

STUDIES OF THE EFFECTS OF ALLOYING IN SOME
Ce BASED HEAVY FERMION ALLOYS

Thesis submitted for the Degree of
Doctor of Philosophy
of the University of London

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May 1989

ABSTRACT.

Structural, magnetic, transport, and heat capacity measurements have been made in order to investigate the effects of alloying on the properties of some Ce based heavy fermion materials. The systems investigated were CeCu_6 , CeAl_2 , CeCu_2 and CeAl_3 .

In the case of CeCu_6 , substitutions on the Cu sites with Au, are found to result in the onset of antiferromagnetic order. The variation in ordering temperature with Au concentration fits well with the theoretical predictions of Doniach's Kondo necklace model. Alloying on the Cu sites rapidly removes the coherence, the dramatic fall in the electrical resistivity seen at low temperature. In contrast alloying on the Ce sites is found to produce only a slow transition from concentrated to dilute Kondo behaviour

CeAl_2 is a heavy fermion which becomes magnetically ordered ($T_N=3.8\text{K}$). Careful measurements reveal a change in slope of the $\rho(T)$ curve at T_N . Substituting either Cu or Co on the Al sites produces modifications in the type of magnetic order, and a reduction in the ordering temperature. The effects of alloying on the onset of coherence and on the peaks observed in the magnetic resistivity of pure CeAl_2 are discussed in terms of changes in the number of conduction electrons and the cell volume. The results are compared with earlier work of Schilling. Substitutions of Fe on the Al sites produce magnetic ordering due to interactions between the Fe atoms on the Al-Fe sublattice. Replacing the Ce with non-magnetic Y results in a loss of magnetic order and indicates the Ce ions are playing a vital role in mediating the Fe-Fe interactions.

CeCu₂ is a magnetic Kondo lattice system ($T_N=3.5\text{K}$). Replacement of Ce with Y produces a steady demagnetisation. The properties of the Y substituted alloys evolve from those expected of a Kondo lattice, through a dilute Kondo impurity regime, to those of the normal metal YCu₂. Substitution of Cu with Ag leads to a weakening of both the Kondo and magnetic interactions. In contrast, addition of Al produces a strengthening of the Kondo interactions, whilst alloying with Pt leads to an enhancement in the strength of ferromagnetic interactions present within CeCu₂. These effects are all attributed to variations in the strength of the hybridisation between the 4f and the conduction electrons.

Changes in the temperature dependence of the electrical resistivity brought about by alloying on the Ce or non-Ce sites in the heavy fermion CeAl₃ have also been studied. The consequences of replacing Ce with Y, Gd and La are compared with substitution of Cu or Sn on the Al sites. It is shown that changes in the temperature dependence of the electrical resistivity are mainly driven by structural distortions and changes in the character of the conduction electrons. These results are then compared with the theoretical predictions given by Maranzana's Kondo sideband model.

ACKNOWLEDGEMENTS

It gives me great pleasure to thank the following people:

My supervisor, Professor B.R. Coles, for his advice, support and guidance throughout the course of this work.

Dr. Howard Stone for his help in preparing and characterizing all the samples.

All the members of the Solid State group, past and present for their help and friendship. In particular, Dr John Chilton, Dr Paul England, Dr Ashok Rastogi and Dr Sindhunil Roy.

Dr Norbert Pillmayr, Dr Ernst Bauer and all members of the Inst. für Experimentalphysik, T.U. Vienna who collaborated on the work on CeCu_6 and CeCu_2 .

All my friends, in and out of London, particularly Nick and Andy who helped spend my grant.

Finally, I would like to thank my parents for their continued encouragement and support. I dedicate this thesis to them.

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Introduction.

This thesis describes a program of measurements carried out on four Ce based heavy fermion systems. This work has involved studying the changes brought about by alloying, in the structural, magnetic, transport and thermal properties of CeCu_6 , CeAl_2 , CeCu_2 and CeAl_3 .

Chapters 4 to 7 of this thesis describe the results of these studies. In each chapter the mechanisms responsible for the observed changes are discussed, and the results are compared with previous experimental and theoretical work in this field.

Information concerning the experimental techniques used during this work, along with details of the preparation and characterization of the samples studied are contained in chapter 3.

As an introduction, chapters 1 and 2 review some of the properties of heavy fermion alloys, and discuss some of the theories which have been developed in order to explain their characteristics.

Chapter 1. Properties of Heavy Fermions.

1:1. Introduction.

1:1:1. Properties of Metals.

The low temperature properties of ordinary metals have characteristics which are well known. For example, an electrical resistivity which is well described by the expression $\rho(T) = \rho_0 + \rho_m(T) + \rho_{ph}(T)$. Where ρ_0 is the temperature independent residual resistivity which is due to scattering from impurities, defects etc. $\rho_m(T)$ is proportional to AT^2 . This AT^2 term in the resistivity can arise from spin density fluctuations and spin density waves in magnetic or nearly magnetic materials, or from electron-electron scattering of more mobile electrons (e.g. s electrons) into less mobile states (e.g. d states) [1:1]. ρ_{ph} is due to scattering by lattice vibrations and is independent of the number of defects within the lattice when their concentration is small. ρ_{ph} is given by the expression $(T/M(\theta_R)^2)f(T/\theta_R)$ [1:2] where θ_R is close to the Debye temperature and $f(T/\theta_R)$ is approximately unity at high temperature and proportional to $(T/\theta_R)^4$ at lower temperature. This empirical observation that the electrical resistivity of a metal can be described by a sum of independent contributions is Matthiessen's law. Thus the electrical resistivity decreases with decreasing temperature approaching some value due to residual resistivity at low temperature. Ordinary metals also exhibit a nearly temperature independent magnetic susceptibility, and a specific heat that varies like $\gamma T + \beta T^3$ where the linear term originates from thermal excitations of electrons around the Fermi energy E_F and the βT^3 arises from lattice vibrations.

The simplest model which can be used to adequately describe many of the low temperature properties of an ordinary metal involves considering the conduction electrons of the metal as a free electron gas of particles which obey Fermi-Dirac statistics and the lattice vibrations of the atomic energy using the Debye model.

1:1:2. The Free Electron Model.

In the free electron model the energy of the electrons $E(k)$ is given by

$$E(k) = \frac{h^2 k^2}{8\pi^2 m} \text{ ----- 1:1(a).}$$

where k = the wave vector of the electrons and h = Planck's constant. The Fermi energy E_F is defined as the top most electron energy level filled in the ground state of the system at $T=0K$.

$$E_F = \frac{h^2 (k_F)^2}{8\pi^2 m} \text{ ----- 1:1(b).}$$

This Fermi energy leads one to define a characteristic temperature T_F , the Fermi temperature where $E_F = kT_F$. For ordinary metals T_F is typically of the order 10^4 to $10^5 K$. For a system of N free electrons in its ground state the occupied orbitals can be represented by a sphere of radius k_F . By considering a free particle Schrödinger equation in three dimensions with the electrons satisfying periodic boundary conditions it is possible [1:2] to show that for each volume element of k -space, $(2\pi/L)^3$, there is a distinct triplet of quantum numbers k_x, k_y, k_z . Thus in a sphere of volume V where

$$V = (4\pi/3) * (k_F)^3 \text{ ----- 1:2.}$$

the total number of orbitals, N is given by

$$N = 2 * V / (2\pi/L)^3 \text{ ----- 1:3.}$$

(the factor two arises from the two allowed spin values of the electron). Defining the density of states $N(E)$ as the number of energy states per unit energy range gives

$$N(E) = dN/dE = (V/2\pi^2) * (8\pi^2 m/h^2)^{3/2} * E^{1/2} = 3N/2E \text{ ----- 1:4.}$$

Using the ideas of this simple model it is possible to derive expressions for many of the low temperature properties expected of a free electron gas in terms of the quantities introduced above.

For example, the magnetic susceptibility is given by

$$\chi(T) = \frac{M}{B} \approx \frac{N(\mu_B)^2}{k_B T_F} \approx (\mu_B)^2 N(E_F) \text{ ----- 1:5.}$$

Where $N(E_F)$ is the density of electron states at the Fermi surface, μ_B is the Bohr magneton. Thus $\chi(T)$ is predicted to be temperature independent with a value (characterized by T_F), which is typically 10^{-5} emu/mol.

At low temperatures the specific heat of a metal is dominated by the contribution due to the electrons. If a metal is heated from absolute zero, only those electrons within $k_B T$ of the Fermi surface can be thermally excited into vacant states. Each of these electrons gains energy of the order $k_B T$. Thus the total electronic thermal energy is given by

$$U = (\text{Number of electrons capable of being excited}) * (\text{Energy gain of each electron})$$

$$\approx \left(\frac{NT}{T_F}\right) * K_B T \text{ ----- 1:6.}$$

This gives a low temperature electronic specific heat

$$C_{el} \approx N K_B (T/T_F) \approx (2/3) N(E_F) (k_B)^2 T \text{ ----- 1:7.}$$

which depends linearly on temperature and is again characterized by T_F . This gives values for C_{el} which are smaller than the classical value $\approx 3Nk_B/2$ by two orders of magnitude (e.g. Cu, $C_{el}=0.7\text{mJ/mol K}$ at 1K compared with the

classically predicted value of 12.47mJ/mol K).

1:1:3. The Debye Model.

When considering the lattice vibrations of a solid, Debye suggested treating a crystal as a continuous, isotropic medium. He further assumed a linear dependence of ω on k (ω =angular frequency of vibrations, k =wave vector) up to some maximum cut off value called the Debye frequency ω_D . To calculate the density of states of modes, note that three vibrational modes can be accommodated for each k . This leads [1:2 page 134] to a density of modes

$$N(\omega) = \frac{V\omega^2}{2\pi^2(v_O)^3} \text{----- 1:8.}$$

where V =the volume of the specimen and v_O =average velocity of modes. Therefore the total number of modes which can be accommodated in a specimen is $3N$ where N is the number of modes for each polarization

$$3N = \int_0^{\omega_D} N(\omega) d\omega = \frac{(\omega_D)^3 V}{2\pi^2(v_O)^3} \text{----- 1:9.}$$

$$\text{Thus } \omega_D = (6\pi^2 N/V)^{1/3} v_O \text{----- 1:10.}$$

One can associate ω_D with a characteristic temperature Θ_D the Debye temperature via

$$h\omega_D/2\pi = k_B\Theta_D \text{----- 1:11.}$$

$$\text{Giving } \Theta_D = (hv_O/2\pi k_B) * (6\pi^2 N/V)^{1/3} \text{----- 1:12.}$$

Using typical values of these quantities for ordinary metals gives $\Theta_D=10^2$ to 10^3 K. One can use the Debye model to calculate the lattice heat capacity. The thermal energy U can be written as

$$U = 3 \int d\omega * N(\omega) * n(\omega) (h\omega/2\pi) \text{----- 1:13.}$$

where $n(\omega)$ = Planck distribution at thermal equilibrium at temperature T giving the occupancy of the phonon modes.

$$n(\omega) = 1/(e^{h\omega/kT} - 1) \text{ ----- 1:14.}$$

The specific heat C_V can then be calculated giving,

$$C_V = (\partial U / \partial T)_T \approx (12\pi^4/5) * (Nk_B) * (T/\theta_D)^3. \text{----- 1:15.}$$

This well known T^3 Debye result fits quite well with the data for temperatures sufficiently less than θ_D .

1:1:4. Summary.

In considering both the free electron gas and the Debye model for the lattice vibrations characteristic temperatures (T_F and θ_D) appear as important parameters. Well above these temperatures, in the high temperature limit the electronic subsystem can be described using classical statistical mechanics. Below these characteristic temperatures and assuming no interaction between the electrons and phonons is present, a combination of the Fermi-Dirac free electron gas model for the electrons and the Debye model for the phonons gives predictions for the properties of ordinary metals, some of which were outlined above.

1:1:5. Heavy Fermions.

Recently a new group of materials have been discovered in which the electronic states have a characteristic energy $E_F = k_B T_F$, orders of magnitude smaller than for ordinary metals. As a result the crossover from behaviour which can be described using classical statistical mechanics to behaviour which requires a quantum statistical interpretation occurs at a much reduced temperature. Writing the electronic energy $E(k)$ in its free electron form

$$E_F = \frac{h^2(k_F)^2}{8\pi^2 m^*} \text{ ----- 1:1(b).}$$

and remembering that the wavevector k_F is determined by the

number of the electrons and the interatomic spacing, and hence takes values which are not much different from ordinary metals, one can ascribe the reduction in E_F to an enhancement in m^* , the effective mass of the electrons. In some cases this leads to m^* values that are 100 to 1000 times the free electron mass. As a result, these materials have been called heavy electron or heavy fermion (hf) systems. These hf materials are intermetallic compounds where one of the constituents is a rare earth (usually Ce) or an actinide (usually U) with a partially filled 4f or 5f electron shell. At high temperatures these materials behave as if these f electrons are localized on their atomic sites, and their properties can be explained using classical statistical mechanics, e.g. observation of Curie-Weiss (C.W.) type temperature dependence in $\chi(T)$.

At low temperature some of the f electrons in hf systems appear to become itinerant. This is indicated by a large but temperature independent magnetic susceptibility $\chi(T)$ (remember for free electron gas $\chi(T) \approx (N(E_F)(\mu_B)^2)$) and a large specific heat which varies linearly with temperature, (again remember for a free electron gas $C_{el} = (2/3)N(E_F)(k_B)^2T = \gamma T$). For hf systems γ has values up to 1000 times the value for a normal metal. Since it is $N(E_F)$, the density of states at the Fermi surface which is related to m^* , and appears in the simple free electron gas expressions for both $\chi(T)$ and C_{el} , hf behaviour can alternatively be attributed to a greatly enhanced electronic density of states at the Fermi surface.

At low temperature these hf systems show features which enable us to subdivide them into 4 groups. The first grouping

are the "normal" heavy fermions. These systems, which include CeAl_3 and CeCu_6 show no definite evidence of a transition into a magnetically ordered or superconducting state down to the lowest temperature measured. The second group contains those hf's which undergo magnetic ordering. These include UCu_5 , UCd_{11} , CeAl_2 and U_2Zn_{17} which all order antiferromagnetically at low temperature. Thirdly, hf's may enter a superconducting state at low temperature e.g. CeCu_2Si_2 and UBe_{13} . The onset of superconductivity is surprising, given that in ordinary superconducting materials the presence of a small amount of magnetic impurity destroys superconductivity. It has been speculated that the superconducting state and the mechanism driving it may be different from those of conventional superconductors, of which more later. Finally there is a group of hf's which show evidence of both superconductivity and antiferromagnetic transitions at different temperatures. These include URu_2Si_2 and $\text{U}_{1-x}\text{Th}_x\text{Be}_{13}$. There have been many hundreds of papers, and several review articles [1:3,1:4,1:5,1:6,1:7] published which discuss the properties of hf systems. The next four sections look at some of the experimental data most relevant to the systems studied in this work. Some important properties of hf materials (e.g. superconductivity) which have not been extensively studied by the writer are only briefly mentioned. The reader is referred to the review articles and the references therein for more detailed discussion of all aspects of hf systems.

The next section looks at the high temperature behaviour of hf's which are common to almost all the known systems.

Section 1:3 will then examine the low temperature properties

of "normal" hf's. Section 1:4 discusses the more complicated behaviour of those systems which show either magnetic or superconducting transitions or which show both magnetic and superconducting transitions at different temperatures. Section 1:5 discusses the correlation between properties of hf systems which may lead to a greater understanding of their behaviour. Finally section 1:6 examines the effects of alloying on hf's.

1:2. High Temperature Properties of Heavy Fermions.

1:2:1. Introduction.

The high temperature properties of a few typical hf systems are summarized in table 1:1. These properties will now be reviewed in a little more detail.

1:2:2. Magnetic Susceptibility.

For all known hf systems at high temperature, the partially filled f electron shells of the individual atoms give rise to localized magnetic moments. These in turn produce a magnetic susceptibility which qualitatively obeys the Curie-Weiss law ($\chi(T) = C / (T - \theta_{C.W.})$ where C is the C.W. constant, and $\theta_{C.W.} (< 0)$ is the C.W. temperature). The effective moments μ_{eff} deduced from C give large values, lying between the value expected for a free atom with a single f orbital occupied of $2.54\mu_B$ and that obtained for a free atom which obeys Hund's rules and has two ($3.26\mu_B$) or three f orbitals occupied ($3.56\mu_B$). For example, in the case of CeAl₃ (see figure 1:1(a)) [1:8,1:9,1:10,1:11], CeCu₂Si₂ [1:12,1:13] and polycrystalline CeCu₆ (see figure 1:1(b)) [1:11,1:12], μ_{eff} has values which lie close to the value expected for a free trivalent Ce ion with a single f orbital occupied. The values obtained by various groups for μ_{eff} and θ_{CW} for different hf

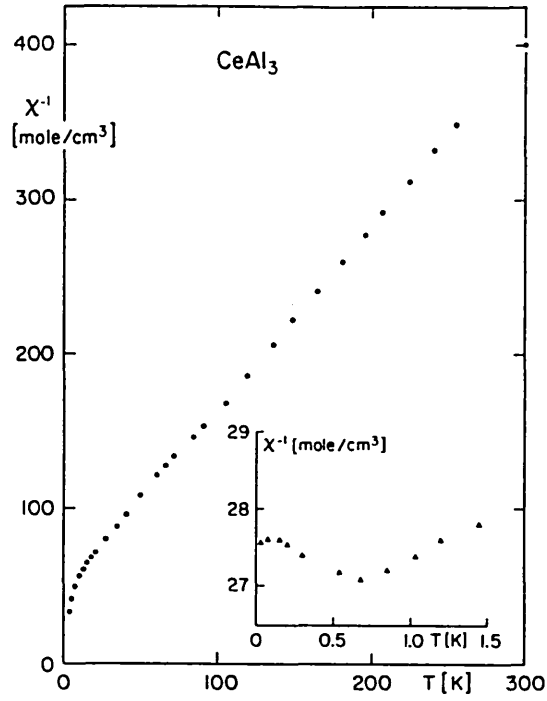


Figure 1:1(a). Temperature dependence of the inverse of the magnetic susceptibility χ^{-1} of CeAl_3 . Data are from Mader and Swift [1:8] and Andres et al. [1:9].

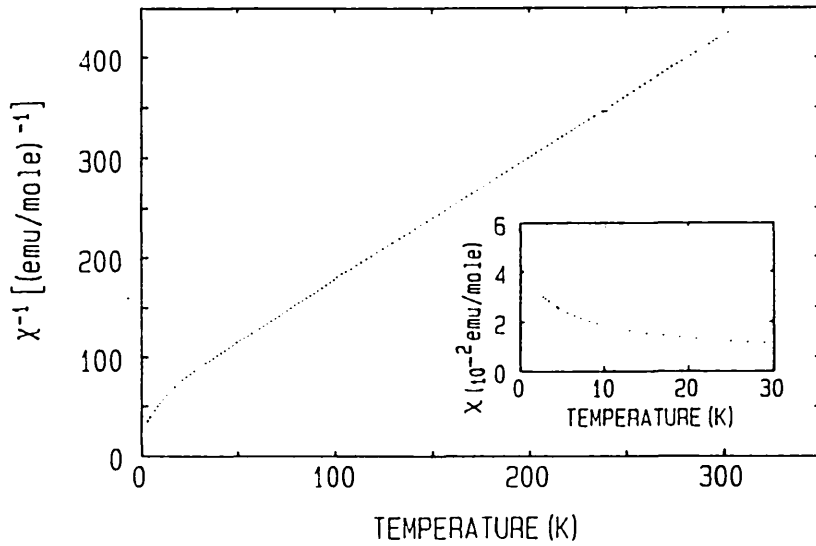


Figure 1:1(b). Temperature dependence of the inverse of the magnetic susceptibility χ^{-1} of CeCu_6 . Data are from Gangopadhyay et al. [1:15].

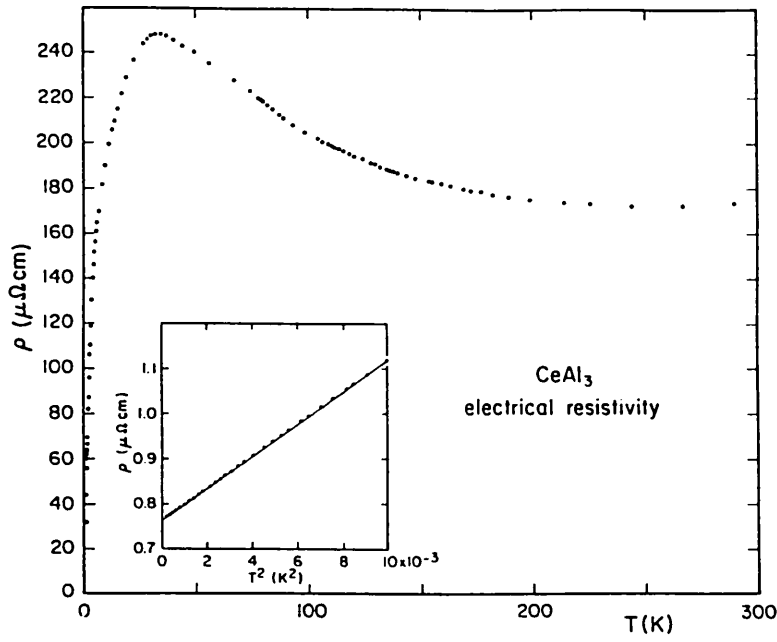


Figure 1:2(a). $\rho(T)$ of CeAl₃ between 1.5 K and 300K [1:20] and below 1.5K [1:9].

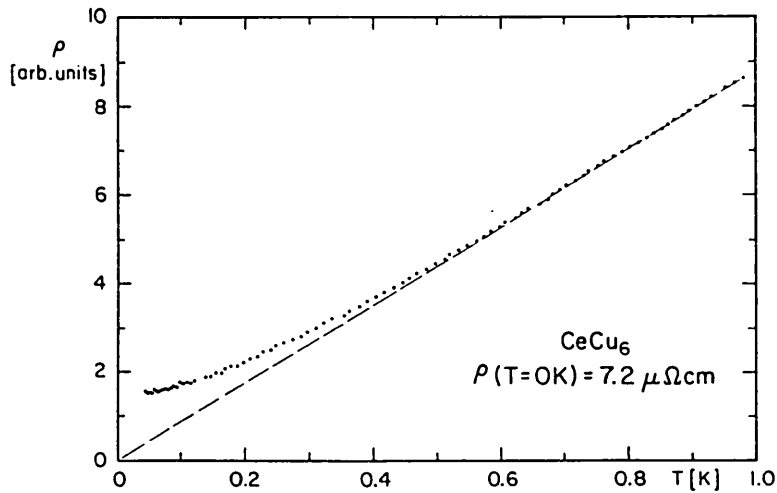
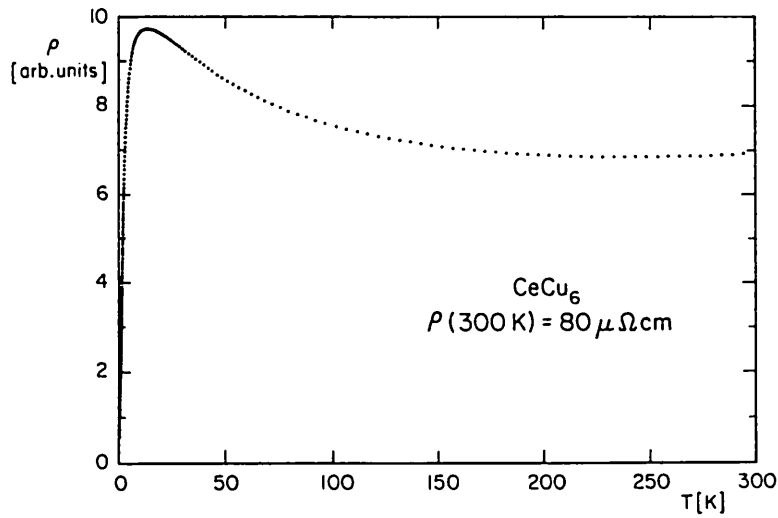


Figure 1:2(b). $\rho(T)$ of CeCu₆ between 0.03 K and 300K and 0.03 K and 1K as reported by Ott et al. [1:21].

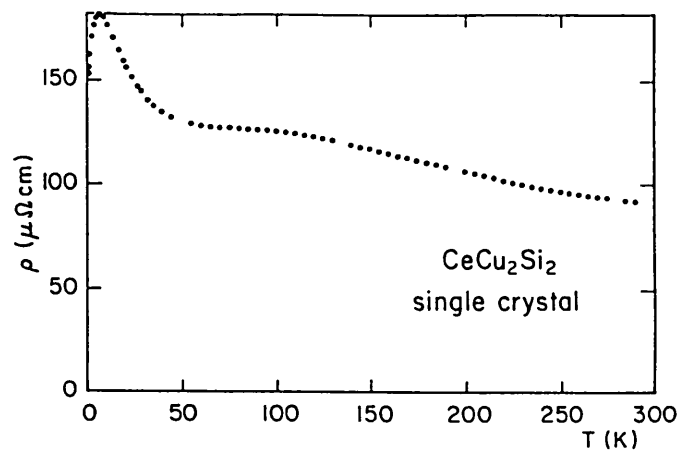


Figure 1:3(a). Temperature dependence of the electrical resistivity of CeCu_2Si_2 between 1.2 and 300K as reported by Stewart et al. [1:22].

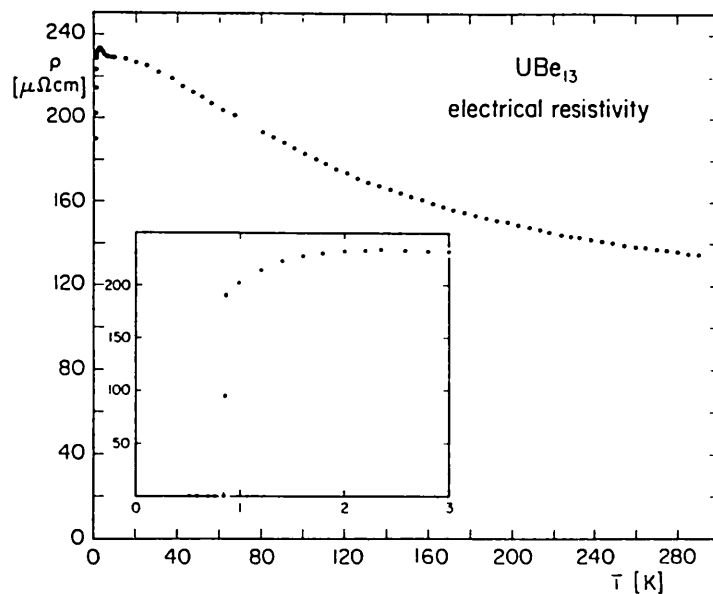


Figure 1:3(b). $\rho(T)$ of UBe_{13} between 0.9 and 300K. The inset shows the transition to the superconducting state. From Ott et al. [1:17].

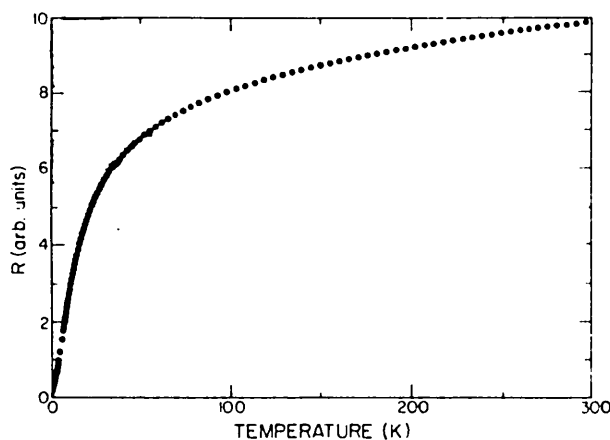


Figure 1:3(c). Temperature dependence of the electrical resistivity of UPt_3 . Data are from de Visser et al. [1:25].

systems vary considerably. This could be due to crystal field effects [1:5] which cause curvature in $\chi(T)^{-1}$ v T plots and are still quite large even at high temperature (e.g. published values for μ_{eff} of UBe_{13} vary from 2.6 to $3.4\mu_B$ with $\Theta_{\text{CW}}=-53$ to -70K [1:16,1:17]). Anisotropy in the susceptibility has also been observed in single crystals of several hf materials e.g. CeCu_2Si_2 [1:13,1:18] and CeCu_6 [1:19]. In the case of CeCu_6 the orthorhombic structure leads to a highly anisotropic behaviour in $\chi(T)$ with μ_{eff} and $\Theta_{\text{C.W.}}$ varying along the 3 crystallographic directions [1:19]. The values obtained for μ_{eff} have been used to determine what valence states are present in a given system. In all cases values for μ_{eff} are not assignable to any integral valence. This suggest that the behaviour of these systems is more complicated than that of a simple collection of local independent f spins. However, this observation is not meant to suggest that the behaviour is strongly mixed valent [1:5].

1:2:3. Electrical Resistivity.

The resistivity of hf's at 300K typically range from 50 to $200\mu\text{-ohm cm}$, some two orders of magnitude larger than normal metals (see table 1:1). Unlike ordinary metals which show decreasing electrical resistivity with decreasing temperature (as outlined in section 1:1), most hf materials have a high temperature behaviour which would be expected if the partially filled f shells were scattering the conduction electrons independently of one another. A high temperature minimum in the resistance is observed in some systems (CeAl_3 [1:20] CeCu_6 [1:21] (figure 1:2)) whilst other systems (CeCu_2Si_2 [1:22], UBe_{13} [1:17], (figure 1:3) UCd_{11} [1:23] and U_2Zn_{17} (figure 1:4)[1:24]) show a rather flat temperature

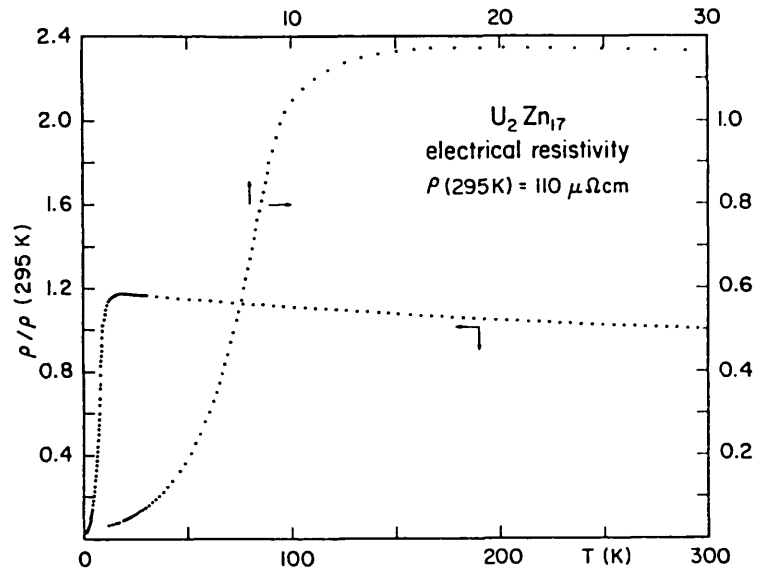


Figure 1:4(a). Temperature dependence of the electrical resistivity of U_2Zn_{17} between 1.5 and 300K. Expanded scale for 1.5 to 30K. Data are due to Ott et al. [1:24].

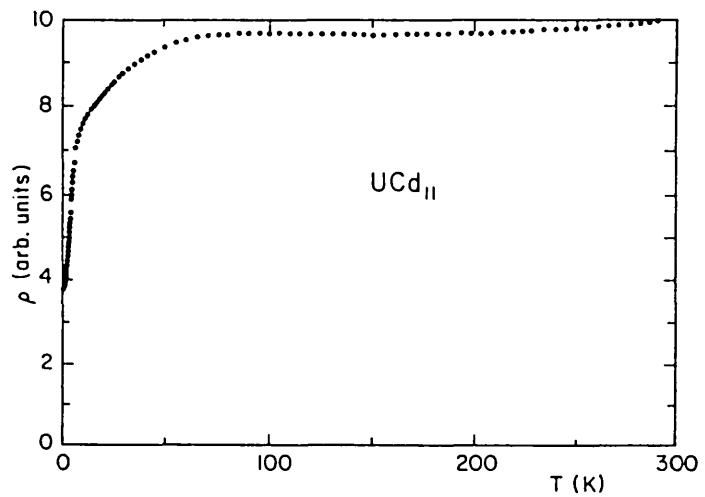


Figure 1:4(b). Temperature dependence of the electrical resistivity of UCd_{11} between 0.3 and 300K as measured by Fisk et al. [2:23].

dependence above 100K. An increase in resistivity at lower temperature is observed in almost all hf systems rising to a maximum in the 50 to 10K range. In most cases this maximum is attributed to a combination of crystal field and Kondo effects. To see this magnetic behaviour more clearly, one must subtract the resistivity of an isostructural non-magnetic reference compound whose resistivity represents the phonon term. For example, in the case of CeCu₆ subtract the resistivity of LaCu₆. One then observes the characteristic Kondo like, logarithmic temperature dependence in the resistivity. (N.B. Unlike other hf's, UPt₃[1:25] and UAu₄Pt[1:26], (see figures 1:3(c) and 1:20(b)) have no minimum in $\rho(T)$. This may be due to an anomalous phonon contribution to $\rho(T)$ or may indicate some kind of inverted Kondo behaviour [1:3]).

Table 1:1. Typical values for the high temperature properties of selected hf systems along with those of Pd. Quantities which vary along different crystallographic axes are separated by slashes.

Material	$-\Theta_{CW}$ (K)	μ_{eff} μ_B/Ce or U	$\rho(T=300K)$ $\mu ohm\ cm$
CeCu ₆	46 [1:15] 59/59/8	2.56 [1:15] 2.6/2.67/2.46[1:19]	80 [1:21]
CeAl ₃	39 [1:10]	2.60 [1:10]	65 [1:9]
CeCu ₂ Si ₂	140 [1:5]	2.68 [1:5]	90 [1:22]
UBe ₁₃	53 [1:17]	3.1 [1:17]	107[1:17]
U ₂ Zn ₁₇	105 [1:49]	3.3 [1:49]	110[1:24]
UCd ₁₁	23 [1:23]	3.45 [1:23]	80 [1:23]
URu ₂ Si ₂	65 [1:62]	3.51 [1:62]	324[1:62]
Pd	86 [1:7]	4.6 [1:7]	10 [1:7]

1:2:3. Summary.

To summarize the high temperature properties of hf include:

1. Curie-Weiss like magnetic susceptibility. Θ_{CW} . The Curie-Weiss temperature is negative and the effective moment lies between $2.54\mu_B$ and $3.6\mu_B$.

2. Large, nearly temperature independent resistivity, whose magnetic component show Kondo logarithmic temperature dependence.

1:3. Low Temperature Properties.

1:3:1. Introduction.

In this section, some of the features of the low temperature behaviour of hf systems which show no evidence of a magnetic or superconducting transition, i.e. "normal" systems, $CeAl_3$ and $CeCu_6$ are reviewed. The enhancement in the values of the low temperature specific heat and magnetic susceptibility, and the appearance of a coherent scattering regime in the transport properties are discussed.

1:3:2. Specific Heat.

For temperature a fraction of the Debye temperature ($T < \Theta_D/50$) the specific heat of an ordinary metal can be written as

$$C = \gamma T + \beta T^3 \text{ ----- 1:16.}$$

where γ is proportional to the electronic density of states and β characterizes the contribution of the phonons to the specific heat. At lowest temperature plotting C/T v T one would expect a slightly increasing positive slope with increasing T and a finite ordinate intercept for $T=0K$. This intercept $\gamma(0)$ would be of the order of a few $mJ/molK^2$ (e.g $Cu \gamma = 0.7 mJ/mol K^2$). For hf materials the situation is distinctly different. For both $CeAl_3$ [1:6,1:27,1:28] and $CeCu_6$ [1:14,1:21] (T) continues to be highly temperature dependent below 10K, with C/T increasing with decreasing temperature (see figure 1:5). In the case of $CeAl_3$ C/T v T

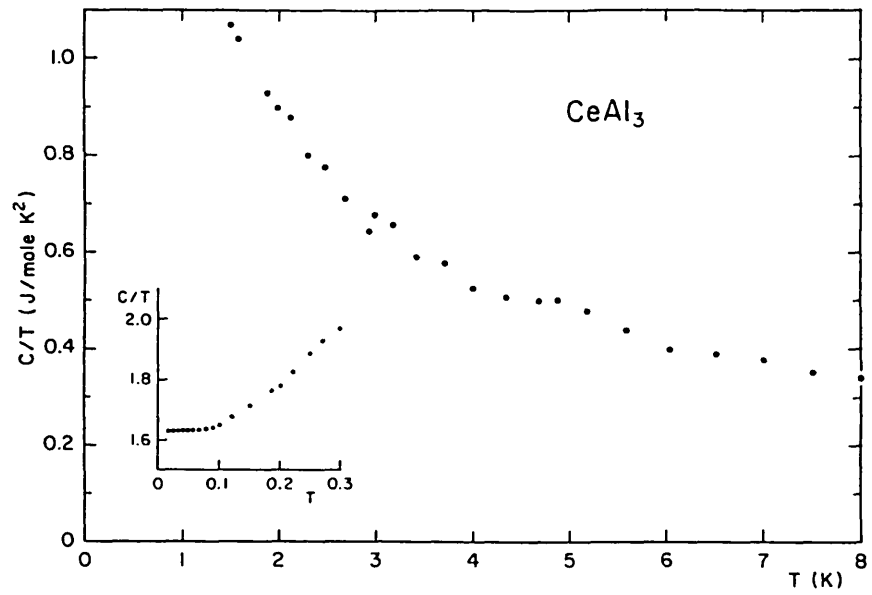


Figure 1:5(a). C/T versus T for CeAl_3 . The data for $T > 1.5$ K are from Ott et al. [1:27], those below 0.3 K are due to Andres et al. [1:9].

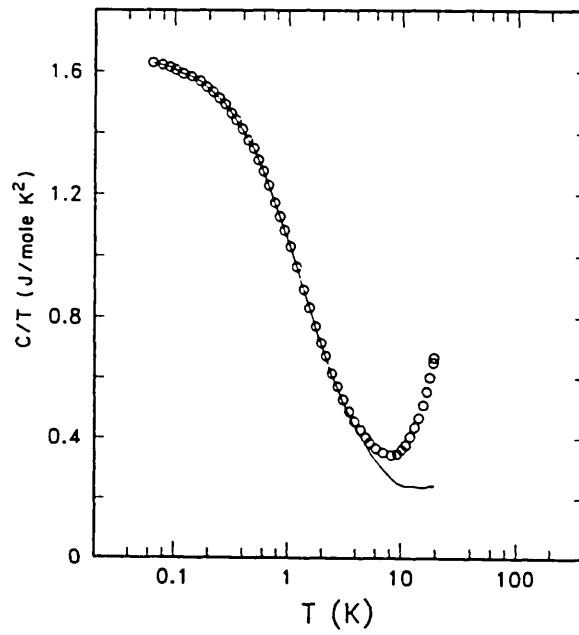


Figure 1:5(b) C/T versus T for a single crystal of CeCu_6 . Data are due to Amato et al. [1:29]. The solid line is the electronic contribution after subtraction of the T^3 phonon term.

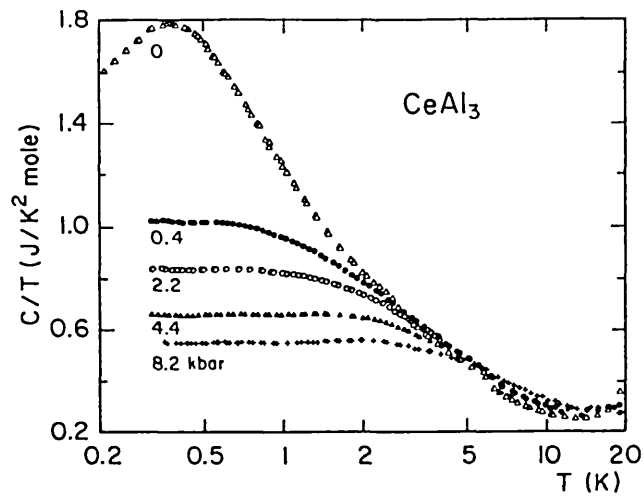


Figure 1:6. Influence of external pressure on the low temperature specific heat of CeAl_3 as reported by Brodale et al. [1:32].

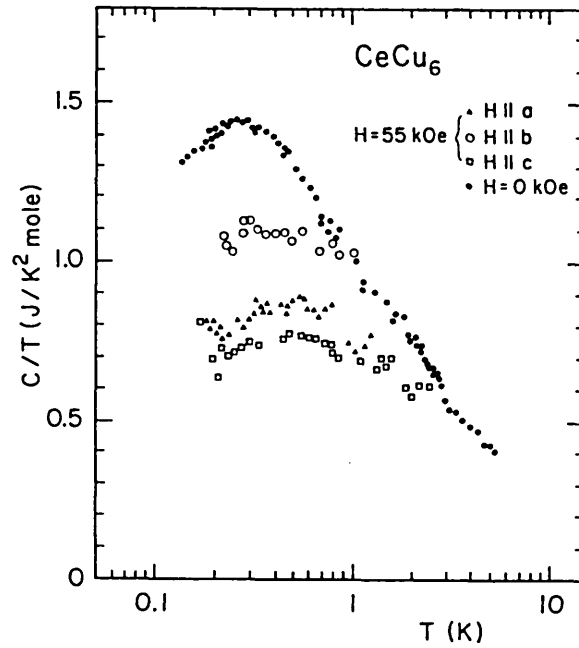


Figure 1:7. Influence of external magnetic fields on the low temperature specific heat of CeCu_6 . Data are from Satoh et al. [1:30].

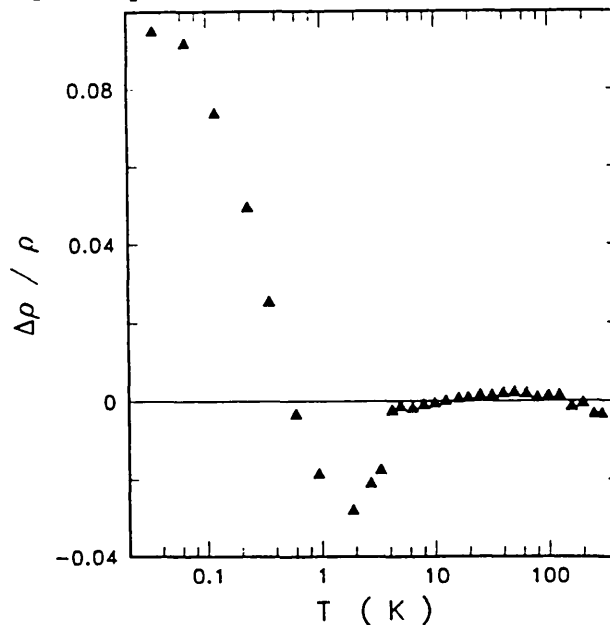


Figure 1:8. Normalised magnetoresistance $\delta\rho/\rho$ for a single crystal of CeCu_6 . $\delta\rho$ is the difference between the resistivity for a field of 1T in the orthorhombic c direction and the resistivity ρ extrapolated to zero field. Data are from Penney et al. [1:40].

passes through a maximum at 0.4K [1:28] before levelling off to give $\gamma(0) \approx 1.6 \text{ J/mol K}^2$ [2:9]. A similar increase in C/T vs T is observed in the CeCu_6 system. However Ott et al. [1:21] and Amato et al. [1:29] report no maximum is observed in C/T whilst Satoh et al. [1:30] suggest the appearance of a maximum around 0.3K, which is far less pronounced than in CeAl_3 . It has been suggested that the peak in C/T indicates the entry into a coherent scattering regime [1:31]. What is clear is that the enormous γ indicates the presence of an extremely large density of states $N(E_F)$ at the Fermi level. The effect of pressure on the low temperature specific heat has been investigated by several groups [1:32,1:33,1:34,1:35]. The low temperature maximum seen in CeAl_3 at normal pressure is dramatically suppressed under pressure (see figure 1:6). The value of $\gamma(0)$ is also reduced dropping to 0.6 J/mol K^2 at 8.8kbar. A similar suppression in $\gamma(0)$ is seen in CeCu_6 where $\gamma(0) = 0.8 \text{ J/mol K}^2$ at $P = 8.8 \text{ kbar}$. The effects of magnetic fields on the specific heat have also been studied [1:30,1:36]. For both CeAl_3 and CeCu_6 (see figure 1:7) the application of magnetic fields suppresses the value of $\gamma(0)$ ($\gamma(0) \approx 1.3 \text{ J/mol K}^2$ for CeAl_3 at 8T; $\gamma(0) \approx 0.5 \text{ J/mol K}^2$ for CeCu_6 at 7.55T).

1:3:3. Low Temperature Susceptibility.

At high temperature the susceptibility of hf materials shows C.W. like behaviour. As the temperature is lowered the magnitude of the susceptibility continues to increase. Deviations from C.W. behaviour are observed although the features are still attributable to the local f configurations. At low temperature $\chi(T)$ begins to saturate and at lowest temperature is reminiscent of Pauli paramagnetic susceptibility. The

absolute values for $\chi(T)$ at low temperature are orders of magnitude larger than those expected for a conventional metal (see table 1:2). It is suggested that the mechanism which prevents the individual Ce^{3+} moments, whose presence at high temperature is indicated by the C.W. behaviour from interacting via the RKKY interaction to give long range magnetic order at low temperature, involves the quenching or compensating of local moments by conduction electrons. This mechanism is discussed in chapter 2.

1:3:4. Electrical Resistivity.

At high temperature the Ce ions in both CeAl_3 and CeCu_6 behave as if they are independent scattering centres, showing dilute Kondo behaviour. The resistivity rises to a maximum at 35K for CeAl_3 (15K for CeCu_6). Below this temperature the resistivity falls through at least two orders of magnitude. This drop is taken to indicate the onset of a coherent scattering regime. That is, the scattering of the Ce ions has become coherent as required by Bloch's theorem. At very low temperature ($\text{CeAl}_3 < 300\text{mK}$, $\text{CeCu}_6 < 100\text{mK}$), the resistivity of both systems smoothly enters a regime where $\rho(T)$ can be approximated well by $\rho(T) = \rho_0 + AT^2$ [1:9, 1:21] where ρ_0 is the residual resistivity determined by impurities and imperfections in the crystal lattice (the value of ρ_0 is close to that of a normal metal). The T^2 term, characteristic of electron-electron scattering in a Fermi liquid, has a large prefactor A (see table 1:2). The value of A is much enhanced over values expected for a conventional metal, (perhaps by an order $(m^*/m)^2$ [1:37]). Kadawoki and Woods [1:38] have noted that A/γ^2 has a universal value that is close to $10^{-5}(\mu\text{ohm cm}^*(\text{mol K}^2/\text{mJ})^2)$ for all the accepted hf systems.

1:3:5. Magnetoresistance.

The magnetoresistance ($\delta\rho/\rho$) of both CeAl_3 and CeCu_6 have been reported [1:39,1:40]. The data for CeCu_6 are shown in figure 1:8. At high temperature the magnetoresistance increases from small negative to small positive values. As the temperature decreases to that at which a peak is seen in the resistivity, the magnetoresistance again changes sign and takes on large, negative values. That is, the field reduces the spin disorder scattering found for Kondo impurities. At still lower temperatures, the effects of spin disorder scattering are frozen out, and the magnetoresistance again becomes positive like a normal metal[1:40]. Finally, at temperatures comparable to those in which the resistivity shows T^2 behaviour a change in slope is seen in $\delta\rho/\rho$ for both CeCu_6 and CeAl_3 .

1:3:6. Hall Effect.

The temperature dependence of the Hall coefficient R_H of CeCu_6 and CeAl_3 are shown in figure 1:9. On cooling from room temperature the Hall constant of CeCu_6 [1:40,1:41,1:42] follows a skew scattering behaviour $\chi\rho_m$, the product of the susceptibility and the Kondo resistivity. The qualitative similarity between R_H and ρ is striking. In the region of 30K, the Hall constant changes very rapidly from a strongly positive to a strongly negative value. At very low temperature the Hall constant reaches a negative minimum at 0.4K. R_H then has a negative slope below this temperature, the temperature at which the system is taken to be in the coherent Fermi liquid state. In the case of CeAl_3 [1:43], the Hall constant can be well fitted to a combination of an intrinsic skew scattering term and a residual term made up

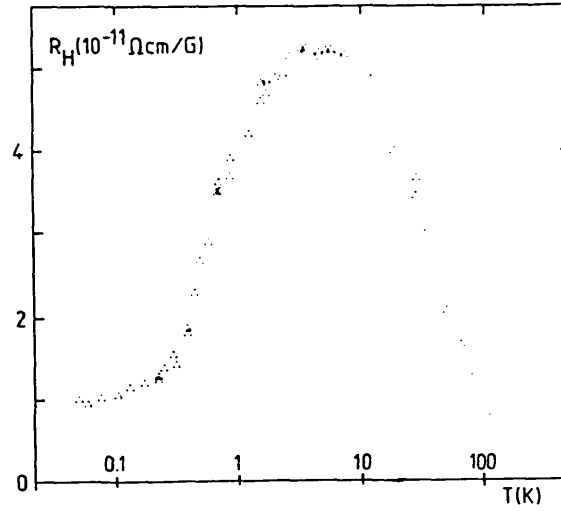


Figure 1:9(a). Initial Hall constant versus $\ln T$ for polycrystalline CeAl_3 . Data are from Lapierre et al. [1:43].

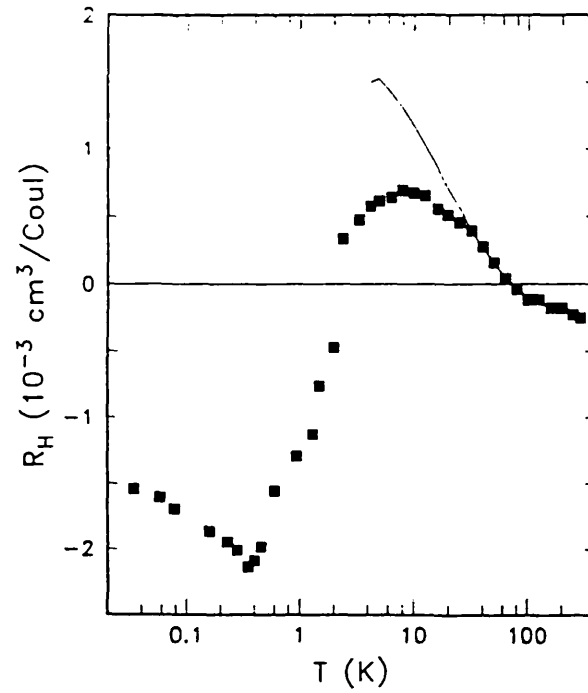


Figure 1:9(b). Hall constant for a single crystal of CeCu_6 for a field of 1T in the orthorhombic c direction. The solid line is a high temperature χ_0 fit. Data are from Penney et al. [1:40].

the ordinary Hall effect and residual skew scattering by defects, impurities etc. The behaviour of R_H at high temperature is similar to that of $CeCu_6$, although there is not the close correspondence between the maximum in R_H (at 5K) and the maximum in the resistivity (at 35K). The same fall in R_H is observed below the maximum, but R_H never becomes negative. At lowest temperature there is again a distinct flattening in R_H as the system enters the coherent regime.

1:3:7. Thermal Conductivity.

Assume the validity of Wiedmann-Franz law

$$\rho\lambda = LT \text{ ----- } 1:17(a).$$

where L is the Lorenz number and the low temperature resistivity can be well approximated by $\rho(T) = \rho_0 + AT^2$ it is expected that

$$\lambda^{-1} = \rho_0/LT + AT/L \text{ ----- } 1:17(b).$$

For $CeAl_3$ (see figure 1:10(a) at low temperature the general behaviour of λ fits well with this expectation [1:20]. At $T \approx 0.4K$ a maximum is observed in λ . Below this maximum the impurity scattering term dominates and λ is linear in T . Above 0.4K the onset of a T^{-1} behaviour typical of a Fermi liquid is observed.

The thermal conductivities of $CeCu_6$ and $LaCu_6$ are shown in figure 1:10b. While $LaCu_6$ has the classical shape of a normal metal, λ of $CeCu_6$ shows unusual behaviour. Below 200mK and between 9 and 110K λ is linear in T . No maximum in λ is observed.

$$\text{Assume } \lambda = \lambda_e + \lambda_p \text{ ----- } 1:18.$$

where λ_e and λ_p are the electron and phonon contribution respectively. At low temperature λ is dominated by λ_e . Below 200mK the resistivity can be well approximated by $\rho(T) = \rho_0 + AT^2$

where ρ_0 is a large residual resistivity and AT^2 is a strong Fermi liquid term. Assuming again the validity of Wiedmann-Franz law. For $T < 200\text{mK}$ $\rho_0 \gg AT^2$ giving $\lambda \propto T$. Between 200mK and 1K λ is expected to be proportional to T^{-1} . It is suggested that the large ρ_0 prevents observation of a maximum. Above 1K, the thermal conductivity is again linear in T , as observed in CeAl_3 .

1:3:8. Thermal Expansion.

The electronic contribution to the thermal expansion can be written as

$$\beta_{el} = \frac{K}{V} \gamma (\partial \ln \gamma / \partial \ln V) * T \text{ ----- 1:19.}$$

where V = molar volume and K = compressibility. This can be rewritten as

$$\beta_{el} \approx \partial \ln N(\epsilon_F) / \partial \ln V \text{ ----- 1:20.}$$

Thus, β_{el} is a direct measure of the volume dependence of $N(E_F)$ (i.e. a large volume or pressure dependence of the density of states at E_F will result in an anomalously large contribution to the thermal expansion). For a normal metal, at low temperature in the free electron model, β_{el} is expected to increase linearly with increasing temperature. Measurements of the thermal expansion α were performed on polycrystalline CeAl_3 [1:34] and CeCu_6 [1:6] (see figures 1:11(a) and (b)). Along different crystallographic axes α may take different values, but assuming good polycrystallinity the behaviour of α gives a reliable estimate of β where $\beta = 3\alpha$. For both CeAl_3 and CeCu_6 , the expansion coefficient α is quite unlike that of an ordinary metal. $\alpha(T)$ has a negative slope between 2 and 10K. The magnitude of α is large (e.g. CeAl_3 $\alpha = 1 \times 10^{-5} \text{ K}^{-1}$ at 2K. At lower temperature $\alpha(T)$ decreases. In the case of CeCu_6 , $\alpha(T)$ approaches zero. On the

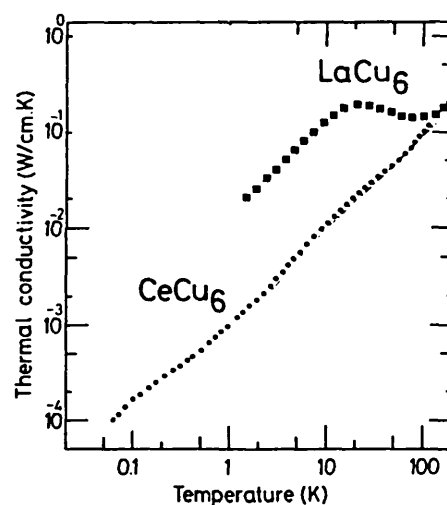
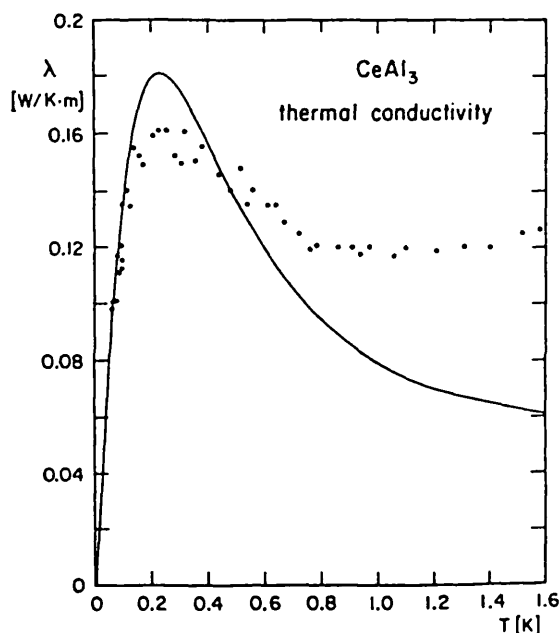


Figure 1:10(a). Low temperature thermal conductivity of CeAl_3 . The solid line is calculated from $\rho(T)$ assuming the law of Weidmann-Franz. Data from Ott et al [1:20].

Figure 1:10(b). Temperature dependence of the thermal conductivity of CeCu_6 as reported by Peysson et al. [1:40].

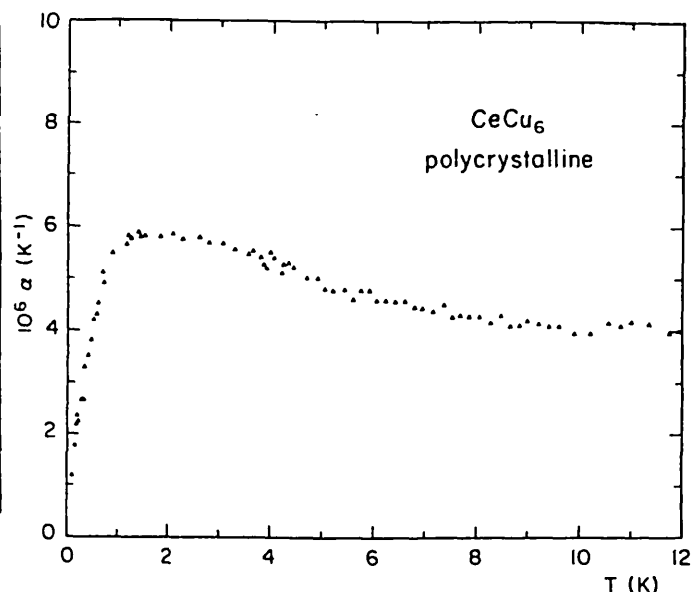
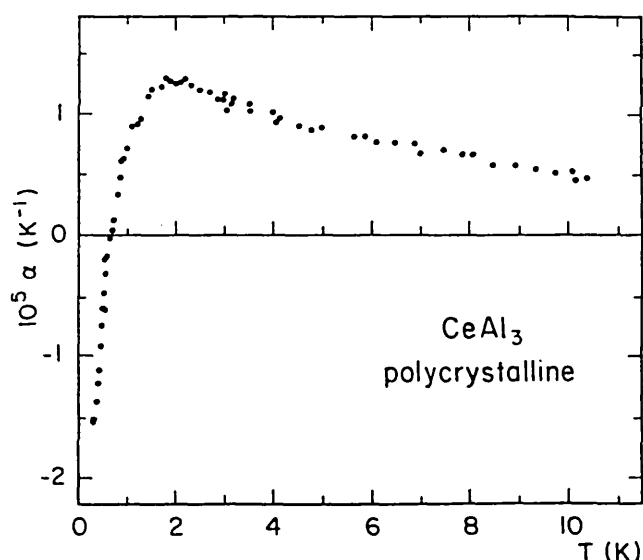


Figure 1:11(a). Linear thermal expansion coefficient of CeAl_3 between 0.3 and 10K as reported by Andres et al. [1:9].

Figure 1:11(b). Linear thermal expansion coefficient of CeCu_6 between 0.05 and 12K as reported by Ott [1:6].

other hand for CeAl_3 $\alpha(T)$ decreases from a positive maximum at 2K, passes through zero and falls to a minimum of $-1.5 \times 10^{-5} \text{K}^{-1}$ at the lowest temperature measured. The large values of α (and consequently β) and its rapid variation with temperature indicate the strong volume dependence of $N(E_F)$. It is possible to extract from this data the value of $\partial \ln \gamma / \partial \ln V = \Gamma_{e1}$, the electronic Gruneisen parameter. For both CeAl_3 and CeCu_6 , Γ_{e1} is two orders of magnitude larger than for a normal metal (N.B. in the free electron model β_{e1} is expected to be 2/3). In addition Γ_{e1} varies considerably below 1K. For CeCu_6 , Γ_{e1} has a positive value of 200 as $T \approx 0\text{K}$. In the case of CeAl_3 , Γ_{e1} changes sign and reaches -200 as $T \approx 0\text{K}$. On the basis of this data C/T is expected to decrease with pressure for CeCu_6 , whilst for CeAl_3 , C/T is expected to increase. In both cases C/T is dramatically suppressed by pressure (see section 1:3:1). This disagreement between prediction and experiment in the case of CeAl_3 may be due to an accidental preferred direction in the polycrystalline sample. Alternatively, the zero pressure state from which Γ_{e1} is calculated may be quenched by a relatively small pressure.

1:3:9. De Haas-van Alphen.

Reinders et al. have performed de Haas-van Alphen (dHvA) measurements on single crystals of CeCu_6 [1:46, 1:47, 1:48]. Measurements were made along the c-axis in fields of up to 14.5T, in the temperature range 20-250mK. Observation of quantum oscillations in CeCu_6 system imply the presence of a sharply defined Fermi surface in the low temperature coherent state. Cyclotron effective masses were determined from the temperature dependence of dHvA amplitudes at constant field. Cyclotron masses between 6 and $80m_0$ were observed and many

body enhancements, 20 times larger than those seen in the reference material LaCu_6 were deduced. From these experiments it was concluded that no "light" electrons (i.e. those with masses $\approx m_0$) exist in CeCu_6 in the low temperature coherent state, and that many body renormalizations influence all the electrons, not just those which are primarily of f character. No field dependence of the cyclotron mass, which was expected from the reported field dependence of the electronic specific heat [1:30] was observed.

1:3:10. Summary.

To summarize the normal state properties of hf systems include:

1. An anomalously large electronic specific heat reflecting a large density of states near the Fermi level.
2. A large nearly temperature independent Pauli paramagnetic susceptibility.
3. Low temperature resistivities of the form $\rho(T) = \rho_0 + AT^2$ with a large coefficient A.
4. Structure in magnetoresistance and Hall coefficient around the temperature where $\rho(T)$ shows T^2 behaviour.
5. A usually negative thermal expansion, several orders of magnitude larger than the positive values seen in ordinary metals.

These properties are listed in table 1:2 below.

Table 1:2. Values for some of the low temperature properties of normal hf are listed along with those of Pd.

Material	$\gamma(0)$ mJ/molK ²	$\chi(0)$ 10^{-2} emu/mol	ρ_0 $\mu\text{ohm cm}$	A $\mu\text{ohm cmK}^{-2}$
CeAl ₃	1620[1:9]	0.36 [1:9]	0.77	35 [1:9]
CeCu ₆	1600[1:29]	0.28 [1:14]	7.2[1:21]	111 [1:21]
Pd	10 [1:7]	0.08 [1:7]	$4.3 \cdot 10^{-4}$ [1:7]	$6.4 \cdot 10^{-5}$ [1:7]

1:4. Ordered Heavy Fermions.

1:4:1. Magnetically Ordered Heavy Fermions.

Several hf materials have a magnetically ordered ground state. All these systems order into some kind of antiferromagnetic structure. These magnetic hf systems can in turn be subdivided into those which show an enhanced specific heat before the onset of magnetic order, and a smaller group in which the magnetic order precedes the formation of the hf state. This first class of compounds includes $U_{2}Zn_{17}$, $NpSn_3$, $CeAl_2$ and UCd_{11} . This section highlights the properties of $U_{2}Zn_{17}$ and UCd_{11} . Finally the behaviour of UCu_5 , the first hf material in which magnetic order precedes the onset of enhancement in the specific heat is reviewed.

1:4:2. $U_{2}Zn_{17}$.

$U_{2}Zn_{17}$ crystallizes into a rhombohedral structure[1:49] with U-U distance of $4.39\text{\AA}$. Figure (1:12(b)) shows the specific heat of $U_{2}Zn_{17}$ with the lattice contribution of isostructural $Th_{2}Zn_{17}$ subtracted(i.e. $C_{el}(U_{2}Zn_{17})/T = (C_{total}(U_{2}Zn_{17}) - C(Th_{2}Zn_{17}))/T$). Above the magnetic transition C_{el}/T is large and temperature independent [1:24]. This gives a parameter denoting the electronic specific heat in the paramagnetic region $\gamma_p = 550\text{mJ/mol-U K}^2$. The transition itself is indicated by a very sharp jump in the electronic specific heat C_{el} at 9.7K. Below 5K the remaining specific heat can be approximated by $C_{el} = \gamma T + \beta T^3$ where γ below T_N is 198mJ/mol-U K^2 about 1/3 of the value of γ above T_N , but still considerably larger than a normal metal. The βT^3 term is a non-lattice contribution (also seen in $NpSn_3$) which may in part be due to magnetic fluctuations. The entropy associated with $\gamma(0)$ below T_N is equal to 1.92J/mol-U K ,

U_2Zn_{17}

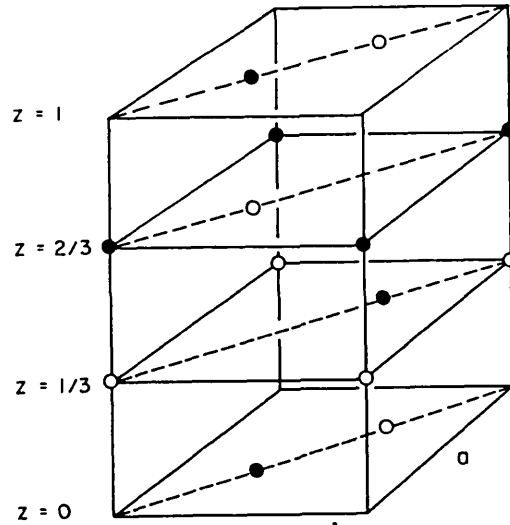


Figure 1:12(a). Representation of the magnetic structure of U_2Zn_{17} below T_N as proposed by Cox et al. [1:49]. The open and closed circles denote the two moment directions of the anti-ferromagnetic structure.

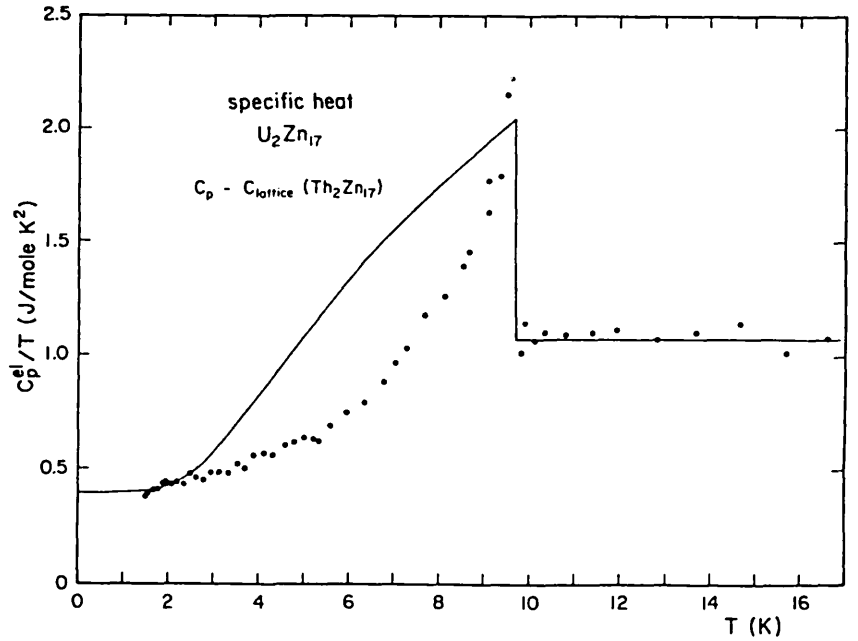


Figure 1:12(b). C_p^{el}/T versus T for U_2Zn_{17} between 1.5K and 16K as reported by Ott et al. [1:24]. The solid line is a BCS-type curve taking into account a non-zero electronic contribution below T_N .

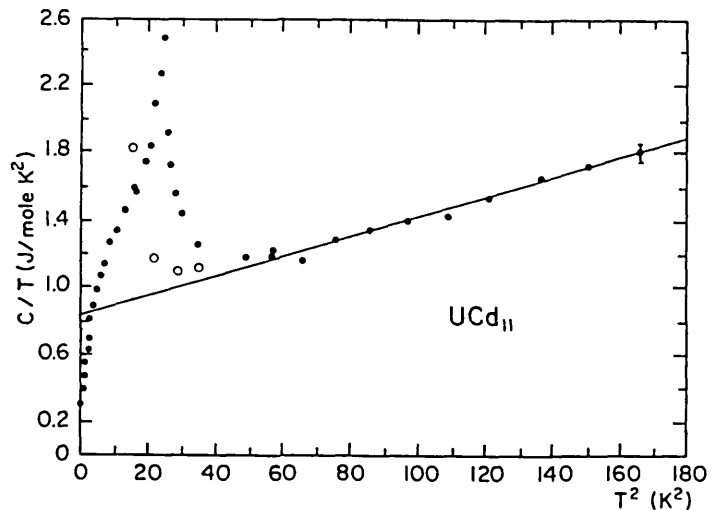


Figure 1:13. C_p/T versus T^2 of UCd_{11} between 0.3 and 13K as measured by Fisk et al. [1:23]. The solid line is a fit of the form $C_p = \gamma T + \beta T^3$.

whilst the remaining part up to the ordering temperature amounts to 1.9525J/mol-U K. The sum of these two contributions (3.8725J/mol-U K) is much less than $2R\ln 2=11.52\text{J/mol-U K}$, the entropy per U atom associated with a doubly degenerate ground state. It is also less than the entropy associated with the electron system in the paramagnetic state. That is, the change entropy associated with the transition, defined as

$$\delta S = \int_{0\text{K}}^{12\text{K}} (C_{\text{measured}}/T) dT - \int_{0\text{K}}^{12\text{K}} (C_{\text{ext}}/T) dT \text{ ----- 1:21.}$$

where C_{ext} is an extrapolation of the high temperature data to $T=0\text{K}$. This gives $\delta S=-1.37\text{ J/mol-U K}$ [2:5]. This has led to speculation that $\chi(T)$ would go on increasing, were it not for the magnetic ordering. Neutron experiments [1:49] reveal U_2Zn_{17} has a relatively simple structure (see figure 1:12(a)). The saturated ordered moment in zero magnetic field is $0.8\mu_B/\text{U}$. This is much reduced compared with the effective moment μ_{eff} of between 2.25 and $3.3\mu_B/\text{U}$ obtained from high temperature susceptibility data [1:6,1:49] and indicates the ordered moment has undergone a considerable reduction during cooling. The resistivity of U_2Zn_{17} is shown in fig (1:4(a)). After passing through a maximum at 17K $\rho(T)$ decreases rapidly only below T_N where a change in slope in $\rho(T)$ is observed. As T approaches 0K, $\rho(T)$ reaches a value two orders of magnitude lower than at the peak value reached at 17K ($\rho=\rho_{\text{max}}/80$ at 1.2K). At lowest temperatures ρ varies as $T^{5/2}$.

1:4:3. UCd_{11} .

UCd_{11} crystallizes into cubic BaHg_{11} structure with the U atoms separated by $6.56\text{\AA}$ [1:50]. Direct overlap of the 5f electron wavefunctions must be negligible and at low

temperature, one would expect a well defined local moment behaviour. Above T_N the specific heat of UCd_{11} (see figure 1:13.) [1:23] shows behaviour which can be well fitted to $C_{el} = \gamma T + \beta T^3$. The extrapolation of C_{el}/T at $T=0K$ gives $\gamma(0)=840\text{mJ/mol K}^2$ indicating a large electronic specific heat. At 5K UCd_{11} undergoes a magnetic phase transition. The temperature dependence of $\chi(T)$ indicates antiferromagnetic ordering. A reduction in μ_{eff} from the value of $3.45\mu_B$ calculated from high temperature susceptibility to $1.2\mu_B$ is observed. As with U_2Zn_{17} the magnetic phase transition reduces γ dramatically. Below 1K $\gamma(T\approx 0K)$ gives a value of 250mJ/molK^2 which is still large compared with a normal metal. However, unlike the sharp transition in U_2Zn_{17} the specific heat of UCd_{11} shows signs of precursor or short range order effects above T_N . Stewart [1:5] suggested this may be partially due to lattice disorder in the samples. Alternatively Fisk et al. [1:23] have suggested that an upturn in C/T seen in other hf systems e.g. $CeAl_3$ may occur in UCd_{11} , and this could in part be the cause of the tail. An estimate of the entropy balance associated with the transition is difficult because of the tail in C but integrating up to a value where C/T is constant (8K) gives

$$\begin{aligned} \delta S &= \int_{0K}^{8K} (C_{measured}/T) dT - \int_{0K}^{8K} (C_{ex}/T) dT \text{ ----- 1:22.} \\ &\approx +1.63\text{J/mol U K} \\ &\approx .28*(R\ln 2) \end{aligned}$$

This positive fraction of $R\ln 2$ indicates local moment behaviour. If part of the tail in the specific heat were due to an upturn in C/T , the $T\approx 0K$ value for γ would be larger than 840mJ/mol K^2 and the net entropy balance would then be

nearer zero or even negative as in U_2Zn_{17} . The electrical resistivity of UCd_{11} (fig 1:4(b)) [1:23] shows no obvious feature accompanying the transition, although an increase in $d\rho/dt$ is seen at the ordering temperature. The fall in ρ from the maximum value is quite sample dependent.

1:4:4. UCu_5 .

Finally in this section the behaviour of UCu_5 , a magnetic hf material which undergoes ordering and then shows hf behaviour is briefly reviewed. UCu_5 crystallizes into a cubic $AuBe_5$ structure with U-U nearest neighbour spacing of $4.96\text{\AA}$ which is again quite large. Magnetic susceptibility and neutron diffraction experiments showed UCu_5 becomes antiferromagnetically ordered at 15K [1:51,1:52]. Later measurements by van Daal et al. [1:53] of the specific heat and electrical resistivity of UCu_5 (see figures 1:14 (a) and (b)) confirmed the antiferromagnetic nature of the ordering. A sharp anomaly in the specific heat is seen at 15K associated with the magnetic ordering. At 4K, C/T begins to increase with decreasing temperature. This contribution was originally ascribed to the onset of a Schottky type contribution to the specific heat due to the spontaneous splitting of nuclear levels in the magnetically ordered matrix. Later however Ott et al. [1:26] showed that the increase in C/T is due to many body effects present in hf materials and that the distinct upturn in C/T is indicative the onset of the hf state. However, this enhancement is reduced by a second phase transition at 1K of unknown origin which involves the heavy mass quasiparticles that lead to the enhanced specific heat. This second transition can clearly be seen in the electrical resistivity. $\rho(T)$ for UCu_5 falls steadily below 10K but then

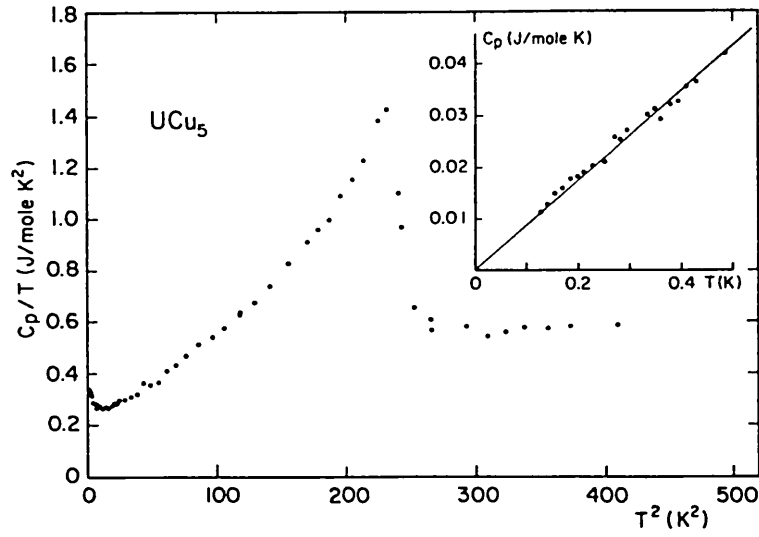


Figure 1:14(a). C_p/T versus T^2 for UCu_5 . The inset demonstrates the linear temperature dependence of C_p as $T \rightarrow 0K$. Data are from Ott et al. [1:26].

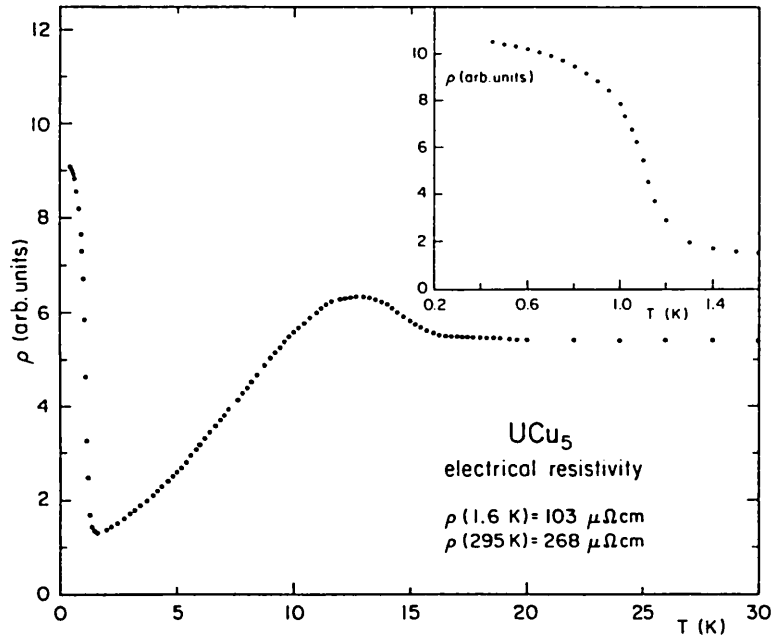


Figure 1:14(b). Temperature dependence of the electrical resistivity of UCu_5 below 30K. The inset shows the low-temperature data on an expanded scale. From Ott et al. [1:26].

passes through a minimum at 1.6K and rises rapidly with decreasing temperature through the second transition. The enhanced γ of 380mJ/mol-U K² at 1.5K is reduced after the second phase transition to 86mJ/mol-U K².

1:4:5. Summary.

The properties of magnetically ordered hf systems are listed below:

1. All magnetic hf's order antiferromagnetically with T_N typically 10-20% of Θ_{CW} .
2. A simple arrangement of ordered moments whose magnitudes are much reduced from values of effective moment calculated from high temperature susceptibility data.
3. Large values for γ just above T_N . Ordering reduces γ . However γ values are still large compared with those of normal metals, suggesting the quasiparticles exist in the ordered hf state.
4. A total entropy that is much less than one would expect from a collection of disordered moments.

Table 1:3. Values of T_N and magnetic moments above and below T_N .

Material	$T_N(K)$	$\gamma (T>T_N)$ (mJ/molK ²)	$\gamma T<(T_N)$ (mJ/molK ²)	μ_{eff} (μ_B/U)	μ_{eff} (μ_B/U)
U ₂ Zn ₁₇	9.7 [1:24]	550 [1:24]	198 [1:24]	2.25 [1:24]	0.8 [1:24]
UCd ₁₁	5 [1:23]	840 [1:23]	250 [1:23]	3.45 [1:23]	----
UCu ₅	15.2 [1:51]	----	380 [1:51] γ enhanced below T_N	3.52 [1:7]	----

1:4:6. Superconducting Heavy Fermions.

The discovery of superconductivity in the hf compound CeCu₂Si₂ by Steglich[1:54] came as a great surprise. The C.W. like behaviour in the high temperature susceptibility suggested the presence of local moments, which are expected to suppress the onset of superconductivity by breaking the Cooper pairs. However a superconducting transition was indeed

observed at $\sim 0.5\text{K}$. In order to highlight the typical properties of superconducting hf materials this section will briefly review the data available on UBe_{13} another hf superconductor. This is because the situation in CeCu_2Si_2 is confused by extreme sample dependence of the properties[1:5].
1:4:7. UBe_{13} .

UBe_{13} is a cubic intermetallic with nearest U-U distance $5.13\text{\AA}$ [1:55]. Thus, one would expect more or less complete localization of the three 5f electrons per U ion. Bulk superconductivity in UBe_{13} was first observed by Ott et al. [1:17]. The electrical resistivity (figure 1:3(b)) increases with decreasing temperature. A narrow bump at 2.5K (as yet unexplained) is followed by a fall in the resistivity and finally the onset of superconductivity at 0.9K . As with CeCu_2Si_2 , UBe_{13} shows good C.W. type behaviour in its magnetic susceptibility at high temperature with an effective moment $\mu_{\text{eff}}=3.1\mu_{\text{B}}/\text{U}$ [1:27]. Specific heat measurements (see figure 1:15(a)) reveal an upturn in C/T with T below 7K , characteristic of a hf. Extrapolating the variation of C/T with T between 1.5 and 1.0K to 0K gives $\gamma(0)\approx 1100\text{mJ/mol K}^2$. A discontinuity in the specific heat is seen at the superconducting transition. The discontinuity of C_{el} is larger than that expected by B.C.S. theory in the weak coupling limit [1:56]. The loss in entropy associated with the transition is the best evidence that the enhanced specific heat above T_{C} is really electronic in nature, and that the superconducting state is formed by heavy mass electrons. This is because the gap formation in the electronic spectrum due to the superconductivity obviously suppresses the specific heat in a way that would be expected

if the specific heat is almost entirely due to C_{el} . The jump in specific heat δC can be used to determine parameter $\delta C/\gamma T_C$ which serves firstly to verify that the superconductivity is truly a bulk property and secondly can distinguish between weak and strong electron-electron coupling. In the B.C.S. theory

$$\delta C/\gamma T_C \approx 1.43 \Rightarrow \text{weak coupling.}$$

$$\approx 1.6 \Rightarrow \text{strong coupling.}$$

For UBe_{13} $\delta C/\gamma T_C \approx 1.65 \Rightarrow$ bulk superconductivity with strong electron-electron coupling. However, problems can arise calculating $\delta C/\gamma T_C$. Firstly γ is temperature dependent so there is the question of which value to use, $\gamma(T_C)$ or $\gamma(0)$. Secondly δC may not be sharply defined. Finally the jump in C and $\gamma(T)$ may be sample dependent. UBe_{13} , in common with all the other hf superconductors, is type II. Measurement of $\rho(T)$ in a magnetic field shows that the superconductivity is extremely stable with respect to magnetic fields [1:57]. In low field, T_C is hardly suppressed at all. The temperature derivative in dH_{C2}/dT at T_C of the order of -0.5MOe/K is very large (see figure 1:15(b)), (at the time the highest value ever observed for a bulk three dimensional superconductor). Other hf superconductors also have large values for dH_{C2}/dT ($CeCu_2Si_2$ -230kOe/K [1:57], UPt_3 -63kOe/K [1:58]) The slope of dH_{C2}/dT changes rapidly around 20kOe dropping to a value $\approx -100\text{kOe/K}$. $H_{C2}(T)$ then varies linearly with temperature between 0.7K and 50mK . The magnitude of H_{C2} , determined resistively at 0K , of 100kOe is large for a superconductor with a T_C of 1K . In contrast to $CeCu_2Si_2$, UBe_{13} has an anomalously large, negative magneto-resistance at low temperature[1:59]. The resistivity (figures

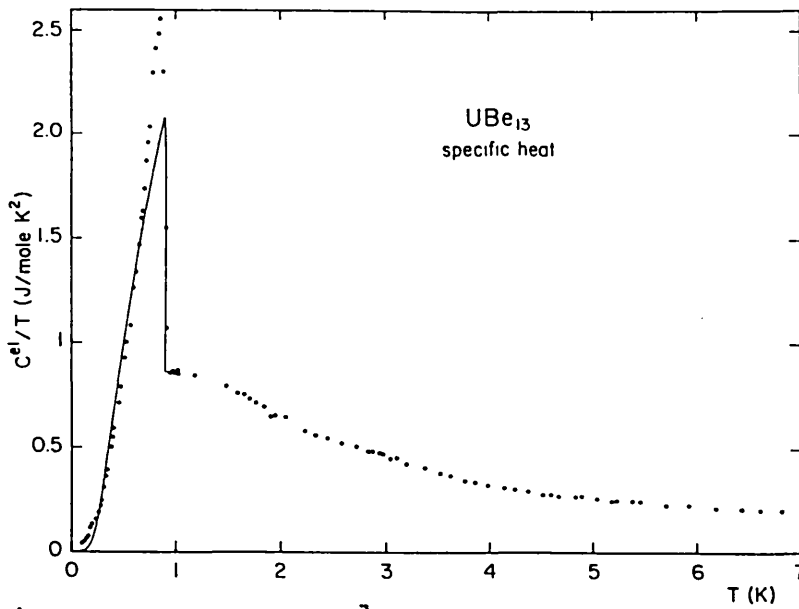


Figure 1:15(a). C_p^{el}/T versus T for UBe_{13} between 0.15 and 7K. The solid line indicates the expected temperature dependence in the superconducting state from BCS theory. Data are from Ott [1:6].

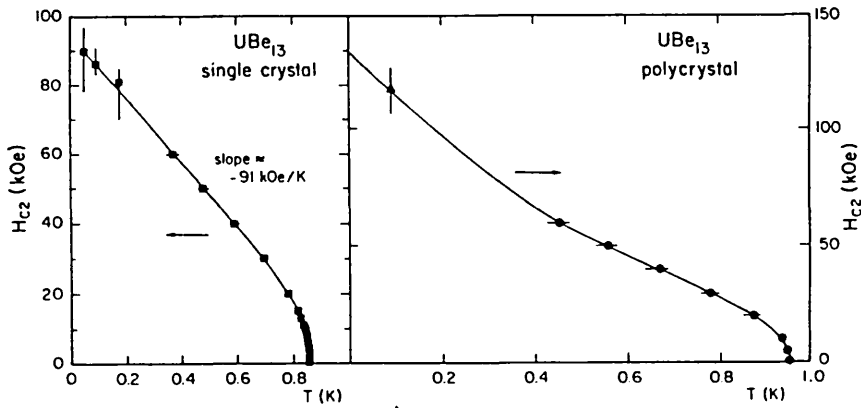


Figure 1:15(b). Temperature dependence of the upper critical magnetic field H_{C2} for poly- and single-crystalline UBe_{13} . Data are from Chen et al. [1:58] and Maple et al. [1:57].

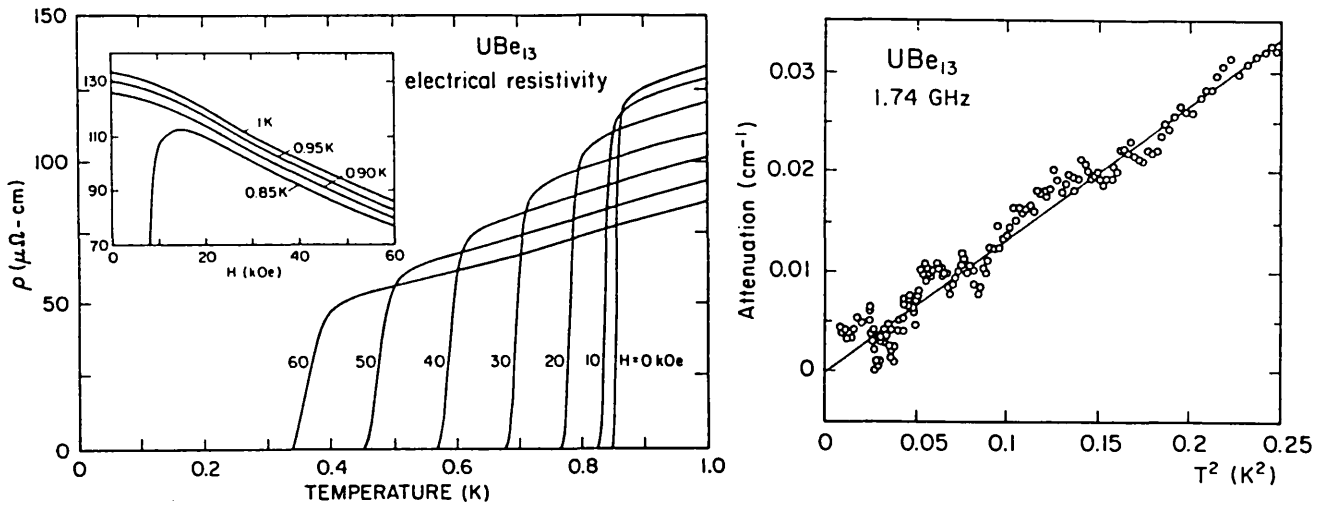


Figure 1:15(c). Influence of external magnetic fields on the low temperature electrical resistivity of UBe_{13} as reported by Maple et al. [1:57].

Figure 1:15(d). T^2 dependence of the ultrasound attenuation of UBe_{13} well below the superconducting transition temperature. Data are due to Golding et al. [1:60].

1:3(b) and 1:15(c)) ($\rho(T_C)=100\mu\text{ohm cm}$) can be lowered either by lowering the temperature or by increasing the field. This shows that UBe_{13} is not an intrinsically dirty or disordered system. It also shows that the coherence effect seen in "normal" hf materials have not set in at T_C in UBe_{13} . That is, increasing H pushes UBe_{13} towards the normal state allowing coherence effects to set in. Perhaps the most interesting of all the experimental properties exhibited by UBe_{13} , is evidence to suggest that the superconductivity observed in this and other hf materials may not be of the s state isotropic type usual in the B.C.S theory. It is suggested that the superconductivity may be anisotropic p or d type. B.C.S. theory leads to the prediction of an exponential temperature dependence of properties such as specific heat, ultrasound attenuation, thermal conductivity and N.M.R relaxation. Anisotropic superconducting states may have point or lines of zeroes in the energy gap and these in turn can lead to a non-exponential temperature dependence in the thermal and transport properties such as those mentioned above. Such non-exponential temperature dependence has been observed. For example, the specific heat in UBe_{13} varies with a T^3 power law [1:59], whilst the ultrasound attenuation follows a T^2 law at temperatures well below T_C (see figure 1:15(d)) [1:60]. These deviations cannot be attributed to impurities and may point to an unusual mechanism driving the hf superconductivity.

1:4:8. Summary.

1. All hf superconductors are of type II.
2. All have low transition temperatures ($\approx 1\text{K}$) with large values of (dH_{C2}/dT) at T_C and $H_{C2}(0\text{K})$. In all cases a discontinuity in C_{e1} and the entropy associated with the transition indicate that it is the heavy electrons which form

the superconducting state.

3. Non-exponential temperature dependence of the specific heat, ultrasound attenuation etc., points to the possibility that they may exhibit p or d-wave superconductivity.

Table 1:4. Some important parameters for superconducting hf.

Material	$\gamma(0)$ mJ/molK	T_C (K)	$-dH_{C2}/dT$ kOe/K	$\delta C/\gamma T$ mJ/molK U or Ce
CeCu ₂ Si ₂	1100	0.65	230[1:57]	.69-1.23[1:5]
UBe ₁₃	1100[1:56]	0.9[1:17]	500[1:57]	1.65 [1:57]
UPt ₃	450 [1:5]	0.54[1:5]	63 [1:58]	0.25-1.0 [1:5]

1:4:9. Magnetic and Superconducting Heavy Fermions.

This section looks at those hf materials which have both a magnetically ordered and a superconducting state at different temperatures and pressures. UPt₃ [1:61] and URu₂Si₂ [1:62] both show evidence to suggest a transition into an antiferromagnetically ordered state is followed at a lower temperature by a superconducting transition.

1:4:9. URu₂Si₂.

Looking in more detail at URu₂Si₂ it can be seen that the properties of both the magnetic and the superconducting state show the typical features of hf materials outlined above. The magnetic transition occurs at 17.5K (see figures 1:16(a) and (b)). A λ like anomaly is seen in the specific heat γ reminiscent of U₂Zn₁₇. Extrapolating the high temperature to T=0K (=180mJ/mol-U K²) gives a negative entropy balance for the transition of -1.38J/mol-U K (c.f. -1.37J/mol-U K for U₂Zn₁₇). The change in γ from the extrapolated high temperature value to that observed at low temperature ($\gamma_{\text{ext}} - \gamma_{\text{obs}}$)/ γ_{ext} is 70% (c.f. 70% for U₂Zn₁₇). The low temperature transition to the superconducting state is seen as a drop in resistivity at 1K. A calculation from the peak

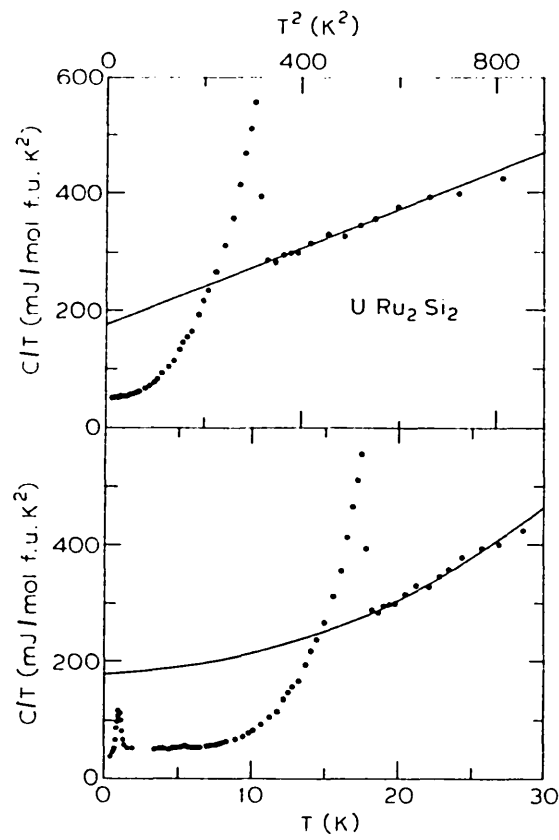


Figure 1:16(a). C_p versus T^2 of URu_2Si_2 (above) yielding γ and Θ_D , and C/T versus T (below) showing the entropy balance. Data are from Palstra [1:62].

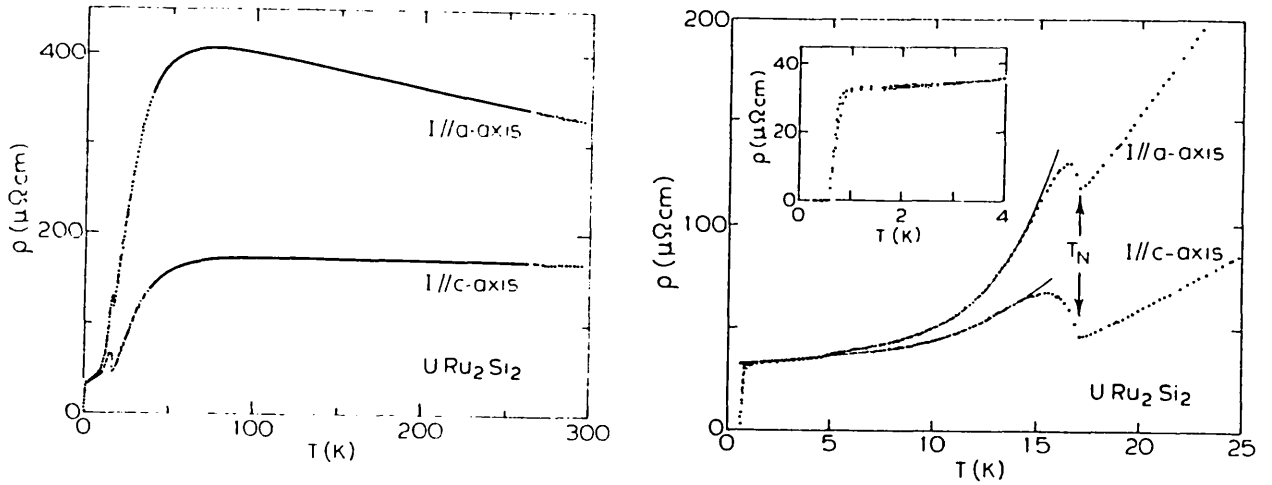


Figure 1:16(b). Temperature dependence of the electrical resistivity of a single crystal of URu_2Si_2 parallel to the a- and c-axes. From Palstra [1:62].

Figure 1:16(c). Low temperature resistivity of a single crystal of URu_2Si_2 parallel to the a- and c-axes showing the magnetic (T_N) and superconducting (T_C) phase transitions. The inset shows the superconducting transition on an expanded scale. Data are from Palstra [1:62].

seen in the specific heat at T_C of the discontinuity in specific heat (δC) suggests bulk superconductivity. This is confirmed by magnetisation measurements at low temperature.

1:5. Regularities and Phenomenological Trends in Heavy Fermion Systems.

Although hf materials show varied and complicated behaviour over a large number of different systems, several properties are common to all the hf alloys. Heavy fermion materials always involve rare earth or actinide elements with partially filled f shells. In all hf compounds the distance between the atoms carrying these electrons is sufficient to prevent the formation of f electron energy bands by direct f-f overlap. This condition requires that the f atom spacing must be greater than $3.4\text{\AA}$ [1:63], the Hill limit. Another feature common to all hf materials is the position in the periodic table of the atoms combining with the Ce or U atoms [1:7]. These are found at the end of the d block (Cu, Zn) or the end of the s-p block (Be, Al). It seems that formation of the hf state requires that only a small number of states are available for hybridisation with the f electrons [1:64]. However these two criteria are not sufficient to predict which compounds will form hf materials and their discovery is still a matter of trial and error. Several authors have searched for experimental trends which allow a better understanding of the hf state. The values of the low temperature specific heat and magnetic susceptibility are enhanced in all the hf materials. However Jones et al. [1:65] have noted that plotting the quantities on a per f atom basis reveals the deviations from normal metal behaviour are not quite as dramatic as might first appear. The Wilson ratio

$$W = \frac{\chi(0)/g^2 J(J+1)\mu_B^2}{\gamma(0)/\pi^2 k_B^2} \text{ ----- } 1:23.$$

gives a measure of the enhancement of the magnetic susceptibility over the specific heat. The value of W for a ordinary metal in a simple free electron theory is given by the solid line in figure (1:17). The values of W for hf materials lies very close to this line. As yet this trend is not well understood.

DeLong [1:66,1:67] has presented a study of the values of χ^* the total (enhanced and uncorrected) magnetic susceptibility and the coefficient of electronic heat capacity γ^* for a large number of narrow band and hf materials. A diagram (see figure 1:18) of an enhanced ratio R vs. γ^* was then constructed, where R is defined by

$$R = \lim_{\substack{T=0 \\ \text{or } T=T_c}} 1/3(\pi k_B/\mu_B)^2 (\chi T/C_{el}^*) \text{ ----- } 1:24.$$

R is evaluated at the lowest possible temperature above the onset of any co-operative phase transition. DeLong observed several trends in this R vs. γ^* :

1. Magnetic order is observed only for $\gamma^* \geq \gamma_m = 4 \times 10^4 \text{ erg/cm}^3 \text{ K}^2$. A number of additional magnetic materials which were difficult to include on the R vs. γ^* plot were also discussed. These included ferromagnetic materials (for which $R \rightarrow \infty$ at the ordering temperature) and certain antiferromagnets (for which γ^* could not be calculated at the ordering temperature). These results show $\gamma^* \geq \gamma_m$ holds for these materials also.

2. There are no superconductors observed in the subregion of magnetic order defined by $\gamma_m^* \leq \gamma^* \leq 10^5 \text{ erg/cm}^3 \text{ K}^2$.

3. A small cluster of superconducting hf's UBe_{13} , CeCu_2Si_2 and UPt_3 all occur near $\gamma^* \approx 1 \times 10^5 \text{ erg/cm}^3 \text{ K}^2$ and $R \approx 1$. This cluster is isolated by a region of magnetic order from other materials exhibiting superconductivity. This isolation of hf superconductors by a region of magnetic order suggest an extremely delicate balance exists between magnetic order and superconducting ground state, if not a common mechanism. To add weight to this argument DeLong examined URu_2Si_2 which shows antiferromagnetic order at 17.5K and superconductivity with $T_c \approx 1.4\text{K}$. Above 17.5K $\gamma^* \approx 3.1 \sim 3.7 \times 10^4 \text{ erg/cm}^3 \text{ K}^2$, $R \approx 1.6$.

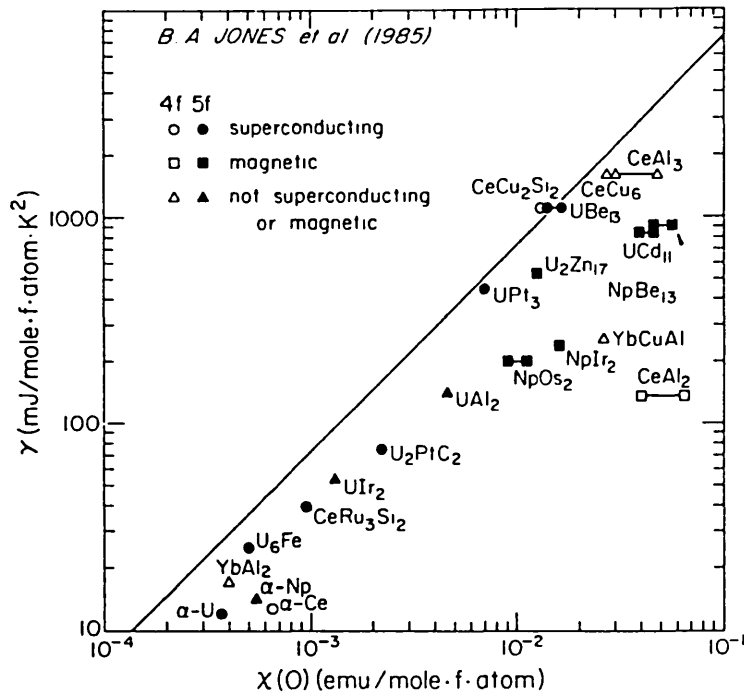


Figure 1:17. The specific heat coefficient versus the susceptibility for some hf systems. The values are extrapolated to zero by a variety of methods. Any free, non-interacting Fermion gas would lie on the straight line. From Jones et al. [1:65].

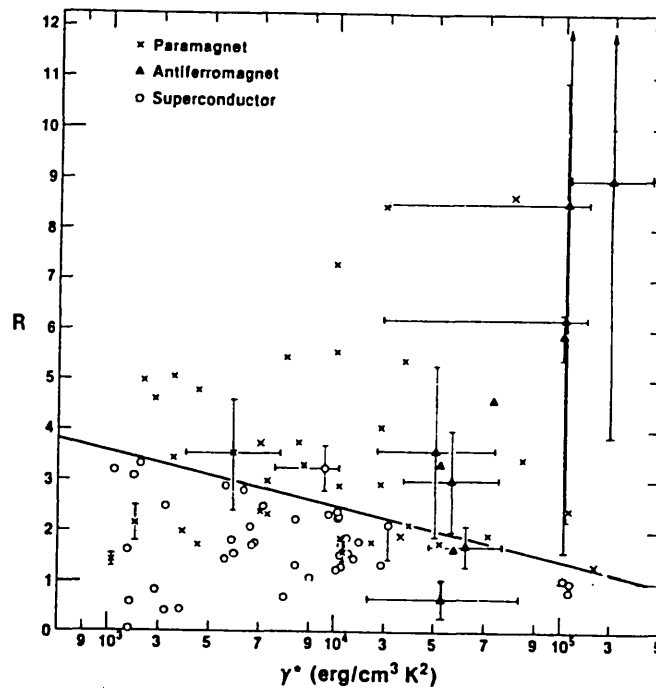


Figure 1:18. Enhancement ratio R versus electronic heat capacity coefficient γ^* for various A15-, AuCu₃-, NaCl-type transition-metal compounds, noble transition elements, Ce, U, Yb and Np compounds, SmS (high pressure), and PuBe₁₃. The solid diagonal line denotes the critical value R_C above which superconductivity does not generally occur. Error bars reflect the difficulties in estimating γ^* for certain antiferromagnets or sample dependence of R and γ^* . N.B. Cu has $\gamma^* \sim 0.7 \text{ mJ/mole K}^2 \leftrightarrow \sim 1 \cdot 10^3 \text{ erg/cm}^3 \text{ K}^2$. From DeLong [1:66].

Below 17.5K $\gamma^* \approx 1 \sim 1.4 \text{ erg/cm}^3 \text{ K}^2$ and $R \approx 3.5$. So the values for URu_2Si_2 are on the borderline of γ_m^* , and are consistent with the idea that in superconductivity and magnetic order in this system are of comparable stability.

4. All superconducting materials fall below a diagonal line indicating a critical value $R_C(\gamma^*)$ above which superconductivity is not seen to occur.

5. Nearly all materials have $1 \leq R \leq 10$.

6. Paramagnetic materials appear throughout the R vs. γ^* plane.

The correlation between the heat capacity data and the observation of magnetic or superconducting ground state can be related to the Fermi temperature T_F and the Debye temperature Θ_D where

$$T_F = \pi^2 k_B \Phi / 2 C_{el} = \pi^2 k_B \Phi / 2 \gamma^* \text{ ----- 1:25(a).}$$

Φ =fermion density Z/Ω (Z =number of fermions per unit volume Ω). Θ_D is extracted from T^3 term of the lattice heat capacity

$$\beta = (12\pi^4/5) * (k_B N_A) * (1/(\Theta_D)^3) \text{ ----- 1:25(b).}$$

It was found that "conventional" superconductivity occurs for $T_F \gg \Theta_D$. Magnetic order commences when $T_F \geq \Theta_D$ and hence superconductivity and magnetic order can be associated with cases where $T_F < \Theta_D$. T_F and Θ_D define characteristic cut off energies for Coulomb and electron-phonon interaction respectively and the nature of the superconducting pairing will depend on their relative sizes. For $T_F \gg \Theta_D$ electron-phonon singlet pairing interaction dominates and "conventional" B.C.S. superconductivity is observed. For $T_F \geq \Theta_D$ Bedell and Quader [1:68] have suggested that singlet and paramagnon triplet pairing interactions will suppress one another allowing magnetic order to occur. When $T_F < \Theta_D$ non B.C.S. superconductivity interactions are suggested to be more favourable in a more stringent competition with magnetic correlations.

1:6. Effects of Chemical Substitution.

1:6:1. Introduction.

Chemical substitution can be used to gain a greater understanding of the hf state. All the work detailed in this thesis has involved investigating the effects of alloying. As an introduction, some examples of the wide range of effects which can result from alloying are presented.

1:6:2. $\text{Ce}_x\text{La}_{1-x}\text{Cu}_2\text{Si}_2$.

For $x \leq 0.2$ this system shows a logarithmic increase in $\rho(T)$ down to low temperature indicating that the Ce ions are acting as individual Kondo scatterers [1:69,1:70]. For $0.2 \leq x \leq 0.7$, Kondo like behaviour is again observed in $\rho(T)$. However at low temperature a maximum in the resistivity and a sharp kink in the magnetic susceptibility indicates the onset of magnetic spin freezing (see figure 1:19). For $x \geq 0.7$ this transition is removed as CeCu_2Si_2 becomes a Kondo lattice, with a suppression in the magnitude of the low temperature Ce magnetic moment and the onset of coherent scattering. It is hoped that some extension of the theory, developed to provide an exact solution to the single Kondo impurity problem, may lead to a greater understanding of the formation of the hf state. For a more detailed discussion see chapter 2.

1:6:3. $\text{U}(\text{Pt}_{1-x}\text{Au}_x)_5$.

Changing the chemical composition of a system can lead to the formation of a hf material. UPt_5 has a cubic AuBe_5 type structure with a U-U distance of $5.25\text{\AA}$. This large separation appears to be more favourable to the formation of a hf state than the case of the hf UPt_3 which has a U-U separation of $4.13\text{\AA}$, about $1\text{\AA}$ less. However specific heat measurements by Ott et al.[1:71] (see figure 1:20) have shown that γ

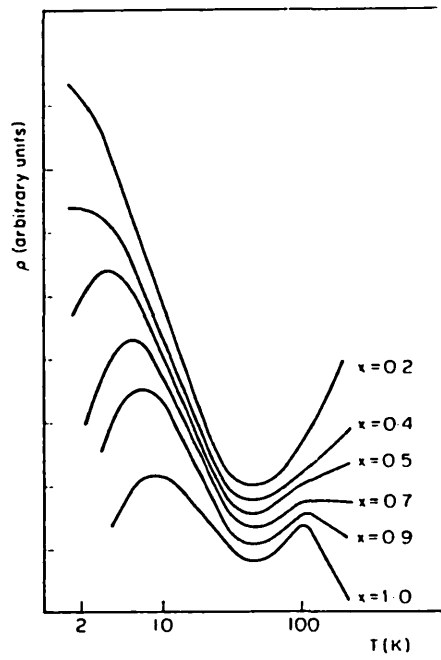


Figure 1:19(a). Temperature dependence of the electrical resistivity of some $\text{Ce}_x\text{La}_{1-x}\text{Cu}_2\text{Si}_2$ alloys. Data are from Aliev et al. [1:69].

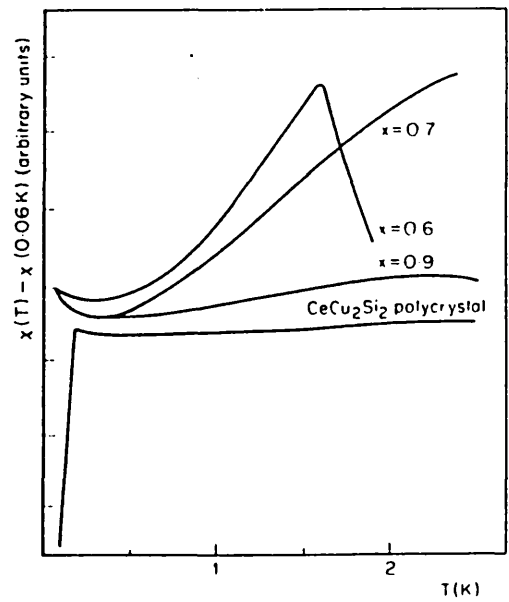
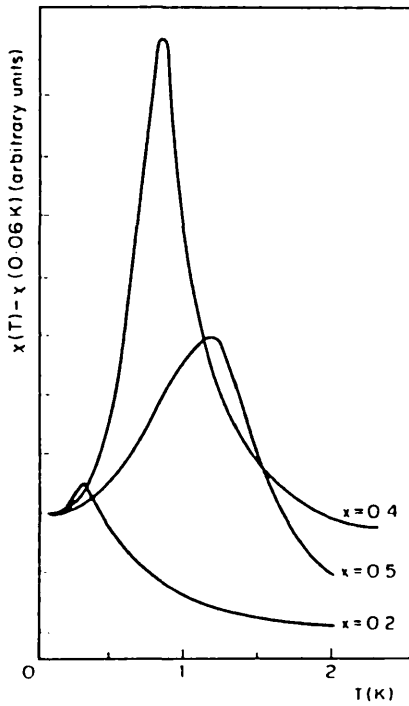


Figure 1:19(b). Temperature dependence of the susceptibility of some $\text{Ce}_x\text{La}_{1-x}\text{Cu}_2\text{Si}_2$ alloys. Data are from Aliev et al. [1:69].

approaches a value of 90 mJ/mol K^2 as $T \rightarrow 0 \text{ K}$. A $T^3 \ln T$ term in the low temperature ($T < 6 \text{ K}$) specific heat is suggestive of the presence of spin fluctuations. De-Visser et al. [1:25] found a T^2 dependence in ρ below 5 K . Ott et al. [1:71] investigated the effect of replacing one Pt atom per formula unit with Au (d U-U UAuPt_4 is $5.285 \text{ \AA}$ a change of 0.7%). The magnitude of $\rho(T)$ of UAuPt_4 is clearly enhanced with respect to that of UPt_5 . The temperature dependence of $\rho(T)$ is reminiscent of the hf UCd_{11} and U_2Zn_{17} . The low temperature resistivity falls but not by the orders of magnitude seen in other hf which indicates the onset of coherence. UAuPt_4 can form an ordered compound when the Au atoms occupy the Be sites that form large tetrahedra in the AuBe_5 structure. Samples of UAuPt_4 of sufficiently high quality are expected to show a much lower residual resistivity and possibly a transition at low temperature into a superconducting state. C/T plots for UPt_5 and UAuPt_4 show that above 15 K the specific heat of UAuPt_4 is only slightly enhanced over that of UPt_5 . However below 15 K the enhancement increases steadily. At 5 K UAuPt_4 shows an upturn in C/T v T similar to that seen in other hf materials. γ as $T \rightarrow 0 \text{ K}$ extracted from measurements made down to 0.15 K show $\gamma(T=0 \text{ K}) = 725 \text{ mJ/mol K}^2$. This is eight times larger than $\gamma(T=0 \text{ K}) = 90 \text{ mJ/mol K}^2$ for UPt_5 .

1:6:4. $\text{U}(\text{Cu}_{1-x}\text{Ni}_x)_5$ and $\text{U}(\text{Cu}_{1-x}\text{Ag}_x)_5$.

Chemical substitution can destroy or enhance the hf state. Both UNi_5 and UCu_5 crystallise into the AuBe_5 structure with U-U distances of $4.796 \text{ \AA}$ and $4.973 \text{ \AA}$ respectively. Continuous replacement of Cu with Ni [1:71] leads to a rapid and drastic changes in the low temperature behaviour of the $\text{U}(\text{Cu}_{1-x}\text{Ni}_x)_5$ system. Substitution of 1% of Ni impurities on the Cu sites

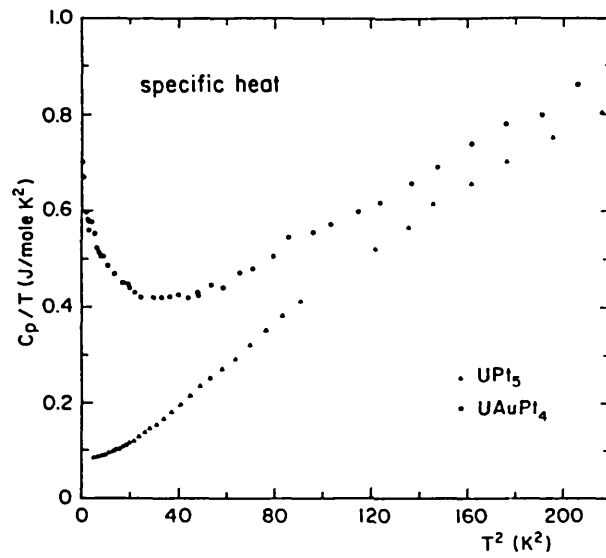


Figure 1:20(a). C_p/T versus T^2 for UPt_5 and $UAuPt_4$ below 15K. Data are from Ott [1:6] and Ott et al. [1:71].

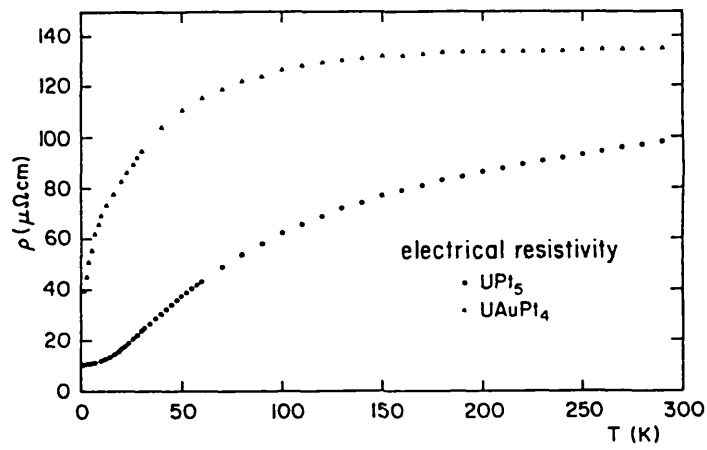


Figure 1:20(b). Temperature dependence of the electrical resistivity of UPt_5 and $UAuPt_4$ between 1.2 and 300K as reported by Ott et al. [1:71].

does not greatly effect the overall specific heat. But these impurities are sufficient to suppress the enhancement in C/T which begins in pure UCu_5 at 4K (see figure 1:21). Resistivity measurements performed on UCu_5 and $U(Cu_{0.95}Ni_{0.05})_5$ [1:6] reveal that the Ni doped material has an absolute resistivity at 1.5K double that of UCu_5 at the same temperature. Thus the fall in $\rho(T)$ associated with the formation of the hf state is also suppressed. In contrast the addition of 20% of Ag on the Cu sites of UCu_5 produces an enhancement in the temperature of the antiferromagnetic transition seen in pure UCu_5 from 15K to ≈ 17.5 K. At lower temperature the second phase transition at 1K which removes the enhancement in the specific heat is suppressed. This leads to a value of $\gamma(T \rightarrow 0K)$ of 310mJ/mol K^2 compared with $\gamma(T \rightarrow 0K)$ of 86mJ/mol K^2 for pure UCu_5 .

1:6:5. $U_2(Zn_{1-x}Cu_x)_{17}$.

Alloying can suppress the magnetic ordering seen in hf materials without much affecting the value of γ above the ordering temperature. Willis et al.[1:72] have examined the effect on the magnetic ordering of U_2Zn_{17} of replacement of U with Th and Zn with Cu(see figure 1:22). Pure U_2Zn_{17} has an ordering temperature T_N of 9.7K. Replacement of 10% of U by Th reduces T_N to 7.5K. The resistivity changes with a fall in ρ at T_N in pure U_2Zn_{17} removed, to be replaced by an increase in ρ at low temperature. Replacement of 2% Zn with Cu removes completely any signs of magnetic order in $\chi(T)$. The shape of $\rho(T)$ curve is unchanged with the drop in ρ moving to lower temperature. γ values above T_N are largely unaffected by substitution on either site. All substitutions reduce T_N , but replacement of Zn with Cu is much more effective in removing

the magnetism than Th on the U sites.

1:6:6. $U(Pt_{1-x}Pd_x)_3$ and $(U_{1-x}Th_x)Pt_3$.

Alloying can help in the understanding of superconducting hf materials like UPt_3 . The presence of spin fluctuation effects have been suggested to help explain the low temperature properties (e.g. the $T^3 \ln(T/T^*)$ term in the specific heat). There has also been speculation that the superconductivity is p wave mediated by spin fluctuations. Several groups [1:73,1:74,1:75,1:76,1:77,1:78] have investigated the effect of substitution of Pt in UPt_3 with isoelectronic Pd. The superconductivity in pure UPt_3 is completely suppressed by small amounts of Pd. No superconductivity was observed in $U(Pt_{0.99}Pd_{0.01})_3$ down to 40mK. Addition of small amounts of Pd ($x \leq 0.10$) also enhances C/T (see figure 1:23). The determination of the low temperature value of γ is ambiguous but amounts to 600 or 700mJ/mol K² (c.f. $\gamma(=0)=422$ mJ mol K² for pure UPt_3). This effect is attributed to a reduction in the spin fluctuation temperature T^* . These results do not point to a close relationship between the superconductivity and the spin fluctuations. The addition of Pd also leads to a rapid increase in the residual resistivity and a replacement of T^2 term in the resistivity with a term linear in T . This points to a strong influence of alloying on the electronic transport properties and could be a reason for the loss of superconductivity. Anomalies in C/T for $0.02 < x < 0.10$ Pd are seen in low temperature data. The temperature at which maximum in C/T , T_{max} occurs is almost constant for $0.04 < x < 0.08$ whilst it falls by $\approx 40\%$ for $x=0.02$ and $x=0.10$. In a field of 5.5T, T_{max} for $x=0.06$ decreases from 5.83 to 5.26K. These anomalies are also seen in thermal expansion

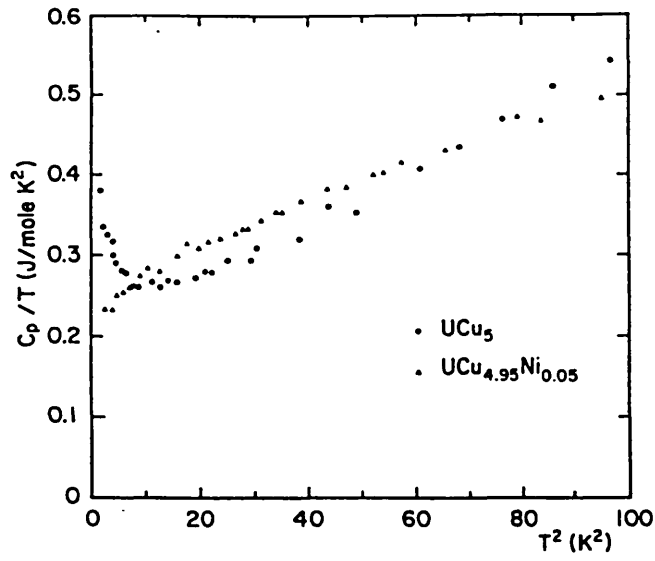


Figure 1:21. C_p/T versus T for UCu_5 and $UCu_{4.95}Ni_{0.05}$ between 1.5K and 10K. Data are from Ott et al. [1:6].

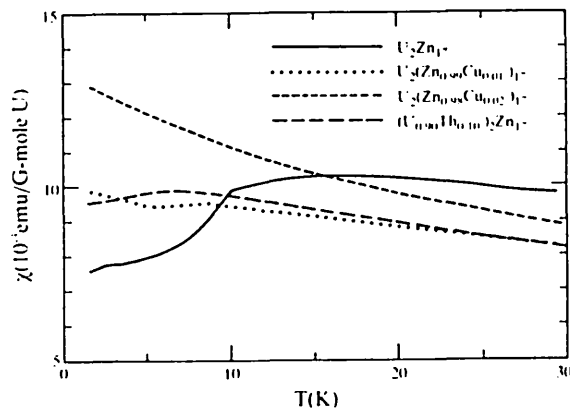


Figure 1:22(a). Magnetic susceptibility for pure and substituted U_2Zn_{17} as measured by Willis et al. [1:72].

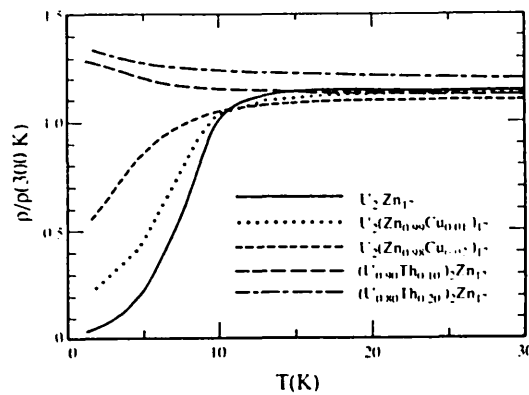


Figure 1:22(b). Electrical resistivity versus temperature for pure and substituted U_2Zn_{17} as reported by Willis et al. [1:72].

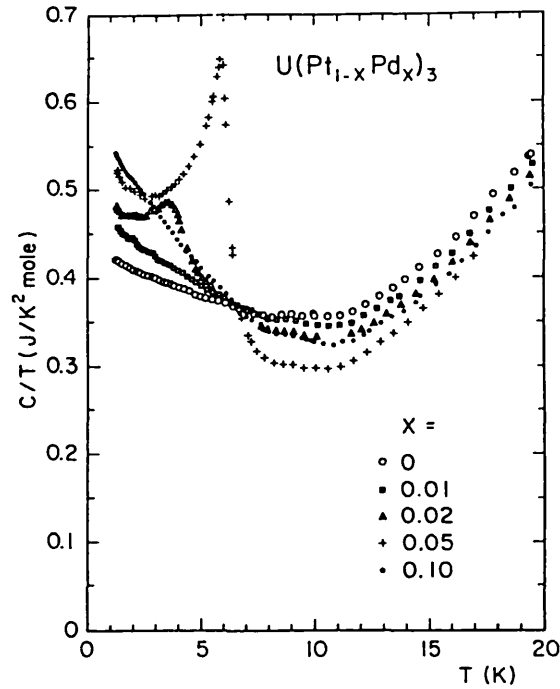


Figure 1:23. Influence of Pd substitution on Pt sites on the low temperature specific heat of UPt_3 as reported by de Visser et al. [1:73].

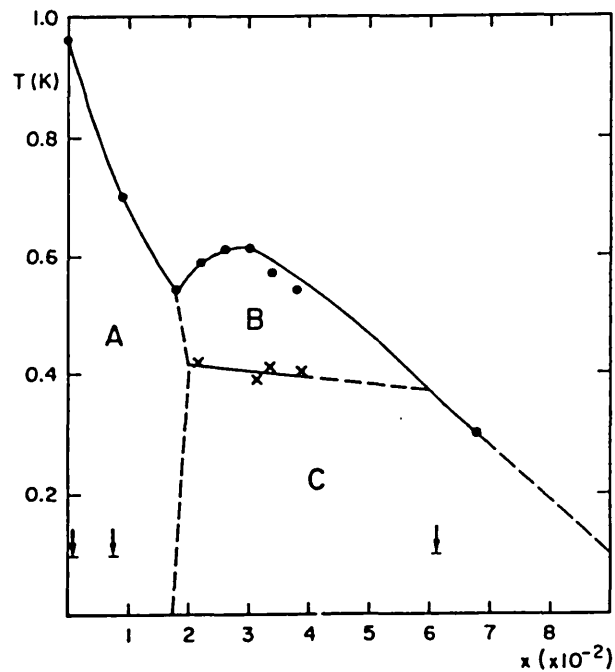


Figure 1:24. Proposed phase diagram $\text{U}_{1-x}\text{Th}_x\text{Be}_{13}$ in the temperature-impurity plane. A, B, and C are different anisotropic superconducting phases. Dashed lines indicate the proposed separation of the phases. The arrows indicate temperatures above which there is definitely only one phase transition.

data and the magnetic susceptibility. The susceptibility of $x=0.06$ sample is enhanced ($\approx 12 \times 10^{-3}$ emu/mol) compared with 6×10^{-3} emu/mol for pure UPt_3 . There is a clear peak in $\chi(T)$ at $\approx 6\text{K}$. All this points to an antiferromagnetic transition. Frings et al. [1:79] confirmed this expectation, reporting that neutron data indicated $\text{U}(\text{Pt}_{0.095}\text{Pd}_{0.05})_3$ is antiferromagnetically ordered at low temperature. Introduction of strain into doped samples (e.g. by grinding) can remove the low temperature anomalies in χ and C/T . Ramirez et al. [1:80] examined the effect on UPt_3 of dilution with Th on U the sites. The addition of a small amount of Th ($x \leq 0.02$) rapidly suppresses T_C to below 50mK. For higher Th concentrations a peak is observed in the magnetic susceptibility at $\approx 7\text{K}$, which coincides with a peak in C/T and an inflexion point in $d\rho/dT$. These features occur at nearly constant temperature up to 10% Th concentration, but disappear for 20% Th. It is suggested that the superconducting transition is replaced by these anomalies which are caused by Fermi surface instabilities (spin density waves) brought about by doping induced strain. These findings for both Pd and Th alloying lend weight to the idea that spin fluctuations in UPt_3 can lead to either superconductivity or a magnetic ground state depending on the details of the Fermi surface, which can be easily modified.

1:6:7. CeCu_2Si_2 .

Varying the stoichiometry of hf materials can drastically effect the low temperature properties. A good example of a hf system in which the properties are extremely sample dependent is CeCu_2Si_2 . Ishikawa et al.[1:81] found that decreasing the Cu content in CeCu_2Si_2 depresses the superconducting

transition from 0.5K for CeCu_2Si_2 to 0.007K for $\text{CeCu}_{1.95}\text{Si}_2$. The sharpest and highest temperature transition (0.67K) they recorded was for Cu rich Si poor $\text{CeCu}_{2.125}\text{Si}_{1.9625}$. Steglich [1:82] reported that T_C was depressed below 0.04K between $\text{CeCu}_{1.95}\text{Si}_2$ and $\text{CeCu}_{1.9}\text{Si}_2$. Variations in Ce and Si content produced less rapid fluctuations in T_C . Later Rauchschalbe et al. [1:83] showed that the transition temperature varied smoothly between 250mK for Cu poor $\text{CeCu}_{1.82}\text{Si}_2$ and 740mK for Cu rich $\text{CeCu}_{2.2}\text{Si}_2$, with the residual resistivity $\rho_0=100\mu\text{ohm cm}$ in $\text{CeCu}_{1.8}\text{Si}_2$ dropping to $1.5 \mu\text{ohmcm}$ for annealed $\text{CeCu}_{2.2}\text{Si}_2$. Thus effects of varying the stoichiometry of hf materials can be as drastic as alloying

1:6:8. $(\text{U}_{1-x}\text{Th}_x)\text{Be}_{13}$.

Alloying in hf materials can produce more complicated effects than just the enhancement or destruction of the ground state properties peculiar to a given system. A good example of this is replacement of U with Th in the hf superconductor UBe_{13} [1:84-1:88]. Addition of a small amount of Th on the U sites in $(\text{U}_{1-x}\text{Th}_x)\text{Be}_{13}$ reduces T_{C1} from $\approx 0.9\text{K}$ for $x=0$ to $\approx 0.5\text{K}$ for $x=0.0175$. Between $0.0175 < x < 0.03$ T_{C1} begins to rise again and passes over a broad maximum centred around $x=0.03$ at a temperature $\approx 0.625\text{K}$. As the Th content is increased above $x=0.03$ T_{C1} again begins to fall with $T_{C1} \approx 0\text{K}$ at approximately 10% Th. In the region for $0.0175 < x < 0.06$ a second feature shows up at a temperature T_{C2} below the first superconducting transition. There is some uncertainty about the interpretation of this second transition. It definitely does not destroy the superconductivity. No ordered moments bigger than $0.01\mu_B/\text{U}$ were detected below T_{C2} using N.M.R, $\mu\text{S.R.}$ or neutron diffraction techniques. A structural transition could

not be definitely ruled out but is thought to be unlikely because in magnetic fields the temperature of the second transition T_{C2} is shifted to lower temperature in a similar way to the first superconducting transition. However Batlogg et al. [1:87] reported measurements on ultrasound attenuation and changes in the sound velocity in $(U_{1-x}Th_x)Be_{13}$. They suggested that the second transition was magnetic in origin with a coexistence of anisotropic superconductivity and antiferromagnetic order below T_{C2} . Joynt et al. [1:87] reinterpreted the data, suggesting the second transition is between different anisotropic superconducting phases and that the low temperature phase is tetragonally distorted. They proposed a phase diagram for in which $(U_{1-x}Th_x)Be_{13}$ has 3 distinct superconducting phases at different temperatures and values of x (see figure 1:24.).

1:6:9. Summary.

Some effects of chemical substitution are summarized below:

1. Substitution on the rare earth or actinide sites leads to a dilution in the number of magnetic centres In this way it is possible to study a continuous progression from a normal metal through the dilute Kondo impurity regime and up to the hf dense Kondo compounds (e.g. $Ce_xLa_{1-x}Cu_2Si_2$, $Ce_xLa_{1-x}Cu_6$, $Ce_xLa_{1-x}La_3$, $Ce_{1-x}LaAl_2$).
2. Alloying has been used to create (e.g. UPt_5+Au), destroy (e.g. UCu_5+Ni) or enhance (e.g. UCu_5+Ag) the hf state.
3. The effects of alloying on the onset of magnetism (e.g. $U_2Zn_{17} + Cu$ and Th) and superconductivity (e.g. $UPt_3 + Pd$ and Th) have been examined to try and elucidate the mechanism responsible for such behaviour.
4. The effect of varying the stoichiometry of the hf material (e.g. $Ce_{1+\delta x}Cu_{2+\delta y}Si_{2+\delta z}$) have been investigated.
5. Complex behaviour involving two or more transitions of different origin can be produced by alloying (e.g. $U_{1-x}Th_xBe_{13}$).

Chapter 2. Theories of Heavy Fermions

2:1. Introduction.

In this chapter, some of the ideas which have been used to develop an explanation of the properties of heavy fermions are discussed. Some of the concepts which will prove helpful in the the analysis of the data presented in later chapters will also be introduced. Section 2:2 looks at some of the different types of electron interactions that can occur within solids. Using some of the ideas introduced in section 2:2, section 2:3 looks at the concept of the virtual bound state and reviews some of the experimental consequences of the formation such a state. In section 2:4 the Kondo effect is introduced. In section 2:5 these ideas are extended to consider a concentrated system of Kondo scattering impurities. In section 2:6 the effects of placing these Kondo scattering centres on a periodic lattice to form a concentrated Kondo lattice are briefly reviewed. Finally, section 2:7 looks at the effects of the competition between the Kondo and RKKY interactions in determining the ground state properties of hf systems.

2:2. Electron Interactions.

2:2:1. Introduction.

In this section the types of coupling between electrons are briefly reviewed. The interactions are of great importance since they are responsible, either directly or indirectly for a wide variety phenomena observed in condensed matter physics. These include the Kondo effect, the virtual bound state (VBS) and magnetic ordering.

We can divide the types of exchange interaction between electrons into three groups. Direct, indirect and hybridisation.

2:2:2. Direct Coupling.

Direct exchange mechanisms occur between electrons which are close enough together that their wavefunctions have significant overlap. In the case of electrons in the same atom (intraatomic coupling), the Pauli exclusion principle results in electrons of the same spin staying out of each others way to a greater extent than electrons with antiparallel spin. Each electron is surrounded by a void (exchange hole) due to local depletion of parallel spin electrons. Thus for electrons of like spin the repulsive Coulomb effect is reduced by the presence of an exchange hole leading to parallel spin alignment. This in turn leads to Hund's rule for filling an electron shell preferentially with like spins. The reduction in the electrons potential energy is at the expense of an increase in kinetic energy. In the case of electrons on different atoms, their greater spatial separation reduces the effect of their mutual interaction. At the same time, the importance of the interaction of the electrons with the ion cores increases. Often the increase in

kinetic energy required to give parallel alignment of electron spins outweighs the gain from the reduced Coulomb force between antiparallel electrons. Thus in the case of interatomic coupling, the electrons may align in parallel or antiparallel depending on the balance between Coulomb force and kinetic energy.

2:2:3. Indirect Coupling.

Non-magnetic ions can act as intermediaries between two well separated ions. For a more detailed discussion see Hurd [2:1]. The Ruderman, Kittel, Kasuya, Yosida (RKKY) interaction [2:2,2:3,2:4] is present in systems containing itinerant electrons. The electrons act as intermediaries between well separated ions which themselves do not interact directly. The RKKY model is an extension of earlier work by Zener [2:5] who suggested an s-d electron interaction model of the form $H_{sd} = -J_{\text{exch}} S \cdot s$ to try and explain the presence of ferromagnetic order in 3d transition metals. Zener suggested an ion possessing net spin will be able to polarize the surrounding electron fluid by means of direct s-d exchange coupling producing parallel alignment of electron spins (i.e. J is positive). The region of spin polarization can likewise couple with the spin of a nearby ion to give ferromagnetic alignment. However, since the d electrons in many transition metals are now known to be itinerant it is unlikely that s-d interaction is the true source of ferromagnetism. This type of model is more appropriate for the rare earths since the 4f moments are well localized. A magnetic ion polarizes the spins of the conduction electrons in its neighbourhood, as the conduction electrons try to screen out the magnetic moment on the ion (in the same way as their charge tries to

screen out the excess charge on the ion). The resultant spin polarization is not well localized in the vicinity of the impurity. According to the RKKY theory this leads to a coupling between atoms a relatively large distance R apart, which varies according to $(1/R^3) * (\cos 2k_F R)$. Thus a second impurity experiences an interaction whose magnitude and sign depends on its distance from the first. The existence of RKKY coupling allows for the possibility of different types of magnetic order e.g. ferromagnetic, antiferromagnetic, spin glass etc.

2:2:4. Coupling Through s-d and s-f Mixing.

Vacancies in partially filled d and f shells can survive the alloying process. This can lead to a mixing or hybridisation of outer orbitals of localized ions with delocalized orbitals containing itinerant electrons. It is possible for an itinerant electron to be temporarily captured in a pseudoatomic state around the ion before tunnelling back out into an itinerant state. The probability of an electron being captured is spin dependent. Since the Pauli exclusion principle allows only electrons of opposite spin to occupy the same orbital, the capture of electrons with spin antiparallel to the localized ion core is favoured.

2:3. Virtual Bound States.

2:3:1. Introduction.

The s-d and s-f mixing introduced in section 2:2:4 and the formation of a VBS are now discussed in more detail.

2:3:2. Virtual Bound State.

Consider the case of an impurity ion dissolved in a metallic host. If the impurity has a strong attractive potential it will form a bound state at energies below the conduction

band. With a strong repulsive potential bound states will be formed above the conduction band. These bound states are of no direct interest since they are either above E_F and are empty, or they lie below E_F forming fully occupied electron shells whose effect can be incorporated with those of the ion. Now consider the case of an ion in solution whose free ion bound states lie within the conduction band of the host. If the state remains a truly bound state it would be of indefinitely narrow energy range and of infinite lifetime. However mixing with the conduction band allows impurity electrons to escape into the conduction band. The lifetime of these states is limited. They are also broadened in energy with a width Δ and extended in space. The extent to which the state is broadened depends on both the degree of coupling with the conduction band and the strength of the potential due to the impurity. Broadening of the hybridised orbitals increases with increasing energy, but for a given energy decreases with increasing angular momentum l . Thus at the other extreme to the truly bound state, hybridisation can lead to electrons becoming completely delocalized. However for higher l states the intermediate situation known as a virtual bound state (VBS) is formed. These states are atomic like in that they are localized about a particular ion, but there is sufficient hybridisation with itinerant states of the same energy that exchange of electrons is quite likely. This is represented schematically by the cross hatched area in figure 2.1(a). Alternatively the formation of a VBS can be considered in terms of the scattering of conduction electrons. Itinerant electrons of intermediate energy comparable to those of pseudoatomic orbitals that can exist

around the ion are temporarily captured around an impurity ion in a VBS before tunnelling back into the electron fluid. Thus the formation of a VBS can be viewed as a resonant scattering event.

2:3:3. Consequences of a VBS.

Consider a number of impurities with unfilled d shells dissolved in a simple metal. At low concentrations the chance of 3d overlap is small. However hybridisation with conduction electrons and 3d shell of the impurity results in quasi-localized states, which in turn can form a mini band of virtual bound states. These VBS can hold 10 electrons divided equally among the two spin alternatives. The spin up and spin down states may be split and separated. The splitting may be due to:

1. Crystal field effects.
2. Coulomb repulsion between the electrons.
3. Direct intraatomic exchange coupling which tends to keep electrons of unlike spin apart.

This splitting may also survive the alloying process. If this splitting is large compared to Δ the width of the resonance, the VBS is magnetic (see figure 2.1(b)).

The formation of a virtual bound state close to the Fermi level effects the Fermi electrons which become temporarily bound. A maximum cross section for scattering results in a maximum phase shift, which in turns leads to maximum in resistivity per scattering impurity. This occurs when the additional density of states at the Fermi surface due to the VBS is a maximum.

The additional density of states at the Fermi surface due to the VBS. will also make a contribution to γ the electronic specific heat.

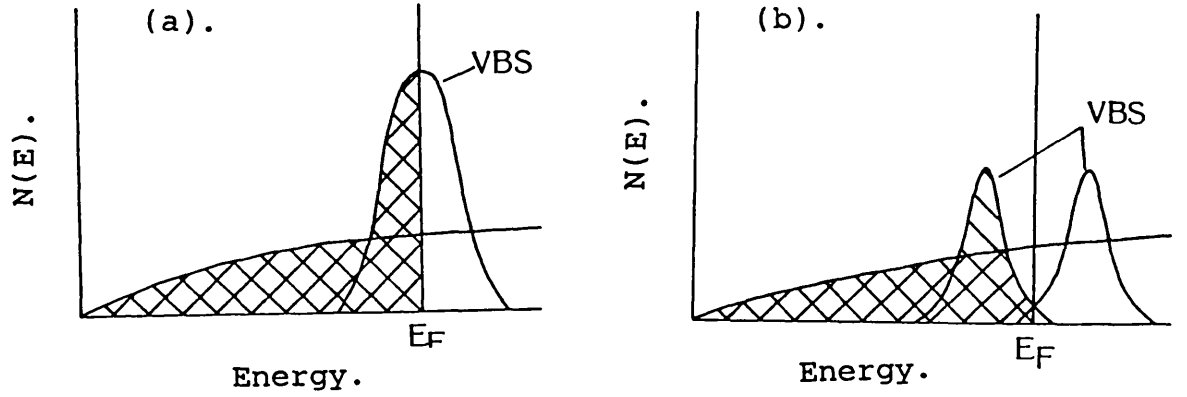
2:3:4. Experimental Manifestations of VBS.

Consider examples of the effects discussed above. First examine the case of the transition metal series Ca - Cu dissolved in Al. Here the Fermi energy is 12eV. The resonance broadening Δ which is greater for higher energies means the VBS is not spin split. Ca as a free atom has an empty d shell. Thus in solution, it is expected that its d shell will lie above the Fermi energy of the host. At the other extreme Cu has a filled d shell which is strongly bound and is expected to be well below the conduction band. Thus going from Ca to Cu it is expected that the energy of each impurity will fall with respect to the Fermi level. The d shell can then mix with the conduction band states and broaden in energy. For an impurity close to the middle of the Ca - Cu series the Fermi level coincides with the centre of the VBS. In this case we observe:

1. a maximum in the scattering in the middle of the series at Cr leading to a maximum in the resistance per impurity (see figure 2.2(a)).
2. no spin splitting with a result that impurity has no magnetic moment.
3. Coles [1:3] has shown that for the case of Fe dissolved in Al, the VBS will make a contribution to the value of γ of 50mJ/molK² per mole of Fe. This is about five times the γ for a pure 3d transition metal because of a narrower bandwidth.

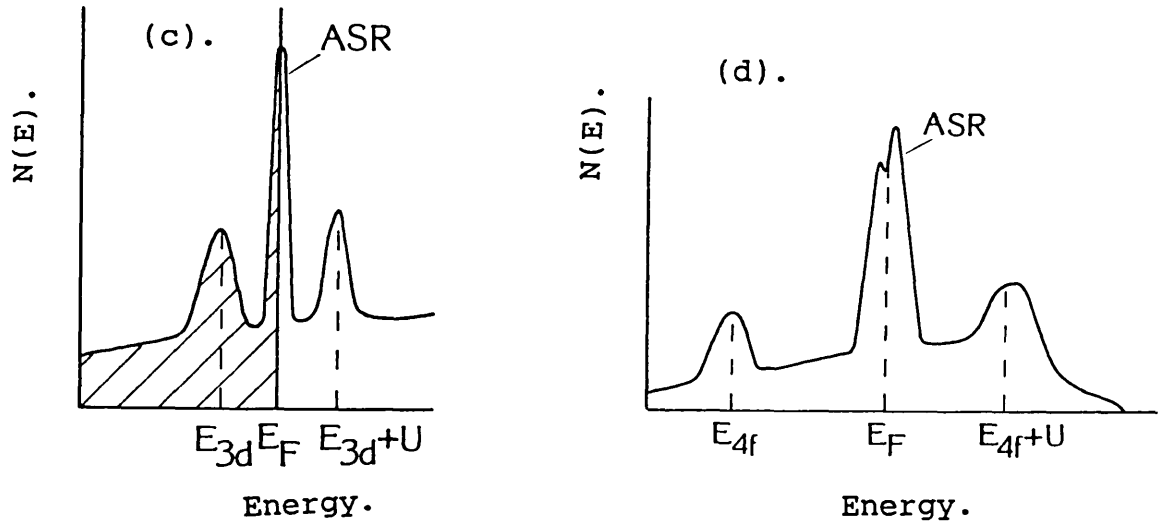
In the case of the same series Ca - Cu dissolved in Cu, where the Fermi energy is lower, the width of the VBS is reduced, and a combination of Coulomb and exchange interactions spin splits the VBS. Thus, we have a situation where the spin split VBS straddles the Fermi level on two occasions across the Ca - Cu series. This has three consequences:

1. Excess of one type of electron spin leads to the impurity being strongly magnetic.



(a). A non-magnetic half filled VBS.

(b). A strongly magnetic VBS. The interactions responsible for the splitting are discussed in the text.



(c). The density of states for a 3d based Kondo system with a narrow ASR superimposed on the two peaks at $E=E_{3d}$ and $E=E_{3d}+U$ which reflect the 3d levels.

(d). The density of states for a non-magnetic Kondo system below the coherence temperature including split off bands at E_{4f} and $E_{4f}+U$ and a many body resonance of width T_K at E_F . The periodicity of the Kondo lattice leads to structure in the ASR.

Figure 2:1(a)-(d). Schematic representations of the density of states of electrons around the Fermi level for different physical situations.

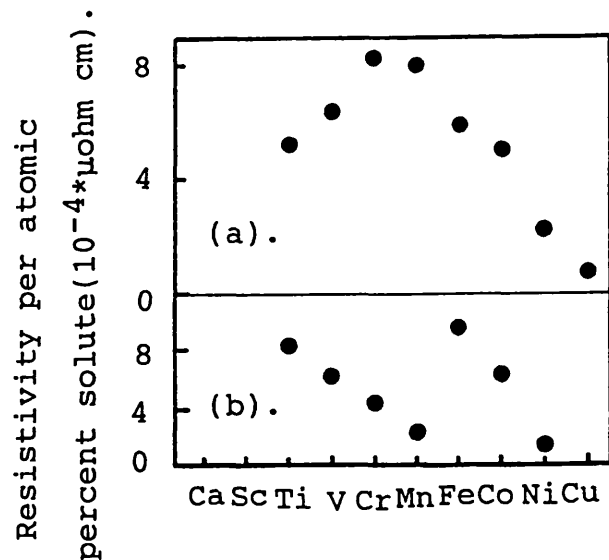


Figure 2:2(a). The resistivity per atomic percent of impurity for elements in the transition metal series Ca-Cu dissolved in Al. Because, for many of the solutes the resistivity is strongly temperature dependent at low temperature the values are for room temperature. Data are taken from Rossiter [1:1] and Bell and Caplin [2:6].

Figure 2:2(b). The resistivity per atomic percent of impurity for elements in the transition metal series Ca-Cu dissolved in Cu. The values are low temperature ones, where the resistivities are almost temperature independent. Taken from [1:1] and [2:6].

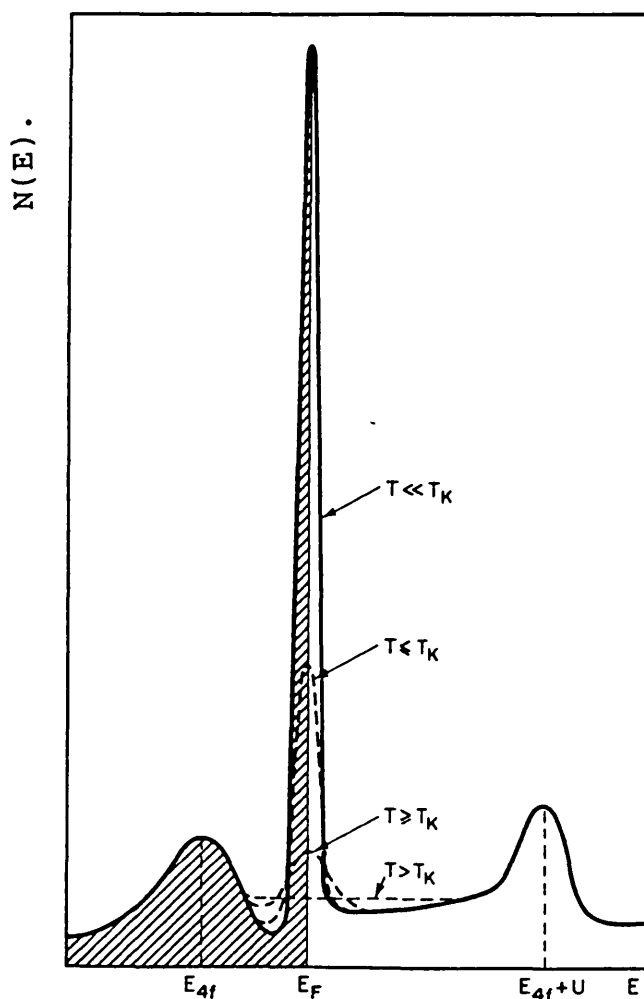


Figure 2:3. Schematic representation of the density of states in a non-magnetic CKS at different temperatures.

2. Two maxima in the resistivity per impurity arise at Ti and Fe as the middle of each spin split VBS straddles the Fermi level (see figure 2.2(b)).

3. Again the 3d impurities contribute to the density states at E_F and hence to the electronic specific heat.

2:3:5. VBS and 4f Impurities.

For most 4f impurities the $4f^n$ configuration of the rare earth ion will be separated from the $4f^{n\pm 1}$ by so large an energy that the hybridisation with the conduction electrons is small giving no contribution to χ . However for Ce (and U) because the $4f^0$ and $4f^1$ ($5f^3$ and $5f^2$) configuration of Ce (U) often have similar energies, the hybridisation of f states with the conduction electrons cannot be ignored.

2:4. The Kondo Effect.

2:4:1. Introduction.

In rare earth metals scattering between the conduction electrons with spin s and localized electrons with spin S can be modelled by the Hamiltonian

$$H \propto J_{\text{exch}} \mathbf{S} \cdot \mathbf{s} \text{ ----- 2:1.}$$

Such scattering can take place with spin flips (Kasuya Yosida spin flip scattering) in which the conduction and the localized electrons both change spin direction, thus conserving the total spin [2:6]) or without spin flips (potential scattering). J_{exch} is always positive for real bound states so parallel alignment of spins is favoured. To first order, such scattering leads to a resistivity term which is temperature independent. Spin flip effects can also be present in solutions of transition metals in simple metal hosts. However in this case J_{exch} need not be positive. To see how this comes about again consider a VBS associated with an impurity which is spin split by exchange and Coulomb interactions. This VBS will be occupied almost exclusively by

electrons of one direction. The Pauli exclusion principle excludes electrons of parallel spin from coming into the VBS. An electron of antiparallel spin may do so, but at a cost of energy equal to U , the Coulomb repulsion. Thus there is a net attraction for electrons of opposite spin i.e. $J < 0$. This mechanism is most effective when the VBS is well split so the electrons occupying the VBS at the Fermi level are predominantly of one spin, but where U is not too large to prevent antiparallel spin electrons from approaching.

Considering only first order spin flip scattering events of conduction electrons produces no temperature dependent term in the resistivity. Kondo considered second order terms in spin flip scattering. This allows for an intermediate state in which energy is not conserved. Kondo showed [2:7] that to second order, the spin flip resistivity is given by

$$\rho_{\text{spin}}^2 = -c|J_{\text{exch}}|^3 s(s+1) \ln T \text{ ----- } 2:2.$$

This leads to a divergence in $\rho(T)$ at $T=0\text{K}$. First attempts to improve the theory simply brought the divergence to a finite temperature T_K (Kondo temperature) given by

$$T_K \sim E_F \exp(-1/|J_{\text{exch}}|N(E_F)) \text{ ----- } 2:3.$$

Grüner and Zawadowski [2:8] have proposed that the divergence at temperatures below T_K is associated with the formation of a narrow many body resonance near the Fermi level E_F . This peak in the density of states is known as an Abrikosov-Suhl resonance (ASR) [2:9-14]. In the case of 3d based Kondo systems this narrow structure is superimposed on two broad peaks at $E=E_{3d}$ and $E=E_{3d}+U$ which reflect the 3d levels (see figure 2.1(c)). For an isolated impurity the amplitude of the resonance $=(\Delta\pi)^{-1}$ where Δ = the width of 3d level due to hybridisation. The width of the ASR is related to $K_B T_K$. Thus

for a Kondo system with $T_K \sim 0.1$ to $10K$ the ASR width is extremely small compared to both the Fermi energy and the width of the s or d bands. Unlike the two broader peaks at $E=E_{3d}$ and $E_{3d}+U$ the ASR is smeared out at temperatures greater than T_K (see figure 2.3). T_K is a characteristic temperature which divides the problem into two regions. A high temperature regime in which the impurities act more or less like independent single impurities and where the conduction electron-local magnetic moment (L.M.M.) interaction can be treated perturbatively giving rise to a logarithmic temperature dependence in $\rho(T)$. Below T_K a strong interaction leads to the formation of a quasibound state. This is a non-magnetic state in which the local spin of the impurity is compensated by a cloud of antiparallel spin polarized conduction electrons.

Nagoaka [2:15] calculated that this state should have a resistivity of the form $(1-A(T/T_K)^2)$ reaching a maximum at $T=0K$.

2:4:2. Exact Solution to the Kondo Impurity Problem.

Wilson [2:16], Andrei [2:17] and Tsvelick and Wiegman [2:18,2:19] have recently developed an exact solution to the single Kondo impurity problem. The theory, involving a single parameter is valid for the whole temperature range from $T \gg T_K$ to $T \ll T_K$ and is in agreement with the earlier results of Kondo [2:7], Nagoaka[2:15], Abrikosov [2:10], Suhl [2:11] and Nozières [2:20] which could only be applied to limited temperature ranges.

2:4:3. Consequences of the Kondo Effect.

A combination of a reduction in the resistivity due to phonon scattering as the temperature of a Kondo system is reduced

together with the rapid increase in spin disorder scattering around T_K produces a minimum in $\rho(T)$ of Kondo systems such as Au-5ppmFe [2:21] (see figure 2:4(a)).

At $T \leq T_K$ an important contribution to the electronic specific heat due to the formation of an ASR around $E=E_F$ is also expected. As the temperature is raised above T_K this narrow highly peaked density of states is reduced and disappear for $T \gg T_K$ (see figure 2:3). This gives a temperature dependent γ . For example as $T \rightarrow 0$, γ in CuFe is appreciably greater than 1 JK^{-2} per mole of 3d element.

2:5. Concentrated Kondo Systems (CKS).

2:5:1. Toward a CKS.

The amplitude of the ASR due to a single impurity is small compared to the initial undisturbed density of states. However for a Kondo system with sufficiently high concentration of noninteracting impurities the reverse can be true. Brandt and Moshchalkov [2:22] have shown that as the number of impurities approaches one per unit cell the density of states at the Fermi level due to the ASR may exceed the initial density of states by 2 to 3 orders of magnitude. Such systems are called concentrated Kondo systems (CKS). It is not possible to make a CKS with 3d elements since the interaction between the VBS which arise from these impurities is strong for even small concentrations (0.01~0.1%) [2:23]. However, the size of 4f shells in rare earth elements are smaller ($0.2\text{--}0.3\text{\AA}$) [2:24] reducing the intersite interactions. Even with one 4f ion per elementary cell the direct 4f shell interactions are negligible and it may be possible to find rare earth intermetallic compounds where the formation of an ASR enhances the density of states at the

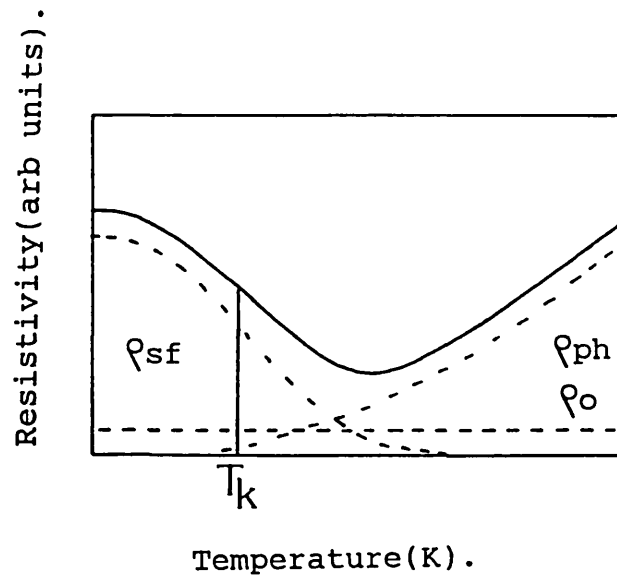


Figure 2:4(a). Schematic representation of the resistivity due to a system of non-interacting Kondo impurities. Contributions are observed from incoherent Kondo scattering ρ_{sf} , phonons ρ_{ph} and a residual component ρ_o . The combined effect is shown as a solid line.

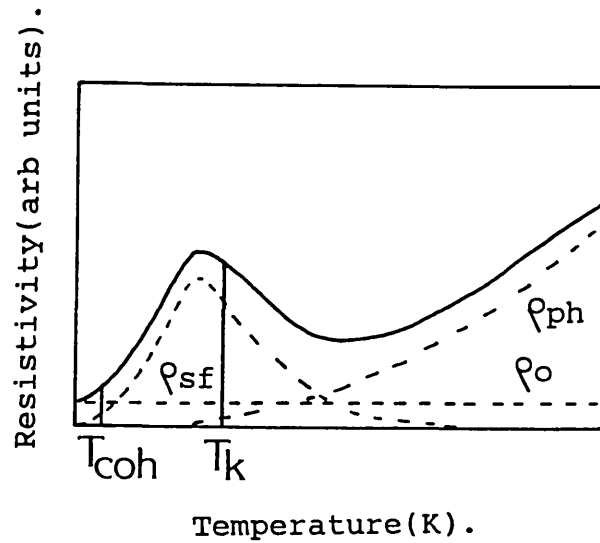


Figure 2:4(b). Schematic representation of the resistivity in a concentrated Kondo system. Once again contributions are observed from incoherent Kondo scattering ρ_{sf} , phonons ρ_{ph} and a residual component ρ_o . At low temperature the incoherent Kondo scattering diminishes as the system forms a Kondo lattice. Below T_{coh} the resistivity exhibits a T^2 temperature dependence typical of a Fermi liquid. The total resistivity is again shown as a solid line.

Fermi level to 100 to 1000 times the value in a normal metal. The position of the ASR relative to the Fermi level has been found to depend on the total magnetic moment j of the 4f shell [2:25]. For a $j=1/2$ CKS, the ASR is placed exactly at E_F , whilst for a CKS with $j>1/2$, the ASR peak is a little above or below E_F .

2:5:2. Magnetism Versus Kondo Interactions.

Even in a system of 4f impurities the competition between the Kondo and indirect magnetic (RKKY) interactions between local magnetic moments must be considered. The intensity of the RKKY interaction is characterized by the temperature T_{RKKY} which is determined by the density of states at the Fermi level $N(E_F)$ the Kondo coupling constant J [2:26] where

$$T_{\text{RKKY}} \sim J^2 N(E_F) \text{ ----- 2:4.}$$

$$\text{and } J \sim V_{\text{sf}} / (E_F - E_{4f}) \text{ ----- 2:5.}$$

V_{sf} is the hybridisation between the 4f and conduction electrons. $E_F - E_{4f}$ is the gap between the 4f and the Fermi level. For most cases the 4f level is deeply immersed in the Fermi sea and J is small [2:22]. Since $T_K \sim \exp(-1/JN(E_F))$, $T_{\text{RKKY}} > T_K$ and a magnetic transition occurs. The frozen local magnetic moments cannot take part in spin flip processes and no enhancement in the density of states at E_F is observed. However for some rare earth compounds E_{4f} is close to E_F resulting in a large J . In this case $T_K > T_{\text{RKKY}}$. Kondo compensation of magnetic moments precedes any magnetic ordering which results in a non-magnetic state at low temperature. One can divide the systems under consideration into three regimes. The classification scheme is shown schematically in figure 2:5.

1. $T_K \gg T_{\text{RKKY}}$ Systems such as $\text{Ce}_{1-x}\text{La}_x\text{Cu}_6$ show no evidence of magnetic order across the entire range of Ce concentration,

down to the lowest temperatures measured.

2. $T_K \ll T_{RKKY}$. At the other extreme one has magnetic metals where indirect exchange coupling dominates Kondo coupling. e.g. Gd($T_C=292.7K$), Tb($T_C=220K$).

3. $T_K \geq T_{RKKY}$. Systems in this regime have a magnetic ground state which is modified because of Kondo compensation of the L.M.M. In this case the Kondo effect reduces the L.M.M. as the temperature is reduced but interactions between the moments are strong enough that a transition into a spin frozen state precedes the formation of a non-magnetic Kondo singlet ground state. Such magnetic CKS include CeAl₂ and CeCu₂ which are the subject of chapters 5 and 6 respectively.

2:5:3. Properties of CKS.

It has been shown above that a non-magnetic ground state is expected for CKS with $T_K \gg T_{RKKY}$. Examples of such systems include CeCu₆ and CeAl₃. The properties of these systems have been discussed at length in chapter 1. The unusual properties observed, which require an explanation are briefly listed below.

1. Lowering the temperature produces a large enhancement in the electronic specific heat e.g. CeCu₆ $\gamma(T \rightarrow 0) = 1500 \text{ mJ/molK}^2$.

2. The magnetic susceptibility shows Curie-Weiss like behaviour at high temperature. This is followed at low temperature by a complete suppression of the effective Ce³⁺ moments and an enhanced Pauli paramagnetism.

3. The resistivity at high temperatures shows a Kondo like logarithmic increase. At lower temperatures resistivity shows a peak followed by a rapid fall. At lowest temperatures, Fermi liquid behaviour is observed in the resistivity with the values of the coefficient A ($\rho(T) = \rho_0 + AT^2$) enhanced.

4. An anomalous increase in R_H , the Hall coefficient is observed as T is decreased from $T \gg T_K$ to $T < T_K$. R_H then becomes strongly negative, with negative extrema at 0.4K. Below this temperature R_H behaves as if CeCu₆ is Fermi liquid.

2:5:4 A Model for CKS.

As a first step to understanding the properties of CKS Brandt and Moshchalkov [2:22] have suggested treating a CKS as a system made up of a large number (N_A) of noninteracting Kondo centres. We can expect a large enhancement in the amplitude of the ASR relative to the dilute impurity case. This may

produce the high density of states round the Fermi level at low temperature T_K required to explain the some properties of CKS listed above. To get some idea if this explanation is on the right track, multiply the values for $\chi_{SI}(0)$ and $\gamma_{SI}(0)$ which are known from the Wiegmann and Andrei exact solution for the Kondo impurity problem by N_A . These values can then be compared with the experimental values for CKS such as $CeCu_6$ and $CeAl_3$. Before doing this, the models used to discuss the Kondo impurity problem the expressions for $\chi_{SI}(0)$ and $\gamma_{SI}(0)$ in the single impurity case will be examined.

2:5:5. $\chi_{SI}(0)$ and $\gamma_{SI}(0)$ in the Single Impurity Problem.

The most frequently used model used to describe the problem of an impurity atom with magnetic moment dissolved in a nonmagnetic host is due to Anderson [2:26]. The Hamiltonian is written

$$H_A = \sum_{k\sigma} E_k c_{k\sigma}^\dagger c_{k\sigma} + V \sum_{k,\sigma} (c_{k\sigma}^\dagger d_\sigma + d_\sigma^\dagger c_{k\sigma}) + \sum_{\sigma} E_d d_\sigma^\dagger d_\sigma + U d_\uparrow^\dagger d_\uparrow d_\downarrow^\dagger d_\downarrow \quad 2:6.$$

where U is the Coulomb repulsion for electrons in localized states and V is the hybridisation between the impurity level and the conduction band states. E_d is the energy difference between the Fermi level and the impurity states. E_k is the energy of an electron of momentum state k . $c_{k\sigma}^\dagger$ and $c_{k\sigma}$ are the creation and annihilation operators respectively for electrons in conduction states, whilst $d_\sigma^\dagger$ and d_σ are the equivalent operators for electrons in the localized impurity states, and k and σ are the band electron wave number and spin respectively. The hybridisation which gives rise to the impurity level broadening can be written in terms of the impurity level width as

$$\Delta \sim V^2 N(E_F) \text{ ----- } 2:7.$$

where $N(E_F)$ is density of states at the Fermi level. For small hybridisation $\Delta \ll \min(E_d, E_d + U)$, and with the help of the Schrieffer-Wolff transformation [2:26], it is possible to deduce the Hamiltonian used in the Kondo model to discuss an $S=1/2$ magnetic impurity. In this case the Anderson Hamiltonian is transformed into a Kondo Hamiltonian [2:7] containing the exchange interaction term introduced in section 2:4:1.

$$H_K = \sum_{k\sigma=\uparrow\downarrow} E_k c_{k\sigma}^\dagger c_{k\sigma} + J_{\text{exch}} \sum_{kk'\sigma\sigma'} S \cdot s_{kk'\sigma\sigma'} c_{k\sigma}^\dagger c_{k'\sigma'} \quad \text{-----} \quad 2:8.$$

The effective exchange parameter can be written in the second Born approximation as

$$J_{\text{exch}} = |V|^2 U / (E_d^*(E_d + U)) \quad \text{-----} \quad 2:9.$$

For $E_d < E_F$ and $E_d + U > E_F$, J is negative and the interaction between the L.M.M. and the conduction electrons is antiferromagnetic. This gives the compensated LMM discussed above. However if the Kondo model is generalized to impurities with arbitrary spin ($S > 1/2$), the complete Kondo compensation of the L.M.M. does not place [2:22, 2:28, 2:29]. As a consequence, one cannot describe the behaviour of a magnetic impurity with spin $j > 1/2$ with the simple substitution $S \rightarrow j$, since for $j > 1/2$ the effective moment of a Kondo impurity is known to tend zero as $T \rightarrow 0$ [2:30]. In this situation, one can use the Coqblin-Schrieffer (C.S.) model [2:31]. The C.S. Hamiltonian

$$H_{\text{CS}} = \sum_{k,m} E_k c_{km}^\dagger c_{km} + J \sum_{k,m} S \cdot \sum_{k',m'} c_{k'm'}^\dagger c_{km} a_m^\dagger a_{m'} \quad \text{-----} \quad 2:10.$$

takes into account the hopping of conduction band electrons between various total angular momentum states. At low temperatures the C.S. model leads to a complete compensation of L.M.M. by conduction electrons with $l > 1/2$ for

$j > 1/2$ case. Rajan [2:32] has calculated the magnetic susceptibility and specific heat using the C.S. model.

He found $\chi_{SI}(0) = j(2j+1)(j+2)(\mu_B g)^2 / 6\pi k_B T_0$ ----- 2:11.

and $C_V(T \rightarrow 0)/T = \gamma_{SI} = j\pi k_B / 3T_0$ ----- 2:12.

where the characteristic temperature T_0 is related to the Kondo temperature through the Wilson number W_N [2:33]

$T_K/T_0 = W_N = 1.2902$ ----- 2:13.

Rajan [2:32] has also obtained expressions for $\chi(T)$ and $C(T)$, which are derived from the exact solution of the Kondo impurity problem in terms of the density of states. These expressions were then inverted to calculate the form of the density of states itself. He found that for $j=1/2$ the density of states is sharply peaked with a maximum exactly at $E=E_F$ whilst for $j > 1/2$ the peak is at $E > E_F$. Similar results were obtained by Nozières [2:20], Nozières and Blandin [2:34] and Newns and Hewson [2:25] in the Fermi liquid theory of magnetic impurities. Therefore it is possible to obtain, from exact solutions for $\chi(T)$ and $\gamma(T)$ a density of states which reflects the formation of an ASR around E_F .

2:5:6. Experiment versus Theory.

Consider the Ce^{3+} ions in the $CeCu_6$ and $CeAl_3$ CKS as N_A non-interacting Kondo impurities. It is suggested [2:22] that

$\gamma_{CKS} = N_A \gamma_{SI}$ ----- 2:14. and $\chi_{CKS} = N_A \chi_{SI}$ ----- 2:15.

For $CeCu_6$ and $CeAl_3$ $j=5/2$, crystal field splitting lifts the six fold degeneracy giving three doublets. For both $CeCu_6$ [2:35,2:36] and $CeAl_3$ [2:22] $T_K \ll \Delta_{CF}$, and both systems can be treated as $j=1/2$ CKS at low temperature.

For $CeCu_6$ with $T_K=3.9K$ $j=1/2$ and $g=2$

$$\gamma = 1.2902 * N_A \pi k_B / 6T_K = 1.87 J/mol K^2$$

$$\chi = j(2j+1)(j+1)(\mu_B g)^2 N_A * 1.2902 / 6\pi k_B T_K = 0.05 emu/mol$$

For CeAl_3 with $T_K=5\text{K}$ $j=1/2$ and $g=2$

$\gamma=1.46\text{J/mol K}^2$ and $\chi=0.03\text{emu/mol}$.

Experimental values for γ and χ taken from 1:3:10 are listed below

CeCu_6 $\gamma=1.6\text{J/mol K}^2$ $\chi(T=0\text{K})=2.8 \times 10^{-2} \text{ emu/mol}$

CeAl_3 $\gamma=1.62\text{J/mol K}^2$ $\chi(T=0\text{K})=3.6 \times 10^{-2} \text{ emu/mol}$

One can see that the agreement is reasonably good.

As an aside, one can also estimate the effective mass of the fermions associated with the ASR.

For a normal metal $m^* \sim 1/\Delta = 0.1 \sim 1m_0$ for $\Delta \sim 1$ to 10eV .

For an ASR with $\Delta \sim k_B T_K$ ($T_K \sim 4\text{K}$) $\sim 10^{-3}\text{eV}$

Find $m_{\text{ASR}}^* \sim m_0 \Delta / k_B T_K \sim (10^2 \sim 10^3)m_0$

2:6. Concentrated Kondo Lattices (CKL).

2:6:1. Introduction.

It has been shown that the treatment of a CKS as a system of N_A noninteracting Kondo centres gives values for γ and χ which are in broad agreement with experimentally determined values. These ideas can also explain such effects as the reduction of γ in high magnetic fields ($\mu H > k_B T_K$) since these fields can suppress the formation of an ASR. However, other low temperature features require more than formation of an enhanced ASR for their explanation.

Disordered CKS have resistivities which increase up to some low temperature saturation value as the temperature is reduced. In contrast periodic CKS, known as concentrated Kondo lattices (CKL) such as pure CeCu_6 and CeAl_3 , in which the Ce^{3+} ions sit on each rare earth lattice site reveal rapid falls in resistivity as the temperature is reduced. At very low temperature $\rho \propto T^2$ (see figure 2:3(b)). In the case of CeCu_6 structure is observed in R_H and $\delta\rho/\rho$ at low

temperature. Satoh et al. [1:30] also claimed a maximum is seen in C/T . In the case of CeAl_3 , maxima are observed in the susceptibility and specific heat at low temperature. In order to explain such behaviour we need to take into account the periodicity of the lattice and coherence effects between neighbouring Kondo compensation clouds.

2:6:2. Coherent Effects in Kondo Lattices.

Remember in rare earth CKS the direct overlap of 4f shells is negligible because the 4f shell radius is small. However the clouds of conduction electrons which develop around each LMM at low temperature during the Kondo compensation mechanism are more extended in space [2:22]. For a sufficiently high concentration of Ce moments the accompanying Kondo clouds can overlap and interact directly. In order to predict the effects of periodicity note that in general, scattering from magnetic impurities is partly elastic and partly inelastic [1:7]. When these magnetic sites are periodic, as in a Kondo lattice, only the inelastic scattering produces real scattering processes contributing to the resistivity. Elastic scattering creates band structure in the electron spectrum. The total cross section for magnetic sites to scatter an electron increases as the temperature is reduced. At high temperature the significant scattering is inelastic whilst at low temperature the scattering is predominantly elastic. Thus as the temperature is lowered, the inelastic scattering cross section first increases reflecting the increase in the total scattering cross section. At low temperature the resistivity falls to zero at $T=0\text{K}$, as inelastic scattering is reduced and elastic scattering dominates. Fluctuations in the band induced at temperatures just above $T=0\text{K}$, produce electron-

electron scattering giving a T^2 dependence in $\rho(T)$.

If 3d impurities are arranged on a proportion of the lattice sites in a crystal, then as the temperature is lowered the VBS associated with each impurity becomes a Bloch state and gives a narrow hybrid band in which only coherent scattering can take place [1:3] (e.g. MnAl_6 and FeZn_{13}).

Consider now a system of 4f impurities Ce^{3+} (e.g. CeCu_6 and CeAl_3) in a regular lattice. At high temperature the resistivity increases logarithmically as the temperature is reduced, indicative of a set of individual Kondo centres. However at lower temperature ($T \leq T_K$) the quasiparticle states associated with each rare earth site will become Bloch states, which together form a narrow band. This band is characterized by a dispersion relation $E(k)$ with a high values of quasiparticle mass in which only coherent scattering can take place. The formation of hf band leads to a transformation in the Fermi surface. The "heavy fermions" are a combination of localized f states and Fermi sd electrons (see figure 2:6). The formation of such states produces:

1. an increase in the mass of the Fermi electrons due to mixing with the localized f electrons.
2. suppression of magnetic moments on the f shell.

Because of the large size of the Kondo clouds, at low temperatures ($T < T_{\text{coh}} \sim T_K/10$ in case of CeCu_6), one has a system of interacting Kondo centres, leading to coherent Kondo spin fluctuations. This coherence leads to the observed Fermi liquid like AT^2 term in the resistivity. At $T < T_{\text{coh}}$ the renormalized Fermi surface is predicted to be anisotropic. For some directions of momentum there is a sharp increase in the mass of the Fermi electrons, while for other directions

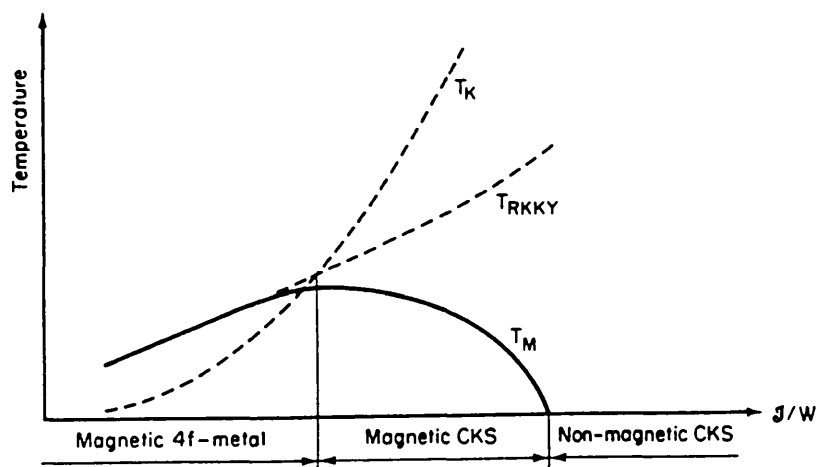


Figure 2:5. The classification of CKS by the relation between two characteristic temperatures- T_K and T_{RKKY} . T_M is a magnetic transition. Taken from Brandt and Moshchalkov [2:22].

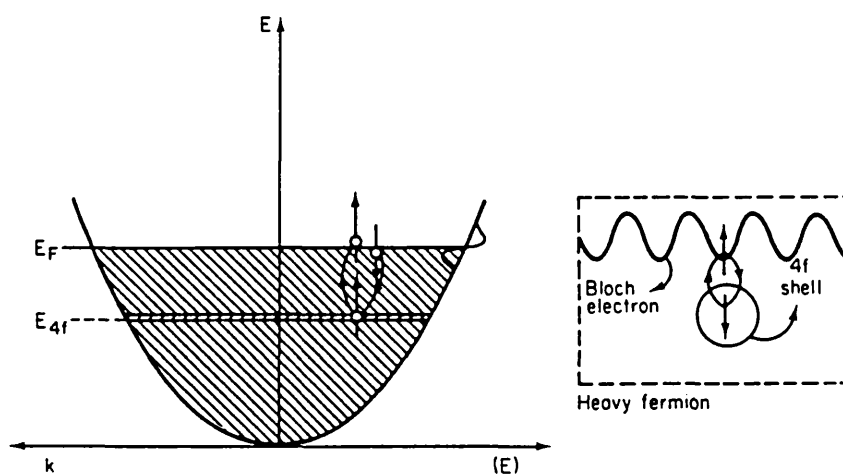


Figure 2:6. Kondo exchange fluctuations leading to heavy fermion formation. From [2:22].

the change in the dispersion law is small [2:22]. Several workers [1:31,2:30,2:37] have suggested that renormalization of the Fermi surface at $T < T_{\text{coh}}$ leads to appearance of structure in the ASR at the Fermi surface (see figure 2.1(d)). If the number of electrons in the conduction band per magnetic centre (n_m)=1 this structure is expected to be a real gap in the ASR at E_F giving an insulating Kondo lattice [2:38,2:39]. For $n_m \neq 1$ a local minimum appears in the ASR at $E=E_F$. The appearance of this structure is associated with a transition from incoherent Kondo singlet regime at $T_{\text{coh}} < T < T_K$ to a truly coherent regime at $T < T_{\text{coh}}$. The opening of this pseudo-gap is predicted to produce a maximum in both the specific heat and the susceptibility and structure in R_H and $\delta\rho/\rho$ around temperatures of order $T_{\text{coh}} \ll T_K$.

2:6:3. Points of Discussion.

1. It has been shown in chapter 1 that for the hf systems CeCu_6 and CeAl_3 , three temperature regimes can be clearly distinguished. A high temperature incoherent scattering region, a transition region, and a low temperature coherent regime. The coherent behaviour occurs at a temperature, an order of magnitude smaller than the Fermi temperature T_F which characterizes the electronic specific heat. This raises the question, is a new temperature scale T_{coh} needed to characterize the coherent state? That is, does the coherent behaviour seen in the low temperature properties occur on some temperature scale T_{coh} which is independent of T_F , or is there simply one temperature scale and coherent behaviour occurs at $T \ll T_F$. It has been shown in section 1:1:5 that for hf materials the cross over from a regime in which behaviour can be described using classical statistics into a regime

requiring quantum statistical mechanics occurs at a reduced temperature T_F . It is believed that this crossover is due to the formation of a many body renormalized quasiparticle band with Fermi degeneracy temperature T_F . The increase in C/T at low temperature is seen as evidence of the creation of this band and yields the crossover temperature T_F . The steepest increase in C/T for $CeCu_6$ system occurs at 2K giving an estimate for $T_F \approx 2K$. At low temperature, the specific heat data can be fitted to $C = \gamma T + \beta T^3$. γ is the electronic contribution proportional to $1/T_F$. For $CeCu_6$ $\gamma(T \rightarrow 0K) \approx 1.6 J/mol K^2$. Using the analysis of Andrei et al. [2:40] ($T_K = 0.68R/\gamma_{max}$) gives $T_K = 3.5K$. Thus $CeCu_6$ is a concentrated Kondo system with $T_K \approx T_F$. Penney et al. [2:34] also point out that $T_K \approx 2K$ which characterizes the specific heat is also the temperature at which most of the dramatic changes in the transport properties occur, e.g. rapid changes in R_H , $\delta\rho/\rho$, ρ . Taken as a whole this data yields a characteristic temperature of 2 to 3K. In the case of $CeAl_3$ C/T is steepest around 3K whilst the value of γ_{max} gives $T_K = 3K$. Thus $CeAl_3$ is also a CKS with $T_F \sim T_K$.

The resistivities of $CeCu_6$ and $CeAl_3$ vary as AT^2 below 0.1 and 0.3K respectively. At higher temperature a somewhat slower, more linear increase is observed [2:22]. A second temperature scale T_{coh} is not required to explain these results. At low temperature, Amato [1:29] claims C/T for $CeCu_6$ varies smoothly with temperature. At the lowest temperature measured (60mK) C/T saturates reaching a constant value, and the limiting behaviour at $T \ll T_F$ is that of a Fermi liquid. Again no additional temperature scale is required. On the other hand Satoh et al. [1:30] asserts that

C/T has a peak at 0.3K. Peaks are also seen in C/T and susceptibility of CeAl₃ at ~0.5K [1:31]. Additionally very low temperatures measurements of the Hall coefficient and the thermopower of CeCu₆ [1:29], which are more sensitive to structure in the density of states near the Fermi level also show rapid changes of character with temperature. Thus the idea (which seems at present to be the ascendancy) of a second temperature scale T_{coh} (typically= $T_K/10$) on the scale of the fine structure in the quasiparticle band may be needed to fully explain this experimental data.

2. The Kondo lattice model described above cannot be used as a general theory for all hf systems. One particular objection is that there are some hf systems which do not have a maximum in their resistivity. e.g. UPt₃. Coles [1:3] has suggested that UPt₃ may show inverted Kondo behaviour, similar to that which has been postulated to occur in RhFe. However it still seems likely that some kind of narrow body resonance near the Fermi level is responsible for the enhancement in the electronic specific heat.

2:7. Kondo versus Magnetism continued.

2:7:1. Introduction.

2:7:2. Variation of T_K and T_{RKKY} with J.

One of the most important aspects of hf system behaviour is the competition between the Kondo and the RKKY interactions. Because of the different functional dependence of T_K and T_{RKKY} on J, it is possible to study the variation of T_K and T_{RKKY} with J. This can be achieved in several ways:

1. Variations in Ce content e.g. Ce_xLa_{1-x}Cu₂Si₂
2. Variations in the hybridisation between the 4f and the conduction electrons can be achieved by application of either external or chemical pressure.

3. The hybridisation can be varied by changing the number of conduction electrons.

2:7:3. Variation of J With Ce Content.

In this section results of experiments on the system $\text{Ce}_x\text{La}_{1-x}\text{Cu}_2\text{Si}_2$ will be used to study the consequences of the variation of J with Ce content. For $x \leq 0.3$ the system shows a logarithmic increase in $\rho(T)$ below 60K followed by saturation at low temperature (see fig 1:19) [2:22,2:41]. For $x \geq 0.4$ $\rho(T)$ has a maximum at $T_{\rho\text{max}}^0$ where $T_{\rho\text{max}}^0$ increases with Ce concentration. One can estimate T_K from $\rho(T)$ by:

1. fitting $\rho(T)/x \propto \ln(T/T_K)$.
2. assuming $T_K \propto T_{\rho\text{max}}^0$.

These procedures give values for T_K $\propto x$ shown in figure 2.7.

For $x \leq 0.2$ the magnetic susceptibility $\chi_{a.c.}$ (fig 1:19) indicates the system is paramagnetic. For $0.2 \leq x \leq 0.7$ the susceptibility increases monotonically as the temperature is lowered down to $T_{\chi\text{max}}^\chi$ where a sharp kink in $\chi_{a.c.}$ is observed. $\chi_{a.c.}$ decreases below $T_{\chi\text{max}}^\chi$. This cusp is taken as an indication of a magnetic transition into a spin frozen state. For $T \geq T_{\chi\text{max}}^\chi$, $\chi_{a.c.}$ can be fitted to $\chi = C/(T - \theta)$ with $\theta < 0$. $|\theta| = 0.18\text{K}$ for $x = 0.2$ and increases with x . Grüner and

Zawadowsky [2:8] have shown that $T_K \propto |\theta|/4$. Thus $\chi_{a.c.}$ results indicate that T_K increases with x in agreement with resistivity results. The temperature of $T_{\chi\text{max}}^\chi$ is assumed to be proportional to T_{RKKY} . Thus these results also indicate that T_{RKKY} increases with x at least up to $x = 0.7$. Above $x = 0.8$ an increase in the Ce (magnetic) content does not increase the magnetic transition temperature. Instead, the cusp at $T_{\chi\text{max}}^\chi$ is smeared out and the value of $T_{\chi\text{max}}^\chi$ is reduced. For $x \approx 1.0$ the system becomes superconducting at 0.5K [1:54]. To understand this look at the variation of T_K and T_{RKKY} with x

calculated from the above data and shown in figure 2:7. The intersection of T_K and T_{RKKY} marks a crossover from a region where the Kondo compensation dominates ($0.8 \leq x \leq 1.0$) to a region in which the RKKY interaction dominates leading to magnetic order ($0.2 \leq x \leq 0.7$). This leads to a phase diagram shown in figure 2:8.

2:7:4. Variation of J With Pressure and Changes in the Number of Conduction Electrons.

Several workers have studied the effects of pressure on dilute magnetic alloys. In particular they have been interested in $J(V)$, the volume dependence of the effective exchange interaction between a single magnetic impurity and the conduction electrons. Schilling and Holzapfel [2:42,2:43] have studied the resistivity of the Kondo system CuFe under pressure. Theory [2:44] predicts that $\rho(T)$ will be a universal function of T_K i.e. $\rho_{spin} = \rho_{spin}(T/T_K)$. They confirmed this, showing that behaviour of systems like CuFe with negative values of J under pressure, can be understood as being due to a shift of ρ_{spin} to higher T as T_K increases. From this, and studies of similar negative J systems, Schilling [2:43] concluded that in such Kondo systems, J universally increases in magnitude with pressure. The increase of $|J|$ is found to be 2 to 5 times the decrease in the cell volume. This increase in J and T_K with pressure is also seen for 4f impurities with negative J , e.g. YCe. For positive J impurities (e.g. Gd in La [2:44]), J decreases with pressure.

The effects of chemical pressure together with changes in the free electron density, brought about by alloying have also been investigated. The alloy series $Cu_{1-x}Au_xFe$ has been

studied by Loram et al. [2:45] and Star [2:46]. The ionic radius of Au is 40% larger than that of Cu. Thus replacing Cu with Au expands the lattice generating negative pressure. This is seen to lead to a reduction in J . So it appears that J is inversely proportional to the average atomic volume V regardless of whether the volume has been altered by application of external pressure or by alloying. Further it does appear that J is a function not of volume alone, but rather of the free electron density (N/V) of the host matrix. Here N is a measure of the number of free electrons in a volume V . Schilling and Crone have studied the $\text{Cu}_{1-x}\text{Al}_x\text{Fe}$ system [2:47]. In this case substituting Al (with three conduction electrons) for Cu (with one conduction electron), leads to an increase in cell volume. If J were a function of $(1/V)$ alone this should be equivalent to a decrease in the external pressure and lead to a decrease in J . However, Schilling and Crone [2:47] have shown that adding 10%Al does in fact increase $|J|$ by the same amount as 100kbars of pressure, even though adding Al to Cu expands the host matrix. Thus, even if the functional dependence of $J=J(N/V)$ is not clear, it does seem likely that increasing the number of free electrons works in the same direction as decreasing the volume by pressure.

Similar effects are observed in rare earth impurity systems. In the system $\text{La}_{1-x}\text{Th}_x\text{Ce}$ [2:48,2:49,2:50], a rapid increase of J and T_K with x , despite a decrease in average atomic volume, indicates that more than lattice pressure is at work. The addition of Th, with one more outer electron than La strengthens the case for $J=J(N/V)$.

At a more fundamental level Schilling has suggested that

changes in $|J|$ with free electron density and pressure may be due to:

1. An increase in V , the hybridisation between the localized and the conduction electrons.
2. A decrease in the separation of the local magnetic level from the Fermi level E_F .
3. A combination of 1 and 2.

2:7:5. Experimental Manifestations of Changes in J with Pressure and Free Electron Density.

Several groups have applied the ideas introduced above to analyse experimental results of alloying in Kondo lattice systems. For example Bauer et al. [2:50,2:51,2:52] studied the effect of Al substitution in CeCu_5 . CeCu_5 is a magnetic Kondo lattice with $T_N=4\text{K}$. CeCu_4Al shows evidence of a magnetic transition at 0.5K , whilst CeCu_3Al_2 is non-magnetic down to 0.3K . The resistivity of the three samples indicates a crossover from magnetic behaviour in CeCu_5 indicated by a kink in $\rho(T)$ at 4K to a non-magnetic Kondo lattice CeCu_3Al_2 with a maximum in $\rho(T)$ 2.8K attributed to the onset of the correlated scattering processes. Thermopower measurements also support a crossover from magnetic to Kondo behaviour. One can determine T_K for the samples using one of two methods:

1. The method of Andrei et al. [2:40] which asserts that $\gamma_{\text{max}} = 0.68R/T_K$. This gives T_K values of 5 and 11K for CeCu_3Al_2 and CeCu_4Al respectively.
2. $T_K \sim |\Theta_p|/4$ [2:8] gives T_K $8\text{K}(\text{CeCu}_5)$, $5\text{K}(\text{CeCu}_4\text{Al})$ and $10\text{K}(\text{CeCu}_3\text{Al}_2)$.

Substitution of Al does not alter the hexagonal structure.

The cell volume increases continuously from CeCu_5 to CeCu_3Al_2 . The behaviour observed in these systems is attributed to changes in the parameter $JN(E_F)$ with Al.

An increase in Al content leads to

1. $N_{\text{CeCu}_5} < N_{\text{CeCu}_4\text{Al}} < N_{\text{CeCu}_3\text{Al}_2}$
2. $V(\text{CeCu}_5) < V(\text{CeCu}_4\text{Al}) < V(\text{CeCu}_3\text{Al}_2)$.

Since $J=J(N/V)$, an increase in N is offset by increase in V . However $N(E_F)$ increases with Al content leading to an overall increase in $JN(E_F)$. Using equations 2:3 and 2:4 one can see T_K increases faster than T_{RKKY} . This leads to a magnetic to Kondo crossover.

2:7:6. Theoretical Understanding.

Doniach [2:54] considered a one dimensional analogue of a Kondo lattice, the Kondo necklace. He found that a second order transition from an antiferromagnetic to a Kondo spin compensated ground state will occur, as the exchange coupling constant J is increased to a critical value J_C . A qualitative understanding of the existence of this transition may be had by comparing the binding energy of a Kondo singlet characterized by T_K given by equation 2:3, with the binding energy of the RKKY antiferromagnetic state characterized by T_{RKKY} of equation 2:4. If $JN(E)$ is less than a critical value the RKKY interaction dominates whilst above this value the Kondo interaction dominates. Thus we see that the ground state is antiferromagnetic for low values of $|J|N(E)$ and a nonmagnetic Kondo singlet for larger values of $|J|N(E)$. These results were confirmed by Jullien et. al. [2:55]. This result was later generalized to the three dimensional case by Lacroix and Cyrot [2:39] using a functional integral method. The solution gives a phase diagram with three phases which are stable in different conditions. For low values of $|J|/W$ (where W band width) the ground state is magnetic whilst if $|J|/W$ is larger than a critical value which depends on the band filling one has a non-magnetic Kondo compensated ground

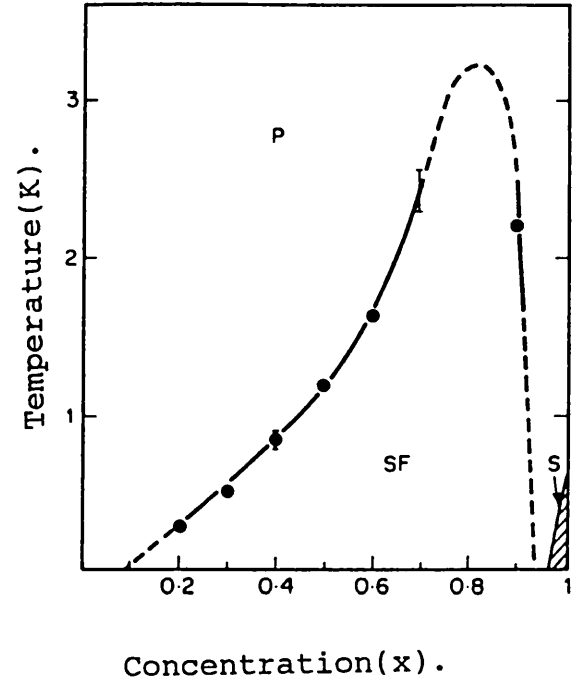
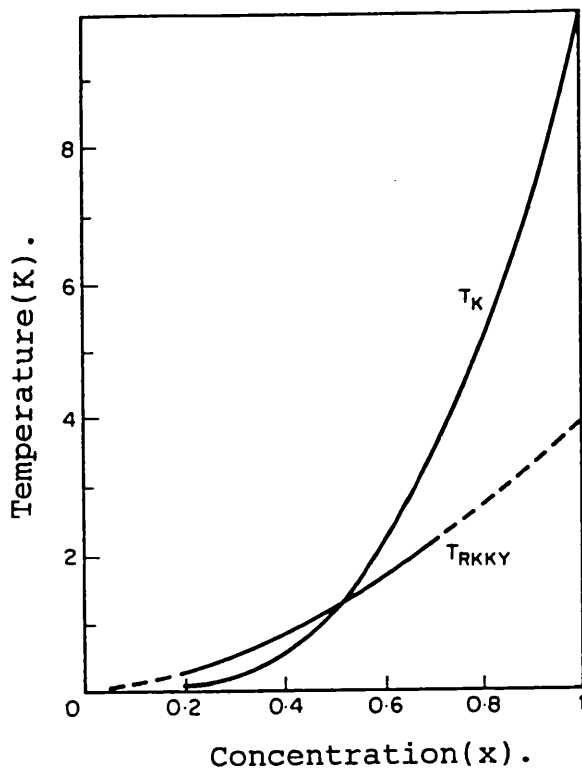


Figure 2:7. (Above left). The variation of the Kondo temperature T_K and the RKKY temperature T_{RKKY} with Ce content x in $Ce_xLa_{1-x}Cu_2Si_2$ alloys. Data are from Aliev et al. [2:41].

Figure 2:8. (Above right). The magnetic phase diagram for the $Ce_xLa_{1-x}Cu_2Si_2$ system. P is the paramagnetic phase, S the superconducting phase and SF the spin frozen state. Taken from Aliev et al. [2:41].

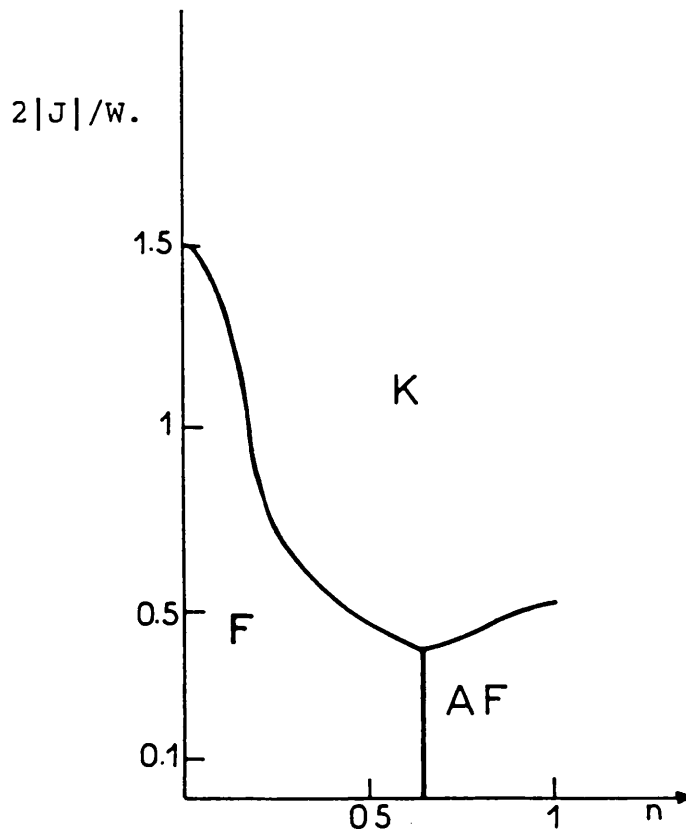


Figure 2:9. The phase diagram showing the stability regions for the Kondo (K), ferromagnetic (F) and antiferromagnetic states (AF). n = the number of conduction electrons per site, J the exchange parameter and W the band width. After Lacroix and Cyrot [2:39].

state. This agrees with Doniach. However the antiferromagnetic ground state is obtained only when the Fermi level is near the middle of the 4f band. When the number of electrons decreases the ferromagnetic state becomes stable. This gives the phase diagram shown in figure 2:9.

Chapter 3. Experimental Apparatus and Sample Preparation.

3:1. Introduction.

This chapter discusses the apparatus used to collect the data presented in this thesis. The principle of operation of each experiment, the construction of the apparatus and the thermometry used are reviewed. Section 2 contains details of the experiment used to collect resistivity versus temperature data. Section three discusses the a.c. susceptibility apparatus and section four contains details of an extraction magnetometer used to collect M V H and M V T data. Section five briefly mentions the other pieces of apparatus used during this work. Finally section six discusses the preparation and characterization of the samples used in this work.

3:2. Electrical Resistivity Apparatus.

3:2:1. Introduction.

All resistance measurements were performed using the standard 4-probe d.c. technique. Figure 3:1 shows a schematic of the equipment used. In figure 3:2 a more detailed diagram of the cryostat insert is shown. The specimen temperature can be varied between 1.6 and 300K.

3:2:2 Apparatus.

3:2:2:1. Micro-ohmmeter.

The resistivity measurements are made using a Keithley 590 micro-ohmmeter. The system has a resolution of 10 μ ohms and an accuracy of $\pm 0.004\%$ of the reading [3.1]. A d.c. pulsed source current of 100mA is used to minimize the effects of joule heating. The pulsed source current along with offset calculated before each reading also minimized the effects due to thermally generated e.m.f.'s. These effects are further reduced by taking forward and reverse readings and averaging the two.

3:2:2:2. The Samples.

Sample dimensions varied between 0.5 and 3.0cm in length and 0.01 to 0.05cm² in cross section giving typical sample resistances of between 2 and 20 milli-ohms. Calculation of accurate values of the absolute resistivity require, both that the samples are uniform i.e. they contain no holes, micro-cracks etc., and that accurate values of the samples cross section and the distance between the sense leads can be obtained. Because of uncertainty in these factors, no firm conclusions have been drawn in this work, from the variations with composition, of the absolute values of the resistivities of a series of samples. However, a comparison

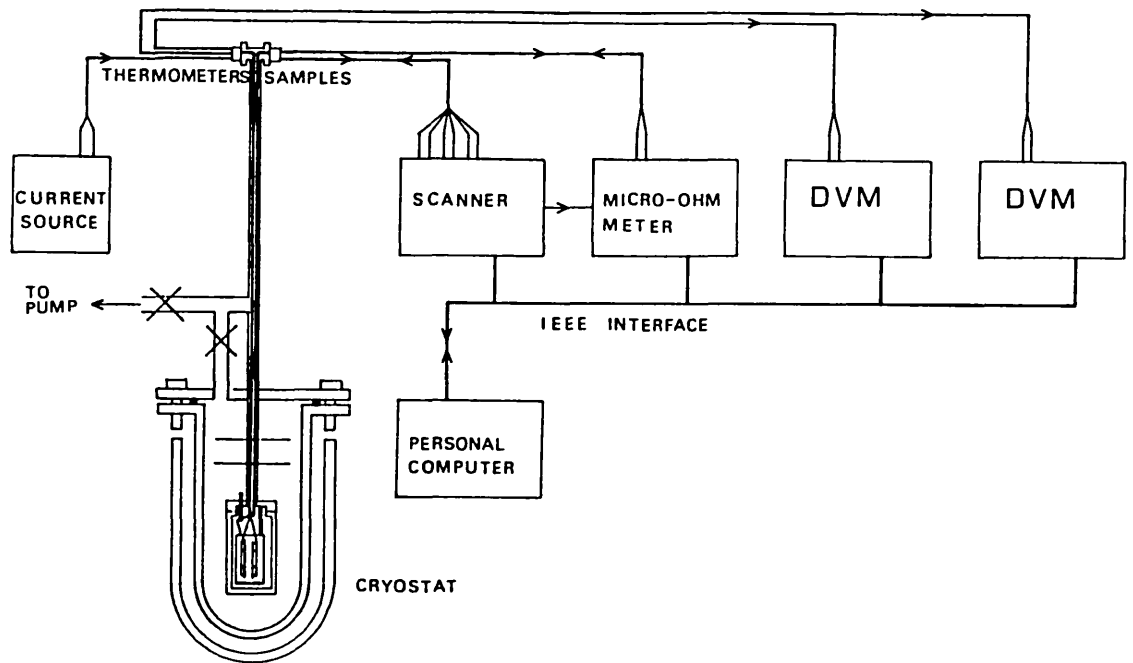


Figure 3:1. Schematic diagram of the apparatus used to perform resistivity versus temperature measurements. For an explanation see section 3:2:1.

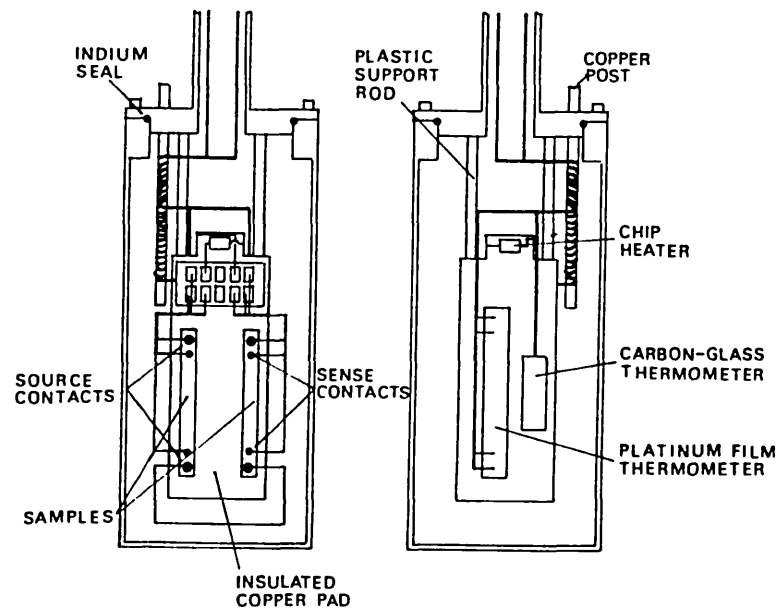


Figure 3:2. Diagram of the sample insert contained within the resistivity apparatus. Left hand shows a front view, with two samples mounted on the copper pad. The right hand side shows the thermometry on the rear of the sample holder.

of the values of absolute resistivity obtained for some of the samples studied in this work, with published data, shows reasonable agreement. In addition, values obtained for the resistivities of two or more different samples of the same composition shows agreement to within $\pm 10\%$.

All the samples are polished and cleaned before contacting to ensure removal of any oxide barrier on the samples surface. Electrical contacts to the samples are made using tinned 40 gauge copper wires attached to the sample using silver epoxy (Epotek H20E silver filled epoxy) giving contact resistances of between 0.1 and 5 ohms. All the leads from the samples are thermally anchored to a copper post to minimize spurious thermally generated e.m.f.'s. The samples are mounted on a plate which is made of copper, covered with a thin layer of paper coated in G.E. varnish. This ensures the samples remain in place and also provides electrical insulation, whilst ensuring the samples are in good thermal contact with the copper pad.

3:2:3. Thermometry.

Two thermometers are employed. The temperature in the region 300-40K is measured using a platinum thin film resistor supplied by R.S.Components Ltd. This thermometer was calibrated via the Z-function [3:2] using measured resistance at 273K and 4.2K. Between 40 and 4.2K the temperature is measured using a commercially calibrated carbon-glass resistor supplied by Cryogenic Calibration Ltd. Both thermometers are thermally anchored to the rear of copper sample pad. Below 4.2K the temperature is measured via the vapour pressure of the helium bath using a manometer and standard tables [3:3].

3:2:3. Experimental Procedure.

Initially the resistance measurements were taken manually. Readings were taken as the samples were cooled from room temperature to 90K using liquid nitrogen coolant in the outer nitrogen jacket. The samples were then cooled to 4.2K and readings taken as the samples were warmed back up to 90K using a heater on the copper plate. Below 4.2K readings were taken as the samples are cooled. Switching between the samples was achieved using a copper switch immersed in oil. More recently the experimental set-up has been automated using a Fast Micro P.C. The temperature and resistance readings are now taken via an I.E.E.E. interface. Switching between samples is carried out using a Keithley 705 scanner with 7059 low voltage card which replaced the manual switch, whilst still ensuring low thermally generated switching e.m.f.'s. The samples are now cooled to 4.2K. Data is then taken below 4.2K. The samples are then returned to 4.2K and data is taken as samples are allowed to warm slowly to room temperature.

3:3. Magnetic a.c. Susceptibility Apparatus.

3:3:1. Introduction.

The magnetic susceptibility measurements were carried out using a mutual inductance method based on the a.c. Hartshorn bridge technique [3:4-8]. Figure 3:3 shows a schematic of the apparatus used. Figure 3:4 shows in more detail, the experimental arrangement inside the cryostat. Measurements can be made between 1.5 and 300K.

3:3:2. General Principle of Operation.

The detection coil system is placed in a cryostat made up of a glass helium dewar surrounded by an outer nitrogen jacket.

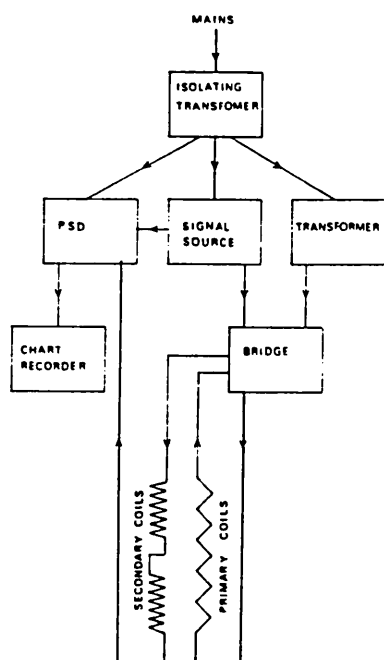


Figure 3:3. Schematic diagram of the a.c. susceptibility apparatus.

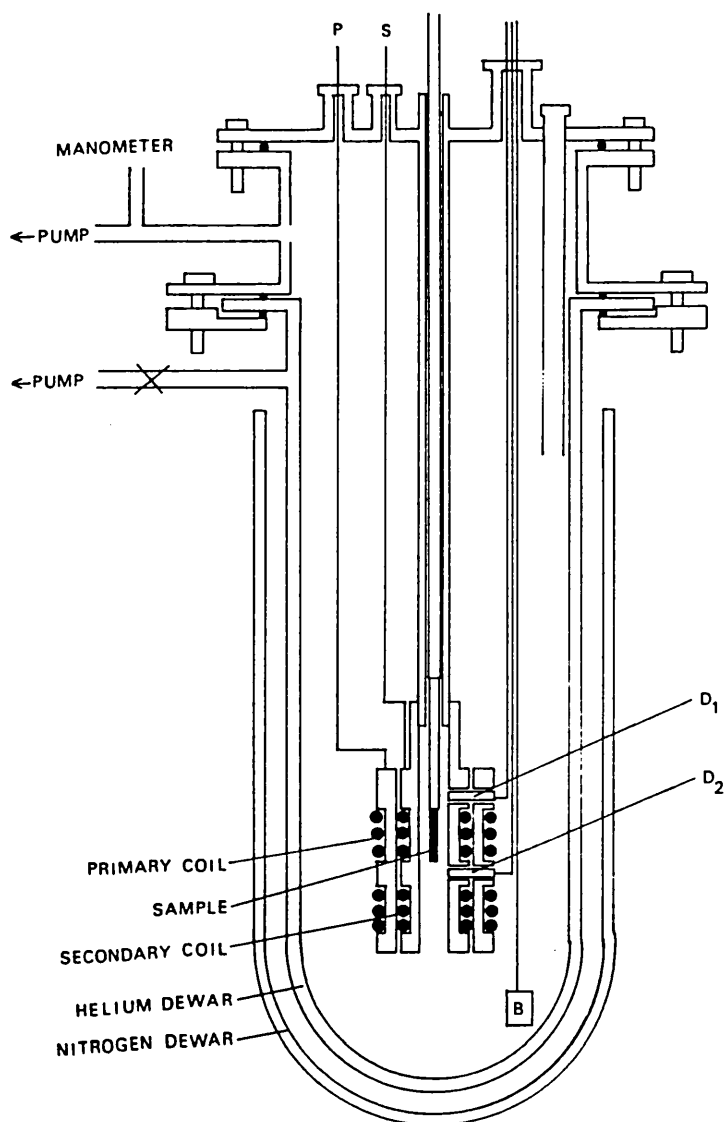


Figure 3:4. A more detailed diagram of the experimental arrangement inside the a.c. susceptibility cryostat. P and S indicate the electrical connections to the primary and secondary coils respectively. D₁ and D₂ indicate the positions of the two diodes which are used as thermometers. B is the helium bath heater.

The system consists of two nearly identical secondary coils and a coaxial primary coil. The secondaries are separated along the axis of the primary and are wound in opposition. All the coils are constructed from enamelled copper wire wound on Tufnol formers. In principle, for two identical secondary coils, the voltage induced in these coils due to the field generated by a passing an a.c. signal through the primary coil is zero. In practice it is hard to construct two identical secondaries. So at any temperature there will be a small offset signal. This offset may vary with temperature and with thermal cycling. However the bridge can be balanced at any temperature using a variable decade resistor to balance the out-of-phase resistive component of the induced signal and a combination of a variable decade resistor and some electronics which together acts as a variable mutual inductance to balance the in-phase component of the signal. The small change in the signal induced in the secondary by the alternating primary coil current produced when a sample is placed inside one of the secondary coils can then be directly related to the magnetic susceptibility of the sample, i.e. the real part of the susceptibility is proportional to δM and the imaginary part of the susceptibility is proportional to $\omega \delta R$ (ω is the frequency of the a.c. primary current). δM , the change in the mutual inductance between the primary and secondary coils results in a offset in the in-phase component of the signal induced in the secondary. δR is the change in the resistive loss and produces an offset in the out-of-phase component.

3:3:3. Apparatus and Calibration.

In an experiment the sample is mounted on a short Tufnol

insert which is in turn connected to a thin stainless steel tube running to the top of the dewar. The sample is held in place on the sample rod using a small amount of G.E. varnish and a strip of P.T.F.E. tape. A small correction to the data, to account for the diamagnetic signal due to the sample rod was found to be necessary, especially when the signal is very small (see fig 3:5). The sample is located in the upper of the two secondaries and its position adjusted to give the maximum signal. To take a reading an alternating current is passed through the primary coil. This current can be varied between 1 and 5mA where 1mA produces a 0.7 Gauss (peak to peak) magnetic field. The primary coil current can be varied from sample to sample in order to give an output signal which can be most conveniently detected and measured. The primary current frequency used for all the measurement throughout this work was 300Hz. Both the in-phase and out-of-phase components of the signal can be detected using a Brookdeal Ortholoc 9502 two-phase lock-in analyser and the output is recorded on a chart recorder. The bridge is balanced with the sample inserted between the secondary coil, the sample is then withdrawn and the susceptibility of the sample is deduced from the offset signal as outlined above. The apparatus was calibrated by measuring the signal generated by a uniform lead sphere as it passed through a superconducting transition [3:10]. This calibration was then checked by comparing the results obtained with known samples against published data. The system is able to detect $\chi_{a.c.}$ values of 4×10^{-6} emu or greater.

3:3:4. Thermometry.

Between 4.2 and 300K the temperature of the sample is

determined using two calibrated diodes (D_1 and D_2) placed above and below the sample. No significant temperature difference is observed between D_1 and D_2 at any point in the temperature range 4.2 to 300K. Below 4.2K the temperature is determined by measuring the vapour pressure of the helium bath via a manometer.

3:3:5. Experimental Procedure.

Readings between 300 and 80K are taken as the apparatus is cooled by placing liquid nitrogen in the outer jacket. When the temperature of the sample reaches 80K, helium is transferred into the inner dewar. If data is to be collected below 4.2K readings are then taken as the temperature is reduced by pumping over the helium bath. The sample is then allowed to return to 4.2K, and data are taken as the sample is warmed back up from 4.2 to 90K. The readings taken in the temperature range 80 to 90K allows the data to be checked for hysteresis.

3:4. Low Field Extraction Magnetometer.

3:4:1. Introduction.

Measurements to determine the variation of magnetisation (M) of a sample with temperature ($M \vee T$) and with field ($M \vee H$) were taken using a low field extraction magnetometer. Zero field cooled and field cooled $M \vee T$ measurements were taken between 4.2K and 200K in fields of up to 100 Oesteds. $M \vee H$ curves were taken at 4.2K in fields of up to 1780 Oesteds.

3:4:2. General Principle of an Extraction Magnetometer.

Faradays law gives the e.m.f. (E) generated in a circuit, by a change in ϕ the flux cutting through the circuit as

$$E = -d\phi/dt \text{ ----- 3:1.}$$

Flux enclosed in a coil made up of N turns each of radius A

in a uniform magnetising field B is given by

$$\phi = NAB \text{ ----- } 3:2.$$

If the magnetising field B changes then the e.m.f. induced

$$E = -NAdB/dt \text{ ----- } 3:3.$$

In the case of two identical coils, wound in opposition and placed in an applied field which is homogeneous and static, no net voltage will be generated in the circuit. Consider now an ellipsoidal sample with a demagnetising factor D which fits tightly inside one of these coils. If such a sample is placed in the upper of the two secondaries then the flux enclosed by that coil is given by [3:8]

$$\phi_{EN} = NBA = N[H_O + 4\pi(D-1)M]A \text{ ----- } 3:4.$$

If the sample is withdrawn to some point well away from the the coil, an e.m.f E is generated in the coil which is given by Faradays law

$$\int_0^T E dt = \int_0^T (d\phi/dt) * dt = \phi_{IN} - \phi_{OUT} \text{ ----- } 3:4(a).$$

$$= N[H_{O1} + 4\pi(D-1)M]A - NH_{O2} \text{ ----- } 3:4(b).$$

Assume $H_{O1} \approx H_{O2}$ then

$$= N[4\pi(D-1)M]A \text{ ----- } 3:4(c).$$

Integrating the e.m.f generated in the coil over the time taken to withdraw the sample gives a measure of the magnetisation of the sample.

$$M \propto \frac{\left[\int \frac{E dt}{NA} \right]}{4\pi(D-1)} \text{ ----- } 3:5.$$

Note that the sample must fit tightly inside the coil, or flux contained within the coil will include stray flux external to the sample. As this also changes when the sample

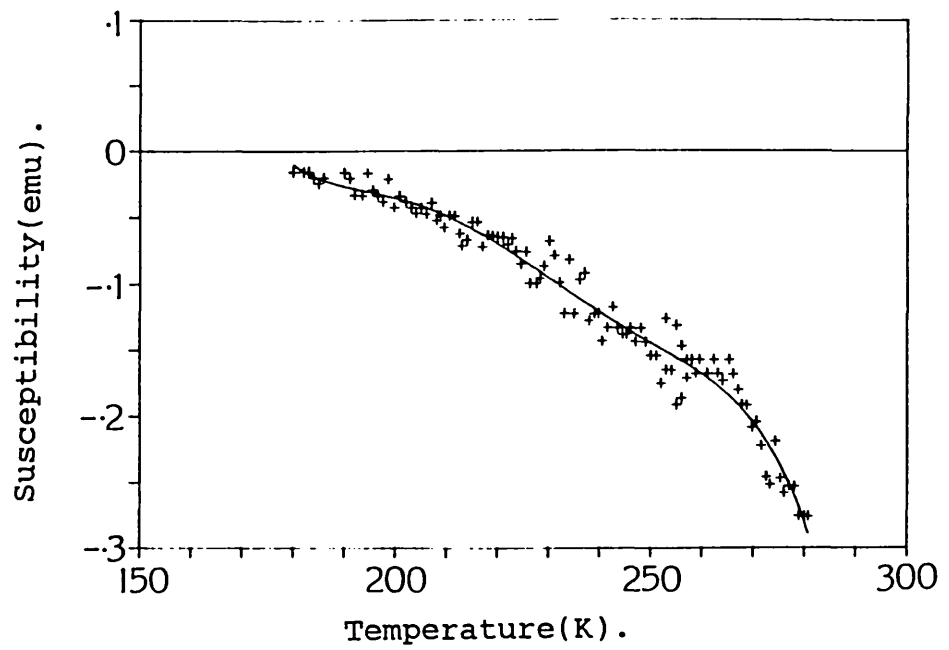


Figure 3:5. Variation with temperature of the diamagnetic signal from the sample rod of the a.c. susceptibility apparatus.

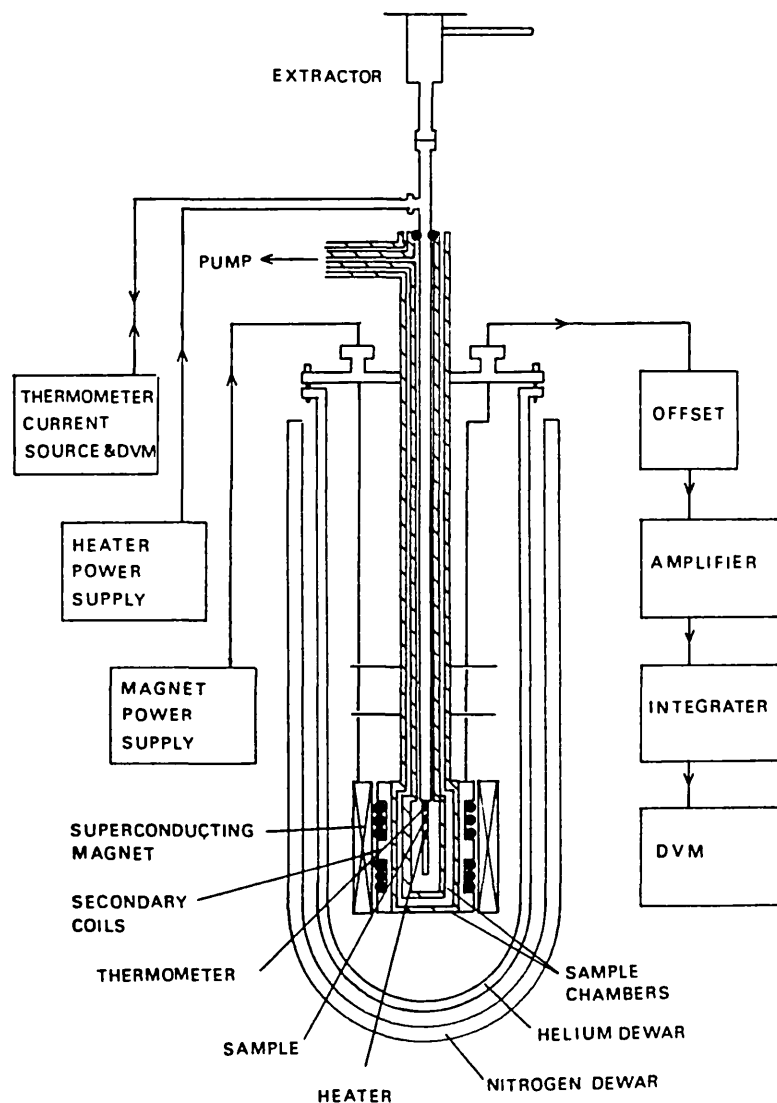


Figure 3:6. Diagram showing the experimental arrangement of the extraction magnetometer.

is removed an error will result. This error can be overcome by calibrating the apparatus with a known sample of similar dimensions to the samples under study. The sensitivity of the apparatus can be doubled by moving the sample from the centre of one of the secondary coils to the centre of the oppositely wound coil. The integration of the e.m.f E can be achieved by connecting the coils in which the voltage is generated to a voltage to frequency converter. The output of this device is an a.c. signal whose frequency is linearly related to the d.c. input voltage. The integration can then be performed electronically by using a frequency counter to count the number of oscillations in this a.c. output in the time interval T .

3:3:3. Cryostat and Coil Design.

Figure 3:6 shows a schematic representation of the extraction magnetometer including some details of the cryostat and coils. The magnetometer cryostat system consists of a glass helium dewar surrounded by a nitrogen jacket. A small superconducting magnet, capable of generating fields of up to 1780 Oersteds is positioned inside the helium dewar. The magnetic coil, is made up of 2640 turns of Niomax A60/15 (60 filaments each of 0.15mm diameter) Nb/Ti superconducting wire wound in 5 layers each of 528 turns on a Tufnol former. Compensation coils made up of 180 turns wound in 3 layers were placed at each end of the magnet to improve the field homogeneity [3:11]. The field generated at the centre of the magnet coil was calculated using the classical expression

$$H = IN/2b \left[\frac{b}{(b^2 + R)^{1/2}} \right] \text{----- 3:6.}$$

Where I is the current, N is the number of turns, $2b$ is the

length of the coil and $2R$ is the diameter of the magnet [3:11,3:12]. The field produced by each layer of the coil was calculated separately to take into account the change in coil radius with the number of layers. Summing these values gives the total field generated by the coil. The secondary pickup coils are positioned inside the bore of the magnet. The secondary coils are wound on a Tufnol former and connected in opposition. Each coil consists of 15000 turns of 48 gauge enamelled copper wire, wound in 30 layers[3:9]. The secondary surrounds the sample chamber. This consist of two concentric cylindrical chambers machined from Araldite. Both these chambers can be independently evacuated. The temperature of the sample can then be varied between 4.2 and 200K by varying the heater current and the introduction of exchange gas, whilst the primary magnet coil and the secondary pick up coils remain immersed in liquid He, without excessive He boiloff.

3:3:3. Sample Holder and Thermometry.

The sample is mounted inside one end of a cage of Cu wires approximately 12cm long. The sample is covered in Apiezon grease to ensure thermal contact with the cage and held in place using a small cotton plug. A sample heater made from a length of manganin wire and a commercially calibrated diode thermometer are positioned at the other end of the Cu cage. This ensures good thermal contact between sample, heater and thermometer, without the need for either the heater or thermometer to placed inside the pick-up coils. This sample holder is connected to a a thin stainless steel rod which runs to the top of the cryostat. The position of the sample within the secondary coils can be varied to give the maximum

output signal. The sample is moved within the secondary coils using an extractor driven by compressed air.

3:3:4. Experimental Procedure and Calibration.

Before an experiment begins, the sample chamber and magnet are cooled to 80K by placing liquid nitrogen in the outer dewar. Liquid helium is then transferred into the magnet chamber. To take a measurement the magnet is energised and the field allowed to settle. The sample is moved from the mid-point of the lower secondary to the mid-point of the upper secondary. The signal induced is first amplified then integrated. The integrated signal is then displayed on a D.V.M. The sample is then returned to its original position. The average of the two signals generated during this cycle is proportional to the magnetisation of the sample as outlined above. To compensate for any spurious signal generated in the secondary coils or during the integration procedure, a reading is taken with the sample stationary. An offset signal is introduced before the amplification stage to give a zero reading on the D.V.M. output.

The output from the magnetometer was calibrated by comparing results taken with this system with published data. The field generated by the superconducting magnet was calculated from the number of turns and their area assuming the magnet was a infinite solenoid.

3:5. Other Apparatus

3:5:1. Vibrating Sample Magnetometer.

Magnetisation measurements were also performed on several samples using a V.S.M. constructed by Dr C.N. Guy. The design and principles of operation of a V.S.M. can be found in references [3:8,3:13]. Details of the operation of the

V.S.M. used are contained in reference [3:14]. The V.S.M. can be operated in two modes:

1. Low Field. The magnet is surrounded by liquid nitrogen. Currents of up to 615mA are passed through the magnet operating in normal mode producing fields of up to 7500e. Data can then be taken between 77 and 200K.
2. High Field. The magnet chamber is filled with liquid helium. Currents of up to 76Amps. are used to produce a maximum field of 6.2T whilst the magnet is run in superconducting mode. Data are then collected at temperatures between 4.2 to 90K.

3:5:2. Specific Heat Measurements.

Specific heat measurements in the temperature range 1.5 to 30K were performed in a fully automated Nernst calorimeter. This apparatus was designed and constructed by Dr N.W. Pillmayr of the Technical University, Vienna. Details of the construction and operation of this equipment can be found in reference [3:15].

3:6. Sample Preparation.

3:6:1. The Argon Arc Furnace.

All the samples studied in this work were prepared by melting the constituent metals together in an arc furnace under an argon atmosphere. Details of the purity and the sources of the original materials used are contained in table 3:1. The furnace consists of a water cooled copper hearth and a tungsten electrode [3:16,3:17]. To prepare a sample the constituent materials were first cleaned. In some cases this involved simply washing in acetone to remove surface grease and dirt. Other metals such as Cu were first etched in dilute aqueous nitric acid before being cleaned with acetone. Others

such as Al were clean on silicon carbide papers to remove a majority of the surface oxides before use. Constituents such as Ce and some of the other rare earth metals used are highly reactive in air. For this reason they are stored under paraffin. These materials were also polished to remove any surface oxides before use. In some cases the Ce was pre-melted into a pellet. This allows oxides trapped within the material to float to the surface of the material where it can then be removed abrasively. The constituent materials are weighed on a balance to an accuracy of $\pm 0.1\text{mg}$. In almost all cases the samples were prepared on stoichiometry. That is, the weight of each element required was calculated and measured out assuming each constituent was made up entirely of the pure material and that all the material would then take part in the reaction to form the desired alloy. Mention is made in the relevant chapters of cases where samples were prepared off stoichiometry to take into account losses of a particular element which may occur during manufacture, or because of metallurgical difficulties peculiar to that system. The constituent metals are placed in a hollow in the copper hearth where they can be melted to form a button. The furnace is sealed, then evacuated and filled with pure argon gas to a pressure of half an atmosphere. This flushing procedure is repeated three times. The furnace is then gettered by heating a titanium pellet for two minutes with an electrode current of 100Amps., to remove any remaining traces of oxygen and to check the furnace is leak tight. The metals are then melted using an electrode current of between 50 and 100 Amperes. The sample button is turned and re-melted at least three times to ensure sample

homogeneity. The sample button is then moved onto the open end of one of a range of copper moulds. The button is melted and vacuum suction cast into the chilled mould. The majority of samples were cast into a square section tapered mould producing a rod shaped sample of 0.01 to 0.05cm² in cross section and between 0.5 to 3cm in length.

Table 3:1. Source and purity of the sample starting materials.

Element	Source.	Purity
Al	Johnson Matthey	Specpure 99.999%
Ag	Koch Light Lab.	99.9999%
Au	Johnson Matthey	99.9999%
Ce	RE-acton	RE-acton 99.9%
Co	Johnson Matthey	Puratronic 99.997%
Cu	Johnson Matthey	Specpure 99.999%
Fe	Johnson Matthey	Specpure 99.9985%
Gd	RE-acton	RE-eacton 99.9%
La	RE-acton	RE-acton 99.9%
Ni	Johnson Matthey	Specpure 99.998%
Pt	Harwell Lab.	99.9999%
Sn	Cominco	Grade 1 99.998%
Y	Rare Earth Prod.	99.99%
Zn	Koch Light Lab.	99.9998%

3:5:2. Annealing.

The samples are all annealed in vacuum in sealed quartz tubes to improve sample homogeneity and help remove unwanted phases which may have formed during manufacture. Choice of annealing schedule depends on the nature of the sample. Details of annealing times and temperatures along with a discussion of the reason for choice of these parameters are contained in

the chapters dealing with the different systems studied.

3:6:3. Metallography and Sample Purity.

All the samples prepared are examined to investigate for the possible presence of unwanted second phases. Metallographic specimens are prepared by mounting a small piece of each sample in Bakelite. These samples are then polished, first on silicon carbide papers with abrasive particles down to 800 grit size (≈ 20 microns). The specimens are then polished on a rotating wheel covered with a diamond polishing powder with particle sizes varying from 14 to 1 micron. This polishing must be carried out carefully to ensure that the surface layer is a representative cross section of the sample bulk. In particular, care must be taken to avoid straining the sample surface or smearing the grain boundaries. These problems can be partly overcome by chemically etching the specimens surface after polishing. The only etching agent used in this work was aqueous ferric chloride. In many cases this etching process also helps to enhance the contrast between different phases and between different grains within a single phase. In the case of many Ce based alloys air etching of specimen samples over a period of a few hours is effective in producing significant contrast between different phases, since Ce rich phases tend to be attacked more rapidly than phases containing less Ce. The samples are examined under an optical microscope. The presence of second phase and oxides and can be detected by considering variation in colour and reflectivity of the samples surface.

Another useful technique for detecting the presence of a magnetic second phase is to perform a magnetic susceptibility experiment. The high temperature susceptibilities of many of

the samples studied in this work are of the order 10^{-3} emu/mol. The presence of a small amount of ferromagnetic material such as pure iron could lead to a signal equal in magnitude to that expected from the sample. Thus an unexpected magnetic transition observed in a new alloy system must be treated with caution, as it could indicate the presence of a second phase.

3:6:4. X-Ray Diffractometry.

X-ray diffractometry can be used to detect the presence of second phase. However, impurity concentrations of between 5 and 10% are required for this technique to be successful. Smaller amounts of second phase may go unnoticed in an X-ray scan.

X-ray diffraction patterns have been obtained for most of the samples studied in this thesis. The equipment used was a commercially available Phillips X-ray machine. To obtain a scan, a small amount of a sample (≈ 0.1 g) is first crushed with pestle and mortar. The powder is then mounted on a single crystal of Si cut along the 011 plane. A collimated beam of radiation from a Cu source then illuminates the sample, and the diffracted beam is detected as the sample rotated between 5 and 65 degrees giving angles of scattering 2θ between 10 and 130 degrees. D spacings are calculated by the machine for significant peaks. For 2θ angles of between 10 and 70 degrees the wavelength used to calculate the spacing is $1.54178\text{\AA}$, an average of the Cu $K\alpha_1$ and $K\alpha_2$ radiation. Above 70 degrees the peaks due to the two wavelengths of radiation can be resolved and d spacings are then calculated using the Cu $K\alpha_1$ wavelength alone.

X-ray patterns are put to two uses:

1. The patterns obtained for each alloy series are compared with the pattern of the parent compounds to determine how far substitutions can be carried before either a structural change occurs or the limits of substitutional solid solution are reached.

2. Comparing the pattern for a substituted compound with the pattern for its pure parent alloy, allows lines of each pattern to be indexed. This is done with the help of Joint Committee on Powder Diffraction Standards card index data base containing details of all previous X-ray diffraction studies. Once the lines have been indexed, and since the structure of the alloy is known, the lattice parameters for the sample can be calculated.

Details of information obtained from X-ray data for the different systems studied are contained in the relevant chapters.

Chapter 4. Studies of the Effects of Alloying on the Properties of CeCu₆.

4:1. Introduction.

The magnetic, thermodynamic and transport properties of CeCu₆ have already been discussed in detail in chapter 1 and will not be repeated here. From these experiments it has been possible to classify CeCu₆ as a non-magnetic Kondo lattice system. An extremely high electronic specific heat parameter ($\gamma(0)=1.6\text{J/molK}^2$) at low temperature also means CeCu₆ is one of the "heaviest" of the hf systems. A qualitative explanation of this large value is found in terms of a low Kondo temperature. Alloying experiments which lead to variations in the physical parameters of the CeCu₆ system allow the study of the importance of these parameters in the formation of the hf state. For example, doping on the Ce sites allows the study of the effects of diluting the number of Ce atoms present per unit cell, and leads to a progression from a dense to a dilute Kondo system. Doping on the Cu sites allows one to investigate the effects on the hf state of changes in the hybridisation between the 4f electrons and the conduction electrons without perturbing the Ce sublattice unduly. Depending on the dopant chosen alloying may also produce chemical pressure effects due to changes in the lattice parameters. This chapter examines some of the effects of alloying on the CeCu₆ system. Section 4:3 discusses the properties of Ce(Cu_{1-x}Au_x)₆ alloys. Section 4:4 contrasts the effects of alloying with Gd or Y on the Ce sites in CeCu₆ with the results of substitutions on the Cu sites with Al, Ni, Zn or Au. Before these results are presented and discussed, previous studies of the variation in the

properties of CeCu_6 with pressure, and alloying experiments which have been carried out (La on the Ce sites and Ag on the Cu sites) will be briefly reviewed.

4:2. Previous Work.

4:2:1. Effects of Pressure on the Properties of CeCu_6 .

As discussed in section 1:3:2, applying pressure to CeCu_6 rapidly suppresses the low temperature value of the specific heat. $\gamma(0)$ is reduced from 1.6J/molK^2 at ambient pressure to 0.8J/molK^2 at 8.8kbar. This indicates that the mechanism which leads to the enhanced specific heat is rapidly modified with pressure. Since the high electronic specific heat is attributed to the formation of a narrow renormalized quasiparticle band close to the Fermi level, suppression of γ suggests that pressure may spread this band over a wider energy range. Thompson and Fisk [4:1], Shibata et al. [4:2] and Yomo et al. [4:3] have studied the temperature dependence of the electrical resistivity of CeCu_6 subjected to hydrostatic pressure (see figure 4:1). All groups observed that with increasing pressure the peak seen near 15K in CeCu_6 at $P=1\text{bar}$ becomes less prominent and is shifted to higher temperature. At 122kbar T_M , the temperature of the maximum, is at 300K. The value of dT_M/dP was calculated to be between 2 and 3K/kbar. All groups adopted the customary view (already discussed in chapters 1 and 2) that the negative $d\rho/dT$ seen above T_M is of Kondo origin and that the Ce 4f level is fully occupied or nearly so, forming a very narrow band close to the Fermi level. Above T_M the resistivity is dominated by Kondo like impurity scattering. Below T_M the Ce ions form a Kondo lattice leading to onset of coherence. T_M is assumed to be proportional to T_K . As pressure is applied,

the Ce 4f level is broadened and brought more nearly into coincidence with the Fermi level. Thus T_K (and with it T_M) increases, driving CeCu₆ into a weakly mixed valent regime, whilst still retaining the Kondo character. Thompson and Fisk calculated change in valency induced by pressure to be given by $V = V_0 + 0.005P(\text{kbar})$ where V is number of electrons per atom. They found for a pressure of 17.4kbar the valency changed by 0.09 electron. Using the assumption that T_K is proportional to T_M , it is also possible to use the shift in T_M with pressure to estimate a change in T_K expected due to changes in the cell volume. This parameter will be useful when considering the variation in T_K , due to changes in the cell volume (brought about by alloying). Assuming $T_K \propto T_M$ implies

$$T_K = C \cdot T_M \text{ ----- 4:1.}$$

where $C = \text{constant}$. Thus

$$\ln T_K = \ln T_M + \ln C \text{ ----- 4:2.}$$

Partial differential w.r.t the logarithm of the volume gives

$$\partial \ln T_K / \partial \ln V = \partial \ln C / \partial \ln V + \partial \ln T_M / \partial \ln V \text{ ----- 4:3.}$$

Using the expressions

$$\partial \ln T_M = \partial T_M / T_M \text{ and } \partial \ln V = \partial V / V \text{ gives}$$

$$\partial \ln T_K / \partial \ln V = \partial T_M / \partial V \cdot V / T_M \text{ ----- 4:4.}$$

Then using $\partial T_M / \partial V = (\partial T_M / \partial P) \cdot (\partial P / \partial V)$ gives

$$\begin{aligned} \partial \ln T_K / \partial \ln V &= (\partial T_M / \partial P) \cdot (\partial P / \partial V) \cdot (V / T_M) \\ &= (\partial T_M / \partial P) \cdot (B / T_M) \text{ ----- 4:5.} \end{aligned}$$

where $B = \text{bulk modulus} = -V(\partial P / \partial V)$

Substituting into equation 4:5 the published values for B , $\partial T_M / \partial P$ and T_M ($B = -500$ to -900 kbar , $\partial T_M / \partial P = 2$ to 3 K/kbar and $T_M = 15 \text{ K}$) gives values for $\partial \ln T_K / \partial \ln V$ between -45 and -180 . Further evidence for an increase in T_K with pressure is found

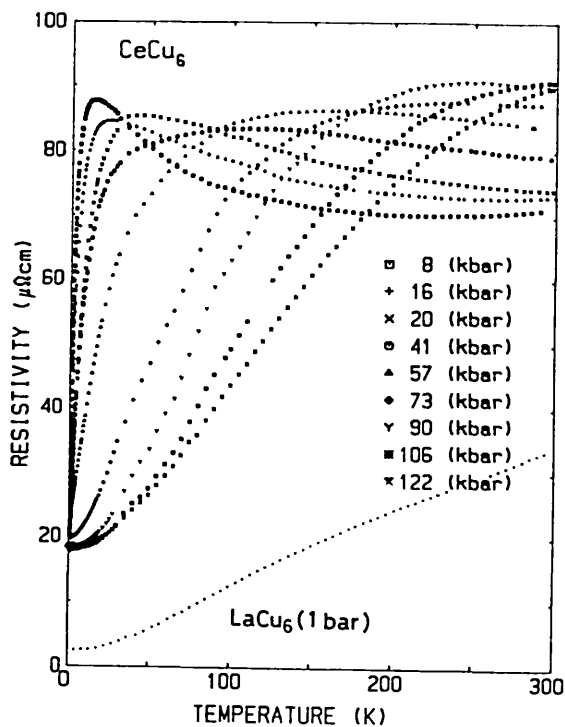


Figure 4:1. Temperature dependence of the resistivity of CeCu_6 at different external pressures. The four sets of pressure data with open marks such as the square, circle, triangle and lozenge indicate one sample and the others are another sample. Data are by Yomo et al [4:3]

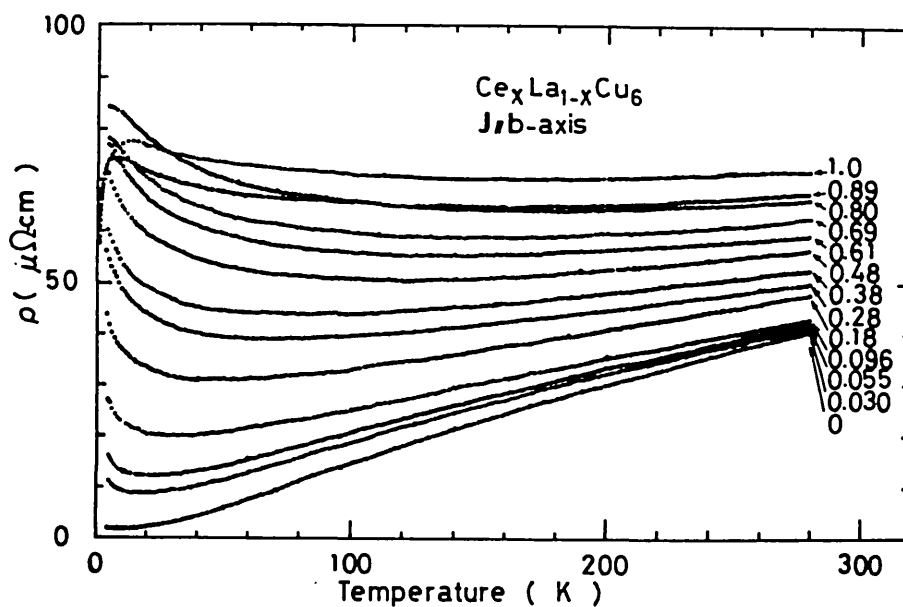


Figure 4:2. Temperature dependence of the electrical resistivity of $\text{Ce}_x\text{La}_{1-x}\text{Cu}_6$. Data are from Onuki et al. [4:5].

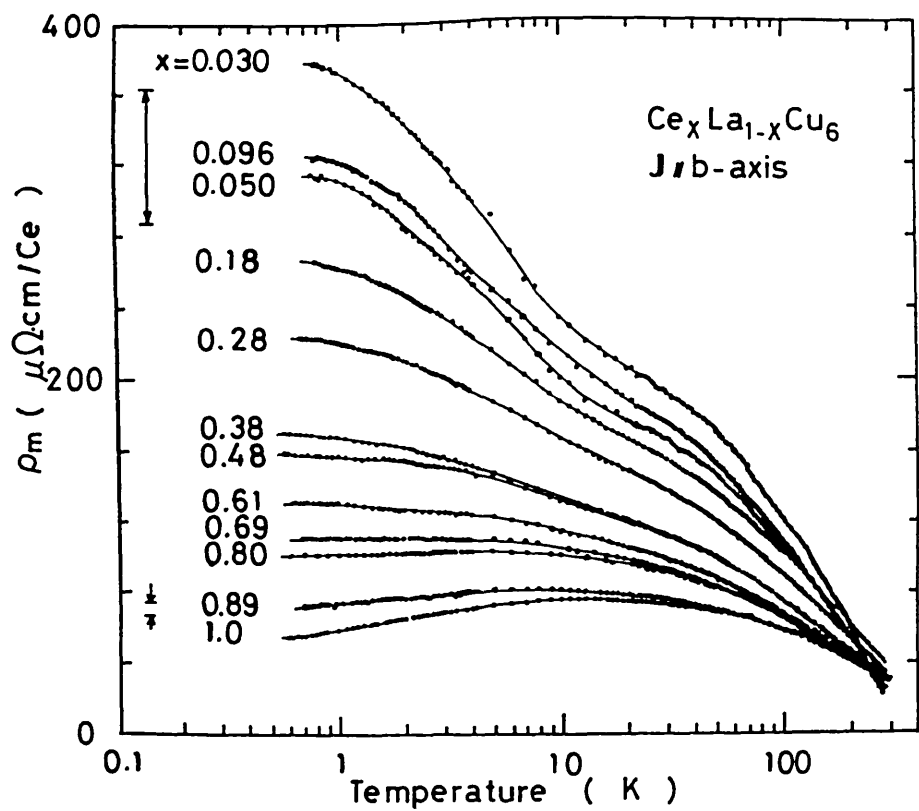


Figure 4:3. Temperature dependence of the magnetic resistivity per molar Ce of $\text{Ce}_x\text{La}_{1-x}\text{Cu}_6$. Data are from Onuki et al. [4:5].

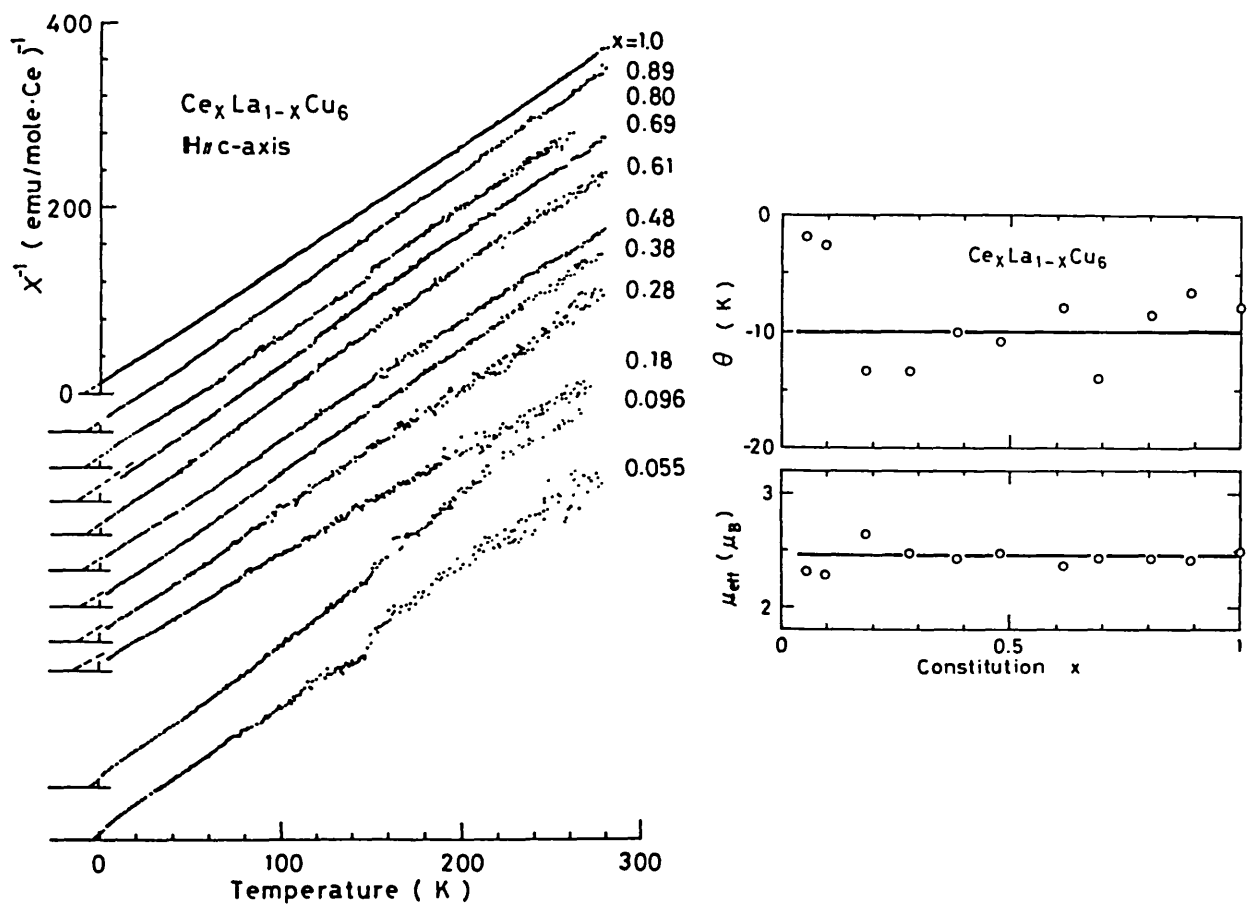


Figure 4:4. Temperature dependence of the inverse magnetic susceptibility in $\text{Ce}_x\text{La}_{1-x}\text{Cu}_6$. Data are from Onuki et al. [4:5].

Figure 4:5. Paramagnetic Curie temperature and Bohr magneton versus concentration x in $\text{Ce}_x\text{La}_{1-x}\text{Cu}_6$. Data are from Onuki et al. [4:5].

in the work of Onuki et al. [4:4] who studied the magnetoresistance of CeCu_6 under pressure. The crossover from negative to positive values at low temperature, which may indicate when CeCu_6 moves from individual into narrow 4f band behaviour, shifts from 0.7K at ambient pressure to 2.2K at 10kbar. This is again ascribed to an increase in T_K .

4:2:2. $\text{Ce}_x\text{La}_{1-x}\text{Cu}_6$.

Several groups have studied the $\text{Ce}_x\text{La}_{1-x}\text{Cu}_6$ system [4:5,4:6,4:7]. Figures 4:2 and 4:3 show the electrical resistivity and magnetic resistivity of selected $\text{Ce}_x\text{La}_{1-x}\text{Cu}_6$ alloys. This allows us to focus on the development of dense Kondo lattice behaviour from the dilute Kondo limit. At high temperature all samples show a logarithmic temperature dependence indicating that the Ce ions are acting as independent Kondo scatterers. At low temperature for $x \leq 0.20$, the magnetic resistivity per mole of Ce atoms has a constant value. For $0.20 \leq x \leq 0.70$ the magnetic resistivity per molar Ce decreases sharply with increase in Ce content. Finally for $x \geq 0.80$ we see a peak in the magnetic resistivity associated with formation of Ce ions into a periodic Kondo lattice. Thus a Kondo lattice is formed for $x \geq 0.8$. This assertion is supported by magnetoresistance data which shows that the minimum seen around 1.5K in magnetoresistance data in pure CeCu_6 , is also observed in the sample with $x=0.89$. However, for higher La concentrations no minimum is observed. Rather, the magnetoresistance is negative, becoming constant at lowest temperature, a behaviour which is characteristic of dilute Kondo systems. The magnetic susceptibility of $\text{Ce}_x\text{La}_{1-x}\text{Cu}_6$ shown in figure 4:4. increases with Ce concentration. The effective moment of the Ce ions at high

temperature ($\approx 2.46\mu_B$) and Curie temperature ($\approx -10K$) are independent of Ce concentration (see figure 4:5). This again indicates that the dilute Kondo regime is continuously connected to the dense Kondo state as a linear function of Ce concentration and that at high temperature the Ce ions behave as independent Kondo scatterers.

4:2:3 Ce(Cu_{1-x}Ag_x)₆.

Gangopadhyay et al. [1:15,4:8] have studied the effects of substitution of Ag on the Cu sites of CeCu₆. Their motivation was to investigate the importance of the hybridisation of the 4f electrons with the conduction electrons in the formation of the hf state, without perturbing the Ce sublattice.

Samples with up to 20%Ag were prepared. All samples showed Curie-Weiss behaviour. A fit to $\chi^{-1}=C/(T+\Theta)$ gave an effective moment of approximately $2.5\mu_B$, which was little changed by Ag substitution, with Θ decreasing from 46K for pure CeCu₆ to 21K for 10% Ag. This contrasts with substitutions of La on Ce sites where both Θ and effective moment were constant up to at least 0.906 La substitution. In the single ion Kondo picture Θ is taken as proportional to characteristic Kondo temperature T_K . Thus, halving the value of Θ with 10% Ag concentration implies a twofold decrease in the Kondo temperature. Similarly, using the idea that $\chi(0)$ is proportional to T_K^{-1} they asserted that a doubling in the value of the measured susceptibility at 2.4K also indicated a decrease in T_K . Using the same arguments as those which explain an increase in T_K with pressure, the decrease in T_K is attributed to negative chemical pressure, since substitution of Ag expands the lattice (10% Ag increases the cell volume by 0.5%). However, alloying is not likely to

produce changes in T_K which are in exact correspondence with changes brought about by pressure. This is because alloying not only expands the lattice, but also changes the character of the conduction electrons at the Fermi level. Reducing T_K should increase the likelihood of the onset of magnetic order at low temperature since the Kondo compensation mechanism is weakened. This is reflected in an increase in the value of the susceptibility. Gangopadhyay et al. also found an increase in the electronic specific heat coefficient, with $\gamma(0)=1.6\text{J/mol K}^2$ for pure CeCu_6 , rising to 2.8J/mol K^2 for CeCu_6 with 10% Ag. Since at the time no evidence for magnetic order was observed they attributed this increase in specific heat to an enhancement in the hf behaviour. However in later work [4:8], a peak was seen in both specific heat and $\chi_{a.c.}(T)$ data suggesting the enhancement in specific heat may simply be a prelude to the onset of magnetic order (see figure 4:6). The maximum in $\chi_{a.c.}(T)$ was seen in both field cooled (F.C.) and zero field cooled (Z.F.C.) data for samples with $x=0.05$ and 0.1 , whilst a peak was only seen in Z.F.C. data for $x=0.15$ and $x=0.2$ samples. This maximum is taken as a sign of the onset of magnetic order. The temperature at which the peak is observed moves up with Ag concentration according to linear relation $dT_{\text{max}}/dx=66\text{mK/at\% of Ag}$. Extrapolating this linear relation back to zero Kelvin suggests that only 1.3% Ag is needed for magnetic order. Gangopadhyay et al. suggest that the susceptibility along with the specific heat data points to antiferromagnetic ordering for low Ag concentration, with ferro or ferrimagnetic order at higher values of x . Ramakrishnan and Chandra [4:9] also investigated the effects of alloying with Ag on Cu sites. They confirmed

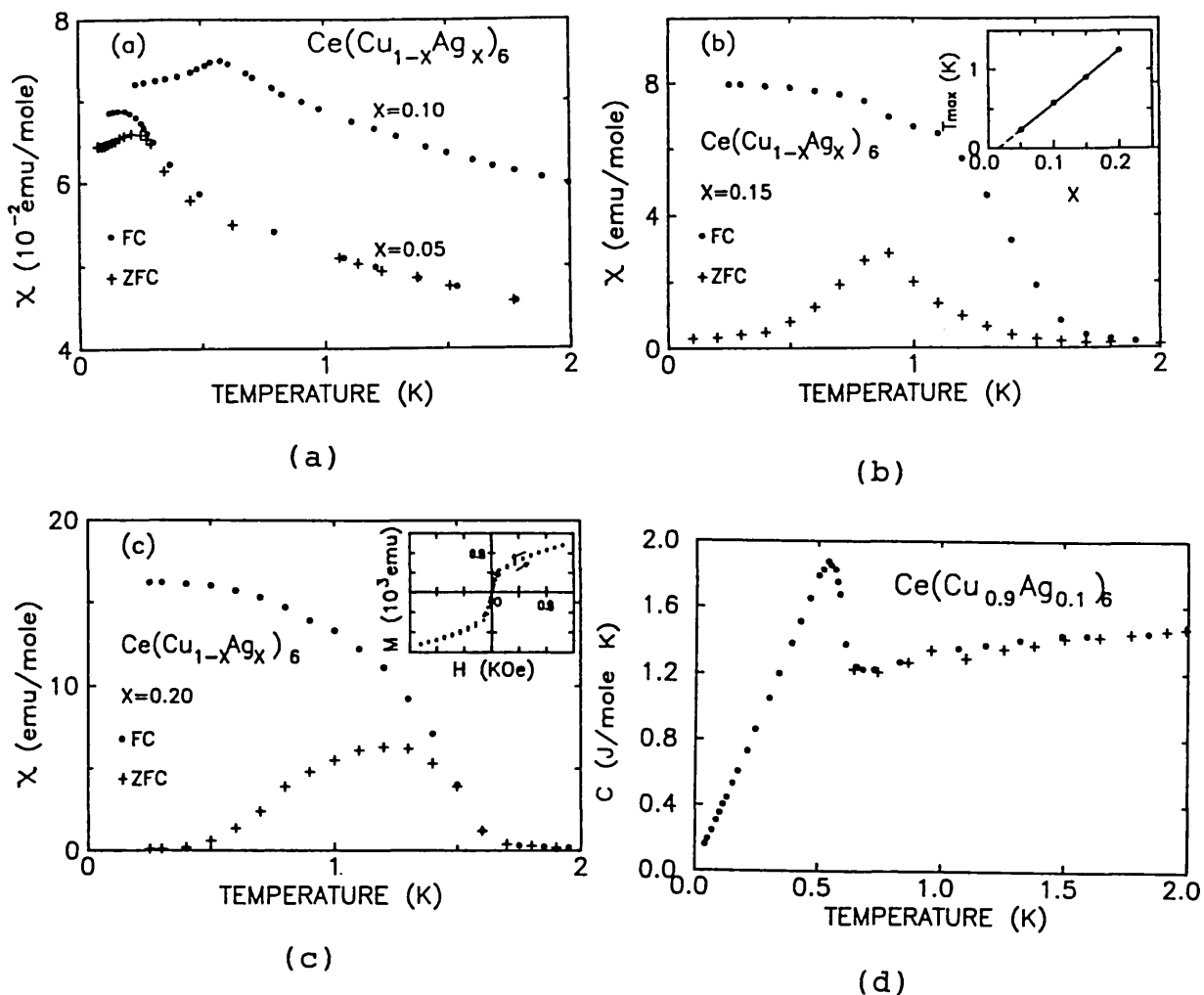


Figure 4:6. (a) The low temperature low-field d.c. susceptibility for $\text{Ce}(\text{Cu}_{1-x}\text{Ag}_x)_6$ samples for $x=0.05$ and $x=0.10$ in a field of 0.80e. Maxima are observed at 0.23 and 0.58K respectively. (b) The same as (a) but for $x=0.15$. The inset shows the variation in the temperature of the maximum with x . (c) The same as (a) but for $x=0.20$. The inset shows the hysteresis curve for $x=0.20$ at 1.4K. (d) The specific heat of $\text{Ce}(\text{Cu}_{0.9}\text{Ag}_{0.1})_6$ versus temperature below 2K showing a sharp anomaly at the temperature of the maximum in the magnetic susceptibility. Data taken from Gangopadhyay et al. [4:8].

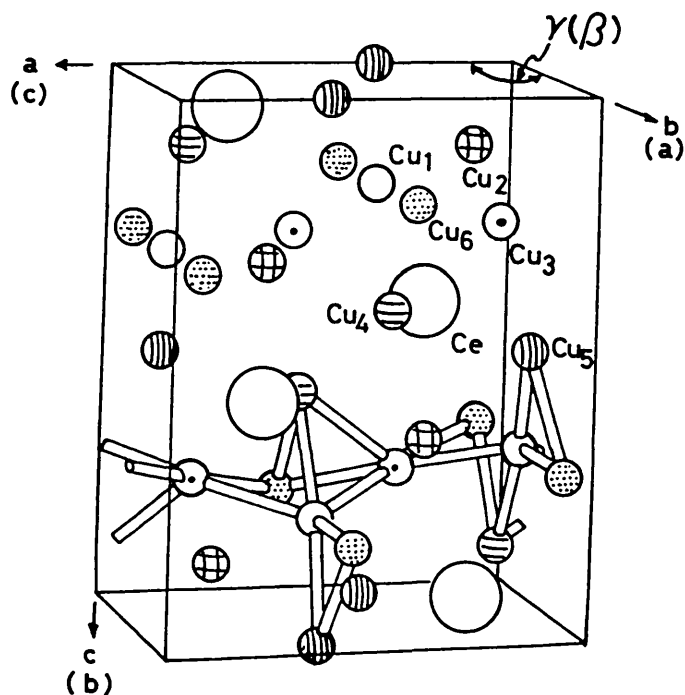


Figure 4:7. The crystal structure of CeCu_6 .

that the effective moment extracted from the high temperature susceptibility of $\text{Ce}(\text{Cu}_{1-x}\text{Ag}_x)_6$ is little changed with increase in x . They also confirmed that the paramagnetic Curie temperature is reduced and that the absolute value of susceptibility is increased as the Ag concentration is increased. They also observed that substitution of as little as 3.5% Ag was sufficient to suppress the maximum seen in the electrical resistivity of pure CeCu_6 at 15K below 1.5K (c.f. 30% La replacement on Ce sites is required to suppress T_M below 1.5K. Thus the position of the maximum in $\rho(T)$ and the onset of coherence was observed to depend critically on Cu conduction band, as well as the Ce sublattice.

4:3. The $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ Alloy System with $x \leq 0.30$.

4:3:1. Introduction.

In this section the effects on the properties of CeCu_6 of replacing Cu with isoelectronic Au are explored. Since Au has a larger ionic radius than Cu one expects to observe an increase in the lattice parameters producing negative lattice pressure. This in turn should lead to a change in the nature of hybridisation between the localized 4f and the conduction electrons, which is crucial in determining the strength of the Kondo effect and RKKY interactions and consequently the formation and nature of the hf ground state.

4:3:2. Sample Preparation.

CeCu_6 has an orthorhombic structure shown in figure 4:7. with lattice parameters shown in figure 4:8. CeAu_6 exists although there is no definite report in the literature of its structure. McMaster et al. [4:10] have tentatively suggested CeAu_6 may have a tetragonal structure. They did at least rule out the possibility that CeAu_6 has the orthorhombic CeCu_6

structure. As a result, no attempt was made to prepare samples with greater than 30% Au. All the samples were prepared by arc melting in an argon atmosphere using the method described in section 3:6. The purity of starting materials is also discussed in 3:6. All the samples were vacuum annealed in sealed quartz tubes for 7 days at 700°C. Metallographic specimens were prepared from the annealed samples. All the samples containing less than 20% Au were found to be nearly single phase, with only small traces of oxides present. Samples containing greater than 20% Au, showed signs of a small amount of a second phase. Examining the phase diagram of the Ce-Cu system [4:11] (shown in figure 4:9) this seems likely to be a little free Cu. X-ray powder diffraction patterns were obtained at room temperature from annealed samples. The X-ray patterns all have the orthorhombic structure of the parent compound CeCu_6 . These X-ray patterns all show a large background signal. The lines are broadened and the intensity of the lines are rapidly reduced as the dopant levels are increased. As a result the patterns could not be used to positively identify the second phase seen in samples with higher Au concentrations. Additionally this meant only the strongest peaks were used to calculate the lattice parameters. For all samples these were found to be the 104, 020 and 213 peaks.

4:3:3. Experimental Results.

4:3:3:1. Lattice Parameters.

The lattice parameters and cell volume of $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ for $x \leq 0.25$ are shown in figure 4:8. The values for pure CeCu_6 are in close agreement with the published data. Addition of Au produces an increase in a and c with increasing Au

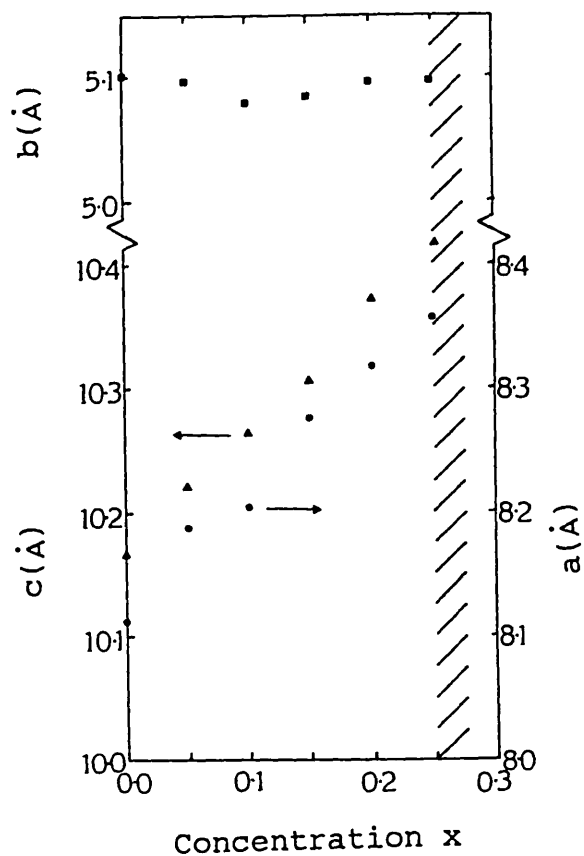


Figure 4:8. (a) Lattice parameters versus Au concentration x for $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$.

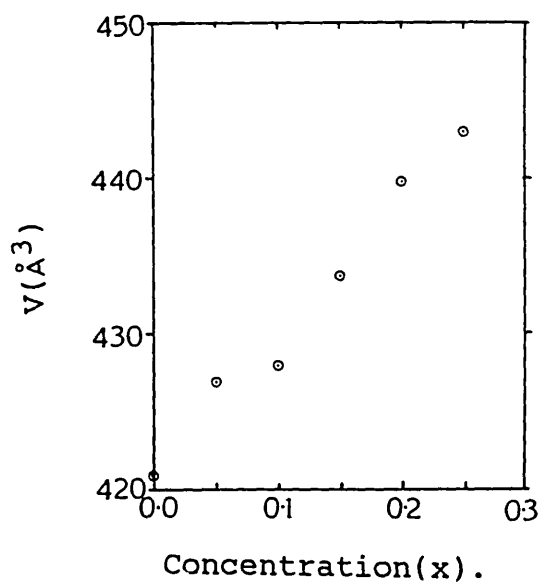


Figure 4:8. (b) Cell volume versus Au concentration for $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$.

Ce-Cu

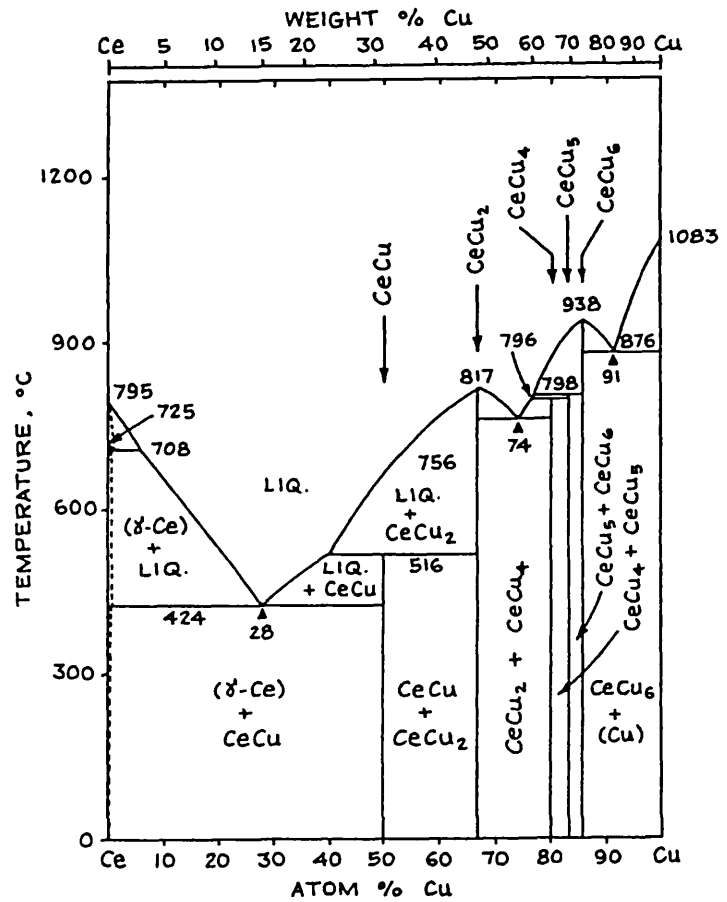


Figure 4:9. Ce-Cu phase diagram from Gschneidner and Verkade [4:11].

concentration, whilst values for b remain almost constant throughout the sample series. These changes produce an almost linear increase in the cell volume. Addition of 10% Au produces an increase in cell volume of 1.65%. (This compares with only 0.5% for 10% Ag. Thus, if the effects observed in the $\text{Ce}(\text{Cu}_{1-x}\text{Ag}_x)_6$ system, and discussed above are entirely due to negative chemical pressure, we can expect alloying with Au to produce similar effects at lower concentration levels). Using the average value of $\partial \ln T_K / \partial \ln V = -124$ obtained in section 4:2:1, a volume expansion of 1.65% is expected to cause a decrease in T_K of roughly 200%. Is this expected reduction in T_K reflected in low temperature properties of $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ which depend on T_K ?

4:3:3:2. Electrical Resistivity.

Figures 4:10, 4:11 and 4:12 show the temperature dependence of the electrical resistivity of $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ alloys for $x \leq 0.25$. The magnetic resistivity results given by $\rho(\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6) - \rho(\text{La}(\text{Cu}_{1-x}\text{Au}_x)_6)$ are shown in figure 4:13. $\text{La}(\text{Cu}_{1-x}\text{Au}_x)_6$ alloys were used as isostructural non-magnetic reference compounds. The structure of LaCu_6 [4:5] is reported to be monoclinic with $a=5.156\text{\AA}$, $b=10.238\text{\AA}$ and $c=8.168\text{\AA}$ with $\beta=91.49^\circ$. As discussed in section 4:3:2. CeCu_6 has an orthorhombic structure at room temperature. However, observation of the temperature dependence of elastic constant by Suzuki et al. [4:12] has revealed a crystal distortion from orthorhombic to monoclinic structure at approximately 165K, with $a=5.089\text{\AA}$, $b=10.137\text{\AA}$, $c=8.073\text{\AA}$ and $\beta=90.83^\circ$. Therefore, both CeCu_6 and LaCu_6 have the same structure below 165K. Further, since no evidence of the structural distortion in CeCu_6 is seen in resistivity data, LaCu_6 is assumed to be

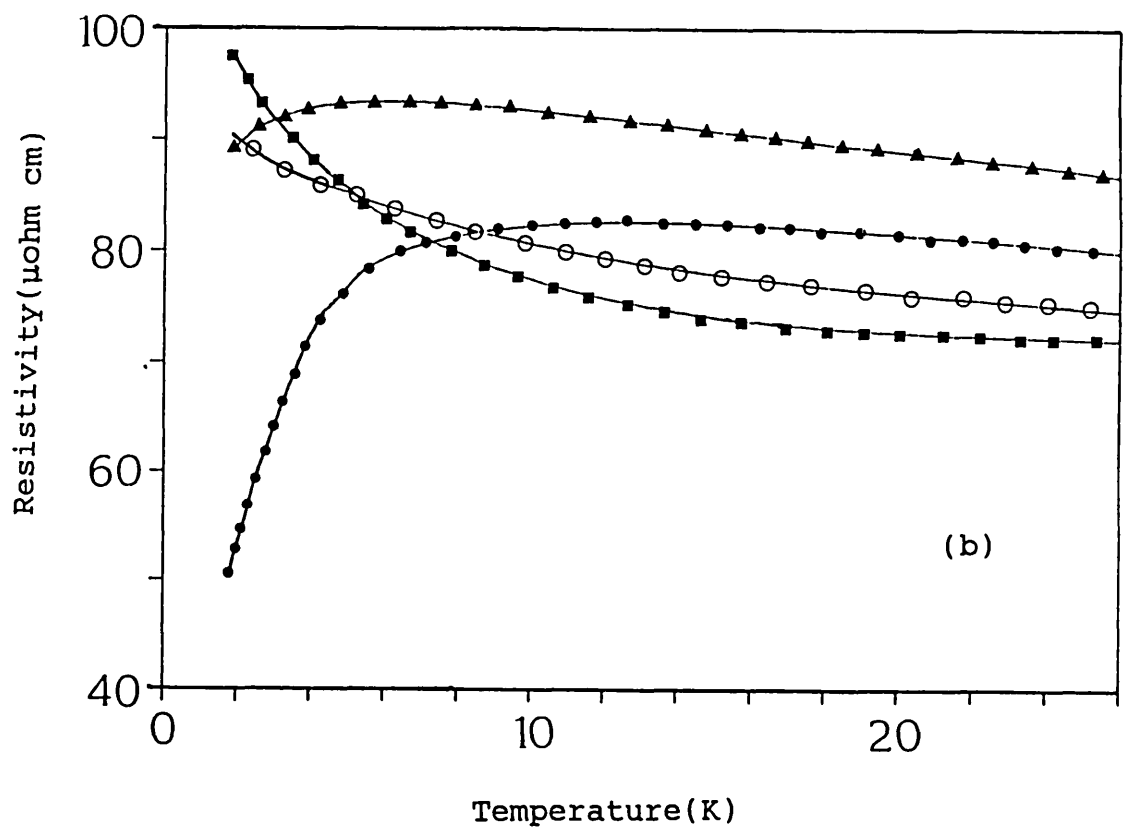
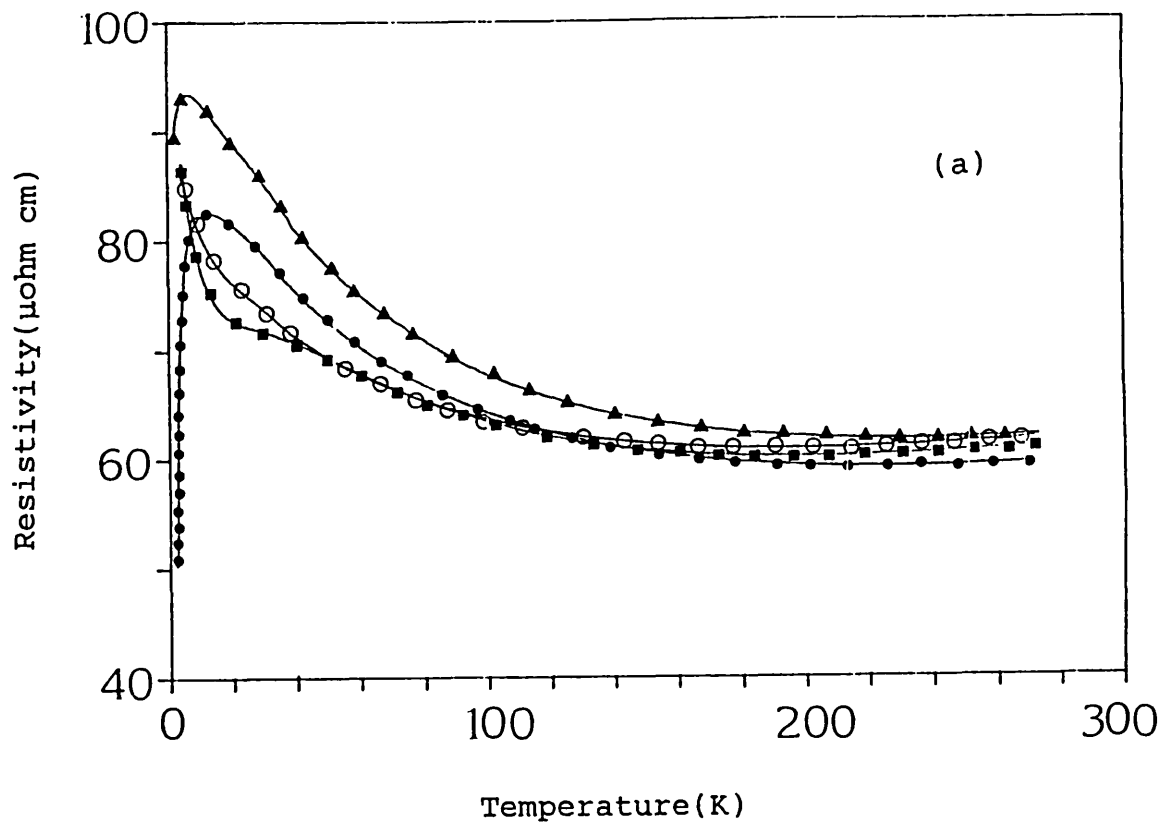


Figure 4:10. (a) and (b) Temperature dependence of the electrical resistivity of $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ for $x=0.00(\bullet)$, $0.02(\blacktriangle)$, $0.05(\circ)$ and $0.10(\blacksquare)$.

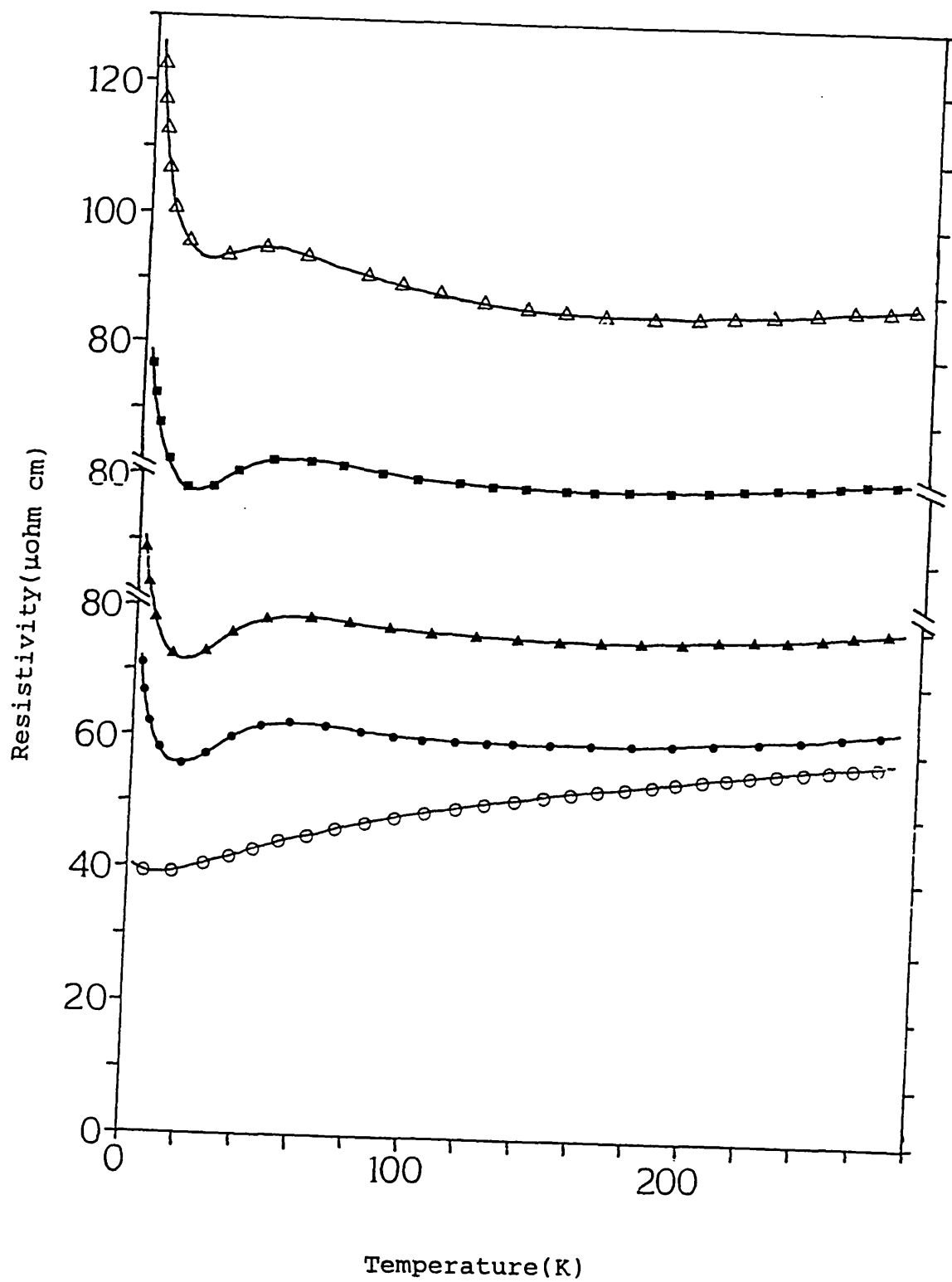


Figure 4:11. Temperature dependence of the electrical resistivity of $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ for $x=0.125(\Delta)$, $0.15(\blacksquare)$, $0.175(\blacktriangle)$, $0.20(\bullet)$ and $0.25(\circ)$.

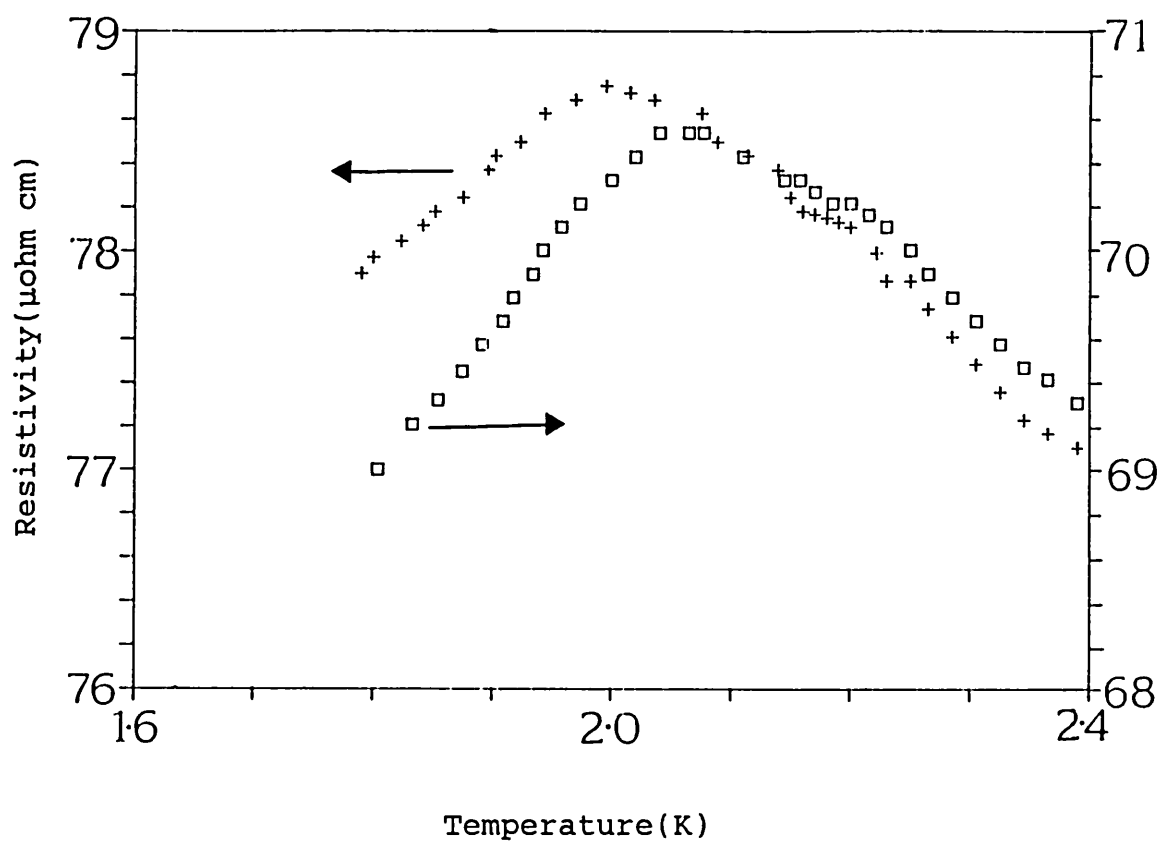


Figure 4:12. Low temperature resistivity of $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ for $x=0.15$ (+) and 0.175 (□).

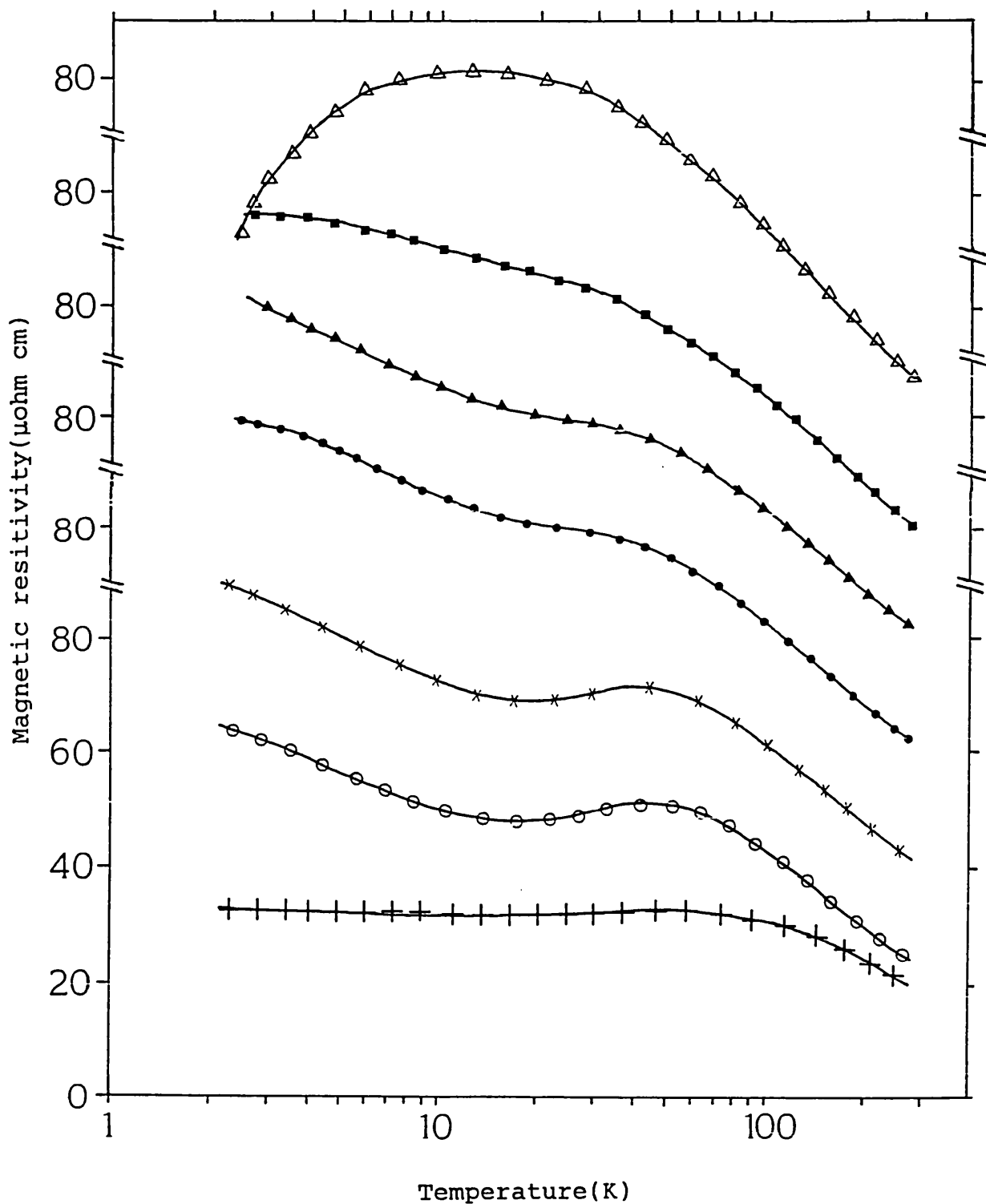


Figure 4:13. Magnetic contribution to the electrical resistivity for $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ in a semilogarithmic representation, where $x=0.00(\Delta)$, $0.05(\blacksquare)$, $0.10(\blacktriangle)$, $0.125(\bullet)$, $0.15(\times)$, $0.20(\circ)$, $0.25(+)$.

a good reference compound to room temperature.

Several features in the resistivity data must be highlighted:

1. The temperature T_M , at which a maximum is seen in the resistivity ($=15K$ for pure $CeCu_6$) is rapidly suppressed as Au is added. For 2% Au $T_M=6K$ whilst it has been suppressed below $1.5K$ for 5%Au.
2. The value of the resistivity at high temperature is almost independent of Au concentration.
3. As the gold concentration is increased, a clear maximum appears in the data around 30 to 50K. The temperature at which this maximum occurs increases with increasing Au concentration (see Table 4:1.).
4. Examining the magnetic resistivity of the alloys shows this feature separates two regions where the resistivity has logarithmic temperature dependence. The slope $d\rho_{mag}/d\ln T$ at high temperature decreases with increasing Au concentration.
5. At concentrations of $.15 \leq x \leq .175$ a maximum in resistivity is seen at approximately 2K.

Table 4:1. Some properties of selected $Ce(Cu_{1-x}Au_x)_6$ alloys taken from transport data.

$Ce(Cu_{1-x}Au_x)_6$ x	0.00	0.05	0.10	0.15	0.175	0.20	0.25
Low $T_{max}(K)$	15	≤ 1.5	--	2.0	2.05	---	---
$\rho_{mag} \text{ Max } (K)$	---	30	35	39	44.5	43.5	49
$\rho_{273K}(\mu ohmcm)$	59.5	61.8	61.0	60.9	58.9	63.0	58.4
$-d\rho_{mag}/d\ln T$	25.5	22.5	20.5	19.9	19.5	18.9	11.4
$S(T)_{max}(K)$	50	---	68	---	---	---	---

4:3:3:3. Thermopower.

The thermopower $S(T)$, of $CeCu_6$ and $Ce(Cu_{0.9}Au_{0.1})_6$ are shown in figure 4:14. The measurements were performed by Dr Ernst Bauer at the Technical University, Vienna. $CeCu_6$ has an unusually large $S(T)$ value. A maximum is seen in $S(T)$ at high temperature in common with many other non-magnetic hf ($CeAl_3$, $CeCu_3Al_2$). This large positive peak is attributed to a competition between incoherent Kondo scattering and C.F. effects. The addition of 10%Au reduces the magnitude of $S(T)$,

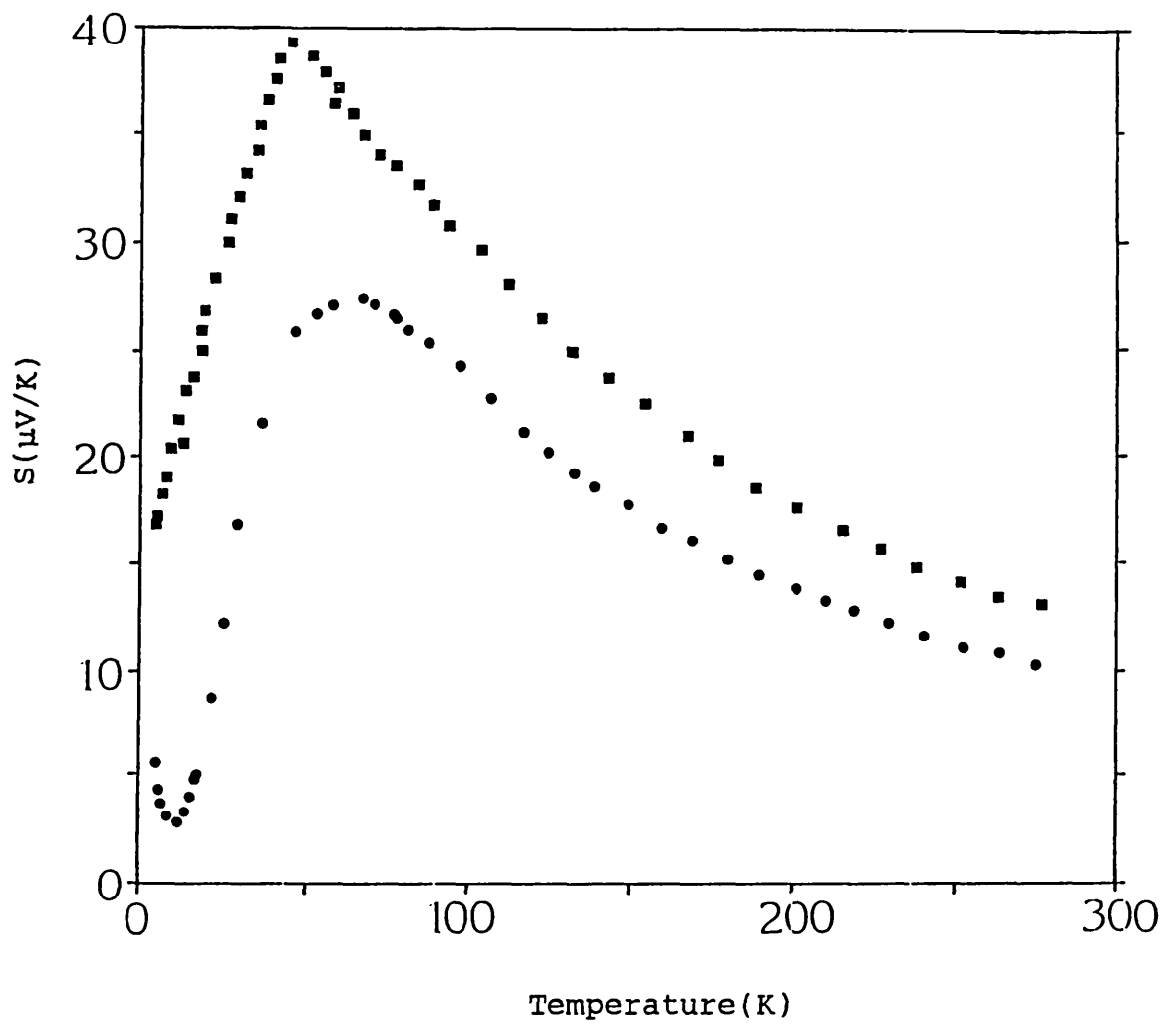


Figure 4:14. The temperature dependence of the thermopower S of $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ with $x=0.00$ (■) and 0.10 (●).

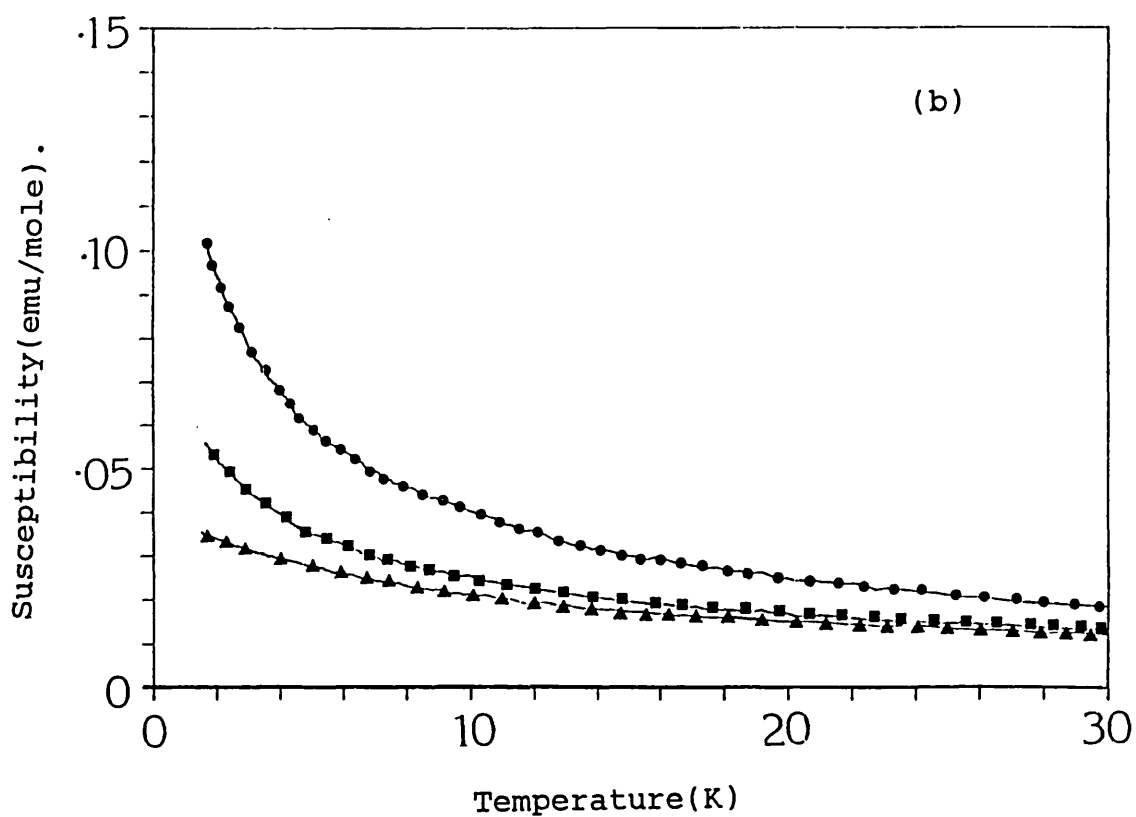
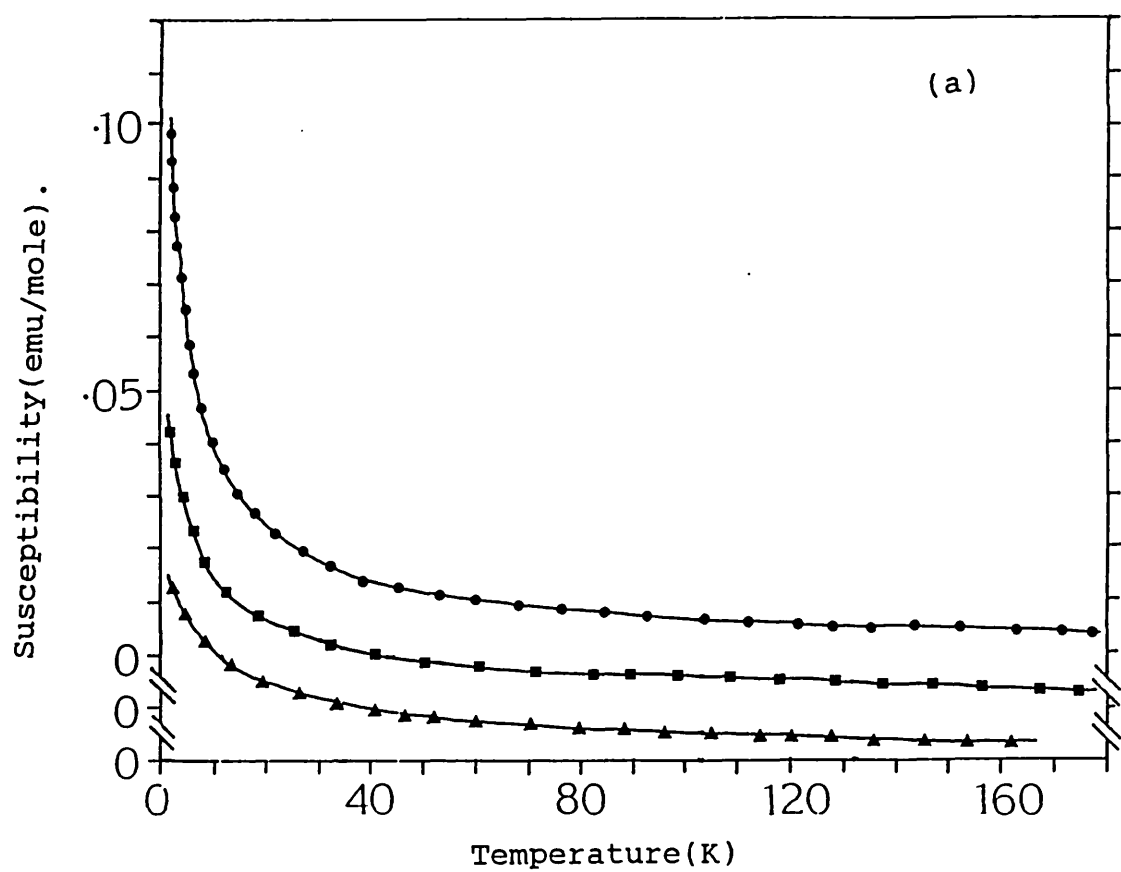


Figure 4:15. (a) and (b) Magnetic susceptibility versus temperature for $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ for $x=0.00$ ($\blacktriangle$), 0.05 ($\blacksquare$) and 0.10 ($\bullet$)

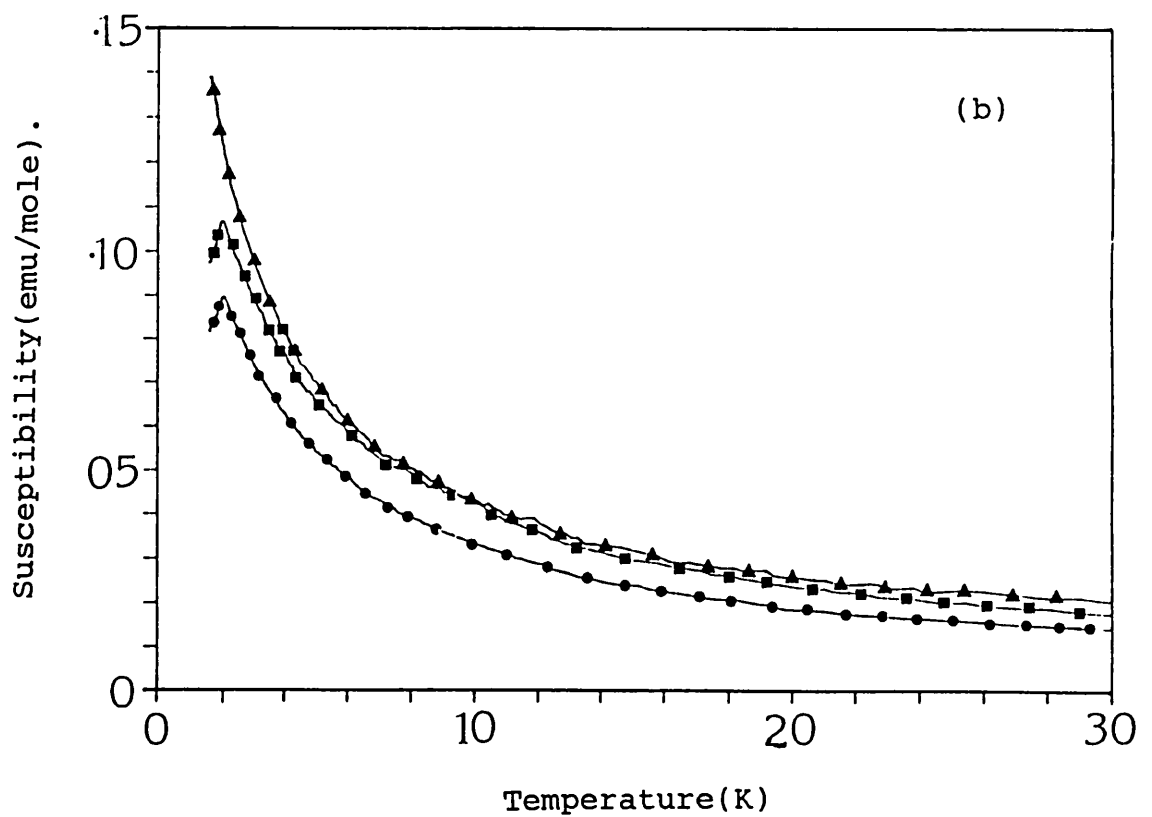
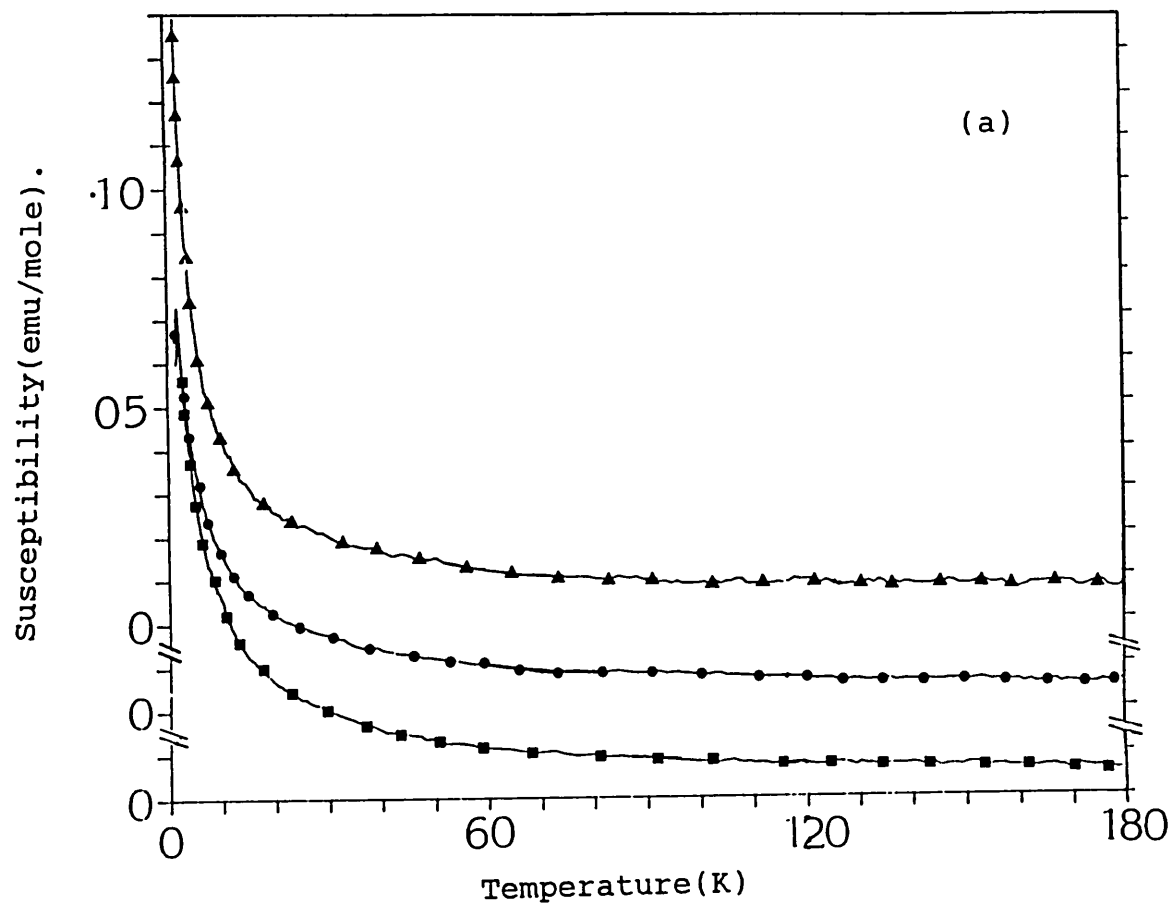


Figure 4:16. (a) and (b) Magnetic susceptibility versus temperature for $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ for $x=0.15(\bullet)$, $0.175(\blacksquare)$ and $0.20(\blacktriangle)$.

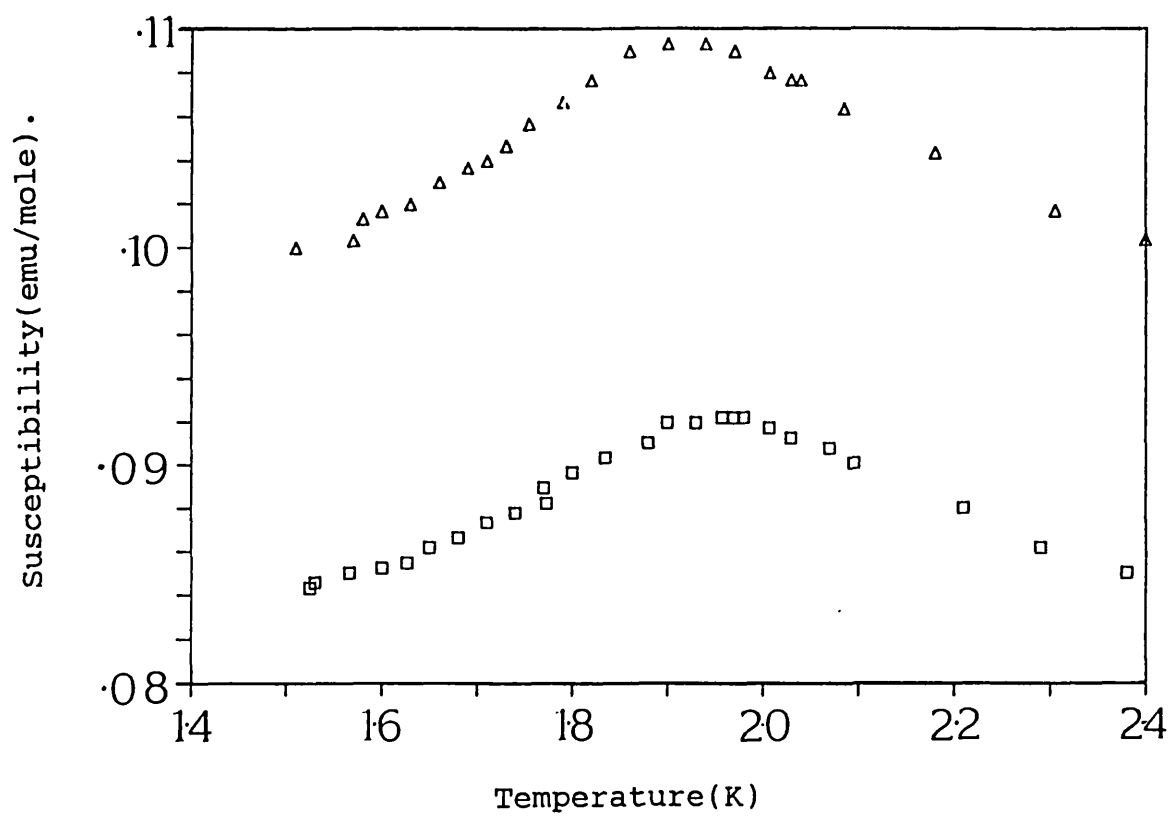


Figure 4:17. Low temperature cusp in the susceptibility of $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ for $x=0.15(\Delta)$ and $0.175(\square)$.

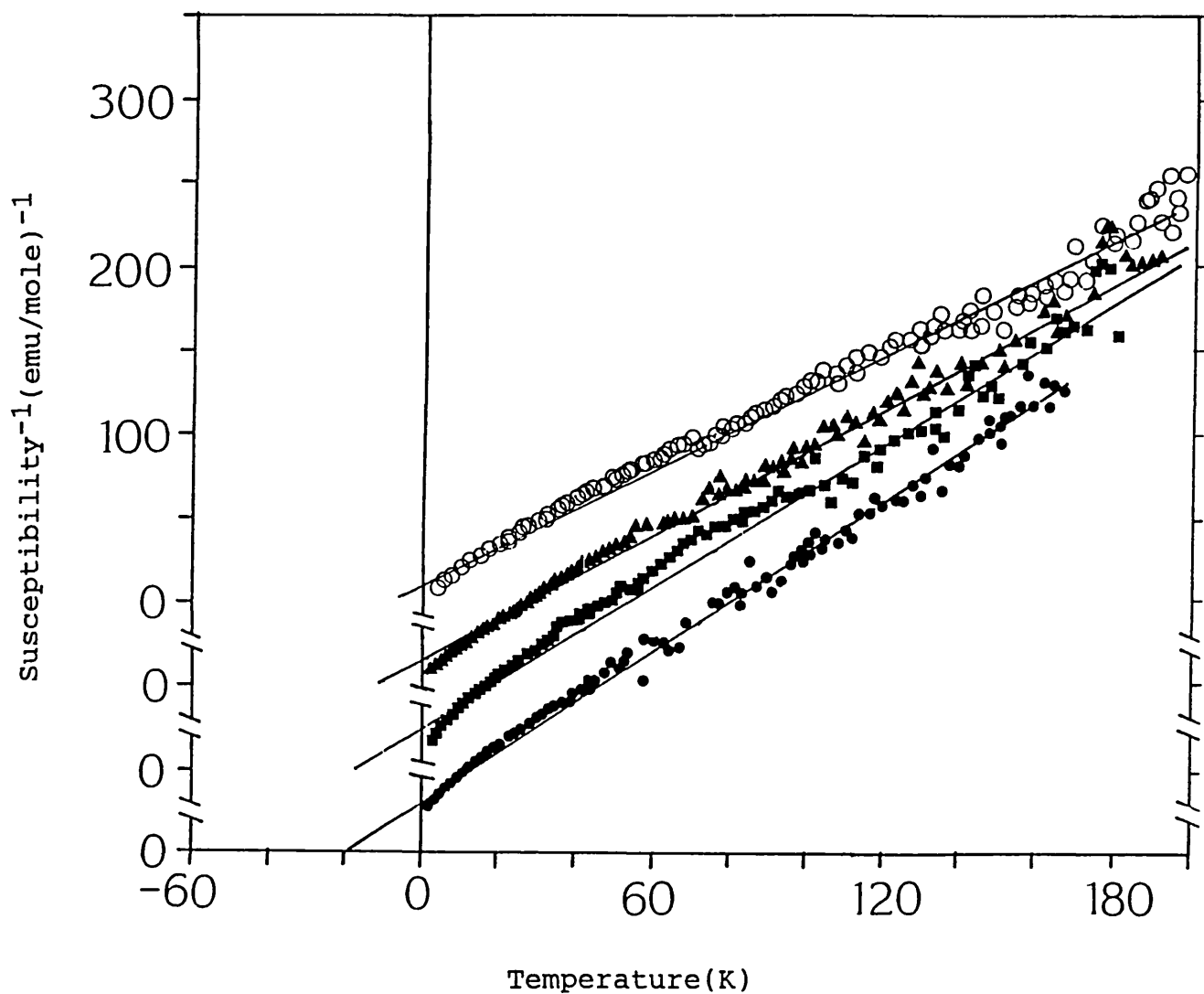


Figure 4:18. Temperature dependence of the inverse magnetic susceptibility of $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ for $x=0.00(\bullet)$, $0.05(\blacksquare)$, $0.10(\blacktriangle)$ and $0.15(\circ)$.

whilst the position of the positive peak is shifted to higher temperature. This behaviour is similar to that observed in $\text{Ce}(\text{Cu}_x\text{Al}_{1-x})_5$ system during the crossover from non-magnetic to magnetic behaviour [4:13].

4:3:3:4. Magnetic Susceptibility.

Figures 4:15., 4:16., 4:17. and 4:18. show χ versus T and χ^{-1} versus T for $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ alloys with $x \leq 0.25$. Again, several features are observed.

1. χ^{-1} v T plots reveal all alloys show Curie-Weiss like behaviour at high temperature. Fits to $\chi^{-1} = C/(T-\theta)$ give values for the effective moment and paramagnetic Curie temperature shown in table 4.2. The value of μ_{eff} for pure CeCu_6 is in close agreement with published data. The value for $|\theta|$ is somewhat smaller than the values observed by other workers.
2. The magnitude of χ at 4.2K (shown in table 4.2.) increases with Au concentration.
3. A peak appears in the susceptibility data at approximately 2K for $0.15 \leq x \leq 0.175$. No maximum is present above 1.5K in χ v T curves outside this concentration range.

Table 4:2. Some magnetic properties of selected $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ compounds.

$\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ x	0.00	0.05	0.10	0.15
$\theta_p(\text{K})$	-20.1	-18.2	-13.0	-8.4
$\mu_{\text{eff}}(\mu_B)$	2.31	2.38	2.54	2.65
$\chi_{4.2\text{K}}(\text{emu/mole})$	0.029	0.038	0.0644	0.076
T_{max}	-----	-----	-----	1.93

4:3:3:5. Specific Heat.

Specific heat measurements were performed on $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ samples for $0.13 \leq x \leq 0.20$, between 1.5 and approximately 20K. Figures 4:19. and 4:20. show the data collected, plotted as C/T versus T^2 . The behaviour of the Au alloys look similar to that of pure CeCu_6 . Between 10 and 20K or the highest temperature reached in the experiment the specific heat has

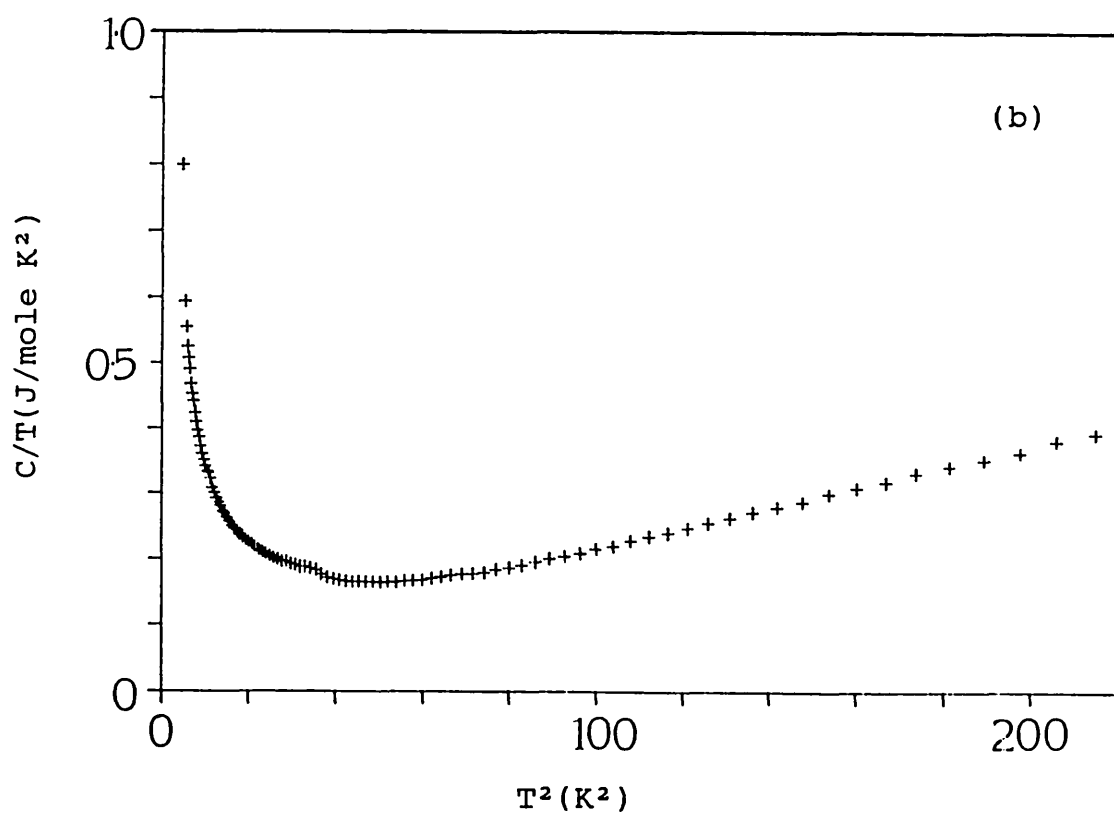
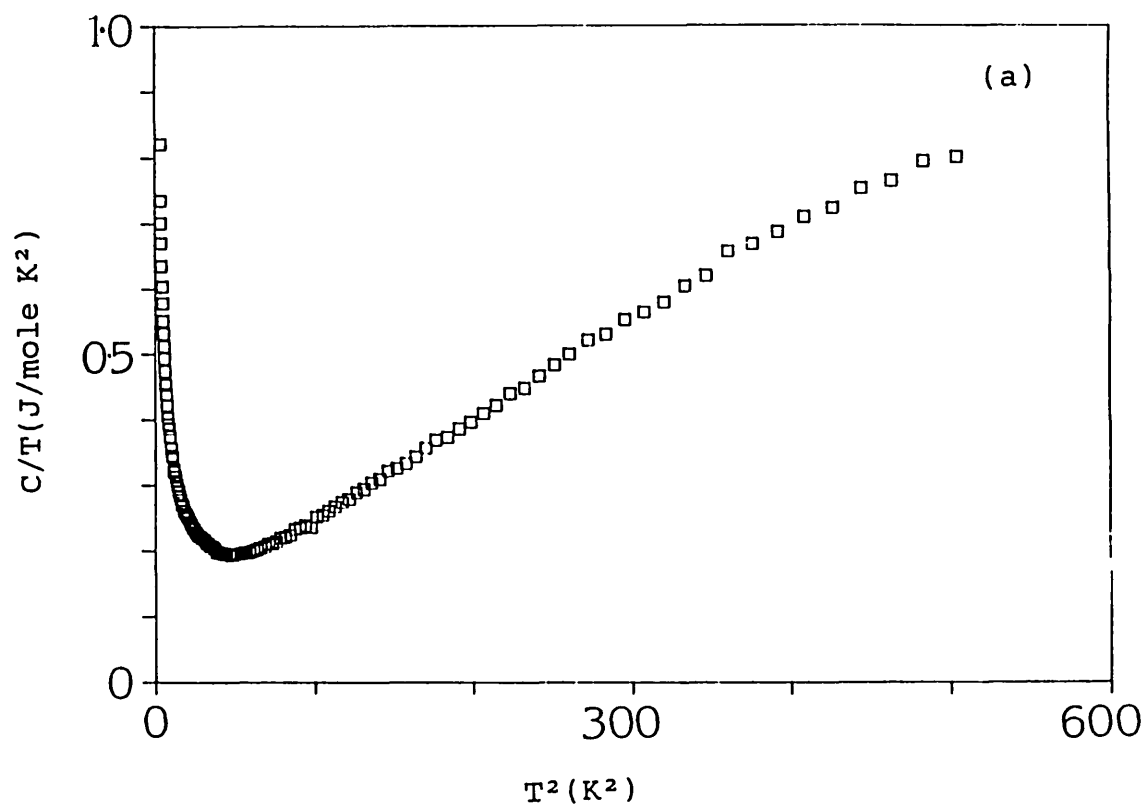


Figure 4:19. (a) and (b) C/T versus T^2 for $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ for $x=0.13(\square)$ and $0.15(+)$.

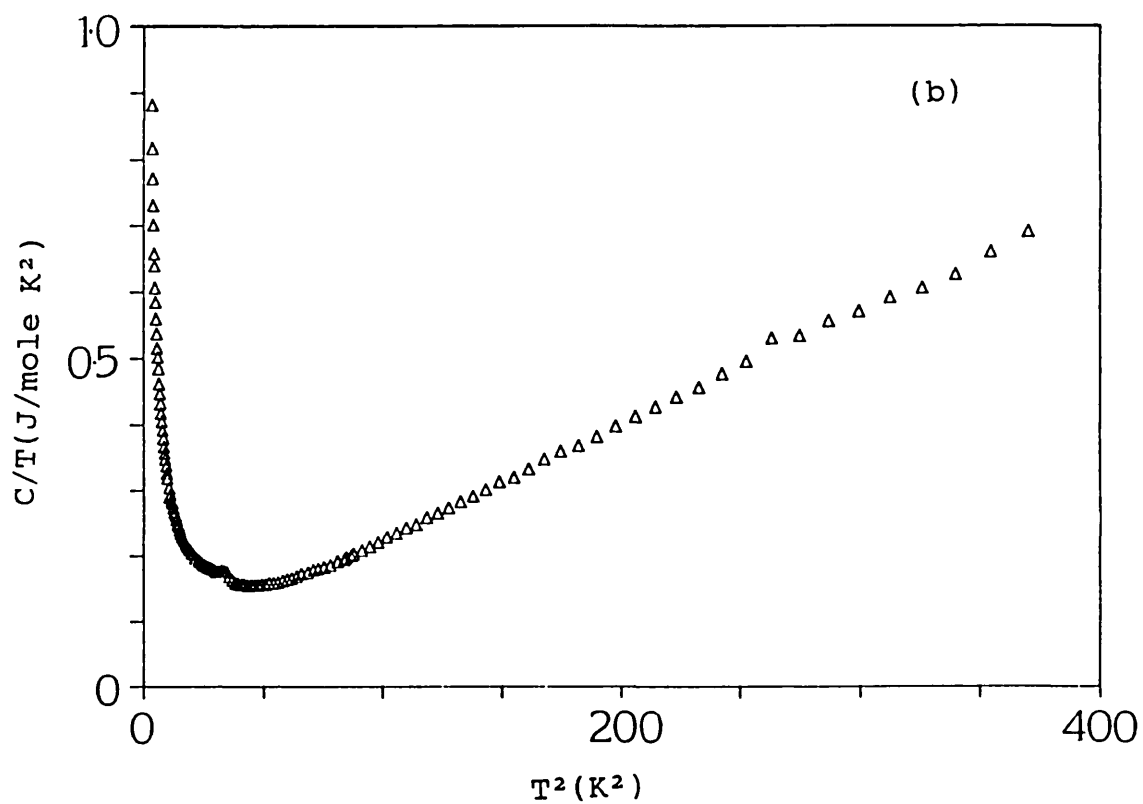
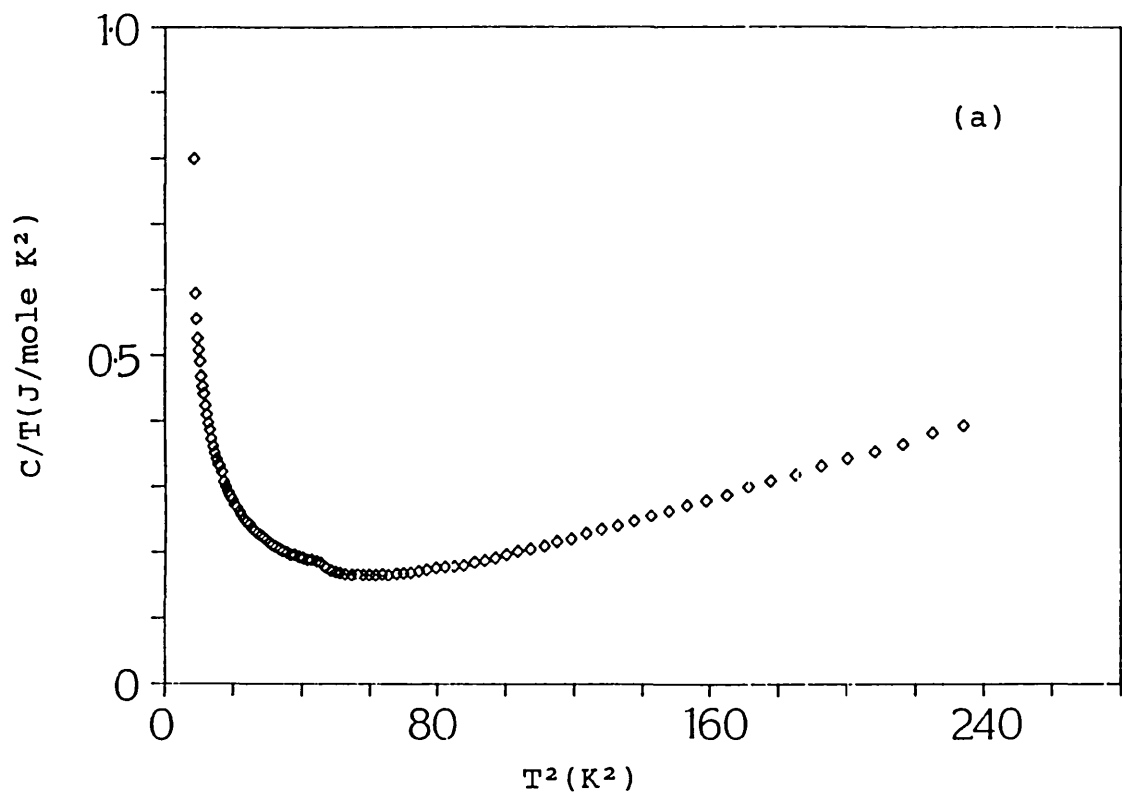


Figure 4:20. (a) and (b) C/T versus T^2 for $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ for $x=0.175(\diamond)$ and $0.20(\triangle)$.

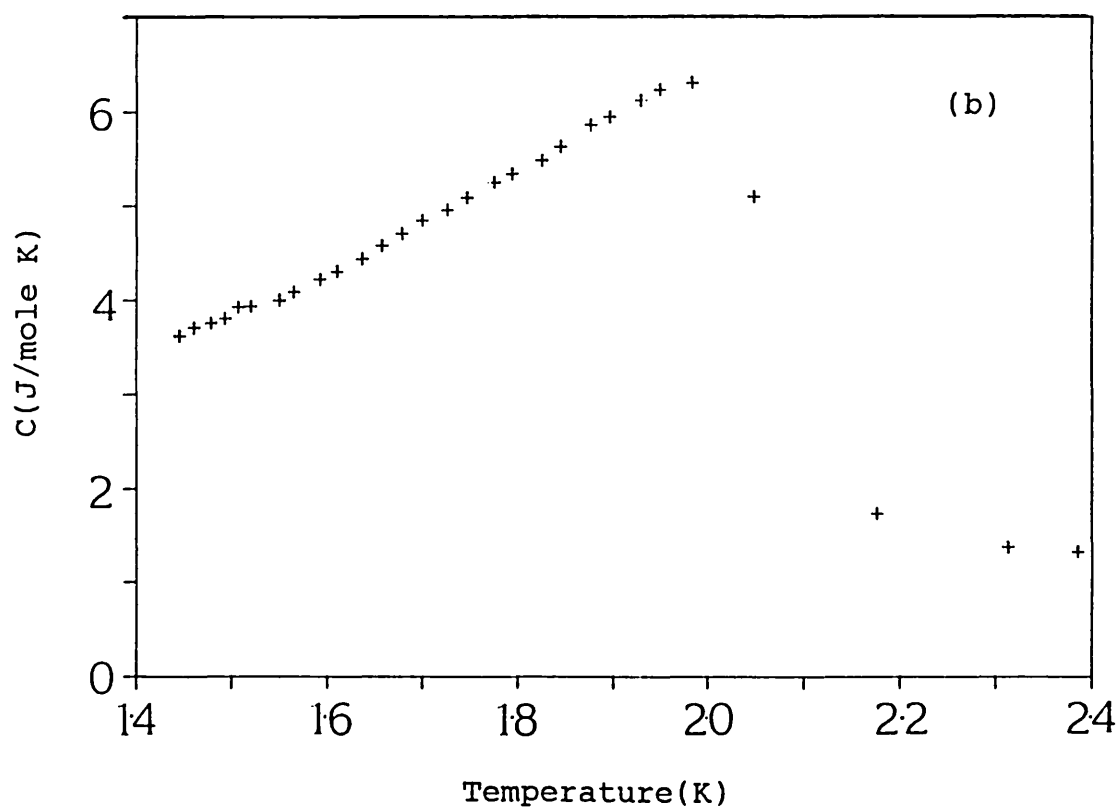
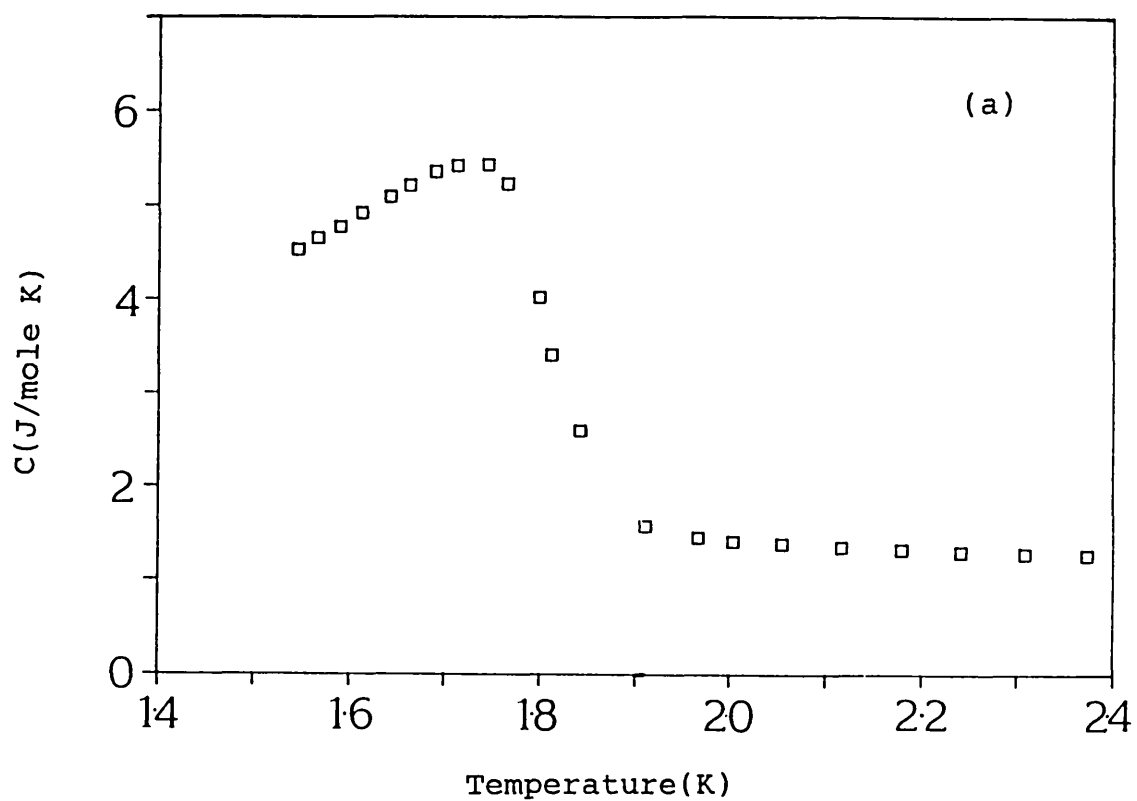


Figure 4:21. (a) and (b) The specific heat C as a function of temperature for $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ for $x=0.13$ ($\square$) and 0.15 ($+$).

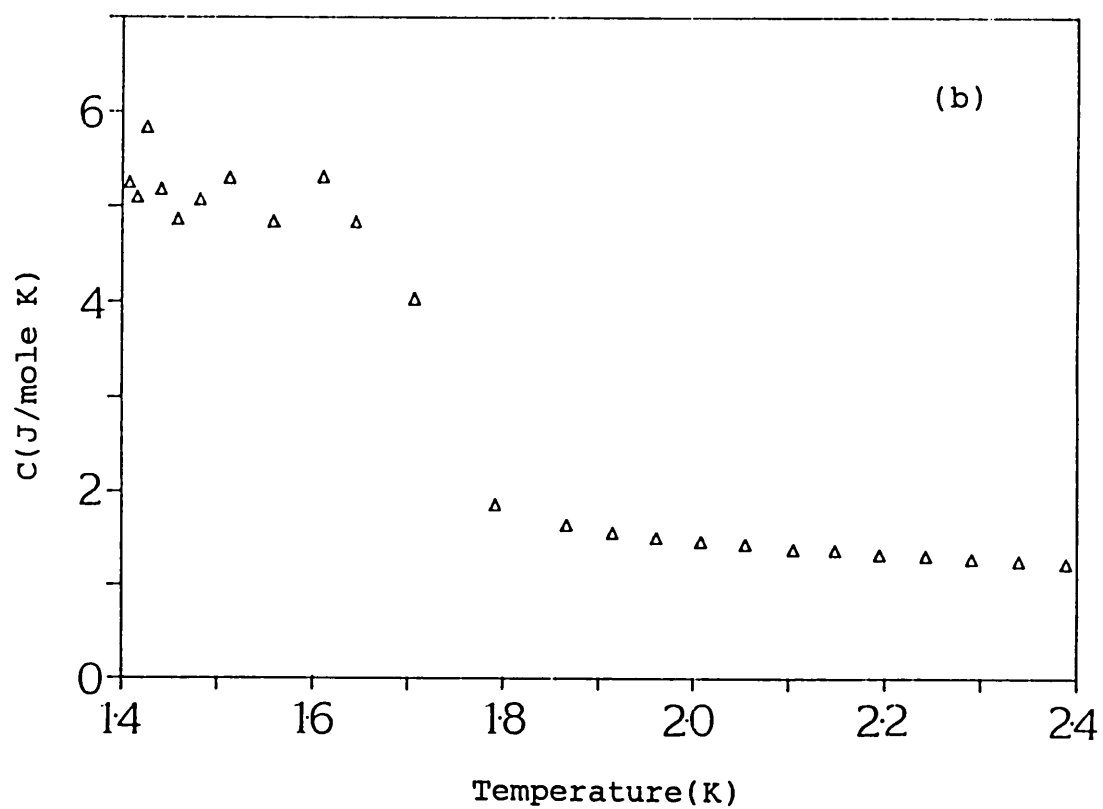
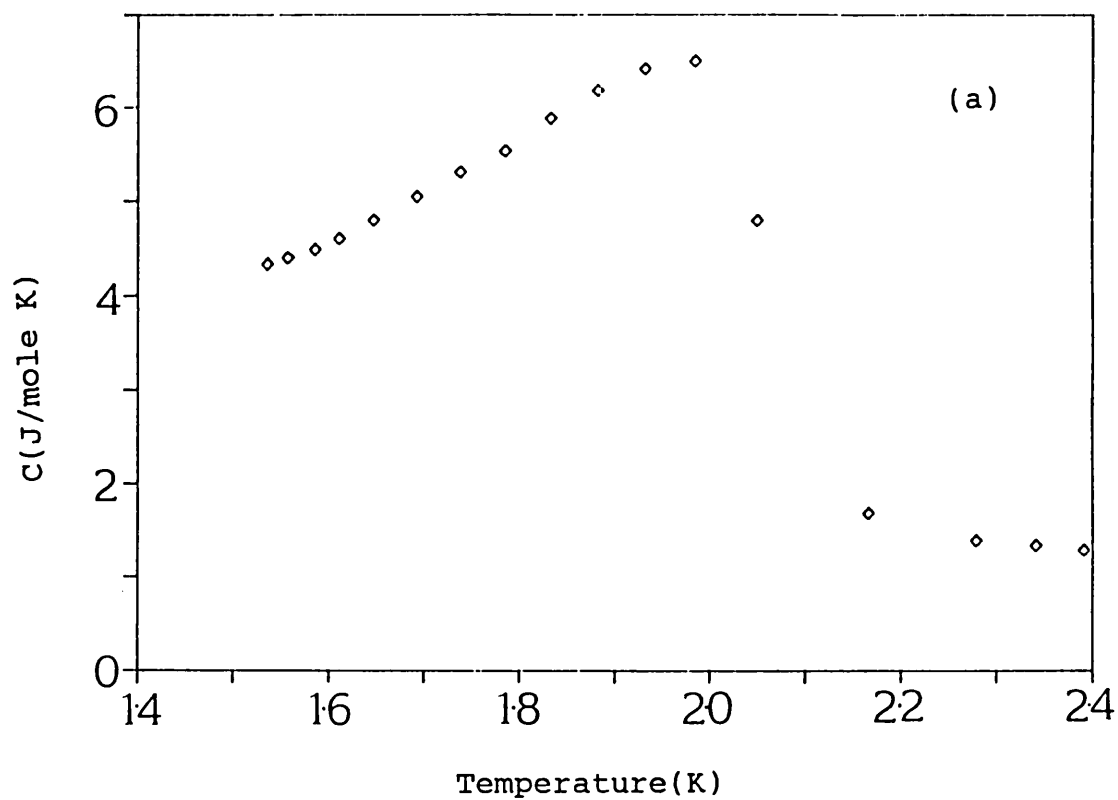


Figure 4:22. (a) and (b) The specific heat C as a function of temperature for $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ for $x=0.175(\diamond)$ and $0.20(\triangle)$.

been fitted to

$$C = \gamma T + \beta T^3 \text{ ----- 4:6.}$$

Values for γ and β for the samples studied in this work and from two samples with lower Au concentration studied by Germann et al.[4:14] are shown in table 4.3. Using the Debye model

$$\beta = (12\pi^4/5) * N K_B * (T/\Theta_D)^3 \text{ ----- 4:7.}$$

where N = number of moles per formula unit

$$= 7 * 6.02217 * 10^{23}$$

and K_B = Boltzmann constant = $1.38 * 10^{-23} \text{ JK}^{-1}$ gives

$$\Theta_D = (13606.18/\beta)^{1/3}. \text{ ----- 4:8.}$$

Values for Θ_D are also shown in table 4:3. The increase in β as Au content is increased corresponds to a steady decrease in Θ_D . This is attributed to the larger Au mass. A decrease is also observed in the high temperature value of γ , from 234mJ/mol K² for pure CeCu₆ to just 46mJ/mol K² for CeCu₆ with 20% Au. It is not possible to categorically state that this reduction in γ indicates the hf behaviour has been removed. This is because γ is temperature dependent and an upturn in C/T at lower temperature may indicate onset of hf behaviour. In fact a sharp rise in C/T at low temperature is observed.

Table 4:3. Some properties of selected Ce(Cu_{1-x}Au_x)₆ alloys extracted from specific heat data.

Ce(Cu _{1-x} Au _x) ₆ x	0.0	.033	.083	.13	.15	.175	.20
γ (mJ/mol K) ²	235	---	145	95	60	47	46
β (mJ/mol K) ⁴	1.14	---	1.32	1.535	1.55	1.67	1.78
Θ_D (K)	228.5	---	217.6	206.5	206.3	201.2	196.9
T_N (K)	0.0	0.25	0.55	1.8	2.0	2.05	1.6

Figures 4:21. and 4:22. show the low temperature specific heat C as a function of temperature. In all 4 samples

measured, a sharp anomaly extending over only 0.2K is observed. For $x=.13$, $.15$ and $.175$ the temperature of this anomaly (T_N) is calculated at the mid-point of the upturn in C . Only a rough estimate of the temperature of anomaly can be made for $x=.20$ sample, since it occurs at around 1.4K, the lowest temperature which can be reached in the experiment.

4:3:4. Discussion.

4:3:4:1. Introduction.

In this section, the features highlighted above will be discussed in more detail. The variations of the resistivity and the susceptibility of pure $CeCu_6$ at high temperature are dominated by localized 4f Ce moments. These moments produce a Curie-Weiss like susceptibility and act as individual Kondo scattering centres producing a region in which the magnetic resistivity shows logarithmic temperature dependence. As expected, substitution of isoelectronic Au for Cu has little effect on the high temperature properties. The value of the high temperature resistivity is almost independent of Au concentration, ρ_{mag} still varies linearly with $\ln T$, whilst the susceptibility still shows Curie-Weiss behaviour with little change in the effective Ce moment.

At lower temperatures the properties of $CeCu_6$ are dominated by two competing interactions:

1. The oscillatory RKKY interaction characterized by $T_{RKKY} \sim J^2 N(E_F)$. This RKKY interaction between Ce 4f moments may eventually lead to magnetic order.

2. The screening of the 4f moments by conduction electrons known as Kondo compensation characterized by $T_K \sim T_F \exp(-1/JN(E_F))$

The strength of both these interactions depend on the value of $JN(E_F)$. Below a critical value $[JN(E_F)]_C$ the tendency is toward magnetic order. Above $[JN(E_F)]_C$ the moments are

completely screened leading to a non-magnetic ground state. In the case of $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$, we are observing the effects of varying this parameter by alloying.

First we discuss how $JN(E_F)$ varies with Au concentration. We have seen in section 2:7:4 that J depends on the parameter N/V . Adding Au does not alter N , the number of conduction electrons. However, adding Au does increase the cell volume and thus reduces J . A reduction in J leads to a weakening of both the Kondo compensation and the RKKY interaction. If the Kondo mechanism was initially weak, a reduction in J will allow the emergence of magnetic ordering. However, if the Kondo mechanism is initially very strong, the reduction in J weakens the interaction between Ce moments to such an extent that even a reduction in the Kondo mechanism will not produce magnetic ordering.

How is this reduction in J reflected in the properties of $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$? Firstly, a reduction in J leads to a reduction in T_K .

4:3:4:2. Reduction in T_K .

It has not been possible to directly measure the variation in T_K with Au concentration via for example the shift in the minimum seen in magnetoresistance. However there are several indications of a steady decrease in T_K with Au concentration:

1. A decrease in T_M . Although the position of T_M has not been unequivocally linked to T_K (see 4:4) there is experimental evidence and a theoretical basis for such an assumption.

2. A decrease in $|\Theta|$. In both the single-ion Kondo model and some models for concentrated Kondo systems $|\Theta|$ is taken to be proportional to T_K . Thus the reduction in $|\Theta|$ from 20.1K for CeCu_6 to 8.4K for 15% Au indicates a 200% decrease in T_K .

3. The value of χ at low temperature increases with Au concentration. In the single-impurity problem χ^{-1} is taken to be proportional to T_K^{-1} . This increase in χ indicates a weakening of the Kondo mechanism at a given temperature, which in turn indicates a reduction in T_K .

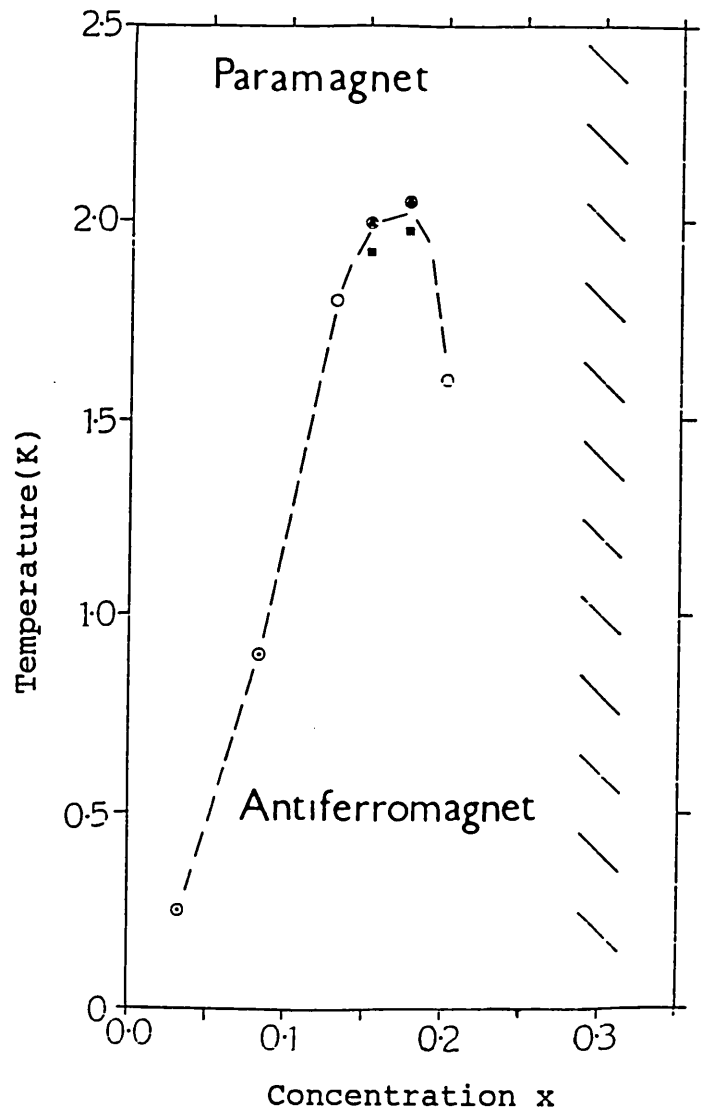


Figure 4:23. Proposed magnetic phase diagram for $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$. Transition temperatures have been determined from specific heat (○), resistivity (■) and magnetic susceptibility (▲) measurements performed during the course of this work and from specific heat data of Germann et al. [4:14] (○).

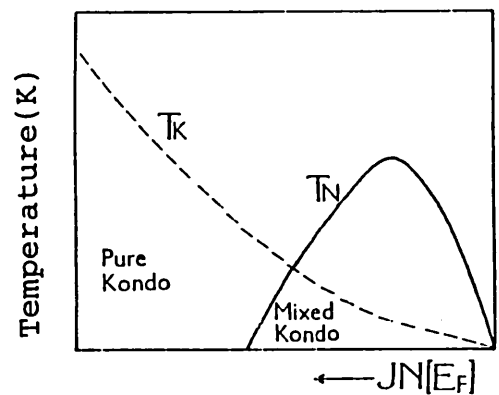


Figure 4:24. Phase diagram constructed using the Kondo lattice model proposed by Doniach [2:44], showing the variation of T_N , T_K and the nature of the ground state of the Kondo lattice with the parameter $JN(E_F)$.

4:3:4:3. The Onset of Magnetic Order.

Because of the different functional dependence of T_{RKKY} and T_K on J , the reduction in J is expected to weaken the RKKY interaction less rapidly than the Kondo interaction, increasing the tendency toward magnetic order. This expectation is confirmed, since, as well as an increase in absolute value of $\chi_{\text{a.c.}}$, a cusp is seen in low temperature data for $0.15 \leq x \leq 0.20$. This cusp suggests the onset of magnetic order. The magnitude of the susceptibility at the peak, seems to rule out ferromagnetic order. The cusp could be indicative of spin glass or antiferromagnetic order. The peak in the resistivity and the sharp anomaly in the specific heat point to long range antiferromagnetic order. The transition temperatures T_N extracted from the positions of peaks in the resistivity and susceptibility data and the mid-points of specific heat anomalies allow the construction of the phase diagram shown in figure 4.23. It can be seen from this diagram there is a steady increase in the transition temperature with increasing Au concentration up to 17.5% Au. Further additions of Au then produces a reduction in T_N . For example, no peak is visible in the resistivity or susceptibility of the 20% Au sample down to the lowest temperature available in these experiments. The onset of a transition is just discernible in the specific heat data. If the rapid reduction in T_N seen between 17.5% and 20% Au is continued to higher Au concentrations, the transition temperature would be reduced to 0K around 30% Au. This reduction in the ordering temperature reflects the further weakening of J with increasing Au concentration. The reduction in the strength of the RKKY this produces is not offset by a decrease in T_K ,

since T_K is already considerably reduced. This then leads to a fall in the ordering temperature.

4:3:4:4. Comparison with Theory.

The behaviour of the $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ system compares well with the Kondo lattice model proposed by Doniach [2:44] and developed by Lacroix and Cyrot [2:39] discussed in section 2.7). The phase diagram indicating the expected variation in T_K and T_N with $JN(E_F)$ bears a close resemblance to the phase diagram of $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ shown in figure 4.24.

4:3:4:5. Magnetic Resistivity.

Finally in this section, the effects of the decrease in J on the magnetic resistivity are examined. Cornut and Coqblin [4:15] have developed a model which considers the effect on the magnetic component of the resistivity, of an interaction between the Kondo effect and C.F. splitting. In their model the magnetic contribution to the resistivity varies linearly with $\ln T$ in both a high and a low temperature region separated by a peak around the C.F. splitting temperature. Hanzawa et al. [4:16] derived a relationship between the "true" Kondo temperature T_K and T_K^H . T_K^H is the apparent Kondo temperature of the system at temperatures greater than the C.F. splittings. They showed that

$$T_K^H = \sqrt[3]{T_K \Delta_1 \Delta_2} \quad \text{-----} \quad 4:9.$$

where Δ_1 is the C.F. splitting between the ground state doublet and the first excited level and Δ_2 is the C.F. splitting between the first and second excited doublet. It is around T_K^H that a peak in resistivity due to the Kondo-C.F. interaction is expected to be observed. In the case of pure CeCu_6 the 4f level is split into three doublets by C.F. The C.F. splitting energies Δ_1 and Δ_2 and the true Kondo

temperature T_K have been calculated from experimental data by several groups. Using specific heat data, Fujita et al. [4:17] estimated Δ_1 and $\Delta_2=65\text{K}$ with $T_K=3.9\text{K}$. A fit to susceptibility data by Takayanagi et al. [4:18] produced $\Delta_1=87\text{K}$, $\Delta_2=210\text{K}$. whilst Walter et al. [2:36] used neutron data to calculate $\Delta_1=65\text{K}$ and $\Delta_2=128\text{K}$. In section 1:3:5. magnetoresistance data was presented which indicated that $T_K \approx 2\text{K}-3\text{K}$. Substituting these values into equation 4:9 gives T_K^H anywhere between 20 and 41K. Onuki et al. [4:19] have chosen a value at the lower end of these estimates to argue that T_K and T_K^H are too close together for the high temperature peak in the resistivity due to a combination of C.F. and Kondo interaction to be resolved from the low temperature peak resulting from the onset of coherence. This produces the single peak structure observed in pure CeCu_6 . Addition of Au leads to a reduction in T_K and a suppression in the low temperature maximum. This should make the observation of any peak due to Kondo-C.F. interaction more likely. However, the effect of substitution on C.F. splitting must also be considered. Oomi et al. [4:20,4:21] have fitted thermal expansion data taken between 6 and 300K to a theory of Ohkawa [4:22]. According to this model, the pressure derivatives of Δ_1 and Δ_2 , $\partial\Delta_1/\partial P$ and $\partial\Delta_2/\partial P$ have the same sign as the thermal expansion coefficient α_M . Oomi found α_M positive indicating Δ_1 and Δ_2 are expected to increase with pressure. Thus alloying with Au, which produces negative chemical pressure should reduce Δ_1 and Δ_2 suppressing the position of the maximum in resistivity expected due to Kondo-C.F. interaction. However, thermopower measurements suggest that substitution of Au increases the C.F. splitting. Within

the framework of the single ion Kondo model, Bhattacharjee and Coqblin [4:23] calculated the temperature dependence of thermopower $S(T)$. They suggested that the positive maximum seen in $S(T)$ of hf materials such as CeAl_3 is related to C.F. splitting by $T_{\text{max}}=(1/3\sim 1/6)\Delta$. In the case of CeCu_6 a peak in $S(T)$ is seen at 50K. This would suggest a C.F. splitting of 150K~300K. This does not agree very well with estimates of C.F. splitting obtained using other methods and discussed above. However a relationship between the peak in $S(T)$ and has been established. In the case of CeCu_6 with 10% Au, T_{max} is at 68K indicating the C.F. splitting increases with Au concentration. Thus, it is suggested that a combination of a decrease in T_K and an increase in C.F. splitting produces the conditions where a well defined peak in the resistivity due to the Kondo-C.F. interaction becomes visible. The increase in C.F. splitting with increasing Au concentration also accounts for the shift to higher temperature of this peak. Cornut and Coqblin also showed that the slopes $d\rho_{\text{mag}}/d\ln T$ at both high and low temperature depend on $J^3N(E_F)$. The reduction observed in $d\rho_{\text{mag}}/d\ln T$ at high temperature with increasing Au concentration fits well with this idea and is a further indication that J decreases as Au is added.

4:4. Alloying, T_M and the Onset of Coherence.

4:4:1. Introduction.

This section will examine one aspect of the effects of alloying on properties of CeCu_6 already touched upon above. Namely, the rapid reduction in the temperature T_M at which the maximum appears in resistivity at low temperature. Also examined, is the suppression in the onset of coherence (which in pure CeCu_6 leads to a rapid fall in the resistivity below

T_M and is associated with the formation of a Kondo lattice). Up until this point the assumption has been made that the temperature of the maximum T_M seen in the resistivity of $CeCu_6$ and many other hf materials (e.g. $CeAl_3$, $CeAl_2$, U_2Zn_{17}) is proportional to (or at least a monotonous function of) T_K . This assumption is based on the premise that T_M marks a crossover from incoherent single ion Kondo scattering at $T > T_M$ to coherent Kondo lattice behaviour at lower temperature $T < T_M$, and has proved useful in giving an indication of the variation of T_K during alloying. Schilling [4:24] has questioned this assumption and discussed the role of other interactions, in particular the RKKY interaction in determining the temperature T_M . T_M is now considered to be a function of both T_K and δ_C the mean RKKY interaction strength. Larsen [4:25] has made a theoretical study of the evolution of the shape of the resistivity per impurity as δ_C is increased by, for example increasing the concentration of magnetic impurities c , whilst keeping T_K essentially constant. The low temperature plateau in the resistivity is depressed. For $\delta_C/T_K \geq 0.5$ a well defined maximum develops, which moves to higher temperature as δ_C/T_K increases (see figure 4:25). Note that T_M can be greater or less than T_K depending on the magnitude of δ_C . For a sufficiently strong RKKY interaction, magnetic freezing occurs giving the well known resistivity behaviour shown in figure 4:26. In this case the position of the maximum does not indicate the onset of magnetic order, but rather the temperature at which the RKKY interaction between the magnetic ions converts the single ion behaviour into correlated ion behaviour. It is clear T_M is not a simple function of T_K and δ_C . Larsen has

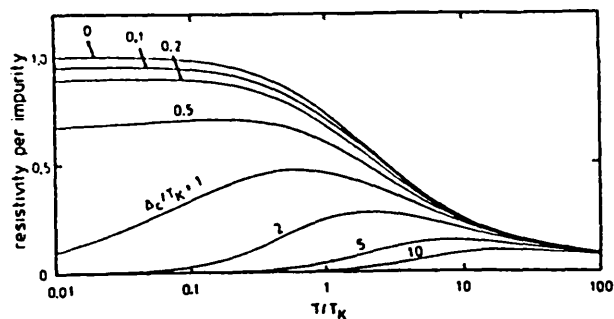


Figure 4:25. Functional dependence of the electrical resistivity per impurity on the relative temperature scale T/T_K and on the relative interaction strength $\delta C/T_K$ according to Larsen [4:25].

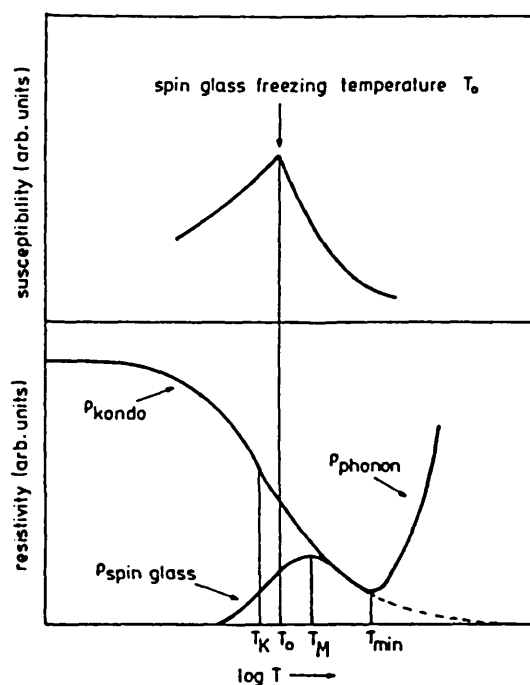


Figure 4:26. Schematic diagram of the resistivity of isolated impurities ρ_{Kondo} and interacting impurities $\rho_{\text{Spin-Glass}}$ as a function of $\log T$. Interactions between impurities give rise to a resistivity maximum and a susceptibility peak at a lower temperature T_0 , taken from Schilling [4:24].

derived the relation $T_M \propto \frac{1}{2\delta_C \ln(\delta_C/T_K)}$.

Returning to hf systems it has been observed that T_M increases linearly with Ce content (see figure 1:19.) in the $\text{Ce}_x\text{La}_{1-x}\text{Cu}_2\text{Si}_2$ system through the region where the system shows spin glass ($0.2 \geq x \geq 0.7$) into the regime ($x \geq 0.8$) where the system forms a Kondo lattice and is non-magnetic. This indicates that the RKKY interaction plays an important role in the origin of the resistivity maximum across the entire alloy system, even when the Kondo compensation has suppressed the magnetic ordering. In conclusion Schilling cautions against blindly using the assumption that T_M is a simple function of T_K alone, and that the presence of other interactions should be borne in mind.

4:4:2. A Comparison Between Alloying on the Ce and Cu Sites in CeCu_6 .

4:4:2:1. Introduction.

The effects of alloying on Ce sites in CeCu_6 with Gd, Y, or La on the position of T_M and the onset of coherence have been studied. The results of doping on the Ce sites are compared with the effects of alloying on Cu sites with iso-electric Au or Ag and with Al, Ni or Zn. In the case of Al, Ni and Zn, alloying not only changes the lattice parameters, but also alters the number of conduction electrons present in the system.

4:4:2:2. Lattice Parameters.

The cell volumes for CeCu_6 doped with Gd, Y and La are shown in figure 4:27. Figure 4:28. shows similar quantities for CeCu_6 with Au, Ag, Al, Ni and Zn.

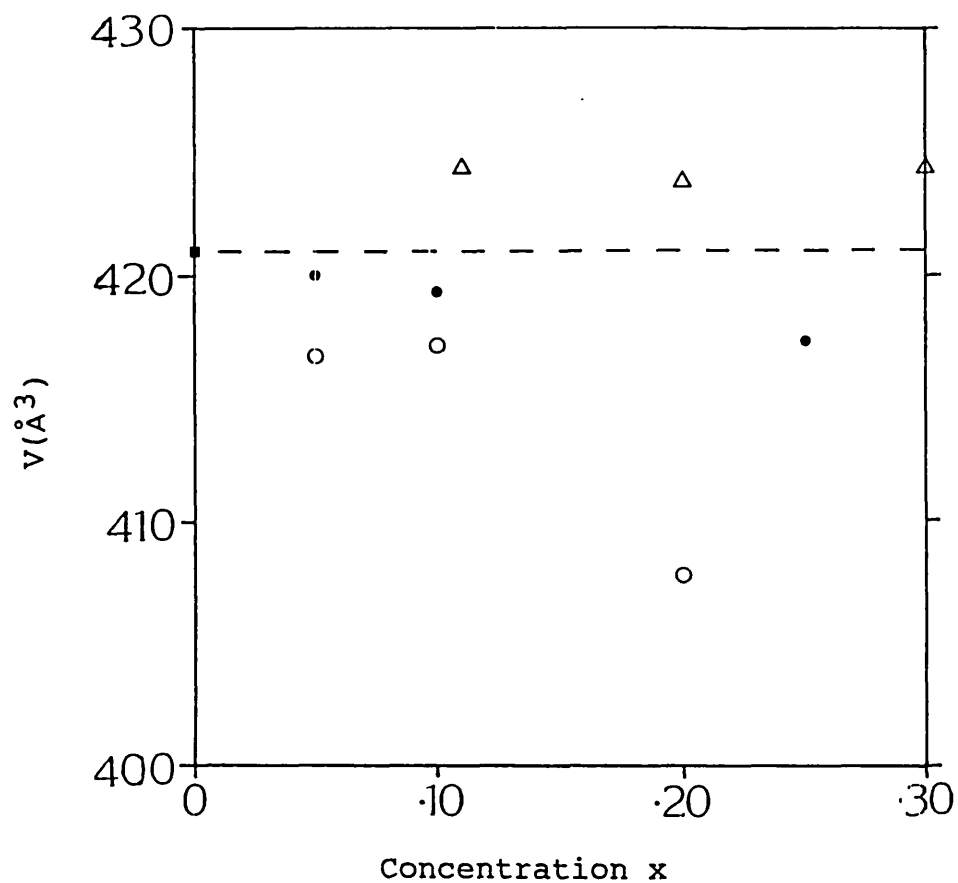


Figure 4:27. Cell volume versus impurity concentration for $\text{Ce}_{1-x}\text{T}_x\text{Cu}_6$ where T is Gd(●), Y(O) or La(Δ).

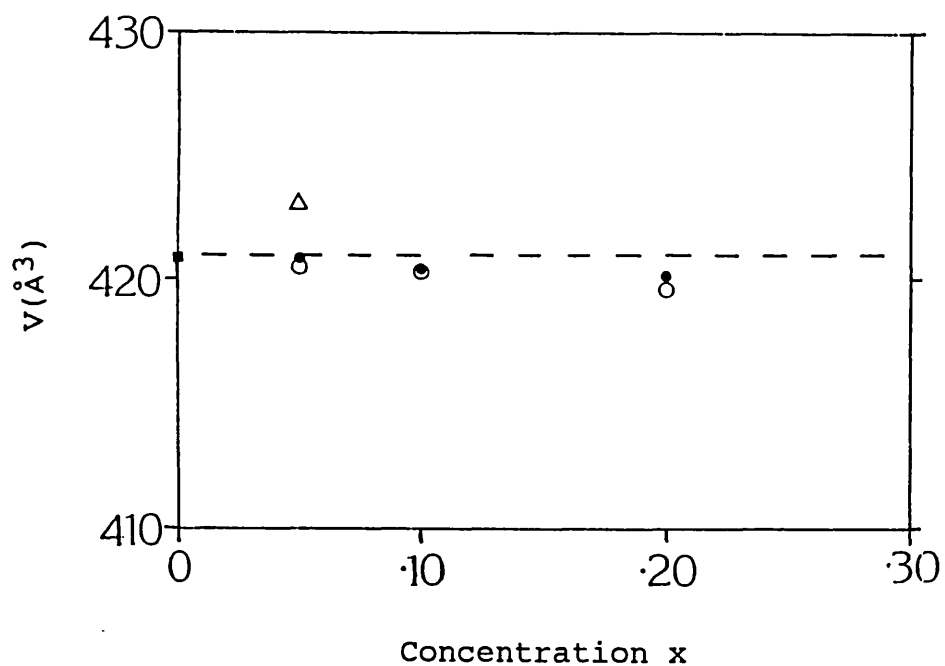


Figure 4:28. Cell volume versus impurity concentration for $\text{Ce}(\text{Cu}_{1-x}\text{M}_x)_6$ where M is Al(●), Ni(O) or Zn(Δ).

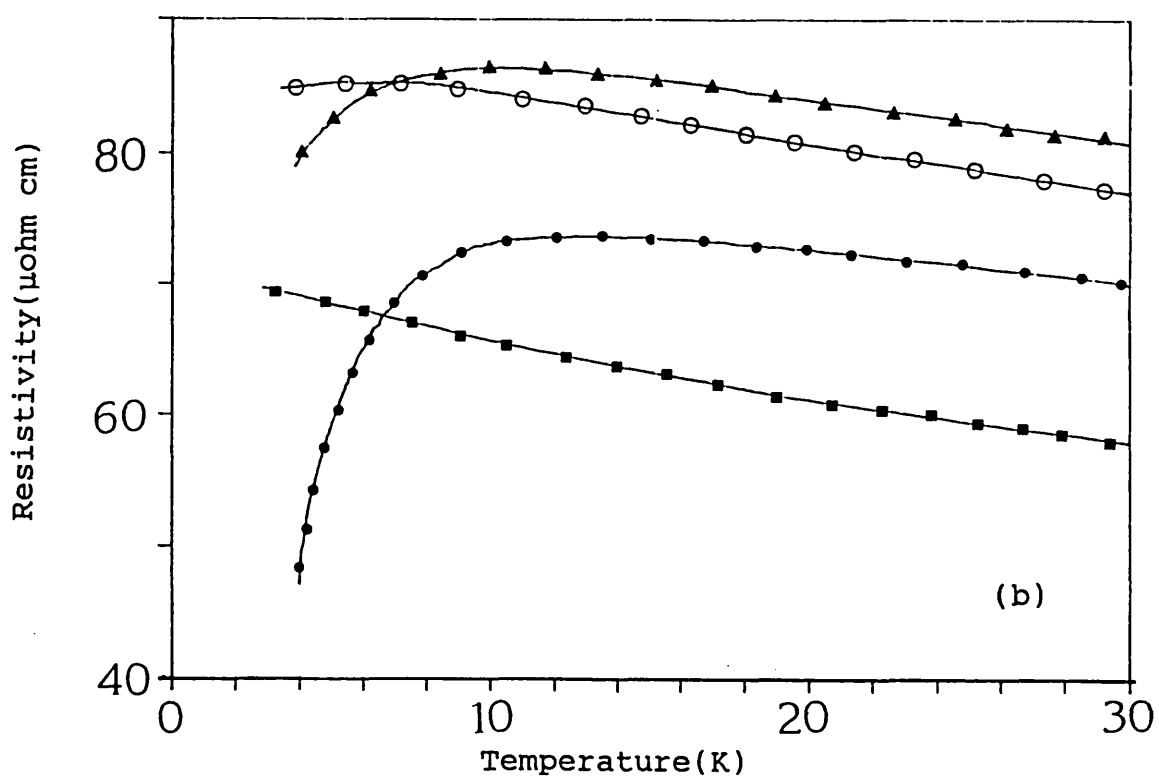
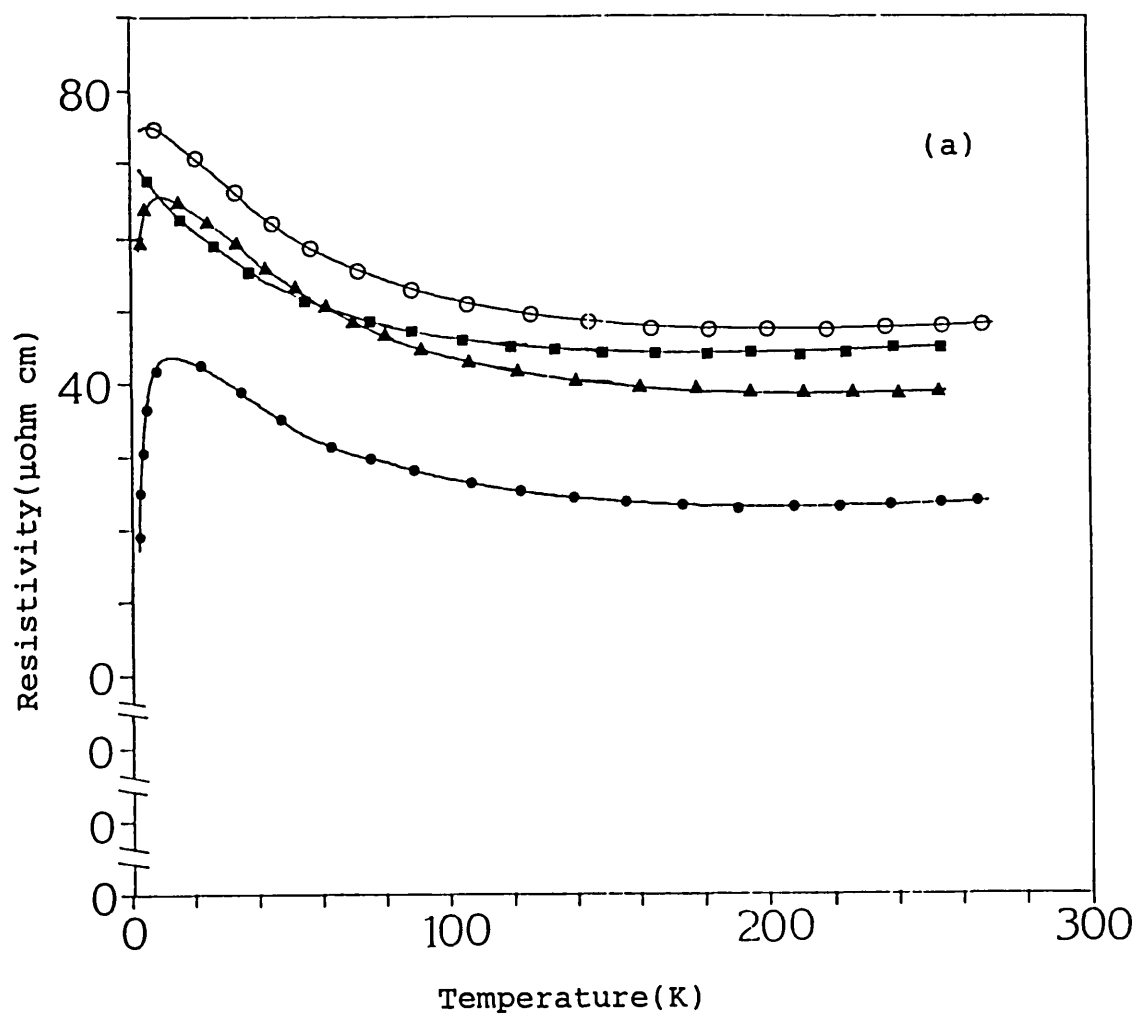


Figure 4:29. (a) and (b) Temperature dependence of the electrical resistivity of $\text{Ce}_{1-x}\text{Gd}_x\text{Cu}_6$ for $x=0.00$ (●), 0.05 (▲), 0.10 (○) and 0.25 (■).

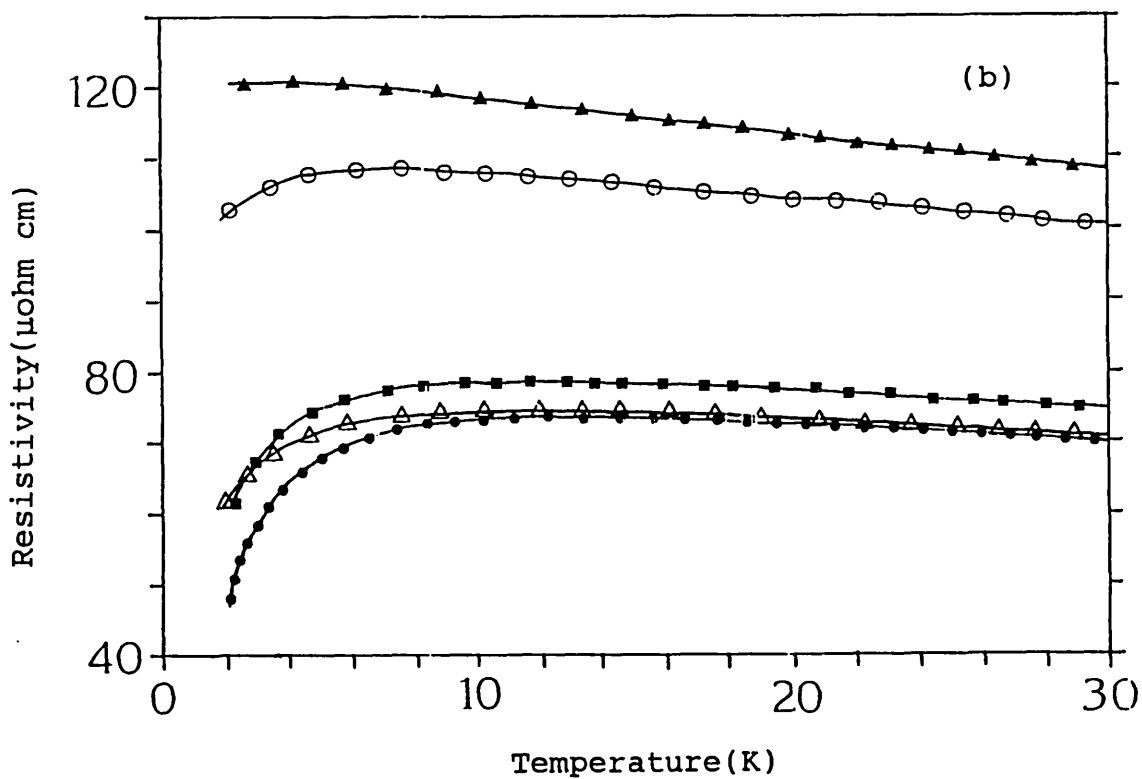
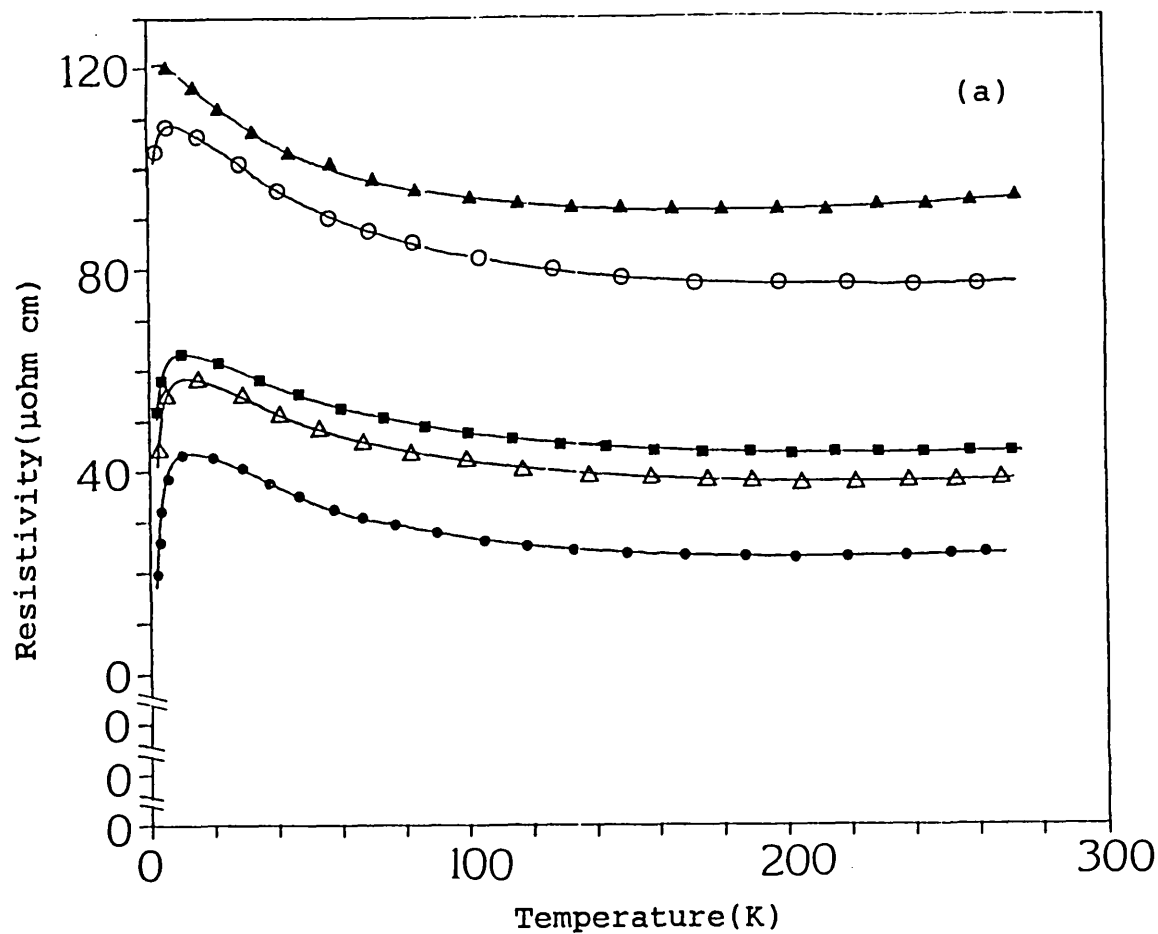


Figure 4:30. (a) and (b) Temperature dependence of the electrical resistivity of $\text{Ce}_{1-x}\text{Y}_x\text{Cu}_6$ for $x=0.00$ (●), 0.02 (△), 0.05 (■), 0.10 (○) and 0.20 (▲).

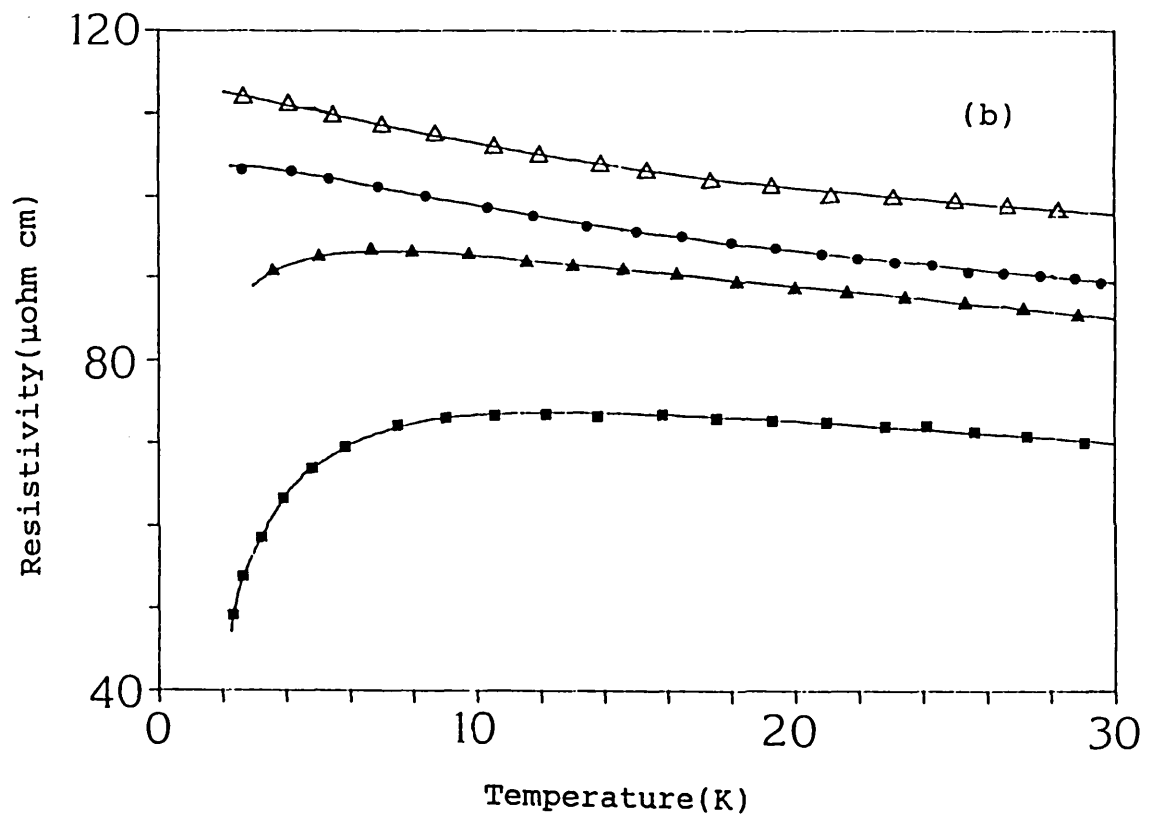
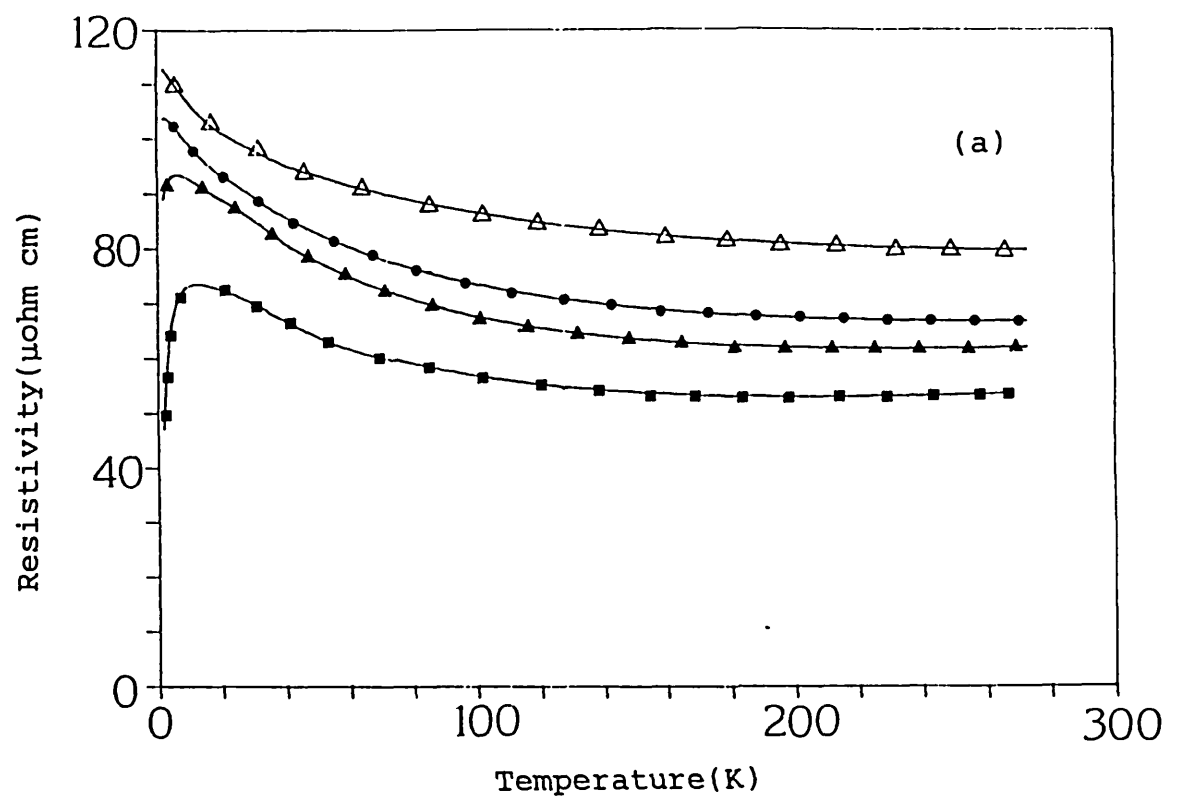


Figure 4:31. (a) and (b) Temperature dependence of the electrical resistivity of CeCu_6 (■) and $\text{Ce(Cu}_{0.98}\text{M}_{0.02})_6$ where M is Au(▲), Al(●) or Ni(△).

4:4:2:3. Resistivity.

The resistivity of CeCu_6 alloyed with Gd, Y, and La, are shown in figures 4:29., 4:30. and 4:2. respectively. The resistivities of CeCu_6 doped with small amounts of Al, Ni and Zn are shown in figure 4:31.

Table 4:4. Parameters taken from electrical resistivity of selected CeCu_6 alloys.

SAMPLE	T_M (K)	$\rho(T_M K)$ $\mu\text{ohm cm}$	$\rho(2.2K)$ $\mu\text{ohm cm}$	$\delta\rho$ $\mu\text{ohm cm}$
pure CeCu_6	14	74	46	28
5% Gd	9	86	79	7
10% Gd	5	85	84	1
25% Gd	below 1.5	--	70	--
2% Y	12	79	61	18
5% Y	10.5	74	61	13
10% Y	8	108.5	101.5	7
20% Y	4	121	120.5	0.5
2% Au	6	93	89	4
5% Au	below 1.5	--	86	--
2% Ni	below 1.5	--	113	--
2% Al	below 1.5	--	104	--
5% Zn	below 1.5	--	109	--

4:4:2:4. Gd.

The value of resistivity at high temperature is almost independent of Gd concentration. The temperature T_M at which the peak in resistivity is observed is slowly suppressed. The values of T_M for various concentrations of Gd are given in table 4:4. The values for the resistivity at T_M and 2.2K along with the difference $\delta\rho$ between these two values are also shown in table 4:4. From these values it can be seen that addition of 10% Gd removes almost completely any low

temperature fall in the resistivity.

4:4:2:5. Y.

The high temperature resistivity of CeCu_6 alloyed with Y shows only a slow rise with Y concentration. As in the case of Gd, T_M and the fall in low temperature resistivity are slowly suppressed as Y concentration is increased (see table 4:4).

4:4:2:6. Au.

The effects on the addition of Au to CeCu_6 were discussed in section 4:2. Table 4:4. shows that as little as 5% Au is sufficient to suppress T_M below 1.5K and remove the onset of coherence.

4:4:2:7. Al, Zn and Ni.

Substitution of only 2% Al, Ni or Zn is sufficient to suppress T_M below 1.5K and completely remove the onset of coherence. No samples with smaller concentrations of dopant were prepared. However, Zemerli and Barbara [4:26] have reported that 0.8% Al destroys coherence and reduces T_M below 1.5K.

4:4:2:8. Discussion.

It has been shown that substitution on Cu sites effects the resistivity much more rapidly than substitution on the Ce sites. Clearly, there is no one simple mechanism which can explain this behaviour. Several factors have to be considered together. These are:

1. Changes in the cell volume which result in changes in the hybridisation between the conduction electrons and the Ce 4f electrons, producing a change in T_K .
2. A decrease in the number of Ce ions, leading to a reduction in both the Kondo like interaction between Ce 4f and conduction electrons and in the Ce-Ce RKKY interaction.

3. The change in the number of conduction electrons.

4. Destruction of the coherent Kondo lattice due to changes in translational symmetry.

It has been shown that alloying with Y reduces the cell volume. Thus it may be expected that chemical pressure will increase hybridisation between 4f and conduction electrons leading to an increase in T_K . This in turn could be expected to lead to an increase in temperature of T_M , as seen in pressure experiments with $CeCu_6$. However, this is seen not to be the case. Instead the dominant mechanism is the dilution of the number of Ce ions. This reduces the Ce-Ce interactions and produces a slow transition from a dense to a dilute Kondo regime. This behaviour has already been observed in the case of alloying with La. Addition of Gd also reduces the cell volume, although less rapidly than Y. Again, a slow transition from a dense to a dilute Kondo regime due to a reduction in the number of Ce ions present seems the best explanation of the observed behaviour.

In the case of Au (and Ag) the Ce sublattice is undisturbed. The number of conduction electrons is also unchanged. Thus it seems in this case, the best explanation of the data is as follows. Expansion of the lattice produces negative chemical pressure. This reduces the hybridisation between 4f and conduction electrons leading to an decrease in T_K .

However, it seems this mechanism may not be sufficient to explain the rapid loss of coherence and reduction in T_M when alloying with Al, Ni or Zn. In the case of Al or Ni the cell volume is slightly reduced, whilst alloying with Zn increases the cell volume. However the fact that the effects of three dopants are similar, and that such small amounts of dopants are required suggests that chemical pressure may not

be a large factor. It should be noted that all the corresponding dopant rich compounds (i.e. CeAl_6 , CeNi_6 and CeZn_6) do not exist. As a result distortions in the orthorhombic structure may be large, for small amounts of dopant. Addition of Al, Ni or Zn also adds to the number of conduction electrons. Thus the nature of the conduction electrons around the Fermi level may be radically altered by small amounts of dopant. This will alter the hybridisation between 4f and the conduction electrons. This could explain the observed results. Alternatively, Germann et al. [4:14] have suggested that even small amounts of a dopant may destroy the translational symmetry of the Kondo lattice, reducing the effectiveness of the Kondo compensation mechanism. However it is difficult to see why Al, Ni and Zn are more effective in this destructive process than Au or Ag.

Chapter 5. Studies of the Effects of Alloying on the Properties of CeAl₂.

5:1 Introduction.

In this chapter the effects of alloying on the properties of CeAl₂, a hf material which orders magnetically at 3.8K are discussed. Section 5:2 contains details of the previous experimental work which has been carried out to determine the properties of this material. Section 5:3 examines the studies which have been made on the effects of pressure on the properties of CeAl₂. The nature of the magnetic ordering, first introduced in section 5:2 is also considered in more detail. Section 5:4 contains details of previous investigations involving substitutions on the Ce sites with La or Y. Sections 5:5 and 5:6 contain details of the effects on the properties of CeAl₂ of replacing Al with Cu or Co. In section 5:7, modifications to the properties of pure CeAl₂ and the emergence of high temperature magnetic ordering, observed when replacing Al with Fe are discussed.

5:2. Previous Work.

5:2:1. Structure.

CeAl₂ crystallizes into a MgCu₂ Cl5 cubic Laves phase [5:1] with lattice constant $a=8.059\text{\AA}$ (see figure 5:1). The cell volume of CeAl₂ is only slightly smaller than the fictitious reference volume expected for integral valence Ce³⁺, obtained by interpolating between the volumes of the unit cell of LaAl₂ and PrAl₂ (see figure 5:2). If 4f electrons are lost from Ce (as in the case of CeFe₂ to the 3d band of Fe), the decrease in the size of Ce atom is expected to result in a substantial reduction in the cell volume. Thus, from an analysis of the cell volume, the Ce in CeAl₂ is shown to be close to integral valency 3+. The Ce³⁺ has a ground state with $j=5/2$ which in free space consists of $(2j+1)=6$ degenerate sublevels. However crystal fields (C.F.) partially lift the degeneracy of the sublevels. White et al. [5:2] showed that for CeAl₂ the magnetic susceptibility below 100K dropped markedly below that expected for a free Ce ion. The cubic C.F. decomposes the ground state of the Ce ion into a doublet Γ_7 and a quartet Γ_8 with either the quartet or the doublet lying lower. Comparison of the experimental data with the theoretically predicted reduction in the susceptibility with either the doublet or quartet lying lowest allowed White et al. to deduce that the doublet must lie lowest. This is appropriate for positively charged Ce ions and negatively charged Al ions. On the basis of neutron diffraction measurements Rainford [5:3] suggested a C.F. splitting of 100K. Hill and Machado da Silva [5:4] performed heat capacity measurements on CeAl₂ in the temperature range 0.5 to 15K (see figure 5:3). A C.F. splitting of 100K should provide a

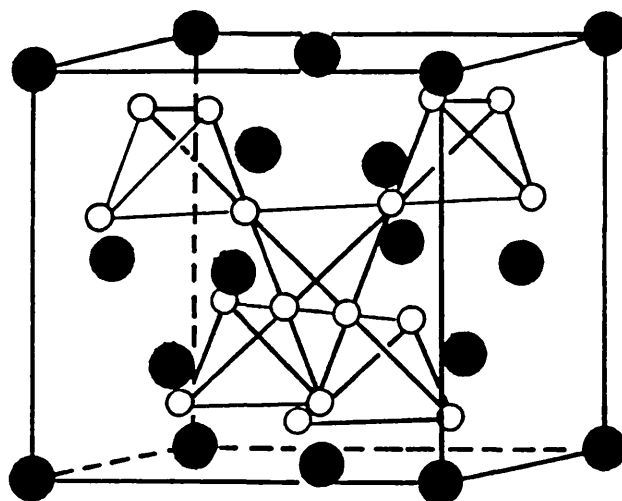


Figure 5:1. Cubic MgCu_2 structure of CeAl_2 . (●) A atoms, (○) B atoms.

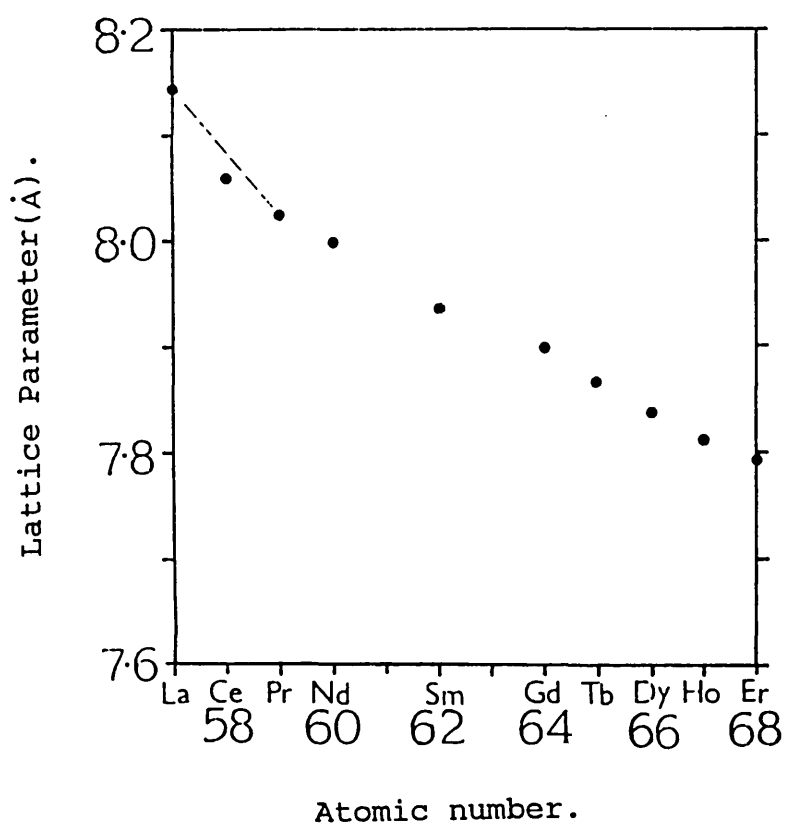


Figure 5:2. Lattice constant versus atomic number of rare earth for selected rare earth- Al_2 compounds. Data are from Wernick and Geller [5:1].

contribution to the heat capacity which is a significant part of the whole at 15K, but which reduces rapidly at lower temperatures. Hill and Machado da Silva treated the magnetic component of heat capacity as if a disordering within the ground state doublet Γ_7 were nearly complete before the population of the quartet became significant and as a result assumed that out of a total possible entropy change of $R \ln 6$ associated with the disorder of an ion with a $j=5/2$ ground state, roughly $R \ln 2$ should be observed under the heat capacity anomaly. Using a C.F. splitting of 100K and a normal lattice specific heat the results of the calculation gave a good agreement with experiment confirming a Γ_7 ground state with a 100K Γ_7 - Γ_8 splitting. A distinct knee in the resistivity at approximately 100K has also been attributed to C.F. effects.

5:2:2. Specific Heat.

The specific heat of CeAl_2 is shown in figure 5:3. Above 4K the specific heat can be well fitted by the expression

$$C = \gamma T + \beta T^3 \text{ ----- } 5:1.$$

where the γ value is estimated to lie between 400 and 500mJ/molK². This large value of γ indicates hf behaviour. A phase transition at 3.8K reduces the value of γ so that as $T \rightarrow 0\text{K}$, γ amounts to 135mJ/molK². As with UCd_{11} (see section 1:4.) a high temperature tail is observed in C/T versus T^2 data which may be due to short range order effects preceding the transition. From this data, one can classify CeAl_2 as a magnetically ordering hf material (sometimes called a magnetic Kondo system).

5:2:3. Resistivity.

The resistivity of CeAl_2 is shown in fig 5:4. Several

important features in $\rho(T)$ must be highlighted:

1. At high temperature the resistivity of CeAl_2 like other hf materials has an anomalously high value, and varies slowly with temperature.
2. A broad knee in $\rho(T)$ is present at approximately 100K.
3. $\rho(T)$ of CeAl_2 falls to a minimum at 15K before rising again to a maximum at 4.3K.
4. Resistance below 4.3K falls rapidly, indicating the onset of coherence.

The resistivity of CeAl_2 can best be analysed by assuming the validity of Matthiessen's rule

$$\rho(T) = \rho_0 + \rho_{\text{mag}} + \rho_{\text{ph}} \text{ ----- 5:2.}$$

where ρ_0 is the residual resistivity, ρ_{ph} is the component of resistivity due to the phonons, and ρ_{mag} is due to magnetic interactions present in the CeAl_2 system.

The variation of ρ_{mag} in CeAl_2 can be more easily discerned if the contributions to the resistivity due to phonons and the residual resistivity are subtracted. In figure 5:5 the resistivities of CeAl_2 - LaAl_2 , CeAl_2 - LuAl_2 and CeAl_2 - YAl_2 are shown. LaAl_2 , YAl_2 and LuAl_2 all have the same MgCu_2 cubic structure as CeAl_2 and are all non-magnetic. All three are candidates for use as non-magnetic reference compounds. Y and La have the trivalent d^1s^2 lanthanide valence electron structure and an empty f-shell i.e. $\text{Y}([\text{Kr}]4d^15s^2)$, $\text{La}([\text{Xe}] 5d^16s^2)$, whilst Lu has a complete f-shell i.e. $\text{Lu}([\text{Xe}]4f^{14}5d^16s^2)$. However $\text{YAl}_2(7.855\text{\AA})$ and $\text{LuAl}_2(7.742\text{\AA})$ have quite different lattice constants than $\text{CeAl}_2(8.056\text{\AA})$. This along with the large mass difference between Y and Lu on the one hand, and Ce on the other make the materials questionable as reference compounds. La has a mass close to that of Ce and LaAl_2 has a similar lattice constant ($8.145\text{\AA}$). However Wohllleben and Wittershagen [5:5] have pointed out

that LaAl_2 appears to have an abnormal resistivity. At high temperature $\rho(T)$ of LaAl_2 deviates from the behaviour of both YAl_2 and LuAl_2 and reaches a value of $100\mu\text{ohm cm}$ (at 900K) very close to that of CeAl_2 . It is suggested that this and other physical anomalies seen in the susceptibility, thermal expansion, superconductivity and L_{III} edges of LaAl_2 indicate that LaAl_2 behaves as if the valency of La is not three but fractionally less, with a configuration $6f^v5d^{1-v}6s^2$ with $v \ll 1$. Nevertheless many other workers seem satisfied that LaAl_2 can serve as a good non-magnetic reference material and have used it as such. Throughout this work LaAl_2 will be used as a reference compound, but consideration will be made as to whether the effects seen are due entirely to LaAl_2 or whether the effects are simply magnified by subtracting LaAl_2 rather than say LuAl_2 . Figure 5:5 shows the magnetic resistivity of CeAl_2 . Three regions are clearly discernible:

1. A high temperature region where the resistance exhibits logarithmic temperature dependence.
2. An intermediate temperature region ($5\text{K} < T < 10\text{K}$) where $\rho(T)$ again varies as $-\ln T$.
3. A low temperature region ($T < 4.5\text{K}$) where $\rho(T)$ falls rapidly and eventually reaches a temperature independent residual value.

It can be seen from fig 5:5 that the drop in $\rho(T)$ at high temperature is much less dramatic if the resistivity of either LuAl_2 or YAl_2 is subtracted away. However this high temperature variation in ρ_{mag} of CeAl_2 is still present. The first attempt to explain the high temperature behaviour of CeAl_2 was made by Rao and Wallace [5:6]. They considered the effect on the resistivity of the interaction between the magnetic moments and the conduction electrons in the presence of crystal fields. $\rho(T)$ for CeAl_2 was assumed to be of the

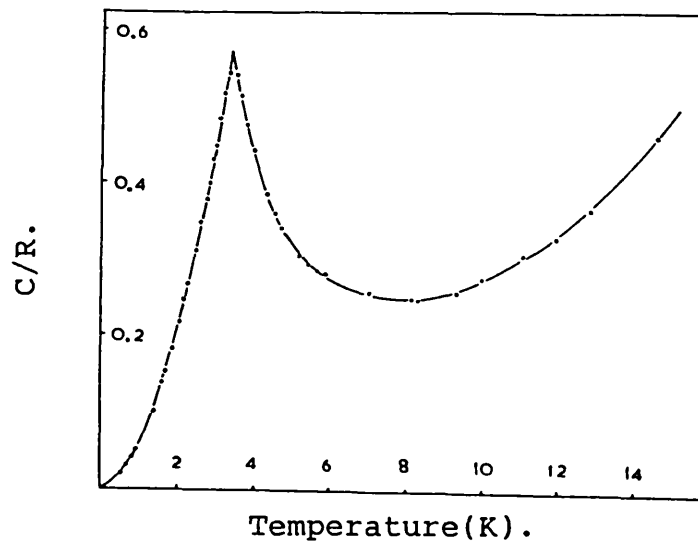


Figure 5:3. The low temperature heat capacity of CeAl_2 measured by Hill and Machado da Silva [5:4].

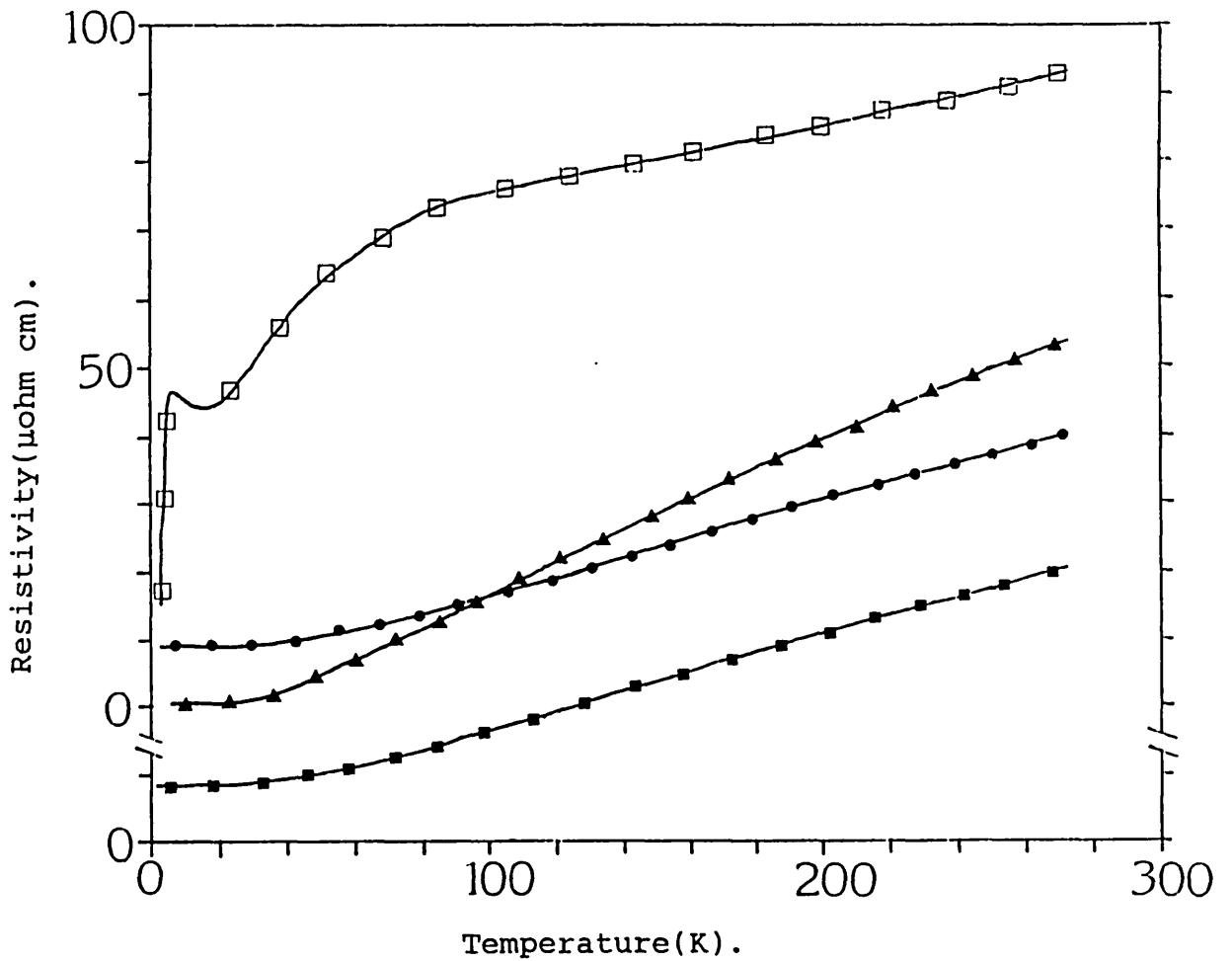


Figure 5:4. Temperature dependence of the electrical resistivity of MAI_2 where M is Ce($\square$), Y($\bullet$), La($\blacktriangle$) or Lu($\blacksquare$).

form of equation 5:2 where

$$\rho_{\text{mag}} = \rho_{\text{spd1}} + \rho_{\text{spd2}} \text{ ----- } 5:3.$$

ρ_{spd1} is evaluated in the first Born approximation assuming that the C.F. result in a Γ_7 doublet ground state. ρ_{spd2} is the second order contribution to the spin disorder resistivity and is estimated by assuming that this term produces a Kondo like contribution, which below 17K leads to an upturn in $\rho(T)$. Above 17K its contribution is taken to be negligible. The phonon contribution is assumed to dominate at high temperature ($T > 100\text{K}$). An estimate of ρ_{ph} was made by scaling the entire $\rho_{\text{ph}}(T)$ curve of YbAl_2 so that the slope of the curve at high temperatures was equal to that of the experimental curve of CeAl_2 . The variation in $\rho(T)$ obtained fitted quite well with the experimental data. In particular, this method was able to reproduce the broad knee seen in the data around 100K. The major failings of this analysis were its inability to predict the upturn at low temperature, and the need to use a scaled value of the resistivity of YbAl_2 as the phonon contribution. This model is also unable to account for the two peaked structure obtained using the unscaled resistivity of isostructural LaAl_2 , LuAl_2 or YAl_2 as the phonon contribution. Cornut and Coqblin [4:15] have developed a theoretical model in which the influence of a combination of C.F. and Kondo effect on the resistivity are considered. They used as a starting point a Hamiltonian which describes the resonant scattering character of the Ce ions and takes into account the combined spin and orbit exchange scattering. For a Ce atom the large spin orbit coupling leads to a ground state of total angular momentum $j=5/2$ which is split by a C.F. In the presence of the C.F. the effective Hamiltonian is

given by

$$H = \sum_{k,m} \epsilon_k n_{km} - \sum_{\substack{k,k', \\ m,m'}} J_{mm'} C_{k',m'}^+ C_{km} (C_m^+ C_m - \delta_{mm'} \langle n_m \rangle) + \sum_{\substack{k,k' \\ m}} \mathcal{V} C_{k',m}^+ C_{km} \quad - 5:4.$$

m is an eigenvalue of a 4f eigenfunction in the presence of a C.F. C^+ and C_{km}^+ are the creation operators for a 4f electron and for a conduction electron partial wavefunction of wavenumber k respectively. The exchange integral

$$J_{mm} = |V_{kf}|^2 / 2 * (1/E_m + 1/E_{m'}) \quad \text{-----} \quad 5:5.$$

where $\mathcal{V}$ gives the direct scattering term and V_{kf} is the mixing parameter between the 4f and the conduction electrons. The third order perturbation resistivity has been calculated exactly. The resistivity has a peak at the temperature around the C.F. level splitting energy Δ . The resulting expression for $\rho(T)$ taking all J_{mm} equal to some value J for the limiting behaviour of $kT \ll \Delta$ and $kT > \Delta$ is

$$\rho = R_S^i + 2AN(\epsilon_F) * (J^2(\lambda_i^2 - 1) / (2j+1) \ln(kT/D^i)) \quad \text{-----} \quad 5:6(a).$$

where R_S^i is the spin disorder resistivity given by

$$R_S^i = A(\mathcal{V}^2 + J^2(\lambda_i^2 - 1) / \lambda_i(2j+1)) \quad \text{-----} \quad 5:6(b).$$

Here A is a constant and λ_i is the degeneracy of the 4f level.

At low temperature $\lambda_i = 2$ since only the doublet ground state is occupied. For high temperature ($> 100K$) $\lambda_i = 2j+1 = 6$ the total degeneracy of the 4f level because all the states are now equally occupied.

So in the two regions $kT \ll \Delta$ and $kT > \Delta$ the resistivity is predicted to show logarithmic temperature dependence with the ratio of the $-\ln T$ slopes equal to 3/5. Thus the shape of the $\rho(T)_{\text{mag}}$ can be explained, at least down to 5K by considering a combination of the Kondo effect and C.F. splitting.

Evidence for the presence of C.F. interactions and the Kondo

effect is also found in the thermopower and thermal conductivity data of Bauer et al. [5:7]. Below 5K a maximum is observed in $\rho(T)$. This can be interpreted as the temperature at which a crossover from incoherent Kondo scattering, to coherent Kondo scattering takes place. Below this temperature one expects to observe a rapid fall in $\rho(T)$ due to coherence. The onset of this fall is observed. However the transition observed in the specific heat at 3.8K indicates that below this temperature, the fall may be due to a combination of coherent behaviour and a reduction in resistivity due to magnetic order. Thus at low temperature CeAl_2 can be classified as a magnetic Kondo lattice. The presence of both Kondo compensation effects and the onset of magnetic order are confirmed by examining the magnetic data available on CeAl_2 .

5:2:4. Magnetic Properties.

Swift and Wallace [5:8] showed that CeAl_2 exhibited Curie-Weiss behaviour at high temperature (see figure 5:6). The effective moment of Ce in this temperature region is approximately $2.5\mu_B$ in good agreement with value predicted for free Ce^{3+} ions, indicating Ce is in a trivalent state. In contrast to earlier work by Williams et al. [5:9], who suggested that CeAl_2 became ferromagnetic at 8K, it was shown via field dependence studies of the magnetic susceptibility that at low temperature CeAl_2 was paramagnetic at 4.12K and develops a weak antiferromagnetic structure at some temperature a little below this. The heat capacity measurements of Hill and Machado da Silva [5:4] had already indicated the presence of a transition at 3.4K. The general shape of the curve was typical of a co-operative phase

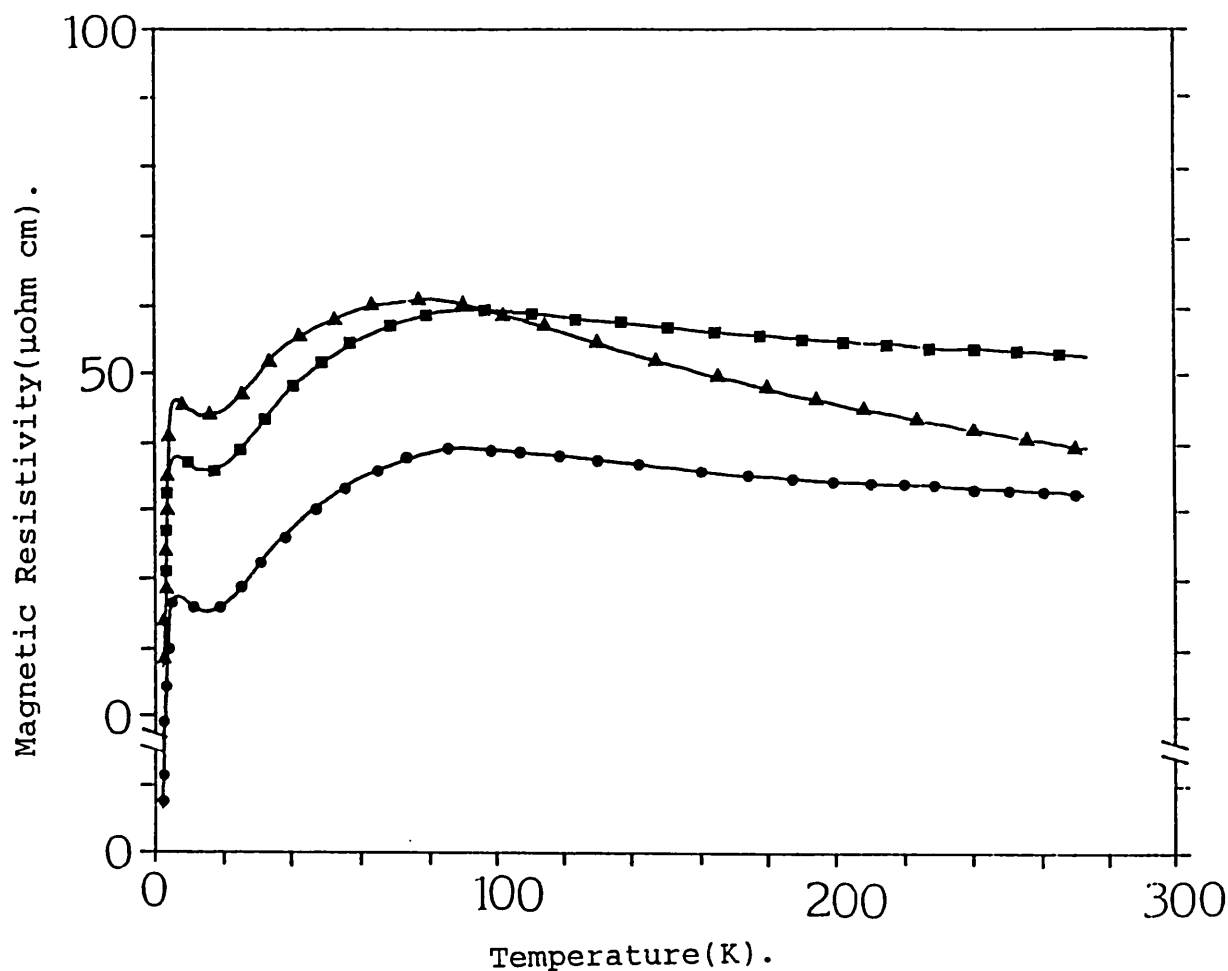


Figure 5:5. Temperature dependence of magnetic resistivity of CeAl_2 . $\rho_{\text{mag}}(T)[\text{CeAl}_2] = \rho(T)[\text{CeAl}_2] - \rho(T)[\text{MAl}_2]$ where M is Y($\bullet$), La($\blacktriangle$) or Lu($\blacksquare$).

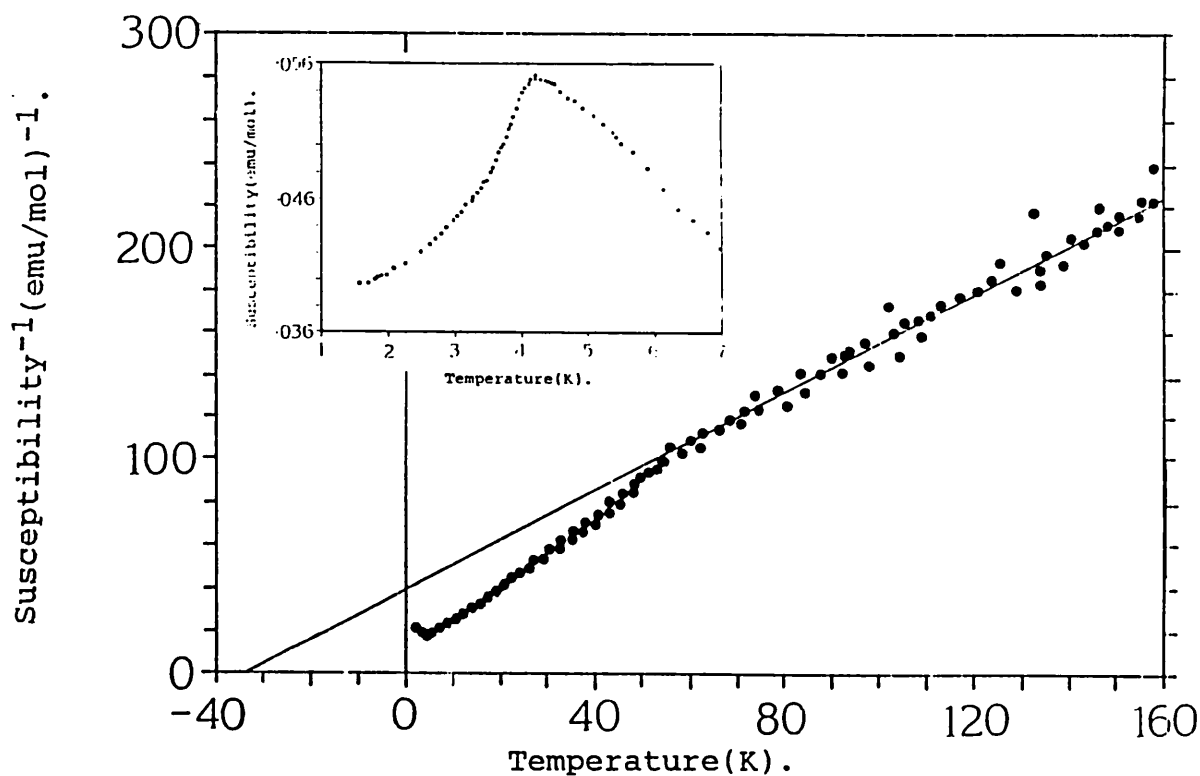


Figure 5:6. The inverse magnetic susceptibility of CeAl_2 versus temperature. The inset shows the low temperature susceptibility on an expanded scale.

transition (fig 5:3). Measurements by Buschow and van Daal [5:10] of $\chi(T)$ also showed evidence of a magnetic transition around 4K. Walker, Purwins, Landolt and Hullinger [5:11] performed dilation measurements on polycrystalline LaAl_2 and CeAl_2 in an attempt to rule out the possibility of a $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$ transition with increasing temperature around 4K (similar to that observed in metallic Ce). Such a transition should be accompanied by a lattice expansion up to room temperature of the order $r(\text{Ce}^{3+}-\text{Ce}^{4+})/r(\text{Ce}^{3+}) \approx 0.1$. The linear thermal expansion coefficient $\alpha(T)$ of LaAl_2 and CeAl_2 were published (fig 5:7). The curve for LaAl_2 reflects the normal behaviour expected for metal above the superconducting transition temperature and the total relative expansion $\delta l/l$ from 2.5 to 300K was found to be 2.52×10^{-3} . For CeAl_2 the corresponding value was 2.37×10^{-3} . The difference between these two values was thought to be too small and of the wrong sign to account for a $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$ transition. However at $3.5 \pm 0.1\text{K}$, $\alpha(T)$ of CeAl_2 has a pronounced negative peak whose shape was characteristic of a broadened phase transition. Specific heat measurements on the same sample agreed with those of both Hill and Machado da Silva and Deenedas et al. [5:12] in the relevant temperature ranges although the peak at 3.36K was found to be a few percent higher than that of Hill and Machado da Silva. Initial susceptibility shows a broad maximum in $\chi(T)$ centred at 4.5 to 4.8K in correspondence with the peak in resistivity of Buschow and van Daal. A distinct change in slope of $\chi(T)$ occurs close to 3.8K which according to Fischer [5:13] indicates a magnetic transition. Barbara, Rossignol, Purwins and Walker [5:14] investigated the static magnetisation of single crystals of

CeAl_2 between 1.5 and 300K in magnetic fields up to 150kGauss, applied in the [100], [110] and the [111] directions. It was shown that the magnetisation of CeAl_2 is anisotropic and behaves qualitatively differently above and below approximately 4K. A maximum in the initial slope of magnetisation versus field curves was observed in close agreement with the maximum in the initial susceptibility reported by Walker et al. Below 3.8K the magnetisation curves are observed to have an inflexion point which is most pronounced at lowest temperatures. The [110] and [111] curves cross near this inflexion point. At higher temperatures the inflexion point was not observed and the slopes of the magnetisation curves decrease monotonically with increasing field with the [111] curve always having the higher value. Despite all this evidence for the occurrence of magnetic ordering neutron diffraction studies at 2.2K had been unable to detect any ordering [5:15]. Barbara et al. [5:16] performed a very careful neutron diffraction experiment in order to determine the exact magnetic structure of CeAl_2 below the phase transition at 3.8K (see figure 5:8). Experiments were performed on crushed CeAl_2 samples at 8.2 and 1.9K i.e. above and below the transition temperature. Published results show a difference between two sets of data revealing extra Bragg peaks, taken to indicate magnetic ordering. The magnetic lines could not be indexed in a magnetic cell commensurate with the chemical cell. Rather they corresponded to a propagation vector (0.612, 0.388, 0.5) which can be decomposed into two vectors (0.5, 0.5, 0.5) and (0.112, -0.112, 0). The first vector indicates antiferromagnetic coupling between the Ce moments of

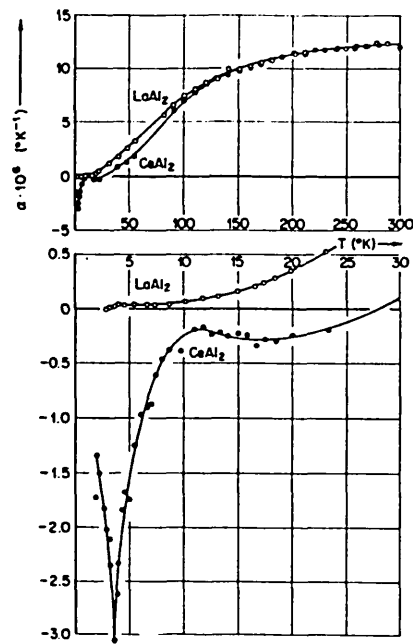


Figure 5:7. Thermal dilation $\alpha = l^{-1}(dl/dT)$ of CeAl_2 and LaAl_2 reported by Walker et al. [5:11].

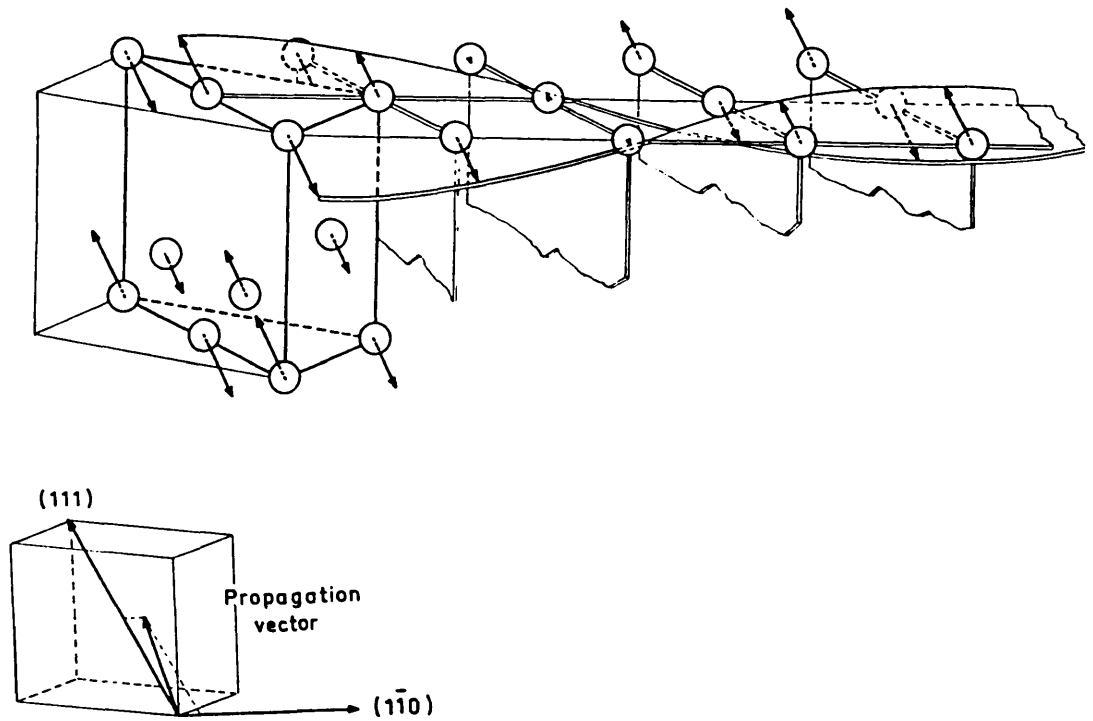


Figure 5:8. The magnetic structure of CeAl_2 proposed by Barbara et al. [5:17].

successive [111] planes, the second vector represents a modulation of this structure along the [110] direction. That is, magnetic moments are constrained to lie along the [111] direction whilst the magnitude of the moments are modulated perpendicular to the [110] direction with a period of 8.93 interatomic distances incommensurate with the crystal structure. The experiment gave a value of $0.89 \pm 0.05 \mu_B/\text{Ce}$ for the maximum amplitude of Ce ordered moment. It was noted that the [111] direction of the antiferromagnetic ordering was consistent with an anisotropy of the initial susceptibility [5:17]. After taking into account the Ce-Ce exchange interaction in CeAl_2 by a molecular field model the maximum value of the Ce ordered moment was calculated to be $0.862 \mu_B$, (c.f. $0.89 \pm 0.005 \mu_B$ of experiment). However this C.F. model could not explain the modulated structure. Instead three conditions were cited as necessary to explain the modulation:

1. The presence of ferromagnetic as well as antiferromagnetic interactions leading to a competition between positive and negative long range interactions.
2. A large anisotropy producing a preferred direction for the magnetic moment and consequently favouring a modulated rather than a helical structure.
3. A reduction in the magnetic moment amplitude.

These three conditions are now discussed in more detail.

1. Exchange Interactions. Williams et al. [5:9] showed all rare-earth Al_2 are ferromagnetically ordered, except YbAl_2 which is not ordered and CeAl_2 . These results are confirmed by neutron diffraction measurements. [5:18-20]. Evidence for the presence of strong ferromagnetic long range interactions in CeAl_2 also comes from an extrapolation to $x=0$ of the Curie temperature of the ternary alloy $\text{Ce}_{1-x}\text{Pr}_x\text{Al}_2$. This would indicate a Curie temperature close to 5K (fig 5:9).

2. Anisotropy. Evidence for a large anisotropy compared to exchange comes from measurements [5:14, 5:21] which show that the magnetisation values remain unequal when a field of 30kGauss is applied along any of the three main directions, i.e. there is no global rotation of magnetic structure and the anisotropy corresponds to at least a field of 30kGauss.

3. Reduction in the magnetic moment. Experiments of Barbara et al.[5:22] used polarized neutron diffraction in a study on a single crystal of CeAl_2 down to $T_N/10$. These experiments confirmed that the sinusoidal modulation remains down to at least 0.4K and that the propagation vector stays invariant. The values of the magnetic moments calculated for the modulated structure of CeAl_2 indicate that the magnetic moments associated with some of the Ce^{3+} sites have values very much smaller than those expected for a Γ_7 Kramers doublet. A thermal reduction in the magnetic moment associated with an increase in entropy [5:23] was ruled out given the low temperatures reached in the experiment and that the specific heat measurements show very little entropy gained from 0 to 0.4K. Instead Barbara et al. appealed to the Kondo effect to explain the moment reduction. A negative coupling of the Ce^{3+} spins and the spins of the conduction electrons may result in Ce^{3+} magnetic moment values intermediate between zero and the maximum value equal to that of C.F. ground state. This ground state of the Ce^{3+} in CeAl_2 arises from a competition between exchange interactions which tend to align moments antiferromagnetically and a Kondo effect which tends to reduce the Ce^{3+} magnetic moment. What is the Kondo temperature T_K i.e. the temperature characteristic of the onset of the spin compensation. The

assumption that the Kondo effect is responsible for stabilizing the ground state implies the Kondo temperature is comparable with the ordering temperature. Is this the case?

5:2:5. Determination of T_K .

Neutron data of Horn et al. [5:24] gave an upper limit to T_K of 6K. Another estimate of T_K comes from examining the results of specific heat of $Ce_{1-x}La_xAl_2$ system [5:25]. Dilution of Ce concentration together with application of high magnetic fields reduces the Ce-Ce interaction effects, leaving us free to deduce a value for T_K . Extrapolating values of T_K obtained back to $x=0$ gives T_K for $CeAl_2$ of $5K \pm 2K$. Magnetisation curves measured at 1.7K under pressures up to 6kbar gives $T_K \approx 4K$, whilst analysis of resistivity data gives $T_K = 5K \pm 2K$. These findings indicate T_K is close to the ordering temperature T_N . Now we ask, what is the evidence for the coexistence of the Kondo effect and magnetic ordering at low temperature which is suggested to be responsible for modulated ordering. Bredl et al. [5:25] showed that for pure $CeAl_2$ at 1.5K (well below the temperature at which the cusp appears indicating we are in the region where magnetic order should have taken place) the specific heat data is well fitted to equation 5:1

$$C(T) = \gamma T + \beta T^3 \text{ ----- 5:1.}$$

with $\gamma = 135 \text{ mJ/K}^2 \text{ mol}$ and $\beta = 140 \text{ mJ/K}^4 \text{ mol}$.

The cubic term is caused by antiferromagnetic spin density waves. The existence of such spin waves is suggested by inelastic neutron scattering data [5:26]. The linear term in the specific heat γT represents a large hf like electronic contribution to the specific heat. γ is found to be almost field independent up to 5T. This weak field dependence rules

out a spin glass behaviour as the origin of the linear term. So we can assume that the Kondo effect is responsible for the linear $C(T)$ and has survived into the ordered phase. The value of γ for pure CeAl_2 estimated by Bredl et al. by extrapolating the value of γ for dilute concentrations of Ce in $\text{Ce}_{1-x}\text{La}_x\text{Al}_2$ back to $x=0$ gave $\gamma=1740\text{mJ/mol K}^2$. Since this value is approximately 10 times the experimentally determined value, it was assumed that approximately 10% of the conduction electrons take part in the Kondo interaction. Ambrüster and Steglich [5:27] extended the range of temperature for which specific heat measurements have been made down to 20mK, in order to determine if a distinct phase showing coexistence of magnetic ordering and the Kondo effect exists down to lowest temperatures probed. They found that above 0.08K the data was well represented by $C(T) = \gamma T + \beta T^3$ and in good agreement with Bredl et al. in the range 0.3 to 1K explored by that group. From this it was inferred that no further phase transition takes place down to 80mK and the Kondo effect is not wiped out. A deviation in $C(T) = \gamma T + \beta T^3$ behaviour in the 20mK-80mK range was attributed to a nuclear contribution from Al^{27} . The excess specific heat above $C(T) = \gamma T + \beta T^3$ law fitted a $C(T)=\alpha T^{-2}$ law with $\alpha=6.4 \pm 0.1 \times 10^{-4} \text{ mJ/mol}$. This result suggests that CeAl_2 exhibits the coexistence of magnetic order and Kondo effect down to 20mK. Later nuclear orientation experiment of gamma ray anisotropy of ^{137}Ce by Benoit et al. [5:28] suggest that CeAl_2 is magnetically ordered down to 5mK.

5:2:6. Summary.

Properties of CeAl_2 can be classified as those of a hf with a magnetic ground state (a magnetically ordered Kondo lattice).

These properties include:

1. Enhanced low temperature electronic coefficient to the specific heat of approximately 400mJ/molK^2 .
2. A magnetic transition at 3.8K which reduces γ to 135mJ/molK^2 .
3. Anomalously high room temperature resistivity.
4. High temperature maximum in ρ_{mag} due to a combination of C.F. and Kondo effects. This maximum divides two regions in which $\rho(T)$ exhibits logarithmic temperature dependence suggesting that the Ce^{3+} are acting as individual Kondo impurities producing incoherent Kondo scattering.
5. A low temperature maximum, followed by a rapid fall in $\rho(T)$ indicating both a transition from incoherent to coherent Kondo scattering and the onset of magnetic order.
6. C-W susceptibility at high temperature confirming the Ce ions are behaving as localized moments.
7. Kondo compensation at low temperature producing a reduction in the Ce moments. However RKKY interaction between the Ce ions is still sufficiently strong to produce complicated antiferromagnetic order below 3.8K .

5:3. Pressure Dependence of the Properties of CeAl_2 and the Nature of the Phase Transition at T_N .

5:3:1. Introduction.

The magnetic structure in CeAl_2 has been shown to result from a delicate balance between several competing interactions. As such, the properties of CeAl_2 are expected to be sensitive to changes in external physical parameters. In this section, some of the many experiments which have investigated the changes in the properties of CeAl_2 at elevated pressures are briefly reviewed. These experiments have allowed the

determination of:

1. The variation of T_N (ordering temperature) with pressure which reflect the strength of the Kondo interaction relative to the RKKY interaction.
2. The nature of the phase transition at T_N .
3. Construction of a temperature - pressure phase diagram for CeAl_2 .

5:3:2. Variation of T_N with Pressure.

Experiments to measure the variation of T_N with pressure were performed by several groups. Specific heat measurements at elevated pressure by Berton et al. [5:29] observed an enhancement in the transition temperature with pressure and a positive value for the pressure dependence of the Neel temperature $t_p = T_N^{-1}(dT_N/dP)_{P=0}$ of 0.0085kbar^{-1} . In contrast, Croft et al. [5:30] suggested that a shift in the inflexion point seen in the susceptibility data implied a depression in T_N with pressure from $3.85 \pm 0.05\text{K}$ at normal pressure to $3.5 \pm 0.15\text{K}$ at 8kbar, giving a negative $t_p = -(0.011 \pm 0.005)\text{kbar}^{-1}$. Recently, experiments by Schefzyk et al. [5:31] and Schefzyk, Lieke and Steglich [5:32] on zero pressure thermal expansion and specific heat around T_N were carried out to finally determine the sign of t_p . They used the Ehrenfest relation

$$t_p = 3V\delta\alpha/\delta C_p \text{ ----- 5:7.}$$

which is valid for a second order transition to determine t_p where

$$\delta\alpha = \lim[T \rightarrow T_N](\alpha(\text{low } T \text{ phase}) - \alpha(\text{high } T \text{ phase})) \text{ ---- 5:8.}$$

=discontinuity in thermal expansion coefficient at $P=0$

$$\delta C_p = \lim[T \rightarrow T_N](C_p(\text{low } T \text{ phase}) - C_p(\text{high } T \text{ phase})) \text{ ---- 5:9.}$$

=discontinuity in molar specific heat at $P=0$

V =molar volume. C_p is always positive since near the Neel

temperature $C_p(\text{A.F.}) > C_p(\text{paramagnetic})$. Therefore the sign of t_p is given by a sign of $\delta\alpha$. Results for $\delta l/l$ and $\alpha = l^{-1}(dl/dt)$ are shown in figure 5:10. $\alpha(T)$ is negative well above T_N . As T_N is approached antiferromagnetic fluctuations become important and cause a large positive contribution to $\alpha(T)$. However this additional thermal expansion consists of two parts:

1. a λ type anomaly indicating a second order phase transition with a positive jump ($\delta\alpha_1$) at $T_{N1} \approx 3.8\text{K}$.
2. a sharp peak signalling a second order phase transition with a negative jump ($\delta\alpha_2$) located on the high side of the λ anomaly at a temperature T_{N2} .

In order to confirm the existence of two phase transitions careful specific heat measurements in the region of the transition were carried out. Again the results showed evidence of contributions from two phase transitions. Compared with thermal expansion results the two contributions were less well resolved, since both the specific heat jumps are positive. From these results Schefzyk et al. were able to confirm estimates of t_p made by both specific heat and susceptibility measurements. These techniques give different signs for t_p because they are sensitive to different effects. $C_p(T)$ appears sensitive to the transition associated with the maximum change in the entropy, i.e. the transition at T_{N1} with a positive jump $\delta\alpha$. This gives $t_p > 0$. On the other hand susceptibility measurements are sensitive to the pressure induced shift of T_{N2} with a negative $\delta\alpha$ and therefore gives values of $t_p < 0$. Numerical values calculated for t_p (t_{p1}, t_{p2}) from thermal expansion experiment for the different transitions agree closely with values calculated for t_p using $C_p(T, p)$ and $\chi(T, p)$ data extrapolated to $P=0$. What are the origins of the two phase transitions? Schefzyk et al.

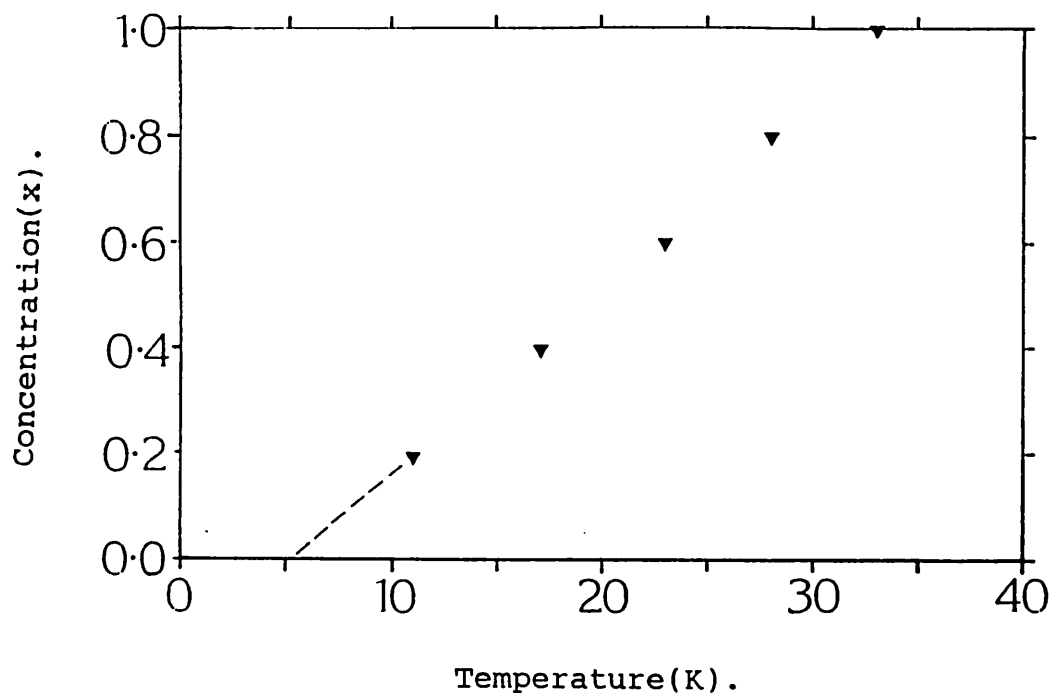


Figure 5:9. Curie temperatures of some $\text{Ce}_{1-x}\text{Pr}_x\text{Al}_2$ samples. Extrapolation of these values to $x=0.0$ gives a Curie temperature of 5K, indicative of the ferromagnetic interactions present in CeAl_2 .

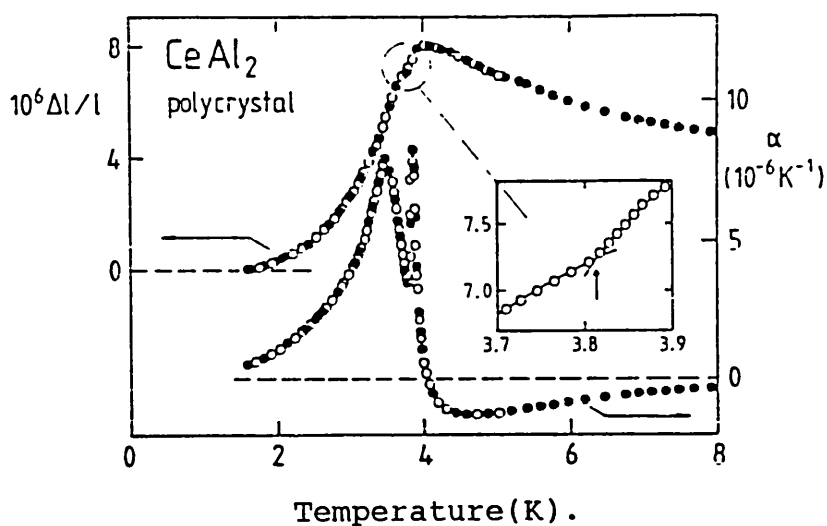


Figure 5:10. Relative length change $\delta l/l$ (left scale) and the thermal expansion coefficient α versus temperature for CeAl_2 . Inset: $\delta l/l$ versus temperature near $T=3.8\text{K}$ on extended scales. Solid lines represent extrapolated high and low temperature behaviour. Arrow indicates change of slope. Taken from Schefzyk et al. [5:32].

investigated the effects of sample quality on two phase transitions. They found either introducing disorder or introducing impurities favours the transition with positive t_p . Barbara et al. [5:33] performed neutron diffraction measurements under perturbations such as uniaxial stress and hydrostatic pressure on CeAl_2 . These experiments showed traces of another magnetic structure of CeAl_2 coexisting with modulated structure. At 25kbar all magnetic lines are characteristic of simple type II antiferromagnetic structure. Releasing the pressure results in the reappearance of the two phase structure in neutron data. A large pressure hysteresis can be explained by the coexistence at normal pressure after a high pressure cycle of more of the high pressure phase, which is stabilized by point defects or impurities. Thus in pure, defect free material, CeAl_2 orders with a sinusoidally modulated structure below T_N . However in most cases the material has some defects or impurities. Then CeAl_2 coexists in two phases in the magnetically ordered state. A sinusoidally modulated phase and a simple type II antiferromagnetic structure with distinct Neel temperatures T_{N1} and T_{N2} and nearly equal internal energies. The proportion of each state depends on the condition and history of the sample.

5:3:2. Variation in the Ce Moment with Pressure.

Barbara et al. [5:17] performed magnetisation measurements on a single crystal at 1.7K for $P < 6\text{kbar}$ and on polycrystalline samples at 1.8K at pressures between 6 and 12kbar. It was shown that the Ce moment associated with the crystal field ground state is a maximum at low pressure. There is evidence for a continuous demagnetisation with pressure. A linear

extrapolation of the decrease of magnetisation with pressure shows that magnetisation of CeAl_2 would be very small for pressures of about 40kbar. Susceptibility measurements by Croft et al. [5:30] also implied a reduction in the Ce moments under pressure.

5:3:3. Variation of Cell Volume with Pressure.

Barbara et al. [5:33] performed lattice parameter measurements at high pressures (≤ 150 kbar) (see figure 5:11). Lattice parameters of CeAl_2 were seen to evolve smoothly in agreement with the results of Vedel et al. [5:35], but in contradiction to Croft and Jayaraman [5:35] who observed a strong volume anomaly at 65kbar. From these results they discounted the occurrence of a transition from integral to mixed valent regime.

5:3:4. High Pressure Resistivity.

Nicholas-Francillon et al. [5:36] investigated the variation in the magnetic component of the resistivity of CeAl_2 with pressure. The resistivities of CeAl_2 and LaAl_2 were measured between 1.3 and 300K at normal pressure, 6kbar and 18kbar. Barbara et al. [5:35] extended the pressure range explored up to 150kbar (see figure 5:12). The resistivity of non-magnetic LaAl_2 was not found to vary with pressure. The variation in resistivity of isostructural CeAl_2 can thus be attributed to magnetic behaviour. It was shown that the maxima seen in magnetic resistivity at approximately 5 and 65K at normal pressure are both moved to lower temperature as the pressure is increased. Subtracting the resistance of LaAl_2 showed that the spin-disorder resistivity almost vanishes at high pressure. Figure 5:13 shows some electrical resistivity versus pressure isotherms. The data taken at 273K shows a

smooth variation, in $\rho(P)_{273K}$ with no indication of crossing a crystallographic phase boundary over the whole pressure range. A continuous anomaly is observed near 80kbar, quite close to pressure at which Croft and Jayaraman observed their strong volume anomaly. It was suggested that this anomaly coincided with a smooth crossover from weak to strong Kondo behaviour. This resistance anomaly was observed to move to lower pressure as the temperature was reduced.

5:3:5. Summary.

All the observations discussed above can be explained by examining the variation in the strength of the Kondo and RKKY interactions with pressure. Spectroscopy [1:6] indicates a close proximity of the Ce 4f level to the Fermi level in CeAl₂. Application of pressure decreases the $E_{4f}-E_{Fermi}$ gap. Pressure also results in an increase in the degree of hybridisation V_{sf} , between f states and the conduction electrons. Both these effects result in an increase in the exchange constant $|J|$ since $|J| \sim V_{sf}^2 / (E_{Fermi} - E_{4f})$. The strength of the Kondo effect is characterized by $T_K \sim T_F \exp(-1/N(E_F)J)$ where T_F is the Fermi temperature and $N(E_F)$ is the density of states at the Fermi level. Thus an increase in pressure will result in an increase in T_K . This in turn leads to a reduction in the Ce moment with pressure. That is, increases in T_K lead to a crossover from a region where the Kondo effect is weak, to a regime where moments are strongly suppressed and the Kondo effect is strong. In paramagnetic CeAl₂ this gives rise to regions I, II and III seen in P-T diagram shown in figure 5:14. In region I at low pressure and high temperature, the Kondo temperature is negligible compared to the thermal energy kT . Thus the

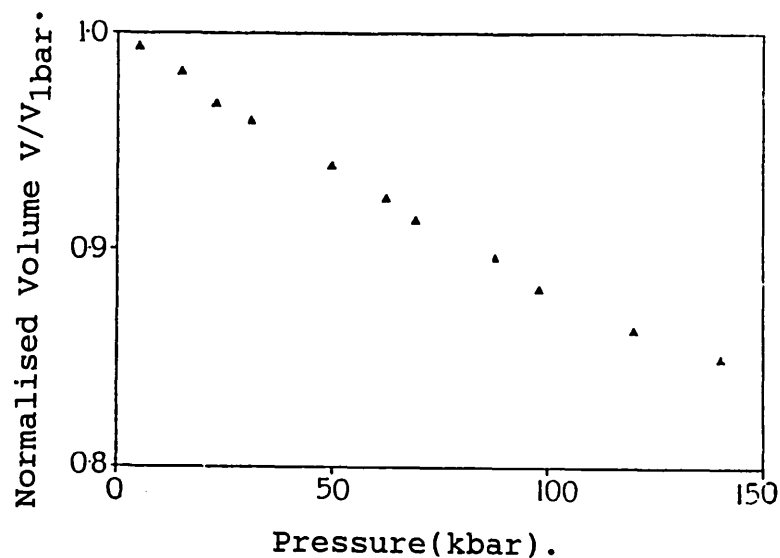


Figure 5:11. Volume-pressure evolution of CeAl_2 at room temperature after Barbara et al. [5:33].

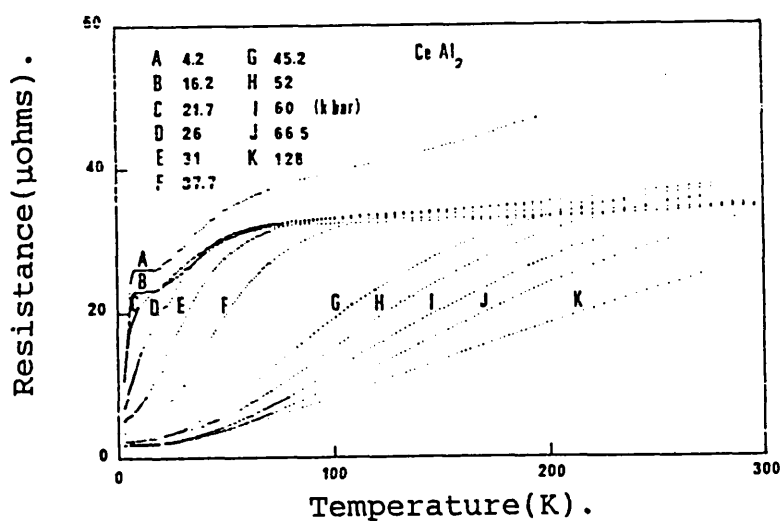


Figure 5:12. Electrical resistance versus temperature of a single crystal of CeAl_2 at different hydrostatic pressures. Taken from Barbara et al. [5:33].

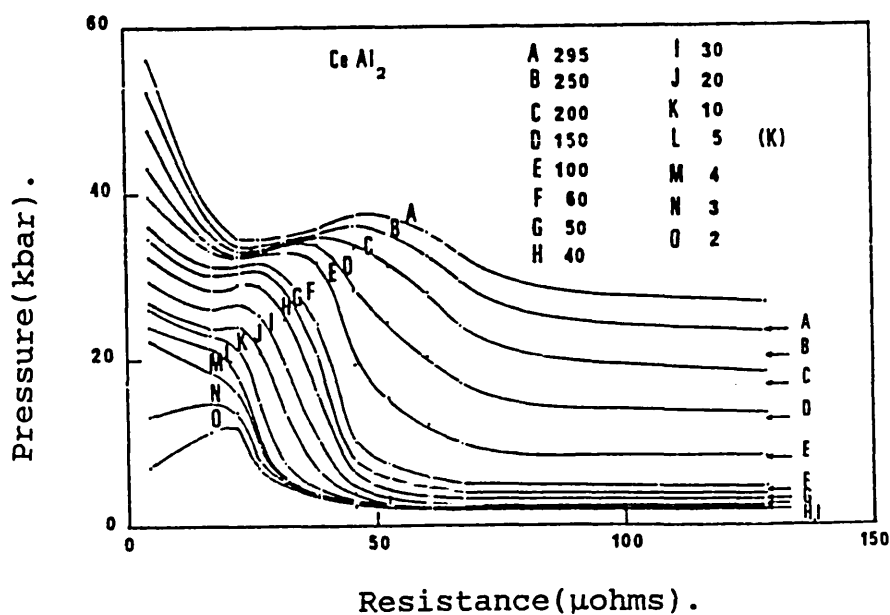


Figure 5:13. Isotherms deduced from results contained in figure 5:12 after Barbara et al. [5:33].

fluctuation time associated with the Kondo effect $\tau_K \sim \hbar/kT_K$ is much larger than the characteristic time of thermal fluctuations $\tau_{\text{Thermal}} \sim 1/kT$ and the Ce paramagnetic moment $\langle M^2 \rangle$ is not much reduced from that expected for free Ce^{3+} . In region II, low pressure, low temperature $\tau_K < \tau_{\text{Thermal}}$ and the Ce paramagnetic moments are reduced. Thus CeAl_2 shows weak Kondo behaviour. Finally in region III (high pressure) the Kondo temperature is enhanced and τ_K is less than τ_{Thermal} for all temperatures, i.e. we have crossed into a regime of strong Kondo behaviour. The gradual loss of spin disorder resistivity with increasing pressure, can now be explained as being due to a smooth transition into this strong Kondo regime with an inflexion in pressure-resistance isotherms indicating the crossover point for any given temperature. According to the theory of Cornut and Coqblin a peak in the magnetic resistivity is expected to occur around the C.F. splitting temperature. So the shift to lower temperature of the high temperature maximum in ρ_{mag} can be attributed to a reduction in the crystal field splitting with pressure. Concerning the ordered phase, the ordering temperature T_N is characterized by $T_N \sim J^2 \mu_{\text{eff}}$. Thus as $|J|$ increases with pressure, if the Kondo effect is weakly enhanced compared to the RKKY interaction and the Ce moment μ_{eff} is only slowly suppressed below its value at normal pressure, we expect T_N to increase with pressure. However a sufficiently strong Kondo effect will result in the increase of exchange being offset and possibly overcompensated for by a reduction in the effective Ce moment. Thus

$$t_p > 0 \Rightarrow \text{RKKY "dominant"}.$$

$$t_p < 0 \Rightarrow \text{"strong" Kondo effect}.$$

Schefzyk et al. [5:31] have shown that at normal pressure CeAl_2 begins to order with a modulated structure for which $t_p = -0.015 \text{ kbar}^{-1}$ (region IV in figure 5:14). This ordering is associated with a sharp feature at T_{N2} . However, if the structure is disturbed in any way, either by defects or impurities the ordering is quenched and leaves a simple type II antiferromagnetic structure which is associated with the transition feature at T_{N1} and a positive t_p . Thus for pure, well formed CeAl_2 we can conclude that the negative pressure dependence of the modulated structure Neel temperature T_{N2} indicates that the Kondo effect is slightly stronger than the RKKY interaction. Introduction of defects or impurities effects the Kondo interaction more greatly than the RKKY interaction and can lead to a positive t_p of type II antiferromagnetic structure. Application of pressure produces an increase in the strength of the Kondo compensation mechanism. This results in the suppression of ferromagnetic interactions necessary for modulated structure and encourages the appearance of the type II structure even in defect free CeAl_2 . Thus for intermediate pressures T_N is reduced and CeAl_2 first exhibits modulated structure (region IV), followed at lower temperature by a coexistence of the modulated and a simple type II structure (region V). In material where conditions have led to the coexistence of the modulated and simple antiferromagnetic structure at normal pressure, an increase in pressure initially results in either an increase or decrease in T_N depending on the ratio of the two phases. However at approximately 5kbar, t_p changes sign for the simple type II structure and t_p is then always

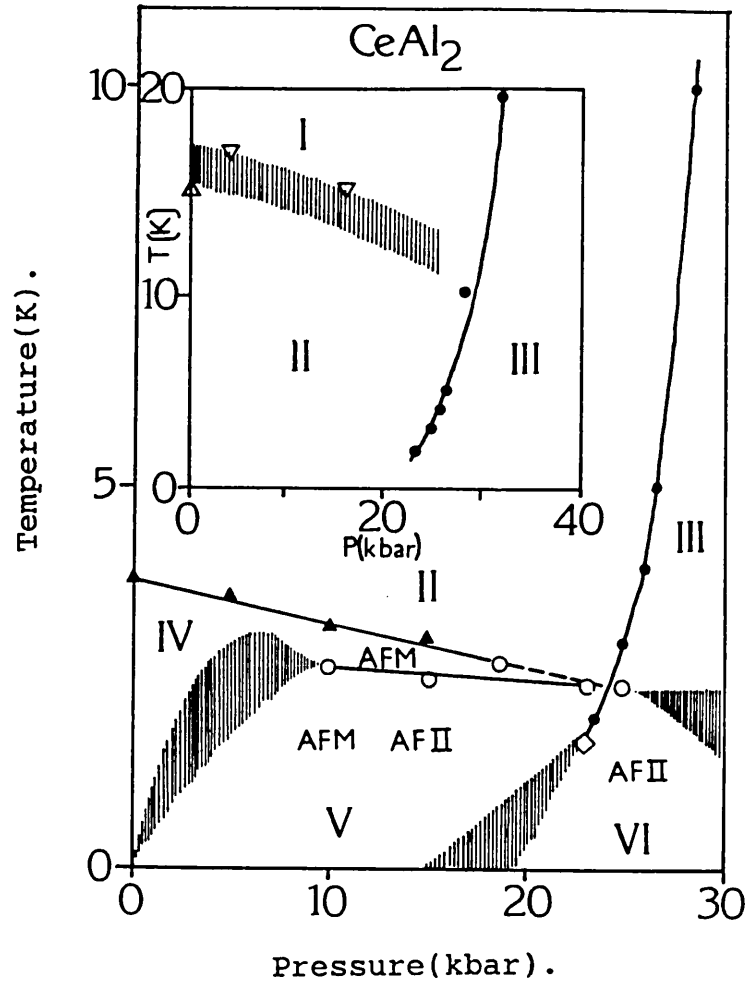


Figure 5:14. Temperature-pressure phase diagram of CeAl_2 for $T \leq 10\text{K}$ and $10\text{K} \leq T \leq 20\text{K}$ (inset). Three different magnetic phases are present: the paramagnetic phase (regions I and II), the modulated phase IV and the type II phase (region VI). Magnetically ordered CeAl_2 shows a coexistence between modulated and type II phases in region V. In the paramagnetic region, two crossover lines are given. One is interpreted as due to the crossover between thermal (I) and weak Kondo behavior (II). The second corresponds to the crossover from weak (II) to strong Kondo behaviour (III). Taken from Barbara et al. [5:33].

negative, giving a reduction in T_N with pressure for either structure. At high pressure ($P \geq 15 \text{ kbar}$), T_N is further decreased and ferromagnetic interactions are reduced to such a degree that only the simple type II structure is observed (region VI). The pressure at which only type II structure is observed, coincides with an extrapolation into the ordered phase, from paramagnetic region, of the boundary marking crossover from weak to strong Kondo effect.

5:4. Effects of Alloying.

5:4:1. Previous Work.

It has been shown in the preceding sections that the properties of CeAl_2 result from a delicate balance between the RKKY and Kondo effects. Replacement of Ce with non-magnetic elements (e.g. La and Y), allows the study of the evolution of the properties of CeAl_2 with changes in the parameters which determine these properties. For example the Kondo temperature T_K which marks the crossover from local moment to a non-magnetic spin compensated regime is given by equation 2:3

$$T_K \sim E_F \exp(-1/N(E_F)J) \text{ ----- 2:3.}$$

Alloying can change the density of states at the Fermi level $N(E_F)$. Alloying can also lead to changes in lattice parameter. This can shift E_{4f} relative to the Fermi level resulting in changes in J . Consider the replacement of Ce with La. Addition of La [5:37] produces little change in $N(E_F)$. However it does produce an increase in lattice parameter which leads to a slight reduction in T_K . At the same time, dilution of the Ce content reduces the strength of the magnetic interactions within the system. The magnetic resistivities of $\text{Ce}_{1-x}\text{La}_x\text{Al}_2$ for selected samples are shown

in figure 5:15. At high temperature all the samples with $x < 0.95$ show logarithmic temperature dependence indicating the Ce^{3+} ions are acting as independent incoherent Kondo scattering centres. For $0.95 > x > 0.80$ $\rho(T)$ shows the typical single Kondo impurity rise at low temperature reaching a temperature independent limit at lowest temperature. For $x < 0.6$ a maximum appears in $\rho(T)$ at low temperature. This maximum grows more pronounced as the Ce content is increased and shifts to higher temperature. This maximum signals the formation of a Kondo lattice. Thus the Kondo lattice state observed for pure CeAl_2 is seen to grow continuously from dilute single impurity regime. The magnetic susceptibilities for $\text{Ce}_{1-x}\text{La}_x\text{Al}_2$ are shown in figure 5:16. At high temperature the values for the effective moment and the paramagnetic Curie temperature are independent of Ce concentration and again confirm that the RKKY interaction is weak, the Ce^{3+} act independently, and that the dilute Kondo regime is continuously connected to the dense Kondo lattice state. At low temperature the onset of long range magnetic order persists down to low Ce concentrations [5:38,5:39] ($x \approx 0.90$). T_N has a quadratic Ce concentration dependence [5:25]. This behaviour comes about because whilst the magnetic interactions are weakened by Ce dilution, T_K , the temperature indicating the strength of the Kondo interaction is also reduced. This behaviour contrasts with replacement of Ce with Y in $\text{Ce}_{1-x}\text{Y}_x\text{Al}_2$ [5:38,5:40]. A much more rapid reduction in T_N is observed. For $x > 0.10$ specific heat and χ results indicate there is no long range order, but do indicate the presence of micromagnetic behaviour. T_G decreases almost linearly with Y concentration until for $x > 0.54$ no magnetic

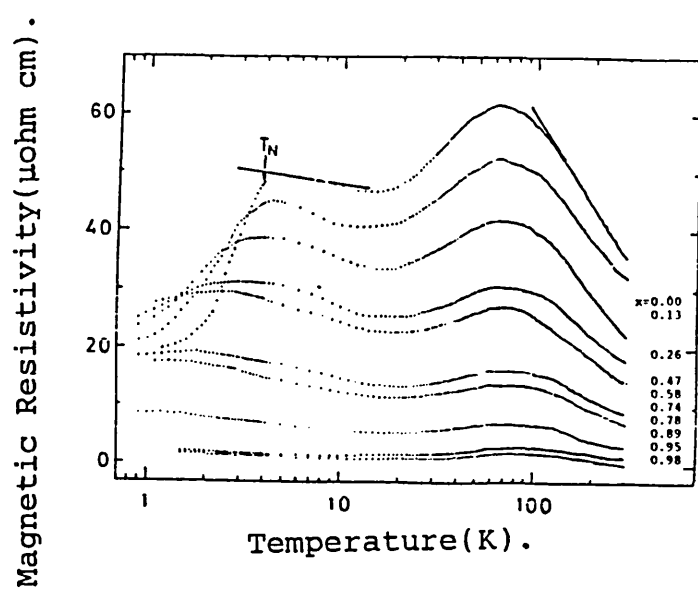


Figure 5:15. Temperature dependence of the magnetic resistivity of $\text{Ce}_{1-x}\text{La}_x\text{Al}_2$. Data are from Onuki et al.[5:6].

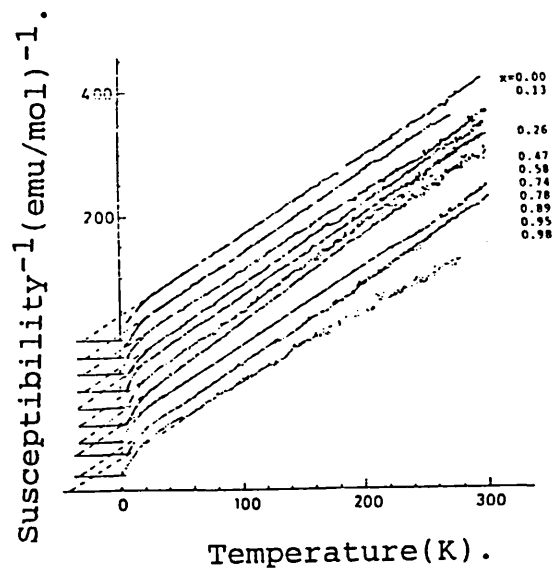


Figure 5:16. Inverse magnetic susceptibility versus temperature for selected $\text{Ce}_{1-x}\text{La}_x\text{Al}_2$ alloys. Data are from Onuki et al[5:6].

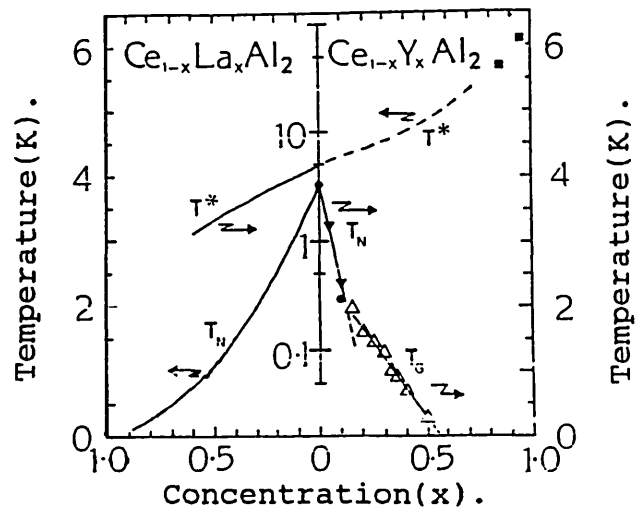


Figure 5:17. Magnetic phase diagram of (a) $\text{Ce}_{1-x}\text{La}_x\text{Al}_2$ and (b) $\text{Ce}_{1-x}\text{Y}_x\text{Al}_2$. T_N , T_G , and T^* indicate Neel, "glass" and spin fluctuation temperatures. After Steglich et al. [5:38].

order is observed. This may be due to an increase in T_K resulting from a decrease in the lattice parameter with Y concentration, coupled with a weakening in the magnetic interaction because of a dilution of the Ce concentration. i.e. the exchange between the Ce moments is overcome by interactions with, and eventual compensation by conduction electrons. The variations in T_K , T_N and T_G for La and Y are summarised in the magnetic phase diagram shown in figure 5:17.

Almost all the alloying studies carried out to date have concentrated on the effects of replacing Ce atoms. It was decided that a study should be made of the effects of alloying on the Al sites. This enables the observation of the effects of changes in the lattice parameters and the density of states at the Fermi level without perturbing the Ce sublattice, whose presence leads to the formation of a Kondo lattice. In the next three sections the effects of alloying with Cu, Co and Fe on the Al sites are examined

5:5. $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$ $x \leq 0.30$.

5:5:1. Sample Preparation and Characterization.

All the samples were prepared using the method described in section 3:6. The samples were all annealed at a temperature of 600°C for seven days. Metallographic specimens revealed the presence of a small amount of oxide in all the samples, but showed no evidence of any other unwanted phases, for up to 20% Cu substitution. For $0.20 < x \leq 0.30$ a small amount ($\approx 10\%$) of some unidentified second phase was observed. X-ray diffraction patterns confirmed that the structure remained cubic C15 throughout the sample series. Lattice parameters of $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$ ($x \leq 0.30$) are shown in figure 5:18. A continuous

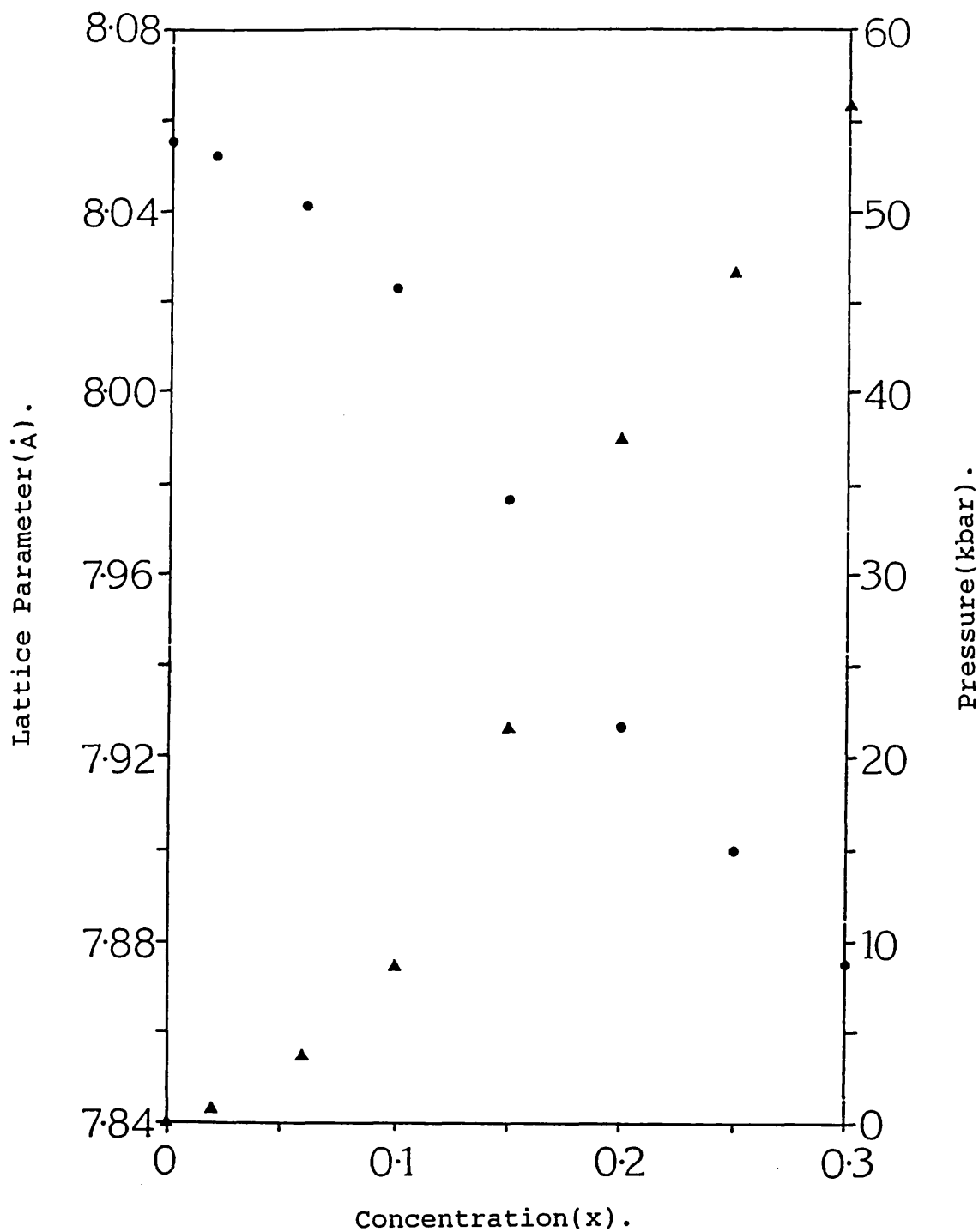


Figure 5:18. Concentration dependence of the lattice parameter of $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$ (●) and the external pressure required to produce such changes (▲).

reduction in the lattice parameter with increase in the Cu concentration is observed. Using the high pressure data of Vedel [5:34] and Probst and Wittig [5:41] the external pressures required to produce such changes in the lattice parameter are also shown in figure 5:18. This gives an idea of the chemical lattice pressure produced in CeAl_2 due to Cu substitution.

5:5:2. Electrical Resistivity.

The variation of resistivity with temperature for samples in the $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$ series with $x \leq 0.30$ are shown in figure 5:19. Subtracting the resistivities of non-magnetic isostructural LaAl_2 doped with similar amounts of Cu shown in figure 5:20 reveals the variation with temperature of the magnetic resistivities (see figure 5:21). The use of $\text{La}(\text{Al}_{1-x}\text{Cu}_x)_2$ as a non-magnetic reference compound seems justified. None of the effects discussed below can be attributed solely to the use of $\text{La}(\text{Al}_{1-x}\text{Cu}_x)_2$ although some of the effects (e.g. the slope of the high temperature magnetic resistivity) would differ slightly if another compound (e.g. LuAl_2 with Cu) were used. Several features present in this data must be highlighted:

1. A careful study of $\rho(T)$ for pure CeAl_2 was made between 4.5 and 2K. No obvious anomaly can be seen in $\rho(T)$ around the magnetic ordering temperature of 3.8K. The derivative $d\rho/dT$ was computed point by point in a 3 point span by performing a second order polynomial fit. The result is shown in figure 5:22 and shows there is a distinct change in slope around 3.75K. This agrees well with the magnetic ordering temperature (3.8K) taken from magnetic susceptibility and is the first time that a clear anomaly in $\rho(T)$ has been observed at T_N in this system.

2. Substitution of Cu removes much of the fall in $\rho(T)$ (called coherence) associated with both onset of magnetic order and the formation of a Kondo lattice. For a more complete discussion see section 5:7:5:2.

3. Addition of Cu leads to a gradual increase in the magnitude of the resistivity at high temperature (see table

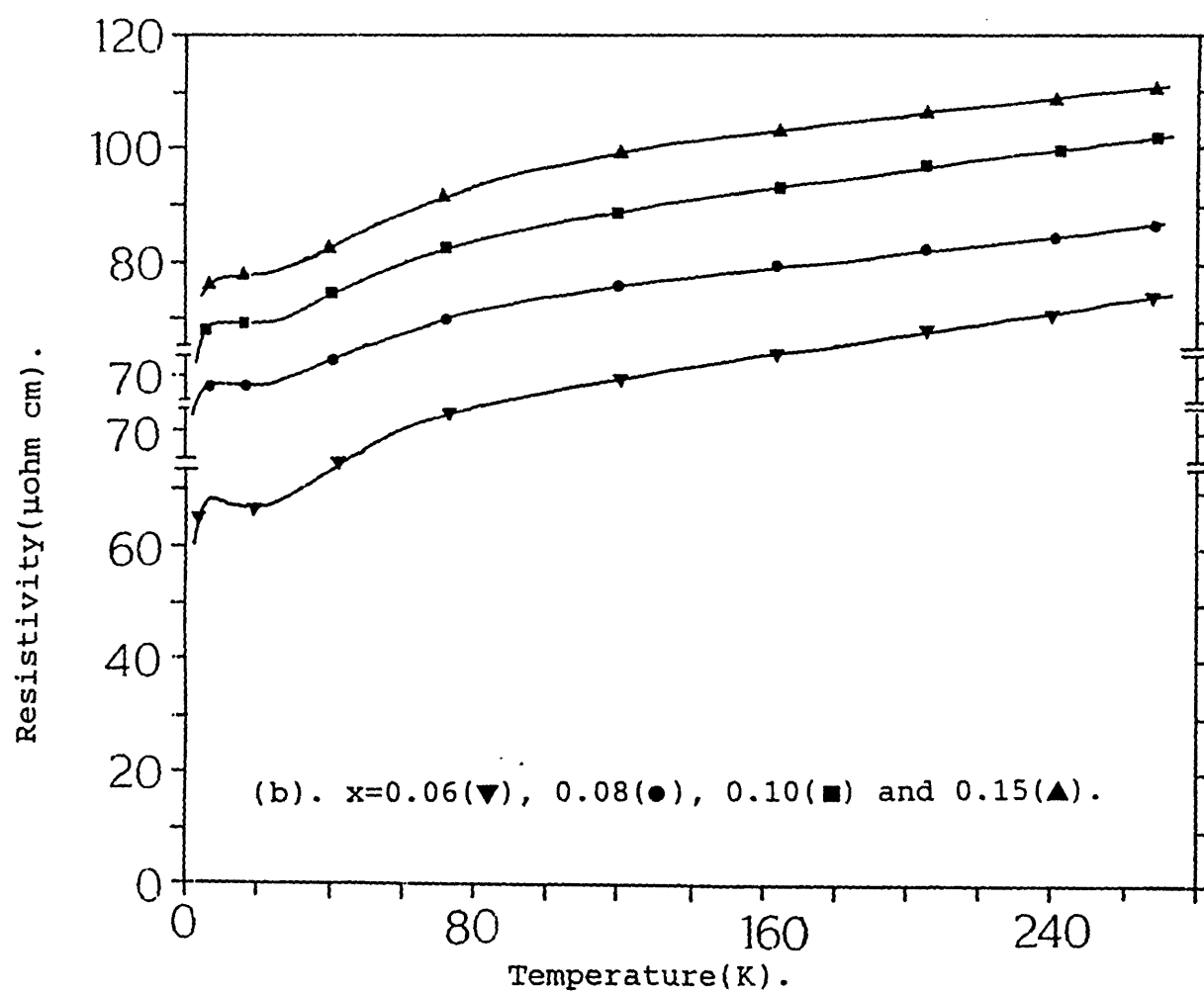
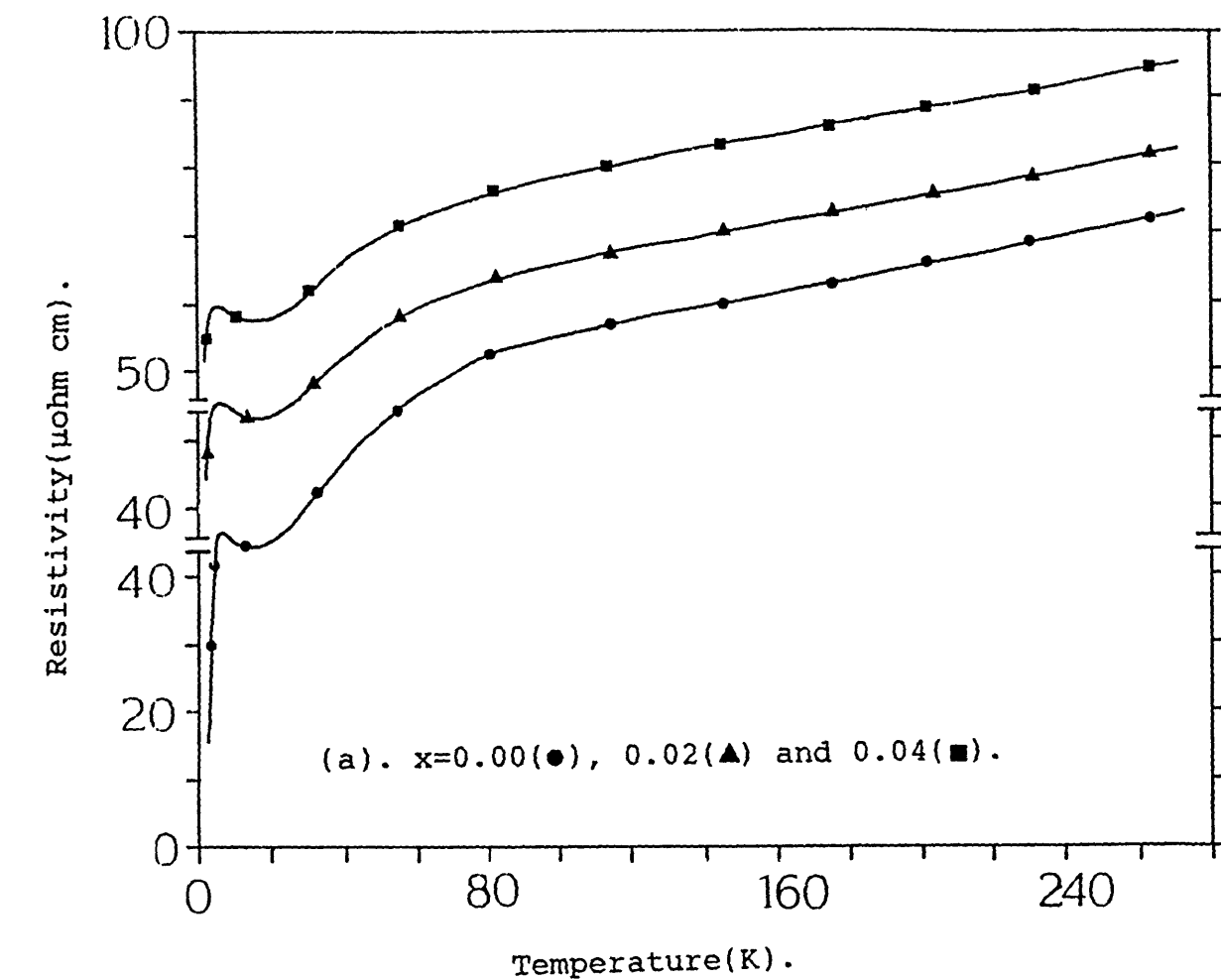


Figure 5:19. (a), (b) and (c) Temperature dependence of the electrical resistivity of $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$.

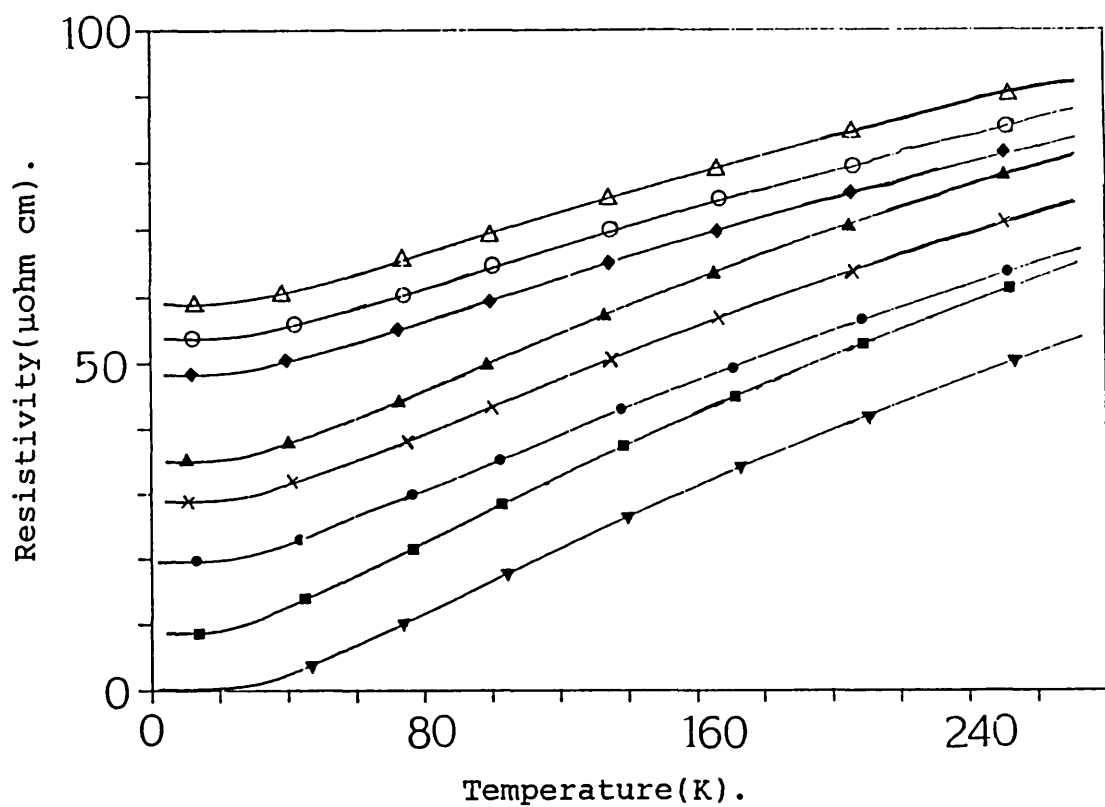
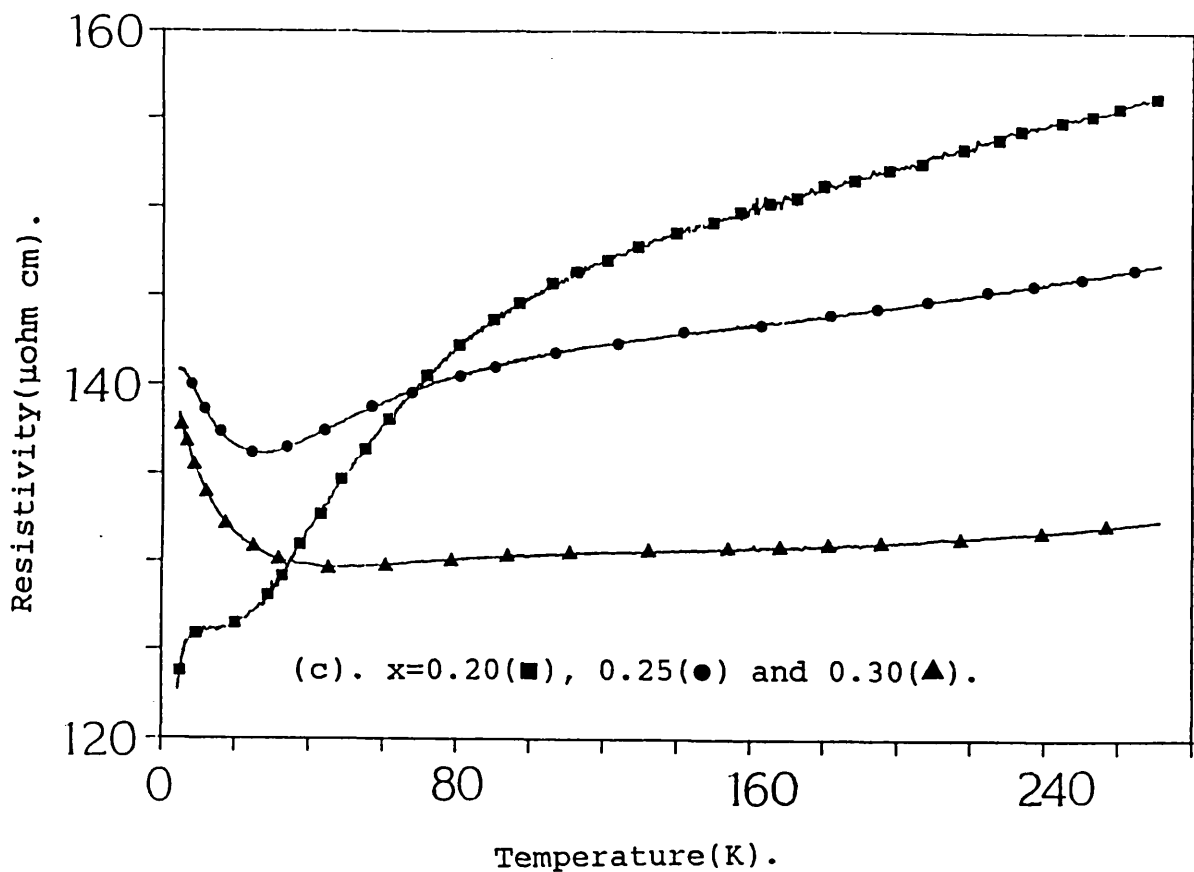


Figure 5:20. Temperature dependence of the electrical resistivity of $\text{La}(\text{Al}_{1-x}\text{Cu}_x)_2$ for $x=0.00(\nabla)$, $0.02(\blacksquare)$, $0.04(\bullet)$, $0.06(\blacktriangle)$, $0.08(\times)$, $0.10(\blacklozenge)$, $0.15(\circ)$ and $0.20(\triangle)$.

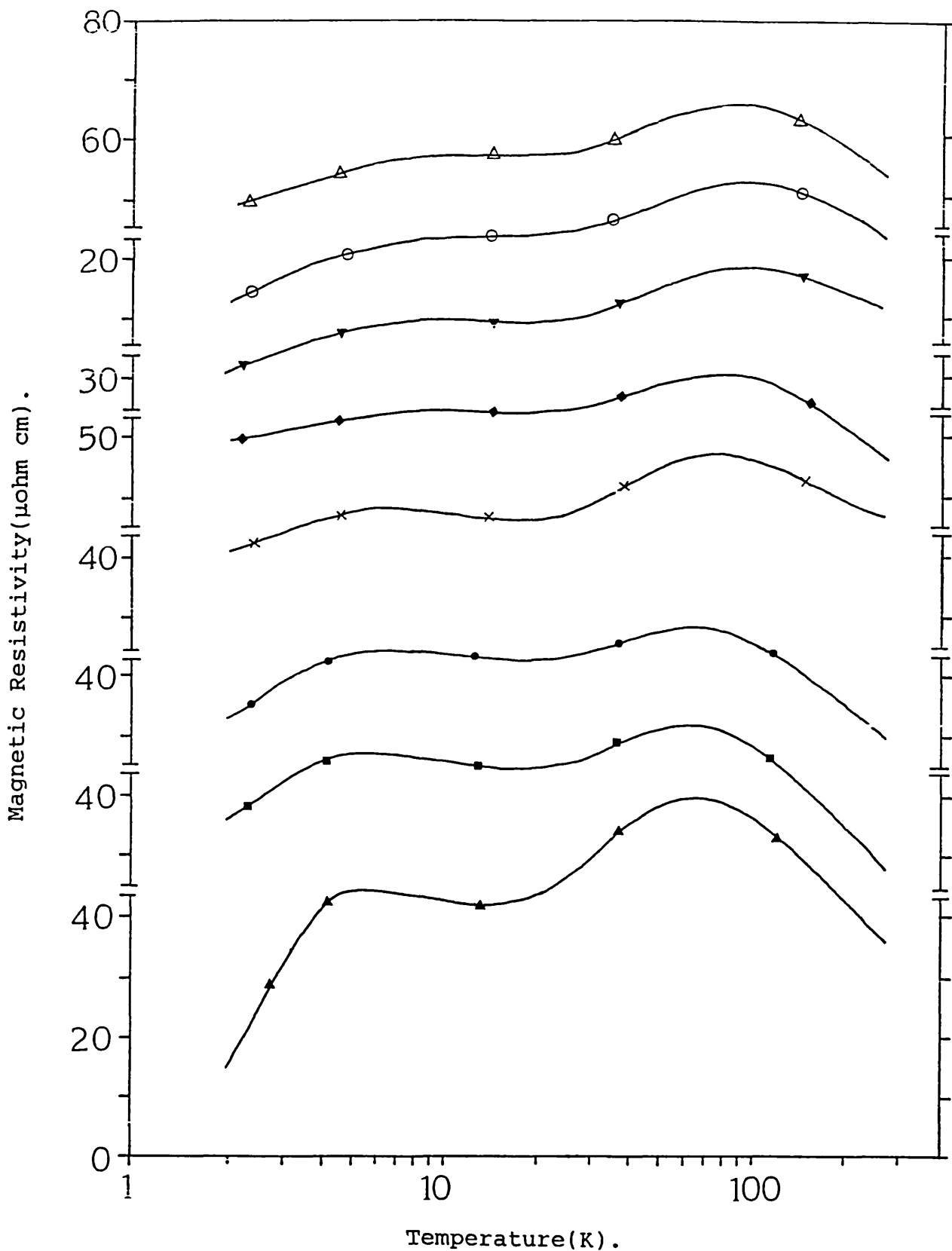


Figure 5:21. (a) Magnetic contribution to the electrical resistivity for $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$ in a semilogarithmic representation, where $x=0.00(\blacktriangle)$, $0.02(\blacksquare)$, $0.04(\bullet)$, $0.06(\times)$, $0.08(\blacklozenge)$, $0.10(\blacktriangledown)$, $0.15(\circ)$ and $0.20(\triangle)$.

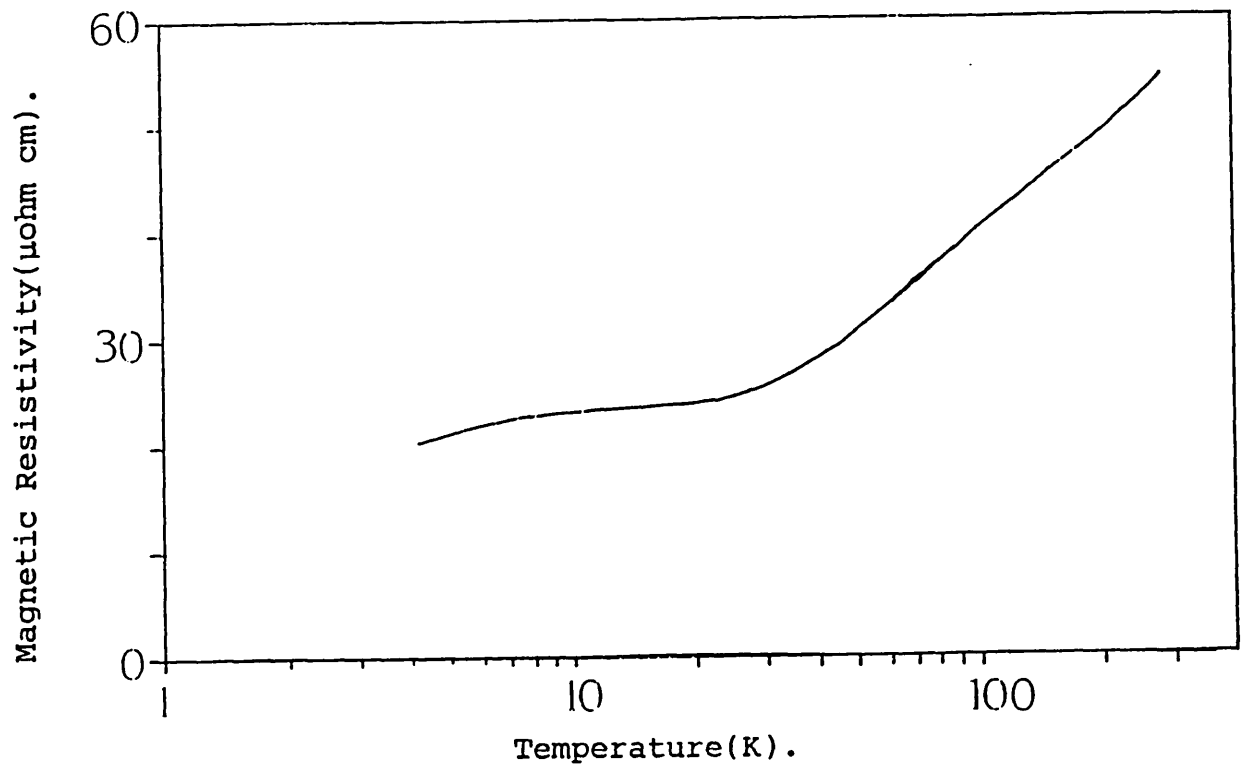


Figure 5:21. (b) The magnetic resistivity for $x=0.15$ with the non-magnetic contribution $\rho(\text{La}(\text{Al}_{0.85}\text{Cu}_{0.15}) - (\rho(\text{LaAl}_2) - \rho(\text{LuAl}_2)))$ as suggested by Wohlleben and Wittershagen[5:5].

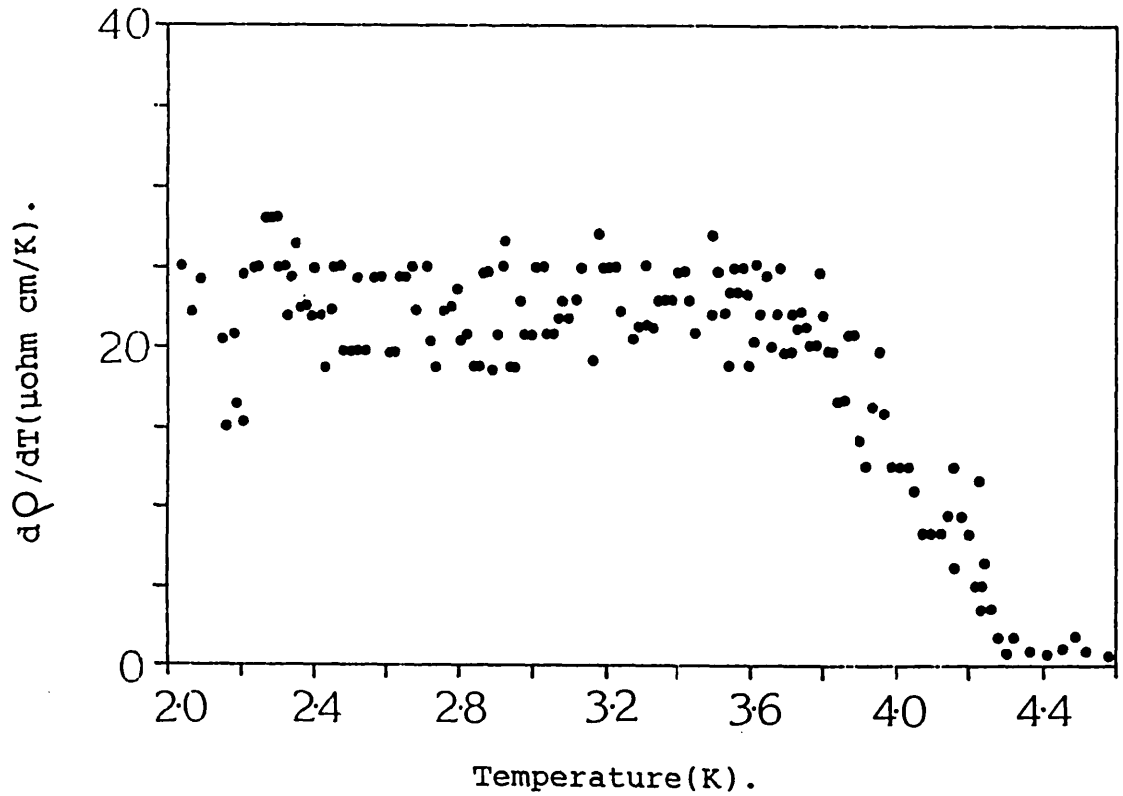


Figure 5:22. Temperature dependence of $d\rho/dT$ for CeAl_2 between 2K and 4.5K.

5:1). This is attributed to the expected rise in the value of the residual resistivity brought about by increases in scattering from impurities and defects in the crystal structure during alloying.

4. In the concentration range $0.00 \leq x \leq 0.20$, addition of Cu gradually removes the low temperature minimum in $\rho(T)$. This indicates the destruction of incoherent Kondo behaviour responsible for the minimum. These effects are discussed in section 5:5:3 with reference to variations in J and $N(E_F)$.

5. The character of the resistivity varies rapidly with concentration between the $x=0.20$ and 0.25 samples. The apparent re-emergence of Kondo behaviour may be connected with dual phase nature of the samples. To date no clear explanation of the behaviour is available.

Table 5:1(a). Important parameters taken from electrical resistivity data for $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$, $x \leq 0.30$.

% Cu	ρ_{273K} (μohmcm)	$\rho_{2.2K}$ (μohmcm)	RR	Mag_{coh} (μohmcm)	T_{max} (K)	T_{min} (K)
0	92.5	15.0	6.17	30.0	5.9	14.2
2	94.5	44.5	2.12	10.0	5.88	15.5
4	95.0	51.5	1.85	8.0	6.48	17.0
6	103.0	60.5	1.70	8.0	6.56	17.4
8	107.0	73.5	1.46	5.5	9.36	17.3
10	112.0	72.5	1.55	7.0	10.0	18.1
15	111.0	75.0	1.48	---	---	---
20	157.0	123.0	1.28	---	---	---
25	141.0	147.0	0.96	---	---	28.2
30	138.4	132.7	0.96	---	---	48.5

5:5:3. a.c. Susceptibility

The a.c susceptibility versus temperature for samples of $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$ with $x \leq 0.30$ are shown in figures 5:23 to 5:25. Pure CeAl_2 shows all the characteristics outlined in section 5:2:4. These include:

1. Curie-Weiss like behaviour at high temperature. A fit to $\chi = C/(T - \Theta_p)$ gives $\Theta_p = -34\text{K}$ and an effective moment of $2.6\mu_B$ taken from C .
2. A broad maximum in $\chi(T)$ centred around 4.3K .

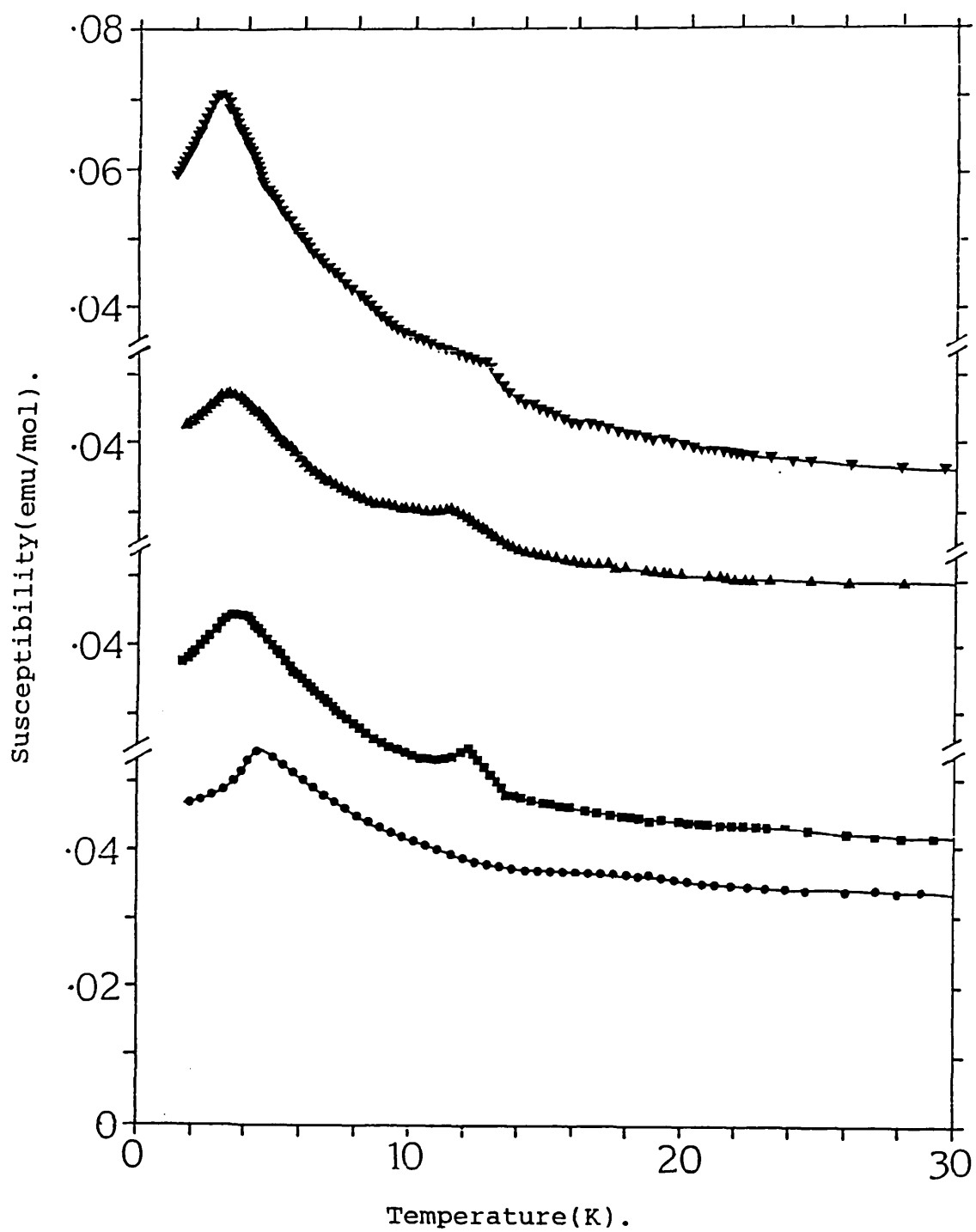


Figure 5:23. Magnetic susceptibility versus temperature of $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$ for $x=0.00(\bullet)$, $0.02(\blacksquare)$, $0.04(\blacktriangle)$ and $0.06(\blacktriangledown)$.

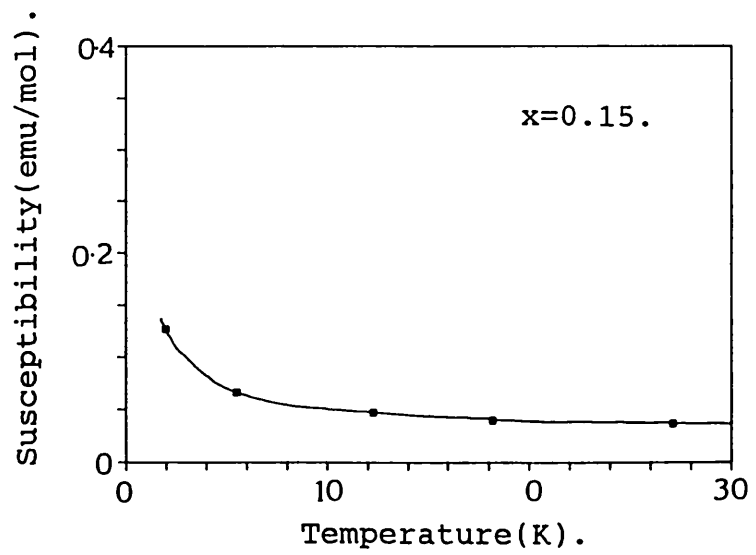
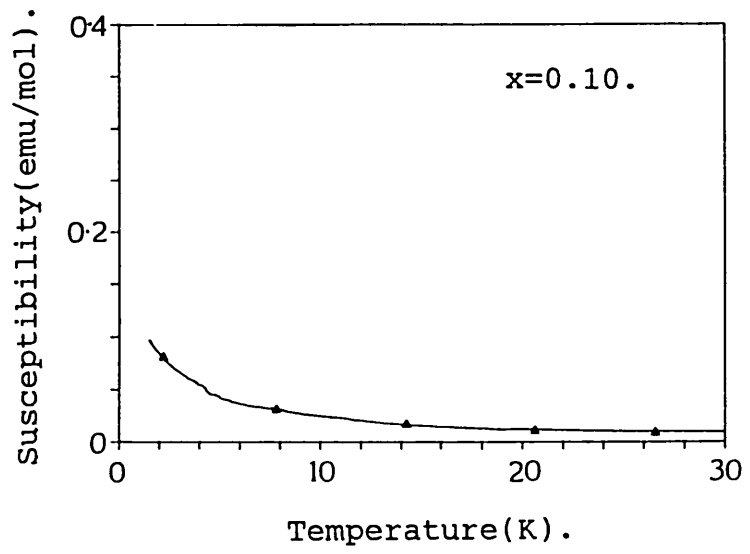
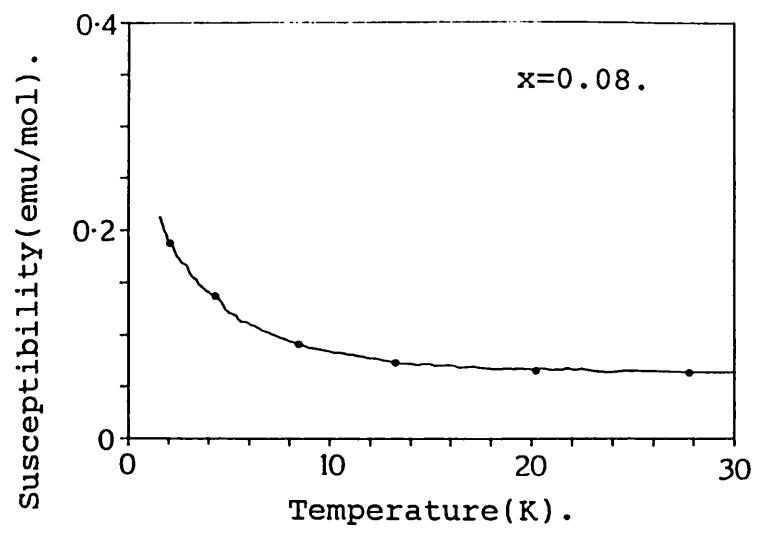


Figure 5:24. (a). Magnetic susceptibility versus temperature of $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$ for $x=0.08(\bullet)$, $0.10(\blacktriangle)$ and $0.15(\blacksquare)$.

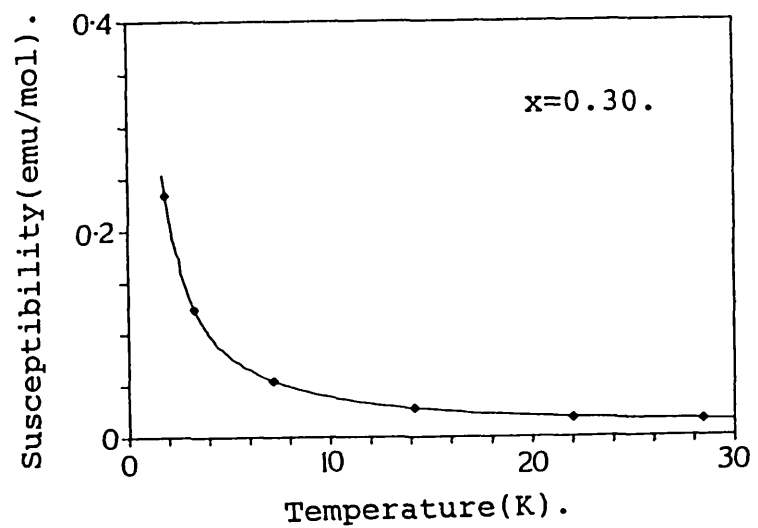
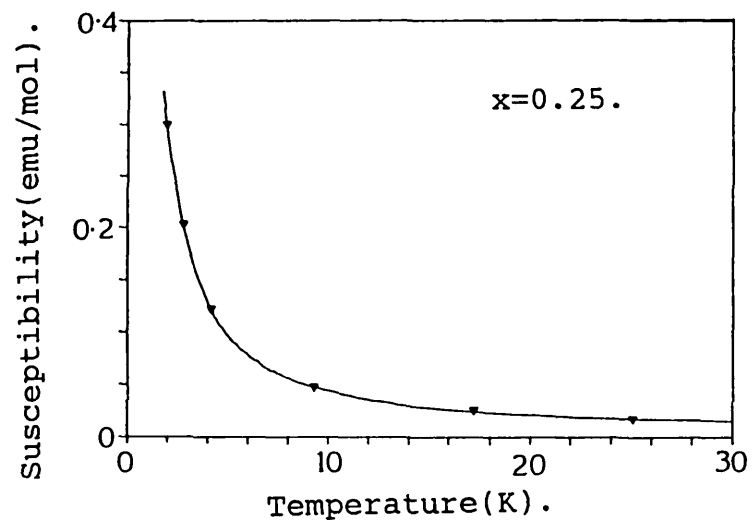
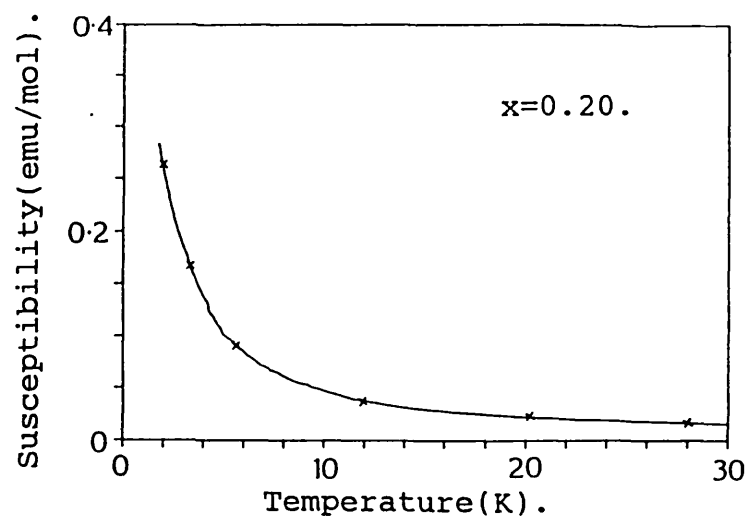


Figure 5:24 (b). Magnetic susceptibility versus temperature of $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$ for $x=0.20(\times)$, $0.25(\blacktriangledown)$ and $0.30(\blacklozenge)$.

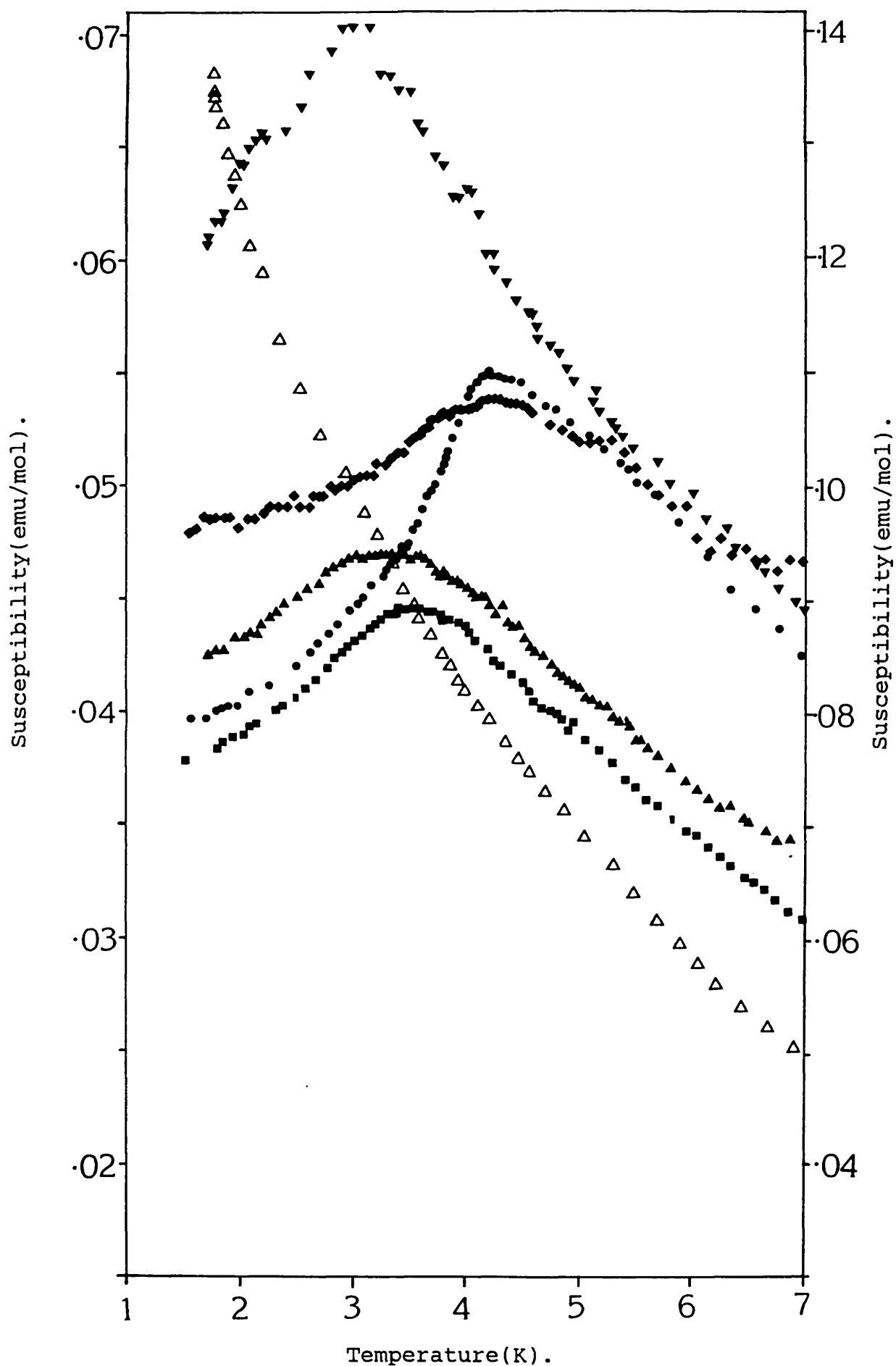


Figure 5:25. Low temperature magnetic susceptibility for $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$. Left hand scale (closed symbols), $x=0.00$ (●), 0.01 (◆), 0.02 (■), 0.04 (▲) and 0.06 (▼). Right hand scale (open symbols), $x=0.08$ (△).

3. A distinct change in slope of χ at 3.8K indicating the antiferromagnetic ordering transition temperature.

Substitution of Cu produces a number of effects.

As Cu is added the low temperature peak in susceptibility is slowly shifted to lower temperature (see table 5:2). For the sample containing 1% Cu an inflexion point indicating magnetic order is seen at 3.5K. For 2% and 4% Cu this peak is broadened but no inflexion point in $\chi(T)$ is observed.

Addition of 6% Cu shows a rapid narrowing of the maximum whilst for concentrations of 8% Cu or more the maximum in $\chi_{a.c.}$ is suppressed down below at least 1.5K.

The magnitude of $\chi_{a.c.}$ at 4.2K increases with Cu concentration so that by 25% Cu it has a value six times larger than pure $CeAl_2$. These findings are compared with those of Croft et al., who studied the effect of external pressure on the Neel temperature of $CeAl_2$. They found (see section 5:3) that a pressure of 8kbars was sufficient to reduce the Neel temperature by $0.4 \pm 0.02K$.

Addition of Cu also leads to the appearance of a second sharp peak in $\chi(T)$ centred at 12K. The temperature at which this peak appears is independent of Cu concentration. The magnitude in this peak first increases with Cu concentration reaching a maximum at 2% Cu, and is then reduced disappearing above 6% Cu. Possible explanations for the appearance of this peak are discussed in 5:5:5:4.

Table 5:2. Important parameters taken from magnetic susceptibility data for $Ce(Al_{1-x}Cu_x)_2$, $x \leq 0.30$.

%Cu	0	2	4	6	8	10	15	20	25	30
$T_{max}(K)$	4.3	3.54	3.32	3.0	--	--	--	--	--	--
$\chi_{a.c. mag}$ (emu/mol)	.055	.045	.047	.075	.137	.098	.215	.285	.335	.255

5:5:4. Magnetisation.

The variation of low field magnetisation with temperature for selected $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$ alloys are shown in figures 5:26 and 5:27. Pure CeAl_2 shows no field cooling effects.

Magnetisation data for sample with $0.01 \leq x \leq 0.06$ show field cooled effects with freezing at 12K. These field cooling effects initially increase in strength with Cu concentration, and are strongest for 2% Cu. For the 2% Cu sample the difference between field cooled and zero field cooled curves is greatest in the lowest field (320Oe.) employed during the experiment. At higher fields the difference between the field cooled and zero field cooled data is reduced until at the highest available field (1780Oe.) no difference between the two curves is discernible. For higher Cu concentrations the difference between the zero field and field cooled data is less pronounced. The disappearance of any feature in susceptibility data above 6% Cu is accompanied by a disappearance in freezing effects seen in magnetisation data.

5:5:5. Discussion.

5:5:5:1. Loss of Magnetic Order with Cu Substitution.

Susceptibility data indicates that addition of Cu leads to a reduction in T_N . By $x=0.06$ susceptibility data suggests that magnetic ordering takes the form of a spin glass. The rapid loss of coherence with Cu substitution (whose appearance is attributed to long range magnetic order) seems to support this analysis. Specific heat measurements by Gratz et al. [5:42] who have also studied the $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$ system have shown that for 2% Cu, a clear anomaly indicating a long range magnetic order is still observed. However for $0.02 < x \leq 0.20$ a broad maximum in C_p is found (see figure 5:28). It was

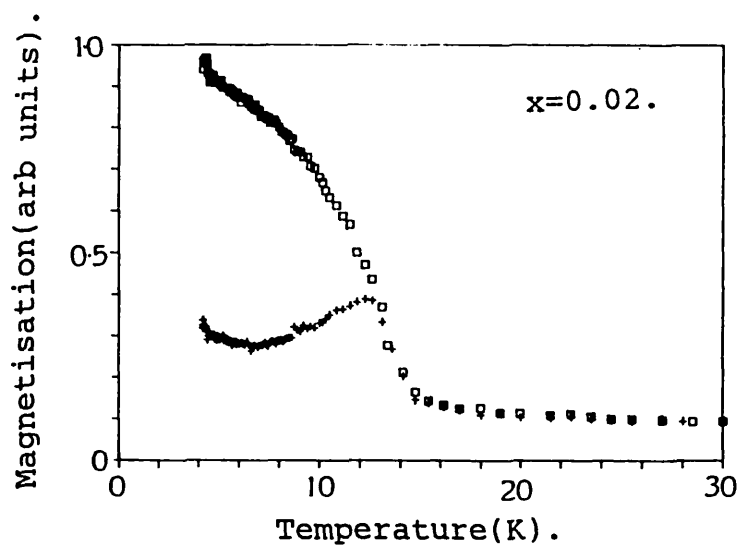
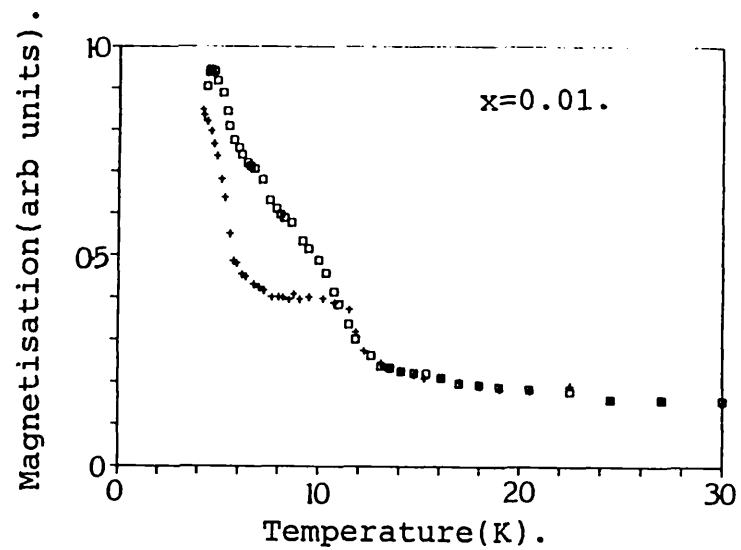
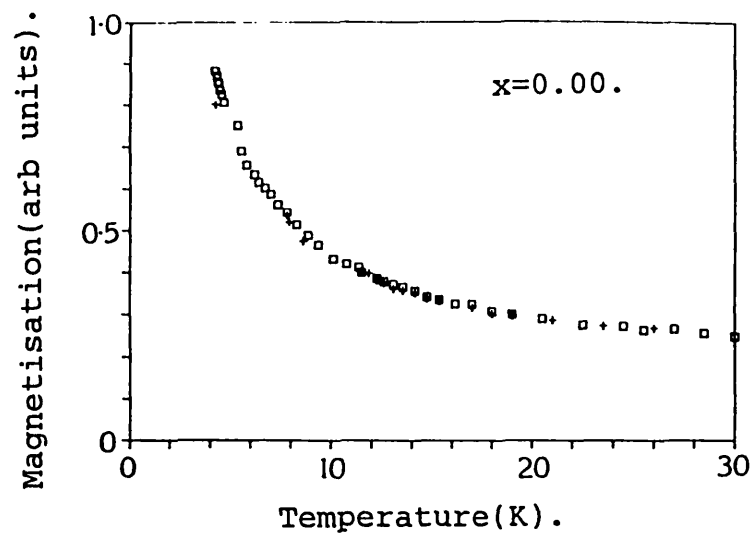


Figure 5:26 (a). Temperature dependence of the magnetisation of $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$ taken in a field of 160Oe. Open squares indicate the data taken after the sample has been cooled in the magnetic field. Crosses indicate the data taken after the sample has been cooled in zero field.

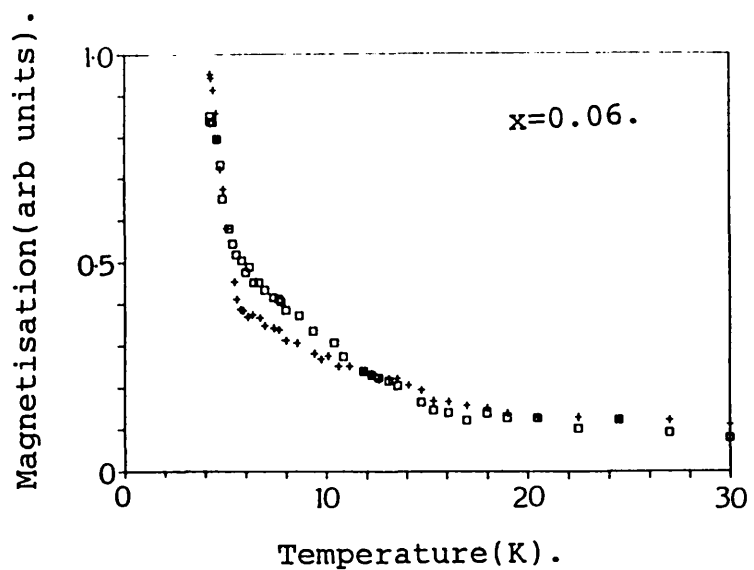
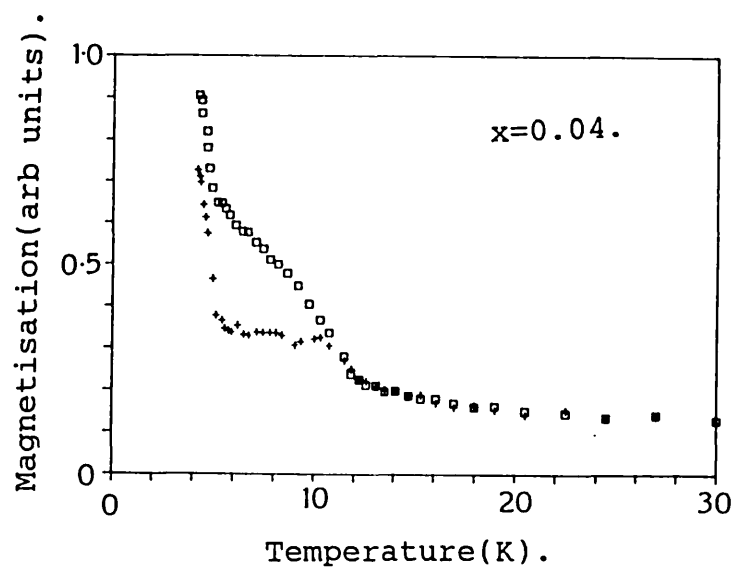
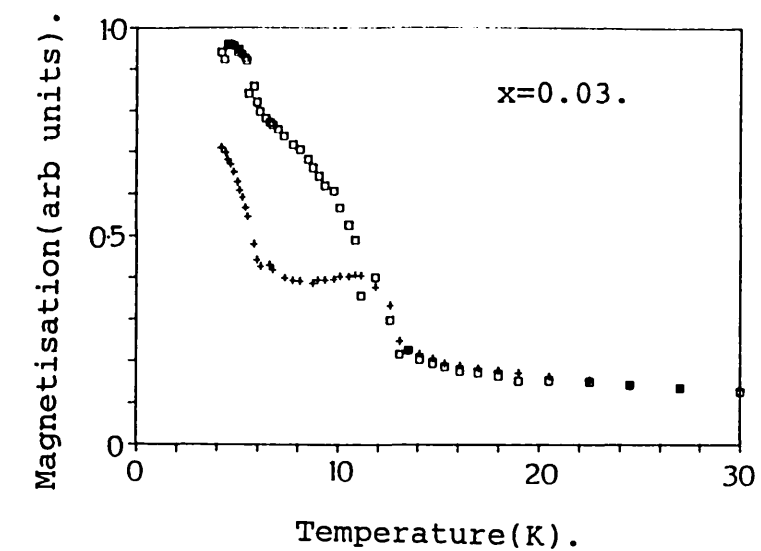


Figure 5:26 (b). Temperature dependence of the magnetisation of $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$ taken in a field of 1600e. Open squares indicate the data taken after the sample has been cooled in the magnetic field. Crosses indicate the data taken after the sample has been cooled in zero field.

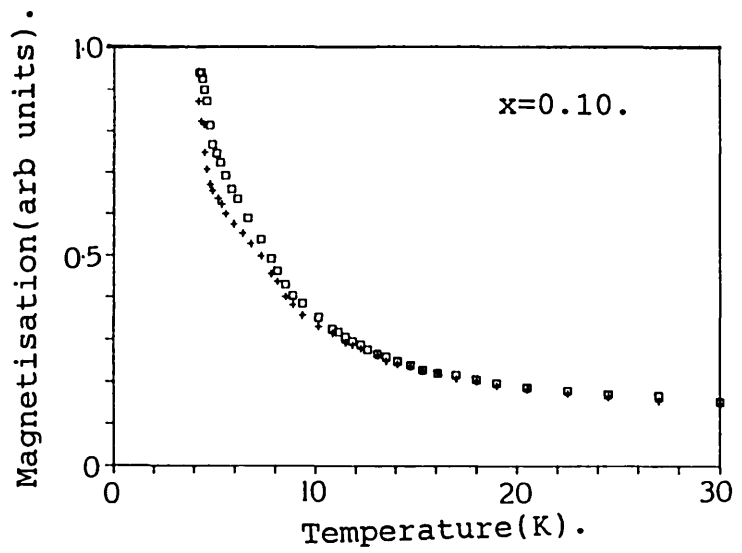
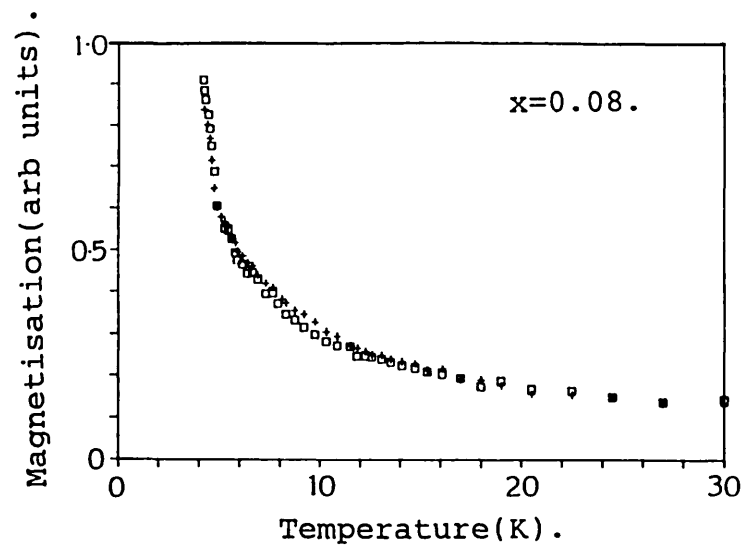


Figure 5:26 (c). Temperature dependence of the magnetisation of $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$ taken in a field of 160Oe. Open squares indicate the data taken after the sample has been cooled in the magnetic field. Crosses indicate the data taken after the sample has been cooled in zero field.

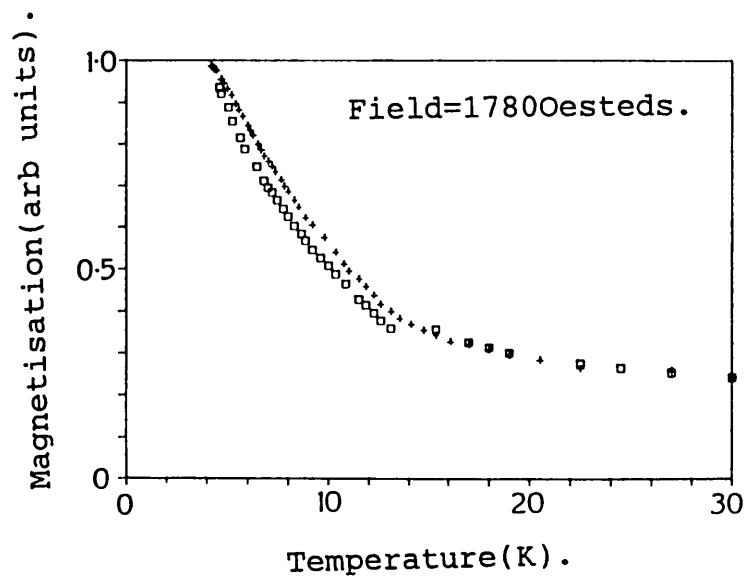
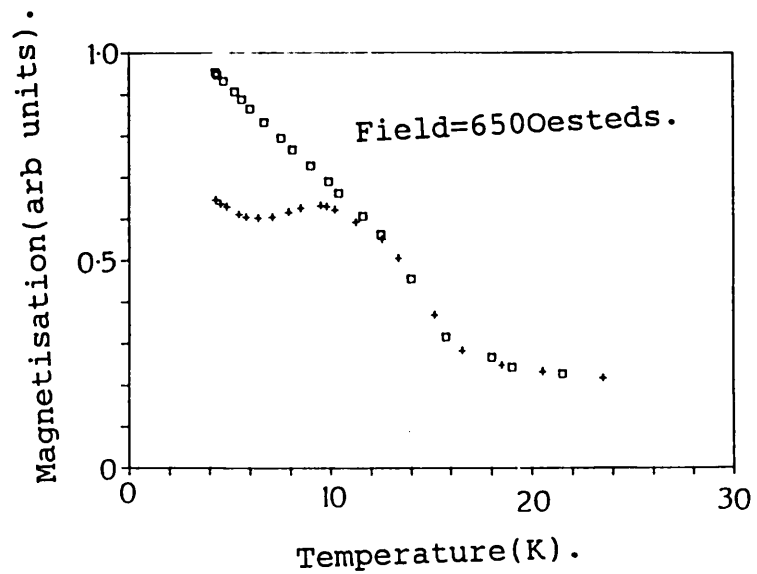
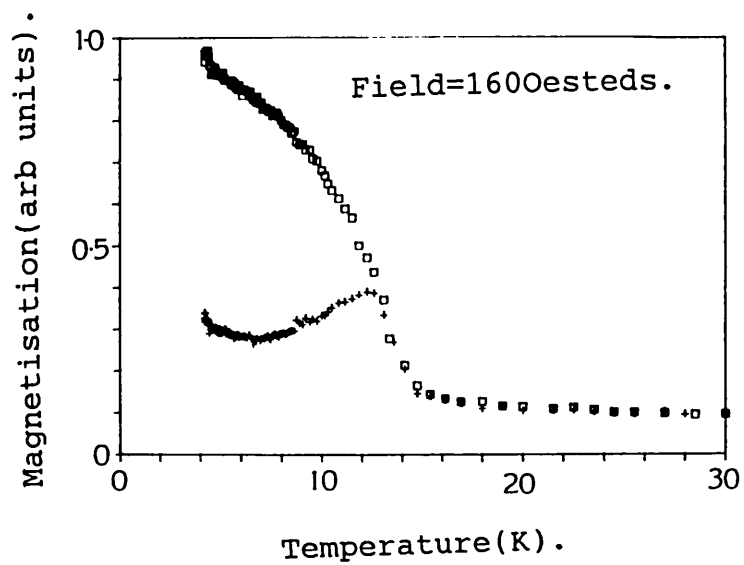


Figure 5:27. Temperature dependence of the magnetisation of the alloy $\text{Ce}(\text{Al}_{0.98}\text{Cu}_{0.02})_2$ taken in different external magnetic fields. Crosses indicate data taken after the sample has been cooled in the external field. Open squares indicate the data collected in the stated field after the sample has been cooled in zero field.

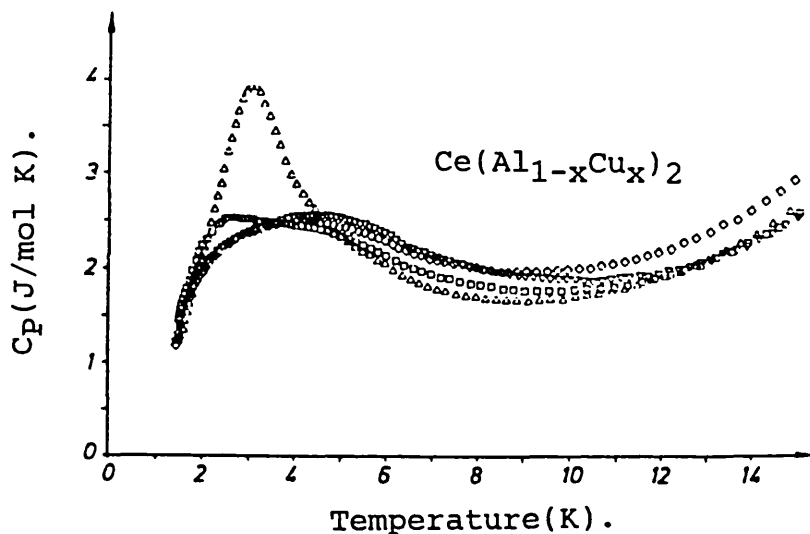


Figure 5:28. The specific heat as a function of temperature for $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$ for $x=0.02(\triangle)$, $0.05(\square)$, $0.10(\nabla)$ and $0.20(\diamond)$. Data are from Gratz et al. [5:42].

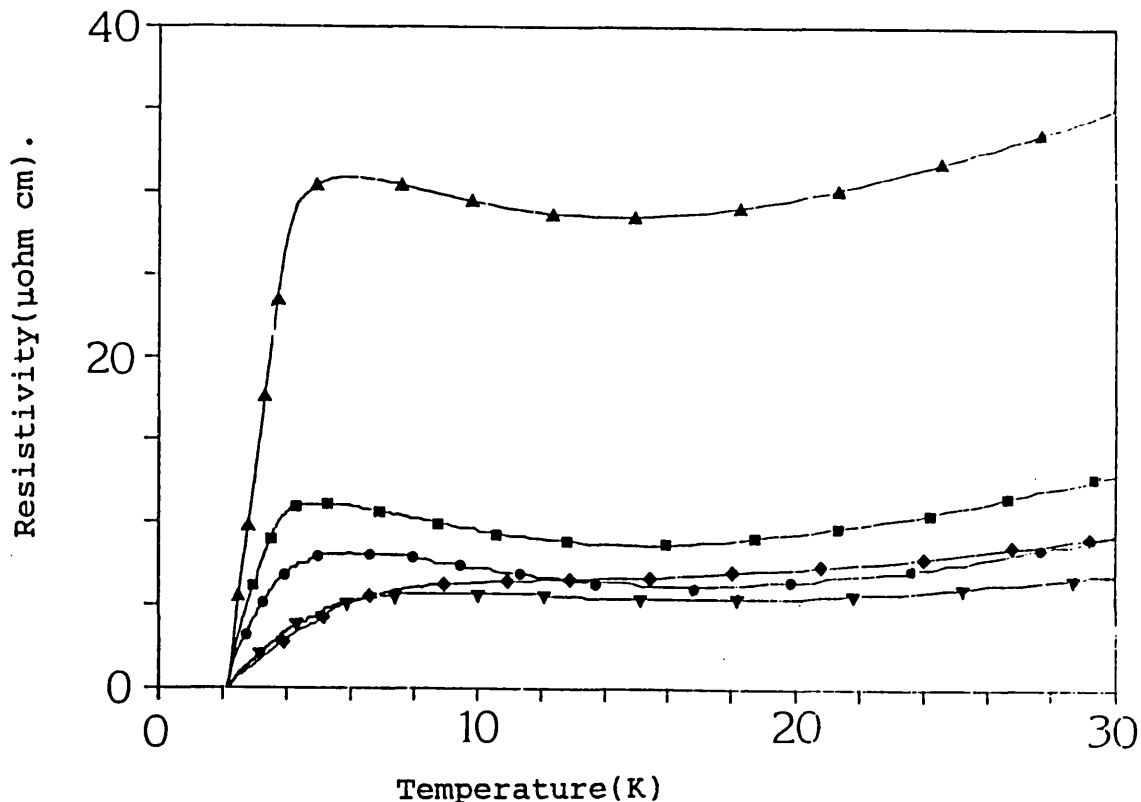


Figure 5:29. Temperature dependence of the electrical resistivities of selected $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$ alloys with their residual resistivities subtracted. $x=0.00(\triangle)$, $0.02(\square)$, $0.04(\bullet)$, $0.08(\nabla)$ and $0.15(\diamond)$.

suggested this bump may be due to spin glass freezing. However, a.c. susceptibility results do not support this analysis, since for $x > 0.06$ no spin glass like cusp is observed. Thus the source of the peak must, for the moment remain a matter for speculation.

5:5:5:2. Loss of Coherence.

The rapid fall in the resistivity observed in pure CeAl_2 below 4.5K associated first with the formation of a Kondo lattice, and then with the onset of magnetic order (see 5:2:3) is suppressed. To see this loss of coherence more clearly, figure 5:29 shows a plot of $(\rho_{\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2} - \rho_{\text{residual}}(\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2))$ for selected values of x . The difference between the value of resistivity at the low temperature maximum and the value of the resistivity at 2.2K (see table 5:1) changes from approximately 30 $\mu\text{ohm cm}$ for pure CeAl_2 to 7 $\mu\text{ohm cm}$ for CeAl_2 with 4at% Cu. This loss of coherence is also reflected in the variation of resistance ratio ($RR = \rho_{273K} / \rho_{2.2K}$) which drops from 5~6 for CeAl_2 to 1~2 for CeAl_2 with 4at% Cu. Since the coherence seen in CeAl_2 is attributed to onset of magnetic order, the loss of coherence supports the idea that addition of even small amounts of Cu are sufficient to either remove magnetic order, or at any rate reduces the ordering temperature below 1.8K. Although coherence is not observed in $\rho(T)$ for $x \geq 0.04$ the resistivities still show a low temperature fall, a behaviour quite unlike that expected of a simple metal. The mechanism which produces this fall in the resistivity at low temperature for up to $x = 0.20$ is unknown. It may be that:

1. Some kind of magnetic ordering takes place at some temperature below 1.5K. However, the suggestion that CeAl_2 with 6% Cu forms a spin glass makes long range order at higher Cu concentrations very unlikely

2. CeAl_2 with a few percent Cu may form a non-magnetic Kondo lattice although the absence of any minima in $\rho(T)$ suggesting the presence of incoherent Kondo scattering make this unlikely.

Chavez-Rivas and Urquijo Islas [5:43] have attributed the low temperature behaviour in $\rho(T)$ for $x \leq 0.10$ to the formation of a spin glass magnetically ordered state, which is assumed to evolve from the antiferromagnetic state of pure CeAl_2 on alloying. They analysed the data using the spin glass theory of Larsen [4:25]. However this analysis is:

1. Unable to account for the continued fall in $\rho(T)$ at low temperature.

2. questionable since no spin glass behaviour is observed in $\chi_{a.c.}$ data above 1.5K for $x \geq 0.06$.

5:5:4:3. Magnetic Resistivity.

The magnetic resistivities for Cu concentrations $0.00 \leq x \leq 0.20$ are shown in figure 5:21. The slopes of $\rho_{\text{mag}}(T)$ in the regions showing linear variation with $\ln T$ (i.e. $d\rho/d\ln T$) are shown in table 5:1 for various Cu concentrations. The ratio of the high and low temperature slopes for pure CeAl_2 is 7 and is in reasonable agreement with the value of $35/3$ predicted by the theory of Cornut and Coqblin [4:15] for a doublet ground state. The slopes of $\rho_{\text{mag}} \propto \ln T$ in both the linear regions are reduced as the Cu concentration is increased. The expression derived by Cornut and Coqblin for the total resistivity shows that the magnitude of the high temperature slope gives a measure of the product $J N(E_F)$. Thus a continuous decrease in slope indicates a decrease in J or $N(E_F)$ with increased Cu concentration. At low temperature the depth of the minima seen in the resistivity of $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$ is continuously reduced until at 15at% Cu no Kondo like rise in $\rho(T)$ is observed. Since both the high and

low temperature maxima are attributed to the same phenomena (see section 5:2:3) of exchange scattering, one would expect the disappearance of the low temperature maximum to be accompanied by a disappearance of the high temperature maximum as well. The remnant high temperature maximum may partially be due to the anomalous resistivity of $\text{La}(\text{Al}_{1-x}\text{Cu}_x)_2$ used as a non-magnetic reference compound. Subtracting $\rho(\text{La}(\text{Al}_{0.85}\text{Cu}_{0.15})_2) - (\rho(\text{LaAl}_2) - \rho(\text{LuAl}_2))$, a correction scheme suggested suggested by Wohllleben and Wittershagen [5:5] reveals the high temperature peak in the resistivity is completely removed by 15at% Cu (see figure 5:21(b)). At the same time, substitution of Cu moves both the low and high temperature maxima seen in ρ_{mag} to higher temperatures (see table 5:1). The low temperature peak moves from 5.8K for pure CeAl_2 to 9.58K for CeAl_2 with 10%Cu. The high temperature maximum moves from 65K for pure CeAl_2 to 93K for 10% Cu. Finally the fact that the difference between ρ_{mag} value at its maximum and the ρ_{mag} value at its minimum is small compared to the ρ_{mag} value at its maximum means that the direct scattering term $\mathcal{V}$ is larger than the J term. The ratio of $\rho_{\text{mag}}(\text{max-min})/(\text{max})$ decrease with Cu concentration, and indicates J decreases with respect to $\mathcal{V}$ as the Cu concentration increases.

Table 5:1(b). Parameters extracted from the magnetic resistivity of $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$.

%Cu	0	2	4	6	8	10	15	20
$T_{\text{max}}(\text{K})$	65.9	66.9	64.0	78.4	77.5	87.0	96.5	96.0
$-\frac{d\rho}{d\ln T}$ High T	21.0	18.8	17.4	10.4	15.4	7.73	---	---
$-\frac{d\rho}{d\ln T}$ Low T	2.98	4.28	2.39	2.96	0.86	1.10	---	---

It has been shown that substitution of Cu reduces the lattice parameter, which in turn generates a lattice pressure which is expected to produce effects which are similar to the application of an external pressure. Nicholas-Francillon et al. [5:36] studied the variation in $\rho(T)_{\text{mag}}$ of CeAl_2 with external pressure. They showed pressure is expected to:

1. move the high temperature maximum to lower temperature due to a decrease in $\Delta_{\text{C.F.}}$.
2. increase the slope of $d\rho/d\ln T$ due to an increase in the exchange constant J

The behaviour of CeAl_2 doped with Cu which produces chemical lattice pressure, reveals trends in the movement of the maxima in $\rho(T)$ and $d\rho/d\ln T$ which are completely the reverse of those expected from external pressure experiments. How can this be explained? We have seen in section 2:7:4. that J depends on the free electron density (N/V) where N is the number of conduction electrons and V a measure of the cell volume, which is inversely proportional to the applied pressure. Gratz et al. [5:42] who have also studied the effects of alloying in CeAl_2 with Cu, have suggested that the experimentally observed changes in the physical properties of the $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$ system may be linked to changes in J , driven by changes in N and V . So, examining the variation in parameter N/V , the free electron density, may be able partially explain the unexpected behaviour of the magnetic resistivity. It is suggested that a decrease in the number of free electrons in the conduction band due to the replacement of Al with Cu outweighs the reduction in the cell volume due to alloying leading to a decrease in (N/V). Looking at the electronic structure of $\text{Al}([\text{Ne}]3s^2p^1)$ and $\text{Cu}([\text{Ar}]3d^{10}4s^1)$, if we simply assume the outer electrons make up the free

electrons substituting Cu for Al reduces the number of free electrons from 3 to 1 for each Al atom replaced. Plotting N/V versus concentration of Cu (figure 5:30) it is clear that the number of free electrons decrease more rapidly than the volume is reduced, leading to a decrease in the free electron density and thus in J . This, along with a reduction in $N(E_F)$, the density of states at the Fermi surface would then explain the decrease in the slope of $d\rho/d\ln T$, and the reduction in ratio of difference in resistivity between the maximum and minimum with respect to height of maximum mentioned above. The reduction in parameters J and $N(E_F)$ also explain the reduced effectiveness of the Kondo compensation mechanism, which in turn results in a rapid rise in the magnitude of $\chi_{a.c.}$ at low temperature. However these ideas are not able to directly explain the increase in $\Delta_{C.F.}$ with Cu concentration which leads to upward shift in $\rho_{mag}(T)$ maximum.

5:5:4:4. Magnetic Freezing at 12K.

Finally in this section, the origin of the peak seen at 12K in susceptibility data and the difference in the F.C.-Z.F.C. data observed in $M(T)$ data is considered. The peak does not seem to be the result of spin glass ordering. The susceptibility taken after the sample had been cooled in a field of 4600e. shows that peak is not shifted in temperature as one would be expected from a spin glass (see figure 5:31). However, whilst field cooling the sample leaves the ordering temperature unchanged, $M(T)$ data in several different fields (see figure 5:27) indicates that the difference between F.C. and Z.F.C. data can be eliminated by the application of a field. The first thought is that this peak may be due to presence of a second phase. However, as stated in section

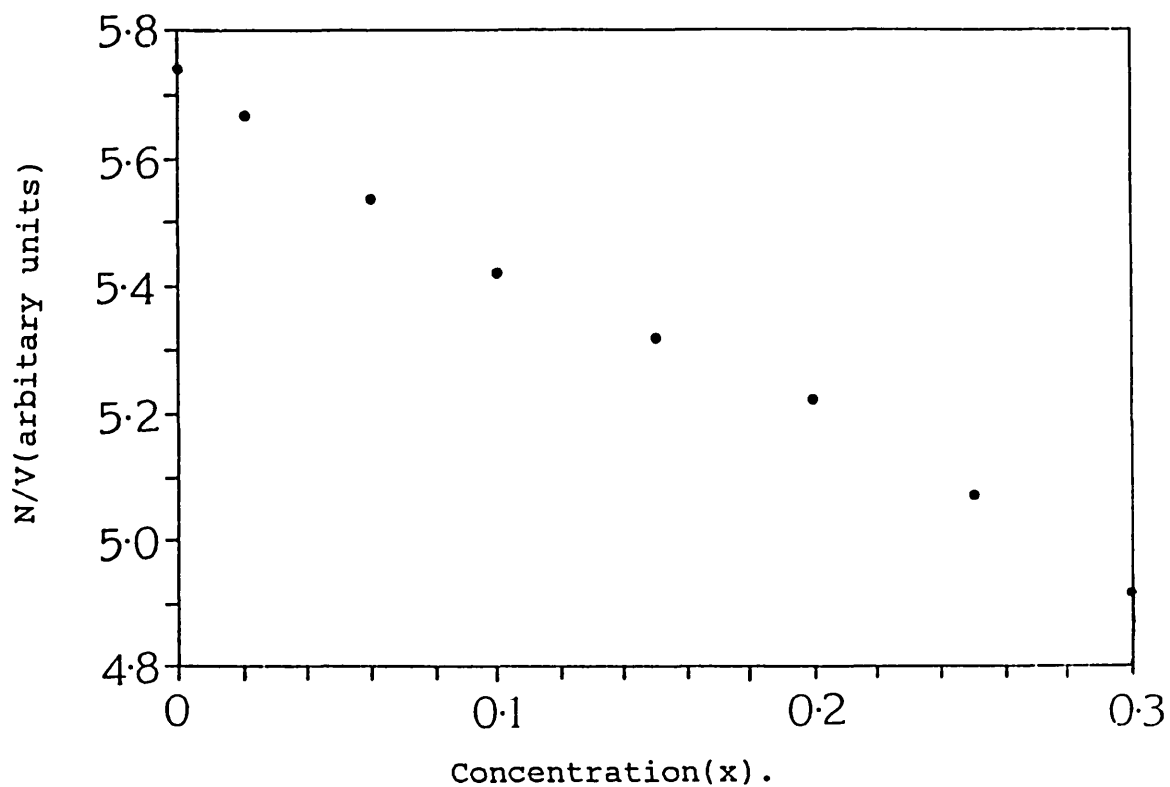


Figure 5:30. Value of the free electron density N/V versus Cu concentration for $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$ alloys

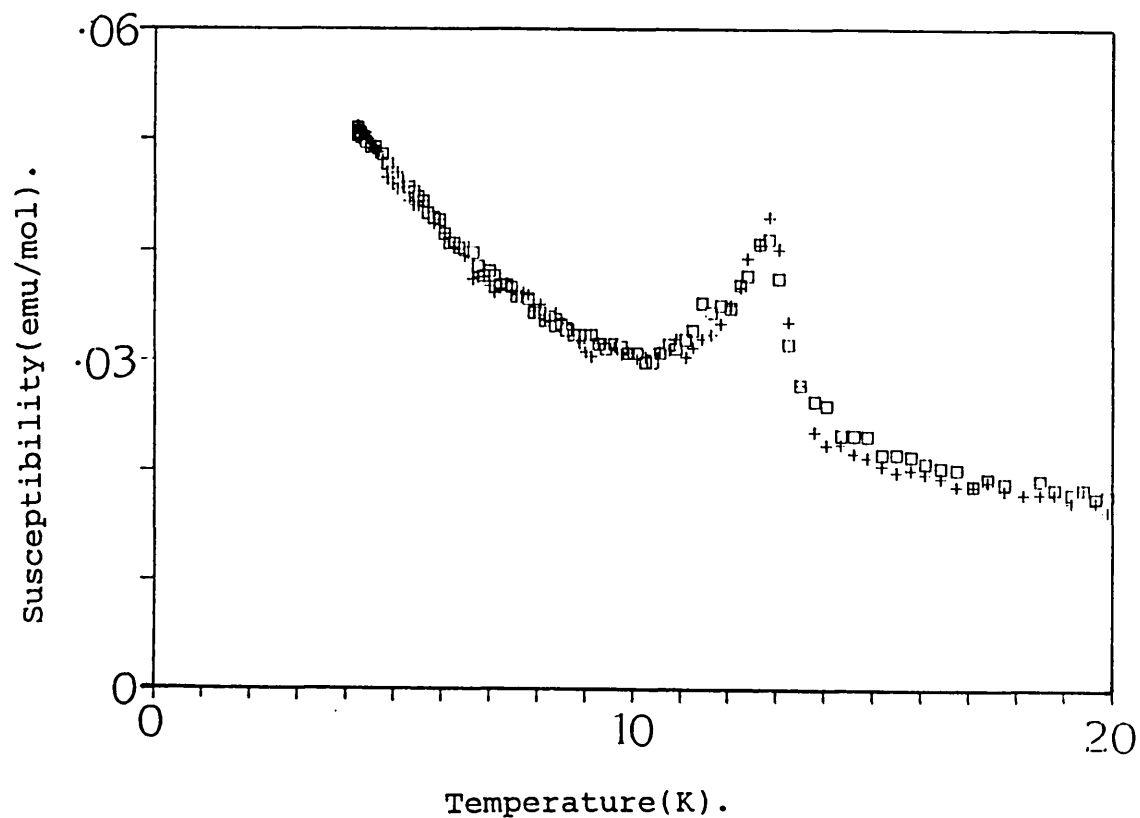


Figure 5:31. Temperature dependence on the magnetic susceptibility of $\text{Ce}(\text{Al}_{0.98}\text{Cu}_{0.02})_2$. Open squares indicate data taken on a sample cooled in a field of 460 Oe. Crosses show data taken on a sample cooled in zero field.

5:5:1 the metallographic specimens of all these samples in the relevant concentration range look single phase except for a small amount of oxides. Similarly there is no sign of a second phase beyond the presence of CeO in the X-ray data. If a small amount of second phase has remained undetected and is present it is difficult to say what it might bearing in mind the results discussed above. Examining the phase diagram of Ce-Al (figure 5:32) the possibilities are $\text{Ce}_3\text{Al}_{11}$, CeAl_3 or CeAl . The properties of these compounds are summarised in table 5:3.

Table 5:3. Magnetic and structural properties of Ce-Al alloys.

Compound	Structure	Prototype	$T_C(K)$	$T_N(K)$	$\Theta_P(K)$
$\text{Ce}_3\text{Al}_{11}$	ortho	$\text{La}_3\text{Al}_{11}$	2.5, 6	----	-24
CeAl_2	f.c.c.	MgCu_2	----	3.8	-34
CeAl	ortho.	CeAl	----	9-10	-19
CeAl_3	hexagonal	NiSn_3	----	----	-24

From this table it is clear that the peak cannot be due to CeAl_3 or $\text{Ce}_3\text{Al}_{11}$ leaving CeAl as the only possibility. Figure 5:33 shows the susceptibility of $\text{Ce}(\text{Al}_{0.98}\text{Cu}_{0.02})$. This has a peak indicating a transition into an antiferromagnetic state at 9K. This is below the peak seen in $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_2$.

Comparing the magnitude of susceptibility of CeAl with 2% Cu with that of peak in CeAl_2 with 2% Cu shows that at least 2.5% of the sample must be CeAl with 2% Cu. One should be able to detect this level of a second phase in a metallographic specimen. Several samples around this concentration range were remade. The unexpected features in $\chi(T)$ and $M(T)$ appeared to a greater or lesser extent in all samples. A 2% Cu sample prepared by E. Bauer of Vienna T.U.

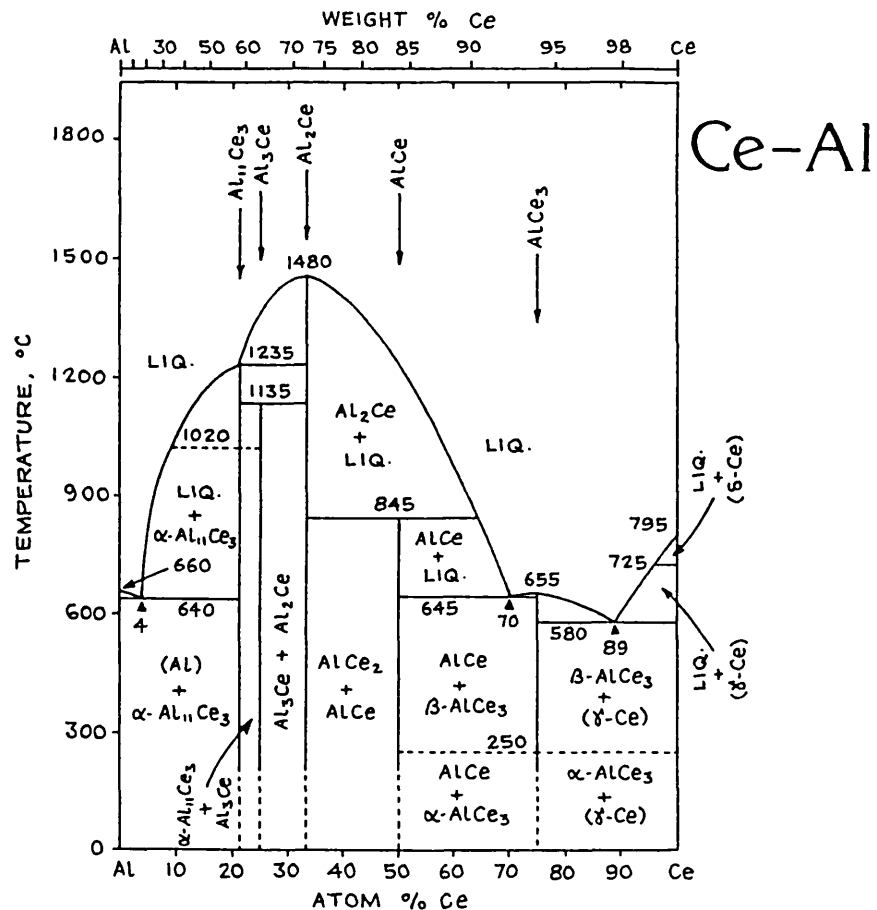


Figure 5:32. Ce-Al phase diagram from Gschneidner and Verkade [4:11].

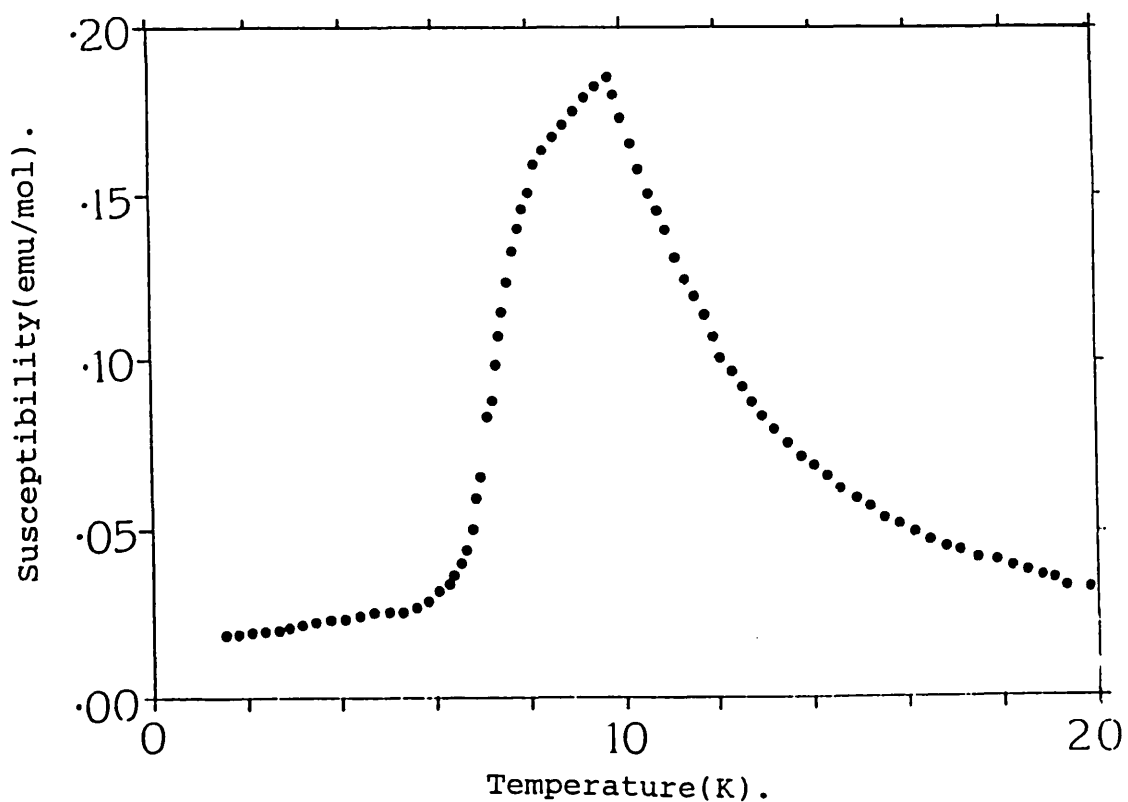


Figure 5:33. Magnetic susceptibility versus temperature for Ce(Al_{0.98}Cu_{0.02}).

using an induction furnace also showed the anomalous features. Two further questions arise when attempting to ascribe this behaviour to the presence of a second phase:

1. Why does the feature appear most strongly around the 2% Cu concentration range, but then weaken and disappear for higher dopant levels?

2. why do samples prepared containing Co showed no similar features in the 2% concentration range (see section 5:6)?

What other possibilities have to be considered. It is known that the low temperature Ce-Ce ordering is extremely complicated. Could the peak indicate a partial freezing of Ce moments. No evidence of such a transition is seen in C_p data of Gratz et al. [5:42] however their data only extends to 15K and any contribution to C_p may be masked by the increasing phonon contribution. It is difficult to understand what mechanism could produce such a dramatic jump in the strength of the interaction between Ce moments, or why the freezing should disappear at higher Cu concentrations. On balance, the most appealing explanation for the observed features is the presence of a small amount of second phase.

5:5:5. Summary.

To summarize, in this section we have seen:

1. the observation of a clear anomaly in $\rho(T)$ at T_N . This highlights the fact that the appearance of coherence in resistivity is due to a combination of the onset of coherent Kondo scattering and magnetic ordering.

2. replacement of Al with Cu leads to a rapid loss of both coherence and magnetic ordering. Alloying on the Al sites with Cu is far more destructive than alloying with for example La or Y, on the Ce sites.

3. the importance of the parameters J and $N(E_F)$ in determining the properties of $CeAl_2$ have been highlighted. Variation of these parameters with alloying has been brought about using both lattice pressure and changes in the number of conduction electrons. Changes in the free electron density are reflected in variations in the magnetic resistivity, and increases in the low temperature susceptibility.

4. unanswered questions arising from this work include the source of the bump in specific heat at low temperature, and the mechanism producing the low temperature fall in $\rho(T)$. It has been shown these features are not due to formation of a spin glass. The nature of magnetic freezing at 12K also remains unclear.

5:6. $\text{Ce}(\text{Al}_{1-x}\text{Co}_x)_2$ $x \leq 0.10$.

5:6:1. Introduction.

5:6:2. Sample Preparation and Characterization.

The samples were prepared by the method described in section 3:6. and were then annealed at 600°C for 1 week.

Metallographic specimens of the samples and a.c.

susceptibility data indicated the presence of at least 3 phases in samples containing 15% or more Co. A peak in the susceptibility data of the $\text{Ce}(\text{Al}_{0.85}\text{Co}_{0.15})_2$ sample at 9K suggests one of these phases is CeAl. Clearly CeAl_2 with Co will be present. The third phase is unknown. These samples were re-annealed for a further 7 days at 700°C however single phase samples could still not be obtained in alloys with $x \geq 0.15$. Thus we limit our discussion to samples containing 10%Co or less. All these samples seem single phase, with only a small amount of Ce oxides present. X-ray diffraction data indicates that all the samples retain the cubic C15 structure of the parent compound. All lines in the X-ray patterns are attributable to either CeAl_2 or CeO. The lattice parameters of $\text{Ce}(\text{Al}_{1-x}\text{Co}_x)_2$ with $\leq 10\%$ Co are shown in figure 5:34. Initially, Co substitution causes the lattice parameter to increase producing negative lattice pressure effects. Continued substitution then leads to a decrease in lattice parameter. Again, comparison of lattice parameter under external pressure allows an estimate of the chemical pressure generated by Co substitution.

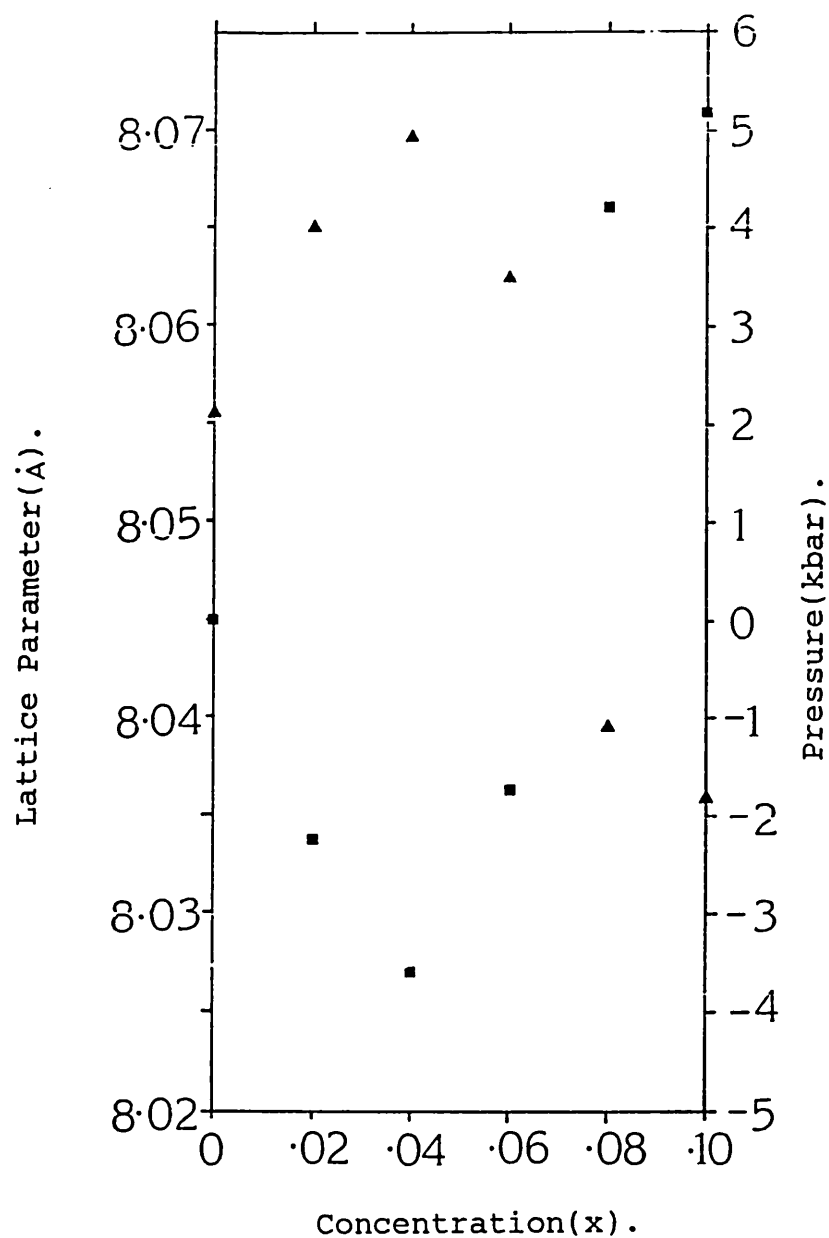


Figure 5:34. Concentration dependence of the lattice parameter of $\text{Ce}(\text{Al}_{1-x}\text{Co}_x)_2$ (▲) and the external pressure required to generate such changes (■).

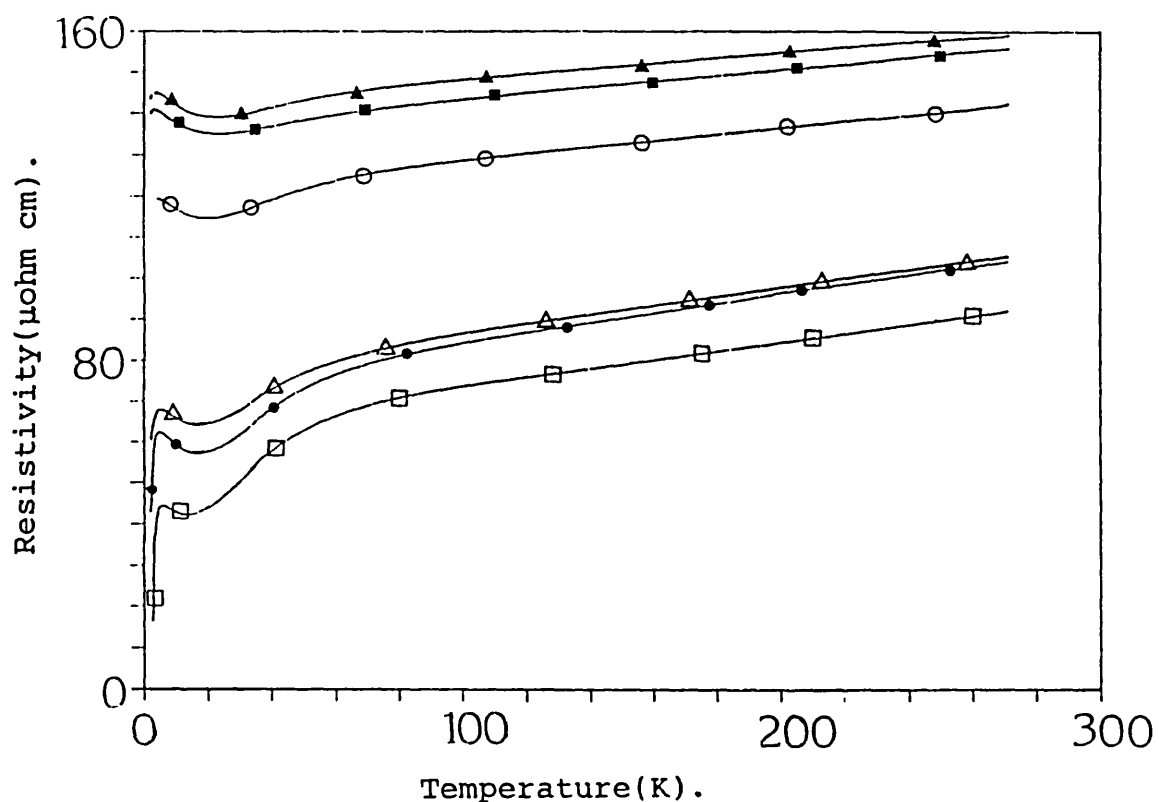


Figure 5:35. Temperature dependence of the electrical resistivity of $\text{Ce}(\text{Al}_{1-x}\text{Co}_x)_2$ for $x=0.00(\square)$, $0.02(\bullet)$ and $0.04(\Delta)$, $0.06(\circ)$, $0.08(\blacktriangle)$, $0.10(\blacksquare)$.

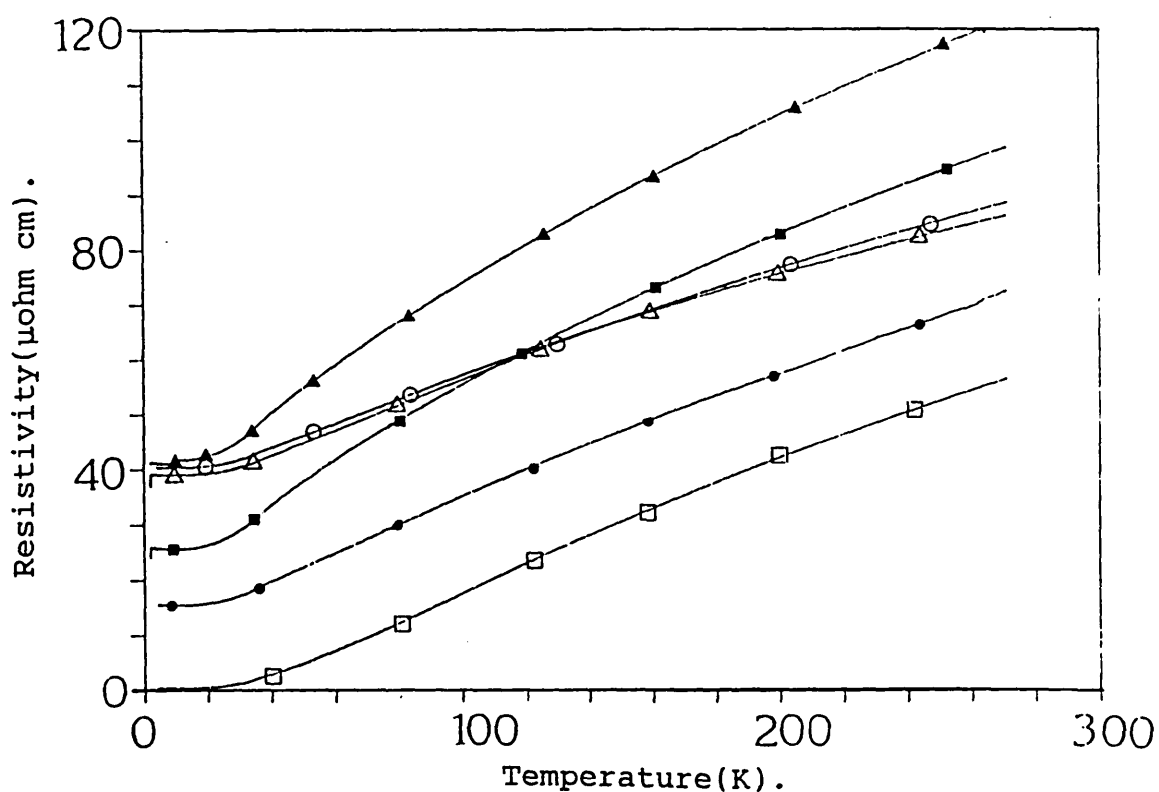


Figure 5:36. Temperature dependence of the electrical resistivity of $\text{La}(\text{Al}_{1-x}\text{Co}_x)_2$ for $x=0.00(\square)$, $0.02(\bullet)$, $0.04(\Delta)$, $0.06(\circ)$, $0.08(\blacktriangle)$, $0.10(\blacksquare)$.

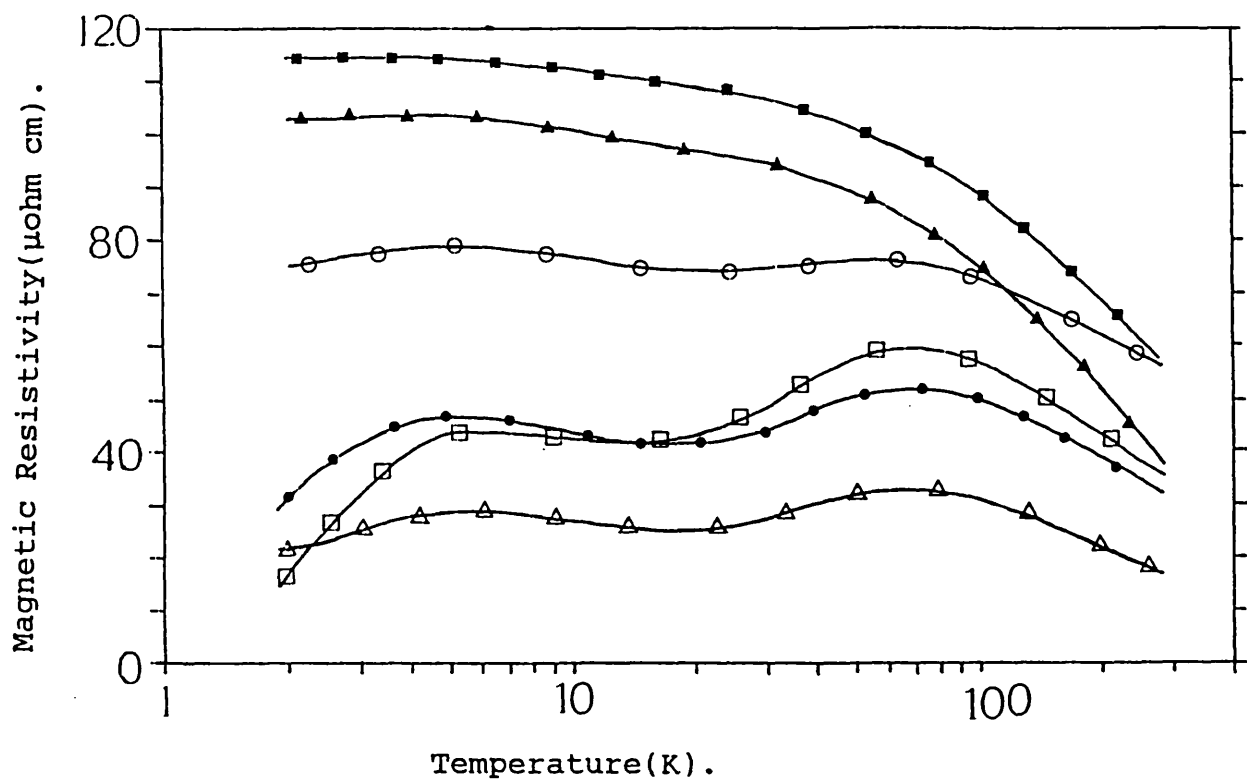


Figure 5:37. (a) Magnetic contribution to the electrical resistivity for $\text{Ce}(\text{Al}_{1-x}\text{Co}_x)_2$ in a semilogarithmic representation, where $x=0.00$ ($\square$), 0.02 ($\bullet$), 0.04 ($\triangle$), 0.06 ($\circ$), 0.08 ($\blacktriangle$), 0.10 ($\blacksquare$).

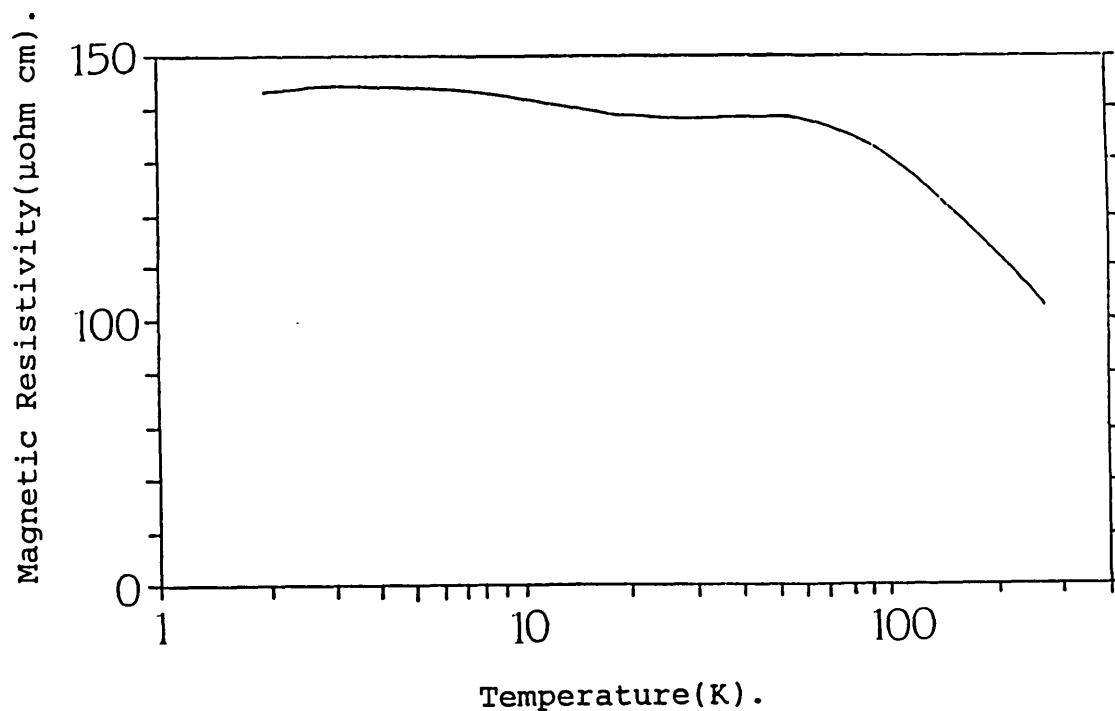


Figure 5:37. (b) The magnetic resistivity for $\text{Ce}(\text{Al}_{0.92}\text{Co}_{0.08})_2$ with the resistivity of non-magnetic LaAl_2 subtracted.

5:6:3. Resistivity.

Variations of the resistivity with temperature are shown in figure 5:35. for $\text{Ce}(\text{Al}_{1-x}\text{Co}_x)_2$ with $x \leq 0.10$. The resistivities of non-magnetic isostructural $\text{La}(\text{Al}_{1-x}\text{Co}_x)_2$ (shown in figure 5:36.) are subtracted to reveal the magnetic resistivities which are pictured in figure 5:37. The behaviour of LaAl_2 with Co is unusual with the residual resistivity passing through a maximum at 4% Co. The resistance ratio $\rho_{273\text{K}}/\rho_{2.2\text{K}}$ first decreases but then increases rapidly. The magnitude of $\rho_{273\text{K}}$ for LaAl_2 with 8% Co reaches an anomalously large value of $160\mu\text{ohm cm}$. However as for CeAl_2 with Cu, none of the effects seen in the magnetic resistivity (see below), can be attributed solely to the anomalous behaviour of the resistivity of the non-magnetic, isostructural alloy (which in this case is $\text{La}(\text{Al}_{1-x}\text{Co}_x)_2$). Several features appear in resistivity of $\text{Ce}(\text{Al}_{1-x}\text{Co}_x)_2$:

1. As with Cu substitutions, replacement of Al with Co rapidly suppresses the fall in the low temperature resistivity associated with the onset of coherence. This indicates that substitution of Co rapidly suppresses the magnetic order which in turn reduces the fall in resistivity associated with magnetic order. The low temperature minimum in $\rho(T)$ appears almost independent of Co concentration with only a slight rise in temperature with Co concentration.

2. The magnitude of the resistivity at high temperature increases with Co concentration and is attributed to the expected rise in the residual component of the resistivity

Several features are evident in the magnetic resistivity:

1. Addition of less than 6% Co leads to only small decrease in the slope of $d\rho/d\ln T$ at high temperature. Further substitutions then lead to a sharp increase in $d\rho/d\ln T$. This suggest the parameter $JN(E_F)$ on which the magnitude of $d\rho/d\ln T$ depends, first decreases slightly then increases with increasing Co concentration.

2. The temperature of the high temperature maximum in ρ_{mag} remains nearly constant for 2% and 4% Co. The temperature at which this maximum occurs is then rapidly reduced. At the same time the minimum seen at low temperature fills rapidly, so that by 8% Co, no peak in $\rho(T)$ at high temperature is observed. Subtraction of resistivity of pure LaAl_2 from

resistivity of CeAl_2 with 8% Co (figure 5:37) reveals a broad plateau at high temperature. This confirms the disappearance of a maximum at high temperature is not due to the use of $\text{La}(\text{Al}_{1-x}\text{Co}_x)_2$ as a non-magnetic reference compound. Since the position of the maximum is related to $\Delta_{\text{C.F.}}$, this behaviour suggests $\Delta_{\text{C.F.}}$ is at first slightly increased then decreases rapidly with Co concentration.

3. At the same time as the high temperature maximum is suppressed, the position of the low temperature maximum is moved to lower temperature.

Comparing the behaviour described above to that of pure CeAl_2 under external pressure suggests the substitution of Co produces first negative chemical pressure, decreasing J, followed by an increase in J as further substitution of Co reduces the lattice parameter below that of pure CeAl_2 leading to positive chemical pressure. This would indicate that if J depends on the parameter (N/V) as asserted by Bauer et al. and again in section 5:5. that the number of free electrons remains roughly constant with Co concentration and that the dominant term driving the change in J is due to variations in V.

Table 5:4. Important values taken from electrical resistivity data of $\text{Ce}(\text{Al}_{1-x}\text{Co}_x)_2$ alloys.

Conc.(x)	0.00	0.02	0.04	0.06	0.08	0.10
$\rho_{273\text{K}} \mu\text{ohmcm}$	92.5	105.0	106.0	142.0	159.5	156.0
$\rho_{2.2\text{K}} \mu\text{ohmcm}$	15.0	43.5	60.0	119.5	143.5	140.0
R R	6.17	2.4	1.77	1.19	1.1	1.1
$T_{\text{MAX}}(\text{K})$	5.9	5.2	5.72	4.5	4.0	3.7
$T_{\text{MIN}}(\text{K})$	14.2	14.7	16.8	19.7	20.1	20.6
$\delta\rho_{\text{COH}} \mu\text{ohmcm}$	30.0	21.0	8.0	2.0	1.0	----
$d\rho/d\ln T \text{ HiT}$	-21.0	-15.4	-13.8	-16.3	-38.7	-32.7
$d\rho/d\ln T \text{ LoT}$	-2.98	-6.1	-4.5	-4.85	----	----
Ratio Hi/Lo	7.07	2.5	3.07	3.36	----	----
$\Delta_{\text{C.F.}}(\text{K})$	65.9	66.0	65.0	51.6	----	----

5:6:4. a.c. Susceptibility.

Figures 5:38 and 5:39 show the susceptibilities versus temperature for $\text{Ce}(\text{Al}_{1-x}\text{Co}_x)_2$ for $x \leq 0.10$. Co substitution causes:

1. a steady suppression of $\chi_{a.c.}$ maximum to below 1.5K. In line with resistivity data this indicates a suppression in magnetic ordering temperature T_N .
2. a reduction in the absolute value of $\chi_{a.c.}$ at 4.2K.
3. the temperature dependence of the inverse of the magnetic susceptibility are shown in figure 5:40 for low temperature. Fits to susceptibility assuming a Curie-Weiss form $\chi(T) = C/(T - \theta)$ were made to both high and low temperature data. Fits to high temperature data yield values for Ce moments close to those expected for Ce^{3+} ions. Fits to low temperature data indicate a reduction in the Ce moment (see table 5:5). A slight decrease in the parameter θ_p calculated from a low temperature fit are also observed.

All this data points to an increase in T_K which is in turn due to an increase in J brought about by changes in lattice parameter. The view that the changes in magnetic resistivity can be interpreted as due to variation J brought about by changes in the lattice parameter are supported by susceptibility data.

Table 5:5. Parameters extracted from magnetic susceptibility data of $\text{Ce}(\text{Al}_{1-x}\text{Co}_x)_2$ alloys.

%Co	0	2	4	6	8	10
$T_{\text{max}}(\text{K})$	4.30	4.2	3.75	2.97	----	----
$\chi_{a.c. \text{ mag}}$ (emu/mol)	.055	.0495	.0595	.043	.046	.046
μ_B lowT	1.94	2.07	2.02	1.59	1.65	1.70
$-\theta_p(\text{K})$	3.84	7.15	5.9	4.04	5.08	3.63
μ_B high T	2.6	2.7	2.65	2.3	2.25	2.3
$-\theta_p(\text{K})$	34.0	31.25	30.5	17.1	21.8	21.5

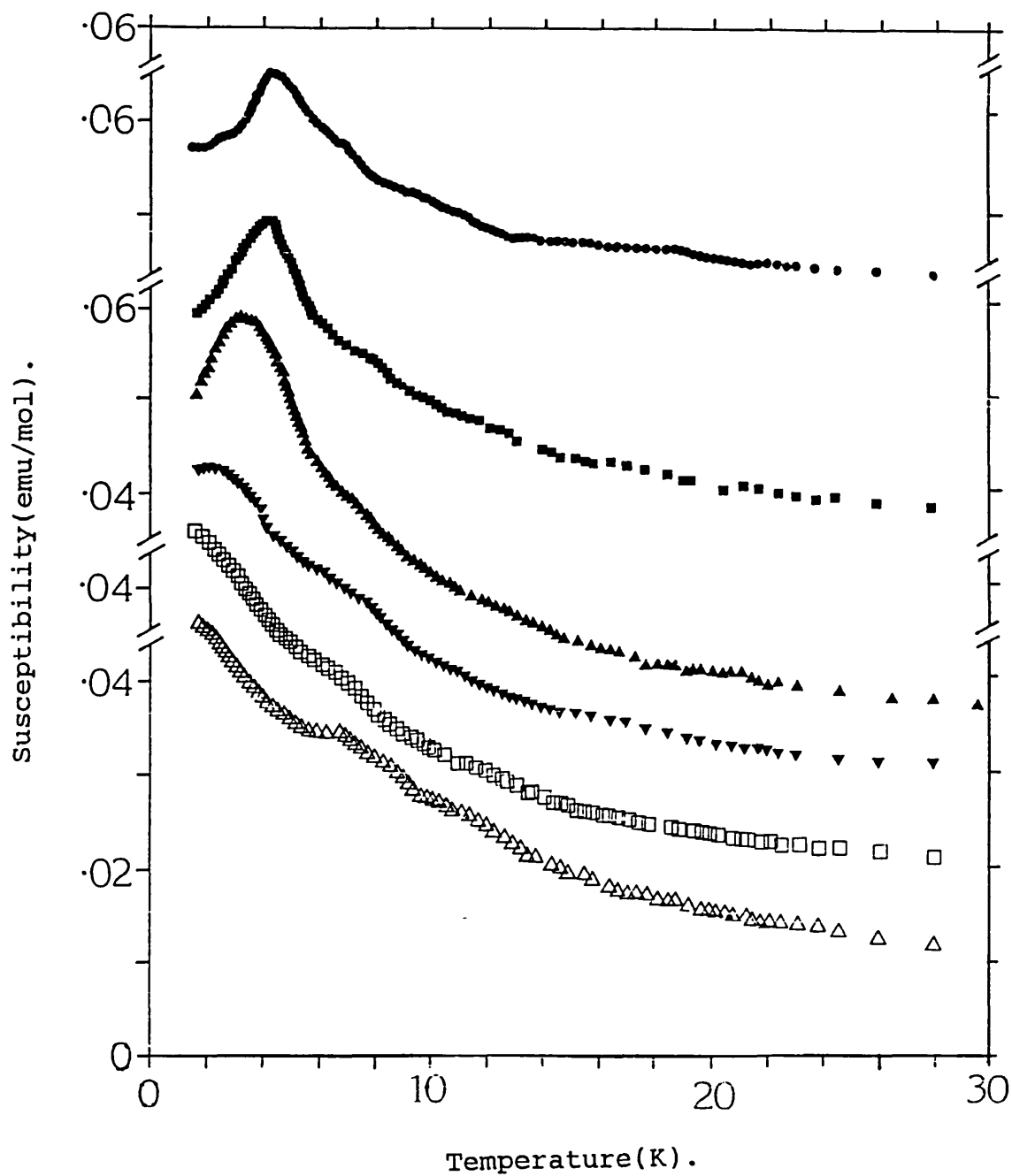


Figure 5:38. Magnetic susceptibility versus temperature of $\text{Ce}(\text{Al}_{1-x}\text{Co}_x)_2$ for $x=0.00(\bullet)$, $0.02(\blacksquare)$, $0.04(\blacktriangle)$, $0.06(\blacktriangledown)$, $0.08(\square)$ and $0.10(\triangle)$.

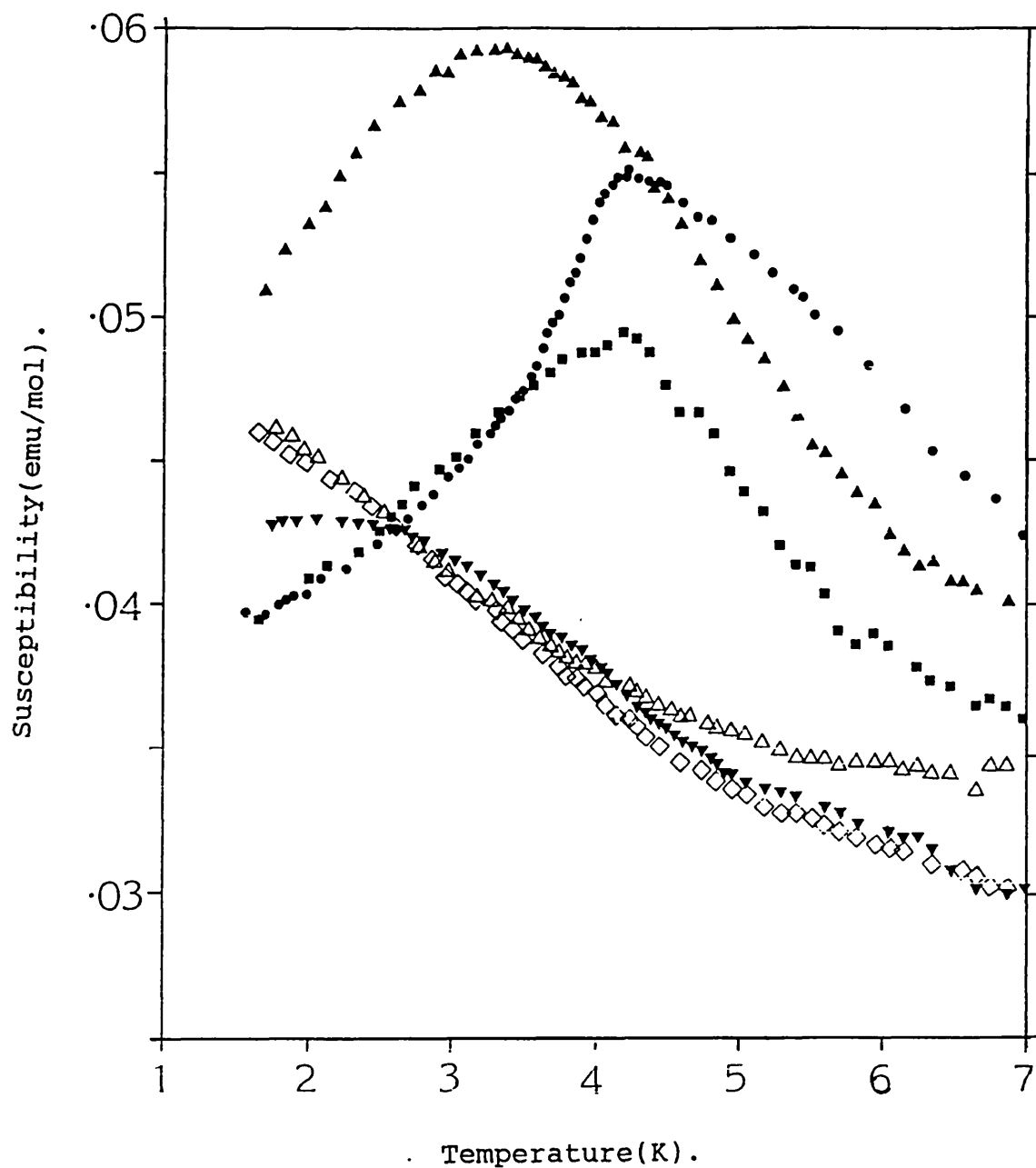


Figure 5:39. Low temperature magnetic susceptibility for $\text{Ce}(\text{Al}_{1-x}\text{Co}_x)_2$ for $x=0.00(\bullet)$, $0.02(\blacksquare)$, $0.04(\blacktriangle)$, $0.06(\blacktriangledown)$, $0.08(\diamond)$ and $0.10(\triangle)$.

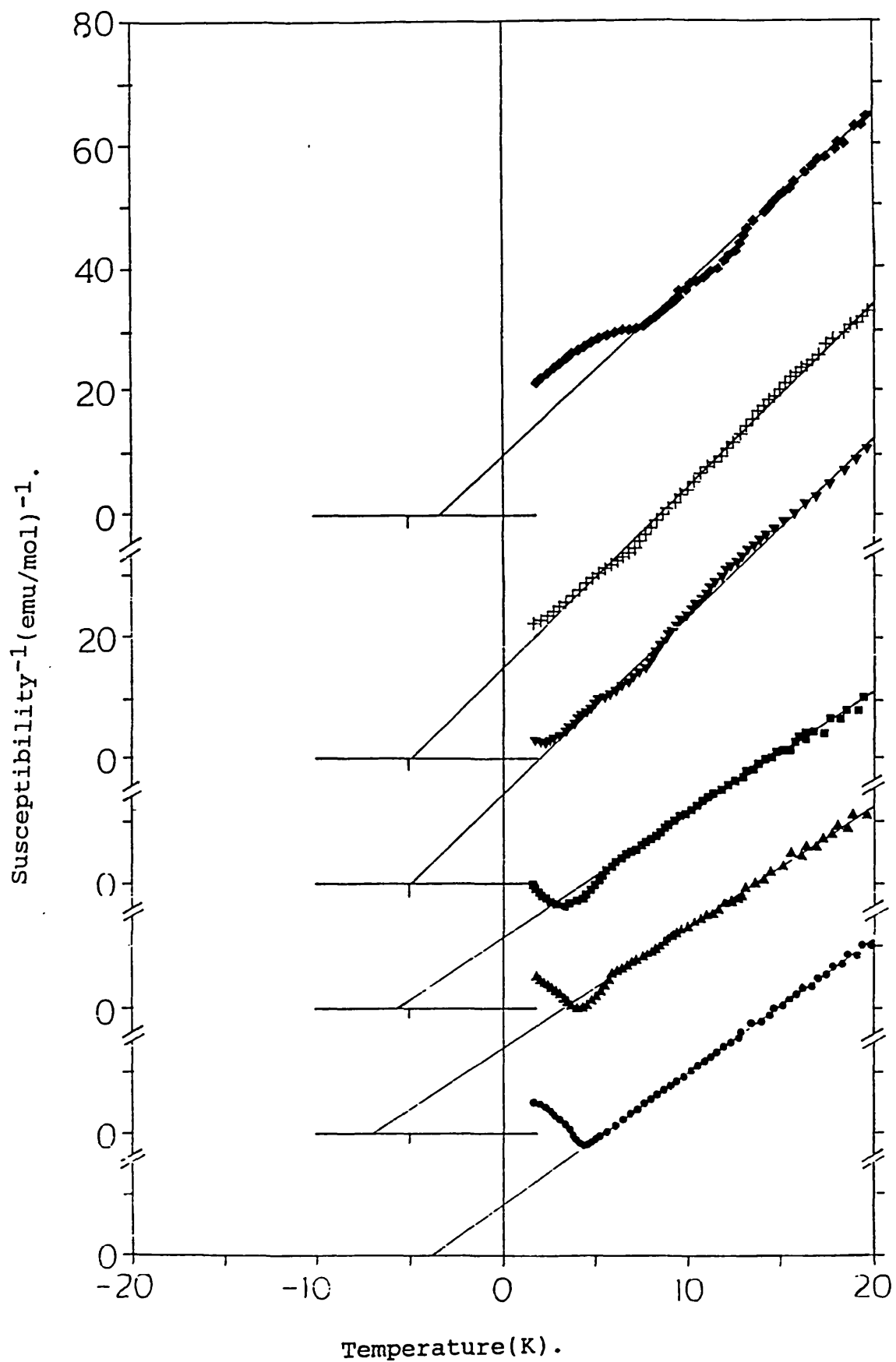


Figure 5:40. Inverse magnetic susceptibility at low temperature of $\text{Ce}(\text{Al}_{1-x}\text{Co}_x)_2$ for $x=0.00(\bullet)$, $0.02(\blacktriangle)$, $0.04(\blacksquare)$, $0.06(\blacktriangledown)$, $0.08(+)$ and $0.10(\blacklozenge)$.

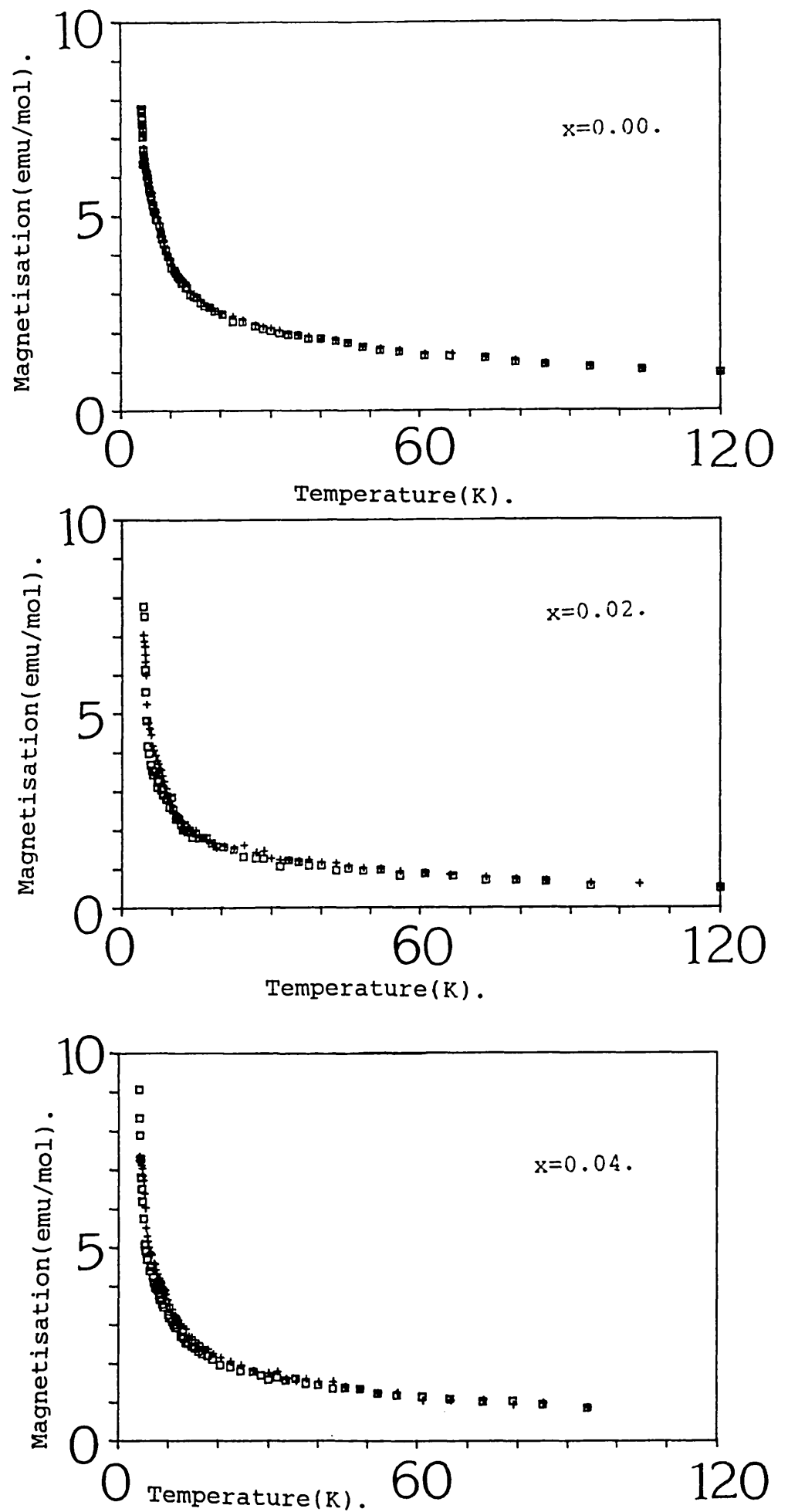


Figure 5:41.(a) Magnetisation versus temperature for selected $\text{Ce}(\text{Al}_{1-x}\text{Co}_x)_2$ alloys. Crosses indicate data taken after the sample has been cooled in zero field. Open squares indicate data collected after the sample has been cooled in magnetic field of 1600e.

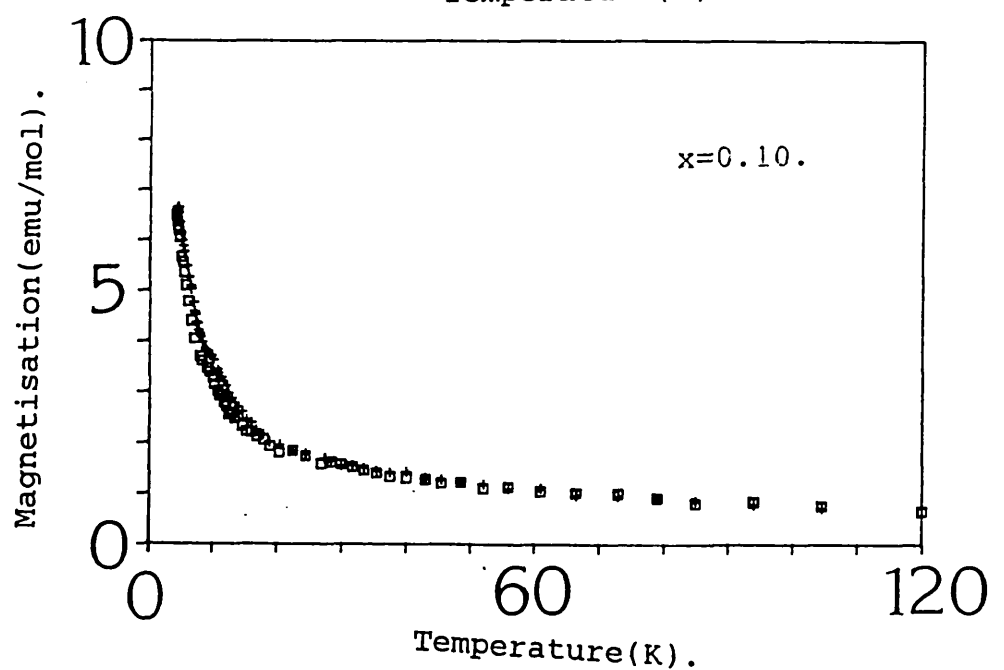
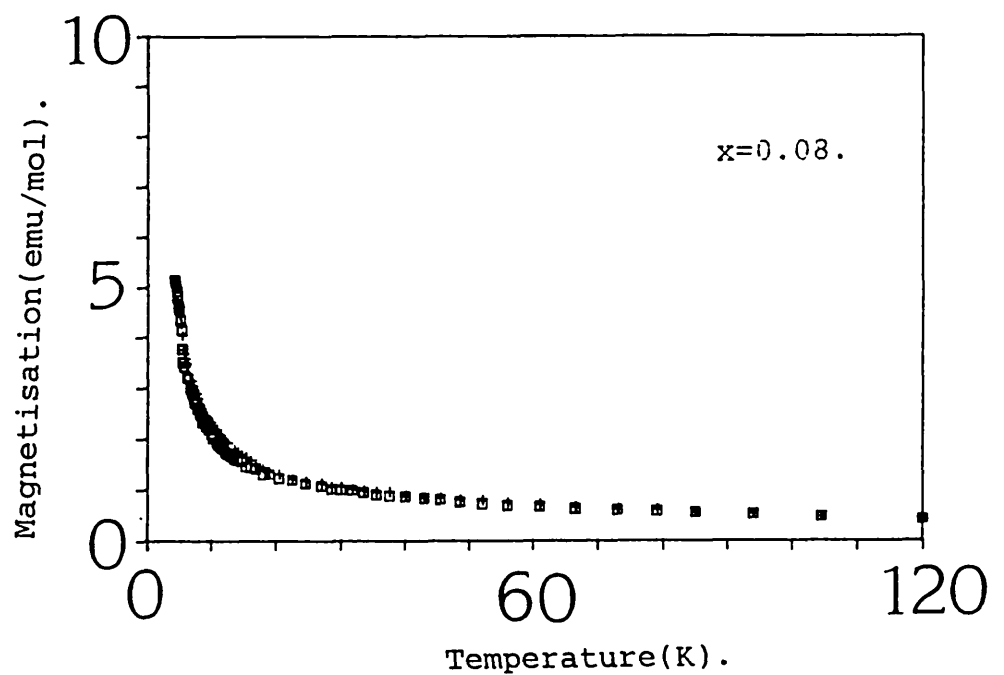
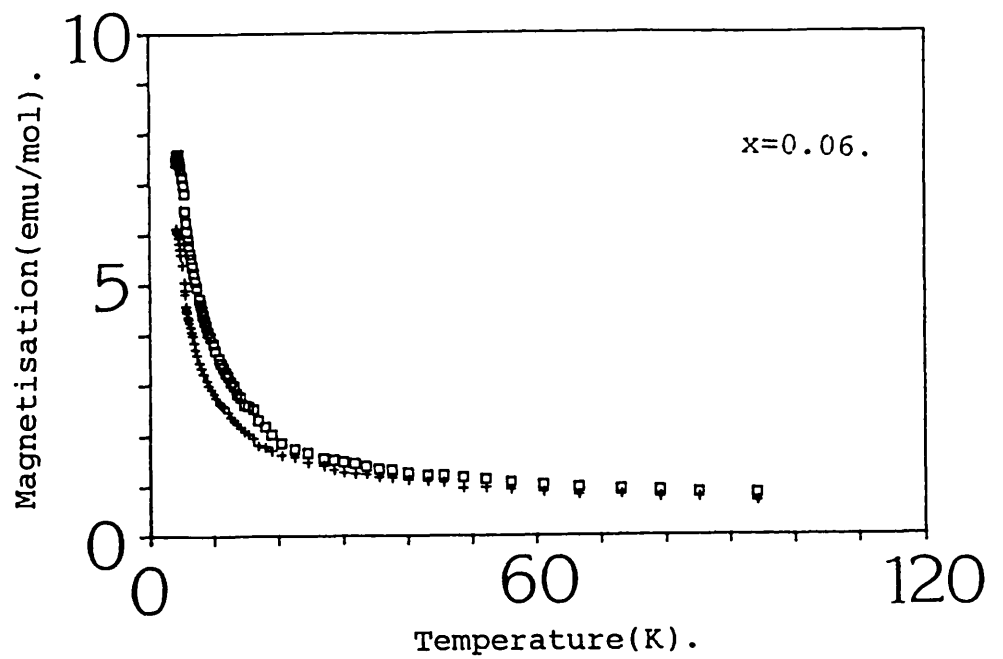


Figure 5:41.(b) Magnetisation versus temperature for selected $\text{Ce}(\text{Al}_{1-x}\text{Co}_x)_2$ alloys. Crosses indicate data taken after the sample has been cooled in zero field. Open squares indicate data collected after the sample has been cooled in magnetic field of 1600e.

5:6:5. Magnetisation.

Magnetisation data (see figure 5:41) also support this hypothesis, with a steady reduction in the magnetic moment due to increase in J reflected in a reduction the absolute values in low temperature magnetisation with Co concentration. Unlike CeAl_2 with Cu zero field and field cooled data shows no magnetic freezing effects.

5:6:6. Summary.

To summarize in this section data has been presented which show:

1. as with Cu, alloying with Co, is equally destructive to the onset of coherence and magnetic ordering.
2. variations in magnetic resistivity and susceptibility are driven by changes in J due to lattice pressure.

5:7. The $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ System.

5:7:1. Introduction.

Pseudobinary systems with composition $\text{R}(\text{Al}_{1-x}\text{Fe}_x)_2$ where R is a rare earth or Zr, Ti, Nb or U have been investigated by several authors. Dwight et al. [5:44] showed via X-ray studies that for either Al or Fe rich $\text{R}(\text{Al}_{1-x}\text{Fe}_x)_2$ where R is (Sc, Y, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm or Lu) the compounds are MgCu_2 type (cubic) Laves phases. In a composition region intermediate between RFe_2 and RAl_2 , the compounds are MgZn_2 type (hexagonal) Laves phase. In general, the stability of the hexagonal compound is shifted to higher Al concentration, as the identity of R changes from Sm to Lu (see figure 5:42). In each case, a boundary region spanning 2 to 10% exists between the different structures in which the samples are made up of the two adjoining phases. For many systems three different (4f-4f, 3d-3d and 4f-3d) exchange interactions together with these structural transitions

produce complicated behaviour. Hilscher [5:45,5:46] and Hilscher et al. [5:47] studied the pseudobinary systems $Y(Al-Fe)_2$ and $Zr(Al-Fe)_2$. Here Y and Zr carry no moment. This allows the properties of the Al-Fe matrix to be studied where either trivalent Y or tetravalent Zr serves to stabilize the Laves phase structure. The effects of the differing electronic structures of Y and Zr can also be examined. YFe_2 is found to order ferromagnetically with a T_C of 540K. The structure remains cubic for replacements of up to 35% Fe with Al and a steady increase in lattice parameter is observed. For $0.35 < x < 0.5$ the structure is C14 hexagonal. For $x > 0.5$ the crystal structure is once again C15 cubic. It was found that for $Y(Al_{1-x}Fe_x)_2$ replacement of Fe with Al produced a steady reduction in the temperature at which long range ordering occurs. No long range ordering was detected for $0.78 > x > 0.65$ or for $x < 0.5$. In a region $0.90 > x > 0.65$ a cluster or spin glass phase forms at low temperature. In contrast, good long range ferromagnetic order persists in the $Zr(Al_{1-x}Fe_x)_2$ system for $x > 0.4$. No magnetic ordering of any kind is observed below this concentration of Fe, and no cluster glass region was detected. The magnetic phase diagrams obtained are shown in figure 5:43. It was suggested that the different magnetic properties seen in the Y and $Zr(Al-Fe)_2$ systems are due to the much stronger hybridisation of Zr 4d electrons with 3d electrons than is the case for the Y system. In $Y(Al_{1-x}Fe_x)_2$ the Fe moments are more localized. Al and Y act as magnetic dilutents. Susceptibility measurements in the paramagnetic region in this system suggest the Fe impurities are dissolved in an YAl_2 matrix and act as good paramagnetic moments. The crossover from the ferromagnetic to the cluster glass state

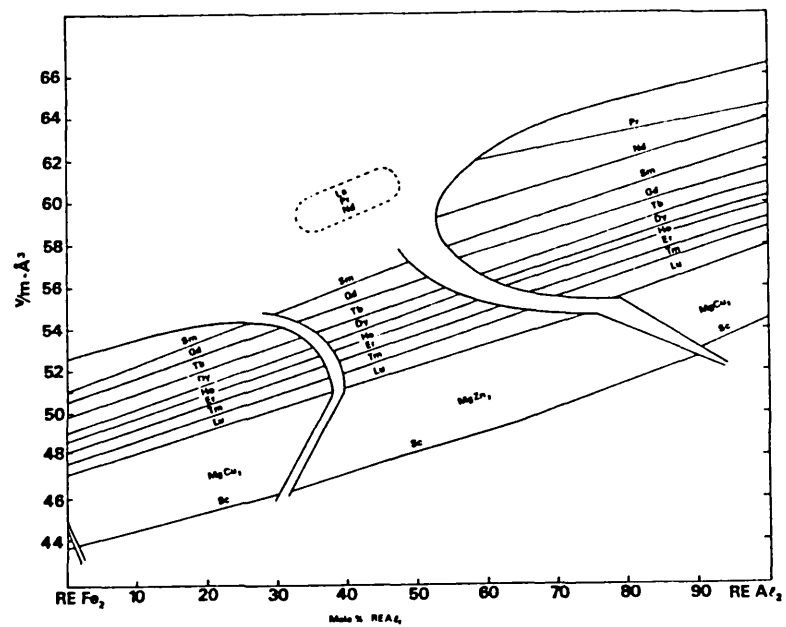


Figure 5:42. Volume dependence per formula weight (V/M) and crystal structure versus composition. Taken from Dwight et al. [5:44].

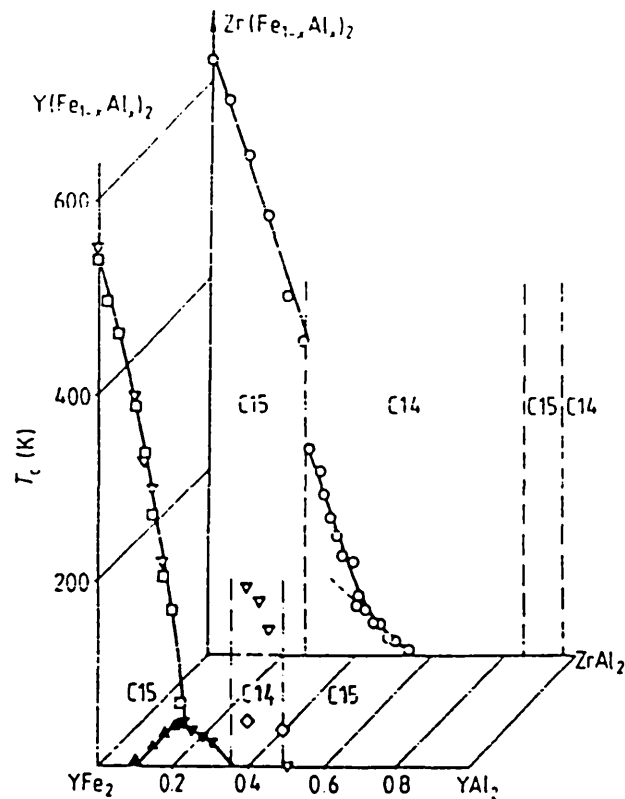


Figure 5:43. Concentration dependence of the Curie temperature T_C of $Zr(Fe_{1-x}Al_x)_2$ (O) and $Y(Fe_{1-x}Al_x)_2$ (◇, □ and ▽); ▽ denotes the freezing temperatures.

may be explained as a competition between ferromagnetic and antiferromagnetic interactions, in analogy with the binary Fe-Al system [5:48,5:49]. The Zr 4d electrons enhance the itinerant character of the 3d Fe electrons due to hybridisation. The Fe moments appear more delocalized. In $\text{Zr}(\text{Al-Fe})_2$ system the C.W. temperatures extracted from susceptibility in the paramagnetic regime, exhibit normal concentration dependence with $\theta_{\text{C.W.}}$ vanishing at the critical concentration ($x_{\text{C}}=0.45$). For $x<0.2$ no evidence for good Fe moments is seen in the susceptibility data.

5:7:2. $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ $x>0.50$.

CeFe_2 is an unusual compound. The moment per formula unit ($2.4\mu_{\text{B}}$) and the Curie temperature (230K) are significantly lower than the values of $3.5\mu_{\text{B}}$ and 600K found in Y or ZrFe_2 . Samples in the alloy series $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ with $x>0.8$ were studied by S.B. Roy, S.J. Kennedy and B.R. Coles. Their findings (see figures 5:44 to 5:46) along with earlier work have been published in references [5:50 to 5:57]. X-ray patterns of Franceschini and da Cunha [5:56], suggest that the solubility limit for Al in Fe rich $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ may be placed around $x=0.875$. This was confirmed in the work of Roy who was not able to produce single phase samples beyond 12% Al. For $0.98>x>0.96$ susceptibility results indicate a sharp paramagnetic to ferromagnetic transition, followed at lower temperature T_{F} by a magnetic transition, whose nature will be discussed shortly. Resistivity measurements reveal a knee in $\rho(T)$ which coincides with T_{C} followed by a local minimum associated with the anomaly at T_{F} . For $x=0.95$ T_{C} and T_{F} are very close together and the knee in $\rho(T)$ is nearly washed out. For $x<0.95$ no evidence of long range order is observed

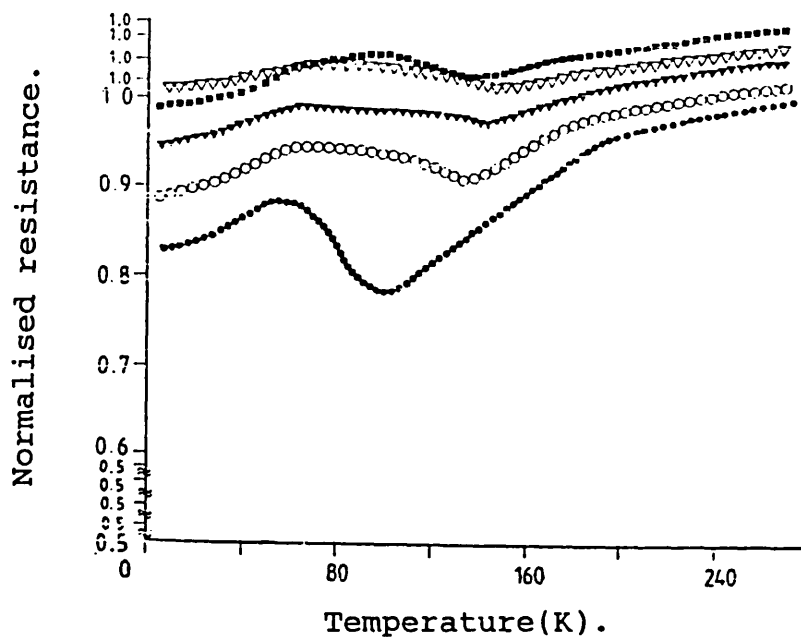


Figure 5:44. The normalised resistivity ($\rho(T)/\rho(280K)$) as a function of temperature of $Ce(Al_{1-x}Fe_x)_2$ for $x=0.96(\bullet)$, $0.95(O)$, $0.94(\blacktriangledown)$, $0.93(\triangledown)$ and $0.92(\blacksquare)$. Data taken by Roy and Coles [5:51].

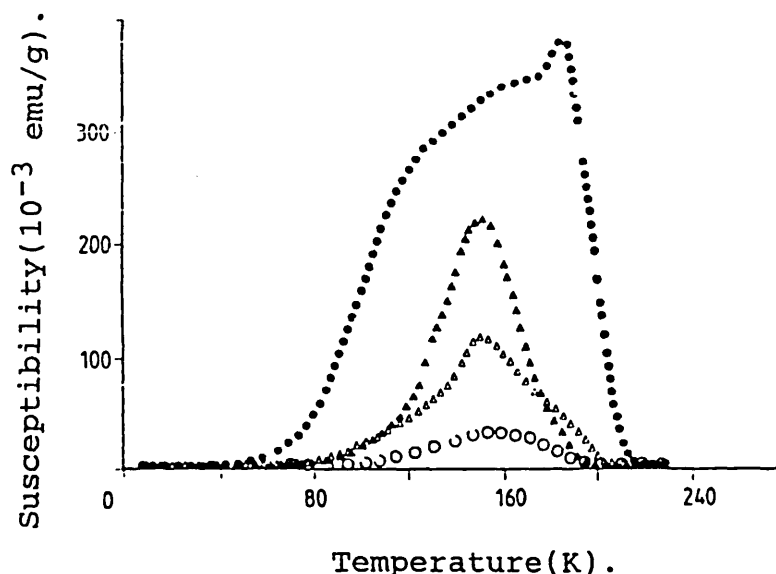


Figure 5:45. The a.c. susceptibility of $Ce(Al_{1-x}Fe_x)_2$ alloys as a function of temperature for $x=0.96(\bullet)$, $0.95(\blacktriangle)$, $0.94(\triangle)$ and $0.93(O)$. Data are from Roy and Coles [5:51].

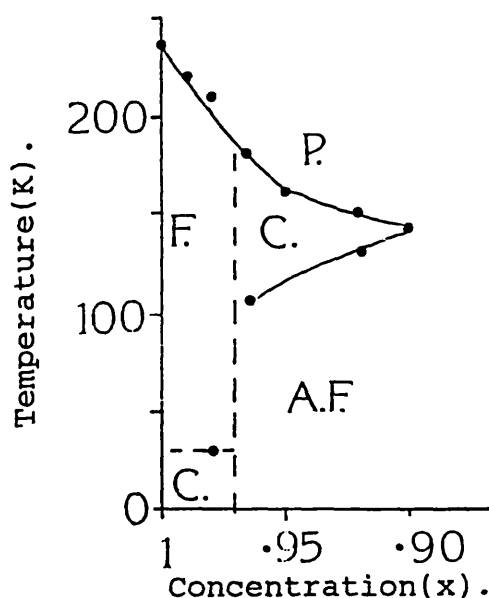


Figure 5:46. Magnetic phase diagram for $Ce(Al_{1-x}Fe_x)_2$ for $x \geq 0.90$. Taken from the data of S.B. Roy, S.J. Kennedy and B.R. Coles.

in $\chi_{a.c.}(T)$ or $\rho(T)$. For $x=0.92$ a single sharp cusp is seen which is shifted to lower temperature with the application of a d.c. magnetic field. This work showed that the ferromagnetism is very unstable to substitution of Al. It was suggested that the lower transition may be due to either:

1. appearance of a reentrant spin glass.
2. a ferromagnetic to antiferromagnetic transition which takes place gradually via a regime of coexistence or superposition in which the canting of the spins in the opposite direction introduces an antiferromagnetic character.

This results in the magnetic phase diagram shown in figure 5:46.

5:7:3. $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ $x \leq 0.50$. Sample Preparation.

Samples in the series $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ for $x \leq 0.50$ were prepared using the method described in section 3:6. The samples were all annealed in vacuum for 7 days at 600°C followed by a further 7 days at 700°C . Metallographic specimens of all the samples were prepared. Small amounts of oxide were observed in all the samples. Samples in the concentration range $x \leq 0.15$ appear essentially single phase whilst those with $0.15 < x < 0.25$ contain a tiny amount ($\geq 5\%$) of an unidentified second phase. All specimens also have several microcracks and exhibit a certain amount of porosity. Above $x=0.25$ a significant amount of second phase was detected. By $x=0.30$ the samples were clearly made up of three phases. Under an optical microscope both the $x=0.35$ and $x=0.50$ samples were seen to contain:

1. Features 1 micron in size, identified as a mixture of peppery oxides and porosity.
2. A main matrix phase together with some interdendritic phase.
3. Embedded in the main matrix, grey particles 2-3 microns across.

X-ray diffraction studies on powdered samples confirm these

findings. For $x \leq 0.20$ patterns retain the cubic structure of the parent CeAl_2 compound, with only a couple of lines which could not be identified with the cubic structure. These lines have been identified as the strongest lines from CeO . Since the intensity of these lines is low and this X-ray technique is particularly sensitive to surface oxide impurities it is suggested that the concentration of these oxides is very small. For $x \geq 0.25$ several foreign lines are present which cannot be attributed to a cubic $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ structure or Ce oxides. These foreign lines grow in intensity as the cubic lines are suppressed, until at $x \geq 0.35$ none of the lines can be unambiguously indexed using CeAl_2 as a prototype compound. It is at this point that it is assumed the majority phase is not cubic $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$. Scanning electron microscope studies have been performed on the $x=0.35$ and $x=0.50$ samples, in an effort to identify the composition of the phases present in these multiphase samples. This analysis identified three composition regions:

1. Ce_3Al with a small (0-10) percentage of the Al replaced with Fe. This phase is identified with the grey blobs embedded in the main matrix, seen under the optical microscope.
2. $\text{CeAl}_{2-x}\text{Fe}_x$ with x ranging from 0.75 to 1.15. This phase makes up the main matrix.
3. $\text{CeAl}_{1.5}\text{Fe}_{0.5}$. This phase is associated with the interdendritic phase.

These observations are in reasonable accord the ternary phase diagram constructed by Zarechnyuk et al. [5:58], shown in figure 5:47 along with a few tentative alterations and additions. This suggests that solubility limit of Fe in CeAl_2 lies between 20 and 25at%, and that single phase samples with cubic structure of CeAl_2 cannot be made with greater Fe concentrations.

5:7:5. Lattice Parameters.

Lattice parameters a_0 for cubic $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ alloys have been calculated from X-ray patterns for $x \leq 0.25$. The results are shown in figure 5:48. Small additions of Fe ($0 \leq x \leq 0.04$) cause the lattice to expand. Further increases in Fe concentration leads to a decrease in the lattice parameter. The same figure includes a line indicating the expected variation in lattice parameter for trivalent Ce^{3+} following Vegard's law. N.B. CeFe_2 is thought to be in the 4+ state. The lattice parameter for CeFe_2 if Ce were in a 3+ state is estimated by plotting the variation in a_0 versus atomic number for several trivalent rare-earth- Fe_2 compounds and extrapolating to the atomic number of Ce. This procedure gives a_0 for $\text{Ce}^{3+}\text{Fe}_2$ of $7.5\text{\AA}$. A small positive deviation from Vegard's law is taken to indicate that Ce persists in the 3+ state up to the solubility limit of approximately 25at%.

5:7:6. Magnetic Susceptibility.

The variation of the magnetic susceptibility with temperature of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ for several samples with $x \leq 0.50$ are shown in figures 5:49 to 5:53. Several important features seen in the data are highlighted below:

1. A peak is seen at 4.3K in pure CeAl_2 , and taken as a precursor to the onset of antiferromagnetic ordering, is continuously shifted to lower temperature as Fe is added. The temperature of the peak T_{max} is given in table 5:6. For $x \leq 0.04$ the shape of the peak is very like that of pure CeAl_2 and may indicate that the compounds still order antiferromagnetically. For $0.04 < x \leq 0.10$ the peak is much sharper and more reminiscent of a spin glass cusp. This may help to explain the apparent change in the rate of reduction of T_{max} when plotted against Fe concentration x (see figure 5:54). For $x < 0.04$ the maximum occurs before the magnetic ordering, whilst for $0.04 \leq x \leq 0.10$ the ordering temperature would be at T_{max} . No low temperature peak associated with antiferromagnetic ordering is observed above 1.5K for $x > 0.10$.

2. For $x=0.02$ a peak is seen in the susceptibility at 12K. This peak is not present in $x=0.00$ or $x \geq 0.04$ samples (c.f $\text{Ce}(\text{Al}_{0.98}\text{Cu}_{0.02})_2$).

$\text{Ce}(\text{Al}_{0.98}\text{Cu}_{0.02})_2$.

3. The magnitude of the susceptibility at the temperature of the maximum $\chi(T_{\text{max}})$ also shows a behaviour similar to that of the $\text{Ce}(\text{Al}-\text{Cu})_2$ system. This magnitude is first depressed, then rises rapidly (see table 5:6).

Table 5:6. Parameters taken from magnetic susceptibility data of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$, $x \leq 0.50$.

%Fe	T_{max} low T (K)	T_{infl} low T (K)	T_{max} high T (K)	T_{F} high T (K)	χ_{mag} low T emu/mol	χ_{mag} high T emu/mol	θ_{CW} (K)
0	4.23	3.85	-----	-----	0.055	-----	-34
2	3.49	3.05	-----	-----	0.0275	-----	-20
4	2.83	-----	-----	-----	0.057	-----	-12
6	2.325	-----	42.5	30.0	0.0595	-----	34
7	-----	-----	92.0	N/A	0.0545	0.044	103
8	2.104	-----	129.0	110.0	0.090	0.29	145
10	1.83	-----	170.0	105.0	0.107	0.38	182
15	-----	-----	235.5	85.0	-----	0.566	---
20	20.65	-----	284.0	45.0	-----	0.43	---
25	20.15	-----	>300.0	18.0	-----	0.40	---
30	20.15	-----	-----	-----	-----	0.29	---
35	20.15	-----	-----	-----	-----	0.23	---
50	19.85	-----	-----	-----	-----	0.40	---

4. For $0.05 \leq x \leq 0.25$ a peak appears in the susceptibility at high temperature. For $x=0.05$ (not shown) this is a sharp cusp whilst for $x=0.06$ this feature is a more rounded cusp. For $0.07 \leq x \leq 0.25$ the shape of this transition changes. As the temperature is lowered a sharp rise in $\chi(T)$ is followed by a much slower fall below χ_{max} . The temperature of the transition can be fixed either at the temperature of the peak in susceptibility or at the point of inflexion in the region of the sharp rise in χ against T . Using either method one observes a rapid rise in transition temperature as Fe concentration is increased. For $x=0.20$ the ordering temperature of 286K is greater than the T_{C} of pure CeFe_2 (230K). The magnitude of $\chi_{\text{a.c.}}$ is less than one would expect from a "good" ferromagnet. Below the peak, the susceptibility response falls so that at low temperature χ has fallen to almost half its peak value. A change in slope in $\chi(T)$ at a lower temperature may be associated with some magnetic freezing or spin canting.

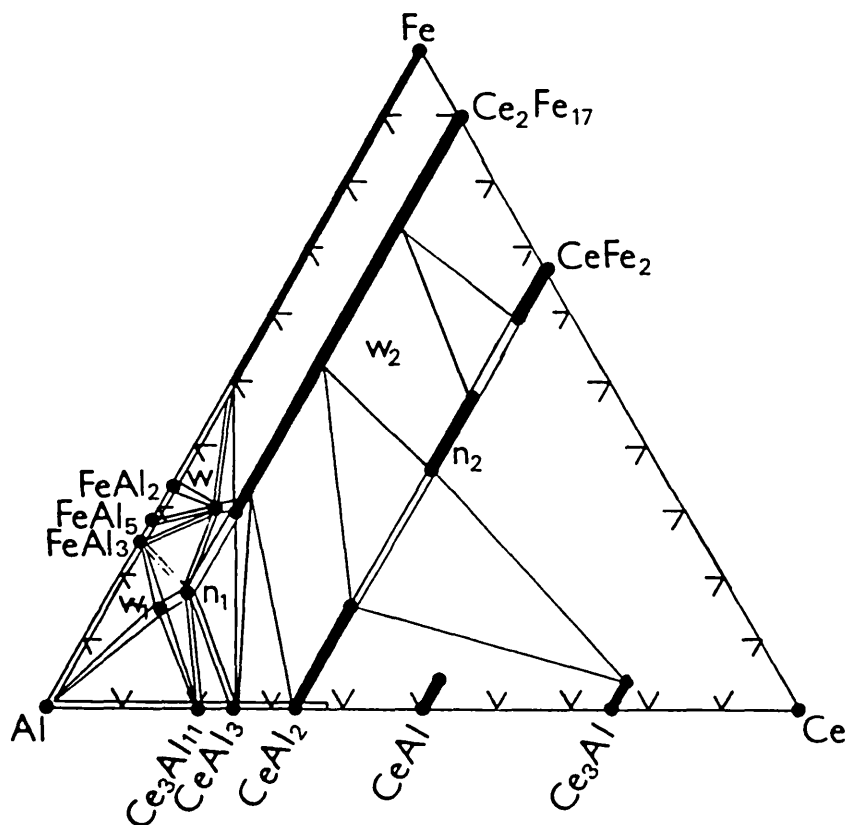


Figure 5:47. Isothermal section of the ternary Ce-Fe-Al system at 500°C after Zarechnyuk et al. [5:58].

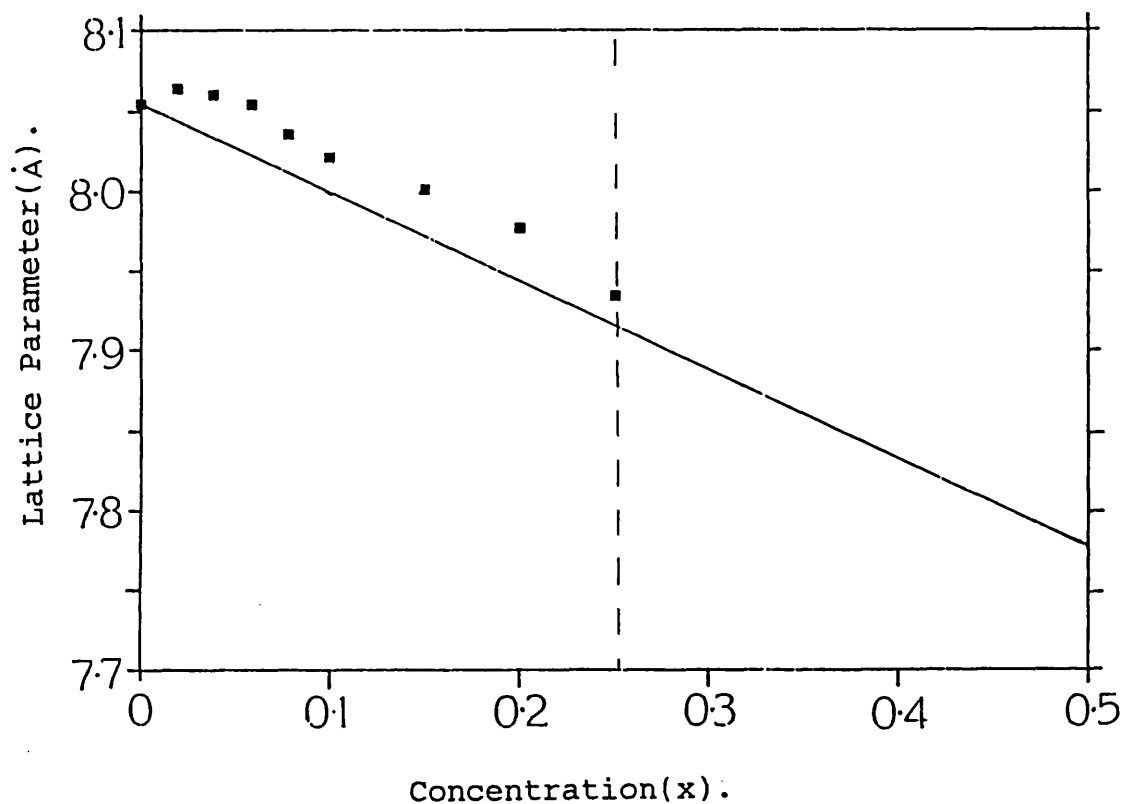


Figure 5:48. Concentration dependence of the lattice parameter of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ (■) for $x \leq 0.25$. The solid line indicates the expected variation in lattice parameter for trivalent Ce following Vegard's law.

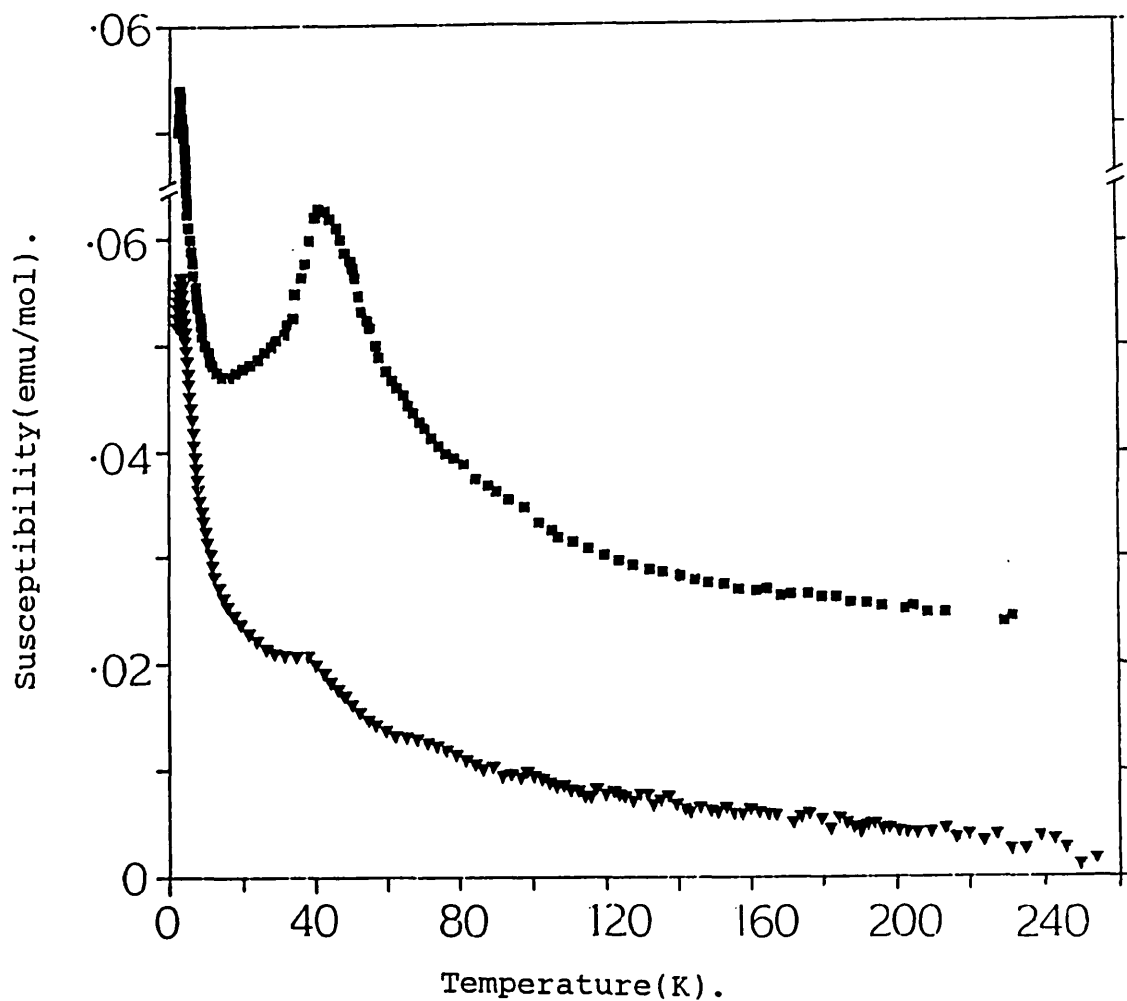
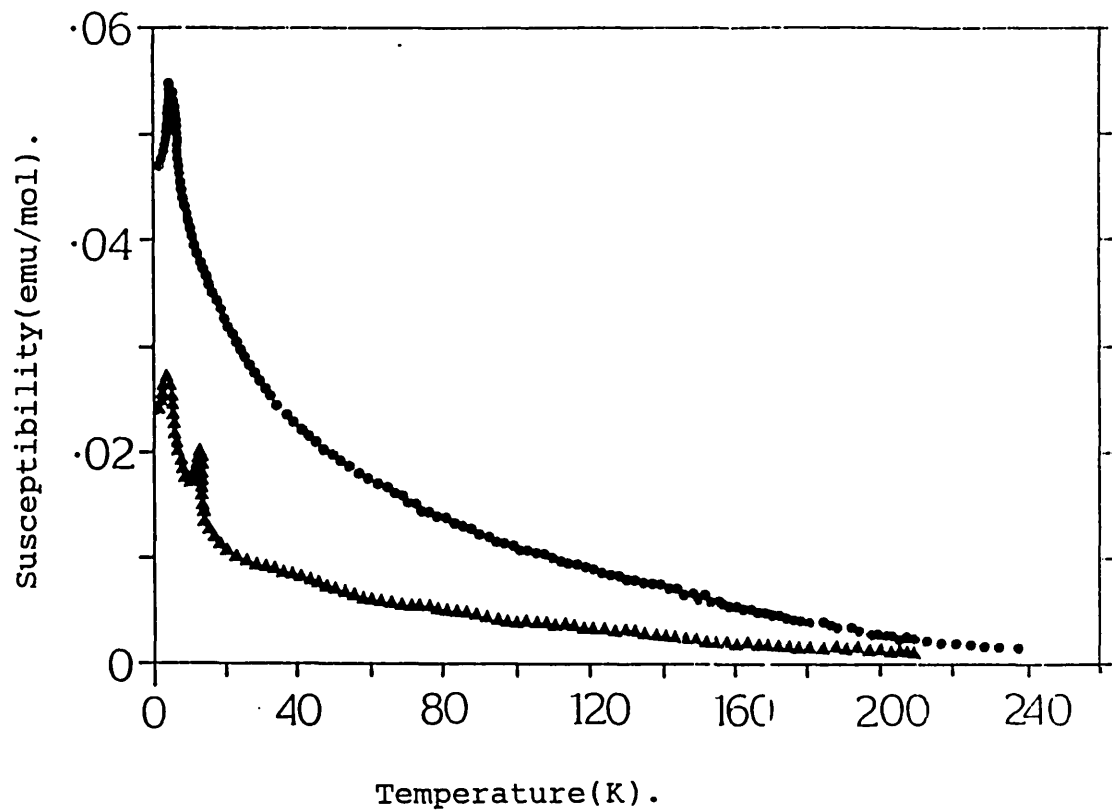


Figure 5:49. (a) and (b) Magnetic susceptibility versus temperature of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ for, $x=0.00(\bullet)$, $0.02(\blacktriangle)$, $0.04(\blacktriangledown)$, $0.06(\blacksquare)$.

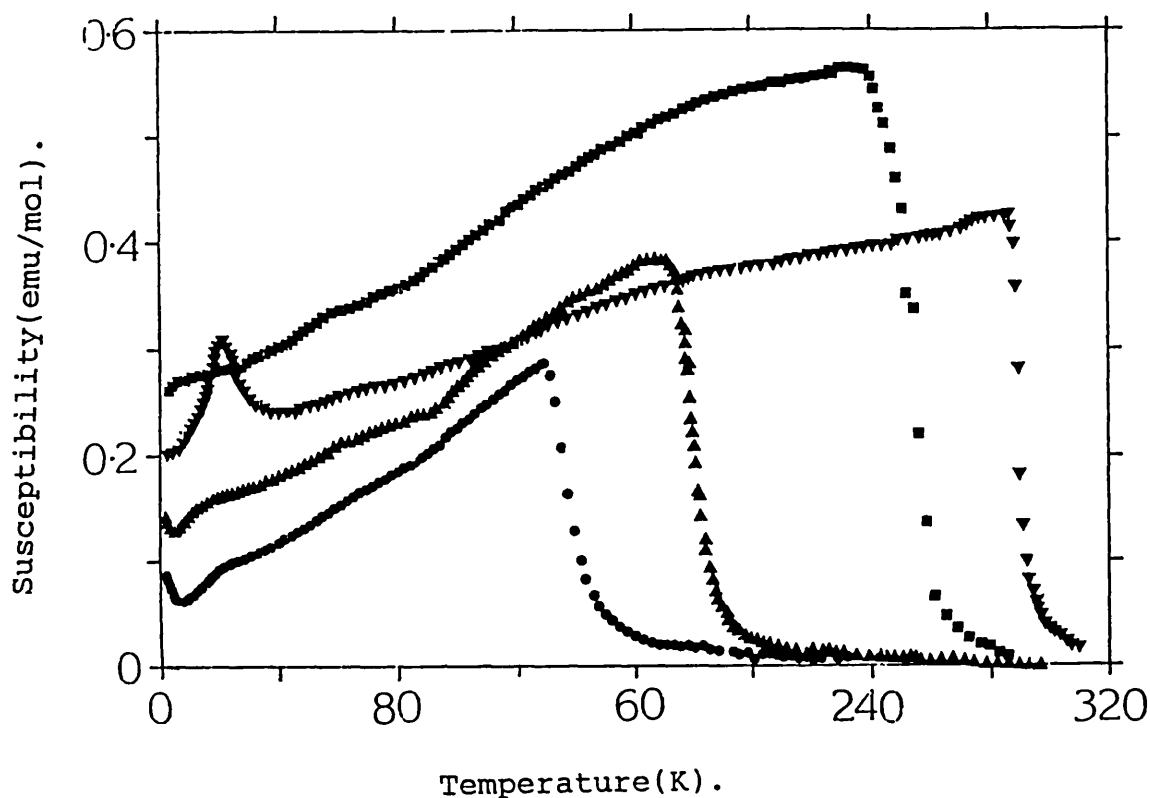


Figure 5:50. Magnetic susceptibility versus temperature of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ for $x=0.08$ (●), 0.10 (▲), 0.15 (■) and 0.20 (▼).

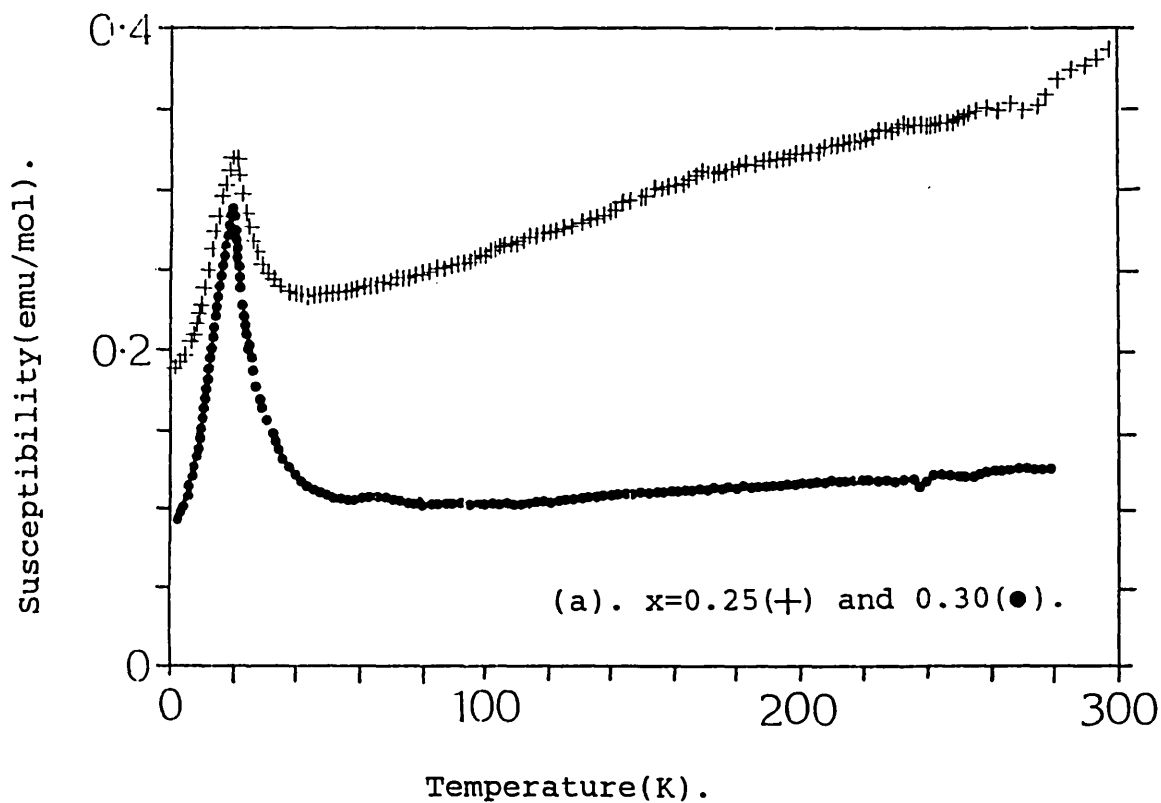
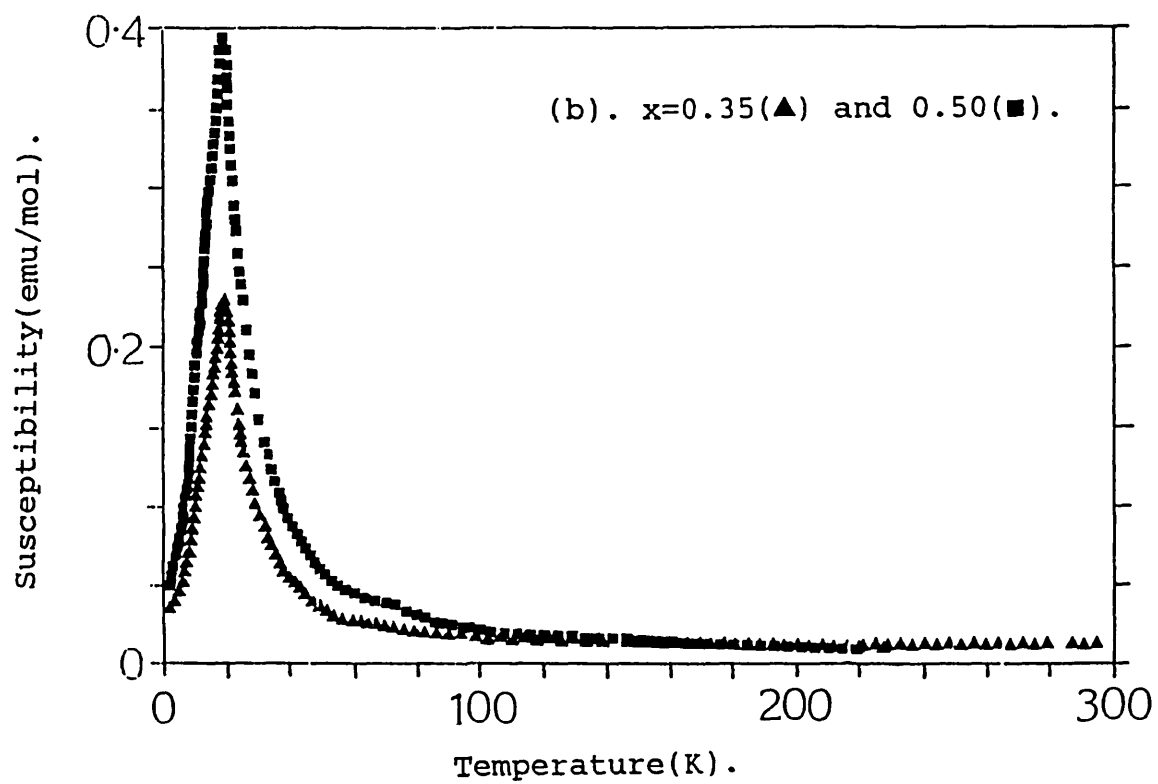


Figure 5:51. (a) and (b) Magnetic susceptibility versus temperature of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ for $x=0.25$ (+), 0.30 (●), 0.35 (▲), 0.50 (■).



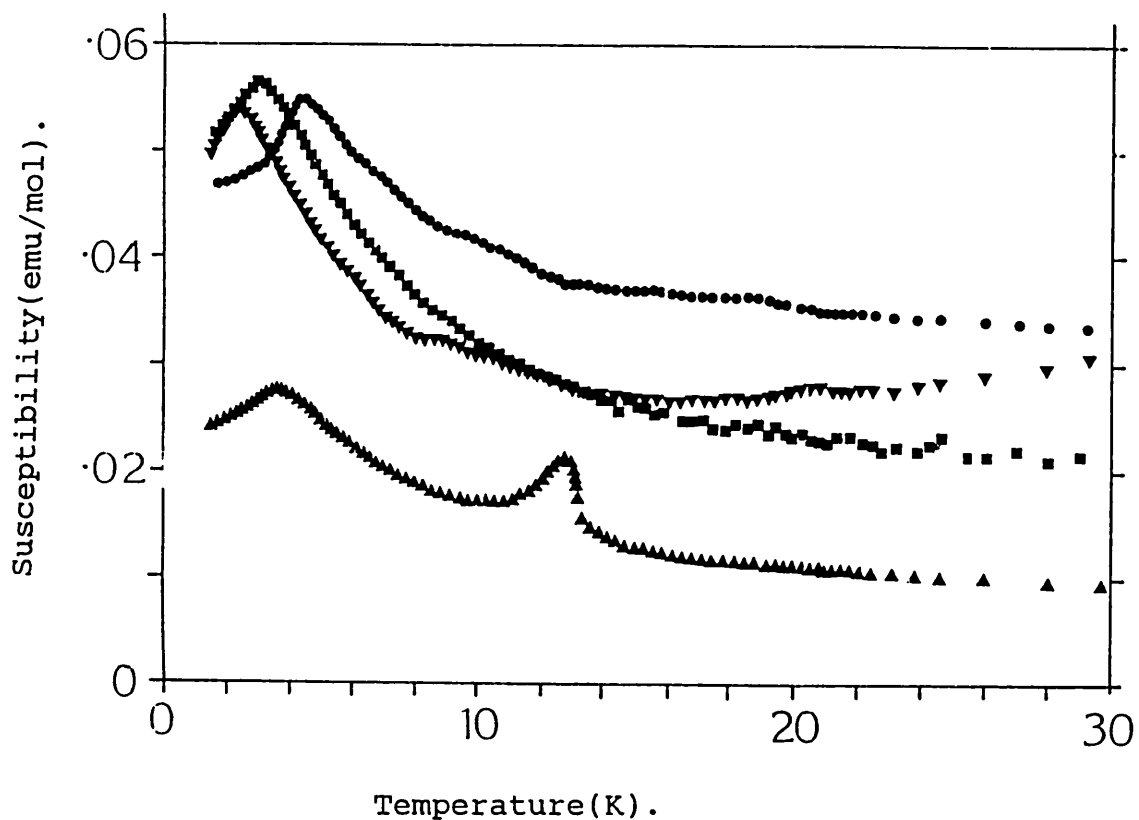


Figure 5:53. Magnetic susceptibility versus temperature between 0 and 30K of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ for $x=0.00(\bullet)$, $0.02(\blacktriangle)$, $0.04(\blacksquare)$, $0.06(\blacktriangledown)$ showing the emergence and eventual disappearance of a peak in $\chi_{\text{a.c.}}(T)$ at 12K.

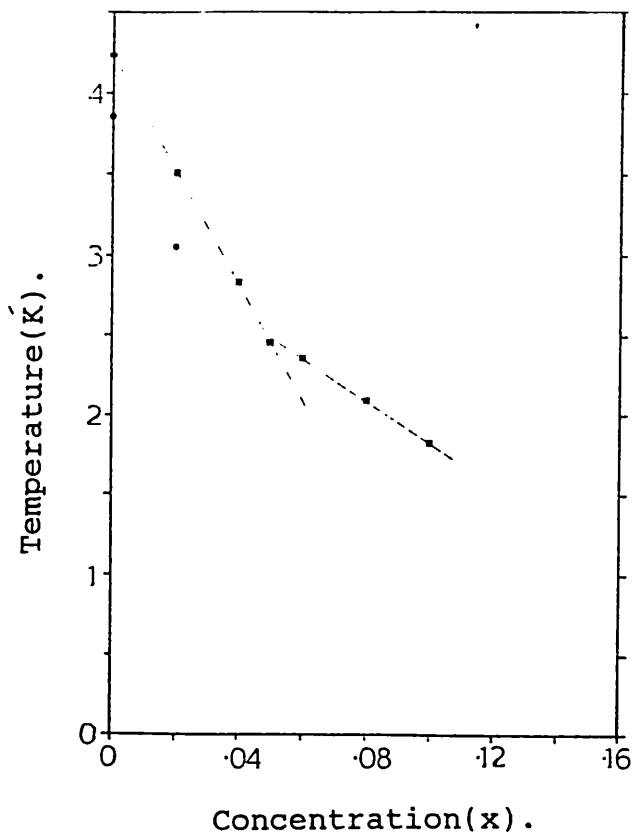


Figure 5:54. Temperature of the maximum($\blacksquare$) or inflexion point($\bullet$) in the low temperature magnetic susceptibility of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ for $x \leq 0.15$ versus concentration.

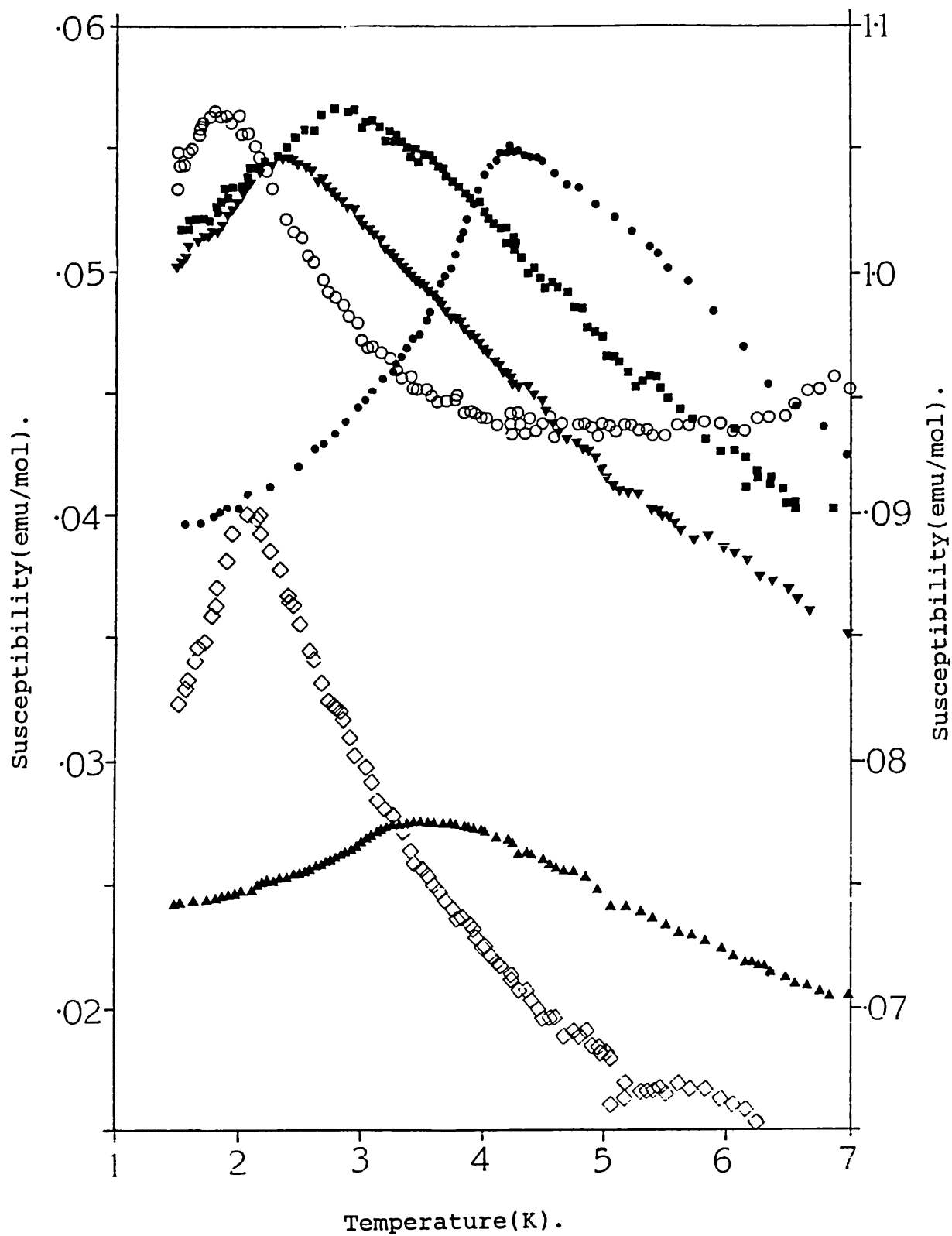


Figure 5:52. Low temperature magnetic susceptibility for $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ for $x=0.00(\bullet)$, $0.02(\blacktriangle)$, $0.04(\blacksquare)$, $0.06(\blacktriangledown)$, $0.08(\diamond)$ and $0.10(\circ)$.

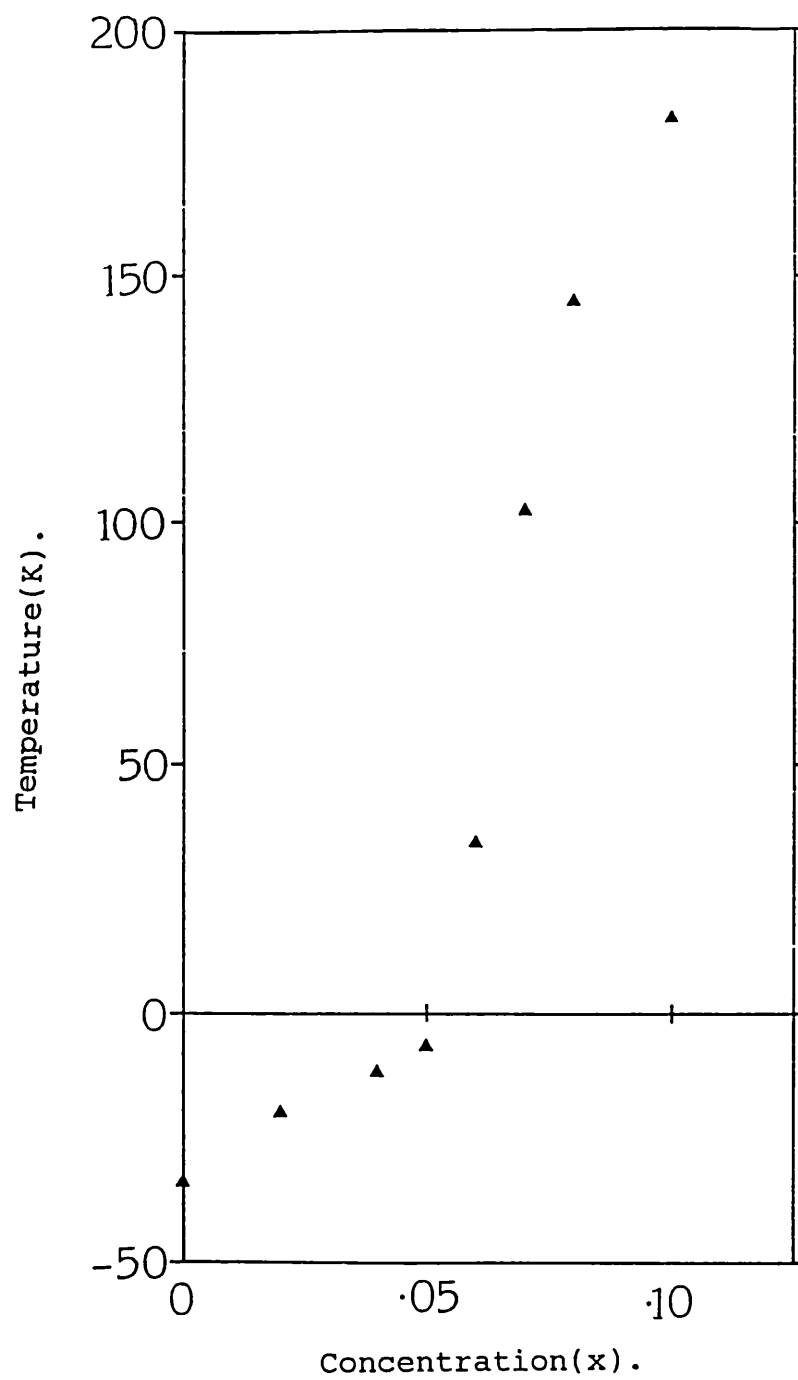


Figure 5:55. Concentration dependence of the paramagnetic Curie temperature of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ for $x \leq 0.15$.

5. Throughout the concentration range $0 \leq x \leq 0.10$ the paramagnetic Curie temperature $\theta_{C.W.}$ exhibits the usual concentration dependence: $\theta_{C.W.}$ vanishes as the critical concentration for the onset of high temperature ordering around $x=0.06$ is approached (see figure 5:55 and table 5:6).

6. For $x \geq 0.30$, the concentration around which the metallographic specimens and X-ray data indicated a break down in the Fe-Al substitution and a loss of the cubic structure one observes rapid changes in $\chi(T)$. The high temperature peak in $\chi(T)$ is rapidly washed away, with only a remnant appearing in the $x=0.30$ data. For $x \geq 0.35$ the magnitude of the susceptibility falls as the temperature is increased above 50K, and is small compared with values of, for example the $x=0.15$ sample. Instead $\chi(T)$ rises to a sharp cusp at around 20K. The temperature of this peak decreases slightly with Fe concentration in the range $0.20 \leq x \leq 0.50$.

5:7:7. Magnetisation.

Figures 5:56-5:58 show the magnetisation versus temperature between 4.25 and 300K for $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ system. Several features are observed.

1. For pure CeAl_2 the magnetisation shows no magnetic freezing effects above 4.2K.
2. In the $x=0.02$ sample a difference in the magnetisation of the field cooled and zero field cooled data is observed, with the onset of irreversible behaviour occurring at the same temperature as that at which the peak is observed in the magnetic susceptibility.
3. For $0.05 \leq x \leq 0.06$ a sharp rise in the magnetisation as the temperature is reduced, is followed at the temperature of the cusp in $\chi_{a.c.}(T)$ by the onset of difference between F.C. and Z.F.C. curves indicating presence of some kind of magnetic spin freezing.
4. For $0.06 \leq x \leq 0.15$ the magnetisation rises sharply at the same temperature as the rapid rise in magnetic susceptibility. At a lower temperature, a difference in the F.C. and Z.F.C. data is observed, again indicating the presence of magnetic freezing behaviour.
5. For $x \geq 0.30$ magnetisation versus temperature again looks very different with magnetisation rising steadily as temperature fall down to 20-25K followed by difference in F.C.-Z.F.C. data below this temperature.

Figures 5:59-5:62 show magnetisation versus field curves for $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ for $x \leq 0.50$ at 4.2K.

1. For 2% Fe distinct curvature is seen in M versus H data along with a small amount of hysteresis.

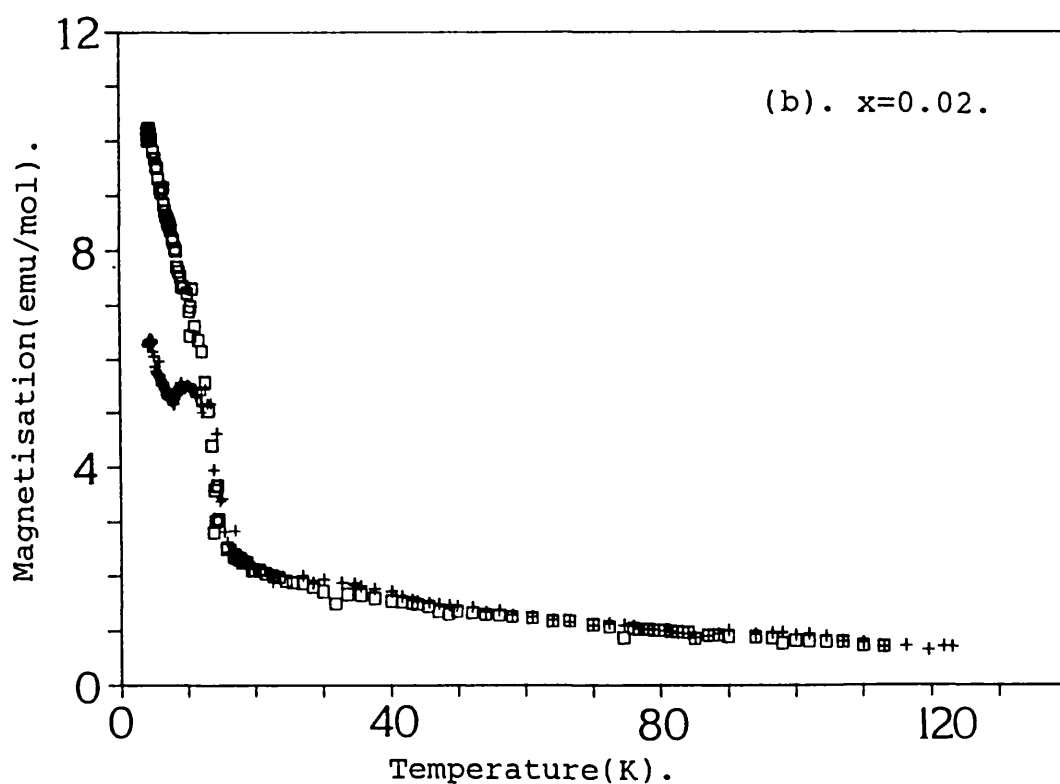
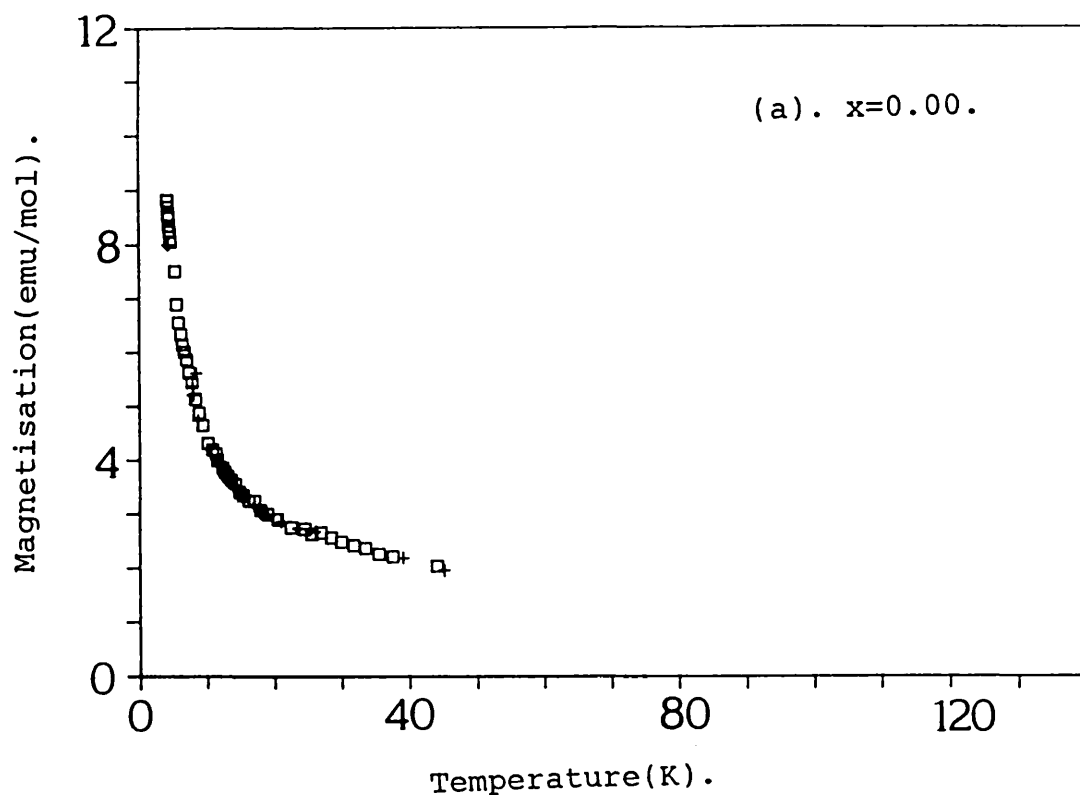
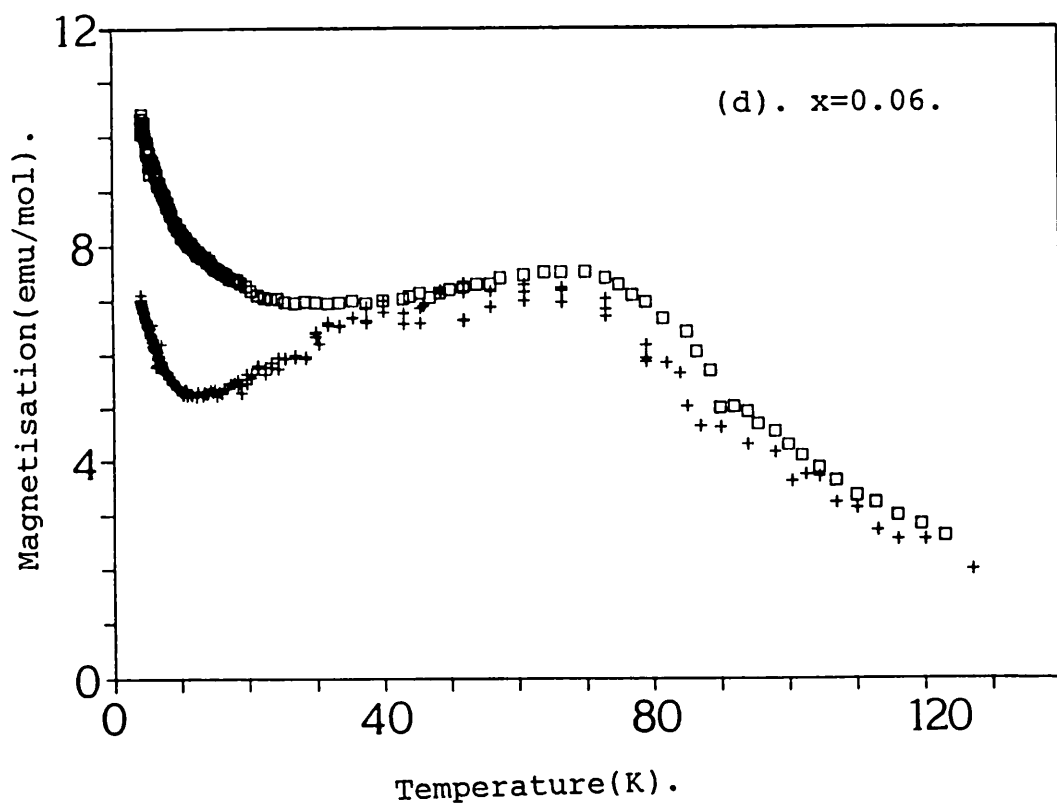
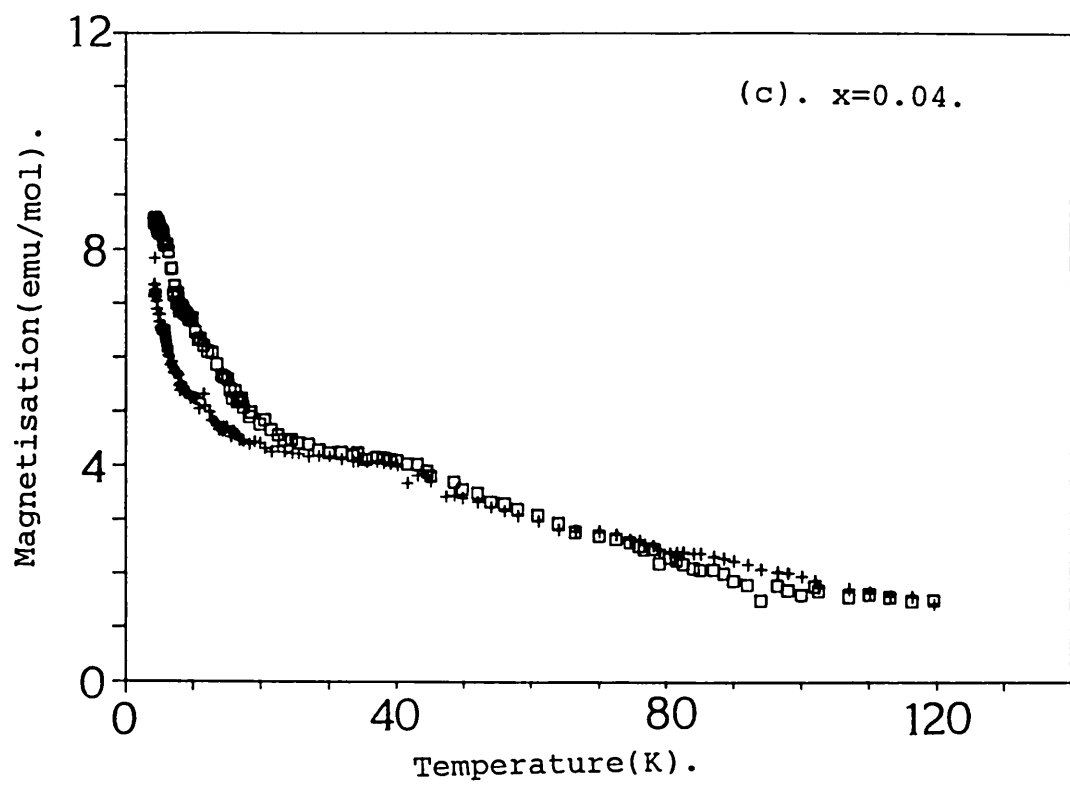


Figure 5:56 (a)-(d). Temperature dependence of the magnetisation of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ taken in a field of 160Oe. Open squares indicate the data taken after the sample has been cooled in the magnetic field. Crosses indicate the data taken on the sample after it has been cooled in zero field.



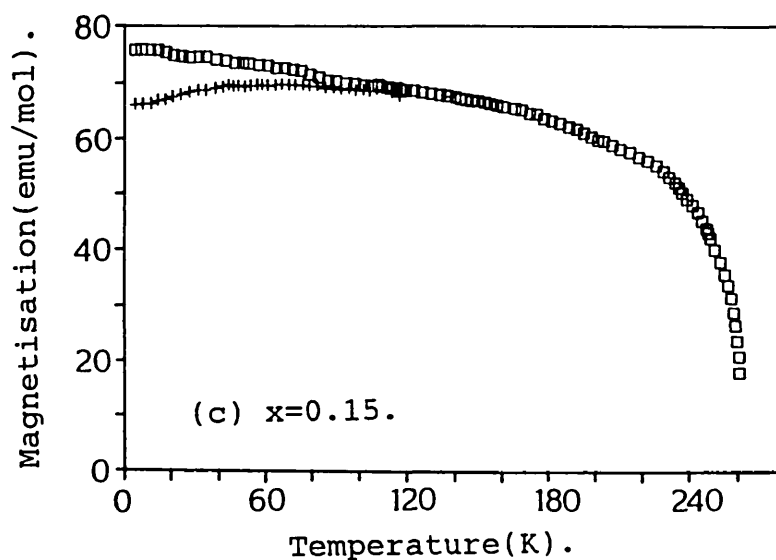
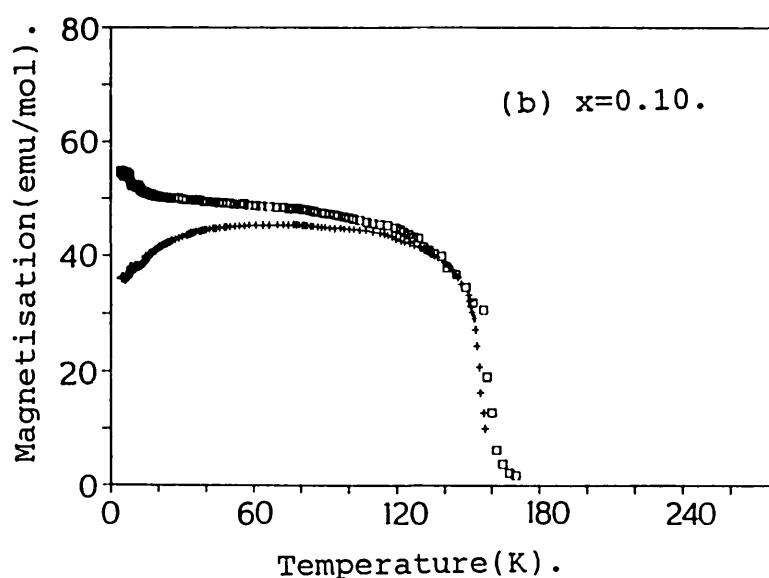
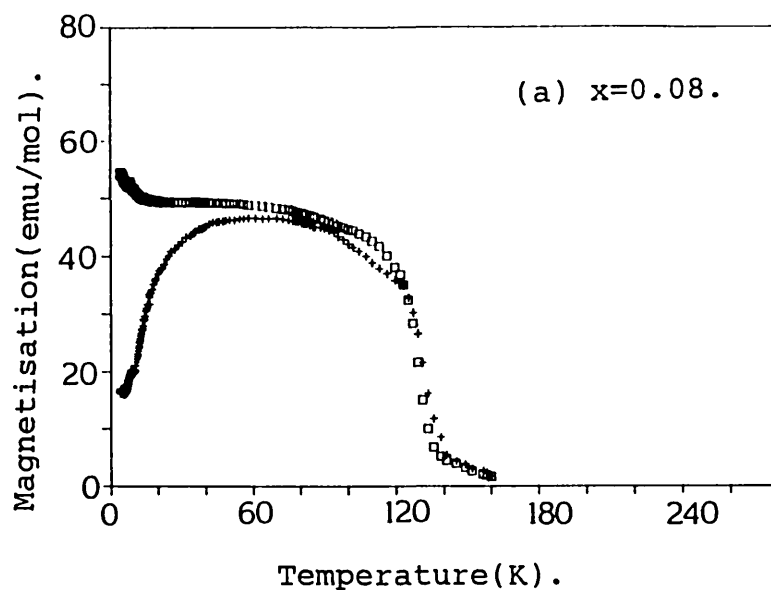


Figure 5:57 (a), (b) and (c). Temperature dependence of the magnetisation of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ taken in a field of 160Oe. Open squares indicate the data taken after the sample has been cooled in the magnetic field. Crosses indicate the data taken on the samples after it has been cooled in zero field.

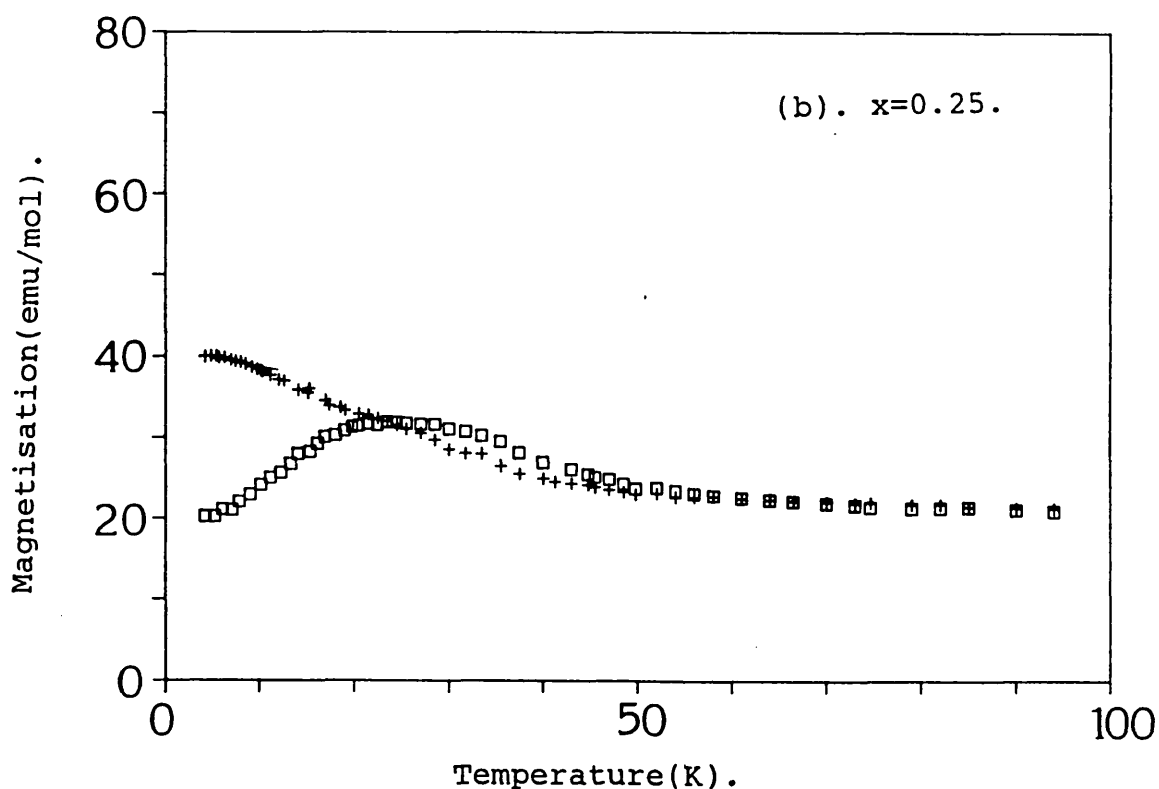
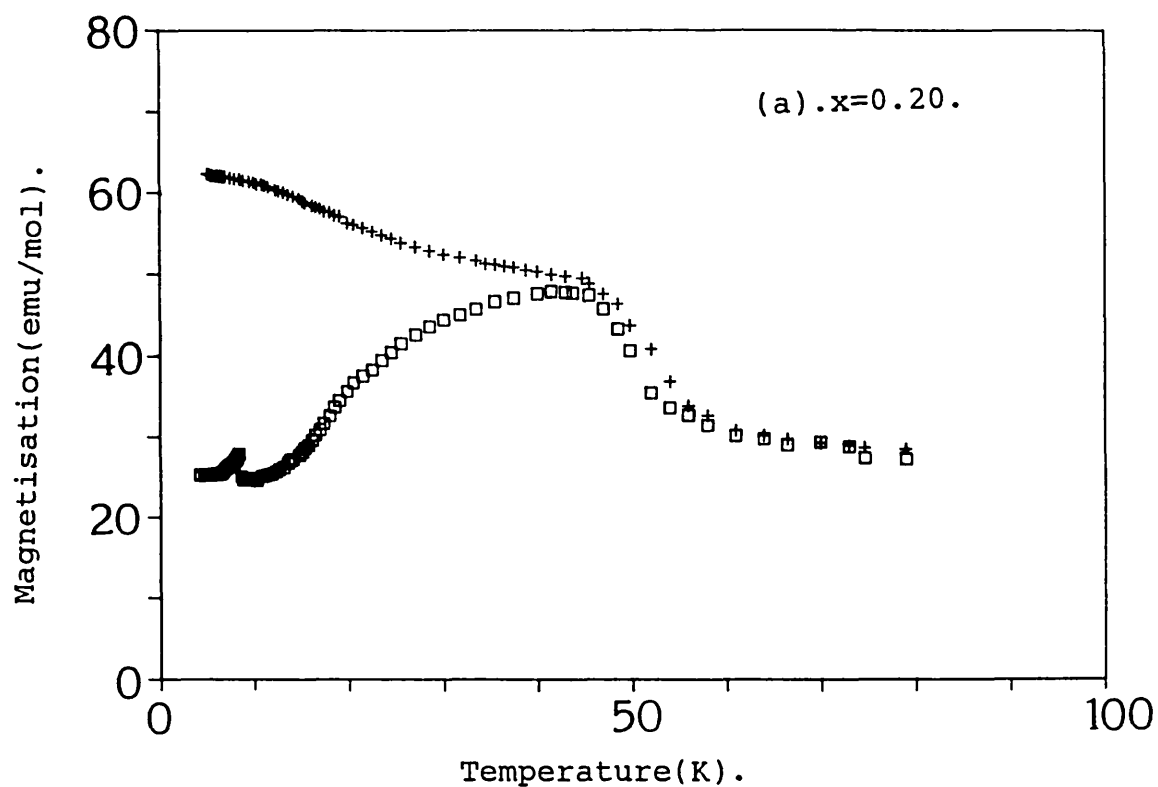


Figure 5:58 (a) and (b). Temperature dependence of the magnetisation of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ taken in a field of 1600e. Crosses indicate the data taken after the sample has been cooled in the magnetic field. Open squares indicate the data taken on the sample after it has been cooled in zero field.

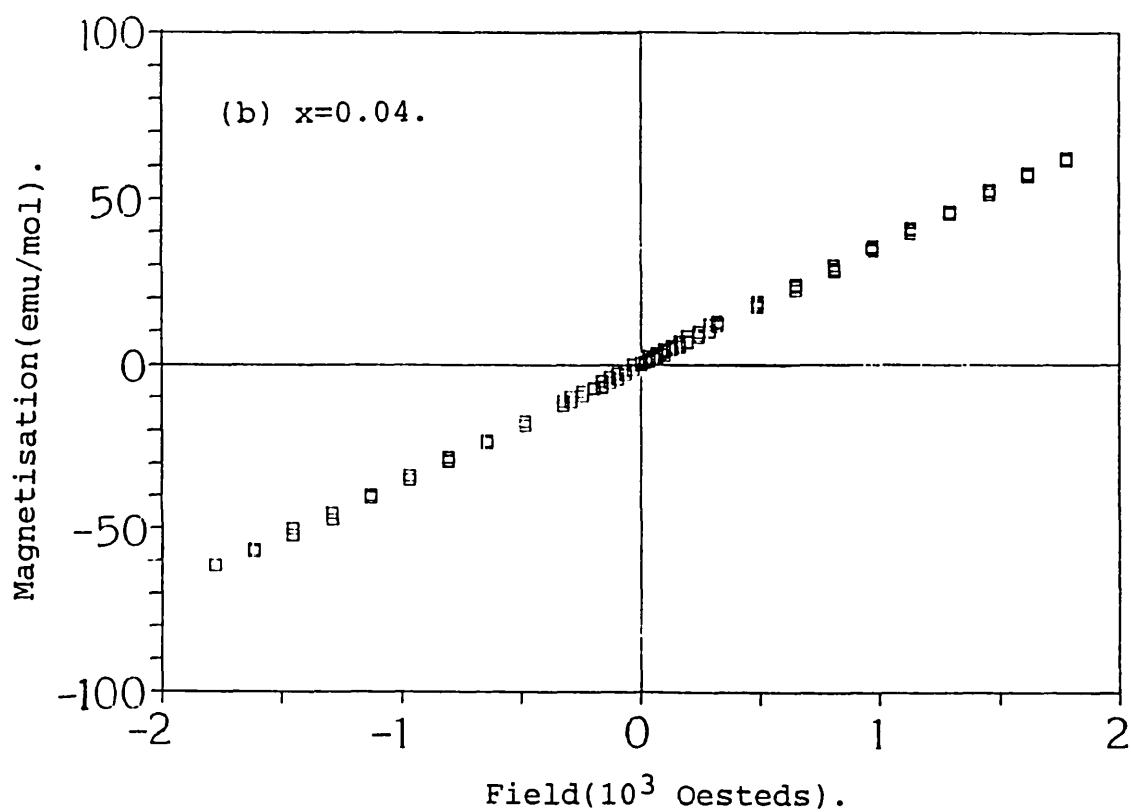
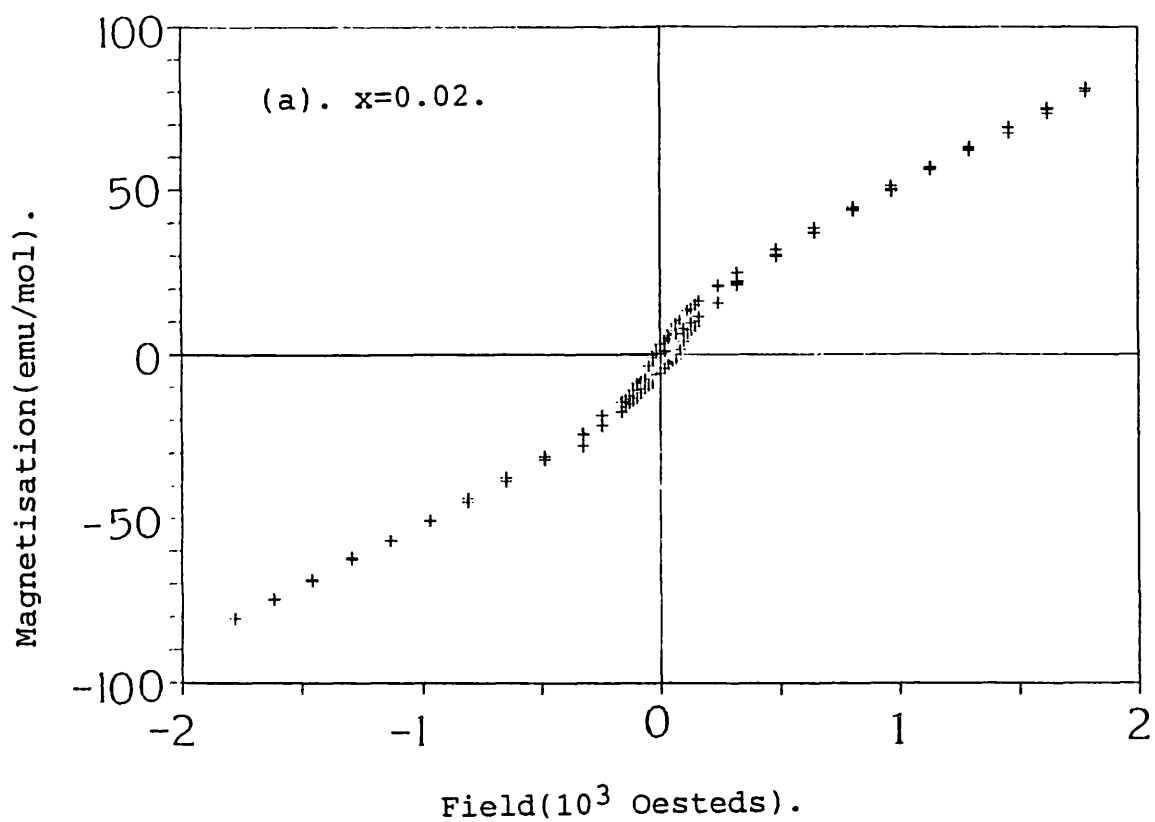


Figure 5:59. (a) and (b) Magnetisation versus field for $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$.

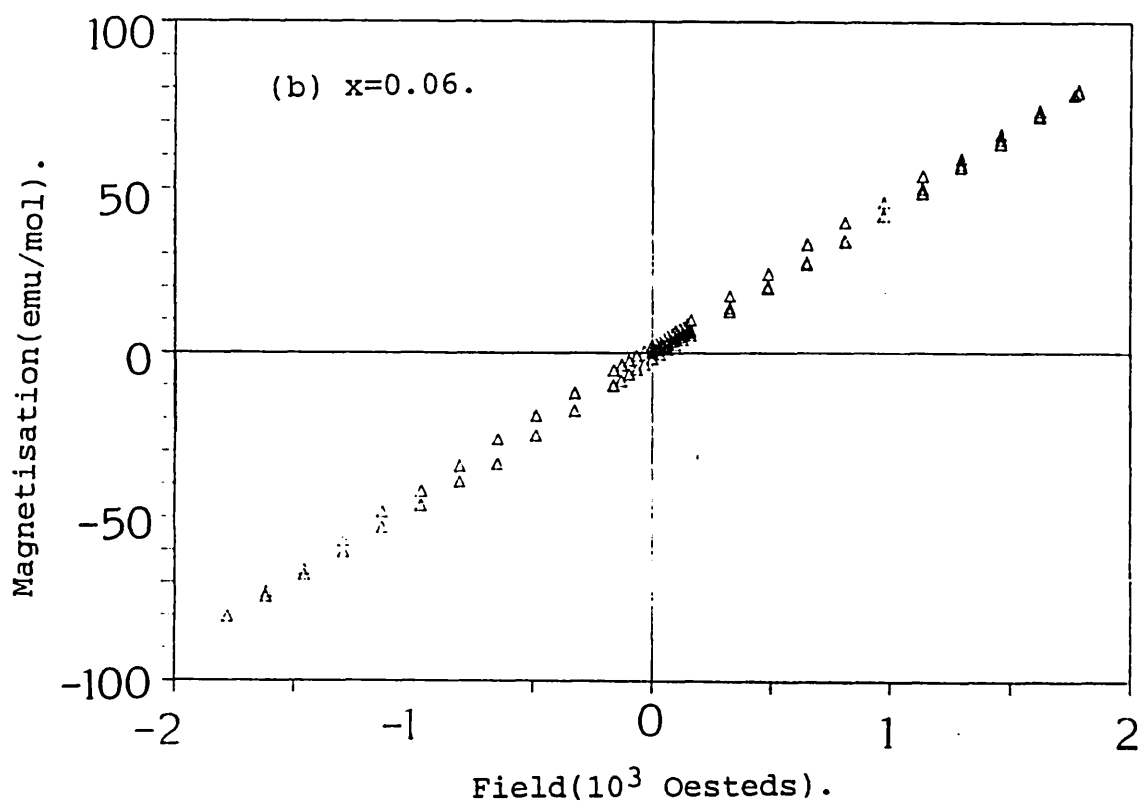
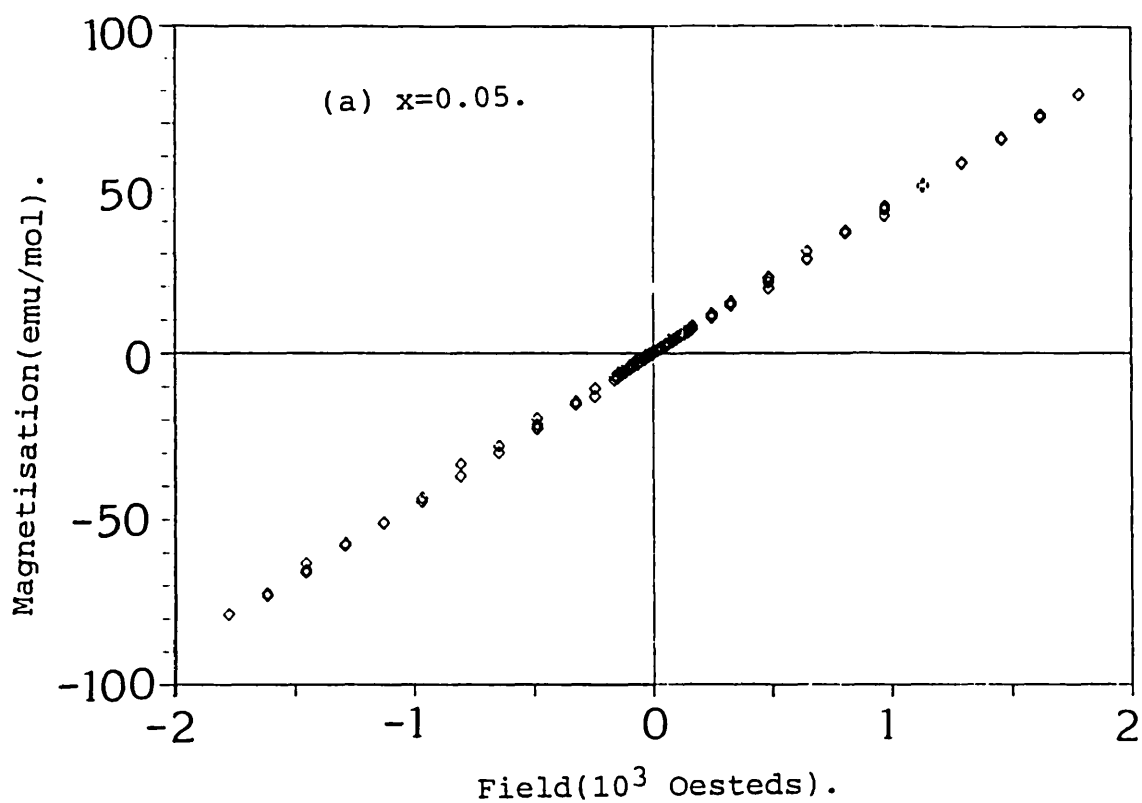


Figure 5:60 (a) and (b). Magnetisation versus field for $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$.

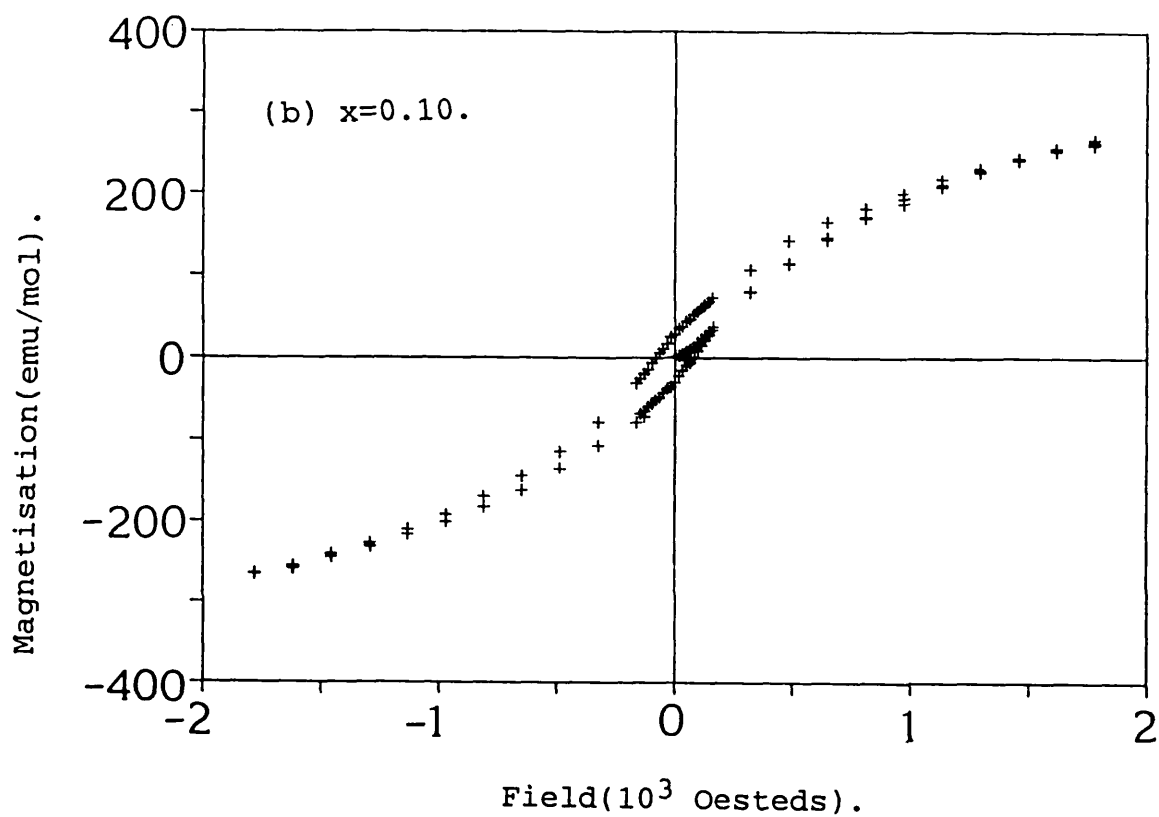
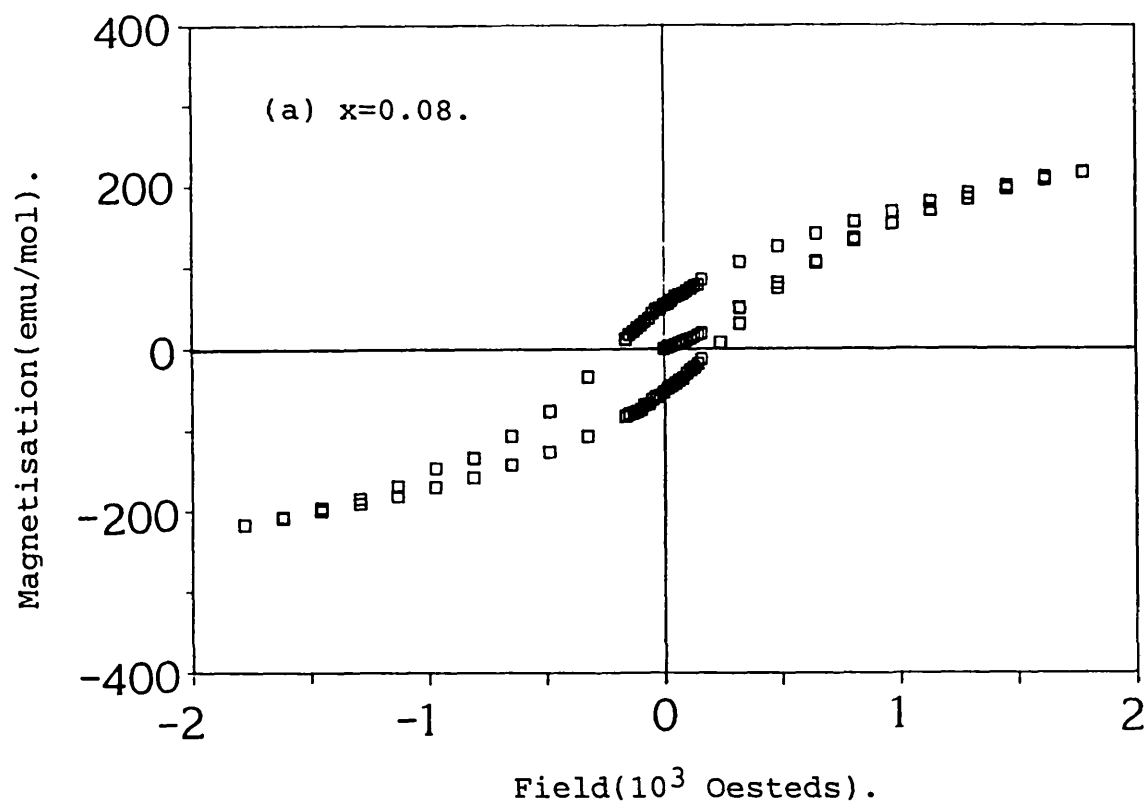


Figure 5:61 (a) and (b). Magnetisation versus field for $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$.

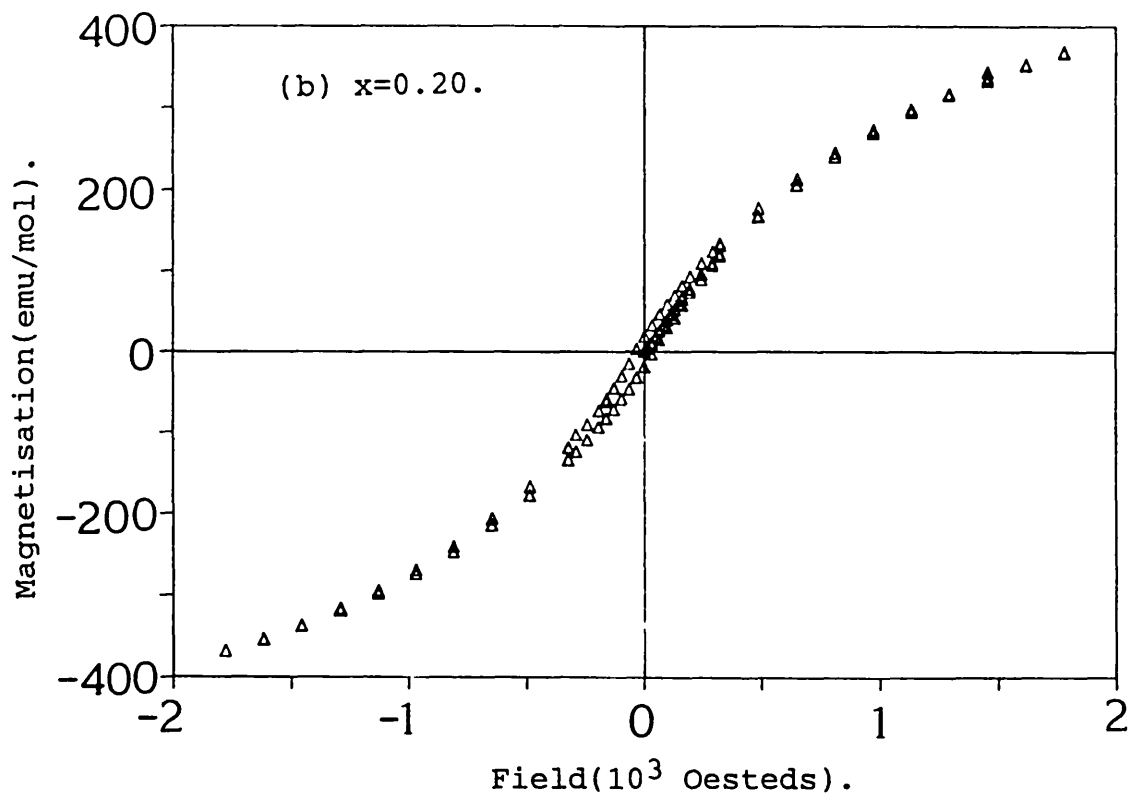
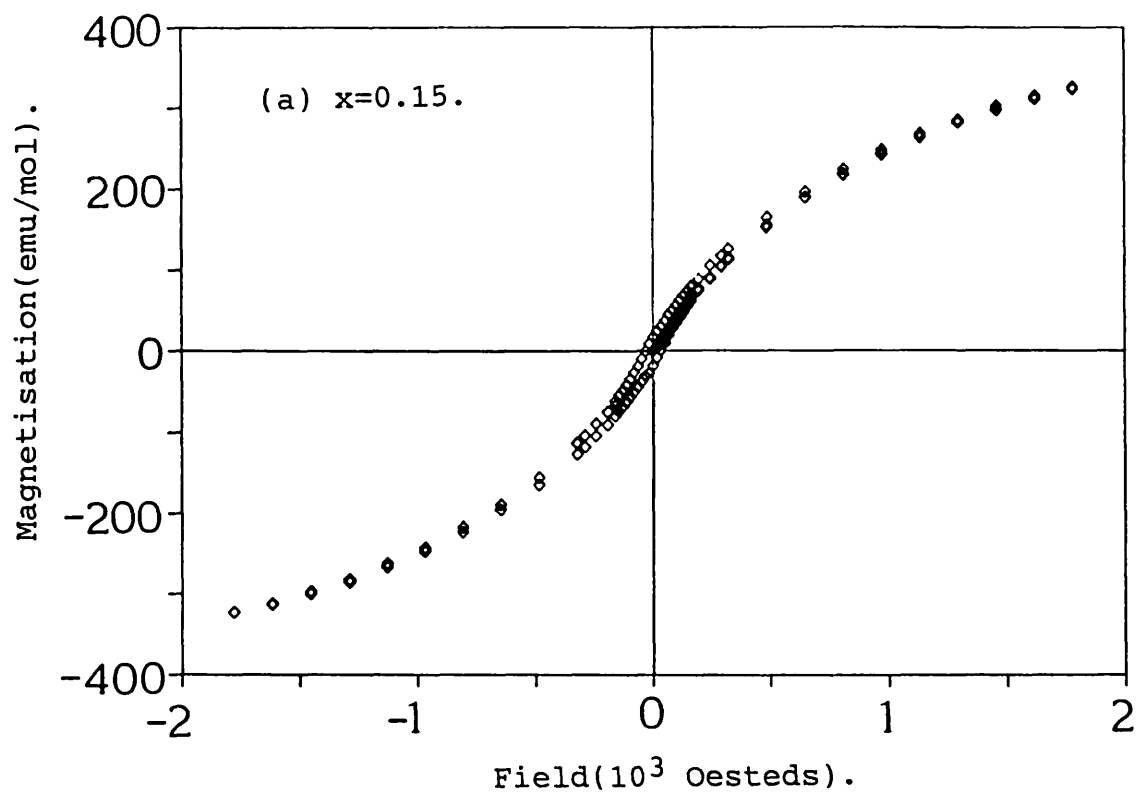


Figure 5:62 (a) and (b). Magnetisation versus field for $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$.

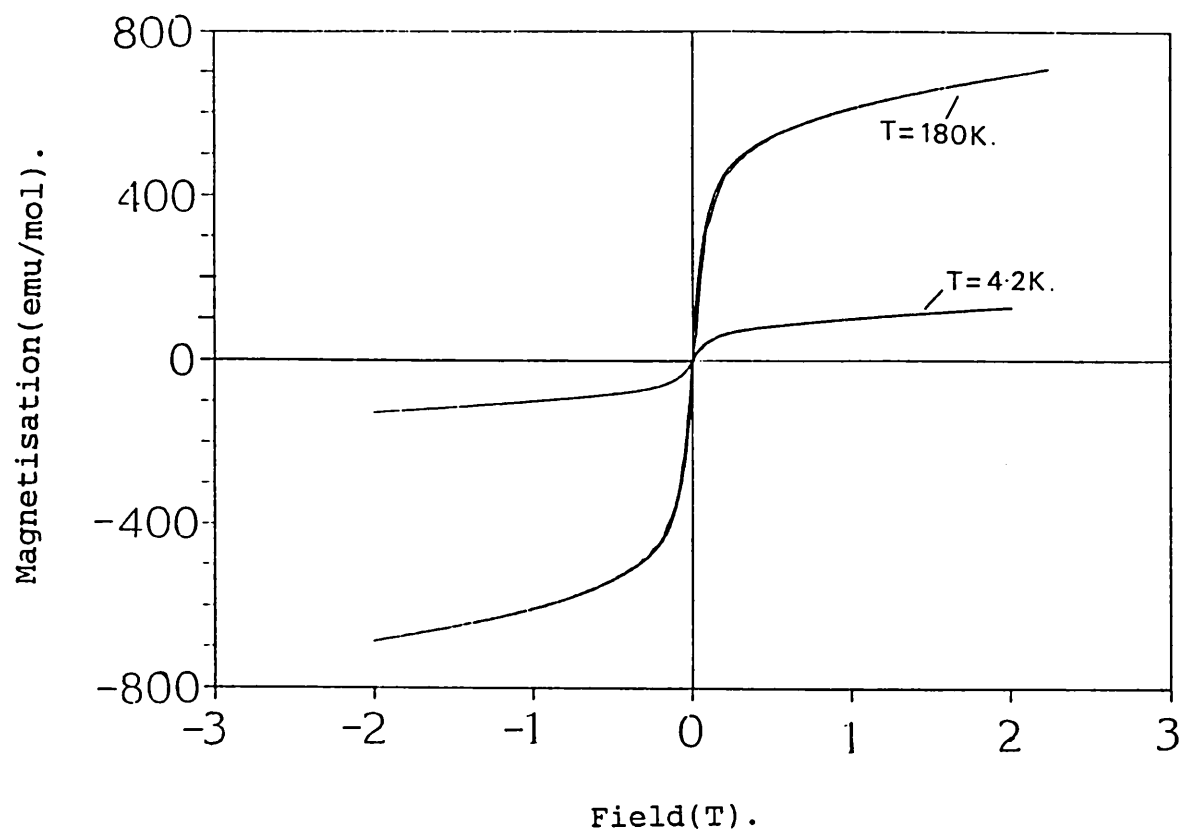


Figure 5:63. (a) Magnetisation versus field for $\text{Ce}(\text{Al}_{0.85}\text{Fe}_{0.15})_2$. Data sweeps taken at 180K and 4.2K.

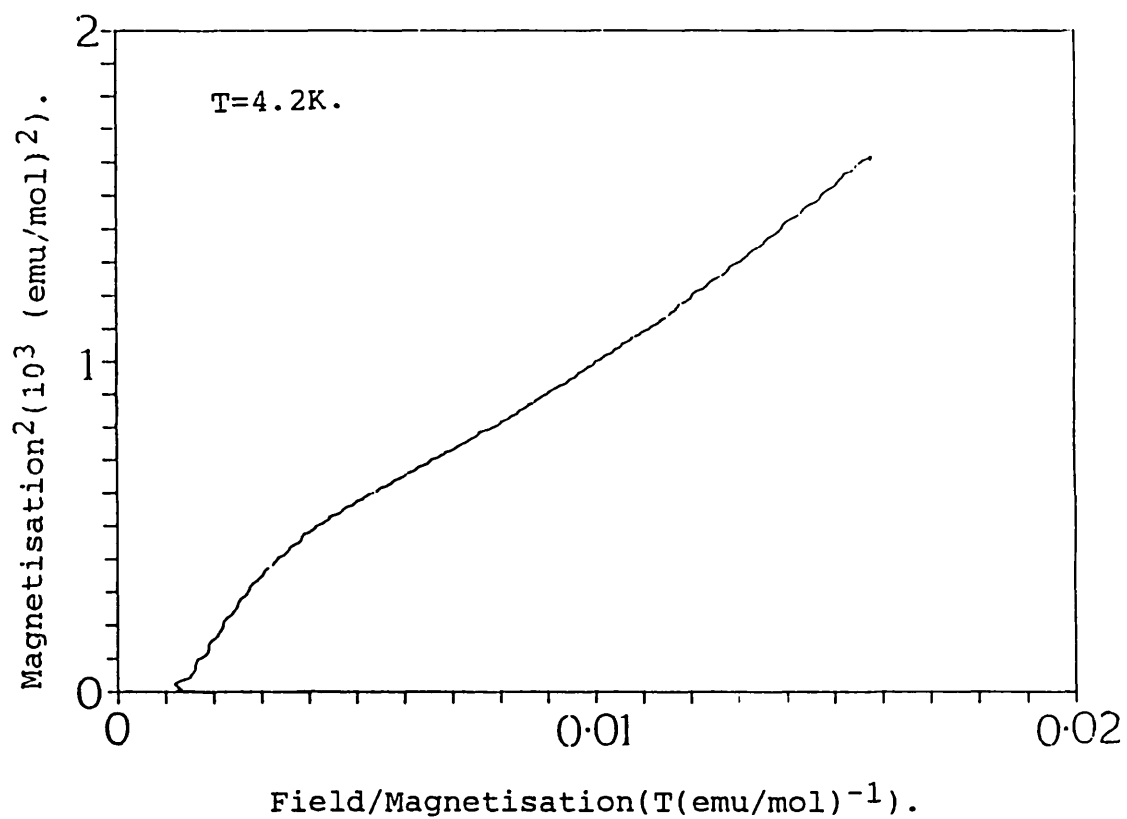
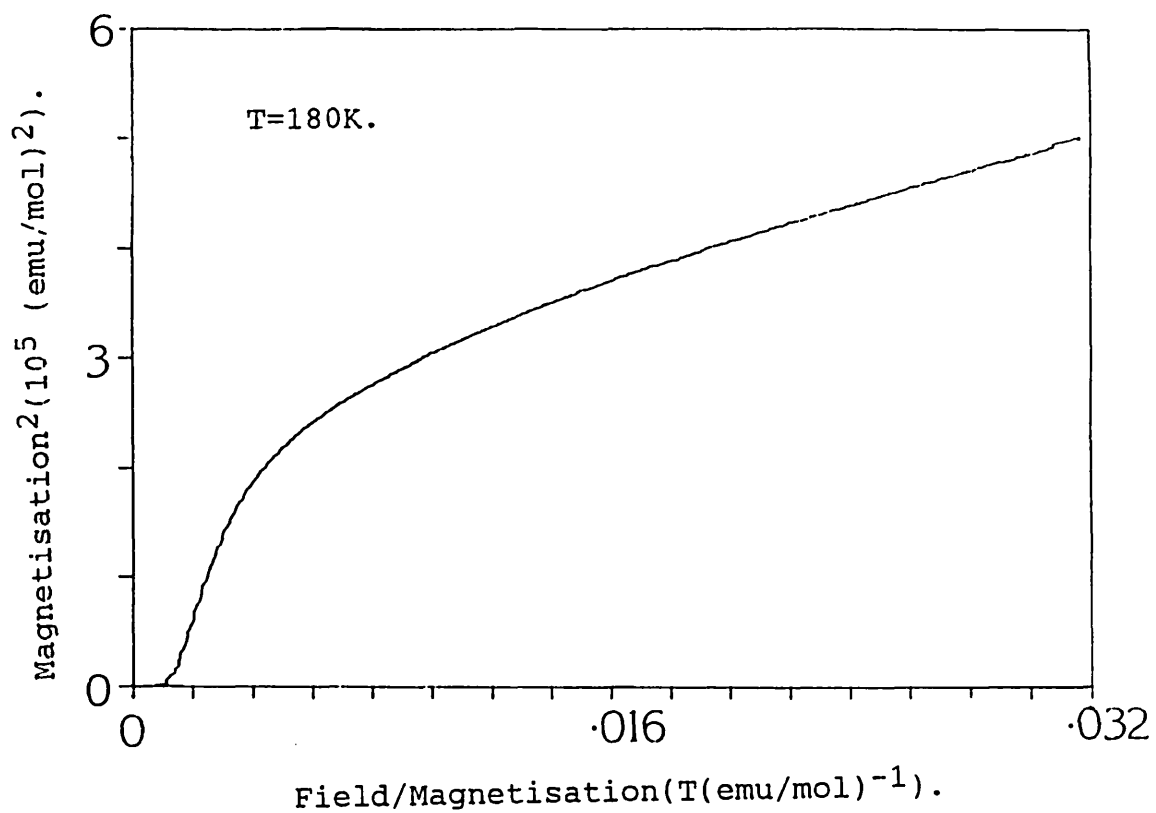


Figure 5:63. (b) and (c). Arrott plots (Magnetisation^2 versus $\text{Field/Magnetisation}$) of the data shown in figure 5:63(a).

2. For $0.04 \leq x \leq 0.05$ Fe no curvature or hysteresis is observed in M v H .

3. For $0.06 \leq x \leq 0.15$ hysteresis is observed in all samples. The coercive field associated with these curves increases to a maximum at $x=0.10$. Beyond this concentration the magnitude of the coercivity decreases with increasing x .

4. High field $M(H)$ curves for the $x=0.15$ sample taken at 180K and 4.2K are shown in figure 5:63. At 180K the magnetisation initially rises sharply with increasing field. Magnetisation reaches 600emu/mol at 1T and then begins to saturate. For the 4.2K curve the magnetisation saturates in much lower field ($\approx 0.3T$) and reaches a value of only 120emu/mol. This data is represented as Arrott plots (M^2 versus M/H) in figure 5:64. Extrapolating high field curves back to zero field show that at 180K long range ferromagnetic order is indicated, whilst at 4.2K the Arrott plot points to short range ordering.

5. For $x \geq 0.30$ M v H data again looks distinctly different. Little curvature is observed but considerable hysteresis is observed.

5:7:8. Resistivity.

Figures 5:64 to 5:67 inclusive show the temperature dependence of the resistivity of the $Ce(Al_{1-x}Fe_x)_2$ system. The behaviour can be divided into 4 distinct regimes.

5:7:8:1. $x \leq 0.06$.

For $x \leq 0.06$ the resistivity shows the same features as pure $CeAl_2$. The absolute value of $\rho(273K)$ increases almost linearly with Fe concentration (see figure 5:68). This is most likely due to an increase in the residual resistivity with greater Fe concentration which produces increases in both structural defects and impurity scattering. At high temperature the resistivity falls with temperature. The distinct knee at approximately 80K associated with a combination of crystal field and Kondo effects and the minimum and upturn in $\rho(T)$ below 16K due to the Kondo effect seen in pure $CeAl_2$ are observed in samples with $x \leq 0.6$. At lower temperature one observes the onset of coherence resulting from a combination of formation of a Kondo lattice

and magnetic order which produces a rapid fall in $\rho(T)$. Addition of small amounts of Fe rapidly reduces the size of this low temperature fall. From susceptibility data it appears that long range magnetic order may persist to around $x=0.04$. Therefore the question of whether the fall in $\rho(T)$ is due to the formation of a Kondo lattice or magnetic order remains unclear.

5:7:8:2. $0.06 < x \leq 0.08$.

For $0.07 \leq x \leq 0.08$ rapid changes in the character in $\rho(T)$ are observed. These appear connected to the changes in $\chi(T)$ discussed in 5:7:6. The low temperature Kondo rise in $\rho(T)$ and the fall below a few Kelvin persist. However, at high temperature the knee in $\rho(T)$ disappears. Examination of the magnetic resistivity reveals that the high temperature peak due to C.F.-Kondo effects is removed. There is a region at high temperature in which ρ_{mag} varies logarithmically with temperature. At first glance one may think this dramatic change in $\rho(T)$ may be due to rapid changes in the nature of the crystal fields. However the observation that the crystal structure remains cubic, together with the smooth changes in lattice parameter makes this unlikely. Initial Fe substitutions suppress coherence producing an increase in magnitude of low temperature resistivity. However a more rapid increase in the magnitude of $\rho(2.2\text{K})$ which begins around 5% Fe is not accompanied by a similar jump in the value of high temperature resistivity, whose increase is almost linear with x . This suggests the appearance of a new scattering mechanism contributing to the value of ρ at low temperature.

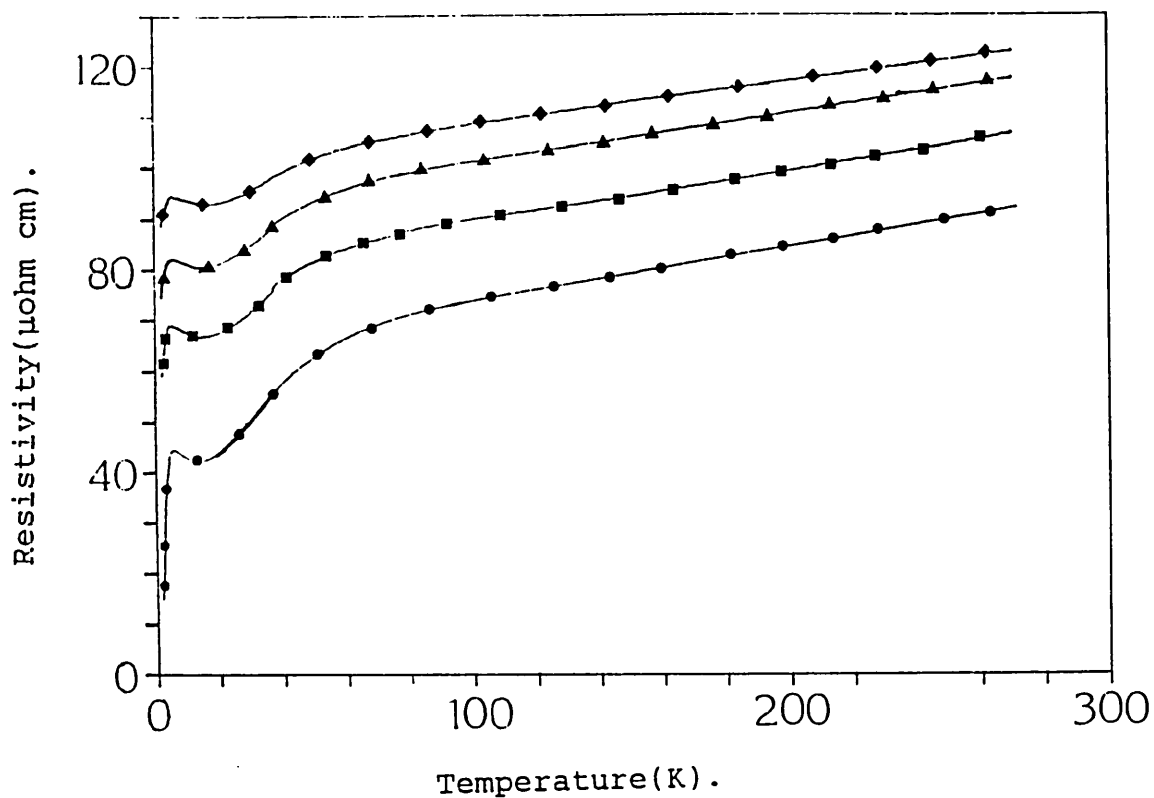


Figure 5:64. Temperature dependence of the electrical resistivity of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ for $x=0.00(\bullet)$, $0.02(\blacksquare)$, $0.04(\blacktriangle)$ and $0.06(\blacklozenge)$.

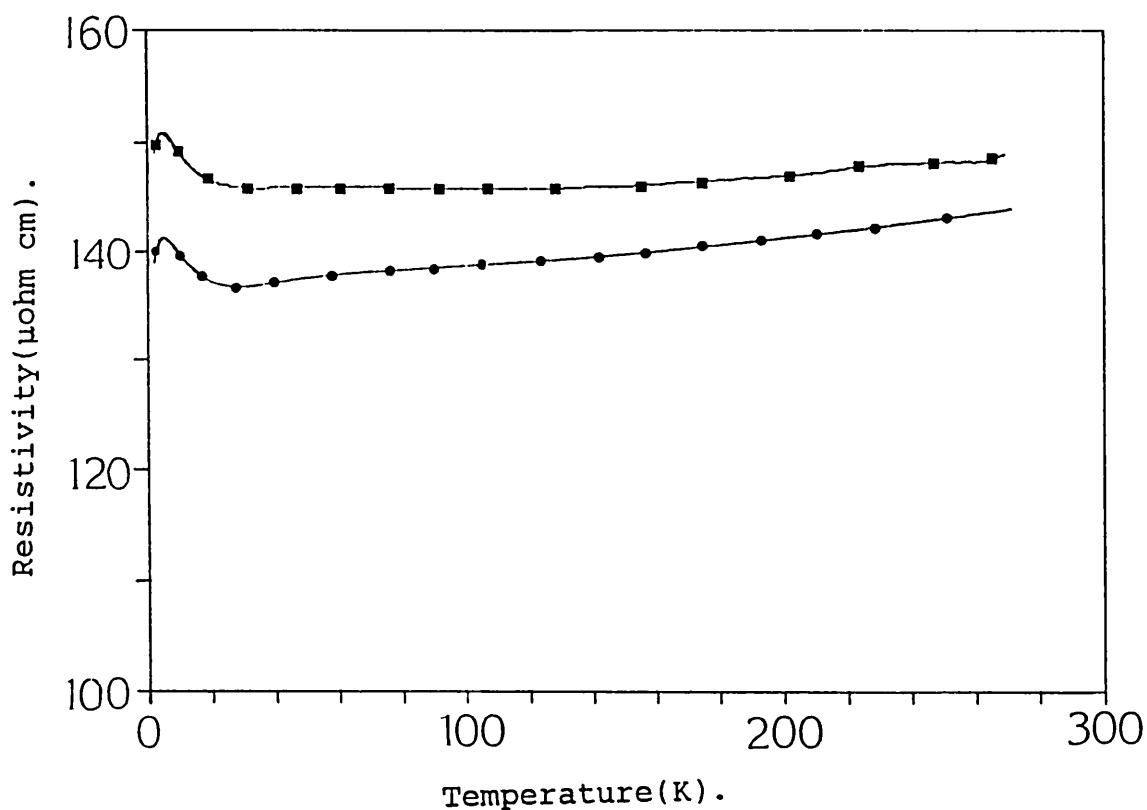


Figure 5:65. Temperature dependence of the electrical resistivity of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ for $x=0.07(\bullet)$ and $0.08(\blacksquare)$.

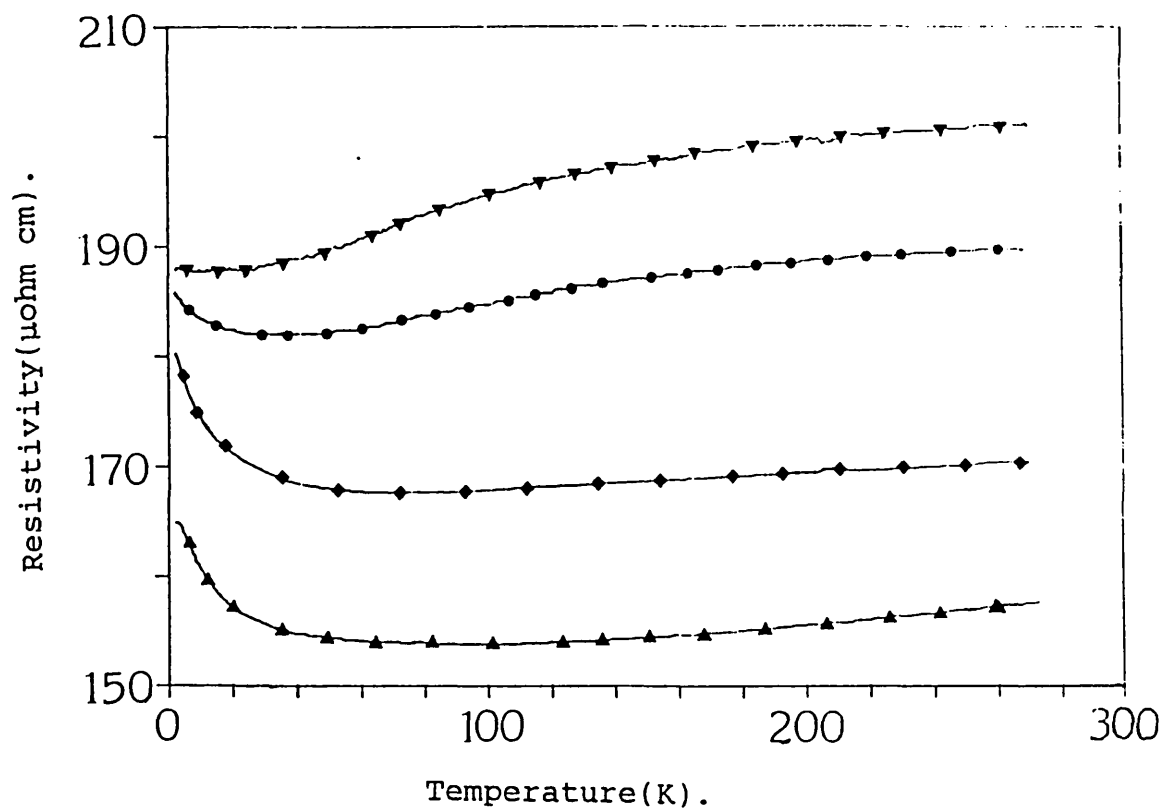


Figure 5:66. Temperature dependence of the electrical resistivity of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ for $x=0.10$ (▲), 0.15 (◆), 0.20 (●) and 0.25 (▼).

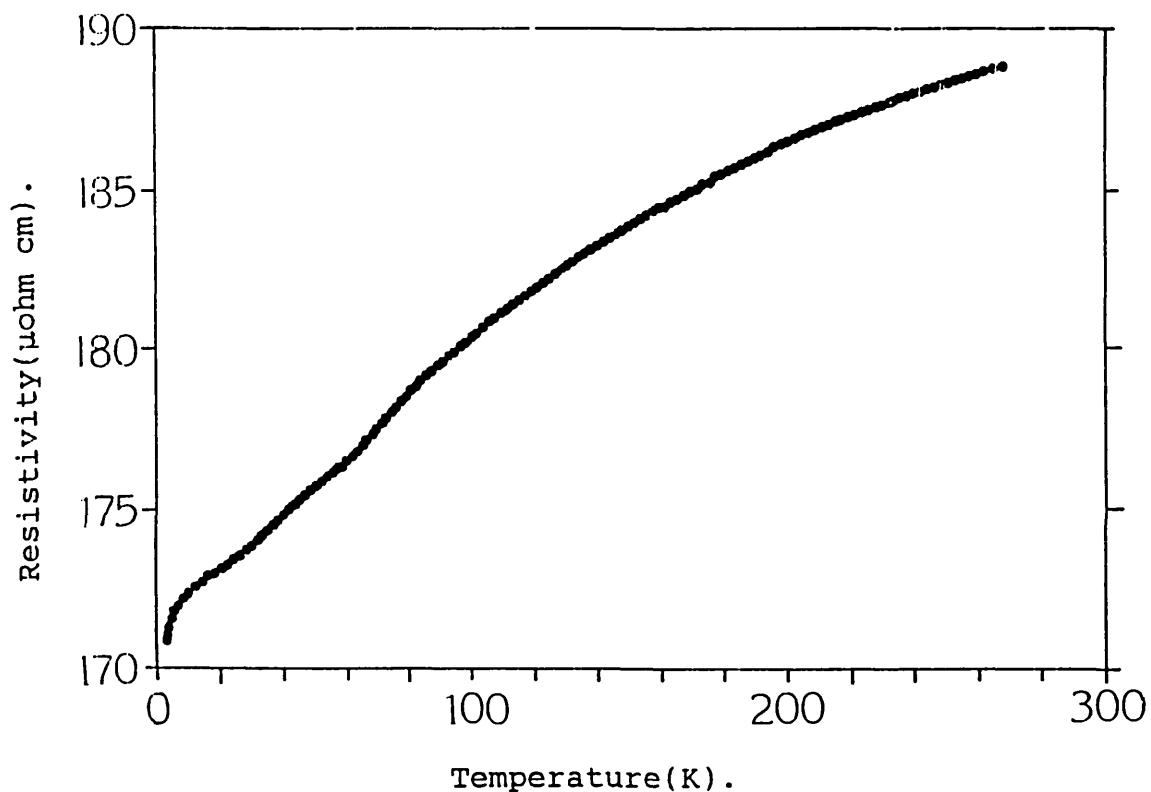


Figure 5:67. Temperature dependence of the electrical resistivity of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ for $x=0.35$.

5:7:8:3. $0.08 < x \leq 0.25$.

For $0.08 < x < 0.15$ the resistivity curves are concave with respect to the temperature axis (i.e. $d\rho/dT$ increases with increasing temperature). For $x=0.15$ the high temperature resistivity is almost linear in temperature, whilst for $0.15 < x \leq 0.25$ the high temperature resistivity is convex ($d\rho/dT$ decreases with temperature). No anomalies are observed at high temperature in the concentration range $0.08 < x \leq 0.25$ at any temperature which can be associated with rapid changes seen in $\chi_{a.c.}$. The temperature at which a minimum in $\rho(T)$ is observed T_{Min} remains at 15K for $x \leq 0.06$ but then increases with increasing Fe concentration reaching a maximum for $x=0.10$ of 100K (see table 5:8). For greater Fe concentrations the minimum decreases in temperature. Comparing the values of T_F (spin freezing temperature) taken from magnetisation measurement with T_{MIN} , it seems the two may be related (see figure 5:69), although T_{MIN} is always smaller than T_F . A more detailed discussion of the origin of this minimum and the sharp jump in $\rho(2.2K)$ will be given later. At lowest temperatures the increase in resistivity $\rho(2.2K)$ with Fe concentration decreases rapidly from the initial value of $d\rho(2.2K)/dx$ of $14.6\mu\text{ohmcm/at\% Fe}$. $\rho(2.2K)$ approaches what appears to be a saturation value of $190\mu\text{ohm cm}$ at $x=0.25$. The resistance ratio ($RR=\rho(273K)/\rho(2.2K)$) falls rapidly with Fe concentration reaching a minimum at $x=0.15$ where the resistivity at 273K is still below the value seen at 2.2K.

5:7:8:4. $0.25 < x \leq 0.50$.

In this concentration region the absolute value of the resistivity at 273K remains high. The resistivity falls steadily with temperature and is relatively featureless. This

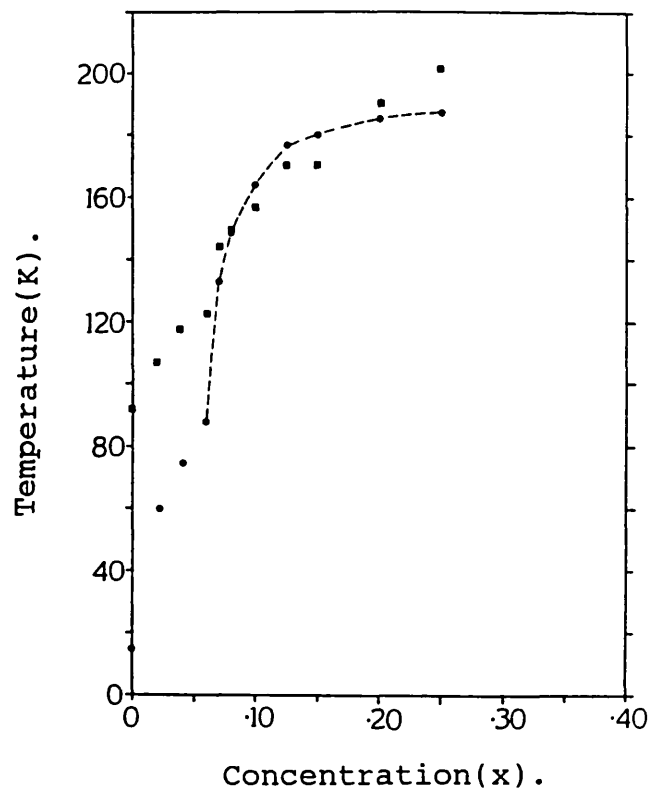


Figure 5:68. Concentration dependence of the magnitude of the electrical resistivity at 2.2K(●) and 273K(■) of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ for $x \leq 0.25$ (N.B. dashed line is only a guide to the eye).

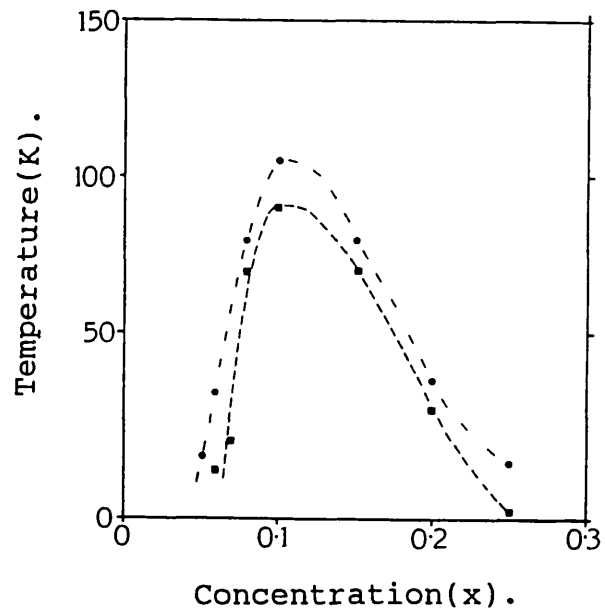


Figure 5:69. Concentration dependence of T_F (●), the magnetic freezing temperature and T_{MIN} (■), the temperature of the minimum in the electrical resistivity (N.B. dashed lines are only guides to the eye).

$\rho(T)$ behaviour reflects the multiphase nature of the samples. No conclusions as to the nature of the magnetic transition seen at approximately 20K indicated by the sharp peak in $\chi(T)$ can be made from this data.

Table 5:7. Parameters extracted from $\rho(T)$ data of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$.

Conc x	ρ_{273K} (μohmcm)	$\rho_{2.2K}$ (μohmcm)	RR	Mag_{coh} (μohmcm)	T_{max} (K)	T_{MIN}
0	92.5	15.0	6.17	30.0	5.9	14.2
2	107.0	59.0	1.81	10.0	5.01	15.5
4	118.0	74.5	1.58	8.0	5.88	15.7
6	123.2	89.0	1.38	6.0	6.42	16.0
7	144.3	133.2	1.09	3.6	5.80	25.0
8	149.5	149.5	1.00	2.8	4.70	100.0
10	157.5	165.0	0.96	0.0	2.66	92.0
15	170.5	177.5	0.95	---	---	70.0
20	190.0	186.5	1.02	---	---	35.0
25	201.2	188.0	1.07	---	---	3.0
30	189.0	171.0	1.105	---	---	----

5:7:9. Discussion.

The data presented in the preceeding section raises several questions. Firstly, what is the origin of the high temperature magnetic transition seen in $\chi_{a.c.}$ and the magnetisation data. The appearance of this ordering with Fe substitution suggests it is certainly due to some kind of interaction between Fe atoms which may be carrying a moment. Further it appears that in the concentration region $0.06 \leq x \leq 0.10$, there is a coexistence of either antiferromagnetic or spin glass ordering between the Ce moments, which is related to the antiferromagnetic ordering seen in pure CeAl_2 at 3.8K, and the high temperature ordering

between the Fe atoms substituted on the Al sites in the lattice. Evidence for ordering between atoms on the Fe-Al sublattice includes:

1. Maximum in $\chi_{a.c.}$ between 60 and 300K.
2. Rapid rise in $M(T)$.
3. Changes in the character of $\rho(T)$.

Data that points towards ordering between Ce atoms like that seen in pure $CeAl_2$ includes:

1. Maximum in $\chi(T)$ between 4.3 and 1.8K.
2. Maximum in $\rho(T)$ between 6.4 and 2.0K.

The maxima in $\chi_{a.c.}(T)$ and $\rho(T)$ are not clear evidence of antiferromagnetic ordering (remember in pure $CeAl_2$ a maximum in susceptibility and resistivity occur before the actual transition). However the sharp cusp in $\chi_{a.c.}$ is strong evidence for spin glass ordering, for example see $x=0.08$ in figure 5:52. In order to confirm the presence of two transitions at the same Fe concentration it will be necessary to determine unequivocally that ordering at low temperature does occur. Specific heat measurements could be expected to provide good evidence of antiferromagnetic ordering. However if spin glass freezing takes place as seems more likely from susceptibility data, one can expect specific heat data will be inconclusive [5:59]. To this end neutron studies on a $Ce(Al_{0.94}Fe_{0.06})_2$ sample will be carried out. It is hoped this technique will be able to determine whether magnetic transitions occur at both high and low temperature and if this is the case, will reveal the nature of the two transitions. If as seems likely the rapid changes in $\chi_{a.c.}(T)$, $M(T)$ and $\rho(T)$ are the result of ordering between the Fe atoms, the next question which must be addressed is,

what is the mechanism which brings about such Fe-Fe interactions. In the case of $Y(Al_{1-x}Fe_x)_2$ and $Zr(Al_{1-x}Fe_x)_2$ systems no long range or spin glass ordering is observed for $x \leq 0.60$ in the former and $x \leq 0.45$ in the latter case. The mechanisms leading to ordering are discussed in 5:7:1, and are ineffective at high Al concentration levels in these systems. Yet in the $Ce(Al-Fe)_2$ system (with lattice parameters greater than in either the Y or Zr systems) some interaction mechanism is effective with as little as 6% Fe. Clearly the presence of the Ce lattice creates conditions in which longer range Fe-Fe interactions become possible. Several systems in which the host matrix provides conditions which allow long range ordering between Fe atoms at concentrations well before Fe-Fe interactions can be expected to arise from nearest neighbour interactions are known. For example PdFe. Pure Pd is a nearly ferromagnetic metal [5:60] sometimes called an incipient ferromagnet. It has a very high paramagnetic susceptibility at low temperature and is easily polarized (i.e. magnetised). For Pd the susceptibility is given by

$$\chi = 2\mu_B^2 N(E_F) / (1 - UN(E_F)) \text{ ----- 5:7.}$$

where the Stoner enhancement factor

$S = (1 - UN(E_F))^{-1}$ is due to intra-atomic Coulomb interaction U between electrons in the same unit cell. For Pd $S \approx 10$. Addition of small amounts of particular elements (Fe, Co, Ni) can lead to ferromagnetism. This behaviour can be explained in term of a local moment model. When an Fe atom is dissolved in Pd it has a magnetic moment which polarizes the local Pd environment by exchange interaction. The total moment associated with the Fe atom is much larger than that

expected from the electronic arrangement in its outer shells. The effective moment in the alloy is of the order of $11\mu_B$. About $3\mu_B$ comes from unpaired spins on the impurity. The rest is made up from ferromagnetically aligned Pd moments each of about $0.05\mu_B$ in the vicinity of the Fe atom. This produces a giant moment consisting of hundreds of Pd atoms with polarized d electrons rigidly coupled to the Fe moment. As the number of Fe atoms is increased, these giant moments can overlap leading to an interaction producing ferromagnetism. An alternative description suggests that the Fe atoms enhance the already large exchange effects in the narrow Pd 4d band leading to a greater splitting of the band. This leads to the appearance of band ferromagnetism. Whichever model is correct we can see that it is conditions within the Pd matrix which allows the emergence of ferromagnetic ordering.

Although it is not suggested that exactly the same mechanism is at work in Al rich $\text{Ce}(\text{Al-Fe})_2$ system, it does seem that the ordering does involve more complicated behaviour than simply nearest neighbour Fe-Fe interactions, and that the Ce sublattice may play an important role. Further evidence to support such an idea was sought. One way to investigate the role the Ce atoms play in the ordering mechanism, is to examine the effects on the ordering of a gradual replacement of the Ce with some non-magnetic material. To this end, several ternary compounds with the composition $\text{Ce}_{1-z}\text{Y}_z(\text{Al}_{0.90}\text{Fe}_{0.10})_2$ were prepared. The magnetic susceptibility versus temperature data for selected samples are shown in figure 5:70. Problems arose in preparing single phase samples with Y concentrations greater than 50%. Metallographic specimens of all compositions were prepared.

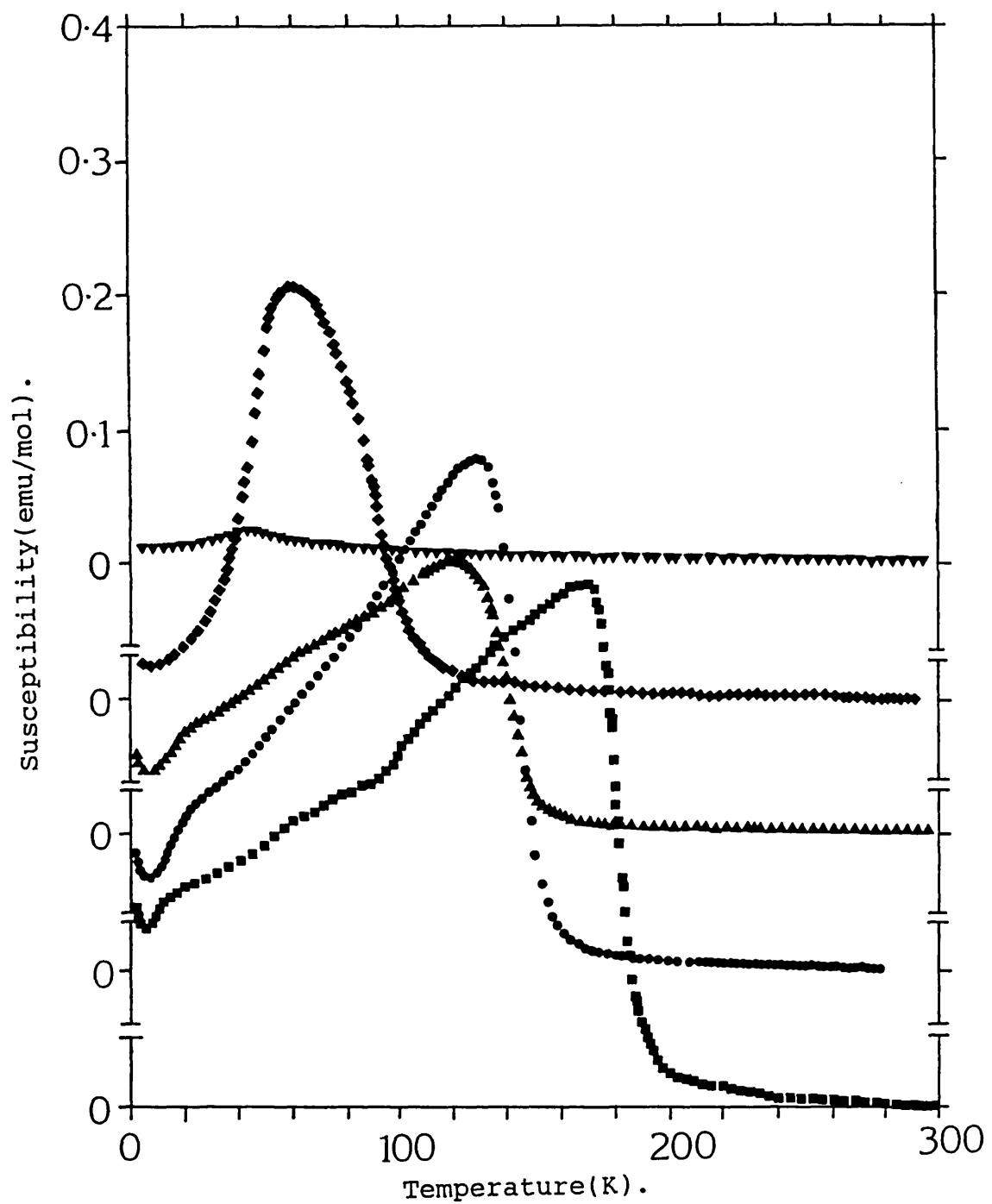


Figure 5:70. Magnetic susceptibility versus temperature for selected $\text{Ce}_{1-z}\text{Y}_z(\text{Al}_{0.90}\text{Fe}_{0.10})_2$ alloys, where $z=0.00$ (■), 0.10 (●), 0.20 (▲), 0.30 (◆) and 0.50 (▼).

These showed that for $z \leq 0.50$ the samples were essentially single phase with only a small amount of oxide contamination. However for $z > 0.50$ all the samples were two phase. Susceptibility measurements of these samples all showed a peak at around 40K, even $Y(Al_{0.90}Fe_{0.10})_2$ which several authors [5:47] have reported as undergoing no magnetic order of any kind down to 1.5K. It is still unclear why such problems arose. In preparing the samples, the Fe and Al was melted together first before adding the Ce and Y. Several samples were also remade slightly off stoichiometry. The samples were annealed for 1 week at temperatures of up to 850°C, 50°C higher than the temperature reported to produce single phase samples. Some of the samples were then quenched in water, whilst others were furnace cooled. We were still unable to eliminate the second phase. As a result of these problems which have yet to be surmounted only the data for $z \leq 0.50$ together with the data due to Hilscher of a $Y(Al_{0.90}Fe_{0.10})_2$ are considered. Examining this data shows that for $z \leq 0.20$ the ordering temperature is rapidly reduced, but the general behaviour of χ with temperature is the same as that of $Ce(Al_{0.90}Fe_{0.10})_2$. For $x=0.30$ the ordering temperature is still further reduced with the shape of $\chi_{a.c.}$ reminiscent of the peak seen in $Ce(Al_{1-x}Fe_x)_2$ with $x=0.06$. In this case it is suggested that magnetic ordering is preceded at lower temperature almost immediately by some kind of magnetic freezing. For $z=0.50$ the peak in $\chi(T)$ is suggestive of spin glass ordering. Extrapolating the ordering temperatures to 0K suggests that magnetic ordering should disappear somewhere around $z=0.60$ (see figure 5:71). It is clear from this data that the Ce is playing an important

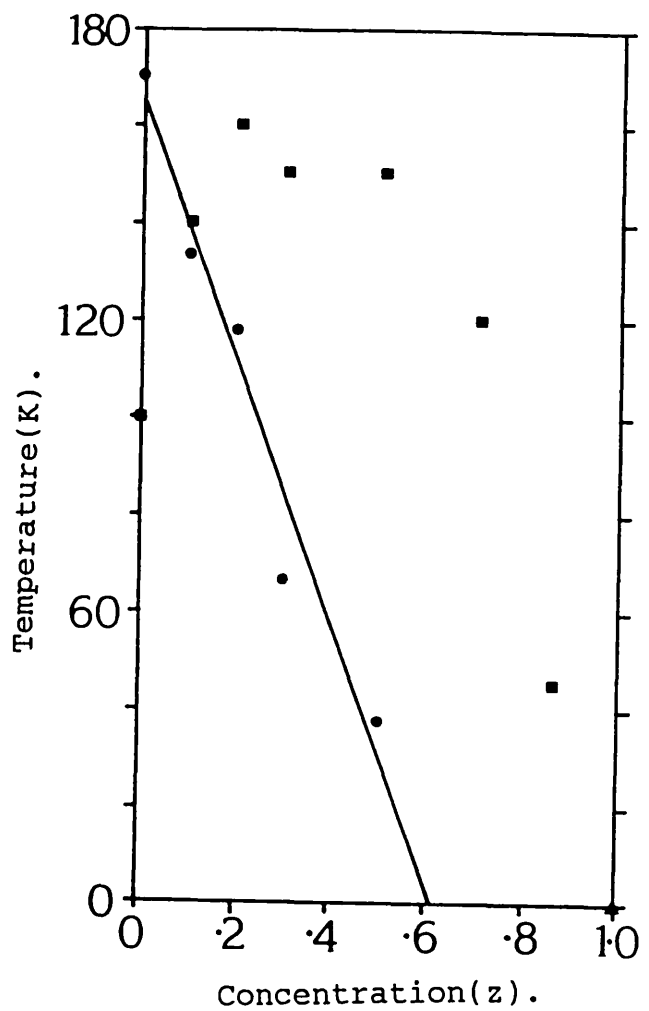


Figure 5:71. Concentration dependence of the temperature of the maximum in the magnetic susceptibility ((●) this work, (▲) Hilscher et al [5:47] of some $\text{Ce}_{1-z}\text{Y}_z(\text{Al}_{0.90}\text{Fe}_{0.10})_2$ alloys. The solid line is a least squares fit to the data points, indicating that the magnetic ordering should be removed completely around $z=0.60$. Also shown is the concentration dependence of the temperature of the minimum in the electrical resistivity (■) of selected $\text{Ce}_{1-z}\text{Y}_z(\text{Al}_{0.90}\text{Fe}_{0.10})_2$ alloys.

role. The presence of ferromagnetic and antiferromagnetic interactions is indicated by the observation of magnetic clustering or spin glass freezing (see below), due to frustration. It seems that exchange between Fe atoms is through the conduction electrons by the RKKY interaction, which is both long range and can lead to coupling of both signs. It may be that the strong s-f hybridisation between Ce 4f shell and the conduction electrons, bootstraps a magnetisation on the Ce atoms themselves and (perhaps antiparallel) leads to a magnetisation on the Fe atoms, which in pure YAl_2 or ZrAl_2 are non-magnetic VBS. Now turn to the question, what is the nature of the magnetic ordering. The emergence of high temperature magnetic ordering in this system is very reminiscent of systems such as AuFe and it seems natural to look to these systems for guidance in interpreting the data presented earlier. The AuFe system has been extensively studied by many workers [5:61 to 5:64]. A magnetic phase diagram for up to 25% Fe is shown in figure 5:72. At low Fe concentrations there is a competition between the Kondo effect and RKKY interactions. But by 0.5% Fe the alloys show a characteristic spin glass cusp in their low field susceptibilities, the temperature of which increases systematically with Fe concentration. This is due to good local moments in the 3d VBS of the solute atoms coupled through the host conduction electrons by the oscillatory RKKY interaction. A combination of ferromagnetic and antiferromagnetic couplings leads to frustration and the onset of spin glass ordering. Above 8% Fe (but less than 15%) the alloys show a rather rounded susceptibility maximum at a temperature which is only a weak function of Fe concentration

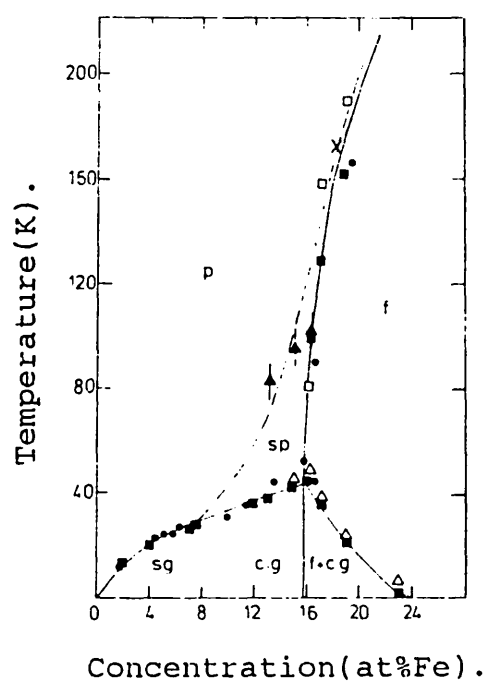


Figure 5:72. Magnetic phase diagram of AuFe solid solutions.
 (●): Mossbauer anomalies; (■): Susceptibility anomalies
 (above 15%, upper points Curie temperatures, lower points T_F ;
 (□): critical peaks in neutron scattering; (X): specific heat
 peak; (△): peak in magnetic resonance line width; (▲):
 minimum in magnetic resonance linewidth; p: paramagnetic; sp:
 superparamagnetic; sg: spin-glass; cg: cluster-glass;
 f: ferromagnetic.

and differs significantly from the observed paramagnetic Curie temperature $\Theta_{C.W.}$. This behaviour is attributed to a proportion of the Fe moments coupling in finite nearest neighbour clusters. Thus the objects freezing at the peak in $\chi(T)$ are clusters of moments. Large paramagnetic Curie temperatures observed in this regime suggest strong ferromagnetic nearest neighbour couplings. The region between $\Theta_{C.W.}$ and T_F is known as the superparamagnetic region. The freezing temperature of these clusters continues to rise smoothly with Fe concentration from that of the more dilute spin glasses. The size of these clusters grows with increasing Fe content until at the percolation limit of $15.5 \pm 0.3\%$ Fe an infinite cluster forms. Above the percolation concentration the alloys show good ferromagnetic response close to the paramagnetic Curie temperature. However the freezing of the finite clusters still takes place, leading to a diminished signal at low temperature. The temperatures at which this freezing occurs and the reduction in signal falls with Fe concentration as the proportion of the Fe moments in such clusters decreases, until above 24% Fe good ferromagnetism is observed. The susceptibility is then characterized by the well defined onset of a very large (demagnetisation limited) response with no fall in signal at lower temperature. There are many parallels between AuFe and the current system under study. In both cases magnetic ordering emerges at low Fe concentration with spin glass behaviour reflected in a cusp in $\chi(T)$. However, unlike AuFe there appears to be only a very narrow concentration range $0.04 < x < 0.06$ in which spin glass freezing takes place. Above this concentration $\chi(T)$ has a rounded maximum with the

freezing temperature taken from the magnetisation versus temperature data occurring at the peak. This strongly suggests cluster glass behaviour, with small groups of Fe atoms coupled directly, with these groups coupled indirectly via the RKKY interaction. Since there is a spread of cluster sizes the freezing transition is less pronounced and more rounded. Above 6% Fe the situation becomes less clear. The large difference between the paramagnetic Curie temperature and the magnetic freezing temperatures may indicate the onset of superparamagnetic behaviour at the temperature at which a rapid increase in $\chi(T)$ is observed, followed by cluster glass freezing at the lower temperature indicated by Z.F.C.-F.C. behaviour in $M(T)$. However if this is the case it is not clear why a sharper single cusp is not seen in $\chi(T)$ at the freezing temperature. It is more likely that the sharp rise in $\chi(T)$ signals the formation of an infinite cluster of moments giving rise to the onset of long range ferromagnetic order. The $\chi_{a.c.}$ response is not as large as those of many "good" ferromagnets. Some of this reduction may be explained by the shape of the samples (relatively short, thick sticks as opposed to the ideal of long thin specimens). In this concentration region many finite clusters which contain large numbers of Fe moments must coexist with the infinite cluster. These resemble the clusters in the $x=0.06$ pre-percolation concentration range. At temperatures immediately below " T_C " these clusters are able to respond fairly freely to applied fields. Thus at 180K the $M(H)$ curve of the $x=0.15$ sample resembles that of a good ferromagnet. At lower temperature the reduction in susceptibility response and the shape of the $M(H)$ curve could be due domain wall pinning observed in many

straightforward ferromagnetic systems. This pinning can arise from a variety of sources, e.g. the onset of some type of anisotropy. The motion of domain walls is more difficult, and leads to a lower initial susceptibility. An alternative explanation of the low temperature anomaly in $\chi(T)$ could be that as the temperature is lowered strengthening of antiferromagnetic interactions lead to a spin canting (as in $\text{Ce}(\text{Fe}_{1-x}\text{Ru}_x)_2$ [5:64]. It seems most likely that the low temperature behaviour can be explained in terms of the formation of a reentrant spin glass phase or a phase in which clusters and long range order coexist. At T_C an infinite magnetic cluster coexists with many finite clusters. As the temperature is lowered these finite clusters will freeze. The coupling between these clusters which below the percolation limit leads to the formation of a cluster glass, must also be present above the percolation limit. As well as interacting with one another it is reasonable to assume they will also interact with the infinite cluster. Thus at low temperature the freezing of the finite clusters constrains not only their response to a magnetic field, but also that of the the infinite cluster. Since it is the infinite cluster which is responsible for much of the magnetisation, it seems reasonable to expect a reduced magnetic response. As the Fe concentration is increased, the finite clusters are increasingly incorporated into the infinite cluster, whilst the surviving clusters become smaller. This is reflected in a fall in freezing temperature at higher Fe concentrations In order to decide definitely on the nature of the magnetic ordering, it will be necessary to determine unambiguously whether or not "good" long range order is present in these

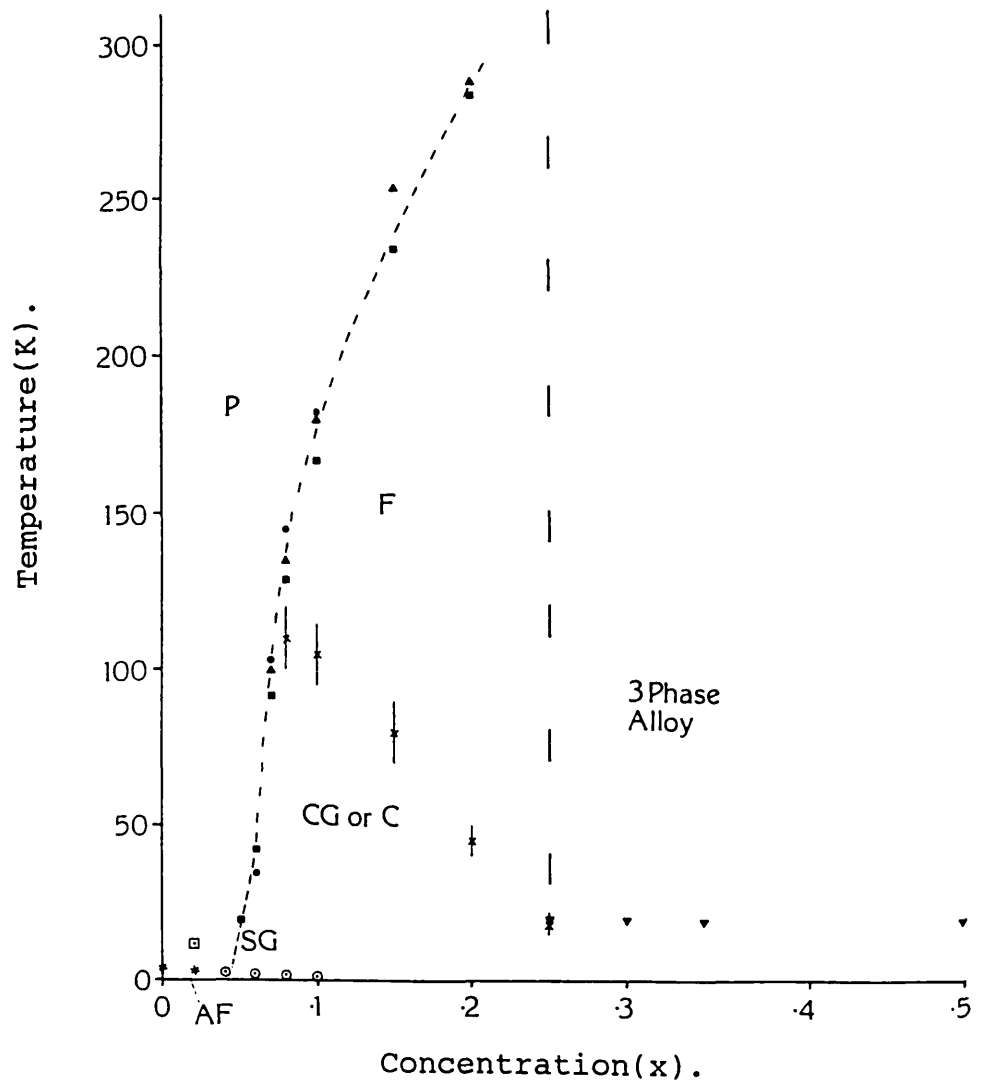


Figure 5:73. Magnetic phase diagram of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ for $x \leq 0.50$. (■), (○), (▼) and (□): susceptibility peaks; (▲) and (*): susceptibility inflexion points; (●) paramagnetic Curie temperature; (X): T_F freezing temperatures taken from magnetisation data; P: paramagnetic; SG: spin glass; CG: cluster glass; C: canting; F: ferromagnetic; AF: antiferromagnet. The concentration region in which the samples are made up of three phases is also indicated.

samples. To this end neutron scattering experiments will be performed on a $\text{Ce}(\text{Al}_{0.85}\text{Fe}_{0.15})_2$ sample. Until these results are available, the nature of the magnetic ordering remains a matter for speculation and the magnetic phase diagram shown in figure 5:73 must be regarded as speculative. Finally it must be noted that in the AuFe system as well as several other dilute magnetic alloys, which have a spin or cluster glass phase at low temperature, one observes a distinctly different resistivity versus temperature dependence from that observed in the $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ system. In the former the resistivity falls at high temperature as the temperature is reduced due to a reduction in phonon scattering. At lower temperatures spin fluctuations (e.g. the Kondo effect) associated with impurities leads to a rise in resistivity similar to that seen in very dilute Kondo systems. A maximum in the low temperature resistivity then appears as a result of a competition between the Kondo effect and spin glass ordering via the RKKY interaction. The temperature at which the maximum occurs T_{MAX} can be greater or less than T_F the freezing temperature deduced from susceptibility measurements. In contrast to this we have seen in section 5:7:8 that a resistivity minimum apparently associated with the Fe-Fe interactions occurs for $0.05 \leq x \leq 0.25$. There are several systems which show resistivity minima at low temperature (see figure 5:74). Examples include:

1. Very dilute systems such as $\text{Au}_{5\text{ppmFe}}$, $\text{Cu}_{110\text{ppmFe}}$, $\text{Y}_{0.995}\text{Ce}_{0.005}$. This resistivity behaviour can be understood as being due to the sum of two components, a negative slope impurity spin scattering resistivity with a characteristic temperature T_K and a positive slope phonon resistivity from the host matrix. This results in the well known Kondo minimum followed at lower temperature by a logarithmic temperature dependence.

2. Resistivity minima have been observed in the CuNi system [1:1,5:66]. Below 10% Ni $\rho(T)$ behaves as a normal metal. Above 45% Ni long range ferromagnetic order sets in producing a knee in $\rho(T)$ at T_C . In the concentration range $0.30 < x < 0.45$ sandwiched between the para and ferromagnetic regimes, one observes a high temperature minimum in $\rho(T)$. This has been attributed to [1:1] the presence of magnetic or nearly magnetic Ni clusters. These giant magnetic polarization clouds exist into the paramagnetic composition range. Thus the character of $\rho(T)$ between 200 and 600K can be interpreted as being due to sum of two contributions. A phonon scattering term which increases with increasing temperature and a spin disorder scattering term from local moment clouds which decreases with increasing temperature.

3. It was suggested by Murani [5:67] and Edwards et al. [5:68] that the minimum observed in $\text{Pd}_{1-x}\text{Au}_x$ and $\text{Pd}_{1-x}\text{Ag}_x$ systems could be understood on the basis of localized d states associated with statistical clusters of Pd atoms. Consider $\text{Pd}_{1-x}\text{Ag}_x$. For Ag rich alloys the Pd d states are supposed localized on the Pd sites and lie at energies below the Fermi level but above the Ag d band. This results in Wolff type scattering [1:1 p. 349]. and ρ increases with temperature. As the Pd concentration is increased the Pd d levels are broadened due to their mutual interaction with neighbouring Pd atoms and lie closer to E_F . At approximately $x=0.50$ Pd d state holes emerge at the Fermi surface and with increased Pd concentration an itinerant Pd d band is formed. In disordered $\text{Pd}_{1-x}\text{Ag}_x$ alloys there will be a statistical variation in the Pd concentration. In regions where the Pd concentration is greater than the nominal concentration, it was proposed that spatially localized "pockets of holes" will appear at the Fermi level. It was suggested that the phase shifts associated with these localized pockets of holes (i.e. conduction electrons scattered by localized spin fluctuations) lead to the observed minimum in the resistivity. At higher Pd concentrations the pockets of holes broaden, and lose their localized character to form a band, and the minimum disappears. This results in a variation in the depth of the minimum shown in figure 5:74.

4. In several systems, a minimum in $\rho(T)$ appears close to the temperature at which magnetic susceptibility reveals spin glass behaviour. For example in the case of RhFe [5:69] the freezing temperature T_F and the temperature of the minimum T_{MIN} increase with Fe concentration. At 25% Fe $T_{\text{MIN}} \approx 33\text{K}$ whilst $T_F \approx 35\text{K}$. No true long range order is observed at this concentration. Data [5:70] for the PtMn system shows that increasing the Mn concentration leads to an increase in T_F . The value of T_{MIN} is greater than T_F for low Mn concentrations (e.g. 5.4% Mn $T_F=7\text{K}$, $T_{\text{MIN}}=10\text{K}$) whilst for higher concentrations T_F is greater than T_{MIN} (12% Mn $T_F=20\text{K}$, $T_{\text{MIN}}=12\text{K}$). Again no long range order is observed in this system. The appearance of minimum in this system around the freezing temperature can be derived from the general theory of resistivity of spin glass systems due to Rivier [5:71]. For other systems, a minimum occurs around the same temperature as magnetic freezing where the onset of magnetic freezing either precedes long range magnetic order at higher

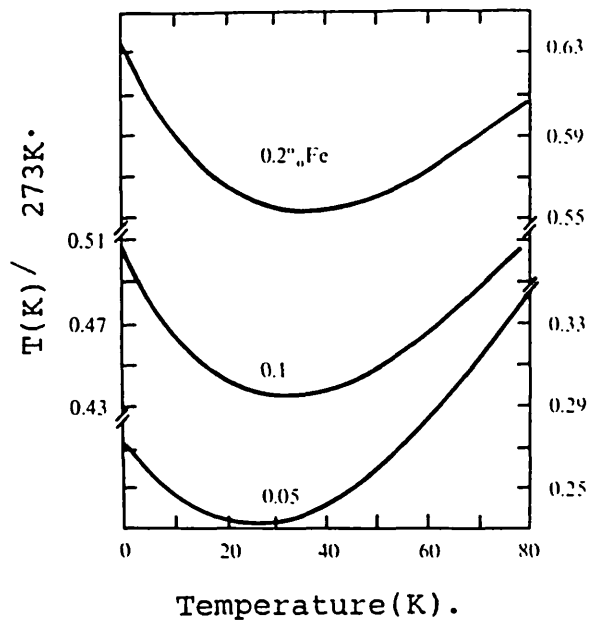
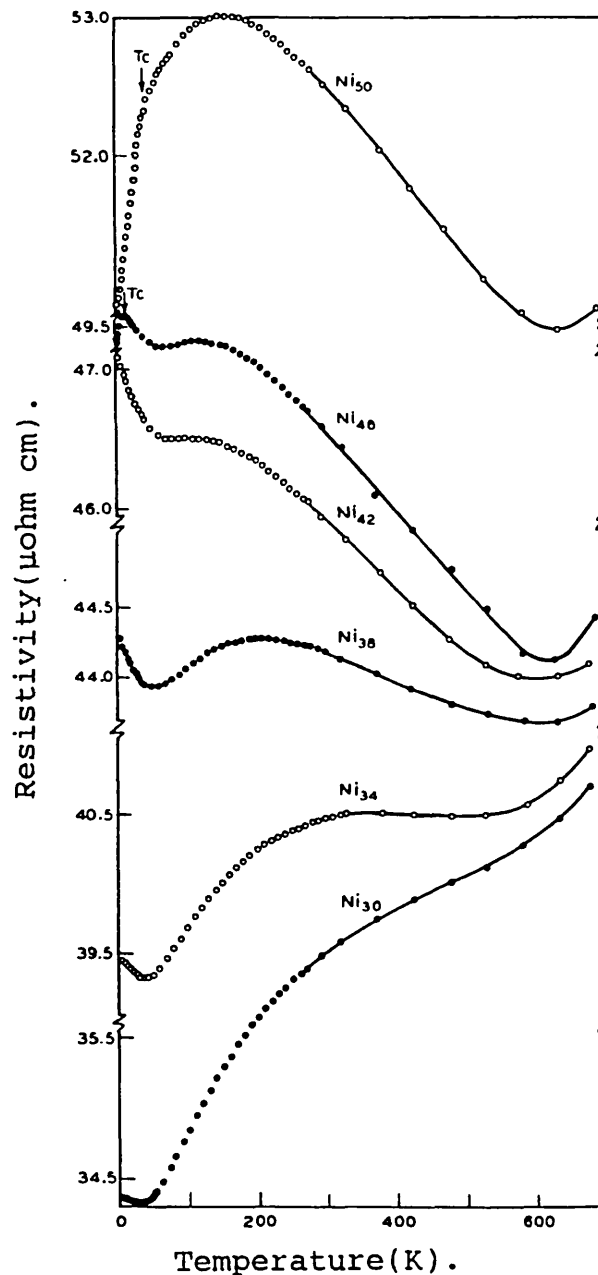
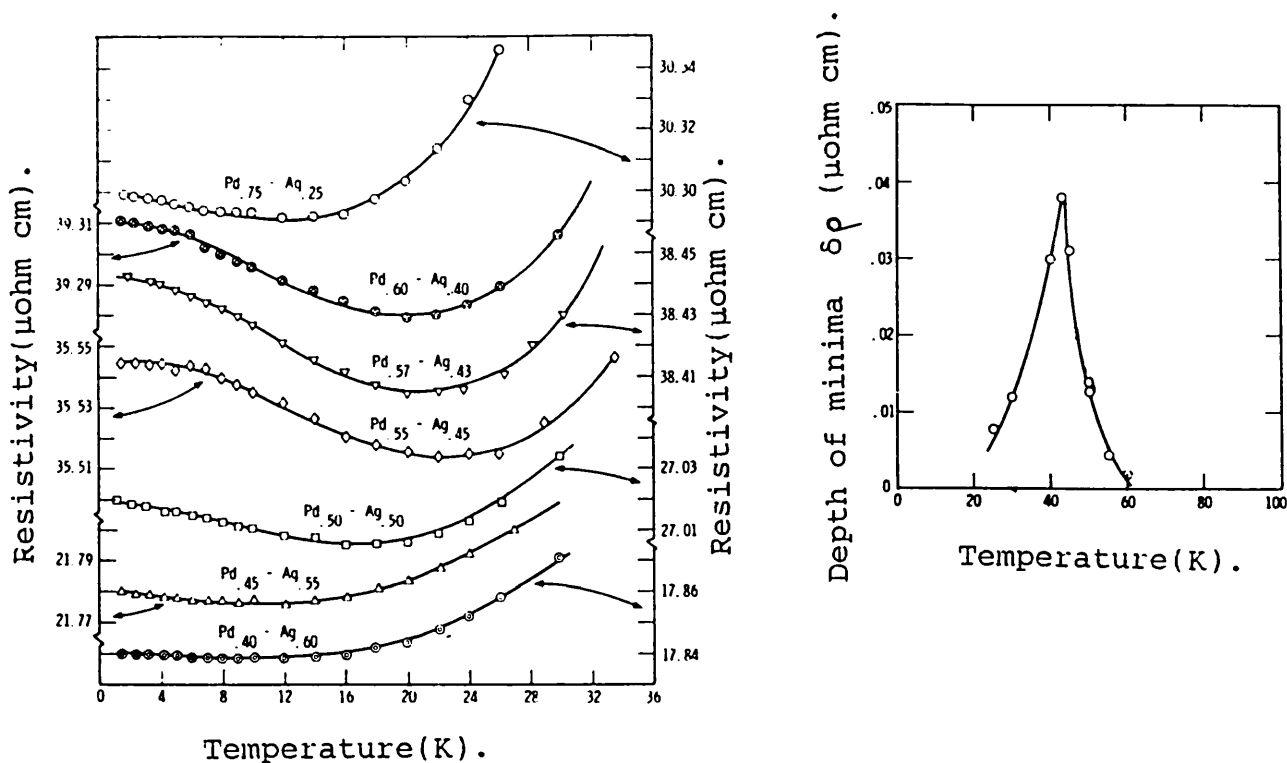


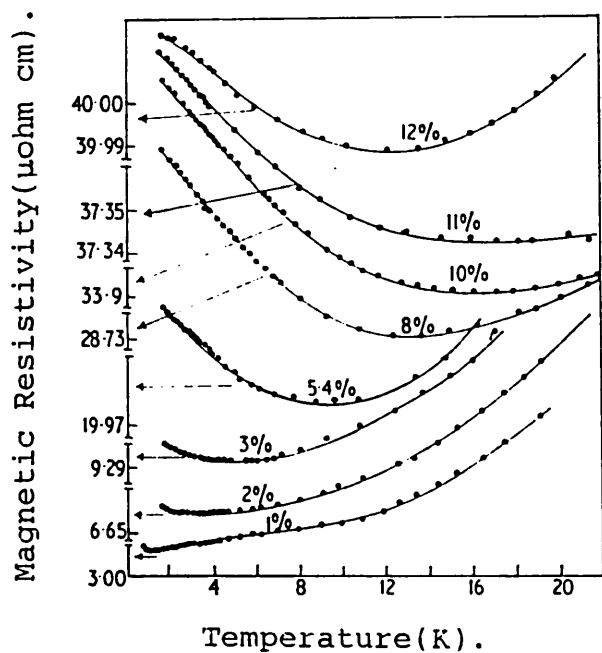
Figure 5:74. (a)-(f). (a): Minimum in the electrical resistivity of some dilute CuFe Kondo alloys as a function of temperature. Data are from Rossiter [1:1].



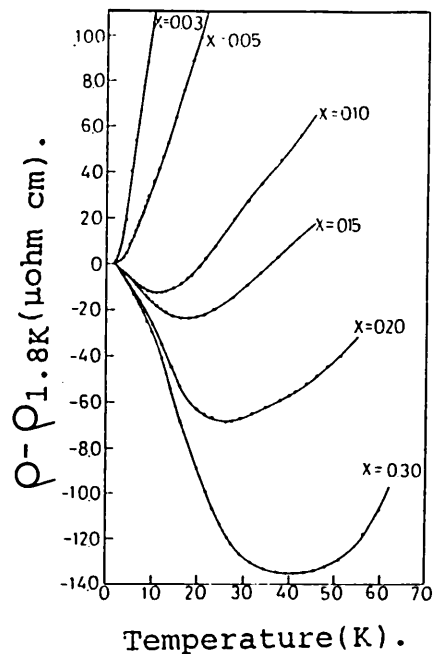
(b): Minima in the temperature dependence of the electrical resistivity of CuNi alloys due to Ni clusters. Data are from Houghton et al. [5:66]. 276



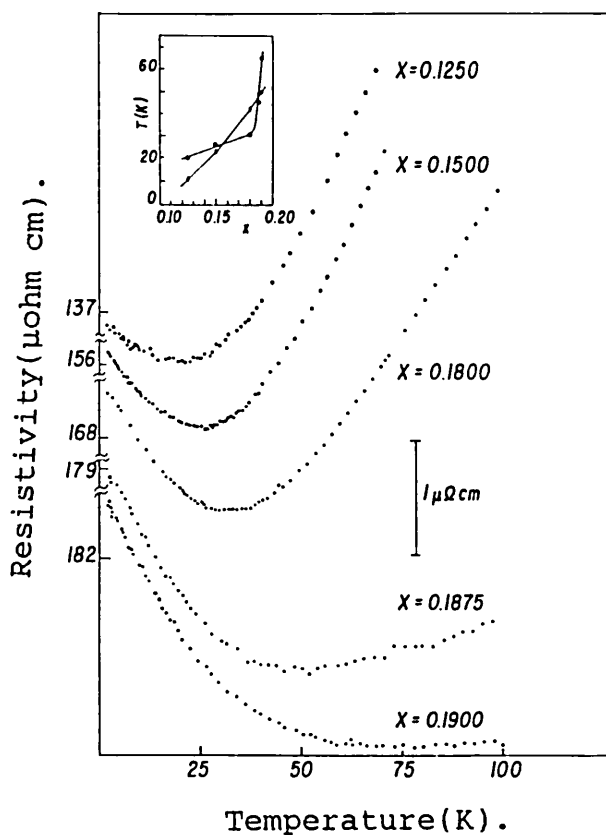
(c): (Left). Temperature dependence of the electrical resistivity for $\text{Pd}_{1-x}\text{Ag}_x$ alloys showing minima. (Right). The depth of the resistivity minima as a function of concentration x . Data are from Edwards et al. [5:68].



(d): Excess resistivity plotted against temperature for PtMn alloys reveals a minimum due to onset of spin glass freezing. Data are from Sarkissian and Taylor [5:70].



(e): Low temperature resistivity behaviour ($\rho - \rho_{1.8K}$) of $U_{1-x}Gd_xAl_2$. Data are from Ping and Coles [5:72].



(f): Low temperature dependence of the electrical resistivity of selected $Y(Al_{1-x}Fe_x)_2$ alloys. Inset shows concentration dependence of the freezing temperature T_F (◆) and T_{MIN} (●).

concentrations of magnetic impurity, or occurs at temperatures above which the system already exhibits long range order i.e. re-entrant behaviour. As an example of the former, consider the spin glass character of UAl_2 doped with Gd studied by Ping and Coles [5:72]. For $(\text{U}_{1-x}\text{Gd}_x)\text{Al}_2$ in the concentration range $0.1 \leq x \leq 0.3$ a well defined cusp is observed in the magnetic susceptibility. These were associated with magnetic spin freezing effects. The temperature at which this cusp occurs increases with Gd concentration. Resistivity data (see figure 5:74) revealed that for $x \geq 0.10$ a well defined minimum occurs at a temperature T_{min} always slightly greater than T_F . This minima is obviously related to the spin freezing in some way. The temperature dependence of the electrical resistivity of $\text{Y}(\text{Al}_{1-x}\text{Al}_x)_2$ in the spin glass concentration has been studied by da Cunha et al. [5:73]. Their results for $x \geq 0.75$ are shown in figure 5:74. For $x=0.0$ $\rho(T)$ is concave, with a single para to ferromagnetic transition well above the temperature range studied. For $0.125 \leq x \leq 0.19$ resistivity is convex. A broad knee around the T_C is followed at lower temperature by a minimum in $\rho(T)$ at a temperature T_{MIN} close to the spin glass freezing temperature T_F . However the variation of T_{MIN} and T_F cannot be easily related (see insert in figure 5:74). For $0.22 \leq x \leq 0.25$ a simple paramagnetic to spin glass transition is observed and the minimum in $\rho(T)$ is replaced by an inflexion point.

It seems clear from the above that whilst the appearance of a minimum in $\rho(T)$ can be related to the onset of magnetic freezing a simple relationship between T_{MIN} and T_F is more difficult to establish because of the superposition of several other sources of electrical resistivity each with its own temperature dependence. For the $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ system with $x \leq 0.25$ it is suggested that the resistivity can be interpreted as being made up from at least three different contributions, namely ρ_{ph} , ρ_0 , ρ_{mag} . ρ_{ph} is simply the contribution to $\rho(T)$ due to the lattice vibrations and is expected to have a similar temperature dependence to that of a non-magnetic isostructural metal e.g. LaAl_2 or YAl_2 . ρ_0 the residual resistivity is scattering due to lattice imperfections and impurities. It is expected to be temperature independent but vary as $x(1-x)$ with Fe concentration x i.e. the Gorter-Nordheim rule. It is the increase in residual resistivity which accounts for the

steady overall increase magnitude of resistivity of $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ with x up to $x=0.25$. ρ_{mag} corresponds to the contribution to the resistivity related to the nature of the magnetic order at a given temperature or Fe concentration. An increase in ρ_{mag} with decreasing temperature can lead to the appearance on a minimum in $\rho(T)$. If the magnitude of ρ_{mag} increases with respect to ρ_{ph} this minimum is shifted up in temperature. A decrease in ρ_{mag} with respect to ρ_{ph} leads to downward shift in T_{MIN} . For $x \geq 0.06$ there is evidence for the formation of magnetic ordering within these materials. For $0.06 \leq x \leq 0.25$, (regardless of the magnetic phases formed at lower temperatures), the first step in this magnetic ordering process must involve the formation of small magnetically ordered clusters. If the cluster size is smaller than the conduction electron mean free path, formation of such clusters can be expected to lead to an increase in ρ_{mag} . Cluster sizes can grow, due to either an increase in Fe concentration or a reduction in temperature, perhaps leading to the formation of an infinite cluster. At any rate cluster sizes may grow to exceed the conduction electron mean free path length. Within these larger clusters the conduction electrons experience a magnetically ordered environment, with a concomitant reduction in magnetic scattering. This leads to, for example, a knee in the resistivity at a paramagnetic-ferromagnetic transition in many ferromagnets In the $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ system, ($0.06 \leq x \leq 0.25$), an increase in Fe concentration can initially lead to an increase not only in the size of the clusters, but in the number of clusters of each size present at a given temperature. This in turn, can be expected to lead to an increase in ρ_{mag} . An increase in

ρ_{mag} , relative to ρ_{ph} shifts T_{MIN} up in temperature. As the Fe concentration is increased still further larger clusters and perhaps even an infinite cluster become larger at the expense of smaller clusters. As discussed above, scattering due to these larger clusters is less than from a collection of smaller clusters containing the same number of individual Fe atoms. Thus at a given temperature further increases in Fe concentration lead to a decrease in ρ_{mag} . This leads to a reduction in T_{MIN} . The overall effect of this behaviour is the observed variation in T_{MIN} with x .

For a fixed Fe concentration, (e.g. $(\text{Ce}_{1-z}\text{Y}_z)(\text{Al}_{0.90}\text{Fe}_{0.10})_2$) addition of Y leads to a breakdown in magnetic order. However statistical variations in the distribution of Fe and Y, can lead to the formation of magnetic clusters at temperatures around the ordering temperature of $\text{Ce}(\text{Al}_{0.90}\text{Fe}_{0.10})_2$ (170K). Since the total Fe concentration is constant at 10%, and the larger clusters present at $z=0.0$ are formed at the expense of smaller clusters the number of small magnetic clusters at a given temperature initially increases with Y concentration. Now, it is these smaller clusters scattering conduction electrons which contribute most effectively to the magnitude of the magnetic resistivity. So T_{MIN} increases with initial Y additions. Only when the Y concentration is increased sufficiently to produce an overall reduction in the number of small magnetic clusters will ρ_{mag} begin to decrease again leading to a decrease in T_{MIN} . Magnetic susceptibility data indicates magnetic ordering removed at between 50 to 60% Y. Thus the observed fall in T_{MIN} for $z \geq 0.60$ agrees well with expected reduction in total number of small magnetic clusters around this concentration (see figure 5:71).

5:7:10. Summary.

Data presented above have shown:

1. Alloying with Fe rapidly destroys the antiferromagnetic ordering between the Ce atoms in CeAl_2 , which is associated with the coherence observed in $\rho(T)$.
2. For $0.06 \leq x \leq 0.25$ we have observed unexpected magnetic ordering between Fe atoms, mediated by RKKY interactions stabilized by the Ce sublattice.
3. Beyond $x=0.25$, the cubic structure breaks down. Unlike many other rare earth(Al-Fe)₂ systems, no intermediate single phase alloy with a stable structure can be prepared between the two end parent compounds.

Chapter 6. Studies of the Effects of Alloying on the Properties of CeCu₂.

6:1. Introduction.

In this chapter the effects of alloying on the heavy fermion/Kondo lattice compound CeCu₂ are discussed. Section 6:2. contains a brief review of properties of pure CeCu₂. Section 6:3. looks at the crossover from a dense to a dilute Kondo system by replacing Ce with non-magnetic Y. The effects of alloying on the Cu sites are examined in section 6:4. In section 6:5. the effects of alloying on the Ce or the Cu sites on the properties of CeCu₂ are contrasted.

6:2. Previous Work.

6:2:1. Crystal Structure.

Storm and Benson [6:1] have shown that all RECu_2 compounds except LaCu_2 crystallize into an orthorhombic CeCu_2 structure (see figure 6:1). Lattice parameters for some RECu_2 compounds are shown in figure 6:2. The lanthanide contraction is apparent. Lattice parameters for CeCu_2 ($a=4.43\text{\AA}$, $b=7.05\text{\AA}$ and $c=7.45\text{\AA}$) indicate the Ce is behaving trivalently (c.f. Eu and Yb which appear to be divalent). The smaller ionic radius of Y leads to a much smaller values for the lattice parameters ($a=4.305\text{\AA}$, $b=6.8\text{\AA}$ and $7.315\text{\AA}$) of YCu_2 .

6:2:2. Electrical Resistivity.

The electrical resistivity of CeCu_2 was first measured by Onuki et al. [6:2] and Gratz et al. [6:3]. The temperature dependence of electrical resistivity of CeCu_2 measured during the course of this work is shown in figure 6:3. To obtain the contribution to the resistivity due to magnetic interactions, the phonon contribution to the resistivity must be subtracted. In the case of CeCu_2 problems arise in choosing a suitable non-magnetic isostructural reference compound. LaCu_2 has a different structure to CeCu_2 , so its use as a reference material is questionable. YCu_2 and LuCu_2 both exhibit quite different lattice constants as well as different phonon spectra associated with the large mass difference between Y and Lu on the one hand, and Ce on the other. This makes the use of YCu_2 or LuCu_2 as reference materials less than ideal. Both PrCu_2 where C.F. effects are limited to $T < 10\text{K}$ [6:4] and NdCu_2 which orders antiferromagnetically at 6K [6:5] can be used. However whichever reference material is used, the magnetic component of the resistivity $\rho_{\text{mag}}(T)$ exhibits

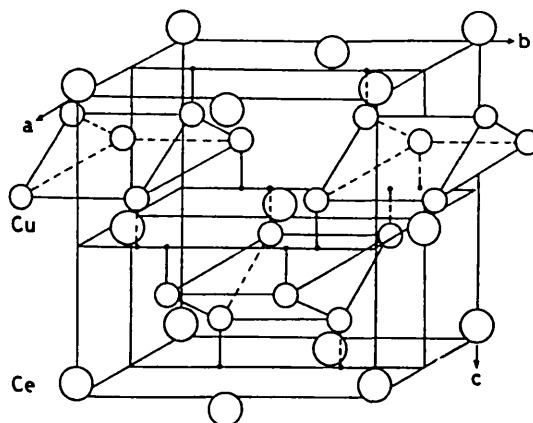


Figure 6:1. Crystal structure of CeCu_2 .

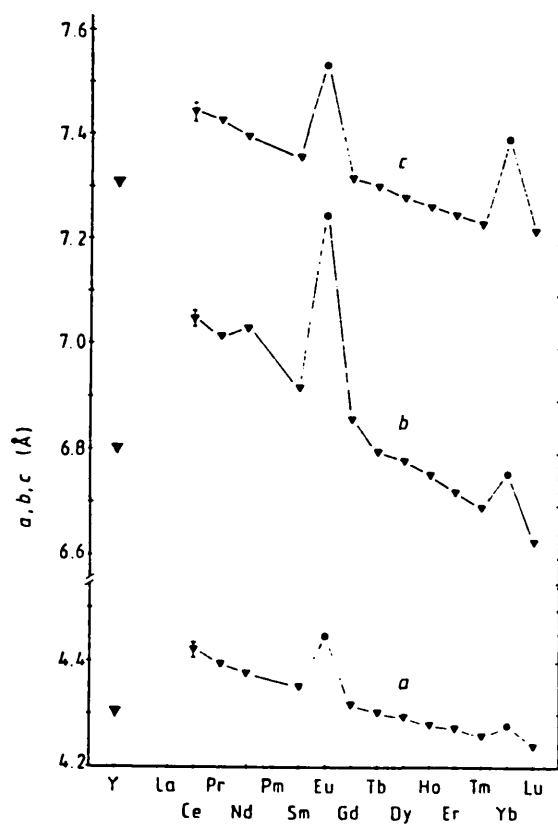


Figure 6:2. Lattice parameters of RECu_2 compounds plotted against atomic number of the RE elements. Taken from Gratz et al. [6:3].

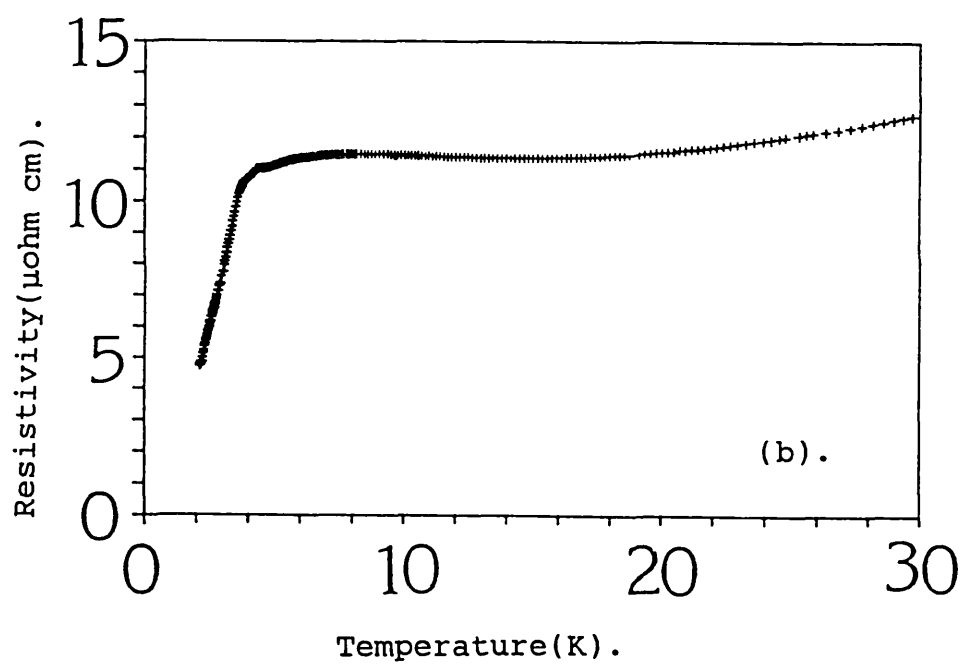
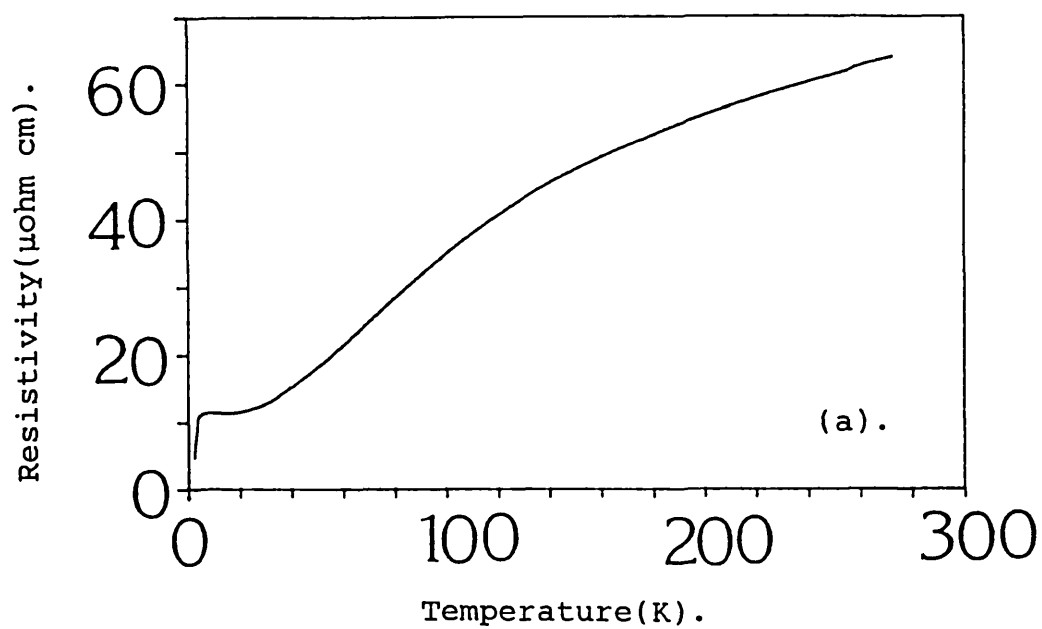


Figure 6:3(a) and (b). Temperature dependence of the electrical resistivity of CeCu_2 .

similar features (see figure 6:4). There exist two distinct regions ($10\text{K} < T < 30\text{K}$ and $160\text{K} \sim 250\text{K} < T < 300\text{K}$) where ρ_{mag} has a negative logarithmic temperature dependence. Such behaviour is characteristic of Kondo scattering of conduction electrons by the localized 4f moments of the Ce ions. These two regions are divided by a broad maximum attributed to a combination of Kondo and C.F. effects. This behaviour is also observed in CeAl_2 and can be well described by the model of Cornut and Cogblin [4:15]. The position of the maximum gives an overall measure of $\Delta_{\text{C.F.}}$, the splitting between the crystal field ground state doublet and the first excited state. The temperature at which the maximum occurs lies between 165K and 250K and is clearly dependent on the material used as a reference compound, but is always present. Following the recent theory of Hanzawa et al. [4:16], Onuki has used this data to estimate a Kondo temperature T_K of 6K and crystal field splitting $\Delta_1 \approx \Delta_2 \approx 650\text{K}$. Below 6K a rapid drop in $\rho(T)$ is observed. This sudden drop is attributed to the formation of a Kondo lattice and the onset of a coherent scattering Kondo lattice. It is suggested that below 3.5K, the fall is due to magnetic ordering.

6:2:3. Thermopower $S(T)$.

The temperature dependence of the thermopower of CeCu_2 as measured by Gratz et al. [6:3] is shown in figure 6:5. Two polycrystalline samples were measured. A tendency to saturation is observed above a peak seen around 230K. $S(T)$ changes sign at around 110K and falls to a negative minimum of $-6\mu\text{VK}^{-1}$ at 35K. This behaviour is observed in several Kondo lattices (e.g. CeAl_2 , CeCu_2Si_2). In general the peak at high temperature is attributed to an interplay between the

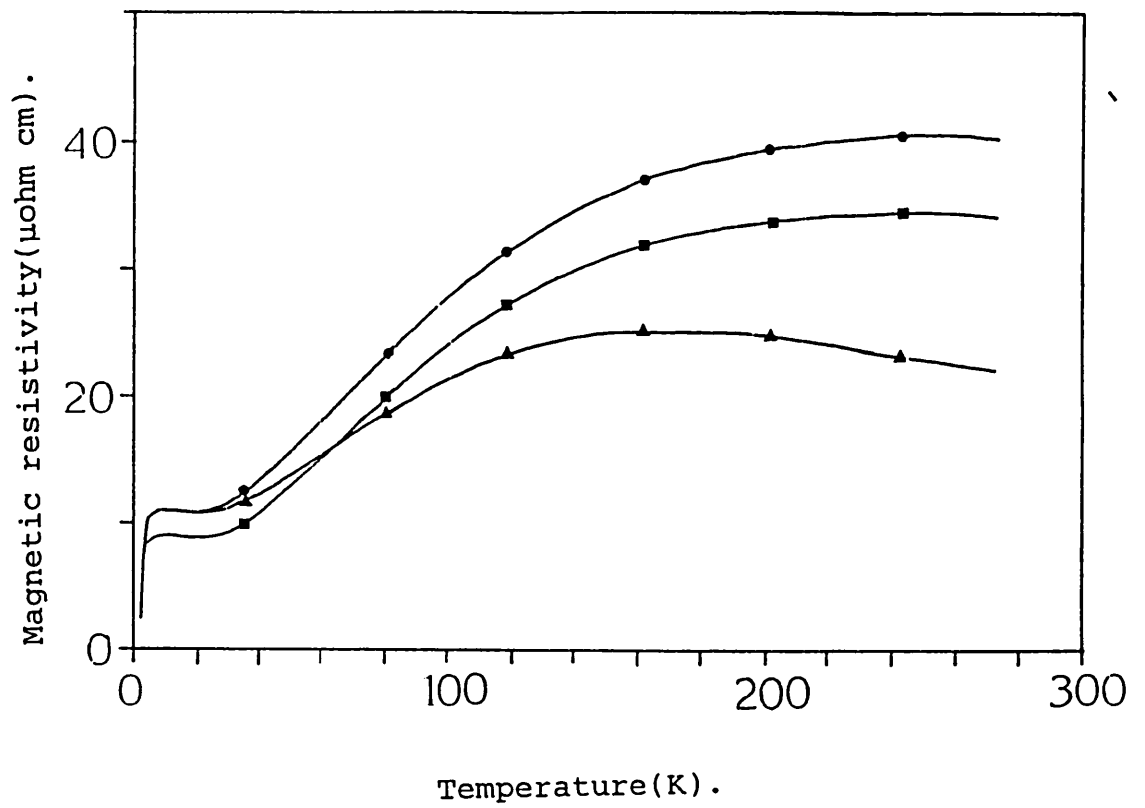


Figure 6:4. Comparison of the magnetic component of the electrical resistivity of CeCu_2 versus temperature determined by subtracting the resistivities of different nonmagnetic alloys YCu_2 ($\blacktriangle$), LuCu_2 ($\blacksquare$) and LaCu_2 ($\bullet$).

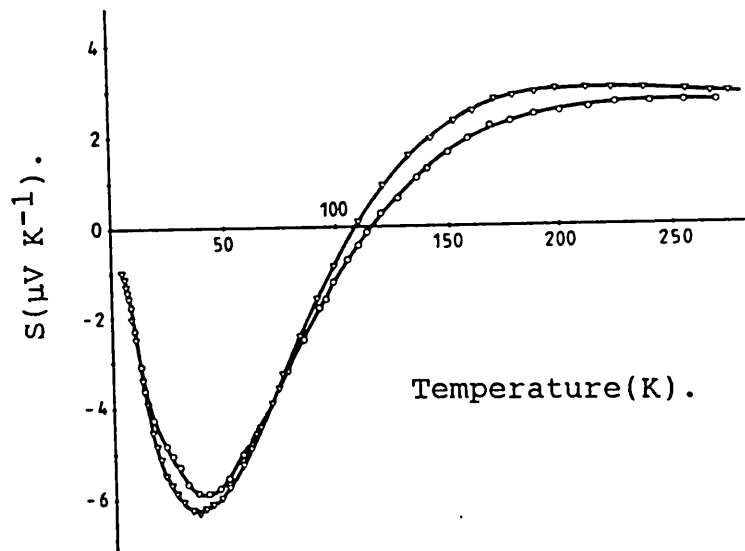


Figure 6:5. Temperature dependence of the thermopower of two different CeCu_2 samples. Taken from Gratz et al. [6:3].

Kondo effect and C.F. splitting. According to the theoretical model of Bhattacharjee and Cogblin [4:23] the temperature of the maximum is related to the overall crystal field splitting according to

$$\Delta_{C.F.} = (3 \sim 6) T_{\max} \text{ ----- } 6:1.$$

This gives $\Delta_{C.F.} \approx 450-900K$

The low temperature minimum occurs at approximately $2T_K$ which implies a $T_K = 17K$.

6:2:4. Magnetoresistance.

Further justification for describing $CeCu_2$ as a Kondo lattice comes from the magnetoresistance data of Onuki et al. [6:2].

A negative magnetoresistance typical of a Kondo lattice is observed. A negative minimum in $\delta\rho/\rho$ is reported to occur at around 3K. Using the theory of Zlatic, this gives an estimate of the Kondo temperature T_K of $T_K \sim 2 * T_{\min} = 6K$.

6:2:5. Specific Heat.

The specific heat of $CeCu_2$ has been reported by Onuki et al. [6:2] and Gratz et al. [6:3] and is shown in figure 6:6.

Above 5K, C/T versus T is almost constant with a value for extrapolated to zero temperature of $180mJ/molK^2$. At 3.5K there is a pronounced (second order type) discontinuity in $C(T)$. The specific heat below 1K can be well described by the expression

$$C(T) = \gamma T + AT^2 \exp(-\Delta E/K_B T) \text{ ----- } 6:2.$$

$$\gamma = 82mJ/molK^2, A = 1.4J/molK^4, \Delta E/K_B T = 1.2K.$$

where the second term can be interpreted as an activation energy in the spectrum of antiferromagnetic spin waves. The existence of such a gap would characterize $CeCu_2$ as an anisotropic antiferromagnet. An estimate of the magnetic entropy associated with the phase transition yields

$\delta S = 3.8 \text{ J/molK}$. This is only two thirds of the entropy equal to $R \ln 2 (5.76 \text{ J/molK})$ associated with a complete removal of the two fold spin degeneracy of a C.F. ground state doublet. This may indicate either:

1. short range ordering above T_N
2. a substantial reduction in the magnetic moments of a Kondo origin.

The mean field type anomaly in C/T makes the former explanation unlikely.

6:2:6. Magnetic Properties.

A distinct change in slope of $\chi(T)$ is observed at the antiferromagnetic transition. Onuki et al.[6:2] have reported the inverse susceptibility of a single crystal along the three crystallographic directions (see figure 6:7). These results showed:

1. Curie-Weiss behaviour above 100K.
2. effective moments μ_{eff} of 2.45, 2.36 and $2.7\mu_B$ for a, b and c axes respectively.
3. paramagnetic Curie temperatures of +17, -25 and -270K for a, b and c.

The observed anisotropy is attributed to C.F. effects associated with the orthorhombic crystal structure.

Paramagnetic Curie temperatures and effective moments for polycrystalline samples [6:3,6:6] have been reported to lie between -30 to -48K and 2.45 to $2.59\mu_B$. These results are consistent with a Ce^{3+} free spin moment of $2.54\mu_B$. Using the ideas of Grüner and Zawadowsky [2:8] who showed for a single impurity Kondo system $T_K \approx \theta_P/4$ gives an estimate for T_K of 7.5 to 12K.

Magnetisation measurements (see figure 6:8) reveal the suppression of the values of magnetic moments compared with those calculated from high temperature susceptibility data.

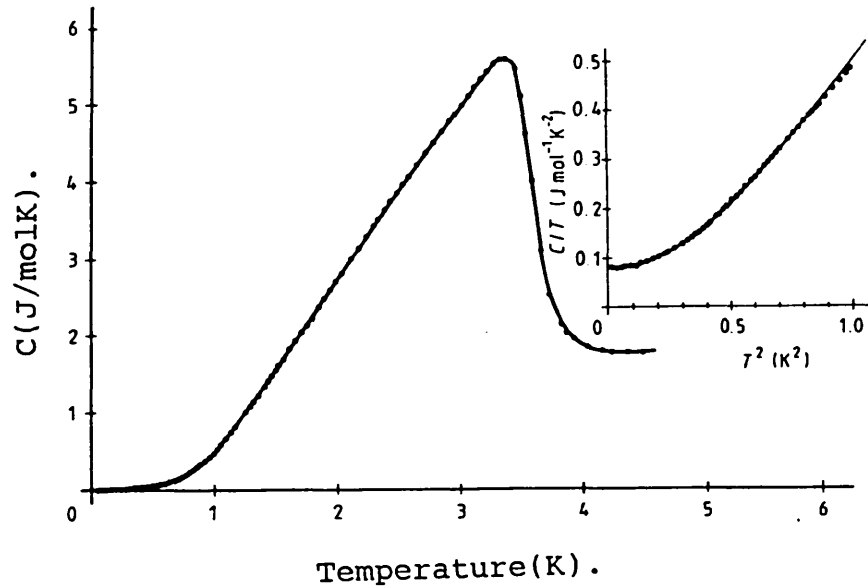


Figure 6:6. Specific heat of CeCu_2 as a function of temperature. Inset: low temperature data in a plot of C/T against T^2 ; the full curve represents $C/T = \gamma + AT^2 \exp(-\Delta E/k_B T)$ with $\gamma = 0.082 \text{ J/molK}^2$, $A = 1.4 \text{ J/molK}^{-4}$ and $\Delta E/k_B = 1.2 \text{ K}$. Data are from Gratz et al. [6:3].

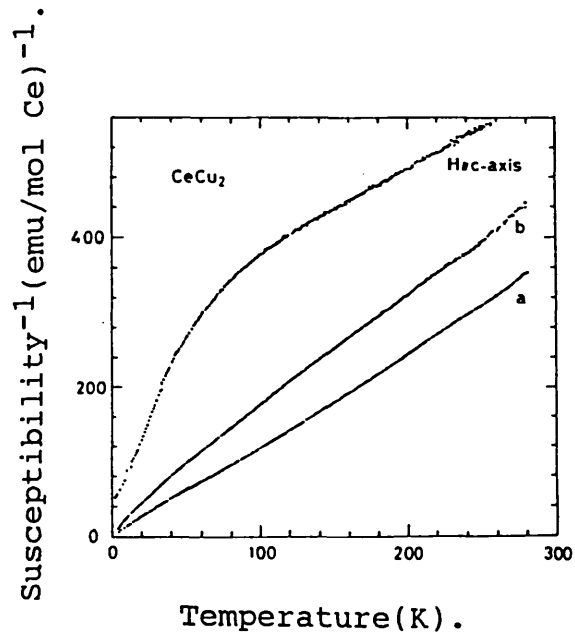


Figure 6:7. Temperature dependence of the inverse magnetic susceptibility of a single crystal of CeCu_2 . Data are from Onuki et al. [6:2].

Onuki et al. [6:2] reported magnetic moments at 4.2K in fields of 75kOe equal to $1.25\mu_B$ and $0.25\mu_B$ along the a and c directions respectively. Sherwood [6:7] reported a value of $0.8\mu_B$ at 4.2K in a magnetic field of 80kOe. for the magnetic moment of polycrystalline CeCu₂. Gratz et al. [6:3] reported metamagnetic behaviour with an inflexion point at 2T. Neutron studies [6:3] revealed small magnetic peaks very close to nuclear Bragg reflections at 1.4K. These could indicate either ferromagnetic ordering ($q=0$) or long range antiferromagnetic order (q small). Magnetisation data seem to rule out the former. A neutron study by Zemerli [6:8] showed CeCu₂ ordered into an antiferromagnetic structure with an incommensurate spin structure.

6:2:7. Summary.

The properties of CeCu₂ discussed above are summarised below:

1. CeCu₂ is a concentrated Kondo lattice with T_K between 6 and 20K.
2. CeCu₂ orders antiferromagnetically at 3.5K with a magnetic structure that is incommensurate with the crystal structure.
3. CeCu₂ has an enhanced value for the electronic specific heat of 180mJ/molK^2 which is reduced by the magnetic transition to 80mJ/molK^2 . The entropy associated with this transition is less than expected.
4. CeCu₂ exhibits Curie-Weiss behaviour at high temperature with Ce moments close to the value expected for free Ce^{3+} ions. These values are reduced by Kondo compensation to $0.8\mu_B$ at low temperature.
5. The transport properties of CeCu₂ show behaviour typical of a Kondo system.
6. The orthorhombic crystal structure leads to a crystal field splitting of 200K or above.

6:3. The Ce_{1-x}Y_xCu₂ System.

6:3:1. Introduction.

In order to study the evolution of a dense Kondo lattice system through to a single impurity Kondo regime it is

necessary to dilute the magnetic scattering centres (in this case Ce) with some non-magnetic rare earth element which forms into a RECu_2 compound with the same structure. Unlike the cases of CeCu_6 and CeAl_2 , where La forms an isostructural compound with roughly the same lattice parameters, LaCu_2 has an hexagonal structure. As a result Y was chosen as a dopant. YCu_2 has the same orthorhombic structure as CeCu_2 . However, as well as the dilution of Ce, additional effects resulting from chemical pressure brought about by the smaller ionic radius of Y are expected to be observed. Work by Schilling [2:44] has shown that pressure is expected to increase the magnitude of exchange constant J, which in turn leads to an enhancement in the Kondo like behaviour.

6:3:2. Sample Preparation.

All the samples in the series $\text{Ce}_{1-x}\text{Y}_x\text{Cu}_2$ were prepared using the techniques described in section 3:6. All the samples were then annealed for 7 days at 700°C . Metallographic analysis revealed no signs of a second phase in any of the samples.

6:3:3. Lattice Constants.

The values of the lattice constants (a, b and c) for all the samples prepared are given in table 6:1, together with the cell volumes. The variations with Y content of these parameters are also shown graphically in figure 6:9. The values were calculated from the 121, 200 and 103 peaks observed in X-ray powder diffraction studies. These three peaks were chosen as they are the strongest to appear in the X-ray patterns of both CeCu_2 and YCu_2 and could be easily indexed across the entire alloy series. It should be noted that both the unit cell volume and the individual lattice parameters decrease smoothly with increasing Y content. The

total change in volume between CeCu_2 and YCu_2 amounts to 8% of the cell volume of CeCu_2 . Within the RECu_2 compounds the lattice parameters of CeCu_2 fit well into that series of compounds with rare-earth ions exhibiting 3+ valency. The smooth variation of a , b , c and cell volume V , must be taken as an indication that no substantial change in the valency of the Ce ions occurs across the alloy series.

Table 6:1. Concentration dependence of the lattice parameters and cell volume V for $\text{Ce}_{1-x}\text{Y}_x\text{Cu}_2$ alloys.

Conc x	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$v(\text{\AA})^3$
0.00	4.43	7.05	7.45	232.7
0.10	4.415	7.05	7.45	231.75
0.20	4.40	7.015	7.42	228.85
0.35	4.40	7.026	7.41	229.0
0.50	4.377	7.0	7.388	226.14
0.70	4.35	6.95	7.35	222.12
0.90	4.32	6.904	7.32	218.3
1.00	4.305	6.80	7.315	214.14

6:3:4. Electrical Resistivity.

The temperature dependence of the electrical resistivity of the $\text{Ce}_{1-x}\text{Y}_x\text{Cu}_2$ series are shown in figure 6:10. YCu_2 shows behaviour typical of a normal metal where $\rho(T)$ can be well described by the sum of a phonon term $\rho(T)_{\text{phonon}}$ and ρ_0 a residual resistivity term. Addition of Ce first increases the residual resistivity term as a result of increased lattice disorder. This leads to an increase in both the absolute value of the resistivity at high temperature ($\rho_{273\text{K}}(T)$) and the minimum value to which the resistivity falls in the temperature range 1.5 to 280K $\rho_{\text{min}}(T)$ (see figure 6:11). The residual resistivity reaches a maximum at $x=0.35$. This

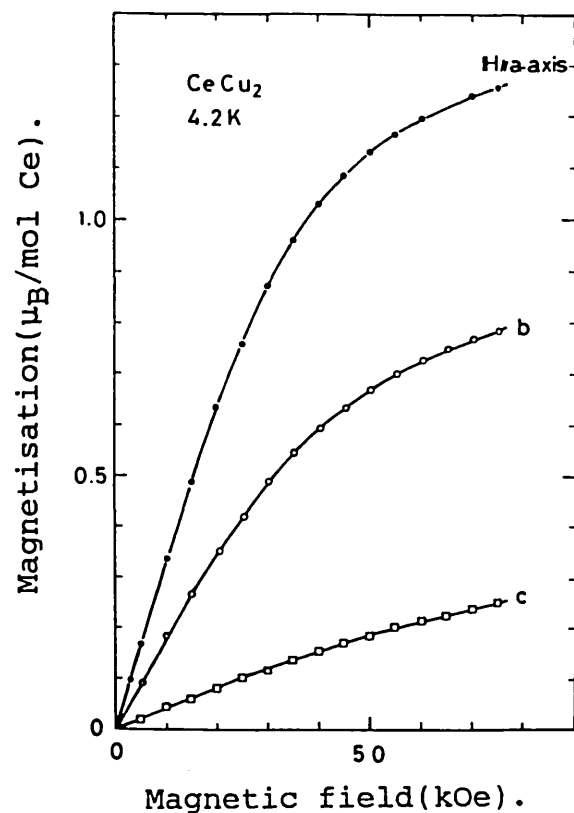


Figure 6:8. Magnetic field dependence of the magnetisation of a single crystal of CeCu_2 . Data are from Onuki et al. [6:2].

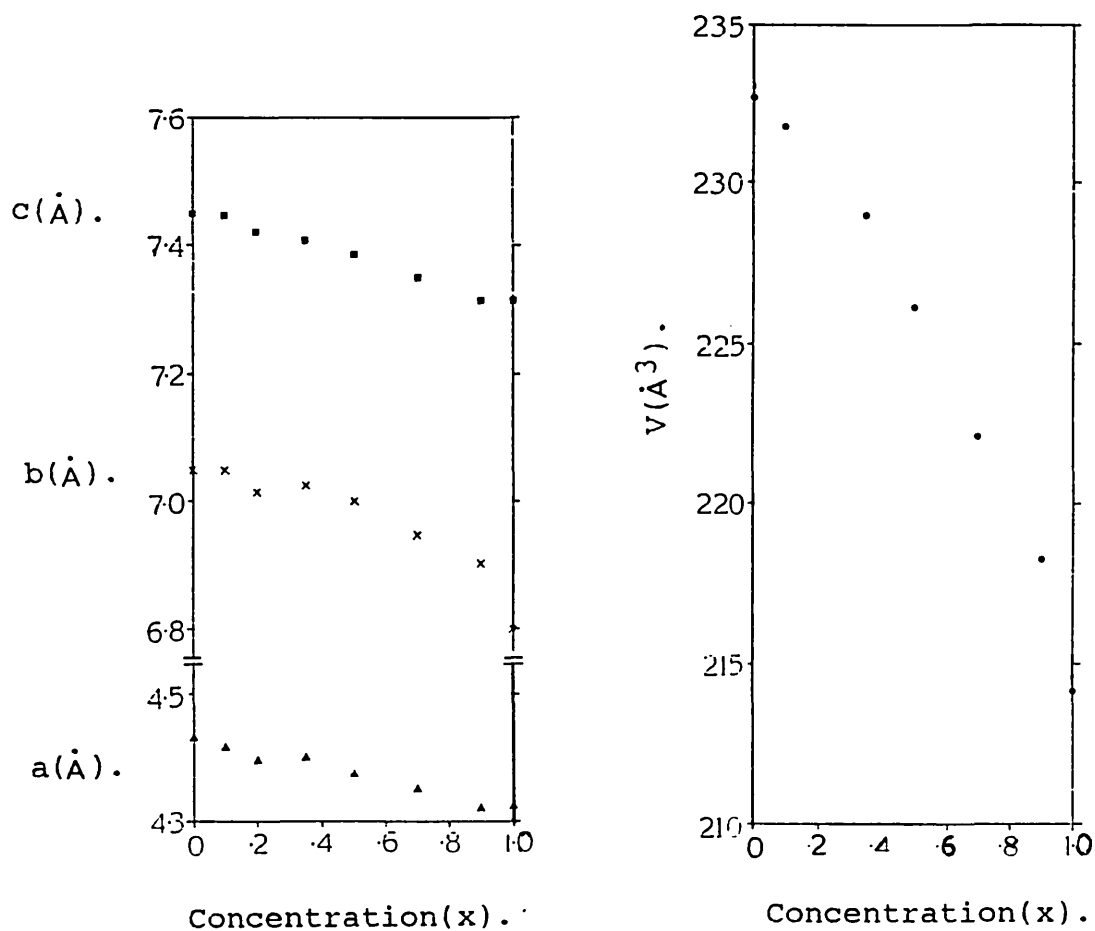


Figure 6:9. Variations in the lattice parameters $a(\Delta)$, $b(X)$, and $c(\blacksquare)$ and the the cell volume $V(\bullet)$ with Y concentration.

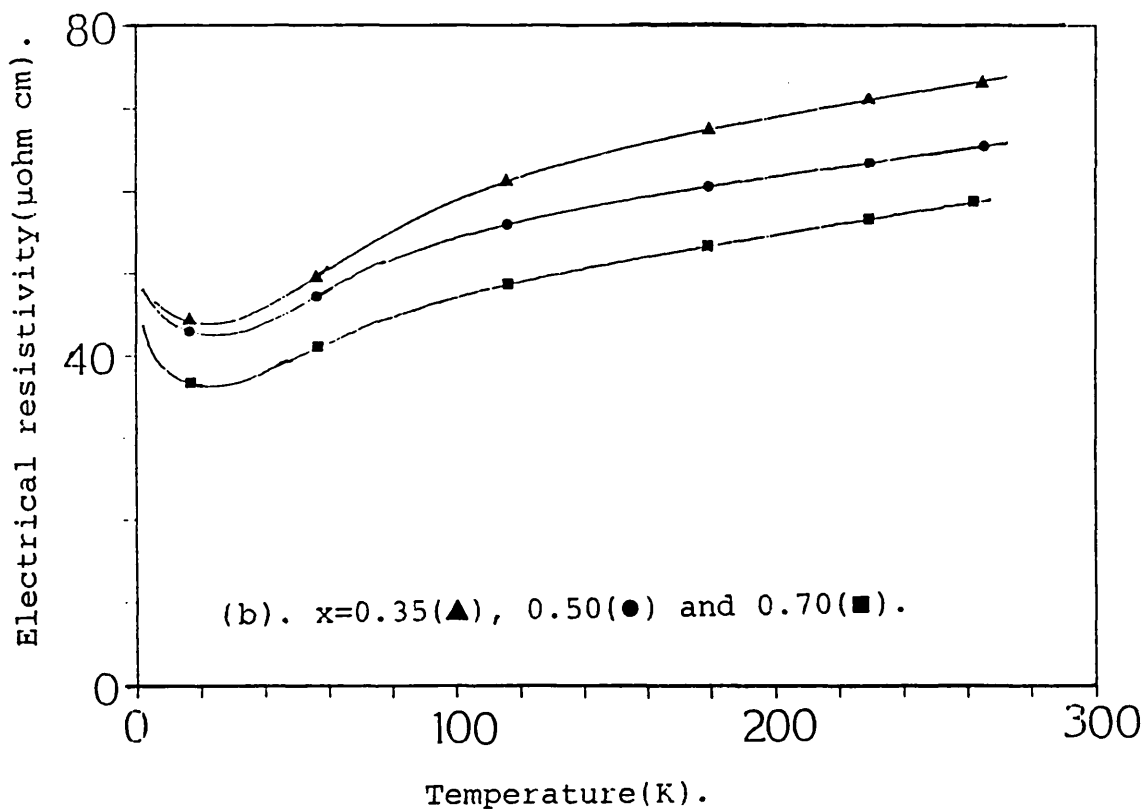
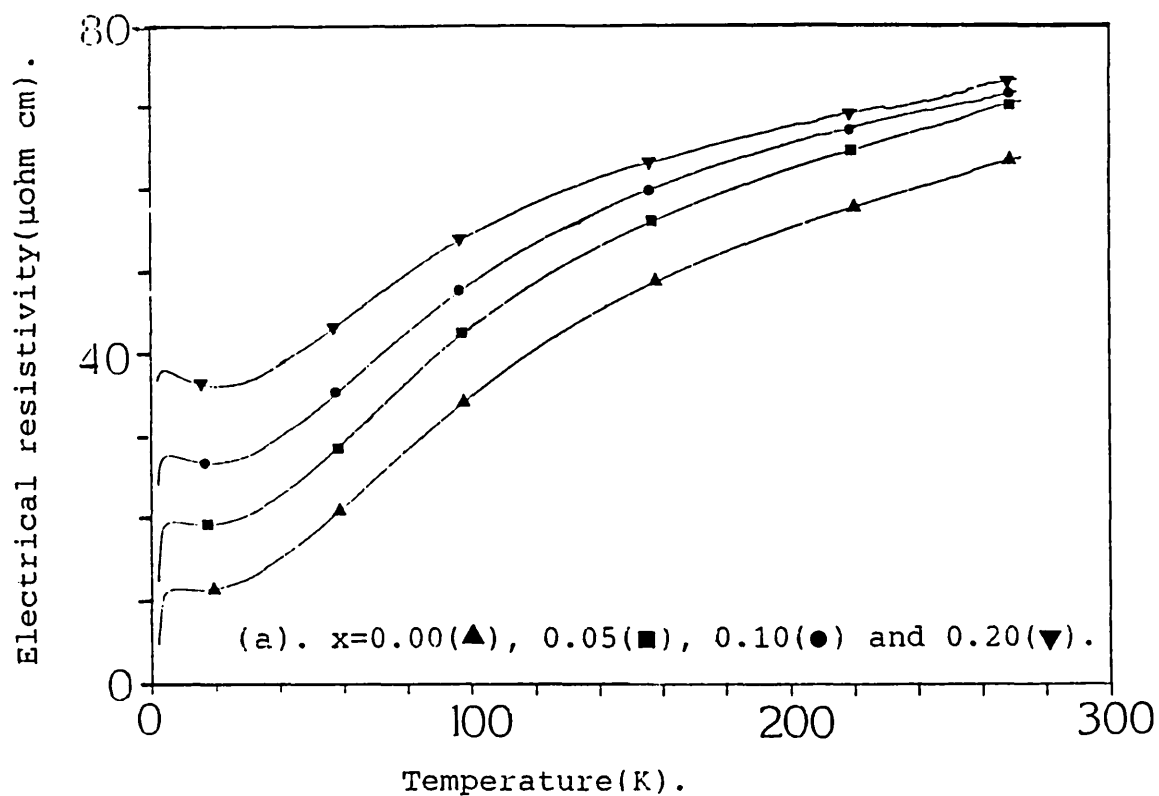


Figure 6:10 (a), (b) and (c). Temperature dependence of the electrical resistivity of $\text{Ce}_{1-x}\text{IrxCu}_2$ alloys.

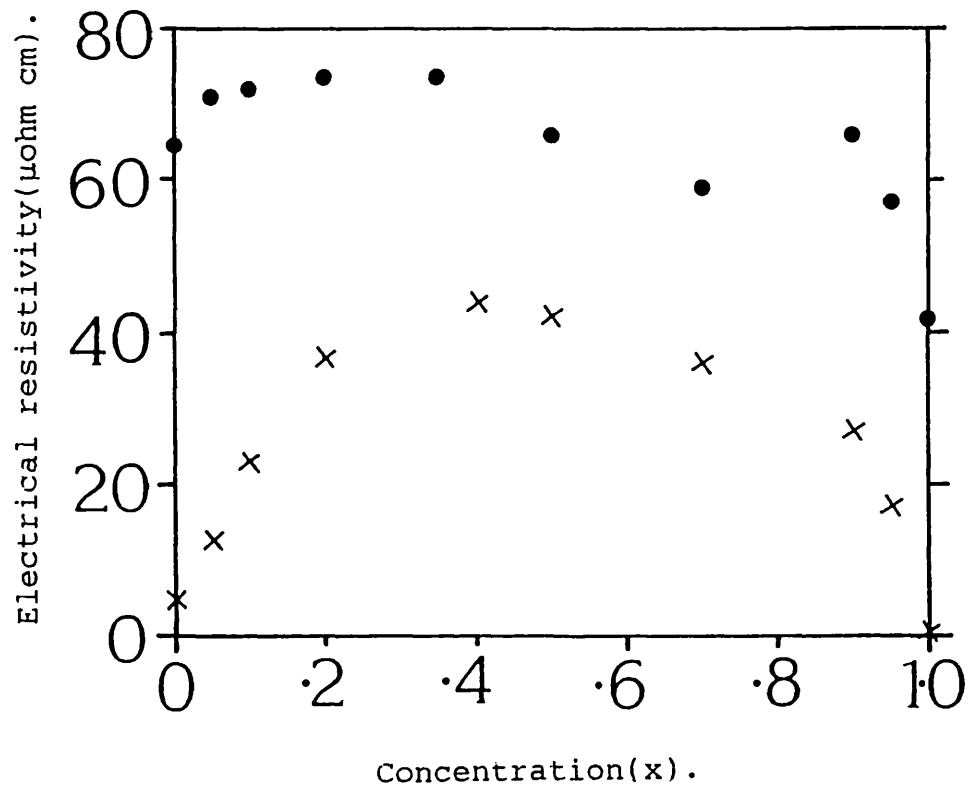
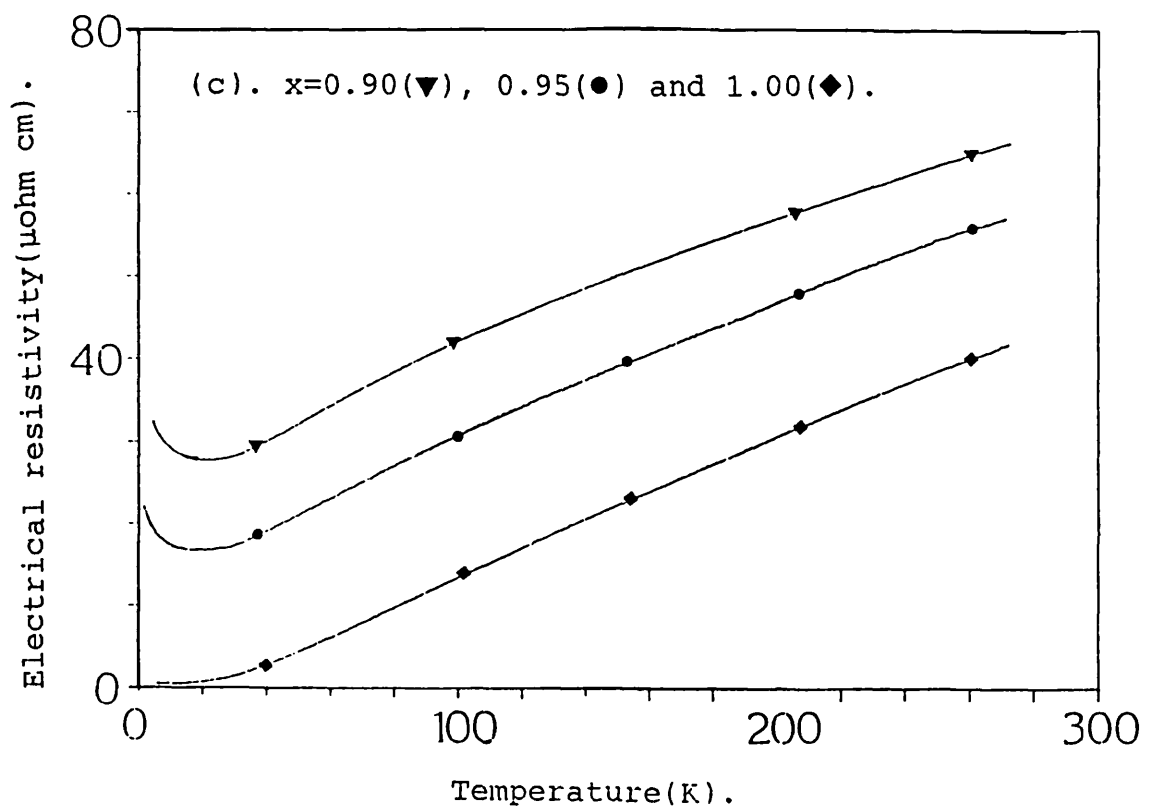


Figure 6:11. Variation in the magnitude of the electrical resistivity at 273K(●) and the minimum value to which the resistivity falls in the temperature range 1.8 to 273K(X) with concentration for $\text{Ce}_{1-x}\text{Y}_x\text{Cu}_2$ alloys.

behaviour is expected due to rising atomic disorder and increased potential scattering due to alloying. As the Ce content is increased still further the disorder decreases and the residual resistivity falls reaching a minimum value of $4.75\mu\text{ohm cm}$ for pure CeCu_2 .

The addition of 5% of Ce to YCu_2 results in the appearance of a minimum in $\rho(T)$ at low temperature. This minimum indicates the presence of incoherent Kondo scattering. As the Ce content is increased the minimum becomes much more pronounced reaching a depth of $8\mu\text{ohm cm}$ at $x=0.30$. At still higher Ce concentrations this minimum becomes less pronounced. For values of $x \leq 0.20$, a low temperature maximum in $\rho(T)$ is observed. This maximum is associated with the formation of the $\text{Ce}_{1-x}\text{Y}_x\text{Cu}_2$ system into a Kondo lattice and the onset of coherent scattering behaviour. At $x=0.00$ $\rho(T)$ has all the features discussed in section 6:2:2. This behaviour clearly indicates a crossover from normal metal (YCu_2 $x=1.0$) through dilute single impurity Kondo behaviour ($0.95 \geq x \geq 0.3$) to a dense Kondo lattice regime ($x \leq 0.2$). The destruction of the onset of coherence by substitution of 20% Y is very similar to concentrations of Y, La or Gd required to destroy coherence in non-magnetic hf systems CeCu_6 (see chapter 4), CeAl_3 (see chapter 7) and the magnetic hf compound CeAl_2 (see chapter 5).

Figure 6:12. shows the contribution to the resistivity which is attributed to magnetic interactions ($\rho_{\text{mag}}(T)$), where $\rho_{\text{mag}}(T) = \rho(\text{Ce}_{1-x}\text{Y}_x\text{Cu}_2)(T) - \rho(\text{YCu}_2)(T)$. Of course the absolute values of the magnetic resistivity and the temperature, T_{max} of the peak observed in ρ_{mag} will depend on the use of YCu_2 as the compound whose resistivity gives a measure of ρ_{ph} (see

section 6:2:2). However the overall shape and the character of the changes observed as a result of alloying will be unchanged by this choice. Across almost the entire series ($0.00 \leq x \leq 0.95$), above 6K, ρ_{mag} looks qualitatively like pure CeCu_2 . Two regions with negative logarithmic slopes are separated by a broad maximum. The temperature at which this maximum occurs is clearly dependent on the concentration of Ce and is shifted from 170K for CeCu_2 to 70K for $x=0.90$ (see table 6:2). For $0.95 \geq x \geq 0.35$ only these two logarithmic regions are observed, whilst for $x \leq 0.20$ deviations from $-\ln T$ behaviour at low temperature associated with the onset of coherent scattering are observed. Cornut and Coqblin [4:15] have related the position of the maximum seen in ρ_{mag} at high temperature to the C.F. splitting $\Delta_{\text{C.F.}}$. Thus the shift of this maximum to lower temperature implies a change in the crystal field scheme across the alloy series. It seems likely that chemical pressure effects produced by Y doping are the source of this modification. No study of CeCu_2 under pressure has been carried out. However Nicholas-Francillon et al. [5:36] have observed a decrease in $\Delta_{\text{C.F.}}$ with increase in external pressure in CeAl_2 a system with similar $\rho_{\text{mag}}(T)$ characteristics. Alloying with Y appears to result in only a small change in T_K (see section 6:3:6 and 6:3:7). Using the theory of Hanzawa et al. [4:16] which asserts that $T_K = \sqrt{T_{\text{Max}} \Delta_1 \Delta_2}$, suggests that alloying with Y also leads to an increase in Δ_2 . According to the theory of Cornut and Coqblin the slope $d\rho_{\text{mag}}/d\ln T$ is proportional to J . The rapid increase in this slope with Y also suggests that lattice pressure leads to a strong increase the parameter J .

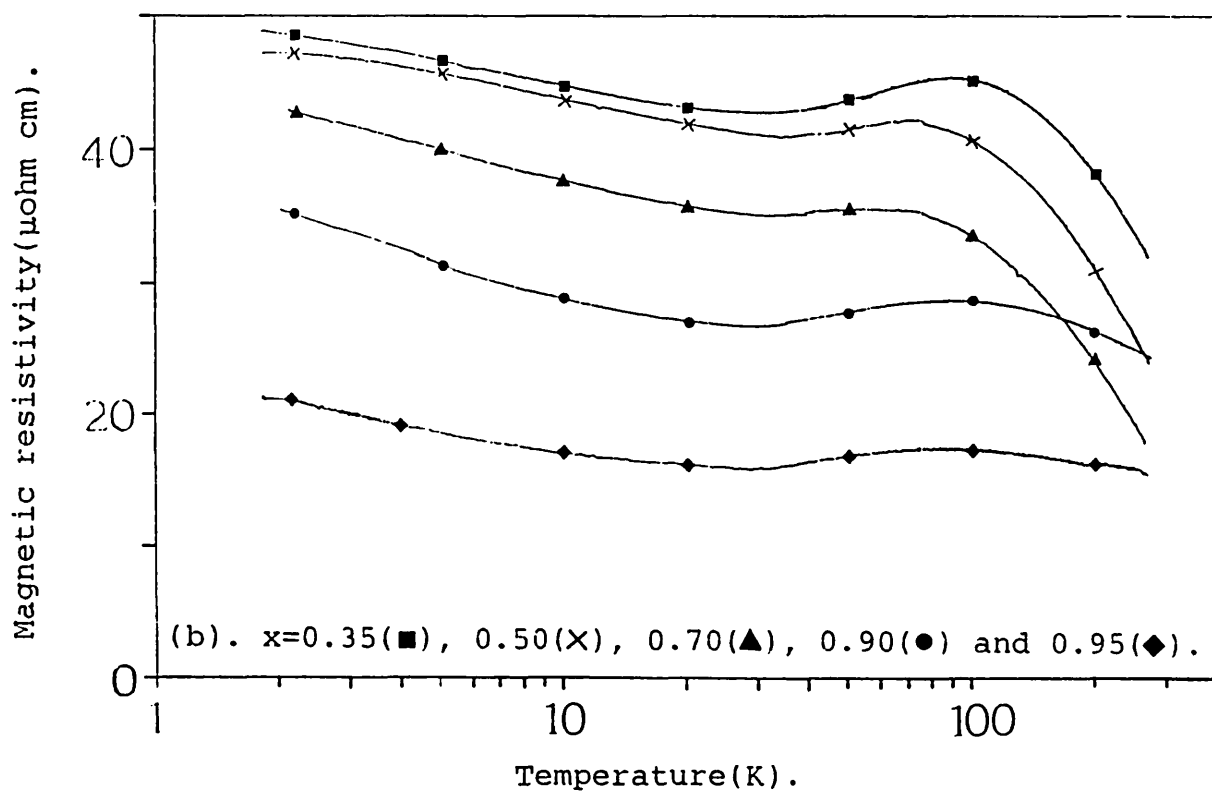
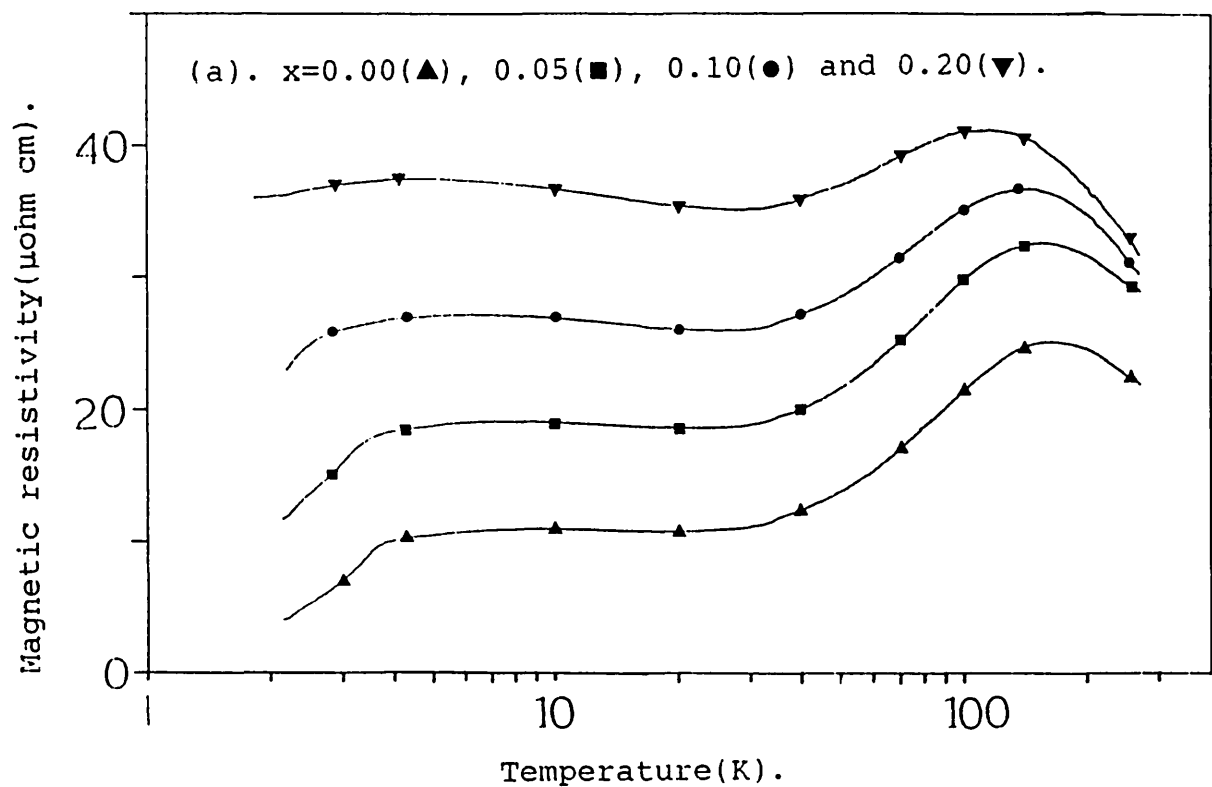


Figure 6:12 (a) and (b). Semilogarithmic representation of the temperature dependence of the magnetic component of the electrical resistivity of $\text{Ce}_{1-x}\text{Y}_x\text{Cu}_2$ determined by subtracting the resistivity of YCu_2 .

Table 6:2. Parameters taken from the transport measurements on $\text{Ce}_{1-x}\text{Y}_x\text{Cu}_2$ alloys.

Conc. x	0.00	0.05	0.10	0.20	0.35	0.50	0.70	0.90	0.95	1.00
$T_{\text{MAX}}(\text{K})$	165	157	148	117	90	72	54	88	--	--
$-\text{d}\rho/\text{d}\ln T$	8.84	8.75	15.5	17.2	17.7	21.9	19.5	6.3	2.8	--
$\rho(273\text{K})$ ($\mu\text{ohm cm}$)	63.9	70.9	72.0	73.4	73.9	65.9	59.0	66.3	57.1	41.9
$\rho(\text{min})$ ($\mu\text{ohm cm}$)	4.75	12.5	23.1	36.8	46.6	48.0	43.7	32.3	22.1	0.45
$S_{\text{MAX}}(\text{K})$	234	--	--	--	150	--	--	101	--	--

6:3:5. Thermoelectric Power $S(T)$.

The crossover from a dense to dilute Kondo system and the variation in $\Delta_{\text{C.F.}}$ suggested by the electrical resistivity results are confirmed by thermopower measurements performed by Bauer et al. [6:9]. Their results are shown in figure 6:13. The behaviour of $S(T)$ for CeCu_2 typical for a Ce based Kondo lattice system has been described in section 6:2:3. In contrast YCu_2 has a shallow minimum at low temperature attributable to phonon drag effects, with $S(T)$ increasing linearly at higher temperature. As Y is added to CeCu_2 the high temperature maximum in $S(T)$ is shifted to lower temperature, with the depth of the negative minimum reduced. This maximum in $S(T)$ has been related to $\Delta_{\text{C.F.}}$, the C.F. splitting ($T_{\text{max}} \propto \Delta_{\text{C.F.}}$ [4:23]). Thus a reduction in $\Delta_{\text{C.F.}}$ as Y concentration is increased can be inferred from these results.

6:3:6. Magnetic Susceptibility.

Figures 6:14 and 6:15 show the temperature dependence of the magnetic susceptibility $\chi_{\text{a.c.}}(T)$ for the $\text{Ce}_{1-x}\text{Y}_x\text{Cu}_2$ series. No obvious maximum which may indicate the onset of magnetic order is observed for any of the samples. However a distinct

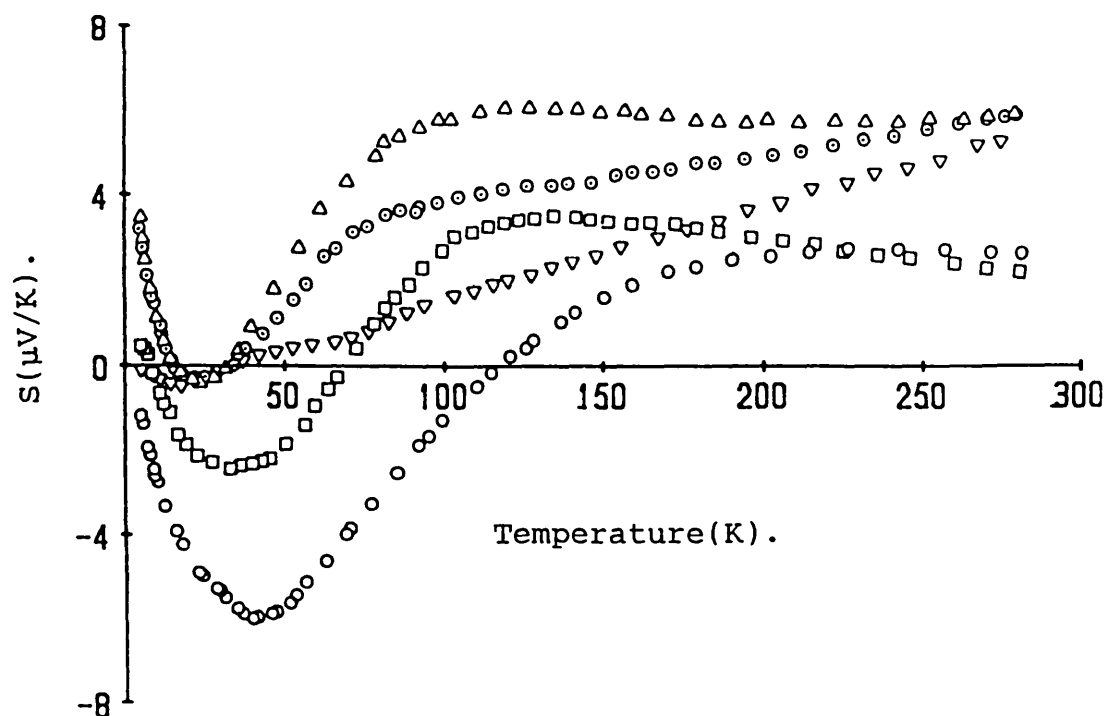


Figure 6:13. The temperature dependence of the thermopower S of $\text{Ce}_{1-x}\text{Y}_x\text{Cu}_2$ alloys, where $x=0.00(\bigcirc)$, $0.40(\square)$, $0.90(\triangle)$, $0.97(\odot)$ and $1.00(\nabla)$.

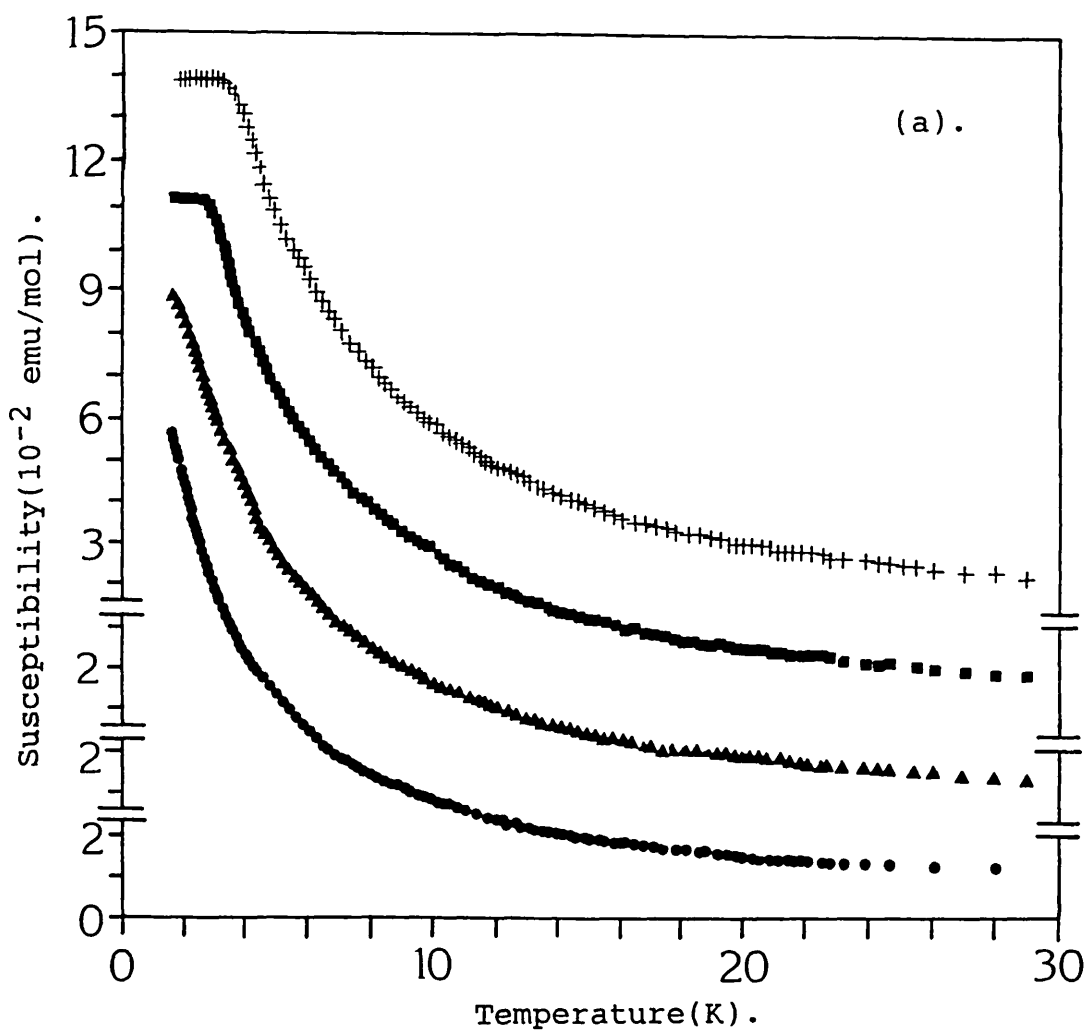


Figure 6:14(a). Temperature dependence of the magnetic susceptibility of $\text{Ce}_{1-x}\text{Y}_x\text{Cu}_2$ alloys where $x=0.00(+)$, $0.10(\blacksquare)$, $0.20(\blacktriangle)$ and $0.35(\bullet)$.

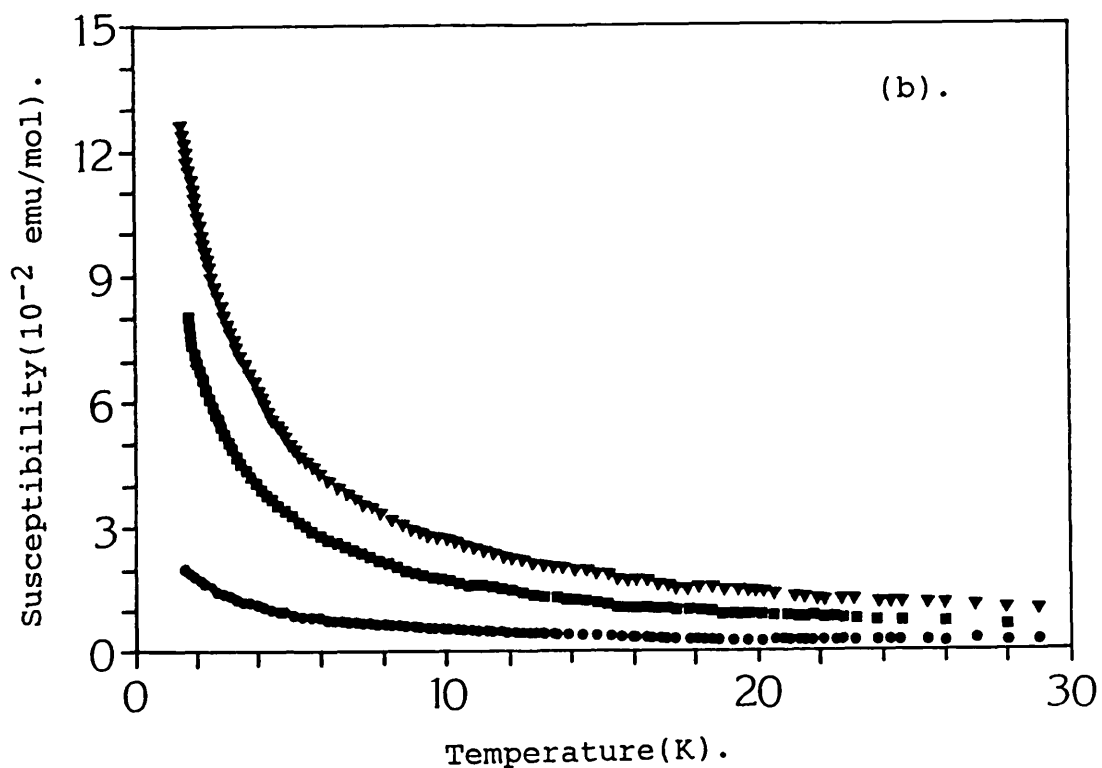


Figure 6:14(b). Temperature dependence of the magnetic susceptibility of $\text{Ce}_{1-x}\text{Y}_x\text{Cu}_2$ alloys where $x=0.50(\nabla)$, $0.70(\blacksquare)$ and $0.90(\bullet)$.

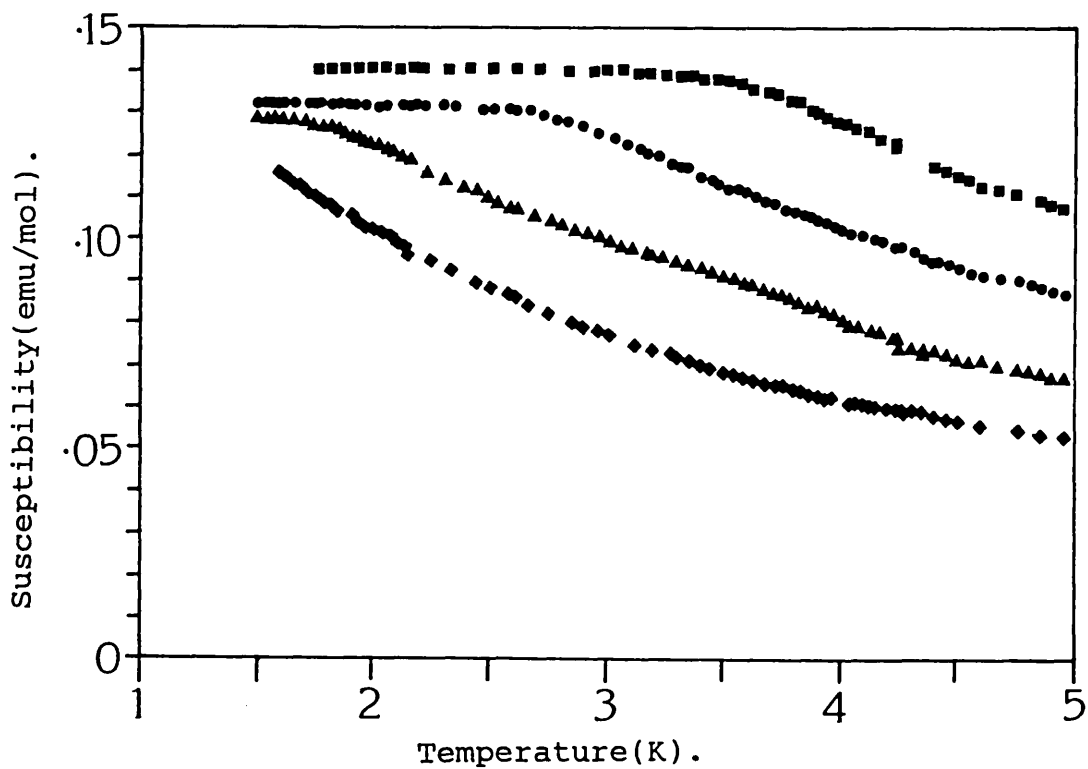


Figure 6:15. The low temperature variation in the magnetic susceptibility of selected $\text{Ce}_{1-x}\text{Y}_x\text{Cu}_2$ alloys where $x=0.00(\blacksquare)$, $0.10(\bullet)$, $0.20(\blacktriangle)$ and $0.35(\blacklozenge)$.

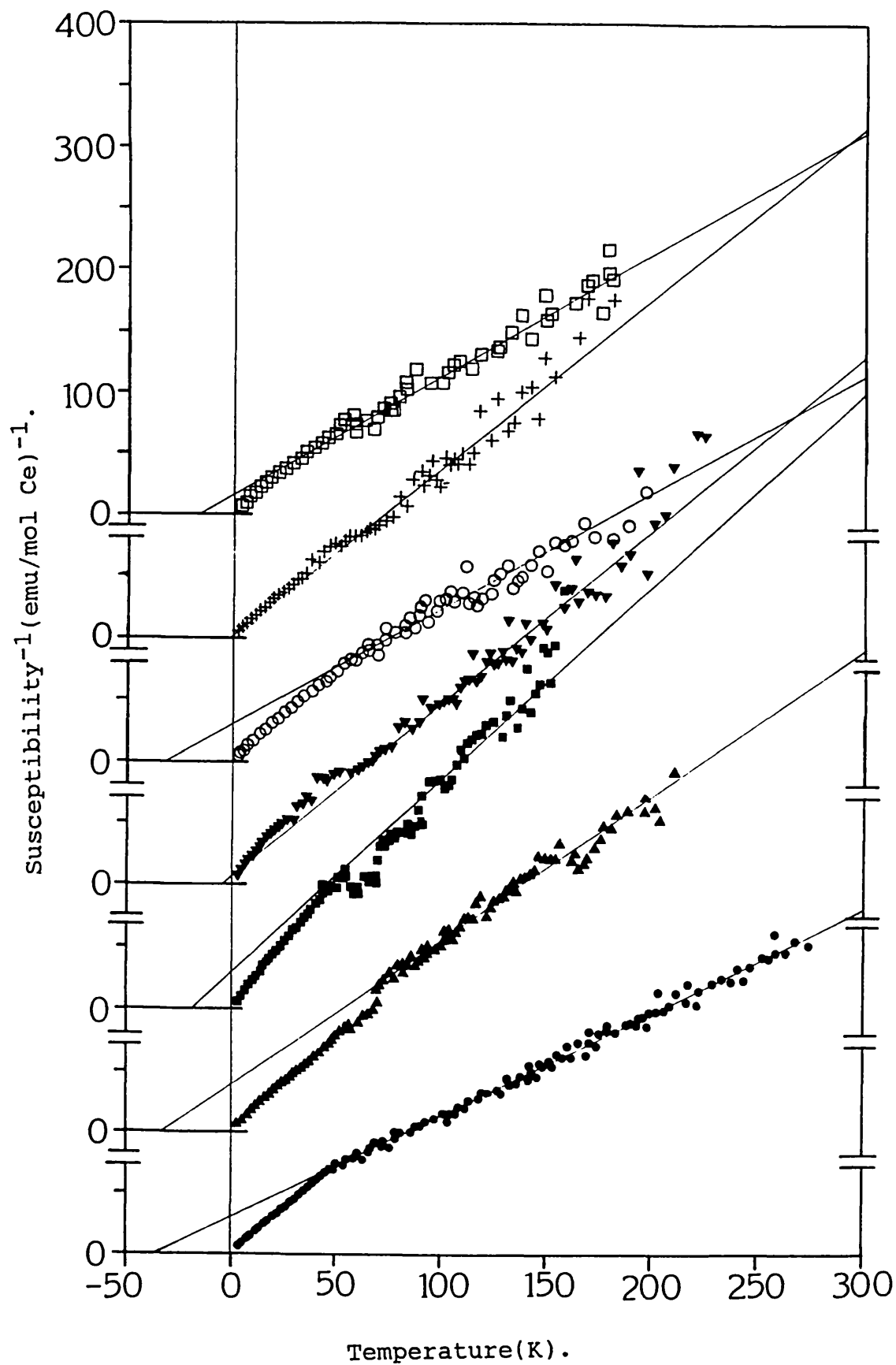


Figure 6:16. Inverse magnetic susceptibility versus temperature of selected $\text{Ce}_{1-x}\text{Y}_x\text{Cu}_2$ alloys where $x=0.00(\bullet)$, $0.10(\blacktriangle)$, $0.20(\blacksquare)$, $0.35(\blacktriangledown)$, $0.50(\circ)$, $0.70(+)$ and $0.90(\square)$.

change in slope in $\chi(T)$ is observed in samples with $x=0.00$, 0.10 and 0.20 at 3.5, 2.58 and 1.89K respectively. Taken along with the specific heat data to be presented in section 6:3:7 it seems likely that these anomalies indicate the onset of long range antiferromagnetic order. For Y concentrations greater than 20% no change in slope or cusp is observed in $\chi(T)$ above 1.5K. This indicates that magnetic order is either completely removed or more likely, as in the case of CeAl_2 doped with Y [5:40], suppressed below 1.5K, and perhaps forced into a spin glass regime. Figure 6:16 shows χ^{-1} versus temperature for the $\text{Ce}_{1-x}\text{Y}_x\text{Cu}_2$ series. The data at high temperature ($50\text{K} < T < 160\text{K}$) has been fitted to a $\chi = C/(T - \Theta_P)$ law. Values for Θ_P and μ_{eff} calculated from C are listed in table 6:3. The values for μ_{eff} remain almost unchanged for

Table 6:3. Important parameters taken from the magnetic susceptibility data for $\text{Ce}_{1-x}\text{Y}_x\text{Cu}_2$ alloys.

Conc x	0.00	0.05	0.10	0.20	0.35	0.50	0.70	0.90	0.95	1.00
$ \Theta_P(\text{K}) $	38.4	--	34.5	20.8	5.09	34.6	1.71	16.3	--	--
$\mu_{\text{eff}}(\mu_B)$	2.65	--	2.62	2.26	2.38	2.92	2.41	2.85	--	--
$\chi_{\text{MAG}}^{\text{emu/mol}}$	.140	--	.132	.129	.117	.127	.080	.020	--	--
$\chi_{\text{MAG}}^{\text{emu/molCe}}$	.140	--	.147	.162	.180	.253	.267	.203	--	--

all values of x, and are reasonably close to the value expected for a free Ce^{3+} ion. These data reinforce the suggestion made from lattice parameter measurements that the Ce valency remains essentially constant at 3+ across the alloy series. Using the ideas of Grüner and Zawadowsky [2:14] whose model for the single impurity Kondo problem suggests Θ_P can be related to T_K by $T_K = \Theta_P/4$ it is suggested that T_K remains roughly constant with a value of $\sim 5\text{K}$ for all

$0.00 \leq x \leq 0.95$.

6:3:7. Specific Heat.

The onset of magnetic ordering suggested by the susceptibility data is confirmed by specific heat measurements of Bauer et al. [6:9] (see figure 6:17). A transition is observed in $\text{Ce}_{1-x}\text{Y}_x\text{Cu}_2$ with $x=0.00$, 0.10 and 0.20 at 3.5, 2.7 and 1.8K respectively. No magnetic ordering is observed above 1.5K for $x \geq 0.3$. Calculations of the magnetic entropy per mole of Ce associated with these transitions, give values of 3.83, 2.94 and 2.38J/molK for $x=0.00$, 0.10 and 0.20 respectively. So, like many other magnetically ordered hf systems (e.g. CeAl_2 , U_2Zn_{17}) these values are much less than the $2\ln R=5.76\text{J/molK}$ associated with a doubly degenerate ground state. The loss of entropy is likely to be due to the reduction of the magnetic moments of the Ce ions because of Kondo compensation. The presence of the Kondo interaction prompts a calculation of T_K , which is found to increase from 3.8 to 4.8K as x increase from 0.00 to 0.20. This seems to confirm the crossover to a stronger Kondo regime. Figure 6:18 shows plots of C/T versus T^2 for selected $\text{Ce}_{1-x}\text{Y}_x\text{Cu}_2$ samples. Extrapolation of the data between 8 and 15K, well above any magnetic transition, to zero temperature gives values for, the electronic component of the specific heat. The values obtained are shown in table 6:4. The large γ value of 105mJ/mol K^2 attributable to a mixing of the itinerant conduction electrons with more localized 4f states seen for CeCu_2 is gradually reduced with Y content. This reduction is not especially rapid and calculated on a per mole Ce basis actually increases.

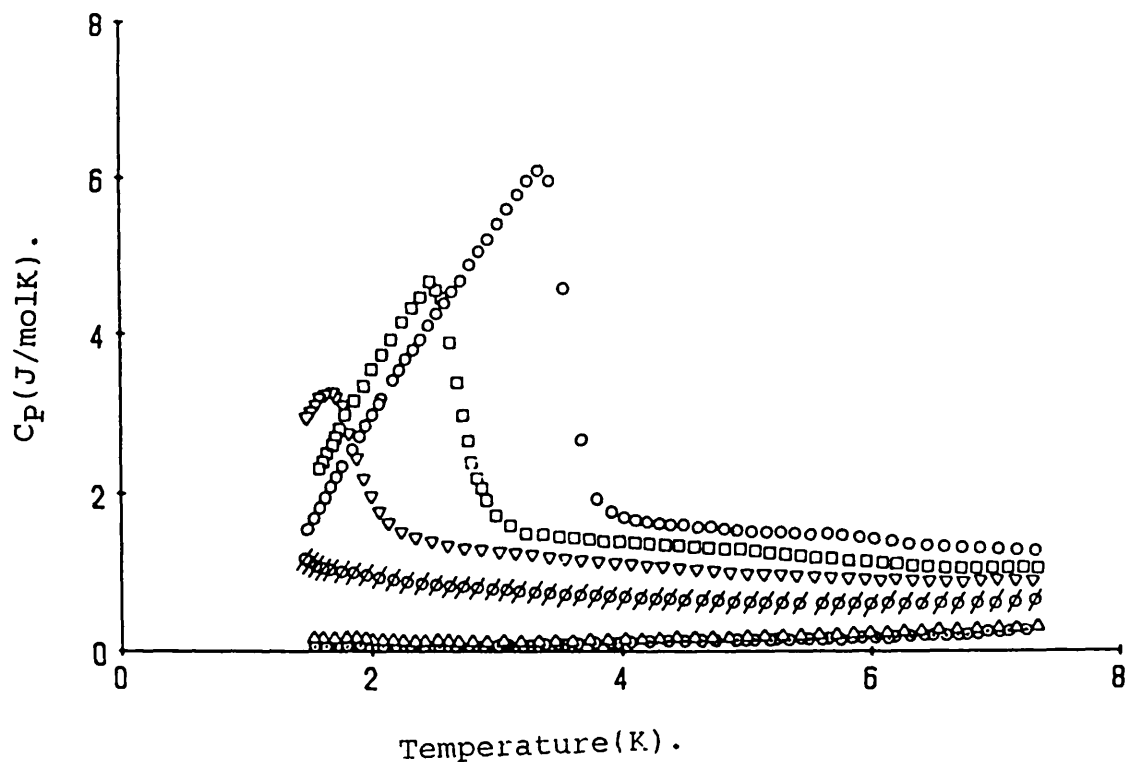


Figure 6:17. Temperature dependence of the specific heat C_p of $Ce_{1-x}Y_xCu_2$ below 8K for $x=0.00$ ($\circ$), 0.10 ($\square$), 0.20 (∇), 0.40 ($\odot$), 0.90 ($\triangle$) and 0.97 ($\odot$). Data are from Bauer et al. [6:9].

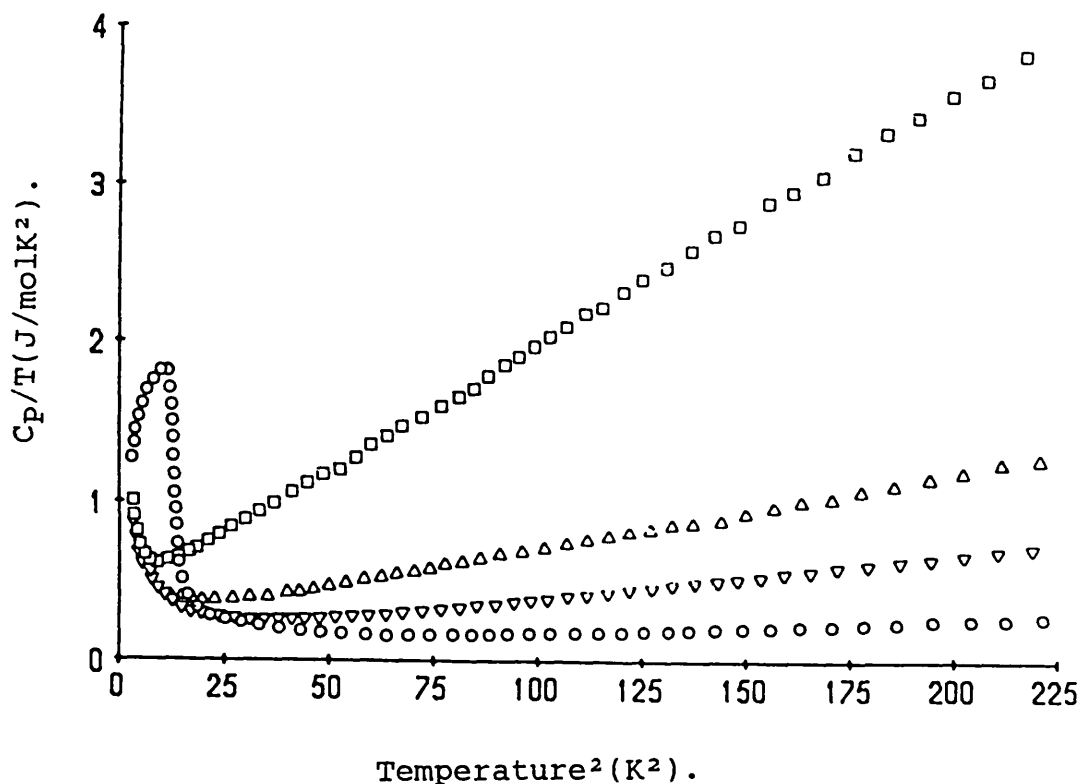


Figure 6:18. The specific heat C_p of $Ce_{1-x}Y_xCu_2$ as C_p/T versus T^2 per mol Ce for $x=0.00$ ($\circ$), 0.90 ($\triangle$), 0.80 (∇) and 0.97 ($\square$).

Table 6:4. The concentration dependence of the electronic contribution to the specific heat γ (per formula unit) and γ (per mol Ce) of $\text{Ce}_{1-x}\text{Y}_x\text{Cu}_2$.

Conc. x	0.00	0.10	0.20	0.40	0.80	0.90	0.97
γ mJ/molK ²	105	91	84	61	27	20	12
γ mJ/molCeK ²	105	102	105	102	135	200	400

6:3:8. Summary.

Addition of Y to CeCu_2 leads to a steady decrease in the cell volume. This steady decrease indicates the Ce atoms remain in a 3^+ state. This assertion is supported by fits to $\chi(T)$ data taken at high temperature which also indicate Ce with a 3^+ valency. Electrical resistivity results reflect single Kondo impurity behaviour in alloys with $x \geq 0.20$. As the Ce concentration is increased still further one observes a crossover to a dense Kondo system. For $x \leq 0.20$, a combination of the onset of coherence and magnetic ordering are responsible for dramatic falls in $\rho(T)$ at low temperature. The magnetic resistivity indicates that for $x \leq 0.8$ addition of Y to CeCu_2 leads to a strengthening of the Kondo interaction. The reduction in T_N and in the magnitude of the signal seen in $\chi_{a.c.}(T)$ data also reflects a strengthening of the Kondo interactions. It may be that chemical pressure effects enhance the coupling constant J between the 4f and conduction band electrons leading to the observed changes. Other effects of pressure include modifications in the C.F. splitting manifested by a shifting of the peaks seen in ρ_{mag} and $S(T)$.

6:4. $\text{Ce}(\text{Cu}_{1-x}\text{M}_x)_2$ where M is Ga, Al, Pt, or Ag.

6:4:1. Introduction.

In this section the effects of replacing the Cu in CeCu_2 with a number of other elements will be discussed. A comparison between the effects of alloying on the Ce and Cu sites on the properties of CeCu_2 will then be made.

6:4:2. $\text{Ce}(\text{Cu}_{1-x}\text{Ga}_x)_2$ $0.00 \leq x \leq 0.50$.

Bauer et al. [6:10] have made a study of the effects of alloying with Ga on the properties of CeCu_2 . The shallow minimum in $\rho(T)$ of pure CeCu_2 enlarges with increasing Ga content (see figure 6:19). For $x=0.30$ and 0.40 a pronounced negative temperature coefficient evolves in $\rho(T)$. Less than 5% Ga substitution is sufficient to remove the onset of coherence at low temperature. The magnitude of $\rho(T)$ also increases reaching values of several hundred $\mu\text{ohm centimetres}$ for $x \geq 0.10$. The strong Kondo interactions present in this system can be seen by plotting the magnetic resistivity $\rho(\text{Ce}(\text{Cu}_{1-x}\text{Ga}_x)_2) - \rho(\text{La}(\text{Cu}_{1-x}\text{Ga}_x)_2)$. Specific heat measurements (figure 6:20) reveal that the antiferromagnetic transition observed in pure CeCu_2 is strongly suppressed with no magnetic order observed above 1.5K in the samples containing 10% or more Ga. Magnetisation measurements indicate a strong increase in the low field magnetic susceptibility at 1.5K with the enhancement reaching a maximum around $x=0.30$. These results suggest a movement away from antiferromagnetic toward ferromagnetic type interactions. However the strength of the Kondo interaction means no ferromagnetic ordering is observed.

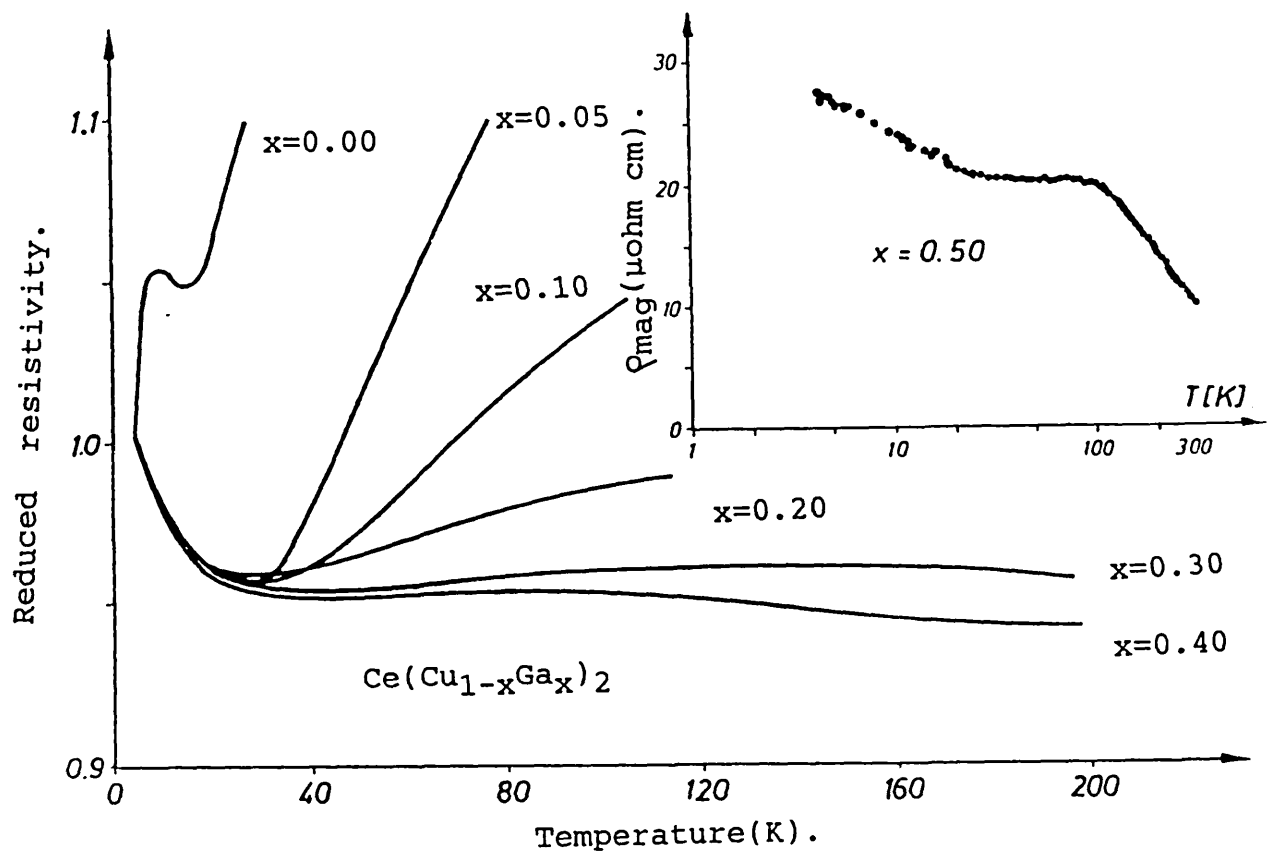


Figure 6:19. The temperature dependence of the reduced electrical resistivity ($Q/Q_{4.2K}$) of $Ce(Cu_{1-x}Ga_x)_2$. The inset shows the magnetic contribution to the electrical resistivity for $x=0.50$ in a semilogarithmic representation. Data are from Bauer et al. [6:10].

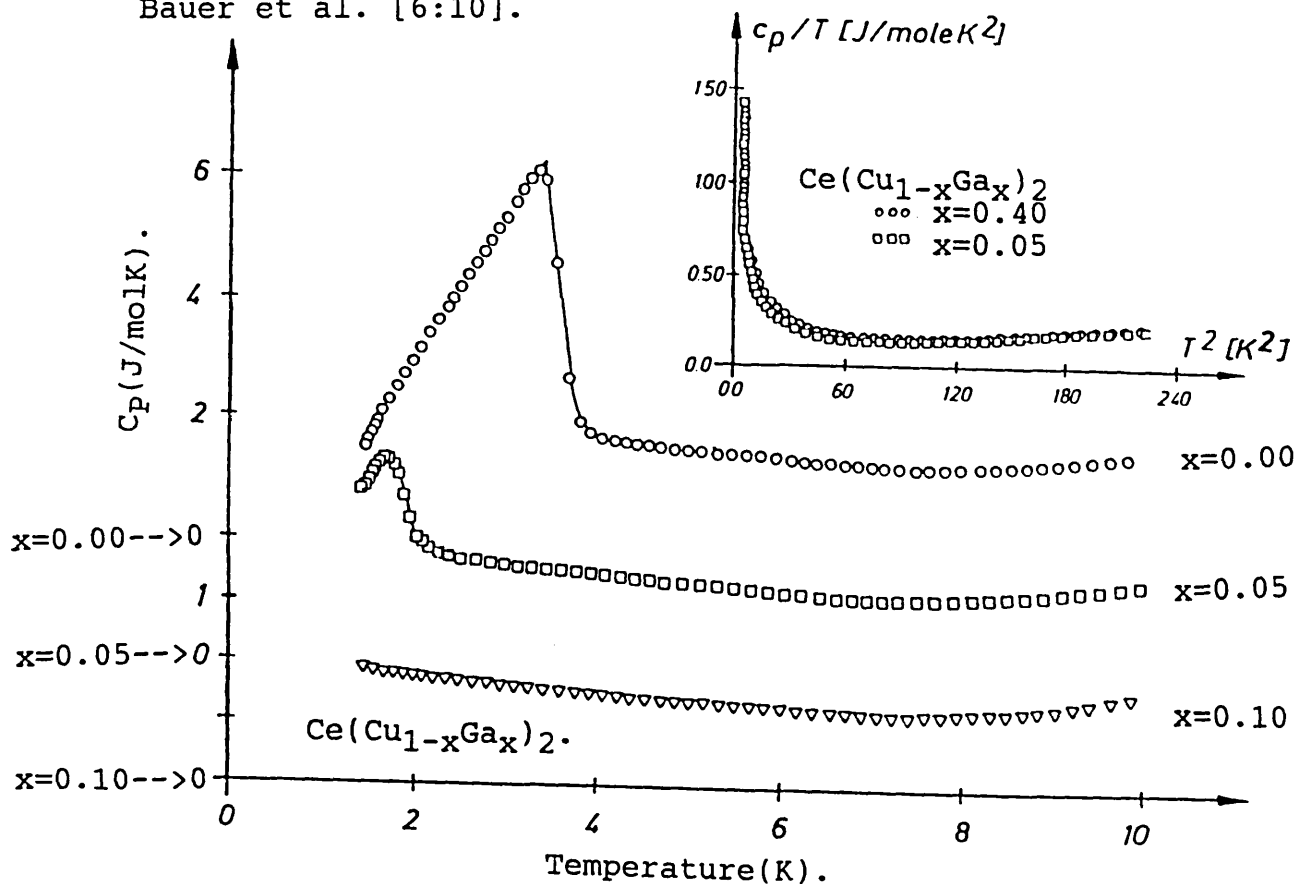


Figure 6:20. The specific heat C_p as a function of the temperature T of $Ce(Cu_{1-x}Ga_x)_2$ for selected values of x . The inset shows C_p/T versus T^2 for $x=0.4$ and $x=0.05$. Data are from Bauer et al. [6:10].

6:4:3. $\text{Ce}(\text{Cu}_{1-x}\text{Al}_x)_2$ $x \leq 0.20$.

6:4:3:1. Sample Preparation.

Because of the different structures of the two end compounds it is not expected that one will be able to substitute large amounts of Al without introducing considerable structural distortion and possibly the appearance of second phase.

As a result, Al substitutions were limited to $x \leq 0.20$. All the samples were prepared using the method described in 3:6. The samples were then annealed at 600°C for 7 days followed by 7 days at 700°C . Metallographic specimens reveal these samples are all single phase with only a small amount of oxide and porosity.

6:4:3:2. Electrical Resistivity.

The results of a study of the electrical resistivity of the $\text{Ce}(\text{Cu}_{1-x}\text{Al}_x)_2$ system are shown in figures 6:21 to 6:24. Al substitutions lead to rapid increases in the magnitude of the electrical resistivity at both 273 and 2.2K. This may be due to a combination of an increase number of structural defects and an increase in potential scattering with alloying. At first, the depth of the shallow minimum in $\rho(T)$ seen in pure CeCu_2 increases with increasing Al concentration, reaching a maximum at $x=0.15$. The position of the minimum in $\rho(T)$ is shifted upward in temperature with Al. At the same time the low temperature maximum seen in pure CeCu_2 is continuously shifted to lower temperature with increasing x . Since this maximum is associated with the formation of a Kondo lattice leading to coherent Kondo scattering and the onset of magnetic order, such a suppression indicates either that Al disrupts the formation of a Kondo lattice and/or removes the magnetic order. The Kondo interactions present in the CeCu_2

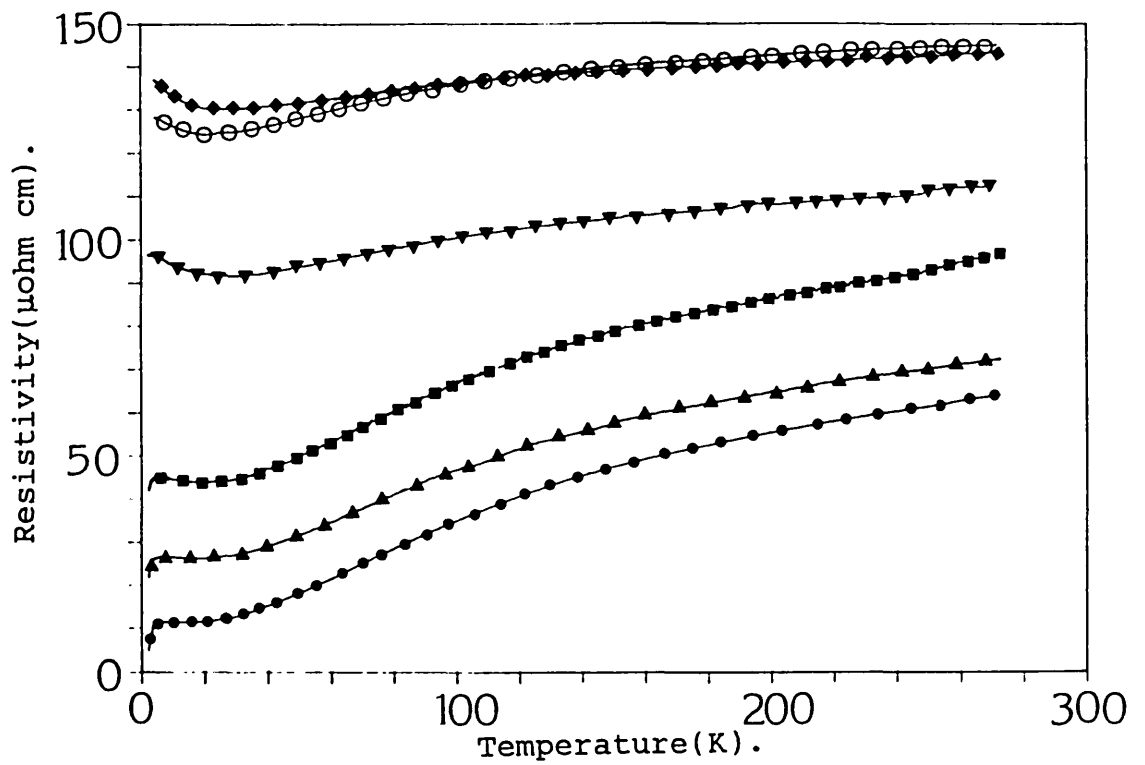


Figure 6:21. The temperature dependence of the electrical resistivity of $\text{Ce}(\text{Cu}_{1-x}\text{Al}_x)_2$ alloys for $x=0.00(\bullet)$, $0.02(\blacktriangle)$, $0.05(\blacksquare)$, $0.10(\blacktriangledown)$, $0.15(\blacklozenge)$ and $0.20(\circ)$.

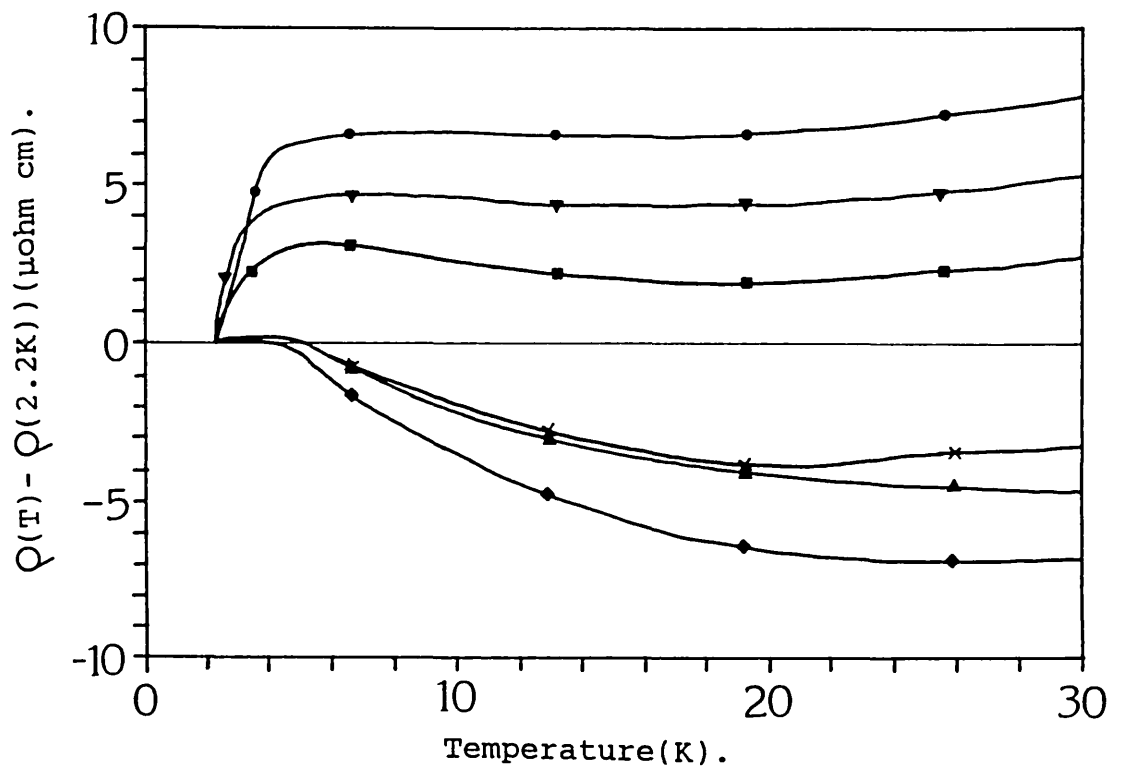


Figure 6:22. The low temperature behaviour of electrical resistivity for $\text{Ce}(\text{Cu}_{1-x}\text{Al}_x)_2$ alloys shown as $Q(T) - Q(2.2\text{K})$. $x=0.00(\bullet)$, $0.02(\blacktriangledown)$, $0.05(\blacksquare)$, $0.10(\blacktriangle)$, $0.15(\blacklozenge)$ and $0.20(\times)$.

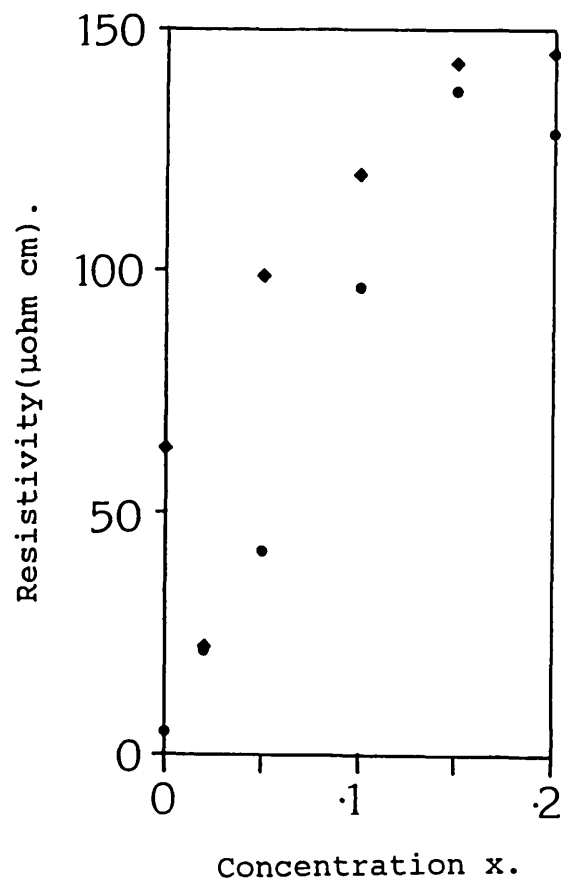


Figure 6:23. Variation with concentration x of the magnitude of the electrical resistivity at 273K(◆) and 2.2K(●) for $\text{Ce}(\text{Cu}_{1-x}\text{Al}_x)_2$ alloys.

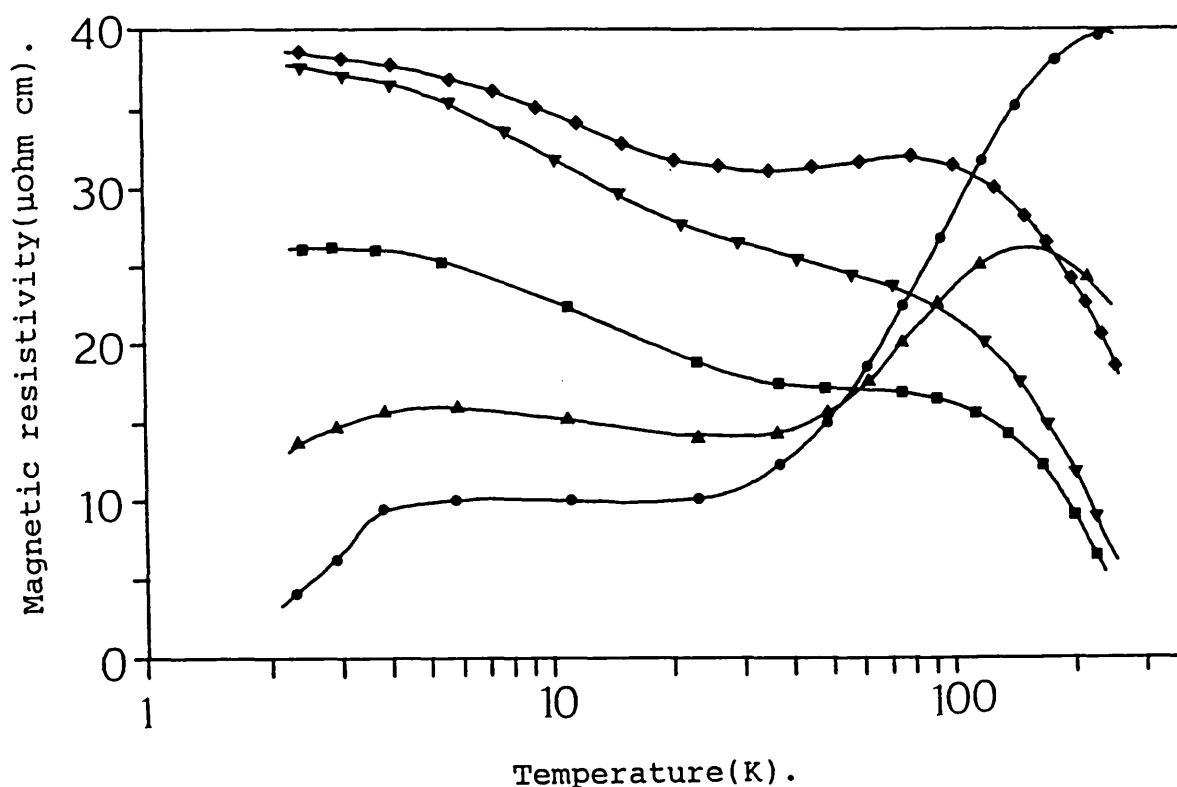


Figure 6:24. Magnetic contribution to the electrical resistivity for $\text{Ce}(\text{Cu}_{1-x}\text{Al}_x)_2$ alloys in a semilogarithmic representation, where $x=0.00(\bullet)$, $0.05(\blacktriangle)$, $0.10(\blacksquare)$, $0.15(\blacktriangledown)$ and $0.20(\blacklozenge)$.

system remain. To see this clearly we plot $\rho_{\text{mag}} = \rho(\text{Ce}(\text{Cu}_{1-x}\text{Al}_x)_2) - \rho(\text{La}(\text{Cu}_{1-x}\text{Al}_x)_2)$. The position of the high temperature maximum is dependent on the behaviour of the resistivity of $\text{La}(\text{Cu}_{1-x}\text{Al}_x)_2$ which appears slightly anomalous. However it is clear that for all values of $x \leq 0.20$ ρ_{mag} exhibits two regimes of logarithmic temperature dependence separated by a broad maximum associated with the crystal field and Kondo interactions.

6:4:3:3. a.c. Susceptibility.

Figure 6:25 shows the temperature dependence of the inverse magnetic susceptibility of selected alloys. The results have been analysed assuming a Curie-Weiss temperature dependence, $\chi(T) = C/(T - \Theta)$. Θ values remain negative for all values of $x \leq 0.20$. No clear trend concerning the magnitude of Θ can be discerned. Again, using the ideas of Grüner and Zawadowsky [2:14] ($T_K = \Theta_P/4$), it is suggested that T_K remains roughly constant with a value of $\sim 5\text{K}$ for all $0.00 \leq x \leq 0.20$.

Table 6:5. Important parameters taken from the magnetic susceptibility data for $\text{Ce}(\text{Cu}_{1-x}\text{Al}_x)_2$ alloys.

Conc x	0.00	0.02	0.05	0.10	0.20
$ \Theta_P(\text{K}) $	38.4	9.56	19.8	8.65	24.42
$\mu_{\text{eff}}(\mu_B)$	2.65	2.66	2.79	2.74	2.57
χ_{MAG} emu/mol	0.14	0.18	0.22	0.30	0.155

Values of μ_{eff} for the Ce^{3+} ions extracted from the high temperature data show Ce moments remain close to those expected for free Ce^{3+} atom. Low temperature magnetic susceptibility of $\text{Ce}(\text{Cu}_{1-x}\text{Al}_x)_2$ alloys with $x \leq 0.20$ are shown in figure 6:26. No anomaly (either a change in slope or a cusp), is observed in susceptibility of samples with $x \geq 0.05$. This indicates the antiferromagnetic order seen in pure CeCu_2

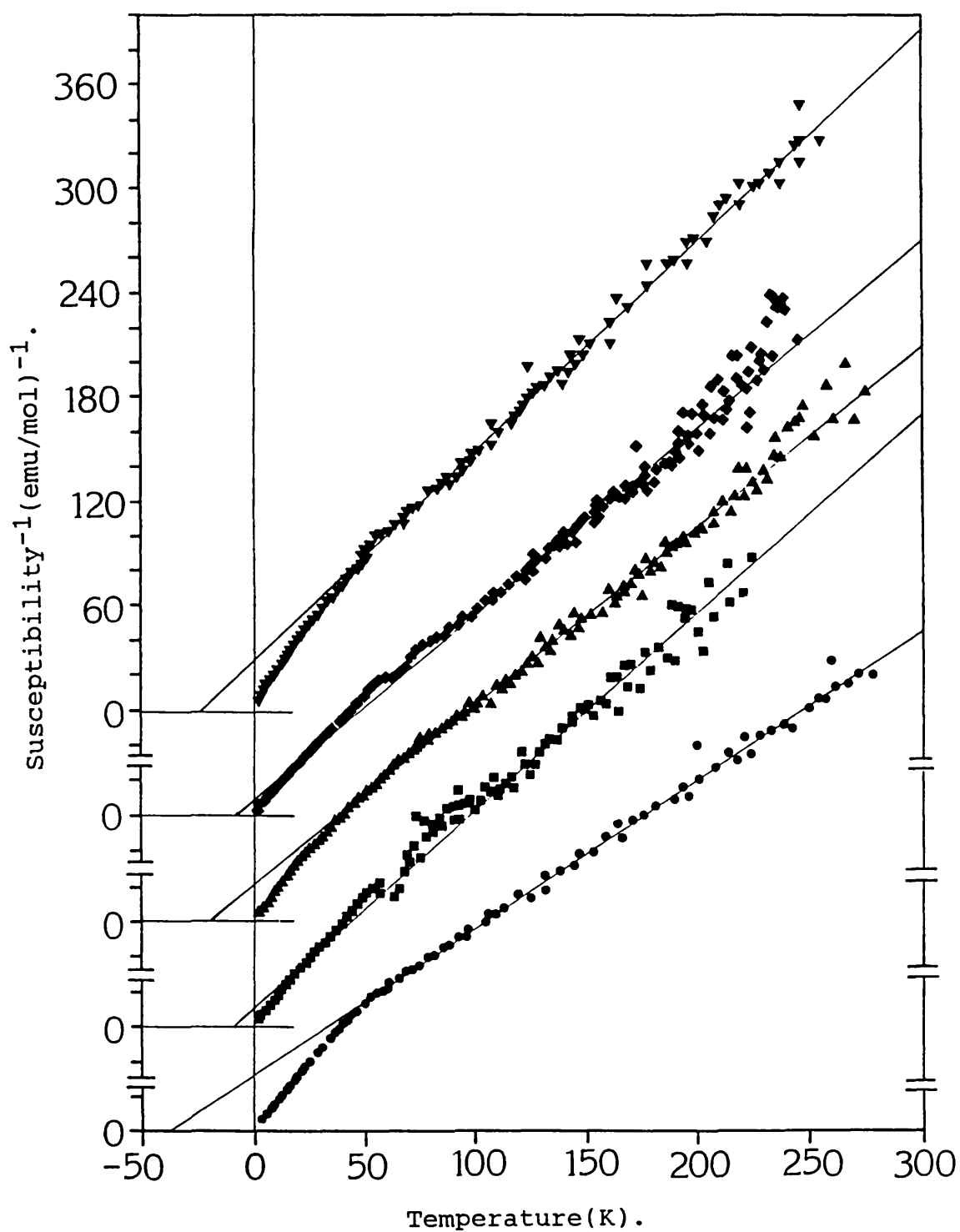


Figure 6:25. Temperature dependence of the inverse magnetic susceptibility of $\text{Ce}(\text{Cu}_{1-x}\text{Al}_x)_2$ for $x=0.00$ (●), 0.02 (■), 0.05 (▲), 0.10 (◆) and 0.20 (▼).

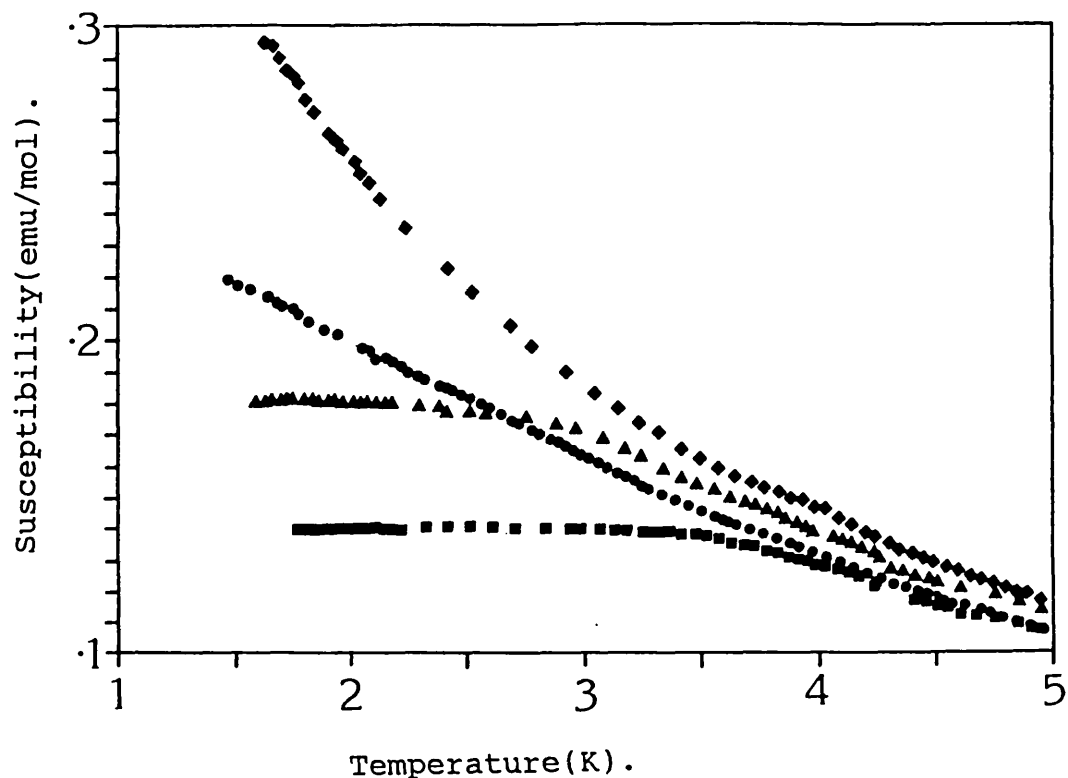


Figure 6:26. Magnetic susceptibility of selected $\text{Ce}(\text{Cu}_{1-x}\text{Al}_x)_2$ alloys at low temperature. $x=0.00(\blacksquare)$, $0.02(\blacktriangle)$, $0.05(\bullet)$ and $0.10(\blacklozenge)$.

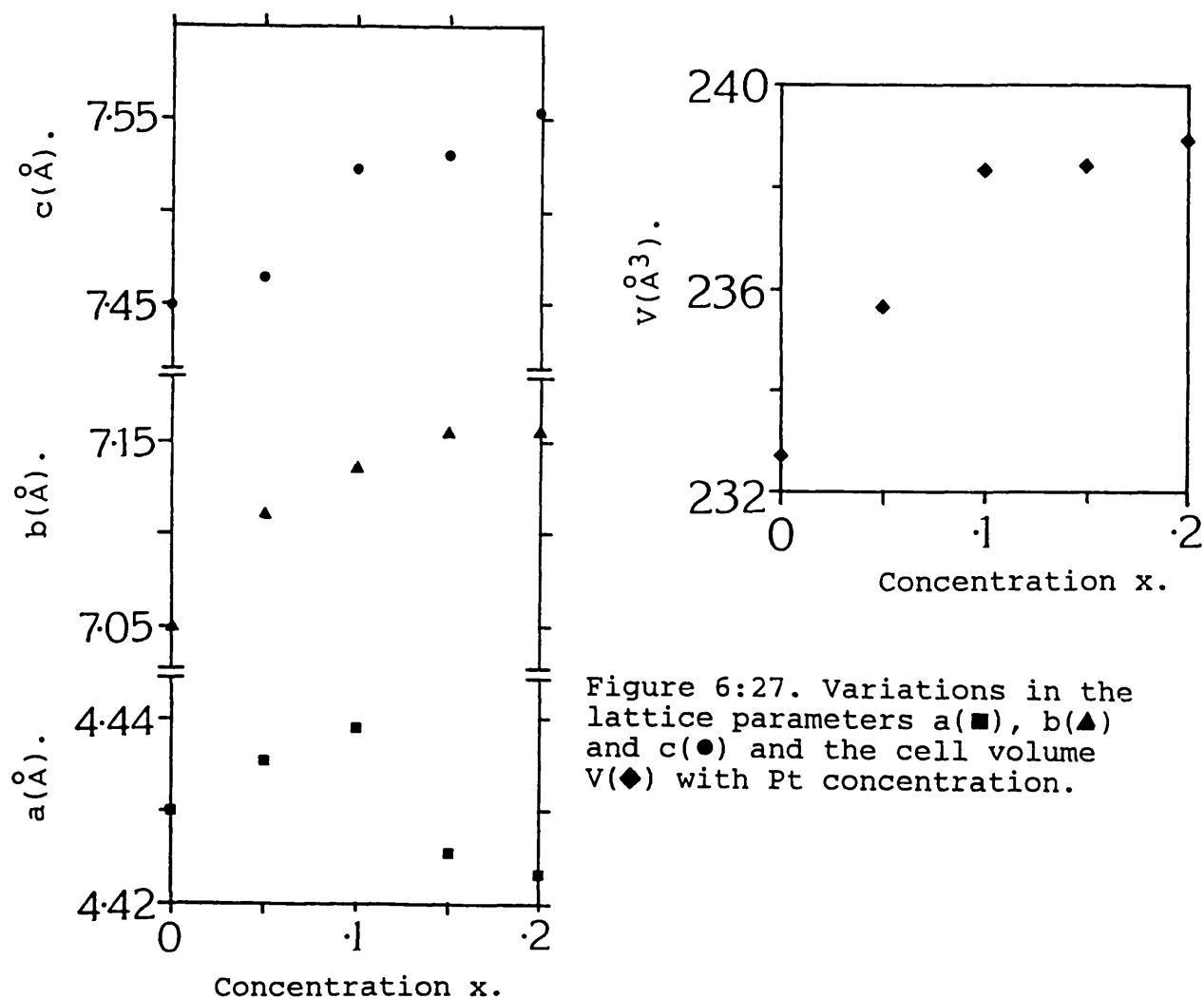


Figure 6:27. Variations in the lattice parameters $a(\blacksquare)$, $b(\blacktriangle)$ and $c(\bullet)$ and the cell volume $V(\blacklozenge)$ with Pt concentration.

is removed or at least suppressed below 1.5K for $x \geq 0.05$. A strong increase in the low temperature magnitude of $\chi_{a.c.}$ is observed, with the maximum enhancement occurring at $x=0.15$. This suggests an increase in the strength of ferromagnetic interactions within the system. As with Ga substitution the presence of Kondo compensation appears to inhibit the onset of ferromagnetic order.

6:4:4. $\text{Ce}(\text{Cu}_{1-x}\text{Pt}_x)_2$ $x \leq 0.30$.

6:4:4:1. Sample Preparation.

CePt_2 has a cubic structure. So once again the substitution of Pt into CeCu_2 is expected to introduce structural distortions and large amounts of Pt may lead to the appearance of a second phase. Samples with $x \leq 0.30$ were made using the method described in section 3:6. All samples were annealed at 700°C for 7 days. Metallographic specimens of all samples were then prepared. For $x \leq 0.20$, the samples appear essentially single phase, with only a small trace of oxide (probably associated with the Ce). For $x=0.30$ the sample was made up of a majority phase and around 5% of a second phase. This amount of second phase, providing it does not become superconducting should have only a small effect on resistivity measurements. However it may have a significant effect on the results of magnetic susceptibility experiment depending on its magnetic character.

6:4:4:2. Lattice Parameters.

For $x \leq 0.20$, addition of Pt leaves the value of the lattice parameter a almost unchanged and produces increases in lattice parameters b , c and the total cell volume (see figure 6:27).

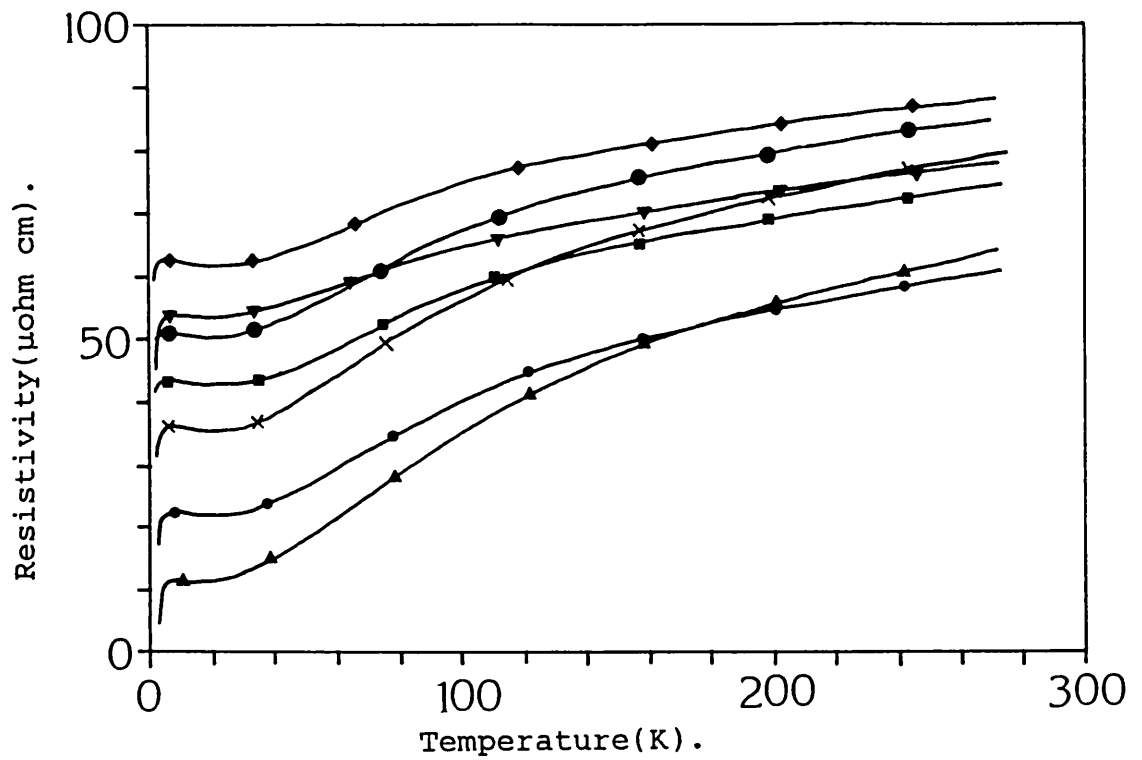


Figure 6:28. The temperature dependence of the electrical resistivity of $\text{Ce}(\text{Cu}_{1-x}\text{Pt}_x)_2$ alloys for $x=0.00(\blacktriangle)$, $0.02(\bullet)$, $0.05(\times)$, $0.10(\blacksquare)$, $0.15(\odot)$, $0.20(\blacklozenge)$ and $0.30(\blacktriangledown)$.

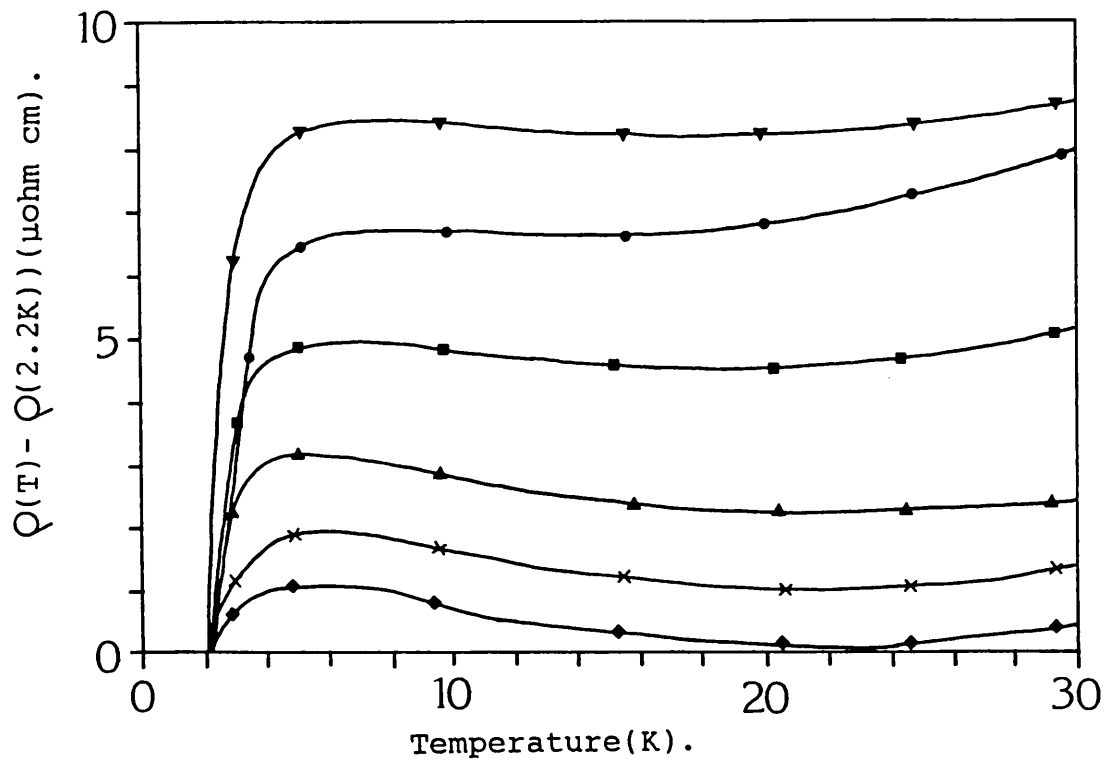


Figure 6:29. The low temperature behaviour of the electrical resistivity for $\text{Ce}(\text{Cu}_{1-x}\text{Pt}_x)_2$ alloys shown as $Q(T) - Q(2.2\text{K})$. $x=0.00(\bullet)$, $0.05(\blacksquare)$, $0.10(\times)$, $0.15(\blacklozenge)$, $0.20(\blacktriangle)$ and $0.30(\blacktriangledown)$.

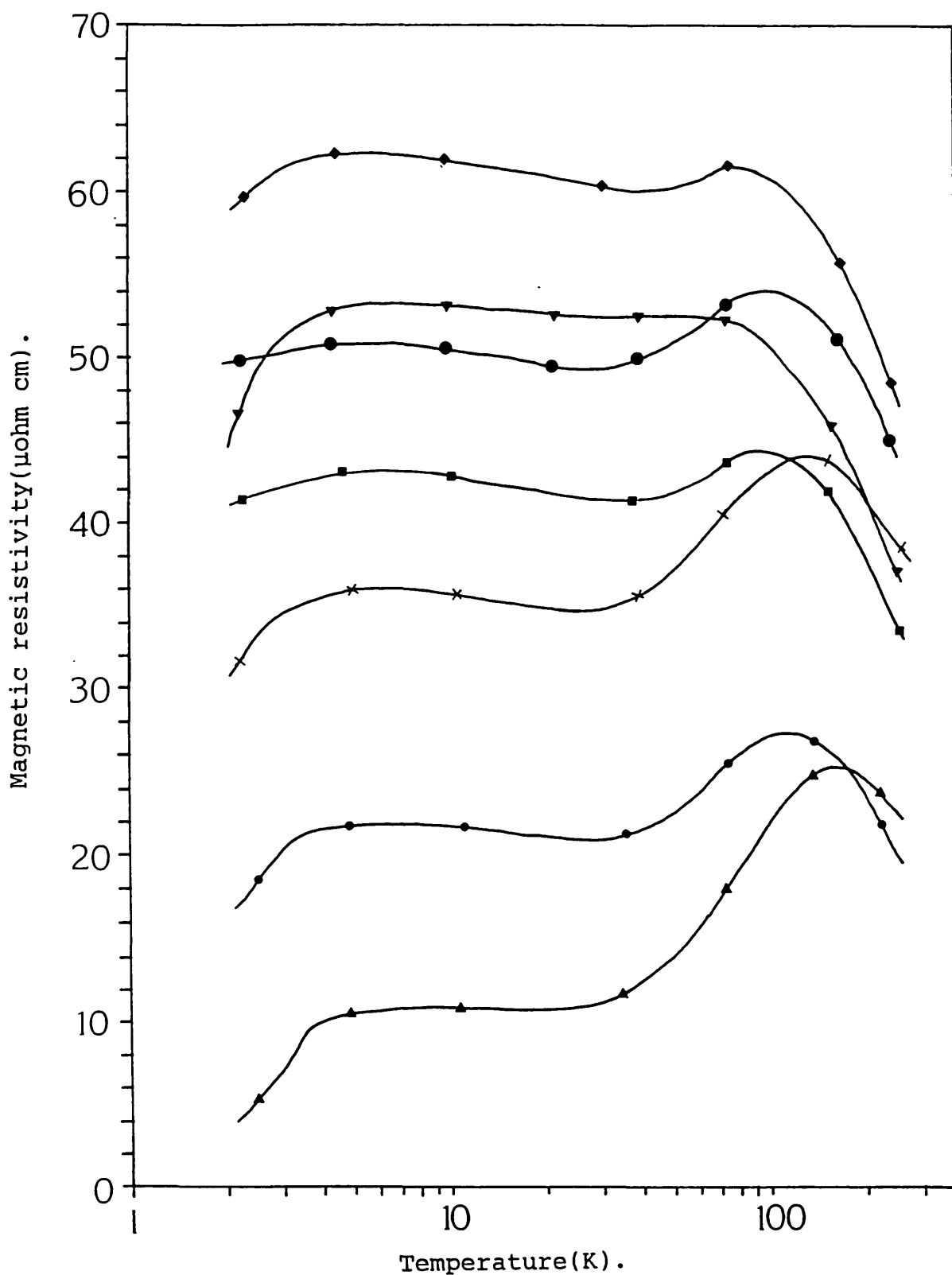


Figure 6:30. Magnetic contribution to the electrical resistivity for $\text{Ce}(\text{Cu}_{1-x}\text{Pt}_x)_2$ alloys in a semilogarithmic representation, where $x=0.00(\blacktriangle)$, $0.02(\bullet)$, $0.05(\times)$, $0.10(\blacksquare)$, $0.15(\odot)$, $0.20(\blacklozenge)$ and $0.30(\blacktriangledown)$.

6:4:4:3. Electrical Resistivity.

The effects of Pt alloying on the electrical resistivity of CeCu_2 are shown in figures 6:28 to 6:30. Addition of Pt does not lead to the rapid increase in the magnitude of $\rho(T)$ observed with the Ga and Al substitutions. Substitutions of Pt do begin to suppress the fall in $\rho(T)$ at low temperature associated with magnetic order and the onset of coherent Kondo scattering. By $x=0.15$ the low temperature fall amounts to only 5% of the value of $\rho(T)$ at its low temperature maximum. However, further additions of Pt then lead to an increase the fall in $\rho(T)$ at low temperature. It may be that this fall is associated with the re-emergence of long range magnetic order. This possibility will be discussed further in section 6:4:4:4. The depth of the minimum in $\rho(T)$ remains shallow with no obvious increase in the strength of the Kondo behaviour. The magnetic component of the electrical resistivity is shown in figure 6:30. These results also indicate the strength of the Kondo interaction remains unaltered.

6:4:4:4. Magnetic Susceptibility.

Temperature dependences of the magnetic susceptibility of $\text{Ce}(\text{Cu}_{1-x}\text{Pt}_x)_2$ alloys are shown in figure 6:31. Addition of Pt reduces the temperature at which the anomaly in $\chi(T)$ indicating the presence of long range antiferromagnetic order is observed. For $x=0.10$ this ordering is removed or at least suppressed below 1.5K. Further additions of Pt ($0.15 \geq x \geq 0.30$) produce a rapid increase in the magnitude of the susceptibility at low temperature (see figure 6:32). This increase is far greater than that observed with Ga or Al substitutions, with the maximum value reached by $\chi_{a.c}$ in the

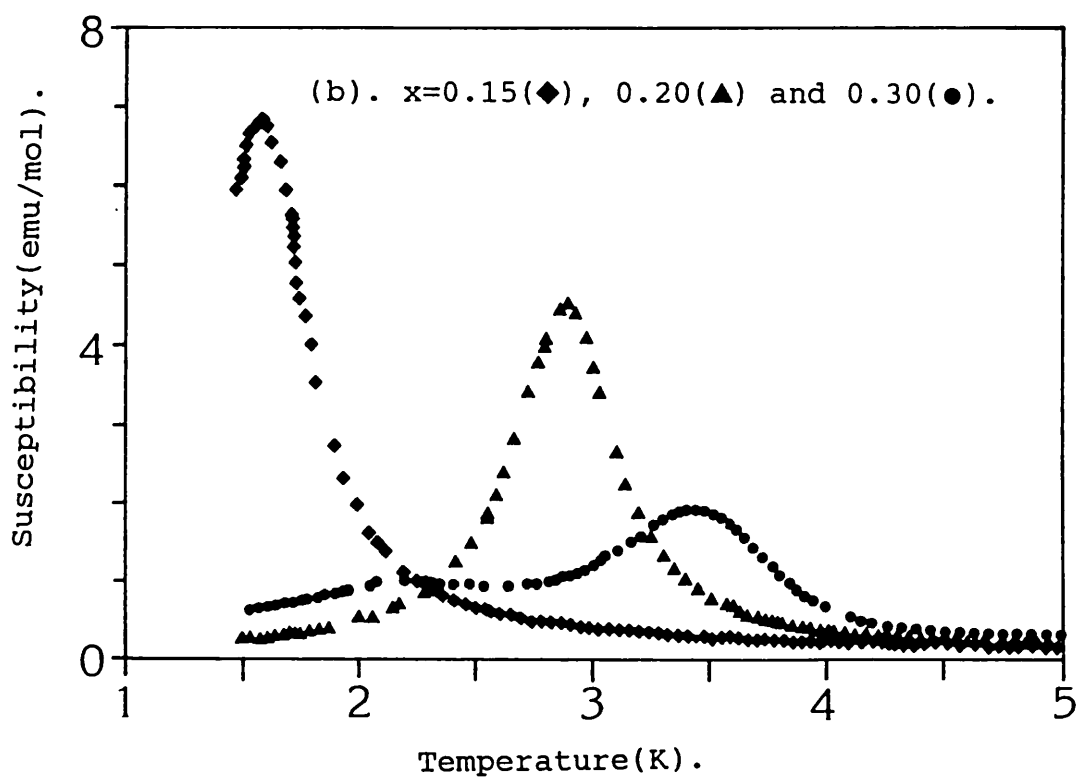
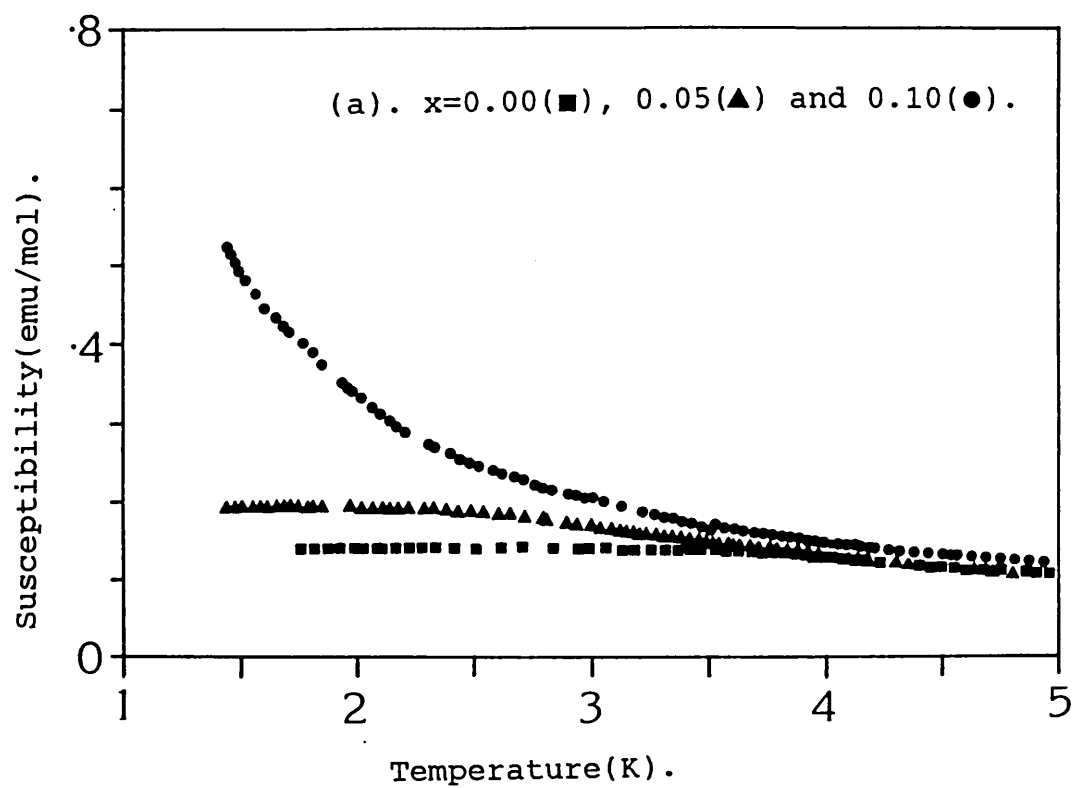


Figure 6:31. (a) and (b) Magnetic susceptibility of selected $\text{Ce}(\text{Cu}_{1-x}\text{Pt}_x)_2$ alloys at low temperature.

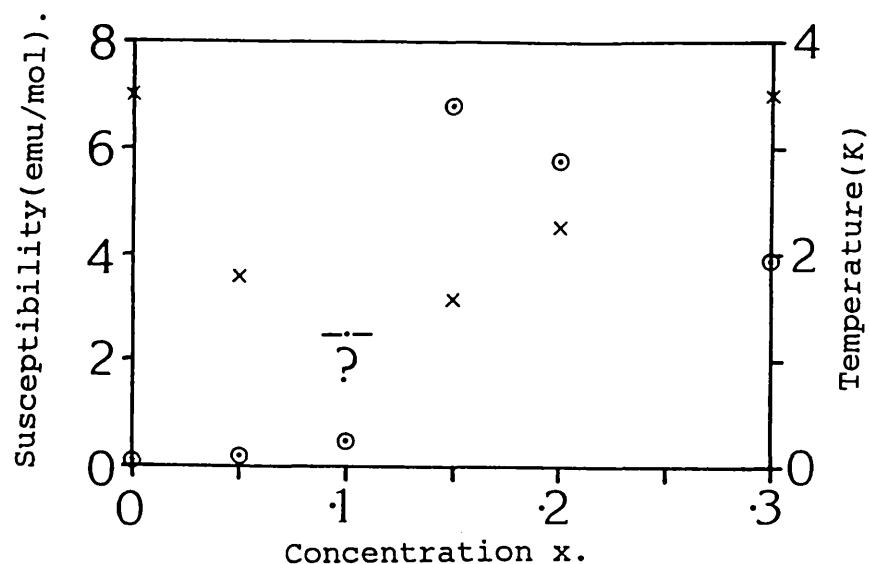


Figure 6:32. Variation with concentration x of the magnitude of the maximum value reached by the magnetic susceptibility ($\odot$) between 273K and 2.2K (left hand scale) and the temperature ($\times$) of the peak observed in the magnetic susceptibility (right hand scale) for $\text{Ce}(\text{Cu}_{1-x}\text{Pt}_x)_2$ alloys.

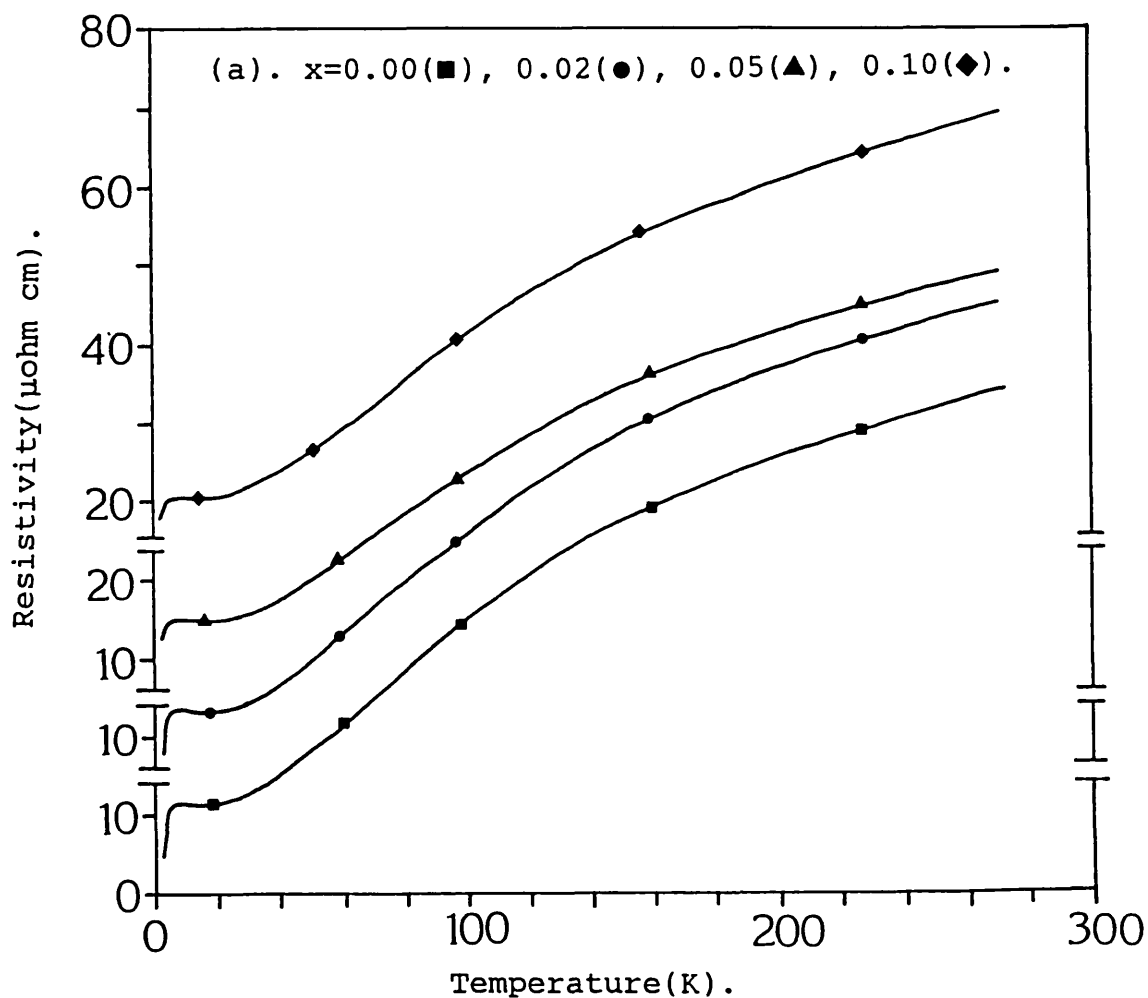


Figure 6:33. (a) and (b) The temperature dependence of the electrical resistivity of $\text{Ce}(\text{Cu}_{1-x}\text{Ag}_x)_2$ alloys.

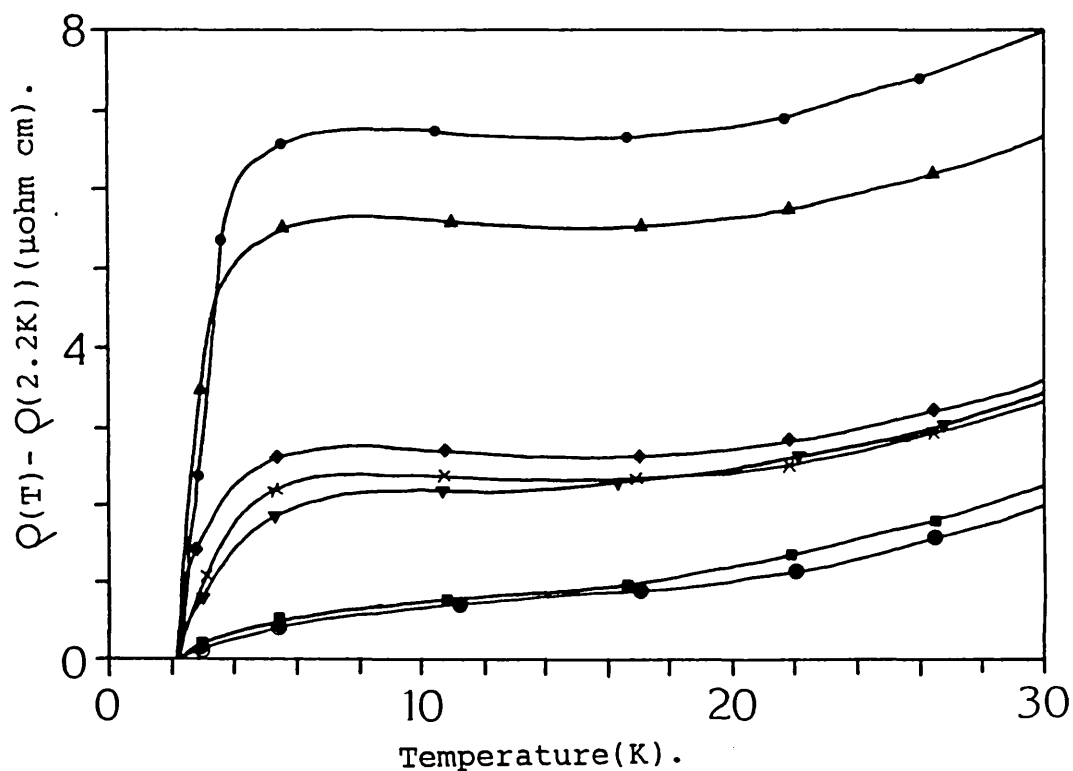
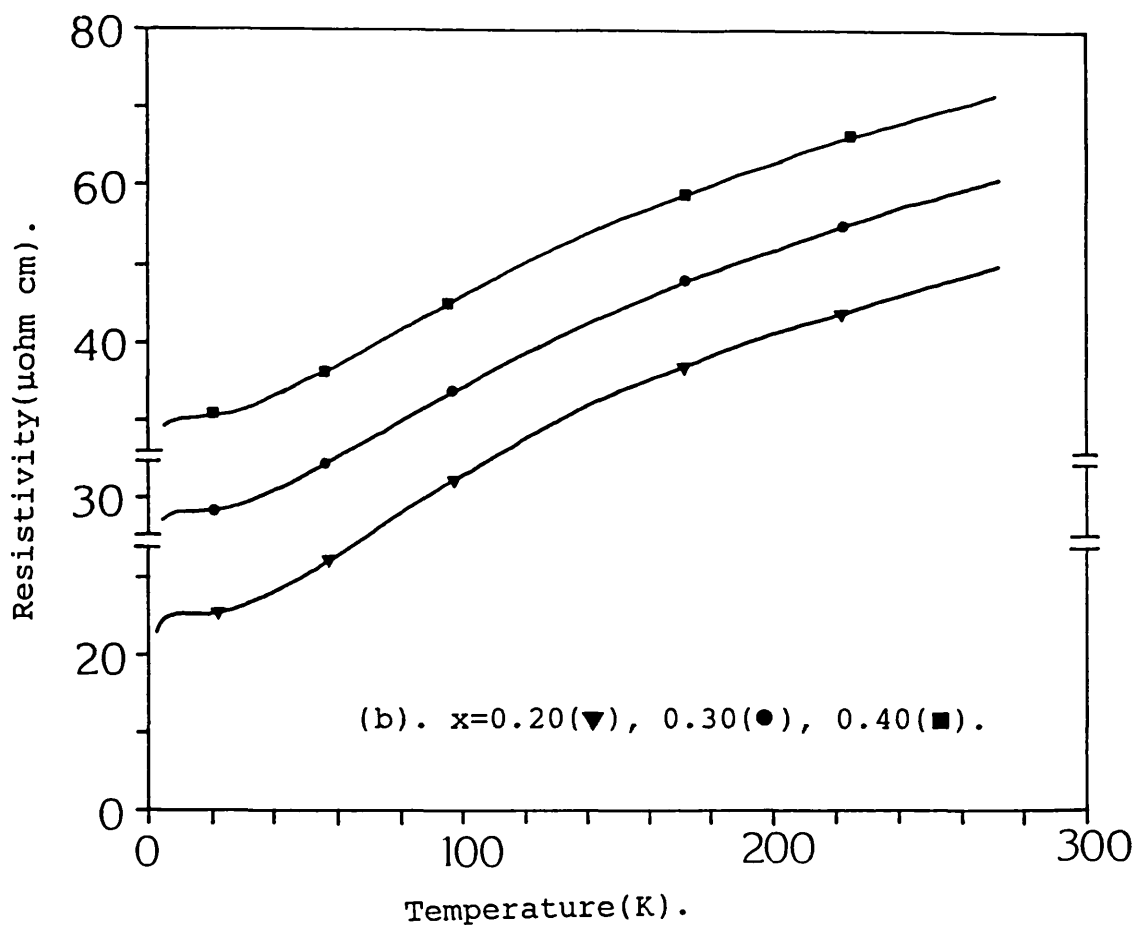


Figure 6:34. The low temperature behaviour of electrical resistivity for $\text{Ce}(\text{Cu}_{1-x}\text{Ag}_x)_2$ alloys shown as $Q(T) - Q(2.2\text{K})$. $x=0.00(\bullet)$, $0.02(\blacktriangle)$, $0.05(\blacklozenge)$, $0.10(\times)$, $0.20(\blacktriangledown)$, $0.30(\circ)$ and $0.40(\blacksquare)$.

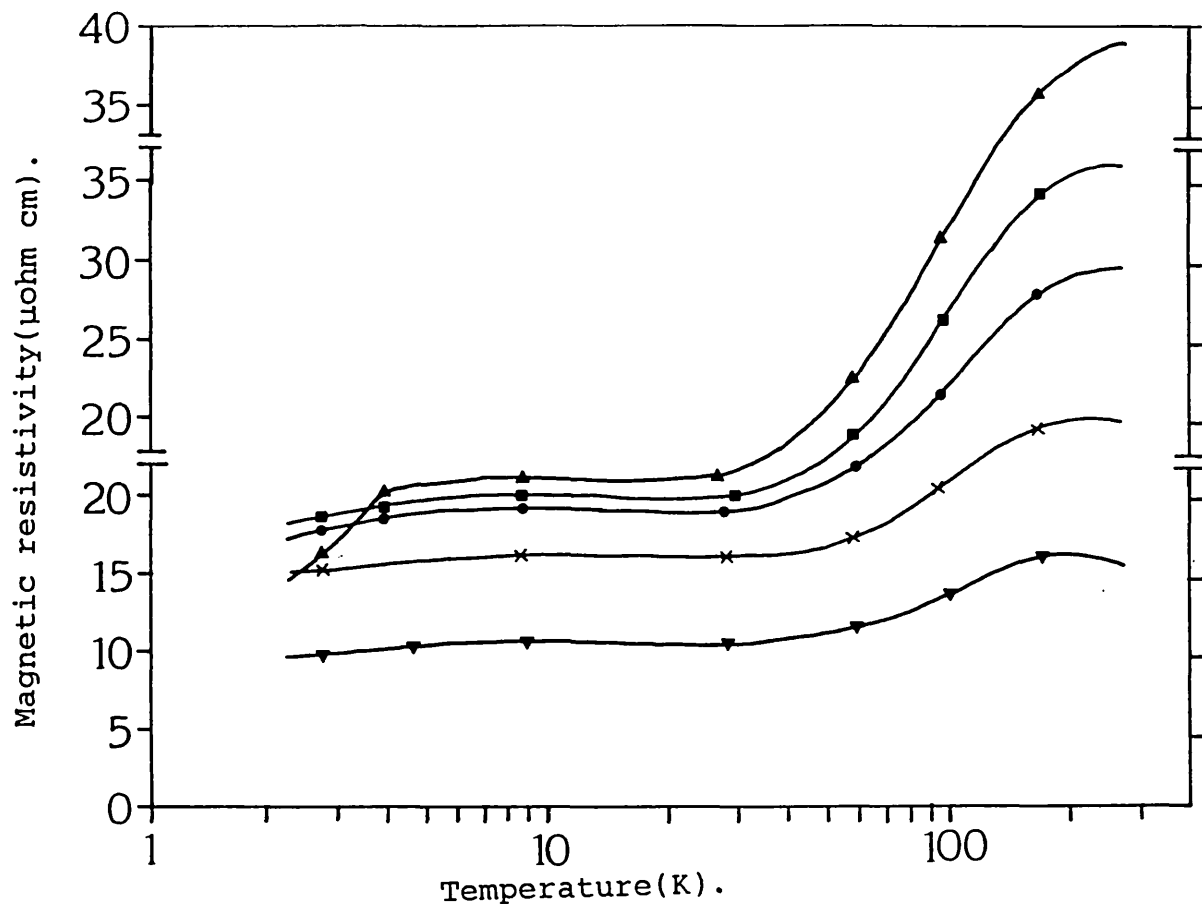


Figure 6:35. Magnetic contribution to the electrical resistivity for $\text{Ce}(\text{Cu}_{1-x}\text{Ag}_x)_2$ alloys in a semilogarithmic representation, where $x=0.00(\blacktriangle)$, $0.10(\blacksquare)$, $0.20(\bullet)$, $0.30(\times)$ and $0.40(\blacktriangledown)$.

temperature range 1.5K to 280K, χ_{MAX} , increasing by at least an order of magnitude. At the same time a peak appears in $\chi(T)$ at low temperature. The concentration dependence of the temperature of this peak and the magnitude of the maximum value of $\chi(T)$ reached at low temperature are shown in figure 6:32.

6:4:4:5. Discussion.

The rapid fall in $\rho(T)$ observed at low temperature, which emerges in samples where $0.15 \leq x \leq 0.30$, takes place at Pt concentrations greater than that required to suppress the fall in $\rho(T)$ associated with the formation of a Kondo lattice and long range antiferromagnetic order. It seems then, that the fall in $\rho(T)$ and the peak in $\chi_{\text{a.c}}$ at higher Pt concentrations are due to the re-emergence of long range or spin glass magnetic order. The nature of this magnetic order is unclear. The shape of the peak in $\chi_{\text{a.c}}$ is reminiscent of a spin glass, but this type of ordering is unlikely to produce such a rapid fall in $\rho(T)$. To date, no definite statement on the nature of the ordering can be made.

6:4:5. $\text{Ce}(\text{Cu}_{1-x}\text{Ag}_x)_2$ $x \leq 0.60$.

6:4:5:1. Sample Preparation.

Samples with $x \leq 0.40$ prepared using the method described in section 3:6. All samples were annealed for 7 days at 700°C for 7 days. Metallographic specimens of all samples reveal the presence of a small amount of oxide, but no unwanted second phase. CeAg_2 crystallizes into the orthorhombic CeCu_2 structure with lattice parameters greater than the corresponding values in CeCu_2 . This results in a larger unit crystallographic cell. X-ray analysis confirms addition of Ag leads to an expansion in the unit cell [6:11].

6:4:5:2. Electrical Resistivity.

Results of electrical resistivity measurements are shown in figure 6:33. The magnitude of the resistivity at 273K increases only slowly with Ag concentration in line with an expected increase in the residual resistivity due to the introduction of crystal defects. The addition of Ag slowly removes the low temperature fall in $\rho(T)$ (see 6:34). This indicates both a loss of magnetic order and a suppression of the coherence connected with the formation of a Kondo lattice. Unlike Ga and Al substitutions, no deepening in the minimum at low temperature is observed with Ag alloying. Magnetic resistivities shown in figure 6:35 support the idea of a weakening the strength of the Kondo interaction. The magnitude of the slopes $d\rho_{\text{mag}}/d\ln T$ in the regions at high and low temperature in which the resistivity has a logarithmic temperature dependence decreases with increasing Ag concentration.

6:4:5:3. Magnetic Susceptibility.

Temperature dependence of the inverse magnetic susceptibility of $\text{Ce}(\text{Cu}_{1-x}\text{Ag}_x)_2$ for $x \leq 0.40$ are shown in figure 6:36. High temperature data shows Curie-Weiss behaviour. Fitting the high temperature data to a $\chi = C/(T - \theta)$ law shows values for θ remain little changed whilst values for μ_{eff} calculated from such fits, are little change from those expected of free Ce^{3+} atoms of $2.54\mu_B$. For $0.00 \leq x \leq 0.05$, addition of Ag leads to a suppression in the temperature at which an inflexion point in $\chi_{\text{a.c.}}$ is observed, and which is taken to indicate the onset of antiferromagnetic order. For $0.05 < x \leq 0.15$ a cusp in $\chi(T)$, indicative of spin glass ordering appears. The temperature of

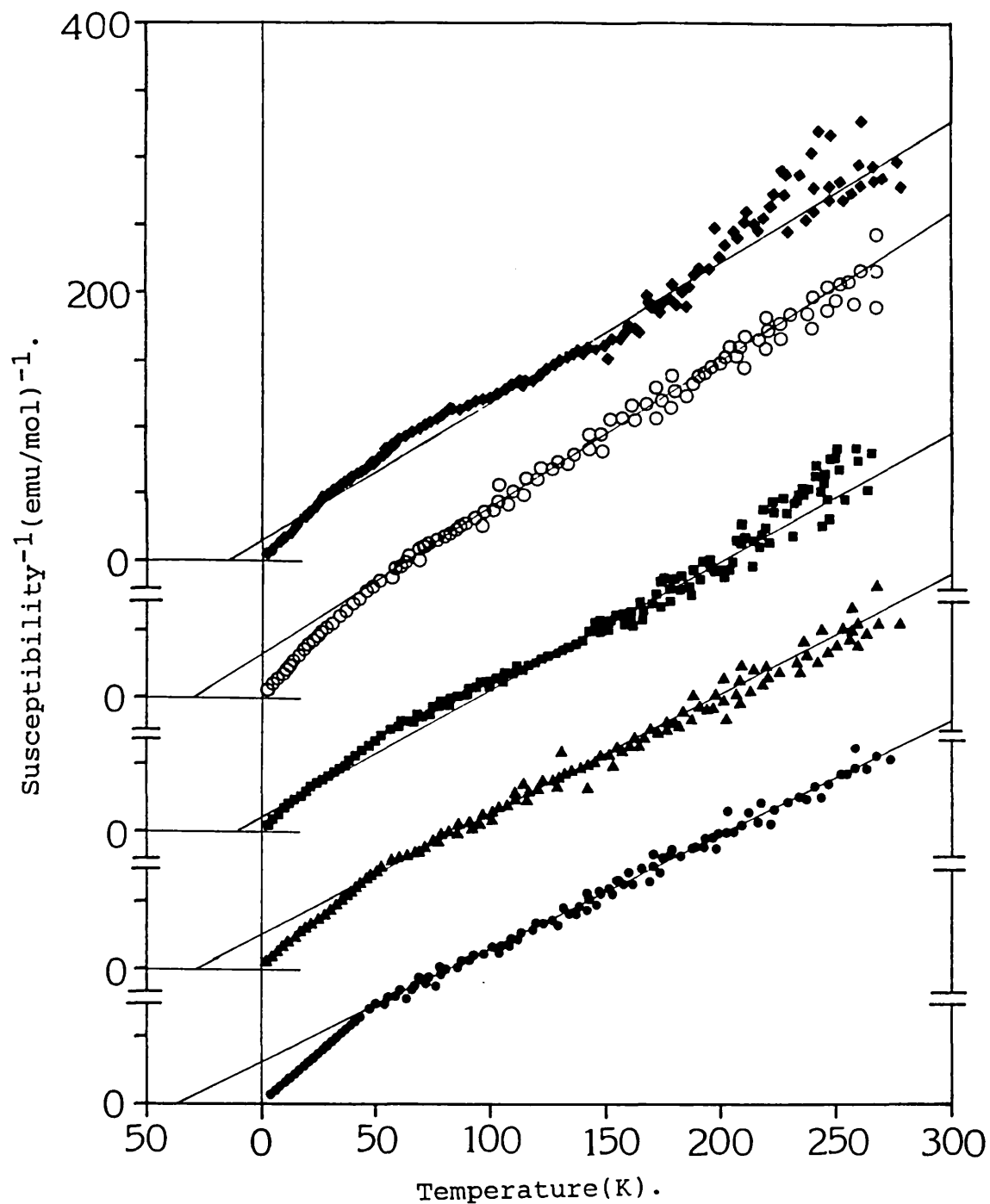


Figure 6:36. Temperature dependence of the inverse magnetic susceptibility of $\text{Ce}(\text{Cu}_{1-x}\text{Ag}_x)_2$ for $x=0.00(\bullet)$, $0.02(\blacktriangle)$, $0.05(\blacksquare)$, $0.10(\circ)$ and $0.20(\blacklozenge)$.

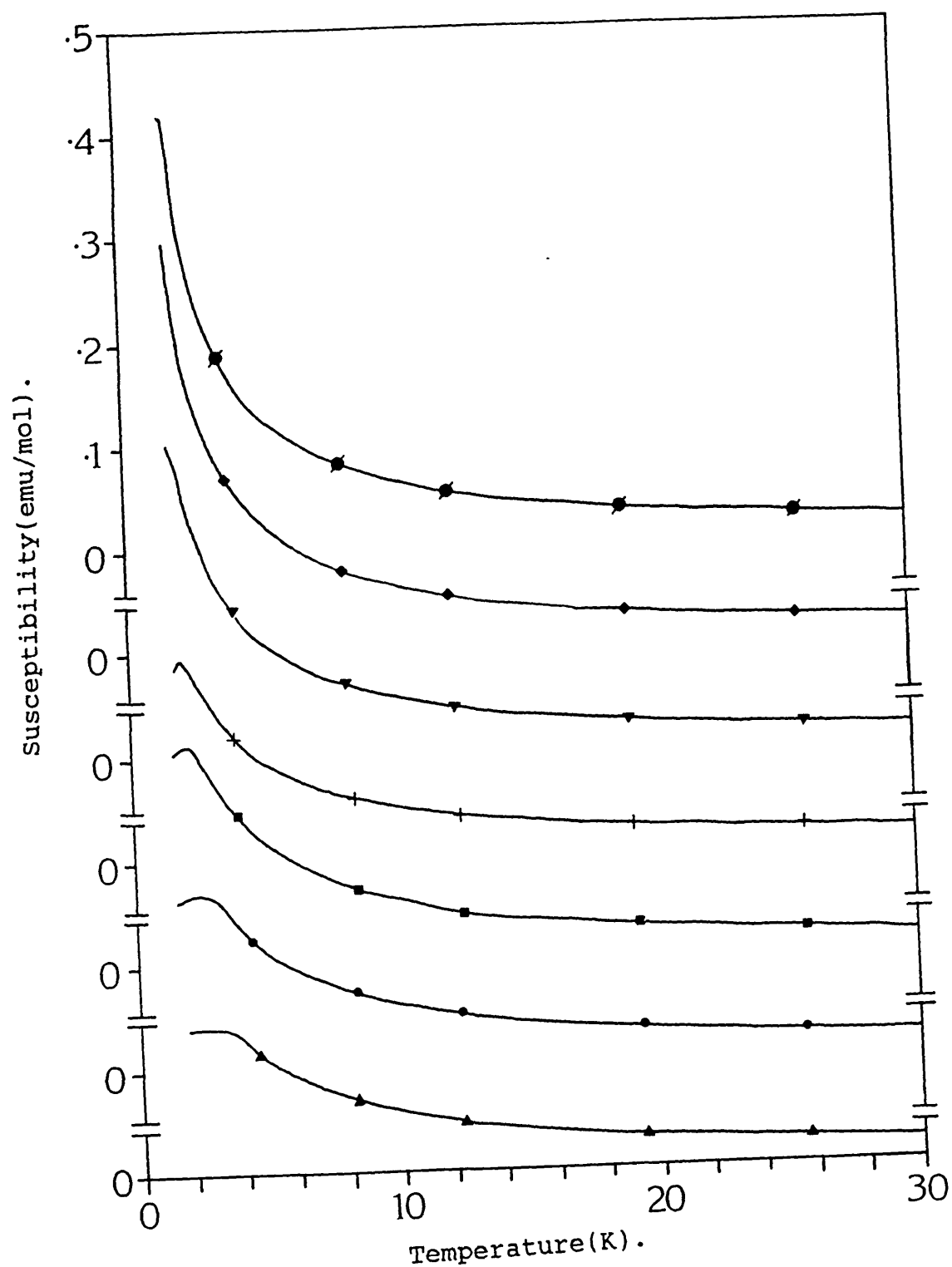


Figure 6:37. Magnetic susceptibility of selected $\text{Ce}(\text{Cu}_{1-x}\text{Ag}_x)_2$ alloys at low temperature where $x=0.00(\blacktriangle)$, $0.02(\bullet)$, $0.05(\blacksquare)$, $0.10(+)$, $0.20(\blacktriangledown)$, $0.30(\blacklozenge)$ and $0.40(\bullet)$.

this peak is reduced with increasing x . For $x \geq 0.20$ no anomaly is observed in $\chi(T)$ at low temperature. At the same time substitution of Ag, produces an increase in the magnitude of the low temperature susceptibility.

Table 6:6. Important parameters taken from the magnetic susceptibility data for $\text{Ce}(\text{Cu}_{1-x}\text{Ag}_x)_2$ alloys.

Conc. x	0.00	0.02	0.05	0.10	0.20	0.30	0.40
$ \Theta_P(K) $	38.4	11.0	12.3	15.7	15.4	10.0	50.0
$\mu_{\text{eff}}(\mu_B)$	2.65	2.63	2.89	2.51	2.78	3.06	2.71
T_{ORD}	3.50	3.00	2.15	1.89	----	----	----
χ_{MAG} emu/mol	0.14	0.17	0.21	0.19	0.30	0.40	0.42

6:4:5:4. Discussion.

The expansion of the unit cell volume resulting from substitutions of Ag seems to weaken the coupling constant J between the conduction electrons and the Ce 4f moments, leading to a weakening in both the Kondo and the RKKY interactions. This results in the disappearance of Kondo like behaviour in ρ_{mag} and an increase in the magnitude of the susceptibility at low temperature. At the same time, the onset of magnetic order is suppressed as the RKKY interaction between Ce moments is reduced. This leads first to the loss of long range order and the appearance of a spin glass, followed at higher Ag concentrations by the complete disappearance of evidence indicating the onset of magnetic order above 1.5K

6:4:5. The Contrasting Effects of Alloying on the Ce and Cu Sites in CeCu_2 .

It seems clear from the results of the previous two sections that alloying on the Cu sites in CeCu_2 has a much greater influence on the properties of the alloy than substitutions

on the Ce sites. In the latter case a dilution in the number of Ce atoms with Y produces the expected reduction in the magnetic ordering temperature with an eventual loss of magnetic order (or at least a suppression of the ordering temperature below 1.5K). At the same time a gradual transition from a dense to dilute Kondo alloy behaviour is observed. The weakening of the Kondo and magnetic interactions within the CeCu_2 system are offset to a degree by the increase in the chemical pressure effects due to the smaller lattice parameter of YCu_2 . In contrast, the effects of alloying on the Cu sites are more rapid, varied and unpredictable in nature. Alloying with Ag leads to an increase in the unit cell volume. This weakens the interaction between the Ce 4f and conduction electrons. As a result both the magnetic order and the Kondo interactions are rapidly weakened. The magnetic order is removed (or at least suppressed below 1.5K) for $x \geq 0.20$, whilst evidence for the presence of Kondo like interactions is removed by $x = 0.40$, despite the presence of a complete and (supposedly) undisturbed Ce sublattice. In the case of alloying with Pt the effects of the resulting lattice expansion are even more dramatic with a rapid weakening of the Kondo interaction producing amongst other things the emergence of strong ferromagnetic like magnetic ordering. In the case of Ga and Al substitutions as little as 5% dopant is sufficient to remove the onset of coherence seen in $\rho(T)$, again despite an undisturbed Ce sublattice. Also observed are dramatic changes in the magnitude and character of the temperature dependence of the resistivity and magnetic susceptibility and a rapid loss of magnetic order.

Throughout this work the importance of the strength and nature of the hybridisation between the Ce 4f and the conduction electrons in dictating the ground state of each system has been emphasized. Once again it has been shown that rapid changes in the properties can be effected by a combination of changes in the lattice constant and the character of the conduction electrons. In this system alloying on the Cu sites can bring about more rapid and dramatic changes as a result of variation in these parameters than alloying on the Ce sites.

Chapter 7. Studies of the Effects of Alloying on the Properties of CeAl₃.

7:1:1. Introduction.

In this chapter the effects of alloying on the properties of the hf CeAl₃ will be examined. Many of the properties of CeAl₃ have already been reviewed in chapter one and will not be repeated here. These properties allowed one to classify CeAl₃ as a non-magnetic heavy fermion.

In section 7:2. however data is presented which suggests that CeAl₃ may order antiferromagnetically at low temperature. A possible mechanism which may explain the suppression of magnetic order in the CeAl₃ alloy is also discussed. Finally in section 7:2. the effects of pressure on the properties of CeAl₃ are reviewed. In section 7:3. the effects of alloying on the Ce or the Al sites are considered and contrasted. These results are also compared with the theoretical predictions of the "Kondo sideband" model due to Maranzana.

7:2:1. Previous Work.

7:2:1:1. Magnetic Ordering in CeAl₃?

One of the greatest difficulties encountered studying CeAl₃ is the preparation of single phase samples. The Ce-Al phase diagram (see figure 5:32) shows the peritectoid formation of CeAl₃ at 1135°C. Almost all polycrystalline samples contain a small amount of either Ce₃Al₁₁ or CeAl₂. Careful annealing can reduce the amount of second phase. However the fact that Ce₃Al₁₁ and CeAl₂ both order magnetically makes the extraction of the magnetic behaviour of CeAl₃, which remains paramagnetic down to at least 30mK problematic. These difficulties are compounded when one begins alloying and will be discussed in more detail in section 7:3:3. The metallurgical problems encountered in the CeAl₃ system also makes the preparation of single crystals of CeAl₃ by conventional techniques difficult. However, Jaccard et al. [7:1,7:2] have recently succeeded in making small single crystals. Ce-Al alloys of different compositions around CeAl₃ were annealed under a high vacuum in order to obtain single crystal grains by recrystallization. The results of the temperature dependence of the resistivity perpendicular and parallel to the c-axis are shown in figure 7:1. Recombining the results according to the equation

$$\rho = 1/3\rho_{||} + 2/3\rho_{\perp}^{ar} \text{ ----- 7:1.}$$

shows that the results give good agreement with previous measurements on polycrystalline samples. At low temperature a rapid change of slope of $\rho_{||}$ is seen near 1.6K. A positive maximum (figure 7:2) is also observed in the magnetoresistance of the single crystal up to this temperature. It is suggested that some form of magnetic

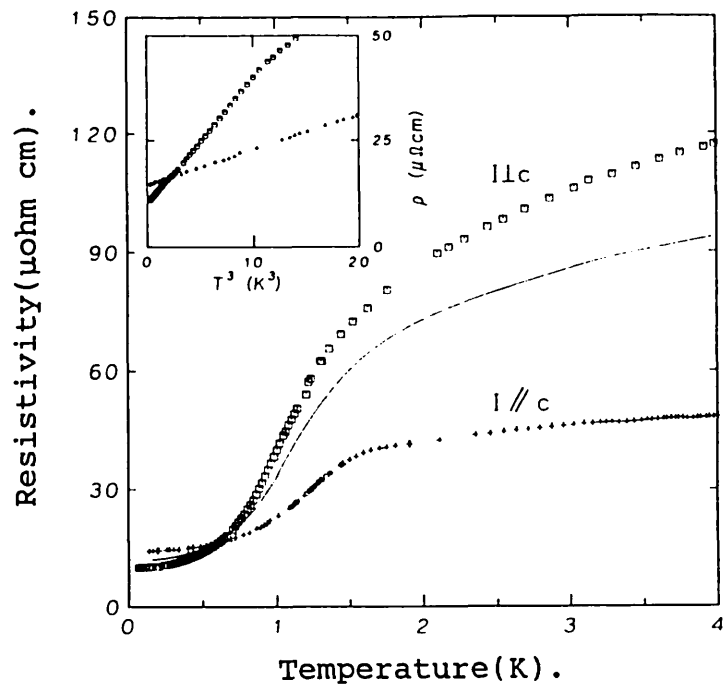


Figure 7:1. Low temperature dependence of the resistivity of CeAl₃ single crystals with the current parallel or perpendicular to the c-axis. Data are from Jaccard et al. [7:1].

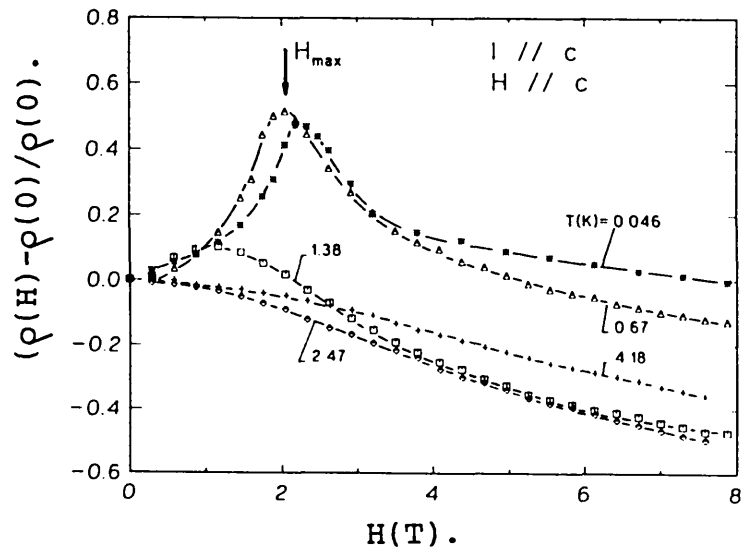


Figure 7:2. Longitudinal magnetoresistance along the c-axis of CeAl₃ at different low temperatures. Data are from Jaccard et al. [7:1].

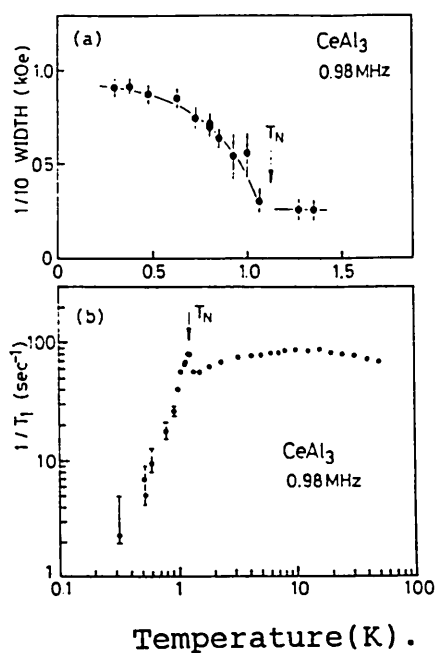


Figure 7:3. (a) Temperature dependence of the 1/10 line width for ^{27}Al spectrum at 0.98MHz. (b) Temperature dependence of the spin lattice relaxation rate $1/T_1$ for ^{27}Al at 0.98 MHz. Data are from Nakamura et al. [7:3]

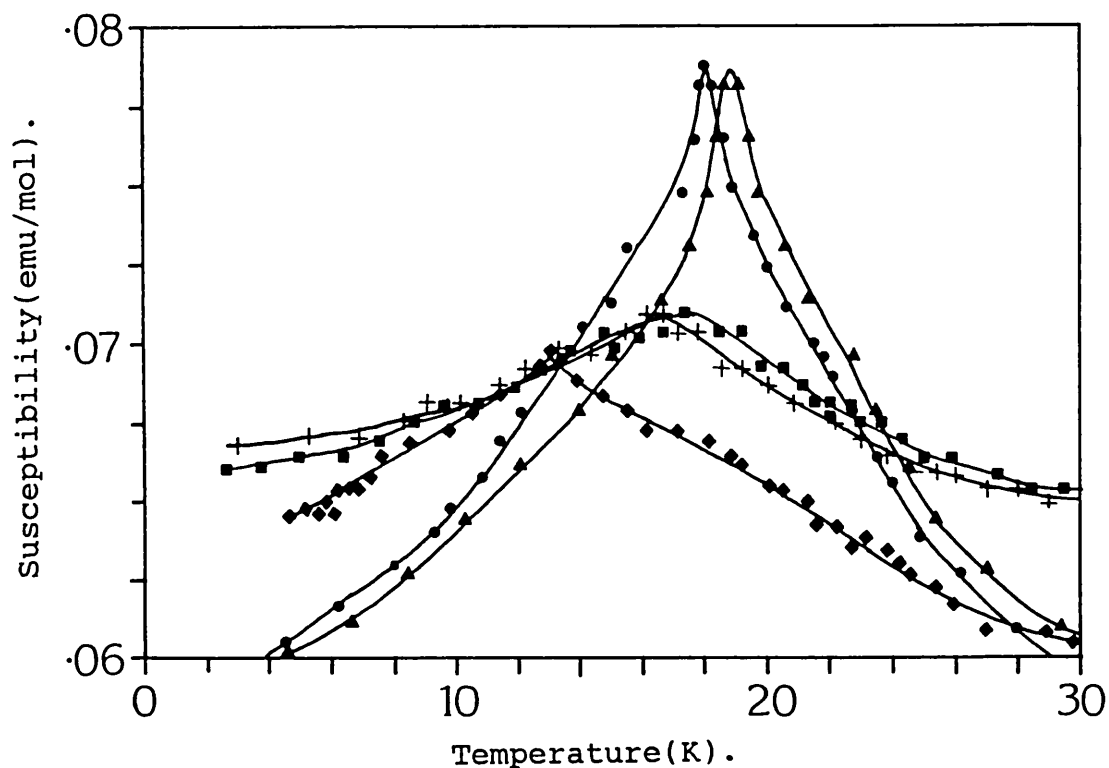


Figure 7:4. Magnetic a.c. susceptibility versus temperature for some $\text{Gd}_{1-x}\text{Y}_x\text{Al}_3$ alloys where $x=0.00(\Delta)$, $0.05(\bullet)$, $0.10(\blacksquare)$, $0.20(+)$ and $0.30(\blacklozenge)$.

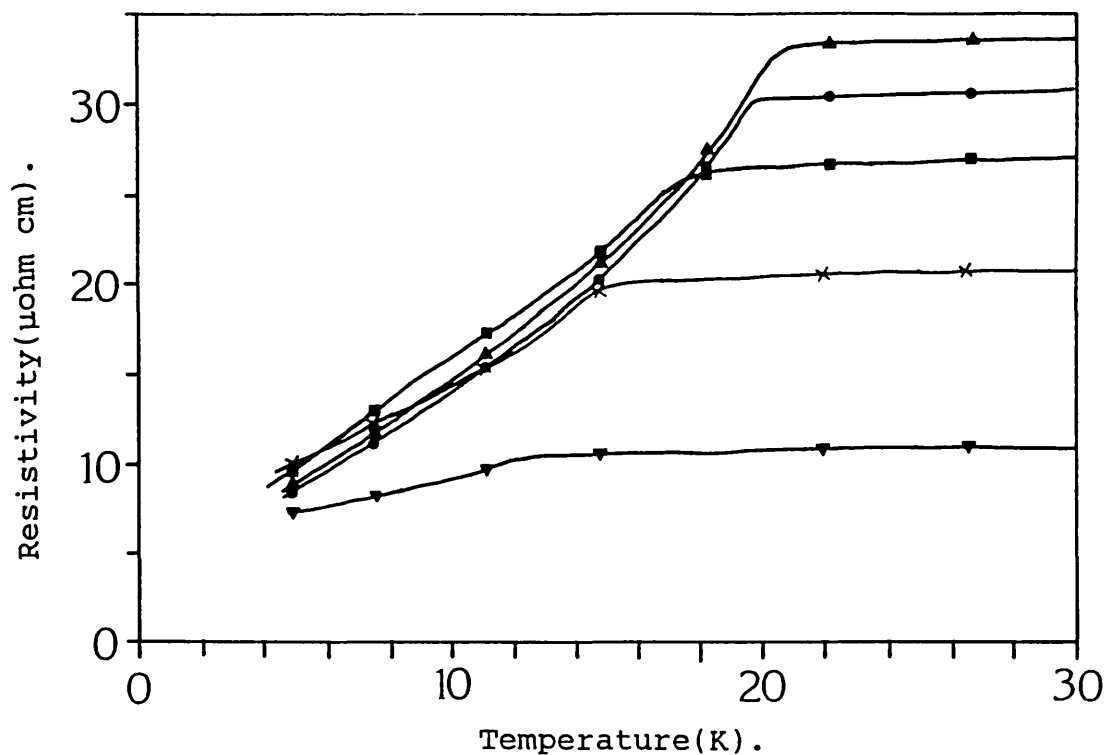


Figure 7:5. Temperature dependence of the electrical resistivity of some $Gd_{1-x}Y_xAl_3$ alloys where $x=0.00(\blacktriangle)$, $0.05(\bullet)$, $0.10(\blacksquare)$, $0.20(+)$ and $0.30(\blacktriangledown)$.

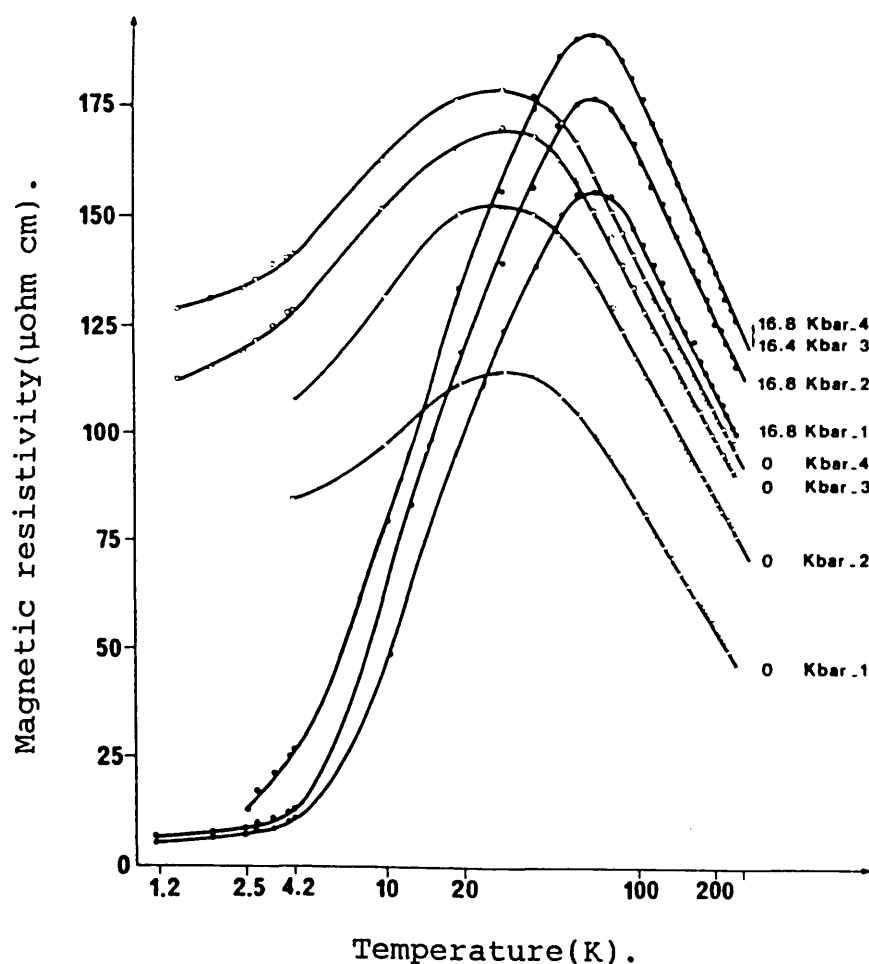


Figure 7:6. Temperature dependence of the magnetic resistivity ($\rho(CeAl_3) - \rho(LaAl_3)$) versus temperature in a logarithmic scale at normal (○) and 16.4-16.8 kbar (●) pressure. Data are from Percheron et al. [7:5].

ordering with very weak moments may be taking place at this temperature. Around the same time Nakamura et al. [7:3] asserted that a ^{27}Al N.M.R. investigation on polycrystalline CeAl_3 indicated that the material ordered antiferromagnetically at 1.2K. Evidence for such ordering takes the form of a marked increase in the line width of the ^{27}Al spectrum below 1.2K and a nuclear relaxation rate $1/T_1$ which exhibits a sharp peak at 1.2K (see figure 7:3). Despite this evidence the question of the appearance of magnetic ordering in CeAl_3 remains a matter for debate.

7:2:2. Frustration in CeAl_3 .

A possible mechanism which may help to explain the suppression of magnetic order in CeAl_3 has been suggested by Coles et al. [7:4]. They considered the corresponding Gd system GdAl_3 . GdAl_3 has a Ni_3Sn structure with a Neel temperature of 17K that is surprisingly low when compared with either the value for $|\Theta|$ of 90K obtained from a fit to a Curie-Weiss law of the high temperature susceptibility data, or the strength of the interactions in ferromagnetic GdAl_2 ($T_C \approx \Theta \approx 170\text{K}$). E.S.R. results were presented which suggested that competing ferromagnetic and antiferromagnetic interactions between neighbouring Gd atoms, frustrates the long range order and it is this which suppresses T_N down to 17K. GdAl_3 is isostructural with CeAl_3 , whilst CeAl_2 ($T_N = 3.8\text{K}$) has the same structure as GdAl_2 ($T_C = 170\text{K}$). If the ratio $T_C(\text{GdAl}_2)/T_N(\text{GdAl}_3)$ is any guide to the temperature at which long range order is expected to appear in CeAl_3 , then one would not observe an ordering temperature much above 0.4K (i.e. $17/170 \approx 3.8/T_{\text{ORD}} \Rightarrow T_{\text{ORD}} = 0.38\text{K}$). By this temperature the Kondo compensation mechanism will have severely reduced the

Ce magnetic moments, making a non-magnetic Kondo lattice more stable. To investigate the influence of frustration within the GdAl_3 system a little further, it was decided to substitute non-magnetic Y on the Gd sites. If the transition temperature of GdAl_3 is suppressed by frustration, one might expect that random substitution of Gd with Y will enhance this frustration, which should in turn rapidly lead to the destruction of the long range order to be replaced perhaps by a spin glass like ordering. However, as figures 7:4. and 7:5. show, the transition temperature is only slowly suppressed by the addition of Y. It is clear from the anomaly in $\rho(T)$ that this is still a transition to long range antiferromagnetic order. What implications these findings have for the frustration model are still unclear.

7:2:3. Effects of Pressure on the Temperature Dependence of the Resistivity of CeAl_3 .

Percheron et al. [7:5] have measured the temperature dependence of the resistivity of both CeAl_3 and LaAl_3 under normal and 16.8kbar pressure. The results of this study are shown in figure 7:6. Their observations include:

1. For $T \geq 50\text{K}$, the resistivity increases with pressure in any given pressure cycle.
2. Conversely, at low temperature, application of pressure leads to a decrease in the magnitude of ρ . This change is huge, with for example $\rho(4.2\text{K}) = 85\mu\text{ohm cm}$ at normal pressure decreasing to $11\mu\text{ohm cm}$ at 16.8kbar.
3. As the pressure is cycled $0 \rightarrow 16.8 \rightarrow 0\text{kbar}$ the resistivity values at any given temperature increase.
4. The position of the maximum seen in ρ_{mag} increases from 34 to 70K as pressure is increased from 0 to 16.8kbar. This shift is independent of the samples pressure history.
5. The slope at high temperature $d\rho_{\text{mag}}/d\ln T$ increases with pressure and with the number of pressure cycles. For example if the initial value of the slope at high temperature at 0kbar is taken to equal to 1, then the slope equals 1.05

after one pressure cycle, 1.085 after two and 1.22 after three cycles.

6. No minimum is seen in $\rho(T)$ between 1.3 and 300K.

The hexagonal C.F. present in the CeAl_3 system splits the Ce^{3+} degenerate C.F. levels with separations Δ_{21} and Δ_{31} (between the ground state and the first and second excited doublets respectively) given by fits to data using the theory of Cornut and Coqblin [4:15].

Table 7:1. Crystal field parameters taken from the resistivity data of Percheron et al. [7:5].

Pressure(kbar)	0kbar	16kbar
$E_1(\text{K})$	-425	-430
$E_2=E_1+\Delta_{21}(\text{K})$	-400	-335
$E_3=E_1+\Delta_{31}(\text{K})$	-375	-325

Application of 16.8kbar is seen to increase the overall crystal field splitting Δ_{31} by a factor of 2. This is in contrast to the decrease in C.F. splitting observed in the CeAl_2 system. It is clear that since changes in $\rho(T)$ as the pressure is released are less than during the application of pressure, that modifications in the material, which bring about these changes are less as the pressure is decreasing. This observation led to the suggestion that the increase in the magnitude of $\rho(T)$ with the number of pressure cycles, can be attributed to the introduction with pressure of another phase either with Ni_3Ti or rhombohedral structure. This transformation occurs due to a decrease in the difference r_o-r_{4f} between the atomic radius r_o and the radius of the 4f shell. The rapid enhancement in magnitude of the fall in $\rho(T)$ observed at low temperature may be due to an increase in the strength of the Kondo interaction, which in turn produces a more non-magnetic Kondo state.

7:3. Effects of Alloying.

7:3:1. Introduction.

In this section the effects of alloying on either the Ce and Al sites of CeAl_3 are discussed. Several studies have been made of the results of replacing Ce, with amongst other elements La, Gd, Th or U. Some of these experiments along with new results replacing Ce with Y are reviewed below. The effects of substituting Al in CeAl_3 with Cu and Sn are contained in 7:3:5. Finally in section 7:3:6, the results of these substitutions are contrasted.

7:3:2. $\text{Ce}_{1-x}\text{M}_x\text{Al}_3$ where M is La, Gd or U.

7:3:2:1. La.

Addition of La leads to an expansion in the cell volume (see table 7:2.

Table 7:2 Lattice parameters for some trialuminide compounds.

Sample	$a(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$
CeAl_3	6.545	4.609	170.98
LaAl_3	6.662	4.609	172.81
GdAl_3	6.332	4.600	159.72
ThAl_3	6.499	4.626	169.2
YAl_3	6.276	4.582	156.29

The temperature dependence of the resistivity of $\text{Ce}_x\text{La}_{1-x}\text{Al}_3$ has been studied by Brandt and Moshchalkov [2:22]. The results of this study are shown in figure 7:7. At low Ce concentrations one observes a high temperature peak at T_2 due to inelastic Kondo scattering by the doublet above the lowest doublet. At lower temperature the resistivity again increases due to Kondo scattering. As the Ce concentration is increased a maximum appears at low temperature T_1 indicating a

crossover from incoherent Kondo scattering to the formation of a Kondo lattice. Both peak temperatures T_1 indicative of the Kondo temperature and T_2 giving a measure of the overall crystal field splitting increase with Ce concentration. At still higher Ce concentrations the two peaks become less distinct until at $x=1.00$ a single peak is observed. This data illustrate the crossover from single Kondo impurity behaviour to a dense Kondo system. Fits to a Curie-Weiss law of the inverse of the magnetic susceptibility of $Ce_xLa_{1-x}Al_3$ give values for $|\theta|$ which increase with Ce concentration.. These values in turn can be used to give a measure of T_K ($T_K \approx \theta/4$). T_K for $CeAl_3$ is observed to be an order of magnitude larger than the alloy with $x=0.01$. Therefore the enhancement in T_K reflected in $\rho(T)$ is confirmed in $\chi(T)$ data.

7:3:2:2. Gd.

Addition of Gd leads to a decrease in the absolute value of the resistivity at low temperature. The temperature at which the maximum is seen in $\rho(T)$ is only slowly shifted to lower temperature (e.g. $Ce_{0.75}Gd_{0.25}Al_3$, $T_{MAX}=31.6K$). Measurements of Edelstein et al. [7:6,7:7] indicated a destruction of the heavy fermion state for Gd concentrations greater than 25%. Magnetic susceptibility data indicated interactions between Gd atoms leading to magnetic ordering The formation of a spin glass like state is observed for $x \leq 0.50$ with the transition temperature increasing with Gd concentration. At still higher Gd levels, a spin glass transition at high temperature precedes a transition into an antiferromagnetically ordered state at lower temperature. This leads to the magnetic phase diagram shown in figure 7:8. However Chilton [7:8] has suggested that these transitions are not due to Gd

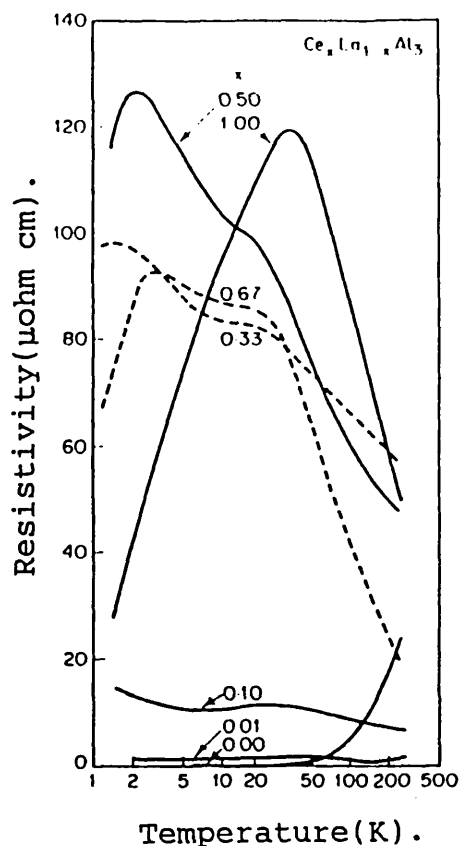


Figure 7:7. The resistivity of $\text{Ce}_x\text{La}_{1-x}\text{Al}_3$ compounds as a function of $\ln T$. Data are from Brandt and Moshchalkov [2:22].

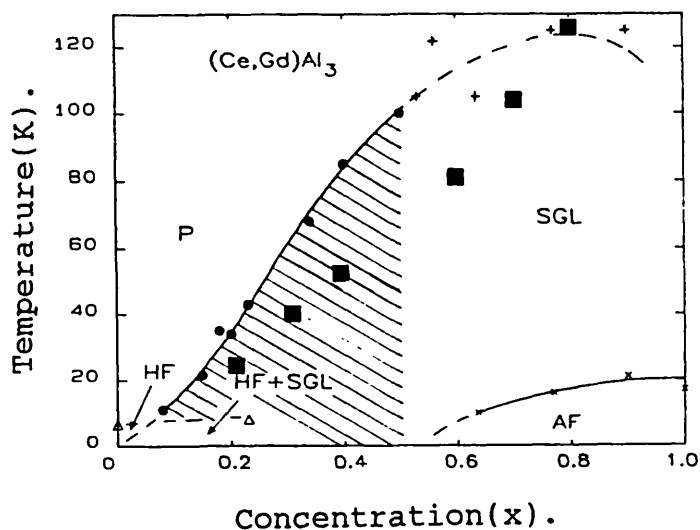


Figure 7:8. Tentative magnetic phase diagram for the $\text{Ce}_{1-x}\text{Gd}_x\text{Al}_3$ system taken from Edelstein et al. [7:6]. The symbols AF, HF, P and SGL represent the antiferromagnetic, heavy fermion, paramagnetic and spin glass-like phases respectively. Superimposed on this diagram are the ordering temperatures of $\text{Ce}_{1-x}\text{Gd}_x\text{Al}_2$ (■) taken from the work of Iwata et al. [7:9].

interactions within $\text{Ce}_{1-x}\text{Gd}_x\text{Al}_3$ but rather the presence of $\text{Ce}_{1-x}\text{Gd}_x\text{Al}_2$ second phase. Edelstein has discussed this possibility, knowing the metallurgical difficulties involved when preparing CeAl_3 alloys, and this explanation of the data was discounted. However superimposing the transition temperatures of $\text{Ce}_{1-x}\text{Gd}_x\text{Al}_2$ taken from the data of Iwata et al. [7:9] show why uncertainties remain in the minds of many, as regards the analysis of Edelstein et al.

7:3:2:3. U.

Addition of U has also been shown [7:8] to leave the character of the resistivity little changed for U concentrations of up to 30%. Again the onset of coherence is still observed and the temperature T_{MAX} is reduced only slightly.

7:3:3. Sample Preparation.

All samples were prepared using the method described in 3:6. The samples were then annealed for 7 days at 600°C . Metallographic specimens were then prepared for all samples. Examination of these specimens revealed all samples contained a small amount of second phase. An estimate of the percentage of second phase present gave an upper limit of around 10%. This estimate is supported by X-ray data which for small dopant levels (>20%) contained no lines which could not be indexed with the CeAl_3 parent compound. The appearance of second phase is not surprising given the difficulties of preparing pure CeAl_3 , which are compounded by doping. The identity of the second phase can be determined by examining the susceptibility of these samples and the Ce-Al phase diagram. Examples of such $\chi(T)$ data are shown in figure 7:9. These data are for samples containing Cu as a dopant which

will be discussed in more detail in 7:3:5. The peaks seen in the $\chi_{a.c.}$ data, even for the smallest dopant concentrations can all be attributed to either Ce_3Al_{11} , $CeAl$ or $CeAl_2$ and are labelled. The strong magnetic character of the second phase masks any interesting behaviour which may be present in susceptibility data. However, unless this second phase becomes superconducting, (which is a possibility when dealing with Sn), it is thought that the amounts of second phase which are present, will not dramatically effect the character of the $\rho(T)$ results and that any major changes in the nature of the resistivity seen in $CeAl_3$ system during alloying are unlikely to be due to second phase. To support this assertion note first that the $\rho(T)$ of a sample of pure $CeAl_3$ despite containing a small amount of Ce_3Al_{11} , is in good agreement with the published data. Secondly the resistivity data of Chilton [7:8] of alloys containing Gd and U which showed only slow variations in the nature of $\rho(T)$ all contained 2nd phase.

7:3:4. $Ce_{1-x}Y_xAl_3$.

7:2:4:1. Electrical Resistivity.

Assuming the system obeys Vegards law, the addition of Y is expected to result in a decrease the lattice parameters. This is expected to produce lattice pressure. Thus the effects of alloying on the Ce sites with Y, are to certain extent at least, expected to mimic the effects of application of external pressure. This is found to be the case. The temperature dependence of $Ce_{1-x}Y_xAl_3$ for $x \leq 0.30$ are shown in figure 7:10. The general behaviour of $\rho(T)$ is unchanged with a Kondo like rise in $\rho(T)$ at high temperature, followed by a peak associated with C.F.-Kondo interactions. The low

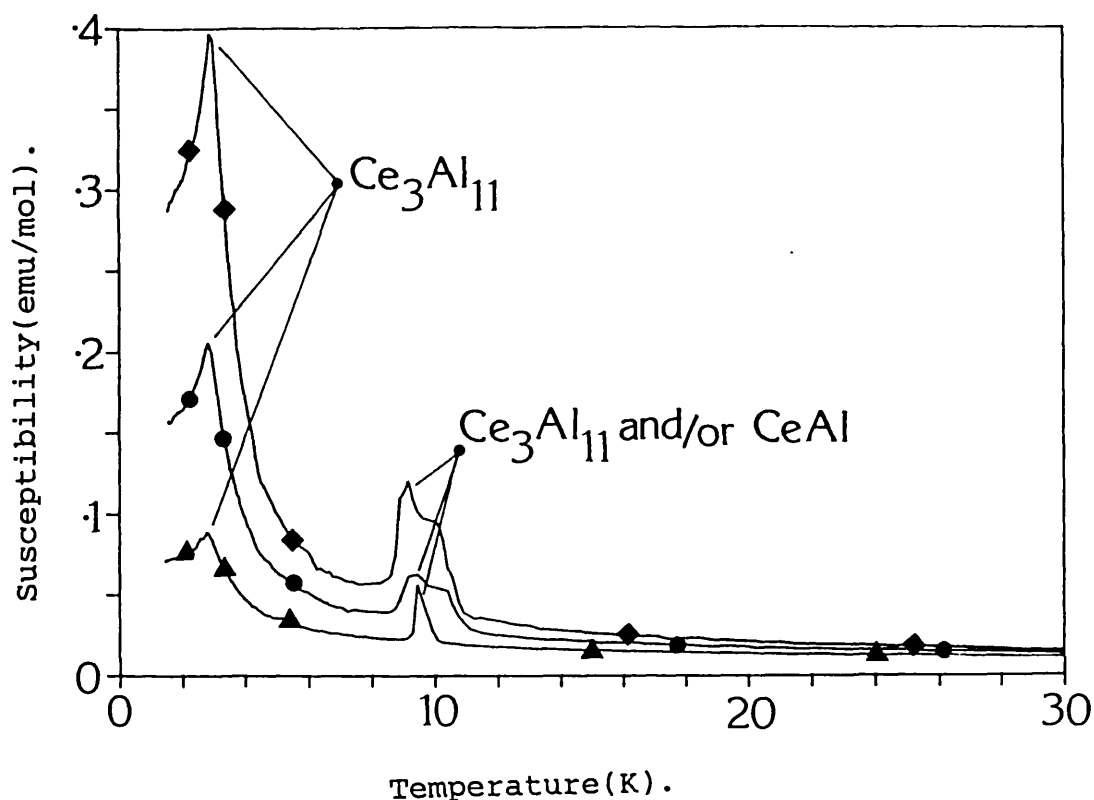


Figure 7:9. Magnetic a.c. susceptibility versus temperature of three $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_3$ samples where $x=0.02$ (▲), 0.05 (●) and 0.10 (◆). The peaks seen in this data are probably due to the presence of a strongly magnetic second phase. The labels indicate the likely nature of the second phase.

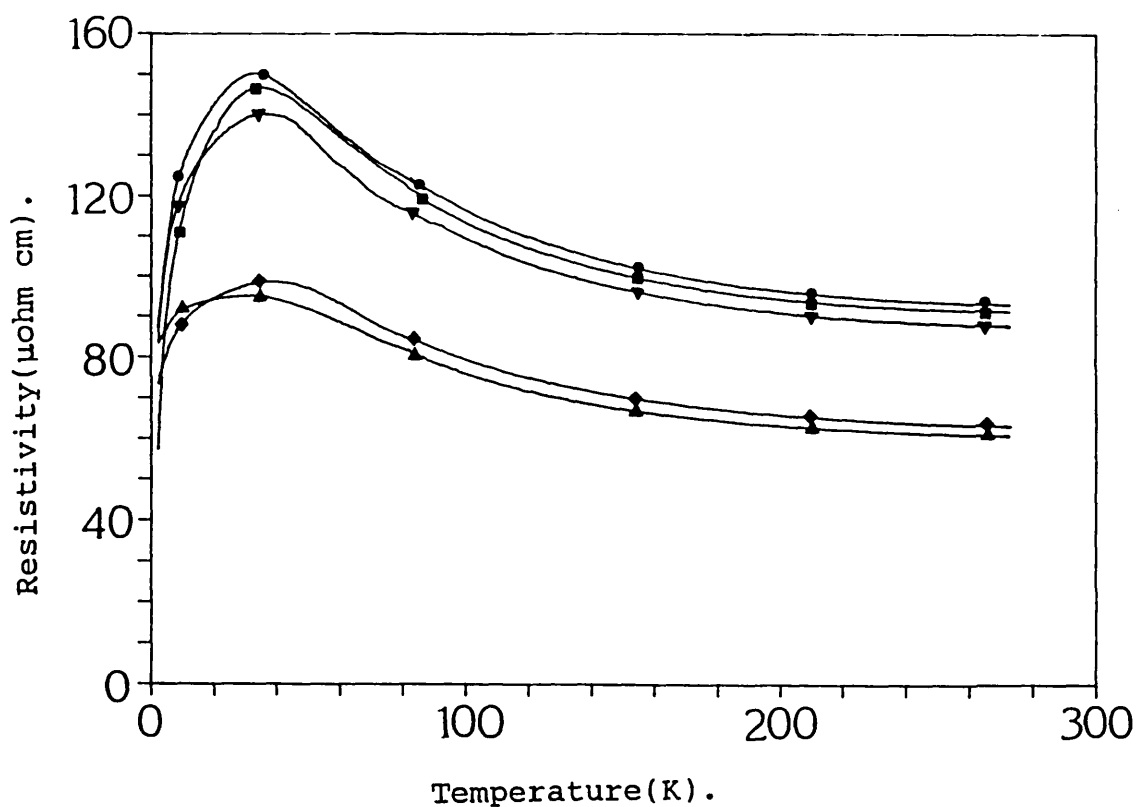


Figure 7:10. Temperature dependence of the electrical resistivity of $\text{Ce}_{1-x}\text{Y}_x\text{Al}_3$ alloys where $x=0.00$ (■), 0.05 (●), 0.10 (▼), 0.20 (◆) and 0.30 (▲).

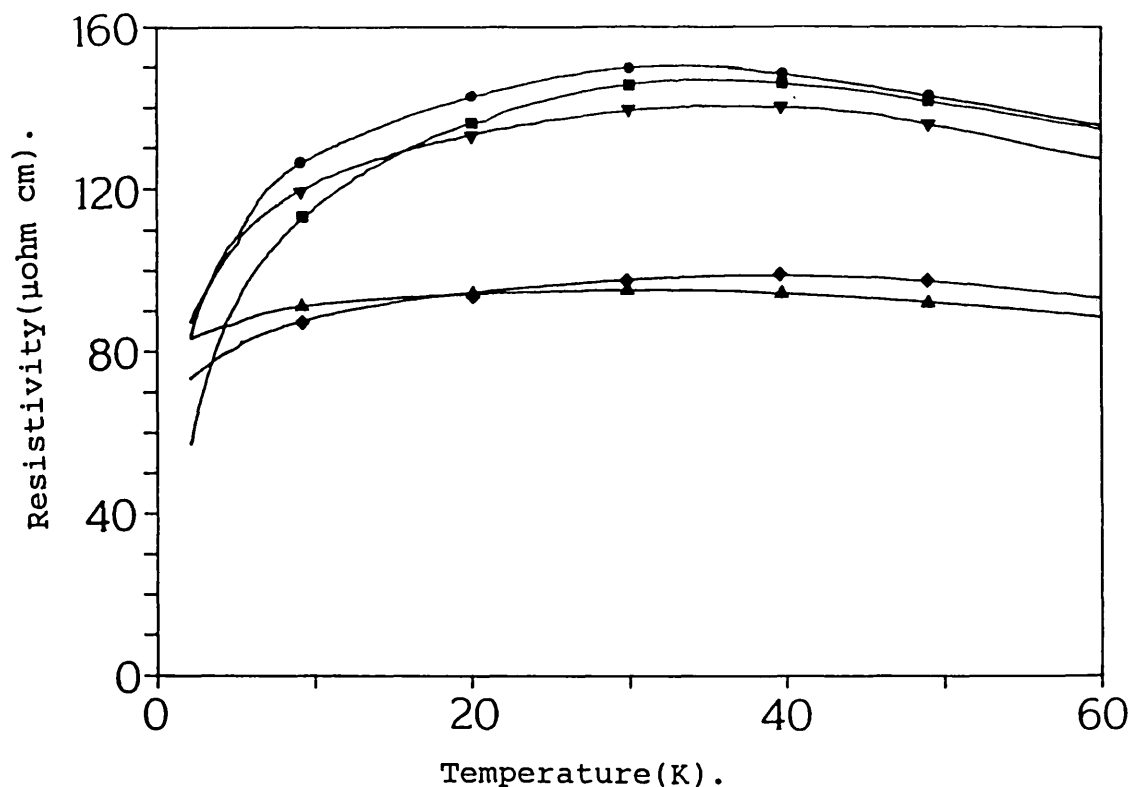


Figure 7:11. The low temperature behaviour of the electrical resistivity of $(\text{Ce}_{1-x}\text{Y}_x)\text{Al}_3$ alloys where $x=0.00(\blacksquare)$, $0.05(\bullet)$, $0.10(\blacktriangledown)$, $0.20(\blacklozenge)$ and $0.30(\blacktriangle)$.

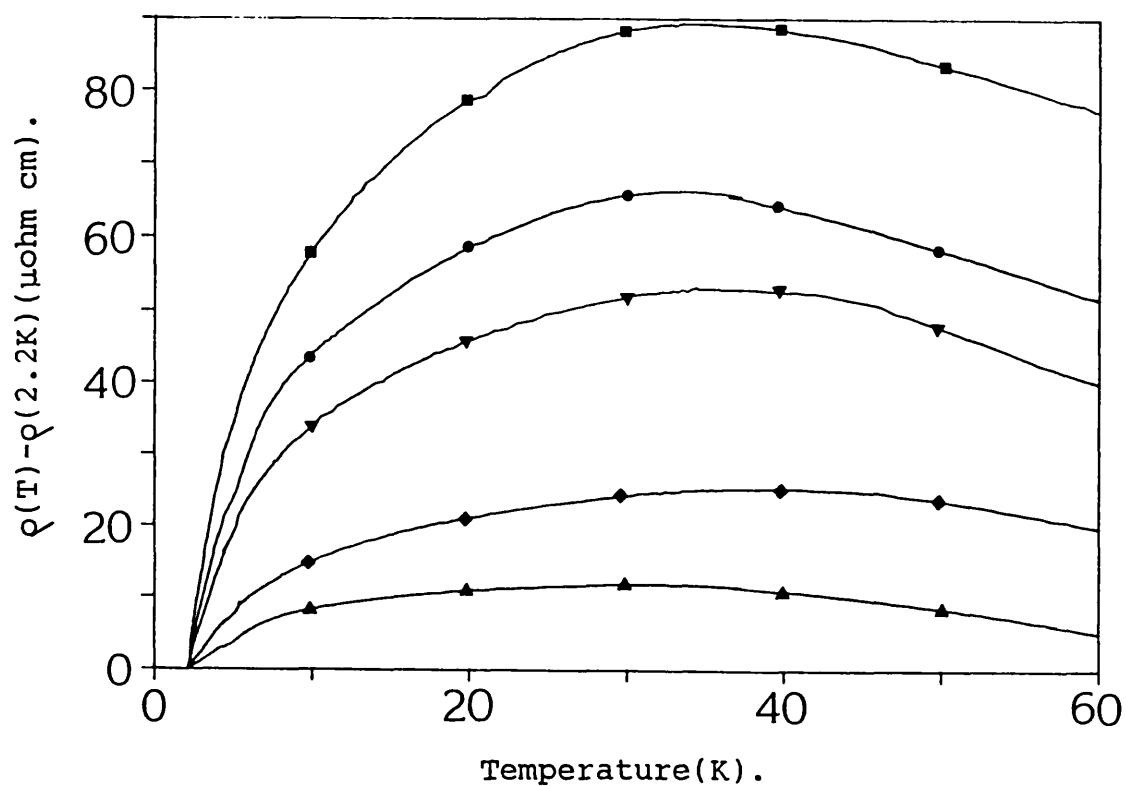


Figure 7:12. The low temperature behaviour of the electrical resistivity of $(\text{Ce}_{1-x}\text{Y}_x)\text{Al}_3$ alloys shown as $\rho(T) - \rho(2.2\text{K})$. $x=0.00(\blacksquare)$, $0.05(\bullet)$, $0.10(\blacktriangledown)$, $0.20(\blacklozenge)$ and $0.30(\blacktriangle)$.

temperature fall in $\rho(T)$ indicates a transition to coherent Kondo scattering. A more detailed examination shows that as Y is added, the peak in $\rho(T)$ is broadened and shifted to higher temperature. See table 7:3. and figure 7:11. This behaviour is observed in CeAl_3 under pressure and is attributed to an increase in the overall C.F. splitting with pressure. Buschow et al. [7:10] has suggested that the width of the peak in $\rho(T)$ is closely connected to the sharpness of the Fermi level at a given temperature, and that the resistivity maximum will in general become flatter the higher the temperature at which it is observed. This is graphically illustrated in this case. As with previous studies of substitutions on the Ce sites, the effects on the onset of coherence of alloying with Y relatively slow to emerge. 30Y is not sufficient to remove the low temperature fall in $\rho(T)$, although the dramatic fall observed in pure CeAl_3 is much reduced (see figure 7:12). Part of this reduction may be due to an increase in the value of the residual resistivity, or to a shift in the onset of coherent Kondo scattering to lower temperature.

7:3:5. $\text{CeAl}_{1-x}\text{M}_x\text{Al}_3$ where M is Cu or Sn.

7:2:5:1. Sn.

The lattice constants for $\text{Ce}(\text{Al}_{1-x}\text{Sn}_x)_3$ are shown in figure 7:13. These lattice constants were calculated from the 101 and 201 lines, the strongest lines in X-ray patterns.

Addition of Sn produces a number of changes in $\rho(T)$ (see figures 7:14 and 7:15) which must be highlighted:

1. Addition of Sn results in a rapid destruction of the onset of coherence. As little as 5% Sn is sufficient to reduce the fall in $\rho(T)$ at low T to only a few $\mu\text{ohm cm}$.
2. Addition of 2% Sn shifts the peak in $\rho(T)$ to lower temperature and leads to the appearance of a shoulder in $\rho(T)$ at low temperature.

3. By 5% Sn two peaks are observed in $\rho(T)$. The lower peak is associated with the onset of coherent Kondo scattering, whilst the upper peak at 28K must be associated with C.F. and incoherent Kondo scattering interactions.

4. For $x=0.10$, much of the high temperature rise in resistivity with decreasing temperature observed in pure CeAl_3 and associated with the incoherent Kondo scattering has been removed. The high temperature peak in $\rho(T)$ is shifted to higher temperature, and is followed at lower temperature by a fall which may be associated with the onset of coherence.

5. The character of $\rho(T)$ is completely changed by 20% Sn substitution. No high temperature rise in $\rho(T)$ which can be associated with incoherent Kondo scattering is observed. At low temperature the complete loss of resistivity results from the onset of superconductivity due to the presence of a small amount of free Sn second phase.

Table 7:3. Parameters taken from the electrical resistivity of some CeAl_3 alloys.

Sample	T_{max}	$T_{2\text{max}}$	$\delta\rho$	$\rho_{\text{mag}}^{273\text{K}}$	$\rho_{\text{mag}}^{2.2\text{K}}$
CeAl_3	35.0	----	90.0	91.0	57.0
CeAl_3+5Y	33.0	----	66.0	93.0	84.0
CeAl_3+10Y	35.0	----	53.0	87.5	87.0
CeAl_3+20Y	39.5	----	25.0	63.0	73.5
CeAl_3+30Y	32.0	----	14.0	61.0	84.0
CeAl_3+2Sn	28.5	3.5	18.0	100.0	127.0
CeAl_3+5Sn	27.5	3.2	2.0	98.5	137.5
$\text{CeAl}_3+10\text{Sn}$	61.0	6.0	30.5	98.0	67.0
$\text{CeAl}_3+20\text{Sn}$	----	----	----	420.0	----
CeAl_3+5Cu	43.5	----	46.5	76.0	33.5
$\text{CeAl}_3+10\text{Cu}$	36.0	infl 5.0	23.0	86.0	28.0
$\text{CeAl}_3+20\text{Cu}$		infl 7.0	6.5	72.0	41.5
$\text{CeAl}_3+35\text{Cu}$		infl 3.5	4.0	87.0	87.0

N.B. infl indicates an inflexion point in the $\rho(T)$ curve.

7:3:5:2. Cu.

The variations in the resistivity versus temperature curves for $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_3$ for $x \leq 0.35$ are shown in figures 7:16 to 7:18. As with Sn, addition of Cu also leads to rapid changes in the nature of the resistivity. These changes include:

1. The low temperature fall in $\rho(T)$ associated with the onset of coherence is continuously removed, with only a small fall observed in $\rho(T)$ for $x=0.35$.
2. As Cu is added the peak in $\rho(T)$ is rapidly broadened and shifted to higher temperature. By $x=0.10$ no peak due to C.F.-Kondo interactions is observed in the raw resistivity data.
3. The underlying rise in $\rho(T)$ at high temperature, associated with incoherent Kondo scattering remains for up to 35% Cu substitution indicating the continued presence of Kondo interactions.

7:3:6. Discussion.

7:3:6:1. Introduction.

It has been shown above, that for a given percentage of dopant, replacement of Al with either Sn or Cu produces much more dramatic effects on the character of the electrical resistivity, than replacement of Ce with Y, Gd, U or La. To understand this first, note that La, Y, Gd or U all crystallize in the isostructural NiSn_3 type compound. In contrast CeSn_3 crystallizes in the AuCu_3 cubic structure, whilst CeCu_3 does not exist. Thus substitution of Sn or Cu are expected to produce much greater structural distortions than substitutions of equal amounts of Y etc. These distortions will in turn lead to more rapid modifications in the nature of the C.F. levels which play an important role in determining the behaviour of $\rho(T)$ (see section 7:2:5). Secondly, in common with $\text{Ce}([\text{Xe}]4f^{15}d^{16}s^2)$, $\text{La}([\text{Xe}]5d^{16}s^2)$, $\text{Gd}([\text{Xe}]4f^75d^{16}s^2)$ or $\text{Y}([\text{Kr}]4d^{15}s^2)$ are expected to be trivalent in the trialuminide compound. Therefore one does

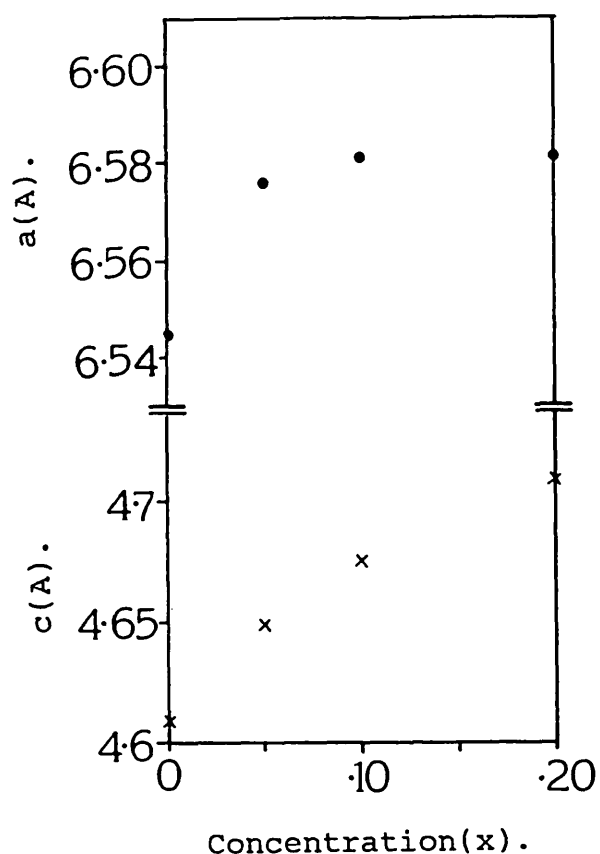


Figure 7:13. Variations in the lattice parameters $a(\bullet)$ and $c(X)$ of $Ce(Al_{1-x}Sn_x)_3$ with Sn concentration.

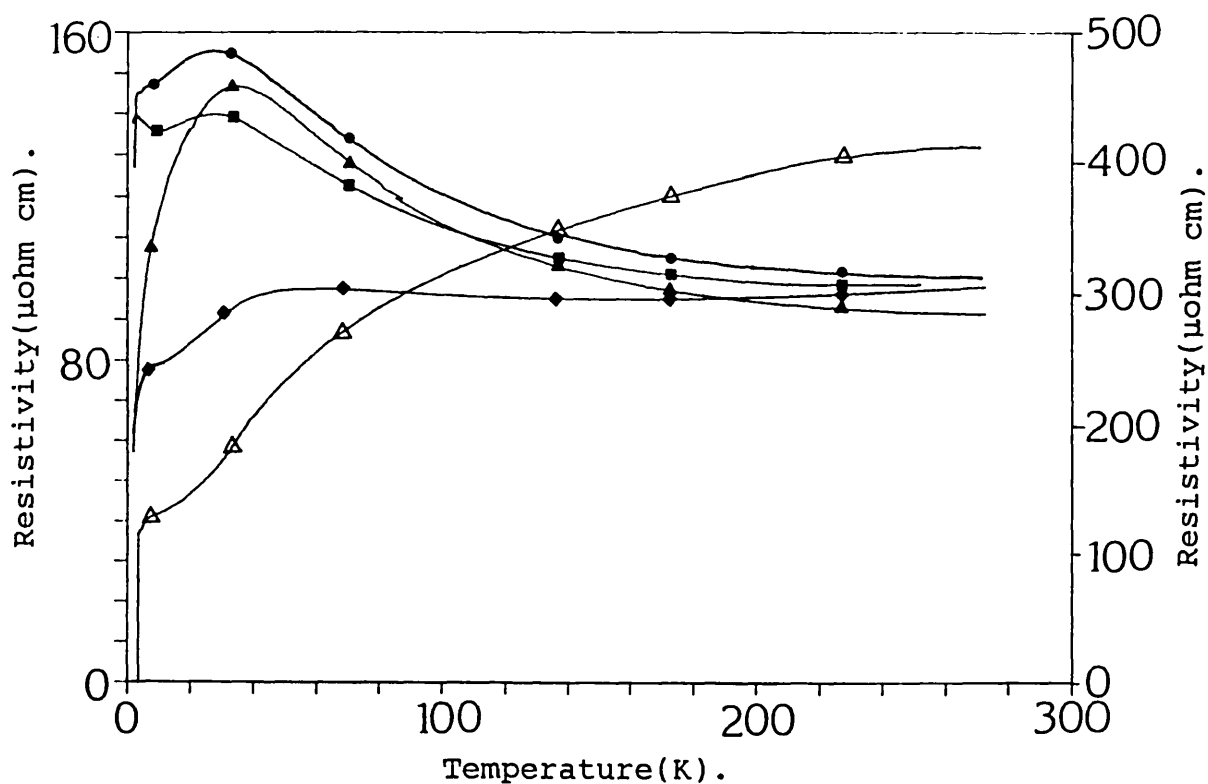


Figure 7:14. Temperature dependence of the electrical resistivity of $Ce(Al_{1-x}Sn_x)_3$ alloys where $x=0.00(\blacktriangle)$, $0.02(\bullet)$, $0.05(\blacksquare)$, $0.10(\blacklozenge)$ and $0.20(\triangle)$. Closed symbols correspond to left-hand scale. Open symbols correspond to right-hand scale.

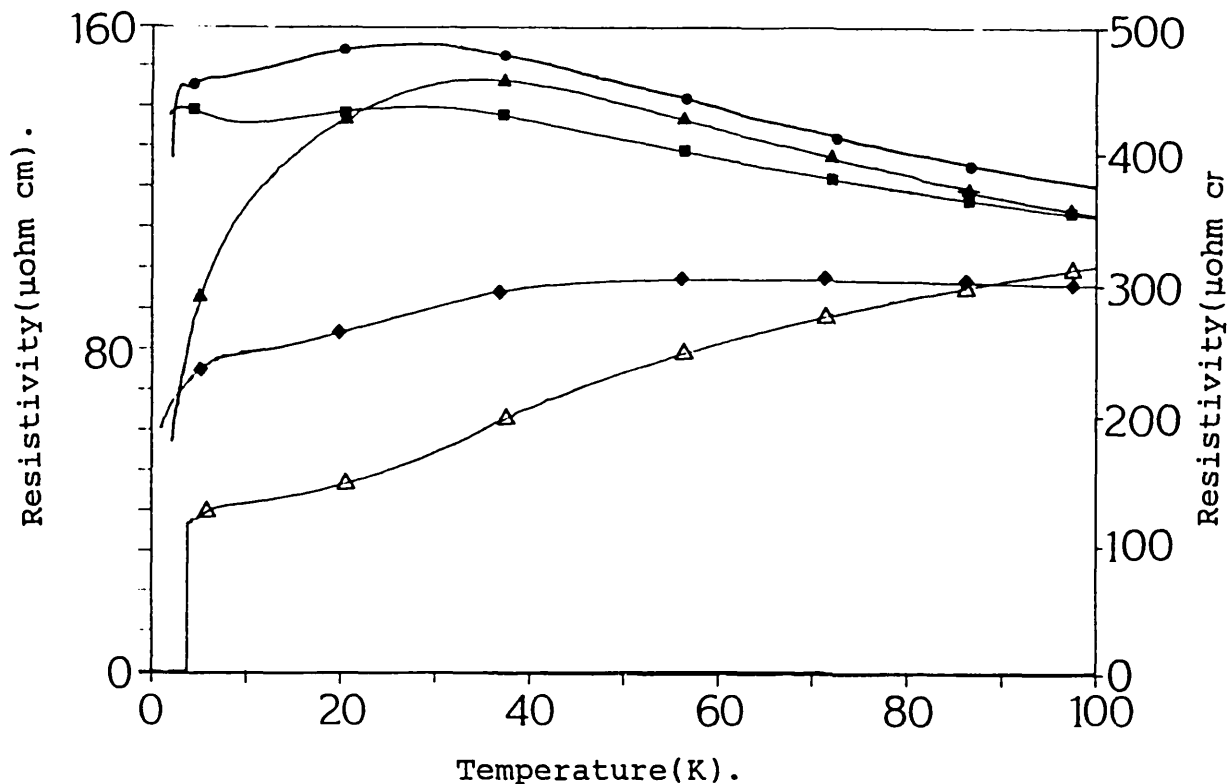


Figure 7:15. The low temperature behaviour of the electrical resistivity of $\text{Ce}(\text{Al}_{1-x}\text{Sn}_x)_3$ alloys where $x=0.00(\blacktriangle)$, $0.02(\bullet)$, $0.05(\blacksquare)$, $0.10(\blacklozenge)$ and $0.20(\triangle)$. Closed symbols correspond to left-hand scale. Open symbols correspond to right-hand scale.

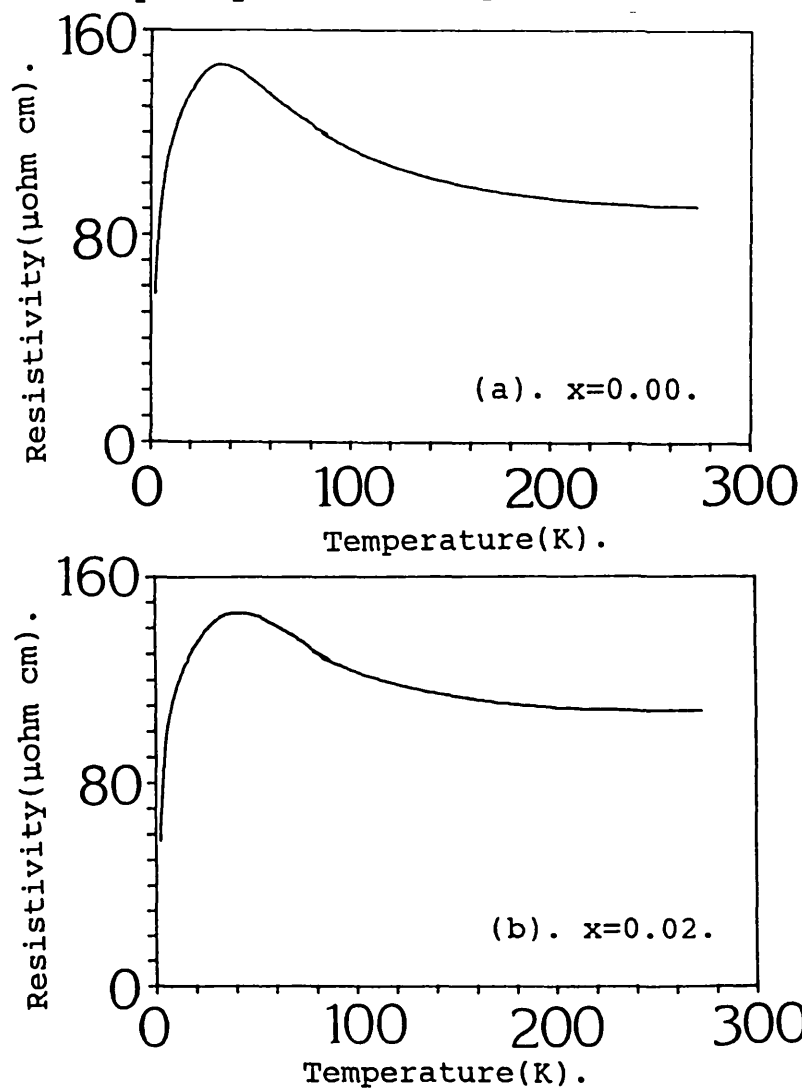
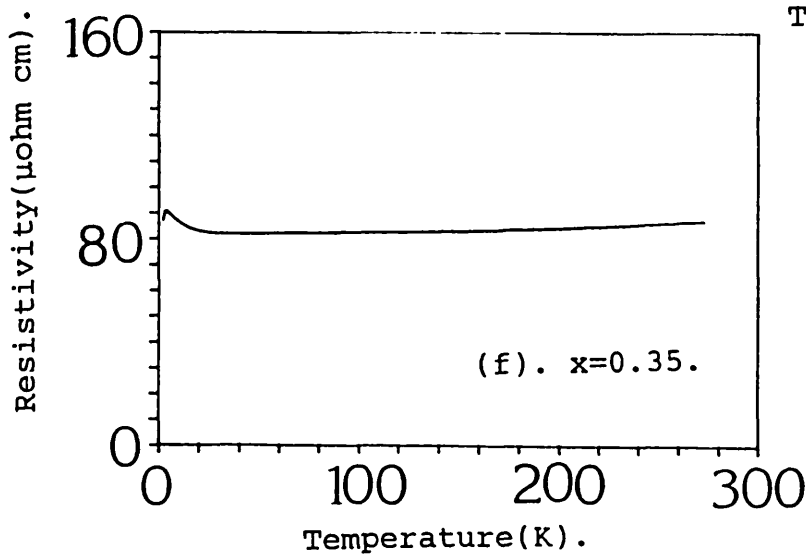
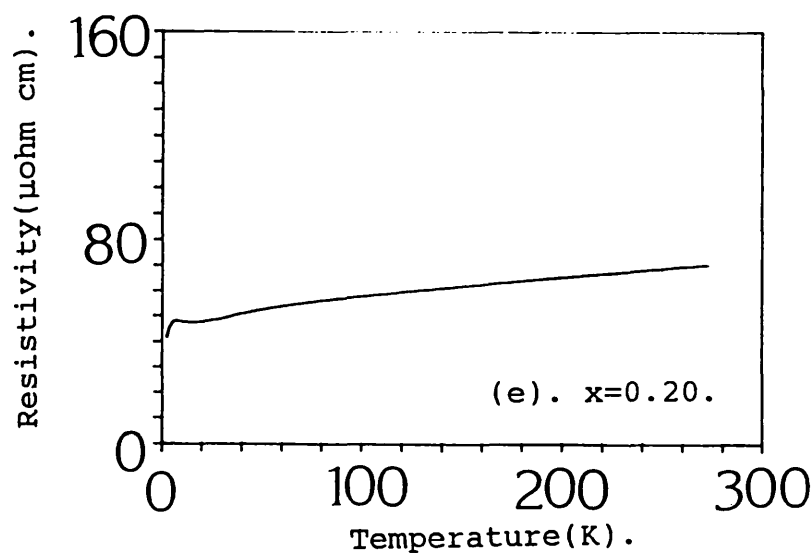
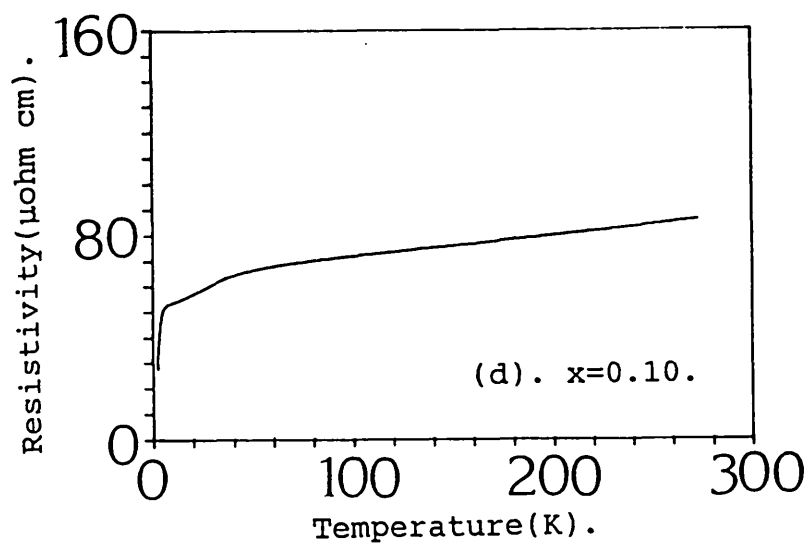
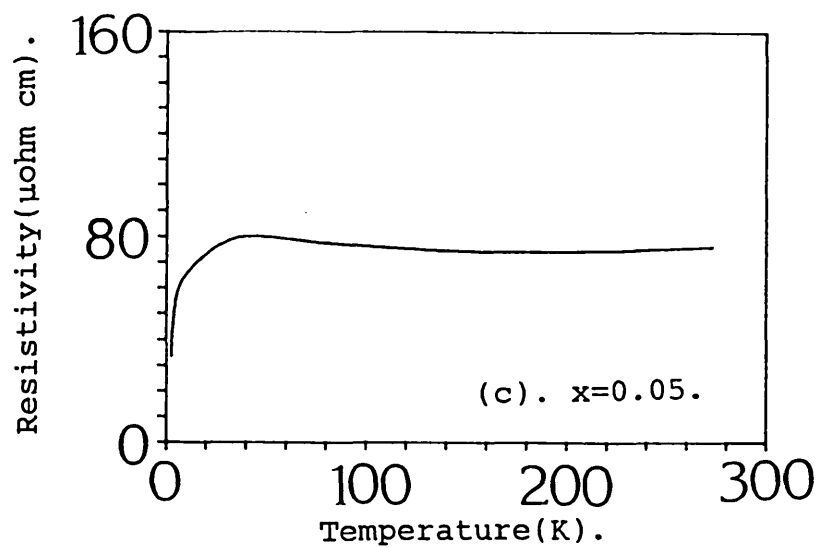


Figure 7:16(a)-(f). Temperature dependence of the electrical resistivity of $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_3$ alloys.



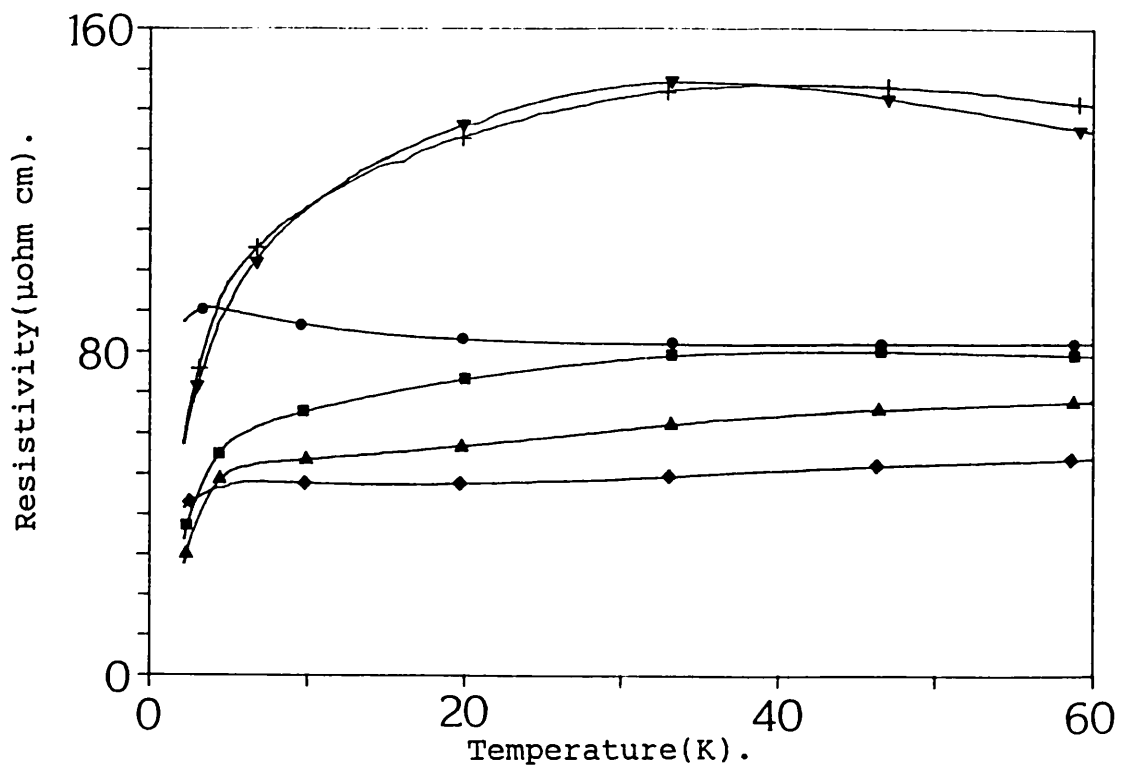


Figure 7:17. The low temperature behaviour of the electrical resistivity of $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_3$ alloys where $x=0.00(\blacktriangledown)$, $0.02(+)$, $0.05(\blacksquare)$, $0.10(\blacktriangle)$, $0.20(\blacklozenge)$ and $0.35(\bullet)$.

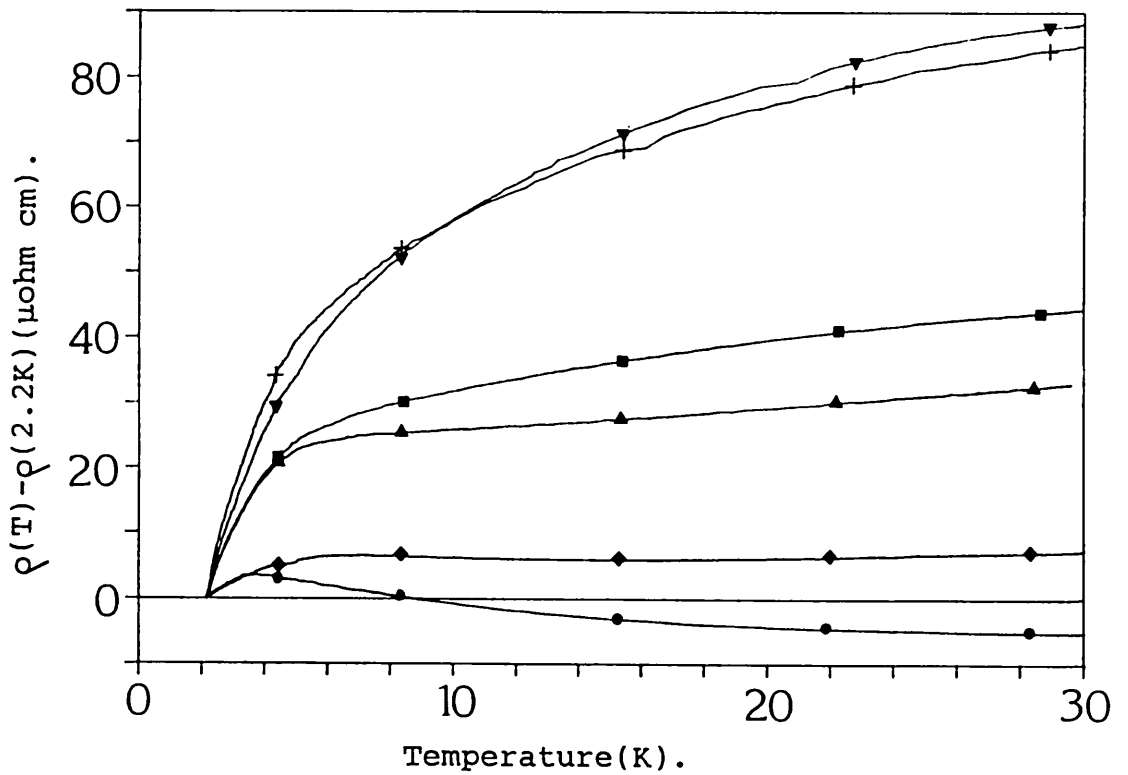


Figure 7:18. The low temperature behaviour of the electrical resistivity of $\text{Ce}(\text{Al}_{1-x}\text{Cu}_x)_3$ alloys shown as $\rho(T) - \rho(2.2\text{K})$. $x=0.00(\blacktriangledown)$, $0.02(+)$, $0.05(\blacksquare)$, $0.10(\blacktriangle)$, $0.20(\blacklozenge)$ and $0.35(\bullet)$.

not expect substitutions of the elements to generate large changes in the density of states at the Fermi energy $N(E_F)$. On the other hand, replacement of $\text{Al}([\text{Ne}]3s^2p^1)$ with $\text{Sn}([\text{Kr}]4d^{10}5s^2p^2)$ or $\text{Cu}([\text{Ar}]3d^{10}4s^1)$ can reasonably be expected to produce large variations in the density of states of the conduction electrons. These changes, will in turn lead to variations in T_K , T_{RKKY} , J and in the character of the resistivity which depend, on these parameters.

7:3:6:2. The Kondo Sideband Model.

The Kondo sideband model proposed by Maranzana [7:11] considered the effects on the resistivity versus temperature curves of systems such as CeAl_3 , of the resonant scattering of conduction electrons, in the presence of C.F. effects. In the case of CeAl_3 the perturbing influence of the C.F. partially lifts the $2j+1$ degeneracy of the Ce^{3+} ion ground state. In zero field this leads to a splitting into three doublets. The localized magnetic moments now depend on the temperature via the Boltzmann average over these three doublets. The overall splitting Δ and the relative positions of the three doublets can be estimated using a point charge model. The crystal field Hamiltonian has the form

$$H_C = \sum_{nm} B_n^m O_n^m \text{ ----- } 7:2.$$

which reduces for the case of the Ce^{3+} ion in an hexagonal C.F. to

$$H_C = B_2^0 O_2^0 + B_4^0 O_4^0 \text{ ----- } 7:3.$$

Buschow et al. [7:10] showed that the relative positions of the C.F. levels is determined by the ratio B_2^0/B_4^0 .

In turn it was then shown that the resistivity of CeAl_3 and similar systems depends rather strongly on the relative positions of the three doublets. The position of the C.F. doublets as a function of B_4^0/B_2^0 were calculated and are

shown in figure 7:19. Numerical calculations of the variation of B_2^0/B_4^0 as a function of c/a (the ratio of dimensions of the lattice parameters a and c) were made, taking into account all atoms lying within a sphere $20\text{\AA}$ of a given point. It was found that the value of B_2^0/B_4^0 was extremely sensitive to variations in c/a . Additionally it is this latter ratio which can be changed by alloying with various elements. Calculations showed that if the c/a ratio is allowed to vary from 0.69 (LaAl_3) to approximately 0.73(YAl_3) one has B_2^0/B_4^0 values varying from -350 to $-\infty$. These values are compared with $B_2^0/B_4^0 = -440$ obtained for the c/a ratio 0.704 (CeAl_3).

Consider now the effects of C.F. interaction on the Kondo scattering process. The essential feature of the Kondo scattering is that it involves intermediate states of the localized spin which differ from the initial and/or final states. When the localized spin can flip without energy expenditure the conduction electrons on the Fermi surface are scattered resonantly. For example, a localized moment with $S=1/2$ has $|+1/2\rangle$ and $|-1/2\rangle$ states that are degenerate. In the Kondo scattering a flip either from $|+1/2\rangle$ to $|-1/2\rangle$ or vice versa takes place and leads to a strong resonance at $T>0\text{K}$ in the transition probability $1/\Gamma_K$ for the scattering of the conduction electrons of energy $E_K=E_F$. The resonance peak broadens at $T=0\text{K}$ and eventually disappears due to the diffuseness of the Fermi level. In the case of CeAl_3 the situation is more complicated. The spin flip scattering can in principle occur between the following sublevels of the ground state manifold of the Ce^{3+} .

$\langle \pm 1/2 | \leftrightarrow | \pm 1/2 \rangle$, $\langle \pm 1/2 | \leftrightarrow | \pm 3/2 \rangle$ or $\langle \pm 3/2 | \leftrightarrow | \pm 5/2 \rangle$.

In the presence of an hexagonal C.F. the scattering is only elastic for $\langle \pm 1/2 | \leftrightarrow | \pm 1/2 \rangle$. Maranzana has shown that for each of the transitions $\langle \pm 1/2 | \leftrightarrow | \pm 3/2 \rangle$ or $\langle \pm 3/2 | \leftrightarrow | \pm 5/2 \rangle$. Kondo exchange scattering leads to a sharp resonance peak at $T=0K$ in the transition probability $1/\Gamma_K$ at an energy shifted away from E_F by an amount equal to the energy separation of the doublet pair. These resonance peaks are designated "Kondo sidebands". With increasing temperature these sidebands broaden and disappear due to the Fermi level becoming diffuse. If the splitting of the Ce^{3+} manifold is such that the doublet $| \pm 1/2 \rangle$ is the highest, then the relaxation time at $T=0K$ does not even show the normal Kondo resonance at $E_F=E_K$ because according to the Boltzmann distribution the doublet is unoccupied at very low temperature. In the other two cases the scattering is inelastic. What sort of effects are expected in $\rho(T)$ for the relaxation times containing resonances? Buschow et al. [7:10] showed that when the relaxation time has a resonance at $E_K=E_F$ one expects to observe two peaks in $\rho(T)$ at temperatures equal to the energy levels in the two pairs of doublets. The width of the peak is closely connected to the sharpness of the Fermi level at a given temperature. If the resonance scattering involves a large separation in energy between the C.F. levels a rather diffuse Fermi level will be involved. For this reason the resistivity maximum will in general become flatter the higher the temperature they are observed.

7:3:6:3. Interpretation of Resistivity Results.

In the numerical calculations of Buschow et al. [7:10] of $\rho(T)$ it was assumed that the total crystal field splitting of the Ce^{3+} ground state is constant and equivalent to about

50K. Results for the relative positions of the three doublets corresponding to the values B_2^0/B_4^0 in the ranges ABC and CDE are shown in figure 7:20.

Above 50K $\rho(T)$ behaviour in all situations is roughly the same, showing an increase in ρ with decreasing temperature expected in a normal Kondo system. This is because at temperatures sufficiently large compared to the total splitting, the Ce^{3+} ground multiplet may be regarded as degenerate.

Below 50K $\rho(T)$ can be seen to differ appreciably in various C.F. schemes. At very low temperature $\rho(T)$ increases markedly with increasing temperature except in the regions AB and at the point D where ρ decreases sharply with an increase of T. In the latter cases the normal Kondo effect is present at very low T also, because the lowest state consists of either a doublet $|\pm 1/2\rangle$ (AB) or coinciding doublets $|\pm 3/2\rangle$ and $|\pm 5/2\rangle$ (D). In these calculations the effect of the sidebands manifest themselves by the presence of either one broad maximum (when B_2^0/B_4^0 has values in the range ABC or at E) or two maxima (for values of B_2^0/B_4^0 near B or D). In the case where two maxima occur the one at lower temperature is sharpest.

7:3:6:4. Comparison with Experiment.

Buschow et al. asserted that in $CeAl_3$ the Ce^{3+} ground state corresponds to the point C

$(Ce_{1-x}La_x)Al_3$.

The c/a decreases with increasing x leading to a shift to the left point C in figure 7:19. Thus the $\rho(T)$ curves must be compared to the theoretical predictions in the region C to B contained in figure 7:20. In this case, agreement between the

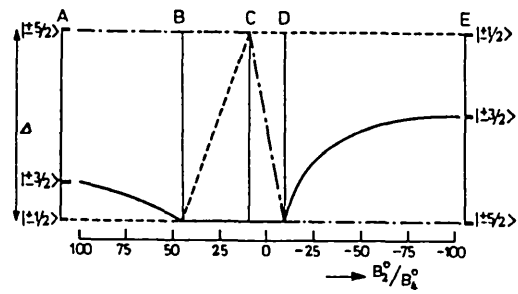


Figure 7:19. The relative positions of the three doublets of the split ground manifold of the Ce^{3+} ion in a hexagonal C.F. as a function of the ratio of the C.F. intensities B_2^0 and B_4^0 . Taken from Buschow et al. [7:10].

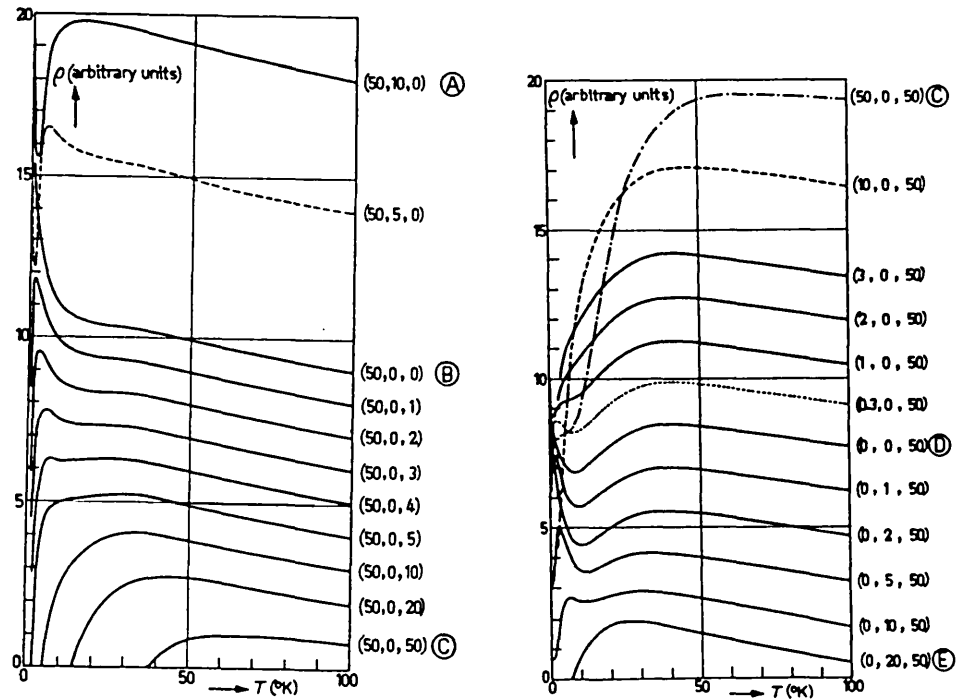


Figure 7:20. Variation of the calculated temperature dependence of the electrical resistivity of CeAl_3 due to the differences in the relative positions of the three doublets. The figures on the right-hand side represent the relative positions (in K) of the levels $|\pm 5/2\rangle$, $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$ respectively. The capital letters denote the corresponding situations in figure 7:19. Taken from Buschow et al. [7:10].

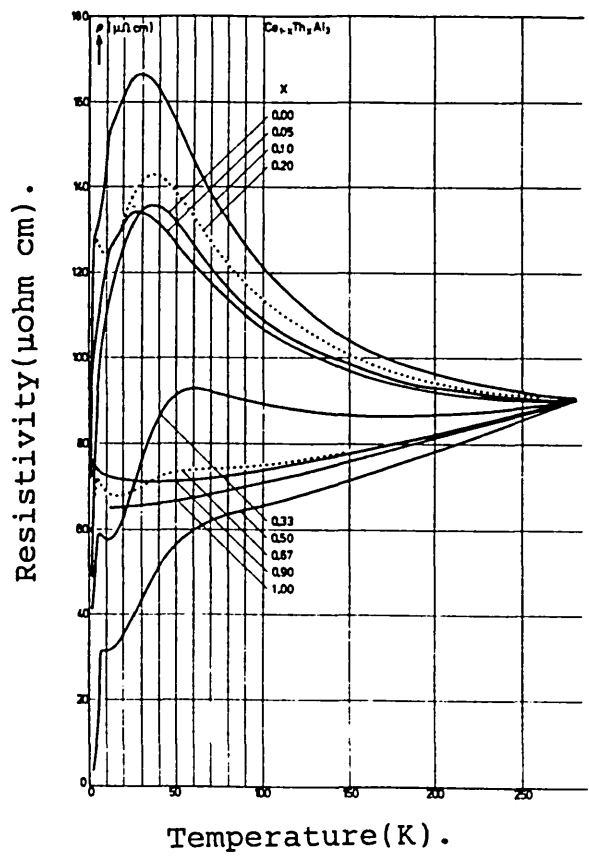


Figure 7:21. The temperature dependence of the electrical resistivity of several $\text{Ce}_{1-x}\text{Th}_x\text{Al}_3$ alloys. Data are from Buschow et al. [7:10].

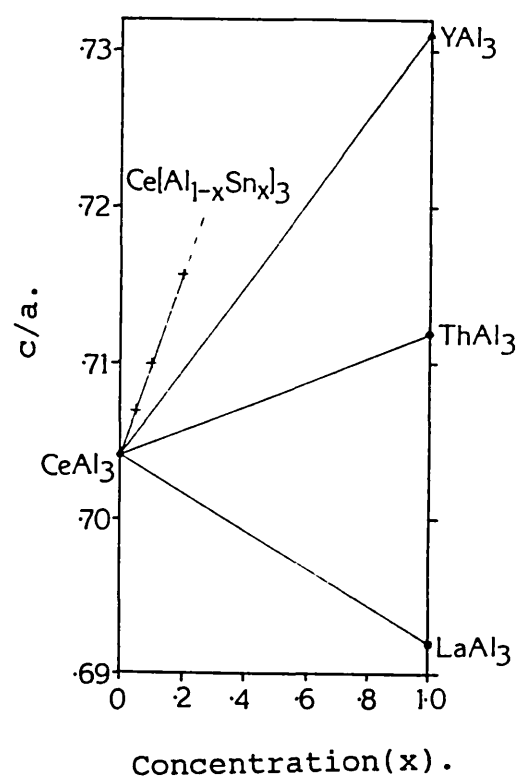


Figure 7:22. Variation of the ratio c/a for several compounds of interest. Values for La, Th and YAl_3 are taken from Buschow et al. [7:10].

theoretical expectations and experimental results seems good.

$(\text{Ce}_{1-x}\text{Y}_x)\text{Al}_3$.

An increase in c/a with Y corresponds to a shift to the left of C in figure 7:19. Thus compare the curves with those in the region C to D in figure 7:20. In successive theoretical curves of figure 7:20 going from C to D one first observes one broad maximum which remains until close to D. As you come close to D the presence of a second maximum at lower temperature becomes noticeable. Behaviour of $\text{Ce}_{1-x}\text{Y}_x\text{Al}_3$ looks similar. With $x=0.00$ to 0.20 , the temperature dependence of ρ does not change appreciably, with ρ characterized by one broad maximum. The presence of a second maximum is reported [7:10] for $x \geq 0.33$.

$\text{Ce}(\text{Al}_{1-x}\text{Sn}_x)_3$.

Alloying with Sn provides the added complication of changes in the conduction electron density of states. However the anticipated increase in $N(E_F)$ due to alloying with Sn is expected to enhance the Kondo sideband effects [7:10].

Replacement of Al with Sn also leads to more rapid changes in the ratio c/a than substitutions of Y. So, disregarding the effects on $N(E_F)$, one would still expect the set of experimental curves for $\text{Ce}(\text{Al}_{1-x}\text{Sn}_x)_3$ to be comparable to the theoretical curves going from C to, or beyond D. Addition of Sn does indeed lead to the appearance of two peaks in $\rho(T)$, with the peak at lower temperature much sharper than that at higher temperature. Very similar behaviour is also observed during the replacement of Ce with Th (see figure 7:21).

However, in the case of alloying with Sn changes in the character of $\rho(T)$ occur at much lower dopant levels than for Th due to the much more rapid increase in c/a (see figure

7:22).

7:3:7. Summary.

In this chapter the effects of alloying on both the Ce and Al sites have been investigated. It has been shown that replacement of Ce with for example Y, produces changes in the resistivity behaviour, which can be attributed to variations in crystal field scheme, driven by variations in the lattice parameters (either by generating lattice pressure or changes in the ratio c/a). The effects of alloying on the Al sites has shown to be much more destructive to the onset of coherence, the rapid fall in $\rho(T)$ at low temperature. At the same time rapid variations in the density of states of the conduction electrons and the ratio c/a lead to much more dramatic changes in the overall character of $\rho(T)$ than replacements on the Ce sites.

Concluding Remarks.

Many of the conclusions which can be drawn from this work are contained in the relevant chapters. However a few, more general remarks can be made. These include:

1. Alloying on the non-Ce sites produces more dramatic effects on the properties of the alloys studied than replacements on the Ce sites.
2. The changes brought about by alloying in the properties of the systems under study are all due to a combination of:
 - (a). changes in the lattice parameters.
 - (b). changes in the nature of the conduction electrons.
 - (c). distortions in the crystal structure.These changes produce variations in the strength of the Kondo and RKKY interactions which in turn dictate the nature of the ground state.
3. Variations with alloying in the properties of the systems studied are reasonably well described by the theoretical work of Doniach, Schilling, Cornut and Coqblin and Maranzana.

As a result of this work a number of experiments are suggested as possible areas of further study. These include:

1. The changes in the electrical properties of CeCu_6+Au and CeCu_2+Ag have been attributed to changes brought about by expansion of the lattice. To confirm this analysis it would be interesting (and experimentally practical) to see whether the application of external or chemical pressure can reverse these effects.
2. It has been shown that alloying with Al or Ni very rapidly destroys the low temperature coherence seen in the $\rho(T)$ curves of pure CeCu_6 . Does alloying also eliminate the enhancement in the γ term seen in the specific heat and if so why?. These experiments are under way.
3. Preparation of single crystals of $\text{Ce}(\text{Cu}_{1-x}\text{Au}_x)_6$ could confirm the changes in the C.F. structure which are thought to produce some of the modifications in $\rho(T)$.
4. Neutron experiments are under way to determine the nature of the magnetic ordering in $\text{Ce}(\text{Al}_{1-x}\text{Fe}_x)_2$ alloys.
5. The preparation of single phase samples of $\text{Ce}(\text{Al}_{1-x}\text{Sn}_x)_3$ would allow for the search for the onset of magnetic order in this system, which could be expected to occur via a similar mechanism to that seen in CeCu_6 .

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