MAGNETIC AND ELECTRICAL MEASUREMENTS ON VERY DILUTE
ZINC AND COPPER BASED ALLOYS.

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

by

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ABSTRACT

A high sensitivity Faraday apparatus has been constructed and used initially to examine the magnetic properties of very dilute (6-133 at. ppb.) ZnCr, ZnMn and ZnFe alloys in fields up to 50 kOe.

For ZnCr and ZnMn, the low field solute susceptibility follows a Curie-Weiss (CW) relation over the 1.3K-15K range; yielding concentration independent values for $\mu_{\text{eff}}$ and $\Theta$ of $3.6u_B$ and 0.45K, and $4.1u_B$ and 0.5K, respectively for Cr and Mn.

In ZnFe alloys isolated Fe atoms display a temperature independent susceptibility throughout the present 1.3K-60K temperature interval, corresponding to a spin fluctuation temperature in excess of 100K. Interactions between pairs of Fe atoms cause a reduction of the characteristic temperature, and we observe magnetic behaviour for such coupled pairs even at 1.3K.

The electrical resistivity due to either Cr or Mn solute in the Zn matrix displays a logarithmic temperature dependence over the interval 1.5K to 4.2K. However interactions between the solute atoms result in a departure from concentration independent behaviour which is evident evn at the lowest concentration. Taking the Caroli mechanism to be responsible for the solute interaction, our data may be reconciled with a recent model, proposed by Matho and Beal-Monod, for the resistivity resulting from exchange scattering from interacting pairs of magnetic solute atoms.
The initial susceptibility (64K - 300K) of a series of $\alpha$-phase Cu$_{1-x}$Al$_x$ alloys, each containing 500 at.ppm. Fe has been fitted to a CW law. The CW $\Theta$ increases monotonically (9K - 34K) with Al concentration (0 - 15 at.%), reducing the temperature dependence of the susceptibility. This increase in the mean characteristic temperature is consistent with that which has been deduced from resistivity measurements on the same alloys, and may be reconciled with the increase in the average density of states of the binary host alloy.
ACKNOWLEDGEMENTS

To my supervisor, Dr. A.D. Caplin, I would like to express my sincere gratitude for the interest and encouragement which he has shown throughout the course of this work. I am also greatly indebted to Professor B.R. Coles for considerable scientific, as well as personal guidance, particularly in the initial and final stages of the work.

I am grateful to Dr. H.E.N. Stone for bringing his considerable experience to bear on the metallurgical aspects of this work and for his assistance in the preparation of the alloys.

I wish to thank in particular Dr. G. Gruner and Dr. A.P. Murani for many valuable and stimulating discussions which took place during the preparation of this thesis, and to all my fellow members of the Solid State Physics group I wish to express my appreciation of their help and co-operation.

I am grateful to the S.R.C. for providing a Research Studentship during the course of this work and to Imperial College Physics department for my appointment to Research Assistant during its later stages.

I would like to thank Mrs. K. Knight for her efficient typing of the manuscript.

Finally I wish to express my deepest gratitude to my parents for their constant encouragement and support and would like to respectfully dedicate this thesis to them.
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page Number</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Abstract</strong></td>
<td>2</td>
</tr>
<tr>
<td><strong>Acknowledgements</strong></td>
<td>4</td>
</tr>
<tr>
<td><strong>Contents</strong></td>
<td>5</td>
</tr>
<tr>
<td><strong>Introduction</strong></td>
<td>10</td>
</tr>
<tr>
<td><strong>Chapter 1 Theory and Past Work.</strong></td>
<td></td>
</tr>
<tr>
<td>1:1 Formation of localised magnetic moments.</td>
<td></td>
</tr>
<tr>
<td>Introduction</td>
<td>13</td>
</tr>
<tr>
<td>The Anderson model</td>
<td>14</td>
</tr>
<tr>
<td>Limitations of the Hartree-Fock approximation in the solution of the Anderson model.</td>
<td>17</td>
</tr>
<tr>
<td>Charge neutrality in the Anderson model</td>
<td>18</td>
</tr>
<tr>
<td>Virtual bound state parameters:</td>
<td></td>
</tr>
<tr>
<td>Experimental determination.</td>
<td>22</td>
</tr>
<tr>
<td>1:2 The resistance minimum and the s-d Hamiltonian.</td>
<td>27</td>
</tr>
<tr>
<td>Perturbation theory of the magnetisation.</td>
<td>35</td>
</tr>
<tr>
<td>Perturbation theory of the specific heat.</td>
<td>39</td>
</tr>
<tr>
<td>Low temperature ($T \ll T_R$) predictions for the properties of the s-d model.</td>
<td>42</td>
</tr>
<tr>
<td>1:3 The relationship between the Anderson and the s-d model Hamiltonians.</td>
<td>51</td>
</tr>
<tr>
<td>1:4 Localised spin fluctuations.</td>
<td>57</td>
</tr>
</tbody>
</table>
1:5 Interaction between solute atoms.

Introduction. 65
Long range interactions between localised moments. 67
Long range interactions between magnetic VBS. 69
Treatment of indirect exchange type interactions in random dilute magnetic alloys. 73
Kondo resistivity due to a pair of interacting impurity spins. 75
Anderson model for n>1 impurities, and the effects of local environment on the magnetic state of the impurity. 81
Some examples of coupling interactions in dilute alloys with the simple metal host matrices. 86

1:6 Previous measurements on the Zn based 3d transition metal systems. 92

1:7 Previous measurements on dilute alloys of Fe in pure Cu and binary CuX host matrices. 100
# CHAPTER 2 EXPERIMENTAL METHODS AND APPARATUS

## 2:1 Gulf spiral Faraday balance

- **Modification to the suspension.**
- **Calibration of the magnetic field.**
- **Temperature measurement.**
- **Experimental procedure.**

## 2:2 Comparison of techniques available for the determination of magnetic susceptibility

- **Force methods.**
- **Induction methods.**

## 2:3 Microbalance Faraday apparatus

- **Introduction.**
- **The balance.**
- **The balance platform.**
- **The superconducting solenoid.**
- **The cryostat.**
- **Suspension tube assembly.**
- **Sample suspension.**
- **Force on the suspension.**
- **The sample chamber.**
- **Helium exchange gas pressure.**
- **Temperature control.**
- **Thermometry.**
- **Calibration of thermometers.**
- **Effect of magnetic fields on the thermometry.**
- **Sample position.**
Sample positioning procedure. 190
Experimental procedure. 193
Modification to the current leads. 202

2:4 Electrical resistivity apparatus. 205

CHAPTER 3 SPECIMEN PREPARATION. 209
3:1 Zinc-3d transition metal alloys. 209
Master alloys. 210
Dilution procedure. 213
Residual resistivity ratio. 217
Fabrication of susceptibility samples. 220

3:2 CuAlFe alloys. 226

CHAPTER 4 EXPERIMENTAL RESULTS AND DISCUSSION. 228
Introduction 228
4:1 Magnetic susceptibility of dilute ZnCr and ZnMn alloys. 229
Discussion of CW parameters for Mn and Cr dissolved in a Zn matrix. 259
Field dependence of the magnetisation of dilute ZnMn and ZnCr alloys. 267
Electrical resistivity of dilute ZnMn and ZnCr alloys. 274
Magnetic susceptibility of dilute ZnFe alloys. 296
Concluding remarks on the properties of dilute alloys of Cr, Mn and Fe in Zn. 324
4.2 Resistivity and Susceptibility measurements on the CuAl Fe system. 328
Resistivity of $\text{Cu}_{1-x}\text{Al}_x + 500\text{ppm Fe}$ alloys. 328
Magnetic susceptibility of $\text{Cu}_{1-x}\text{Al}_x + 500\text{at. ppm}$ alloys. 331
Concluding remarks on the properties of Fe solute atoms dissolved in $\alpha$-phase $\text{Cu}_{1-x}\text{Al}_x$ alloys. 361

APPENDIX A. 362
REFERENCES. 365
INTRODUCTION

The prime objective of the present work has been to further the experimental investigations of the so-called single, or isolated, magnetic impurity problem where, ideally, a single transition metal atom is placed within the free electron like conduction electron band of a simple host metal and admixture between the localised and continuum electron states is permitted to a greater or lesser degree.

In the first part of chapter 1 (section 1:1 to 1:4) we include a review of the theoretical work which has been developed toward a more complete understanding of this problem, and which, broadly speaking, stems from the now classic publications of Friedel, Anderson and Kondo.

The choice of Zn as a host matrix for 3d transition metals from the centre of the series is based primarily on its interesting intermediate position as a divalent host metal, thus lying between the extensively studied Cu-3d series of dilute alloys, where 3d elements near the centre of the series would appear to support well defined magnetic moments, with corresponding low characteristic temperatures, and the Al-3d series where, although investigated to a somewhat lesser degree, these solute atoms fall into the non-magnetic or enhanced localised spin fluctuation regimes, with correspondingly high characteristic temperatures. Except for ZnMn, the Zn-3d series has until now been the subject of surprisingly few investigations, the main reason probably lies in the relatively poor
solubility of these solutes, which demands high resolution experiments on rapidly quenched alloys of very low concentrations (c < 200 at.ppm.) if meaningful results are to be obtained at all.

The effect of the electronic environment on the behaviour of the magnetic, or nearly magnetic, solute atom may be observed by using a binary alloy as the host matrix. The electronic structure of the alloy is then varied by changing the relative composition of the host. Since the characteristic temperature for Fe atoms dissolved in the Cu matrix is already within the readily accessible experimental temperature range (ie 1K - 300K) and an increase in the host matrix density is expected, a priori, to increase the characteristic temperature still further, the relatively high solubility of Al in Cu suggested α-phase CuAl alloys containing low levels of Fe solute as a suitable choice for investigation. However, since these measurements were obtained it has become apparent that at the levels of Fe concentration employed, interactions between these nearly magnetic atoms will have a very important role to play in modifying the true single impurity properties of those atoms.

A review of some of the mechanisms which can give rise to interactions between solute atoms has been included in chapter 1 (section 1:5) and the previous experimental work on the dilute Zn-3d series of alloys as well as the experimental properties of dilute CuFe and CuX-Fe alloys has
been outlined in section 1:6 and 1:7 respectively.

As we have already pointed out, ideally we would like to measure the properties due to a single magnetic solute atom in the host matrix, however in practice the limit to the degree of dilution which may be achieved is set by the sensitivity of the particular apparatus which is to be employed.

In chapter 2, after describing the original Faraday apparatus, we go on to discuss the various techniques which may be employed in the measurement of the magnetic susceptibility and in the final section we describe in some detail the design, construction and operation of the new Faraday apparatus which was used to obtain the data on the extremely dilute Zn-3d alloys.

In chapter 3 we describe the metallurgical procedures which were developed in order to prepare, with a high degree of reliability, the low concentration Zn-3d alloys. The high level of purity with which Zn may be readily obtained as well as the fact that, in solution, Fe atoms have an essentially non-magnetic behaviour are added advantages which accompany the choice of this metal as host matrix. In section 3:2 we describe the preparation of the binary CuAl alloys containing the low concentrations of Fe.

Finally, in chapter 4, we present our experimental results, together with discussions and the conclusions which may be drawn from them. In the first section (section 4:1) we deal with the Zn-3d alloys, whilst the second section (section 4:2) comprises of the data on the Cu$_{1-x}$Al$_x$+500 at. ppm Fe alloys.
CHAPTER 1
THEORY AND PAST WORK

1:1 Formation of localised magnetic moments.

Introduction

The essential feature of a 3d atom present in a simple metal host is that the unperturbed 3d - level, which in an isolated atom may give rise to a net magnetic moment (Hund's rule), has an energy which falls within the range of the host conduction band, and is therefore strongly admixed with the continuum states.

Friedel (1) first introduced the concept of a virtual bound state (VBS), which he regarded as arising from the resonant scattering of conduction electrons by the impurity potential. Although such a state is not tightly bound (in the atomic sense) to the 3d atom it is localised within the vicinity of the impurity and, under certain conditions, is capable of maintaining a magnetic moment. If such a moment can be detected experimentally, e.g. through a temperature dependent contribution to the magnetic susceptibility, then the state of the impurity corresponding to simultaneous occupation of the virtual bound levels for antiparallel spin directions must be energetically unfavourable. Interactions and correlations between electrons at the impurity site are clearly an important aspect of this problem.

Friedel argues qualitatively that the VBS may split due to the exchange interaction. If \( p \) is the number of electrons (or holes, whichever is the smaller) and \( \Delta E \) is the energy
gained when two antiparallel spins set themselves parallel, then a localised moment will exist if the total energy gained is greater than the width of the VBS, \( w \) i.e., if \( p \Delta E > w \).

Blandin and Friedel (2) later obtained this condition as a result of a more detailed calculation.

A more quantitative formulation of the problem of local moment formation was achieved by Anderson (3) and also by Wolff (4) and Clogston (5). Although these authors approach the problem from different viewpoints they both are based on the VBS ideas of Friedel. The Anderson model, where the extra orbital(s) are orthogonal to the conduction band states, is the most appropriate when considering 3d transition metal atoms in a simple metal host matrix. Where dilute alloys of one transition metal in another are concerned, the Wolff-Clogston model, in which the VBS is derived by resonant scattering of the conduction electrons from the perturbing impurity, is preferable.

The Anderson model

Anderson considers a single localised d-orbital, \( \Phi_d \), located within the conduction band of the host, at an energy \(-E_d\) with respect to the Fermi level. The conduction band is assumed to be free-electron like. In the absence of any interaction between the localised orbital and the conduction band, the impurity is taken to be in the magnetised state. The spin degeneracy is removed by the coulomb repulsion, \( U \), between electrons of opposite spin at the impurity site, so that the spin-up (say) level, has energy \(-E_d + U\), which
is above the Fermi level, and is consequently unoccupied. All other two-body interactions between electrons are neglected.

The full Anderson Hamiltonian may be expressed in the form

$$H = H_s + H_d + H_{sd}$$

1(1)

$$H_s = \sum_{k\sigma} \epsilon_k n_{k\sigma}$$ and is the energy of the one-electron states of the conduction band.

$$H_d = E_d \left(n_{\uparrow} + n_{\downarrow}\right) + U n_{\uparrow} n_{\downarrow}$$

1(2)

represents the energy of the unperturbed localised d-orbital, including the coulomb repulsion term which renders the magnetic state energetically more favourable.

The final term, $H_{sd}$, represents the admixture between conduction states and the localised state

$$H_{sd} = \sum_{k\sigma} V_{kd} \left(C^\dagger \sigma C_{d\sigma} + C^\dagger \sigma C_{d\sigma}^* C_{k\sigma}\right)$$

1(2a)

which is expressed in the usual 2nd quantised form. Physically, this interaction is in competition with the coulomb repulsion, and allows electrons to hop on and off the impurity, with the result that the energies of the localised levels are no longer well defined, they are broadened into virtual states with a reduced separation between that for spin up and that for spin down fig. (1:1).

Anderson solves the Hamiltonian within the Hartree-Fock approximation. In this case the d-state energies may be written

$$E_{d\sigma} = E_d + U \left<n_{d-\sigma}\right>$$

1(3)

where the average occupation of each spin state, $\left<n_{d\sigma}\right>$, must be determined self-consistently in order to discover
the conditions for the persistence of the magnetic moment, that is \( \langle n_{d\sigma} \rangle \neq \langle n_{d-\sigma} \rangle \)

The additional density of d-states is found to be

\[
\rho_{d\sigma} = \frac{1}{\pi} \frac{\Delta}{(E-E_{d\sigma})^2 + \Delta^2}
\]

1(4)

where the VBS width, \( 2\Delta \), increases with the strength of the admixture term, and the host density of states at the d-state energy, according to

\[
\Delta = \bar{\n} \langle v_{kd}^2 \rangle_{av} \rho_o(E_{d\sigma})
\]

1(5)

The number of electrons in each d-state is obtained by integration of eqn. 1(4) over all energies up to the Fermi energy, corresponding to the shaded portion of fig. (1:1), with the result that

\[
\langle n_{d\uparrow} \rangle = \frac{1}{\pi} \cot^{-1} \left[ \frac{E_d - E_F + U \langle n_{d\uparrow} \rangle}{\Delta(E_F)} \right]
\]

\[
\langle n_{d\downarrow} \rangle = \frac{1}{\pi} \cot^{-1} \left[ \frac{E_d - E_F + U \langle n_{d\downarrow} \rangle}{\Delta(E_F)} \right]
\]

1(6)

\[\text{fig. (1:1) Density of states distribution in magnetic case (after (3))}\]
Simultaneous solution of eqns. 1(6) reveals that even when the unperturbed localised levels are symmetrically placed with respect to the Fermi energy (the most favourable case), the impurity can no longer support a magnetic moment when, for a given strength of the coulomb repulsion, the broadening of the levels exceeds a well defined limit

\[ \Delta > \frac{U}{\tau} \]

1(6a)

in which case there exists only the non-magnetic solution

\[ \langle n_{df} \rangle = \langle n_{d\uparrow} \rangle . \]

We note that the magnetic limit, \( \frac{U}{\Delta} > \tau \), is equivalent to requiring that the time for which both levels are simultaneously occupied, \( \sim \frac{\hbar}{U} \), is short compared to the lifetime of a single electron on the impurity \( \sim \frac{\hbar}{\Delta} \).

Limitations of the Hartree-Fock approximation in the solution of the Anderson Hamiltonian

The tendency for the impurity to form a magnetised state is over-estimated as a result of the use of the Hartree-Fock (HF) approximation. Furthermore the sharp boundary between magnetic and non-magnetic solutions is unphysical since we might expect that the probability of simultaneous occupation of both spin up and spin down levels reduces in a smooth fashion as the strength of the coulomb repulsion is increased.

The HF approximation neglects correlations between electrons with opposite spins and thus arrives at an artificially high value for the energy gained when two such electrons align their spins on the impurity site. Correlation effects lead to the eventual break-down of HF in the magnetic limit, since here the total time spent by a given electron
hopping on and off an impurity $\left( \sim \frac{\hbar}{\Delta} \right)$ is sufficient for it to react to the instantaneous potential due to the other VB level, rather than the time average of this quantity, i.e., $\frac{1}{\Delta} \gg \frac{1}{U}$.

Schrieffer and Mattis (6) show, in the "low-density limit", where the total number of electrons in a single orbital is less than 0.3, and the predominant correlations are 2-particle, that the effect of coulomb correlations beyond the HF approximation is to result in an effective coulomb repulsion given by

$$U_{\text{eff}} = \frac{U}{1 + \frac{U}{2d} \tan^{-1} \left( \frac{E_d}{\Delta} \right)} \quad \text{(7)}$$

so that the Hartree instability is not reached, even as $U \rightarrow \infty$, and the orbital must remain in the non-magnetic state. In the case of several degenerate orbitals, the exchange splitting, $J$, will favour the parallel alignment of electrons localised at the impurity and so the magnetic case is still possible, even in the "low density limit". The work of Kjöllerström et al. (7) verifies the results from the single orbital.

**Charge Neutrality in the Anderson model**

From the point of view of scattering theory, when a 3d atom is placed in the matrix of a simple host metal, the electrons of the 3d – level delocalise into the conduction band, leaving an excess charge, $Ze$, at the impurity site, which represents a perturbation to the otherwise periodic potential of the host matrix. The fundamental condition of charge neutrality requires that the total screening charge, $S$,
arising from such a perturbation should just compensate
the excess charge at the impurity. Friedel (1) calculates
S in terms of the phase shifts $\eta_l$ of the $l$th partial wave
component of the free conduction electron state, and invokes
charge neutrality to establish the Friedel Sum Rule
(underlined)
\[
S = \frac{1}{\pi} \sum_{l,\sigma} (2l + 1) \eta_{l,\sigma} (E_F) = Z
\]

Now let us consider the Anderson model for the physically
more realistic case of a $(2l + 1)$ degenerate localised impurity
orbital. This was discussed by Anderson (3) and more fully
by Yosida et al. (8) and Klein and Heeger (9).

The basic Hamiltonian still retains its original form,
except that the 2nd term must be re-written in order to take
account of the intra-atomic like exchange, $J (~> 0)$, favouring
parallel spin electrons localised in different orbitals at
the impurity site. i.e.,
\[
H_d = \sum_{i\sigma} E_{d\sigma} n_{i\sigma} + U \sum_{ij} n_{i\sigma} n_{j-\sigma} + \frac{1}{2}(U-J) \sum_{i \neq j} n_{i\sigma} n_{j\sigma}
\]

Within the H.F. approximation, the solution of the
Hamiltonian is exactly analogous to that for the single
orbital, provided that there is no crystal field splitting
of the d-orbital energy levels, so that $E_{i\sigma} = E_{d\sigma}$ for all $i$,
where
\[
E_{i\sigma} = E_d + (U-J) \sum_{j \neq i} \langle n_{j\sigma} \rangle + U \sum_{j} \langle n_{j-\sigma} \rangle
\]

The added density of states is just a factor $(2l + 1)$
greater than for the single orbital, due to orbital
degeneracy, and the instability condition for the presence
of a magnetic moment becomes,

$$(U + 4J) \frac{\rho_d(E_F)}{10} \gg 1 \quad 1(11)$$

which may also be written, eqns., 1(3), 1(4), 1(6)

$$(U + 4J) \sin^2 \frac{\prod N_d^{TOT}}{\prod \Delta} \gg 1 \quad 1(12)$$

reducing to

$$\frac{(U + 4J)}{\prod \Delta} \gg 1 \quad 1(13)$$

in the most favourable case when the VBS is symmetric about $E_F$.

The total number of occupied states introduced by the 3d impurity is

$$N_d^{TOT} = 5 \sum_{\sigma} n_{\sigma} = \frac{5}{\prod} \sum_{\sigma} \cot^{-1} \left[ \frac{E_d\sigma - E_F}{\Delta(E_F)} \right] \quad 1(14)$$

Returning to the Friedel Sum Rule, we expect that, in the case of a 3d impurity, there will be resonant scattering of the $l=2$ partial wave for incident energies in the region of the original 3d atomic level, causing the latter to broaden into a V.B. level. All other phase shifts are relatively small, being the result of simple potential scattering, so

$$\eta_l = \eta_l^0 \quad l \neq 2 \quad 1(15)$$

$$\eta_2 = \eta_2^0 + \eta_2^{resonant}$$

where (10) $\eta_2^{resonant} = \cot^{-1} \left[ \frac{E_d\sigma - E}{\Delta(E)} \right] \quad 1(16)$

and $E$ is the energy of the incoming partial wave.

Substituting eqns. 1(15) into the Friedel Sum Rule
and neglecting $\eta_0^x$ we find

$$Z = \frac{5}{\pi} \sum_\sigma \cot^{-1} \left[ \frac{E_d^\sigma - E_F}{\Delta(E_F)} \right]$$

the R.H.S. of which is identical to the expression for the total number of localised electrons derived from the Anderson model (eqn. 1(14)). Thus the vital condition for charge neutrality is implicit in the Anderson model, and $N_{dTOT} = Z$.

**Virtual bound state parameters: Experimental determination**

The experimental methods available for the determination of the parameters $(U+4J)$, $E_d$ and $\Delta$ of the Anderson model fall into two groups.

i) Optical absorption and electron photo-emission - 'direct' methods which, in principle, can probe an energy range large enough to examine the whole structure of the VBS.

ii) Specific heat, magnetic susceptibility and residual resistivity - 'indirect' measurements, sensitive only to the structure of the VBS at the Fermi surface.

The optical methods require alloys with high concentration $(c \geq 10\%$ usually) in order to observe the changes in the energy spectrum of either the inter-band absorption coefficient, or the number of photo-electrons ejected from the metal surface per photon absorbed. However, in practice (11, 12) the modification to the pure host metal spectrum is found to be remarkably insensitive to the solute concentrations and it is possible to extrapolate the data on several alloys to the dilute limit.
The choice of the host metal is restricted to those where the d-band is sufficiently well separated from the Fermi level that the small spectral changes due to the solute VBS are not lost in the gross structure arising from host d-band absorption. The noble metals Ag, Au and Cu are most suitable in this respect.

The optical absorption spectrum of Ag Mn alloys (11) has two peaks centred at 3eV and 1.8eV from the Fermi energy, corresponding to a total spin splitting of 4.8 eV for the Mn VBS. The photo-emission data (13) confirms the existence of a VBS which is centred approximately 3eV below the Fermi surface, and although there is some overlap with the contribution from the Ag 4d band, the width of the state, $2\Delta$, is estimated to be 1 eV. Having fixed $E_d$ and $\Delta$, the net spin on each Mn atom will be determined by the separation of spin-up and spin-down halves of the VBS which is, in turn, a measure of $(U + 4J)$. In order to achieve $\mu_{\text{eff}} = 4.7 \mu_B$ in agreement with the bulk susceptibility data of Hurd (14), Myers (15) has calculated that a splitting of $\sim 6$ eV is necessary. The d-band absorption edge in Cu is 2.2eV below $E_F$. No structure is seen in Cu Mn alloys within this energy of the Fermi surface which is consistent with a large splitting of the VBS as in Ag Mn.

The photo-absorption spectrum of Cu Ni (0.5 - 4 at%) alloys (16), when compared to that for pure copper has a single additional peak centred around -0.72eV, ($E_F =0$), corresponding to a spin degenerate VBS of width $2\Delta \sim 0.5$eV. Photo-emission measurements (17) on more concentrated alloys (13% and 27% Ni) display a structure corresponding to
$E_d = 0.95 \text{eV}$ with $2\Delta = 0.8 \text{eV}$. Integrating a Lorentzian VBS characterised by these parameters gives 8.9 and 8.5 electrons localised in the VBS, in satisfactory agreement with residual resistivity measurements.

Friedel (1) has shown that the impurity resistivity, in terms of the phase shifts, $\gamma_{l,\sigma}$, of the $l$th partial wave of the conduction electron state, may be written

$$\Delta R = \frac{4}{Ze^2 K_F} \sum_{l,\sigma} (l + 1) \sin^2 \left( \gamma_{l,0} - \gamma_{l+1,\sigma} \right) E_F$$

1(18)

for a free electron host with $Z$ electrons per atom. Assuming all non-resonant phase shifts are small, for a 3d impurity this expression becomes

$$\Delta R = \left[ \frac{4}{Ze^2 K_F} \right] 5 \left\{ \sin^2 \gamma_{2\uparrow} + \sin^2 \gamma_{2\downarrow} \right\} E_F$$

1(19)

The phase shift, for each spin direction, is related via the Friedel Sum Rule to the average number, $\langle n_{d\uparrow} \rangle$ or $\langle n_{d\downarrow} \rangle$, of d-electrons localised at the impurity site

$$\gamma_{2\uparrow} (E_F) = \frac{\pi}{5} \langle n_{d\uparrow} \rangle, \quad \gamma_{2\downarrow} (E_F) = \frac{\pi}{5} \langle n_{d\downarrow} \rangle$$

1(20)

i.e.,

$$\Delta R = \left[ \frac{4}{Ze^2 K_F} \right] 5 \left\{ \sin^2 \frac{\pi}{5} \langle n_{d\uparrow} \rangle + \sin^2 \frac{\pi}{5} \langle n_{d\downarrow} \rangle \right\}$$

1(21)

and in the non-magnetic case, where $\langle n_{d\uparrow} \rangle = \langle n_{d\downarrow} \rangle = \frac{N_d \text{TOT}}{2}$ and $N_d \text{TOT}$ is the average total number of localised d-electrons

$$\Delta R = \left[ \frac{4}{Ze^2 K_F} \right] 10 \sin^2 \frac{\pi}{10} \frac{N_d \text{TOT}}{10}$$

1(22)
On this basis the residual resistivity vs. atomic number for 3d solutes in various hosts may be explained. For those hosts (Cu, Au) where a net moment is observed for solutes near the centre of the 3d series, eqn. 1(21) will apply resulting in small $\Delta R$ around Mn, (where $\langle n_{d\uparrow} \rangle \approx 5$ and $\langle n_{d\downarrow} \rangle \approx 0$), and the characteristic double peaked distribution in $\Delta R$ vs. atomic number. On the other hand, in the case of Al host, the maximum in the residual resistivity around Mn implies a spin-degenerate VBS and eqn. 1(22) applies.

A measurement of the residual resistivity leads to a determination of the number of localised d-electrons and therefore gives information on the relative disposition of the VBS with the Fermi level.

As we have already discussed, the HF approximation is expected to be valid only in the extreme $(U/\pi \Delta \ll 1)$ non-magnetic limit. For this regime, Klein and Heeger (9) have evaluated the specific heat contribution from the impurity

$$\Delta C = \frac{\pi^2}{3} k_B^2 T \rho_d(E_F)$$  \hspace{1cm} 1(23)$$

provided

$$\left| \frac{E_F - E_d}{\rho_H(E_F)} \left( \frac{\partial \rho_H}{\partial E} \right)_{E_F} \right| \ll 1,$$

which will be true for 'simple' metals eg., Cu, Ag and Au where the density of states, $\rho_H$, varies slowly at the Fermi surface. Thus the change in the coefficient of the linear term of the temperature dependence on alloying measures, in a 'straightforward' way, the extra density of states at the Fermi surface due to the impurity VBS, $\rho_d(E_F)$. In combination with residual resistivity measurements this can be used to
provide an estimate of the single particle half-width, \( \Delta \), using

\[
\rho_d(E_F) = \frac{10}{\pi \Delta} \sin^2 \left( \frac{\pi N_d \text{TOT}}{10} \right)
\]

\[1(24)\]

In the case of Be Ni alloys (9) - (band structure calculations \( \frac{\partial \rho_H}{\partial E} \) \( \sim \) 0 for Be) -

specific heat measurements yield \( \rho_d(E_F) = 1.15 \) states/eV/Ni atom and \( 2\Delta = 0.8 \) eV. Similarly for Ni dissolved in Cu

\( \rho_d(E_F) \sim 1 \) state/eV/Ni atom and \( 2\Delta \sim 0.6 \) eV. The good agreement, in the latter case, with optical data demonstrates that in the non-magnetic regime the HF approximation provides an adequate basis for evaluating the properties of the VBS.

In contrast to the specific heat, the magnetic spin susceptibility of a VBS is enhanced over the 'straightforward' Pauli spin paramagnetism which would be expected from the additional density of states at the Fermi surface, and this is a consequence of the self-consistent manner in which the occupations of spin up and spin down halves of the VBS are adjusted when the magnetic field is applied.

\[
\chi_d^{\text{spin}} = \eta_s \chi_0 \text{ Pauli} = \eta_s a_B^2 \rho_d(E_F)
\]

\[1(25)\]

where \( \eta_s = \frac{1}{1 - \left( U + 4J \right)} \rho_d(E_F) \)

\[1(26)\]

We note that the enhancement factor diverges as the criterion for the existence of a net magnetic moment is approached.

Dworin and Narath (18) have calculated the orbital susceptibility of the VBS and find
\[ \chi^\text{orb}_d = \eta^\text{orb}_d 2u_B^2 \rho_d(E_F) \quad \text{(27)} \]

where \[ \eta^\text{orb}_d = \frac{1}{1 - \frac{(U-J)}{10} \rho_d(E_F)} \quad \text{(28)} \]

Far from the HF instability the orbital component will represent a large contribution to the total susceptibility of the VBS, but this is increasingly swamped by the spin susceptibility as the condition for spin splitting of the VBS is approached. From their NMR measurements of the Knight shift in Cu Ni alloys Dworin and Narath conclude that \( (U + 4J) \approx 6\text{eV} \) and \( (U - J) \approx 3\text{eV} \).

In summary, from the measurements quoted above, \( U + 4J \approx 4 \) for 3d transition metals in noble metal hosts, and \( \frac{\Delta}{\kappa} \) this is consistent with the observed magnetic behaviour of solutes Cr, Mn and Fe in the centre of the series.
1.2 The resistance minimum and the s-d Hamiltonian

Prior to the publication of Kondo's now famous paper (19), the occurrence of a minimum in the resistivity of certain dilute alloys (20) and nominally 'pure' metals (21) had gone without satisfactory explanation. The experimental evidence was clarified by the work of Sarachik et al. (22), who were able to demonstrate a one to one correspondence between the presence of a resistance minimum and a temperature dependent magnetic susceptibility (implying the existence of a localised moment on the impurity) for a range of Nb-Mo alloys containing a small fraction of Fe atoms.

Kondo's contribution was, by reconsidering the then well known s-d model Hamiltonian (23) (24) (25), to provide a theoretical basis for the existence of a minimum in the resistivity due to exchange scattering of electrons from a localised impurity spin.

In its most general form this Hamiltonian may be written

$$H_{sd} = - J(r) \mathbf{S} \cdot \mathbf{s}$$  \hspace{1cm} (19)

where $\mathbf{S}$ and $\mathbf{s}$ represent the impurity spin and the conduction electron spin respectively. The spatial extent of the localised spin is represented in the spatial dependence of the s-d exchange coupling constant, $J(r)$. In the s-d model the existence of the impurity spin is assumed a priori and, furthermore, the lifetime of this spin is taken to be infinite.

$J(r)$ may include contributions from both the direct exchange (23) interaction (ferromagnetic, $J(r) > 0$) between the localised spin and the conduction electron spin, as well as the effective indirect exchange (antiferromagnetic $J(r) < 0$)
due to the Anderson admixture of localised and conduction electron states. (The latter mechanism for effective exchange coupling will be more fully discussed in a later section).

In most theoretical treatments of the s–d model, \( J(r) \) is approximated to be an isotropic zero range delta function potential so that the exchange interaction takes place only at the impurity lattice site, and is independent of the momentum wavevector of initial or final conduction electron scattering states. Such an approximation is clearly a drastic simplification of the real situation, particularly in the case of a 3d solute. The finite range of the s–d exchange potential may be included schematically by having a momentum space cut-off for \( J(k,k') \) so that \( J(k,k') = J -D < E_k \) and \( E_k < D \)

\[
= 0 \quad \text{otherwise}
\]

where \( k \) and \( k' \) are the initial and final states for the conduction electron. The cut off energy \( D \) may be associated with the Fermi energy of the conduction band.

Yosida (25) showed that, when treated in the first Born approximation, the s–d interaction of eqns (9) and (10) leads only to a temperature independent contribution to the resistivity

\[
R = R_0 J^2 S(S+1)
\]

where \( R_0 \) depends solely on the properties of the host conduction band.

Kondo (19) reconsidered this problem, but extended the calculation to the second order Born approximation for the transition rate \( (k \rightarrow k') \) between conduction electron states.
induced by the s-d interaction. In this approximation the scattering process proceeds via an intermediate state (q). In order to calculate the resistivity it is necessary to sum the individual transition probabilities for each distinguishable scattering channel, bearing in mind the dynamical character of the localised spin which allows for conduction electron spin flip scattering processes to take place (with the corresponding change in the z-component, $S_z$, of the impurity spin).

To see how a logarithmic divergence in the scattering amplitude may arise it is sufficient to consider only those processes which result in an electron in an initial state $k_+$ being scattered to a final state $k'_+$. Energy is conserved, the scattering process is elastic, and so $E_k = E_{k'}$. There are two distinguishable processes

1) An electron $k_+$ is scattered to $q_+$, and then the electron in $q_+$ is scattered to $k'_+$. The transition probability for this process will be dependent on the probability that $q_+$ is an empty state, $(1-f(q))$, where $f(q)$ is the Fermi function. On the other hand when $q_+$ is first scattered to $k'_+$ and subsequently $k_+ ightarrow q_+ q_+$ must initially contain an electron. The matrix elements for these direct and exchange processes may be written, respectively

$$a_{2D} = \left( \frac{J}{2N} \right)^2 \cdot S_z^2 \cdot \sum_{q} \frac{1 - f(q)}{E_k - E_q}$$

$$a_{2E} = \left( \frac{J}{2N} \right)^2 \cdot S_z^2 \cdot \sum_{q} \frac{f(q)}{E_k - E_q}$$

The sum of these two terms gives the total scattering
amplitude for scattering through an intermediate state without spin flip occurring which is

\[ \left( \frac{J}{2N} \right)^2 S_z^2 \sum_{q} \frac{1}{E_k - E_q} \]  \hspace{1cm} 1(13) \]

and we note that, as with simple potential scattering, where the scattering centre lacks internal degrees of freedom, the Fermi function has cancelled out leaving a small, energy independent scattering amplitude, which in turn results in a temperature independent contribution to the total resistivity (as with simple potential scattering).

2) The second scattering mechanism allows the electron, \( k_+ \), to be spin flip scattered into an empty state \( q_- \), the \( z \)-component of the impurity spin being increased by unity \( S_z \rightarrow S_z + 1 \); subsequently \( q_- \rightarrow k'_+ \) and the impurity spin \( z \)-component is reduced to its original value. In the exchange process \( q_- \rightarrow k'_+ \), while \( S_z \rightarrow S_z - 1 \), and then \( k'_+ \rightarrow q_- \) so that \( S_z - 1 \rightarrow S_z \). This time the Fermi function does not cancel out and the total scattering amplitude is, excluding a small energy independent component which may be absorbed into eqn. 1(13)

\[ 2 \left( \frac{J}{N} \right)^2 S_z^2 \sum_{q} \frac{f(q)}{E_k - E_q} \]  \hspace{1cm} 1(14) \]

The non-cancellation of the Fermi function can be shown (26) to be due to the non-commutivity of the raising and lowering operators for the impurity spin. i.e.

\[ \left[ S_+, S_- \right] \neq 0 \]  \hspace{1cm} 1(15) \]

where \( S_\pm = S_x \pm i S_y \).

but, perhaps more physically, indicates that the scattering
of the electron in state \( k \) is influenced by the occupation of all the other electron states \( g \), and so we are dealing with an explicitly many-body problem where, because of the 'structure' of the impurity spin (i.e., \( 2S+1 \)-fold spin degeneracy), the scattering of \( N_e (\sim 10^{23}) \) electrons cannot be regarded simply as the superposition of \( N_e \) independent single electron scattering processes, as is the case for the more usual potential scattering problem.

The presence of \( f(q) \) in the expression for the scattering amplitude with intermediate spin-flip (eqn. 14) has a dramatic effect on the summation over intermediate states, \( g \). Replacing the summation by an integration and considering the simplest case of a free electron half filled host conduction band \(-D < E_k < D\) with a uniform density of states \( n(\omega) \)

\[
\sum_{q} \frac{f(q)}{E_k - E_q} = n(\omega) \int_{-D}^{+D} \frac{f(q)}{E_k - E_q} dE_q
\]

(16)

\[ \frac{1}{E_k - E_q} \]

FIG(1:2) BEHAVIOUR OF FACTOR \((E_k - E_q)^{-1}\)
At $T=0\ K$, then $E_k = E_F$, $f(q)$ is a step function and only the shaded area in fig.(1:2) contributes to the integral, which will clearly diverge. If $E_k \neq E_F$ the integral is finite and proportional to $\ln \left| \frac{E_k - E_F}{D} \right|$, which is strongly energy dependent when $E_k \approx E_F$. Thus at finite temperatures, when $|E_k - E_F| \approx k_B T$ we obtain in the scattering amplitude, and therefore also in the resistivity, a term proportional to $\frac{\ln k_B T}{E_F}$ or $\frac{\ln k_B T}{E_F}$ (see fig.(1:2)).

Working out the details for all the scattering processes to 2nd order, Kondo (27) obtains for the impurity resistivity

$$\rho = \rho_0 (1 + 4n(o)J\ln \frac{k_B T}{E_F})$$

1(17)

where

$$\rho_0 = \frac{2\pi n(o)J^2 S(S+1)}{ZNe^2 h}$$

and so when $J<0$ the resistivity diverges at low temperatures as $T \rightarrow 0$. Eqn. 1(17), in combination with the usual phonon contribution to the low temperature resistivity ($\propto T^5$) accounts for the observation that the temperature of the resistance minimum, $T_m \propto c^{1/5}$.

The temperature dependent term in eqn. 1(17) begins to diverge, and dominates the impurity resistivity below a characteristic temperature, now called the Kondo temperature

$$T_K = \frac{E_F}{k_B} \exp \left[ - \frac{1}{n(o)|J|} \right]$$

1(18)

and the infinite resistivity predicted by eqn.1(17) for the resistivity at $T=0$ is, in fact, physically unacceptable since no scattering mechanism can result in a cross-section
which exceeds the (finite) 'unitarity limit' of $\frac{4N}{k_F^2} (2j+1)$.

Thus we see, even at this early stage, that at low enough temperatures $T \ll T_K$, no matter how small the characteristic parameter $n(o)J$, the s-d interaction will lead to a strong coupling between the localised spin and the conduction electrons, which cannot be treated successfully using a perturbational type of theory.

Heeger (26) pictures the Kondo divergence as the manifestation of an indirect electron-electron interaction mediated via the impurity spin in the following manner; electron (1) spin flip scatters with the impurity so that a subsequent scattering of electron (2) is influenced by the fact that the previous event had taken place, resulting in an indirect interaction between the electrons. Gainon and Heeger (28) argue that from this point of view the "memory" of the spin in the intermediate state will be important. If this memory is made sufficiently short, either by intrinsic (ie admixture) coupling to the conduction electrons (localised spin fluctuations - see later), or by direct relaxation of the impurity spin to the lattice, then this indirect interaction and therefore the Kondo divergence itself should be suppressed. These authors find that the addition of as little of 0.1 at.% of Pt impurities to dilute CuMn alloys causes a marked suppression of the logarithmic temperature dependence in the Mn impurity resistivity (measurements on a Cu + lat.%Pt alloy confirmed that the Pt
impurity itself gives rise only to a temperature independent contribution to the total resistivity) and explain this feature as being due to the increased relaxation rate of the Mn spin which results from the indirect (via the induced conduction electron spin polarisation (see later) around each Mn spin) coupling of the Mn spin into the strong spin-orbit interaction at distant Pt impurities.

The approximation of eqn.1(10) for \( J(\mathbf{k},\mathbf{k}') \) corresponds to the exchange potential scattering only the \( l=0 \) partial wave of the conduction electrons. In theoretical treatments where \( S=1/2 \), corresponding to a single non-degenerate orbital this may be appropriate. However Blandin (29) and also Schrieffer (30) argue that the exchange potential should reflect the symmetry of the VBS which gives rise to the impurity spin itself, i.e. \( \mathbf{\lambda} = 2 \) for a 3d solute. Blandin points out that if we make the approximation

\[
J(\mathbf{k},\mathbf{k}') = J P_l(\cos \Theta) \tag{1(19)}
\]

(where \( P_l(\cos \Theta) \) is the Legendre polynomial corresponding to the \( l \)th partial wave) then eqn.1(17) is modified to become

\[
\rho = c \rho_0' \left[ 1 + 4n(o)J' \ln \frac{k_B T}{E_F} \right]
\]

with

\[
\rho_0' = (2l+1) \frac{2\gamma n(o)m J' 2S(S+1)}{ZNe^2 h}
\]

\[
J' = \frac{J}{(2l+1)} \tag{1(20)}
\]
Perturbation theory of the magnetisation

Yosida and Okiji (31) have calculated the perturbation to $\langle S_z \rangle_0$, the thermal average z-component of the localised spin, due to the s-d interaction to 4th order in $J_n(o)$

\[ \langle S_z \rangle = \langle S_z \rangle_0 + \langle S_z \rangle_1 + \langle S_z \rangle_2 + \langle S_z \rangle_3 + \langle S_z \rangle_4 \]

where $\langle S_z \rangle_n$ is of order $(J_n(o))^n$ and $J_n(o) \ll 1$.

The first order correction is zero and

\[ \langle S_z \rangle = \langle S_z \rangle_0 \left\{ 1 + \frac{J_n(o)}{2} \left[ \frac{(J_n(o)\ln k_B T)}{E_F} \right] + \left( \frac{J_n(o)\ln k_B T}{E_F} \right)^2 + \left( \frac{J_n(o)\ln k_B T}{E_F} \right)^3 \right\} \]

Assuming this geometric progression to persist to all orders in $J_n(o)$

\[ \langle S_z \rangle = \langle S_z \rangle_0 \left[ 1 - \frac{(J_n(o))^2}{2} \right] \frac{\ln E_F}{k_B T} \frac{E_F}{E_F} \left[ 1 + \frac{J_n(o)\ln E_F}{k_B T} \right] \]

Since $J_n(o) \ll 1$ for the perturbation expansion to be valid at all, we have the result that $\langle S_z \rangle$ is reduced below the value $\langle S_z \rangle_0$ in the absence of the s-d interaction. This may be regarded as a consequence of the spin flip scattering processes which results in $S_z$ not being a good quantum number in addition to the usual thermal randomisation which results in the unperturbed time average $\langle S_z \rangle_0$.

The s-d interaction represents a coupling between the local spin and the conduction electron spin and so there will
be an antiparallel polarisation of the latter with respect to the local spin even when $T \gg T_K$. Yosida and Okiji find that the total conduction electron polarisation due to a single impurity when $T \gg T_K$ is directly related to the expectation value of the impurity spin in the presence of the s-d interaction by

$$\langle \sigma \rangle = \frac{Jn(o)}{2} \langle S_z \rangle$$  \hspace{1cm} \text{(123)}$$

We see from eqn. 1(22) that, as with the calculation of the resistivity, the perturbation theory solution breaks down at $T = T_K$ and may not be used to predict the behaviour of the system below this temperature.

Giovannini et al. (32) have calculated the impurity magnetisation for $T \gg T_K$ to second order perturbation theory with $S = 1/2$, for both the high field ($\mu H \gg kT$) and low field ($\mu H \ll kT$) limiting cases. They obtain

i) $\mu_B H \ll k_B T$

$$M = 2u_B^2 n(o)H + \mu_B \left[ 1 + \frac{Jn(o)}{1 + Jn(o)\ln \frac{E_F}{k_B T}} \right] B_{\frac{1}{2}}(gx)$$  \hspace{1cm} \text{(124)}$$

ii) $\mu_B H \gg k_B T$

$$M = 2u_B^2 n(o)H + \mu_B \left[ 1 + \frac{Jn(o)}{1 + Jn(o)\ln \frac{E_F}{k_B H}} \right] B_{\frac{1}{2}}(gx)$$  \hspace{1cm} \text{(125)}$$

where $B_{\frac{1}{2}}(gx)$ is the Brillouin function for $S=\frac{1}{2}$.

The first term in each of the above two expressions arises from the Pauli paramagnetism of the conduction electrons, and this uniform polarisation will exert an effective magnetic field at the impurity site via the s-d interaction.
Loram et al. (33) point out that the results, eqn. 1(22) and 1(23), of Yosida and Okiji are equivalent to those of Giovannini et al. if we take as the exchange field acting on the local spin as

\[
H_{\text{EX}} = \frac{\frac{1}{2} J_n(o) H}{1 + J_n(o) \ln \frac{E_F}{k_B T_{\text{EFF}}}} \tag{1(26)a}
\]

with

\[
k_{\text{EFF}} = \left( (k_B T)^2 + (g u_B H)^2 \right)^{1/2} \tag{1(26)b}
\]

Thus in eqn. 1(22), \( \langle S_z \rangle_0 \) is the expectation value of \( S_z \) of a free spin in contact with a thermal bath at temperature \( T \) and a total magnetic field \( H + H_{\text{EX}} \), i.e.

\[
g u_B S_B S \left( \frac{g u_B (H + H_{\text{EX}})}{k_B T} \right)
\]

where \( B_S(x) \) is the Brillouin function for a spin \( S \). The expression for the total magnetisation, using eqns. 1(21) and 1(23) may thus be written

\[
M = 2 u_B^2 n(o) H
\]

\[
+ c \left( 1 + \frac{J_n(o)}{2} \right) \left( 1 + \frac{J_n(o)}{2} \left( J_n(o) \ln \frac{k_B T}{E_F} + \ldots \right) \right) \langle S_z \rangle_0
\]

which may be written, if we include only terms like \((J_n(o) \ln \frac{k_B T}{E_F})^n\) in the summation

\[
M = 2 u_B^2 n(o) H + c g_{\text{EFF}} u_B S_B (g_{\text{EFF}} x)
\]

where

\[
g_{\text{EFF}} = g \left[ 1 + \frac{\frac{1}{2} J_n(o)}{1 + J_n(o) \ln \frac{E_F}{k_B T_{\text{EFF}}}} \right] \left( \frac{k_B T_{\text{EFF}}}{k_B T} \right)
\]

\[
x = g u_B H \frac{1}{k_B T}
\]

\[
1(28)
\]
and c is the concentration of impurity spins. Eqn. 1(28) thus provides us with an expression for the impurity magnetisation which covers the whole range of x and which reduces to eqns. 1(24) and 1(25) for \( S = \frac{1}{2} \) and \( x \ll 1 \) or \( x \gg 1 \) respectively.

From eqn. 1(28) we may deduce the low field or initial, \( x \ll 1 \), susceptibility of an impurity spin S.

\[
\chi(x \to 0) \approx \frac{g_{\text{EFF}}^2 u_B^2 S(S+1)}{3k_B T} \left[ 1 + \frac{Jn(o)}{1 + Jn(o) \ln \frac{E_F}{k_B T}} \right] \frac{g_{\text{EFF}}^2 S(S+1)}{3k_B T} \\
= \left[ 1 - \left( \ln \frac{T}{T_K} \right)^{-1} \right] \chi_0
\]

(1(29))

(using eqn. 1(18) to complete the last step). Once again we observe that the perturbational solution diverges as \( T \to T_K \).

Scalapino (34) has calculated the initial susceptibility due to a single impurity orbital in the Anderson model in the limit of weak admixture, \( V_{kd} \), between the localised impurity state and the conduction electrons, and obtains a similar expression to eqn. 1(29). The equivalence between the s-d model and the extreme magnetic limit of the Anderson model for the impurity will be discussed in a later section.

If we use eqn. 1(29) to plot graphically \( \chi^{-1} \) vs T,
then over the limited temperature range \(7 \leq \frac{T}{T_K} \leq 100\),
the points deviate by less than \(\pm\%\) from a straight line,
which would correspond to a Curie Weiss (CW) behaviour for
the susceptibility, which in terms of the parameters of
the s-d model is given by

\[
\chi(x \to 0) = \frac{(\mathcal{A}^2/1.22)}{2k_B(T + 4.5T_K)}
\]

Loram et al. (33) have found the magnetisation vs.
field and the initial susceptibility due to small
concentrations (c < 0.01 at.%) of Fe dissolved in Au to be
well fitted by eqns. 1(28) and 1(30) respectively with
\(S = 1.29\) and \(T_K = 0.1 K\). (We note however that more recently
Swallow and White (35) have found it equally possible to
interpret these same magnetisation measurements within
the framework of the localised spin fluctuation theory - to
be discussed).

A temperature dependent (CW like) susceptibility has
long been the experimentalists criterion for the existence
of a localised moment on the impurity and there are many
examples of a CW susceptibility in the literature. For a
comprehensive survey the reader is referred to the exhaustive
review due to Rizzuto (36) and also that due to van Dam and
van den Berg (37).

Perturbation theory of the specific heat

Kondo (27) has calculated the modification to the free
energy of the conduction electron gas due to the introduction
of a localised impurity spin, \( S \), which is coupled via the s-d exchange interaction to the conduction electron spins. This enables Kondo to obtain an expression for the total change in the entropy of the system, which is

\[
\Delta S(T) = k_B \ln(2S+1) + \frac{k_B \eta^2 S(S+1)(Jn(o))^3}{\left[ 1 + Jn(o)\ln \frac{E_F}{k_BT} \right]^3} \tag{131}
\]

and since \( J < 0 \) we see that even when \( T \gg T_K \) the entropy will be reduced over the 'free' spin value, \( k_B \ln(2S+1) \).

The excess specific heat, \( \Delta C \), can be calculated directly from the entropy

\[
\Delta C = T \frac{d}{dT} (\Delta S) \]

\[
= \eta^2 S(S+1)(Jn(o))^4 k_B \left[ 1 - 4Jn(o)\ln \frac{k_BT}{E_F} \right] \tag{132}
\]

Once again the perturbational treatment gives rise to a logarithmic term which results in an unphysical divergence in the specific heat below the Kondo temperature.

Susceptibility measurements on dilute CuMn alloys \( (39) \) indicate that \( T_K \) for this system is only a few millidegrees. Heeger \( (26) \) reports a logarithmic rise with decreasing temperature in the range 5K - 2K, for the excess impurity specific heat of dilute CuMn alloys, in agreement with the predictions of eqn. 1(32), although the value of \( J \) inferred from the measurement \( (-0.9eV) \) implies, using eqn. 1(18), much too large a value for \( T_K \).
For the high temperature \((T \gg T_K)\) perturbational theory of other physical properties, such as the thermopower and RKKY spin polarisation around each impurity the reader is referred to Kondo's review article (27).
Low temperature \( (T \ll T_K) \) predictions for the properties of the s-d model.

Although Kondo's original 3rd order perturbation treatment of the s-d interaction explained in principle the existence of the resistance minimum phenomenon, it is clear from the previous sections that a perturbational treatment alone cannot predict either the \( T \ll T_K \) properties, or provide any information on the nature of the ground state of the coupled system as the temperature is reduced to absolute zero.

For several years after Kondo's initial publication (19) there was an intense theoretical interest in the \( T \ll T_K \) solution of the s-d Hamiltonian, and although, most recently, a new generation of theoretical techniques and approaches to the problem (39) have superceded these so-called 'wilderness' methods (40), they have played an important role in the development of the theory of the s-d model, and for this reason we shall briefly trace their history. For a more complete survey the reader is referred to the reviews of Kondo (27), Heeger (26) and Fischer (41).

Mattis (42) demonstrated in a formal proof that the ground state at \( T = 0 \) of an \( S = \frac{1}{2} \) impurity spin with antiferromagnetic exchange coupling to the conduction electrons must be a non-magnetic singlet, although this knowledge alone does not of course reveal any of the low temperature properties of the ground state.

As we have already mentioned the s-d interaction gives
rise to indirect interactions of arbitrarily high order between conduction electrons via the spin flip processes at the impurity, and as such the s-d model presents a true many-body problem to which no exact solution has yet been found. In all cases the starting point of the theory involves some simplification of the full many-body correlations, and the physical significance of these approximations is quite often far from being clear. The solution of this approximate model is then obtained with varying degrees of mathematical rigour, usually for the restricted case $S = \frac{3}{2}$ and $J$ a constant which is independent of the temperature.

Nagaoka (43) formulated the many body problem in terms of Greens functions and wrote down a truncated series of equations of motion which apparently (41) correspond to retaining only the correlation between the impurity spin and a single conduction electron. At high temperatures a perturbational solution reproduces Kondo's original result, but the solution becomes unphysical below $T_K$ (eqn. 1(18)). For $T < T_K$ Nagaoka devised a self-consistent solution which suggested that below $T_K$ a long range anti-parallel spin polarisation cloud would build up in the conduction electron gas, tending to reduce the effective magnitude of the spin ('spin-compensation') and possibly resulting in its complete cancellation at $T = 0$. It has since been argued (44) that any $T < T_K$ conduction electron spin correlations must be spatially extended since only electrons occupying states within $k_B T_K$ of the Fermi energy are available to take
part in the scattering processes at the impurity site. Application of the uncertainty principle thus demands that the range of the non-perturbative correlations is of the order \( \frac{E_F}{k_F^2 B^2 K} \), where \( k_F \) is the Fermi momentum.

Hamann (45) has re-examined the Nagaoka equations and obtains an expression for the impurity resistivity which is valid over the whole temperature range, both above and below \( T_K \)

\[
\rho = \frac{\rho_0}{2} \left[ 1 - \frac{\ln \left( \frac{T}{T_K} \right)}{(\ln^2 \left( \frac{T}{T_K} \right) + \pi^2 S(S+1))^\frac{1}{2}} \right] \tag{133}
\]

This expression corresponds to a resistivity which decreases smoothly from the unitarity limit value of \( \rho_0 \) at \( T=0 \), the transition extending over several decades of temperature centred on \( T_K \). The Kondo temperature would thus appear to determine the scale of the temperature dependence in the resistivity, which is seen to be a universal function of \( \left( \frac{T}{T_K} \right) \). According to Hamann's expression \( \frac{\rho_0}{\rho} \rightarrow \infty \) as \( T \rightarrow 0 \), which is at variance with Star's recent measurements on dilute CuFe alloys (46) which show only a quadratic temperature dependence of the resistivity due to isolated Fe atoms over the 50mK to 1K temperature range (\( T_K \approx 25K \)). Loram et al. (47) have been able to fit expression 1(33) to their resistivity data for Fe dissolved in pure Au and binary CuAu alloys, but only in the \( T \gg T_K \) region and even then the value of \( S \) required to achieve a satisfactory fit is not in good agreement with that obtained.
more directly in their susceptibility measurements on
dilute AuFe alloys (33).

Zittartz and Muller-Hartmann (48) have solved the
Nagaoka equations exactly and deduce an expression for
the excess specific heat of an $S = \frac{1}{2}$ impurity which is
valid at very high or very low temperatures, i.e.

$$\ln \left| \frac{T}{T_K} \right| \gg 1$$

$$\frac{\Delta C}{k_B} \sim \frac{T^{2S(S+1)}}{\ln^4 \left( \frac{T}{T_K} \right)} \quad (34)$$

This expression is in agreement with the numerical
calculation of Bloomfield and Hamann (49) also based on the
Nagaoka equations, which predicts a peak in $\Delta C$ vs $T$ at
about $\frac{T_K}{3}$ and $\Delta C \propto \left( \frac{T}{T_K} \right)^{0.57}$ when $10^{-4} \leq \frac{T}{T_K} \leq 10^{-1}$.

However, Zittartz and Muller-Hartman find that the reduction
in the entropy of the coupled system at $T=0$ is calculated to
be only $k_B \ln \frac{27}{16}$, rather than the value $k_B \ln 2$ which would
be expected for the spin compensation of an $S = \frac{1}{2}$ impurity
into a ground state singlet at $T = 0$. Zittartz (50) finds
that the magnetic susceptibility predicted in the exact
solution becomes (unphysically) negative at $T=0$, which is
a further indication that the Nagaoka equations themselves
are inadequate for a proper description of the $T \ll T_K$
behaviour of the $s-d$ model.

The conduction electron spin polarisation, $p_z(r)$,
induced around the impurity in the presence of a small
external magnetic field has been evaluated for the exact
solution of the Nagaoka equations (51). Apart from the
usual Pauli term, $p_z(r)$ is found to contain no
non-oscillatory terms, therefore as far as the Green's function theory is concerned this result rules out Nagaoka's original picture of a 'spin condensation' for $T < T_K$ in which a bare, high temperature spin is increasingly compensated as $T \to 0$ by a polarisation cloud of conduction electrons with their spins locked antiparallel to the direction of the local spin. However one still has a spatially extended equal time correlation between the conduction electron spin and the impurity spin.

The suggestion of a non-magnetic ground state singlet from the Nagaoka equations and also Mattis' theorem prompted a second class of attempts to solve the Kondo problem. In such 'ground state' theories various authors attempted to construct the wavefunction of the ground state ($T=0$) of the coupled conduction electron / local spin system, with the required singlet symmetry.

In the Appelbaum-Kondo (AK) theory, the energy of the trial wavefunction is minimised using a variational calculation and the binding energy of the ground state at $T=0$ is found to be

$$
\mathcal{E}_B = - E_F \exp \left\{ - \frac{2/3}{\ln(\alpha)} \left( \frac{1}{|J|} \right) \right\}
$$

The $T \ll T_K$ specific heat and resistivity associated with the ground state have been calculated (52) and

$$
\Delta C \propto T \ln \left( \frac{T}{T_K} \right) \quad T \ll T_K
$$

$$
\rho = \rho_0 \left[ \cos^2 \gamma - \frac{16}{3} \cos^2 \gamma \left( \frac{T}{T_K} \ln \frac{T}{T_K} \right)^2 \right]
$$
where $\eta$ is the phase shift due to potential scattering.

The nature of the ground state theories would suggest that their predictions are most likely to be valid as $T \to 0$, however the recent low temperature measurements of the excess impurity specific heat (53) and resistivity (46) of dilute CuFe alloys imply that these quantities follow simple power laws as $T \to 0$, in contrast to the logarithmic nature of expressions 1(36) and 1(37).

In contrast with the Greens function theory, most 'ground-state' theories predict a finite value $\frac{\mu^2}{3kT_K}$ for the magnetic susceptibility at $T=0$.

The susceptibility and conduction electron spin polarisation around a partially polarised impurity spin has been worked out within the framework of AK theory by Heeger et al. (54). They find

$$\chi = \chi_p + \chi_L + \chi_Q$$ 1(38)

where $\chi_p$ is the usual Pauli susceptibility of the free electron gas, $\chi_L$ is that due to the localised spin and $\chi_Q$ is the contribution arising from the polarisation of the AK ground state correlations in the conduction electron gas—referred to as the 'quasiparticle'. At $T=0$ $\chi_L = \chi_Q$, so that only half of the excess impurity susceptibility is predicted, in this model, to be localised at the impurity site.

The conduction electron polarisation around the impurity, $\sigma_z(r)$, also comprises of three terms

$$\sigma_z(r) = \sigma_p + \sigma_{RKKY} + \sigma_q$$ 1(39)
The first two terms correspond to the usual Pauli and RKKY contributions, while $\sigma_q(r)$ is a non-oscillatory long range spin polarisation

$$\sigma_q(r) \propto \langle S_z \rangle \left( \sin \frac{k_F r}{r} \right)^2 \ln^2 \frac{r}{\xi}$$

where the 'range'

$$\xi \approx \left( \frac{2E_F}{\varepsilon_B} \right) \frac{\hbar^2}{k_F^2}$$

Hamann and Appelbaum (55) have pointed out that the AK theory has serious shortcomings and that a proper calculation would lead to a modified ground state energy, $\varepsilon_B$ (eqn. 1(35)). For this reason the various predictions outlined above must be regarded as inconclusive, although they have stimulated considerable experimental activity, particularly in the search for the conduction electron quasi-particle.

Golibersuch and Heeger (56) compared the then currently available data on the bulk susceptibility (57) (58) and hyperfine field at the $^{57}$Fe nucleus as measured by the Mössbauer technique (59) (60). The latter quantity is proportional to the mean polarisation, $\langle S_z \rangle$, of the spin localised at the Fe site and is thus, in turn, proportional to the component of the bulk susceptibility which is localised on the impurity Fe site. The hyperfine field was found to be $\propto (T + 32)^{-1}$ over the entire temperature range $T \geq T_K$. On the other hand the low temperature bulk susceptibility (58) appeared to be proportional to
\[(T + 18)^{-1}\], indicating the presence of an extra contribution in the bulk susceptibility which was not localised to the impurity site, and which was identified with the build up of the so called Quasi-spin in the conduction electron gas (eqn.1(38)). The more recent measurements of Tholence and Tournier (61) however show that the results of Daybell and Steyert are heavily influenced by impurity interactions and that the susceptibility due to isolated Fe impurities has \[(T + 30)^{-1}\] temperature dependence down to be at least 1.3K, in agreement with the hyperfine field data.

Golibersuch and Heeger also examined the host NMR line shift and lineshape in CuFe alloys for evidence of the extended quasi-spin polarisation cloud. A long range non-oscillatory polarisation such as that suggested in eqn.1(40) should give rise to a Knight shift in the resonance of the Cu nuclei, however although a small shift is observed it is approximately a factor 30 too small to correspond to the predictions based on AK theory, (62). The major effect is an excess line broadening which sets in below about 20K, indicating enhancement of the RKKY oscillatory conduction electron spin polarisation around the Fe impurity, however this may be the result of impurity interactions which are now known to dominate the properties of CuFe alloys in this concentration/temperature regime.

In conclusion it is now apparent that the predictions of the first generation (pre ~ 1969) of attempts to solve
the low temperature ($T \ll T_K$) properties of the s-d model Hamiltonian do not concur with the picture of simple power laws which is emerging from the experimental data on very dilute alloys. Anderson, however, has stated a belief (39) that the second generation of attempts will lead to non-singular, simple power law predictions for the various physical properties in better agreement with experiment.
1:3 The relationship between the Anderson and the s-d model Hamiltonians

So far we have discussed two apparently dissimilar models for the magnetic impurity problem. On the one hand we have the Anderson model, in which electrons may hop between the localised d (or f) states and spatially extended conduction states, more or less freely, depending on the strength of the mixing interaction, $V_{kd}$ (or $V_{kf}$). On the other hand, in the s-d model, conduction electrons are exchange scattered by a localised impurity spin whose only structure is the $(2S + 1)$-fold spin degeneracy, and there is no mixing of s and d electron states in the Anderson sense.

The suggestion that the mixing interaction could lead to an effective anti-parallel exchange coupling between the localised and conduction electron spins was first proposed by Anderson and Clogston (63), however it was Schrieffer and Wolff (64) who first demonstrated the equivalence between the Anderson Hamiltonian in the extreme magnetic limit (ie $\frac{U}{\hbar \Delta} \gg 1$) and the s-d Hamiltonian in a quantitative way.

Schrieffer and Wolff write the Anderson Hamiltonian as the sum of two terms

ie $H_A = H_0 + H_1$  

$H_0$ contains the terms which correspond to the energy of the conduction electrons and d electrons in the absence of the mixing. $H_1$ represents the admixture and is 1st
order in $V_{kd}$. They show that provided $\frac{|E_d|}{\Delta} < 1$ and $\frac{|E_d + U|}{\Delta} < 1$
it is possible to perform a canonical transformation
on $H_A$ such that

$$H_A = H_0 + H_2$$

1(42)

where $H_2$ contains only second order terms in $V_{kd}$, and
reduces to an effective s-d interaction between the
localised and conduction electrons which has an exchange
coupling constant

$$J_{\text{EFF}}(k_F, k_F) = \frac{2|V_{kd}|^2 U}{E_d(E_d + U)}$$

1(43)

which since $E_d < 0$ must be negative!

The conditions for the validity of eqn.1(43)
correspond to the unperturbed spin up and spin down
orbitals lying on opposite sides of the Fermi level, and
separated from it by an energy which is large compared
to the width of the VBS in the presence of the admixture
perturbation. This is only true for the extreme magnetic
limit of the HF solution, where the solute has an effective
moment which is not greatly reduced from the free ion value.

Schrieffer (65) has extended the method to apply a
canonical transformation to the full Anderson Hamiltonian
for a $(2l + 1)$-fold degenerate impurity orbital. If the
quantum number $m = m_1, m_2, ..., m_{2l + 1}$ labels each spin degenerate
orbital he finds

$$J_{\text{EFF}}^m(k_F, k_F) = \frac{2|V_{k_F m}|^2 U}{E_m(E_m + U)}$$

1(44)

where $E_m$ is the energy of the $m$th orbital.
where $m$ is a singly occupied orbital and $S$ is the 'Hund's rule' spin for an isolated solute atom in the absence of admixture, and

$$J_{\text{EFF}}^m(k_F, k_F) = 0 \text{ otherwise.} \quad (45)$$

Schrieffer pictures the spin-flip interaction as arising from the mixing term of the Anderson Hamiltonian in the following manner. An electron in the conduction state $|k, \lambda m \uparrow\rangle$, say, hops onto the impurity $|\lambda, \mu m \uparrow\rangle$ orbital. If this orbital already contained an electron in $|\lambda, \mu m \downarrow\rangle$, then this may hop off into $|k', \lambda m \downarrow\rangle$, ($|k| = |k'|$), the net result being a conduction electron spin flip scattering, and provided the Hund's rule coupling is strong, a change in $S_z$ by $\pm 1$ for the impurity. If the orbital $|\lambda m \rangle$ is initially empty, then only the $|\lambda m \uparrow\rangle$ electron (ie the one which hopped on) may leave the ion and still conserve orbital angular momentum for the complete scattering process. The Pauli exclusion principle clearly disallows exchange scattering from an already doubly occupied orbital. Since spin-flip scattering does not take place in the last two instances $J_{\text{EFF}}^m$ will be zero.

Schrieffer argues that since an impurity with spin $S$ must have $2S$ singly occupied orbitals each of which is capable of spin flip scattering the residual resistivity at $T = 0$ will be

$$\Delta R = \rho_0 2S \quad (46)$$

where $\rho_0$ is the unitarity limit for scattering from a
single localised orbital in the conduction band of the host. Correspondingly for 3d solutes in simple metal hosts we expect the form shown below for $\Delta R$ vs atomic number of the impurity.

![Graph showing $\Delta R/\rho_0$ vs atomic number of impurity: Ti, V, Cr, Mn, Fe, Co, Ni.](image)

Schrieffer pointed out that in the case of Al host this fig. (1:3) reproduces the single peaked behaviour in the vicinity of Mn which is observed experimentally, and which had been previously explained in terms of a non-magnetic VBS passing through the Fermi level in accordance with charge neutrality constraints (eqn. 1(8)). Schrieffer proposed that an alternative explanation, in the light of the non-magnetic many-body singlet ground state which theory had predicted for the s-d model, that some 'non-magnetic' impurities, in the sense that they displayed temperature independent properties within the conventional experimental range of temperatures, may in fact be regarded as the end product of a very high temperature
spin correlated state arising from the Kondo effect. Values of \( T_K \) which range from \( 10^{-3} \) to \( 10^{3} \)K can result from relatively small changes in \( J_{\text{EFF}} \) because of the exponential dependence of \( T_K \) on the exchange coupling constant (eqn. 1(18)).

In the symmetric case when \( E_d = -\frac{U}{2} \)

\[
T_K = T_F \exp \left\{ - \frac{|E_d| S}{\Delta} \right\}
\]

which implies that a high spin value favours a low characteristic temperature, in qualitative agreement with the properties of 3d transition metal solutes in noble metal hosts where the characteristic temperature is smaller for Mn than for either Fe or Cr solute.

The Anderson Hamiltonian, eqn. 1(1), is expected to contain the essential physics of the single impurity problem, and in the extreme magnetic limit we have seen that the Schrieffer-Wolff transformation may be applied to reduce the Anderson Hamiltonian to that of the s-d model, which is the starting point of most of the theories of the isolated magnetic impurity.

Grüner (71) includes a review of the predictions of the extreme non-magnetic \( \left( \frac{U}{\text{\Delta}} \ll 1 \right) \) limit of the Anderson Hamiltonian and finds good agreement with the experimental data on impurities in this regime.

Probably the most intractable regime for the solution of the Anderson Hamiltonian is the intermediate regime \( \frac{U}{\text{\Delta}} \approx 1 \), where the impurity is nearly-magnetic and the
many body d–d electron correlations at the impurity site are very important and result in the inadequacy of the Hartree–Fock approximation. Some success in understanding the behaviour of nearly-magnetic impurities has been possible using the localised spin fluctuation theory (LSF), which is a dynamic extension of the non-magnetic limit of the Anderson model, which allows for the possibility of a temporary moment occurring on the impurity site even when $\frac{U}{\Omega} < 1$. 
Localised spin fluctuations

The HF treatment of the Anderson Hamiltonian results in a sharp transition from the non-magnetic to the magnetic state of the impurity at the HF instability $\frac{U}{\Pi \Delta} = 1$. Experimentally (66) the effective magnetic moment on Fe atoms dissolved in $\varepsilon$-phase CuZn alloys is observed to decrease smoothly as the host alloy composition moves toward the Zn rich end of the phase and no sudden extinction of the moment occurs. The HF treatment is incomplete because it excludes the dynamic aspects of local moment formation which are particularly important when the impurity is on the verge of magnetism and $\frac{U}{\Pi \Delta} \approx 1$.

When $U=0$ the ground state of the VBS is non-magnetic but as $U$ is increased excitations which have unequal numbers of spin up and spin down electrons become of lower and lower energy so that any perturbation tending to decouple the spin up and spin down halves of the VBS will have an enhanced effect. The lifetime of such a temporary moment, or ISF, increases with the strength of the coulomb interaction $U$, (67)

$$\tau \text{lsf} = \frac{\Pi \rho_d^{(o)}}{1 - U \rho_d^{(o)}}$$

and becomes infinite when the HF instability is reached. As we have discussed already, correlations between the electrons which are not included in the HF approximation lead to an effective value for the coulomb interaction which is reduced so that $U_{\text{eff}} \cdot \rho_d^{(o)} \rightarrow 1$ only as $U \rightarrow \infty$. 
Thus for real alloys it seems that the concept of a stable moment with infinite lifetime is never valid, but there will be a smooth transition from non-magnetic to magnetic characteristics for the impurity with increasing $\gamma_{\text{lsf}}$.

The electrical resistivity of dilute AlMn and AlCr at low temperatures shows a weak temperature dependence which is well accounted for in terms of ISF at the Mn or Cr sites. Caplin and Rizzuto (68) find

$$\rho = \rho_0 (1 - \frac{T}{\Theta}^2)$$

where $\Theta \approx 530K$ for Mn and $\Theta \approx 1200K$ for Cr.

Thermal fluctuations in the number of spin up and spin down electrons in the VBS will occur at finite temperatures corresponding, when $U = 0$, to the energy of the VBS fluctuating $\pm k_B T$ about the Fermi energy. The impurity scattering cross-section for conduction electrons is related to the VBS occupation for each spin via the appropriate phase shift $\gamma_{\text{lsf}}$ and the thermal averaging of the cross-section leads to an extremely weak $T^2$ temperature dependence in the resistivity

$$\rho = \rho_0 (1 - \frac{\mathcal{N}^2}{3} \frac{(k_B T)^2}{\Delta})$$

for a half-filled Lorentzian VBS with half-width $\Delta$.

When $U$ is finite, it is energetically favourable for there to be unequal numbers of spin up and spin down electrons on the impurity, resulting in spin fluctuations of larger amplitude and enhanced lifetime, $\gamma_{\text{lsf}}$. Caplin and Rizzuto argue that the amplitude of the fluctuations in the energy of
the VBS is increased to \( \pm \eta \kappa T \) where the enhancement factor \( \eta \) is the same as that which occurs in the static polarisation of the VBS in an external magnetic field at \( T=0 \), i.e.

\[
\eta = \frac{1}{1 - \frac{U_0}{\eta D}}
\]  

Thus, including the enhanced ISF to account for the nearly magnetic behaviour of the impurity VBS, one obtains an enhanced temperature dependence in the resistivity, corresponding to

\[
\rho = \rho_o \left( 1 - \frac{\eta^2}{2} \left( \frac{\eta kT}{\Delta} \right)^2 \right)
\]  

thermal averaging of the impurity cross-section over \( \eta kT \).

The effective width \( \Gamma = \frac{\Delta}{\eta} \) for the VBS when the correlations which lead to ISF are included is simply related to the ISF lifetime since \( \gamma_{\text{lsf}} = \frac{1}{\Gamma} \).

Rivier et al. (67) (68) pointed out that the ISF concept was capable of providing an alternative picture for the transition from magnetic to non-magnetic behaviour, predicted in terms of spin-compensation below some characteristic (Kondo) temperature in the s-d model theories.

The ground state at \( T=0 \) is taken to be non-magnetic in the Friedel-Anderson sense, but subject to ISF with typical lifetime \( \gamma_{\text{lsf}} \). If the ISF are long compared to other relevant times, e.g. the time taken for the spin to equilibrate in an applied magnetic field, then the ISF will be
indistinguishable from a genuine spin and will result in a Curie-Weiss term in the susceptibility or a logarithmic temperature dependence in the resistivity, the 'hallmarks' of a magnetic impurity. At finite temperatures thermal fluctuations in the conduction electron gas result in a conduction electron having an intrinsic spin memory time $\sim \frac{k}{k_BT}$. If the LSF are longer lived than this time, then the conduction electron does not have time to see that the impurity spin is transient before losing memory of its own spin, leading to magnetic characteristics at temperatures $k_BT > k\gamma_{\text{lsf}}^{-1}$. The smooth transition between non-magnetic and magnetic regimes for the impurity is centred on the LSF temperature

$$T_{\text{lsf}} \sim \frac{k}{k_BT} \gamma_{\text{lsf}} = \frac{\Gamma}{k_B}$$

which, in the sense of indicating the temperature below which the 'magnetic' qualities of the impurity are progressively diminished may be compared to the Kondo temperature, $T_K$, of the s-d model.

As Grüner has pointed out (71) there is no direct evidence for the existence of a high temperature spin on Mn as an impurity in Al, which the above philosophy would lead one to expect. However when one compares the experimental data for CuFe, the archetypal Kondo alloy, with that for AlMn, traditionally regarded as a spin fluctuation system, the same kind of temperature dependences are observed in both the impurity resistivity (46) (68) and the impurity
susceptibility (53) (70), but always over lower temperature ranges in the case of CuFe. This observation suggests that despite the apparent fundamental differences between the two theoretical approaches which attempt to explain the properties of these alloys, on experimental grounds the only difference appears to be in a lower characteristic temperature in the case of Fe in Cu than for Mn in Al.

Indirect support for a high temperature magnetic state for Mn is given by the residual resistivity measurements on Al-3d alloys (72) (73) which, when plotted as a function of atomic number through the 3d series, display the same double peaked behaviour which is observed in the case of Cu-3d alloys (which also persists to much lower temperatures than in the case of Al-3d) and which is traditionally taken as evidence of a spin split VBS appropriate to the magnetic HF limit for the impurity. Similarly the residual resistivity measurements extrapolated to T=0 for Cu-3d alloys (36) show a single peaked behaviour just like that observed at low temperatures for the Al-3d series of alloys and traditionally taken to indicate the spin degenerate non-magnetic HF limit for the impurity localised state.

The amplitude of the charge oscillation around 3d impurities dissolved in the Al matrix (74), as measured using the NMR technique, shows the same characteristics as the residual resistivity, i.e. at T=0 a single peak when plotted as a function of 3d atomic number, but at T=420K a double peak structure is again apparent, indicating a double peak in the impurity density of states for the 3d solutes at high enough temperature.
Most recently Rivier and Zlatic (75) have been able to show that the resistivity of an alloy due to LSF on the impurity orbital is given as a universal function of \( \frac{T}{T_{lsf}} \). The resistivity has a finite (equal to the unitarity limit) value at \( T=0 \) and then decreases as \( T^2, T, \ln T \) and \( T^{-1} \) progressively as the temperature is increased. Babic et al. (72) (76) have observed a linear temperature dependence in the impurity resistivity of AlMn at temperatures in excess of about 120K and extending up to 200K (the limit of the measurement). The linear region has also been observed by Rizzuto et al. (77) in dilute Au V and CuFe alloys and the experimental evidence, from a wide spectrum of different properties, for universal behaviour of transition metal impurities in the various host matrices has been thoroughly reviewed by Rizzuto (36) and Rizzuto et al. (77).

Caroli et al. (78) have evaluated the impurity due to LSF on the impurity, taking into account the \((2\ell+1)\) - fold orbital degeneracy of the localised state and also the strength of the Hund's rule exchange interaction, \( J_{mm'} > 0 \), between the \( m \) and \( m' \) orbitals of the impurity state. For the enhanced impurity spin susceptibility they find

\[
\frac{\Delta \chi}{\alpha} = \frac{2u_B^2 (2\ell+1)}{\pi k_B T_{lsf}}
\]

In the zero Hund's rule coupling limit, i.e. \( J_{mm'} = 0 \), the impurity contribution to the linear term in the specific...
heat of the alloy is

$$\Delta S_c = \frac{(2\lambda+1)T K_B}{T_{lsf}} \left[ 1 - \frac{2T^2}{5} \left( \frac{T}{T_{lsf}} \right)^2 \right]$$

while in the limit of strong Hund's rule coupling

$$\Delta S_c$$ is reduced to

$$\Delta S_c = \frac{(U+4J_{mm'}) R_d K_B}{T_{lsf}} \left[ 1 - \frac{4T^2}{5} \left( \frac{T}{T_{lsf}} \right)^2 \right]$$

In order to compare this theory with experimental data on LSF systems, Caroli et al. use the dimensionless parameter

$$\tilde{\gamma} = \frac{\gamma_H^{-1} \Delta S}{\chi_H^{-1} \Delta \chi}$$

where $\gamma_H^{-1}$ and $\chi_H^{-1}$ are the specific heat and susceptibility due to the host conduction band electrons. In the limit $J_{mm'} = 0$, $\tilde{\gamma} = 3/2$, but for strong Hund's rule coupling

$$\tilde{\gamma} = \frac{3}{2(2\lambda+1)} = 0.3$$

for 3d transition metal impurities.

The data for AlMn and AlCr alloys is consistent with strong Hund's rule coupling at the impurity site for Mn, $\tilde{\gamma} = 0.3$, while for Cr $\tilde{\gamma} = 0.8 \pm 0.1$ indicating intermediate strength for this interaction.

The importance of Hund's rule exchange coupling and the existence of both Hund's rule and anti-Hund's rule states
for the impurity has most recently been emphasised by Caplin and Coles (79).
1:5 Interactions between solute atoms

Introduction

Although it has long been recognised that in alloys of sufficiently high concentration the bulk properties may be dominated by the effects of interactions between the solute atoms, it is only in the last 3 years or so that the role of interactions has been more fully appreciated in the supposedly "dilute" random alloys (c < 1000 ppm. say).

Broadly speaking it is possible to separate the various interactions into two categories.

First there are the long range interactions which take place between solute transition metal atoms whose magnetic moment has survived. These interactions are mediated by the conduction electrons, in which a long range oscillatory spin polarisation is induced as a result of the s-d coupling interaction between the local spin and the spin on the conduction electron. At low enough temperatures the effective internal fields to which these interactions give rise lead to ordering of the solute atom moments, although well before the onset of long range order the interactions can lead to a modification of the ideal single impurity properties, eg. the logarithmic resistivity calculated by Kondo (eqn.1(17)).

The second group of interactions may have their origin in a long range perturbation of the conduction electron gas or may involve a direct interaction between first neighbour impurities, but do not in themselves give rise to a long
range order. After Rizzuto (36) we will refer to these interactions as 'coupling' interactions and these interactions are generally important between pairs or small groups of solute atoms to result in a change in the magnetic state of the solute atoms involved away from that of the truly isolated ones, in such a manner that each solute atom is required to be given a different characteristic temperature according to its location with respect to all the other solute atoms in the alloy. Since even in a random alloy there is a finite probability ($\propto c^2$) of two solute atoms occupying adjacent lattice sites the effect of these 'pair coupling' interactions may be felt even at very low concentration and the use of intense magnetic fields ($H \geq 50kOe$) has proved invaluable in differentiating the contributions to the bulk properties of the alloy coming from more and less magnetic impurities (with lower and higher characteristic temperatures, respectively) and the separation of the properties of the truly isolated solute atom. It should be noted that the coupling interactions can be artificially enhanced as a result of metallurgical factors, eg. poor solubility of the impurity, partial precipitation as a result of heat treatment of the alloy. In experiments on magnetic impurities dissolved in binary host matrices a reduced solubility of the impurity or a non random distribution through the host matrix of the impurity due to clustering of the components of the host may influence the bulk properties in a rather complex manner.
Long range interactions between localised moments

The first interaction of this type which we will consider is the so-called Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction.

In alloys of transition metals it is possible to treat the interaction between the local moment and the conduction electrons in a completely parallel way to the hyperfine interaction between the nuclear spin and the conduction electrons (80) (81).

Zener (82) first investigated the effect, to 1st order perturbation of the conduction electron energies only, of an exchange interaction

\[ H = J \mathbf{S} \cdot \mathbf{s} \]  

between the conduction electron spin, \( \mathbf{s} \), and the localised spin \( \mathbf{S} \) on the paramagnetic ion. His work suggested that a spatially uniform polarisation of the conduction band would occur as a result of this perturbation.

Yosida (82) extended this calculation to take into account the first order perturbation of the conduction electron wavefunction

\[ \phi_k = \phi_k^0 + \sum_{k'} \frac{H_{kk'}}{E_k - E_{k'}} \phi_{k'}^0 \]  

with the result that the modified conduction electron density (spin dependent) around the magnetic impurity atom is
given by

$$\Phi^+(r) = \frac{n}{\sqrt{V}} \pm \frac{3n}{2E_F} \cdot \frac{N^{-1}J(o)}{\sqrt{V}} S_z$$

$$\pm \frac{3n N^{-1}}{2E_F \sqrt{V}} \sum_q J(q)f(q) \left[ \exp(iq \cdot r) + \exp(-iq \cdot r) \right] S_z$$

with $f(q) = 1 + \frac{4k_F^2 - q^2}{2k_F} + \ln \left| \frac{2k_F + q}{2k_F - q} \right|$.

1(59)

The first, second and third terms in eqn. 1(59) correspond to the unperturbed conduction electron density, that due to the 1st order perturbation in conduction electron energy and that due to the 1st order perturbation of the conduction electron wavefunction. The magnitude of the last two terms is comparable so that one expects a considerable modification of Zener's result.

The final expression for the spin dependent conduction electron density around the impurity depends, particularly as $r \to 0$, on the chosen form of $J(q)$. The simplest choice $J(q) = J(o) = \text{const.}$ leads to a divergence in the conduction electron spin polarisation as $r \to 0$. Yosida chooses

$$J(q)f(q) = 2 \frac{J(o)}{2k_F} \quad q < 2k_F$$
$$J(q)f(q) = 0 \quad q > 2k_F$$

1(60)

to obtain

$$\phi(r) - \phi(r) = 2 \rho_0 \frac{12n}{E_F} \frac{J(o)}{N} \frac{2k_F r F(2k_F r)}{S_z}$$

where $F(x) = \frac{x \cos x - \sin x}{x^4}$

1(61)
At large distances $k_F r \gg 1$ the spin polarisation oscillates rapidly ($2k_F d \sim 7$ when $d$ is the first neighbour spacing for pure Cu) and the mean amplitude $\propto (k_F r)^{-2}$. The total charge density $q_+(r) + q_-(r) = 2 Q_0$ and remains unchanged in the presence of the perturbation (at least to 1st order).

The RKKY polarisation results in an indirect coupling of solute spins with an interaction energy $(k_F r \gg 1)$

$$E(r) \approx \frac{9N}{8} \left(\frac{n}{N}\right)^2 \frac{J^2(0)}{E_F} \frac{\cos(2k_F r) S_1 S_2}{(k_F r)^2}$$

which taking values for the parameters appropriate for CuMn, $E_F \sim 7eV \quad |J| \sim 0.2eV$ gives

$$E(r) \sim 810^{-2} \cos(2k_F r) \frac{u_1 \cdot u_2}{(k_F r)^3} \quad 1(63)$$

where $u_1$ and $u_2$ are unit vectors parallel to the spins on Mn atoms 1 and 2.

**Long range interactions between magnetic VBS**

Friedel (1) showed that the potential scattering of conduction electrons by the impurity potential would give rise to a long range oscillatory perturbation of the conduction electron charge density which would be specified in terms of the phase shifts $\gamma_2 \sigma$ of the $\ell = 2$ component of the partial wave expansion for an electron of spin $\sigma$.

$$\Delta q_\sigma(r) \approx -5 \frac{k_F^2}{4 N^2} \sin \gamma_2 \sigma \frac{\cos(2k_F r + \gamma_2 \sigma)}{(k_F r)^3} \quad 1(64)$$
Blandin and Friedel (2) and Caroli and Blandin (83) pointed out that if the phase shifts for spin up and spin down electrons were not equal, i.e. the VBS is spin de-coupled, then the conduction electron spin density

\[ S(r) = \% (\Delta \rho_+(r) - \Delta \rho_-(r)) u_1 \]

is non-zero and, for \( r \rightarrow \infty \), oscillatory like eqn. 1(61). A second localised moment may couple to this polarisation via an exchange interaction of the type eqn. 1(57), resulting in an interaction energy

\[ E(r) \approx 5 \frac{k_F^2 JS}{8 \frac{2(\frac{k_F}{r})}{3}} \left\{ \sin \eta_2 \cos(2k_Fr + \eta_2) - \sin \eta_2 \cos(2k_Fr + \eta_2) \right\} u_1 \cdot u_2 \]

Again taking suitable parameters for CuMn, \( \eta_2^\uparrow = \eta_2^\downarrow = 0 \)

\[ E(r) \approx 9 \times 10^{-1} \frac{\cos(2k_Fr + 2\eta)}{(kr)^3} u_1 \cdot u_2 \text{ eV} \]

Caroli (84) considers a second type of interaction between magnetic VBS which corresponds to consecutive resonant scattering of the conduction electrons from each of the VBS in turn. The effect of resonant scattering from the first solute atom is to modify the initial free electron wavefunction to \( (r \rightarrow \infty) \)

\[ \psi_k(r) \approx \exp(i\mathbf{k} \cdot \mathbf{r}) + \frac{\exp(ikr)}{kr} \exp(i\eta_{l\sigma}) \sin \eta_{l\sigma} \]

\[ \eta_{l\sigma} \]
When the electron proceeds to be scattered by the second impurity the admixture matrix element $V_{kd}$, which in the single impurity solution of the Anderson model (see above) determines both the width (eqn.1(5)) and location (eqn.1(6)) of the virtual levels, must be calculated using eqn.1(68) for the conduction electron wavefunction

$$V_{kd}(2) = \langle \varphi_k | V | \psi_d \rangle$$

$$= V_{kd}(1) \left\{ \exp(ikR) + \frac{\exp(ikR)}{kr} \exp(i \frac{\gamma_{ks}}{2}) \sin \frac{\gamma_{ks}}{2} \right\}$$

Thus we see that, unlike the RKKY or Blandin and Friedel type of interactions, the Caroli mechanism is capable of affecting the basic magnetic character of the solute atom, via a modification of the width $\Delta$ from that appropriate to the single impurity limit, in the presence of the interaction. The use of the modified wavefunction, eqn.1(68), is equivalent to taking account of the modification of the density of conduction electron states at the 2nd impurity (see eqn.1(64)) due to the resonant scattering from the first. A change in the Anderson model parameters $\Delta$ (and $E_F - E_d$) will, via the Schrieffer-Wolff transformation eqn.1(43), result in a change in the Kondo temperature according to eqn.1(18), appropriate to the s-d model. From the point of view of the LSF model also, the modification of the impurity VBS density of states will affect the spin fluctuation lifetime $\tau_{lsf}$ of eqn.1(47) and thus the characteristic temperature
Finally we note that the Caroli interaction provides a mechanism for the impurity magnetic state to be modified even when the solute atoms are not sufficiently close for there to be a direct interaction between them through overlap of the VBS wavefunctions. (The effect of direct interactions will be considered in more detail later).

Caroli proceeds to evaluate an expression for the interaction energy between two solute atoms separated by distance $r$. In the case of fivefold degenerate orbitals and for large $r$ he obtains

$$E(r) \propto \frac{25E_F}{2\pi} \sum \sigma \sigma' \sin \gamma_{2\sigma}^{(1)} \sin \gamma_{2\sigma}^{(2)} \cos(2k_F r + \frac{\gamma_{2\sigma}^{(1)}}{2} + \frac{\gamma_{2\sigma}^{(2)}}{2}) \frac{u_1 \cdot u_2}{(k_F r)^3}$$

which for Mn dissolved in Cu reduces to

$$E(r) \propto 10 \cos(2k_F r + \frac{\gamma}{5}) \frac{u_1 \cdot u_2 \text{ eV}}{(k_F r)^3}$$

Comparing equations 1(63), 1(67) and 1(71) one observes that going from RKKY to double resonance scattering interactions, the magnitude of the interaction increases dramatically, being a factor of 100 larger in the last case for Mn in Cu. This will be generally true for 3d series transition metals which
carry a moment and for which the VBS straddles the Fermi energy. On the other hand for rare earth transition metals, the s-f admixture to the tightly bound magnetic 4f shell is relatively much weaker with the VBS levels being far removed from the Fermi energy. Consequently the phase shifts \( \eta_{3\sigma} \approx 0 \) or \( \eta \) depending on whether the orbital contains an electron or not and \( \sin \eta_{3\sigma} \approx 0 \) in eqns. 1(66) and 1(70) drastically reducing the strength of the hybrid resonance-exchange and the double resonance interaction energies. In this instance the RKKY double exchange scattering provides the strongest source of interaction.

**Treatment of indirect exchange-type interactions in random dilute magnetic alloys.**

All of the mechanisms described so far for interaction between magnetic solute atoms give rise to an interaction energy between two local moments \( \mu_1 \) and \( \mu_2 \) which can be written in the form

\[
E(r_{12}) = A \cos(k_F r_{12} + \phi) \frac{\mu_1 \cdot \mu_2}{r_{12}^3}
\]

for sufficiently large separation, \( r_{12} \). This energy may be regarded phenomenologically in terms of an effective internal field \( H_i(r_{12}) \) exerted by one impurity at the site of the second.

\[
E(r_{12}) = \mu_2 \cdot H_i(r_{12})
\]

where \( H_i(r_{12}) = A \cos(2k_F r_{12} + \phi) \frac{u_1}{r_{12}^3} \)
For the impurity sited at an arbitrary origin in a random alloy of finite concentration there will be a probability distribution, $P(H_i)$, for the net effective field at the origin due to all the other impurities. The calculation of this distribution will involve a lattice sum of individual contributions like eqn.1(73) which takes into account the statistical nature of both the occupancy of any given lattice site (except the origin) by an impurity and the orientation of the magnetic moment on that impurity. A complete theory must also include the correlations between the orientation of the magnetic moments which arise as a result of the interaction.

Klein and Brout (85) and Klein (86) have developed an approximate theory in which the orientation of $\mu$ are restricted to + and - (Ising model), and only two particle correlations $\langle \mu_i \mu_j \rangle$ are taken into account. They find that the impurities which fall within a critical radius of the origin

$$R_c \simeq 0.5 \ c^{-1/3} \ d$$

where $c$ is the fractional concentration and $d$ is the lattice constant, are strongly correlated to the moment at the origin and determine the character of the distribution $P(H)$, whilst all spins outside this volume are essentially uncorrelated and provide the spread in fields which changes $P(H)$ ($r_{oj} \ll R_c$ only), from a discrete distribution to a continuous one, ($r_{oj} \leq R_c$ and $r_{oj} > R_c$). The particular concentration dependence of $R_c$ means that the mean number
of strongly correlated spins is independent of the concentration, and for CuMn it is equal to 3.3 (including the spin at the origin). The solid may thus be pictured as being composed of small inter-related clusters of interacting spins.

Liu (87) has made further contributions toward a statistical theory for the internal field distribution and Souletie and Tournier (88) have pointed out that in general, an interaction between solute atoms with $r^{-3}$ spatial dependence will give rise to simple correspondences in the magnetic properties of alloys of a given system with varying concentration $c$. These authors are able to scale such quantities as the impurity specific heat, magnetisation and initial susceptibility of such alloys as AuFe, CuMn and AgMn as universal functions of the reduced temperature, $T/c$, or reduced external field, $h/c$.

In these alloys, where the concentration is not high enough for true long range order to occur, but is sufficiently high for the correlations which we have described above to be significant at low temperatures, cooling in the presence of an external magnetic field results in a 'frozen in' moment when the field is reduced to zero at low temperatures. Coles has referred to such alloys as 'magnetic spin glasses'.

'Kondo' resistivity due to a pair of interacting impurity spins

We have already described Kondo's classic calculation of the resistivity in the case of a single magnetic impurity, exchange coupled to the conduction electrons, and demonstrated
the divergence of the resistivity as $T \to 0$ for negative exchange coupling constant, $J$, eqn. 1(17).

Beal-Monod (89) and Matho and Beal-Monod (90) have examined the problem of exchange scattering of conduction electrons from a pair of impurity spins, $S_1$ and $S_2$ which are themselves coupled through some kind of exchange interaction with a Hamiltonian which may be written

$$H_W = -W S_1 S_2$$

Their expression for the scattering rate from the coupled impurity pair contains two terms, the most important one of which (for dilute random alloys $c \ll 1\%)$ corresponds to localised scattering of the conduction electron from one impurity spin at a time, the second spin exerting its influence through the interaction of eqn. 1(75) to produce a modification of the truly isolated scattering characteristics.

Beal-Monod and Matho evaluate the resistivity of the pair in the two limiting cases of $\beta W \ll 1$, strong anti-ferromagnetic (AF) coupling and $\beta W \gg 1$ strong ferromagnetic (F) coupling of $S_1$ and $S_2$ ($\beta = (k_B T)^{-1}$). They obtain

$$R_b \approx R_u \left( \frac{\gamma}{\pi} \pi \beta^2 S_{eff}^2 \right) \left( \beta W \right)$$

$$X \left\{ \begin{array}{ll}
1 + \gamma \ln \left( \frac{T}{T_F} \right) + \gamma \ln \left( \frac{T^2 + T_W^2}{T_F^2} \right), & W > 0 \\
1 + 2\gamma \ln \left( \frac{T^2 + T_W^2}{T_F^2} \right), & W < 0
\end{array} \right.$$

1(76)
where $R_u$ is the unitarity limit for isolated impurities, $\mathcal{U} = n(o)J$ and $k_B T_W \ll W$. A major modification to the single impurity expression, in the same notation,

$$R_0 = R_u \left(\frac{4}{3} \mathcal{U}^2 S(S+1) \right) \left[ 1 + 2 \mathcal{U} \ln \frac{T}{T_F} \right]$$  \hspace{1cm} (77)

is through the effective spin amplitude, $S_{eff}^2$

$$\frac{S_{eff}^2}{S(S+1)} \longrightarrow \frac{S + \frac{1}{2}}{S+1} \quad \beta W \to \infty$$  \hspace{1cm} (F)

$$= 1 \quad W = 0$$

$$\longrightarrow 0 \quad -\beta W \to \infty$$  \hspace{1cm} (AF)  \hspace{1cm} (78)

In the expression (77) above, when $T = T_K$, the Kondo temperature for an isolated impurity, the magnitude of the temperature dependent term is twice that of the temperature independent one. Applying the same criterion to eqn. (76) it is possible to extract the effective Kondo temperature for the pair, $T_K$, which is shown graphically as a function of the coupling strength $\sim T_W$ in the figure below.

![Graph](attachment:image.png)

**fig. (1:4) (After ref. (90)),** $k_B T_W \ll W$
Both ferromagnetic and antiferromagnetic coupling results in a lower $T_K$ compared to $T_{K_0}$, and in the antiferromagnetic case $T_K = 0$ for $W \gg k T_{K_0}$ implying that the perturbation expansion for the resistivity (or any other property) no longer diverges even at $T=0$, for sufficiently strong AF coupling. It should be stressed that the reduction of the effective $T_K$ for the pair does not necessarily reflect a change in the magnetic state of each impurity, which is still characterised by $T_{K_0}$. However if $W S_1 S_2$ arose as a result of the Caroli mechanism $T_{K_0}$ may well change for the reasons which have already been outlined.

Matho and Beal-Monod proceed to construct a model for the resistivity of dilute random alloys, taking account of the coupling between pairs of solute atoms.

The resistivity due to scattering from a particular impurity in the alloy may be expanded as a power series in the concentration and, provided the concentration is low enough, the low order terms alone will provide a reasonable approximation

$$\rho(c,T) - c\rho_V = cA(T) + c^2 B(T) + \ldots$$  \hspace{1cm} 1(79)

$A(T)$ is the single impurity expression for the resistivity eqn. 1(77), and $B(T)$ will be determined statistically by considering the probability distribution $D(W)$ of the coupling between the solute atom at the origin and each of those distributed throughout the rest of the alloy.
\[ B(T) = \sum_{\{W\}} N D(W) \mathcal{S}_R(W) \]  

where \( N \) is the total number of lattice sites, \( \{W\} \) is the set of possible values of the coupling and the modification to the single impurity resistivity, \( \mathcal{S}_R(W) \), can be deduced from eqn. 1(76) and eqn. 1(77). Descending from high temperatures, at fixed concentration, \( B(T) \) represents the first correction to the single impurity resistivity as soon as some of \( \{W\} \) exceed the thermal excitation energy \( k_B T \).

In order to find the value of eqn. 1(80) an explicit spatial dependence for \( W(r) \) must be assumed. Matho and Beal-Monod specify \( W(r) \) as the RKKY interaction, so that

\[ W(r) = 2W \frac{\sqrt{2} \cos(2k_F r + \phi)}{N(r)} \]  

where \( N(r) = \frac{4\pi r^3}{3V_0} \) is the number of lattice sites enclosed in a sphere of radius \( r \).

Evaluating \( B(T) \) and inserting the value into eqn. 1(79) the resultant expression for the resistivity is identical to that which would have been obtained by considering the following, much simpler model. Around the origin there will be a finite number of sites, called 'superthermal' sites, for which the coupling to the impurity at the origin will exceed the thermal excitation energy, ie. \( W(r) > k_B T \) for \( r \leq r_c(T) \) where \( r_c(T) \) is the thermal-pair - correlation length.
From eqn. 1(81) it is apparent

\[
\frac{4/3}{V_0} \sum r_p^2 (T) = N_s(T) = 2 \frac{W_1}{k_B T}
\]

and the number of superthermal sites increases with decreasing temperature. The model requires that if a second impurity is located on a superthermal site then the resistivity takes the strong coupling limit \( \beta |W| > 1 \), which assuming equal probability of AF or F coupling, has a mean value (eqn. 1(76) and eqn. 1(78))

\[
R_1 = \frac{1}{2} \left( \frac{S + \frac{1}{2} + 0}{S + 1 + 0} \right) R_o = \frac{1}{2} R_o.
\]

For impurities not located within the thermal pair correlation length of the origin the coupling may be neglected entirely and the resistivity takes the single (isolated) impurity limit of \( R_o \). Thus in a given random dilute alloy it is possible to evaluate the mean number of solute atoms which, at a given temperature, will have a second impurity within the sphere of superthermal sites, and this will be equal to \( N N_s(T)c^2 \) (provided we are in a concentration and temperature interval where the pair approximation is valid ie where \( N_s(T)c < 1 \)). This enables us to write down the total resistivity of the alloy as a sum of contributions from "isolated" and "coupled" impurity atoms, which reduces to

\[
\rho(c, T) = cR_o = Nc R_o \left[ 1 - \frac{N_s(T)c}{2} \right]
\]

which implies a suppression of the zero coupling limit of the \( \ln T \) temperature dependence which will be (initially)
proportional to \( c^2 \) at a given temperature. The temperature dependence of \( N_s(T) \), eqn. 1(82), means that reducing the temperature, more and more impurities must be classified as 'couples' with the result that the deviation from the ideal single impurity resistivity becomes progressively larger, and the impurity resistivity itself may, for sufficiently large concentrations, pass through a maximum within the experimental temperature range. Beal-Monod and Matho (90) suggest possible extensions of the pair model to the \( n = N_s(T)c > 1 \) regime, and are able to obtain a reasonable fit to the experimental values of the resistivity for dilute (\( c < 2000 \text{ ppm.} \)) AuMn, AgMn and CuMn alloys. For CuMn at \( T=1K \) the radius of the sphere enclosing the super-thermal lattice sites is about \( 35 \text{ Å} \), assuming the Caroli mechanism, eqn. 1(70), to give rise to the coupling between the Mn spins.

Anderson model for \( n > 1 \) impurities, and the effects of the local environment on the magnetic state of the impurity

In this subsection we briefly review some of the attempts to solve the Anderson model for \( n > 1 \) impurities, and then go on to examine some of the experimental data on alloys where the local influence of one impurity on another is able to affect the magnetic state of that impurity.

Alexander and Anderson (91) extended the single non-degenerate orbital Anderson model (3) to the case of a pair of neighbouring non-degenerate orbitals. The
Hamiltonian was taken to be

\[ H = H_s + H_d + H_{sd} \tag{1(82)} \]

where the individual terms are the same as those for a single impurity (eqns. 1(2) and 1(2a)), except that the d-orbital energy,

\[ H_d = E_0 \sum_j \left( n_{1\sigma} + n_{2\sigma} \right) + U(n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow}) + \sum_j \left( V_{12} c_{1\sigma}^* c_{2\sigma} + V_{21} c_{2\sigma}^* c_{1\sigma} \right) \tag{1(83)} \]

has an additional term which corresponds to a direct interaction between the orbitals via the transfer integral

\[ V_{12} = V_{21} = \int \phi_1^*(r) \phi_2(r) \, dr \tag{1(84)} \]

between them. The nature of the coupling between the two orbitals as a result of the direct transfer interaction was found to be dependent on the relative disposition of the spin up and spin down components of the VBS. When either component lies close to the Fermi energy, parallel alignment of the net moment on each orbital is favoured, whereas for symmetrical disposition of the VBS about, and remote from, the Fermi energy antiferromagnetic alignment occurs. In the latter case the condition for the occurrence of a net moment (c.f. eqn. 1(6a)) is made more stringent.

Moriya (92) extended this calculation to deal with the direct transfer interaction between two adjacent five-fold degenerate impurity orbitals. His results are
summarised in the diagram below which gives the sign and the relative magnitude for the effective coupling between two impurity orbitals which contain \( n_1 \) and \( n_2 \) d electrons respectively. The curves, which are evaluated for \( \frac{U + 4J}{\Delta} = 10 \), are not very sensitive to the exact value of this latter parameter, at least in their qualitative form.

![Diagram](image)

On the basis of fig. (1:5), the direct transfer interaction will lead to the parallel alignment of the magnetic moment on adjacent pairs of Fe, Co or Ni atoms, whereas for Cr or Mn, where the VBS is close to being half full antiparallel alignment would result. Moriya also points out that the d-d transfer interaction will also give rise to a change in the net moment on the impurity, which will be the greatest in those cases where the isolated (\( V_{ij} = 0 \) for all \( j \)) degenerate orbital is close to the critical boundary.
for the spin degeneracy of the VBS to be lifted.

Kim (93) considers the effect of the local environment in determining whether or not a given impurity carries a magnetic moment in a more explicit manner. He begins with a Hamiltonian which is a generalisation of that used by Anderson (3) to N impurity states and includes, in addition to the normal s-d admixture term, $H_{sd}$, a term

$$H_{dd} = \sum_{ij\sigma} T_{ij} d_i^{+} d_j$$

(85)

corresponding to the direct d-d admixture between neighbouring orbitals.

In the presence of all the other N-1 impurities the density of states $\rho_{di}(\omega)$ at the Fermi energy for the ith orbital will be changed from its value $\rho_{di}(\omega)$ when only the ith orbital is present. Thus, in the presence of the other impurities the criterion for the existence of a moment on the ith atom, $U_i \rho_i(\omega) > 1$, is modified compared to that for the isolated atom, i.e. $U_i \rho_i^0(\omega) > 1$. The modification of the magnetic state of the ith impurity is equivalently monitored through the change in the VBS width induced by the presence of the other impurities. Kim shows that there are three main contributions, i.e.

$$\Delta_i = \Delta_i^0 + \delta\Delta_i^{(1)} + \delta\Delta_i^{(2)} + \delta\Delta_i^{(3)}$$

(86)

$\delta\Delta_i^{(1)}$ arises as a result of the indirect interaction between impurities, mediated by the conduction electrons.
and is effectively the change in $\Delta_i^0$ (as given by eqn. 1(5)) due to the change in the local host density of conduction states at the $i$th impurity, brought about by the presence of the other $N-1$ impurities in the conduction band. The oscillatory nature of the latter perturbation (1) is reflected in $\delta\Delta_i^{(1)}$ and

$$\frac{\delta\Delta_i^{(1)}}{\Delta_i^0} = \frac{1}{k_F^2} \sum_{j \neq i}^{N} \cos(2k_F r_{ij})$$  \hspace{1cm}  1(87)

Counting only the contribution from $Z$ nearest neighbours at distance $d$, eqn. 1(87) reduces to

$$\frac{\delta\Delta_i^{(1)}}{\Delta_i^0} = 4Z \cos(2k_F d) \frac{(2k_F d)^2}{(2k_F d)^2}$$  \hspace{1cm}  1(88)

$\delta\Delta_i^{(1)}$ can thus account for both an increase and a decrease in $\Delta_i^0$ and is qualitatively capable of explaining both the demagnetisation, eg Au V (98), or the magnetisation, eg CuNi (100), of the isolated impurity VBS due to the presence of nearest neighbour solute atoms in alloys of finite concentration.

$\delta\Delta_i^{(2)}$ arises from the direct transfer interaction and, for the simplifying condition that the neighbouring impurity VBS are situated at the Fermi energy

$$\delta\Delta_i^{(2)} = \sum_{j \neq i} T_{ij}^2 \frac{1}{\Delta_j^0}$$  \hspace{1cm}  1(89)
Again, including only the $Z$ nearest neighbours with $T_{ij} = T$ and $\Delta^0_j = \Delta^0$ independently of $j$

\[ \frac{\delta \Delta^{(2)}_i}{\Delta^0_i} = Z \left( \frac{T}{\Delta^0} \right)^2 \geq 0 \quad 1(90) \]

This mechanism can thus only broaden the $i$th VBS.

The relative magnitudes of $\delta \Delta^{(1)}_i$ and $\delta \Delta^{(2)}_i$ depend on the relative strengths of the indirect and direct impurity interactions. For impurity pairs which are not nearest neighbours the indirect mechanism will dominate the modification of $\Delta^0_i$. For nearest neighbour rare earth transition metal atoms the indirect mechanism still dominates, but in the case of 3d impurities, where the VBS is not so strongly localised, the direct transfer mechanism may be the most important.

$\delta \Delta^{(3)}_i$ is a cross term which has a magnitude intermediate between $\delta \Delta^{(1)}_i$ and $\delta \Delta^{(2)}_i$.

Some examples of 'coupling' interactions in dilute alloys with simple metal host matrices

1) Au V The impurity contribution to the low temperature magnetic susceptibility and specific heat of Au V alloys in the concentration range 0.2 - 10 at.% (94) was found to increase more slowly than linearly with increasing V concentration. It was found possible to interpret this result in terms of a model where isolated V atoms are nearly magnetic ($T_{lsf} = 270K$) whereas those which have one
(or more) V atoms as a nearest neighbour are non-magnetic ($T_{lsf} = 2500K$). The characteristic temperatures $T_{lsf}$ are derived from the enhancement of the impurity susceptibility as given in eqn. 1(53) due to LSF. Souletie and Tournier (95) were able to obtain a fit to the concentration dependence of their own, and also Creveling and Luo's (96) susceptibility measurements at low temperatures using a double CW law of the form

$$\Delta \chi = \frac{N_1 \mu_1^2}{3k(T+\Theta_1)} + \frac{N_2 \mu_2^2}{3k(T+\Theta_2)}$$  \hspace{1cm} (91)

where $N_1 = c(1-c)^{12}$ and $N_2 = c - c(1-c)^{12}$ are the numbers of isolated (in the sense of no nearest neighbour V atoms) and non-isolated V atoms, respectively. Assuming $\mu_1 = \mu_2 = 3u_B$ they found $\Theta_1 = 225K$ and $\Theta_2 = 1120K$.

The NMR Knight shift and nuclear relaxation rate of $^{51}V$ in Au V alloys (97) also indicates that V atoms in groups of two or more are less magnetic than those with no nearest neighbours.

Van Dam (98) (99) finds that for $c \leq 1$ at.%V the impurity susceptibility actually increases more rapidly than the V concentration, whilst above this concentration ($1 \leq c \leq 10$ at.%) the increase is less rapid than linear. He explains this behaviour in terms of a model where isolated V are nearly magnetic, those with nearest neighbours are non-magnetic and those with next nearest neighbour V atoms are magnetic. The main justification for the last situation
is that Au₄V, in which the V atoms are separated by a
distance which is nearly the same as next nearest neighbours
in a disordered alloy, undergoes a ferromagnetic transition
with Tc = 60K implying that the local environment is
favourable for the V atom to be magnetic. Van Dam's model
is illustrated schematically in fig. (1:6) below where the
magnetic or non-magnetic character of the V atom is
interpreted in terms of smaller or larger Kondo temperature.

![Diagram](image)

fig. (1:6) Magnetic character of a V atom with another
placed at distance r. (after ref. (98))

Increasing the concentration of the alloy results in
passing from isolated V properties to a region where next
nearest neighbour V interactions predominate and at still
higher concentrations (c ≥ 1 lat.%) the behaviour is
dominated by nearest neighbour V interactions.

ii) Cu Ni

The isolated Ni atom in Cu Ni is further into the
non-magnetic regime than V in Au (as can be judged by the
very much smaller enhancement of the low temperature susceptibility in the former case (36)) and Perrier et al.,(100) find that in order for impurity interactions to result in a given Ni atom becoming magnetic, \( n \geq 8 \) nearest neighbour Ni atoms must be present. With such a large number of nearest neighbours Perrier et al. have shown that, even in a random alloy, the Ni atoms bearing a magnetic moment will occur in clusters having a typical moment of about 6 \( u_B \) (for Cu + 50 at.\% Ni and taking the Ni moment as 0.6 \( u_B \)). This is consistent with the results of neutron scattering experiments on ferromagnetic Cu + 50 at.\% Ni alloys (101) which demonstrates that the magnetisation is not spatially uniform through the alloy but occurs in 'clouds' with total moment of about 8 - 10 \( u_B \), within a sphere of radius about 8\( \bar{R} \).

The magnetisation of Cu Ni + Fe alloys (102) may be interpreted in terms of a model in which a Ni atom is non-magnetic unless either (a) it has \( n \geq 8 \) Ni nearest neighbours or (b) it has one (or more) Fe atom as a nearest neighbour.

iii) Cu Co

The magnetisation measurements of Tournier and Blandin (103) may be interpreted in terms of isolated Co atoms being non-magnetic (\( T_{lsf} \approx 550K \)), those which have a single nearest neighbour Co being nearly magnetic (\( T_{lsf} \approx 7K \)) whilst those with two (or more) nearest neighbour Co being
magnetic (the M vs H plots even at 0.1K showed distinct curvature, with the saturation magnetisation $\propto c^3$). The authors point out that assuming that a magnetic Co atom has a saturation moment of $1.72u_B$ (equal to that of pure ferromagnetic Co), then the magnetisation data suggests rather more than the number of nearest neighbour Co pairs and groups of 3 expected in a perfectly random alloy. This might imply that either some tendency exists for the Co atoms to cluster, or that interactions are still important when next nearest Co neighbours are included.

iv) Au Co

Perhaps not too surprisingly the magnetic state of isolated Co atoms, and the effect of Co nearest neighbours in modifying the magnetic state of a given Co atom in Au is not very different from the situation for Cu host matrix. Once again magnetisation measurements (104) are consistent with different characteristic temperatures for isolated Co atoms ($T_{lsf} \approx 190K$), Co atoms with one Co nearest neighbour ($T_{lsf} \approx 23K$) while groups of 3 or more Co atoms remain magnetic even down to 0.05K, where the M vs H data show a remnant magnetisation in H = 0 which is proportional to $c^3$, indicative of the onset of ordering of the moments on groups of three atoms.

v) Cu Fe

The case of Fe dissolved in a Cu host matrix will be discussed more fully in a later section, but the magnetisation
measurements of Tholence and Tournier (61) are consistent with a characteristic temperature (in this case the CW theta) of \( \approx 30K \) for an Fe atom which has no other Fe atoms within a sphere radius \( 11 \AA \), and \( 0 - 5K \) otherwise.
Previous measurements on the Zn based, 3d transition metal alloy system

Only recently have measurements been performed on alloys of sufficiently low concentration for the data to be relatively free from the effects of interactions between the impurity atoms. A comprehensive tabulation of all previous data on these systems has been compiled by Ford, Rizzuto and Salamoni (105), hereafter FRS, and in the following we shall refer mainly to the measurements carried out on the most dilute alloys.

The electrical resistivity of the Zn Mn system has been extensively investigated and a resistance minimum is clearly observed, even in the earlier measurements (106), which indicated that interactions between the Mn atoms lead to a broad maximum in the impurity resistivity in the region of 4K for concentrations greater than about 0.15 at.% Mn.

FRS have measured the resistivity of 4 ZnMn alloys with concentrations ranging from 0.1 at.ppm. to 16 at.ppm., using a high resolution (1 in 10^6) D.C. technique, over the temperature range 0.35K to 5K. Whilst the impurity resistivity has a logarithmic temperature dependence above about 0.5K, below this temperature there is a concentration independent saturation in the resistivity for the 2 and 16 at.ppm. samples. The temperature dependence is claimed to be a good fit to the Hamann expression, eqn.1(33), for temperatures above 0.5K with $S=3/2$ and $T_K = 1K$. The authors observe that the deviation at the lowest temperatures follows a $T^2$ dependence, with a
characteristic temperature $\Theta \sim 2.5K$ when compared to expression 1(48).

Although the pure $\ln T$ temperature dependence for the resistivity between about 0.5 and 5K seems to be well established for ZnMn alloys of sufficiently low concentration, the precise form of the deviation below about 0.5K seems to be not so well established.

Newrock et al. (107) have used a somewhat less sensitive (5 parts in $10^{+4}$) A.C. eddy current technique to determine the resistivity of 4 ZnMn alloys with concentrations ranging from 7.8 at.ppm. to 38 at.ppm. Mn, down to a lowest temperature of 0.1K. Although some curvature in the excess resistivity at low temperatures occurs for the 3 most concentrated alloys, the deviation seems to begin at lower temperatures for the lower concentration alloys and in the case of the 7.8 at.ppm. ZnMn alloy the pure logarithmic behaviour persists right down to 0.1K, within experimental accuracy.

In order to try to establish conclusively the temperature and concentration dependence of the resistivity, Pilot et al. (108) have measured alloys containing 3 and 6 at.ppm. Mn down to 0.05K using the high resolution technique. They observe a 'flattening off' of the resistivity below about 2K which is concentration independent for the two samples reported. The evidence for the quadratic temperature dependence at the lowest temperatures is still not clear-cut since if it exists at all it appears to be reached only well below 0.1K and is therefore experimentally observed only over a rather small temperature interval. Comparison with eqn. 1(48) yields a
characteristic temperature in the quadratic region of $\Theta \sim 0.9K$. These authors also attempted to fit the Hamann expression to the data at the higher temperatures, but the fit was not satisfactory using any reasonable value of the Mn spin between 0.5 and 1.5.

Wassermann et al. (109) have measured the modification to the impurity resistivity and the depression of the superconducting transition temperature as a result of various annealing processes on a 20 at. ppm. ZnMn alloy. The alloy was initially quenched from the melt and cold-rolled. After 24 hrs. at 400°C in an atmosphere of argon, they find a pronounced drop in the temperature dependence of the resistivity and almost no reduction in the superconducting transition temperature from the value for pure zinc. During the course of the present work, see later, it was found that even nominally "high-purity" argon could contain sufficient oxygen as an impurity to oxidise a large proportion, if not all, the Mn or Cr present in a dilute molten ZnMn or ZnCr alloy within a few minutes. Since Wasserman uses argon as a heat exchange gas during the annealing processes, it seems likely that at least some of the effects he observes are due to the oxidation of the Mn during these long annealing process.

The resistivity of several ZnCr alloys in the concentration range 0.5 at. ppm. to 108 at. ppm. was measured by FRS down to 0.3K. The results are very similar to those obtained for the ZnMn, ie a high temperature logarithmic regime, with deviations below about 0.6K to a $T^2$ temperature dependence. The best fit of the Hamann expression in the high temperature region
suggests $T_K$ is about 3K, whilst the characteristic temperature from the $T^2$ region is $4.5 \pm 0.5K$.

Extending the measurements down to 0.05K, Pilot et al., for Cr concentrations of 0.5 and 0.7 at.ppm. also see a deviation from logarithmic behaviour, which, as with their ZnMn data only follows a $T^2$ dependence over an extremely limited temperature range below 0.1K, if at all. The characteristic temperature of the $T^2$ region would appear to be the same for ZnCr as ZnMn, ie about 0.9K.

The first resistivity measurements on dilute ZnFe alloys (Caplin, (110)) showed clearly that, due to the low solid solubility of Fe in zinc, for concentrations in excess of about 200ppm. the properties of the alloy will depend sensitively on its metallurgical history. For lower concentrations a very weak (about $1/1000$th of that for the same concentration of Mn or Cr) logarithmic term is observed. When the magnitude of this term is compared with resistivity (66) and susceptibility (111) measurements on CuZn Fe alloys, it implies the existence of a small ($p_{eff}^2 \approx 0.07$) residual moment on the iron. The more recent resistivity measurements (FRS) show a $T^2$ region extending up to about 1.5K, with a characteristic temperature of $\Theta \approx 85 \pm 10K$, and above this temperature a logarithmic temperature dependence is again observed.

The resistivities of ZnV and ZnCo (FRS) are temperature independent ($\Theta \geq 1000K$).

The residual resistivities at 4.2K for the Zn-3d systems have been measured (FRS and (112)) and these are shown in fig.(1:7). FRS have used their fit to the Hamann formula to
**Fig. 17** RESIDUAL RESISTIVITY (42K) FOR 3d SOLUTE IN Zn.

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>Zd</th>
<th>$\rho_d/\rho$ EXP</th>
<th>$\rho_d/\rho$ FRIEDEL</th>
<th>$\alpha_{\text{EXPT}}$</th>
<th>$\alpha_{\text{THEORY}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnV</td>
<td>2</td>
<td>6.5</td>
<td>2.84</td>
<td>2.29</td>
<td></td>
</tr>
<tr>
<td>ZnCr</td>
<td>4</td>
<td>18.5</td>
<td>7.45</td>
<td>2.50</td>
<td></td>
</tr>
<tr>
<td>ZnMn</td>
<td>5</td>
<td>23.5</td>
<td>8.24</td>
<td>2.85</td>
<td></td>
</tr>
<tr>
<td>ZnFe</td>
<td>7</td>
<td>14.8</td>
<td>5.38</td>
<td>2.75</td>
<td></td>
</tr>
<tr>
<td>ZnCo</td>
<td>8</td>
<td>6.2</td>
<td>2.84</td>
<td>2.18</td>
<td></td>
</tr>
<tr>
<td>ZnNi</td>
<td>9</td>
<td>1.9</td>
<td>0.78</td>
<td>2.44</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 1.1** RESIDUAL RESISTIVITY OF Zn-3d ALLOYS AT $T=0$ K (105°)
deduce the resistivity at OK for ZnMn and ZnCr, for other members of the series this value is essentially the same as that measured at 4.2K. These experimental values of $\left(\frac{\rho_d}{\rho_n}\right)_{T=0}$ are compared in table (1:1) with the value derived from the formula due to Friedel (1) for a non-magnetic VBS in a free electron host metal

$$\frac{Q_d}{c} = \frac{h}{10 Zhe^2k_F} \sin^2 \frac{\pi Z_d}{10}$$

There is an approximately constant ratio $\alpha \approx 2.5$ between the experimental and calculated values of the resistivity which may be phenomenologically explained by assuming that the effective number of conduction electrons, $Z_h$, per Zn atom is 0.8. Farrell et al. (113) found that in order to bring about agreement between the experimental and calculated resistivities of dilute alloys of non-magnetic (eg. Cu, Au, Ag and Al) solutes in Zn a value of $Z_h = 0.6$ electrons/atom was required (again treating $Z_h$ as a parameter). The band structure calculation due to Allen et al. (114) shows large deviations of the density of states curve for the Zn conduction band from the free electron model.

The magnetic susceptibility measurements on ZnMn alloys in the concentration range 0.04 to 0.4 at.% between 4K and 300K (115) show evidence of strong correlations between the Mn spins at the lowest temperatures, with the result that the susceptibility of the most concentrated alloy passes through a maximum at $T \approx 6K$, indicative of the onset of antiferromagnetic order below this temperature. The CW fit to the
high temperature data yields $S = 3/2$.

Newrock et al. (107) observe a CW temperature dependence of the susceptibility of ZnMn alloys in the concentration range 7.6 - 182 at.ppm. The concentration independent intercept $\Theta = 1.1K$ and the Curie constant implies $p_{\text{eff}} = 4.2u_B$, although the authors quote their raw data in terms of the s-d model expression for the susceptibility (eqn 1(30)) ie $T_K = 0.24K$ and $p_{\text{eff}} = 4.66u_B$.

There is no previous data for ZnCr alloys and only a preliminary and inconclusive measurement on a single Zn + 0.1 at.% Fe alloy (111).

Martin (116) (117) observes a low temperature specific heat anomaly in dilute ZnMn alloys (0.05 and 0.1 at.% Mn), corresponding to $S = 3/2$ for Mn. The temperature at which the maximum is in the excess impurity specific heat occurs is a linear function of the concentration, characteristic of impurity interactions via RKKY coupling leading to a 'freezing out' of the spin degrees of freedom, rather than spin compensation at the impurity site.

There are no reliable specific heat data on either ZnCr or ZnFe.

The thermo-electric power is very sensitive to the magnetic state of the solute atoms in a dilute alloy, and 'giant' thermopowers, of either positive or negative sign, are observed with the maximum falling close to the characteristic temperature of the solute. e.g. $\sim 20K$ for CuFe and
~1K for AuFe (see refs. (26) (71) and references therein). Measurements between 0.4K and 8K for a Zn + 12 at.ppm. Mn specimen (118) show a large negative thermopower which has a sharp decrease below 1K.

The depression of the superconducting transition temperature of Zn on alloying with Cr, Mn, Fe, Co and Ni has been measured by Boato et al. (119) who found that \( \frac{dT_c}{dc} \approx 170, 315, 13, 6.4, 2.9 \) K per at.% respectively. The very large rate of depression in the case of Cr and Mn is consistent with \( T_K \approx T_{c_0} \), the superconducting transition temperature for the pure host matrix (≈ 0.85K for Zn). Boato and Rizzuto (120) find that the suppression of \( T_c \) by 100 at.ppm. Mn in Zn is decreased when Al is added, which they interpret as an increase of the Kondo temperature for Mn with increasing Al concentration.
Previous measurements on dilute alloys of Fe in pure Cu and binary CuX host matrices.

Since we have measured some properties of the ternary system Cu$_{1-x}$Al$_x$+Fe, a discussion of previous measurements on dilute CuFe alloys will be relevant.

The resistivity measurements of Daybell and Steyert (121) first suggested that a Kondo temperature $T_K \approx 16$K was appropriate for this system, making it well suited for the experimental study of the Kondo effect, and especially the nature of the transition from the high temperature magnetic ($T \gg T_K$) to the low temperature non-magnetic ($T \ll T_K$) state. Most of the earlier measurements were complicated by the effects of impurity interactions which, as we have already seen, led to some false conclusions concerning the validity of some of the predictions of the s-d model theories for the $T \ll T_K$ properties. However, following the systematic study of concentration dependent effects in the magnetisation of CuFe alloys by Tholence and Tournier (61) there now exists, in addition to the susceptibility, reliable data for the isolated atom contribution to both the specific heat (53) and the resistivity (46).

Tholence and Tournier have investigated the magnetisation of a range of dilute CuFe alloys ($1 \ll c \ll 600$at.ppm.Fe) in the temperature interval 0.05K to 30K and in fields up to 60kOe. The initial susceptibility for $T \gg 1.3$K, (below this temperature the nuclear susceptibility of the Cu nuclei represents a large contribution to the total susceptibility of the alloy) was
found to contain both a term proportional to the concentration of Fe, c, and also one proportional to \( c^2 \). The magnetisation vs. field plots showed distinct curvature which was saturated by fields in excess of about 40kOe at 1.3K, with the magnetisation still increasing as a linear function of the field at higher fields. The intercept at \( H = 0 \) on the magnetisation axis, extrapolated from the magnetisation at 1.3K in fields in excess of 40kOe was found to be proportional to the square of the concentration, whilst the high field gradient of the magnetisation vs. field was found to increase linearly with the concentration. Tholence and Tournier concluded that the two contributions to the magnetisation, \( \alpha c \) and \( c^2 \), corresponded to isolated Fe atoms and Fe atoms in coupled pairs, respectively. Since the saturation in the magnetisation at 1.3K was related to the Fe atoms coupled in pairs, then the effect of the coupling interaction is such that pairs are still 'magnetic' at 1.3K implying a much lower characteristic temperature for the pairs than for the 'nearly magnetic' isolated Fe atoms. The inverse of the high field susceptibility was found to be a linear function of the temperature from 1K to 30K, consistent with a CW behaviour with \( T = 29K \) and \( \mu_{\text{eff}} = 3.4u_B \) for isolated Fe atoms. On the other hand the contribution to the total susceptibility from the pairs was found to follow a CW law with \( 0 < T < 5K \).

From the magnitude of the pair saturation magnetisation Tholence and Tournier determined the concentration of the pairs \( c_2 = 130 c^2 \), which assuming that equal numbers of pairs
have the two Fe spins coupled antiparallel or parallel corresponds to $c' = 520c^2$ for the concentration of Fe atoms which are coupled into pairs. Assuming a purely random distribution of Fe atoms through the Cu matrix, the concentration $c'$ implies that a given Fe atom will be coupled to another if the second Fe atom is located on one of the 520 lattice sites closest to the first. This represents a sphere of radius $\approx 1\% R$ for the coupling interaction to be effective in modifying the state of the Fe atoms concerned. If we allow for a non-random distribution, i.e., there is a tendency for Fe atoms to cluster, this critical separation would be reduced.

The Mössbauer spectra (122) at room temperature for CuFe alloys $c > 0.2$ at.% Fe shows distinctly the presence of two different types of sites for the Fe atoms. A single unsplit absorption line corresponds to isolated Fe atoms, whilst, due to their asymmetrical environment, Fe atoms which are one of a pair, or even larger group of Fe atoms, experience an electric field gradient which leads to quadrupole splitting of the Mössbauer absorption line, and a total spectrum for the alloy which is a superposition of a singlet and a doublet. The intensity of the doublet increases with the concentration of Fe. Analysis of the spectrum of the alloys at 1.3K (where for $c > 0.5$ at.% the alloys are magnetically ordered) shows that the distribution of saturation hyperfine fields at the Fe nucleus has one peak at 80kOe corresponding to isolated Fe atoms, another at 150kOe corresponding to Fe atoms which are coupled to
their nearest neighbour, whilst still higher values are observed for Fe atoms in larger clusters.

The transition to the non-magnetic ground state singlet and the disappearance of the high \( T \gg T_K \) temperature spin predicted (though through very different mechanisms) by both the s-d model and LSF theories is most readily demonstrated in the case of CuFe by the specific heat measurements of Triplett and Phillips (53). A broad peak in \( \Delta C_V \) with a concentration independent position for the maximum at about 9K is observed for CuFe alloys containing 81 and 195 at.ppm. of Fe. Fitting the data in the region of the peak to a Bloomfield-Hamann curve (49) resulted in \( T_K = 28K \) and, from the area under the curve, the total change in entropy \( \Delta S = 1.01 \text{ln}4 \) which corresponds very well to the removal of the magnetic entropy associated with a spin \( S = 3/2 \). This spin value is in good agreement with the spin on the isolated Fe atom in Cu obtained by Tholence and Tournier. It should be noted, however, that the Bloomfield-Hamann theory does not give the correct temperature dependence for \( \Delta C \) as \( \frac{T}{T_K} \to 0 \). This theory suggests \( \Delta C \propto \left( \frac{T}{T_K} \right)^{0.57} \) but the experimental data correspond to \( \Delta C \propto T \), for temperatures as low as 0.06K.

As we have already mentioned, the susceptibility of dilute CuFe alloys is dominated below about 1K by the contribution from the Cu nuclei. The impurity specific heat is, however, related to the impurity susceptibility by the thermodynamic relationship
Triplett and Phillips are thus able to use the field dependence of the low temperature excess specific heat, to show that

\[ \chi = \chi_0 \left( 1 - 15 \left( \frac{T}{29} \right)^2 \right) \]  \hspace{1cm} (94)

for \( T < 0.7K \). Thus, in addition to the impurity specific heat itself, the impurity susceptibility can be described by a simple power law at low enough temperatures \( \left( \frac{T}{T_K} \right) \ll 1 \).

Star (46) has observed that below \( \sim 1K \) the resistivity of a Cu + 50 at.ppm. Fe alloy has a quadratic temperature dependence

\[ \rho = \rho_0 \left( 1 - \left( \frac{T}{19} \right)^2 \right) \]  \hspace{1cm} (95)

For the same alloy below about 0.01K there is a positive deviation from this temperature dependence which can be accounted for as being a small log \( T \) contribution from the coupled pairs of Fe atoms with their correspondingly much reduced characteristic temperature.

The pattern of simple power laws which has emerged for the temperature dependences of various properties of the isolated Fe atom in Cu at temperatures \( T \ll T_K \) is also reflected in the magnetic susceptibility of isolated V atoms in Au (98) and Mn atoms in Al (70), both of which display a quadratic temperature dependence of the form

\[ \chi = \chi_0 \left( 1 - AT^2 \right) \]  \hspace{1cm} (96)
at sufficiently low temperatures. As we have already discussed there is some evidence that the resistivity of dilute ZnCr ZnMn and ZnFe alloys tends to a quadratic temperature dependence at the lowest temperatures and all of these data provide an experimental basis for the idea that the behaviour of a given solute in a given host matrix may be specified just in terms of a single characteristic temperature, for example, the Kondo temperature of the s-d model, or, in terms of the lifetime, $\tau_{\text{lsf}}$ of the spin in the LSF model, $kT_s \approx \frac{k}{\tau_{\text{lsf}}}$ (67).

Both the Kondo temperature, eqn.1(18), and the enhancement factor eqn.1(50), of the LSF theory depend on the density of states of the host matrix. This quantity may be varied directly if a binary alloy is used as the host matrix, although there may be additional complications in the interpretation of the data due to metallurgical problems, eg. a tendency for one or other of the binary components to cluster around the magnetic impurity atoms, or a much reduced solubility of the latter in the presence of the 2nd component of the binary host.

Window (123) has examined the Mössbauer spectra of alloys of 0.1 and 1 at.% of $^{57}$Fe in various binary alloys CuX, where X represents 2 - 10 at.% of either Al, Zn or Au (among others). The room temperature spectrum in the case of Cu + 10 at.% Al shows only a well defined doublet structure, implying that all of the Fe atoms in this matrix experience an electric field gradient due to having an asymmetrical environment. Window suggests that the site is probably one where the Fe atom is surrounded by 4 nearest neighbour Al atoms, with several of
these units forming a planar structure (Guinier-Preston zone) in a matrix of depleted CuAl alloy. In the case where X is either Zn or Au the spectrum at 300K has essentially the same character as that already described for the pure Cu host matrix. Analysis of the low temperature spectra on alloys containing 1 at.% of Fe at 1.4K showed that the distribution of hyperfine fields at the $^{57}$Fe nuclei is least changed from that for the pure Cu host in the case of the CuZn matrix, but has a larger probability for the lower values ($< 80$ kOe) of hyperfine fields in the case of X = Al.

The magnetic susceptibility (111) and resistivity (66) of alloys consisting of ~0.1 at.% Fe dissolved in ε-phase CuZn host matrices (Cu concentration ranges from 21% to 14%) has been extensively discussed by Caplin et al. (124) (125).

The impurity susceptibility is found to follow a CW law with 0 < Θ < 1 in all cases, however the effective moment on the Fe atom is reduced from 1.4 $\mu_B$ to less than about 0.4 $\mu_B$ as the concentration of Cu is decreased across the phase, i.e. as the electron per atom ratio is increased. Simultaneously the impurity resistivity shows a smooth reduction in the logarithmic slope, at such a rate that $\frac{2 \rho}{\ln T} p_{\text{eff}}^2 (\propto J^3)$ remains a constant, independent of the Cu concentration. This, in turn, implies that the progressive demagnetisation of the Fe VBS takes place without the strength of the s-d exchange coupling constant, J being affected. For any given alloy the value of $p_{\text{eff}}$ was found to be temperature independent in the temperature range examined ($T > 2$K) implying a rather low characteristic temperature for the Fe atom ($<< 1$K).
Mössbauer measurements (126) were able to confirm that the disappearance of the magnetic moment occurred simultaneously at every Fe site due to host average properties, rather than the question of any given Fe site being magnetic being decided by its immediate local environment.

Loram et al. (47) have measured the resistivity of a series of CuAu alloys (0, 5, 10 and 100 at.% Au) containing low concentrations of Fe (10 ≤ c ≤ 1000 at.ppm.) and are able to deduce, by comparison with the various expressions which have been derived for the resistivity in the s-d model (43) (52), that the Kondo temperature, $T_K$, decreases rapidly with increasing Au concentration from a value $T_K = 24K$ in pure Cu to 0.24K in pure Au. Although the theoretical expressions for the resistivity, and therefore the absolute values of $T_K$ must be regarded with some suspicion, Loram et al. do find that when the impurity resistivity of each of their alloys is plotted as a function of $\frac{T}{T_K}$, the data falls on a single universal curve. This property of the data indicates that the resistivity may be scaled by a single parameter, which decreases strongly with increasing Au concentration of the host alloy. Star (46) has commented that since the solubility of Fe in Au is much higher than in Cu, the Fe atoms may reside in Au rich regions of the host metal in a highly non-random fashion so that local environment effects may complicate the interpretation of the resistivity data. Ekström and Myers (127) have measured the susceptibility of a single Cu + 10 at.% Au alloy containing 189 at.ppm. of Fe, as well as some dilute CuFe alloys (80 ≤ c ≤ 300 at.ppm.). In each case they have fitted the Fe impurity susceptibility to a double CW
expression of the form

$$
\Delta \chi = \frac{C_1}{T + \Theta_1} + \frac{C_2}{T + \Theta_2} + \chi_0
$$

1(97)

For the pure Cu matrix $\Theta_1 \simeq 25K$ while $\Theta_2 \simeq 2-4K$. so that the first and second terms would appear to represent the contribution from isolated Fe atoms, and those coupled in pairs, respectively. From $C_1$ the authors find $p_{\text{eff}} = 3.4 \pm 0.1$ $\mu_B$, in good agreement with the value due to Tholence and Tournier(61). The results for the binary host alloy yield values of $\Theta_1$ and $\Theta_2$ which are essentially unchanged, however $\frac{C_2}{C_1}$ has increased. Ekström and Myers put forward two possible explanations, either the presence of the Au causes increased clustering of the Fe and so an increased value for $C_2$, the pair contribution or, alternatively, the potential scattering from Au atoms attenuates the pair coupling interaction between the impurities so that the second term now represents a contribution from isolated Fe atoms in Au rich regions, while the first represents that from isolated atoms in Cu rich regions. Since the mean free path in the Cu+10%Au alloy is still greater than the critical separation for pair coupling to occur, we tend to favour the first possibility. In either case the scaling observed in Loram's data may be accounted for by a reduction in the mean Kondo temperature $<T_K>_{av}$. (128) for the Fe atoms with increasing Au concentration.

The susceptibility of Fe dissolved in CuAl host matrices was first measured (between 114K and 300K) by Huck et al. (129). At such high temperatures the departure of the susceptibility from a Curie law is small so that these workers were able to
observe that the susceptibility varied proportional to the reciprocal of the temperature for each alloy including CuFe. Golibersuch (129) replotted this experimental data in the $\Delta X^{-1}$ vs $T$ format which shows up much more clearly the departures from Curie behaviour. In spite of some curvature in the data it is clear that the negative intercept on the temperature axis is increasing with increasing Al concentration in the host (alloys of 0, 5 and 10 at.% Al in Cu were measured). The effective moment on the Fe atom remains essentially independent of the host matrix composition in this range.

Zrudsky et al. (130) have measured the impurity contribution to the specific heat of Fe dissolved in CuAl alloys (0, 5 and 10 at.% Al), however the Fe concentration (0.07 at.%) is too high for the temperature dependence of the specific heat at low temperatures to be representative of the isolated Fe atom. In fact these workers find $\Delta C \propto T^{1/2}$ as $T \to 0$, demonstrating very clearly how the presence of the interactions can lead to dramatically altered impurity properties.

Gruber and Gardner (131) have measured the excess susceptibility due to Fe (and also Mn) dissolved in liquid CuAl alloys whose composition covered the whole range from pure Cu to pure Al. The excess susceptibility was found to scale with impurity concentration up to 5 at.% of Fe (or Mn). In solid alloys, as we have already discussed, each impurity is subject to statistical variation in its surroundings, but in a liquid such variations are averaged over a time scale $\sim 10^{-12}$ sec. because of the rapid diffusion of the atoms. In addition, the absence of a periodic lattice makes the free electron model for the conduction electrons, on which most of
the theoretical calculations are based, a more justifiable approximation. For the Cu rich host alloys the excess susceptibility is found to decrease with increasing temperature in a fashion which may be fitted to the predictions of the s-d model (eqn. 1 (29) and 1 (30)). The magnetic moment deduced from such a fit remains essentially constant at $5 \mu_B$ for Fe, although $T_K$ increases from 16K in pure Cu to 237K for the Cu + 40 at.% Al host. For the Al rich hosts the susceptibility is found to increase with increasing temperature. The authors observe that this characteristic may possibly result from a temperature dependence of the model parameters i.e. $V_{kd}$, $Q$, or $U$, but point out that the NMR data (132) on the host resonance line shift for the same liquid alloys shows that the amplitude of the conduction electron spin polarisation around each transition metal impurity decreases with increasing temperature, irrespective of whether the susceptibility is increasing or decreasing. Gruber and Gardner argue that if the increase in the susceptibility were due to a parametric temperature dependence then the conduction electron polarisation, which scales with the local susceptibility, would also increase at higher temperatures, which is not observed. The authors argue that the thermal disruption of the many body correlations at high temperatures (the experiments cover the range 800K to 1200K) may explain the results. In the LSF model a reduction of the spin fluctuation lifetime with increasing temperature can only lead to a decreasing susceptibility. However, in the s-d model, if the low temperature (in the $T \ll T_K$ sense) correlations, which lead to the reduction and eventual
disappearance of the impurity spin, are progressively curtailed as a result of the large thermal energies (~0.1eV), then the impurity spin will be restored to a larger fraction of its unperturbed value, and a net increase in the impurity susceptibility may result. Gruber and Gardner argue that such a thermal disruption of the conduction electron correlations around the impurity need not necessarily result in a change in the amplitude of the conduction electron polarisation which is proportional to the change in the impurity susceptibility which results.
CHAPTER 2
EXPERIMENTAL METHODS AND APPARATUS

Introduction

The measurements on the \( \text{Cu}_{1-x} \text{Al}_x \text{Fe}_{0.05} \) series of alloys reported in this work were made using a Faraday balance originally constructed by Griffiths (133) and subsequently used (with some modification) by Waszink (134), Williams (135), and Dunlop (136).

Preliminary measurements on several zinc alloys, containing between 10 at. ppm. and 100 at. ppm. of chromium were also made. Their success was limited due to inadequate sensitivity of the balance. For concentrations below about 25 at. ppm. accurate force measurement was virtually impossible due to eddy currents induced in the sample.

The measurements reported for the zinc + 3d element alloys were made using a newly constructed Faraday apparatus which is described in the latter part of this chapter. A short survey of the various methods available for the measurement of magnetic susceptibility is also included.

2:1 GULF SPIRAL FARADAY BALANCE

The balance itself consists of a helical elinvar spiral (fig. (2:1)) which supports the rigid quartz suspension link, together with the nulling coil, force calibration scale pan and copper damping discs. The sample is hung from the lower end of the modified suspension. A small galvonometer mirror is attached to the spiral and directs the focussed image of a light bulb filament onto a split differential selenium
photocell, positioned approximately 80 cm. from the spiral. A galvonometer monitors the output current from the photocell.

A vertical force may be exerted on the balance by passing a small current through the nulling coil, which is positioned in the field of a loudspeaker magnet. Such a force will cause a slight extension of the spiral together with a rotation of the mirror, thus displacing the image of the filament and changing the output current from the photocell.

Initially, when the applied magnetic field is zero, the photocell output is reduced to zero by passing a suitable current through the nulling coil. This current is noted in terms of the equivalent voltage drop, $V_o$, across a standard resistor in the nulling coil current circuit.

When the magnetic field is applied, any additional vertical force on the specimen or suspension will lead to a finite output current from the photocell. This change in the vertical force will be exactly compensated for by changing the current in the nulling coil to some new value, $V_m$, whereupon the photocell output current is again zero. The total force on the balance of magnetic origin is thus proportional to $V_m - V_o$, and by the use of this null - technique we ensure that the measurement of the total magnetic force always takes place under conditions of constant sample and suspension position in the magnetic field.

The nulling coil current is calibrated by lowering a known weight (about 100 mgm. of platinum) onto the perspex scale pan by means of a small relay.

A combination of eddy current damping of vertical
Fig.(2:1) Gulf Spiral Faraday Balance
Figure 2.2

(a) Copper End Cap

(b) Modified Suspension

(c) Original Suspension

(d) Definition of Axes
Fig. (2.3) Field dependence of the force on the modified suspension.
oscillations and effective decoupling of vertical and torsional modes results in a very low level of residual noise in the output current of the photocell. Under ideal conditions this is equivalent to random fluctuations of only \( \pm 2 \mu \text{gms} \) in the total force on the balance. In practice drifts in the thermomolecular forces on the suspension and a small temperature dependence in the characteristics of the elinvar spiral limit the accuracy of force measurements to \( \pm 10 \mu \text{gms} \).

**Modification to the suspension**

The total magnetic force, \( F_m \), measured by the balance comprises two contributions

(i) the force on the specimen, \( F_s \)

(ii) the force exerted on the specimen holder, suspension link and balance mechanisms, \( F_o \)

thus: \( F_m = F_o + F_s \)

The errors arising in \( F_s \) due to uncertainty in \( F_o \) are minimised by arranging for this correction to be relatively small and temperature independent.

The original design (fig.(2:2)c) utilises a quartz sample holder, keyed directly onto the lower end of the quartz suspension link. The value of \( F_o \) was large (\( \sim 1 \text{dyne at maximum field} \)) and showed a temperature dependence of \( \sim 20\% \) between room temperature and 2K due to the presence of paramagnetic impurities in the quartz.

The modification (fig.(2:2)b) involved shortening the copper link between the spiral and the top of the quartz rod,
raising the latter by approximately 10 cms. The quartz bucket was replaced by a loop of fine aluminium wire from which a rigid aluminium suspension link of 10 cm. length is hung.

A blank run (i.e. no sample) established the new field dependence of $F_o$. This is shown in fig.(2:3). The magnitude is reduced by a factor of five compared to its previous value, and there is no significant temperature dependence between room temperature and 4.2K.

At room temperature the result of changing the vertical position of the suspension, (with the magnet current constant), was to change $F_o$ by approximately 1% per mm. Subsequent uncertainty in the position of sample and suspension is less than 0.5 mm., consequently the correspondingly small adjustment of $F_o$ is not significant and may be neglected.

A further advantage of the present arrangement lies in the fact that a much larger specimen may be accommodated within the apparatus. This allows an increase in the signal to noise ratio of about ten, which was essential to the measurement of the weak temperature dependence of the force in the case of the $\text{Cu}_{1-x}\text{Al}_x\text{Fe}_{0.05}$ alloys.

Calibration of the magnetic field.

An inhomogeneous magnetic field was provided by an electromagnet in conjunction with a constant current power supply controlled externally by a resistor network described elsewhere (135).

The size of the sample is limited by the dimensions of
the copper end-cap ($\phi \sim 10$ mm). Adequate clearance was ensured by machining the niobium field calibration sample into the form of a solid cylinder of 12.2 mm. length and diameter 4.5 mm. This cylinder was then hung from the final suspension link by means of a small aluminium loop, located in a groove to prevent the sample slipping out during the course of an experiment.

The position of the magnet was adjusted so that the axis of the cylinder lay along the $z$-axis (fig. (2:2)d). The vertical force on the sample was then measured as a function of the position, $Z_c$, of its centroid, for various fixed magnet currents.

We observe

(i) the position for maximum force, $Z_c$, is independent of magnetic current.

(ii) a displacement of 1 mm. from $Z_c$ reduces the force by approx. 0.4%.

Provided the magnetic susceptibility of the sample has one unique value through its volume, namely $X_g$ emu/gm, the total vertical force, $F_z$, may be written exactly as

$$F_z = m X_g I$$

where

$$I = \frac{1}{V} \int_{\text{CYLINDER}} H_x \frac{\partial H_x}{\partial z} + H_y \frac{\partial H_y}{\partial z} + H_z \frac{\partial H_z}{\partial z} \, dv$$

and $V$ is the volume of the cylinder (using $F = (\mathbf{M} \cdot \nabla) \mathbf{H}$ and $\text{curl} \mathbf{H} = 0$, see next section).

With the niobium cylinder positioned at $Z_c$, $F_z$ was measured as a function of magnet current and the corresponding
values of the integral evaluated taking $X_g = 2.34 \times 10^{-6}$ emu/gm. (137) for pure niobium. The maximum force exerted on this sample was 45 dynes. A palladium sample of similar geometry showed no lateral deflection until the force reached ~60 dynes. The critical force for lateral instability (138) in the sample for this balance would appear to be approx. 100 dynes. Clearly, this field calibration is only valid for subsequent samples of identical geometry positioned at $Z_c$.

For points near the z axis the latter two terms in the integral are relatively small and, from the point of view of data analysis, it is convenient to write the integral in the form

$$I = H_x^c \left( \frac{\partial H_x}{\partial z} \right)_{EFF}$$

2:(2)

$H_x^c$ is the component of magnetic field along the x direction at $Z_c$, the centroid of the sample. This field (maximum value 7.5 kOe) was measured directly using a Hall probe gaussmeter (Bell type 620 which had previously been checked against an NMR probe (error 0.1%) $\left( \frac{\partial H_x}{\partial z} \right)_{EFF}$ is a measure of the effective field gradient experienced by the specimen as a whole and is defined by eqn.2(2). Examination of the dependence of $\frac{F_z}{\left( \frac{\partial H_x}{\partial z} \right)_{EFF}}$ on $H_x$ enables a correction for the effects of ferromagnetic contamination of a sample to be made in the normal way.

Temperature measurement.

(i) Radiation heating.

Any thermometer mounted directly on the sample itself
would interfere with the force measurement, directly through frictional forces in the connecting leads and, indirectly, through its own magnetisation.

Thermometers are therefore attached to the end-cap, fig.(2:2)a, and the sample maintained in thermal contact with it through the presence of a heat exchange gas in the suspension tube. Normally about 1Torr of pure helium is admitted for this purpose. In the present balance the sample is partially shielded from energy radiated from the upper (warmer) parts of the suspension tube by a lead foil wrapped around the suspension about 15 cms. from its lower end - initially placed there to reduce lateral deflections of the suspension. Even so measurements on a Au + 0.3 at.% Cd alloy by Dunlop (136) indicate that the sample is some 0.3K warmer than the end-cap due to radiation heating.

(ii) Thermometry.

Initially the temperature of the copper end-cap (fig. (2:2)a) was measured using a Au + 0.03 at.% Fe vs. Chromel thermocouple (TC 1) referenced to 273 K by means of an ice bath. The thermocouple cold junction was moved from its original position above the cone joint onto the end-cap itself, at the same level as the specimen. Since changing the sample meant the removal of this cap, the junction was attached using GE 7031 varnish. This ensured a good thermal contact which was easily demountable using a mixture of equal parts toluene and ethyl alcohol to dissolve the varnish.

For the measurements in the temperature range 2K to 30K performed on the ZnCr alloys a further Au - 0.03 at.% Fe vs.
Chromel thermocouple (TC 2) was added (fig.(2:2)a). The junction between the component wires were made by first tinning the Chromel wire with silver solder and then using a low melting point solder to join on the gold-iron wire. The wires were then twisted together and carefully wound around a thin walled plastic straw, using GE varnish to hold them in position. The straw slotted into a small nut soldered to the base of the end-cap, and ensured that the reference junction was held at the very bottom of the helium dewar, as well as preventing the thermocouple being strained when the dewars were lifted into position. The upper junction was fixed to the end-cap, again at sample level, using more varnish. The differential thermocouple e.m.f. was fed to the input of a DC voltage amplifier (x 1,000) via two twisted 42 swg copper wires, thermally anchored to the German silver downtube. Errors due to temperature differences between the two copper junctions to the thermocouple were eliminated by winding them both on a single piece of 16 swg enamelled copper wire, located a few cms. above the cone joint.

A 1 watt heater, was conveniently positioned by taping it about 3 cms. from the lower end of the straw.

(iii) Thermometer calibration.

The output of TC 1 was measured relative to the icepoint, with the sample junction held at 4.2K and also 77K. A calibration was obtained by comparing these values with those tabulated by Berman (supplied to A.M. Stewart) and applying a small linear interpolation on the differences.

The output of TC 2 was converted directly to the
equivalent temperature using data again due to Berman (139).
For temperatures between 4.2K and 20K the temperatures
indicated by the two thermocouples differed by no more than
0.2K.

Experimental procedure.

The cone joint was first demounted, thus exposing the
previous sample, and degreased using carbon tetrachloride.
The new specimen was then hooked onto the end of the suspension
and adjusted to hang with its axis vertical.

The magnet was then wheeled into position and the exact
location of the specimen at the field calibration point \( Z_0 \),
executed using a standard procedure, adopted to maximise the
reproducibility of the positioning technique. The probable
error in any one co-ordinate of the sample centroid is about
\( \pm 0.5 \) mm. (In practice this was found to introduce an error
of \( \pm 3\% \) into the absolute value of the specimen magnetic
susceptibility).

After noting the position of the magnet, it was wheeled
away and the cone joint reassembled using high vacuum silicone
grease. The thermocouple junctions are then varnished to the
end-cap, exchange gas introduced into the suspension tube and
a check made that both sample and suspension hang freely
within the downtube. The dewars are raised into position and
the magnet relocated.

Force measurements were obtained over the whole tempera-
ture range 1.7K - 300K in two stages :-

(i) Nitrogen run.

Force measurements were obtained at all nine calibrated
settings of $H_x$ at room temperature, and temperatures in the range 77K - 64K (Stewart (140) reports large temperature gradients in the nitrogen bath at temperatures below the triple point). The temperature was stabilised ($\pm$ 0.01K) by pumping on liquid nitrogen using a diaphragm manostat to control the pressure. Intermediate temperatures were stabilised ($\pm$ 1K) sufficiently to enable a measurement to be made at fields of 5.64 kOe, 6.72 kOe and 7.41 kOe at each temperature.

(ii) Helium run.

Temperatures in the range 4.2K to 1.7K were stabilised by pumping on liquid helium, again using a manostat, thus enabling the full field dependence of the force to be obtained. Between 4.2K and 20K the temperature could not be stabilised and consecutive pairs of measurements were made at 5.64 kOe and 7.41 kOe as the temperature rose at an ever increasing rate. The susceptibility (in this field range) as a function of the temperature was then interpolated from the two sets of force data. Above 20K the temperature rises too quickly for meaningful measurements of the force to be made.
2.2 COMPARISON OF TECHNIQUES AVAILABLE FOR THE DETERMINATION OF MAGNETIC SUSCEPTIBILITY.

The various methods available for the direct measurement of magnetisation fall into two principle categories, (i) those involving the measurement of the force experienced by a specimen placed in an inhomogeneous magnetic field. (ii) those involving the measurement of the change in the magnetic induction in the region of a specimen placed in an homogeneous magnetic field.

Force methods.

A magnetic moment at a point in a region of inhomogeneous magnetic field will experience a force

\[ F = (M \cdot \nabla) H \]

where \( M \) is the magnetic moment, permanent or induced, and \( H \) is that part of the field not caused by the moment (141).

The two principle methods used are the Faraday and the Gouy methods.

The Faraday sample, generally, is small enough that the field may be considered uniform over its volume and for positions along the z axis (fig. 2.4a) the only non-zero component of the force is

\[ F_z = M_x \frac{\partial H_x}{\partial z} \]

For an isotropic sample of mass \( m \), and susceptibility, \( \chi_g \, \text{emu/gm} \),

\[ M_x = m \chi_g \frac{H_x}{1 + 4\pi D \chi_g} \]
For weakly diamagnetic or paramagnetic specimens the demagnetisation is negligible and

\[ F_z = m \chi g H_x \frac{\partial H_x}{\partial z} \]  \hspace{1cm} 2:(6)

\( \chi \) is the susceptibility. The Gouy specimen is sufficiently long for \( \left( \frac{H_2}{H_1} \right)^2 \ll 1 \) (Fig. 2:4b). If it has uniform cross section \( A \) and susceptibility \( \chi_v \) emu/cc. which is field dependent, then eqn. 2:(6) may be integrated to give

\[ F = \frac{\chi_v}{2} A \left( H_1^2 - H_2^2 \right) \approx \frac{\chi_v}{2} A H_1^2 \]  \hspace{1cm} 2:(7)

Although sample positioning is less critical for the Gouy method (Fig 2:4) there are several factors which render it unsuitable for measurements on metallic alloys:

(i). difficult to evaluate results when \( \chi = \chi(H) \)

(ii). not always possible to fabricate a specimen \( \sim 10 \) cm. long which is uniform in composition and density along its length.

(iii). a large isothermal specimen chamber is required.

In the Faraday method the product of field and field gradient is most easily found by measuring the force on a sample of known susceptibility and standard geometry, placed at the point in the magnetic field where the vertical force
is maximised and forces in lateral directions are zero; the
method is thus essentially comparative. Small errors in the
positioning and geometry of subsequent samples will lead to
an error in the susceptibility measured, to an extent dependent
on the field profile in the region of the sample. (For a full
discussion of positioning errors and lateral stability of the
sample the reader is referred to (140).) Optimum design of
electromagnet pole pieces to provide a large volume of constant
$H_x \frac{\partial H_x}{\partial z}$ are discussed in refs. (143), (144)
and (145).

With a given magnet system and sufficient isolation of
the apparatus from sources of vibration the sensitivity of the
Faraday method is limited by that of the force detection, and
also the mass of the sample. Previously, many techniques have
been used, (see for example Sucksmith (146), Hutchinson and
Reekie (147), Griffiths (133), Gerritsen and Damon (148)
but more recently (Morris and Wold (149), Delby and Elkstrom
(150)) automatic vacuum microbalances have been adapted and
a sensitivity of $10^{-10}$ emu/gm. achieved.

The force is measured in a steady field with the sample
stationary, however in order to subtract the forces due to
other than magnetic origin the field must be swept to zero.
For specimens of low resistivity the currents induced may lead
to serious over-damping of the balance making accurate force
measurement difficult if not impossible. Where the force
measuring system maintains the sample at a constant position
via a feed back system (e.g. automatic microbalance) no such
problem arises.
Induction methods.

Measurements of the susceptibility based on a determination of the mutual inductance of a system of coils containing the specimen (151) require the use of an AC magnetic field of frequency typically 100 Hz. This proves a major limitation where alloys of low impurity concentrations and consequently high conductivity are concerned because of the effects of eddy currents. (e.g. Zn + 10 at.ppm. Cr has skin depth ~3mm. at 100 Hz.)

Deaver and Goree (152) and Hirschkoff et al. (153) make use of a superconducting flux transformer whose primary is in the form of a pair of nearly identical coils connected in series opposition ('astatic pair'). This arrangement reduces spurious variations in the flux linked to the secondary due to temporal fluctuations in the magnetising field, magnetic disturbance from external sources or small vibrations of the primary coil itself.

In the first method, fig.(2:5)a, the flux linked to the secondary coil $L_3$, $\Delta \Phi$ is due to moving the specimen from $L_1$ to $L_2$ in the presence of uniform field $H$ Oe. The necessary stability is provided by using a superconducting solenoid capable of fields up to 40 kOe operated in persistent current mode. $P$ is a superconducting modulator in the form of a small tin rod. When this is heated and cooled periodically through its transition temperature the variation of flux in $C$ causes an alternating voltage, $V_c$, to appear, which is proportional to $\Delta \Phi$. The initial flux change at the primary may be compensated by coil $B$, thereby reducing $V_c$ to zero, whereupon the current through $B$ is a direct measure of $\Delta \Phi$ and thus of
the magnetisation of the specimen. The resolution is primarily limited by the degree of isolation from external magnetic disturbances which can be achieved. Making use of superconducting shields and a ferromagnetic flux return path for the solenoid the authors report $10^{-10}$ emu/gm., due mainly to irregularities in the switching of the modulator. This would be equivalent to field fluctuations of only 100 microgauss amplitude at the primary.

Hirschkoff's method, fig.(2:5)b, is particularly suited to measurements in the millidegree region, since only very small quantities of energy are dissipated in the specimen. A niobium cylinder surrounds the primary with the dual purpose of trapping an extremely stable magnetising field and providing shielding for the sample coil from external magnetic fluctuation. Changes in the magnetisation of the specimen (at constant field) due to changes in its temperature result in flux changes in the primary coil. The corresponding flux changes at the secondary, located in one hole of a symmetric SQUID, (Superconducting Quantum Interference Device) are cancelled by the action of a feedback circuit which is capable of maintaining the flux through the SQUID to approx. $10^{-2} \Phi_0$ ($\Phi_0$ is the flux quantum = $2.1 \times 10^{-7}$ gauss cm$^2$). Changes in the feedback current are thus proportional to changes in the magnetisation of the sample. The 'astatic pair' allows the device to be used as a differential magnetometer of asymmetry $\sim 1\%$, thus by placing an identical shaped specimen of the pure host metal in the second half of the primary, the contribution to the susceptibility due solely to the magnetic impurity of a dilute alloy may be directly measured.
**Fig. 2.5a** Induction method after Draver and Goree (152)

**Fig. 2.5b** Induction method after Hirschkoff et al. (153)
The actual value of the trapped field may differ by as much as 20% from that above the superconducting transition, but by following an identical procedure in each experiment a rather reproducible field may be generated. Changing the field, of course, requires that the niobium shield is heated beyond its transition temperature. Since the total trapped flux must remain constant, the presence of the sample will itself change the incident magnetising field, though the effect may be neglected for small weakly magnetic samples (154). The sensitivity of the system is approx. \(10^{-6}\) emu in the total susceptibility of the specimen.

Bissell and Sandiford (155) also use a method employing a SQUID to measure directly small changes in flux, in this case due to lowering the specimen into the primary of the flux transformer in the presence of a magnetising field of approx. 1 Oe provided by a superconducting solenoid. The susceptibility of brass is measured to a precision of 10% i.e. about \(10^{-8}\) emu/gm.

Several magnetometers of the vibrating coil or vibrating sample type have been described, (Smith (156), Kaeser et al. (157), Arrot and Goldman (158), Foner (159) and Murani (160).) The general method is to detect the AC voltage induced in a detection coil due to oscillatory relative motion between the magnetised sample and the coil. The vibrating sample method has the intrinsic advantage of limiting the induced voltage due solely to non-uniformities in the applied field to that arising from sympathetic vibration of the detection coil as a result of insufficient mechanical decoupling from the sample support (159)(160). This
synchronous pick-up may be further limited by using a series opposed pair for the detection coil. Measurements on samples of high conductivity are complicated by the effects of induced currents in the sample (158) (159).

The vibrating coil technique may be used in preference at very low temperatures (< 0.3K) where energy dissipated and reaching the sample as a result of small vibrations can cause a serious increase in its temperature (157). Eddy current problems also disappear in this arrangement. Both Kaeser and Foner claim sensitivities as high as approx. 10^{-10} emu/gm. in a field of 10 kOe.

A null technique is made possible by winding a small coil directly around the sample (158), (160). A DC current is passed through the coil to cancel the magnetic moment of the specimen whereupon the induced voltage at the detection coil is zero and the current is a direct measure of the magnetisation. An advantage is that the position of the sample w.r.t. the detection coil is not now critical, although the specimen must be reproducibly positioned within the nulling coil. Murani obtained reproducibility of a given specimen after removal and replacement of 0.5% and an overall sensitivity approaching 10^{-9} emu/gm. The total magnetisation of the sample must be small enough that the nulling current does not cause any significant heating of the sample.

McGuire (161) describes an automated induction magnetometer in which the specimen is slowly (~5 secs.) moved between two series opposed detection coils in the presence of the magnetising field. The voltage so induced is integrated to provide a direct measure of the magnetisation of the specimen.
The effect of spurious AC voltages of frequency $\geq 1$ Hz is lessened by the integration process, but the motion of the specimen, particularly its end-points, must be very reproducible if small changes in the specimen magnetisation as the temperature is varied are to be followed. End-points chosen to maximise the total flux change will minimise sensitivity to subsequent positional errors.

These problems are eliminated in the "very low frequency vibrating sample magnetometer" method described by Foner and McNiff (162). The amplitude of the oscillation ($T \approx 1$ sec. - 10 sec.) is sufficient to take the specimen beyond the centre of each half of the detection coil, and the integrated voltage is displayed on an X, time plotter. The maximum total flux change under given conditions of temperature and field is then readily observable and errors due to drift in the integrator circuit are also eliminated. The smallest detectable change in the susceptibility by such flux integration technique is approx. $10^{-8}$ emu/gm.

Clearly the most suitable technique is a function of

(i). the objectives of the measurement.

(ii). the nature of the specimen.

In this work the prime aim is to obtain precise measurement of the temperature dependence of the contribution of small concentrations ($< 100$ at.ppm.) of magnetic atoms to the total magnetic susceptibility of an alloy.

This requires:

(i). measurement of magnetisation (in fixed field) to the highest possible resolution as the temperature is raised.
(ii). measurement of the magnetisation (at fixed temperature) to similar resolution as a function of field to avoid errors due to Brillouin curvature.

(iii). high relative accuracy between samples, enabling the host contribution to be measured separately and subtracted from the total susceptibility of the alloy.

The specimens are characterised by:

(i). low resistivity $\rho \ll 0.5 \, \mu\Omega\cdot\text{cm.}$ at 4.2K

(ii). weakly magnetic $|\chi_g| \ll 10^{-7} \, \text{emu/gm.}$

(iii). machinable or cast to desired geometry.

The Faraday technique is capable of the highest resolution ($10^{-10} \, \text{emu/gm.}$) and measurements are easily made as a function of field without the need for elaborate magnetic screening or extremely stable fields. The highest field is limited only by the magnet system employed. The use of an automatic microbalance also means that the low resistivity of the alloys does not present any problem. The reproducibility of the data due to positional errors may be reduced to $\ll 0.5\%$ by careful design of the magnet system.

An important advantage of the Faraday method lies in its relative simplicity, given the range of commercial microbalances now available (Cahn, Sartorius, Beckman) we have only to assemble a suitable magnet/dewar system and provide an isothermal chamber in which to suspend the specimen.
Introduction

The main features of this newly constructed apparatus are:-

(i) automatic measurement of the force on the sample by a commercial microbalance.

(ii) provision of the necessary inhomogeneous magnetic field by a superconducting solenoid, constructed with two independent windings, one providing a uniform field, the other providing a uniform field gradient within the field volume.

(iii) a stainless steel cryostat, including an insert dewar, which provides a 4.2K bath for the magnet, but still allows regulation of the temperature of a specimen placed in the field volume. An internal transfer of liquid helium from the bath into the insert is effected by means of a needle valve and capillary.

(iv) a facility for changing samples under operational conditions.

In a typical run, lasting 48hrs. and consuming 25l. of liquid helium, one might measure the magnetisation of up to six samples, in a maximum field of 50kOe and in the temperature range 1.3K to 300K.

The smallest resolvable change in the force ($10^{-3}$ dyne) corresponds, for a lgm. sample in a field of 10kOe and maximum field gradient, to a change in the magnetic susceptibility of $10^{-10}$ emu/gm.
The balance.

An electronic microbalance (Beckman-Riic LM600) is used to measure the magnetic force on the sample.

The balance beam, attached to the restoring coil is supported by a torsion ribbon so that the coil rotates between the poles of a permanent magnet. A mirror fixed to the beam reflects light from a lamp onto a pair of photocells, connected in opposition. Any rotation of the beam results in a net photocell output which is roughly proportional to the out of balance torque. An opposing torque is automatically provided by amplifying the photocell output and feeding the resultant current back through the restoring coil. At equilibrium the electromagnetic torque is equal and opposite to the applied torque and the standing current in the coil requires only a very small deflection of the beam from its unloaded position because of the high gain of the feedback loop. The restoring current develops a potential drop across a pre-set resistor which is measured either by an internal potentiometer coupled to a duodial on the control unit, or externally by a digital voltmeter. In the latter mode the force on the scalepan may be directly, and continuously, displayed, making the change in the force due to application of the magnetic field particularly easy to measure.

The noise component in the voltage output from the preset resistor is reduced at the expense of increased response time, by a capacitor connected in parallel to the resistor. An x-t plotter was used to observe the response at the balance output when the calibrating weight (see below) was dropped onto the scalepan. The output filter used (filter 3...
as indicated on control unit) reduced the noise to \( \pm 1 \mu \text{gm.} \) under favourable conditions and resulted in a response time of \( \sim 5 \text{ secs.} \)

With the 10mg. range selected, a differential pan loading of \( 1\mu \text{gm.} \) will correspond to a change in the voltage drop across the preset resistor of 10 \( \mu \text{V} \). The balance is capable, on this range, of a linear output for differential pan loads up to 300mg. (3v drop across the resistor) but the range of the D.V.M. (Dana model) limits the maximum force which is resolvable to \( 1\mu \text{gm.} \), at 20mgm. The total beam loading of the balance must not exceed 20gms.

Fig.(2:6) shows the balance platform with the microbalance head in position. The microbalance stands on three spherical feet located in V-shaped grooves machined in short pegs fixed to the balance plate. Secure mounting is ensured by two padded aluminium clamps. A rubber "O" ring provides the vacuum seal between the platform and the clear perspex housing which is also clamped in position. This housing, together with the suspension tube may be evacuated and filled with exchange gas via one of the pumping ports located on the underside of the plate. The draught shields provided with the microbalance are not required and their removal allows for easy access to the beam and stirrups.

Each stirrup was originally constrained to be approximately normal to the beam by the action of the stray field of the permanent magnet in the microbalance head on a small ferromagnetic pin attached to the stirrups. These were removed to avoid the possibility of spurious forces due to the stray field of the solenoid at the pin. A fine aluminium wire (42swg)
Fig. (2:6) BALANCE PLATFORM ASSEMBLY
FIG (2:7) MODIFICATION
TO SCALEPAN AND STIRRUP

Fig (2:8) SUPERCONDUCTING SOLENOID
glued to each extremity of the beam performs the same function as the pins fig. (2:7). A check was made that no errors are introduced by the stirrup resting against this wire, although in practice this very rarely occurred and the stirrups hung freely in the correct position.

The hooks from which the sample suspension and the counterweight are hung pass through a 1mm. diameter hole drilled in the centre of each scalepan. The spherical solder blob at the top of the 30swg constantan wire rests on the floor of the scalepan and provides a non-rigid attachment to the latter. The counterweight hook hangs through a \( \frac{3}{8} \)\" diameter hole in the plate and is accessible by removing the glass tube which is sealed with 'pycene' to a short copper tube soldered into a standard \( \frac{3}{4} \)\" Edwards vacuum fitting. The sample suspension hook also passes through a \( \frac{3}{4} \)\" aperture and is just long enough for the hook to lie approx. lcm. below the end of the copper bellows which form the upper section of the demountable joint between the balance housing and the suspension tube.

A relay lowers a known mass of platinum wire (14.558mgms.) onto the scalepan, thus allowing the balance to be calibrated at any stage during the run. The relay is energised externally via a nine pin seal in the balance platform, which also provides the connection between the microbalance head and the control unit. A check was made that no errors were introduced due to the stray magnetic field of the relay.

In practice the balance proved very stable and the calibration drifted by less than one part in a thousand during
the course of a run.

**The balance platform.**

Since the position of the magnetic field centre is fixed relative to the suspension tube, we must be able to make precise adjustments (~±0.1mm.) to the position of the microbalance head in order to correctly locate the sample, and also to avoid contact between the suspension and the inner wall of the suspension tube.

The balance plate is bolted to the top flange of the inner of two concentric brass cylinders. A screw allows the inner cylinder to be moved in the vertical direction with respect to the outer cylinder, and a close fit between the two prevents the balance plate from rocking out of the horizontal plane. The relative vertical height is indicated to ±0.01mm. on a dial gauge D, fig. (2:6).

The outer cylinder is fixed to a horizontal aluminium plate, P1, which rests on 2 P.T.F.E. rods (2mm. diameter) located in grooves machined in the top of an aluminium frame P2. By turning screw S1, P1 moves relative to P2 along the horizontal direction in the plane of the diagram, and scale Al indicates their relative position.

The aluminium frame, P2, may be rolled smoothly along the horizontal direction perpendicular to the plane of the diagram on roller bearings (3 in all) running along two horizontal parallel hardened steel rods, R1 and R2. The rods are each mounted on lugs welded to the main supporting frame, and clearly bear the whole weight of the balance platform assembly. Small adjustments to the position along this
direction are made using a screw S2 and observed on a scale similar to A1 (but not shown) fixed to the side of the platform. Once positioned along the rods, the platform may be clamped so that no further movement is possible. When a specimen is withdrawn from the apparatus the whole platform assembly may be rolled well clear of the suspension tube, enabling the withdrawal of the suspension from above (see later).
The superconducting solenoid.

A cross-sectional view of the solenoid is shown in fig.(2:8). The two independent windings are each wound using a multifilamentary superconductor which contains 61 filaments of Nb-Ti (approx 50at.%) superconducting alloy extruded within a high purity copper matrix. The overall diameter of the wire is 0.5mm. and the area ratio of superconductor to copper is about 1.3:1.

The copper matrix serves two main purposes (163)

(i) provides a large thermal mass to absorb the heat liberated during 'flux jumps' which occur as the current in the solenoid is being swept up. The probability of a premature quench due to thermal runaway is thus reduced.

(ii) in the event of the magnet quenching, the current is diverted into the low resistance path provided by the copper, so protecting the windings from damage due to the large interlayer voltages which would otherwise arise.

a) Main field winding.

This winding has an inductance of 0.7 Henries and comprises a main section (MM) of 5984 turns in series with two correction coils each of 414 turns, CC and CRC. Both the field profile fig.(2:9) and the field rating of 523 Oe/Amp. (± 0.2%) are computed from the coil geometry and supplied by B.O.C. Ltd., who check the field/Amp calibration using a cryogenic Hall probe (Siemens). The quench field (with gradient coils energised to 1000 Oe/cm.) is approx 49 kOe.
Fig. (2.9) MAIN FIELD PROFILE
The main field winding may be operated in the persistent current mode, thus reducing the helium boil off due to the current leads and allowing the power supply to be disconnected. The persistent current heat switch is in parallel to the main winding and is wound, together with the 100mW heater, around a nylon post situated at the top end of the solenoid former. A field decay of less than 1 part in $10^{10}$ per sec. has been reported (152) for solenoids operated in the persistent mode, but in the present case a decay of 1 part in $10^5$ per sec. was observed for fields of 30 kOe, being worse at higher fields. This is probably due to a small (about 1 ohm) resistance in the joints between the persistent current switch and the solenoid winding. The normal state electrical resistance of the switch is 2 ohm. A thyristor (mounted onto the underside of the main bath top plate) is connected in parallel with the persistent current switch and protects it from damage due to the large inductive voltages which would otherwise occur between the end of the main field winding in the event of power supply failure or accidental disconnection of the external current circuit whilst the solenoid is energised. In the latter case it also protects the operator.

b) Gradient field winding.

A pair of series opposed coils, AA and A'A' (anti-Helmholtz pair), each consisting of 743 turns produces a field of the form $Gz^2$ where $Z = 0$ is the centre of symmetry for the main field. The magnetic field gradient, $G$, is linear to within 0.3% over the 20mm. diameter sphere centred at $Z = 0$ and is produced at the rate of 11.87 ($\pm$ 0.2%) Oe/cm. per Amp
flowing in the gradient field winding. The critical current (84Amps) corresponds to a maximum attainable field gradient of approx. 1 kOe per cm. Once again the discharge rate is limited by a 1 volt constraint imposed by a thyristor connected in parallel with the winding.

c) Solenoid performance.

During the measurement of the force on a specimen in a given field, it is necessary to record the force, $F_0$, due to the main field only, both before and after measuring the force, $F_T$, when the gradient field is swept up to its chosen value. Each time a new main field value was set, the first cycling of the gradient field resulted in a change in $F_0$ which was larger than could be explained in terms of the steady drift in $F_0$ before cycling the gradient field. The change in $F_0$ is only 2 or 3 per cent of $F_T - F_0$ but is significant especially at high fields or when strongly magnetic samples are being measured. The second and successive cycling of the gradient field produces no systematic change in $F_0$.

The cause of this effect is not understood, although it may be possible that some small redistribution of the current in the main field winding takes place when the gradient field is energised for the first time. During the course of all the measurements reported here, the gradient field was always cycled once before taking the value of $F_T - F_0$.

d) Power supplies.

The current to the main field winding is supplied by a
B.O.C. 100A supply (type FS 100A). The DC current is stabilised to better than 1 in $10^3$ over one hour, no effects attributable to a ripple imposed on the magnetic field were ever observed. A built-in electro-mechanical sweep unit enables the current to be raised or lowered between zero and a preset value over a predetermined period ranging between 1 min. and 100 mins. In the event of a magnet quench a voltage trip circuit automatically switches off the supply.

The relationship between the current output and the helipot setting was investigated by recording the potential difference across a 0.01 (50A) standard wire-wound resistor. In this range (0 - 50A) the current was a linear function of the helipot setting to at least 0.01A (the limit of resolution of the helipot). The absolute value of the current output was, however, 0.25% higher than indicated and in addition there was a current offset of + 68mA at all currents, which corresponds to an additional magnetic field of 36 Oe for the main field winding.

The magnetic field was found to be a linear function of the current in the main coil to better than 0.1% (10kOe - 50kOe) by measuring the magnetisation of a pure Al specimen (resistance ratio = 5000). The absolute value of the susceptibility was found to be 3% more paramagnetic than observed by Hedgecock and Li (70), but low field curvature indicated the presence of a small amount of ferromagnetic impurity in the Al.

A current supply capable of 20A output was constructed to energise the gradient field winding, the circuit diagram is shown in fig.(2.10). The drift in the current was 2 parts in $10^3$ over a period of 10 mins.
A manganin strip in series with the external current circuit serves as the feedback resistor and its surface area is such to allow 10 sq. cms. per watt dissipated at maximum current (J. Good private communication). The manganin potential leads are spot welded to the strip to minimise spurious thermoelectric emf's in the feedback voltage (100mV @ 20A). The reference voltage (and hence the output current) is adjusted manually using the wire-wound potentiometer, P.

Most of the measurements were in fact made using a stabilised current supply kindly loaned to the author by Dr. J. Good. An electronic voltage sweep unit enabled the current to be raised to a preset value (100A max.), in a highly reproducible fashion (better than 2 parts in $10^4$). The current was monitored by measuring the voltage drop across an internal shunt, which was calibrated for currents up to 50Amps by comparison with the $0.01\Omega$ standard.
Fig.(2:10) 20A CURRENT SUPPLY
Fig. (2:11) SCHEMATIC DIAGRAM OF APPARATUS

- Balance Head
- Balance Platform
- Support Frame
- Over Pressure Safety Valve
- Top Plate
- Radiation Shield
- Hg Level Detector
- Current Lead Guides
- Insert Dewar
- Copper Heat Exchanger
- Main Bath Heater
- N₂ Level Detector
- Radiation Plate
- Interspace
The Cryostat

The main dewar, with the insert dewar and solenoid in position is shown in fig.(2.11). The liquid nitrogen jacket and liquid helium vessel are of integral construction and share a common vacuum interspace. The interspace is periodically pumped to a pressure of \(2 \times 10^{-6}\) Torr through the pump-down boss located on the side of the cryostat. A 77K radiation shield, fixed to the lower rim of the nitrogen jacket prevents 300K radiation from being directly incident onto the base of the helium vessel.

The main bath top-plate, seated on a rubber "O" ring seal, provides support for both the solenoid assembly and the insert dewar.

Insert dewar

The use of an insert dewar is the standard method for providing a thermally isolated region in which the experiment may be performed, within the bore of an operational superconducting solenoid. In this particular apparatus it houses the suspension tube and sample chamber. The insert dewar support flange is bolted onto an "O" ring seal, where the dewar passes through the top plate, the dewar itself hanging vertically with its tail end inside the solenoid bore.

The capillary (~1mm. diameter) indicated in fig.(2.12), bridges the interspace of the insert dewar and allows liquid helium to be syphoned from the main helium bath into the insert. When such an "internal transfer" is complete, the capillary is closed by screwing down a needle valve located on the external wall of the insert dewar interspace.
The needle point is soldered to a stainless steel link tube which may be raised and lowered by the screw mechanism located on the main bath top plate, thus opening and closing the valve. A positive action is ensured by an outer stainless steel guide tube and PTFE spacing washers along the link tube. The influx of air, which could lead to a blocked capillary, is prevented by a sliding "O" ring seal near the top of the link tube and after an initial "bedding-in" of the needle in its seat, the valve has proved completely reliable.

Initially, once the helium level dropped below that of the intake hole (see fig.(2.12)) no more liquid helium could be drawn into the insert and further low temperature measurements curtailed. However experience showed that the solenoid could be operated, at up to 50% maximum current, whilst only half submerged in liquid helium. By transferring the helium pick up point to a position half way down the solenoid casing it was then possible to extend the useful run time by 12 hours without the consumption of any more helium. This was done using a two-piece, thermally insulated extension tube, carefully soldered into the intake hole. The two sections were joined using about 5cms. of heat-shrink tubing so that the L-shaped piece was easily detachable and the insert could be withdrawn through the top plate without remelting the solder joint, thus avoiding the danger of blocking the (highly inaccessible) internal capillary. In the absence of thermal insulation, heat is conducted through the walls of the 2.5mm. diameter extension at the rate of 100 mW/cm. run/ K temperature difference, sufficient to severely reduce the efficiency of internal transfer. Thermal insulation of the
vertical leg is provided by a sealed interspace, cryopumped under operational conditions and several layers of PTFE. tape are wound around the horizontal portion. 

The solenoid assembly

The solenoid mounting studs are bolted to a rigid brass plate, which is in turn suspended from the top plate by means of four symmetrically positioned stainless steel tubes. The initial alignment of the solenoid axis parallel (±1°) to that of the insert dewar was accomplished by adjusting the mounting studs to obtain an even clearance of about 0.5mm. between the insert and the solenoid bore.

The B.O.C. current lead design is based on the work of Scott (164). The rigid brass conductor is in the form of two anglepieces soldered back to back, so that a large surface area is available for heat exchange with the evaporated helium gas. One such conductor runs down the centre of each of the four solenoid support tubes, insulated from it by a PTFE liner as shown in fig.(2.13)a. To reduce joule heating under the surface of the liquid helium the final few centimetres of brass are shorted out by a copper fly lead. The current terminals on the top plate are also connected to the brass conductor using a copper lead.

In principle the brass leads are cooled by a stream of evaporated helium, forced up the inside of the support tube by a slight overpressure due to the head of liquid helium above the lower end of the tube. In practice the surface of the liquid helium is generally below the ends of the support tubes and the cold gas absorbs very little of the heat dissipated in the brass, resulting in high boil-off levels.
Fig. (2:12) INTERNAL TRANSFER ASSEMBLY
Fig. (2:13)a CURRENT LEAD DESIGN

BRASS CONDUCTOR
COPPER BRAID 'FLY-LEAD'
PTFE TUBE
STAINLESS STEEL

Fig. (2:13)b HELIUM BOIL OFF vs. CURRENT
IN MAIN FIELD WINDING

2.0 l/hr.
at 4.2K

Boil Off Rate

25
20
15
10
5
0

l/min at N.T.P

0 20 40 60 80 100

CURRENT, AMPS.
when the solenoid is energised. The principles of current lead design and possible modifications are discussed later, and the present boil-off rate is shown as a function of the current in fig. (2.13)b

Radiation shield.

The main bath radiation shield is attached to the solenoid support tubes. It consists of a thick layer of styrofoam, sandwiched between two highly polished stainless steel discs. A central hole allows the withdrawal of the insert dewar, but is necessarily oversize to permit the platform section of the insert to be passed through.

In an effort to reduce the static boil off from the cryostat a two-piece styrofoam plug was used to close the annular gap around the insert dewar at the main radiation shield and two further aluminium radiation plates were attached lower down the support tubes.

Electrical circuits.

A nine pin sealed lead-through on the top plate provides electrical access to the main bath circuitry.

This includes the heater for the persistent current switch in the main coil winding of the solenoid, the main bath heater and the liquid nitrogen detector.

The pre-cooling procedure for the solenoid requires the transfer of liquid nitrogen into the main bath (see later). Much of this nitrogen may be "blown-out" but perhaps ½l. is left below the level of the end of the blow out tube and must be boiled away using the main bath heater.

The main bath heater consists of six 6 watt wire-wound 22A resistors mounted on a dished circular copper sheet
(0.01" thick) which is located at the bottom of the main bath beneath the tail of the insert dewar (see fig.(2.11)). Current is supplied via 36swg manganin wire by a 50v DC supply.

The liquid nitrogen detector, which is in fact an OA-95 point contact diode, is attached centrally to the underside of the copper heater disc and so rests at the lowest point of the main bath.

The V-I characteristics of the diode under reverse bias conditions were measured with the diode submerged in liquid nitrogen (IN), and also a few millimetres above the surface (OUT). These are shown in fig.(2.14)a. When the current exceeds 20mA the low thermal conductivity of the vapour as compared with the liquid environment results in a relatively much higher diode temperature at thermal equilibrium. This increase in temperature results, at constant current, in a reduced voltage drop across the diode when it is raised above the nitrogen liquid surface. The rate of transition between the IN and OUT equilibrium states increases with the power dissipated in the diode. $T_{\frac{1}{2}}$ was measured as being the time required for the voltage drop to change from $V_{IN}$ to $\frac{V_{IN} + V_{OUT}}{2}$ and is shown as a function of the standing current through the diode. In practice $I_0 \approx 80mA$ is a convenient current and the diode gives a clear indication of the presence or otherwise of liquid nitrogen in the main bath.

This current was provided by a Minireg constant current supply, the output voltage of which was monitored by a digital voltmeter.
The liquid helium level in the main bath (and also the insert dewar - see later) was conveniently monitored by a set of 9 carbon resistors (Allen Bradley nom. 110Ω miniature) mounted at strategic heights in the main bath on a vertical copper nickel tube passed down through the vacuum sealed, 1 cm. diameter access port in the top plate.

As in the case of the diode, and for similar reasons, when the power is dissipated internally is sufficiently high (\( \approx 60\text{mW} \) i.e. \( I \geq 15\text{mA} \)), as the carbon resistor emerges from the liquid helium its resistance falls due to an increase in its internal temperature. The variation of the voltage drop when \( I = 30\text{mA} \) is shown in fig.(2.14)b. The IN resistance of \( \approx 200\Omega \) corresponds to an internal temperature of about 20K, and the voltage change takes place over a distance comparable to the dimension of the resistor normal to the liquid surface.

The circuit shown in fig.(2.15) is used to check the IN/OUT condition of each of the depth gauge resistors. TR1 provides a standing 15mA current which is switched to flow through the appropriate resistor. The voltage drop, \( V_R \), is applied to the base of TR 2. A zener diode and potential divider provides a steady voltage \( V_Z \approx \frac{V_{IN} + V_{OUT}}{2} \) to the base of TR 3.

If the depth gauge is below the helium surface, \( V_R = V_{IN} \) which is \( > V_Z \), hence only TR 2 conducts and the green indicator bulb is lit. If the resistor is above the surface \( V_R < V_Z \), TR 3 conducts and the red indicator bulb is lit.
Fig. (2:14) a Liquid Nitrogen Detector Characteristics

Voltage drop volts

I = 30 mA

Fig. (2:14) b Liquid He Detector Characteristic

Position, mm.
Fig. (2:15) LIQUID HELIUM LEVEL DETECTOR CIRCUIT
Suspension tube assembly.

The suspension tube assembly comprises of two concentric stainless steel tubes as shown in fig.(2.16).

The outer tube hangs vertically within the insert dewar, supported by flange A which is bolted onto the "0" ring seal at the top of the insert. The electrical wiring to the suspension tube passes through flange A via two nine pin seals S1 (liquid helium sensors) and S2 (heaters and thermocouples for the sample chamber).

The diameter of the inner wall of the insert dewar is only 1.25", consequently a brass union is used to reduce the diameter of the lower 50cm. of the outer tube from 1" to 0.625". This arrangement permits a sufficient volume of liquid helium to be internally transferred above the sample chamber for all the measurements below 4.2K to be carried out. The pressure inside the insert is reduced by pumping through P1 and measured by means of a dial gauge connected to P2. The helium level in the insert is monitored by five carbon resistors (DG1 to DG5) mounted externally along the outer suspension tube. The 42swg enamelled return leads (5+ common return) are contained within a nylon insulating sheath which is wound around the 1" tube and held in position using masking tape. Between the brass union and the brass sample chamber they are varnished directly onto a stainless steel guide tube (diameter 2mm.).

The upper end (0.75" dia) of the inner tube forms the lower section of the demountable joint, and is thus coupled to the balance platform. During the positioning of the sample, which normally takes place with the suspension tube and balance
housing evacuated, small lateral movements (few mm.) are accommodated by the flexible copper bellows and a sliding "O" ring seal at flange B allows relative movement between inner and outer tubes when the balance platform is raised and lowered. The relative position is indicated on a vertical metal scale mounted on flange B by a pointer attached to the inner tube.

The lower 60cm. of the inner tube has diameter 0.5" and the internal wall of the brass union is chamfered to lower the chances of the sample being unhooked from the suspension whilst being lowered into the apparatus. In the event of this occurring, a circular section of Lectrokit circuit pegboard (fig.(2.17)) which is glued across (using GE7031) the otherwise open end of the 0.5" tube enables the sample to be retrieved by extracting the inner tube from the apparatus. (Before replacement the tube must first be warmed to room temperature and all traces of moisture removed by washing with acetone and drying with a hot air blower.)

During the operation of changing samples (see later) the static boil-off from the main bath (∼2-4 l.p.m. at N.T.P.) is vented through P3. The pure helium gas flows down the cylindrical gap between inner and outer suspension tubes, through the holes in the pegboard endpiece and up the inside of the inner suspension tube (flow rate ∼10-20 cm/sec). This counterflow severely restricts the influx of air and so avoids errors in the measurement due to oxygen being condensed onto the sample as it is lowered into the suspension tube.

A transverse cryogenic Hall probe (Siemens) is mounted horizontally on the inside surface of the pegboard endpiece
Fig. (2:16) SUSPENSION TUBE ASSEMBLY

DEMOSTANLE JOIIT

HEIGHT SCALE

FLANGE B
S1
S2
FLANGE A

P3
P2
P1

INSERT DEWAR INTERSPACE

TAPER

INNER SUSPENSION TUBE

OUTER SUSPENSION TUBE

SAMPLE CHAMBER
Fig.(2:17) SAMPLE CHAMBER

- SUSPENSION TUBE
- DEPTH GAUGE
- BRASS
- COPPER COIL FOIL
- SUSPENSION
- CARBON RESISTOR TEMPERATURE SENSOR
- PERSPEX
- HALL PROBE
- CIRCUIT BOARD

THERMO COUPLES
HEATER (1 WATT)
so as to leave as many of the small holes as possible unblocked by the plastic substrate. A perspex sheet (0.75mm. thick) protects the active element and the connecting leads (42swg enamelled Cu) pass out through a slot cut in the wall of the tube.

A carbon resistor, CR2, (Allen Bradley miniature 110Ω nominal) is located in a slot in the side of the inner tube and the enamelled copper current leads (42swg) are thermally anchored by winding a few turns around the tube just above the resistor and fastening them with GE7031.

The electrical leads to both these components are connected externally via S3 (fig.(2.16)), a six pin sealed lead-through. At the point (just below flange B) where the nylon sheathed wires must run within the suspension tube they are prevented from interfering with the sample suspension by an expanding stainless steel circlip which pins them close to the wall.

**Sample suspension.**

The first sample suspension used is shown in fig.(2.18)a. The main section of the suspension is a quartz fibre of 0.1mm. approx. diameter. The fibre is quite supple and extremely strong under tension, but localised shearing forces must be avoided.

The upper hook is fabricated from constantan wire (32swg), chosen for its strength, since during specimen changes this hook must be gripped firmly with tweezers. After stripping the cotton insulation from the wire any kinks may be removed by heating to a dull red heat whilst applying a tension of 20 to 30lbs wt. This hook together with the aluminium hook
at the lower end of the suspension are each glued on with a single drop of diluted GE 7031 varnish.

The radiation shields are made by gluing a thin aluminium disc (BACO-FOIL) to an aluminium frame as shown in fig.(2.18)b. A segment cut in the disc allows the shield to be mounted centrally on the fibre using a little varnish. With the suspension in position, the lower shield is approx. 6cm. above the brass union, and the two shields are separated by about 15cm. The diameter of each shield (0.5") is the same as that of the lower section of the inner suspension tube, thus preventing the direct passage of any room temperature radiation below the brass union.

A rigid aluminium link (32swg) completes the final 20cm. (approx.) of the suspension and avoids the effects of possible ferromagnetic contamination of the quartz, on the force on the suspension. The aluminium wire is relatively soft and only \( \sim 100 \) gm. wt. tension and a small cool flame is sufficient to remove any curvature. The angular shape of the connecting hooks ensures that no slip occurs during the course of a run at any of the linkages.

With specimen of mass less than 0.5gm. it was found that the fibre did not hang perfectly straight, and measurements were not possible because of contact between the suspension or sample and the inner wall of the suspension tube. To overcome this difficulty a \( \sim 1 \) gm. aluminium (resistance ratio of \( \sim 5000 \)) ballast rod (diameter 2mm.) was added just below the radiation shields and the quartz fibre shortened by the corresponding amount (\( \sim 10 \)cm.).

The total length of sample + suspension was adjusted so that with the inner suspension tube located in its lowest
Fig. (2:19) Force on Suspension

Suspension Force

(Magnetic Field)$^2 (\text{magms-wt.})$
position relative to the outer suspension tube (i.e. with the pegboard endpiece resting on the inner surface of the sample chamber), the sample could be 'bottomed' onto the Hall probe by lowering the balance platform to within 2 or 3mm. of its lowest position. This standard length was found to be 126.7mm. (273K).

The relatively small expansion coefft. of quartz at temps. below 273K is an advantage, the total expansion of the composite suspension between OK and 77K is <0.1mm. and from 77K to 273K is <1mm.

**Force on the suspension.**

The suspension as a whole may be regarded as a Gouy specimen, and furthermore, since the field is already reduced by a factor of ~40 at the top of the final aluminium link, we might expect the force on the suspension due to the main field only to be given by

\[ F_s = \frac{1}{2} A \chi_v H^2 \]  

where \( A \) is the cross-sectional area of the aluminium link, \( \chi_v \) is the magnetic susceptibility of aluminium per unit vol. and \( H \) is the uniform field in the region of the sample hook.

This assumption was checked experimentally and the results are shown in fig.(2.19). The straight line is given by \( F_s = 0.58 H^2 \) (\( F_s \) in \( \mu \)m, \( H \) in kOe) and the corresponding value for \( \chi_v \) is 19.4 \( 10^{-7} \) emu/cc. which is in satisfactory agreement with that quoted by Hedgecock and Li (70), 19.1 \( 10^{-6} \) emu/cc. at \( T = 50K \)

This property of the suspension, used in conjunction with the facility to apply a uniform field and a uniformly varying
field - Gz independently (the z axis is defined in fig.(2.8)) allows the contribution to the total force on the balance due to that on the suspension alone to be almost entirely eliminated.

When the field gradient is zero
\[ F_{o} = -\alpha H^2 + \xi F \]  \hspace{1cm} (2.9)
where \( \alpha = 5.7 \times 10^{-10} \text{dyne/kOe}^2 \), \( H \) is the field strength at A (fig.(2.18)a) and \( \xi F \) represents a relatively small force on the sample and the suspension hook due to the main field not being perfectly uniform. From the field profile (fig.(2.9)) we may deduce that \( H \) is not more than 0.5% (approx.) different from the known field strength (523g/amp) at \( Z = 0 \).

When the field gradient winding is energised the field strength at A is reduced and
\[ F_{G} = -\alpha(H-lG)^2 - \lambda_{\text{HOOK}}HG + \xi F + F_{S} \]  \hspace{1cm} (2.10)
where \( l \) is the distance between the point A and \( Z = 0 \), the field centre. The second term is the 'Faraday' force on the suspension hook, \( \lambda_{\text{HOOK}} = \lambda \) multiplied by the volume of the hook \( (\sim 10^{-3} \text{cc.}) \). \( F_{S} \) is the force on the sample - which will be discussed in greater detail below.

Subtracting (2.9) from (2.10)
\[ F_{G} - F_{o} = F_{S} + \Delta, \text{where} \]
\[ \Delta = (2\alpha l - \lambda_{\text{HOOK}})GH + \alpha l^2 G^2 \]  \hspace{1cm} (2.11)
Typically \( \lambda_{\text{HOOK}} \approx 2 \times 10^{-9} \text{emu. (± 10%)} \) and since \( l = 2 \text{cm} \pm 0.2 \text{cm} \), we also find \( 2\alpha l \approx 2 \times 10^{-9} \) (± 10%). Hence the absolute value of the bracket in eqn. (2.11) is reduced to within approx. \( 2 \times 10^{-10} \) emu. of zero and
\[ \Delta = 2 \times 10^{-10} GH + 2 \times 10^{-9} G^2 \text{ dynes} \]
\( \Delta \) is evaluated for typical and maximum values of \( G \)
and \( H \) in the table below. \( F_s \) is the force on a 1 gm. sample of magnetic susceptibility \( 10^{-7} \) emu/gm. in the same field conditions. Clearly \( \Delta \) is not a significant correction, and furthermore any temperature dependence (which will be proportionally the same as that of the susceptibility of aluminium, i.e. \( \sim 2\% \) between 1K and 77K) is entirely negligible.

| \( H \) kOe | \( G \) Oe/cm | \( |\Delta| \) millidyne | \( F_s \) millidyne |
|----------|----------|----------------|---------------|
| 10       | 500      | 1              | 500           |
| 30       | 500      | 3              | 1500          |
| 50       | 1000     | 10             | 5000          |

Suspension force for typical and maximum \( H \) and \( G \), compared with sample force when \( m \Delta g = 10^{-7} \) emu.
The Sample Chamber.

The brass sample chamber is shown in fig. (2.17). The choice of material is an important consideration since when the magnetic field is being swept, heat energy will be dissipated in the walls of the sample chamber due to the current induced (Faraday's Law). For a given geometry and fixed field sweep rate the power dissipated is proportional to the reciprocal of the electrical resistivity of the material. From the point of view of providing an isothermal environment for the sample the high thermal conductivity of copper (∼3 watts/cm/°K at T = 10K for machining copper rod (165)) is a distinct advantage. However if the power dissipation is to be limited to a reasonable level (so as not to cause a significant increase in the temperature of the sample chamber) the maximum sweep rate would have to be inconveniently small.

The high electrical resistivity of brass (4.3 μΩcm at T = 4.2K) enables the field to be swept at the maximum rate (45KG/min) while only 2mW (approx.) of power are dissipated. The usual experimental procedure involved only the field due to the gradient windings being swept up and down, resulting in a lower rate of change of field in the vicinity of the sample chamber and no heating effect was ever observed due to this source.

In order to take measurements above 4.2K a heater (∼10 turns 44 swg constantan delivering 1 watt at approx. 100mA) is wound around the lower end of the sample chamber. To stabilise the temperature in the region of 20K approx. 100mW is dissipated.

Thermal gradients along the sample chamber due to the
relatively poor thermal conductivity of brass (0.1 watts/cm$^0K@10K$ (165)) are avoided by cladding the body of the chamber with a layer of copper coil-foil. Good thermal contact to the brass is provided by a liberal application of GE 7031 and since the direction of the copper wires is parallel to the applied magnetic field no induced currents may circulate in the copper when the field is changed.

The coil-foil was fabricated by winding a length of 37 swg enamel-covered copper wire tightly onto a 1" diameter PTFE rod, and applying two or three coats of varnish, allowing time for each to dry before the next application (about 12 hrs. at room temperature was sufficient). The foil is removed by slitting the coil parallel to the axis and peeling it away from the PTFE former. Three fins were folded into the foil to improve the heat exchange between the sample chamber and the helium vapour passing up the insert dewar.

Good thermal contact between the various temperature sensors and the brass sample chamber is obtained by first mounting them in a groove machined in the side of the chamber before encasing the whole in coil-foil. The groove is located directly opposite the sample position and a thin layer of cigarette paper (soaked in 7031 varnish) provides electrical insulation from the brass and also from the coil-foil. The connecting leads emerge from under the coil-foil near the top flange of the sample chamber and are protected from damage during the lowering of the suspension tube assembly into the insert dewar by passing them through nylon sheaths pushed through holes drilled in the top flange.

The Au 0.03at. % Fe vs chromel thermocouple is supported
by winding it in a spiral together with 4 30 swg silk covered constantan wires. The thermocouple junction is held against the bottom of the insert dewar by the spring-like quality of the spiral. The constantan leads supply the current to the 150Ω (nom.) wire-wound resistor which is used as a small heater (1.5 watt @ 100mA) to boil away surplus helium at the end of the pumpdown and also to the liquid helium sensor DG1.

**Helium exchange gas pressure**

A small pressure (~ 1 Torr) of pure helium gas admitted to the suspension tube and balance housing provides for the heat exchange necessary to maintain thermal equilibrium between the sample and the sample chamber.

At this pressure, although the mean free path (0.003cm at 80K) is still relatively small compared to the diameter of the suspension tube, the presence of large temperature gradients along the walls of the tube may still give rise to thermomolecular flow leading to a large vertical force being exerted on the suspension (166). Gerritsen and Damon (148) found the thermomolecular force to be a maximum for a gas pressure of about 0.1 Torr. This maximum was proportional to the circumference of the suspension regardless of its composition. The maximum force on a 0.28 mm. diameter quartz suspension, with its lower end at 77K was 1 dyne in the downward direction. Krupp et al. observed that for pressure above that for maximum force, the force was proportional to the inverse of the exchange gas pressure, (167).

In practice the thermomolecular contribution to the total force on the balance is not constant during the course of measurement, and is by far the major source of drift in the
output of the balance. Even when the temperature of the sample chamber is stabilised ±0.1K, the slow change in the temperature distribution along the suspension tube will result in a drift of a few μgms. per minute in the recorded force. By taking a force reading with the applied field gradient zero both before and after the measurement of the force with both field and field gradient applied, the thermomolecular forces may be subtracted out and a linear interpolation between initial and final readings reduces the error due to any residual drifts to a minimum. Gerritsen observed that lateral deflection of the suspension, (including the sample) due to its not hanging axially within the suspension tube caused the magnetic force on the specimen to be a function of exchange gas pressure. No such variation could be observed in the pressure range 0.1 Torr to 3 Torr investigated for the present apparatus.

In order to establish the relationship between the actual sample temperature and that of the sample chamber it is necessary to measure the apparent susceptibility of a material whose true behaviour is already well established. Murani (160) found that the susceptibility between 1.5K and 4.2K of an alloy of gold containing 0.3 at.% gadolinium followed the Curie-Weiss law with an intercept θ ≈ 0.05K.

The susceptibility of a specimen of Au + 0.1at.% Gd. was measured between 1.5K and 4.2K in the present apparatus. The inverse of the impurity susceptibility \( (\chi_{\text{Alloy}} - \chi_{\text{Au}})^{-1} \) fig. (2.20) was proportional to the temperature in this interval with an intercept on the temperature axis of 50 ± 5mK. This is not significantly different from Murani's result indicating that radiation heating of the sample is not
Fig. (2.20) INVERSE SOLUTE SUSCEPTIBILITY OF Au + 0.10% Gd SPECIMEN vs. T

\[ \frac{1}{\Delta X} \] vs \( T \) (Temperature K)
Fig. (2.21) AuFe (0.03 at%) vs. Chromel Thermocouple Calibration.

Thermoelectric EMF.

Temperature K
a significant effect, leading to upper limit of 50mK for the temperature difference between sample and thermometry.

**Temperature control.**

By careful adjustment of the current supplied to the sample chamber heater it is possible to stabilise the temperature during the course of a single measurement to within 0.2K over the whole range 4.2K-300K. Between 4.2K and 25K the drift in the error signal displayed on the centre zero meter of the carbon resistor resistance bridge (see below) provides a useful 'feedback' signal when trimming the heater power.

Below 4.2K the temperature is stabilised to within 10mK for the duration of several force measurements, by maintaining a constant pressure above the boiling liquid helium in the insert. A rubber diaphragm manostat controls the pressure, and the temperature is obtained by reference to the standard helium vapour pressure tables. At temperatures below 1.6K there is a divergence between the temperature indicated by the vapour pressure at P2 (fig.(2.16)), and that recorded by the carbon resistor immersed in the liquid helium bath. This may be due to the existence of a pressure gradient along the insert dewar (which is part of the pumping line), so that the pressure as measured at P2 is slightly lower than that just above the liquid surface. At the lowest temperature (1.3K) the discrepancy amounts to about 50mK.

**Thermometry.**

In all, three temperature sensors are used to measure
the temperature of the sample chamber.

i) Au + 0.03 at.% Fe vs Chromel thermocouple; this thermocouple was constructed using the same technique as already mentioned. The two copper (42 swg enamelled) junctions with it are located in close proximity in the groove cut in the side of the isothermal sample chamber. The output voltage is amplified X 1000 using a differential D.C. chopper amplifier (ANCOM 15C-3) and displayed on a Dana model 4700 D.V.M. The noise in the amplifier voltage output was < 0.2 μV (referred to input) and was due solely to thermals along the thermocouple leads.

ii) Cu vs Constantan thermocouple. (42 swg copper, 38 swg constantan). The reference junction was held at 77.4K by submersion in a dewar full of liquid nitrogen. Previous experience with the Au - Fe vs Chromel thermocouple referenced to the ice-point (discussed earlier) showed that the boiling point of liquid nitrogen could be raised by as much as 1K by contamination with liquid air and so only fresh nitrogen was used, and a paper plug was inserted into the top of the nitrogen dewar. The output voltage was displayed in the same way as that of the above thermocouple.

iii) Carbon resistor (Allen Bradley nom. 110Ω resistance at 300K) The resistance (including that of the connecting leads) was measured using a commercial A.C. resistance bridge, operating at 375 Hz (Oxford Instrument Co.). The power dissipated in the resistor during the course of measuring its
resistance is less than $10^{-10}$ watts and so does not increase the internal temperature.

The connecting leads to each of the above sensors are thermally grounded to the upper part of the specimen chamber (168), (169). The possibility of the temperature of the sensor being artificially raised above that of the sample chamber due to heat conducted down the leads is thus avoided.

**Calibration of thermometers.**

In the temperature range 4.2K to 1.5K the initial susceptibility of the Au + 0.1 at.% Gd sample was established to be

$$\chi_i = \frac{23.45 \times 10^{-6}}{T_s + 0.052} - 1.43 \times 10^{-6} \text{emu/gm}.$$  

At temperatures above 4.2K the measured susceptibility can be used to give an absolute measurement of the temperature of the sample chamber, $T_s$, and so provide the basis of an independent calibration of the gold-iron versus chromel-p thermocouple and also the carbon resistor.

The thermocouple calibration is shown in fig. (2.21) and agrees to within 1% of that obtained by Rosenbaum (170) for a Au + 0.02 at.% Fe (annealed) vs. chromel-p thermocouple, in the temperature range 4.2K to 25K.

The carbon resistor was also calibrated in the usual manner by measuring its resistance as a function of the temperature in the range 2K to 4.2K (using He$^4$ vapour pressure) and also at the boiling point of liquid nitrogen. Since the resistance bridge makes only a two terminal measurement, a small correction of $4.5^2$ is necessary to allow for lead
resistance. The data was fitted using a computer program based on the method of least squares, to the equation
\[ \log R + \frac{A}{\log R} = \frac{B}{T} + C; \]
where A, B and C are the constants to be determined (171). The two calibrations for the resistor agreed to within 0.3K for temperatures below 14K, but for higher temperatures the agreement became rapidly worse. A criticism of the latter calibration is that it is extremely sensitive to the exact value of the resistance at 77.4K, a temperature which is remote from the region of interpolation (4.2K - 25K). A more reliable calibration would be obtained if the resistance could be measured in the pumped hydrogen range (11K to 20K), but with the present experimental arrangement this would be difficult.

In practice the carbon resistor was used to measure the temperature below 1.6K, using a calibration in the range 2K to 4.2K. The root mean square deviation of the calibration data from the fitted curve corresponds to a temperature uncertainty of about ±5mK.

The copper vs. constantan thermocouple was calibrated by measuring the output emf when the sample chamber junction was held at 4.2K and the reference junction at 77.4K. This was compared to the data of Powell et al. (172) and a linear interpolation made to account for the small difference (about 1.4%).

Temperatures between 4.2K and 25K were measured with a resolution of 0.1K using the Au Fe (0.3at.%) vs. chromel-p thermocouple. The absolute accuracy of the calibration
is \( \sim 1\% \) of the temperature. Above 25K the temperature is taken from the Cu vs constantan thermocouple and the absolute uncertainty is about \( \pm 0.5\text{K} \).

**Effect of magnetic fields on the thermometry**

1) **Au Fe vs. chromel thermocouple**

Dilute Au Fe alloys display a giant negative thermopower (about \(-13 \mu V/K\)), characteristic of the Kondo effect (37), which has a maximum value in the region of 1K (173). The long range correlations which build up between the local moment and the conduction electron spins in the region of and below \( T_K \) are destroyed by the application of a sufficiently intense magnetic field and the Kondo effect is progressively suppressed as the field is increased from zero. In view of the origin of the giant thermopower, it is not so surprising that Berman et al. (174) find that although at 2K \( \frac{\Delta S}{S} \), the fractional change in the thermopower is about 20\% for a 20kOe field, by 5K it has fallen to 5\% and decreases still further at higher temperatures. Von Middendorff (175) has measured the effects of a magnetic field on a Au Fe (0.07 at.\%) vs. chromel thermocouple and finds that in fields up to 60kOe, the fractional change in the thermopower has reduced to rather less than 5\% by 20K.

The present measurements on dilute ZnMn and ZnCr alloys were made in fields of 2 - 5 kOe (see table 4:1) and in the same temperature interval, from 4K to 15K,
von Middendorff's data would indicate that \( \frac{\Delta S}{S} \) will be at most a 1% change from the zero field thermopower, which is a small deviation. However, the calibration procedure for the present thermocouple, which was discussed earlier, means that the calibration itself is relevant to an applied field of 3.7 kOe, the field in which the force measurements on the Au Gd sample were obtained. We thus see that the error involved in neglecting the difference between the applied field during the ZnMn and ZnCr measurements and that relevant to the thermocouple calibration will be entirely negligible (\( \frac{\Delta T}{T} \leq 0.5\% \)).

The measurements on the dilute Zn Fe alloys were taken in a field of typically 25 kOe. For this field strength, von Middendorff's data would imply \( \frac{\Delta S}{S} \approx 10 - 15\% \) at 5K, decreasing to about 1% by 15K. However, the error in the temperature due to neglecting this field dependence is no more than 0.2 to 0.3K at any temperature in this range, the apparent temperature deduced from the zero field calibration being greater than the true temperature of the thermocouple junction. A systematic error of this magnitude in our Zn Fe data will not affect the general discussion which we make in chapter 4 or the conclusions which we draw, but will probably result in a systematic error of a similar magnitude in the \( \Theta \) value derived from a Curie-Weiss fit to the low temperature (\( T \leq 25K \)) data.

ii) Cu vs. constantan thermocouple

Schlosser and Kunnings (176) have investigated the effect of magnetic fields up to 100 kOe on a Cu vs
constantan thermocouple. They find that, when a reference temperature of 273 K is used, a field of 30 kOe results in a change in the apparent temperature indicated by the thermocouple which increases from 0.2K at 10K to 0.6K at 60K and stress that since the field dependence is due to a modification of the Kondo effect due to traces of magnetic impurities in either the copper or the constantan, the precise modification of the thermoelectric emf as a function of temperature and applied field may differ for different thermocouples.

At 30K and 30kOe the apparent temperatures (deduced from zero field calibrations) indicated by the Au Fe vs. chromel and copper vs. constantan thermocouples differ by about 1K, which confirms that the effects of the magnetic field of this magnitude and at this temperature are not large. A systematic error in the T > 30K data on the ZnFe alloys of this order does not affect our conclusions.

iii) Carbon resistors

Several workers (see (177) and references therein) have measured the magneto resistance of carbon resistor temperature sensors, and above 4.2K both negative and positive magneto-resistances are reported. The most recent work favours a negative magneto resistance (177) of approximately -3% over the range from 6K to 12K for a field of 15 kOe.

We have measured the magneto resistance of a nominal 100Ω Allen Bradley 1/10 th watt resistor at 4.2K and 1.3K. The results are shown in fig. (2:22). We find a positive
magneto resistance (field orthogonal to the current) which is increased at the lower temperature for the same field strength. The magnetoresistance in 40kOe corresponds to an apparent change in the temperature of 50 mK at 4.2K and 35 mK at 1.3K.
Fig. (2.22) Magnetoresistance of Allen-Bradley Nominal 110Ω Carbon Resistor

\[ \frac{\Delta R}{R(H=0)} \]

- \( T = 1.3K \)
- \( T = 4.2K \)

Magnetic Field kOe

0 5 10 15 20 25 30 35 40 45
Sample Position

Consider a uniformly cylindrical sample of length $L$ and cross-section $A$ positioned along the $z$ axis as shown below.

The centre of symmetry for the main field $H_m(z)$ is $z = 0$ and the uniformly varying field is of the form $-Gz$.

When only the main field is applied the force experienced by the cylinder is

$$ F_0 = \int_{-Z_0}^{-Z_0+L} A \chi_v H_m \frac{\partial H_m}{\partial z} \, dz \quad (212) $$

$\chi_v$ is the volume susceptibility of the specimen. Now, energising the gradient coils the total field and total field gradient are respectively

$$ H_{TOT} = H_m - Gz $$

$$ \frac{\partial H_{TOT}}{\partial z} = \frac{\partial H_m}{\partial z} - G \quad \text{note} \quad \frac{\partial H_m}{\partial z} \ll G $$

and the force becomes

$$ F_G = \int_{-Z_0}^{-Z_0+L} A \chi_v (H_m - Gz)(\frac{\partial H_m}{\partial z} - G) \, dz \quad (213) $$

Expanding $(213)$ and subtracting $(212)$ we obtain in order of decreasing magnitude
Provided the specimen is within the 20 mm. diameter sphere of the field volume, and assuming a magnetic susceptibility which is independent of the field

\[ I_1 = -A \chi_v \int_{-Z_0}^{-Z_0+L} H_m G \, dz \approx -V \chi_{vH_m(o)} G \]  

where \( V \) is the volume of the cylinder. This approximation will lead to an absolute error in the field independent susceptibility of approx. 0.2% due to non-uniformity of field gradient over the sample volume, but will not contribute to the relative error between two samples of the same dimensions.

When the susceptibility is field dependent, the apparent value \( \chi_v^{app} \) is related to the true function \( \chi_v(H) \) as

\[ \chi_v^{app} = \frac{I_1}{V H_m G} = \frac{1}{\Delta H} \int_{H_1}^{H_2} \chi_v dH \]  

where \( \Delta H = H_2 - H_1 \) where the latter are the field strengths at the top and bottom of the sample respectively.

In order to examine the relative importance of the last two terms we need only consider the case where magnetic susceptibility is independent of applied field, then
Let the $z$ - co-ordinate of the centroid of the cylinder be at $z = -\Delta z$ i.e. $Z_0 = \frac{L}{2} + \Delta z$

$$\left| \frac{I_2}{I_1} \right| = \frac{G}{H_m} \frac{L}{2} \left[ 1 - 2Z_0 \frac{L}{I} \right]$$

Not surprisingly the positioning is less critical when the field gradient is small compared to the field strength at the sample. This term represents the major contribution to the relative error between samples of similar geometry, errors in resetting the field and field gradient are typically 0.2%

3rd term.

A crude approximation to the main field gradient in the region of field volume is given by

$$\frac{\partial H_m}{\partial z} = 10^{-3} H_m \text{ Oe/cm } z > 0$$

$$= -10^{-3} H_m \text{ Oe/cm } z < 0$$

by substituting into the 3rd term of eqn. 2(14) it may be shown that

$$\left| \frac{I_3}{I_1} \right| \approx \frac{10^{-3}}{4} \left\{ 1 - 4 \left( \frac{\Delta z}{L} \right)^2 \right\}$$

The correction is a maximum when $z = 0$ because of the even symmetry of the main field about $z = 0$ but is in any
case negligible.

Typical magnitudes of the above two corrections are presented in the table below when \( \Delta z = \pm 1 \text{mm.} \) and \( L = 1 \text{ cm.} \)

<table>
<thead>
<tr>
<th>( H_m ) kOe</th>
<th>( G0e/cm. )</th>
<th>( I_2/I_1 % )</th>
<th>( I_3/I_1 % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>250</td>
<td>0.5%</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>500</td>
<td>0.25%</td>
<td>0.03%</td>
</tr>
<tr>
<td>50</td>
<td>1000</td>
<td>0.2%</td>
<td></td>
</tr>
</tbody>
</table>

Sample positioning procedure.

For both the main field and the gradient field it is true that

\[
\left( H_z \frac{\partial H_z}{\partial z} \right)_z = - \left( H_z \frac{\partial H_z}{\partial z} \right)_{-z}
\]

and so the total magnetic force on the specimen whose centroid is at \( z = 0 \) will be zero in the presence of one or other of these fields. In practice, when we traverse the sample along the \( z \)-axis (by adjusting the vertical position of the balance platform) there will be a particular location for which the total magnetic force on the balance is just equal to that on the suspension alone. The latter may be evaluated from the empirical relationship displayed in fig.(2.19).

1) Gradient field only

The rate of change of the magnetic force on the specimen is shown to be

\[
\Delta F_s \approx m \sum g^2
\]

when the gradient field is of the form \(-Gz\). If we take
G = 500g/cm. and \( m\chi_g = 10^{-6}\text{emu} \) we find that \[ \frac{\Delta F_s}{\delta z} \approx 25\mu g/m/mm \]

which is adequate to locate the specimen to within \( \pm 0.1\text{mm.} \) of the symmetrical position, being limited essentially by the noise in the microbalance output. This is \( \pm 2.5\mu g/m. \) since the balance platform is being moved and some disturbance of the microbalance is unavoidable.

11) Main field only

In this case \[ \frac{\Delta F_s}{\delta z} \approx \frac{m\chi_g}{500} \cdot H_m^2 \] and the main limitation is now the uncertainty in the suspension force, say \( \pm 5\% \). This leads to the same sample being positioned \( \pm 0.3\text{mm.} \), independently of the strength of the applied field. Clearly, since at \( T = 4.2K \) \( m\chi_g \sim 10^{-8}\text{emu} \) for the Zn - 3d alloys the above methods are not sufficiently precise. For these alloys a geometrical method was employed: First the position of the field centre was located by applying a gradient field \( (H = -Gz) \) and raising the Hall probe from its lowest position (when the circuit board is hard against the floor of the specimen chamber) until the Hall voltage was reduced to zero. In this way the field centre was found to be \( 11.9 \pm 0.2\text{mm.} \) above the lowest position of the Hall probe element. To within the quoted accuracy no dependence in the position of the field centre on the strength of the field gradient, \( G \), was observed.

To position a sample the balance platform is lowered until a sudden increase of the noise in the balance output indicates contact between the base of the sample and the
surface of the Hall probe, which is set at its lowest position. If the length of the sample has been previously measured, the balance platform may then be raised by the corresponding distance to place the mid-point of the sample at the field centre.

A cylindrical specimen 10.2 mm. in length, 5 mm. in diameter with $\chi_\text{m} \approx 10^{-5}$ emu/gm. was positioned using each of the three techniques. The geometrical method and the field gradient method agreed to within 0.1 mm. but the position suggested by the main field technique was significantly different (1 mm). This could be the result of a small ($1 \text{ in } 10^4$) unsymmetrical component in the main field profile in the region $-1 \text{ cm} < z < 1 \text{ cm}$, fig. (2:9).

In the case of the zinc alloy, the main source of the $\pm 1$ mm. uncertainty in the position of the centroid was due to the irregular shape of the sample bundle.
Experimental Procedure

Initial setting up

The main cryostat was supported within the aluminium box frame by three brackets welded to a steel band clamped around its circumference. The axis of the cryostat, and therefore of the insert dewar also, could be tilted about the vertical direction by adjusting the bracket supports mounted on the box frame.

To ensure that the insert dewar axis was vertical an 'electrical plumbline' was lowered into the insert and suspended from the balance platform. Adjustments were made to the supports until the co-ordinates of the centre of the circular cross-section of the insert, as indicated on the balance platform scales, were not a function of the height of the steel ball bearing (1" diam.) which served as the conducting bob.

The suspension tube assembly was then lowered into position and the various pumping and helium gas return lines plumbed in. The main bath helium gas return line includes a spring loaded valve to prevent large pressures building up as a result of the solenoid quenching. The final few inches of any connections to the apparatus were completed with flexible copper bellows in order to reduce the transmission of pump vibration to the microbalance head.

The microbalance head was located on the balance plate and the external circuitry already described, mounted in a modular fashion in a Langley equipment rack.
Helium Run

Because of the financial commitment involved in transferring $^{17}$ of liquid helium into the cryostat, a more disciplined approach than is normally necessary must be adopted during the pre-transfer procedure, in order to increase the chances of a successful run.

Normally some eight or nine specimens are prepared so that in the event of one or two being unsatisfactory (due to contamination or loose bundling etc.) there are still sufficient for measurements to continue uninterrupted whilst the solenoid remains operational.

The dimensions of each sample are recorded, using a travelling microscope, and the sample is placed between layers of Kleenex tissue in a labelled box. A counterweight is fashioned from a length of soft solder for each sample.

The order of measurement for the samples should clearly be such that those requiring the highest applied fields are measured when the liquid helium level in the main bath is still relatively high.

The first sample to be measured is hooked onto the suspension, and the latter lowered slowly into the suspension tube by means of a small pulley attached to the ceiling directly above the tube. When the level of the top hook of the suspension is only a few centimetres above the top of the suspension tube a length of 32 swg wire is positioned diametrically across the entrance and held firmly in position with sellotape. The suspension can then be unhooked from the pulley and hooked over the wire, thus allowing the
balance platform to be rolled forward into position. With the 500 mg. range selected the suspension and counter-weight are gently located onto the balance hooks which hang from either scalepan.

The demountable joint is closed and the balance platform adjusted so that the suspension hangs axially within the suspension tube with the sample a few mm. above the Hall probe.

The balance housing and suspension tube are slowly evacuated so as not to cause undue disturbance of the micro-balance and suspension. The pumping is continued for several hours to ensure that the volume is thoroughly out-gassed.

Meanwhile the main vacuum space and insert dewar are checked for leaks and re-pumped to a pressure of $\sim 2 \times 10^{-6}$ Torr if necessary. The balance housing, suspension tube and needle-valve are also leak tested. The capillary throughput is checked by evacuating the main bath and observing the rate of drop in the insert dewar pressure when the needle-valve is opened (For helium $\sim 10$ Torr/sec.).

The needle-valve is closed and the main bath and insert dewar are flushed three times with helium gas. It is rather important that the insert contains only pure helium gas because during the cooling of the solenoid to 4.2K the inner wall of the insert dewar is thermally isolated by the vacuum jacket and remains above 77K. The capillary, however, is connected across the vacuum to the outer wall and therefore acts as a 'cold finger' for the volume in the insert dewar. Consequently any condensable gases will preferentially solidify in the capillary and may lead to its blockage. A secondary advantage of careful flushing is the reduction of
helium boil-off from the insert dewar at temperatures below the \( \lambda \)-point (2.17K), (165). Bowers and Mendelssohn (178) found that contamination by solid air could lead to a tenfold increase in the rate of superfluid film flow across metallic surfaces.

The various electrical circuits are checked for continuity and the precool initiated by transferring approx. 20l. of liquid nitrogen into the nitrogen jacket. Over the course of the next 36 hrs. or so the temperature of the solenoid, as indicated by the resistance of the gradient coil winding, drifts down to somewhere in the region of 125K.

At this point the main bath is isolated from the helium gas return line and liquid nitrogen introduced via a 1 cm. diameter copper-nickel tube which slides down through the access port in the top-plate to below the level of the solenoid. About 6l. are transferred and the resistance of the gradient coils drops to about 11\( \Omega \), the 77K value. The liquid nitrogen level is a few cm. above the base of the solenoid.

In the region of 77K a temperature rise of 10K for the solenoid results in approx. 20% increase in its heat capacity ((165). p.336 assuming mean \( T \sim 350K \)). During the time required to expel the last drop of liquid nitrogen the solenoid temperature may well rise to approx. 85K. Therefore, before removing the nitrogen, we first reduce the temperature of the solenoid to approx. 66K by pumping on the liquid nitrogen to a vapour pressure \( \sim 150 \text{Torr} \) (The triple point for nitrogen (63.15K) corresponds to a vapour pressure of 94 mm.). To remove the bulk of the remaining liquid nitrogen the main bath is pressurised with helium gas from a cylinder and the nitrogen
blown out through the copper-nickel tube. A rubber hose attached to the top end of the tube directs the jet away from the balance platform and into a small dewar. The remaining $\sim \frac{1}{4} l$ is boiled away using the main bath heater at full power whilst simultaneously maintaining the vapour pressure at approx. 150Torr. This process takes about 1 hr. and meanwhile a final check of the electrical circuits is made. When the liquid nitrogen detector indicates that all the nitrogen has evaporated, the main bath is completely evacuated and a final check on the capillary throughput is made. The main bath volume is returned to atmospheric pressure with helium gas from the return line and the two piece helium transfer syphon introduced in place of the copper-nickel tube.

The transfer rate of liquid helium is initially monitored by the gas flow rate in the return line. This is maintained at about 40 l.p.m. at N.T.P. ($\equiv 3 l/\text{hr. liquid}$) whilst the magnet cools from an initial temperature of about 75K to 4.2K. A copper ruffle fastened around the middle of the solenoid impedes the flow of cold gas and helps reduce the volume of liquid helium required to cool the solenoid to about 4 l, see fig.(2:11).

Once the helium level detector at the bottom of the main bath indicates that liquid helium is collecting, the boil off rate drops to about 12 l.p.m. and is independent of the rate of transfer of liquid helium. The remaining 10 l in the transport dewar are transferred as quickly as possible ($\sim 1 l/\text{min}$) in order to minimise losses due to heat conducted down the syphon tube.
The internal transfer of liquid helium is effected by opening the needle-valve and simultaneously pumping on the insert dewar volume. The initial temperature of the end cap is about 90K and because, under vacuum conditions, there is only poor thermal contact between inner and outer suspension tubes, about 1Torr of pure helium gas is introduced to the balance housing and suspension tubes from the main bath boil-off. If the exchange gas is introduced after the internal transfer the sudden liberation of heat from the inner tube to the insert helium bath results in a violent boil-off of most of that helium. In the case of a full pump-down helium is transferred to the level of the brass union in the suspension tube assembly. After isolating the insert from the pump and closing the needle-valve ~100mW. is dissipated at the insert bath heater to bring the pressure back to 760Torr and the vigorous boiling action ensures that a uniform temperature of 4.2K exists when the insert is opened to the return line.

The sample is now positioned according to the methods previously described, the exchange gas pressure adjusted to 0.5-1Torr as indicated by the Speedivac guage (0-20Torr) and the microbalance is calibrated.

The magnetic field is increased in steps through its whole range and, for each setting, the force change $\Delta F$, on applying a preset field gradient is largely governed by the magnitude of the susceptibility of the sample and the degree of precision required.

The main field winding is put into persistent mode for the duration of the pump-down. First the power supply is
used to set up the desired current through the main coil and then the persistent current switch heater is turned off. After about 2 mins. the switch has cooled and the superconducting circuit is completed. The power supply may now be swept down to zero output. The magnitude of the field is chosen with reference to the measurements at 4.2K so as to make negligible any correction for Brillouin curvature in the sub 4.2K region. In general, so as to limit the effect of errors in the sample position to less than 1%, field gradients larger than 0.1 H gauss/cm. are avoided where possible.

In the case of the measurements on ZnMn and ZnCr, $\Delta F$ was measured as a function of applied field at the lowest temperature directly after the pump-down. In order to return the main field winding to external control the power supply output is reset to the level corresponding to the persistent current in the winding and the persistent current switch heater turned on. Within a few seconds the persistent current switch becomes resistive and a voltage spike may be observed across the output terminals of the power supply as any small inequality between persistent and controlled current is eliminated.

For the high resolution measurements on ZnFe alloys, the effect on $\Delta F$ due to decay of the field strength in persistent mode was significant when compared to the very small temperature dependence of these alloys. In order to establish the rate of field decay the value of $\Delta F$ was measured at 4.2K immediately before and after the pump-down sequence. A uniform rate of decay was assumed when interpolating the intermediate field strength, at the intermediate temperature of the pump-down.
After completion of all measurements at or below 4.2K the insert bath heater is used to boil away any excess helium which remains above the level of the sample chamber. Once again the main field windings are operated in the persistent current mode and the sample chamber temperature is raised to the appropriate values using the heater described previously.

At all temperatures the approach to thermal equilibrium between the sample and the sample chamber is accompanied by a simultaneous drift in the thermomolecular force on the suspension, as the temperature profile along the suspension tube is re-established. The latter process has a time constant of approx. 15 secs. and once the drift rate is sufficiently small for \( \Delta F \) to be measured no effects due to non-equilibrium conditions in the sample temperature are observed.

The procedure for the specimen interchange is as follows:

1) Sample chamber temperature raised to approx. 100K
2) The main bath helium boil-off is partially diverted through the balance housing and the pressure in the suspension tube slowly increased to 1 atmos.
3) The demountable joint is broken and the entire boil-off diverted through P3(fig.(2.16)). The sample and suspension are disengaged from the balance and hooked over a wire positioned across the top of the suspension tube as before.
4) The balance platform may now be rolled clear and the suspension slowly removed using the pulley.
5) After the new sample has been lowered into the apparatus the pan load difference is adjusted to be a few mgms. by
trimming the counterweight. The boil-off is returned to the helium recovery line and the demountable joint closed.

6) The balance housing and suspension tube is evacuated as before and pumped on for a period of 10 mins. to ensure complete removal of any oxygen from the region of the sample (still held at \( \geq 100K \)).

7) About 1Torr of helium is admitted to the balance space and the whole measurement cycle repeated.
Modification to the current leads

In order to reduce the heat input into the cryostat due to the current leads it is important that there is good heat transfer to the evaporated helium gas. This ensures that as much as possible of the enthalpy of the boiled-off gas is utilised and so reduces the heat input directly into the liquid helium. Deiness (179) uses tubular current leads and finds that a surface area of 20 sq.cm. per electrical watt dissipated in the current leads is sufficient to ensure adequate heat exchange.

Eckert et al. (180) have obtained good heat exchange by constructing each lead from a large number (25) of copper wires which are connected, electrically and thermally at short intervals by copper cooling plates. The copper cooling discs are connected at right angles to the wires and so act as radiation shields in addition. These authors have attempted to solve the problem theoretically using an analogue computer and their results indicate that there is some advantage in reducing the cross-sectional area of the current lead at the 'cold' end. This is easily done in their case by progressively reducing the number of copper wires. A reduction in the boil-off rate is also achieved when superconducting wire is connected in parallel with the copper wire at the cold end of the current lead.

In the present apparatus, although the current leads must be capable of carrying a current of 100 amps, the typical operating level is approximately half of this, and, particularly in the case of the current leads to the main field solenoid, which is operated in the persistent current mode during the
pump-down and warm-up, the current is zero for a large proportion of the total time.

According to Scott (164 ) brass is a more suitable material than copper where a wide range of current levels is required to be supplied to the solenoid. The smaller thermal conductivity of the brass results in, for leads optimised to a given current, a lower boil-off rate when the current level is below the optimum. Furthermore, for brass leads, the current may be overrated two or three times the optimum level without the serious over-heating, and consequently severe boil-off rate which occurs in copper leads.

Dr. J. Good (private communication) has investigated the performance of a rather simple form of current lead fabricated from brass strip. The strip is mounted within the dewar but is not enclosed inside a guide tube as was Scott's design. The boil-off rate per amp. at optimum current, 3cc.liquid/hr., is about the same as that observed by Deiness and also by Scott, when the helium level is above the ends of the guide tubes and there is good heat transfer. The guide tubes thus seem to be unnecessary, and even a problem when the helium level is too low. According to Good, for a given geometry of current lead, the optimum current, $I_0$, i.e. that for which the boil-off rate per amp. is lowest, occurs for a potential drop of 75mV per lead.

$$I_0 \frac{\rho l}{A} = 0.075$$

where $\rho \approx 5 \mu\text{cm.}$ is the mean resistivity of the brass along the current lead under operating conditions, i.e. with
the equilibrium temperature profile between 4.2K and 300K.

If we optimise the main field current leads to 50 amps and the gradient field to 30 amps, taking \( l = 75 \text{ cms} \).

\[
\begin{align*}
A_{50} &= 0.25 \text{ sq.cm.} \\
A_{30} &= 0.15 \text{ sq.cm.}
\end{align*}
\]

Using 1mm. thick brass strip, a width of 2.5cm. and 1.5cm. is required for \( I_0 = 50 \) and \( I_0 = 30 \). The total surface area of these strips is 375 sq.cm. and 225 sq.cm. respectively so that we have 50 sq.cm./watt dissipated which should ensure very adequate heat transfer. A length of Nb-Ti multifilamentary superconducting wire soldered along the lower part of each strip and in parallel with the copper fly-leads will also help to reduce the helium consumption.
2.4 Electrical resistivity apparatus

The electrical resistivity of all the present alloys was measured using an apparatus originally designed by A.D. Caplin, but subsequently rebuilt with some modification by A.J. Barber (199). This apparatus utilises the standard 4-terminal D.C. technique and includes an isothermal (copper) sample chamber which is capable of housing up to six specimens during a single run. These samples are connected in series with each other and also with an external 0.012 manganin standard resistor which is submerged in a thermostatically controlled water bath maintained at about 25°C. The current passing through the samples is obtained by measuring the potential difference across this standard resistor, and is supplied by a Tinsley regulated current supply, type 5753, with a stability of better than 1 part in $10^5$ over a 1 hr. period. A Julie zener provides the necessary stable reference voltage to the current supply.

The potential drop across each sample and the standard resistor is measured in turn using a Tinsley Stabaumatic potentiometer, type 5545, in conjunction with a galvanometer amplifier which allows the out of balance voltage observed with a sensitivity of 10nV/cm deflection on the galvanometer scale. The potential differences may thus be measured with a resolution of $\sim 2.10^{-9}$V, and the potentiometer itself has 7 decade resistors which step between 10nV and 10mV.
Tektronics, Inc.

Dimensions: 574.0x830.0

Page 206

Diagram: TEFLON DISC, STAINLESS STEEL TUBE, COPPER TUBE, SAMPLE CHAMBER, HEATER, THERMOCOUPLE JUNCTION, COPPER BLOCK, PINS PROVIDING CURRENT AND POTENTIAL CONNECTION, BATH HEATER AND THERMOCOUPLE REFERENCE JUNCTION, LOW M.PT. SOLDER, ANNEALED Pt

Fig. (2:23)a Resistivity Apparatus

Fig. (2:23)b Resistivity Sample
Although, by using the sample heater, fig. (2:22)a the temperature of the sample chamber may be stabilised (± 0.2K) at temperatures above 4.2K, the present measurements were restricted to the pumped liquid helium range and stabilised by using a rubber diaphragm manostat. A Au Fe vs. chromel thermocouple, referenced to 4.2K, provides the facility to measure temperatures in excess of 4.2K, whilst below this temperature reference to the standard vapour pressure tables for liquid helium enabled the temperature to be ascertained.

In order to check that the internal temperature of the specimen was not raised significantly (<1mK) above that of the liquid helium both by Joule heating, a check was made that the potential difference was in fact proportional to the current in the experimental current range. The current used was typically 200 - 500 mA.

The resistivity of the present Zn based alloys varied (at 4.2K) between $7.5 \, \Omega \cdot \text{cm}$ and $75 \, \Omega \cdot \text{cm}$ according to their concentration. Typically the resistivity sample was in the form of a cylindrical rod with dimensions 6 cm. X 1 mm. diameter which allowed the resistance to be measured with a precision of between 1 part in $10^3$ and 1 part in $10^4$ for the lowest (~5ppm.) and highest (~50 ppm.) transition metal concentrations, respectively. Between 4.2K and 1.5K the resistance increases by 1 part in 10 for these alloys, so that even for the most dilute alloy the temperature dependence could be measured to within 1%.
In the majority of cases (see tables (3:3) and 3:4)) the resistivity specimens were cut from the same alloy casting as was used to provide a susceptibility specimen. Potential leads, consisting of annealed 0.15 mm. diameter Pt wire were spot-welded approximately 4 mm. from each end of the rod, fig. (2:22)b. Current leads of tinned Cu wire were soldered using a cool iron and low melting point indium-tin solder so as to form a complete dome at either end of the specimen. This arrangement results in a more uniform current distribution in the specimen at small distances from the current contact than would a spot-welded current lead and, in addition to providing increased mechanical strength, allows the potential leads to be attached more closely to the ends of the specimen, thus increasing the total potential drop to be measured.

After each low temperature run the resistance of each specimen was determined at 273K by removing the glass dewars and immersing the sample chamber in an ice/water mixture. This procedure enabled a far more accurate determination of the resistance ratio, \( \Delta \rho \) in chapter 3, than could be obtained using a simple 'dipstick' arrangement devised to check the absence of oxidation during the casting procedure, and the concentration as deduced from this more accurate resistance ratio was used in any subsequent calculations involving the resistivity data.
3:1 Zinc-3d Transition metal alloys

The maximum solubility of Cr and Fe in Zn is small; the residual resistivity ratio measurements of Boato et al. (112) indicate a solubility limit, for alloys quenched directly from the melt, of about 300 at.ppm. in both cases. The effect of heat treatment (at 10°C below the solidus) was to lower the solubility limit still further to 20 at.ppm. and 50 at.ppm. respectively. Ford et al. (105) detected the effects of precipitation after cold working ZnMn and ZnCr alloys with concentrations in excess of 20 at.ppm., and also as a result of relatively short, strain relieving heat treatments. Caplin (110) reports that the temperature dependence of the electrical resistivity of dilute ZnFe alloys is also very sensitive to the metallurgical treatment.

Alloys of Mn, Cr and Fe in Zn, with concentrations ranging from 5 at.ppm. to 200 at.ppm. were prepared by successive dilutions of the appropriate master alloy. In view of the above observations the measurements were made on alloys quenched directly from the melt, in the 'as cast' condition.

The composition of the alloys was monitored by measuring the resistivity ratio, $\Delta \rho$, of each alloy,

$$\Delta \rho = \frac{R_{4.2}}{R_{273} - R_{4.2}}$$

where $R_{4.2}$ and $R_{273}$ are the resistances, at 4.2K and 273K respectively, of the alloy.
Master alloys

The starting materials for these alloys were supplied by Koch-Light Laboratories Ltd., and their respective forms and overall levels of purity are shown in the table below.

<table>
<thead>
<tr>
<th>PURITY</th>
<th>FORM</th>
<th>PICKLING REAGENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>6N</td>
<td>8mm rod</td>
</tr>
<tr>
<td></td>
<td>5N8+</td>
<td>shot</td>
</tr>
<tr>
<td>Cr</td>
<td>5N</td>
<td>flake</td>
</tr>
<tr>
<td>Mn</td>
<td>4N5+</td>
<td>flake</td>
</tr>
<tr>
<td>Fe</td>
<td>4N8+</td>
<td>1mm wire</td>
</tr>
<tr>
<td>Ag</td>
<td>5N</td>
<td>rod</td>
</tr>
</tbody>
</table>

Table 3:1 Zn-3d alloys, starting materials

The primary alloys were each prepared in the form of a 5gm. ingot with the nominal concentrations indicated in table 3:2. In order to remove any surface contamination, the zinc shot and the appropriate mass of transition metal were given a prolonged pickle in the reagent indicated in table 3:1 (about 20% of the metal dissolved). After rinsing in deionised water and acetone, the materials were dried, weighed and placed in a 5mm I.D. quartz tube which had previously been etched for several hours in aqua regia (3:1 ; HCl : HNO₃). The tube was evacuated and then heated to a temperature of 200°C, whilst pumping continuously to remove all traces of volatile contamination. Once the pressure had fallen to below 10⁻⁵ torr the tube was sealed off.

In the case of the ZnMn and ZnFe masters the tube was held at 700°C in a vertical furnace for several hours, and
shaken vigorously at regular intervals to ensure good mixing. If an attempt is made to quench the tube directly into water from this temperature, the silica generally cracks before the melt has solidified. The sudden influx of steam results in great turbulence of the molten metal and consequently a very irregular solid shape. Therefore, for a few minutes immediately prior to quenching, the furnace temperature is reduced to about 50°C above that of the liquidus, and the ingot is then cast in the shape of the tube.

Solid chromium dissolves very slowly in molten zinc. Stone and Dunlop (31) found that a temperature in excess of 1100°C was required to ensure that no chromium remained undissolved when preparing a 7 at.% ZnCr alloy.

The tube containing the zinc and chromium pieces was placed in the furnace at 900°C and the temperature was raised in stages to 1200°C, where the vapour pressure of pure zinc is about 8 atmos. (18). The temperature was maintained at this level for 90 mins. before lowering it briefly to 500°C and quenching the tube in water as before.

A disc was removed from the cross-section at either end of each of the master alloys, and examined microscopically, both before and after, etching with a 5% solution of HCl in alcohol.

There was no evidence of free chromium in the ZnCr master, and the distribution of 2nd phase appeared to be uniform throughout the fine-grained crystal structure that was common to all three ingots.

The cylindrical master alloys were each mounted in
plastic and a flat surface ground and polished along their whole length (~2cms). The hardness was measured at several points along the surface using a Vickers machine. The area of the indentation (for a typical load of 5Kgm.) means that in the case of the ZnFe and ZnCr alloys the hardness represents the mean value for the mixture of second phase and solid solution.

The variation in hardness of the ZnFe master indicated that the 2nd phase was not evenly distributed through the alloy. This resulted in some disagreement between nominal and analysed Fe concentrations of the final specimens, although (fig.(3:4)) the linear relationship between the residual resistivity ratio and analysed concentration, demonstrates that for concentrations below 135 at.ppm. Fe, the alloys are good solid solutions.

The concentration of the ZnMn alloy is below the solubility limit for Mn in Zn (0.5 at % at 415°C (183)) and no second phase is present.

<table>
<thead>
<tr>
<th>MASTER</th>
<th>ZnCr</th>
<th>ZnMn</th>
<th>ZnFe</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOMINAL CONCENTRATION (at.ppm.)</td>
<td>5436</td>
<td>4241</td>
<td>25830</td>
</tr>
<tr>
<td>HARDNESS (VICKERS SCALE)</td>
<td>65(±5)</td>
<td>57(±3)</td>
<td>60-80</td>
</tr>
</tbody>
</table>

Table 3:2 Primary Zn-3d master alloys

The figures in brackets are the maximum variation of the hardness. Samples of 5N8+ shot and 6N zinc rod, which
had been melted and cast in a similar fashion had hardness values of 35±1 and 36±1 respectively in the same units.

**Dilution procedure**

If we were to dilute the primary master alloy directly to achieve the final concentrations, the mass of master (for a 5gm. specimen) is rather small to permit of easy handling and accurate weighing. Therefore a secondary master of intermediate concentration is cast and the final alloys obtained by diluting portions of this with the 6N zinc rod. In order to avoid ferromagnetic contamination, only Cu-Be implements were used.

Rizzuto (private communication) and others (105), (112), mixed the master alloy and pure zinc at 450°C in a pyrex container under an atmosphere of 'pure' argon. After a thorough mixing the argon is quickly evacuated and the molten alloy cast into a graphite (Aquadag) covered pyrex tube, which had previously been out-gassed for 30 mins. at 480°C. Immediately after casting an atmosphere of argon is re-admitted, thus packing the melt into the casting tube, which was then quenched in a water bath.

Attempts to reproduce this method to dilute the ZnCr master were unsuccessful mainly, it would seem, because the argon (although nominally 'high purity' grade) oxidised a large proportion of the Cr atoms during the mixing process. Whenever argon was present during the mixing stage a grey powdery layer appeared on the surface of the melt, and when the residual resistivity ratio for the alloy was subsequently measured it was found to correspond to an alloy containing
anything up to 50% less than the nominal concentration of the Cr atoms. We note that if the total number of molecules of oxygen and water included in the argon atmosphere (~100cc) is to be less than, say, 10% of the number of Cr atoms in a 5 gm. melt of a nominally 10 at.ppm. ZnCr, the purity of the argon must exceed 1 part in \(10^4\). Ford et al. (105) have acknowledged that the anomalous change in their resistivity data for ZnCr alloys of \(< 25\) at.ppm. is most probably due to sample oxidation of this origin.

As a result of these observations, a modified technique was developed which avoided, as much as possible, the use of argon or any other heat exchange gas during the melting and mixing of the alloy. The design of the pyrex glassware is shown in fig. (3:1) and all measurements reported here are on alloys prepared using the following technique.

The casting tube is steeped in aqua regia for several hours and then, after rinsing in water and acetone, joined to the 10 mm. diameter mixing tube. The use of Aquadag in the previous arrangement led to unavoidable contamination of the surface of the alloy with graphite, as well as making the outgassing of the casting tube difficult. Provided the casting tube was drawn with a very slight taper the graphite layer was found to be unnecessary. The alloy could be extracted by sliding short sections of the glass tube from the thinner end of the rod, without the introduction of further strain into the specimen.

After cleaning and weighing, the pieces of zinc rod and master alloy are introduced via the upper tube which is then
sealed off as shown. The glassware is evacuated and pumped continuously with the casting tube positioned within a horizontal furnace. The optimum furnace temperature was found to be about 380°C. At higher temperatures (>420°C) there is a strong possibility that the casting tube will crack during the quench, which has a similar effect to that already described, while at lower temperatures (<350°C) the melt may not run the full length of the casting tube (20 cms.).

The external (to the furnace tube) parts of the glassware are outgassed by heating them to about 550°C (dull red) for 5 minutes, whilst taking care not to allow the component metals to melt prematurely.

The metals are molten together for a period of 5 mins. under vacuum conditions (p<10^-4 torr). They are thoroughly mixed by rotating the glassware back and forth as indicated by the arrow in fig. (3:1). A Gaz portable burner is ideal for this purpose, but care must be taken to prevent the collapse of the mixing tube, due to local overheating of its walls. Pyrex softens at about 650°C (184°C). In the absence of the argon atmosphere, the mean free path of the zinc atoms is rather large, and coupled with the high vapour pressure for zinc, may lead to excessive mass transport of zinc from the melt. This is minimised by heating all parts of the glassware equally and only sufficiently to keep the alloy in the molten state. It is estimated that about 5% of the zinc could be lost from the melt in this way.

Next the springloaded stop-cock, A, is closed and the pump shut off at B, so that 1 atmosphere of argon may be admitted to the ballast volume and pumping line from the cylinder, via C.
Fig.(3.1) Casting Arrangement for Zn-3d Alloys

- Horizontal Furnace
  - T = 380°C
- Pyrex Casting Tube
- Thermocouple
- Load and Seal
  ±45° to Mix
- Heat
- Melt
- Quench Bath
- Diffusion Pump
- Ballast Volume
- 0-760 mm. Hg
- Gauge
- Argon Cylinder
Finally, the glassware is removed from the furnace and held vertically so that the melt is funneled into the neck of the casting tube. Stopcock A is re-opened and the pressure of the argon rams the liquid metal into the tube, which is then lowered (over a period of ~2 secs.) into the water bath below. Contact between the melt and the argon is thus limited to the end surface of the cast rod, and the absence of oxidation during the mixing process is apparent from the untarnished, silvery surface of the melt, and the reproducibility of the residual resistivity ratio per nominal at ppm of solute.

Residual resistivity ratio, $\Delta \rho$.

Directly after quenching, the resistance of a section of each alloy was measured, at 4.2K and 273K using a 4-terminal d.c. arrangement incorporated in a 'dipstick' which could be lowered directly into a liquid helium transport dewar. The value of $\Delta \rho$ obtained in this way was reproducible to better than ± 2%.

The homogeneity of several of the alloys was checked by measuring $\Delta \rho$ separately for the upper, middle and lower sections of the rod. No significant difference in the three values was ever observed.

In order to eliminate that part of the residual resistivity of the alloy which is not due to the 3d solute, but which arises from the strains incorporated during the casting procedure or the (mainly non-magnetic) remnant impurities in the 6N zinc, a specimen of pure zinc was cast and $\Delta \rho$ was found to be
$0.3 \times 10^{-3}$, corresponding to a resistance ratio $R_{273}/R_{4.2}$ of about 3000.

(i) ZnCr alloys.

$\Delta \rho$ is shown plotted vs. the concentration of Cr as determined by chemical analysis for alloys prepared without the use of argon during the mixing stage in fig.(3:2). The error bars for high concentrations correspond to the $\pm 5\%$ uncertainty claimed by the analyst (185), whilst those for the low concentrations are based on the scatter in two or three separate determinations on the same alloy. The straight line drawn through the data corresponds to a residual resistivity ratio per atomic % Cr of $3.30 \pm 5\%$ and the final concentration of each alloy is calculated as

$$c = \frac{\Delta \rho - \Delta \rho^Zn}{3.3 \times 10^{-4}} \text{ at.ppm.}$$

As shown in table (3:3) there is good agreement between nominal concentration and the final concentration based on the residual resistivity ratio.

(ii) ZnMn alloys.

$\Delta \rho$ is plotted as a function of both nominal (filled circles) and analysed (open circles) concentration of Mn in fig.(3:3). The lower sensitivity of the analysts methods (chemical analysis $c > 30$ at.ppm., spectrographic at lower concentrations) in the case of Mn is reflected in the scatter. The residual resistivity per atomic % Mn, $3.65 \pm 5\%$, is based on the nominal concentrations only, but is clearly not
inconsistent with the analysed concentration points. Table (3:4) summarises the final concentrations of the ZnMn alloys.

(iii) ZnFe alloys

$\Delta \rho$ is shown as a function of analysed Fe concentration in fig.(3:4). The residual resistivity ratio per at.% Fe is $2.80 \pm 5\%$. The large discrepancies between nominal and final concentrations are due simply to the inhomogeneity of the primary master alloy, Fe(M), which was apparent from the Vickers hardness data and confirmed by the analyst, table (3:5).

A portion of the ZnFe primary master was analysed using the emission spectroscopy technique for traces of Mn or Cr. None were observed, the lower limit of detection is 1 ppm and 0.1 ppm respectively.

Two portions of the 6N Zn rod, one from each of the batches used, were similarly analysed and again the results were negative.

The residual resistivity per at.% of solute at 4.2K is tabulated below (assuming the resistivity of pure zinc at 273 K is $5.5 \mu\Omega\cdot\text{cm}$.\(\text{(112)}\)) and compared with Ford et al.'s (106) data.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present data</td>
<td>18.0</td>
<td>20.1</td>
<td>15.2 (±5%)</td>
</tr>
</tbody>
</table>
| Ford et al. | 17.7| 19.1| 14.8 (μΩcm /at.%)

Table 3:6 Residual resistivities ($T=4.2K$) for 3d solutes in Zn.
In conclusion we expect that the absolute accuracy of the determination of the final concentrations has a ±5% uncertainty, whilst the relative accuracy is limited only by the uncertainty in \( \Delta \rho - \Delta \rho_{\text{Zn}} \) ie ~±2%.

Fabrication of susceptibility samples.

In the case of ZnMn and ZnCr, the alloy rods were cut into 1 cm. sections and etched (to remove about 10% of their mass) in 10% aqueous HCl. Seven such sections were then tied into a bundle using a few mgms. of fine Al wire to form a sample of mass 0.6 - 1 gm.

For the high resolution measurements on ZnFe, where it was desirable to use the largest possible samples, the sections were increased to 1.8 cm. in length and the typical mass of a specimen was 2 - 3 gm.

These specimen bundles were found to be quite stable provided the final etching of the alloy sections was sufficiently vigorous to leave the surface in a roughened condition.
Fig. (3:2) Resistivity ratio vs. concentration for ZnCr alloys

Analyzed concentration Cr at. ppm.
\[ \Delta \rho \]

ZnMn

- NOMINAL CONC.
- ANALYSED

Fig. (3:3) Resistivity Ratio vs. Concentration for ZnMn Alloys
$\Delta \rho$

ZnFe

**Fig. (3:4) Resistivity Ratio vs Concentration for ZnFe Alloys**

Analysed Concentration (At. PPM)
### Table (3:3) ZnCr alloys, concentrations

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>FUNCTION</th>
<th>NOMINAL</th>
<th>ANALYST</th>
<th>FINAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMnI</td>
<td>Master (1)</td>
<td>4240</td>
<td>4290</td>
<td>-</td>
</tr>
<tr>
<td>Mn500</td>
<td>Master (2)</td>
<td>438</td>
<td>373</td>
<td>-</td>
</tr>
<tr>
<td>Mn100</td>
<td>Master (2)</td>
<td>91</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>Mn5(63)</td>
<td>X, R</td>
<td>63</td>
<td>70</td>
<td>60.3</td>
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<td>Mn5(39)</td>
<td>X, R</td>
<td>39</td>
<td>39</td>
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<td>23</td>
<td>19</td>
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<td>X, R</td>
<td>16</td>
<td>6</td>
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<tr>
<td>Mn5(6.6)</td>
<td>X, R</td>
<td>6.7</td>
<td>6</td>
<td>6.8</td>
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</table>

**Cr CONCENTRATION AT.PPM.**

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>FUNCTION</th>
<th>NOMINAL</th>
<th>ANALYST</th>
<th>FINAL</th>
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</thead>
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<tr>
<td>MI</td>
<td>Master (1)</td>
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<td>-</td>
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<td>415</td>
<td>380</td>
<td>-</td>
</tr>
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<td>MIII056</td>
<td>R</td>
<td>56</td>
<td>49</td>
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</tr>
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<td>MIII023</td>
<td>R</td>
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<td>23.3</td>
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<td>MIII09</td>
<td>X, R</td>
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<td>9.7</td>
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### Table (3:4) ZnMn alloys, concentrations

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<th>ALLOY</th>
<th>FUNCTION</th>
<th>NOMINAL</th>
<th>ANALYST</th>
<th>FINAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMnI</td>
<td>Master (1)</td>
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<tr>
<td>Mn500</td>
<td>Master (2)</td>
<td>438</td>
<td>373</td>
<td>-</td>
</tr>
<tr>
<td>Mn100</td>
<td>Master (2)</td>
<td>91</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>Mn5(63)</td>
<td>X, R</td>
<td>63</td>
<td>70</td>
<td>60.3</td>
</tr>
<tr>
<td>Mn5(39)</td>
<td>X, R</td>
<td>39</td>
<td>39</td>
<td>38.9</td>
</tr>
<tr>
<td>Mn5(23)</td>
<td>R</td>
<td>23</td>
<td>19</td>
<td>22.6</td>
</tr>
<tr>
<td>Mn5(16)</td>
<td>X, R</td>
<td>16</td>
<td>6</td>
<td>16.7</td>
</tr>
<tr>
<td>Mn5(6.6)</td>
<td>X, R</td>
<td>6.7</td>
<td>6</td>
<td>6.8</td>
</tr>
</tbody>
</table>
### Table (3:5) ZnFe alloys, concentrations

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>FUNCTION</th>
<th>NOMINAL</th>
<th>ANALYST</th>
<th>FINAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>FE(M)</td>
<td>Master (1)</td>
<td>2.58(at%)</td>
<td>2.80(at%)</td>
<td>-</td>
</tr>
<tr>
<td>FE1260</td>
<td>Master (2)</td>
<td>1260</td>
<td>1604</td>
<td>-</td>
</tr>
<tr>
<td>FE1390</td>
<td>Master (2)</td>
<td>1390</td>
<td>1224</td>
<td>-</td>
</tr>
<tr>
<td>FE866</td>
<td>Master (2)</td>
<td>866</td>
<td>636</td>
<td>-</td>
</tr>
<tr>
<td>FE216</td>
<td>X</td>
<td>216</td>
<td>356</td>
<td>356</td>
</tr>
<tr>
<td>FE98</td>
<td>X</td>
<td>98</td>
<td>132</td>
<td>133</td>
</tr>
<tr>
<td>FE95</td>
<td>X</td>
<td>95</td>
<td>104</td>
<td>115</td>
</tr>
<tr>
<td>FE77</td>
<td>△</td>
<td>77</td>
<td>109</td>
<td>110</td>
</tr>
<tr>
<td>FE103</td>
<td>X</td>
<td>103</td>
<td>85</td>
<td>84</td>
</tr>
<tr>
<td>FE62</td>
<td>X</td>
<td>62</td>
<td>74</td>
<td>69</td>
</tr>
<tr>
<td>FE81</td>
<td>△</td>
<td>81</td>
<td>64</td>
<td>64</td>
</tr>
<tr>
<td>FE40</td>
<td>X</td>
<td>40</td>
<td>54</td>
<td>58</td>
</tr>
<tr>
<td>FE36</td>
<td>△</td>
<td>36</td>
<td>40</td>
<td>42</td>
</tr>
<tr>
<td>FE30</td>
<td>△</td>
<td>30</td>
<td>29</td>
<td>28</td>
</tr>
</tbody>
</table>

### Table (3:6) CuAl-Fe alloys, concentrations

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>Al CONC. (at. %)</th>
<th>Fe CONC. (at. ppm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuFe0.05</td>
<td>0.0</td>
<td>535</td>
</tr>
<tr>
<td>CuAl5Fe0.05</td>
<td>5.1</td>
<td>566</td>
</tr>
<tr>
<td>CuAl10Fe0.05</td>
<td>10.1</td>
<td>556</td>
</tr>
<tr>
<td>CuAl15Fe0.05</td>
<td>15.1</td>
<td>544</td>
</tr>
</tbody>
</table>
The Cu-Al phase diagram (183), indicates that the solubility limit for aluminium in copper is 16at.% at 1037°C. In all, four ternary alloys were prepared, each containing nominally 500 at.ppm. of iron, with aluminium concentrations of 0, 5, 10 and 15 at.%.

These alloys were prepared by Dr. H. E. N. Stone by melting a Cu Fe master alloy together with the appropriate quantities of copper and aluminium in a sintered alumina crucible under a vacuum of 10⁻⁵torr. The starting materials were as indicated in the table below.

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>SUPPLIER</th>
<th>PURITY</th>
<th>FORM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>K-L</td>
<td>5N8</td>
<td>BAR</td>
</tr>
<tr>
<td>Fe</td>
<td>K-L</td>
<td>4N8</td>
<td>1mm. WIRE</td>
</tr>
<tr>
<td>Al</td>
<td>J.M.</td>
<td>SPECPURE</td>
<td>7mm. ROD</td>
</tr>
</tbody>
</table>


Table (3:7) CuAl Fe alloys, starting materials

The melt was allowed to solidify in the bottom of the crucible, and each 10 gm. button so formed was cut into two roughly equal portions, which were then subjected to a heavy pickle in 50% aqueous nitric acid.

The susceptibility specimen was prepared from one half-round by first cold rolling into an approx. circular cylindrical shape, taking the usual precautions to prevent mechanical inclusion of surface contamination. After a further
pickle, this could be held in a collet and machined to a cylinder of the standard dimensions (12.2 mm. X 4.5 mm.). A small groove machined near the top of the cylinder at this stage provides a location for the Al loop used to suspend the specimen in the susceptibility apparatus. After a thorough pickle the sample was sealed inside an evacuated quartz capsule and held at 950°C for three days in order to ensure a homogeneous composition. After heat treatment the capsule was quenched directly into water.

Dr. D. C. Golibersuch used the second half round of each button to fashion a resistivity specimen. The alloy was cold-rolled and drawn, with intermediate anneals, into a wire form. After pickling the specimens were given the same heat treatments as already described for the susceptibility sample.

A set of binary Cu-Al alloys (0 to 15at.% Al) were prepared in an exactly similar way.

The composition of each alloy was determined by chemical analysis and the results are shown in table (3:8).
CHAPTER 4

EXPERIMENTAL RESULTS AND DISCUSSION

Introduction

The first section of this chapter is devoted to the results of the high resolution resistivity and susceptibility measurements performed on the very dilute ZnMn and ZnCr alloys. Part of the original motivation for investigating ZnCr was the result of Ford et al. (105) who observed a factor of two decrease in the logarithmic derivative of the resistivity, with respect to the temperature, for concentrations below about 40 at. ppm. As we shall see, the present results show no evidence of such drastic concentration dependence in either the Curie constant from the susceptibility data or the slope of the resistivity and we have already concluded (see chapter 3) that oxidation of the Cr during specimen preparation will have strongly affected Ford et al.'s results in the extreme low concentration region.

The second section deals with the susceptibility measurements on the dilute ZnFe alloys, which demanded the full precision of which the present apparatus is capable in order to follow the very small temperature dependence which was observed at temperatures less than 25K.

In the final section we briefly recount the resistivity data on $\alpha$-phase Cu$_{1-x}$Al$_x$ + 500 at. ppm. Fe alloys, taken by D. C. Golibersuch, which prompted the measurement of the susceptibility of the same set of alloys on the Gulf spiral Faraday balance. Since these latter measurements were
performed the work of Tholence and Tournier (61) among others has served to greatly clarify the influence and role of interactions between Fe atoms in a Cu matrix, so that although the present results are still of some interest, they do not allow of direct observation of 'single impurity' behaviour.

4:1 Magnetic susceptibility of dilute ZnCr and ZnMn alloys

The magnetic susceptibility of four ZnCr alloys with concentrations 8.8, 10.0, 26.8 and 35.1 at.ppm. Cr, and four ZnMn alloys with concentrations 6.8, 16.7, 38.9 and 60.3 at.ppm. Mn, was measured over the temperature interval 1.3K to 15K.

The theoretical expressions available (eqn. 1(29) and 1(30)) for the susceptibility refer to the zero field limit or initial susceptibility and it is therefore desirable that the magnetic field is sufficiently low to make negligible any correction to the experimental data to account for the saturation of the localised moments. By first measuring the field dependence of the magnetisation of each alloy at 4.2K, fig.(4:1) and fig.(4:3), it was possible to choose a suitable value for the magnetic field. The actual values used are shown in table (4:1) and even at the lowest temperatures the correction for Brillious curvature is negligible, being less than about 1% of the impurity contribution to the total susceptibility of the alloy.
The initial susceptibility is plotted as a function of temperature for ZnCr alloys in fig. (4:5) and ZnMn alloys in fig. (4:6). The strong temperature dependence is characteristic of the presence of a local moment on the impurity and, as we have already discussed in chapter 1, for high temperatures $T \gg T_K$, the perturbational solution to the s-d model is valid, and results in the expression eqn.1(29) for the initial susceptibility. This expression is, in turn, closely approximated over a wide temperature range by a CW law, eqn.1(30).

In view of this, in order to establish whether or not the s-d model may account for the behaviour of Mn or Cr dissolved in Zn, we have compared the temperature dependence of the present data with that of the CW law

$$\chi = \frac{A}{t + \Theta} + \chi_H$$

where $\chi_H$ is a temperature independent susceptibility generally associated with that due to the host matrix, but
which may contain, in addition, any temperature independent components of the impurity susceptibility which we shall denote by $\chi_0$ in the following

\[ \chi_H = \chi_m + \chi_0 \]  

(4.2)

where $\chi_m$ is the temperature independent susceptibility due to the host matrix alone.

Since the s-d model itself contains some oversimplifications with regard to the true situation of a transition metal atom dissolved in a simple metal host (e.g. infinite lifetime for the spin, zero range for the s-d interaction) and the calculation of the susceptibility itself assumes a uniform density of conduction electron states, it is not obvious that a rigid interpretation of the Curie constant, $A$, and of expression 4(1) in terms of eqn.1(30) is very meaningful. For this reason we shall use $\Theta$ itself as the characteristic temperature for the solute, and calculate the effective moment on the impurity, $P_{\text{eff}}$, using the straightforward expression

\[ A = \frac{N u_{\text{eff}}^2}{3k_B} \]  

(4.3)

where $u_{\text{eff}} = P_{\text{eff}}u_B$ and $P_{\text{eff}}$ is the effective number of Bohr magnetons per solute atom. Also in the following we shall assume that the orbital angular momentum is quenched by the crystalline fields so that $P_{\text{eff}}^2 = 4S(S+1)$, where $S$ is the impurity spin.

If $A$ is the Curie constant in units of emu/gm per at.ppm. of impurity in Zn, then

\[ P_{\text{eff}}^2 = 5.231 A \cdot 10^8 \]  

(4.4)
Fig. (4:1) Magnetisation vs. Field at $T = 4.2 \text{K}$

Magnetisation vs. Field for $\text{ZnCr}$ alloys

- $5 \times 10^{-4} \text{ emu/gm.}$
- Field, kOe
- Magnetisation
- 35.1 at. ppm. Cr
- 26.8
- 10.0
- 8.8
Fig. (4.2) Magnetisation vs. Field at $T=1.3K$

For $	ext{ZnCr}$ Alloys

Magnetisation

Magnetic Field, 10e-}

0

10

20

30

40

10^{-4}$ emu/gm.

$\circ$ 35.1 at. ppm. Cr

$\triangle$ 26.8 "

$\square$ 10.0 "

$\triangledown$ 8.8 "

0

-5

-10

-15
Fig. (4.3) Magnetisation vs. Field at 4.2 K for Zn Mn Alloys

- 60.3 at. ppm. Mn
- 38.9
- 16.7
- 6.8

Magnetisation vs. Magnetic Field (10^4 emu/gm.)
Fig. (4:4) Magnetisation vs. Field at \( T = 1.3 \text{K} \) for \( \text{ZnMn} \) alloys

- 38.9 at. ppm Mn
- 16.7
- 6.8

Magnetisation vs. Magnetic field, kOe
Fig. (4.5) Magnetic susceptibility of Zn-Cr alloys vs. temperature

Magnetic susceptibility

30 \times 10^{-8} \text{ emu/gm}

Temperature K

-10

0

5

10

15

-35.1 \text{ at. ppm. Cr}

26.8

10.0

8.8
Fig. (4:6) Magnetic Susceptibility of Zn-Mn Alloys vs. Temperature

- 60.3 at. ppm. Mn
- 38.9 "
- 16.7 "
- 6.8 "

Temperature K
<table>
<thead>
<tr>
<th>Alloy</th>
<th>concentration</th>
<th>$A \times 10^8$</th>
<th>$\Theta$</th>
<th>$\chi_H \times 10^8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnMn</td>
<td>60.3</td>
<td>198</td>
<td>0.49</td>
<td>-15.4</td>
</tr>
<tr>
<td></td>
<td>38.9</td>
<td>122</td>
<td>0.42</td>
<td>-15.7</td>
</tr>
<tr>
<td></td>
<td>16.7</td>
<td>53.3</td>
<td>0.51</td>
<td>-16.2</td>
</tr>
<tr>
<td></td>
<td>6.8</td>
<td>19.6</td>
<td>0.37</td>
<td>-16.1</td>
</tr>
<tr>
<td>ZnCr</td>
<td>35.1</td>
<td>86.9</td>
<td>0.39</td>
<td>-15.3</td>
</tr>
<tr>
<td></td>
<td>26.8</td>
<td>62.6</td>
<td>0.26</td>
<td>-15.3</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>23.2</td>
<td>0.37</td>
<td>-15.6</td>
</tr>
<tr>
<td></td>
<td>8.8</td>
<td>22.3</td>
<td>0.53</td>
<td>-16.4</td>
</tr>
<tr>
<td>at. ppm.</td>
<td>emu/gm</td>
<td>K</td>
<td>emu/gm</td>
<td></td>
</tr>
</tbody>
</table>

Table(4:2) Curvefit results on data $1.3K < T < 15K$
The parameters of the fit, $A$, $\chi_H$ and $\Theta$ were determined using a computer program based on the method of least squares, and the results of such a curve fit to the raw $\chi$ vs $T$ data for each alloy over the whole temperature range are shown in table (4:2).

Before going on to inspect the data more closely for deviations from this CW fit we would like to make the following points about the data of table (4:2)

i) The value of $A$, for both ZnCr and ZnMn, is a linear function of the concentration, and from a plot of $A$ vs. concentration we find

ZnMn  $P_{\text{eff}} = 4.11 \pm 0.1 \mu B, S=1.61 \pm 0.04$

ZnCr  $P_{\text{eff}} = 3.55 \pm 0.1 \mu B, S=1.34 \pm 0.04$

ii) There is no experimentally significant concentration dependence in the value of $\Theta$, the mean values of which are

ZnMn  $\Theta = 0.45 \pm 0.05K$

ZnCr  $\Theta = 0.39 \pm 0.10K$

iii) The temperature independent term, $\chi_H$, becomes less diamagnetic with increasing impurity concentration.

iv) For every alloy the root mean square deviation of the experimental data from the fitted CW curve corresponds to a scatter in the raw force measurement which is less than $\pm 1 \mu g m$, and typically $\pm 0.5 \mu g m$. This is just the typical noise level in the output from the microbalance under operational conditions (due to vibration and thermo-molecular forces), suggesting that there are no serious departures of the experimental points from the fitted CW curve.
In order to examine the data more closely for deviations from CW dependence we have, for each alloy, divided the data into two sets, one comprising of data in the temperature range $1.3K \leq T \leq 4.2K$ and the other of data in the $4.2K \leq T \leq 15K$ range. Each set contains two separate determinations of the susceptibility at each of about ten different temperatures within the range. The results of the CW curve fit to each set in turn are shown in table (4:3) for ZnMn alloys and table (4:4) for ZnCr alloys. The values of $\mu_{\text{eff}}$ and $\Theta$ which may be deduced from this data are given in table (4:5) below.

<table>
<thead>
<tr>
<th></th>
<th>$\mu_{\text{eff}}$ (\mu_B)</th>
<th>$\Theta$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15K-4.2K</td>
<td>4.2K-1.3K</td>
</tr>
<tr>
<td>ZnMn</td>
<td>4.1</td>
<td>4.1</td>
</tr>
<tr>
<td>ZnCr</td>
<td>3.6</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Table (4:5) CW parameters for split temperature range

The ZnMn data shows no appreciable dependence of the CW parameters on the temperature range of the fit. For ZnCr alloys the parameters change more noticeably with the temperature range, especially the value of $X_H$ which is consistently less diamagnetic in the fit at the lower temperature range for a given alloy. On the other hand, the low temperature data is least sensitive to the exact choice of $X_H$, since the impurity contribution to the total susceptibility, $\chi - X_H$, is largest in this region.
Table (4:3) Results of computer fits to data of ZnMn alloys

<table>
<thead>
<tr>
<th>Concentration at ppm.</th>
<th>A (10^8) emu/gm</th>
<th>(\Theta) K</th>
<th>(\chi_H) (10^8) emu/gm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) 4.2K ≤ T ≤ 15K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60.3</td>
<td>197</td>
<td>0.54</td>
<td>-15.2</td>
</tr>
<tr>
<td>38.9</td>
<td>129</td>
<td>0.67</td>
<td>-16.0</td>
</tr>
<tr>
<td>16.7</td>
<td>52.4</td>
<td>0.52</td>
<td>-16.1</td>
</tr>
<tr>
<td>6.8</td>
<td>21.7</td>
<td>0.77</td>
<td>-16.2</td>
</tr>
<tr>
<td>2) 1.3K ≤ T ≤ 4.2K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60.3</td>
<td>207</td>
<td>0.55</td>
<td>-16.8</td>
</tr>
<tr>
<td>38.9</td>
<td>123</td>
<td>0.42</td>
<td>-15.7</td>
</tr>
<tr>
<td>16.7</td>
<td>51.5</td>
<td>0.46</td>
<td>-15.8</td>
</tr>
<tr>
<td>6.8</td>
<td>20.6</td>
<td>0.43</td>
<td>-16.3</td>
</tr>
</tbody>
</table>

Table (4:4) Results of computer fits to data of ZnCr alloys

<table>
<thead>
<tr>
<th>Concentration at ppm.</th>
<th>A (10^8) emu/gm</th>
<th>(\Theta) K</th>
<th>(\chi_H) (10^8) emu/gm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) 4.2K ≤ T ≤ 15K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35.1</td>
<td>92.7</td>
<td>0.65</td>
<td>-15.6</td>
</tr>
<tr>
<td>26.8</td>
<td>62.7</td>
<td>0.31</td>
<td>-15.3</td>
</tr>
<tr>
<td>10.0</td>
<td>25.1</td>
<td>0.69</td>
<td>-15.7</td>
</tr>
<tr>
<td>8.8</td>
<td>22.5</td>
<td>0.44</td>
<td>-16.5</td>
</tr>
<tr>
<td>2) 1.3K ≤ T ≤ 4.2K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35.1</td>
<td>79.5</td>
<td>0.29</td>
<td>-13.8</td>
</tr>
<tr>
<td>26.8</td>
<td>57.5</td>
<td>0.16</td>
<td>-14.4</td>
</tr>
<tr>
<td>10.0</td>
<td>21.9</td>
<td>0.30</td>
<td>-15.4</td>
</tr>
<tr>
<td>8.8</td>
<td>19.6</td>
<td>0.37</td>
<td>-15.9</td>
</tr>
</tbody>
</table>
Shifting the value of $X_H$ to a more diamagnetic value, compatible with the $T > 4.2K$ curve fit, will also tend to increase the apparent value of $p_{eff}$ and $\Theta$. In order to test the data fairly for low temperature deviations from CW it would be desirable to first reduce the number of variables in the fitted curve. The high temperature data $T > 4.2K$, where $X - X_H$ is smallest, is most sensitive to the exact choice of $X_H$ and the CW curve fit to data in this temperature range will therefore provide the best estimate for $X_H$ for a given alloy.

Using this value for $X_H$, in figs.(4:7) to (4:14) we show $(X - X_H)^{-1}$ vs. $T$. In each case it is possible to connect both high and low temperature data with a single line, indicating CW temperature dependence. The deviations of the data points from this line are shown for ZnMn alloys in fig.(4:15) and ZnCr alloys in fig.(4:16). We do observe some small systematic deviations about the CW line, but in all cases these deviations are only of the same magnitude as the experimental uncertainty, based on a scatter of $\pm 1$ ugm in the measured force. Thus it would seem that any departure from the high temperature CW behaviour at temperatures below 4.2K as a result of impurity interactions are essentially negligible in the present concentration and temperature ranges.

We base our final estimates of the CW parameters on the data as shown in figs.(4:7) to (4:14).
\[ [X - X_H(>4.2K)]^{-1} \]
\[ [\text{emu/gm.}]^{-1} \]

**Fig. (4-7) CW FIT TO DATA OF Zn + 35.1 \text{at.ppm Cr-ALLOY}**

\[ X = \frac{90.3}{T + 0.44} - 15.63 \cdot 10^{-8} \text{emu/gm.} \]

**Temperature K**
Fig. (4.8) CW FIT TO DATA OF Zn + 26.8 at. ppm. Cr ALLOY

\[ X = \frac{62.5}{T + 0.25} - 15.31 \times 10^{-8} \text{ emu/gm.} \]

\[ \left[ X - X_H (> 4.2 \text{K}) \right]^{-1} \]

\[ \left[ \text{emu/gm.} \right]^{-1} \]

TEMPERATURE K
Fig. (4.9) CW FIT TO DATA OF Zn + 10.0 at. ppm Cr ALLOY

\[ \chi = \frac{24.5}{T + 0.45} - 15.74 \times 10^{-8} \text{ emu/gm.} \]

\[ \left[ \chi - \chi_H (>4.2 K) \right]^{-1} [\text{emu/gm.}]^{-1} \]
Fig. (4:10) CW FIT TO DATA OF

\[ Zn + 8.8 \text{ at. ppm. Cr alloy} \]

\[
\frac{1}{[X - X_H(>4.2K)]}^{-1}
\]

\[
\frac{1}{[\text{emu/ gm.}]}^{-1}
\]

\[
X = \frac{22.5}{T + 0.45} - 16.46 \\
\times 10^{-8} \text{emu/gm.}
\]

TEMPERATURE K
Fig. (4:11) CW FIT TO DATA OF Zn + 60.3 at. ppm. Mn ALLOY

\[ \frac{1}{X - X_H (>4.2 \text{K})} \]

\[ \left[ \text{emu/gm.} \right]^{-1} \]

\[
X = \frac{195}{T + 0.46} - 15.15 \times 10^{-8} \text{emu/gm.} \]

TEMPERATURE K
Fig. (4.12) CW FIT TO DATA OF Zn + 38.9 at. ppm Mn.

\[ X = \frac{124}{T + 0.44} - 15.95 \]

\[ [X - X_H (> 4.2 \text{K})]^{-1} \]

[emu/gm]^{-1}
Fig. (4:13) CW FIT TO DATA OF

\[ Zn + 16.7 \text{ at. ppm, Mn alloy} \]

\[
\left[ \frac{X - X_H (>4.2K)}{X} \right]^{-1}
\]

\[
\left[ \text{emu/gm.} \right]^{-1}
\]

\[
X = \frac{52}{T + 0.45} - 16.06 \times 10^{-8} \text{ emu/gm.}
\]

TEMPERATURE K
Fig. (4.14) CW FIT TO DATA OF \[ Z_n + 6.8 \text{ at. ppm. Mn alloy} \]

\[ [X - X_\text{H (>4.2K)}]^{-1} \]

\[ [\text{emu/gm.}]^{-1} \]

\[ X = \frac{20.8}{T + 0.49} - 16.23 \times 10^{-8} \text{emu/gm} \]

TEMPERATURE K
Fig. (4.15) Deviation from CW fits: Zn-Mn alloys
Fig. (4.16) Deviation from CW fits: ZnCr alloys
Fig. (4:17)
 EFFECTIVE MOMENT OF Mn & Cr IN Zn

CURIE CONST.

150 \times 10^{-8} \text{ EMU/GM}

100

50

200

0

conc. at. ppm.

20 40 60

\begin{align*}
\text{ZnCr} & & P_{\text{EFF}}(U_B) & & S \\
& & 3.6 \pm 0.2 & & 1.35 \pm 0.05 \\
\text{ZnMn} & & 4.1 & & 1.60
\end{align*}
Fig. (4:18)
COMPUTED HOST SUSCEPTIBILITY, $X_H[T>4.2K]$, VERSUS ALLOY CONCENTRATION

$X_H$ $\times 10^{-8}$ emu/gm

ZnCr

ZnMn

CONCENTRATION AT. PPM.
TEMPERATURE INDEPENDENT COMPONENT IN THE SUSCEPTIBILITY OF ZnMn ALLOYS

Fig. (4.19)

[Graph showing temperature independent component with lines for 60.3 at. ppm, 38.9 at. ppm, 16.7 at. ppm, and 6.8 at. ppm.]
Fig. (4.20) Relative positions of the Mn and Cr VBS w.r.t. the Fermi energy of Zn
Fig. (4.17) shows that for both the ZnCr and the ZnMn series the Curie constant, $A$, scales linearly with the concentration, corresponding to

\begin{align*}
\text{ZnMn} & \quad P_{\text{eff}} = 4.1 \pm 0.2 u_B \\
& \quad S = 1.60 \pm 0.05 \\
\text{ZnCr} & \quad P_{\text{eff}} = 3.6 \pm 0.2 u_B \\
& \quad S = 1.35 \pm 0.05
\end{align*}

where the quoted uncertainty includes the possibility of systematic error in the concentration as a result of the uncertainty in $\frac{\Delta \rho}{c}$, the residual resistivity ratio per atomic% of solute.

The mean values for $\Theta$ are

\begin{align*}
\text{ZnMn} & \quad \bar{\Theta} = 0.48 \pm 0.05 K \\
\text{ZnCr} & \quad \bar{\Theta} = 0.44 \pm 0.05 K
\end{align*}

We note that these values for $P_{\text{eff}}$ and $\bar{\Theta}$ are not significantly different from those obtained from the CW curve fit to data over the whole temperature range, which is a further indication that deviations from CW behaviour at low temperatures is negligibly small.

The computed values for $\chi_H$ are shown in fig. (4.18), and for both ZnMn and ZnCr alloys there is a clear trend towards a less diamagnetic value as the solute concentration is increased. This effect amounts to a temperature independent contribution of about $100 \times 10^{-4}$ emu/mole Mn, and with less
certainty because of the large scatter in the data, to about \(150 \times 10^{-4}\) emu/mole Cr. In addition there appears to be a sharp initial increase in the temperature independent component of the susceptibility of the alloys for the lowest concentrations of the solute.

Claus (186) has discussed the significance of the temperature independent susceptibility which is derived from a CW curve fitting process when \(X_H\) itself is one of the variable parameters. If there are impurity interactions at the lowest temperatures, leading to an enhancement of the temperature dependence of the excess impurity susceptibility, and consequently a departure from CW behaviour, then a least squares curve fit of the type which we have employed will compensate for this deviation by adjusting the value of \(X_H\), thereby giving a false impression for a temperature independent component in the susceptibility, \(X_0\), besides that due to the host matrix, \(X_m\), see eqn.4(2). In order to see if the present increase in \(X_H\) with the concentration of solute, fig.(4:18), is an artificial result of the curve fitting procedure, we have plotted in fig.(4:19) the raw data for the total susceptibility of each of the ZnMn alloys as a function of \(T^{-1}\). The temperature independent component can now be obtained directly from the highest temperature data by extrapolation to infinite temperature \((T^{-1} \to 0)\), since any kind of temperature dependent local moment type of contribution should disappear in this limit. The extrapolated values, \(X(T^{-1} \to 0)\), show the same trend as the computed values of \(X_H\). In addition we note the absence of downward curvature in figs. (4:7) to (4:14), as being in
favour of the absence of interactions and the conclusion that $X_H$ does not appear to be a false artefact of the curve fitting process.

Discussion of CW parameters for Mn and Cr dissolved in a Zn matrix.

The magnetic behaviour of an isolated solute atom in a simple metal host matrix is specified by its effective moment $p_{\text{eff}}$, the CW $\Theta$, which is generally taken as a measure of the characteristic (or Kondo) temperature for the solute atom and possibly an additional small temperature independent component to the impurity susceptibility, $X_0$.

To summarise, from the present data we find

<table>
<thead>
<tr>
<th></th>
<th>$p_{\text{eff}}$</th>
<th>$\Theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnMn</td>
<td>4.1 uB</td>
<td>0.5 K</td>
</tr>
<tr>
<td>ZnCr</td>
<td>3.6 uB</td>
<td>0.45 K</td>
</tr>
</tbody>
</table>

Our value for Mn, $p_{\text{eff}} = 4.1$ uB, is close to that obtained by Newrock (107) of 4.2 uB, and shows a substantial reduction from the effective moment of Mn atoms dissolved in noble metal host matrices. Our value of $p_{\text{eff}} = 3.6$ uB for Cr in Zn is also smaller, though the reduction is not so marked.

<table>
<thead>
<tr>
<th></th>
<th>Au</th>
<th>Ag</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>5.3</td>
<td>5</td>
<td>4.4</td>
<td>4.1</td>
</tr>
<tr>
<td>Cr</td>
<td>3.9</td>
<td>4</td>
<td>3.6</td>
<td>3.6 (uB)</td>
</tr>
</tbody>
</table>

Table (4.6) Comparison of $p_{\text{eff}}$ for Mn and Cr in noble metal hosts and Zn (Data taken from ref(36))
The progressive demagnetisation of the 3d solute atom on passing to solvents with higher conduction electron density of states at the Fermi surface can be understood from the Anderson model as arising from a broadening of the VBS, see eqn.1(5), and the ensuing reduction in the energy separation of spin up and spin down halves of the VBS. In this sense the Zn matrix represents the intermediate case between monovalent hosts (table(4:6)) and a trivalent host like Al where the VBS width is even larger resulting in a non-magnetic spin degenerate VBS for the impurity. This picture is an oversimplification, even in terms of the Anderson model, since one might expect that departures from free-electron behaviour for the conduction electrons in Zn (114) would result in a reduced (compared to the free electron model) density of states at the Fermi energy, as well as affecting the matrix element $V_{kd}$ for the conduction to localised state admixture.

The residual resistivity ratio measurements of Ford et al. (105) correspond, after allowance has been made for the contribution due to s-wave scattering, to the (time averaged) total number of d electrons on the impurity site being 4 and 5 for Cr and Mn respectively. In terms of the Anderson model the difference between the (time averaged) spin up and spin down populations is related to the spin on the impurity by

$$n_{d\uparrow} - n_{d\downarrow} = 2S \quad 4(5)$$

which allows us to calculate the individual VBS population
for each spin component

<table>
<thead>
<tr>
<th></th>
<th>$n_{d\uparrow}$</th>
<th>$n_{d\downarrow}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>4.1</td>
<td>0.9</td>
</tr>
<tr>
<td>Cr</td>
<td>3.35</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Assuming a Lorentzian form for the VBS and using the relation

$$
\rho_{ds} (E_F) = \frac{1}{\pi \Delta} \sin^2 \left( \frac{n_{ds} \pi}{5} \right)
$$

we may deduce the relative positions of each component of the VBS relative to the Fermi surface; this is shown in fig.(4:20)

The values of the CW $\Theta$ which we have obtained for Mn and Cr solutes in Zn are very close, which is in contrast to the situation which is observed in the Cu host matrix (see table (4:7)), where the characteristic temperature is two orders of magnitude larger for Cr than Mn. The characteristic temperatures of AuMn (187), $10^{-13} \text{K}$ from resistivity measurements, and AuCr (188), $0.01 \text{K}$ from nuclear orientation, are less well established but the data suggests that the value for Cr is several decades larger than that for Mn. The temperature dependence of the resistivity of AlMn and AlCr corresponds to a characteristic temperature for Cr which is a factor of two larger than that for Mn. These data are summarised below, where we have included, in anticipation of a full discussion of the ZnFe susceptibility results the characteristic temperature of
isolated Fe atoms in Zn.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Host</th>
<th>Au</th>
<th>Cu</th>
<th>Zn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0.01</td>
<td>1.3</td>
<td>0.45</td>
<td>1200</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>$10^{-13}$</td>
<td>0.01</td>
<td>0.48</td>
<td>530</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.4</td>
<td>29</td>
<td>120</td>
<td>$10^3$ (K)</td>
<td></td>
</tr>
</tbody>
</table>

Table (4:7) Characteristic temperatures of Cr, Mn and Fe dissolved in Au, Cu, Zn and Al. (36)

The characteristic temperatures for Mn and Fe both show a progressive increase as the host is varied along the series from Au through to Al. For the Cr solute, however, ZnCr alloys break this progression and seem to have too small a value for the characteristic temperature. One might consider a characteristic temperature of about 10K would fit the pattern set by Mn and Fe solute. It may be significant that Zn is a h.c.p. metal and, as Hirst has pointed out (189), the orbital angular momentum is not necessarily quenched for 3d solutes in host matrices possessing such high symmetry. Any residual orbital angular momentum is coupled to the impurity spin angular momentum via the spin-orbit interaction and under certain circumstances this might result in a modification of the spin flip scattering of the conduction electrons and the Kondo effect itself.

The paramagnetic increase in the temperature independent contribution to the susceptibility of ZnMn and ZnCr alloys (fig. (4:18)) must either be associated with a modification
of the Fermi surface of Zn due to the presence of impurity atoms, or be a component of the impurity susceptibility itself.

There are other alloy systems where a temperature independent term, $\chi_0$, in addition to a CW temperature dependence has been observed for the excess impurity susceptibility. Some examples are shown in table (4:8).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Peff</th>
<th>$\Theta$</th>
<th>$\chi_0$</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>RhMn</td>
<td>2.5</td>
<td>50</td>
<td>8.10^{-4}</td>
<td>(186)</td>
</tr>
<tr>
<td>CuFe</td>
<td>3.4</td>
<td>26</td>
<td>11</td>
<td>(127)</td>
</tr>
<tr>
<td>CuAuFe</td>
<td>24</td>
<td>-</td>
<td>8</td>
<td>(127)</td>
</tr>
<tr>
<td>SnMn</td>
<td>4.33</td>
<td>-</td>
<td>4</td>
<td>(190)</td>
</tr>
<tr>
<td>uB</td>
<td>K</td>
<td></td>
<td></td>
<td>emu/gm mole solute</td>
</tr>
</tbody>
</table>

Table(4:8) Temperature independent contributions to the impurity susceptibility.

The value of $\chi_0$ in the present results is a factor of ten (or more) larger than these values.

The Fermi surface of Zn is rather complicated (191) and in particular the axial ratio, $\frac{c}{a} = 1.83$, is very close to the critical value for the existence of the needle shaped portions of the Fermi surface in the 3rd band. As a result of their eccentricity (192) these needles would be expected to make rather a large contribution to the conduction electron diamagnetism when the magnetic field is parallel to the c-axis (ie along the length of the needle), and Verkin (193)
associated the peak in the diamagnetic susceptibility, \( \chi \), which occurs at about 112K, with the disappearance of the needles due to the thermal expansion of the lattice, which affects the \( \frac{c}{a} \) ratio.

When an impurity atom is added to pure Zn the resultant changes in the dimensions of the needles depends on a delicate balance between changes in the electron per atom ratio and changes in the axial ratio \( \frac{c}{a} \). For example Cu impurities result in a net increase in the needle dimensions because of a strong reduction of \( \frac{c}{a} \) on alloying, which over-compensates for the reduced mean electron per atom ratio (194).

In view of this discussion it is rather difficult to predict a priori what the effect of a given impurity will be on the Fermi surface of Zn and therefore on the conduction electron diamagnetism. The dHvA measurements of Holt and Myers (195) show that the period, \( P_1 \), which corresponds to electrons in the needle orbits is not very much different for pure Zn than for Zn alloys containing up to 90 at.ppm. Mn or 1400 at.ppm. of Ag (The value of \( P_1 \) with \( H//c \)-axis was increased by 5% in the former case and decreased by 5% in the latter.) These effects appear to be small, however it is rather difficult to relate quantitatively the change in the susceptibility of the matrix for a given change in the dimensions of the Fermi surface.

In conclusion therefore, it seems that we cannot rule out the possibility that the large temperature independent
term in the susceptibility is at least in part due to the modification of the host matrix properties on alloying, although since fig. (4.20) shows a large density of $\delta$-states at the Fermi energy for the VBS it also seems probable that some part of the temperature independent term $\chi_H$ will be associated with the impurity itself.

We comment finally on the apparent strong increase in the temperature independent susceptibility $\chi_H (> 4.2K)$ on first alloying at the lowest concentrations. Since the susceptibility of the ZnMn and ZnCr alloys was measured in fields of less than 5kOe (table (4.1)), whilst that for pure Zn (and also ZnFe alloys which have a temperature independent component which does extrapolate back to the pure Zn value, see fig. (4.44)) was measured in a field strength of about 25kOe, the effect might be due to a field dependence in the temperature independent susceptibility. Unfortunately we did not obtain the full field dependence at low temperatures of the susceptibility of pure Zn, however we have observed a field dependence in the susceptibility (at 4.2K and 1.3K) of ZnFe alloys of a similar magnitude (about 2 or 3% up to 25kOe), although the susceptibility is generally more diamagnetic at 5kOe than 25kOe, in the opposite sense from that required to explain the present effect.

Another possibility is that the limited temperature range over which the data was obtained (the same temperature range applies to every sample) has led to an artificial temperature independent component of about $0.7 \times 10^{-8}$ emu/gm,
arising from the computed fit to each sample, in addition to that which increases with the concentration of the solute, which we have discussed already and which, on the basis of fig. (4:19), seems to be a real effect. In order to resolve this possibility we would require more data above 15K to extend the temperature range of the fitted curve.

Finally one may speculate that the effect is due to the strong spin flip scattering, introduced even at the lowest solute concentrations, on the orbital motion of the conduction electrons in the applied magnetic field. Then, in the case of ZnFe, where the very shallow resistance minimum (110) is observed the spin flip amplitude must be correspondingly weaker and the effect will not be nearly so marked.
Field dependence of the magnetisation of dilute ZnMn and ZnCr alloys.

The magnetisation as a function of field shown in figs.(4:1) to (4:4) has been corrected for the host matrix magnetisation using the computed values of $X_H$. The impurity magnetisation, normalised for each alloy to 1 at.ppm. per gm. alloy is shows for Cr impurities in fig.(4:21) and Mn impurities in fig.(4:22).

In the case of Mn solute at 1.32K it is apparent that we are very close to attaining the saturation magnetisation, which allows us to make an estimate of the Mn spin which is independent of the CW curve fitting procedure. Taking the highest observed magnetisation of $2.6 \times 10^{-5}$ emu/gm/at.ppm. Mn and equating this to $N g u B S$, with $g=2$, we obtain $S=1.52$, confirming the value obtained from the CW fits.

Since the T=1.32K data for Mn solute provides the most complete magnetisation curve we have used it to compare some expressions for the magnetisation.

If we interpret our CW parameters rigorously in terms of the s-d model, ie using

$$
\frac{N}{3k} \frac{u^2 / 1.22}{(T+4.5 T_K)}
$$

then for Mn $S=1.83$ and $T_K = 0.11$, and for Cr $S=1.55$ with $T_K = 0.10$.

Curve I in fig.(4:22) is the magnetisation of a free spin with $S=1.83$ in the absence of interaction with the
conduction electrons, calculated using the Brillouin function $B_{1.83}(g_x)$ with $g=2$. The interaction between conduction electrons and local moment leads to a substantial reduction in the magnetisation at all fields. At 40k0e the measured magnetisation is $\sim 15\%$ reduced from the free spin ($S=1.83$) saturation magnetisation.

Curve II is the magnetisation deduced using the expression

$$M = N g_{\text{eff}} B_{1.83} B_{1.83}(g_{\text{eff}} x)$$

where $g_{\text{eff}}$ is a temperature and field dependent g-factor as discussed in chapter 1, see eqn.1(28). Loram et al. (33) have found this expression to describe quite well the magnetisation of Fe impurities in a Au matrix, but in the present case there appear to be substantial deviations for intermediate magnetisations ($1 < g_{\text{eff}} x < 5$).

We have already found that the initial magnetisation of the Mn atoms follows a CW law. This we can regard phenomenologically as a reduction in the magnetisation of the free spin (Curie law) due to the increased randomisation of $S_z$ in the presence of the spin flip scattering resulting from the s-d exchange coupling. This interaction may be accounted for in terms of an effective temperature for the impurity spin, $T^* = T + \Theta$, which is otherwise taken to be a free spin, then $M = \frac{CH}{T^*} < \frac{CH}{T}$ where $C$ is the Curie constant and $H$ is the (tending to zero) applied field. Curve III in fig.(4:22), which follows the experimental data more closely than curve II is
\[ M = N g u_B 1.60 B_{1.6}(g x^*) \]

where \[ x = \frac{u_B 1.6 H}{k_B T^*} \]

ie free spin behaviour but with \( T \rightarrow T^* \).

Figs. (4:23) and (4:24) show all the magnetisation data at 1.32K and 4.2K, for each alloy, plotted as a function of \( gx^* \). For both Mn and Cr solutes, in the region of overlap of the 4.2K and 1.32K data, \( 0 \leq gx^* \leq 1.7 \), the magnetisation is, within experimental uncertainty, a universal function of this parameter. Although as might be expected, (on the basis of the initial susceptibility being described by \( \frac{C}{T^*} \)), the appropriate free spin Brillouin function, with \( T \) replaced by \( T^* \), fits the low field data (\( x^* \leq 0.6 \)), there are more marked deviations at higher fields. The latter deviations are not surprising in view of the fact that the magnetic field itself would be expected to progressively modify the coupling between the local spin and the conduction electrons through a freezing out of the spin flip scattering process.

If we suppose, as eqn.1(26)b suggests, that the effective temperature at a given absolute temperature, \( T \), is increased at higher fields, then this would bring the theoretical curves in figs.(4:23) and (4:24) into closer agreement with the experimental data by reducing the predicted magnetisation at the highest fields. We should note, however, that this agreement may be fortuitous, since it is by no means obvious that it is permissible to use a Brillouin function to describe the magnetisation of a system of non-half integral spins.
Fig.(4.21) SOLUTE MAGNETISATION vs. FIELD FOR ZnCr ALLOYS

- MAGNETISATION per at. ppm SOLUTE
  - 25 x 10^{-5} emu/gm alloy
  - 1.3 K
  - 4.2 K

- MAGNETIC FIELD KOe
  - Data from each alloy within point

- Symbols:
  - ○ 35.1 at. ppm Cr
  - △ 26.8
  - □ 10.0
  - ▽ 8.8
Fig. (4.22) Solute magnetisation vs. field for Zn Mn alloys

10^{-5} \text{emu/gm alloy}

N_0 \mu_B = 1.60

Magnetic field, KOe

38.9 at. ppm. Mn

16.7

6.8

Data from each alloy within point
Fig. (4.23) Solute magnetisation of Zr-Mn alloys

Comparison of field dependence with $B_{1.60}(x)$

$N_{g_B} 1.60$

$B_{1.60}(x)$

Data at $T = 1.3K$

Data at $T = 4.2K$

$x = \frac{g_{u_B} 1.60 H}{k_B (T+0.48)}$
Fig. (4.24) Solute magnetisation of ZnCr alloys
Comparison of field dependence with $B_{1.35}(x)$

$\nu = 0.1 + 0.15(T - 0.44)$

- Data at 1.3K
- Data at 4.2K
Finally we note that an attempt to describe our data within the framework of the LSF model, by using a temperature and field dependent enhancement factor in the same way as Swallow and White (35) who were able to describe the magnetisation of dilute AuFe alloys, proved unsuccessful, the predicted magnetisation at 40kOe being some 10% too high.

Electrical resistivity of dilute ZnMn and ZnCr alloys

The resistivity of 5 ZnMn alloys with concentrations 61.0, 41.9, 22.6, 17.1 and 7.4 at.ppm. of Mn and of 5 ZnCr alloys with concentrations 51.9, 27.1, 26.5, 24.2 and 10.0 at.ppm. of Cr was measured over the temperature interval 4.2K to 1.3K using the 4 terminal D.C. technique and apparatus outlined in chapter 2.

The resistance ratio of each of the resistivity specimens, some (see table (3:3) and table (3:4)) of which were cut from the same alloy as was used to provide a susceptibility specimen, was determined with a relative precision of ±0.1%. (The resistance of each specimen at 273K was obtained by immersing the sample chamber of the resistivity apparatus in an ice/water bath, after the resistances at 4.2K and below had been measured).

The concentrations of the alloys used throughout this section are based on the resistivity ratio of the actual resistivity specimen (after subtracting the resistivity ratio of a sample of 6N Zn), rather than that measured for a section of the alloy immediately after quenching. For most of the alloys these two determinations of the concentration differed by less than 1 at.ppm. To convert the high precision
residual resistivity ratio measurements into solute concentration we have used the figures 3.30 and 3.65 for the residual resistivity ratio per at.% of Cr and Mn respectively, as were deduced from the data in chapter 3, see figs. (3:2) and (3:3).

In figs. (4.25) and (4.26) we show the resistivity of the ZnCr and ZnMn alloys respectively. In each case we have subtracted the resistivity of a sample of the original 6N Zn which was melted and quenched from the melt in exactly the same way as the alloys.

Fig.(4.27) shows the total uncorrected resistivity of the most dilute alloy which was measured (Zn + 7.4at.ppm. Mn) together with the resistivity of the 6N Zn specimen. In this temperature range the temperature dependence due to the phonon resistivity is still very small and represents an almost negligible correction to the strong logarithmic dependence associated with the Mn atoms. Also the magnitude of the residual resistivity due to non-magnetic impurities and imperfections in the crystal structure of the 6N Zn represents a temperature independent correction of less than 10% to the resistivity of even this most dilute alloy.

The resistivity data in figs.(4:25) and (4:26) show no significant departures from a purely logarithmic temperature dependence, even for the highest concentrations at the lowest temperatures. The logarithmic variation of the resistivity is compatible with the well defined local moment on the Mn and Cr solute in Zn in this temperature region, as
Fig (4.25) Solute Resistivity of ZnCr Alloys
Fig. (4.26) Solute Resistivity of \( \text{Zn-Mn} \) Alloys

61.02 at. ppm.
Fig. (4.2) Comparison of temperature dependence of the solute and lattice resistivity.

Resistance

6N pure Zn (Batch 5561)

Zn + 7.41 at. ppm Mn
Fig. (4.28) Temperature dependence of the resistivity in Zn-Mn alloys.

\[ \frac{d\rho}{d\log T} \]

\[ \text{at. ppm. Mn} \]
Fig. (4:29) TEMPERATURE DEPENDENCE OF THE RESISTIVITY ZnCr ALLOYS

\[ \frac{d\rho}{d\log T} \]

at. ppm. Cr
Fig. (4.30). Concentration dependence of the log. derivative of the resistivity ZnMn alloys.

\[
\frac{1}{C} \frac{d \ln \rho}{d \ln T} = \frac{\text{NO-CM}}{\text{DEC.T-AT.PPM.}}
\]

C, at. ppm. Mn
Fig. (4:31)
CONC. DEPENDENCE OF THE LOG. DERIVATIVE OF THE RESISTIVITY, ZnCr ALLOYS

\[-\frac{1}{C} \frac{d\rho}{d\log T}\]

N2-CM
DEC.T-AT.PPM.

\(\pm 1\%\)

C, at.ppm. Cr
Fig. (4:32) Probability that a given Mn atom has no near neighbour Mn on the closest 1700 lattice sites, as a function of Mn concentration.
implied by the CW temperature dependence in the susceptibility.

If interactions between the local moments are entirely negligible we should observe that the logarithmic derivative of the resistivity, \( \frac{\partial \rho}{\partial \log T} \), should scale linearly with the concentration. Figs. (4.28) and (4.29) show, for Mn and Cr solutes respectively, \( \frac{\partial \rho}{\partial \log T} \) as a function of the solute concentration, and for both solutes we observe a progressive reduction with increasing concentration. For ZnCr alloys in particular we do not observe the dramatic decrease by a factor of two in the value of \( \frac{\partial \rho}{\partial \log T} \) per at.ppm. Cr observed by Ford et al. (105) for alloys with concentrations below about 30 at.ppm. The present data are in closer agreement with the higher concentration range of alloys \((c \geq 30 \text{ at.ppm. Cr})\) measured by Ford et al. and these authors now concede (105) that the explanation of the apparently anomalous behaviour of their low concentration alloys lies in a systematic error in the Cr concentration through oxidation of the melt during the casting of the alloys.

Although both Newrock et al. (107) and Ford et al. report for ZnMn and ZnCr alloys in this concentration \((c < 100 \text{ at.ppm.})\) and temperature range, a pure logarithmic temperature dependence for the resistivity, neither group reports any concentration dependence in \( \frac{\partial \rho}{\partial \log T} \). On the other hand Hedgecock and Rizzuto (106) have observed for ZnMn alloys with concentrations \(c \geq 500\text{at.ppm. Mn}\), a maximum in the impurity resistivity in the region of 1K,
moving to higher temperatures as the concentration is increased. These latter authors explain this phenomenon in terms of the onset of magnetic order through indirect interaction between the Mn spins, brought about by the long range conduction electron spin polarisation (eg RKKY) which is induced about each magnetic solute atom. The effective internal field which results at each Mn site due to the conduction electron spin polarisation tails from all the other Mn impurities progressively freezes out the spin flip component of the impurity scattering and thus depresses the logarithmic term in the resistivity. Collings, Hedgecock and Muto (115) have observed that the magnetic susceptibility of a 0.43 at.% ZnMn alloy has a maximum at a temperature of 6 ±1K with anti-ferromagnetic ordering below this temperature.

In figs.(4:30) and (4:31) we show, for Mn and Cr solute respectively, \( \frac{1}{c} \frac{\partial \rho}{\partial \log T} \) versus the concentration, c. A linear decrease in the former parameter is observed, consistent with

\[
\frac{\partial \rho}{\partial \log T} = \alpha c + \beta c^2
\]

\[4(10)\]

\( \alpha \), the intercept on the \( \frac{1}{c} \frac{\partial \rho}{\partial \log T} \) axis, is the logarithmic derivative of the resistivity due to truly isolated Mn atoms, ie in the limit of infinite dilution, \( c \to 0 \). We find that the values of \( \alpha \), as with the CW \( \Theta \) values, for Mn and Cr are very similar

<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>-0.472</td>
<td>-0.460</td>
</tr>
</tbody>
</table>

\( \Omega\)-cm/decade T/at.ppm.
From these values for $\alpha$, and using the expression (17) for the impurity resistivity we obtain $J(Mn) = 0.16$ eV and $J(Cr) = 0.19$ eV for the respective s-d coupling constants.

For both Mn and Cr the deviation from the infinite dilution limit for $\frac{\partial \rho}{\partial \log T}$ is proportional to the square of the concentration, this is characteristic of the modification of the isolated atom behaviour being due to interactions between pairs of impurities, as in eqn. 1(83). We observe

\[
\begin{array}{ccc}
  \text{Mn} & \text{Cr} & \\
  \beta & +0.8 \times 10^{-3} & +1.0 \times 10^{-3} \pm 0.2 \times 10^{-3} \\
  \text{mm-cm/decade T/(at.ppm.)}^2 & & \\
\end{array}
\]

The effect of interactions between pairs of solute atoms is to reduce the modulus of the logarithmic derivative of the resistivity. The model calculation which we discussed in chapter 1, due to Matho and Beal-Monod (90), also predicts that an interaction between two localised spins of the form $H_w = -W S_1 \cdot S_2$ (see eqn. 1(75)) will lead, in the limiting case $|W| \gg 1$ to a mean reduction of 50% from the single impurity resistivity $R_0$, eqn.1(77), provided that $W \equiv W(r_{12})$ is an oscillatory function of the spatial separation of $S_1$ and $S_2$, so that equal numbers of the impurities are coupled ferromagnetically as are coupled antiferromagnetically, see eqns. 1(76) and 1(78) and the subsequent text. As with CuMn, the dominant contribution to $W(r_{12})$ between Mn (or Cr) spins in a Zn matrix will be from the Caroli double resonant scattering mechanism, eqn. 1(70).
In terms of the Matho and Beal-Monod model for interacting pairs of impurity spins, let $2c_2$ be the concentration of Mn (or Cr) atoms which have a nearest neighbour Mn (or Cr) atom occupying one of the superthermal lattice sites, i.e. $c_2$ is the concentration of pairs of Mn (or Cr) atoms. The radius of the sphere which encloses the superthermal lattice sites is given by eqn. 1(82) and the superthermal volume expands proportionally to $T^{-1}$. For simplicity, however, we shall take the number of superthermal sites to be constant over the experimental temperature range, which enables us to write down for the logarithmic slope of the resistivity of an alloy of concentration $c$

$$\frac{\delta \rho}{\delta \log T} = \alpha(c - 2c_2) + \left(\frac{\alpha}{c_2}\right)^2 c_2$$  \hspace{1cm} \text{4(11)}

where the first and second terms of the above equation correspond to the contribution from Mn (or Cr) impurities with no superthermal nearest neighbour, and those which do have a superthermal nearest neighbour, respectively. According to the calculations of Matho and Beal-Monod the temperature dependence of the resistivity in the latter case will be, on average, halved, hence the factor $\frac{\alpha}{c_2}$.

The experimental results for ZnMn alloys may be expressed as

$$\frac{\delta \rho}{\delta \log T} = -0.472 c + 0.8 \times 10^{-3} c^2$$  \hspace{1cm} \text{4(12)}

so by comparison with eqn. 4(11) we can deduce that

$$c_2 = 1.7 \times 10^{-3} c^2 \hspace{1cm} \text{4(13)}$$

or

$$c_2 = 1700 c^2$$
where \( c \) now is measured as the atomic fraction of impurities in the alloy.

The expression \( 4(13) \) means that, within the 1.3K to 4.2K temperature range, a given Mn atom will couple to its nearest neighbour Mn atom if this second atom is situated on one of the 1700 lattice sites closest to the first. These sites are the so-called superthermal sites on which the strength of the coupling via \( W(r_{12}) \) to the atom at the origin exceeds the thermal energy appropriate to the present temperature range.

In fig. (4:32) we have plotted the percentage of Mn atoms in a ZnMn alloy of concentration \( c \) which do not have a nearest neighbour Mn on a superthermal site, taking our expression \( 4(13) \) for the concentration of coupled pairs. Such atoms may be regarded as isolated, and it is apparent from fig. (4:32) that for \( c \geq 1000 \text{ at.ppm.} \) Mn the overwhelming majority of the Mn atoms will have their properties modified by pair (and higher order) couplings. This prediction, based entirely on the results of our resistivity measurements for \( c < 60 \text{ at.ppm.} \), is consistent with the observation, by Hedgecock and Rizzuto (106) of the onset of a maximum in the resistivity occurring in the same 1.3K to 4.2K regime for ZnMn alloys containing in excess of about 1200 at.ppm, and suggests that the same interaction mechanism is responsible, presumably the long range Caroli mechanism, eqn.1(70), which is the dominant one also in CuMn alloys.
For the hexagonal close packed Zn crystal structure \( c = 1.86 \) and \( a = 2.66 \, \text{Å} \), the volume per lattice point is \( 15 \, \text{Å}^3 \). The criterion, eqn. 4(13), that the neighbouring atom of a pair is situated on one of the 1700 closest lattice sites corresponds to a critical separation of \( \sim 18 \, \text{Å} \), below which the properties of the Mn atoms are strongly modified, in this temperature range.

The coefficients, \( \alpha \) and \( \beta \), are not much different for Cr than for Mn, and the reduction of \( \frac{\partial \epsilon}{\partial \log T} \) would correspond to a concentration of pairs given by \( c_2 = 2170 \, c^2 \) and a critical radius of separation of \( 20 \, \text{Å} \), which is not significantly different, in view of the semiquantitative nature of the analysis which we have pursued.

Taking expression 1(70) derived by Caroli for the interaction energy between two magnetic solute atoms resulting from double resonant scattering, we can insert \( E_F = 9.4 \, \text{eV} \) and \( k_F = 1.57 \times 10^3 \, \text{cm}^{-1} \) for the free electron parameters appropriate to a Zn matrix, and our susceptibility data, in conjunction with the residual resistivity, yield \( n_{d\uparrow} = 4.1 \) and \( n_{d\downarrow} = 0.9 \) d electrons for a Mn solute, which leads, using the Friedel sum rule, eqn. 1(8), to

\[
E(r) \approx 30 \cos \left( \frac{2k_F r + 2\pi}{(k_F r)^3} \right) u_1 u_2 \, \text{eV} \quad 4(14)
\]

for the coupling energy due to the Caroli mechanism between Mn atoms in the Zn matrix. In the notation of the Matho and Beal-Monod (MB) model eqn.1(81) combines with eqn.1(75)
and reduces to

\[ H_w = \frac{2\sqrt{2}}{N(r)} (3.10^{-13}) \cos (2k_F r + 2\pi) S_1 \cdot S_2 \text{ ergs} \]

so that \( W_1 = 3.10^{-13} \) ergs, and the number of superthermal lattice sites, eqn. 1(82), is given by

\[ N_s(T) = 4 \frac{\pi r_c^3}{V_0} = 2 \frac{W_1}{k_B T} = 6.10^{-13} \]

The value of \( r_c \) deduced from the above equation increases from 15 \( \hbar \) to 23 \( \hbar \) as the temperature is reduced from 4.2K to 1.3K, and for \( T=2K \), the mean reciprocal temperature over this temperature range, \( r_c = 20 \hbar \), which is in excellent agreement with the estimate of \( r_c = 18 \hbar \) deduced solely on the basis of the resistivity data and the MB model.

In the above discussion we have not considered the possibility that the pair coupling interactions actually lead to a change in the characteristic or Kondo temperature of pairs compared to that for truly isolated Mn or Cr atoms. The Caroli interaction, as we have discussed in chapter 1, is certainly capable of modifying the Anderson parameters, \( \Delta \) and \( E_d \), of the impurity VBS and thus \( T_K \). Since the scale of the resistivity is determined by \( T_K \), see eqn. 1(33) for example, if the pair interactions would result in either a large reduction or a large increase in \( T_K \) for the coupled solute atoms, then in the temperature range of the present experiment, their contribution to the temperature dependence would be decreased compared to the isolated atoms, which is
the effect observed in our data. However, at somewhat higher temperatures, ZnMn alloys with concentrations well in excess of 1000 at.ppm. have an excess impurity susceptibility which follows a Curie law rather closely (115), ruling out an increase in the characteristic temperature of pair coupled solute atoms which would result in a large CW component, having a large $\Theta$ value. In order to decide if there is a substantial reduction in $T_K$ for pairs, directly, one would need to look at the properties of extremely dilute alloys at temperatures $T \ll 0.4K$ where the isolated solute atoms would contribute a temperature independent component to the susceptibility, whereas the pairs, if they had a much reduced characteristic temperature would still appear magnetic. Since the resistivity data which we have obtained can be explained rather well in terms of the MB model, where $T_K$ for the isolated atom is assumed to be unchanged in the presence of pair coupling, it would seem in fact that the characteristic temperature of the isolated Mn atom is rather insensitive to the Caroli interaction with its neighbours.

In conclusion then it would appear that the concentration dependence observed in the present resistivity data may be explained, even semi-quantitatively, by the MB model for coupled pairs of impurity spins, assuming the Caroli interaction to be responsible for the coupling, and using the present susceptibility data to deduce the strength of this interaction.
We would now like to discuss the resistivity results in conjunction with the susceptibility data in more detail. Firstly we make the general observation that the interaction effects are not so apparent in the susceptibility data as in the resistivity. The Curie constant, for example, is much more closely a linear function of the concentration (see fig.(4:17)) than was \( \frac{d\rho}{d\log T} \).

We have already seen that the s-d model is capable of accounting for the gross features of the present data on dilute ZnMn and ZnCr alloys, ie the CW temperature dependence of the susceptibility and the logarithmic temperature dependence of the resistivity. We shall now use the predictions of the s-d model in greater detail to see if they are capable of explaining the behaviour of these alloys.

The Curie constant per atom for a given solute in a given matrix is, in the absence of interactions, dependent only on \( S(S + 1) \) where \( S \) is the spin on the solute atom. On the other hand, again for isolated impurities \( \frac{1}{c} \frac{d\rho}{d\log T} \) is proportional to the product \( J^3 S(S + 1) \), where \( J \) is the antiferromagnetic coupling constant between the local moment and the conduction electron spin (eqn.1(17)). The constant of proportionality depends only on the host matrix properties. Thus for susceptibility and resistivity measurements on a single alloy with fixed concentration

\[
G = \frac{\frac{d\rho}{d\log T}}{\text{Curie constant}} \propto J^3
\]

4(18)

If we now change the solute, but keep the host matrix
unchanged, e.g. Mn and Cr in Zn, the constant of proportionality in eqn. 4(18) above is unchanged and

\[ \frac{G(Mn)}{G(Cr)} = \left[ \frac{J(Mn)}{J(Cr)} \right]^3 \quad 4(19) \]

In fig. (4.33) we show the Curie constant for each alloy, normalised to account for any small (<5% in practice) differences in the concentrations of susceptibility and resistivity specimens cut from the same alloy, versus \(\frac{\partial \rho}{\partial \log T}\) for that alloy, corrected for the reduction due to interactions between impurity pairs which we have already discussed. The linear relationship, confirming eqn. 4(18), is evident for alloys of a given solute and, from the respective gradients we deduce \(\frac{G(Mn)}{G(Cr)} = 0.81\), corresponding to \(J(Mn) = 0.93 J(Cr)\). Since the s-d coupling constant for Cr is larger than that for Mn, the s-d model expression for the Kondo temperature, eqn.1(18)

\[ T_K = T_F \exp \left[ -\frac{1}{n(0) |J|} \right] \quad 4(20) \]

would predict that \(T_K\) would be somewhat larger also. From the above equation it follows that

\[ \frac{T_K(Mn)}{T_K(Cr)} = \left[ \frac{T_K(Mn)}{T_F} \right] \left(1 - \frac{J(Mn)}{J(Cr)}\right) \quad 4(21) \]

so that taking \(T_F \approx 10^5 K\) and \(T_K(Mn) \approx 0.5K\) we obtain \(T_K(Cr) = 2.3 T_K(Mn)\). This factor of two increase in \(T_K\) for Cr is not evident in the present susceptibility data, which imply \(T_K(Mn) \approx T_K(Cr)\).
This inconsistency which is apparent in the more detailed comparison of the s-d model to the experimental data may be attributable to the failure of the model to take into account the effects of any residual unquenched orbital momentum which may be important for Cr (Mn ion has $L=0$) when dissolved in a high symmetry host such as Zn, (189).
Fig. (4.33)
NORMALISED CURIE CONSTANT vs. (CONC)\(^{-1}\) DEPENDENT PART
OF LOG. DERIVATIVE OF THE RESISTIVITY

\[
d\frac{\theta}{d\log T}
\]

NORMALISED CURIE CONST. EMU/GM •

\[\text{CURIE CONST. (normalised)}\]

\(\text{EMU/GM}\)

- ZnCr
- ZnMn
Magnetic susceptibility of dilute ZnFe alloys

The magnetic susceptibility of pure Zn and of five ZnFe alloys of concentration 58, 69, 84, 115 and 133 at.ppm. was measured in a fixed field of 25kOe and over a temperature interval from 1.3K to 60K. The results are shown in figs. (4:34) and (4:35). Also shown in fig. (4:35) is the susceptibility, as measured in a magnetic field of 14kOe, of a ZnFe alloy containing 356 at.ppm. Fe which, since its apparent resistance ratio per at.% is reduced below that found in alloys with $c \leq 133$ at.ppm., see fig.(3:4) and table (3:6), is beyond the solubility limit for Fe in Zn alloys quenched directly from the melt using the present technique.

The strong temperature dependence which we observed in the case of ZnMn and ZnCr alloys is clearly absent for Fe solute when $c \leq 133$ at.ppm. However, below about 25K there is a small but well defined upturn, which is absent from the pure Zn control sample, but which increases with the Fe concentration to about $5 \times 10^{-9}$ emu/gm in the case of the 133 at.ppm. alloy. A change in the susceptibility of this order is by the usual standards a rather small effect, however by making several determinations of the force at each temperature on relatively massive ($\sim 3$ gm) samples and utilising the inherent stability of the persistent current mode for the main field windings it was possible to attain a precision in excess of $10^{-10}$ emu/gm in the total susceptibility of the ZnFe alloys. This is evident in fig. (4:36)
where we show as an example susceptibility as a function of temperature for the 84 at.ppm. alloy on an expanded scale. The increasingly diamagnetic susceptibility for the alloy above about 30K is also reflected in that for pure Zn which is included in the diagram for comparison.

Contamination of the 133 at.ppm. Fe alloy by only 0.3 at.ppm. of Cr or Mn would be sufficient to account for an upturn of the observed magnitude. The quoted Mn contamination of the Fe used was 3ppm, which would correspond to only 0.0004 ppm in a 133 at.ppm. alloy. In addition a section of the ZnFe master alloy was examined by the Imperial College Analytical service for traces of Mn or Cr, which were not detected. The lower limit of detection for Mn (1 ppm.) and Cr (0.1 ppm.) would correspond to a maximum contamination level of 0.005 ppm. Mn or 0.0006 ppm. Cr in the 133 at.ppm. Fe alloy.

Having established that the low temperature upturn in the susceptibility is not the result of spurious contamination by Mn or Cr, we must distinguish whether this effect is a genuine characteristic of the isolated Fe atom, or alternatively, if it should be ascribed to a relatively small number of 'magnetic pairs' of Fe atoms, or even clusters containing higher numbers of Fe atoms. In CuFe alloys the modification of single impurity properties by 'pair coupling interactions' is so as to reduce the characteristic temperature of the Fe solute by about one order of magnitude, the CW $\Theta$ for isolated atoms is about 30K whilst that for the pairs is
Fig. (4:34) MAGNETIC SUSCEPTIBILITY ZnFe ALLOYS

-16 \times 10^{-8} \text{ emu/gm}

Temperature K
Fig. (4:35) Magnetic susceptibility of ZnFe alloys

- Zn + 356 at. ppm Fe
- Zn + 133 at. ppm Fe
- 6N pure Zn

Temperature K

10⁻⁸ emu/gm
Fig.(4.36) Susceptibility of pure Zn (*)
and Zn + 84 at. ppm Fe (•) vs. Temperature

Temperature K

$10^{-9}$ emu/gm.
between 2K and 5K depending on the concentration of the alloy (61) (127).

In a random solid solution, the number of Fe atoms which have a nearest neighbour within a given radius increases with the square of the concentration. Thus, if the upturn is attributable to pair coupling effects we would expect that it would scale with the square of the concentration of the alloy, on the other hand, a true single impurity property must increase in magnitude linearly with the concentration of the alloy.

In figs. (4:37) and (4:38) we have plotted the raw data for the temperature dependence of the susceptibility of each alloy relative to 1.3K and normalised to the concentration and the square of the concentration respectively. With the exception of the 133 at.ppm. sample there seems to be a remarkable scaling of the alloys with concentration alone. At first sight this could be taken as evidence for single impurity characteristics, especially in view of the markedly worse coincidence of the data when scaled against the concentration squared, fig. (4:38). However it is rather difficult to understand why the 133 at.ppm. Fe alloy has such an enhanced temperature dependence, implying a significant number of pairs or clusters, when an alloy of 115 at.ppm. Fe falls in nicely with the alloys of lower concentration. One might argue that the distribution of Fe atoms within the alloy will depend sensitively on the exact details of its metallurgical history (e.g. speed of quenching) but it is difficult to be quantitative about such effects and all the alloys were certainly prepared
using the same basic technique, which we have already
described in chapter 3.

The solid line through those alloys (58, 69, 84, 115
at. ppm. Fe) which do appear to scale with the concentration
is the result of a least squares fit to a CW relation, for
which we find the CW $\Theta$ to have a value of $\sim 4K$. The Curie
constant corresponds to a tiny effective moment of only
$p_{\text{eff}} = 0.3 \ u_B$ which is in remarkable agreement with the
value of $p_{\text{eff}} = 0.26 \ u_B$ deduced by Caplin, by scaling the
magnitude of the logarithmic temperature dependence in
the resistivity in dilute ZnFe alloys to that for Fe
dissolved in \(\varepsilon\)-phase CuZn alloys where, towards the Cu rich
end of the phase, the Fe atom carries a moment of $\sim 1.5 \ u_B$.

Since the effects we are observing are so small,
before drawing any firm conclusions about the concentration
dependence of the upturn we should examine the consequences
of subtracting the small temperature dependence which we
have observed in the 6N pure Zn sample. This amounted to
only $5 \times 10^{-10}$ emu/gm between 1.3K and 25K. In figs. (4:39)
and (4:40) we show the excess temperature dependent part
of the susceptibility of the alloys relative to the Zn
data normalised to the concentration and to the concentration
squared respectively. The distinction between the quality
of the fit is now much less clear-cut and it is rather
difficult to claim an ambiguous evidence in favour of either
$c^1$ or $c^2$ concentration dependence. The inadequacy of
the present data in this respect is clearly shown in fig.(4:41)
where we have plotted the total increase in the excess
Fig. (4.37) Low temperature upturn, Zn Fe alloys

\[ \Delta = X(1.3K) - X(T) \]

\( \Delta / C \text{ emu/gm} \) at. ppm.

- ○ 58 at. ppm. Fe
- ■ 69
- △ 84
- ▽ 115
- ● 133
Fig. (4.38) Low Temperature Upturn, ZnFe Alloys

\[ \Delta = X(1.3K) - X(T) \]
\[ \Delta = X(1.3K) - X(T) \]

- 58 at. ppm. Fe
- 69 "
- 84 "
- 115 "
- 133 "

\[ \frac{\Delta - \Delta_{Zn}}{c} \]

emu/gm

at. ppm.
Fig. (4:40) Low temperature upturn vs $C^2$

$$\Delta = X(1.3K) - X(T)$$

Symbols:
- 58 at. ppm. Fe
- 69 "
- 84 "
- 115 "
- 133 "

Other symbols and annotations are not clearly visible due to the image quality.
Fig. (4.41) Concentration Dependence of Excess Susceptibility in $\text{ZnFe}$ Alloys
impurity susceptibility, normalised to the Fe concentration. On this graph a horizontal line corresponds to a single impurity effect (ie $\propto c^1$), whilst a straight line through the origin would be consistent with pairs (ie $\propto c^2$) of Fe atoms. Line I, which is nearly horizontal, showing a large intercept on the $\Delta X/c$ axis, can be drawn if we reject the point corresponding to the 133 at.ppm. alloy. Line II, implying magnetic pairs, is equally satisfactory if we reject the point corresponding to the 115 at.ppm. sample.

In addition to the temperature dependence of the susceptibility in a fixed field, we have also measured the magnetisation (up to 45 kOe) at 4.2K and 1.3K. We shall now examine this data in some detail to see if it is capable of resolving whether the low temperature upturn is due to properties of an isolated Fe atom, demanding from the CW fit a small $p_{eff}$ at each impurity site, or if this effect is the result of a small fraction of the Fe atoms which, as a result of pair coupling interactions, have a somewhat larger effective moment (corresponding to two ferromagnetically coupled Fe atoms ie $\sim$ few $u_B$) and a small enough characteristic temperature so that 'magnetic' properties are still observed at the lowest temperature (1.3K) in the present experimental range. Isolated Fe atoms, in this picture, would have a somewhat higher characteristic temperature (cf Fe in Cu matrix) and contribute 'non-magnetic' properties, eg temperature independent enhanced Pauli
susceptibility in the low \((T \leq 25K)\) temperature range.

First we shall consider the magnetisation vs. field data for the 356 at.ppm. alloy which is shown, along with that for the 133 ppm. alloy for comparison in fig. (4:42). Since the 356 at.ppm. alloy exceeds the solubility limit we must expect that there will be a partial precipitation of the Fe, leading to Fe enriched regions, or clusters, and thus a considerably enhanced probability of small separations between Fe nearest neighbours. The very strong temperature dependence of the susceptibility (fig.(4:35)) which we have already seen for this alloy confirms our assumption that pairs or groups of interacting Fe atoms are more magnetic than the isolated Fe atoms.

The magnetisation as a function of field for the 356 at.ppm. alloy, fig. (4:42), shows a distinct curvature, characteristic of the kind of saturation of spins which we have already discussed in the case of ZnMn and ZnCr. This aspect of the data is not apparent for the 133 at.ppm. alloy. At 1.3K for 356 at.ppm. alloy saturation appears to be approaching completion in the region of 20k0e. In the case of the Mn solute, fig.(4:22), at 1.3K the impurity magnetisation was very nearly saturated in a field of 40k0e and the value of the spin was \(S = 1.6\). Since the magnetic component of the ZnFe alloy saturates in half the field strength, a very crude estimate would place its spin value at \(S \approx 3\), which is not inconsistent with the magnetic component being ferromagnetically coupled pairs of Fe atoms. The saturation of the magnetisation of the 356 at.ppm. Fe alloy is not complete at 4.2K in a field of 40k0e which is
also consistent with a very low characteristic temperature placing $\Theta < 2K$. (If $\Theta = 0$, ie free spin behaviour, we would expect saturation around 60kOe and as $\Theta$ increases the saturation field at 4.2K would decrease, $\Theta = 2K$ would correspond to saturation in a field of 40kOe at 4.2K).

The magnetisation vs field data for the 356 at.ppm. Fe alloy is thus consistent with interactions between the Fe atoms, at least at this level of concentration, being dominated by ferromagnetic pairs of Fe atoms, resulting in a magnetic pair with, effectively, a spin of about 3 and a characteristic temperature below 2K. This information provides us with a possibility of distinguishing whether the low temperature upturn observed in the most dilute alloys is due to isolated atoms or a relatively much smaller number of magnetic pairs, regardless of the ambiguity in the concentration dependence of the upturn. The point is that, as we have seen, the magnetisation due to a spin of about 3 will become completely saturated at 1.3K, and at least 50% saturated at 4.2K at fields in the region of 40kOe. This being so, the change in the impurity component of the susceptibility between 4.2K and 1.3K, which at a given field, $H$, is given by

$$\Delta \chi(H) = \frac{M(1.3,H) - M(4.2,H)}{H}$$    \hspace{1cm} 4(22)
Fig. (4.42) MAGNETISATION vs. FIELD

Zn Fe ALLOYS

MAGNETISATION
emu/gm.

356 at. ppm Fe, T = 1.3 K
T = 4.2 K
133 at. ppm Fe, T = 1.3 K
T = 4.2 K
Fig. (4.43) Reduction of the apparent temperature dependence, $S_X$, Eqn 4.22, with increasing field strength.

$S_X(H)$, emu/gm.

- ▲ 133 at. ppm. Fe
- • 115
- ▼ 84
- ■ 69

$H$, kOe
where $M(T, H)$ denotes the total magnetisation of the alloy at temperature $T$ and field strength $H$, will be progressively reduced in higher and higher fields, and equal to zero for fields in excess of that required to saturate the magnetisation of the spins at 4.2K.*

On the other hand, the magnetisation due to a tiny spin, $p_{\text{eff}} = 0.3 \, \mu_B$ implies $S = 0.02$ a factor of 100 smaller, will be, for all practical purposes a linear function of the applied field for the range of fields and temperatures which are accessible in the present apparatus. In this case we should therefore observe a $\chi'(H)$ which is independent of applied field.

In fig. (4:43) we show $\chi'(H)$ as a function of the field for each ZnFe alloy ($c \leq 133$ at.ppm) and we see a strong reduction with increasing field which is inconsistent with the small spin value demanded by the single impurity interpretation.

Another criterion for separating small spin character from large spin character in this magnetisation data lies in the temperature dependence of the high field differential susceptibility. In the case of the small spin, for the reasons already outlined above, we should observe the

*Since we are subtracting the magnetisation at 1.3K from that at 4.2K, in the same field strength, any inherent field dependence in the susceptibility of the Zn host matrix is automatically discounted from $\chi'(H)$. For details of this field dependence see the Appendix A.
same change in the high field slope between 4.2K and 1.3K as we observe in the susceptibility measured at any single fixed field value in the present experimental range. We shall define the high field differential susceptibility, between 23k0e and 38k0e as

$$\Delta X^{23/38}(T) = \frac{M(38,T) - M(23,T)}{38 - 23} \cdot 10^{-3}$$

where $M(H,T)$ is the same parameter as we have used in eqn. 4(22).

In table (4:9) below we compare the difference,

$$\Delta X^{23/38}, \text{ in } X^{23/38}(T) \text{ between } T=4.2K \text{ and } T=1.3K,$$

with the corresponding change in the susceptibility as measured in a single fixed field of 25k0e, ie $\delta X(25)$ as given by eqn. 4(22). $\Delta X^{23/38}$ or $\delta X(25)$ positive corresponds to increased paramagnetic susceptibility at 1.3K compared to the 4.2K value.

We see that the main feature of the susceptibility as measured at 25k0e, namely the upturn at low temperatures (T $\leq$ 25K), is absent.

<table>
<thead>
<tr>
<th>Fe concentration at ppm.</th>
<th>$\Delta X^{23/38}$ emu/gm.</th>
<th>$\delta X(25)$ emu/gm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>69</td>
<td>$-0.033 \times 10^{-8}$</td>
<td>$+0.05 \times 10^{-8}$</td>
</tr>
<tr>
<td>84</td>
<td>$-0.043$</td>
<td>$+0.09$</td>
</tr>
<tr>
<td>115</td>
<td>$-0.080$</td>
<td>$+0.12$</td>
</tr>
<tr>
<td>133</td>
<td>$-0.012$</td>
<td>$+0.21$</td>
</tr>
<tr>
<td>356</td>
<td>$-0.565$</td>
<td>$+2.56$</td>
</tr>
</tbody>
</table>

Table (4:9) Temperature dependence of the high field differential susceptibility of ZnFe alloys
in the high field differential susceptibility. Infact
\[ \chi^{23/38} \text{ is more diamagnetic at 1.3K than at 4.2K, exactly} \]
the opposite effect. This feature is, however, reconcilable
with the incomplete saturation of the magnetic pairs at
4.2K, where they will still contribute a small positive
component to the differential susceptibility as given by
eqn. 4(23). At 1.3K, since they are essentially saturated
by fields in excess of 20kOe, between 23kOe and 38kOe the
pair magnetisation is essentially independent of the applied
field in this region and so does not contribute to the
differential susceptibility at this temperature and field
interval. The total differential susceptibility, as given
by eqn. 4(23) is therefore reduced at 1.3K compared to its
value at 4.2K, and this effect is particularly noticeable
in the 356 at.ppm. Fe alloy (see table (4:9)) where the
number of impurity pairs is enhanced due to the concentration
exceeding the solubility limit.

To summarise the magnetisation vs. field data, we
have shown that two aspects, namely
i) the reduction of the apparent temperature dependence
of the susceptibility as measured in a single, fixed field
with increasing magnitude of that field
ii) the absence of a paramagnetic upturn at low
temperatures in the high field differential susceptibility
are incompatible with the existence of a small spin
\[ S \approx 0.02 \] on each of the Fe atoms.
The substantial reduction in the apparent temperature dependence between 4.2K and 1.3K in fields in excess of 40kOe (see fig. (4:43)) is consistent with the saturation of the magnetisation associated with a moment of several $\mu_B$. A moment of this size is apparent in the Zn + 356 at.ppm. Fe magnetisation, fig. (4:42) which, since it corresponds to $S \approx 3$ would seem to arise from ferromagnetically coupled pairs of Fe atoms ($S \approx 3/2$ for each). In view of this observation it is not unreasonable to ascribe the features of the ZnFe alloys with $c \leq 133$ at.ppm. to the existence of magnetic coupled pairs of Fe atoms also. The low characteristic temperature (since spin saturation effects are observed right down to 1.3K) and high spin value of these pairs would then lead to just the low temperature upturn in the susceptibility which we have observed, figs. (4:34) and (4:35).

If we assume $S=3$ it is possible, from the Curie constant which we have obtained from the CW fit to obtain a rough estimate (probably good to about a factor of two) for the total number of coupled pairs.

For a 100 at.ppm. ZnFe alloy the Curie constant, based on the CW fit shown in fig. (4:37), would correspond to about $2.10^{15}$ spins with $S=3$, ie a concentration of pairs $c_2 = 0.2$ at.ppm. Thus when $c$ is expressed as an
atomic fraction, \( c_2 = 20c^2 \). This rather small, ( compared to CuFe, for example, where \( c_2 = 560c^2 \)), concentration of pairs implies that the Fe atoms must approach one another rather closely before the interactions between them are strong enough to modify the magnetic state of the isolated atom. In fact, since the number of nearest neighbours for a h.c.p. lattice is 12, the above concentration for pairs suggests that the Fe atoms have actually to be nearest ( or maybe next nearest ) neighbours in order for the pair coupling interaction to be effective.

In CuFe alloys (61), the critical radius of separation, below which neighbouring Fe atoms are effectively coupled as a pair with a reduced characteristic temperature is 11Å, implying a long range, indirect via the conduction electrons, interactions are responsible for the pair coupling. An obvious candidate for such a mechanism would be that described by Caroli (84). For Fe dissolved in Zn, however, since coupled pairs of Fe atoms appear to be limited to nearest and possibly next nearest neighbour positions, coupling via direct overlap of the localised Fe 3d electron wavefunctions as discussed in chapter 1, must also play an important role.

Finally we would like to briefly discuss a very recent
model which has been proposed to account for the magnetic properties of the intermetallic compound Al₂Mn (196). The magnetic susceptibility of this compound is consistent with a CW behaviour which would correspond to a small effective moment per Mn atom, \( p_{\text{eff}} \approx 0.1 \mu_B \), in addition to a small CW intercept, \( e \approx 1 \mu \). In the model, the ground state configuration for the impurity has \( n \) electrons and \( S = 0 \). However, in the presence of a finite admixture, \( V_{kd} \), between conduction and localised electron states, it is possible for the impurity to undergo a transition, via an intermediate state containing \( n + 1 \) electrons and with energy \( U \) above the ground state, to an excited state, \( W \) above the ground state \( (W < U) \) which contains \( n \) electrons but has \( S = 1 \). \( W \) thus represents an intraatomic exchange type of interaction. If the lifetime of the impurity in the \( S = 1 \) state is long enough (i.e., the spin has time to equilibrate in an applied magnetic field), then the susceptibility may be CW like with \( p_{\text{eff}} = 2\sqrt{2} \mu_B \). Those impurities with \( S = 0 \) contributing only a temperature independent term in the excess susceptibility. If we take the compound as a whole and divide the Curie constant by the total number of Mn atoms then the apparent value of \( p_{\text{eff}} \) per solute atom may be arbitrarily small depending on the extent of the \( S = 1 \) state admixture. However since the magnetic behaviour is essentially due to spins with \( S = 1 \) (and not the spin value evaluated from the apparent \( p_{\text{eff}} \)) we would expect a saturation of the impurity magnetisation consistent with \( S = 1 \).
Qualitatively our ZnFe data is similar to that for Al₆Mn, i.e. small apparent $p_{\text{eff}}$ and small $\Theta$ value. The curvature in the impurity magnetisation, as evidenced by the reduced temperature dependence at high fields, fig. (4:43), can also be reconciled (although one might argue that the reduction is too strong for $S=1$). However an essential requirement for this model to be appropriate for the present data is that the temperature dependence in the impurity susceptibility should scale linearly with the concentration, since we are dealing with the property of an isolated solute atom. As we have demonstrated, figs. (4:39) to (4:41), on the basis of the present data there is no unambiguous evidence for linear concentration dependence for all five alloys which have been measured.

Since we already have the precedent that pair coupling interactions between Fe atoms in a Cu matrix lead to a reduction in the characteristic temperature, and since Fe is a notoriously difficult solute from the metallurgical point of view with low solid solubility and a tendency to cluster, we favour the explanation of the present low temperature upturn in the susceptibility as being due to a small fraction of the total number of Fe atoms coupled into pairs with a large spin $S \approx 3$ and a reduced characteristic temperature ($\Theta < 2K$). The field dependence of the impurity magnetisation at fixed temperature, and the ambiguity in the concentration dependence of the susceptibility at fixed field respectively are inconsistent with the other two alternatives of either a small $p_{\text{eff}}$ on each Fe atom or a small admixture of an $S=1$ excited state into
Fig. (4.44)

TEMP. INDEPENDENT CONTRIBUTION TO THE MAGNETIC SUSCEPTIBILITY AT 25K OF ZnFe ALLOYS

\[ \chi_{25K} \]

\[ \text{GRADIENT} = 10^{-6} \text{ EMU/GM/AT\%} \]

Conc. at. ppm.
an essentially non-magnetic \((S=0)\) ground state.

We shall now discuss the second prominent feature of our susceptibility data for ZnFe alloys as shown in figs. (4:34) and (4:35), namely the large temperature independent component in the excess impurity susceptibility which is observed in all alloys at \(T \gg 20K\).

The susceptibility is plotted as a function of the Fe concentration in fig. (4:44) and, with the exception of the 133 at.ppm. alloy, we observe a linear increase in this temperature independent component in the excess susceptibility corresponding to \(65.10^{-4}\) emu/mole Fe \((\pm 10\%)\). The scaling of this term as a linear function of the Fe concentration implies that it is associated with isolated Fe atoms, and its magnitude, if we interpret the whole \(65.10^{-4}\) emu/mole Fe as being an enhanced Pauli-like susceptibility, suggests that the isolated Fe atom is very close to the HF condition (eqn.1(69)) for the magnetic VBS to be stable. The temperature independent component exceeds that observed for either V in Au, \(42.10^{-4}\) emu/mole V (98), or Mn in Al, \(14.10^{-4}\) emu/mole Mn (70) both of which systems are generally considered to be on the borderline between magnetic and non-magnetic behaviour, where enhancement of the Pauli-like susceptibility by localised spin fluctuations is considerable (eqn. 1(53) for \(T \ll T_{\text{lsf}}\)). If we use the expression due to Caroli et al., eqn. 1 (53), we find that an enhanced Pauli term of \(65.10^{-4}\) emu/mole Fe corresponds to a characteristic spin fluctuation temperature of 180 K.

The resistivity of ZnFe alloys, \(c = 300\) at.ppm. and \(c = 100\) at.ppm. (105) was observed to follow a quadratic
temperature dependence below 1.5K, of the form, eqn. 1(48), characteristic of localised spin fluctuations with a characteristic temperature $85 \pm 10K$, somewhat lower than that predicted by the present data. However it seems possible that the low temperature excess resistivity could contain a contribution ($\propto \log T$) coming from the still magnetic coupled pairs of Fe atoms, c.f. Star's resistivity measurements on dilute CuFe alloys at $T < 0.2K$ (46). Such a contribution would tend to increase the temperature dependence of the resistivity, and thus reduce the apparent value of $\theta$ in eqn. 1(48), the characteristic temperature.

If we use the expression 1(25) for the temperature independent susceptibility of a non-magnetic VFS in the absence of LSF to evaluate the effective width $\Gamma = \frac{\Delta}{\kappa}$, then taking the mean number of localised electrons to be 7 we obtain $\Gamma = 0.01eV$ which yields a smaller characteristic temperature, eqn. 1(52), of 120K, closer to that obtained from the resistivity.

In view of our earlier discussions on the effect of alloying on the host matrix susceptibility of Zn we must view the above estimates of the characteristic temperature of Fe in Zn with some caution, since we cannot ascertain what proportion of the total $65.10^{-4}$ emu/mole Fe excess susceptibility should be associated with the Fe solute atoms themselves. Since the characteristic temperature, assuming no matrix contribution, agrees to within a factor of two
with that derived from the resistivity, this contribution may indeed be small and we note also that if part of the excess temperature independent susceptibility is associated with the host, then the characteristic temperature evaluated from the now reduced impurity component would be increased, resulting in a worsened consistency with the resistivity data.
Concluding remarks on the properties of dilute alloys of Cr, Mn and Fe in Zn.

In the course of the present measurements we have been able to observe the properties of isolated solute atoms which fall into the "magnetic" category (Mn and Cr) where a well defined magnetic moment may be associated with the impurity site, as well as those which may be described as "nearly magnetic" (Fe) where, although, within the experimental temperature range there is no direct evidence of a localised impurity moment, the properties of the solute are enhanced over truly non-magnetic behaviour (in the Anderson HF sense) as a result of dynamic localised spin fluctuations. Alternately, and perhaps equivalently, we may say that we have made observations on solute atoms whose characteristic (or Kondo) temperature has been either small compared to the experimental temperature range as well as one case where the characteristic temperature would appear to be outside, but larger than that range.

The gross features of Cr and Mn solute atoms in Zn (1.3K - 15K) appear to be adequately described by the perturbational solution of the s-d model and we have observed Curie-Weiss behaviour with a well defined, though substantially reduced from the Hund's rule values, magnetic moment of 3.6μB and 4.1μB respectively. The Curie-Weiss θ values are very similar in each case with θ = 0.45 and 0.48 for Cr and Mn respectively. The Mn value is intermediate between that found for Mn atoms dissolved in Cu and that for Mn in Al host, however that for Cr is
lower than the value appropriate to Cr dissolved in a Cu host.

The impurity resistivity of dilute ZnCr and ZnMn alloys has a pure logarithmic temperature dependence (1.5 - 4.2K) and by extrapolating the data to infinite dilution a more detailed comparison with the predictions of the s-d model ($T \gg T_K$) may be attempted. This reveals some inconsistencies which may possibly be associated with a residual orbital angular momentum on the Cr solute atom. The present data is, however, incapable of testing this last hypothesis.

The nearly magnetic properties of isolated Fe atoms in Zn are best discussed in terms of the LSF theory. The enhancement of the temperature independent excess susceptibility corresponds to a characteristic (or localised spin fluctuation temperature) in the region of 150 K. However uncertainty in the contribution arising from modification of the Zn conduction electron band structure due to alloying makes it necessary to regard this figure as a lower limit. The present data is inadequate to resolve the possibility of the existence of a small quadratic temperature dependence in the susceptibility at $T \ll T_{\text{lsf}}$, or of a CW term with $\Theta \sim T_{\text{lsf}}$ in the $T \gg T_{\text{lsf}}$ regime.

Although at the outset of this work alloys of extreme dilution were deliberately chosen in order to avoid interactions between the solute atoms being a significant effect, such modifications of true isolated solute atom properties have been discernible in the case of each solute
which we have measured and impurity interactions have played an important role in our discussion of results.

Whilst the susceptibility data on Cr and Mn gave no strong evidence for solute interaction being a significant factor, the temperature dependence of the impurity resistivity was reduced with increasing solute concentration. This reduction could be accounted for in terms of the pair-coupling model for "magnetic" solute atoms put forward by Matho and Beal-Monod. We obtained good quantitative agreement between our data and this model by taking the coupling mechanism to be the long range indirect double resonant scattering process between two magnetic VBS proposed by Caroli. The quantitative estimate of the phase shifts due to scattering from the impurity localised state which was based in part on our own susceptibility data.

The behaviour of Fe in Zn appears to be similar to that of Fe in Cu in the sense that the pair coupling interactions modify the magnetic state of the otherwise isolated Fe atom so as to reduce its characteristic temperature (deduced from magnetisation measurements) to below about 2K (which is an upper limit estimate only). However, one important difference would seem to be that since an, albeit crude, estimate of the total concentration of pairs of Fe atoms implies that the coupled pairs of Fe atoms must occupy nearest or maybe next nearest neighbour lattice sites in the Zn matrix, direct electron
transfer interaction between the Fe VBS would appear to play a more important, if not dominant, role in the coupling mechanism than compared to Fe pairs in Cu where the large critical radius for coupling to occur implies that a long range indirect (Caroli) mechanism dominates the majority of pair couplings.
Resistivity and Susceptibility measurements on the CuAlFe system.

The resistivity measurements reported below were made entirely by Dr. D. C. Golibersuch, but since they provided the motivation for our susceptibility measurements they will be included in this section as a preface to the magnetic data.

Resistivity of Cu$_{1-x}$Al$_x$ + 500 ppm Fe alloys

The resistivity of a series of 5α-phase CuAl alloys each containing nominally 500 at. ppm. Fe was measured using the D.C. apparatus already outlined in chapter 2 over the temperature range 1.5K to about 30K. The concentration of Al in the alloys was varied between 0 at.% and 9.6 at.%

In order to establish the component of the resistivity due to the Fe atom the resistivity of a series of α-phase CuAl binary alloys was also measured and subtracted from that of the ternary alloy corresponding to the same α-phase composition.

In fig.(4:45) we show the impurity (ie Fe) contribution to the resistivity for the pure Cu matrix and for the Cu + 9.6 at.% Al matrix, normalised in each case to 0.05 at.% Fe. For the purpose of comparison of the temperature dependence, the two curves have been brought into coincidence at 1.6K by a simple displacement parallel to the resistivity axis. The reduction of the temperature dependence of the Fe resistivity on the addition of Al to the host matrix is evident, and greatly exceeds that which
Fig. (4:45) COMPARISON OF TEMPERATURE DEPENDENCE IN THE RESISTIVITY OF $\text{Cu}_{1-x}\text{Al}_x\text{Fe}_{0.05}$ ALLOYS

$\rho_{Fe}$ (NORMALISED TO 0.05 at% Fe)

- $\text{CuFe}_{0.053}$
- $\text{Cu}_{90}\text{Al}_{10}\text{Fe}_{0.048}$

$0.05 \ \mu\Omega$-cm.
Fig. (4:46) RESISTIVITY vs REDUCED TEMPERATURE

<table>
<thead>
<tr>
<th>At%Al</th>
<th>T_e [°K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>1.9</td>
<td>1.2</td>
</tr>
<tr>
<td>4.1</td>
<td>1.5</td>
</tr>
<tr>
<td>8.0</td>
<td>1.9</td>
</tr>
<tr>
<td>9.0</td>
<td>2.7</td>
</tr>
</tbody>
</table>
could be explained simply in terms of the uncertainty in
the Fe concentration.

The most important aspect of the resistivity data is
shown in fig. (4:46) where the normalised resistivity of
each of the 5 alloys measured is plotted as a function of
the reduced temperature $\frac{T}{T_\text{c}}$. A universal behaviour of
the resistivity is clearly observed and the values of $T_\text{c}$
necessary to bring about coincidence of the data are
tabulated below

<table>
<thead>
<tr>
<th>at.% Al</th>
<th>$T_\text{c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>1.9</td>
<td>1.2</td>
</tr>
<tr>
<td>4.1</td>
<td>1.5</td>
</tr>
<tr>
<td>8.0</td>
<td>1.9</td>
</tr>
<tr>
<td>9.6</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Table (4:10) Scaling factors for resistivity data of
$\text{Cu}_{1-x}\text{Al}_x + 500$ at.ppm. Fe alloys

The solid line in fig. (4:46) represents the universal
curve obtained in a similar manner by Loram et al. (47)
from a study of the resistivity of dilute alloys of Fe
in $\text{Cu} + 5\% \text{Au}$ and pure Au hosts.

Magnetic susceptibility of $\text{Cu}_{1-x}\text{Al}_x + 500$ at.ppm. Fe alloys

The scaling of the temperature dependence observed
in the resistivity suggested that it might be worthwhile
to measure the susceptibility of these alloys and examine
the data for evidence of a similar effect. Consequently
the susceptibility of four alloys, each containing 500 at.ppm.
of Fe and with host matrices of Cu, Cu + 5 at.% Al, Cu +
10 at.% Al and Cu + 15 at.% Al (for the actual analysed
concentration see table (3:6)) was measured in the temperature
range from 1.8K to room temperature using the Gulf spiral
Faraday balance. Using the modified suspension it was
possible to make measurements on samples with mass
approximately 1.5 gm. so that the force sensitivity of
~ 20 µgms was sufficient to follow, with adequate resolution,
the temperature dependence of the susceptibility.

The maximum field obtainable using the electromagnet
(7.4 kOe) is too low to enable us to saturate out the
contribution to the magnetisation due to interacting pairs
of Fe atoms, even at the lowest temperature, (Tholence and
Tournier (61) observed that a field in the region of 40kOe
was required to saturate the pair magnetisation even at
1.3K), and, using the figure $c_2 = 260 c^2$ obtained by the
above authors for the concentration of coupled pairs of
when $c = 500 $atom only 75% of Fe atom
Fe atoms will be sufficiently well isolated from their
nearest impurity atom neighbour for their properties to
remain unmodified by the presence of interactions. The
susceptibility data which we shall present here is thus
clearly not representative of the behaviour of the isolated
Fe atom in the various host matrices and interactions will
have an important role to play in the interpretation of
the data.

In figs. (4:47) and (4:48) we show the magnetisation
vs field curves for the two alloys at the extremes of the
host matrix composition range which we have investigated, 
ie Cu with 500 at.ppm. Fe and Cu + 15 at.% Al with 500 at.ppm. 
Fe, at various temperatures between 1.8K and 300K.

In each case the room temperature M vs H is linear 
between 2kOe and 7.4kOe and there is a positive intercept 
on the magnetisation axis of $0.4 \times 10^{-4}$ emu for the Cu host 
and $0.5 \times 10^{-4}$ emu for the Cu + 15 at.% Al host. This is due 
to small particles of ferromagnetic contaminant and only 
0.03% of all the Fe in the alloy need by in this form to 
account for an intercept of this magnitude. ($< 0.5$ at.ppm.).

At the lowest temperatures there appears to be a 
distinct curvature at fields less than about 5kOe, which 
is present for both Cu and Cu + 15 at.% Al hosts.
Golibersuch (129) has reported a low field ($H \leq 4kOe$ at 1.2K) 
curvature in the host NMR linewidth in CuFe alloys of 
similar concentration to the present alloys, and he explains 
this feature in terms of a partial precipitation of the Fe 
solute leading to the formation of superparamagnetic clusters 
having very large effective moments. According to Golibersuch 
the low field curvature in the NMR data, which is saturated 
out for fields greater than about 4kOe at 1.2K is consistent 
with a precipitation of approximately 1% of the total Fe 
present in the alloy into clusters comprising of typically 
30 Fe atoms coupled ferromagnetically to result in a net 
giant moment of $66u_B$ (taking the magnetic moment per Fe atom 
to be $2.2u_B$). The curvature in the present magnetisation 
vs. field data at 1.8K (figs. (4:47) and (4:48)) is 
saturated out for fields in excess of about 5kOe which is
Fig. (4:47) Magnetisation vs. Field for Cu + 0.05 at% Fe
Fig. (4.48) Magnetisation vs Field for CuAl$_{15}$ + 0.05 at% Fe

Magnetisation (emu)

Magnetic Field (kOe)

0 1 2 3 4 5 6 7 8

77 K

300 K

1.9 K
Fig. (4.49) ZERO FIELD INTERCEPT (EXTRAPOLATED) ON MAGNETISATION \( (\text{FROM } H \geq 5 \text{kOe}) \)

\[ M(H \to 0) \text{ emu/gm.} \]

\[ 15 \times 10^{-4} \]

\[ 10 \]

\[ 5 \]

\[ \log T \]

- \( \bigcirc \) Cu \( \text{Fe}_{0.05} \)
- \( \bigtriangleup \) Cu\(_{95}\)Al\(_{15}\)Fe\(_{0.05}\)
- \( \square \) Cu\(_{80}\)Al\(_{10}\)Fe\(_{0.05}\)
- \( \triangledown \) Cu\(_{85}\)Al\(_{15}\)Fe\(_{0.05}\)
consistent with the NMR data and suggests that a typical cluster size of about 30 Fe atoms would be appropriate to explain this data also. Of course in a particular alloy of given concentration one would expect a distribution in the size of the clusters depending on the particular heat treatment which the alloy had been subjected to, but the present alloys were given the same homogenising heat treatment as that described by Golibersuch (129) for his NMR specimens.

Golibersuch also observed a strong increase in the zero field intercept of the linewidth of the Cu host NMR signal (as obtained by extrapolation from the $H \gg 5\text{kOe}$ linewidth vs. field data) as the temperature was reduced through about 30K to 1K, below which temperature it remained essentially constant. (fig. (18) of ref. (129)). In fig. (4:49) we show the corresponding data from the magnetisation measurements. The zero field intercept of the magnetisation, as obtained by extrapolation of the $H \gg 5\text{kOe}$ magnetisation data, is shown as a function of the temperature, and the rapid increase at temperatures below about 10K corresponds to the increasing degree of saturation of the magnetisation due to the superparamagnetic clusters which is possible as the temperature is reduced, in the fixed field range 5 - 7.5 kOe from which the extrapolation to zero field is made. The NMR data suggest that below 1K (for $H \gg 5\text{kOe}$) the magnetisation due to the clusters is completely saturated (the zero field extrapolated linewidth no longer increases as the temperature is reduced)
and at 1.8K the cluster magnetisation is about two-thirds of its full saturation value. From the present measurements fig. (4:49) the cluster magnetisation at 1.8K is $10^{-3}$ emu/gm which, again taking the magnetic moment per Fe atom in a cluster to be $2.2u_B$, requires that approximately 1% of the total Fe present in the alloy contributes toward the formation of the clusters. This is the same degree of precipitation which Golibersuch suggests would account for the NMR data.

On the question of superparamagnetic clustering we note finally the absence (fig.(4:49) of any large systematic effects in the zero field extrapolated magnetisation as the proportion of Al in the host alloy is increased from 0 to 15 at.%. This would suggest, at least at this level of Fe concentration that the partial precipitation of Fe into clusters is not very sensitive to the addition of Al.

The values of the magnetic susceptibility as a function of the temperature, which we shall now discuss, are based on the magnetisation as measured in fields in the range 5kOe to 7.5kOe. The actual method of obtaining this susceptibility in each temperature range has been discussed in detail in chapter 2, section 2:1. Not only are these fields, as remarked earlier, too small to separate out the magnetisation due to coupled pairs of Fe atoms but, from fig. (4:49) it is clear that above about 50K the measured susceptibility will also contain a contribution from the superparamagnetic clusters. Even
below this temperature the magnetic field is never strong enough to saturate out completely the superparamagnetic contribution to the total susceptibility of the alloy. Assuming 1% precipitation of the Fe into clusters with an effective moment of 70\(\mu_B\) the superparamagnetic contribution at 100K will be about \(10^{-8}\) emu/gm.

First of all let us consider the susceptibility data for the Cu + 500at.ppm. Fe alloy. There are two possibilities for the analysis which will allow for the effects of the interactions between the solute atoms, which we know to be present in the data. Both methods may be understood as approximations to the model that the characteristic temperature of a particular solute atom in an alloy of fixed composition will be decided by the local environment of that particular solute atom with respect to all the other solute atoms in the host matrix, which was discussed by Souletie and Tournier(95). This results in a range of characteristic temperatures for the solute atoms which may be specified by a probability distribution \(P(\Theta_{\text{loc}})\), the probability that a given solute atom has a particular value of the local characteristic temperature \(\Theta_{\text{loc}}\).

The first approach, used by Souletie and Tournier to interpret the high temperature behaviour of the susceptibility of CuFe alloys in the concentration range 100 - 600 at.ppm. Fe, considers that an alloy of given concentration will be specified by a mean characteristic temperature for the solute atoms (which even at fixed concentration may
depend upon the details of its metallurgical treatment)

\[
\bar{\Theta} = \int \Theta_{loc} P(\Theta_{loc}) \, d\Theta_{loc} \tag{4(21)}
\]

and at temperatures remote from the permitted range of \( \Theta_{loc} \) it should be possible to describe the distribution, at least to a first approximation, by the single parameter \( \bar{\Theta} \) alone. Thus at sufficiently high temperatures it should be possible to fit the total excess impurity susceptibility, \( \chi_{Fe} \), to a single CW term

\[
\chi_{Fe} = \frac{C}{T + \bar{\Theta}_X} + \chi_0 \tag{4(22)}
\]

where \( \bar{\Theta}_X \) is the mean value of the local characteristic temperatures which are appropriate to the susceptibility of the solute atoms. In general, for any physical property, \( \bar{\Theta} \) will depend on the concentration of the alloy, since this will affect the distribution of solute atoms within the host matrix. Souletie and Tournier observed that as the concentration of the CuFe alloys was increased \( \bar{\Theta}_X \) was reduced from the infinite dilution (isolated impurity) limit of 29K, to 14K for a Cu + 600 at.ppm. Fe alloy.

The second approach, used by Ekström and Myers (127) for example, takes account explicitly of the presence of coupled pairs of Fe atoms by fitting the susceptibility data to a composite CW expression

\[
\chi_{Fe} = \frac{C_1}{T + \Theta_1} + \frac{C_2}{T + \Theta_2} + \chi_0 \tag{4(23)}
\]

which is essentially replacing the distribution of \( \Theta_{loc} \).
with two permissible values, $\Theta_1$ corresponding to effectively isolated impurities, and $\Theta_2$ appropriate for those solute atoms which are coupled through interactions with their nearest neighbour solute atoms. Ekström and Myers obtained fitted values of $\Theta_1 = 26K$ and $\Theta_2 = 2-4K$ depending on the concentration of the alloy, which are consistent with the schematic model proposed by Tholence and Tournier (61), where Fe atoms separated by less than a critical distance (11R) are coupled by interactions so as to form a magnetic or nearly magnetic pair with a reduced characteristic temperature (0-5K) compared to that of the weakly magnetic isolated Fe atom (29K).

From fig. (4:46) we have already seen that it is possible to scale the temperature dependence of the resistivity using the single parameter $T_R$. This implies that the temperature dependence of the resistivity may be specified, at least in this temperature range, in terms of a single mean characteristic temperature, $\bar{\Theta}_R$, which is the mean of the distribution of local characteristic temperatures of the solute atoms appropriate to the solute resistivity, in an alloy containing 500 at.ppm. solute.

In order to facilitate a comparison of the resistivity and susceptibility data we have chosen to analyse the latter using the first scheme, which also avoids the uncertainties which may arise in assessing the significance of a computer fit to experimental data which allows for 5 variable parameters (eqn.4(23)).
Using the computer program already discussed we have fitted the susceptibility data of the Cu + 500 at.ppm. Fe sample in the high temperature range between 65K and 300K to a CW relationship. In fig. (4:50) we have plotted \((\chi_{\text{alloy}} - \chi_H)^{-1}\) vs. \(T\) where \(\chi_H\) is the temperature independent term in the total susceptibility of the alloy as computed in the least squares fit to the CW law. The solid line is the CW fit to the high temperature data (open circles).

The value of the Curie constant was found to correspond to an effective moment of \(2.8\mu_B\) per Fe atom and the value of \(\Theta_X\) was found to be 9K. This latter value is somewhat lower than that reported by Souletie and Tournier (14K) for a CuFe alloy of similar concentration, however it is clear that even at fixed concentration the distribution of Fe atoms, and hence \(\Theta\), may be affected by the metallurgical treatment of the alloy, and indeed Tholence and Tournier observed that the pair contribution to the magnetisation of a given alloy was increased if the alloy was annealed subsequent to its first quenching from the melt. If the number of coupled pairs is enhanced by the heat treatment then one might expect that \(\Theta\) would be reduced, and the data reported by Souletie and Tournier is for alloys measured in the as cast condition with no annealing. The present alloys, as discussed in chapter 3, received a prolonged anneal.

We now turn to the susceptibility data for the ternary alloys, and we have fitted this data, again over the high
Fig. (4:50) CW FIT TO DATA OF \( \text{Cu Fe}_{0.05} \) ALLOY

\[
\left( X - X_H \right)^{-1} \left[ \text{emu/gm} \right]^{-1}
\]

DATA INCLUDED IN FIT

\[
X = \frac{939}{T + 9} - 7.1 \times 10^{-8} \text{ emu/gm}.
\]
Fig. (4:51) CW FIT TO DATA OF Cu$_{95}$Al$_5$Fe$_{0.05}$ ALLOY

\[ \chi = \frac{848}{T+13} - 7.7 \times 10^{-8} \text{emu/gm} \]

\[ \left[ \chi - \chi_H(>64K) \right]^{-1} \]

\[ \left[ \text{emu/gm} \right]^{-1} \]

DATA INCLUDED IN FIT

TEMPERATURE K
Fig. (4:52) CW FIT TO DATA OF

\[ \text{Cu}_{0.90}\text{Al}_{1.0}\text{Fe}_{0.05} \text{ ALLOY} \]

\[ \left[ X - X_H (> 64 \text{K}) \right]^{-1} \]

\[ [\text{emu}/\text{gm}]^{-1} \]

DATA INCLUDED IN FIT

\[ X = \frac{1060}{T + 22} - 8.6 \times 10^{-8} \text{emu/gm} \]

TEMPERATURE \( K \)
Fig. (4.53) CW FIT TO DATA OF Cu$_{85}$Al$_{15}$Fe$_{0.05}$ ALLOY

\[ \frac{1}{X-X_H(>64\,K)} \]

\[ \frac{1}{[\text{emu/gm.}]} \]

DATA INCLUDED IN FIT

\[ X = \frac{972}{T + 34} - 10.5 \times 10^{-8} \text{ emu/gm.} \]

TEMPERATURE K
Fig. (4:54) CW curve fitted to data of CuFe and CuAl_{15}Fe_{0.05} alloys.

\[ \frac{10^{-9}}{\Delta X} \]

\[ \frac{\text{emu/gm}}{\text{at. ppm Fe}} \]

- CuFe\textsubscript{0.05}
- CuAl\textsubscript{15}Fe\textsubscript{0.05}

TEMPERATURE °K

347
| ALLOY         | COMPOSITION | FITTED PA\n\n|--------------|-------------|----------------|
|              | HOST SUSC.  | $\Theta$ \n\n|              | $P_{\text{eff}}$ |  |
| CuFe$_{0.05}$ | 0.00        | 587            | -7.1 | 9      | 2.8 ±0.1 |
| CuAl$_5$Fe$_{0.05}$ | 4.76        | 492            | -7.7 | 13     | 2.9      |
| CuAl$_{10}$Fe$_{0.05}$ | 8.74        | 632            | -8.6 | 22     | 2.8      |
| CuAl$_{15}$Fe$_{0.05}$ | 14.66       | 641            | -10.5| 34     | 2.7      |

**At. %** | **At. ppm** | E.M.U.$10^{-8}$ | **°K** | **U_B**

| 14.66 | \n\n| 641   | \n\n| E.M.U.$10^{-8}$ | \n\n| °K | \n\n| U_B | \n\n|
Fig. (4.55). Dil. Fe in Cu$_{1-x}$Al$_x$ alloys
More paramagnetic

Host

$10^{-8}$ E.M.U./GM.

$10^{-8}$ E.M.U./gm.

Fig. (4:56)
Fig. (4.57) Temperature independent component II

\[ \frac{\text{Susceptibility of } \text{Cu}_{1-x}\text{Al}_x\text{Fe}_{0.05} \text{ alloy}}{1000 \ (K)^{-1}} \]
temperature range 65K to 300K, to the same CW expression as before. In figs. (4:51) to (4:53) we show
\((\chi_{\text{Alloy}} - \chi_{\text{H}})^{-1}\) vs. \(T\) for each of the alloys and in fig. (4:54) we compare the CW fits (solid lines) obtained for the pure Cu and the Cu + 15at.% Al host matrices, normalised in each case to 1 at.ppm. of Fe. The actual parameters obtained as a result of such fits are displayed in table (4:11) where they are compared with those for the pure Cu host matrix.

Firstly we observe (see fig. (4:55)) that the effective moment per Fe atom is not significantly reduced by the addition of up to 15at.% Al, there is however a strong increase in \(\Theta_X\) on the addition of Al, tending to reduce the temperature dependence of the susceptibility. In this respect the susceptibility data show a marked similarity to the resistivity data discussed in the previous section. It is noticeable in figs. (4:50) to (4:53) that as the concentration of Al is increased the deviation from the high temperature CW fit are more marked and begin at higher and higher temperatures. This is not surprising since the simplest approximation, which we have employed, of replacing the range of local characteristic temperatures specified by \(P(\Theta_{\text{loc}})\) by the single mean value \(\Theta_X\) becomes inadequate at low enough temperatures, where a better description of the experimental data would require the next order of approximation to the \(P(\Theta_{\text{loc}})\) distribution, corresponding to the two component CW expression (eqn. 4(23)).
Since $\bar{\Theta}_X$ is increasing with the Al concentration the validity of the single parameter approximation would be expected to break down at higher temperatures.

Gruber and Gardner (131) have measured the susceptibility of liquid CuAl alloys containing low levels of Fe impurities and observe a similar behaviour, namely an essentially constant, though somewhat higher, value for the magnetic moment and a strongly increasing characteristic temperature $\Theta$ for host alloys containing up to 20% Al. The measurements of Huck et al (197) as replotted by Golibersuch (129) also indicate an increase in the CW theta value with increasing concentration of Al.

Before going on to discuss the increasing value of $\bar{\Theta}_X$ with increasing Al concentration we shall first briefly discuss the temperature independent contribution to the susceptibility of the present alloys. We have measured separately the susceptibility at room temperature of a series of binary CuAl alloys which contain no Fe. These are displayed as a function of Al concentration in fig. (4:56) where the computed values of $X_H$ are also plotted for comparison. The large open circles are the values of the host susceptibility for the actual Al concentrations of the ternary alloys, calculated on the basis of a least squares fit (solid line) to the experimentally determined susceptibilities of the binary alloys (solid points). Both the experimental and computed values of the host susceptibility show a trend toward increasingly diamagnetic
values as the concentration of the Al is increased, but the computed values remain typically $10^{-8}$ emu/gm more paramagnetic than would be expected on the basis of the susceptibility of the binary alloys. In fig. (4.57) we plot the total susceptibility of the alloys vs $\frac{1}{T}$ and the intercept at $\frac{1}{T} \rightarrow 0$ confirms the computed value of the temperature independent component. The excess temperature independent component over that deduced from the 'pure' binary alloys corresponds to about $10.10^{-4}$ emu/mole Fe, remarkably close to the value obtained by Ekström and Myers (127).

Both the resistivity and the susceptibility data show clear evidence of an increase in the mean characteristic temperature on alloying with Al. In the case of the resistivity, if $\bar{\Theta}(0)$ is the mean characteristic temperature for a pure Cu host matrix and $\bar{\Theta}(Al)$ is that for the host matrix which contains Al then it is apparent that

$$T_R = \frac{\bar{\Theta}(Al)}{\bar{\Theta}(0)}$$

Similarly we can define a scaling factor $T_X$ for the susceptibility measurements as

$$T_X = \frac{\bar{\Theta}(X)(Al)}{\bar{\Theta}(X)(0)}$$

and we obtain the following values:

<table>
<thead>
<tr>
<th>Al conc., at.%</th>
<th>$T_X$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>4.8</td>
<td>1.45</td>
</tr>
<tr>
<td>8.7</td>
<td>2.45</td>
</tr>
<tr>
<td>14.7</td>
<td>3.80</td>
</tr>
</tbody>
</table>
In fig. (4.58) we have plotted $T_x$ and $T_{\xi}$ as a function of the Al concentration in the host matrix and we observe that the mean characteristic temperature for both the resistivity and the susceptibility increases in just the same manner! ie whatever the mechanism for the increase in $\overline{\Theta}_x$ or $\overline{\Theta}_\xi$ it produces the same change in each for a given Al concentration.

There are two distinct possibilities for accounting for the increase in $\overline{\Theta}$.

The first regards the increase in $\overline{\Theta}$ as being due to a change in the local environment of each Fe atom due to the presence of neighbouring Al atoms in the binary host matrices. In this model the actual form of the distribution function $P(\Theta_{loc})$ of the local characteristic temperatures is changed, and, since Fe as a solute in Al is non-magnetic and has a high characteristic temperature, one might conjecture that those Fe atoms which are sited in Al rich parts of the alloy with a large number of Al atoms in their vicinity would have a rather large value of $\Theta_{loc}$ leading to a net increase in $\int \Theta_{loc} P(\Theta_{loc}) d\Theta_{loc}$ and thus $\overline{\Theta}$. According to Window (123) the Mössbauer spectrum of a binary Cu + 10 at.% Al host matrix containing 0.1 at.% and 1.1 at.% of Fe indicates that the Al atoms tend to cluster around the Fe atoms to form a pre-precipitate of Guinier-Preston zones. This data suggests that the Fe atoms certainly do not see a random distribution of Al in the binary host matrix, but it does not provide any information on the effectiveness of the presence of the Al neighbours in
increasing the value of $\Theta_{\text{loc}}$ for the Fe atom.

The exponential damping ($\sim e^{-\frac{r}{\lambda}}$) of the long range interaction between the Fe solute atoms as a result of the reduction in the mean free path for conduction electrons, $\lambda$, is not sufficient to explain the increase in $\overline{\Theta}$ as being due to a reduction in the number of coupled pairs of Fe atoms having low characteristic temperatures. The value $\overline{\Theta}_x = 34K$ for the Cu + 15 at.% Al would require that there is no coupling between the Fe atoms yet the increase in the mean free path (from 900 $\AA$ for Cu + 500 at.ppm. Fe to $\sim 30 \AA$ for Cu + 15 at.% Al with 500 at.ppm. of Fe) corresponds to a reduction in the critical radius for pair coupling to take place of only $\sim 10\%$.

The second model interprets the increase in $\overline{\Theta}$ not as being due to a change in the form of $P(\Theta_{\text{loc}})$ but rather a change in each value of $\Theta_{\text{loc}}$ as a result of the change in the average properties of the host matrix on alloying with Al, in particular the host matrix density of states for conduction electrons. The s-d model predicts a CW like behaviour of the high temperature magnetic susceptibility (see chapter 1) and would therefore appear to account for the present data. The Kondo temperature, which scales the temperature dependence of the resistivity and of which the CW theta is generally taken to be a measure is related to the host matrix density of states through the expression (eqn. 1(1))

$$T_K = T_F \exp \left\{ - \frac{1}{n(o)|J|} \right\}$$

4(25)
Fig. (4.58) Scaling of characteristic temperatures with Al concentration

$T_x$ or $T_e$
$J = -0.69 \pm 0.05 \text{ eV}$

Figure (4.59)

- **SUSCEPTIBILITY DATA**
- **RESISTIVITY DATA**

$\frac{1}{n[0]} \left[ \frac{\text{STATES}}{\text{eV} \cdot \text{ATOM}} \right]^{-1}$
where $J$ is the s-d exchange coupling constant. If we neglect the increase of $T_F$ on alloying and suppose that the sole effect of adding Al is to increase the mean density of states of the host matrix at each Fe site then

$$\theta_{loc} \propto \exp\left\{-\frac{1}{n(o)|J|}\right\}$$  \hspace{1cm} (4.26)

so that using eqn. 4.21

$$\bar{\theta} \propto \exp\left\{-\frac{1}{n(o)|J|}\right\}$$  \hspace{1cm} (4.27)

For pure Cu, density of states $n^P(o)$

$$\bar{\theta}(Cu) \propto \exp\left\{-\frac{1}{n^P(o)|J|}\right\}$$  \hspace{1cm} (4.28)

For binary host matrix, with variable density of states $n(o)$

$$\bar{\theta}(Al) \propto \exp\left\{-\frac{1}{n(o)|J|}\right\}$$  \hspace{1cm} (4.29)

so that dividing eqn. 4.29 by eqn. 4.28

$$\frac{\ln T_X}{\ln T_Q} = -\frac{1}{n(o)|J|} + \frac{1}{n^P(o)|J|}$$  \hspace{1cm} (4.30)

In fig. (4.59) we show both $\ln T_X$ and $\ln T_Q$ plotted as a function of the reciprocal of the density of states, $\frac{1}{n(o)}$, as determined directly from the specific heat data of Wu and Green (198). The linear relationship in fig. (4.59) implies that, in spite of the clustering
tendencies noted in the Mössbauer data, the direct local effects of a given Fe atom having Al atoms on neighbouring sites appear to be weak, and the variation in the mean characteristic temperatures may be accounted for solely in terms of the average density of conduction electron states. The value of the s-d coupling constant, $J$, appears to be independent of the composition of the host matrix and has the value $0.69 \pm 0.05 \text{eV}$. 
Concluding remarks on the properties of Fe solute atoms dissolved in $\alpha$-phase Cu$_{1-x}$Al$_x$ alloys

In conclusion, the present data suggests that both local and host average properties are important to an understanding of the behaviour of Fe atoms dissolved in binary Cu$_{1-x}$Al$_x$ hosts, at this level of Fe concentration.

The local environment of a given Fe solute atom in a pure Cu matrix, with respect to the other Fe atoms which may, or may not, occupy close by sites in the lattice, can affect the local characteristic temperature, $\Theta_{\text{loc}}$, of the Fe atom, reducing it for those Fe atoms for which the separation is less than some critical value. However when we then add Al to the matrix, although there is evidence (from the Mössbauer data) that some degree of clustering of the Al atoms around the Fe atoms does indeed take place, it would seem possible to understand the resulting increase in the mean characteristic temperature as derived from either resistivity or susceptibility measurements, consistently in terms of the increase in the host average density of conduction electron states. Our susceptibility data show that the characteristic temperature for the Fe solute increases by a factor of almost 4 on going from a Cu to a Cu + 15 at.% Al host matrix, which corresponds to an increase in the host matrix density of states of approximately 15%. 

Field dependence in the magnetisation of dilute ZnFe alloys.

we have observed that the magnetisation of the ZnFe dilute alloys is not a linear function of the applied field, and furthermore the field dependence does not correspond simply to the saturation of the magnetisation due to the magnetic moment on coupled pairs of Fe atoms.

In fig. (A:1) we show

\[ \chi(H) = \frac{M(H) - M(0)}{H} \]

as a function of the applied field H for the Zn+69 at.ppm. Fe and the Zn+133 at.ppm. Fe alloys as well as for a ZnAg solid solution containing nominally 400 at.ppm. Ag. In all cases \( \chi(H) \) becomes 2 or 3% less diamagnetic relative to its \( H \rightarrow 0 \) value by 25 kOe. In the case of the two ZnFe alloys (which are typical) the saturation of the temperature dependence in \( \chi(H) \) at high fields, as shown in fig. (4:43) is easily observable. In fig. (A:2) we plot the differential susceptibility

\[ \frac{\Delta M}{\Delta H} = \frac{M(H_2) - M(H_1)}{H_2 - H_1} \]

as a function of \( H_2 \) and the same characteristic field dependence is observed in each alloy with a rather sharp change in \( \frac{\Delta M}{\Delta H} \) at 20 -25 kOe.

Since the same field dependence is observed in each of these alloys it would appear to be a property of the Zn host matrix itself although, unfortunately, we were not able to obtain actual measurements of the high field susceptibility of pure Zn in order to check this hypothesis directly.
Fig. (A:1) $\chi(H)$ vs $H$ for Zn dilute alloys

Magnetic Field

$0 \quad 10 \quad 20 \quad 30 \quad 40$ kOe

$\chi(H)$

$-15.5$

$-16.0$

$-16.5$

$10^{-8}$ emu/gm

$\text{Zn} + \text{Fe}$ (133 at. ppm)

4.2K 1.3K

Ag nom. 400 at. ppm
Fig. (A:2) Differential Susceptibility, $\frac{\Delta M}{\Delta H}$, for Zn Dilute Alloys.
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