

MAGNETISATION STUDIES
OF SOME
CRYOGENIC ALLOYS

A Thesis submitted
for the degree
of
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by

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ABSTRACT

The flux pinning properties of superconducting alloys of indium with thallium, lead and cadmium in the vicinity of the martensitic phase transformation have been investigated. It is found that flux pinning reaches a peak in the partially transformed alloys of In-Tl and In-Pb but that precipitation of Cd-rich phase complicates the situation in In-Cd. These superconducting measurements also allow the position of the low temperature phase boundaries to be determined in the hitherto uninvestigated In-Pb and In-Cd alloys.

The magnetic properties of a wide variety of commercial austenitic iron-chromium-nickel stainless steels have also been studied. All the standard AISI 300 grade steels were found to have significant magnetisations on cooling to 4.2°K . In the 18Cr/10Ni grades, a ferromagnetic martensitic transformation may occur in an anti-ferromagnetic or paramagnetic austenite matrix. The occurrence of the transformation has been related both to the chemical composition variation within standard grades and to the room temperature deformation properties. At higher alloy contents, such as AISI 309 (23Cr/14Ni), the austenite phase remains stable on cooling to 4.2°K and is anti-ferromagnetic, as in the 18/10 steels. On further increasing the alloy content to AISI 310 (25Cr/20Ni) and Incoloy 800 (20Cr/32Ni), however, the austenite becomes reversibly ferromagnetic. This change is believed to be due to the existence of two electronic states in $\gamma\text{-Fe}$ whose relative stability is a function of alloying content. An analysis of previous deformation work shows that all steels which were found to be anti-ferromagnetic in the present study become martensitic after tensile destruction at 4.2°K , while those which are ferromagnetic are structurally stable. This behaviour is also believed to be related to the two electronic states of $\gamma\text{-Fe}$ and suggests the importance of the magnetic energy in determining the equilibrium structure of these steels.

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CHAPTER 1

INTRODUCTION TO THE THESIS

INTRODUCTION

The existence of superconductivity has been known for about 60 years but the hopes of an early technology based on superconductivity were not fulfilled since it was found that comparatively modest external fields or transport currents were sufficient to quench the superconducting state in the materials then available. A major increase of interest, however, followed the discovery of the high field current carrying capacities of certain materials, notably Nb_3Sn , in the late 1950's. These practical discoveries were closely paralleled by major theoretical advances and it is now well understood that to obtain these important lossless transport currents a metallurgically inhomogeneous, not to say dirty, structure is essential. The situation is closely analogous to the mechanical properties of metals where almost all important combinations of strength, toughness and ductility depend on the presence of controlled internal defect arrays. The influence of such internal defects on the superconducting properties has been considerably studied though the details of many interactions are still obscure and, accordingly, this thesis was undertaken so as to investigate the particular influence of martensitic boundaries on the superconducting properties of some indium-based alloys.

During the construction of the magnetometer and solenoid system necessary for these measurements, large eddy current and spurious magnetisation effects were observed, which greatly interfered with the operation of the magnetometer. These effects were traced to the ferromagnetic martensitic breakdown of the supposedly non-magnetic austenitic stainless steel solenoid former. Such stainless steels are widely used in cryogenic apparatus, principally because of their low thermal conductivity, wide availability and reasonable fabrication properties. In large scale engineering use, these alloys are even more advantageous, since they retain excellent strength and toughness at temperatures down to 4°K . The present prospects of major engineering uses of superconductivity mean that increasing attention must be paid to the electrical and magnetic properties of these steels, which have hitherto been generally assumed to give no problems. Current major projects in the U.K. which exemplify this are the

Rutherford High Energy Laboratory 70 kOe 1.5m Hydrogen Bubble Chamber and the 3250 h.p. homopolar motor with superconducting field coils for Fawley power station.

In view, therefore, of this engineering interest, the scope of the thesis was expanded to cover the low temperature properties of commercial austenitic iron-chromium-nickel steels. An interesting point of contact between the two subjects of this thesis is provided by the martensitic nature of the particular steel which prompted the original interest. Martensitic transformations themselves occupy a special place in cryogenics since, being diffusionless, they are the only structural change that can occur at low temperatures.

CHAPTER 2

THE REVERSIBLE PROPERTIES OF SUPERCONDUCTORS

2.1 Introduction

The superconducting state is characterised by two important, independent properties. The first of these, the complete absence of electrical resistance below a transition temperature T_c , was discovered by Kammerlingh Onnes in mercury in 1911 (1). The second, that of complete flux expulsion in small magnetic fields, was discovered by Meissner and Ochsenfeld (2) rather later, in 1933.

Twenty four elements and many hundreds of alloys and compounds have been found to be superconducting. The highest known T_c is 20.7°K (3) for a ternary Al5 compound of composition $\text{Nb}_3(\text{Al}_{0.2}\text{Ge}_{0.8})$. The superconducting properties of many of these materials have been tabulated by Roberts (4).

A number of recent books and reviews discuss aspects of superconductivity - among these, books by Lynton (5) and de Gennes (6) discuss the general properties while the review of Goodman (7) deals in detail with the reversible properties of type 2 superconductors. The particular influence of metallurgical structure and defects on superconducting behaviour has been reviewed by Livingston and Schadler (8).

2.2 The reversible properties of superconductors

2.21 The Meissner effect

A perfect normal conductor in an external magnetic field could either trap or expel the field from its bulk, depending on whether the field was applied before or after cooling through the transition temperature. The discovery that a superconductor expels the magnetic field (the Meissner effect) in either situation was important in differentiating the superconducting from the perfect conducting state and showing that the superconducting/normal phase transition was thermodynamically reversible.

Since the Meissner effect shows that the magnetic induction B within the superconductor is zero, the superconductor possesses a diamagnetic magnetisation $-4\pi M$ equal to the external field and has the ideal diamagnetic susceptibility of $-1/4\pi$.

Following Gorter and Casimir (9) we may now write the Gibbs free energy of the superconductor in an external field H as

$$G_s(H) = G_s(0) - \int_0^H M(H) \cdot dH \quad 2.1$$

referring to unit volume. Equation 2.1 may be evaluated as

$$G_s(H) = G_s(0) + H^2/8\pi \quad 2.2$$

As the normal state susceptibility is of the order 10^{-4} - 10^{-5} , it may be neglected and the thermodynamic critical field, H_c , is given by :-

$$G_s(H_c) = G_n(0)$$

$$G_n(0) - G_s(0) = H_c^2 / 8\pi \quad 2.3$$

The entropy difference, ΔS , between the two states is given by $-(\partial G / \partial T)_{H,P}$ and is

$$\Delta S = S_n(0) - S_s(0) = -H_c(dH_c/dT)/4\pi \quad 2.4$$

The superconducting state has a lower entropy and therefore possesses a higher degree of order than the normal state.

Equation 2.3 shows that the normal state is restored for a sufficiently large external field H_c at temperatures below T_c . The variation of H_c with temperature is closely approximated by the parabolic equation

$$h = 1 - t^2 \quad 2.5$$

where h and t are the reduced parameters $H_c(T)/H_c(0)$ and T/T_c .

F. and H. London (10) were able to show that the magnetic field does in fact penetrate a bulk superconductor over a small but finite

a.) Type 1 superconductor.

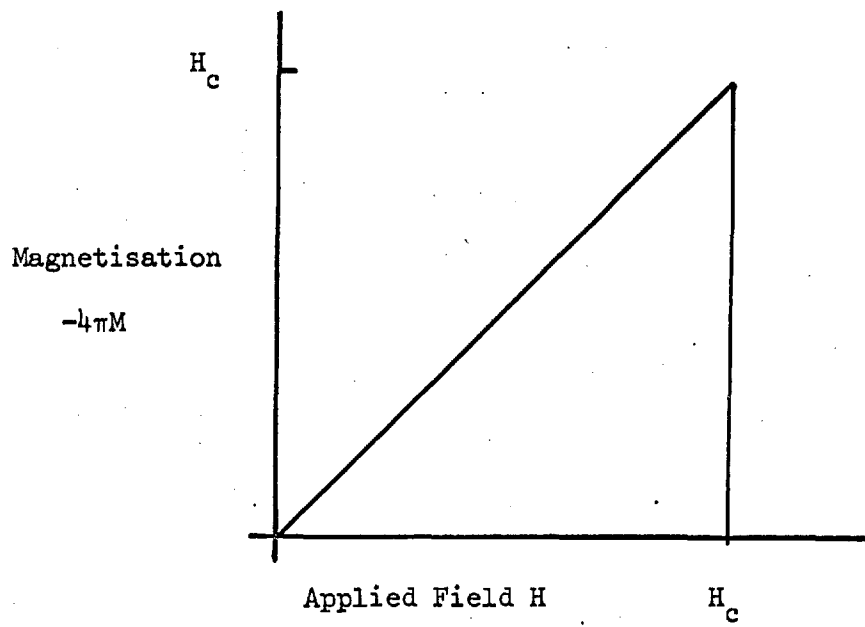
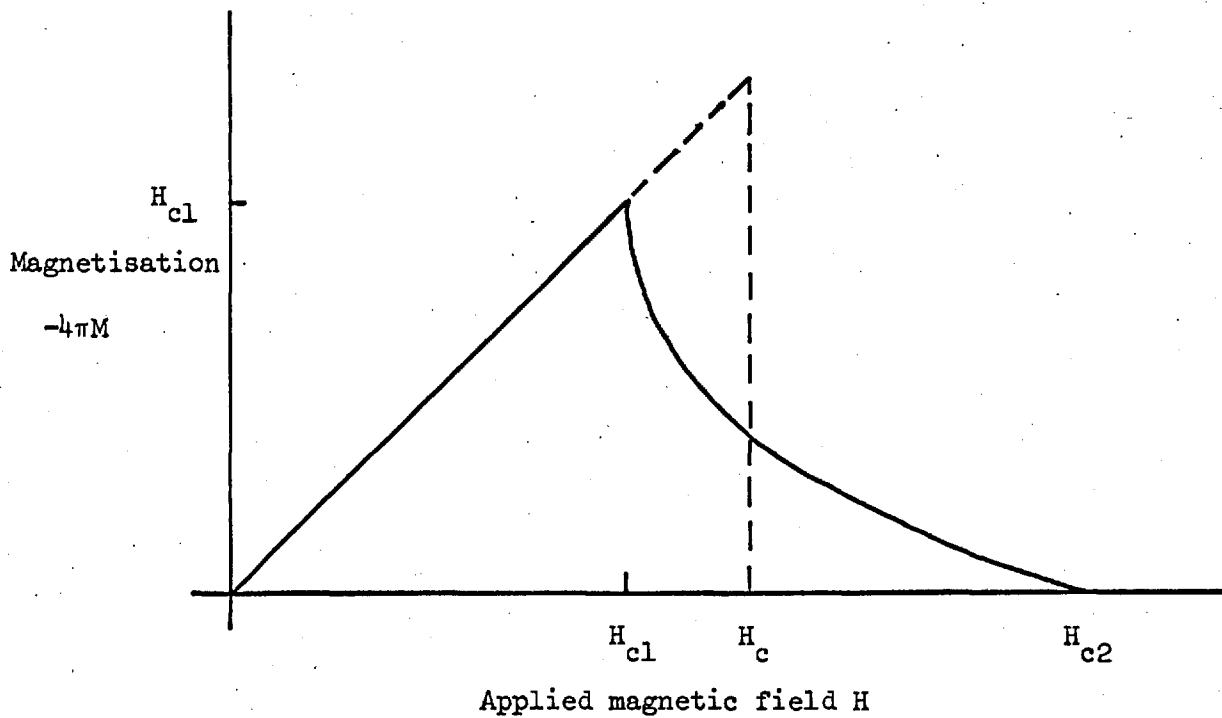


Figure 2.1 Magnetisation curves for ideal superconductors.



b.) Type 2 superconductor.

length λ_L , known as the penetration depth, where

$$\lambda_L = (mc^2 / 4\pi n_s e^2)^{1/2} \quad 2.6$$

m and e are the electronic mass and charge respectively, n_s is the number density of superconducting electrons and c is the velocity of light. The form of field penetration is exponential and λ_L is defined as the depth at which the field has fallen to $1/e$ of its external value. The penetration depth is also a measure of the depth to which the circulating supercurrents, which shield the external field, flow. λ_L is seen to be dependent on temperature through the dependence of n_s on T . Typical values of the penetration depth for pure metals are around 500 Å (5).

2.22 Magnetisation curves

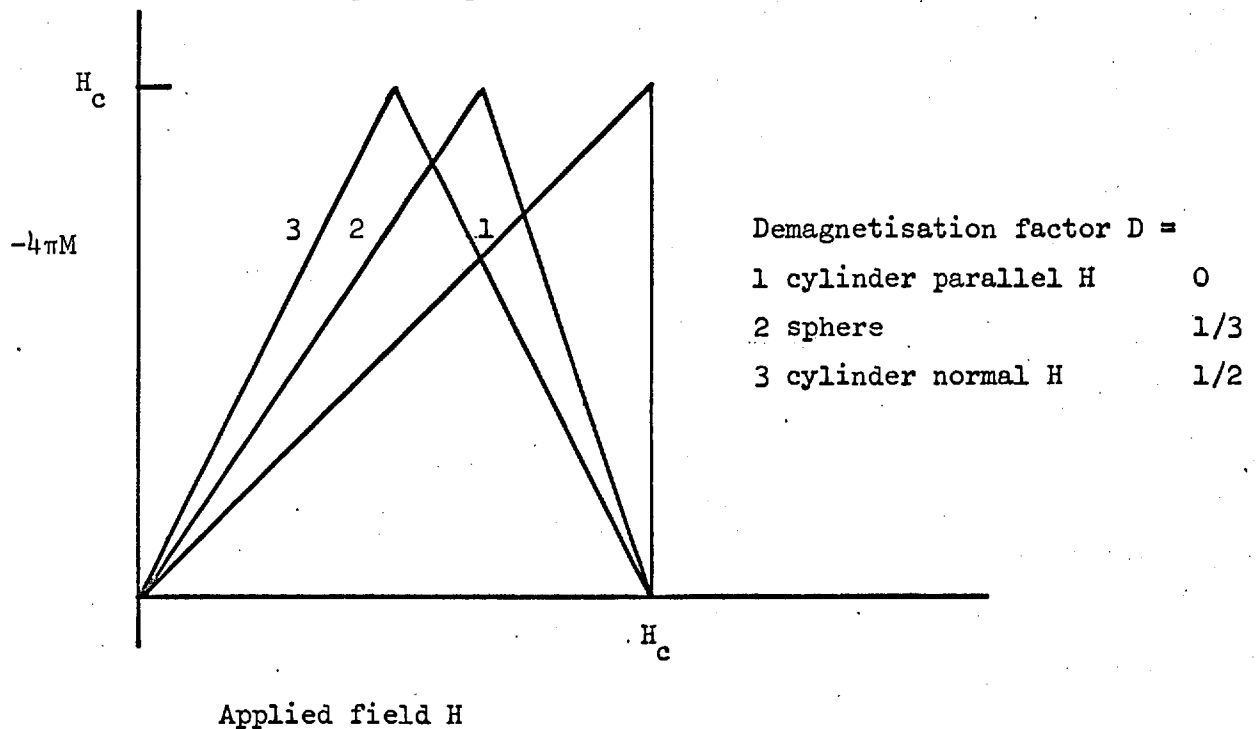
2.22a Type 1 and type 2 superconductors

Two types of superconductors are now recognised to exist on the basis of their behaviour in a magnetic field. Representative magnetisation curves for samples of each type are shown in figure 2.1 and it can be seen that each has an initial perfect diamagnetic portion. For a type 1 superconductor perfect diamagnetism is retained until the critical field, H_c at which point the whole sample enters the normal state. For a type 2 superconductor, however, partial flux penetration begins at a lower field H_{c1} and bulk superconductivity is not destroyed until an upper critical field H_{c2} . Between H_{c1} and H_{c2} the superconductor is in the so-called mixed state (section 2.24f) but this partial flux penetration does not invalidate the thermodynamic analysis of the preceding section and H_c may still be obtained from the area under the magnetisation curve, $(H_c)^2/8\pi$. H_c is then formed by drawing a type 1 curve of the same area as the type 2, as shown by the dotted line construction in figure 2.1b.

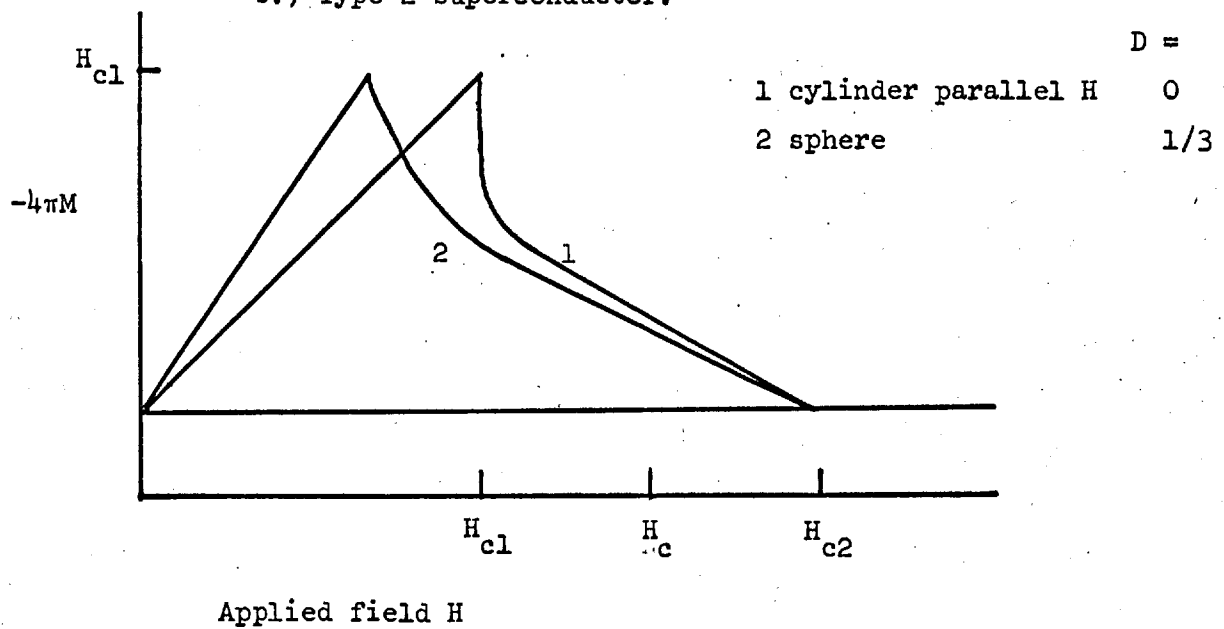
2.22b Demagnetising effects

The preceding magnetisation curves (figure 2.1) are valid only

a.) Type 1 superconductor.



b.) Type 2 superconductor.



< Figure 2.2 Demagnetisation curves of superconductors.

for the case of an infinitely long cylinder in a parallel applied field. For all other geometries the specimen magnetisation distorts the external field which is then position dependent. Standard treatments (5) show that the internal field, H_i , seen by a specimen of arbitrary shape is related to the external field, H by

$$H_i = H - 4\pi DM_i \quad 2.7$$

where D is the demagnetising factor and is generally approximated to an ellipsoid of revolution. Bozorth (11) has tabulated demagnetisation factors for ellipsoids of various axial ratio. With a finite demagnetising factor the maximum surface field reaches H_c at a lower value of the external field $H_c(1 - D)$ and partial penetration of the field occurs at this point. The form of magnetisation curve for a cylinder in transverse field ($D = \frac{1}{2}$) is shown in figure 2.2. Between $H_c/2$ and H_c the cylinder is in the intermediate state, a fine array of alternate superconducting and normal regions. The scale of these regions is controlled by the surface energy of the superconducting/normal interface.

Demagnetising effects control the magnetisation curve of a type II superconductor in a similar way (figure 2.2b) but the mixed state structure by which field penetration occurs is fundamentally different from the intermediate state (section 2.24f).

The demagnetising factor of the specimens used in this study was calculated to be 0.03 from the tables of Bozorth (11). In fact, due to the detection coil arrangement used (section 4.33), the effective demagnetisation factor was less than this and demagnetisation effects were only observed in the type I specimens of indium cadmium (section 5.21)

2.23 The Bardeen-Cooper-Schrieffer theory

A microscopic theory of superconductivity which is able to explain the major features of the superconducting state is due to Bardeen, Cooper and Schrieffer (BCS) (12). The BCS theory is based on an earlier suggestion by Fröhlich (13) that a lattice-electron

interaction was responsible for superconductivity. Fröhlich and Bardeen (14) showed that the passage of an electron through the crystal lattice distorts the lattice in an oscillatory manner by the exchange of short life time (virtual) phonons. Under certain conditions a moving electron will then be "clothed" by a positive screening charge which may lead to an attractive interaction with another electron which overcomes their normal coulombic repulsion.

Cooper (15) was able to show that if such an attractive interaction occurred between two electrons just above the Fermi surface then a bound state of lower energy would be formed. This state occurs for electrons in a thin shell above the Fermi level of width $\hbar\omega$ where $\hbar\omega$ is the average phonon energy. The ground state of lowest energy at 0°K is then occupied by electrons of opposite spin and momentum.

BCS synthesised these contributions and made the further assumption that because the superconducting/normal state energy difference was so small, all interactions, except that responsible for superconductivity, were the same for both states at 0°K. Using the Cooper pair interaction they found that the energy difference $W(0)$ between the superconducting and normal states was

$$W(0) = -2 N(0)\hbar\omega / \exp (2/N(0)V) \quad 2.8$$

At finite temperatures excitation of electron pairs across the energy gap 2Δ is possible where

$$2\Delta = 4\hbar\omega \exp (-1/N(0)V)/k_B \quad 2.9$$

and the transition temperature T_c is given by

$$T_c = 1.14\hbar\omega \exp (-1/N(0)V)/k_B \quad 2.10$$

$N(0)$ is the single electron density of states at the Fermi surface at 0°K and V is the electron phonon interaction parameter.

Although not susceptible to direct experimental proof as V is not in general directly measurable, the BCS theory has been very successful in explaining the major properties of superconductivity including the Meissner state, perfect conductivity and the temperature variation of the critical field. As discussed by Lynton (5), later additions to the theory, necessary to explain the properties of particular superconductors, have involved very little change in the basic theory.

2.24 The Ginzburg-Landau-Abrikosov-Gorkov theory

While the BCS theory is successful in explaining superconductivity in microscopic terms a more convenient approach to the magnetic properties of superconductors follows from the earlier phenomenological theory of Ginzburg and Landau, later developed by Abrikosov and Gorkov. The combined approach is widely known as the GLAG theory.

2.24a The Ginzburg-Landau theory

Ginzburg and Landau (16) (G-L) used the Landau-Lifshitz (17) theory of phase transformations to obtain the free energy of a superconductor in terms of an order parameter ψ . According to this theory the free energy of a superconductor can be expanded in terms of ψ only, viz.,

$$G_s(0) = G_n(0) + \alpha(T)|\psi|^2 + \beta/2(T)|\psi|^4 + \dots \quad 2.11$$

where $\alpha(T)$ and $\beta(T)$ are temperature dependent constants and ψ is normalised as $|\psi|^2$ so as to be equal to n_s , the concentration of superconducting electrons. For temperatures close to T_c and for small ψ , equation 2.11 is valid when only the first two terms of the expansion are included. The important step in the theory, however, was to represent the behaviour of the superconductor in an external magnetic field when ψ ceases to be a completely rigid function. Associated with this gradient in ψ is a term analogous to the kinetic energy of a particle in the Schrödinger equation $p^2/2m = 1/2m (-i\hbar\nabla^2\psi - e^*\underline{A}\psi/c)^2$. The total free energy is then given by adding this term and the magnetic field energy $H^2/8\pi$ to equation 2.11 viz.,

$$G_s(H) = G_s(0) + H^2/8\pi + 1/2m (i\hbar\nabla\psi - e^*\underline{A}\psi)^2 \quad 2.12$$

where $\underline{A}$ is the vector potential of the applied field given by $\underline{H} = \text{curl } \underline{A}$ and e^* and m^* are general constants which were not necessarily envisaged as the electronic ones.

Minimising this equation over the whole superconducting volume with respect to ψ and $\underline{A}$ gives the two Ginzburg Landau equations :

for ψ

$$1/2m (-i\hbar\nabla\psi - \frac{e^*\underline{A}}{c} \psi)^2 + \frac{\partial G_s(0)}{\partial \psi^*} = 0 \quad 2.13$$

for $\underline{A}$

$$\begin{aligned} \nabla^2 \underline{A} &= - \frac{4\pi}{c} \underline{J}_s \\ &= \frac{2\pi e^*\hbar}{mc} (\psi^*\nabla\psi - \psi\nabla\psi^* + \frac{4\pi e^{*2}}{mc^2} |\psi|^2 \underline{A}) \end{aligned} \quad 2.14$$

2.24b The Gorkov formulation

Gorkov (18) was able to show that equations very similar to the G-L equations could be derived from BCS theory. In particular

$$G_s(H) = G_n + A|\Delta|^2 + \frac{B}{2}|\Delta|^4 + C \left| (-i\hbar\nabla - \frac{2e^*\underline{A}}{c}) \Delta \right|^2 + \frac{H^2}{8\pi} \quad 2.15$$

where ψ can be considered as interchangeable with Δ , half the energy gap from equation 2.8. A, B and C are constants, given physical significance when the superconductor is a pure metal as

$$\begin{aligned} A &\approx -N(0) (1 - t) \\ B &\approx 0.098N(0) / (k_B T_C)^2 \\ C &\approx N(0) \lambda \xi_0 \end{aligned}$$

where λ is the electronic mean free path and ξ_0 is a characteristic length to be discussed. The generalised values of A, B and C are discussed by Goodman (7).

2.24c The characteristic lengths

Solution of equation 2.13 in the presence of a small perturbation in ψ leads to a parameter ξ with the dimensions of length which is the characteristic distance over which $|\psi|^2$ may vary. (This concept was first introduced by Pippard (19)). ξ is called the coherence length and is a function of temperature, viz :

$$\xi(T) = 0.74 \xi_0 (1 - t)^{-1/2} \quad 2.16$$

where ξ_0 , the 0°K coherence length for a pure metal, is given by

$$\xi_0 = \frac{\hbar V_f}{\pi \Delta(0)} \quad 2.17$$

V_f is the Fermi velocity and $\Delta(0)$ the energy gap at 0°K.

In the limit of a weak field $|\psi|^2$ tends to the rigid, zero field value $|\psi_0|^2$. Equation 2.14 may then be replaced by a London type equation which contains a penetration depth $\lambda(T)$ given by

$$\lambda(T) = \left(\frac{mc^2}{16\pi e^2 |\psi_0|^2} \right)^{1/2} \quad 2.18$$

where e^* has now been replaced by $2e$ in accordance with microscopic theory. The formal similarity of this to equation 2.6 for λ_L is clear but more exact solutions show $\lambda(T) = f|\psi|^2$ and thus $f(H)$, a result which is not provided for in equation 2.6 where n_s is only a function of temperature. Since $\lambda(T)$ also has a $(1 - t)^{-1/2}$ dependence near T_c the temperature dependent parameters $\lambda(T)$, $\xi(T)$ may be related to the dimensionless Ginzburg Landau parameter κ which is independent of temperature over this limited range.

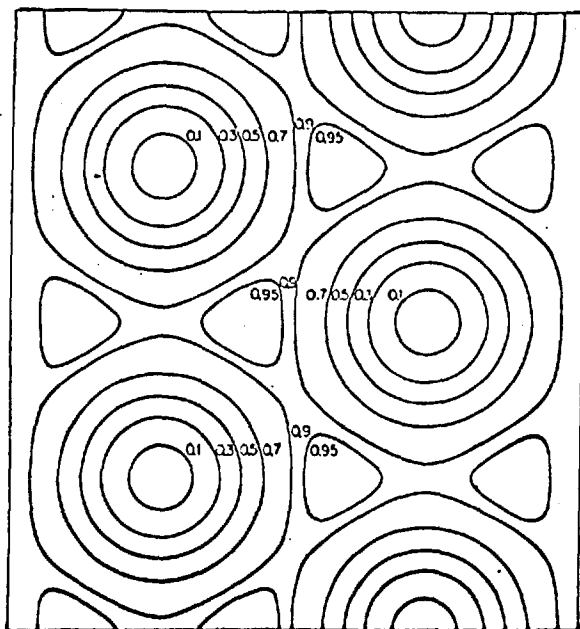
$$\kappa = \frac{\lambda(T)}{\xi(T)} \quad 2.19$$

2.24d The bulk nucleation field

If an infinitely large superconductor is placed in a magnetic

Figure 2.3

The spatial variation of $|\Delta|^2$ (Kleiner et al,22)

Figure 2.4

The structure of a fluxoid (de Gennes,6)

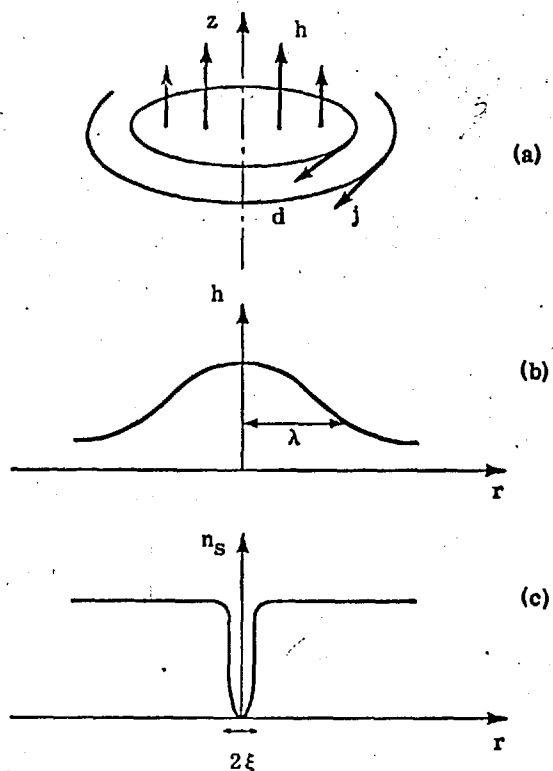


Figure 3-4

Structure of one vortex line in a Type II superconductor. The magnetic field is maximum near the center of the line. Going outwards, h decreases because of the screening in an "electromagnetic region" of radius $\sim \lambda$ (the penetration depth) (Fig. 3-4b). On the other hand, the number of superconducting electrons per cm^3 n_s is reduced only in a small "core region" of radius ξ (Fig. 3-4c).

field sufficiently large to quench superconductivity, the first non-zero solution of the order parameter ψ in equation 2.13 to be obtained in decreasing field is at a field H_{c2} given by

$$H_{c2} = \sqrt{2\kappa} H_c \quad 2.20$$

Thus for $\kappa > 1/\sqrt{2}$ there is a field value H_{c2} , greater than H_c , at which superconductivity is first nucleated.

2.24e The surface nucleation field

St. James and de Gennes (20) were able to show that, for a superconductor of finite size in a magnetic field with a component parallel to the external surface, superconductivity was first nucleated in a surface sheath of depth $\sim \xi$ at a field $H_{c3} > H_{c2}$. H_{c3} was found to reach a maximum of $1.695 H_{c2}$ in parallel applied field, falling off to $H_{c3} = H_{c2}$ in transverse field.

Real solutions of H_{c3} exist for all κ values but the surface sheath is only observed for $\kappa > 0.42$ at which point $H_{c3} = H_c$. For $\kappa < 0.42$, H_{c3} is the lowest field to which the superconductor may be supercooled. The surface sheath is a common feature of magnetisation curves for superconductors with $\kappa > 0.42$.

2.24f The Abrikosov flux line model

Abrikosov (21) was able to solve the G-L equations for $\kappa \gg 1$ in the region near H_{c2} and found a periodic variation of $|\psi|^2$ of the order of ξ in a direction perpendicular to the applied field. This periodic variation had the form of a square lattice but more recent calculations (22) have shown that a triangular lattice has a lower energy. Figure 2.3 shows contours of $|\Delta|^2$ (interchangeable with ψ) normalised to $|\Delta|^2 = 1$. The local magnetic field h varies linearly with $|\Delta|^2$ between the values

$$\begin{aligned} \text{(i)} \quad h &= H \text{ at } |\Delta|^2 = 0 \\ \text{(ii)} \quad h &= H - \frac{\sqrt{2}(H_{c2} - H)}{2\kappa^2 - 1} \text{ at } |\Delta|^2 = 1 \end{aligned}$$

At H_{c2} , $h = H$ throughout the specimen (neglecting surface effects, section 2.24e) and the energy gap 2Δ becomes zero. The lattice spacing of $|\Delta|^2$ increases as the field is lowered below H_{c2} and the bulk magnetisation close to H_{c2} is given by

$$-4\pi M = \frac{H_{c2} - H}{\beta(2\kappa^2 - 1)} \quad 2.21$$

where β had the value 1.18 for the square lattice and 1.16 for a triangular lattice (22).

The regions of $|\Delta|^2$ varying over ξ are known as flux lines or fluxoids. In a high κ material flux lines may be visualised as having a normal core containing a field $\sim 2H_{c1}$ with a diameter $\sim 2\xi$ over which the energy gap varies from that characteristic of the superconducting state to zero. The normal core is shielded from the superconductor by circulating supercurrents to a depth λ . A visualisation is shown in figure 2.4.

Convincing evidence for this structure has come from the flux line decoration experiments of Tr uble and Essman (23) which have enabled the flux line lattice to be observed directly.

2.24g Flux quantisation

London (24) had already showed that the flux trapped inside a multiply connected superconductor was quantised in units of ϕ_0 , where

$$\phi_0 = \hbar c / 2e = 2.07 \times 10^{-7} \text{ gauss cm}^2 \quad 2.22$$

Calculations of the line energy ζ of a flux line show that it is the sum of three terms (6):

- (i) the normal state energy of the normal core $\frac{H_{c2}^2}{8\pi}$
- (ii) the field energy $h^2/8\pi$ over the dimensions of the flux line
- (iii) the shielding kinetic energy density outside the core (similar to the third term in equation 2.12)

The general result is

$$\zeta = \left(\frac{\phi_0}{4\pi\lambda} \right)^2 \ln \left(\frac{\lambda}{\xi} \right) \quad 2.23$$

The important feature of this equation is that ζ varies as ϕ_0^2 and each flux line thus carries only one flux quantum, ϕ_0 .

2.24h The lower nucleation field

The free energy of a superconductor containing n flux lines is given by

$$G_s = n\zeta + \sum_{ij} U_{ij} - BH/4\pi \quad 2.24$$

where $\sum_{ij} U_{ij}$ is the sum of the interfluxoid interactions and $BH/4\pi$ is the external magnetic pressure tending to push the fluxoids together. The first term is the sum of all the line energies, the second sums the inter flux line interactions and the third term represents the driving force of the external magnetic field, the magnetic pressure which packs the fluxoids more closely.

$\sum_{ij} U_{ij}$ is not in general known but in the limit when n tends to zero it may be neglected and we then have $G_s = B(\zeta/\phi_0 - H/4\pi)$. For $H < 4\pi\zeta/\phi_0$, G_s is increased for $B > 0$ and Meissner flux exclusion occurs. For values of $H > 4\pi\zeta/\phi_0$, however, a non-zero value of B is energetically more favourable and the first nucleation field H_{c1} is given by

$$H_{c1} = 4\pi\zeta / \phi_0 \quad 2.25$$

which with equation 2.23 gives

$$H_{c1} = (H_c \ln \kappa) / \kappa \quad 2.26$$

The more exact calculations of Abrikosov give

$$H_{c1} = (H_c (\ln \kappa + 0.08) / \sqrt{2}\kappa \quad 2.27$$

As the interaction term $\sum_{ij} U_{ij}$ is small at low fluxoid densities, initial

flux penetration is rapid but the gradient of the magnetisation curve finally levels out to that given by equation 2.21. At H_{c2} the internal field is everywhere equal to H_{c2} and the specimen is normal.

2.24j Type I and type II superconductors

Hardern and Arp (25) extended Abrikosov's solutions of the Ginzburg Landau equations to values of κ between 0.1 and 100 and found that at $\kappa = 1/\sqrt{2}$

$$H_{c1} = H_{c2} = H_c \quad 2.28$$

This value of κ marks the division between type I superconductors with $\kappa < 1/\sqrt{2}$, and type II superconductors with $\kappa > 1/\sqrt{2}$. This result was implicit in the original Ginzburg Landau paper where it was calculated that the surface energy between a superconducting and normal interface went to zero at $\kappa = 1/\sqrt{2}$, but such negative surface energy superconductors were not physically considered. In fact the fundamental difference in the magnetic properties of type I and II superconductors is seen to be in the surface energy. Since we know from equation 2.2 that the free energy of a superconductor is raised by $H^2/8\pi$ in a magnetic field, the existence of a complete Meissner effect in type I superconductors is explained by the existence of a positive surface energy. When the surface energy becomes negative a stable state of flux penetration is set up (the mixed state of a type II superconductor). In terms of the parameters λ and ξ , we then have type I behaviour when $\xi > \lambda$ and the field decays withing the normal boundary and type II behaviour when $\xi < \lambda$ and the field decays within the superconductor.

2.24k The general validity of the GLAG theory

The preceding discussion of the GLAG theory has emphasised the essential correctness of their approach in explaining the observed magnetic properties of the superconducting state. Though originally derived for rather restricted situations (G-L: small ψ near T_c ,

Abrikosov: $\kappa \gg 1$) Goodman (7) considers that the numerical predictions of the theory are not in error by more than 50% at any temperature. Considerable generalisation of the theory to arbitrary temperature, κ and mean free path has been performed and the references quoted in Section 2.1 may be consulted for further details. Here we shall merely remark that because λ and ξ are a function of temperature the values of κ defined by equations 2.20, 2.21, and 2.27 are replaced by the temperature dependent parameters κ_1 , κ_2 and κ_3 . In the limit $t = 1$, $\kappa_1(1) = \kappa_2(1) = \kappa_3(1) = \kappa$.

ξ and λ are also a function of mean free path and a convenient expression due to Goodman (7) gives the effect of alloying on κ

$$\kappa = \kappa_0 + 7.5 \times 10^3 \rho \gamma^{\frac{1}{2}} \quad 2.29$$

where κ_0 is the pure metal parameter

ρ is the normal state resistivity in ohm cm.

and γ is the normal state temperature coefficient of the electronic specific heat in c.g.s. units.

Considerable variation of κ is possible with typical values being 0.4 for Pb (5), 1 - 1.5 for the present In-Pb and In-Tl alloys, 13 for Pb-Bi ϵ phase (26) and 35 for Nb_3Sn near T_c (27). The values of ξ and λ thus also vary over a wide range and this can have important consequences for the irreversible properties, as discussed in the next section.

2.3 The irreversible magnetic properties of superconductors

In practice, the GLAG theory is found to be inadequate to deal completely with the magnetic properties of superconductors since it predicts that the magnetisation in a given field is determined only by the thermodynamic critical field H_c and by the Ginzburg-Landau parameter κ . The predicted magnetisation curve is thus reversible; experimentally, however such ideal curves are rarely observed. The cause of this irreversibility arises in the pinning of flux both at the surface and in the bulk of the superconductor and forms the subject of this section.

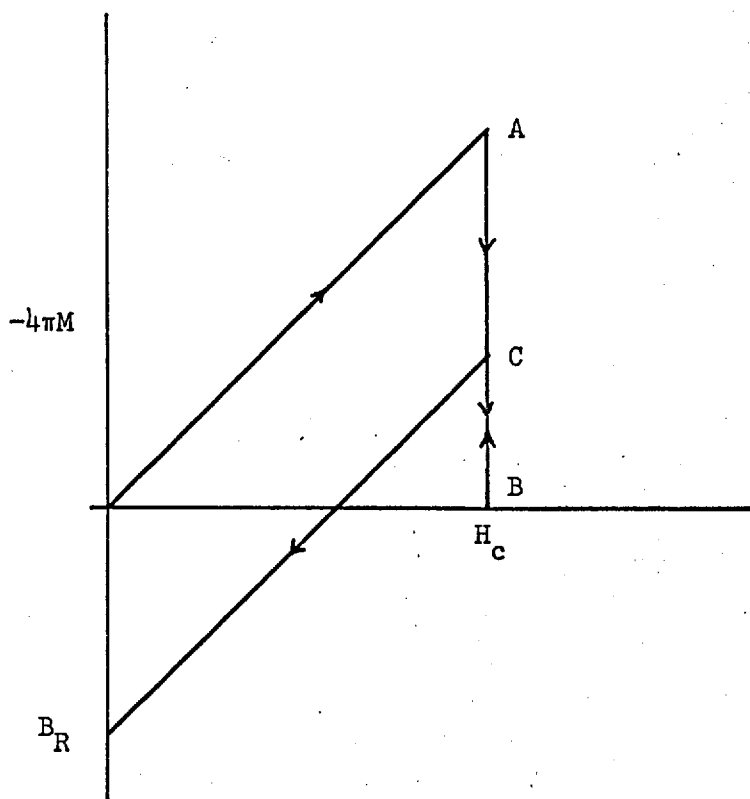


Figure 2.5 Magnetisation hysteresis due to multiple connectedness

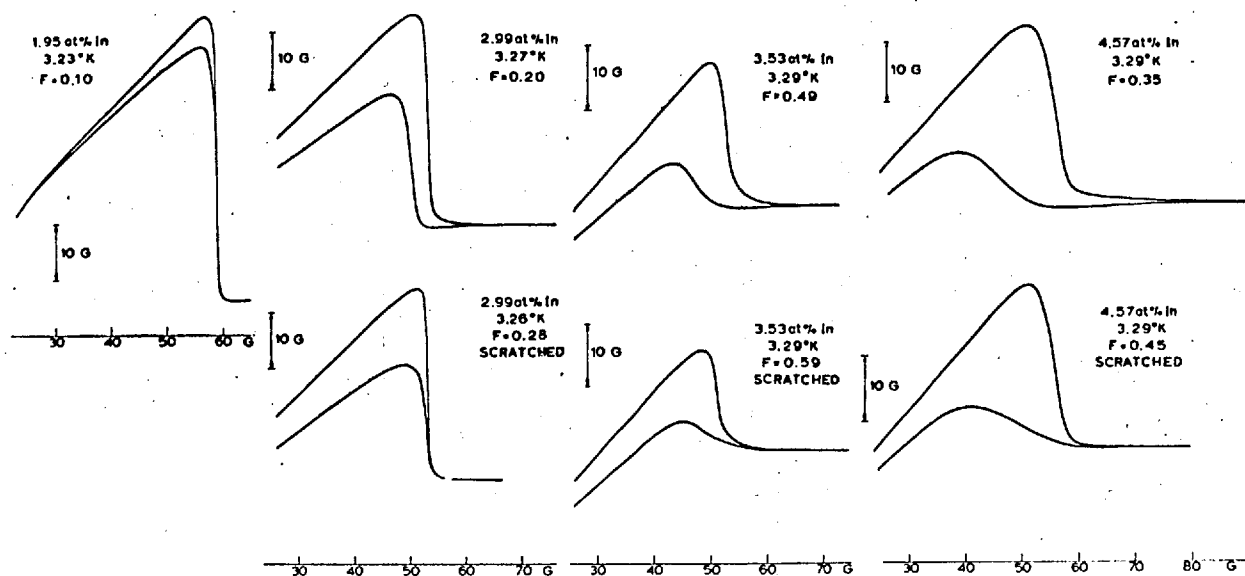


Fig. 1. Magnetization curves taken in increasing field (upper curves) and decreasing field (lower curves), $-4\pi M$ against applied field, both in gauss. M is the magnetization. The specimens of Sn In were at approximately 3.3°K and ranged in composition from 1.95 at.% In ($\kappa \sim 0.4$) to 4.57 at.% In ($\kappa \sim 0.7$). F is the ratio of the remanent flux density (frozen flux) to the critical field H_c . H_c is taken to be the field at which the magnetization has fallen to half its maximum value in an increasing field. The field was increased from zero after it had been lowered once from above H_c , thus inducing the zero field frozen flux. The lower curves were produced by specimens almost identical with those used to produce the upper ones but which had been scratched with shallow helical grooves, as described in the text.

Figure 2.6 Magnetisation hysteresis due to the surface sheath (Jones & Park,³⁰)

2.31 Multiple connectedness

The simplest form of magnetic hysteresis arises in the presence of an internal homogeneity which is completely surrounded by superconductor and which for simplicity we may regard as a cavity. Since the superconductor surrounds the cavity we speak of the superconductor as multiply connected.

On cooling such a sample below T_c in the absence of a field, the induction is of course everywhere uniform and equal to zero. On raising the field, the shielding surface currents of the Meissner state maintain the internal induction everywhere at zero. At the critical field H_c , superconductivity is quenched and the internal induction now becomes everywhere equal to the external field. The field increasing curve of such a sample is therefore no different from that of a homogeneous bulk superconductor.

When the field is reduced below H_c , however, flux is expelled from the superconductor but not from the cavity. A Meissner current is thus induced at the surface between the cavity and the superconductor which shields the superconductor from the trapped field. These currents maintain the trapped field at a value of H_c even after the external field has been reduced to zero. Since the total magnetisation of the specimen is the resultant of the external and internal Meissner currents, the field decreasing magnetisation is different from that of the first ascent and a hysteresis has occurred, as may be seen from figure 2.5. The proportions of the superconducting and normal volumes are given by $BC : AB$.

In general, multiple connectedness hysteresis will be present in any specimen containing internal inhomogeneities, which are themselves surrounded completely by a superconductor with a higher critical field. In type II superconductors, multiple connectedness is not expected above H_{c1} since fluxoids can, in principle, then move freely through the specimen bulk to equalise internal flux gradients. At κ values > 0.42 (section 2.24e), a superconducting surface sheath forms at the surface and may remain stable to a field $H_{c3} > H_{c2}$ or H_c , at which bulk superconductivity is destroyed. This sheath is itself multiply connected and will thus be

Figure 2.7

The Surface Barrier

(Bean & Livingston, 31)

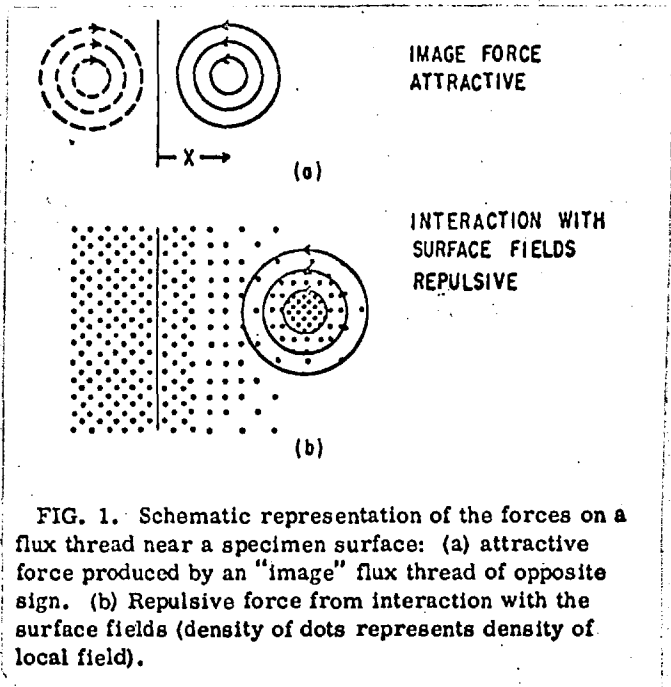


FIG. 1. Schematic representation of the forces on a flux thread near a specimen surface: (a) attractive force produced by an "image" flux thread of opposite sign. (b) Repulsive force from interaction with the surface fields (density of dots represents density of local field).

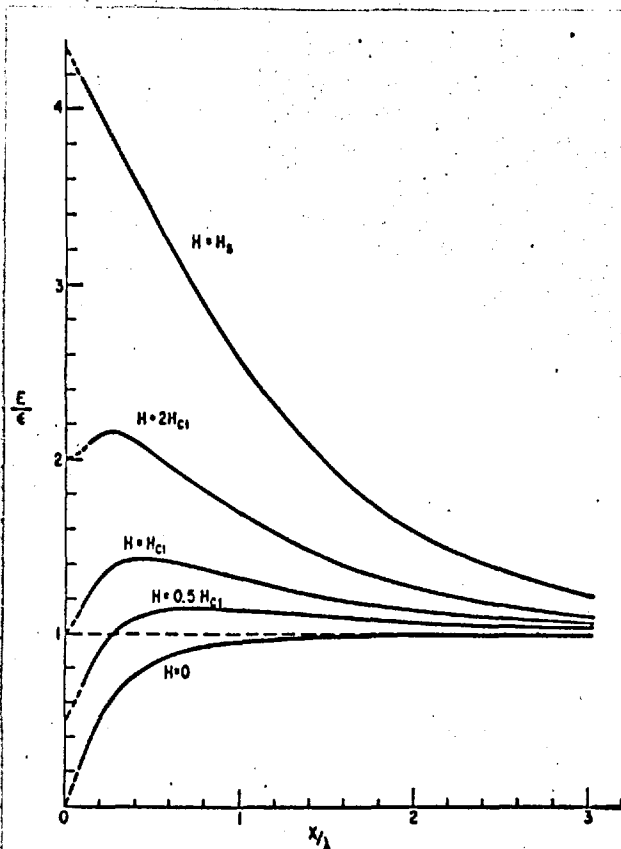


FIG. 2. Dependence of the line energy E of the flux thread on x , distance from the surface, for various applied fields. Results presented are for $\lambda = 10\xi$.

able to shield the bulk from small changes in the external field to a value determined by its critical current.

The effect of the sheath on the magnetisation hysteresis has been studied by plating the external surface with normal or magnetic metals (28,29) and by overlaying the surface with a diamond pattern of grooves (30). In the case of plating, the proximity of the normal metal to the superconductor destroys the sheath, while in the case of grooving, as is illustrated in the experiments of Jones and Park (30) shown in figure 2.6, the sheath current is forced to flow across surfaces at $\sim 70^\circ$ to the field direction so that the local sheath critical current is greatly reduced and the currents decay with a finite time constant. The ability of such a sheath state to cause magnetic hysteresis is thus a very sensitive function of surface condition.

2.32 The surface barrier

A further source of surface-induced hysteresis arises from modifications to the line energy of a fluxoid (equation 2.24) in the neighbourhood of the surface. A consequence of the second G-L equation (equation 2.14) is that no supercurrent can flow normal to the specimen surface and Bean and Livingston (31) have proposed that this condition can be satisfied by the presence of image fluxoids outside the specimen of opposite sign to the internal fluxoids, as in figure 2.7a. Close to the surface, this results in an attractive force on the internal fluxoid which inhibits its movement into the bulk. These authors find that the change in line energy for a single fluxoid is

$$\Delta g_I = (\phi_0 / 4\pi\lambda)^2 K_0(2x/\lambda) \quad 2.30$$

where K_0 is a modified Bessel function.

The same authors also propose an interaction between the internal fluxoids and the external field, which penetrates the superconductor as $H \cdot \exp(-x/\lambda)$, as illustrated in figure 2.7b. In the more common experimental situation, where the external field and the fluxoids have the same

sign, they find that the resulting interaction is repulsive. The magnitude of the interaction, again for a single flux line, was calculated to be

$$\Delta g_H = -\phi_0 H \exp.(-x/\lambda)/4\pi \quad 2.31$$

The sum of these two equations ($\Delta g_I + \Delta g_H$) for $\lambda/\xi = 10$ (i.e. $\kappa = 10$) is plotted in figure 2.7c, which shows that for all values of the external field considered, $\Delta g_I + \Delta g_H$ tends to zero within a few λ of the surface. The important result of the calculation is, however, that the barrier to flux entry does not disappear until a field H_s which may be considerably greater than H_{cl} . De Gennes (6), who has independently considered this problem, suggests that H_s is of the same order as H_c .

In practice, such macroscopic superheating fields are seldom met since local surface irregularities and the effect of the specimen ends ensure that local fields of H_s are realised at much lower values of the external field. Flux may enter at these irregularities and propagate into the bulk when the thermodynamic field H_{cl} is reached. On reducing the field, however, the irregularities responsible for early flux entry now block flux escape and the barrier does not reduce to zero until $H = 0$. Bean and Livingston comment that, under these circumstances, the field increasing curve is likely to be closer to the thermodynamically reversible curve.

Experimentally, the combination of a surface sheath and surface barrier appears to account for much of the hysteresis observed in bulk reversible superconductors (that is, those without a remanent induction B_R). The situation has been extensively investigated in alloys of lead by Malseed and Rachinger (32) who found that the surface barrier could be much reduced by longitudinal grooving of the surface, while the surface sheath was substantially unaffected until a diamond pattern of grooves was added, as already discussed. Some similar experiments on the alloys investigated in this thesis are reported in section 5.21.

2.33 The pinning of flux lines within the specimen bulk

Considering now the bulk pinning of flux lines, we recall that the free energy per unit length of flux line may be obtained from equation 2.24 and is

$$g = \zeta + \sum_{ij} U_{ij} - \phi_0 H / 4\pi \quad 2.32$$

Near the surface, of course, we must also add the surface barrier terms derived above, but, within a bulk reversible superconductor, g is expressed only by the 3 terms above, which represent the fluxoid line energy, the interfluxoid forces and the magnetic pressure of the external field, respectively.

In general a defect may affect g in several ways; we consider now two interactions proposed by Kramer and Bauer (33) for the particular case of the single fluxoid/single dislocation interaction but which are of more general importance.

- 1). Since the volume of the normal core of a flux line is less than that of the superconductor it replaces, there is a stress field associated with the fluxoid which can interact with defect stress fields.
- 2). There is also an elastic modulus variation between the two states, which causes the fluxoid to behave like an elastic inhomogeneity and display an induced stress field.

In the particular case of the single fluxoid/single dislocation interaction the authors find net long range forces when the two are parallel but only local torques when the two are normal to each other. The forces found are, however, rather small, of the order $10^{-8} - 10^{-9}$ dynes /cm. This is in reasonable agreement with the value found experimentally for screw dislocations by Freyhardt and Haasen (34). Narlikar and Dew-Hughes (35) have calculated that a 1% reduction in electron mean free path in a dislocation tangle gives an interaction of the same order but the practical measurement of such a reduction has not been attempted.

When dealing with coherent and incoherent precipitates, compositional fluctuation, inclusions of normal or insulating particles and second phase precipitates in general, the interactions proposed by Kramer and Bauer still operate. In addition, though, the change in the condensation core energy of the fluxoid $\sim H_c^2 \xi^2/8$ per unit length and the kinetic energy associated with the screening supercurrents should be taken into account. In a recent review, Livingston (36), considers that experiments to date clearly suggest that maximum pinning occurs for defects with radically different electronic properties from the matrix (e.g. voids or insulators) since the fluxoid core energy disappears in the normal metal or void. Livingston calculates that such an interaction, giving a local reduction of $H_c^2 \xi^2/8$ per unit length, will result in a pinning force of $\sim 10^{-6}$ dyne/cm for a superconductor with $H_c = 3000$ Oe and $\xi = 100$ Å. A flux thread intersecting one such void every 1000 Å would then have a pinning force of 10^{-1} dyne/cm and result in a bulk critical current density $J_c = 10 f_p / \phi_0 = 5 \times 10^6$ A/cm².

While such a calculation can give a plausible figure for J_c , it is not in practice possible to calculate J_c from first principles. To do this we should also have to take into account the detailed interaction between the fluxoid lattice and its imperfections (37) and the defect lattice and its irregularities. A first principle calculation would also have to consider the existence of a surface barrier and/or surface sheath at the defect/superconductor boundary and at present such detailed calculations have not been performed.

Nevertheless the bulk critical currents and pinning observed in many alloys have been satisfactorily related to the particular microstructure. In the well studied Pb-Bi eutectic, Campbell et al (26) and Kramer and Rhodes (38) have found that J_c is proportional to the total surface area of the normal bismuth particles and Levy et al (39) have generalised this result to a wide range of eutectics. Narlikar and Dew-Hughes (35) have demonstrated a clear connection between a steep rise in B_R and the formation of dislocation cells in cold-worked niobium, while Bean et al (40) have observed very large increases in the critical current of samples of Nb₃Al and V₃Si after the introduction of point defects by neutron irradiation. The effects of precipitation have been studied by many authors, particularly

by Livingston in lead based alloys (41, 42). Much information about flux pinning in particular systems has been given in reviews by Livingston and Schadler (8), Livingston (36) and Dew-Hughes (43).

The importance of a disparity between the electronic properties of the pinning centre and the matrix has already been mentioned but a further important feature is the size of the pin relative to the coherence length ξ of the superconducting matrix. Livingston (36) and Campbell et al (26) suggest that pinning centres with a diameter much less than ξ do not trap flux effectively since the normal core of the flux line has a radius of ξ and appreciable reduction of energy will occur only in defects of this size or larger. In principle maximum pinning would occur if the defect and flux-line lattices could be perfectly matched, but as the flux-line lattice spacing goes as $(\phi_0/B)^{1/2}$, such matching can only occur for one value of B. The optimum sizes of pinning centre are therefore given by the range of parameters occupied by the flux-line lattice, which vary from $\sim \lambda$ near H_{c1} to $\sim \xi$ at H_{c2} .

2.34 The equilibrium between pinning forces and flux line forces

2.34a Depinning forces

The pinning of flux within the specimen bulk results in a flux gradient as the distance from the specimen surface is increased. Arising from this gradient is an imbalance in the inter-fluxoid interactions $\sum_{ij} U_{ij}$ and this imbalance leads to a macroscopic force, commonly referred to as a Lorentz force, which acts so as to unpin fluxoids and even out the flux gradient. Friedel et al (44) have shown that the driving force on an individual flux line resulting from an array of straight flux lines is given by :

$$F_L = - (\phi_0/4\pi) \partial H(b)/\partial x \quad 2.33$$

where $H(b)$ is the external field in equilibrium with the flux density B in the reversible specimen.

The existence of such a gradient is equivalent to a macroscopic internal current parallel to the slab surface which is given by (8)

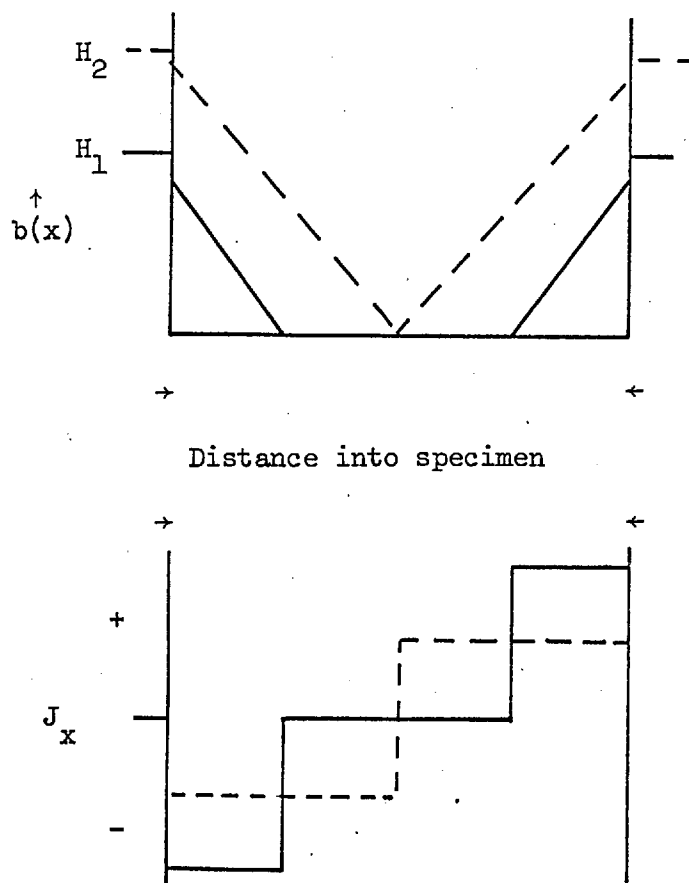


Figure 2.8 Flux gradients and critical currents in an irreversible superconductor

Figure 2.9

Experimentally observed
Flux gradients in Nb/60Ti.
(Coffey, 49)

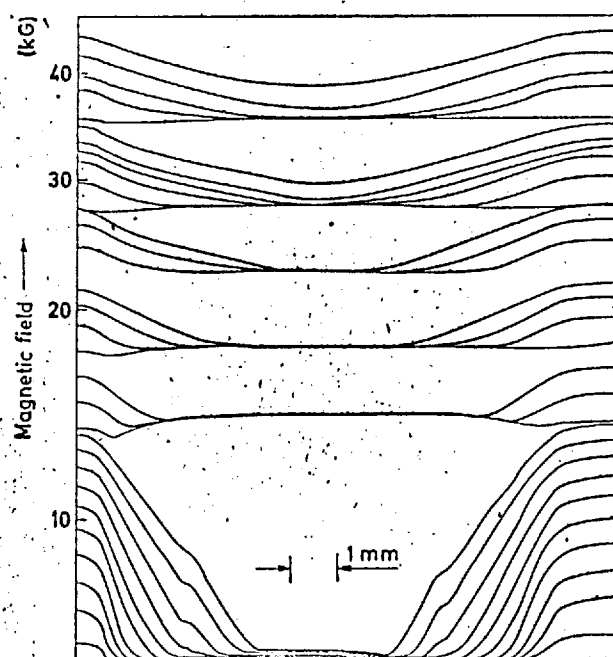


Figure 3. Detailed tracings of field distribution data in a niobium-titanium (60 per cent) sample indicating six flux jumps. Field was increased at ~ 300 G/min between tracings. Note deeper penetration of field before flux jumps at higher fields and flux flow after last two jumps

$$J = 10/4\pi (\partial b/\partial x) \text{ amps/cm}^2 \quad 2.34$$

which in the 3-D case can be generalised to $\underline{J} = 10/4\pi \text{ curl } \underline{b}$. This result is important since it demonstrates the relation between bulk internal currents and magnetisation hysteresis. An ideally reversible type 2 superconductor can only carry lossless currents below H_{c1} ; above H_{c1} , flux moves freely through the bulk magnetic field, generating a finite E.M.F. The whole technology of high field current carrying superconductors thus depends on an irreversible magnetisation curve.

An additional source of energy capable of unpinning fluxoids was proposed by Anderson and Kim (45), who suggested that at finite temperatures above 0°K thermal activation could excite fluxoids over their pinning barriers with a rate given by

$$R = W_0 \exp. (-E/kT) \quad 2.35$$

where W_0 is the vibration frequency of the flux line and E is the height of the energy barrier. Small rates of flux creep have been measured (46) in practice by observing the decay of magnetisation currents over long periods (see also figure 2.9) but the time scale of most magnetisation measurements is shorter than the time constant associated with flux creep and it is thus not normally observed when plotting magnetisation curves.

2.34b The critical state

At any combination of field and temperature there exists a value of the Lorentz force (or some fraction of it, depending on the time scale and possibility of thermal activation in the experiment) which will just overcome the pinning force F_p on a flux line. Bean (47) introduced the idea of a critical state in which the flux density gradient was everywhere given by the relation $F_p = F_L$, or was equal to zero. This critical gradient corresponds to the maximum internal current which can be carried without loss and is known as the critical current J_c . The relation between the flux gradient and the internal current is illustrated in figure 2.8.

Since under critical state conditions $F_p = F_L$, we may write

$F_p = - (\phi_0/4\pi) \partial H(b)/\partial x$ from equation 2.33. After re-arrangement and substitution of $\partial H(b)/\partial b$, $\partial b/\partial x$ for $\partial H(b)/\partial x$ we obtain the internal flux gradient $\partial b/\partial x$:

$$\frac{\partial b}{\partial x} = - \frac{4\pi}{\phi_0} \cdot \frac{F_p}{\partial H(b)/\partial b} \quad 2.36$$

where $\partial H(b)/\partial b$ is the gradient of the reversible magnetisation curve. The first integration of this equation gives the local induction b and the second then sums b over all x to give the macroscopic induction B , which allows a direct comparison with the experimentally observed magnetisation.

Solutions of this equation were first proposed by Bean (48) for the mathematically simple case of (i) a high κ superconductor, so that $\partial H(b)/\partial b$ can be approximated by a straight line in the mixed state and (ii) for F_p independent of B . This leads to a flux profile linear with penetration into the specimen, as has been shown in figure 2.8.

Physically this linear dependence, corresponds to a pin density very much greater than the fluxoid density such as a heavily cold-worked specimen not far from H_{c1} . The low field profiles observed by Coffey (49), who has driven a very small Hall probe through a fine slit in a cold-worked Nb-Ti sample, are shown in figure 2.9 and confirm two features of the Bean analysis, namely a flux profile which is either finite and linear or equal to zero. It can be seen, however, that at higher fields $\partial b/\partial x$ decreases implying a reduction in J_c as H increases and, in addition, on five occasions a large discontinuous change in the flux profile has occurred. It is interesting that after the last two of these so-called flux jumps, the flux profile is almost flat so that the bulk magnetisation corresponds to the Abrikosov reversible magnetisation. Some flux creep can also be seen after these latter flux jumps.

The dependence of J_c on B observed in the latter curves does not invalidate the concept of the critical state and in practice many variations of J_c with B have been proposed : viz. B^{-1} (Silcox and Rollins (50)), $B^{-\gamma}$

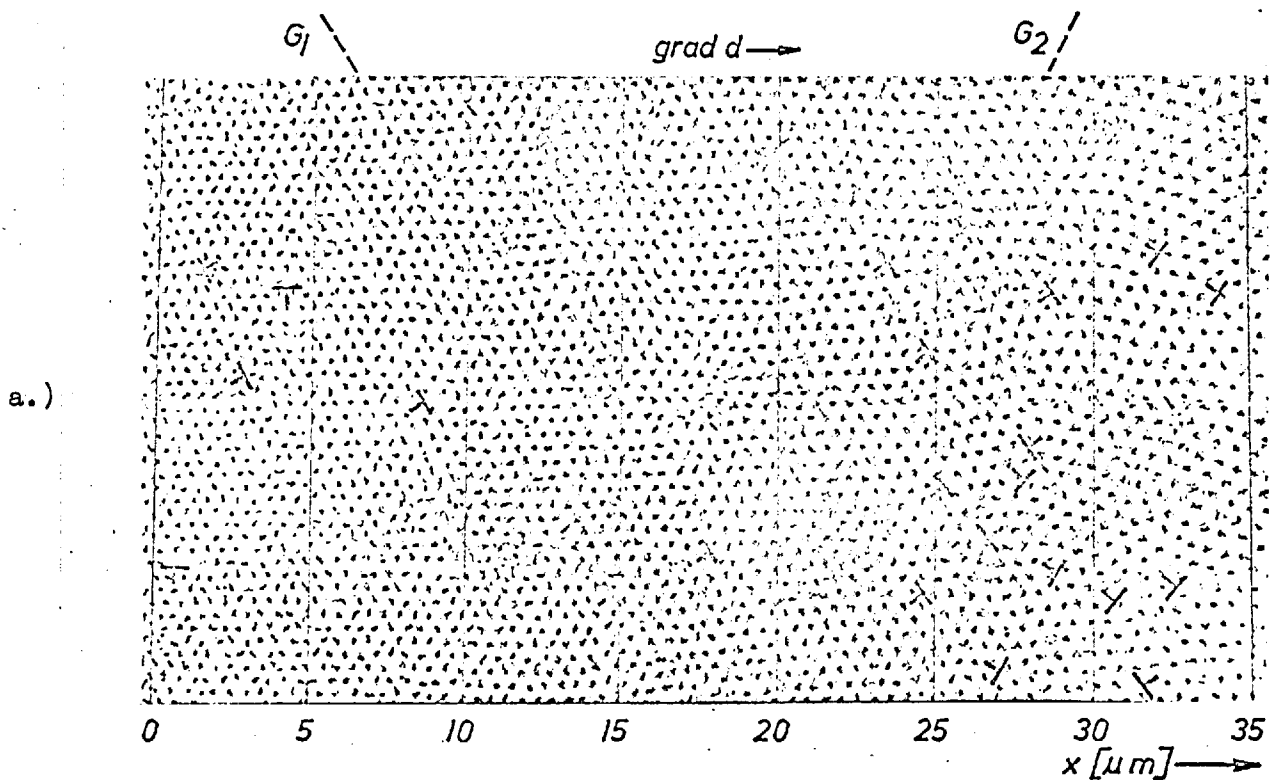


FIG. 8. Area of the FLL with an extremely high, approximately constant flux-line density gradient from right to left. The dislocation cores are indicated by the symbol $\perp$. Dislocations on the glide planes G_1 and G_2 have a resultant Burgers vector perpendicular to the gradient. Note the transition to the flux-line fluid at the right-hand side of the picture. Replica.

Figure 2.10 The flux line lattice (Trauble & Essmann, 37)

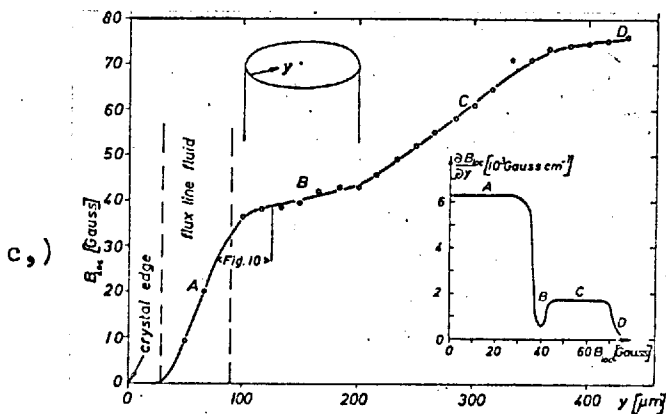


FIG. 7. Local induction B_{100} ($\sim$ flux-line density) in the remanent state of a lead-indium crystal as a function of y . Averaged induction $B = 70$ G. Evaluated from replica from the top surface of a cylindrical crystal. On the right-hand side the corresponding $\partial B_{100}/\partial y$ diagram.

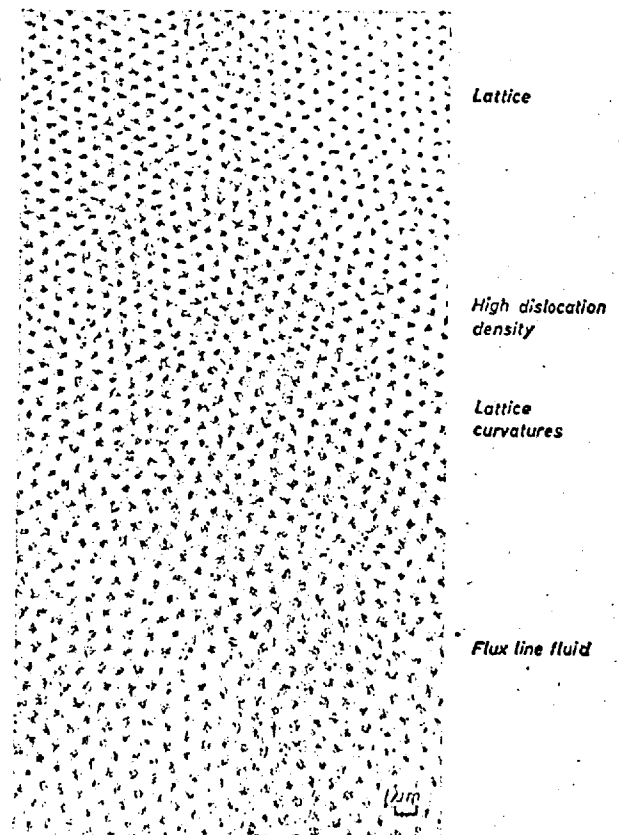


FIG. 10. Transition zone from the triangular lattice to the FL fluid. For position on crystal surface see Fig. 7. Replica.

b.)

(Irie and Yamafuji (51)), $(B + B_0)^{-1}$ (Kim and Anderson (52)) and M_{rev}/B^2 (Campbell et al (26)). This variation arises naturally from the variety of pinning centres possible in different materials and their effectiveness relative to the electronic properties of the superconducting matrix. Thus no single form of $J_c(B)$ is valid over the whole range H_{c1} to H_{c2} for all materials.

2.34c The fluxoid lattice

While the experiments of Coffey (49) were able to reveal details of the flux line gradient on a scale of $\sim 1/10$ mm (1000μ), the flux line decoration experiments of Träuble and Essmann (37) and Sarma and Moon (53) can reveal individual flux lines on a scale of $\sim 1/10 \mu$. In the micrographs shown in figure 2.10 (37), the individual fluxoids in the remanent state of a cold-worked Pb/6 In specimen have been revealed by decorating the surface with ferromagnetic particles $\sim 100 \text{ \AA}$ in diameter and evaporating a carbon film to fix the pattern for later examination at R.T. with an electron microscope. In the first micrograph, figure 2.10a, a well developed triangular lattice is seen which supports a flux gradient from right to left by extensive faulting with edge dislocations. In the second micrograph figure 2.10b, the transition from the well-defined lattice through a highly faulted structure to a flux line fluid is shown. A further region $\sim 30\mu$ wide between the fluid and the surface was found in which no fluxoids exist. The flux gradient arising from this fluxoid arrangement is shown in figure 2.10c.

The samples investigated by Träuble and Essmann to date have all been essentially weak pinning materials and this may well explain the perfection of the flux line lattice observed. In the present sample of Pb/6.33 In, which presumably contained a dislocation structure responsible for the existence of the flux line gradient, no metallography was performed to relate the flux line distribution to the defect distribution.

An interesting anomaly is found however when the pinning force is estimated from the individual fluxoid-defect interaction at the boundary of the flux line fluid and flux free regions and when it is inferred from the critical state equation (eqn. 2.36). A value of $\sim 4 \times 10^{-4}$ dyne/cm

is obtained for the first case which is two order of magnitude greater than that in the second. The authors consider that this reduction may be due to the presence of flux line dislocations which allow easy flux movement down the flux line gradient. It is also likely, as Livingston (36) has pointed out, that considerable cancellation of inter-fluxoid forces occurs in the lattice arrangement.

Nevertheless it is not clear that the flux lines are capable of being formed into a lattice in the presence of an extended defect array. Thus, in the cold-worked samples of Nb/25 Zr studied by Sarma and Moon (53), no evidence of a flux line lattice is visible (with a resolution of the order of $500 \text{ \AA}$) and the pattern obtained is very similar to the dislocation cell structure. Pinning appears to be particularly strong at the nodes of cells. In more recent work, Sarma (54) has correlated the flux density patterns obtained from samples of V_3Si and Pb-Ca alloys, finding pinning due to grain boundaries in V_3Si and to segregated Ca_3Pb in Pb-Ca. In this case the fluxoid replica was compared directly to the microstructure beneath, as revealed by light microscopy, but the comparative coarseness of the replica structure precluded the calculation of internal fluxoid gradients as in figure 2.10c. In the case of the cell structure revealed in Nb-Zr by electron microscopy, of course, such direct comparison cannot be made. The current introduction, however, of the million volt electron microscope might well allow thicker specimens characteristic of the bulk to be examined, so that a direct correlation between fluxoid and defect structure on a scale of $100 - 1000 \text{ \AA}$ can be made.

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CHAPTER 3

THE PHYSICAL METALLURGY OF SOME CRYOGENIC ALLOYS

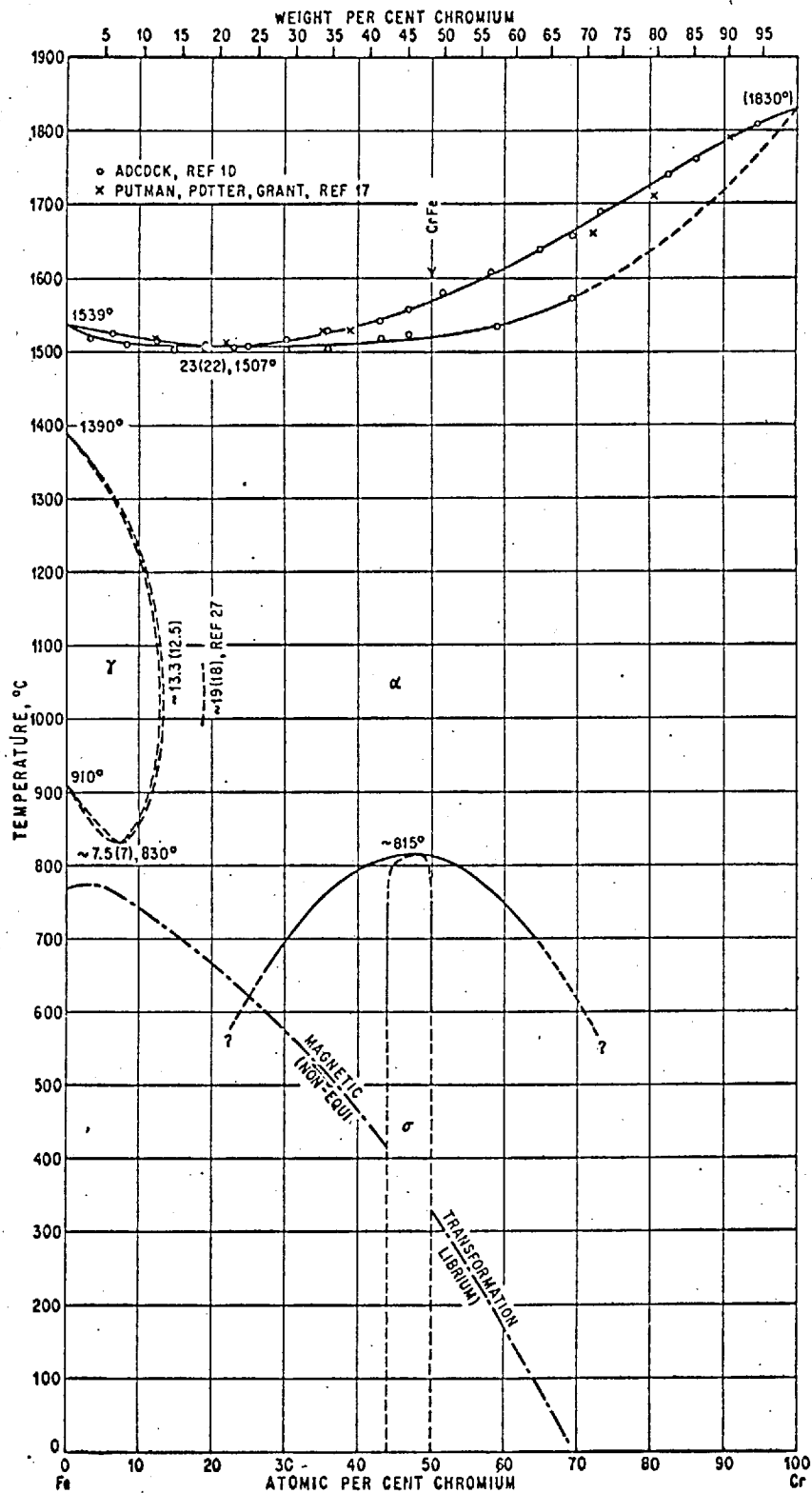


Fig. 309. Cr-Fe. (See also Fig. 310.)

Figure 3.1 The Iron-Chromium phase diagram. (Hansen, 1).

3.1 Austenitic stainless steels

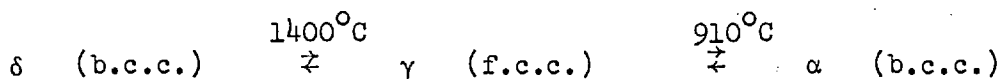
3.1.1 Introduction

Stainless steels acquire their name from the corrosion resistant properties that chromium confers when alloyed to iron. Protection in corrosive environments is believed to be due to a tough insoluble surface film containing chromium oxides which becomes effective at approximately 10 - 12 wt% Cr and which represents the useful lower limit of chromium additions to stainless steel. Nickel is widely used in stainless steels to control their structure but is not essential for corrosion resistance, although it brings improvements in alkaline and weakly oxidising environments.

The composition of stainless steels varies widely from a simple Fe/12 Cr alloy to multi-element alloys which may contain less than 40% iron. For convenience the common practice of referring to a steel by two numbers denoting its chromium and nickel contents in weight per cent will be used; viz 18:10 = 18 wt% Cr /10 wt% Ni. Other significant additions may also be specified; viz 16/12/3 Mo for an AISI 316 steel.

3.1.2 The equilibrium structure of iron-chromium-nickel alloys

The microstructure of the stainless steels is based on the allotropic changes occurring in pure iron:



In alloy systems, solutions based on b.c.c. iron are known as ferrite and those based on f.c.c. iron as austenite.

The different effects of adding chromium and nickel to iron are illustrated by the phase diagrams in figures 3.1 and 3.2 (1). Chromium is a ferrite forming solute and hence the γ phase region is restricted to a loop, while the α and δ phase fields become continuous at compositions greater than 12.5 wt% Cr. It is also

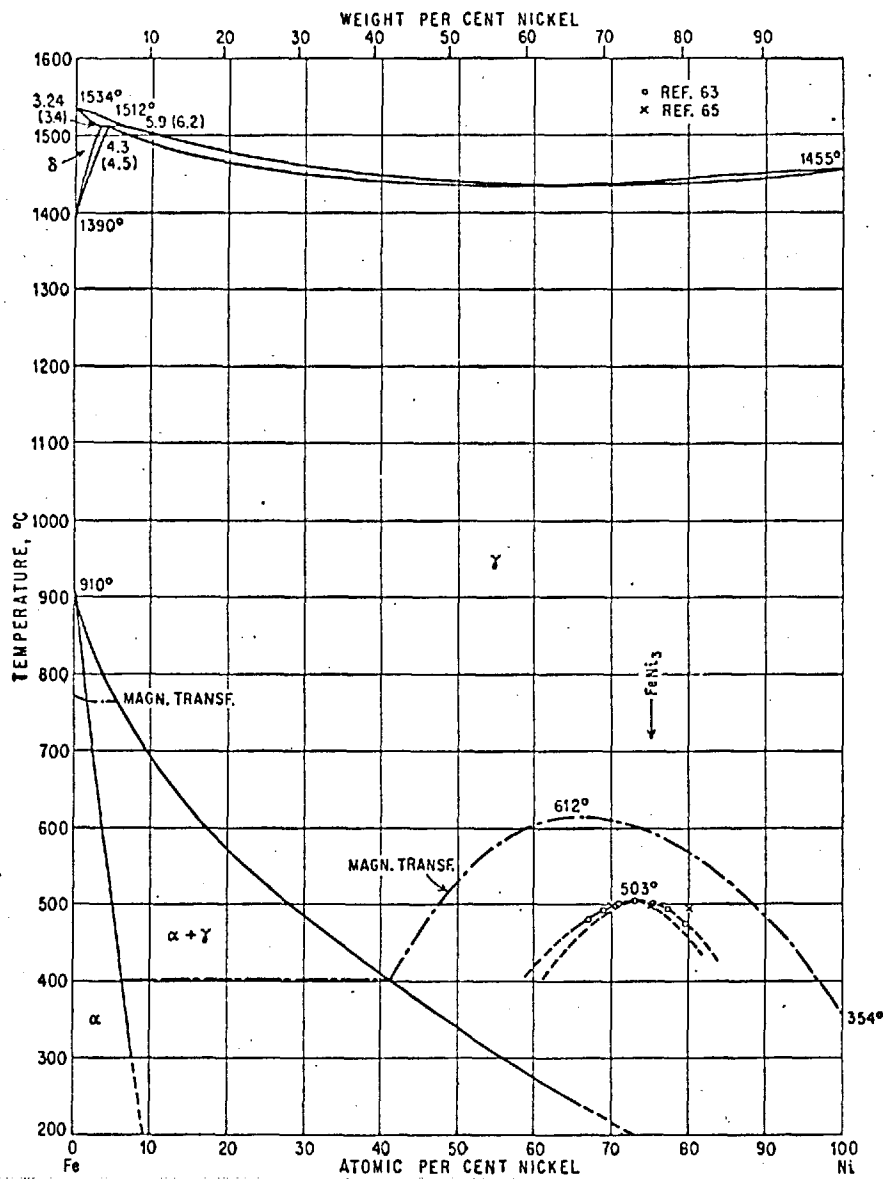
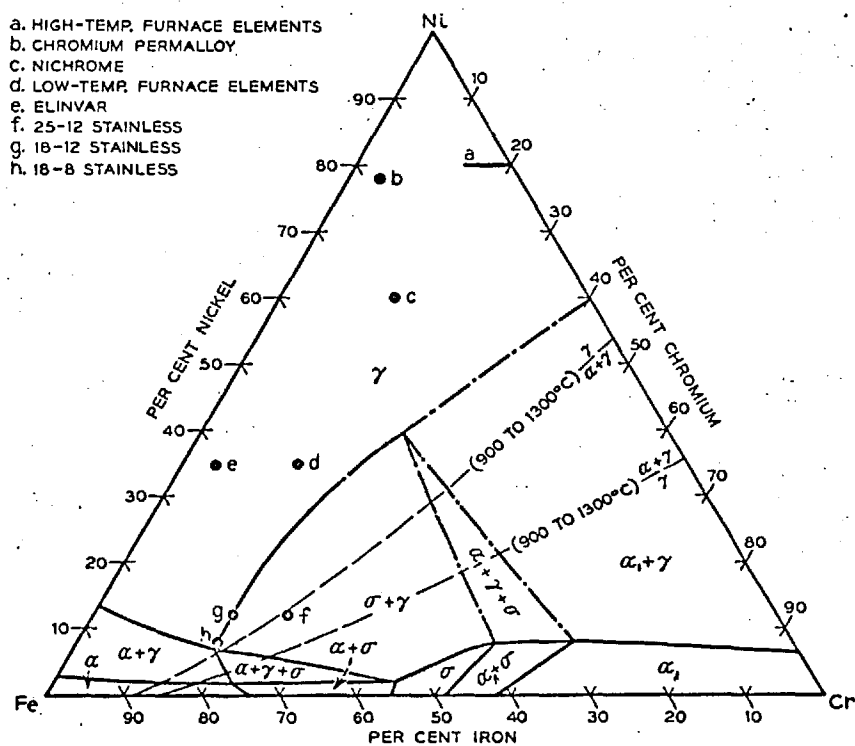


Figure 3.2 The iron-nickel equilibrium diagram. (Hansen, 1).

Figure 3.3 Isothermal sections through the Fe-Cr-Ni equilibrium diagram. (Bozorth, 3).



important to notice the presence of the brittle σ phase which forms at the composition FeCr.

The addition of nickel to iron on the other hand stabilises the austenite, thus restricting ferrite to the high and low temperature parts of the diagram (Figure 3.2). The $\gamma \rightarrow \alpha$ transformation at temperatures below approximately 500°C is very sluggish and at 350°C, for example, alloys need to be held for up to 2 years to obtain the equilibrium phase structure (2). Figure 3.2 also shows that the magnetic transformation depends markedly on structure and that the Curie point of the austenitic alloys is lower than that of the ferritic alloys.

An isothermal section through the Fe-Cr-Ni ternary equilibrium diagram at 600°C is shown in figure 3.3 (3). This shows the presence of the α , γ and σ phases which are also present in the binary Fe-Cr and Fe-Ni diagrams. Also shown are dashed lines representing the approximate position of the γ and $\alpha + \gamma$ phase fields over the range 900 - 1300°C.

3.13 The martensitic transformation in Fe-Cr-Ni alloys

On continuous cooling of iron nickel alloys the γ phase decomposes to ferrite by a diffusionless martensitic transformation as illustrated in figure 3.4 (1). The temperature at which the transformation starts on cooling is known as M_s and that at which it finishes M_f , which does not necessarily imply that 100% transformation has taken place. Figure 3.4 shows the 10, 50 and 90% points of this transformation. On heating the martensite a reverse shear transformation back to austenite occurs. The reverse transformation is accompanied by a hysteresis of approximately 200 - 400°C, depending on composition, and is increased by cyclic thermal treatments. A similar martensitic shear transformation occurs in Fe-Cr-Ni ternary alloys and in the stainless steels. The martensitic phase, denoted α' , is of prime interest to the present work because it is ferromagnetic below approximately 600°C.

It is a consequence of the martensitic shear transformation

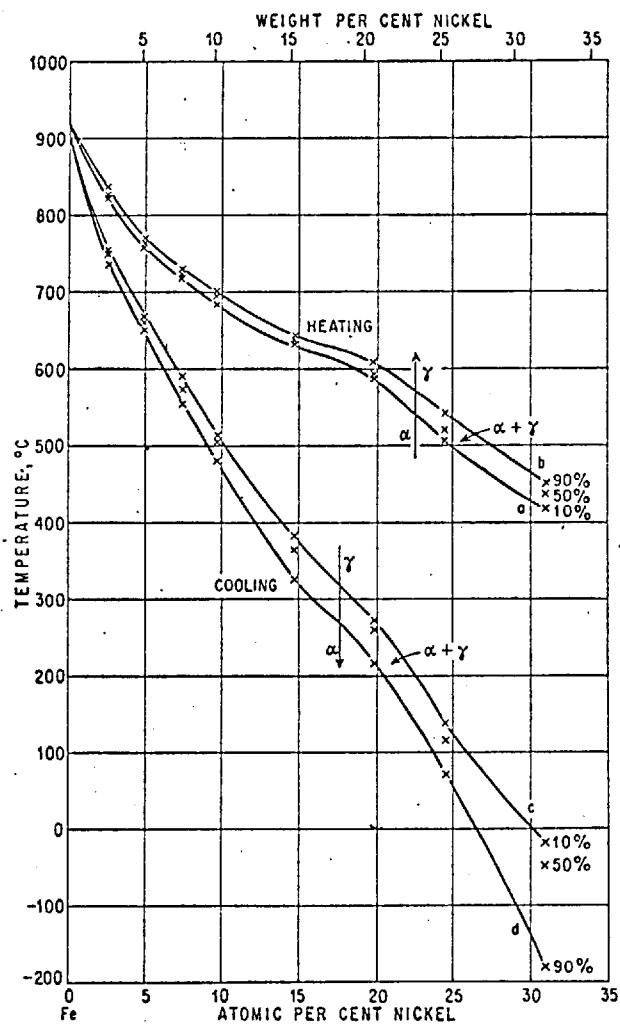
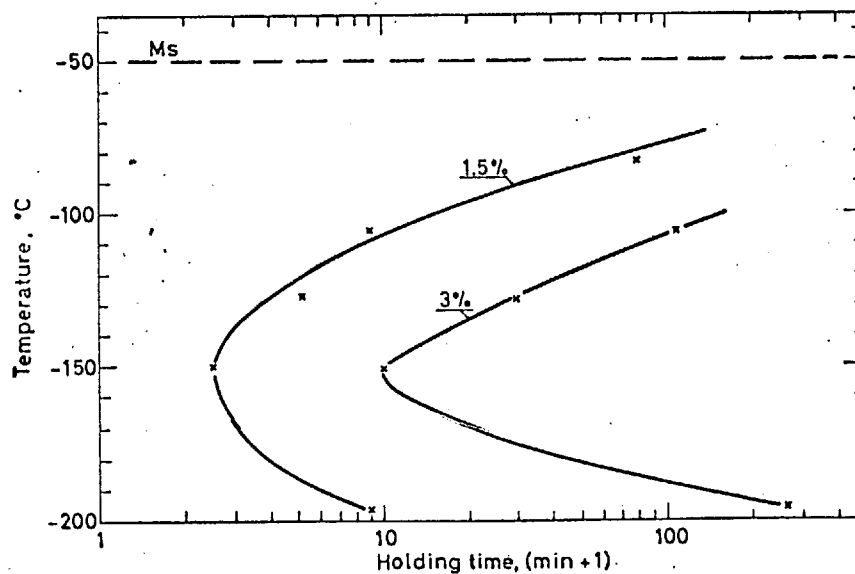


Figure 3.4 The $\gamma \rightarrow \alpha$ transformation on continuous cooling in Fe-Ni.

(Hansen, 1).

Figure 3.5 Isothermal transformation in an 18/8 steel. (Lagneborg, 6).

LAGNEBORG: MARTENSITE TRANSFORMATION IN 18-8 STEEL

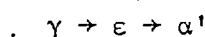
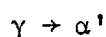


that the martensite phase forms with a distinctive orientation relationship to the parent phase and that there is a coherent interface between the two structures.

The plane of the austenite which lies parallel to the plane of the interface is known as the habit plane and its Miller index is characteristic of the particular martensitic transformation. Several different orientation relationships and morphologies have been observed in Fe-Cr-Ni alloys and stainless steels. Thus Reed (4) has found that α' forms as plates within $\{111\}_\gamma$ sheets. Kelly and Nutting (5) have found α' as needles after deformation where the α' is oriented in $\langle\bar{1}10\rangle$ in $\{111\}_\gamma$ sheets. Lagneborg (6) has noted that whereas α' forms as plates on cooling, deformation of the same steel produces needles. He has also observed a $\{259\}_\gamma$ habit plane for both morphologies with the orientation relationships $\{111\}_\gamma // \{101\}_{\alpha'}$ and $\langle\bar{1}10\rangle_\gamma // \langle\bar{1}11\rangle_{\alpha'}$. Small additions of molybdenum were observed to change the $\{259\}_\gamma$ habit to $\{225\}_\gamma$. Venables (7) has also observed a $\{225\}_\gamma$ habit in an 18/8 alloy.

A complication in the low temperature decomposition to α' is the existence of an additional martensitic product ϵ which has the h.c.p. structure and is paramagnetic (8). ϵ is oriented in the γ matrix so that the close packed planes and directions of each structure are parallel, i.e. $\{111\}_\gamma // \{0001\}_\epsilon$ and $\langle\bar{1}10\rangle_\gamma // \langle\bar{1}2\bar{1}0\rangle_\epsilon$. ϵ may be formed from γ by faulting on alternate $\{111\}_\gamma$ planes and if this periodicity is not maintained faulted ϵ results. The ease of faulting depends on the stacking fault energy and Schumann and von Fircks (9,10) have recently proposed two schemes by which the occurrence of ϵ martensite depends on chemical composition. Briefly, increasing the carbon contents is considered to play the major role in raising the stacking fault energy and thus suppressing the ϵ phase. They have also considered the Cr/Ni composition, however, at a constant carbon content and find that at concentrations less than 15.5 Cr/9 Ni, where the Cr/Ni ratio is held at $\sim 2:1$, no ϵ is formed. At higher contents they succeeded in measuring separate M_s temperatures by dilatometry for the transformations $\gamma \rightarrow \epsilon$ and $\epsilon \rightarrow \alpha'$. $M_s(\epsilon)$ is higher than $M_s(\alpha')$.

The close relationship between α' and ϵ has been noted by many workers (4,6-15.) Thus Lagneborg (6) has observed the appearance of faulted ϵ sheets above the $M_s(\alpha')$, followed by growth of α' crystals within the sheets on further cooling. Reed (4) has noticed similar behaviour in 18/10 steels, as have Breedis and Robertson (13,14) with 16/12 single crystals. That ϵ is a transitional phase is indicated by studies which show that as the total martensite content increases, the ϵ content declines, being practically zero at high α' concentrations (4,11,12.) Two modes of transformation are thus well-established :--



without the exact details of the changeover between the two being exactly defined.

A martensitic phase transformation can also be induced by deformation below a critical temperature M_d which is greater than M_s . In the case of the 18/8 steels this is the only way to obtain 100% transformation (6,11,15.) Deformation below M_d causes transformation along active slip planes and the microstructural inhomogeneity of the transformation in polycrystalline material has been explained on the basis that martensite forms most readily in those grains where $\langle 111 \rangle \gamma$ is parallel to the tensile axis and least readily when $\langle 100 \rangle \gamma$ is parallel to the tensile direction (6).

Deformation above M_d may both enhance subsequent transformation on cooling below M_s and then at higher strains lead to suppression of the transformation by reducing the M_s (15). This latter effect is known as mechanical stabilisation. Lagneborg (6) has shown that 4% deformation causes maximum transformation in a subsequently cooled 18/8 steel while 25% deformation leads to complete stabilisation. Similar results have been presented by Fiedler et al (15).

These effects have been explained in terms of the internal dislocation structure and the consequent internal stress field (6,15,16). Above M_d it is postulated that small deformations produce additional nucleation sites on active slip planes which become operative on subsequent cooling. Mechanical stabilisation is associated

with the formation of a dislocation cell structure whose stress field opposes the creation of martensite (16).

Many workers have found that the amount of α' (11,12,17,18) formed by deformation is increased as the temperature is lowered. Measurements below 77°K (11,12,18) have shown, however, that the extent of the transformation declines at very low temperatures and it is suggested this may be related to a reduction in the amount of transformation which occurs isothermally in these alloys, as discussed in the following section.

Low temperature isothermal transformation of $\gamma \rightarrow \alpha'$, following some degree of athermal transformation during the cool down, has been observed in a number of investigations. Fiedler et al (15) and Lagneborg (6) have made detailed measurements on materials similar to 18/8 steels and Figure 3.5 shows a time-temperature-transformation (TTT) diagram due to Lagneborg. The TTT curve shows a maximum isothermal rate at ~120°K in the presence of a small quantity of athermally produced martensite. Fiedler et al (15) found that the isothermal transformation rate for their steels was still increasing at 77°K but did not determine the rate at lower temperatures. Their measurements show that the isothermal transformation may also be mechanically stabilised by prior deformation of the austenite at room temperature. No observations of the isothermal formation of ϵ have, however, been reported.

The reverse transformation of ϵ or α' to austenite has not been studied in great detail but the investigations of Cina (12,19), Breedis (20) and Reed (4) show that α' reverts to γ over a range of temperature between 500° and 700°C. ϵ was shown to revert at rather lower temperatures, 150° to 400°C. Thus steels which are quenched to cryogenic temperatures to produce martensite are most unlikely to revert to austenite on warming to room temperature.

TABLE 3.1 Composition of austenitic stainless steels

The AISI 300 Series

AISI No.	C max.	Cr	Ni	Significant additions
301	0.15	16 - 18	6 - 8	
302	0.15	17 - 19	8 - 10	
303	0.15	17 - 19	8 - 10	0.15 min S
304 (L)	0.08(0.03)	18 - 20	8 - 12	
305	0.12	17 - 19	10 - 13	
308	0.08	19 - 21	10 - 12	
309 (S)	0.20(0.08)	22 - 24	12 - 15	
310 (S)	0.25(0.08)	24 - 26	19 - 22	1.5 Si max
314	0.25	23 - 26	19 - 22	1.5 - 3 Si
316 (L)	0.08(0.03)	16 - 18	10 - 14	2 - 3 Mo
317	0.08	18 - 20	11 - 15	3 - 4 Mo
321	0.08	17 - 19	9 - 12	(5 x C) Ti min
347	0.08	17 - 19	9 - 13	(10 x C) Nb or Ta min
348	0.08	17 - 19	9 - 13	(10 x C) Nb or Ta min 0.10 Ta max

All steels contain 2% Mn max., 1% Si max., 0.045% P max. and 0.030% S max. except where otherwise stated.

3.14 Commercial materials

3.14a The AISI 300 specifications

Two British Standard specifications, B.S. 970 (21) and B.S. 1449 (22), govern the production of the austenitic Fe-Cr-Ni stainless steels. However, the more widely used EN58 specification is governed by the obsolete B.S. 970 and the recent B.S. 1449 uses a scheme based on the American Iron and Steel Institute (AISI) 300 specifications. As the AISI 300 specifications are widely used throughout the U.K. and in many other parts of the world, they have been adopted in this study. The alloy compositions of this specification are shown in Table 3.1 (23). From this it may be seen that in addition to the main constituents (Fe, Cr, and Ni), the steels also contain specified additions of C, Mn and Si. A further addition of approximately 0.02 wt% N is likely in air melted steels and up to 0.2 % may be added deliberately to improve the strength in the so-called "Hi-proof" steels.

The standard heat treatment for these steels is a $\frac{1}{2}$ hour fully softening anneal at 1050° - 1150°C followed by a water-quench, or quick air-cool, to retain the austenitic structure at room temperature. This treatment does not leave the steel in thermodynamic equilibrium and hence Fe-Cr-Ni ternary equilibrium diagrams are of limited use in dealing with commercial steels. To deal with this multi-element non-equilibrium situation, the concept of an alloying balance has been developed.

3.14b The alloying balance

The alloying balance represents an empirical approach to the complex alloying behaviour of commercial stainless steels by considering additional elements in terms of the behaviour of chromium and nickel. Thus at high temperatures silicon, molybdenum, titanium and niobium behave like chromium and are ferrite formers, while carbon, nitrogen and manganese stabilise austenite, like nickel. The final structure of a commercial steel depends sensitively on the balance

Figure 3.6

The Schaeffler diagram.
(Schaeffler, 24).

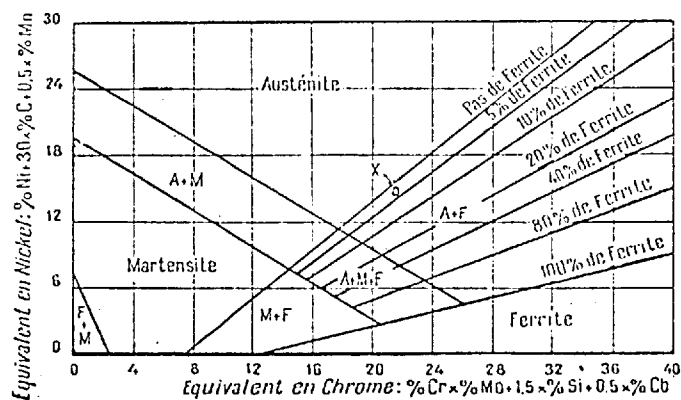


Figure 3.7

The structure of
18/10 steels at
1150°C.
(Pryce & Andrews, 25).

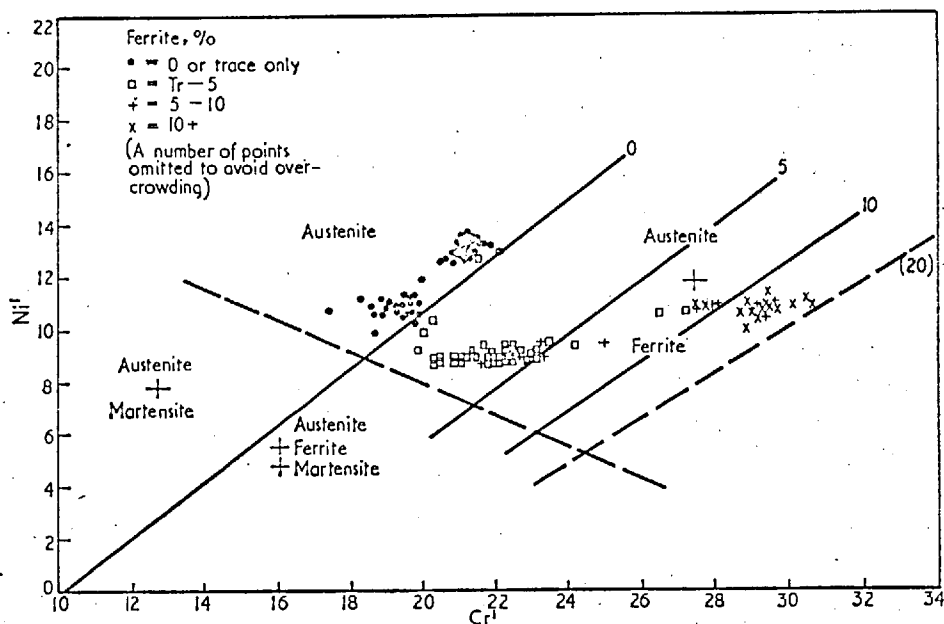
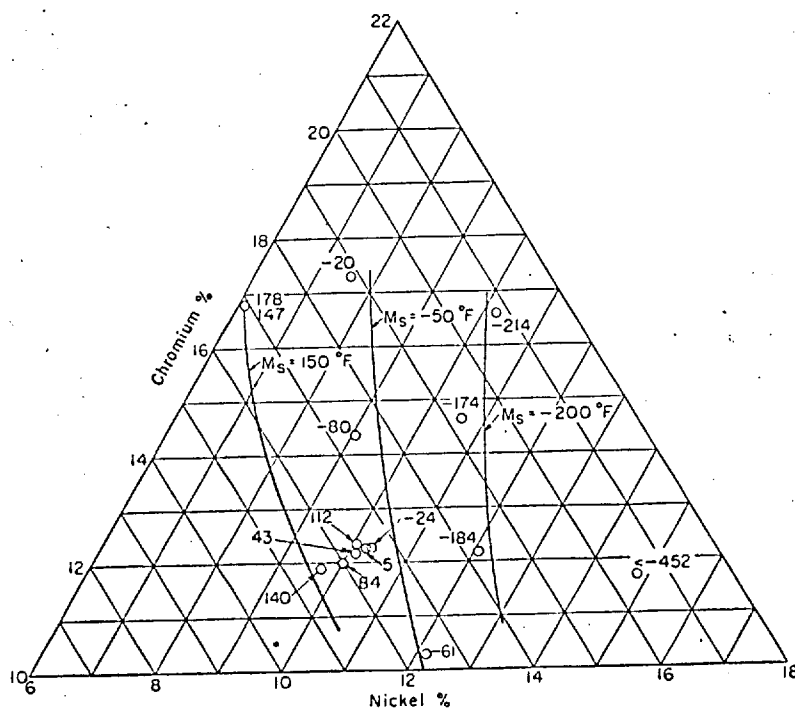


Figure 3.8

The M_s as a function
of composition.
(Eichelmann & Hull, 27).



Corrected to a Nominal Composition of 1.33% Mn, 0.47% Si, 0.068% C+N and Balance Fe.

between the ferrite formers and the austenite stabilisers.

Numerical relationships between the two have been derived for special cases of importance. An early approach, due to Schaeffler (24) is illustrated in figure 3.6 and predicts the structure of welded material after cooling to room temperature. The empirically determined equivalents are:

$$\text{Cr equivalent} = \text{Cr} + \text{Mo} + 1.5 \text{ Si} + 0.5 \text{ Nb} \quad 3.1a$$

$$\text{Ni equivalent} = \text{Ni} + 30 \text{ C} + 30 \text{ N} + 0.5 \text{ Mn} \quad 3.1b$$

A similar approach, shown in figure 3.7, is due to Pryce and Andrews (25) and is aimed at predicting the structure of stainless steels during hot rolling at 1150°C , when it is desirable to avoid δ -ferrite. Under these conditions Pryce and Andrews propose the following equivalents:

$$\text{Cr equivalent} = \text{Cr} + 3 \text{ Si} + \text{Mo} \quad 3.2a$$

$$\text{Ni equivalent} = \text{Ni} + 0.5 \text{ Mn} + 21 \text{ C} + 11.5 \text{ N} \quad 3.2b$$

The significant variation between the two sets of coefficients for C, N and Si (equations 3.1 and 3.2) means that considerable care must be taken to select the correct equivalents for a given set of experimental conditions. It is interesting to note that a typical 18/10 steel containing 0.08 C, 1 Si and 1 Mn would contain $\sim 5\%$ δ -ferrite if welded and cooled to R.T. but would be wholly austenitic at 1150°C . Since it is often desirable to have a small quantity of δ -ferrite in austenitic welds in order to prevent hot-cracking, this particular steel could have desirable properties in both situations. Further refinements of these equations have since been proposed, to deal with the free carbon and nitrogen content in niobium and titanium stabilised steels (25, 26).

3.14c The M_s temperature

While a considerable number of individual M_s determinations have been made in the structural work already cited (Section 3.13) only two attempts have been made to predict the compositional dependence

of M_s in the austenitic stainless steels. Eichelmann and Hull (27) make a clear distinction between the high and low temperature effects of chromium and silicon. While these solutes behave as ferrite formers at high temperatures, at low temperatures it is found that they both depress the M_s temperature, as do manganese, nickel, carbon and nitrogen. Using 25 different heats they analysed the effect of carbon, nitrogen, nickel, chromium, manganese and silicon on the M_s temperature and obtained the following equation for the M_s (which for convenience has been transformed from $^{\circ}\text{F}$ to $^{\circ}\text{K}$)

$$M_s (^{\circ}\text{K}) = 41.7 (14.6 - \text{Cr}) + 61.1 (8.9 - \text{Ni}) + 33.3 (1.33 - \text{Mn}) \\ + 27.8 (0.47 - \text{Si}) + 1667 (0.068 - (\text{C} + \text{N})) + 255 \quad 3.3$$

Equation 3.3 is valid over the composition range 10 - 18 wt % Cr, 6 - 12 wt % Ni, 0.6 - 5 wt % Mn, 0.3 - 2.6 wt % Si, 0.004 - 0.12 wt % C and 0.01 - 0.06 wt % N and showed an average deviation of 21°C between the measured and calculated values. Figure 3.8 shows their results plotted on a ternary diagram and reduced to a standard base composition, from which the corrections of equation 3.3 were derived. An important feature of equation 3.3 is the coefficient outside each bracketed term, which represents the relative effectiveness of each element in depressing the M_s in $^{\circ}\text{C}/\text{wt per cent}$. Equation 3.3, like 3.1 and 3.2, shows the pronounced stabilising effect of C and N.

The detailed validity of equation 3.3 has been challenged by Monkman, Cuff and Grant (29) who measured the M_s of 49 different alloys low in manganese and silicon, over the range 12 - 18 Cr, 5 - 12 Ni and 0.035 - 0.176 C + N. They found an average deviation of 37°C when comparing their measured M_s with those predicted by a least squares analysis of their data using equation 3.3. This deviation is approximately twice that reported by Eichelmann and Hull(27) and was attributed to a highly non-linear variation of M_s with carbon and nitrogen, whereas equation 3.3 depends implicitly on a linear relation between M_s and composition. They did, however confirm the assumption of linearity in the separate effects of nickel and chromium. They concluded that further improvement of such first

degree formulae was unlikely, because the exact behaviour of carbon and nitrogen in the presence of other alloying elements was still a relatively unknown factor.

A particular point of the above criticism of Eichelmann and Hull's equation concerns the carbon coefficient which, with nitrogen, is approximately 30 times stronger than any other element in depressing the M_s . Thus although Eichelmann and Hull measured the effect of carbide precipitation on the M_s in a few alloys, they made no provision for considering the different effects of carbon in solid solution and as precipitated carbide over the wide range of carbon content considered (0.004 - 0.12). There appears to be some disagreement as to the exact amount of carbon in solution in 18/8 steels, with Pryce and Andrews (25) giving approximately 0.03 % at 1150°C whereas Rosenberg and Irish (30) put it at approximately 0.06 % at 1100°C, and it will be subject to further modification in the presence of strong carbide formers such as niobium and titanium. Whatever the exact figure, it is clear that a large difference in behaviour is to be expected between the two and it is not allowed for in equation 3.3.

Nevertheless, Fiedler et al (15) and Angel (28) claim good agreement between measured M_s temperatures in their 18/8 steels and those calculated from equation 3.3 and it may be that over the range of carbon compositions typical in the 18/8 - 18/10 steels (0.08% max.) sufficient is retained in solution after a fully softening treatment that Eichelmann and Hull's equation is still capable of giving useful results. The introduction of the hi-proof grades of stainless steel with up to 0.20% N in solution shows that nitride precipitation is not likely to be a problem for the nitrogen contents picked up in air-melting the normal 18/8 - 18/10 steels.

3.15 The use of austenitic stainless steels at cryogenic temperatures

Austenitic stainless steels are widely used as structural components at temperatures down to 0°K because they combine high strength with good toughness and do not show a ductile/brittle transition. Further, their welding and forming properties are good

and they may be extensively cold worked at room temperature without serious increases in notch brittleness at cryogenic temperatures. They are also rustless, which is an important advantage in components which must be cycled from sub-zero to room temperature, with consequent condensation of water vapour.

Combined with these excellent mechanical properties are some very useful physical properties. The steels have low thermal conductivities which makes them extremely useful as thermal insulators. Their residual electrical resistance is high (approximately $60\mu\Omega$ cm at 4°K), thus reducing eddy current losses in field changing situations. In addition, since austenite is not ferromagnetic the steels are desirable in many situations where magnetic measurements are made.

Finally, the 18/10 type steels are available in a wide variety of forms such as sheet, bar, plate, tube, etc., so that small scale users are able to build cryostats, transport dewars, support systems and other items from stock material.

3.15a Mechanical properties

The low temperature mechanical properties of the AISI 300 steels have been studied mainly at 77° and 20°K . Data up until 1960 have been summarised in two handbooks (32, 33) and much recent work appears in the conference reports, published in Advances in Cryogenic Engineering (34 - 43).

A typical 18/10 steel such as 304L has a yield stress (Y.S.) of $\sim 80,000$ p.s.i. (55 kg/mm^2) and an ultimate tensile strength (U.T.S.) of $\sim 240,000$ p.s.i. (170 kg/mm^2) at 4.2°K (43). These represent increases of $\sim 30\%$ and 140% respectively over the room temperature values for this steel. Elongation at 4.2°K declines somewhat compared to R.T. Values, but 30 - 40% can still be achieved. Impact properties of ~ 60 ft. lbs, with a Charpy V notch, are typical of the excellent toughness retained by these materials at 4.2°K .

Since, however, all the 18/10 steels are known to undergo a stress induced transformation, and some a spontaneous transformation of variable extent at low temperatures, these properties may be

subject to some modification for different grades and casts. Guntner and Reed (43) have investigated the properties of 304 and 304L steels which underwent a spontaneous martensitic transformation on cooling and concluded that the formation of 11% martensite in 304 and 7.5% in 304L caused no significant loss of toughness. Thus, apart perhaps from the low alloy grades 301, 302 and 303 (Table 3.1), the spontaneous martensitic transformation on cooling is not likely to lead to significant changes in the mechanical properties of the 18/10 steels.

Weil and his co-workers (36, 37, 40, 41) have investigated the creep and fatigue properties of 18/10 steels at 77°K and 20°K and confirm that considerably less martensite forms in the high nitrogen steels.

Of the higher alloy steels only type 310 has been studied in any detail. This steel has a Y.S. of 95,000 p.s.i. a U.T.S. of ~180,000 p.s.i., an elongation of 70% and a Charpy V notch of ~45 ft lbs at 4.2°K and is thus only slightly inferior to type 304 in strength. It has been found impossible to produce martensite in type 310 even after tensile deformation to destruction at 20° and 4.2°K (42, 48).

3.15b Magnetic properties

A paramagnetic/antiferromagnetic transition has been reported by several workers (43 - 47) for some austenitic stainless steels at low temperatures. Thus Kondorsky and Sedov (45) found a Néel temperature (T_N) of 40°K for an 18 Cr/9 Ni alloy and a susceptibility of 6×10^{-4} at 10°K. Meiklejohn (46) has reported the same value of T_N for a type 347 alloy, while Gonser et al (47) obtained $T_N = 38°K$ for a type 304 steel. Mikesell and Reed (43) found Néel temperatures of 40°K for types 302 and 303 and Kohlhaas et al (44) report a value of 38°K for a 17/13 commercial material. The Néel temperature is not therefore particularly sensitive to small changes in chemical composition around the 18/10 mark. Kohlhaas et al do find however that the Néel temperature drops as they go through the sequence 17/13 (38°K), 16/14 (21.5°K), 16/16 (18°K), 17/18 (13°K), finally finding that a 23 Cr,

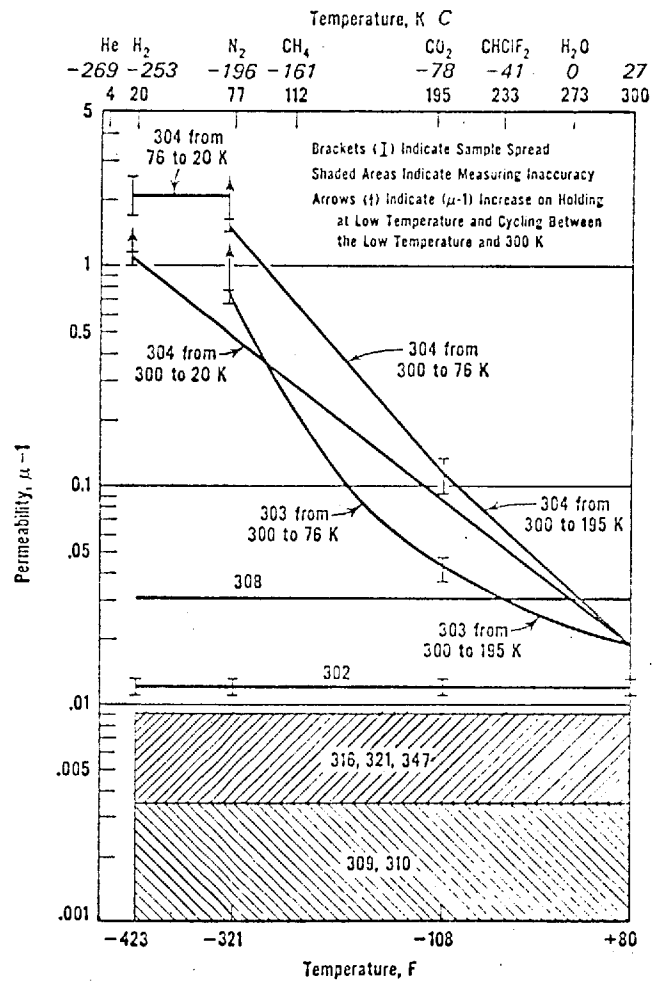


Figure 3.9

The permeability of the AISI 300 stainless steels after cryogenic cycling. (Reed and Mikesell, 18).

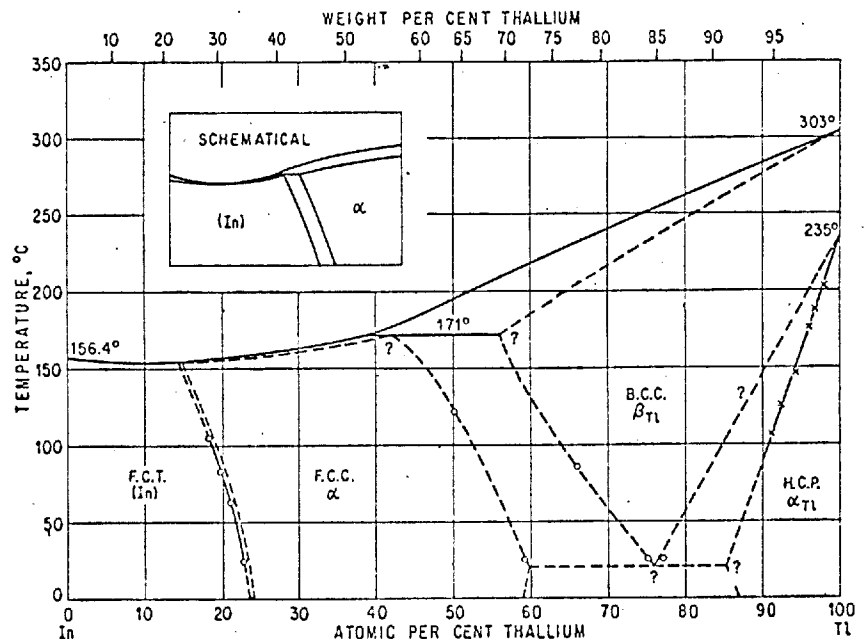


Figure 3.10

The In/Tl equilibrium diagram. (Hansen, 1).

22 Ni, 2.5 Si alloy is still paramagnetic at 4.2°K . All the susceptibilities measured fall in the range $6 - 22 \times 10^{-4}$ and are thus unimportant except for the most precise magnetic work.

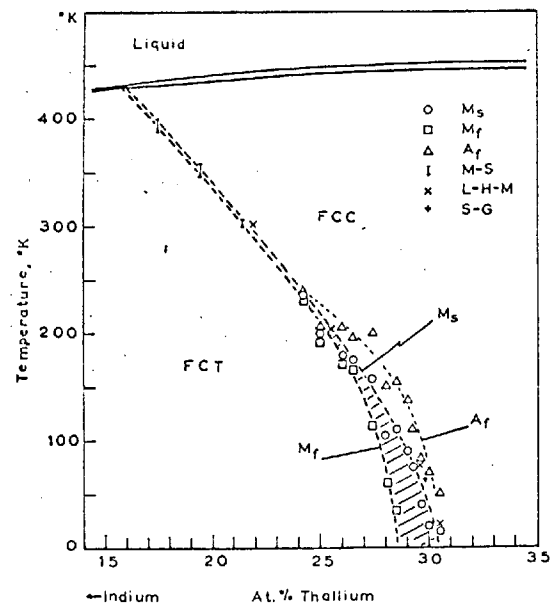
For nearly all practical purposes, however, the magnetic properties of these steels are associated with the ferromagnetic martensite α' . For convenience the progress of the transformation to α' is thus often studied by magnetic methods, but in spite of the large number of such investigations only one systematic study of the spontaneous magnetisation of the AISI 300 steels at low temperatures has been reported. Reed and Mikesell (18) studied the permeabilities of a wide range of AISI 300 steels after extensive cooling and warming cycles between 77°K , 20°K and room temperature. The steels studied were types 302, 303, 304, 308, 309, 310, 316, 321 and 347. On the basis of measurements made with a Magnegauge at room temperature they found that only types 303 and 304 showed an increased permeability after cryogenic treatments. This was attributed to the presence of α' martensite and confirmed by metallographic examination. Figure 3.9 shows their results presented graphically.

Their cycling experiments showed that cycling to and from 77°K produced a larger permeability than cycling to and from 20°K , which they associate with a greater rate of isothermal transformation to martensite at 77° than 20°K . It was also found that samples cycled 5 times a day had a greater total transformation than those cycled once, and that transformation was still occurring in type 304 steels after over six months of such treatments.

The results shown in figure 3.9 are ambiguous, however, in that the permeability figures are stated for an unknown field value. The Magnegauge uses a torsion balance to measure the force needed to detach the specimen from a standard bar magnet, the field of which was unstated. It is most unlikely that the specimens were saturated (as the present experiments have indicated that a field of greater than 10 kOe is needed to saturate stainless steels at room temperature) and thus the figures given have only a very limited design significance.

Figure 3.11

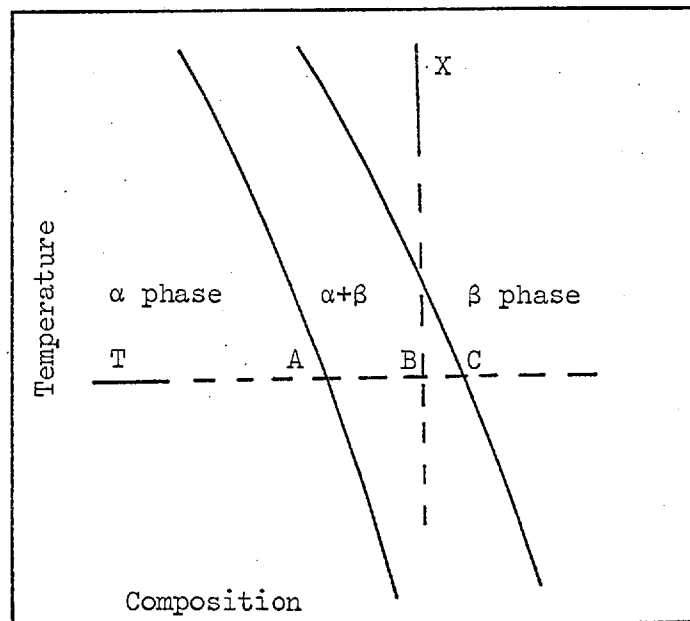
The In/Tl realisation diagram.
(Pollock and King,50).



Realisation diagram of the fct to fcc phase transformation in In/Tl alloys. M_s = temperature of transformation on cooling; M_f = temperature of completion of transformation on cooling; A_f = completion of transformation in the reverse direction on heating; M-S [19];

Figure 3.12

The Lever Rule



Further, although tests were made at 77°K with type 304 to check that the formation of martensite was irreversible on warming to room temperature, all further tests were then carried out at room temperature so that no reversible magnetic effects would have been observed using the Magnegauge. Nevertheless, figure 3.9 is quoted in the commercial handbook "Mechanical and Physical properties of the Austenitic Chromium - Nickel Stainless Steels at Sub-zero Temperatures", published by the International Nickel Company Ltd.(42) and thus at the start of the present work no particular problems with the use of type 321 (EN58B) stainless steel in the vicinity of a cryogenic magnetometer system was envisaged, either by us or the manufacturers of our solenoid system.

3.2 Indium alloys

3.21 The metallography

3.21a Indium thallium

The equilibrium diagram proposed by Hansen (1) for the indium-thallium system is shown in figure 3.10. Pure indium has a body-centred tetragonal structure (b.c.t.) with a c/a ratio of 1.52 but is more generally represented as face-centred tetragonal (f.c.t.) with an axial ratio of 1.08. An f.c.c. intermediate solid solution is formed at R.T. when the composition exceeds ~ 24 at % Tl. The boundary between the tetragonal and cubic phase slopes towards higher thallium concentrations and thus over the range $\sim 15 - 22$ at % Tl alloys may be f.c.c. at high temperature and f.c.t. on cooling to room temperature. Guttman (49) has shown that on the basis of surface relief effects this cubic/tetragonal transformation can be classed as martensitic. Because of the diffusionless nature of such a change, the progress of the transformation at cryogenic temperatures is of considerable interest and the position of the phase boundaries has been determined down to helium temperatures. The results of Pollock and King (50) who studied the onset of transformation, M_s , its completion, M_f , and the equivalent reverse transformation points A_s and A_f , by light microscopy, are given in figure 3.11. This shows that at 9.5°K , the lowest temperature studied, all alloys with less than 28.75

at % Tl are tetragonal and those with greater than 30.75 at % Tl are cubic. At intermediate compositions the tetragonal and cubic phases co-exist. Their general findings have been confirmed by dilatometry down to 4.2°K (51) and agree with boundaries derived from superconducting transition temperatures (52).

The boundaries shown in figure 3.11 do not however conform to the "Lever Rule" for metallurgical systems and the thermodynamic significance of the transformation has thus been the subject of some speculation. According to the Lever Rule the proportion of the phases α and β present in a two phase mixture of the alloy x (figure 3.12) are given by $\alpha : \beta$ as $BC : AB$, and their compositions should be A (α) and C (β). Since both phases in a martensitic phase transformation have the same composition this rule is clearly inapplicable.

According to the classical thermodynamics of phase transformations, a transformation is assigned an order depending on which derivatives of the Gibbs Free Energy with respect to temperature and pressure are discontinuous at the transformation point (53). The first order derivatives are thus

$$\text{Entropy } S = - \left(\frac{\partial G}{\partial T} \right)_P$$

$$\text{Volume } V = \left(\frac{\partial G}{\partial P} \right)_T$$

$$\text{Enthalpy } H = \left(\frac{\partial G/T}{\partial 1/T} \right)_P$$

Experimentally a discontinuous change in volume can be measured directly, while a discontinuity in enthalpy takes the form of a latent heat. During the transformation the two phases will exist in equilibrium at a particular temperature or pressure. Examples of first order transformations are melting, evaporation and allotropy.

Some transformations such as the ferromagnetic/paramagnetic transition and the helium I/helium II transition at the λ point are continuous

with respect to their first order derivatives but possess discontinuities in their second order derivatives, viz:-

$$\begin{aligned} \text{specific heat /temperature} \quad \frac{C_p}{T} &= \left(\frac{\partial S}{\partial T} \right)_P \\ \text{compressibility} \quad \chi &= \left(\frac{\partial V}{\partial P} \right)_T \\ \text{specific heat} \quad C_p &= \left(\frac{\partial H}{\partial T} \right)_P \end{aligned}$$

Thus a second order transformation is conveniently characterised by a discontinuity in the specific heat. In a second order phase change the transformation is nucleated homogeneously throughout the material and the transformation takes place uniformly throughout the volume, so that at no time do the initial and final phases co-exist in equilibrium.

Guttman (49) had declared the transformation in indium-thallium to be second order because in none of his alloys could he find evidence for co-existence of the two phases. Later work by Burkart and Read (54), however, showed a change of length at the transformation temperature, from which they derived a latent heat, while Prédél (55) has recently made direct measurements of the latent heat by precision calorimetry. Pollock and King (50) do not however consider that their microscopic evidence of two co-existing phases at cryogenic temperatures confirms the first order nature of the change because the accommodation stresses needed to maintain a coherent interface between parent and product phase effectively introduce the constraint of pressure into the balance of temperature and composition. Further, since a martensitic change is diffusionless, the phases have the same chemical composition and the phase change is thus best considered as if it were a polymorphic change in a one component system with two degrees of freedom, temperature and pressure. The presence of a two phase field may now reflect not the order of the transformation but the temperature range over which the change takes place.

The significance of the pressure effect at temperatures below about half the melting point ($0.5 T_m$) is that this is generally recognised as the temperature below which recovery does not take place. Thus the transformation stresses, which are a result of the coherent interface between the martensite and parent phase, remain unrelieved and cause the reaction to enter a temperature - pressure balance. Evidently these effects are still reasonably small in indium thallium as the transformation hysteresis is around 40°C at low temperatures and the plates still form and disappear in the same order after several thermal cycles (50). As mentioned in section 3.13 the equivalent transformation interval for iron-nickel alloys, with $M_s \sim 0.2 T_m$, is of the order of 200°C and prolonged annealing at low temperatures (600 days at 300°C) is required in order to break down the coherent interface between the martensite and its parent and form two chemically distinct phases (2). It thus seems likely that, except in those cases where a martensite is formed by suppression of a diffusion controlled reaction, the two phase region represents the effects of the transformation stresses. The curves plotted in figure 3 should thus be referred to as "realisation diagrams", following the notation of Hansen(1).

Experimental observations (49, 54, 56, 57) of the transformation at room temperature and above have shown that the martensite forms as bands extending from one grain boundary to another. These bands form on the $\{110\}$ planes of the f.c.c. matrix and are themselves internally twinned on $\{110\}$ planes at 60° to the main bands. During transformation on continuous cooling, growth of individual bands may occur or new bands may form at 60° or 90° to the original bands. On the reverse transformation the bands disappear in the reverse order to which they formed i.e. last in, first out (58). Provided no drastic temperature cycling occurs, the transformation may be repeated exactly, the f.c.c. matrix retaining a memory of the transformation (54). On cooling, the transformation is generally complete after 7° or 8°C , on heating the temperature interval is a little less.

Low temperature observations (50) have shown that at thallium contents higher than 26.5 wt % Tl where the M_s is less than $0.5 T_m$

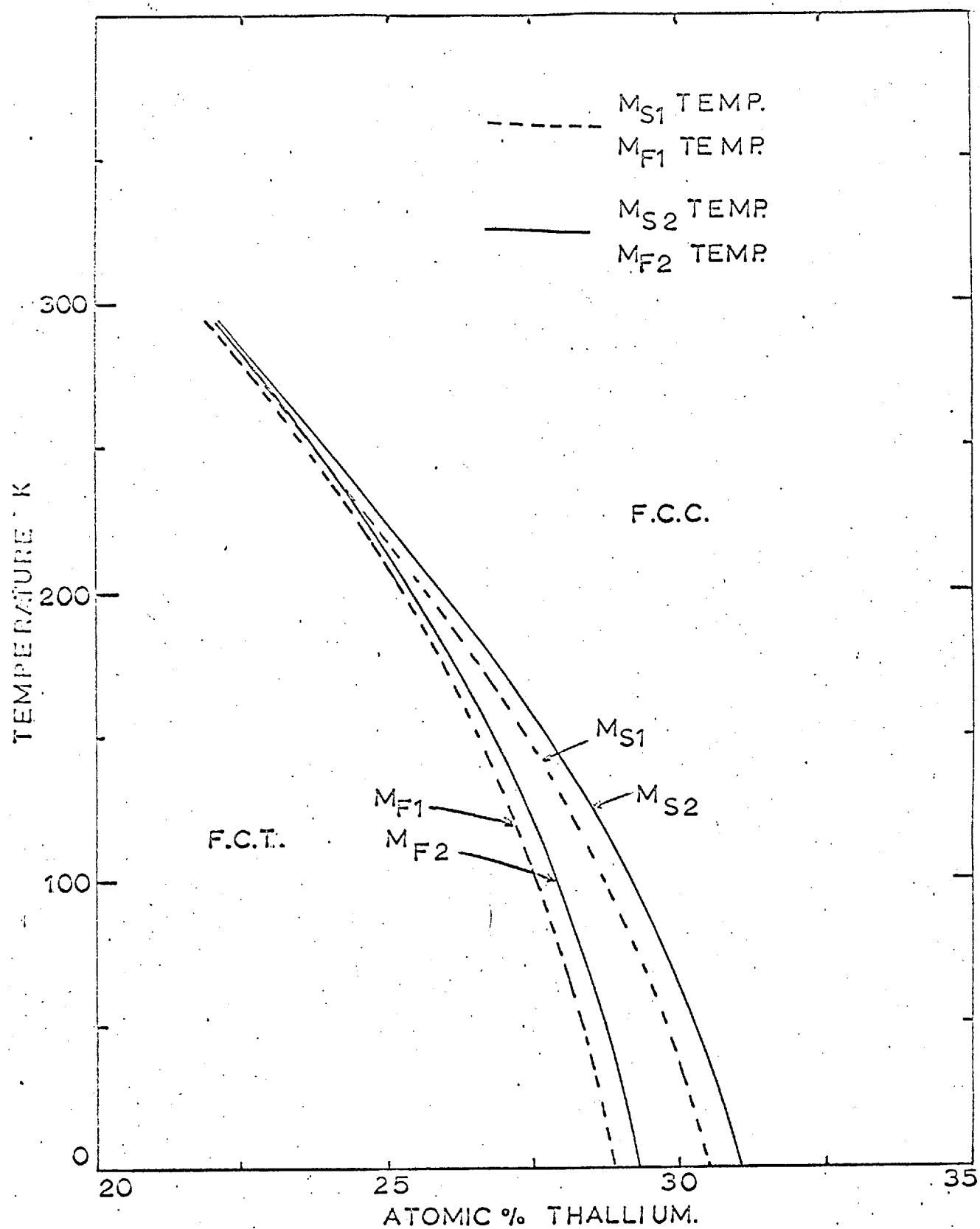
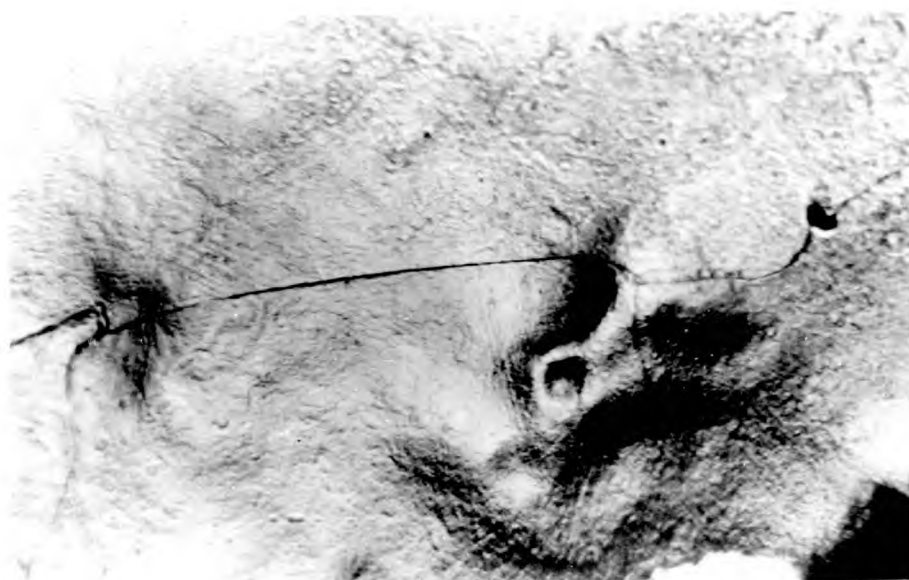
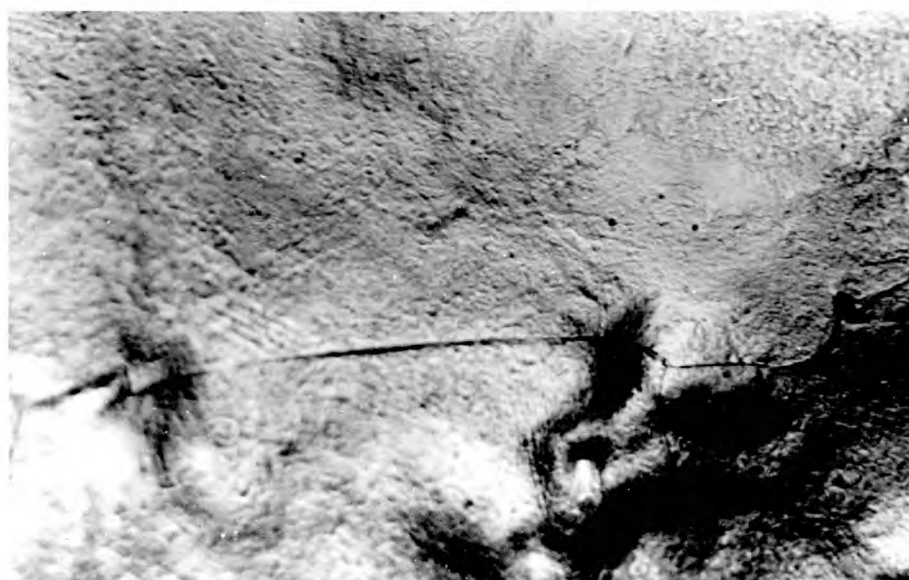


Figure 3.14 The realisation boundaries of the cubic to tetragonal transformation in In/Tl on (1) first cooling and (2) subsequent cooling cycles. (Pollock, 68).

Figure 3.13. Martensitic transformation
cooling an In/29.5 at% Tl alloy.



3.13 (a) x525 40°K

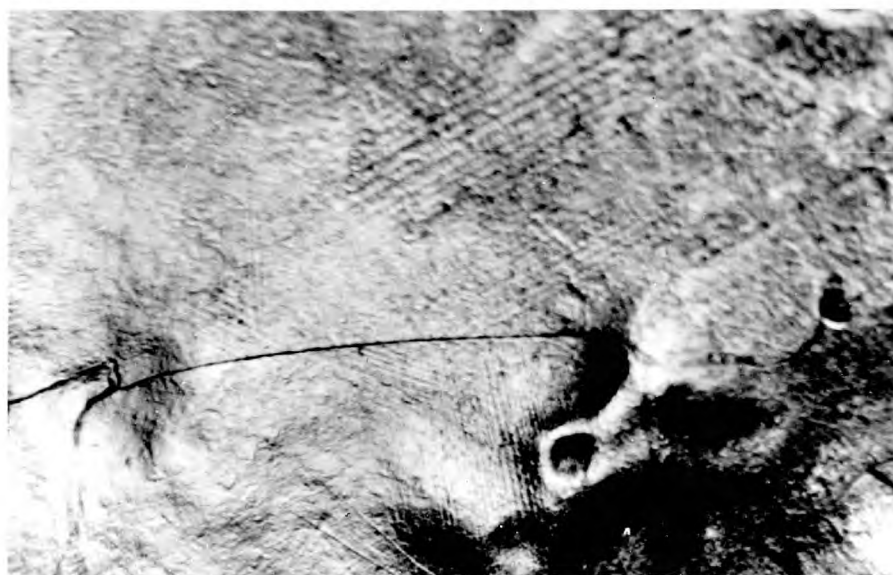


3.13 (b) x525 35°K

Figure 3.13. (continued)



3.13 (c) x525 25°K



3.13 (d) x525 9.5°K

bands do not nucleate right across the grains and the temperature interval over which the transformation extends becomes much broader (figure 3.11). A sequence of such observations for an In/29.5 at % Tl alloy is shown in figure 3.13 and it can be seen that martensite plates are nucleated in several regions of different orientation within each grain. On cooling, further martensite is formed both by growth of these plates and the formation of new ones. It is evident that even on cooling to 9.5°K the transformation is incomplete. The crystallographic relationships and the cyclic reversibility are in all respects unchanged at low temperatures, however. An interesting point concerning these observations is that the second cycle measurements of M_s , M_f etc. occur at temperatures 15° to 20°C higher than the first. Figure 3.14 shows that this is equivalent to a shift in the diagram to higher thallium contents of approximately 0.5 at %. Subsequent cycles repeat the second cycle behaviour.

3.21b Indium-lead and indium-cadmium

Very little metallographic work has been performed on the martensitic phase transformations in indium-lead and indium-cadmium. The equilibrium diagram proposed by Hansen(1) for indium-lead is shown in figure 3.15. The primary solid solution has the f.c.t. structure with $c/a > 1$ ($1.075 \rightarrow 1.087$) while the adjoining intermediate solid solution, α_1 , is also f.c.t. with $c/a < 1$ (~ 0.93). It is the change from α_1 to indium on cooling which is martensitic in nature. Several studies have been made of this system by Raynor and his co-workers (57, 59, 60) but the position of the phase boundaries and the order of the transformation are still open questions. Light microscopy shows that the transformation proceeds by a double shear similar to that in indium-thallium with a $\{111\} \alpha_1$ habit plane. By variation of the thermal and mechanical history of samples, it was found possible to get widely different proportions of the two tetragonal phases to co-exist at room temperature. The realisation phase boundaries shown in figure 3.16 were only found to be well-defined after heavy cold work and this dependence of the boundaries on previous thermal and mechanical treatment indicates the very small free energy difference between the two phases.

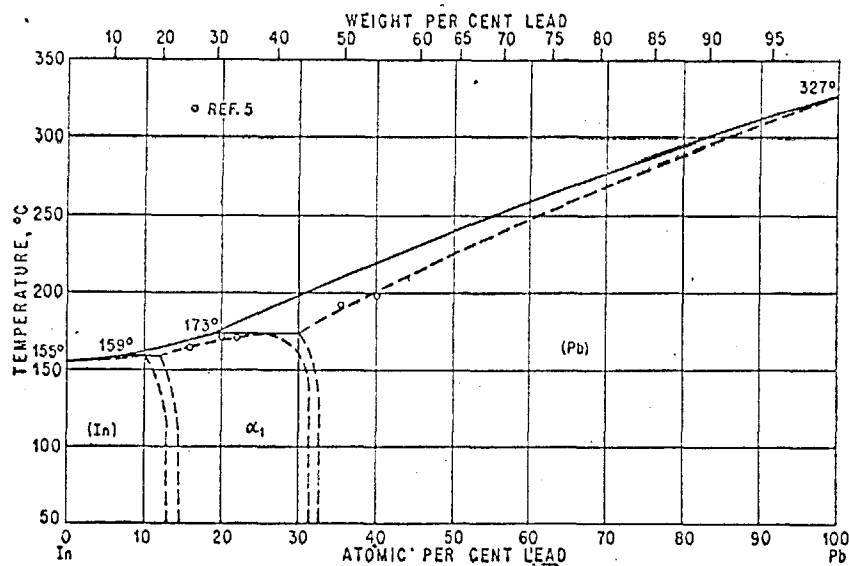


Figure 3.15
The Indium-Lead
equilibrium diagram.
(Hansen, 1).

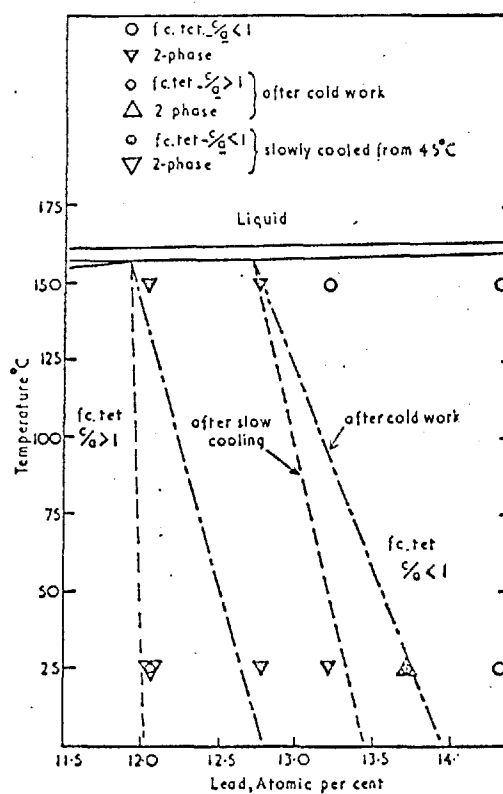


Figure 3.16
The boundaries of the martensitic
phase transformation in In-Pb.
(Raynor and Graham, 60).

Figure 3.17

The Indium-Cadmium equilibrium diagram, according to Heumann and Predel (61).

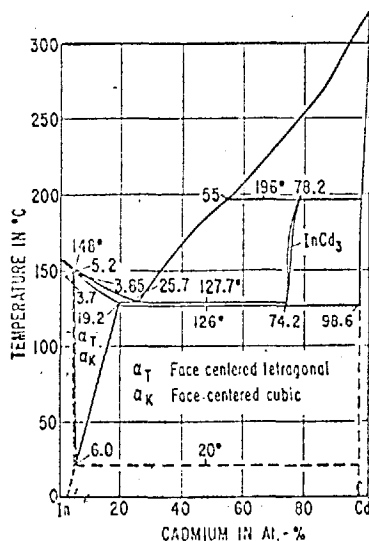


Figure 3.18

Details of the cubic to tetragonal transformation from above.

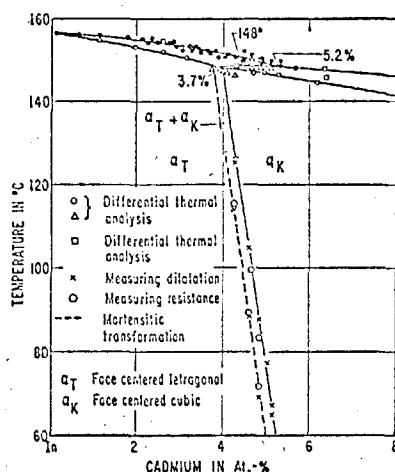
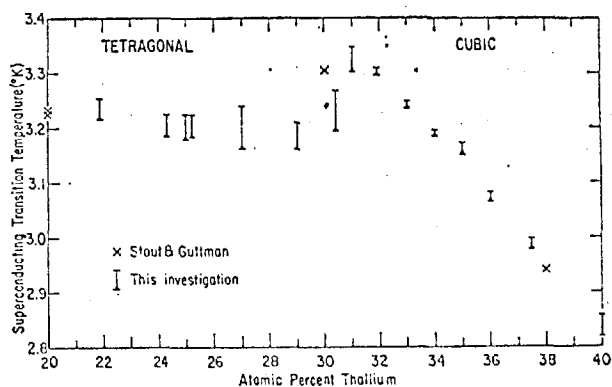


Figure 3.19

Transition temperatures in indium-thallium, according to Luo et al. (65).



Superconducting transition temperature as a function of composition for some In-Tl alloys in the neighborhood of the tetragonal-cubic transformation. The spreads indicate total transition widths, rather than experimental errors.

The phase diagram determined by Heumann and Predel (61) for indium-cadmium in the vicinity of the martensitic transformation is shown in figure 3.17. The change is here cubic to tetragonal on cooling and the two phase region is extremely narrow. At 20°C and 6 at % Cd (figure 3.18) the indium solid solution begins to precipitate a cadmium-rich solid solution by a normal diffusion and growth reaction. Little information has been given about the metallography of the martensite and no studies have been made at low temperatures. In other work (55) Predel has measured a latent heat for the martensitic transformation on cooling an In/4.75 at % Cd alloy, indicating a first order change. The reverse transformation he believes, however, to occur with the help of diffusion.

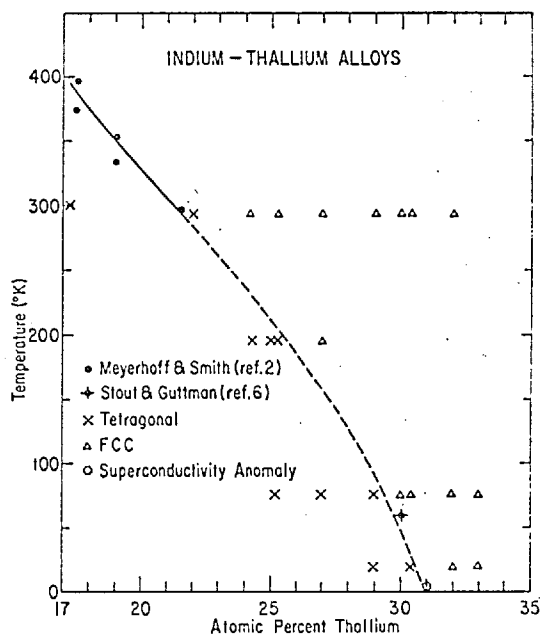
3.22 Superconducting properties

A number of investigations of the low temperature properties of indium alloys have been made. As with the metallography, the majority of these refer to the indium-thallium system which is nominally isoelectronic since both elements come from the same subgroup of the Periodic Table. The metallographic investigation of indium-thallium which led to the discovery of the martensite (49) was conducted in parallel with an investigation of the superconducting behaviour of some single and polycrystalline alloys over the range 0 - 50 at % Tl (62). These measurements showed that there was a general drop in the superconducting transition temperature (T_c) as the %Tl increased but that in the region of In/30 at % Tl the T_c rose to a peak before falling off again in the cubic phase. Resistive measurements (63) as a function of temperature on a polycrystal of 30 at % Tl showed an anomaly at approximately 62°K which was associated with the M_s . The rise in T_c was then interpreted in terms of the phase structure at low temperatures, so that alloys with up to and including 30 at % Tl were tetragonal and a 38 at % Tl alloy was cubic.

This peak in T_c was studied further by Merriam et al (64,65) with a greater number of alloys and with the aid of X-ray diffraction down to 20°K for structure identification. These results

Figure 3.20

The cubic-tetragonal boundary
in In/Tl according to Luo et al.(65)



Temperature dependence of the tetragonal-cubic transformation in In-Tl, to 3°K. The phase boundary is shown as a single line in the figure: this should not be regarded as an implication that no two phase region exists.

Figure 3.21

Transition temperatures in In/Cd
according to Merriam (69).

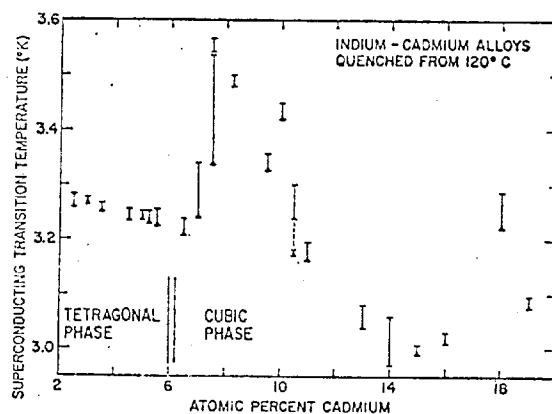
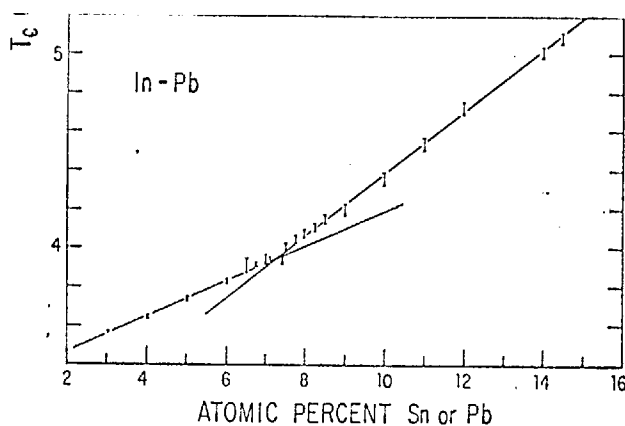


Figure 3.22

Transition temperatures in In/Pb
according to Merriam (71).



Superconducting transition temperature vs composition for solutions of Pb and Sn in In. The spreads shown are total transition widths, and do not indicate experimental error.

(figure 3.19) showed that if a smooth line was drawn from the room temperature position of the cubic/tetragonal boundary (49) through the low temperature points obtained from X-ray diffraction, the composition intercept at 3°K coincides with the peak in T_c at 31 at. % Tl (figure 3.20). While the cubic phase evidently has a higher T_c than the tetragonal phase the shape of the T_c peak was explained in terms of the strains set up by the martensitic transformation. Earlier work (66, 67) had shown that strains internally produced in In/Hg and In/Sn alloys by a fast quench rate led to a rise in T_c . Thus it was postulated that alloys between 29 and 31 at. % Tl with very broad transitions were severely strained and that the cubic/two phase boundary lay at 31 at. % Tl where broad transitions gave way to narrow ones belonging to single phase and unstrained cubic alloys. The confirmatory metallographic evidence for the two phase region at cryogenic temperatures has already been described (50) (Section 3.21a) and T_c measurements (68) on the same alloys used for metallography, indicate that the broad transitions between 29 and 31 at. % Tl are in the two phase cubic-tetragonal region.

Measurements in the indium-cadmium system are complicated by the precipitation of cadmium-rich solid solution at 6 at. % Cd (figure 3.17). By quenching specimens from 120°C Merriam (69) was able to inhibit precipitation, and obtain values of T_c which he considered characteristic of the cubic phase. No features were seen however which could be attributed to a cubic/tetragonal two phase region. His results (figure 3.21) show that T_c declines as the cadmium content increases but that there is a similar increase to that in In-Tl on passing to the cubic phase.

Much less comprehensive investigations have been made of the superconducting properties of indium-lead alloys. Meissner et al (70) made measurements on five alloys spaced throughout the system but none bear directly on the region of the phase transformation while the later measurements of Merriam (71) cover only the range of composition from pure indium to In/14.75 at. % Pb (figure 3.22). The kink observed at approximately 7 at. % Pb is paralleled by a similar kink in a lattice parameter plot and is believed to originate

in a Brillouin zone overlap. Similar effects have been found at In/2 at % Cd (69), In/4.4 at % Tl (64) and in the In/Sn system (71). Beyond this kink the variation of T_c is quite linear up to the highest composition studied. Recent magnetisation measurements up to 12 at % Pb confirm these T_c findings (72)

The magnetic and current carrying properties of superconductors are particularly susceptible to internal stress fields (73) and thus in alloys containing martensitic interfaces enhanced flux pinning may be expected. Stout and Guttman (62), however, did not investigate the flux trapping properties of their single and polycrystals as they were more interested in the form of flux penetration into their samples as a function of alloying addition. This work preceded Abrikosov's (74) paper on the nature of type II superconductivity and consequently the beginning of type II behaviour was not recognised as such. From the form of their magnetisation curves it can be seen to lie between 5 and 10 at % Tl. In the experiments of Love et al (75) at a similar time (1952) the same aim was paramount and it is interesting to note one of the reasons put forward to explain gradual flux penetration at thallium contents >5 at % Tl in what we now know to be type II superconductors. It was suggested that at absolute zero a solid solution should either separate out into its separate constituents or become an ordered structure. The gradual flux penetration observed in these alloys might then be attributed to the microscopic strains involved in either of these processes. They did however note that the remanent induction reached a maximum in their 15 and 20 at % Tl alloys, rather than their 5, 10, 28.5 and 37 at % Tl materials and this was attributed to the presence of martensitic interfaces within these specimens.

In more recent experiments, van Gurp (76) has demonstrated the flux pinning properties of an In/20 at % Tl single crystal rather elegantly by measuring the critical current as a function of the alloy's orientation in a magnetic field. The crystal was grown with a $[111]$ orientation and contained parallel bands of martensite $\sim 20\mu$ apart, themselves internally twinned with fine twins 0.5 - 3μ wide at 60° to the main bands. The curve of J_c versus θ (figure 3.23)

Figure 3.23

The critical current of a fully martensitic In/20 Tl [111] single crystal as a function of orientation in a magnetic field.

(van Gurp,76).

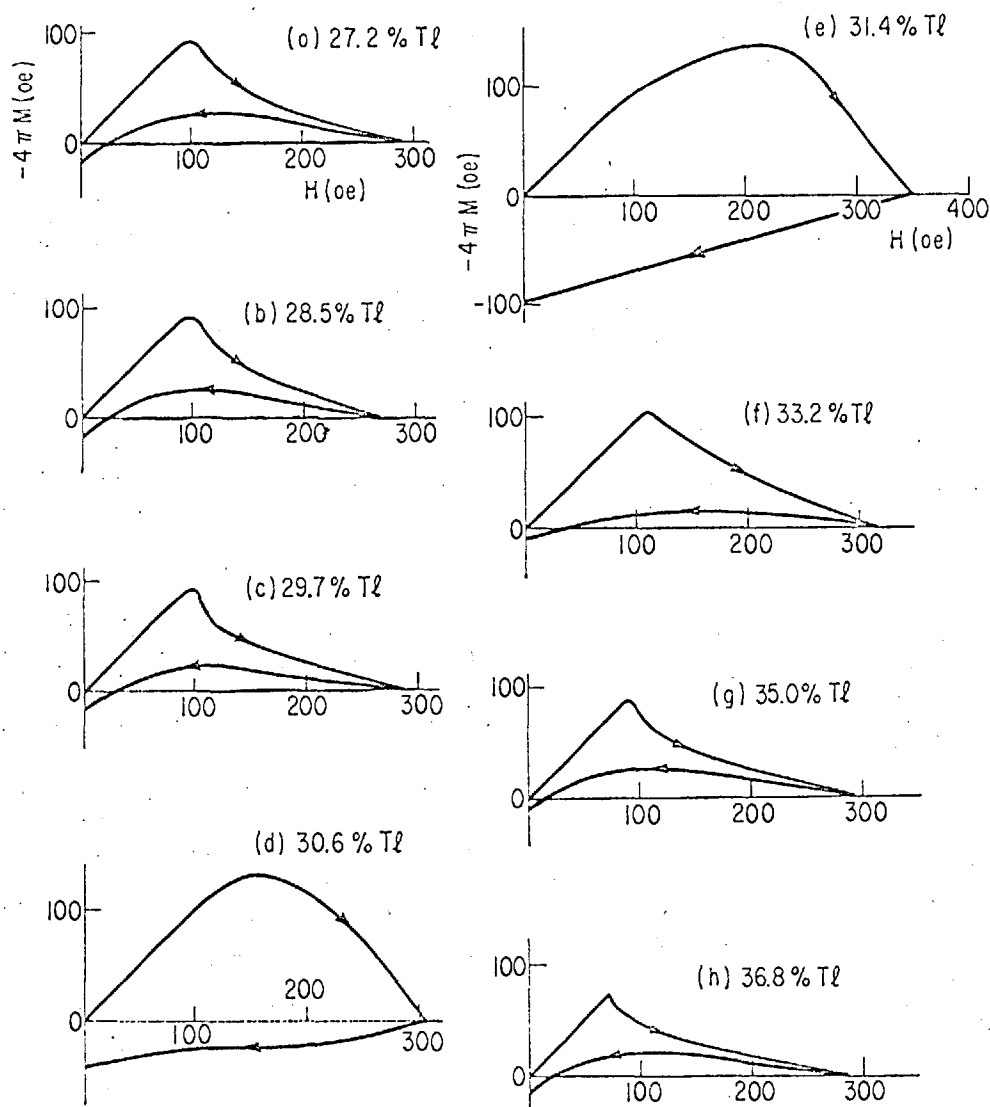
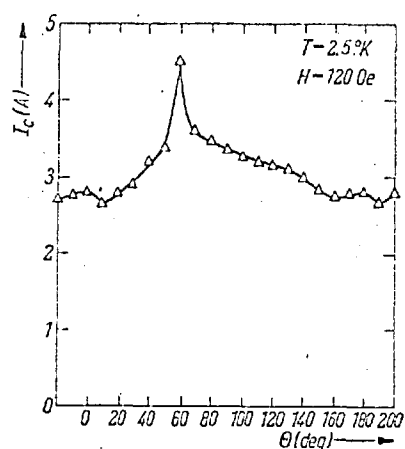


Figure 3.24 Magnetisation curves of In/Tl alloys at 2.2°K. (Livingston,77).

shows a pronounced peak at 60° when the fluxoids are parallel to the fine twins and thus pinned along their whole length. A smaller peak is observed at 0° when fluxoids are parallel to the main bands.

Consideration of the total strain energy (50, 64, 77) within a martensitic crystal suggests however that whereas in a fully martensitic crystal stress fields are associated with the coherent interfaces between both the main bands and the sub-bands, a partially transformed crystal will also have a stress field resulting from the coherent interface between the two different structures. This analysis is suggested not only by the study of the transition breadths shown in figure 3.19 but even more strongly by the magnetisation measurements of Livingston (77) (figure 3.24). These curves show a pronounced hysteretic form at 30.6 and 31.4 at % Tl and much more reversible behaviour at compositions on either side of this. A visual inspection of these curves suggests in fact that a fully martensitic alloy traps no more flux than a cubic one (cf. 29.7 at % Tl vs 35.0 at % Tl). This conclusion is an interesting one when compared to the results of van Gorp (76) and Love et al (75), described above.

This striking correlation between an increased hysteresis and the two phase region prompts a similar study in indium-lead and indium-cadmium. In indium-lead the previous work of Raynor et al (57, 59, 60) (section 3.21b) showed that at room temperature varying proportions of the two tetragonal phases could be obtained, depending on the previous thermal and mechanical treatments. Thus the free energy difference between the phases must be quite small and it might therefore be expected that the internal stress field resulting from a partial transformation will be rather less than in indium-thallium. This provides an additional reason for interest in magnetisation measurements in this two phase region.

In indium-cadmium, the possibility of cadmium precipitation and the narrowness of the two phase region (approximately 1 at %) may make unambiguous magnetisation measurements difficult. Because

of the fast quenching rate needed to suppress precipitation, low temperature metallography of the martensitic phase transformation will not be possible. However, a comparative study of the different effects of martensite pinning and second phase pinning may be possible. Magnetisation measurements will also enable the point of changeover from type I behaviour to type II to be determined, as this has not been established with certainty. Chiou et al (78) place it at In/3.5 at % Cd $\pm$ 0.5 % but Merriam (69) claims that an In/4.5 at % Cd alloy was still type I at 2°K. A further point of interest is that measurements on the lead-bismuth system have indicated that flux pinning reaches a peak in the region of changeover from type I to type II behaviour and that this is related only to the κ value and not to any new microstructural defect array (79).

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CHAPTER 4

EXPERIMENTAL APPARATUS AND TECHNIQUES

TABLE 4.1 Source of stainless steels

Manufacturers Specification	Equivalent AISI No.	Shorthand description
<u>Firth Vickers Stainless Steels Ltd.</u>		
Staybrite F.D.P.	321	18/10/Ti
" F.S.L. (L)	304L	18/10 low C
" F.C.B.	347	18/10/Nb
F.V. Inmac 5	310	25/20
F.V. 309	309	22/14
F.V. Inmac 2 W	-	20/7/2 W
<u>Samuel Fox & Co. Ltd.</u>		
Hi proof 304	304	18/10 with high N
" 316L	316L	16/12/3 Mo high N and low C
<u>International Nickel Ltd.</u>		
Incoloy 800	-	20/32

4.1 Preparation and composition of alloys

4.1.1 Stainless steels

All the stainless steels examined in the present work were commercial materials and were received in a variety of forms from the sources listed in Table 4.1. They were turned down to rods of diameter between 3.94 and 4.20 mm, each sample being slightly different in diameter, to allow easy identification. Magnetisation specimens 30 mm long were cut from these rods and small specimens about 4 mm long from adjacent positions were used for metallographic examination. The latter were sealed in the same silica capsule as the magnetisation specimens during subsequent heat-treatments.

Cast analyses were supplied with all but one of the steels, but it was uncertain how representative they were of the actual specimens used. Further, since preliminary experiments showed that the magnetisations at 4.2°K were in direct disagreement with previous work (1), the possibility that some samples were wrongly labelled could not be dismissed. All steels were therefore analysed chemically by the Analytical Services Laboratory of this department. These results confirmed that no substitution had taken place and are discussed in detail in Chapter 6.

4.1.2 Indium alloys

Indium alloys were melted from 5N Specpure indium and cadmium supplied by Johnson Matthey Chemicals Ltd., 5N thallium supplied by Koch Light Laboratories Ltd. and 6N lead from the Consolidated Mining & Smelting Company of Canada. Special precautions were taken with the indium-thallium alloys because of the toxic nature and easy oxidation of thallium. To reduce the handling of thallium metal to a minimum an In/52 wt% Tl master alloy was prepared by melting predetermined weights of the pure metals in an evacuated pyrex capsule at approximately 250°C. The alloy was kept molten for half an hour with intermittent shaking to ensure a good mixing and then quenched into an ice-water bath. The alloy was then homogenised in

the same capsule for two weeks at 145°C and extruded to rod. Preweighed amounts of the master alloy were then melted with pure indium to give a series of indium-thallium alloys between In/26 Tl and In/33 Tl. The melting and homogenising procedure followed that discussed above for the master alloy. Finally, the alloys were extruded to 4 mm diameter rods from which magnetisation specimens 30 mm long were cut. Hemispherical ends were turned on these specimens to reduce their demagnetisation factor and the specimens were strain-relieved by a two day anneal at 145°C before measurement.

A series of indium-based alloys containing 11 to 17.5 at % Pb and 2.1 to 7 at % Cd were obtained from Mr. C.J. Gillham of this department. These alloys had been cast in pyrex capsules from predetermined weights of the pure metals, there being no special problems associated with them. The melting procedure was similar to that for indium-thallium and the alloys were homogenised for seven weeks at 135°C. Extrusion to 4 mm diameter and specimen preparation was as described above for the indium-thallium alloys. The indium-cadmium alloys were however, kept at 120°C until immediately prior to measurement, when they were quenched into liquid nitrogen in an attempt to prevent precipitation of the cadmium-rich solid solution phase (2).

Since widely different compositions had been reported by the Analytical Services laboratory for the same indium-thallium alloys (3), a full chemical analysis of the indium-based alloys was not attempted. It is interesting to note that Livingston (4) has also reported unreliable analyses for these alloys. All ingots were weighed after homogenising and those with weight differences of more than 0.1% were rejected. The nominal compositions were therefore accepted to ± 0.25 at % for the In-Cd and In-Pb alloys and to ± 0.5 at % for the In-Tl alloys made from the master alloy.

4.13 Metallographic examination

The micro-structure of the stainless steels and the indium alloys

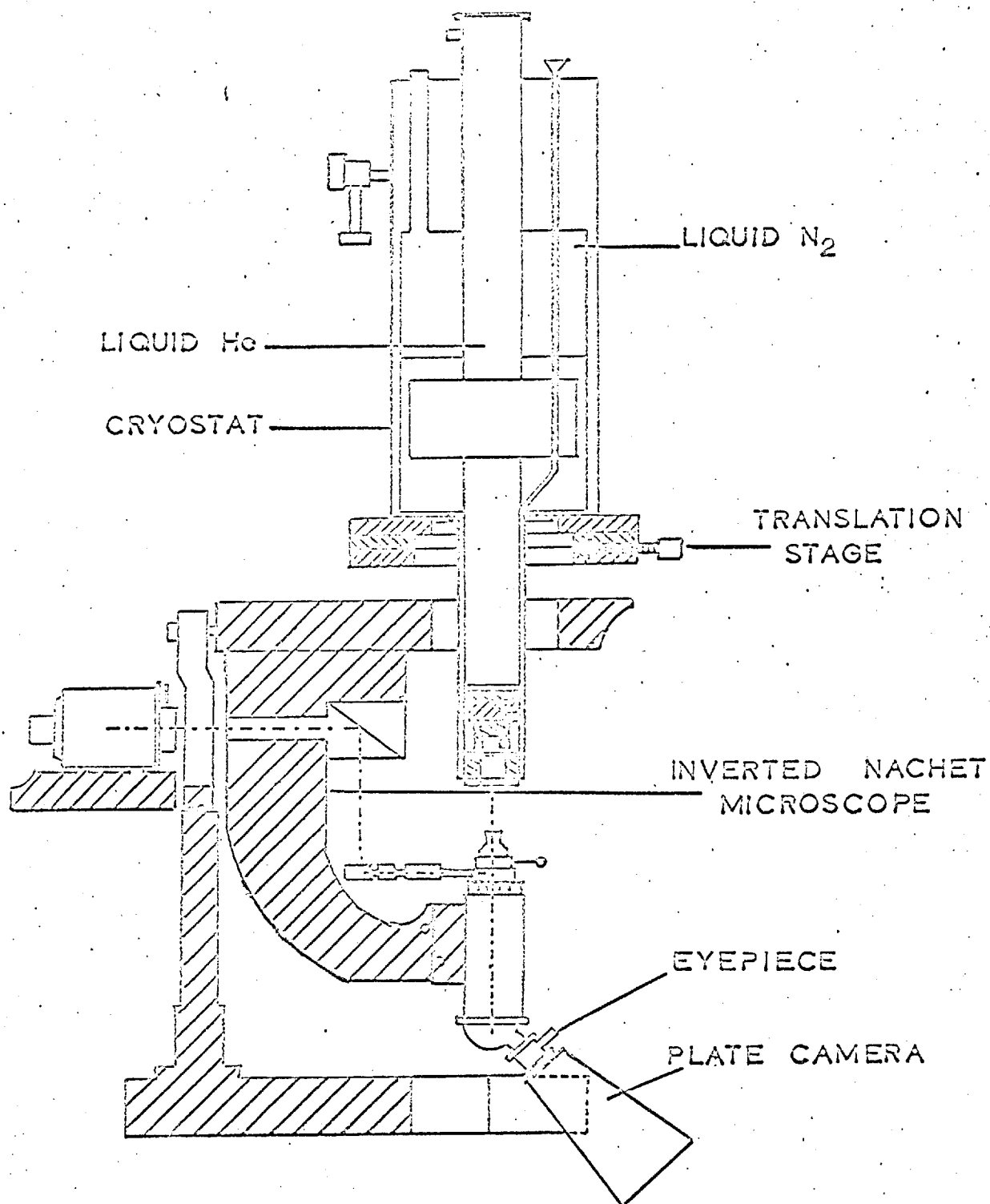


Figure 4.1 Cross-section through the helium stage on the microscope
(Pollock,7)

was examined at room temperature using a Nachet T46 metallurgical microscope. Selected specimens were then photographed with a Reichert photomicroscope. In addition some alloys were also examined metallographically at cryogenic temperatures using the liquid helium stage developed by King and Pollock (5). A cross-section of this apparatus is shown in figure 4.1. The microscope is again a Nachet T46 with facilities for polarised light and Normarski Interference and is inverted so that it may be used with the tail section of a standard helium dewar. The specimen is in contact with a copper block which is attached to the bottom of the helium reservoir. With liquid helium or liquid nitrogen as the coolants, specimens can be held at 6.5° or 78°K respectively while intermediate temperatures can be obtained with a heater embedded in the specimen mount. Magnifications up to x 330 were used and the temperature was measured with a calibrated Au/0.03 at % Fe vs. chromel thermocouple.

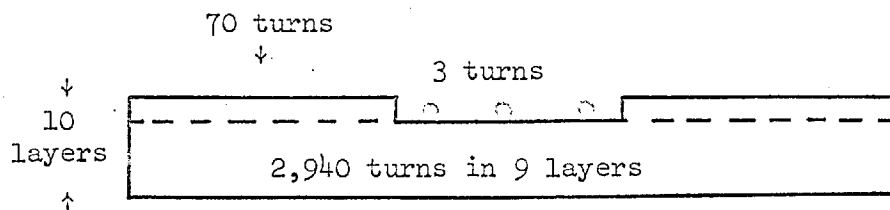
Some attempts were made to follow permeability changes on cooling stainless steel micro-specimens in the microscope by monitoring the inductance of a coil surrounding the specimen. The changes were, however, obscured by stray magnetisations due to the surrounding metal work of the microscope and support system.

Specimens of stainless steel for metallographic examination were prepared using standard grinding techniques involving progressively finer SiC papers and diamond paste down to 1 μ . The steels were then electropolished using a saturated solution of chromium trioxide in acetic acid

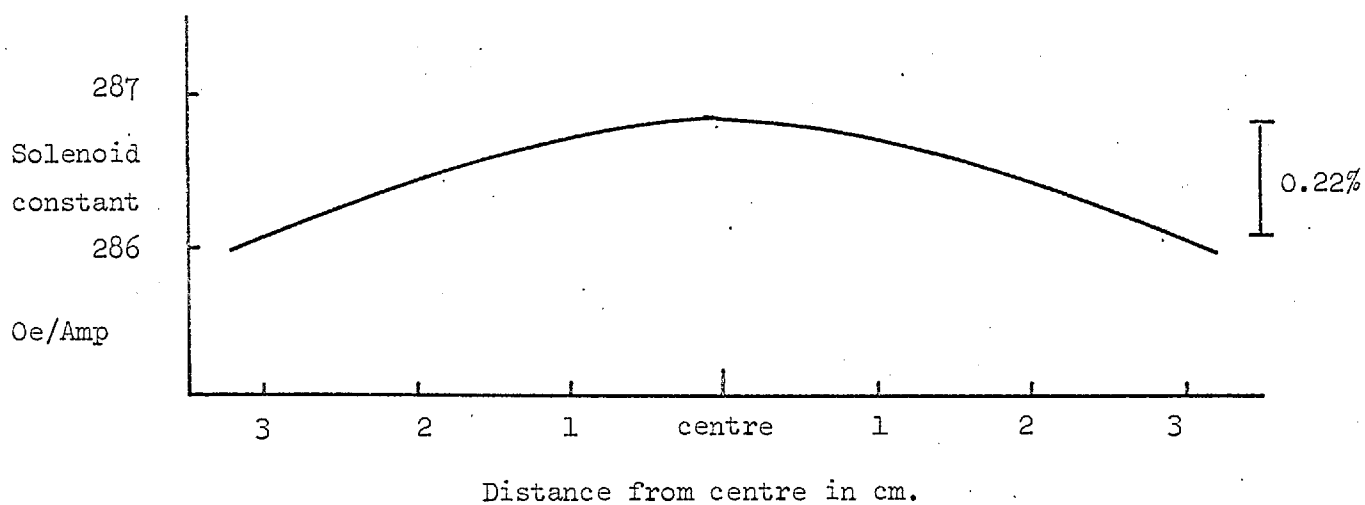
- a) 133 ml acetic acid
- b) 7 ml water
- c) 25 gm chromium trioxide.

A good polish was obtained in a static bath at approximately 100°C using a copper cathode at 16v. Polishing times were kept to less than a minute because it was found that polishing for longer times produced irregular surfaces. It had been thought that mechanical polishing might nucleate surface martensite but no transformation was observed in these alloys. Saturation magnetisation measurements

Figure 4.2 THE SUPERCONDUCTING SOLENOID



a) The winding geometry



b) The computed field profile of the solenoid

made on selected steels confirmed this finding since no magnetisation changes were detected after mechanical polishing. This eliminated the need for extensive electro-polishing to remove uncharacteristic surface layers.

Various attempts were made to electro-polish magnetisation specimens of indium-thallium alloys using an electrolyte described by Guttman (6)

- a) 75 ml diethylene glycol
- b) 5 ml concentrated nitric acid
- c) 2 ml concentrated hydrochloric acid

Techniques (7) which proved satisfactory for polishing small metallographic specimens produced an irregular polish with intermittent tarnishing along the length of magnetisation specimens. Because of these difficulties, and the anomalously high values of H_c obtained by Doidge et al (8) on electropolished specimens of In/33 and In/38 Tl, no further attempts were made to electropolish the indium-thallium magnetisation specimens.

4.2 Magnet systems and dewars

4.2.1 The superconducting solenoid

Magnetisation measurements at liquid helium temperatures were made using a 30 mm bore superconducting solenoid system designed and constructed to our specifications by the Oxford Instrument Co. Ltd. using Niomax Nb/44 wt% Ti wire wound on a tufnol former. A number of problems arose from the use of this solenoid which had a profound effect on the content of this thesis and these are described in the Appendix.

The coil was computed to give a field of 287 Oe/amp, falling off by 0.12 % at 30 mm on the solenoid axis (Figure 4.2). The design used nine close packed layers with the tenth spaced so as to provide the required homogeneity. No primary standard was available to check the design figure of the field at 4.2°K. However, the copper solenoid described in section 4.22 had been calibrated against the

proton resonance of heavy water (9) and it was possible to measure the susceptibility of type 316LN stainless steel in both magnets. Using the computed field value for the superconducting solenoid no difference could be detected in the susceptibility at 3kOe. When the sensitivity of the magnetometer was taken into account it was found that the computed value of the field, 287 Oe/Amp, was accurate to within $\pm 1\%$. Thus the design value of the solenoid was accepted and the field was measured by monitoring the potential drop of the solenoid current across a standard 0.02 ohm resistor. The potential drop was fed to the X axis of the X-Y recorder.

The remanent field of the solenoid was estimated by dropping superconducting specimens into the pick up coils when the solenoid current was zero, and found to be less than 1 Oe.

The solenoid current was supplied from an Oxford Instrument Co. Ltd. 30 Amp stabilised power supply controlled by an electronic sweep generator permitting a range of sweep times from 5 seconds to 30 minutes.

The solenoid system was enclosed in a standard metal dewar, also constructed by the Oxford Instrument Co. Ltd.. This was of composite construction with an aluminium outer skin and nitrogen radiation shield and a thin wall stainless steel helium dewar. No magnetisation was ever detected due to the helium dewar. The dewar was generally filled with helium gas in the liquid helium space and then cooled overnight with liquid nitrogen supplied by an automatic pump. This ensured that the solenoid and probe were very close to 77°K after approximately 10 hours and that no water vapour or air could condense or freeze on the solenoid or magnetisation probe and impede their operation on transferring liquid helium. A small overpressure of gaseous helium was maintained overnight from an inflated football bladder to prevent the entry of air as the cryostat cooled.

4.22 Water cooled copper solenoid

Magnetisation measurements on the stainless steel specimens

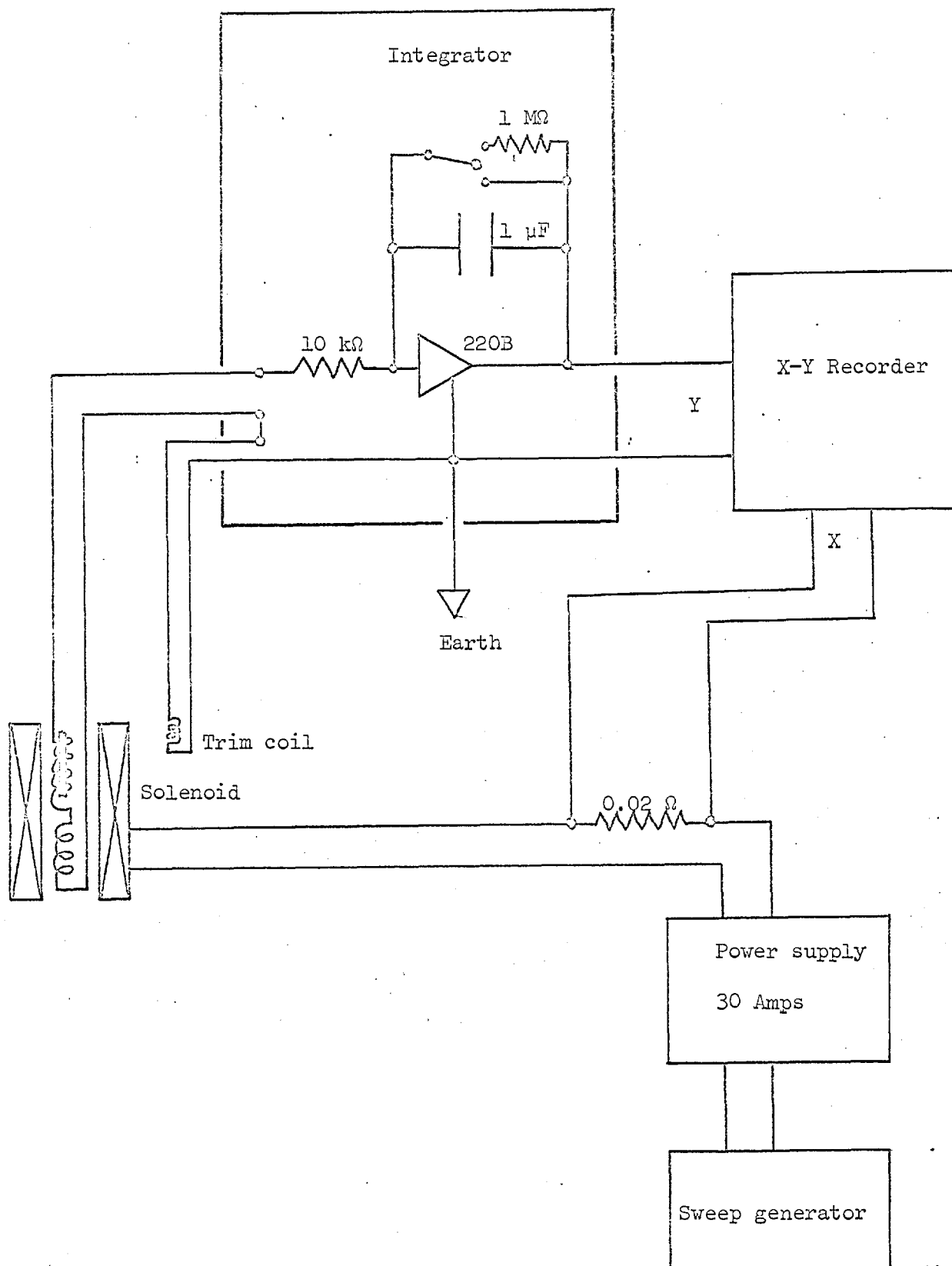


Figure 4.3 Block diagram of the magnetometer and solenoid circuits.

at room temperature and 77°K were performed in a water cooled copper solenoid, located in the Physics Department at Imperial College (9). Since the length and diameter of the dewar associated with the solenoid are similar to that of the superconducting solenoid, the same magnetisation probe could be used for both magnet systems. The solenoid gave 89.2 Oe/amp and the field was 0.5% down at 30mm on the solenoid axis. Current was supplied from an E.M. Wareham Ltd. 35 Amp stabilised power supply. In the early experiments the supply was controlled with a motor driven helipot. However, the use of this sweep generator caused irregular and, on occasions, large discontinuous jumps in the current output with a consequent interference with the magnetometer. This led to a basic sensitivity of only approximately ± 10 gauss on many occasions. Later experiments were performed using the electronic sweep generator referred to in Section 4.21. Before modification the voltage output of this sweep was insufficient to sweep the magnet supply over its full range and some room temperature magnetisation measurements were made to a maximum field of 1890 Oe. A later modification of the unit allowed a noise free sweep over the full range to 3150 Oe when the precision of the magnetisation measurement was limited by the inherent magnetometer errors.

4.3 The D.C. Integration Magnetometer

The integration magnetometer was constructed specially for this work and will therefore be described in some detail.

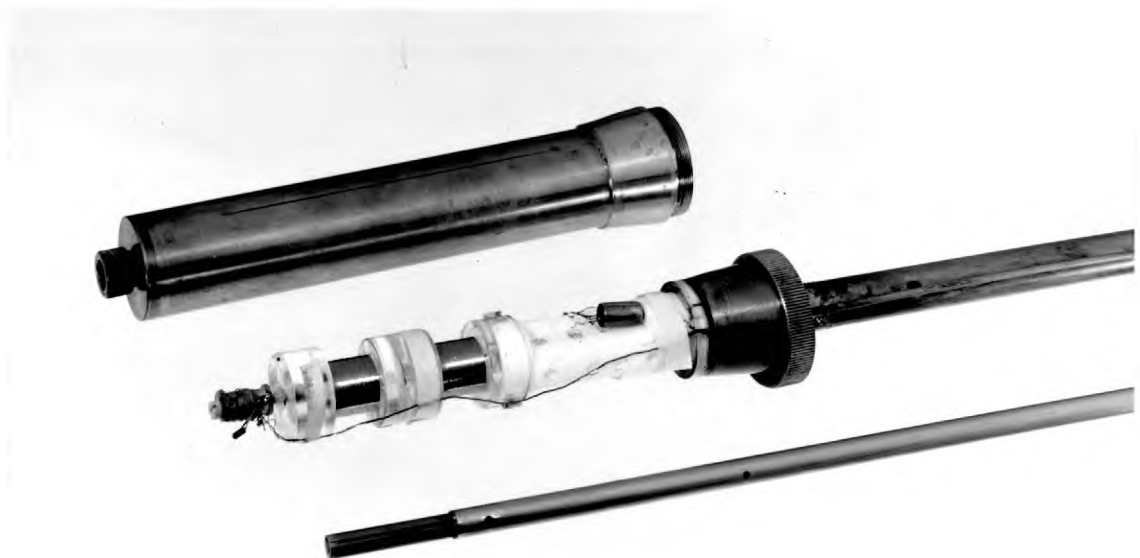
4.31 Principles of operation

A block diagram of the magnetometer and solenoid system is shown in figure 4.3. The coil detection system is composed of two similar coils wound in opposite senses and situated symmetrically along the solenoid axis. On changing the solenoid field a voltage e_c is induced in the coil pair

$$e_c = - \frac{d\phi_1}{dt} + \frac{d\phi_2}{dt} \quad 4.1$$



Figure 4.5 The magnetisation probe



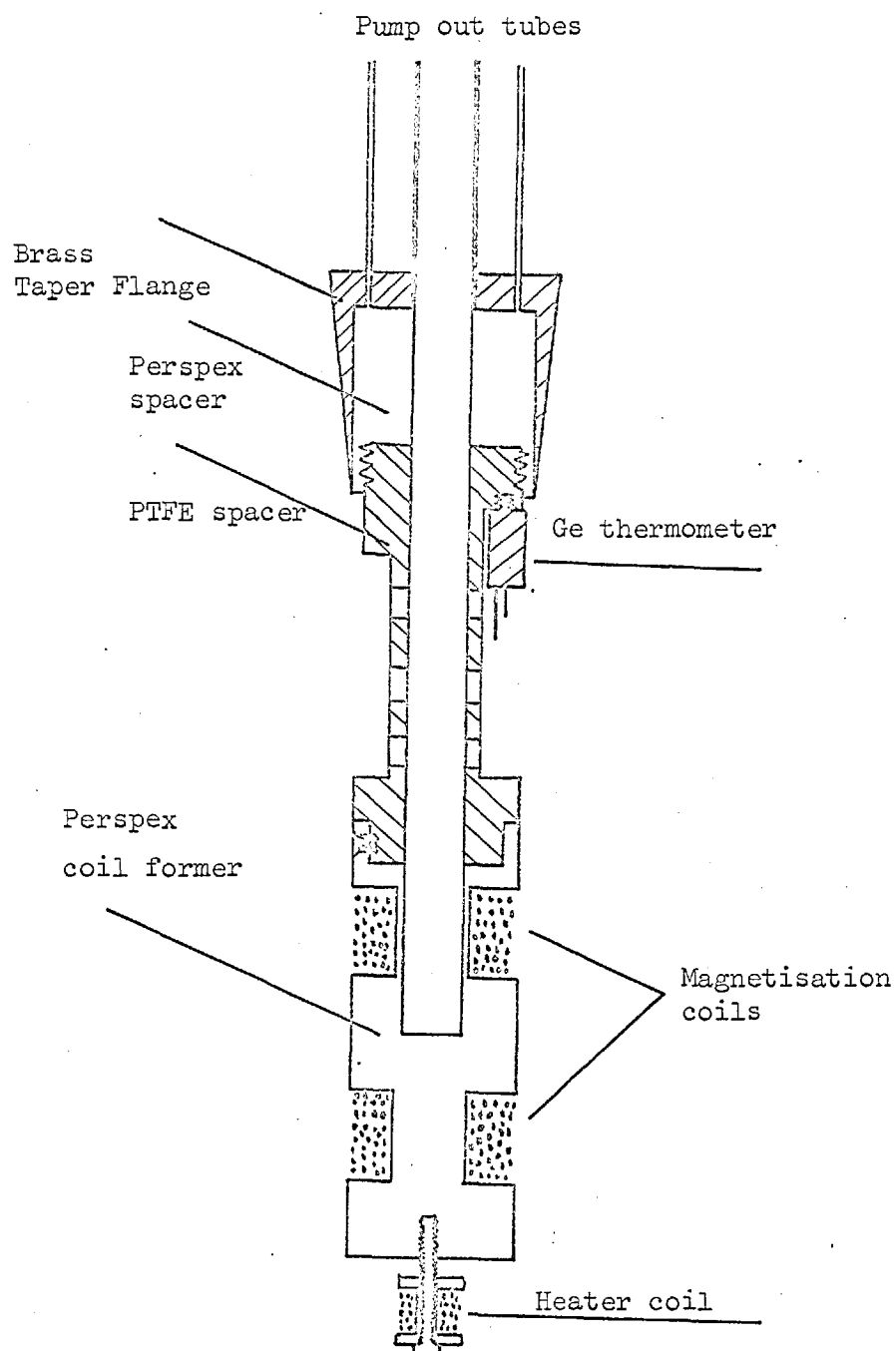


Figure 4.5 Cross-section of the specimen chamber.

where the subscripts 1 and 2 refer to the separate coils. Equation 4.1 may be relaxed by

$$e_c = -N_1 A_1 \frac{dH_1}{dt} + N_2 A_2 \frac{dH_2}{dt} \quad 4.2$$

where NA is the turns area product of each coil and dH/dt is the rate of field change. In the absence of any external magnetic moments the coil products may be balanced so that $e_c = 0$. When a specimen with magnetic moment $4\pi M$ is introduced into one of the coils, the output voltage is now given by

$$e_c = -NA_s \frac{4\pi dM}{dt} \quad 4.3$$

providing the coils have negligible mutual inductance. A_s is the cross-section of a specimen, the length of which should be $\sim 1.5 \times$ the coil length.

If the balanced coil pair is now connected to the integrating circuit of figure 4.3, the output voltage of the integrator is given by

$$\begin{aligned} e_o &= -\frac{1}{RC} \int_0^t e_c dt \\ &= \frac{4\pi M N A_s}{10^8 RC} \end{aligned} \quad 4.4$$

where RC is the time constant of the circuit and the factor of 10^8 is introduced if e_o is measured in volts, $4\pi M$ in gauss and A in cm^2 .

4.32 The Magnetisation probe

A magnetisation probe which supports the detection coils, enables specimens to be exchanged and allows the temperature to be varied both above and below 4.2°K , is shown in the photographs in figure 4.4. A cross-section of the specimen chamber is also shown in figure 4.5.

The chamber is isolated from liquid helium by a double walled can which mates on to a flange constructed from admiralty brass and with a 6° taper. This brass flange is internally bored out so as to accept a perspex spacer which thermally insulates the specimen chamber from the helium bath. A 1.5 mm dia. copper finger extends from the helium bath through the spacer and acts as a heat sink for the germanium thermometer leads which are wrapped tightly round it and covered with Apiezon M grease. Below the perspex spacer is another spacer, made from P.T.F.E., which supports the germanium thermometer, and to which the pick-up coils are attached with 2 6BA nylon screws. Beneath the coil former is a small 100 ohm heater and a carbon resistor which acts as a sensor when the temperature of the chamber is being controlled with the Minireg. (Section 4.34).

The specimen change tube shown in figure 4.4b slides to a stop half way between the coil positions. It is constructed from $\frac{1}{4}$ " dia. thin wall stainless tube (which had no detectable magnetisation), into which a 4.5 mm I.D. split high conductivity copper tube is cemented with G.E. varnish. Magnetisation specimens are held in the specimen tube by Apiezon M grease.

The double-walled can is constructed from 0.25 mm hard drawn brass tube with admiralty brass flanges and has no detectable magnetisation (Appendix 2). When first constructed the can exploded on returning to room temperature after a period in liquid helium and this was attributed to microleaks in the hard soldered joints. To counter this, a small cone joint was added to the outside can so that the inter-wall space could be leak tested. Special care was taken with the soldering and the flux was used dry so that no steam bubbles were trapped below the molten metal (which can give rise to possible leaks on cooling). The cone joints are sealed with silicone vacuum grease which sets to a glass on cooling, providing a vacuum tight joint and on cooling to helium temperatures, the air between the walls of the can condenses to provide a hard vacuum, thus insulating the specimen chamber from the helium bath. The temperature of the chamber may now be raised above that of the bath as described in the next section.

Connections to room temperature are made by three cupro-nickel tubes soldered to the brass taper flange. The two small bore tubes carry the electrical leads, leaving the central tube free for the specimen change tube and for pumping out the specimen chamber. Electrical connections are taken to pin seals and feed-throughs mounted in standard Edwards $\frac{1}{2}$ " vacuum fittings. The specimen chamber is pumped out and helium exchange gas admitted by a $\frac{1}{4}$ " tap on the top plate. The top plate contains in addition two O-ring seals, one of which accepts the specimen change tube and the other the helium transfer syphon. The syphon has a guide tube which extends to the bottom of the large brass tube. In normal use ~ 1.25 litres of liquid helium are needed to cool the magnet and probe to 4.2°K and a further litre to fill the reservoir.

The consumption of liquid is very dependent on the temperature range desired. At 4.2°K the double-walled can is not needed, superconducting specimens may be demagnetised by withdrawing them from the liquid and the helium lasts about 3 hours. When the can is fitted, helium consumption is principally limited by the frequency of changing specimens as the probe contains helium exchange gas at reduced pressure (section 4.23) and this must be brought to 1 atmosphere, by admitting room temperature helium gas before the specimen can be withdrawn. It has not been found possible to measure more than 2 specimens with one change of liquid helium.

4.33 Operational details

The pick up coils were each wound from 25,000 turns of 49 gauge (0.035 mm dia.) enamelled high conductivity copper wire and connections made to copper posts set in the perspex former. A continuous pair of twisted 36 gauge (0.22 dia) copper wires connect the pick-up coils to the amplifier input where a series connection is made to a small balance coil located in the fringing field of the solenoid. The orientation of this coil can be varied to obtain a final balance between the pick-up coils. Both coils are fully shielded and grounded to the common earth point of the amplifier power supply.

Fietz (10) has discussed the sources of error involved in D.C. Integration and the methods used to minimise them. Important among these are the specifications for the feedback components. In particular the integrating capacitor should be a high grade polystyrene type with a leakage resistance greater than 10^{12} ohms. The shorting switch must have a similar resistance. Both of these components had measured insulation resistances $>10^{13}$ ohms. In addition the temperature coefficients of the components used in the feedback network were better than ± 100 p.p.m. so that temperature changes contributed voltages smaller than the normal drift voltage of the amplifier.

The D.C. amplifier chosen for the integrator is however the most critical element in the system on account of its very low drift. The rated specification of the amplifier, an Analogue Devices 220B Operational Amplifier, gives a drift of less than $0.25 \mu\text{V}/^\circ\text{C}$ or better than $1 \mu\text{V}/\text{day}$. By using high conductivity copper wire throughout the input circuit, minimising the number of connections and making them with low thermal E.M.F. solder (11), the complete system drift with the coils in helium could consistently be reduced to the equivalent of 10^{-7}V , referred to the input, over a time of 10 - 15 minutes. On occasions this could be reduced to $5 \times 10^{-8}\text{V}$ over the period of 5 - 10 minutes.

To take full advantage of the exceptional performance of the amplifier, and the precautions employed to minimise thermal E.M.F.s in the input circuit, requiring a careful amplifier zeroing and coil balancing procedure. Zeroing of the amplifier input was accomplished by an internally injected voltage derived from a Bourns 3052 100K ceramic trimpot connected across the $\pm 15\text{V}$ supply of the amplifier. This offset voltage could be observed either by switching the integrator to act as a simple amplifier with a gain of 100 or by integrating for a short time. Resolution of the trimpot is such that 1 full turn causes a change of $\sim 3\text{mV}$ in the injected voltage.

The coils were balanced by switching the integrator as above to give a gain of 100 and observing the imbalance voltage $N'A'dH/dt$

as the field was swept. N^2A , the imbalance area turns product of the coils, was reduced to zero by first removing turns from a deliberately overwound specimen coil. This involved the withdrawal of the whole magnetisation probe from helium about 3 or 4 times and the consumption of about 3 or 4 litres of helium. Final balancing on each cool down was done with the external trim coil whose orientation could be varied through 360° . The output of this was equivalent to about 5 specimen coil turns. Only small adjustments to the trim coil were needed from experiment to experiment and the final balance was sensitive to $\sim \pm 10^\circ$ of arc.

It was during these first coil balancing experiments that problems with the superconducting solenoid were first encountered. A discussion of both the ideal curves expected and those obtained in practice when eddy currents and parasitic magnetisations were present is given in Appendix 1.

The aim of the balancing procedure was to reduce the coil imbalance error to less than the amplifier drift error. Given that the maximum rate of field sweep possible with the available solenoid was 10 Oe/sec and the basic amplifier drift is 10 μ V/sec (with a time constant of 10^{-2} sec) we have from equation 4.4:-

$$\begin{aligned} \text{Imbalance output} &= \frac{N.A.\Delta H}{10^8.RC} \\ &= 1.75 \mu\text{V/turn/Oe field change} \end{aligned}$$

Thus balancing to the nearest half turn ensures that the imbalance output remains less than amplifier drift. This is easily done using the same procedure as for minimising amplifier drift.

The basic sensitivity of the apparatus is obviously time dependent. With specimens 4 mm in dia. and 30 mm long, the integrator output was measured as ~ 2.5 mV/gauss. If the amplifier drift is regarded as being the principal source of error, for the present, the output drifts at 600 μ V/min or $\sim \frac{1}{2}$ gauss/minute.

In fact when operating with the germanium thermometer in position a ferromagnetic moment of approximately 3 gauss was registered at the pick-up coils. This did not saturate until about 500 Oe and had a remanence of about 1 gauss and thus imposed the effective limit of accuracy for short time, low field, measurements. The presence of a ferromagnetic impurity in such an expensive and sensitive thermometer was both surprising and disappointing. The likely source of the magnetisation is iron impurity in the brass case and this point is discussed further in Appendix 2.

The precision of the magnetisation measurements could be increased by using the magnetometer ballistically, that is by withdrawing the specimen from the pick-up coils so that all residual drift, coil imbalance and spurious magnetisations could be identified. This procedure was not as convenient as the normal operation but it enabled the precision of the measurements to be increased to $\pm \frac{1}{2}$ gauss or better at all fields.

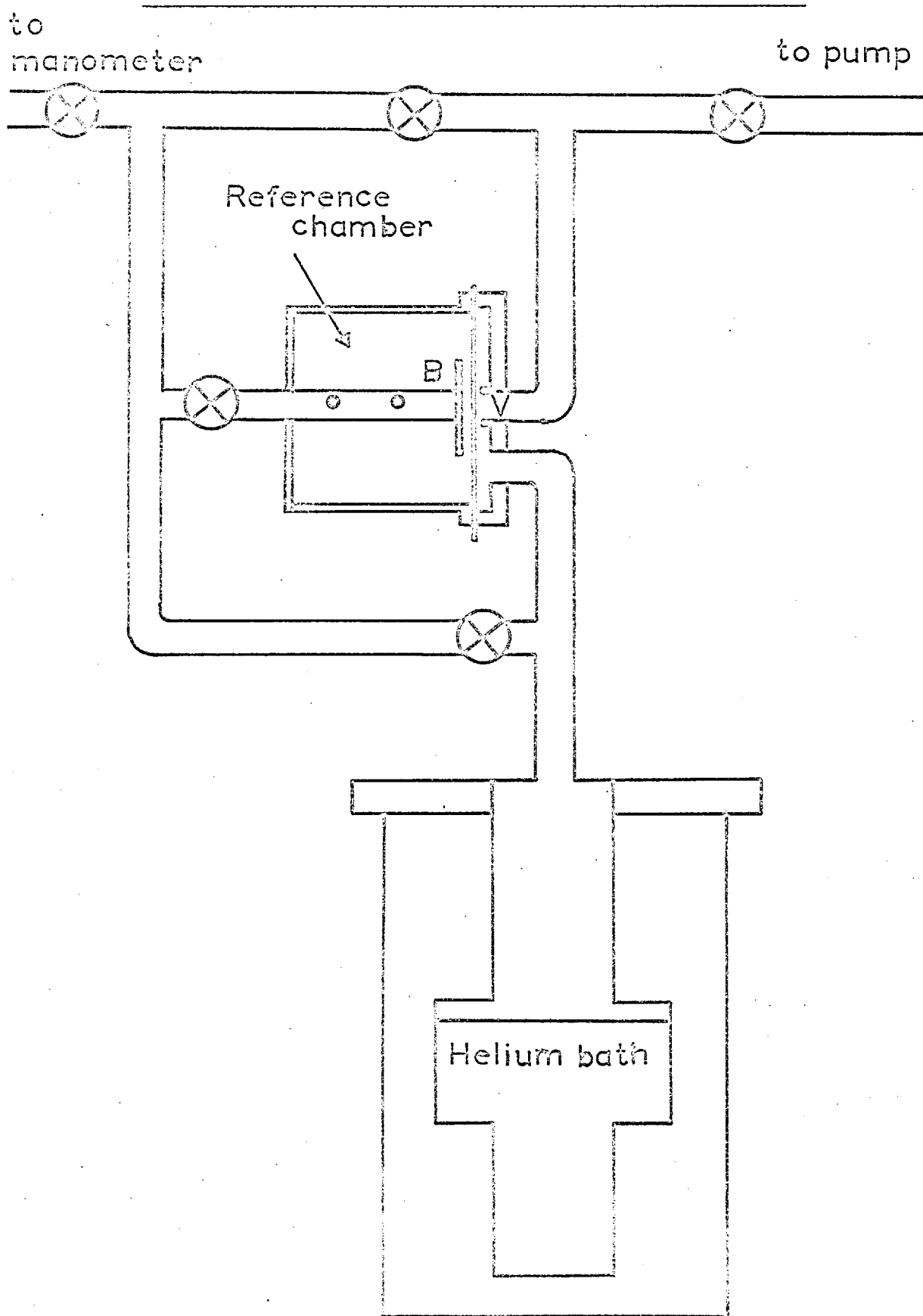
The integrator output was calibrated by comparing the voltages due to a high purity Nickel specimen (99.998% Koch Light Laboratories Ltd.) at the maximum fields possible (3 kOe R.T., 4 kOe 4.2°K) and by measuring the Meissner state output of a superconducting specimen, for which $-4\pi M = H$. Using the saturation moments given by Bozorth (12) for nickel and making demagnetisation corrections (12) these two outputs were found to agree to within 3%. This is in good agreement with Pietz (10) who has suggested that the absolute errors of this technique are in the region of 5%.

4.34 Control and measurement of temperature

For operation in the temperature region above and below 4.2°K, the specimen chamber was filled with helium exchange gas at a pressure of approximately 5 mm Hg and the temperature regulated electronically or by controlling the pressure of the liquid helium bath using a manostat.

A manostat was built which followed the general design of Sommers (13) and utilised a rubber diaphragm to separate two chambers, one of which

Figure 4.6 The Manostat used for maintaining a constant temperature in the helium bath.



contains the desired reference pressure to which the helium bath is to be pumped (figure 4.6). The rubber diaphragm is made from 1/32" neoprene sheet and is free to oscillate over a distance of $\sim 1/16$ " in either direction between a backstop (B) in the reference chamber and a smooth valve seat (V) which shuts off the line to the vacuum pump. The pumping line from the liquid helium bath feeds into the same chamber as the pump so that, when the cryostat pressure is greater than the reference pressure, the diaphragm is forced clear of the valve seat and the pump reduces the pressure of the helium bath. When the desired pressure is achieved, the diaphragm enters a state of stable oscillation which controls the pressure at a very nearly constant value. Over periods of 10 - 15 minutes the probe temperature was found to vary by less than 0.005°K over the range $1.2^{\circ} - 4.2^{\circ}$.

Some early experiments were also made with a feedback stabilised D.C. power supply (Weir Electronics Ltd., Minireg) which was controlled by a 47 ohm Allen Bradley carbon resistor feeding power into a small 100 ohm non-inductive heater, mounted beneath the pick up coils (figure 4.5)(9). This arrangement was found to control the probe temperature to better than 0.010° between 4.2° and 8°K for periods of 5 - 10 minutes. Since few magnetisation curves were, however, measured above 4.2°K , it was mainly used to demagnetise specimens by warming them above their critical temperatures prior to the recording of each magnetisation curve.

The temperature of the specimen was measured with a Texas Instruments germanium resistance thermometer, which had been standardised against a manufacturer's calibrated thermometer to an estimated accuracy of $\pm 0.003^{\circ}\text{K}$ over the range $1.2 - 8^{\circ}\text{K}$ (9). The resistance of the thermometer was measured with a Wheatstone bridge constructed from 0.01 % precision grade resistors and utilising a dual range four dial 0.01 % resistance box as the variable arm. A three wire connection to the bridge was made so as to avoid introducing the lead resistance into the bridge balance.

Unfortunately, the potential accuracy of the thermometer could

not be realised in practice, as , when the thermometer was mounted in the copper block close to the specimen, a ferromagnetic magnetisation of over 30 gauss at 4k Oe was measured. In order to reduce this to tolerable proportions, as described in the last section, the thermometer was removed to a position on the P.T.F.E. spacer. Measurements on the same alloy on different cool-downs showed that the temperature indicated by the thermometer was reproducible to $\sim 0.005^{\circ}\text{K}$ but, during attempts to measure the transition temperatures of the samples, as in section 4.42, it was found that the specimen was about 0.1°K colder than the indicated thermometer temperature, as judged from the transition in pure indium.

This is a disappointing result but since the prime demand of the system was that the temperature should be reproducible and stable, the arrangement was accepted. In no case does any subsequent argument depend sensitively on the magnitude of the temperature errors found in this way.

4.4 Other magnetic measurements

4.41 Saturation magnetisation measurements

Some saturation magnetisation measurements were made at room temperature using a Sucksmith (14) type of magnetic balance built by Dr. H. Smith of this department (15). The magnetic field was provided by an electromagnet with shaped pole tips to give a constant field gradient dH/dx over the length of the specimen. When the field is applied a magnetic specimen experiences a force F proportional to the total magnetic moment of the specimen.

$$F = \sigma \cdot m \cdot dH/dx \quad 4.5$$

where m is the mass of the specimen and σ its magnetic moment/unit mass. The force F produces a proportional elastic distortion D in a spring which supports the specimen and D is measured by a direct reading transducer. Thus

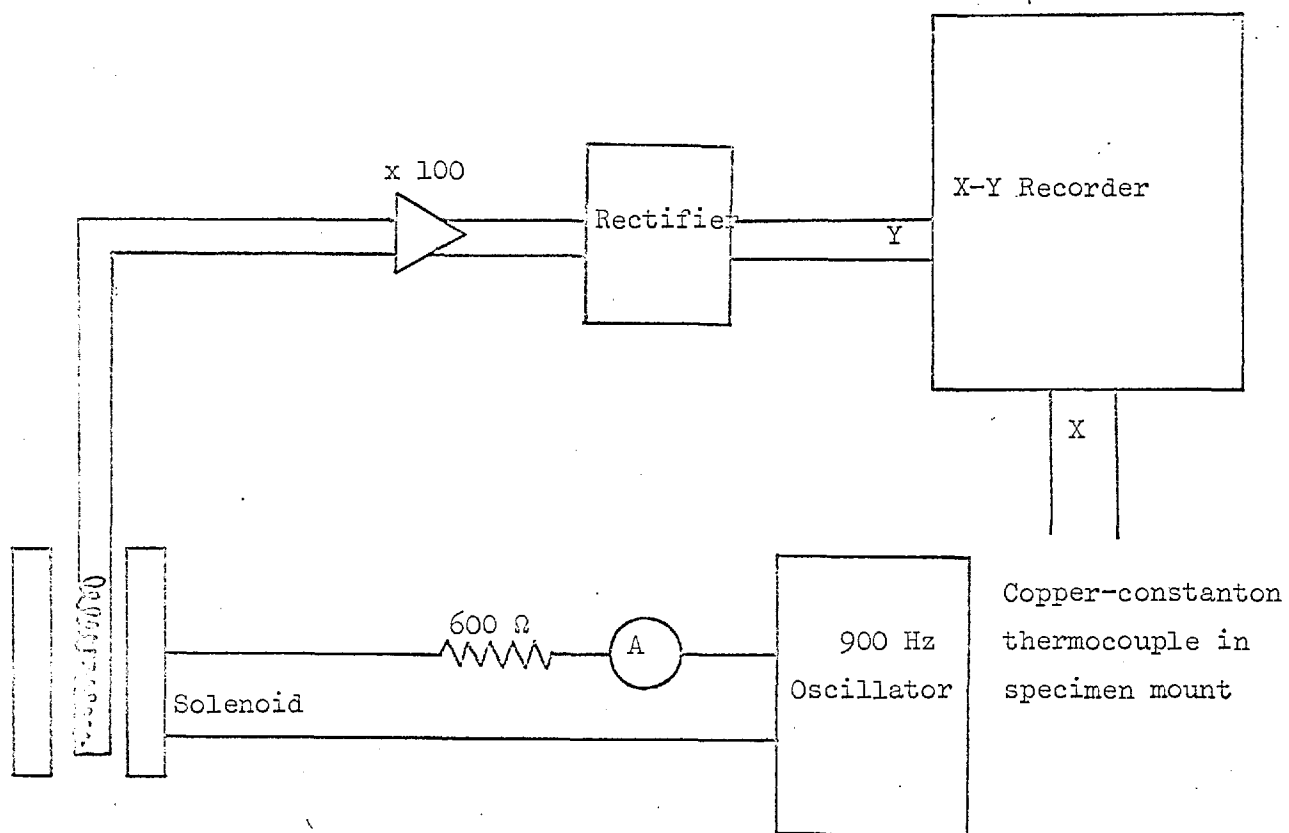


Figure 4.7 A.C. Susceptibility apparatus for Curie point measurements.

$$F \propto D = K \cdot \sigma \cdot m \cdot dH/dx$$

4.6

where K is an instrumental constant.

The Sucksmith balance was calibrated by measuring the displacement of a standard nickel specimen in a field great enough to saturate it. The field of 12,000 Oe which was available was found to be sufficient to saturate both nickel and the steels used in this investigation. However, no simple method was available by which the pole pieces of the magnet could be demagnetised and thus a previously demagnetised specimen always possessed a magnetisation when the transducer was zeroed with the magnet current set at zero. Thus the magnetisations measured on this instrument are always overestimated by an amount which depends on the initial slope of the magnetisation curve of the specimen concerned.

Fortunately the permeability of the steels containing α' martensite (which were the only ones ferromagnetic at room temperature) was relatively low and, from measurements on cold-rolled steels with 100% α' martensite (Section 6.51b), it is estimated that this error was always less than 5 % of the magnetisation measurement.

4.42 Curie Point determinations

At a late stage in the experimental work, an attempt was made to measure the Curie Point of the stainless steels 310 and Incoloy 800, by using the pick-up coils of the D.C. Magnetometer as an A.C. detector. A simple set up was used which is shown in figure 4.7. An A.C. drive signal from an audio frequency oscillator was supplied to the superconducting solenoid via a series 600 Ω resistor to minimise changes in signal amplitude as the solenoid was cooled. The solenoid field was ~ 0.3 Oe at 900 Hz. The output from the pick-up coil pair (without the external trim) was amplified, rectified and fed to the Y axis of the X-Y recorder. The specimen was placed in a modified specimen holder with a copper/constantan thermocouple glued with G.E. varnish to one end. The thermocouple voltage was fed to the X axis of the recorder and the reference junction maintained at 0°C .

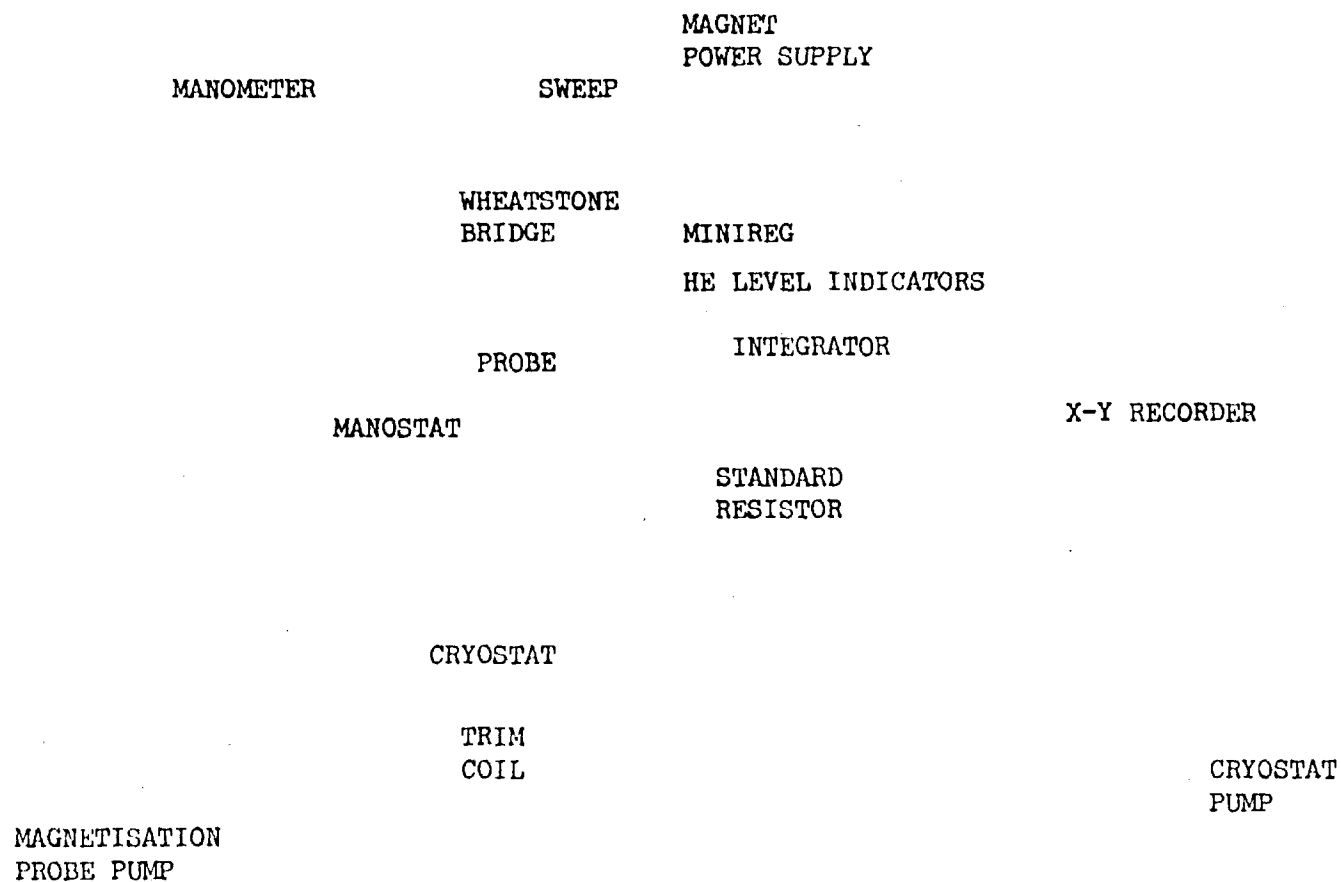
In operation down to 77°K the specimen probe and solenoid were slowly immersed in a glass dewar containing liquid nitrogen with about $1/2$ atmosphere of helium exchange gas in the specimen chamber. Cooling from room temperature to 77°K took from twenty minutes to half an hour. Measurements were also made down to 4.2°K when helium was being transferred into the cryostat. The cooling time was then approximately 80 minutes.

Samples of the curves obtained from this apparatus are given in figure 6.23 which show that, as the material is cooled below its Curie point, the coil signal increases sharply due to the large permeability increase.

4.5 General assembly of the experimental apparatus

A general view of the apparatus built and assembled for this project is shown in figure 4.8.

FIGURE 4.8 GENERAL VIEW OF THE EXPERIMENTAL APPARATUS.





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CHAPTER 5THE LOW TEMPERATURE PROPERTIES OF SOME INDIUM-THALLIUM, INDIUM-LEADAND INDIUM-CADMIUM ALLOYS

5.1 Introduction

This chapter describes measurements of the flux trapping properties of superconducting alloys of indium-thallium, indium-lead and indium-cadmium in the region of the martensitic phase transformations as discussed in Section 3.22. At the outset it was envisaged that the study would be extended to the flux trapping properties of the high field superconducting compounds Nb_3Sn and V_3Si , in which a crystallographically similar martensitic transformation has been reported (1,2,3). The scope of the programme was modified, however, following experimental difficulties encountered with the superconducting solenoid, caused by the presence of eddy currents in copper and the low temperature instability of austenitic stainless steel. These difficulties are described in detail in Appendix 1. The present chapter is thus limited to a study of the flux trapping in the alloys of indium, while additional work on the low temperature magnetic properties of stainless steels is reported in chapter 6.

5.2 Results

5.21 Methods and definitions

The preparation of the specimens for this study has already been described in section 4.12 together with the D.C. integration magnetometer (section 4.3) with which a continuous record of the specimen magnetisation was obtained. Measurements on the indium thallium and indium cadmium alloys were all made below 4.2°K by isolating the specimens from the helium bath with the double-walled can and reducing the pressure of the bath with a vacuum pump controlled by a manostat. When necessary samples were demagnetised at the start of each curve by heating the chamber above the transition temperature of the alloy and then allowing it to cool in zero field. Measurements on the indium lead alloys were made at 4.2°K without the can being fitted and specimens were demagnetised by withdrawing them from the liquid.

In order to compare the flux pinning properties of different alloys at different reduced temperatures (the magnetisation of the

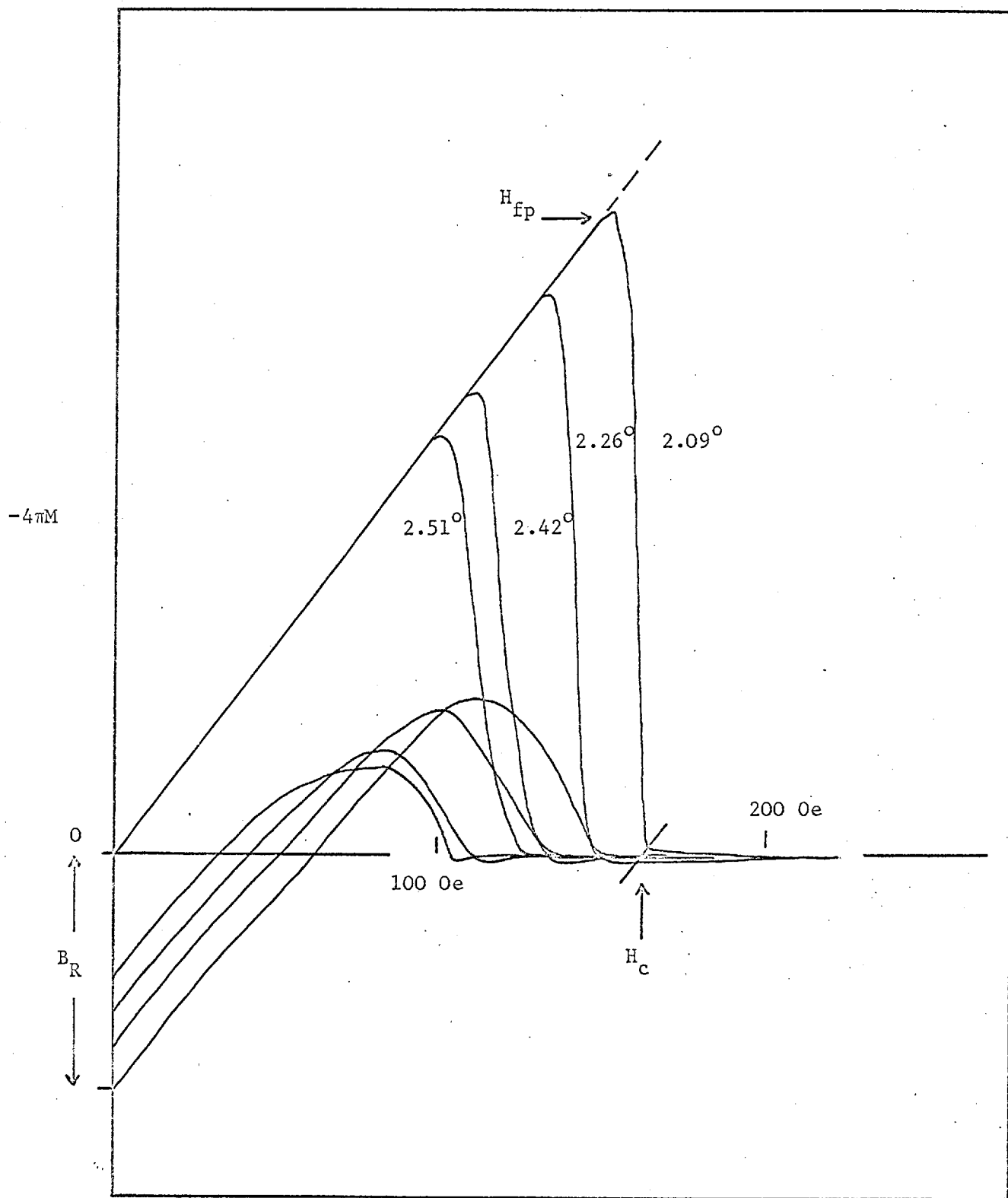
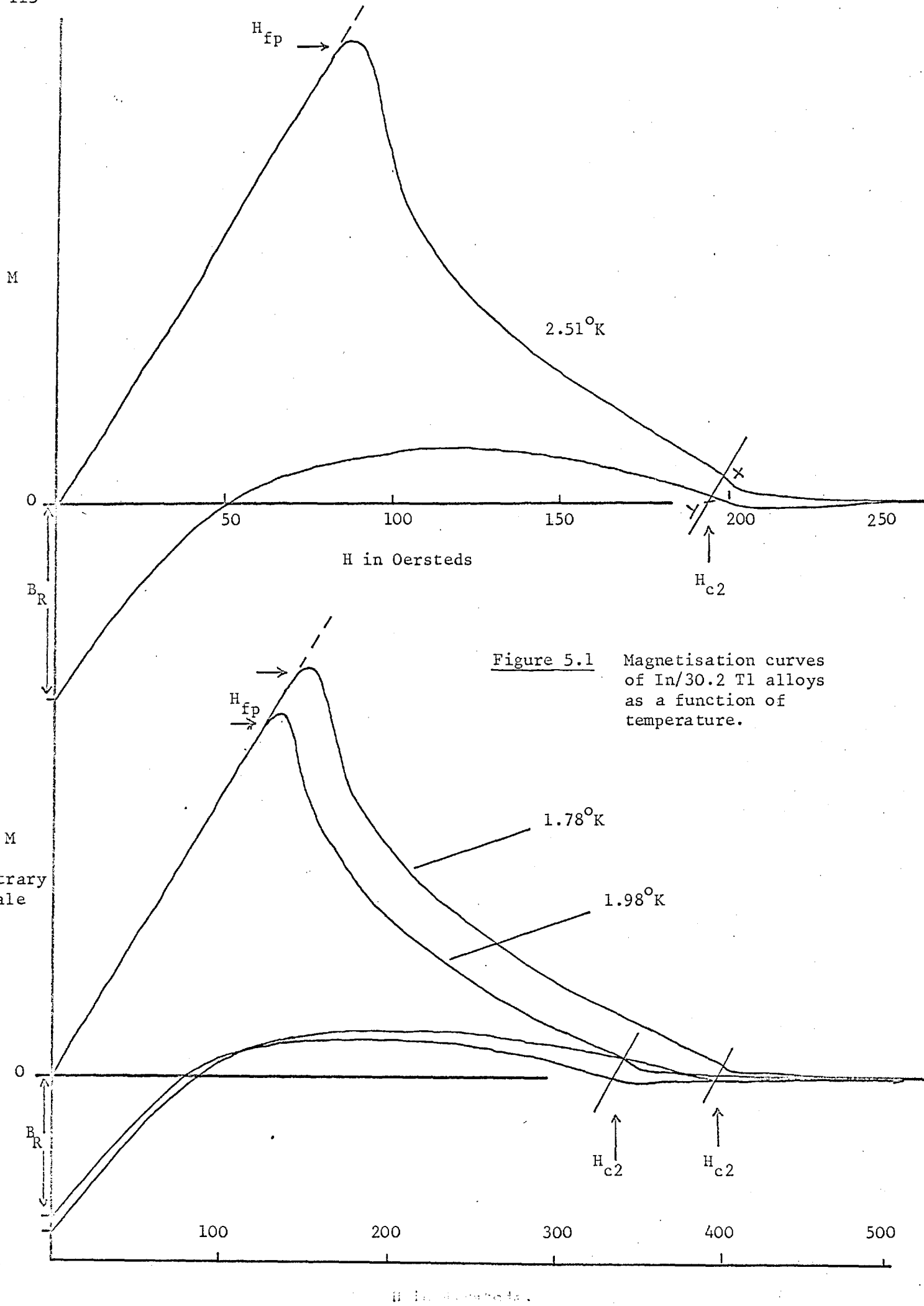


Figure 5.2 Magnetisation curves of In/6.07 Cd as a function of temperature.



thermometer precluded accurate measurements of the transition temperature, as described in section 4.34) a flux pinning parameter was sought which was substantially independent of temperature. The normally measured parameter B_R , the remanent induction in zero field, is a function of temperature, like H_{c1} and H_{c2} . H_{c1} was not accurately measurable in these alloys since they were all hysteretic to a greater or lesser extent. H_{c2} was, also, not found to be simply defined in all cases, since double transitions appeared in some of the alloys and in one (In/13Pb on its second measurement, after 8 months at room temperature) the transition was so broad that distinct values of H_{c2} could not be separated.

In order to avoid these difficulties, the quantity H_{fp} , the field at which flux begins to enter the specimen, as judged by the first deviation from the diamagnetic Meissner slope, was measured and the ratio B_R/H_{fp} was selected as the flux pinning parameter. This has the merit that in weak flux pinning materials such as the present alloys H_{fp} is very close to the maximum magnetisation and thus the ratio B_R/H_{fp} indicates how efficient the specimen is in trapping flux on an approximate scale of 0 to 1.

Examples of the magnetisation curves are given in figures 5.1 and 5.2, together with the definitions of the quantities B_R , H_{fp} and H_{c2} and their variation with temperature. B_R was measured accurately at the end of each sweep, either by heating the sample above T_c while it was still within the pick up coils (In/Tl and In/Cd) or by withdrawing it from the coils (In/Pb). In this way all residual drifts, coil imbalance errors and stray magnetisations were eliminated. The latter were typically of the order 2 - 3 gauss. H_{fp} was determined as already described, but H_{c2} was not always easy to measure because of the presence of a surface sheath current. When this sheath current is present, the magnetisation does not fall to zero at H_{c2} but persists to a higher field H_{c3} , as discussed in section 2.24e. The transition of the bulk of the specimen occurs when the magnetisation passes through the point of inflexion marked X in figure 5.1. The true value of the internal field within the specimen is now obtained by drawing a straight line XY with the Meissner slope (i.e. a diamagnet) and taking H_{c2} as the point Y at

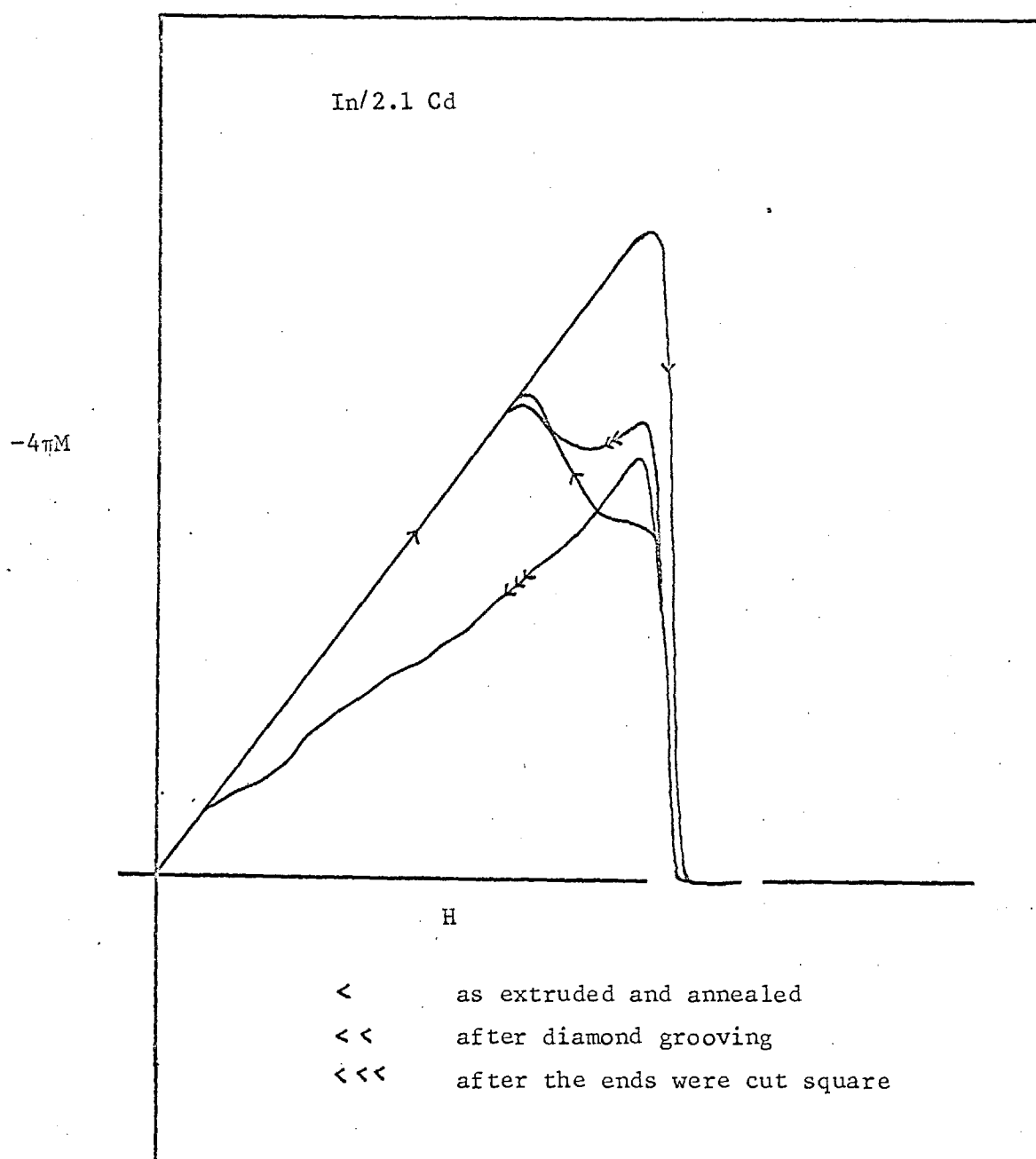


Figure 5.4 The effect of surface grooving and end shape on magnetisation hysteresis.

Figure 5.3 The effect of surface condition on the magnetisation hysteresis.

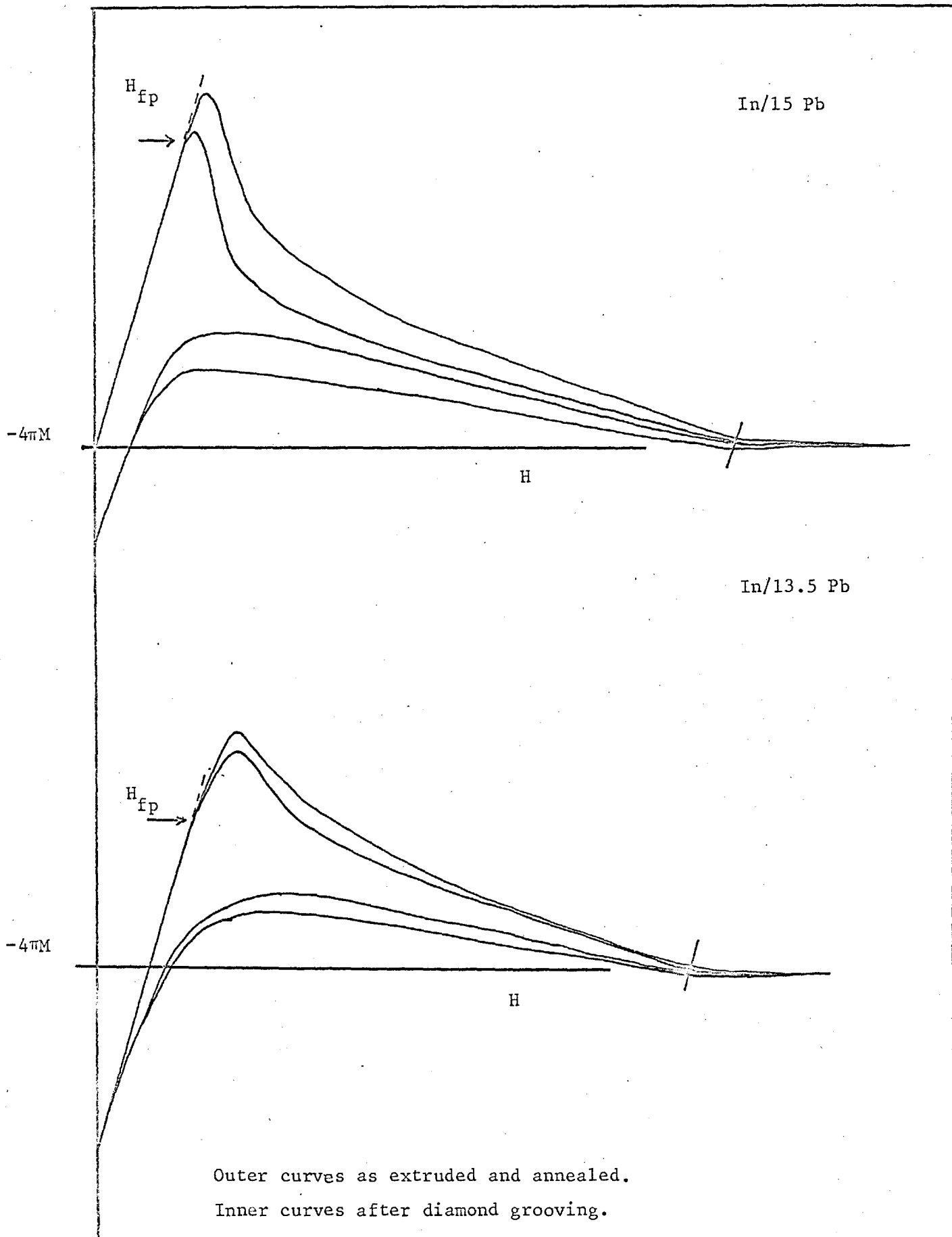


TABLE 5.1 The flux pinning parameter B_R/H_{fp} as a function of temperature

Indium Thallium

B_R/H_{fp} as $f(T)$

In/28.5 Tl	0.25 (2.54°K), 0.23 (1.97°)
In/29.3 Tl	0.40 (2.48), 0.40 (1.94)
In/29.8 Tl	0.42 (2.55)
In/30.2 Tl	0.42 (2.51), 0.41 (1.98), 0.41 (1.78)
In/30.6 Tl	0.21 (2.45), 0.22 (1.96)
In/26.0 Tl	0.29 (2.29)
In/27.0 Tl	0.25 (2.31) 0.25 (2.34)
In/29.0 Tl	0.24 (2.31)
In/30.0 Tl	0.32 (2.64) 0.31 (2.30)
In/30.5 Tl	0.27 (2.33)
In/31 Tl	0.31 (2.31)
In/33 Tl	0.22 (2.31)

Indium Cadmium

In/2.1 Cd	0 (2.38), 0 (2.49)
In/2.5 Cd	0 (2.36)
In/3.0 Cd	0 (2.32) 0 (2.38)
In/4.0 Cd	0.02 (2.31) 0.01 (2.37)
In/5.0 Cd	0.04 (2.41)
In/6.1 Cd	0.35 (2.51) 0.35 (2.42), 0.34 (2.26) 0.34 (2.09), 0.34 (2.01), 0.36 (1.72) 0.35 (1.51), 0.35 (1.34)
In/6.5 Cd	0.61 (2.55), 0.59 (2.41)
In/7 Cd	0.62 (2.38), 0.62 (2.38)

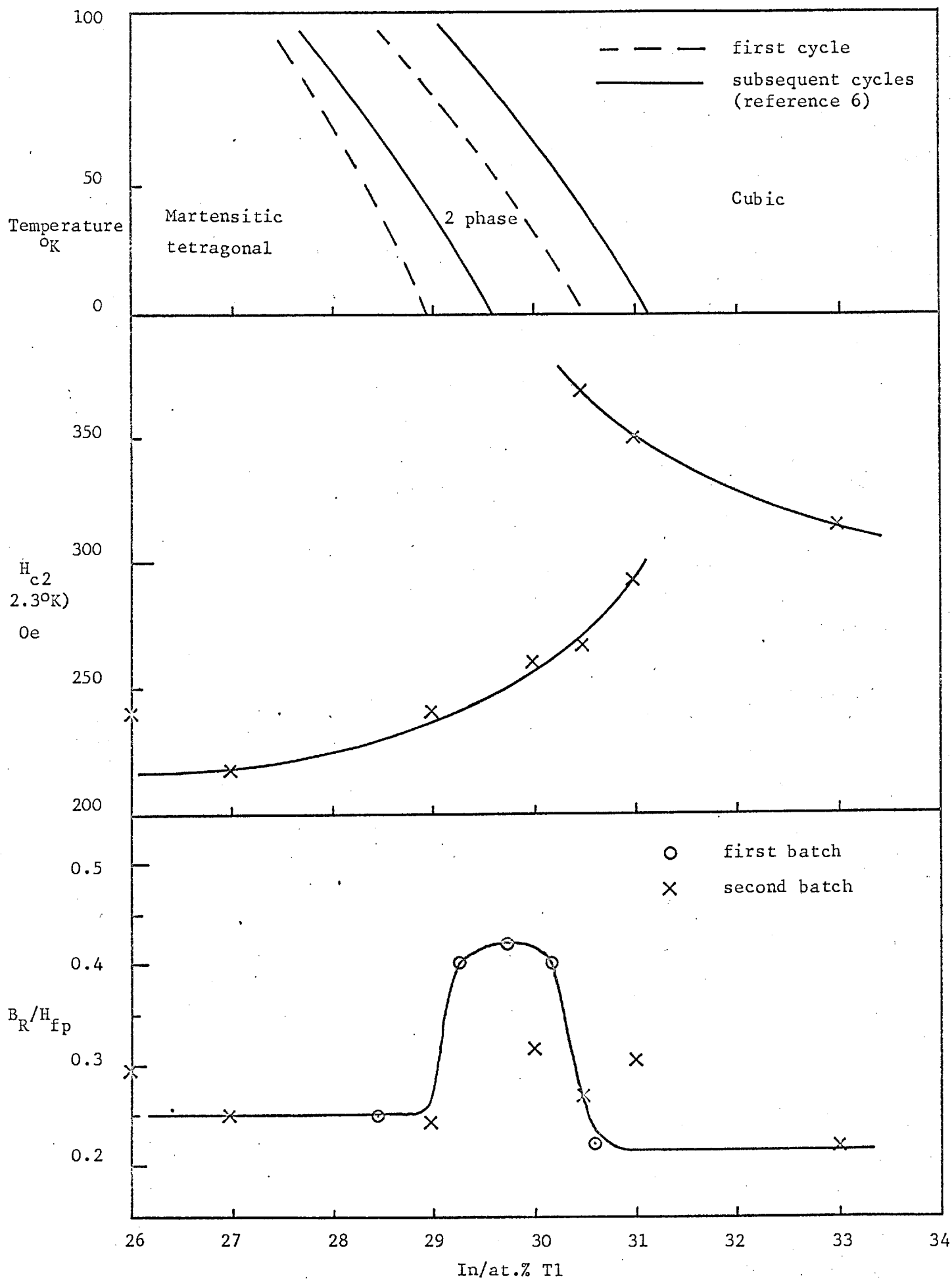
which it crosses the H axis. This procedure was also used for determining H_c in the presence of a surface sheath for the type I indium cadmium alloys.

Many alloys of indium thallium and indium cadmium were measured at at least two temperatures, and thus provided a test of the temperature independence of the pinning parameter. As may be seen from the results in table 5.1, B_R/H_{fp} does not vary by more than ± 0.01 which is of the order of the measuring accuracy. On the basis of these results, the In-Pb alloys were only measured at the single temperature of 4.2°K .

All the alloys used in the present study were extruded through the same die and acquired a series of longitudinal scratches, typically $0.05 - 0.1$ mm deep. It was thus not surprising to find that lightly scoring further longitudinal grooves with a razor blade caused no visible effect on the magnetisation curve of an In/13.5 Pb specimen. When, however, following the experiments of Jones and Park (4) described in section 2.3, a diamond pattern of grooves was overlaid on the longitudinal grooves, a marked decrease was observed in both the mixed state hysteresis and the surface sheath magnetisation above H_{c2} , as shown in figure 5.3a. This figure also shows, however, that no change occurs in any of the quantities B_R , H_{fp} or H_{c2} . A similar result was found after scoring a diamond pattern on the surface of an In/15Pb specimen (figure 5.3b), though in this alloy a small reduction in H_{fp} was found. The latter results in an increase of 0.02 in the value of B_R/H_{fp} . Since this variation is well within the experimental scatter of the results for these alloys (figure 5.6a), it is evident that the present criterion for measuring flux pinning is not significantly affected by the surface condition of these specimens.

A similar experiment was carried out on an In/2.1 Cd specimen to determine the origin of a "double hump" effect which was observed in the field decreasing portions of the essentially bulk reversible curves of In/2.1, In/2.5, In/3 and In/4 Cd. Figure 5.4 shows that lightly scoring circumferential grooves on the specimen surface accentuates the double hump but reduces the overall hysteresis. When the hemispherical ends of the specimen were cut off using a razor blade, the hysteresis

Figure 5.5 The compositional variation of B_R/H_{fp} , H_{c2} and the cubic/tetragonal phase boundaries in In-Tl.



is markedly increased, while the double hump is eliminated. This finding is in agreement with the general conclusions of Malseed and Rachinger (5) that, because of the large size of flux tubes in type 1 superconductors, compared to the small size of fluxoids in type 2 superconductors, geometrical effects caused by the sample shape are very important in determining the extent of the hysteresis. The double hump obtained in these curves is thus attributed to the particular sample shape used. It is important to note again, however, that these geometrical effects did not influence the value of B_R , H_{fp} or H_c .

5.22 Superconducting magnetisation measurements

5.22a Indium-thallium

Twelve alloys of indium-thallium were made in two batches of five and seven. After homogenisation they were slow cooled to room temperature and allowed to age for approximately one week before measurement. As discussed in the previous section, measurements on the first batch were made at several different temperatures to check that B_R/H_{fp} was not a function of temperature and measurements on the second batch were subsequently made at 2.3°K.

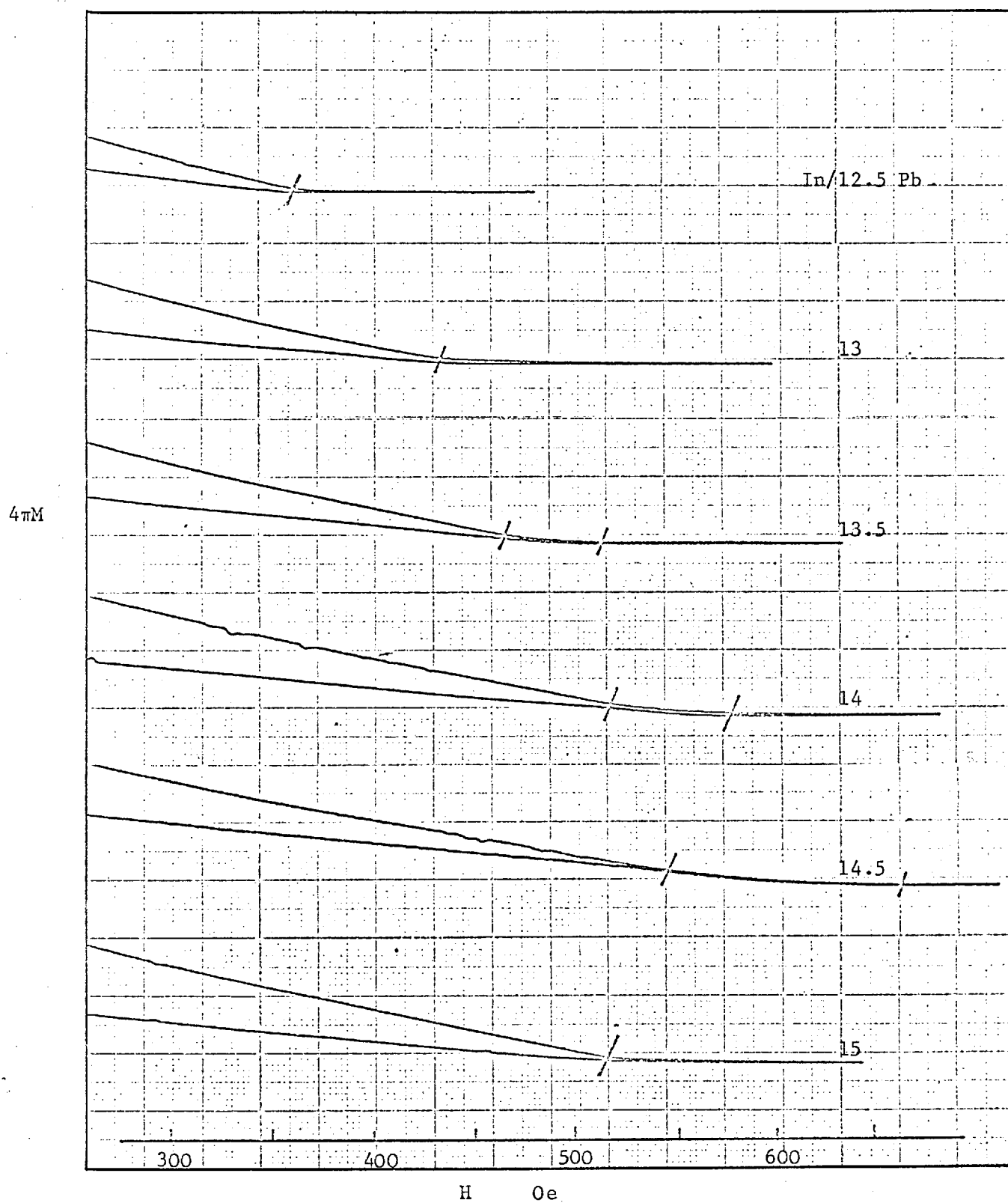
The magnetisation curves (see for example figure 5.1) obtained showed that all the alloys were type 2 superconductors. The values of B_R/H_{fp} vs. composition derived from the curves are plotted in figure 5.5a and show two features;

1) B_R/H_{fp} is constant within the single phase regions (which have been judged from the data of Pollock and King (6), plotted in figure 5.5c) but has a higher level in the martensitic tetragonal phase than in the untransformed cubic phase.

2) There is a pronounced peak in the two phase region.

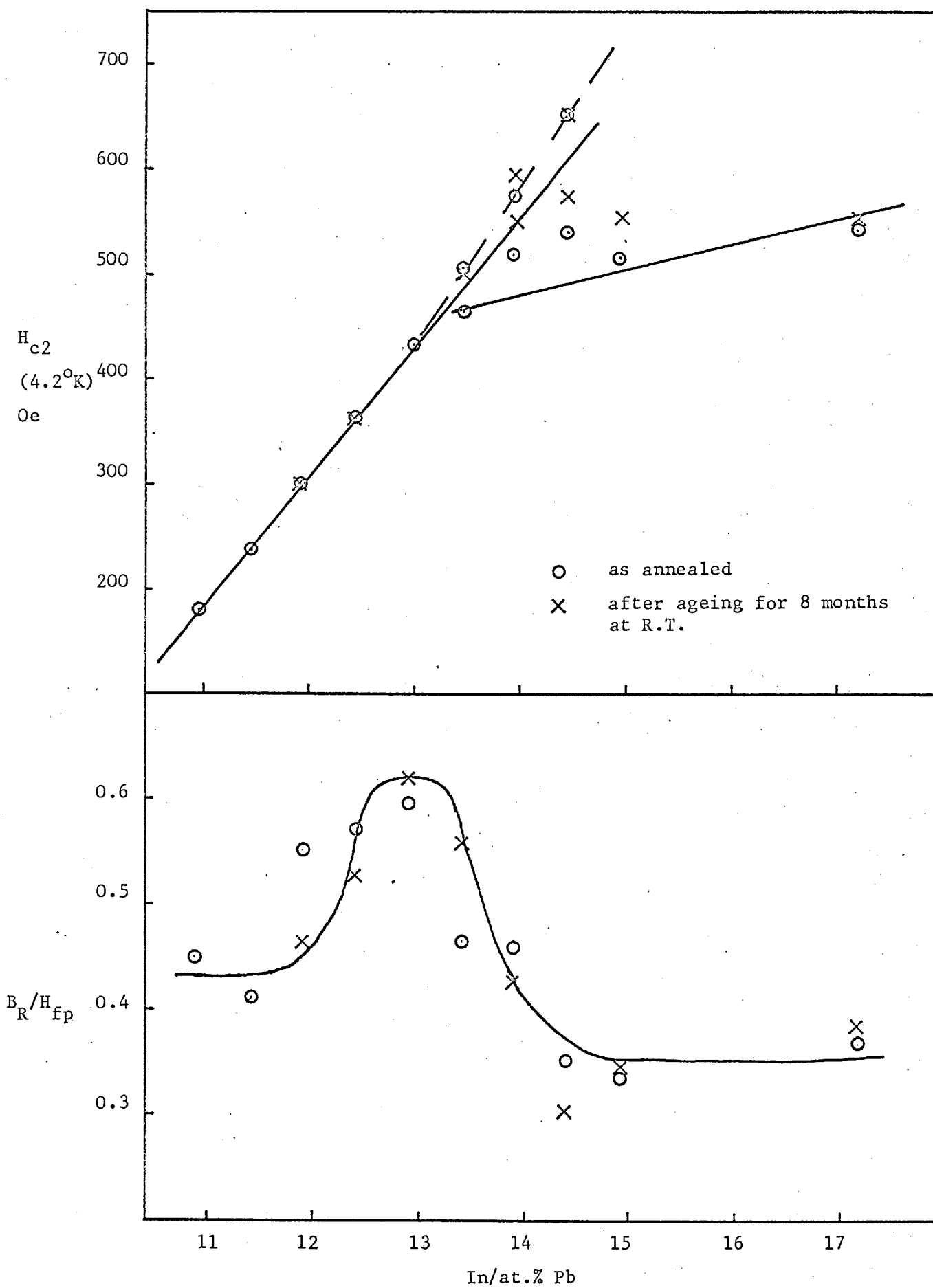
The H_{c2} values of the In-Tl alloys at 2.3°K are plotted against composition in figure 5.5b. When determining H_{c2} for the In/30.5 and In/31 Tl alloys, it was found that two bulk transitions could be

Figure 5.7 Double transitions at H_{c2} in In-Pb alloys near the partially transformed region.



Transitions at H_{c2} indicated by the diamagnet.

Figure 5.6 The compositional variation of B_R/H_{fp} and H_{c2} in In-Pb.



detected, as described for the In-Pb alloys in the next section. Both values are plotted in figure 5.5b. The resultant plots again show two significant features :

1) H_{c2} lies on a rising curve in the tetragonal phase and on an initially higher but decreasing curve in the cubic phase.

2) The slope of each curve is increased in the two phase region.

5.22b Indium-lead

Ten alloys of indium-lead were examined. As with the indium-thallium alloys, these were slow cooled after homogenising and allowed to stand at R.T. for a week before measurement. The magnetisation curves showed all the alloys studied to be type 2 superconductors.

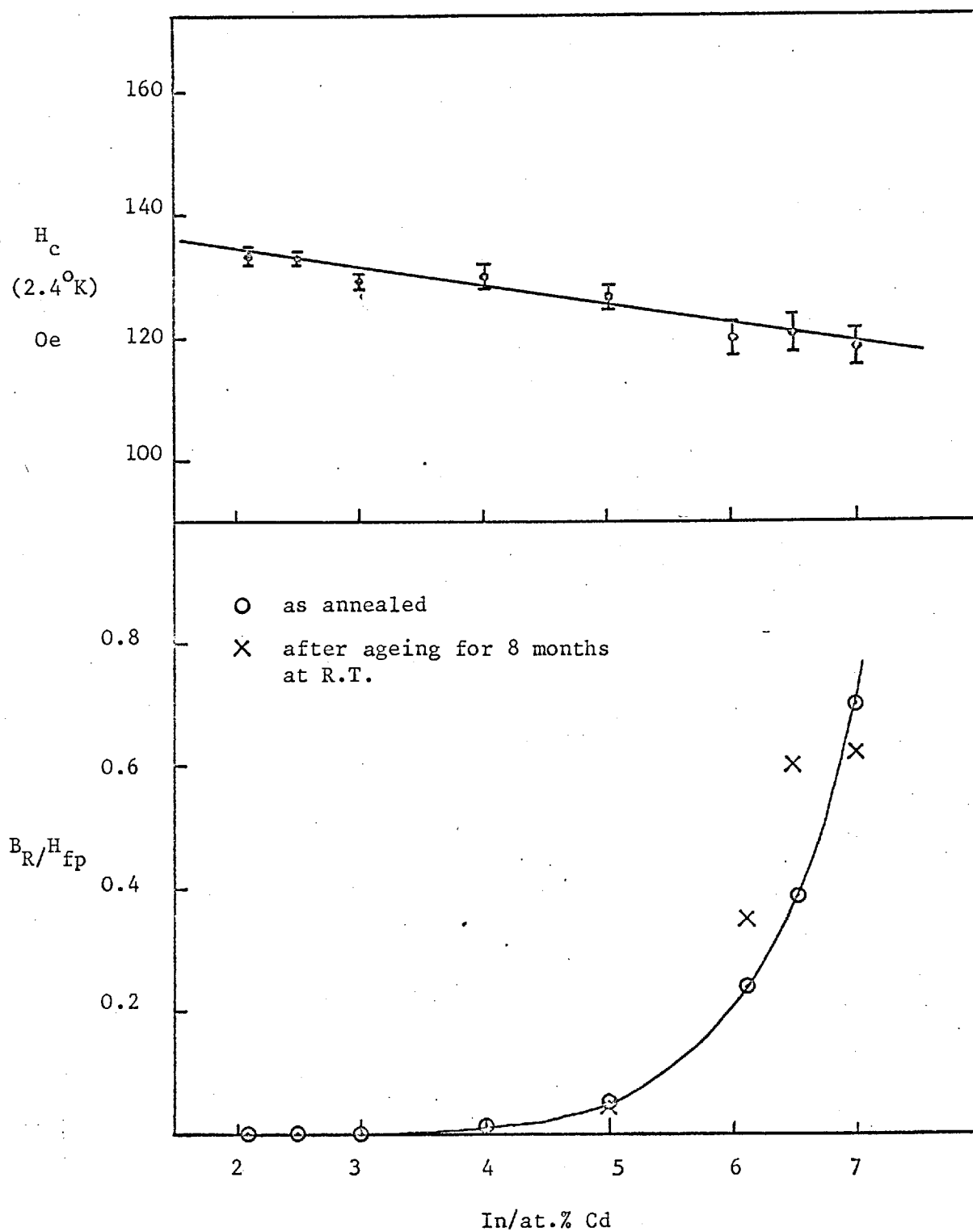
Values of B_R/H_{fp} vs. composition are plotted in figure 5.6a and again show two features :

1) There are two regions over which B_R/H_{fp} is effectively constant, the region below In/12 Pb having a higher value than that above In/15 Pb.

2) A pronounced peak appears in the region of In/13Pb.

Examination of a number of magnetisation curves of these alloys showed that between In/12.5 Pb and In/15 Pb the transitions at H_{c2} broadened and allowed two bulk transitions to be detected as may be seen from the high field portions of the magnetisation curves which are reproduced in figure 5.7. The curves of In/12.5 and In/13 Pb show a single characteristic bulk transition at H_{c2} before entering the sheath state. The In/13.5, In/14 Pb and In/14.5 Pb, while possessing this characteristic bulk transition, have a magnetisation which continues to decrease until it reaches zero at some higher field. Although the presence of surface sheath currents was observed in the magnetisation curves of these specimens, it is clear that this further decrease after a first bulk transition cannot be explained by sheath currents as these possess a paramagnetic moment in decreasing field, whereas the present curves are diamagnetic in this region in both increasing and decreasing field. This form of curve is consistent with the existence of bulk regions of the

Figure 5.8 The compositional variation of B_R/H_{fp} and H_{c2} in In-Cd.



specimen with differing values of H_{c2} and it is noteworthy that at In/15 Pb a single transition is again observed. Two values of H_{c2} were also derived in this way for the In/30.5 and In/31 Tl alloys.

The values of H_{c2} vs. composition are plotted in figure 5.6b and show three features :

- 1) At compositions up to In/13 Pb the H_{c2} values lie on a steeply rising (~ 135 Oe/at % Pb) linear plot.
- 2) At compositions beyond In/15 Pb H_{c2} appears to rise only gradually with increasing lead content.
- 3) At intermediate compositions two transitions are observed. The higher values lie on a steeper deviation from the first curve while the lower values are somewhat scattered but appear to conform to the shallower second plot.

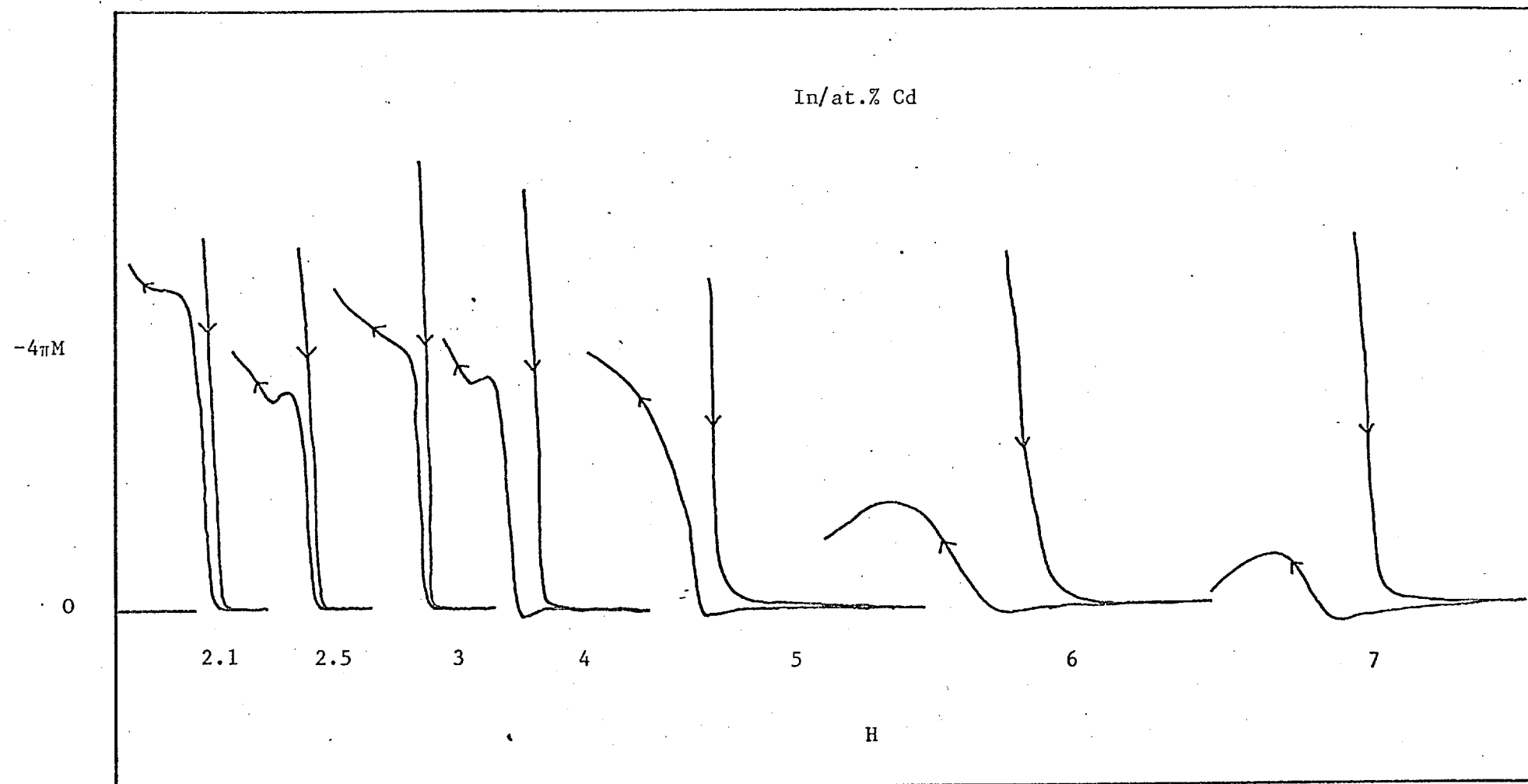
These magnetisation curves were remeasured after the samples had been aged for eight months at R.T. Although this treatment caused changes in individual values of B_R/H_{fp} , the general form of the plot was unaffected. The single values of H_{c2} were also unaffected but the lower of the double transitions show a consistent rise of about 40 Oe.

5.22c Indium-cadmium

The magnetic properties of eight alloys of indium-cadmium were investigated. Four of these, the In/5, 6, 6.5 and 7 at % Pb samples, were quenched directly from their homogenising temperature of 120°C into liquid nitrogen, so as to inhibit possible precipitation of the cadmium rich phase. After quenching, the specimens were rapidly inserted into the specimen holder and quickly cooled to the measuring temperature of $\sim 3.5^\circ\text{K}$.

Values of B_R/H_{fp} are shown in figure 5.8a. B_R was immeasurable for the three samples of In/2.1, In/2.5 and In/3 Cd, but, starting at In/4 Cd, B_R/H_{fp} rises smoothly and steeply, reaching a value of 0.62 at In/7 Cd. After ageing at room temperature for eight months, the alloys containing more than 6 at % Cd showed definite changes in B_R/H_{fp} , registering an

Figure 5.9 The appearance of a superconducting surface sheath in In-Cd alloys.



increase for the In/6 and In/6.5 Cd samples but a decrease for the In/7 Cd sample.

The values of H_c at 2.4°K vs. composition are plotted in figure 5.8b. This plot shows a general linear trend downwards at a rate of 3 Oe/at % Cd, i.e. a very shallow slope. There is no obvious deviation in this plot to correlate with the increase of B_R/H_{fp} observed in figure 5.8a. Examination of the magnetisation curves showed that all the In/Cd alloys were type 1 superconductors in the temperature range studied. Analysis of the portions of the curves near H_c shows, however, that a surface sheath appears on the curves at In/4 Cd, as may be seen from figure 5.9. The arrival of the sheath also coincides with an increase in the intermediate state hysteresis.

5.3 Discussion

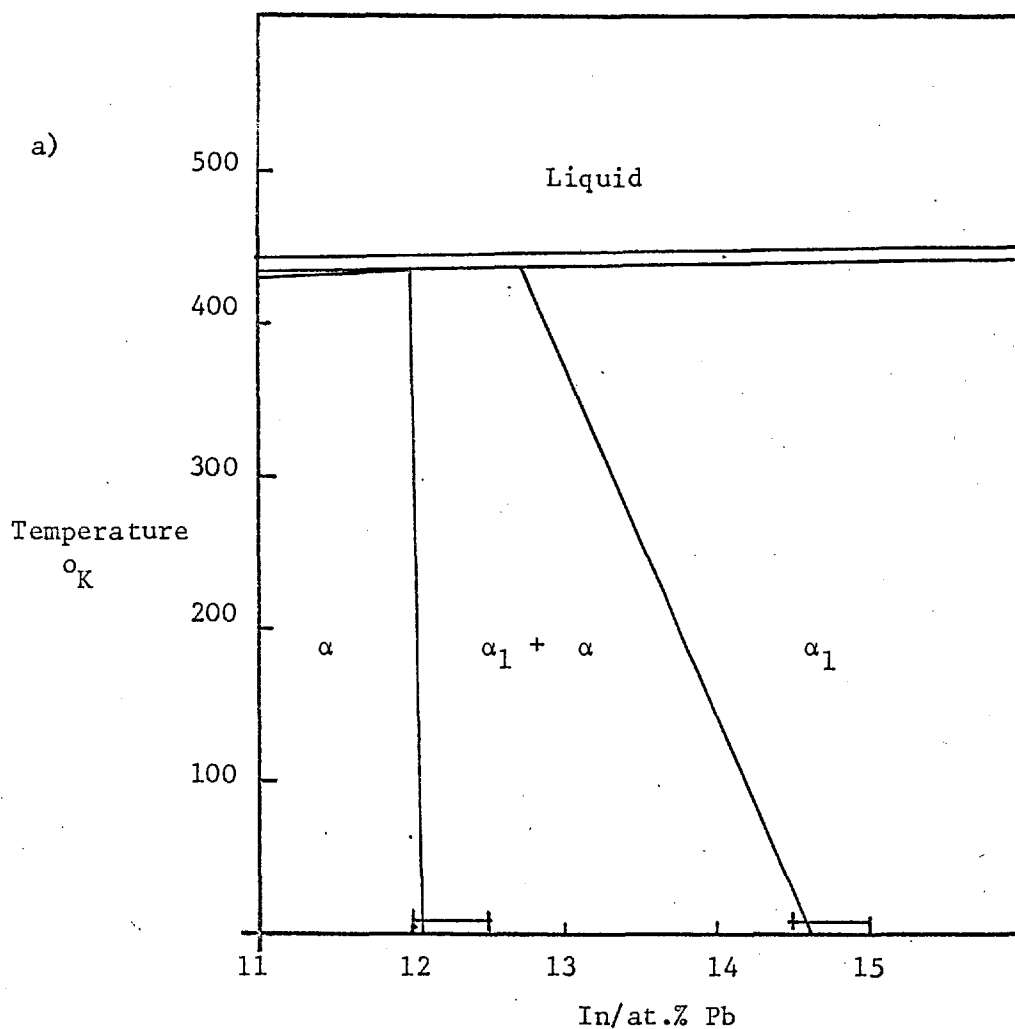
5.3.1 The low temperature phase boundaries

The experiments of Coles, Merriam and Fisk (7) in the indium-mercury system have demonstrated that the measurement of superconducting transition temperatures (T_c) can be used as an effective tool to establish the position of the phase boundaries in the solid state. This is because the T_c , like the lattice parameter, is generally a function of composition and, thus, in an equilibrium two phase region two constant values will be obtained. As discussed in section 3.22, Luo, Hagen and Merriam were unable to detect two distinct T_c values but used the criterion of transition breadth to place the position of the cubic/tetragonal or cubic/two phase boundary in In-Tl at 3°K . These measurements were later reinterpreted (9) in terms of a two phase cubic + tetragonal region using the magnetisation data of Livingston (10). Livingston did not, however, detect two transitions at H_{c2} , because he used a point by point ballistic magnetometer, and the nature of the two phase region was thus not confirmed until the low temperature metallographic studies of Pollock and King (6). The plot of $H_{c2}(2.3^\circ\text{K})$ obtained in the present work and shown in figure 5.3b has the same form as that of the plots of transition temperature obtained by Merriam et al (9) and by Pollock (11). This is to be expected since the critical fields H_c , H_{c1} and H_{c2} are related to T_c by the parabolic relation

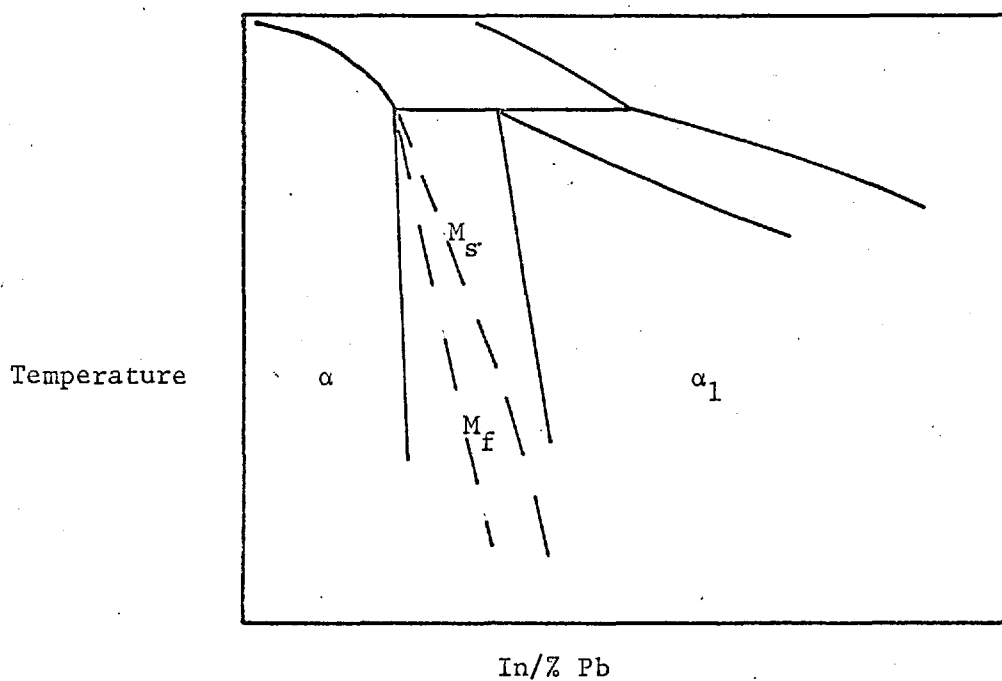
$h = 1 - t^2$ (equation 2.5). An advantage demonstrated by the present continuous recording magnetometer measurements is that two transitions, characteristic of the cubic and tetragonal phases, could be detected in the In/30.5 and In/31 Tl alloys. It is important to note, however, that the values of H_{c2} are not constant within the two phase alloys, but continue the trends established in the single phase regions with a further upward deviation, which may be attributed to the presence of internal stresses. It is therefore reasonable to assume that the composition of each phase varies continuously across the two phase region; i.e. that the Lever rule (figure 3.12) does not apply. This implies that the transformation must be martensitic in nature as is indeed confirmed by the low temperature metallographic results (6).

As discussed in the following section, the flux trapping properties of these alloys are relatively insensitive to composition within a given single phase region, but within the two phase region a pronounced increase in flux trapping is to be expected. The variation of B_R/H_{fp} vs. composition may thus be used as a further indication of the position of the phase boundaries at low temperatures. In In-Tl then, the steep increase of B_R/H_{fp} enables the tetragonal/cubic + tetragonal boundary to be fixed between 29 and 29.3 at % Tl. There is some experimental scatter in the values around In/31 Tl as the steep descent of the curve suggests the boundary to lie at In/30.5 Tl while the magnetisation curves show two transitions at H_{c2} for In/31 Tl. The behaviour of In/33 Tl is typical of a cubic alloy but in the absence of intermediate values, the cubic/tetragonal + cubic boundary cannot be fixed precisely. It is likely, however, to lie in the region of In/31.5 Tl. The position of the two phase region as determined by the transition temperature measurements of Merriam et al (9) was In/30.1 - 31.7 $\pm$ 0.4 Tl while the metallographic investigation gave reproducible boundaries (on cycling backwards and forwards through M_s and A_f) of In/29.25 - In/31.25 Tl. The present results are thus clearly in general agreement with these investigations. The small discrepancies between them may well be explained by the nature of the martensitic transformation itself, which is sensitive to small differences in internal stresses, grain size and the number and form of nucleation sites.

Figure 5.10 Realisation diagram for the $\alpha_1 \rightarrow \alpha$ transformation in In-Pb



b) Suggested relation between equilibrium and realisation boundaries.



5.31b Indium-lead

Examination of the data obtained for indium-lead, given in figure 5.6, shows similar behaviour to that of indium-thallium. For instance, the values of H_{c2} fall on two general trends which belong to the indium solid solution (α) and to the intermediate solid solution (α_1), respectively. Two separate values of H_{c2} can again be detected for alloys with compositions for which B_R/H_{fp} shows a pronounced increase. Furthermore the variation of H_{c2} with composition in this two phase region is consistent with the martensitic nature of the transformation, which has previously been established above room temperature (12).

The position of the low temperature phase boundaries may now be determined as for indium-thallium, using both the variation of H_{c2} and B_R/H_{fp} with composition. The In/13.5/14/14.5 Pb alloys are definitely two phase, since two values of H_{c2} can be detected. B_R/H_{fp} declines to its base line value of ~ 0.35 in the region of In/14.5 Pb and thus since the H_{c2} transition of In/15 Pb is quite sharp, the $(\alpha + \alpha_1) / \alpha_1$ phase boundary is placed between In/14.5 and In/15 Pb. Similarly, at lower lead contents B_R/H_{fp} rises above its baseline value of ~ 0.44 at between In/12 and In/12.5 Pb and the phase boundary $\alpha / (\alpha + \alpha_1)$ is therefore placed between these two compositions.

The positions derived for the low temperature phase boundaries are shown in figure 5.10a, together with the previous high temperature data of Raynor and Graham (figure 3.16) to give a composite realisation diagram for the indium-lead system. It is seen that the steepness of the $\alpha / \alpha + \alpha_1$ boundary precludes a complete transformation from α_1 to α on continuous cooling and the 100% α alloys were thus formed from the melt. However, the significance of the boundaries drawn by Raynor and Graham for the region close to the solidus is unclear, as they appear to suggest that only alloys with greater than In/12.75 Pb transform martensitically on cooling, whereas the present variation of B_R/H_{fp} suggests that all alloys above In/12 Pb do so. It is interesting to note that Heumann and Predel (13) have found a peritectic reaction between 10.3 and 12.7 at % Pb at 159°C , but unfortunately they did not study the solid state phase boundaries. In view of these inconsistencies a possible form of the M_s curve for these alloys is

shown in figure 5.10b. It should be emphasized, though, that this curve is speculative and that further high and low temperature metallography should be carried out in order to establish the diagram unambiguously.

5.31c Indium-cadmium

Figure 5.8b shows that the plot of H_c (2.4°K) for indium-cadmium decreases linearly with composition up to 7 at % Cd. This is in general agreement with the transition temperature measurements of Merriam (14), reproduced in figure 3.21, which also show a linear decline of T_c with composition over the range In/2 to In/6 Cd. At compositions above In/6 Cd, Merriam reports significantly increased values of T_c , which he attributes to the presence of the cubic phase, α_K . The fact, therefore, that only one transition at H_c was observed in the present magnetisation work, is good evidence for the conclusion that all the present alloys were tetragonal at 2.4°K .

The phase diagram proposed by Heumann and Predel has already been shown in figures 3.17 and 3.18. An important feature of this diagram is the occurrence of a peritectic horizontal at 148°C in the neighbourhood of the indicated two phase $\alpha_T + \alpha_K$ region. A careful study of their paper shows, however, that this two phase region is not a conventional one, since it is bounded on the indium-rich side by the M_s curve obtained on continuous cooling and, on the cadmium-rich side by the finish of the reverse transformation on heating. While the authors comment that these M_s and A_f points fit in well with the peritectic, no direct measurements were made within 25°C of the peritectic temperature. They also propose a eutectoidal decomposition at 20°C and In/6 Cd on the basis of an extrapolation of the A_f curve to the Cd-rich boundary of the cubic phase. Some cadmium precipitation was indeed observed after ageing for long periods at room temperature in the present In/6, In/6.5 and In/7 Cd alloys, while the superconducting measurements indicate that the alloys are tetragonal rather than cubic at low temperatures. No precipitation was, however, found in the lower Cd alloys and evidently the cooling rates employed in the present work were sufficient to suppress any such eutectoid transformation, the alloys passing through an extrapolation of the M_s . The presence of some cadmium precipitation will, of course,

displace the composition of the indium solid solution slightly to higher indium contents but will not affect the general interpretation.

The thermodynamic significance of a eutectoid, which is formed from an extrapolation of the realisation boundaries of a diffusionless transformation is, in any case, not clear and it must be concluded that the breakdown of the tetragonal indium solid solutions still has a number of unexplained aspects. The major question is, of course, why does a transformation proceed by martensitic shear at temperatures close to the melting point when the thermal energy is high? The presence of a peritectic horizontal in In-Pb and In-Cd (and also in In-Hg (7) and In/Sn (15)) suggests that the reaction can proceed by diffusion. Further measurements just below the peritectic, possibly with long anneals in the two phase region, would be extremely useful in clarifying this point. This treatment would be particularly interesting for In-Tl, which has received considerable attention from nearly every other aspect, (see section 3.21) but for which no peritectic appears to have been established (16).

5.32 Flux pinning in indium-thallium and indium-lead

Flux pinning by internal defects has been previously discussed in section 2.3. We now wish to discuss the flux pinning measurements obtained in the present work in terms of the internal defects existing within the present alloys. To do this it is convenient to consider the alloys of indium-cadmium separately from those of indium-thallium and indium-lead, since the work already described has indicated that no partially transformed In-Cd alloys were obtained and all the specimens were found to be type 1 superconductors.

5.32a Identification of flux pinning centres

Analysis of the results for In-Tl and In-Pb is aided if the alloys are considered under three headings :

(i) Single phase, untransformed alloys

These comprise the f.c.c. alloy In/33 Tl, the tetragonal α phase

alloys In/11 - In/12 Pb and the tetragonal α_1 alloys In/15 and In/17.25 Pb. Each of these alloys was melted from high purity materials (> 5 9's purity) and annealed at greater than $0.95 T_M$, prior to measurement. Their principal internal defects are therefore considered to be grain boundaries and a relatively low density of dislocations.

The fluxoid-dislocation interaction has been discussed in section 2.33 but the details of the fluxoid-grain boundary interaction are rather more obscure. Due to their small effective width of 2 or 3 atoms in well-annealed material (17), grain boundaries are not expected to trap flux effectively, except in materials with a very small coherence length (say V_3Ga with $\xi = 50 \text{ \AA}$ (18)). In practise, however, bulk reversible magnetisation curves of well-annealed single phase crystals are very seldom reported and a number of workers have reported B_R as an inverse function of grain size (19, 20). It is probable that this flux trapping occurs either by preferential segregation of impurities or because the given mechanical treatments required for controlling the grain size may also influence the resultant dislocation density. An estimate of the coherence length of the present samples (based on a weighted mean of the penetration depths in pure In and Tl (21) and the κ values of the magnetisation curves) gives $\xi = 500 - 1000 \text{ \AA}$. This would appear to rule out grain boundaries as major sources of flux pinning. It may well be, however, that normal handling procedures prior to measurement of these soft materials introduce defect arrays which cannot anneal out in the short time before cooling to liquid helium temperatures. Whatever the true cause, the remanent inductions observed in the present work are typical of those reported by other workers for alloys of Pb-In (22), Sn-In (4) and Pb-Bi (5, 23).

(ii) Single phase martensitic alloys

Since the transformation in In-Pb does not go to completion (section 5.31) the only fully martensitic alloys obtained were the indium-thallium alloys with less than 29 at % Tl. In addition to the presence of dislocations and grain boundaries, these alloys contain coherent twin boundaries associated with the martensite. In these banded martensites (as opposed to the lenticular type) the main martensite bands have a twin relationship to each other and are themselves also sub-divided by

internal twins. Because these coherent boundaries separate two identical crystal structures across a common plane, the interfacial stress field will be very small (~ 2.5 ergs/cm for an In/20.75 Tl single crystal (24)). Thus even though van Gorp (25) has shown that these boundaries can form a significant barrier to flux motion in a transformed single crystal, when the interfaces are parallel to the fluxoids, in a randomly oriented polycrystal the effect will be averaged out and the additional flux pinning may be quite small.

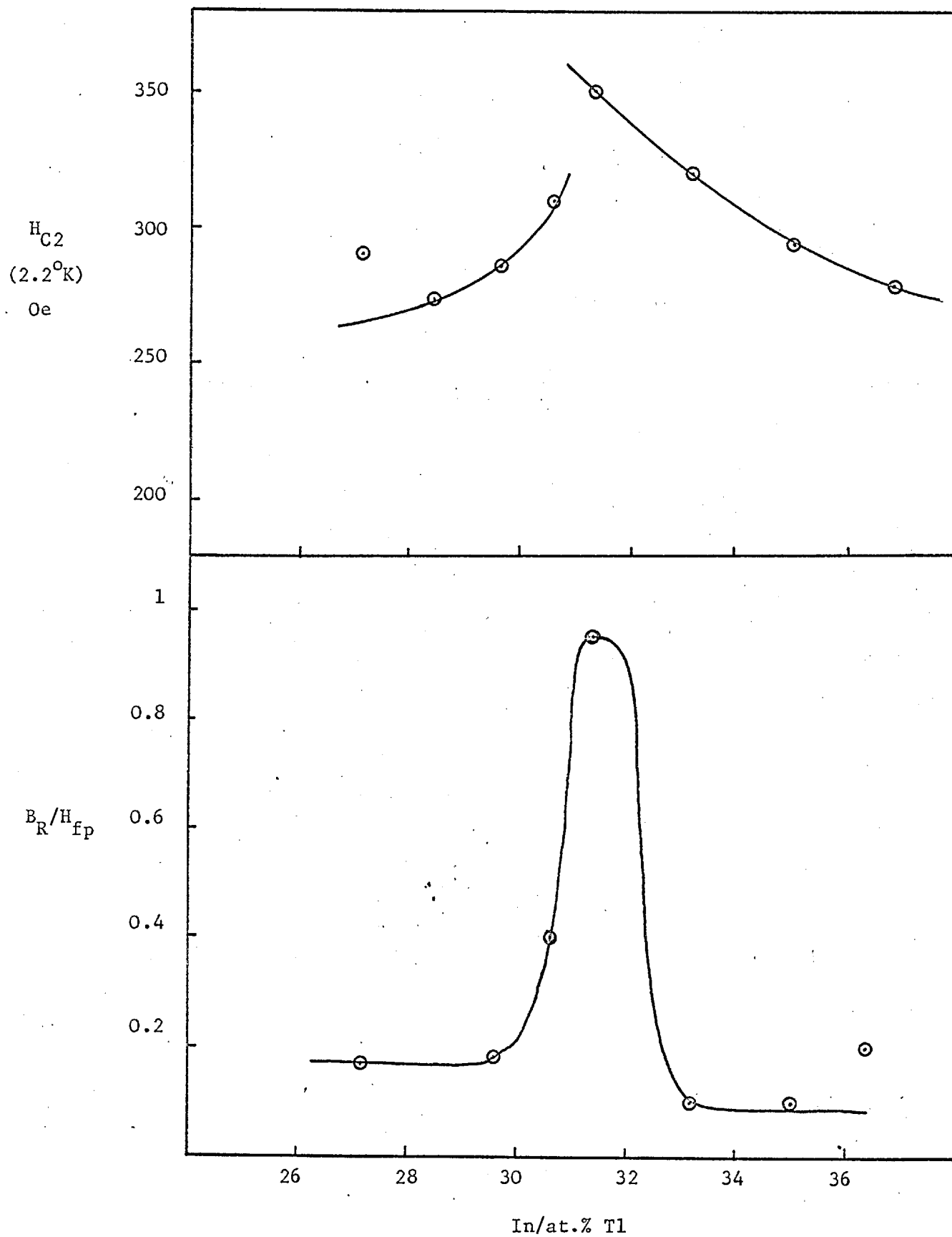
(iii) Partially transformed alloys

The partially transformed alloys of In-Tl and In-Pb (In/29 - 31 Tl, In/12.5 - 14.5 Pb inclusive) contain not only the microstructural features of (i) and (ii) but also further coherent boundaries which separate the martensitic and parent phase regions. The stresses associated with these boundaries are considerably greater than those discussed in (ii) above, because of the mismatch between the two crystal structures, and their flux trapping properties will therefore be increased. In addition the boundary separates two regions of different superconducting properties so that the flux line energy varies between the two phases and there will also be a surface barrier to the free movement of flux across the interface.

5.32b The effectiveness of the pinning centres

Absolute calculations of the magnitude of the various pinning effects outlined above still present some considerable mathematical problems when applied to the total hysteresis observed in a weak pinning sample. Campbell et al (26) were able to get good agreement for the very strong pinning ($B_R > 20 H_{cl}$) observed in the Pb-Bi eutectic by considering only a surface barrier of the sort proposed by Bean and Livingston (section 2.32) which opposes the free movement of fluxoids across the boundary between the superconducting ϵ phase and the normal Bi particles. It was thus found possible to ignore the effects of a dislocation cell structure, the presence of grain boundaries and the consequent changes in the line energy of the fluxoids. In the weak pinning situation found in the present work, where B_R is $< H_{cl}$, such a calculation is not possible, but the relative importance of the different

Figure 5.11 The compositional variation of B_R/H_{fp} and H_{C2} for In-Tl after Livingston (10).



pinning centres can still be estimated. It can be assumed that there is a basic pinning present in all the specimens due to the dislocation structures and/or grain boundaries discussed above. In addition, for the fully martensitic alloys of In/Tl, there should be an extra small pinning due to the presence of twin boundaries. It can indeed be seen from figure 5.5a that the baseline value of B_R/H_{fp} in the transformed tetragonal phase is a little higher than that in the cubic phase (~ 0.25 vs. ~ 0.22). This difference may be relatively underestimated, however, since there is a discontinuous increase in κ on going from the tetragonal to the cubic phase (κ (f.c.t.) In/27 Tl ≈ 1.1 vs. κ (f.c.c.) In/33 Tl ≈ 1.5). In the absence of any microstructural differences, an increase in structure sensitivity for the higher κ sample would be expected since ξ is decreasing. This is confirmed when the values for In-Pb are examined. In this case both the α and α_1 phases have similar microstructures and the change in κ is similar but opposite to that obtained in In/Tl (κ In/11 Pb ≈ 1.5 vs. κ In/15 Pb ≈ 1.1). As expected, it is seen from figure 5.6a that B_R/H_{fp} in the α phase is somewhat higher than in the α_1 phase (~ 0.42 vs. ~ 0.35).

Since the κ values of the two phases in each system are similar, it is to be expected, therefore, that the pinning caused by a variation of superconducting properties will be the same in each case. It can be seen, however, that the increased pinning in the two phase region is $\sim 100\%$ for In-Tl but only $\sim 50\%$ for In-Pb, when the phase with $\kappa = 1.5$ is taken as the baseline in each case. The X-ray measurements of Raynor and Graham (12) and Moore et al (27) have shown that the volume difference between the two phases in In-Tl is 0.5%, whereas in In-Pb it is only 0.15%. It thus seems likely that the greater pinning observed in In-Tl is to be attributed to an elastic interaction between fluxoids and the larger stress field of the coherent parent-product interface.

This conclusion is supported when the previously described magnetisation curves of Livingston (10) (figure 3.24) are analysed for their variation of H_{c2} and B_R/H_{fp} with composition. The change of shape in the magnetisation curves of the In/30.6 and In/31.4 Tl samples was not duplicated in the present work, although it is clear from the plots of B_R/H_{fp} and H_{c2} in figure 5.11 that these effects can be associated with a two phase cubic/tetragonal structure. These differences could arise either from preferred orientation effects in Livingston's alloys (the

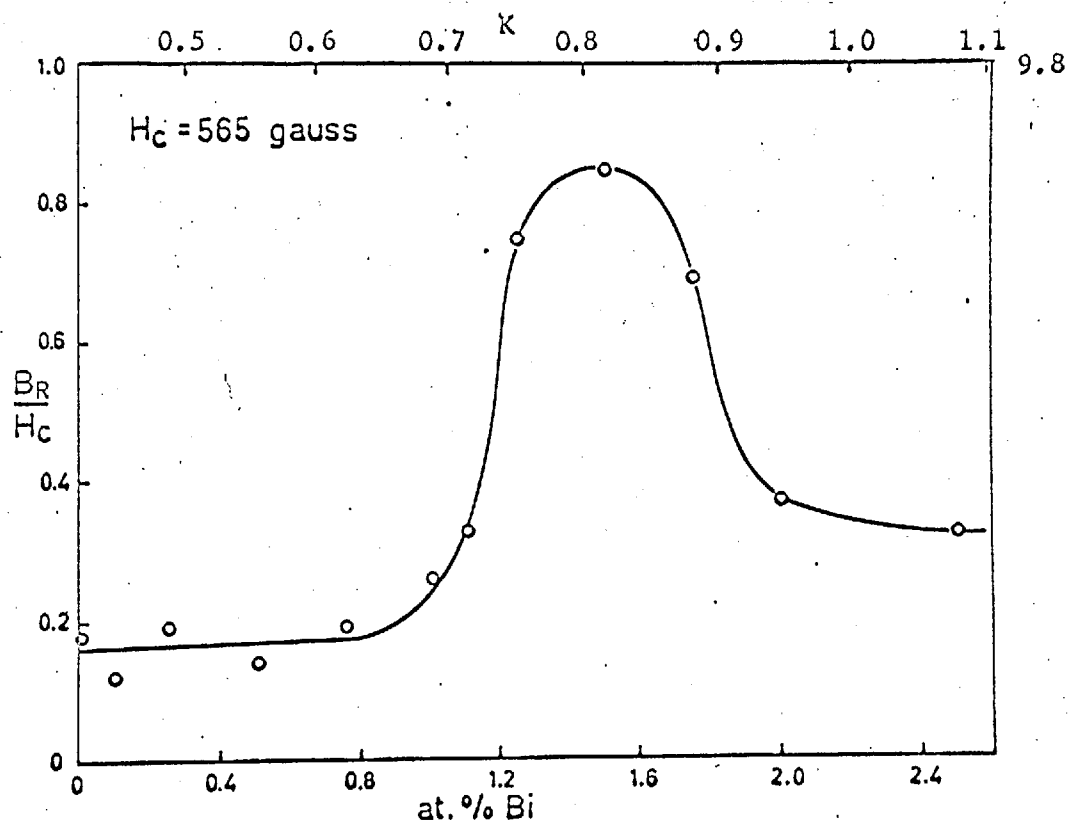
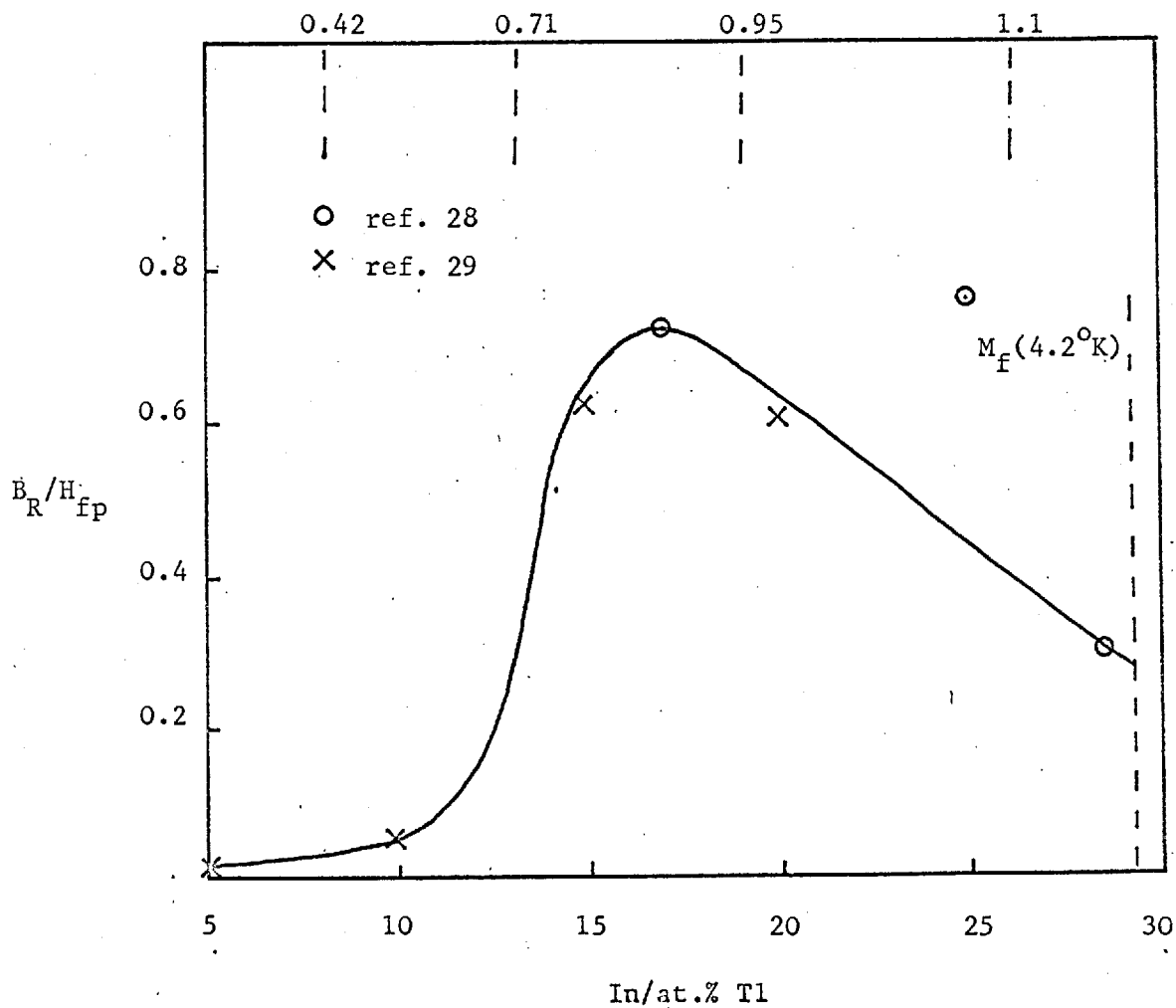


Figure 5.12 The variation of B_R/H_{fp} with κ value
Ginzburg-Landau parameter κ



present alloys had an equi-axed grain structure, 0.2 - 0.4 mm in diameter) or perhaps from nucleation of the martensite at a larger number of sites. It is obvious from the general considerations of section 2.33 that maximum flux trapping will occur when the whole sample is divided into a two phase cubic-tetragonal structure on a scale between ξ and λ and, in a martensitic transformation, the number and distribution of nuclei are expected to be very sensitive to the precise metallurgical state of the specimen. Small differences in handling which can significantly alter the nucleation conditions may thus cause large differences in such structure sensitive properties as the magnetisation, but since no details of the specimen preparation or treatment are given by Livingston, this point cannot be pursued in any detail. Nevertheless, it is clear that the present results are in general agreement with those reported by him.

5.32c Anomalous pinning at lower Tl contents in In-Tl

A feature noted in the review of the literature in section 3.22 was an apparent anomaly in the flux trapping properties of In-Tl alloys with Tl contents lower than those studied in the present work. Thus Love et al (28) found greater flux trapping in the alloys of In/15 and In/20 Tl than in their In/28.5 Tl alloy and Livingston (10) has noted that the flux trapping properties of the alloys round In/28 Tl are low. Similar results are obtained when the magnetisation curves of Stout and Guttman (29) are examined. Van Gorp (25) did not reproduce a magnetisation curve for his In/20 Tl single crystal but noted that it was hysteretic. Values of B_R/H_{fp} have thus been derived from this previous work and are shown plotted against composition in figure 5.12. This plot shows a steep rise in the region of In/14 Tl, reaching a peak at $\sim$ In/17 Tl. Beyond this composition, in spite of the high value at In/25 Tl, there is a more gradual decline to the low value of B_R/H_{fp} found at In/28.5 Tl which is close to the limit of the single phase field. It can be seen from the realisation diagram (figure 3.11) that beyond $\sim$ In/15 Tl all the alloys have transformed to the tetragonal structure martensitically which could account for at least part of the steep rise in B_R/H_{fp} . As the M_s is depressed below $\sim 0.5 T_m$ (at $\sim$ In/26 Tl), however, the strains involved in the transformation increase as they can no longer be continuously relieved but it can be seen that B_R/H_{fp} continues to decline.

It is believed that the explanation for this behaviour lies primarily in the variation of κ with composition. Values of κ have been estimated from the change from type 1 superconductivity without a surface sheath to type 1 behaviour with a sheath ($\kappa = 0.42$) and from the change to type 2 superconductivity ($\kappa = 0.71$). In addition the values quoted by van Gorp (25) and those found in the present work have been added to figure 5.12, which shows that κ varies only gradually with composition and that the broad peak at $\sim \text{In}/14$ to $\text{In}/22$ Tl corresponds to κ values of ~ 0.7 to 0.95 .

A similar peak has been found by Malseed and Rachinger (5) in single phase alloys of Pb with up to 2.5 at % Bi where κ varies from ~ 0.4 to 1.1 . Their results in figure 5.13 also show a marked increase in flux trapping for κ values between 0.7 to 0.95 , that is over the same region as found in the present work. The origin of this peak was considered to arise from two causes. The initial increase in B_R/H_c occurs as κ rises towards 0.71 with consequent reductions in the positive surface energy of the flux tubes and their equilibrium size. Smaller pinning forces are then needed to trap flux tubes and B_R rises. The decline of B_R/H_c at κ values greater than 0.71 has been discussed by Kramer (30), who has shown that the sum of the core and kinetic energies of a flux line varies with κ so as to cause attractive interactions at $\kappa < 0.71$ and repulsive interactions at > 0.71 . Near this value, the inter-flux line forces are very small, and the lines are easily captured by pinning sites. The finite breadth of the peak observed by Malseed and Rachinger thus results from a particular combination of pinning forces and inter-fluxoid interactions.

In the In-Tl system the breadth of the peak of B_R/H_{fp} can also be associated with the critical composition ($\sim \text{In}/16$ Tl) at which the tetragonal phase first forms martensitically. The shallow decline at compositions above $\sim \text{In}/22$ Tl then results from the competing effects of stronger inter-fluxoid interactions on the one hand and a greater unrelieved strain energy on the other. The enhanced values of J_c observed by van Gorp (25) in $\text{In}/20$ Tl thus lie in the composition range where the flux pinning mechanism is in transition. It would therefore be of interest to repeat this experiment with an alloy of higher Tl content, say $\text{In}/26$ -

28 Tl where κ is in the region of 1.1.

5.33 Flux pinning in indium-cadmium

As discussed in section 5.22c all the present In-Cd alloys are considered to be tetragonal at the measuring temperature of 2.4°K , so that they do not therefore span any two phase region of the type found in In-Tl or In-Pb. A further reason for considering the In-Cd alloys separately, is the complication introduced by precipitation of cadmium-rich phase in the alloys containing more than 6 at % Cd.

The flux pinning properties of these alloys are therefore expected to be more complex than those of In-Tl and In-Pb and, in addition, since it was also found that the In/4 Cd alloy had a κ value in the region of 0.42, a rise in the flux trapping properties at greater Cd contents is to be expected, even in the absence of new microstructural pinning centres. This κ -dependent hysteresis has already been discussed in the previous section. We therefore identify four flux-trapping situations :

(i) The alloys of In/2 - In/3 Cd have well annealed single-phase tetragonal structures and their principal internal defects are likely to be dislocations and grain boundaries.

(ii) The alloys of In/4 to In/7 Cd are fully martensitic according to the phase diagram of Heumann and Predel (31) and will thus contain many coherent twin boundaries.

(iii) Precipitation was observed in the In/6, 6.5 and 7 Cd samples after ageing for some months at R.T. This precipitation was small in extent and occurred principally in the grain boundaries. The new pinning centres introduced by this precipitation may well therefore act as a special case of enhanced grain boundary pinning.

(iv) Above about In/6 Cd where κ is in the region of 0.6, κ dependent pinning will increase strongly. This may be modified somewhat by the effect of Cd precipitation which will have the effect of reducing the Cd-content of the matrix, though such reduction is not evident from the linear plot of H_c with composition in figure 5.8b.

Turning now to the plot of B_R/H_{fp} vs. composition in figure 5.8a, it can be seen that B_R was not measurable for the alloys of In/2 - 3 Cd and

it is thus clear that at these low κ values (< 0.4), the presence of dislocations and grain boundaries does not lead to flux trapping. Small values of B_R/H_{fp} are registered for the In/4 and In/5 Cd samples which are expected to contain twin boundaries. On remeasuring the In/5 Cd sample after ageing at R.T. no change in B_R/H_{fp} was found, indicating that quenching strains introduced by the initial quench to 77°K did not enhance flux trapping and metallographic observation at R.T. confirmed that no precipitation had occurred in the alloy.

The alloys of In/6. 6.5 and 7 Cd were also quenched initially to 77°K, to inhibit Cd precipitation, and then remeasured after ageing for 8 months at R.T. The values obtained from the initial quench fall on the smoothly increasing curve drawn in figure 5.8a but, after ageing small changes were observed which indicated a somewhat steeper slope in B_R/H_{fp} with a flattening off after In/6.5 Cd.

It is likely therefore that the steep rise in B_R/H_{fp} beyond In/5 Cd is due to two causes. The first of these is the general increase in structure sensitivity as κ increases. Superimposed on this will be the effect of Cd precipitation in the grain boundaries. This is effective on two accounts, since the Cd particles are normal above 0.5°K (32) and the surface area/volume ratio within the grain boundaries is high.

An uncertainty which the present measurements answer is the nature of the change reported by Chiou et al (33) in the region of In/3.5 $\pm$ 0.5 Cd. Their conclusion was that the broadening of resistive transitions at this composition indicated the onset of type 2 superconductivity. The present measurements, shown in figure 5.9, indicate that the change is, however, that from a type 1 superconductor without a surface sheath at In/3 Cd to one with a surface sheath at In/4 Cd. The critical composition of In/3.5 $\pm$ 0.5, therefore, corresponds to the critical κ value of 0.42 (section 2.24e).

5.4 Conclusions and suggestions for future work

5.41 Conclusions

(i) The compositional dependence of the parameters B_R/H_{fp} and H_{c2} was used to establish the low temperature limits of the two phase region, giving values of In/29.2 to In/31.5 Tl at 2.3°K and In/12.25 to In/14.75 Pb at 4.2°K, respectively. The metastable tetragonal solid solution in In-Cd was found to extend at least to In/7 Cd at 2.4°K.

(ii) An increase in the degree of flux pinning was found in alloys of In-Tl and In-Pb which were only partially transformed to the martensitic structure at liquid helium temperatures. This pinning is attributed to the existence of a stress field at the coherent interface between the transformed and untransformed regions and to the κ difference between the two phases across this boundary.

(iii) In the In-Cd system a steep rise in the flux pinning between In/5 and In/7 Cd was observed. This could not be attributed solely to the presence of twin boundaries in the martensitic phase since a normal precipitate of Cd-rich phase occurred in the alloys beyond In/6 Cd. A superconducting surface sheath, corresponding to $\kappa = 0.42$, was observed to appear at between In/3 and In/4 Cd.

5.42 Suggestions for future work

(i) The thermodynamic significance of the peritectic horizontals reported in the region of the martensitic phase transformation for In-Pb and In-Cd is not clear. Differential thermal analysis of alloys solidified from the melt, followed by X-ray and resistivity measurements in the solid state would be extremely useful in investigating the relationship between the M_s and the peritectic. This would be particularly interesting in the region immediately under the peritectic and in In-Tl for which a peritectic has not yet been established.

(ii) The interaction between fluxoids and twin boundaries in a fully martensitic alloy of In-Tl has been examined by van Gorp.

An analysis of flux trapping in previous work shows, however, that the values of J_c obtained by van Gurp may be anomalously high since the alloy used lies in the type 1/type 2 changeover region. This interaction should therefore be re-examined with a single crystal of higher thallium content of say In/28 Tl. The pinning effects of grain boundaries are also not fully explained and it would therefore be useful to investigate the orientation dependence of J_c of bi-crystals in a magnetic field. In the fully transformed alloys of In-Tl these two experiments could be combined in the same alloy so as to allow a comparative study of the effects of twin and grain boundaries.

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31. T. Heumann, B. Predel Z. Metallk. 53, 240 (1962)
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CHAPTER 6

THE LOW TEMPERATURE MAGNETIC PROPERTIES OF AUSTENITIC

IRON-CHROMIUM-NICKEL STAINLESS STEELS

6.1 Introduction

The reason for the present interest in the low temperature magnetic properties of the austenitic stainless steels has been alluded to in the introductory chapter and discussed in some detail in Appendix 1. In the initial stages of the work four steels, types 304L, 321, 347 and 310, were examined, the interest being practical and precautionary with a view to their use in the manufacture of a solenoid former. From this study it became clear that none of these was suitable for this application. Following a discussion of these findings at a special session on cryogenic materials at the 1969 Spring Meeting of the Institute of Metals, it became apparent that, apart from the work of Reed and Mikesell (1), little was known about the low temperature magnetic properties of these steels in spite of their widespread use at cryogenic temperatures. The general opinion, however, was that the higher nickel alloys, such as Incoloy 800, should be completely stable against martensitic decomposition(2). It was also revealed at this meeting that the high nitrogen versions of 304 and 316L (hereafter suffixed with an N), were being considered as structural members in the proposed High Field Bubble Chamber project of the Rutherford High Energy Laboratory (3). These alloys were therefore also examined, together with samples of AISI 309 and Inmac 2W, which were included to provide a wider coverage of chromium and nickel contents. Other alloys such as AISI 308 (20/11), 314 (25/20/3Si) and 317 (19/13/3Mo) were sought but proved impossible to obtain.

The development of the work was thus first prompted by the behaviour of commercial materials and finally circumscribed by their availability. It is shown however that both a practical and a more academic interest attaches to the behaviour of the steels. The study undertaken here also provided an interesting contrast to the work on indium alloys described in the preceding chapter.

Table 6.1 Steels used in the present study.

Steel	Shorthand composition
304L	18/10/low carbon
304N	18/10/ high nitrogen
309	23/14
310	25/20
316LN	16/12/3 Mo/ high nitrogen
321	18/10/ Ti
347	18/10/ Nb
Incoloy 800	20/32
Immac 2W	19/8/2W

Figure 6.1 Position of these steels on the Fe-Cr-Ni ternary.

304L ○ 321 ×
 304N 347 +
 316LN △ Immac 2W ▽

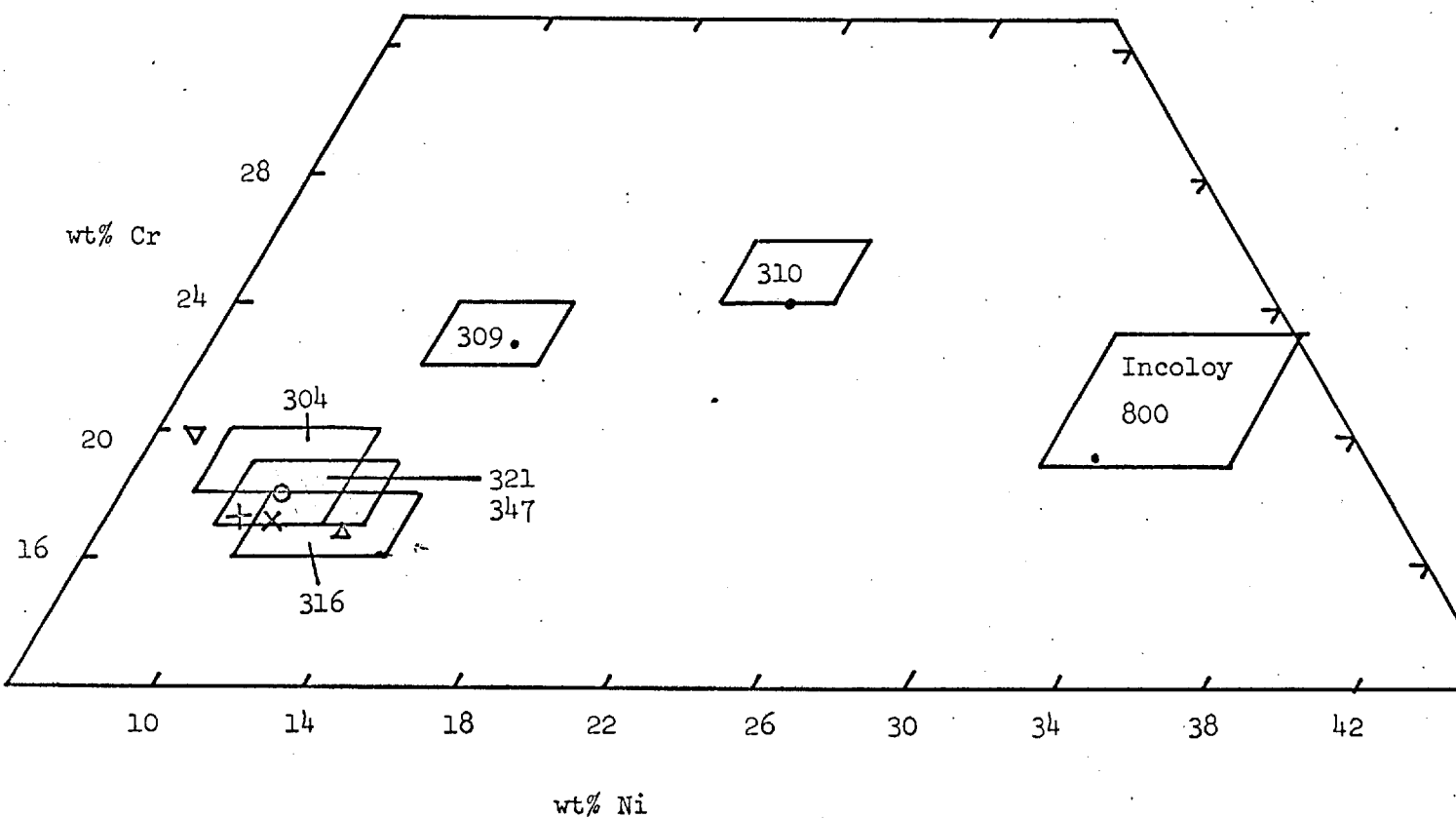


Table 6.2 Heat and sample analyses of stainless steels.

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Alloy	C		Cr		Ni		Si		Mn		S		P		Others	
	Heat	Sample	Heat	Sample	Heat	Sample	Heat	Sample	Heat	Sample	Heat	Sample	Heat	Sample	Heat	Sample
304L	0.025	0.07	18.47	17.98	10.83	10.53	0.47	0.77	1.18	1.37	0.012	0.08	0.019	0.02	-	-
304N	0.05	0.08	18.4	17.92	10.0	10.47	0.43	0.49	1.50	1.60	0.02	0.02	0.025	0.01	0.18N	-
309	0.12	-	22.44	-	14.25	-	0.54	-	1.23	-	0.011	-	0.02	-	-	-
310	0.07	0.14	24.62	23.95	20.70	21.09	0.76	0.75	1.68	1.65	0.008	0.03	0.019	0.007	-	-
316LN	0.025	0.05	16.81	16.77	12.31	12.43	0.36	0.38	1.60	1.49	0.01	0.03	0.021	0.02	0.18N - 2.40Mo	
321	0.05	0.10	18.11	17.22	9.96	10.18	0.58	0.60	0.78	0.77	0.011	-	0.024	0.02	0.43Ti	0.41Ti
347	0.06	0.14	17.60	17.18	9.56	9.65	0.61	0.72	0.63	0.70	0.012	0.02	0.013	0.02	0.82Nb	0.68Nb
Incoloy 800	-	0.14	-	19.18	-	31.36	-	0.56	-	0.76	-	0.004	-	0.02	-	-
Immac 2W	0.31	-	19.71	-	7.32	-	1.34	-	0.88	-	0.003	-	0.026	-	2.02W	-

6.2 Results

6.21 Alloy notation

The chemical compositions of the alloys used in this study are listed in table 6.1 while their permitted composition limits are plotted on a ternary Fe-Cr-Ni diagram in figure 6.1. As some of the alloys, notably 316LN, contain up to ~ 3.5 wt % of other elements, their position on this figure should be treated as a general guide only. The spread of the alloys in figure 6.1 shows that while the 16 - 20 Cr/8 - 12 Ni region is well covered, steels 309, 310 and Incoloy 800 only sparsely cover their part of the ternary diagram.

6.22 Chemical analysis

Heat analyses were supplied by the manufacturers for all materials except Incoloy 800. In addition, a wet chemical analysis was performed on all samples except the last two steels to be received, i.e. type 309 and Immac 2W, by the Analytical Services Unit at Imperial College. The heat and sample analyses for the important elements chromium and nickel always agreed within 0.8 wt % and generally to within 0.5 %. Such variations are to be expected within large casts. The specimen analyses gave carbon contents uniformly higher than those reported by the suppliers and indicated that all the steels except type 304N, were above the permitted maximum in their respective specifications. The stated tolerance on the carbon determinations at Imperial College was 0.002 wt %. The nitrogen contents of the alloys were not checked because suitable facilities were not available at Imperial College.

6.23 Heat treatments

Four magnetisation and four metallographic specimens were prepared for each alloy and given treatments to simulate practical conditions of the material. Hence, two specimens were left in the as-machined condition, while the third was fully softened, by heating.

for $\frac{1}{2}$ hour at 1075°C and water quenched, and the last was sensitised by heating for one week at 700°C to induce the precipitation of chromium and other carbides. Although this latter treatment should be strictly avoided in practice, it was aimed at giving some indication of what might happen if the steels were accidentally given a wrong heat treatment, particularly if the alloy was at the low end of its particular composition. Metallographic and magnetisation specimens of each alloy were heat treated in vacuum in the same silica capsules.

6.24 Metallography of samples before cryogenic cooling

All steels, except 309 and Immac 2W, were examined metallographically using light microscopy before they were cooled to sub-zero temperatures. All the structures revealed by this examination were single phase austenite with precipitated particles of carbides, phosphides or sulphides. No trace of either δ -ferrite or martensite was observed, which was later confirmed by the lack of a ferromagnetic component in the room temperature magnetisation plots of the as-received specimens (Section 6.31b).

The grain size of each sample was determined by comparing the polished structures with those of a standard ASM net (4). Where necessary the grain structure was revealed by an electrolytic etch with a 10% oxalic acid solution at 2v. The grain size results are given in table 6.3, and show a maximum range of four units between steels of any one condition. This range is quite normal for wrought

TABLE 6.3 ASM Grain size number of stainless steels

<u>Type</u>	<u>As machined/sensitised</u>	<u>Fully softened</u>
304L	5	3
304N	5	4
310	6	4
316LN	4	3
321	6	4
347	8	7
Inc. 800	7	4

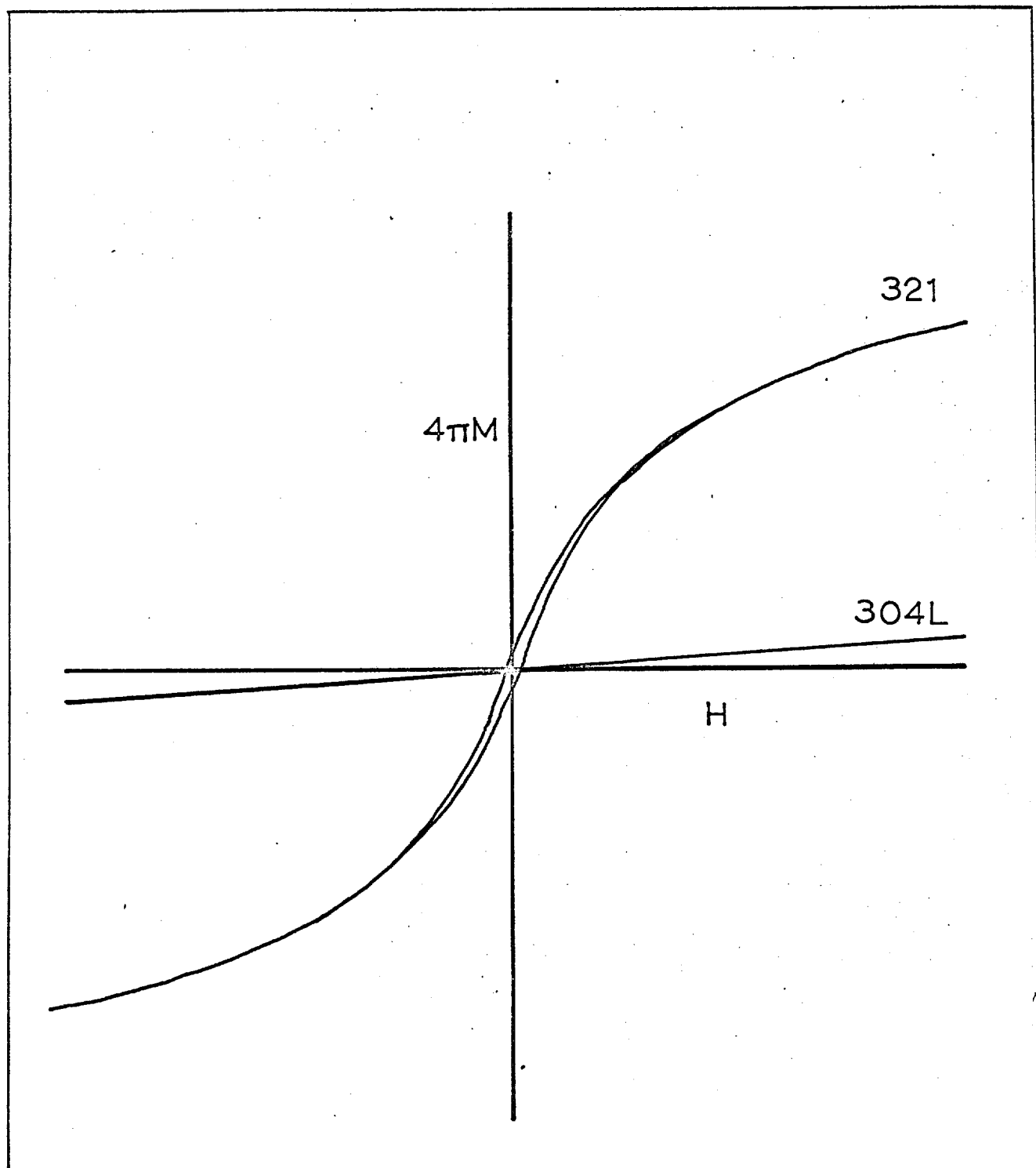


FIGURE 6.2 Typical magnetisation curves at 4.2°K

materials. As the recrystallisation temperature is considerably above the sensitising temperature of 700°C (5), the as-machined and sensitised steels have the same grain size.

According to Eichelmann and Hull (6) the M_s temperature of martensite is increased by $\sim 4^{\circ}\text{C}$ per unit increase in grain size number. The relationship between such small changes in M_s and the additional amount of martensite formed on quenching to 77°K or 4.2°K is probably complex and not subject to precise control in cryogenic applications, where cool down and warm up procedures may vary widely and some of the transformation may occur isothermally. Since the grain size of these steels can only be controlled by extensive cold work and recrystallisation, this parameter was not introduced as an experimental variable in the present study.

6.3 Preliminary results

6.31 Magnetic measurements

6.31a Measurements at 4.2°K

The first steels obtained for this programme were three weldable quality 18/10 steels (AISI 304L, 321 and 347) and one high alloy steel (AISI 310). Specimens of these steels were cooled to 4.2°K in about three minutes and their magnetisation loops plotted over the range $0 - 4\text{kOe} - 0$ using the D.C. integration magnetometer and superconducting solenoid described in chapter 4. Typical magnetisation curves are shown in figure 6.2. Within the limits of error, the plot for steel 304L is linear with field, suggesting that it is paramagnetic (or antiferromagnetic). The curve for steel 321, which is also typical of steels 310 and 347, is a non-linear function of applied field, indicating that the magnetisation of these steels is ferromagnetic in character.

For purposes of comparison with later magnetic measurements made at room temperature and 77°K , the magnetisation of these steels at a field of 2290 Oe is quoted in table 6.4. This particular field

was selected because it represents the highest field to which the copper solenoid, used for the measurements at 77°K and R.T., could be swept with a motor driven helipot while still retaining a reasonable sensitivity (± 5 gauss).

The results of table 6.4 show that all four steels have a detectable magnetisation at 4.2°K, which can vary over an order of magnitude between different grades (304L and 310) or between different specimens of the same grade (347). In order to fully evaluate the

TABLE 6.4 Magnetisation at 4.2°K and 2290 Oe

<u>Condition</u>	<u>304L</u>	<u>310</u>	<u>321</u>	<u>347</u>
softened	14 gauss	228	177	37
as machined	9	223	208	29
sensitised	16	290	124	360

significance of these results, it was clearly necessary to study the magnetisation of these steels at higher temperatures and to examine the effect of cooling on their microstructures.

6.31b Measurements as a function of temperature

Using the copper solenoid described in section 4.22, magnetisation loops were plotted at room temperature for previously uncooled samples of all steels in table 6.2, except 309 and Immac 2W. These comprised the second set of as-machined samples of 304L, 310, 321 and 347 and an original as-machined set of 304N, 316LN and Incoloy 800. These measurements, again referred to a field of 2290 Oe, are shown in table 6.5.

The initial measurements at R.T. show that the steels were essentially non-magnetic (i.e. non-ferromagnetic) in the as-machined condition. The figures which are qualified with a "less than" sign refer to

TABLE 6.5 Magnetisation of previously uncooled steels in the
as machined condition at 2290 Oe.

Steel	before cooling	Measurements at R.T.			at 77°K
		(a)	(b)	(c)	
304L	<18 gauss	<18	4	4	16
304N	<17	<17	7	10	13
310	<19	<19	8	<19	28
316LN	<20	<20	8	12	18
321	<18	167	279	316	335
347	<20	35	137	164	176
Inc. 800	<18	<18	10	9	658

Cooling treatments were given as

- a) quick cool and warm up, to and from 77°K
- b) quick cool, 14 hour soak at 77°K, slow warm up
- c) quick cool and warm up, to and from 4.2°K.

Further details are given in the text.

The set of steels measured here are designated the second set.

measurements made when discontinuities of the order of ~ 10 gauss occurred in the field sweep. Later measurements using an electronic sweep (Section 6.41b) gave magnetisations less than half the equivalent value in table 6.5. In any case these higher values correspond to a permeability of 1.005, or a susceptibility of $\sim 4 \times 10^{-4}$, and are thus clearly incompatible with the presence of any bulk δ -ferrite or α' martensite. Since, as discussed in Section 6.51, the saturation magnetisation of α' martensite lies in the region of 16,000 gauss, a magnetisation of 10 gauss at a field of 2290 Oe corresponds to a detection limit of 0.1 % of ferromagnetic constituent.

After the room temperature measurement three successive and different cooling treatments were given to each steel. The first of these was a quench to 77°K followed by a rapid return to R.T., effected by simply dropping the specimen into a flask of liquid nitrogen, leaving for one minute and then removing the specimen and warming with a hot air blower. The second treatment, which was much used subsequently, involved a down quench as above, followed by an overnight (16 hours) soak at 77°K. This treatment was performed in a 1 litre thermos flask and at the end of the soaking period the liquid nitrogen was poured away and the flask stoppered, so that the warm up to R.T. was very slow, taking about 4 - 5 hours. The object of this treatment was to maximise the amount of athermal martensite by giving a fast down quench, while the long soak at 77°K and the slow warm up to R.T. were designed to maximise isothermal transformation, assuming a C-type TTT diagram with a nose between 77°K and R.T. The third treatment was similar to the first, except that the temperature of the quench was lowered to 4.2°K and the specimens took about three minutes to cool. The magnetisation curves were plotted on the return to room temperature, following each treatment.

The results given in table 6.5 show two types of behaviour.

1) Steels 321 and 347 have magnetisations which are ferromagnetic in nature after cryogenic cycling and are an increasing function of such cyclic cooling.

2) Steels 304L, 304N, 310, 316LN and Incoloy 800 have reproducibly low magnetisations after cryogenic cycling and their magnetisation

TABLE 6.6 Magnetisation measurements at 2290 Oe
as a function of temperature.

a) Previously uncooled steels

Steel		R.T.	77°K	4.2°K
304N	softened	10 gauss	10	-
	as machined 1	17	22	21
	sensitised	< 17	17	-
316LN	softened	12	16	-
	as machined 1	< 20	18	30
	sensitised	8	25	-
Incoloy 800	softened	14	635	1970
	as machined 1	18	570	1492
	sensitised	18	692	2180

Testing sequence was R.T., 77°, 4.2°K.

b) Previously cooled steels

Steel		R.T.	77°K	4.2°K
304L	softened	15 gauss	16	14
	as machined 1	< 18	11	9
	sensitised	9	18	16
310	softened	< 11	24	228
	as machined 1	19	29	223
	sensitised	11	32	290
321	softened	242	309	177
	as machined 1	210	236	208
	sensitised	141	167	124
347	softened	47	97	37
	as machined 1	35	102	29
	sensitised	422	461	360

Testing sequence was 4.2°, R.T., 77°K. The 4.2°K values are from Tab. 6.4.

curves were linear with respect to field within the margins of error.

It is particularly interesting to note that 310 falls into the second category, as the first as-machined specimen of this steel possessed a ferromagnetic magnetisation of 223 gauss on previously cooling to and measuring at 4.2°K (table 6.4). On cooling these specimens to 77°K again and repeating the measurements at this temperature, the magnetisation of 310 increased to 28 gauss but the M/H curve remained linear. The magnetisation of Incoloy 800, however, became an order of magnitude larger (658 gauss) and characteristically ferromagnetic, while those for 321 and 347 showed only small increases above their previous values.

In order to throw further light on this varied behaviour, all remaining specimens were then tested at room temperature and 77°K . These comprised the as yet uncooled samples of 304N, 316LN and Incoloy 800 and the specimens of 304L, 310, 321 and 347 previously measured at 4.2°K (table 6.4). The results of these measurements, also referred to a standard field of 2290 Oe, are shown in table 6.6 and now show that three different types of behaviour occur among the steels.

1) All specimens of 321 and 347 develop ferromagnetic magnetisations on cooling to 77° and/or 4.2°K . These magnetisations increase with continued cryogenic cycling and lie in a regular increasing sequence which is not affected by the measuring temperature.

2) Steels 304L, 304N have small, non-ferromagnetic magnetisations at all temperatures studied.

3) 310 possessed a ferromagnetic magnetisation when tested at 4.2°K , but was paramagnetic at R.T. and 77°K . Incoloy 800 had a similar small paramagnetic magnetisation at R.T. but on cooling, first to 77°K and then to 4.2°K , exhibited the largest magnetisations recorded in this study (~ 600 gauss at 77°K , ~ 1800 at 4.2°K). Subsequent re-measurements at 77°K and 4.2°K for both 310 and Incoloy 800, gave magnetisations which agreed with the respective values in tables 6.5 and 6.6 to within the experimental error. It is therefore clear that the ferromagnetic magnetisations found in these steels are reversible with temperature.

6.31c Isothermal effects

No direct evidence for isothermal increases in magnetisation was sought in the course of these experiments, but during measurements at 77°K on the sensitised sample of type 347, a spontaneous increase of magnetisation was observed during the plot of one complete hysteresis loop. The increase during the time taken to plot the loop, $\sim 7\frac{1}{2}$ minutes, was from 461 to 478 gauss. The specimen was then up-quenched to room temperature and returned to 77°K when the magnetisation loop was repeated, giving a value of 570 gauss. After leaving the specimen at this temperature for 4 hours the magnetisation further increased to 600 gauss. It is evident that while quenching is more potent in increasing the magnetisation of this alloy, quite significant isothermal increases are observed on holding at 77°K.

6.32 Metallographic observations

Up to this point, and following the survey of these steels by Reed and Mikesell (1), the only mechanism considered that would produce a ferromagnetic magnetisation in these steels was the formation of α' martensite. While the presence or absence of the phase would explain the results on the 18/10 steels, a fully reversible martensitic transformation would be required to extend this explanation to account for the results for 310 and Incoloy 800.

Even though this possibility appeared unlikely, it was checked by examining both steels in the low temperature stage of a light microscope (Section 4.13). No microstructural changes of any type were observed in either steel when continuously viewed at magnifications of $\times 330$, while cooling from R.T. to 77°K over a period of 2 to 3 minutes. Hence the low temperature ferromagnetic behaviour of Incoloy 800, and the increased magnetisation of 310 at 77°K, are not to be associated with any martensitic transformation.

Samples of all the steels were now examined metallographically at room temperature after several quenching treatments to 77°K. Martensite was found to have formed in all samples of 321 and 347 but none could be observed in any sample of the remaining steels even

Figure 6.3 Martensite in the 18/10 stainless steels.



a.) Steel 347 fully softened x300

b.) Steel 321 fully softened x300



c.) Steel 321 fully softened x540



after quenching to 4.2°K. These results are in accord with the results of the magnetic measurements already described. On quenching to 77°K or 4.2°K spontaneous transformation to martensite occurs through thermal stress-induced activation of nucleation sites. This process is essentially athermal, but may be supplemented by isothermal activation of such sites too. On warming to room temperature, further martensite may be formed isothermally, with a consequent further change in the internal stress distribution. On re-quenching, further martensite plates may form athermally and/or isothermally in order to relieve the local internal stresses when they reach a critical value. It is evident that some degree of auto-catalysis is inherent in the formation of martensite during each quench and this catalysis makes it impossible to test the efficacy of the various quench procedures used, unless the steel can be taken back to the original state each time.

The martensitic structures obtained in these steels are illustrated by the micrographs in Figure 6.3. These refer to the softened specimens of 321 and 347 after many cooling cycles to 77°K. The microstructures are similar to those reported by Lagneborg (7) and Reed (8) and consist of α' contained within sheets of ϵ . The ϵ sheets appear as pairs of parallel sided lines on the two dimensional polished surface, while the α' forms within these sheets in preferred orientations. It was observed that on the first or second quench many pairs of ϵ sheets were formed, but that they contained little α' . On repeated quenching, subsequent transformation was predominantly α' , which formed between the ϵ sheets. After many cooling cycles the ϵ sheets tended to acquire a "filled" appearance as shown in figure 6.3c.

It can be seen from figure 6.3a and b that steel 347 contains a much larger total volume of martensite than steel 321. Table 6.6 shows, however, that 321 had a considerably larger magnetisation than 347 (309 gauss vs. 97). This can be explained by the relative lack of α' between the ϵ plates in steel 347 even after examination at magnifications up to $\times 2000$. The relative proportion of ϵ to α' is thus very high for this specimen, suggesting that the stacking fault energy is very low and thus causing a smaller total magnetisation than

would be expected from the amount of decomposition indicated in the micrograph.

6.4 Detailed experimental programme

At the completion of the experimental programme described in the previous section, it now became of interest not only to study further the occurrence or non-occurrence of a martensitic transformation in the 18/10 steels, but also to investigate the magnetic properties of austenite itself, in view of the reversible ferromagnetic transition found in the two high alloy steels. To these ends a sequence of cryogenic cycling treatments were planned for the 18/10 steels and some experimental modifications were made to allow a more accurate measurement of the small paramagnetic susceptibilities of austenite. In addition, a wider range of steels was sought and two further steels, 309 (23/14) and Immac 2W (19/8/2W) were obtained.

The experimental modifications involved the use of an electronic sweep generator which gave a much smoother variation of magnet current and so eliminated the large discontinuities associated with the previous use of the copper solenoid. At the time of the cryogenic cycling experiments, the voltage output of this sweep was insufficient to sweep the current supply over its full range and a maximum field of 1890 Oe was obtained but for the susceptibility measurements the sweep was modified so that the full field of 3150 Oe could be smoothly applied. With this sweep unit, the magnetometer sensitivity was estimated to be ± 2 gauss. The sensitivity was further increased to $\pm \frac{1}{2}$ gauss by using the magnetometer ballistically as described in section 4.33.

6.41 Magnetisation measurements after cryogenic cycling treatments

Measurements of the magnetisation at R.T. after cryogenic cycling were made using both the Sucksmith balance (described in section 4.41) and the integration magnetometer. The advantage of the Sucksmith balance lay in its measurement of the saturation magnetisation of the ferromagnetic steels which may then be related directly to the α' content of the steel, using the calculation described in section 6.41d. Since the maximum length of specimen accepted by the balance is limited

to 5 mm the metallographic samples were used for this study and thus provided parallel measurements to the magnetisation results reported in section 6.3.

The cycling treatment employed was similar to that described in section 6.31b, involving a quick cool to 77°K, a long soak of about 14 hours at this temperature and a slow warm-up to R.T. taking 4 to 5 hours.

6.41a Sucksmith measurements

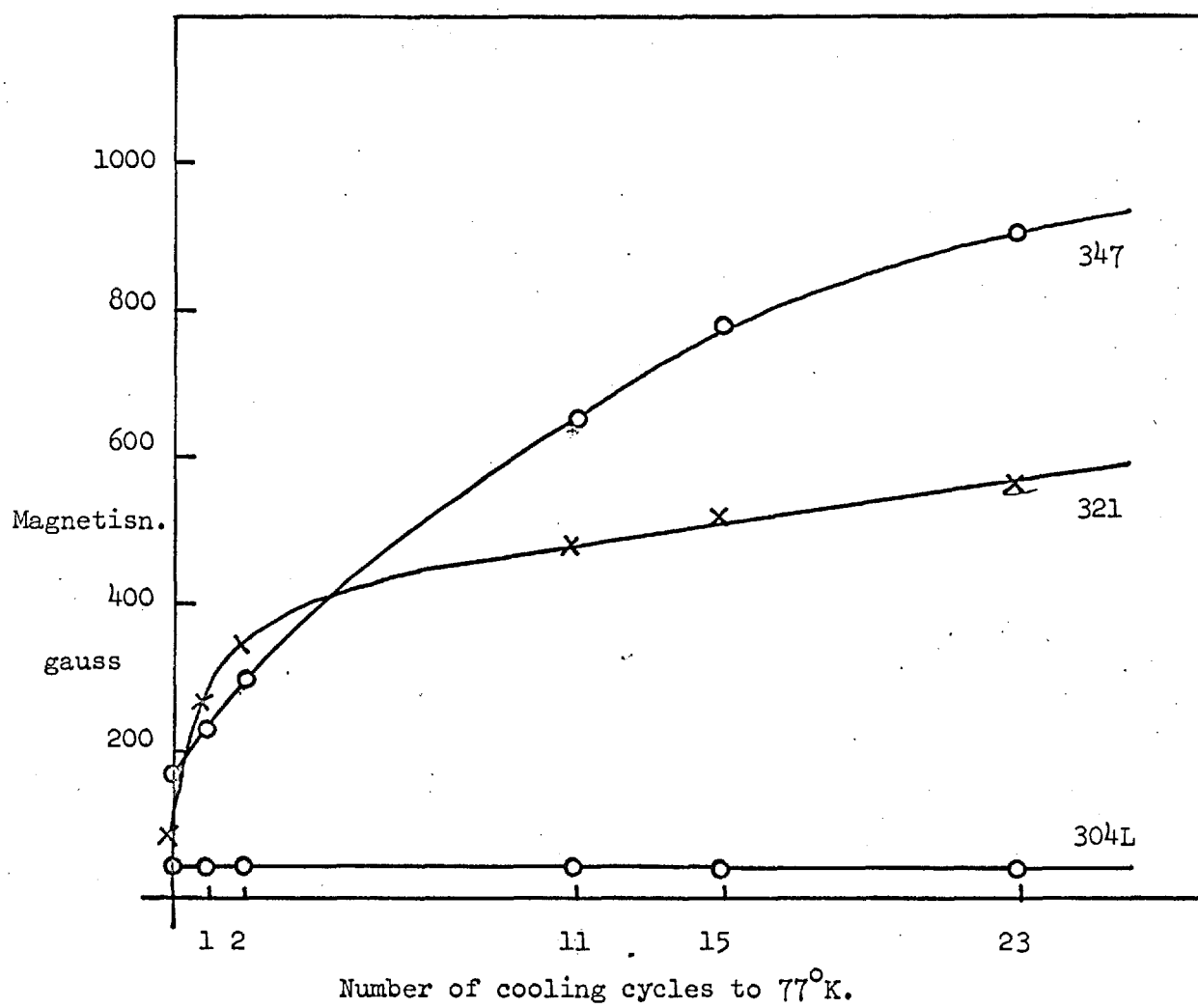
The previously uncooled and as-machined set of metallography specimens was selected for this study and the initial measurements before cooling were made by firmly gluing the specimens with Bostik cement to a long brass rod, connected to the suspension of the balance. This procedure proved time-consuming, however, and was inherently suspect in that a strongly magnetic specimen might be moved relative to the rod when the field was applied. After these measurements, therefore, a LOBA clearance hole was drilled through the specimens so that they could be bolted to the end of the brass rod. One face of the specimen was then polished for metallographic examination.

TABLE 6.7 Magnetisation measurements on as machined metallography specimens at a field of 12k Oe in the Sucksmith balance

Steels		After drilling As machined and polishing	No. of quenches to 77°K				
			1	2	11	15	23
304L	29 gauss	45	45	45	47	47	45
304N	25	32	32	32	32	33	32
310	25	24	24	24	25	29	27
316LN	27	34	34	34	32	34	34
321	44	79	283	372	491	527	563
347	51	169	230	356	655	782	904

The results shown in table 6.7 suggest that some ferromagnetic phase was present in types 321 and 347 even before drilling. This could

FIGURE 6.4 Sucksmith magnetisation measurements on as
machined steels at room temperature



be attributed to $\sim 0.1\%$ of δ -ferrite but is more likely to be due to α' martensite induced at the surface by the machining operation. It may appear strange at first that no such increase was observed in the integration measurements on the specimens reported in table 6.5. However, although the diameters of both sets of specimens are the same, their lengths are 4 and 30 mm respectively, giving a surface area/volume ratio of $\sim 1.5 : 1$. The Sucksmith measurements should thus be more sensitive to the surface condition of the specimens. As the detector coils for the integration measurements were only half the length of the specimens, they were comparatively insensitive to end and demagnetisation effects and hence the equivalent surface area/volume ratio for these measurements is no doubt considerably in excess of $1.5 : 1$. It is clear, however, that no α' martensite existed in the bulk of any sample. After drilling and polishing, all samples except type 310 registered an increase in their magnetisation. This increase was particularly large in steel 347, for which metallographic observation showed ϵ and α' martensite to be present.

On continued cycling between R.T. and 77°K further marked increases in magnetisation of some 6 - 8 times the drilled and polished value were registered for steels 321 and 347. No further changes were detected for steels 304L, 304N, 310 and 316LN and observation of the polished surfaces of these steels revealed no traces of either ϵ or α' martensite after these cyclic treatments. Observation of both 321 and 347 revealed considerable amounts of both ϵ and α' martensite with morphologies similar to those shown in figure 6.3.

The Sucksmith magnetisation measurements for steels 321 and 347 are plotted against the number of cooling cycles in figure 6.4. This figure indicates that the amount of α' martensite formed after each quenching treatment falls off steadily but that the steels are still unstable even after ~ 20 cycles to 77°K . It is also interesting to note that steel 321 has a much steeper initial rate of α' formation than 347, but that this rate falls off rapidly, to give a lower total content after a small number of cycles.

Figure 6.7 Magnetisation curves of 347 at 4.2°K.

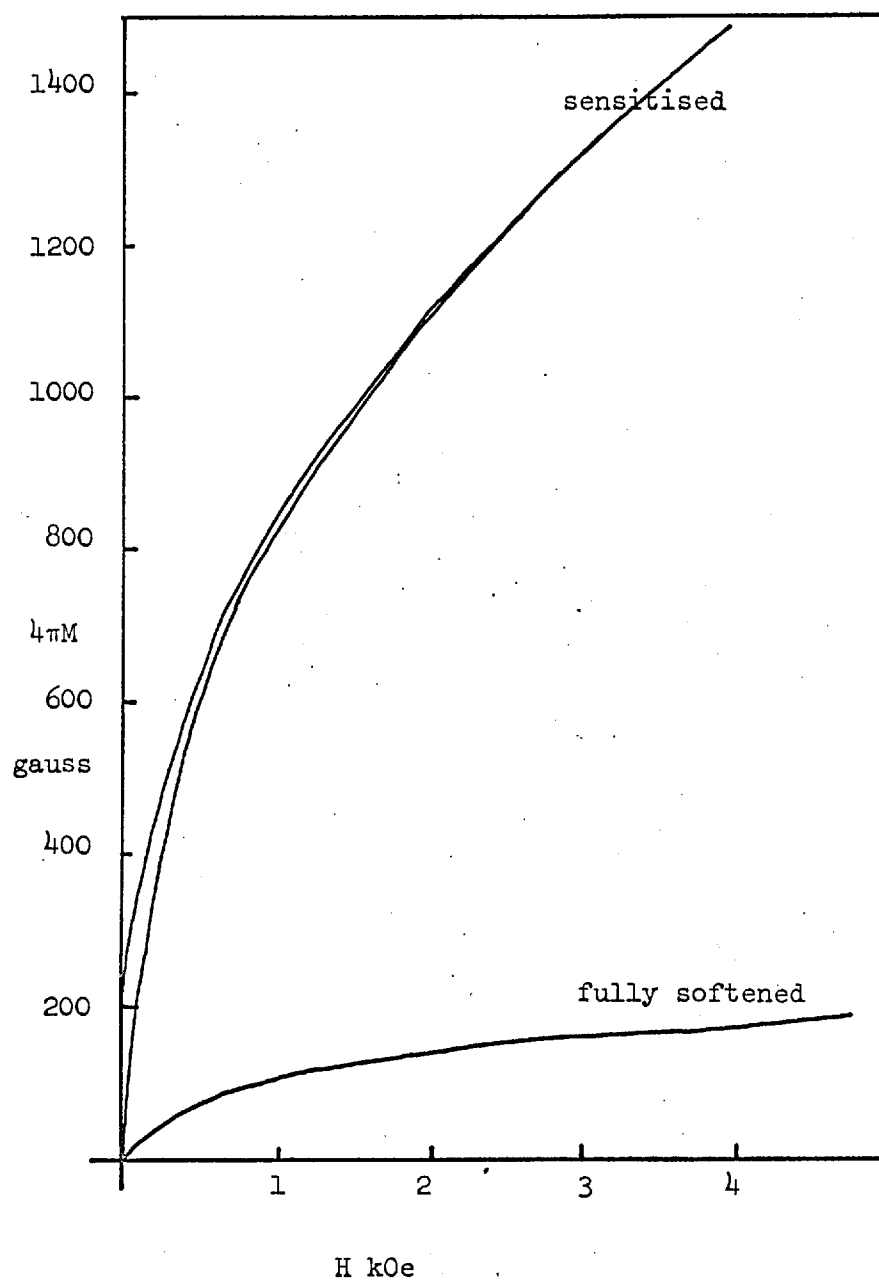


Figure 6.5 Magnetisation curve of 304L sensitised at 4.2°K

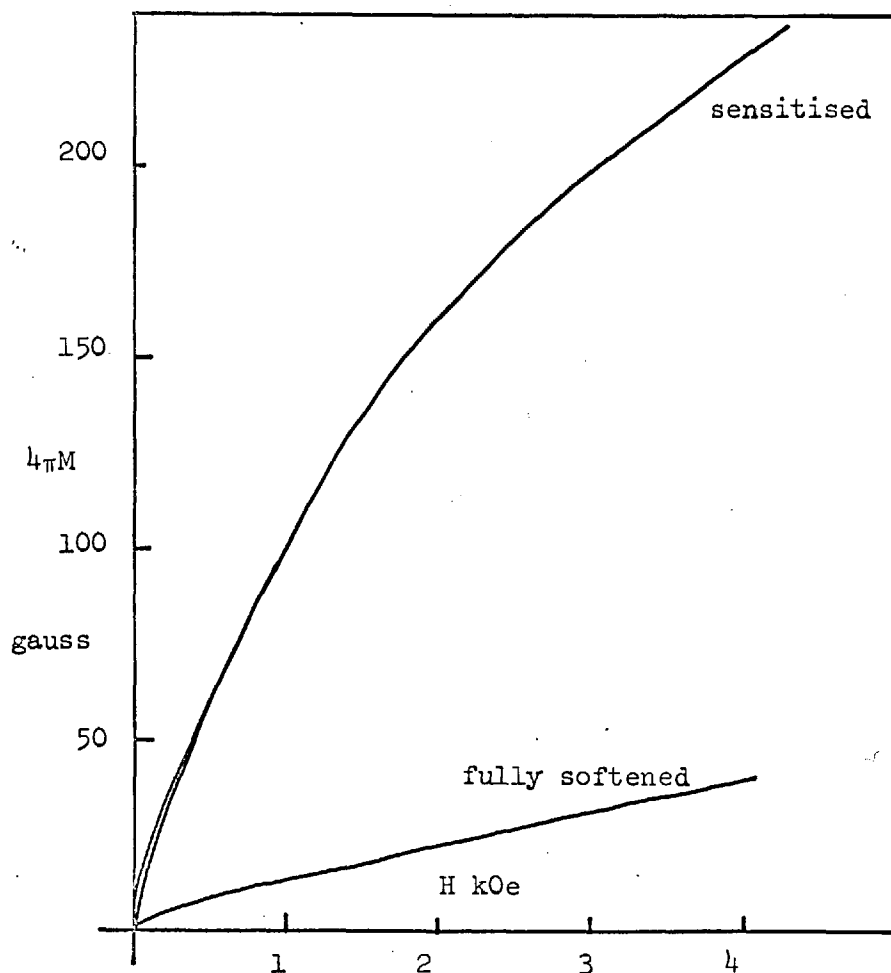


Figure 6.6 Magnetisation curves of 321 at 4.2°K.

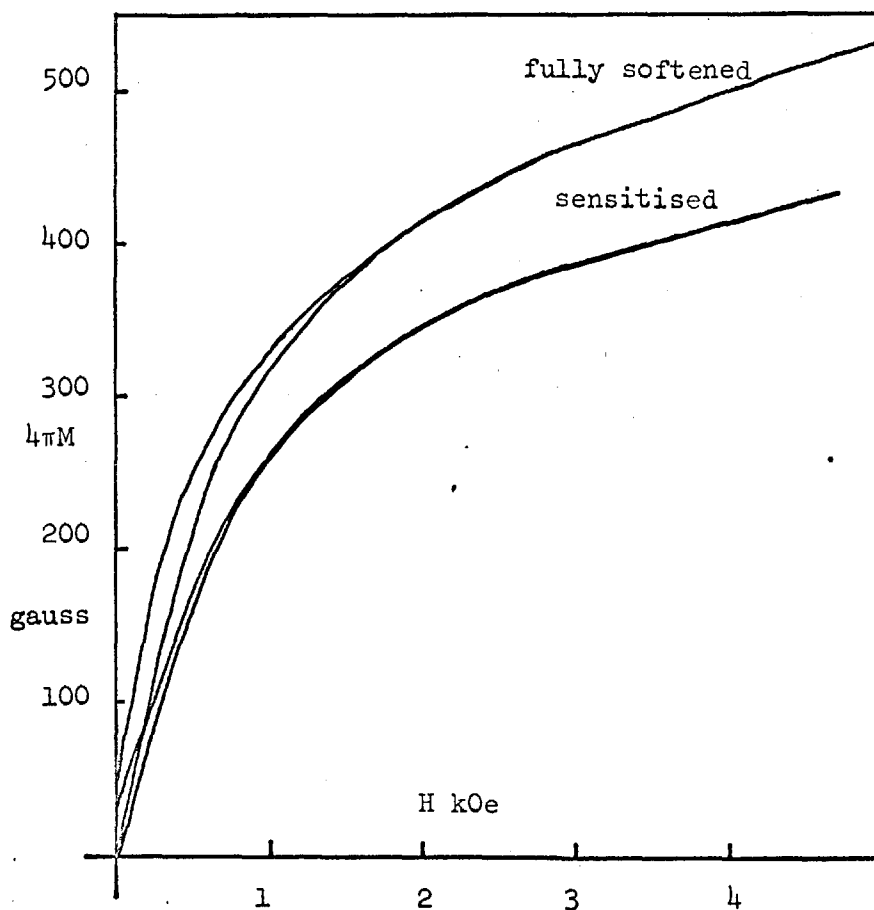


TABLE 6.8 Room Temperature magnetisation after cryogenic cycling

Steel		At 1890 Oe	Previous measurements at 2290 Oe
304L	fully softened	5.5 gauss	15
	as machined 1	5.5	<18
	as machined 2	5.5	4
	sensitised	138	9
304N	softened	3.5	10
	as machined 1	3.5	17
	as machined 2	3.5	10
	sensitised	14	<17
316LN	softened	4	12
	as machined 1	4	<20
	as machined 2	4	12
	sensitised	6	8
321	softened	381	242
	as machined 1	288	210
	as machined 2	335	316
	sensitised	312	141
347	softened	127	47
	as machined 1	368	35
	as machined 2	388	164
	sensitised	1115	422

6.41b Integration measurements

The integration measurements were made at room temperature on all magnetisation specimens of steels 304L, 304N, 316LN, 321 and 347 after 10 similar cooling cycles and the results are shown in Table 6.8. When these results are compared with the previous R.T. values in the second column of the table, it can be seen that (even at a field approximately 15% lower than before) all specimens of 321 and 347 register an increase in magnetisation. The table also shows that the sensitised specimen of 304L has now become unstable, its magnetisation increasing from the previous low value of 9 gauss to 138 gauss. This interesting result may perhaps be explained by the formation of a large amount of α' isothermally at a temperature mid-way between room temperature and 77°K. It was with this possibility in mind that the composite quench used was designed, but it is nevertheless not clear why no detectable athermal transformation occurred during the two previous cryogenic quenches recorded in tables 6.4 and 6.6.

The magnetisations recorded for the remaining steels (304N, 316LN and 304L except sensitised) are rather lower than before, indicating the greater sensitivity of the measurements made with the electronic sweep. These steels were also quenched three times to 4.2°K but in no case was any detectable change in the magnetisation observed. It was therefore concluded that these specimens were stable against martensitic decomposition at cryogenic temperatures.

6.41c The effect of carbide precipitation

The magnetisation curves of the fully softened and sensitised specimens of steels 304L, 321 and 347 on a subsequent quench to 4.2°K are given in figures 6.5 - 6.7. These show a fairly gradual approach to ferromagnetic saturation, as might be expected for steels with a considerable internal stress distribution. The most striking feature of the curves, however, is that whereas sensitising markedly increases the ferromagnetic behaviour of steels 304L and 347, where the magnetisation increases by a factor of ~ 6 and 8 times respectively over the fully softened condition, this treatment actually reduces the magnetisation in steel 321.

Figure 6.8 Carbide precipitation in stainless steels

a.) Steel 304L



(i) Fully softened x200

(ii) Sensitised at 700°C for one week x540

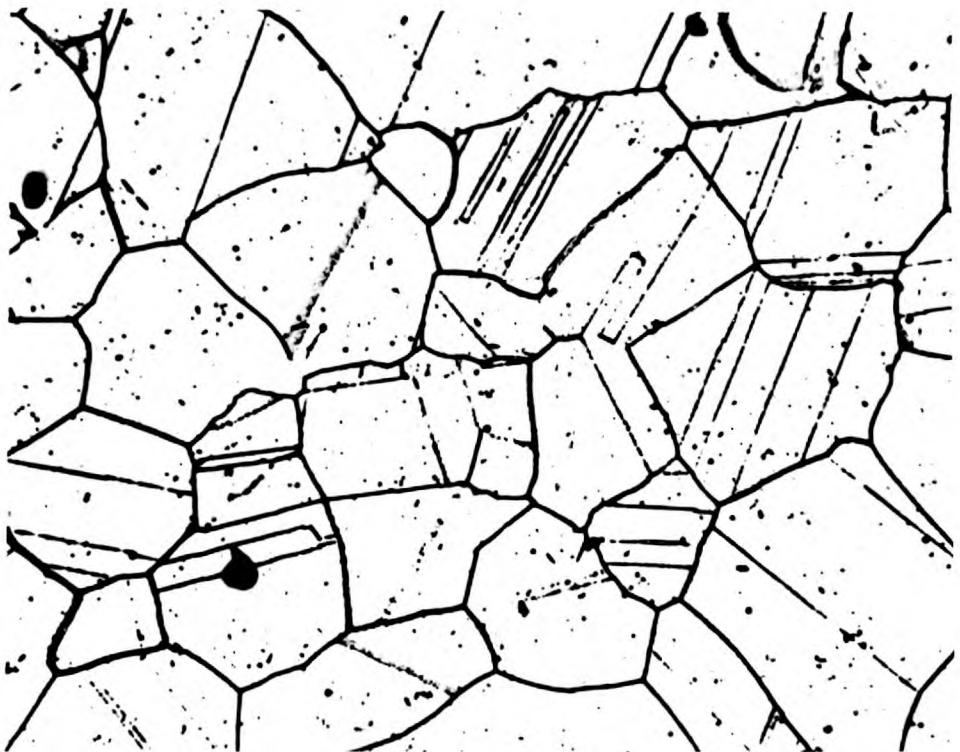
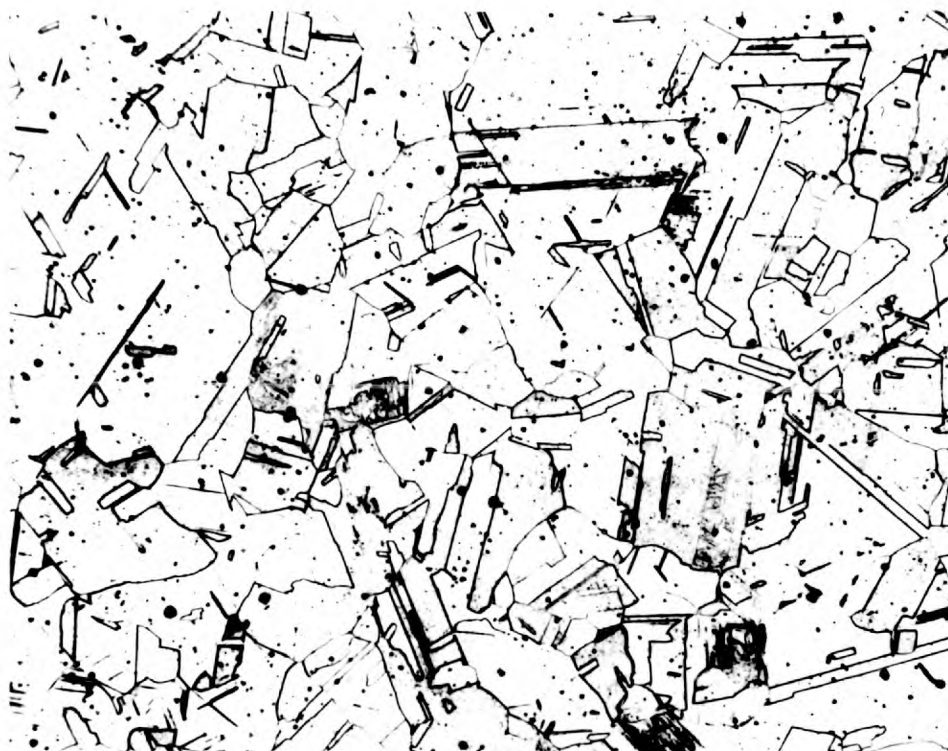


Figure 6.8 Carbide precipitation in stainless steels

b.) Steel 321



(i) Fully softened x200

(ii) Sensitised for one week at 700°C x540

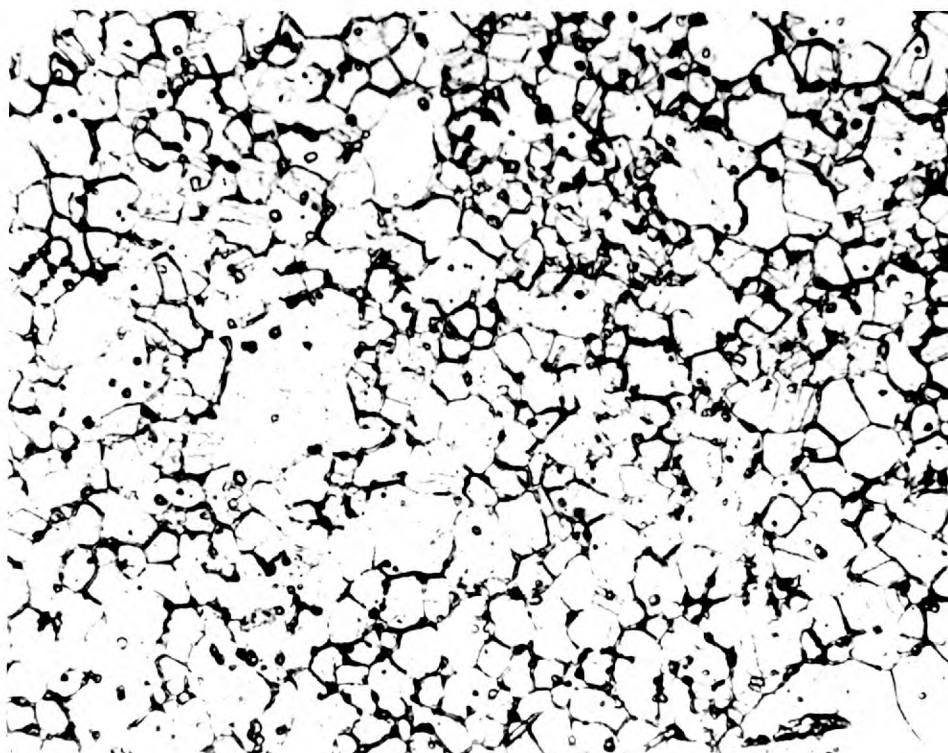
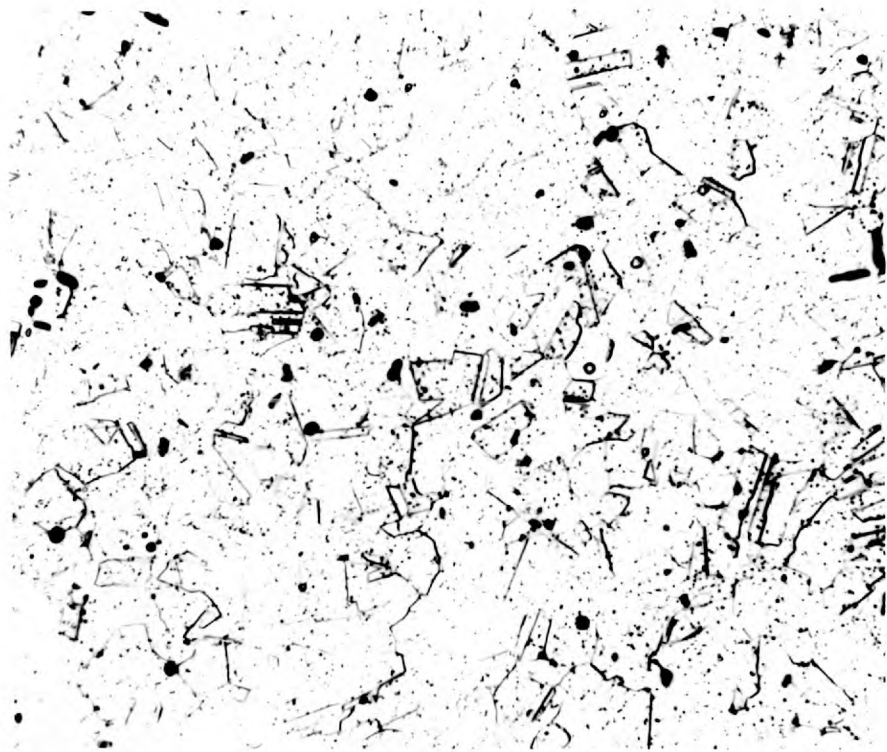


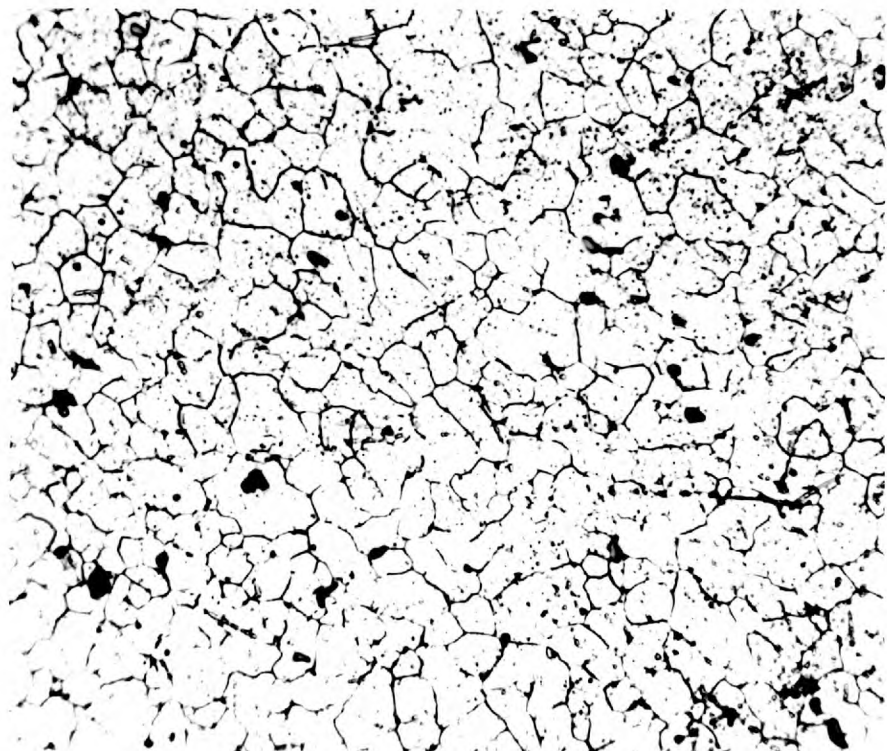
Figure 6.8 Carbide precipitation in stainless steels

c.) Steel 347



(i) Fully softened x540

(ii) Sensitised for one week at 700°C x540



This is an interesting result, because in a plain carbon stainless steel the reduction of carbon content in the austenite matrix caused by sensitising would be expected to increase the M_s considerably (equation 3.3). Each of these three steels, however, is specially formulated so that the actual amount of carbon in solution in the austenite is close to or below the solubility limit of $\sim 0.02\%$ (9) at the sensitising temperature. For 304L this is achieved by simply reducing the carbon content below 0.03% , but for 321 and 347 a higher carbon limit of 0.08% is tolerated, provided the titanium or niobium content is five and ten times the carbon content, respectively, so that the excess carbon is fixed as TiC or NbC . The precipitation of $Cr_{23}C_6$, and potential intergranular corrosion, should thus be avoided.

Metallographic examination of these steels revealed, however, that considerable precipitation had occurred in each during sensitising (figure 6.8). This precipitation was particularly heavy for 304L, but was also obvious in the finer grained 321 and 347. When the heat and specimen analyses for carbon, niobium and titanium for these steels are compared, a considerable variation is found. Table 6.9 reproduces the relevant data from table 6.2 together with the AISI specified limits and shows that, according to the specimen analyses all of the steels contain more than the permitted carbon content, the deviations from specification being greatest in steels 304L and 347.

TABLE 6.9 Chemical composition of weldable stainless steels

Steel	C content			Nb or Ti content		
	Specific ⁿ	Heat anal.	Sample	Specific ⁿ	Heat	Sample
304L	0.03 max	0.025 %	0.07	-	-	-
321	0.08 max	0.05	0.10	5 x Cmin	0.43 Ti	0.41
347	0.08 max	0.06	0.14	10 x Cmin	0.82 Nb	0.68

If the specimen analyses are accepted, the magnetic behaviour of type 304L can be understood by considering that the gross precipitation which occurs on sensitising (figure 6.8) removes the excess carbon ($\sim 0.05\%$) from solution to form Cr_{23}C_6 . According to equation 3.3 the removal of 0.05% C, and its equivalent of 0.78% Cr, from solid solution should increase the M_s temperature of the austenite by 117°K , and thus increase the amount of α' formed on cryogenic cycling.

The minimum weight proportions of titanium & niobium needed to combine with all the available carbon in steels 321 and 347 are $4 : 1$ and $8 : 1$, respectively (9). According to the sample analyses in Table 6.9, the required $4 : 1$ ratio is just achieved in 321, but the equivalent ratio for 347 is only $4.85 : 1$. Thus the niobium content of the latter steel is clearly inadequate to prevent the precipitation of some Cr_{23}C_6 during sensitising, thereby raising the M_s temperature and causing the steel to become more ferromagnetic after cryogenic cooling, as in the case of 304L.

In the light of the evident precipitation which has occurred on sensitising 321 at 700°C , figure 6.8b, it is interesting to note that this sample has a magnetisation some 15% lower than the fully softened specimen. This suggests that the $\text{Ti} : \text{C}$ ratio in this steel is sufficiently balanced so that only TiC can precipitate. Since both titanium and carbon are in random solid solution at the softening temperature, carbon and titanium atoms which are rejected from solution on the subsequent rapid cool to R.T. will be able to diffuse only short distances and the resulting precipitates will be very fine. The long sensitising treatment would then cause coarsening and spheroidisation which would make the precipitates more visible to light microscopy but, if all the excess carbon had already been fixed in the fully softened condition, no changes in the M_s of the austenite could occur. The magnetisation differences observed may then reflect fine differences in cryogenic treatment between the two specimens, such as variations in the slow warm up employed in the cycling treatments.

An interesting footnote to the preceeding discussions is that NbC is superconducting below about 10°K (10) but it is obvious from

figure 6.7 that any diamagnetic magnetisation due to the precipitate is masked by the large ferromagnetic moment of the α' martensite. It would be interesting, however, to study the magnetisation of a stable austenitic version of 347 at 4.2°K.

6.4ld The quantitative determination of α' martensite

The magnetisations of these steels may be related to the α' martensite contents causing them, using a method due to Curtis and Sherwin (11), which was developed for the estimation of δ -ferrite in stainless steel welds. This is based on earlier work by Seitz (12), who considered that in the b.c.c. lattice iron, nickel and chromium each contributed 2.2, 0.6 and 0.22 Bohr magnetons (μ_B), respectively, to the saturation magnetisation σ_0 at absolute zero. Thus

$$\sigma_0 = (2.2W_{Fe}/A_{Fe} + 0.6W_{Ni}/A_{Ni} + 0.22W_{Cr}/A_{Cr})N_0 \mu_B \quad 6.1$$

where A_x , W_x are the atomic weight and weight fraction respectively of each element in the alloy and N_0 is Avogadro's number. The remaining elements C, N, Si, Mn, Mo, S and P were considered to have a neutral dilution effect and a linear relation was found between the δ -ferrite content of an austenitic weld and its saturation magnetisation as calculated from equation 6.1. Similar good agreement has been found when determining α' martensite contents in stainless steels (13) and the saturation magnetisations of the 18/10 steels used in this study have thus been calculated according to equation 6.1 and are shown in Table 6.10.

TABLE 6.10 Saturation magnetisation of stainless steels

Steel	σ_0 from eqn. 6.1	Density	$4\pi M_s$
304L	162.4 c.g.s.units	7.90 gm/c.c.	16,100 gauss
304N	163.4	7.90	16,200
316LN	152.5	7.96	15,250
321	165.2	7.90	16,400
347	164.9	7.93	16,400

$$4\pi M_s = 4\pi \cdot \sigma \cdot \rho.$$

TABLE 6.12 Permeability of martensitic steels at 4.2°K

Steel		μ at 100 Oe	μ at 1 kOe
304L	sensitised	1.35	1.10
321	fully softened	2.75	1.34
	sensitised	1.95	1.27
347	fully softened	1.40	1.11
	sensitised	5.15	1.82
"non-magnetic" steel 304N		$\mu = 1.003$ at all fields	

Figure 6.9 Permeability versus α' content

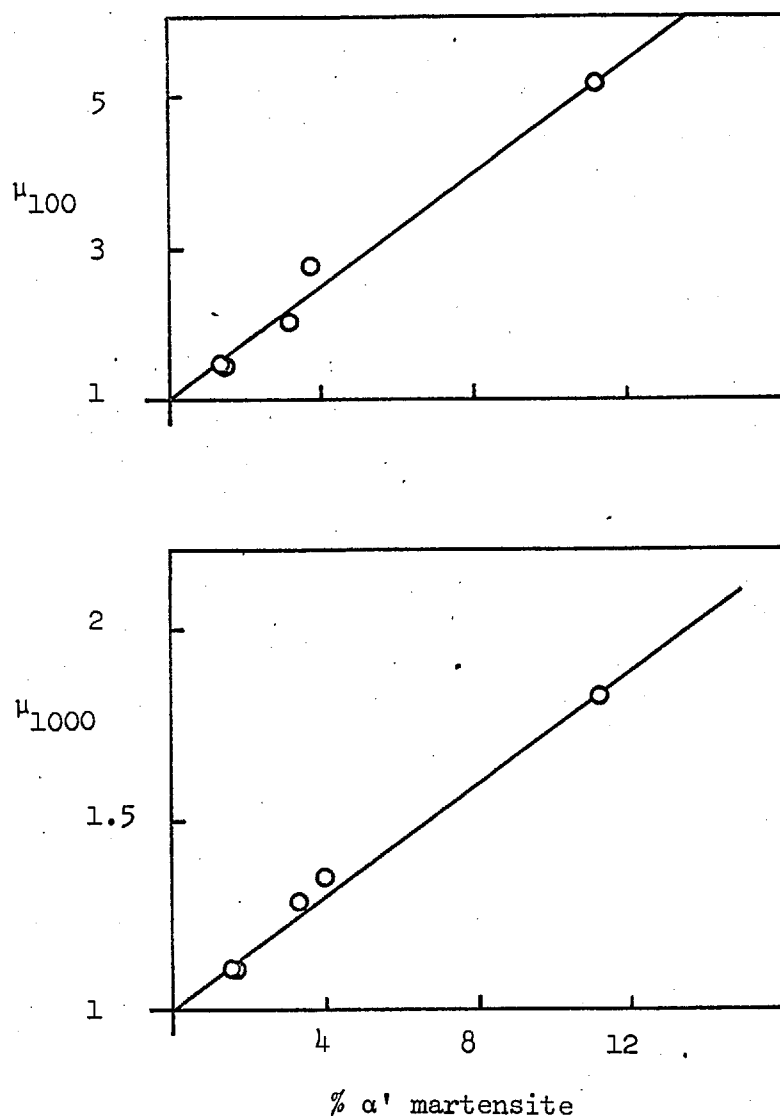


TABLE 6.11 α' martensite contents of steels

a) Sucksmith measurements at 12 kOe

Steel	$4\pi M$	α' content
321 as machined	563 gauss	3.4 %
347	904	5.5

b) Integration measurements at 1890 Oe

Steel	$4\pi M$	α' content
304L softened	5.5 gauss	< 0.1 %
as machined 1	5.5	< 0.1
as machined 2	5.5	< 0.1
sensitised	1.38	1.4
321 softened	381	3.7
as machined 1	335	3.4
as machined 2	288	2.9
sensitised	312	3.1
347 softened	127	1.3
as machined 1	388	3.9
as machined 2	368	3.7
sensitised	1115	11.2

These measurements have been assessed as 60 % of the saturation magnetisation.

The densities have been taken from the commercial specification sheets (14).

Table 6.11 shows the derived α' contents of these steels after the cryogenic cycling treatments of sections 6.41a and b. The Sucksmith measurements have been converted directly, as all the samples were saturated at the measuring field of 12 kOe. The integration measurements were assessed at 60% of saturation at 1890 Oe by observing the magnetisation of the Sucksmith specimens as a function of field.

This calculation emphasizes the smallness of the transformations as, if the sensitised samples are excluded from consideration, the maximum α' content found is less than 4%. As Guntner and Reed (15) have found that up to 11% α' does not significantly affect the low temperature notch toughness properties of these steels such transformations are not expected to significantly affect the mechanical properties. Permeability figures have been derived from the full magnetisation curves of figures 6.5 - 6.7 at fields of 100 and 1000 Oe and these are shown in table 6.12. These show a variation from 1.35 to 5.15 at 100 Oe falling to values less than 2 at 1000 Oe but these values, while not high, are clearly significant in magnetic field situations, particularly field changing situations.

Figure 6.9 shows that when the permeability is plotted against α' content a linear-relationship holds. This is, of course, to be expected at high fields, on the basis of the calculation used to derive the α' content in the first place. That it is also true at low fields emphasizes the discrete nature of the magnetisation in these steels. Evidently at low α' concentrations there is little interaction between neighbouring ferromagnetic plates. This is in line with the work of Henkel (17) who has shown that appreciable magnetostatic interactions between plates do not occur at concentrations less than 15%.

6.42 Susceptibility measurements

In order to study the magnetic properties of austenite, the fully softened and sensitised specimens of 304N, 309, 310, 316LN, Incoloy 800 and Immac 2W were selected for measurement. In addition, the fully

TABLE 6.13 Susceptibility of austenite in stainless steels as a function of temperature

Steel	R.T.	77°K	4.2°K
304L softened	f. 1.86×10^{-4}	f. 4.91×10^{-4}	f. 7.16×10^{-4}
sensitised	mF	mF	mF
304N softened	1.99	4.15	5.68
sensitised	f. 2.66	f. 4.53	f. 5.70
309 softened	1.66	4.97	18.7
sensitised	2.06	5.31	16.6
310 softened	1.79	6.63	F
sensitised	1.86	9.95	F
316LN softened	2.05	5.50	9.02
sensitised	f. 2.78	f. 5.70	f. 9.02
321 softened	mF	mF	mF
sensitised	mF	mF	mF
347 softened	mF	mF	mF
sensitised	mF	mF	mF
800 softened	4.25	F	F
sensitised	4.25	F	F
2W softened	1.59	3.85	8.22
sensitised	f. 1.72	f. 4.90	f. 7.42

Notes :

- f - traces of ferromagnetic component - χ derived after extrapolating this out.
- mF - large scale martensitic ferromagnetism.
- F - bulk austenitic ferromagnetism.

Figure 6.13 Magnetisation curves of Immac 2W.

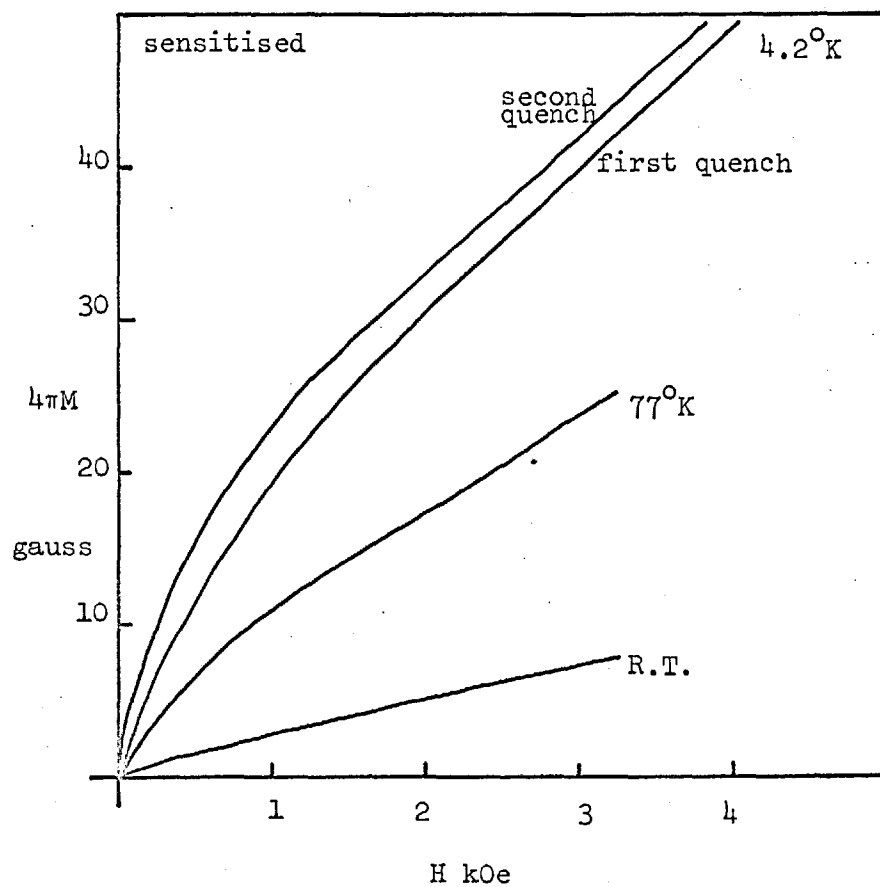
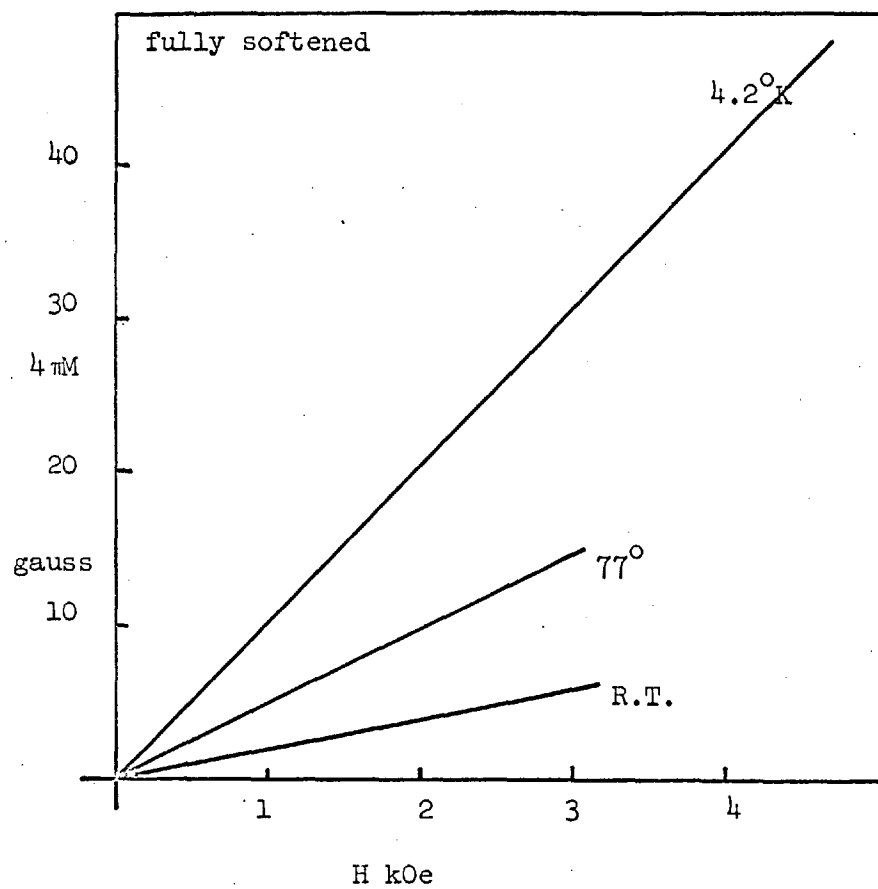


Figure 6.12 Magnetisation curves of 316LN.

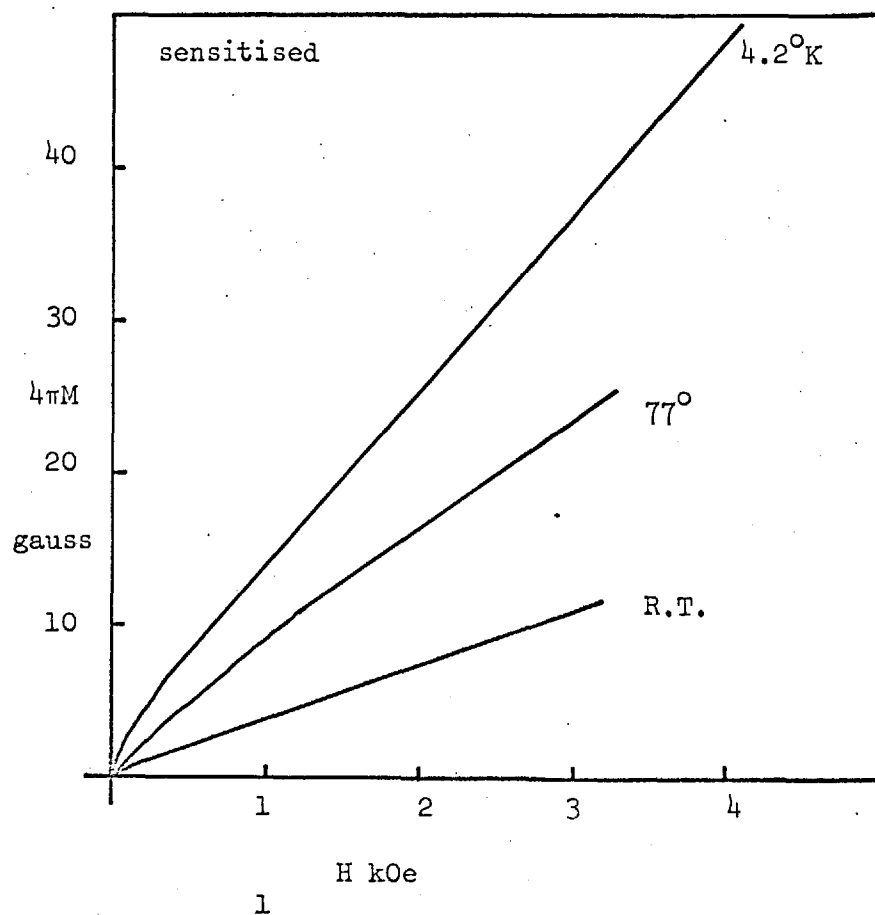
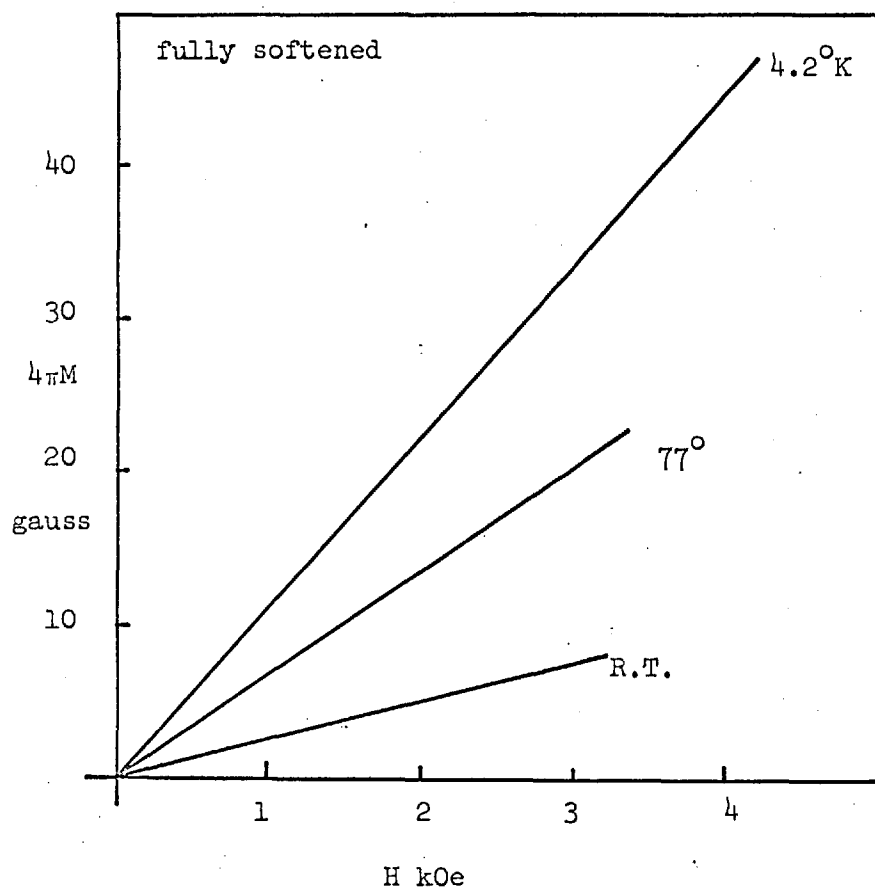


Figure 6.11 Magnetisation curves of 304N.

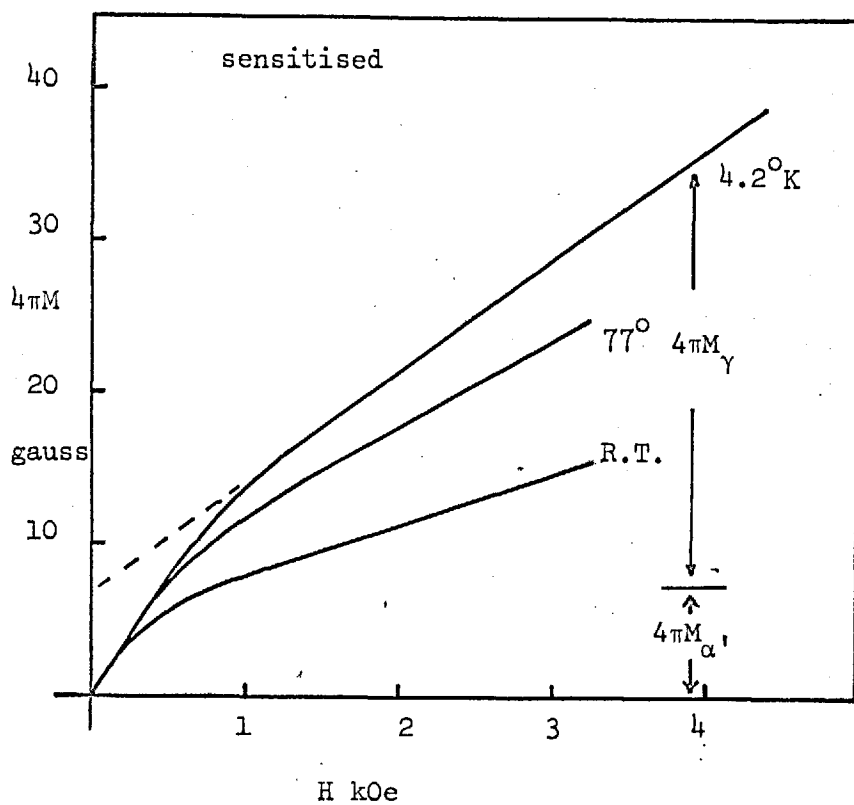
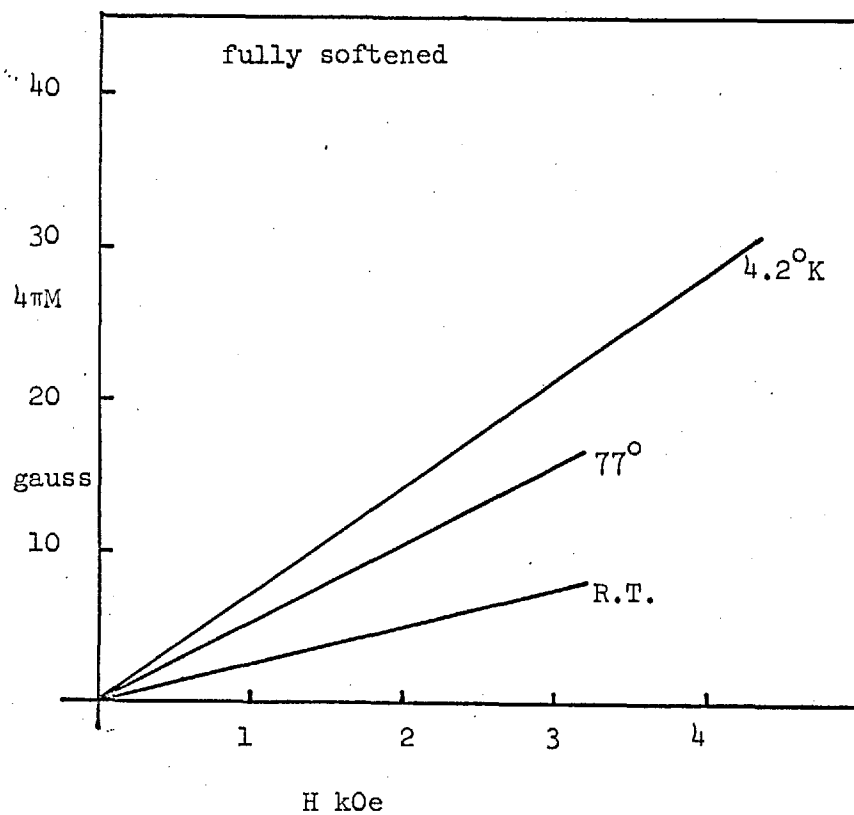
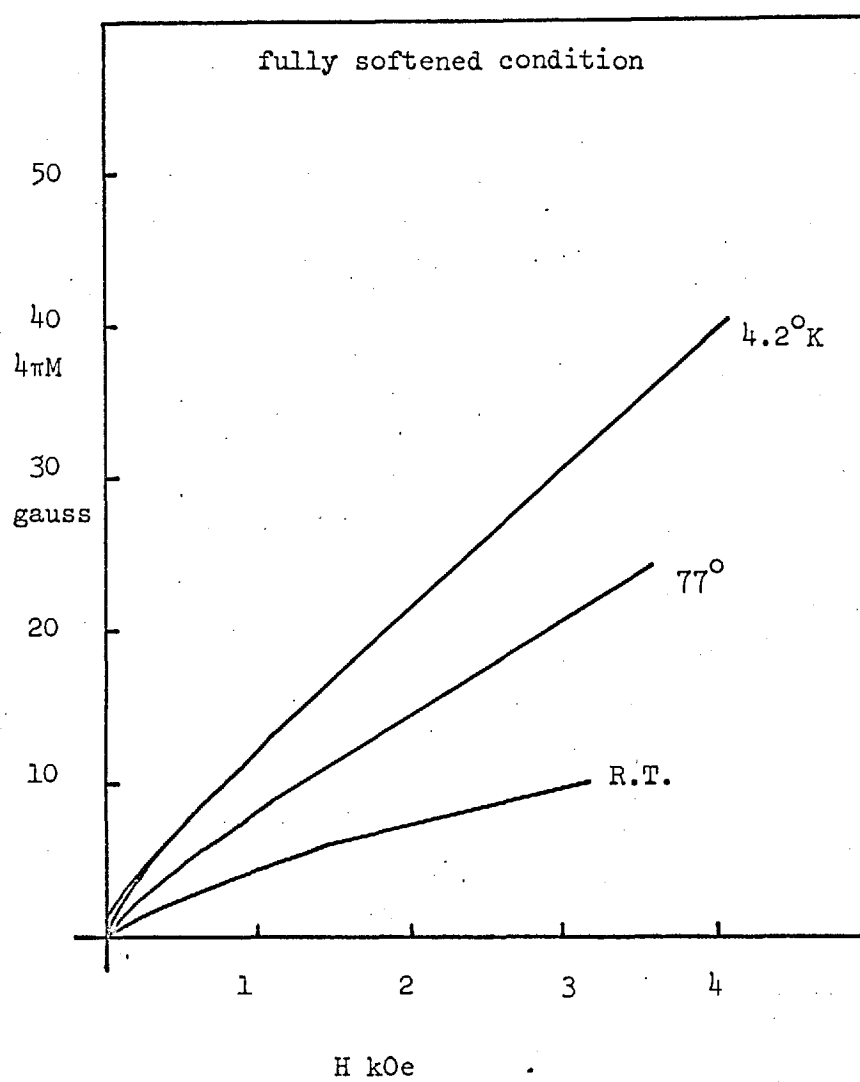


Figure 6.10 Magnetisation curves of 304L.



softened specimen of 304L was measured but the sensitised specimen and those of 321 and 347 were excluded as their ferromagnetic magnetisations obscured the susceptibility of austenite. The as machined specimens were rejected so as to avoid effects due to unknown internal stress distributions.

6.42a Results

The magnetisation curves for steels 304L, 304N, 316LN and Immac 2W are shown in figures 6.10 - 6.13. Their magnetisations are small and characteristic of the paramagnetic (or anti-ferromagnetic) state and increase as the temperature is lowered. Small departures from linearity at low fields were observed, however, for the softened specimen of 304L and the sensitised specimens of 304N, 316LN and Immac 2W, indicating the presence of a small superimposed ferromagnetic magnetisation. A linear extrapolation of the relevant curves indicates that the ferromagnetic component of the magnetisation is less than 15 gauss, which corresponds to less than 0.1% α' martensite or δ -ferrite. Neither of the phases could be detected, however, by light microscopy. While in principle sensitising at 700°C could cause δ -ferrite to form if the high temperature alloying balance of the steel is very fine it is much more likely that this magnetisation is due to α' martensite since, as discussed in the previous section, the removal of both chromium and carbon from solid solution will tend to raise M_s . An examination of figure 6.13 shows that on a second quench to 4.2°K, the ferromagnetic component of the magnetisation curve of Immac 2W had increased by 0.02% which could only be due to the formation of α' martensite.

The susceptibility values, $\chi = M/H$, derived from these curves are shown in table 6.13. The 4.2°K values of $5 - 8 \times 10^{-4}$ are in general agreement with the previous work referred to in section 3.15b. For those specimens with a small ferromagnetic component, χ was derived by extrapolating the high field slope of the magnetisation curve to zero field, as illustrated in figure 6.11.

The magnetisation curves of the high alloy steels 309, 310 and Incoloy 800 are shown as a function of temperature in figures 6.14 -

Figure 6.16 Magnetisation curves of Incoloy 800.

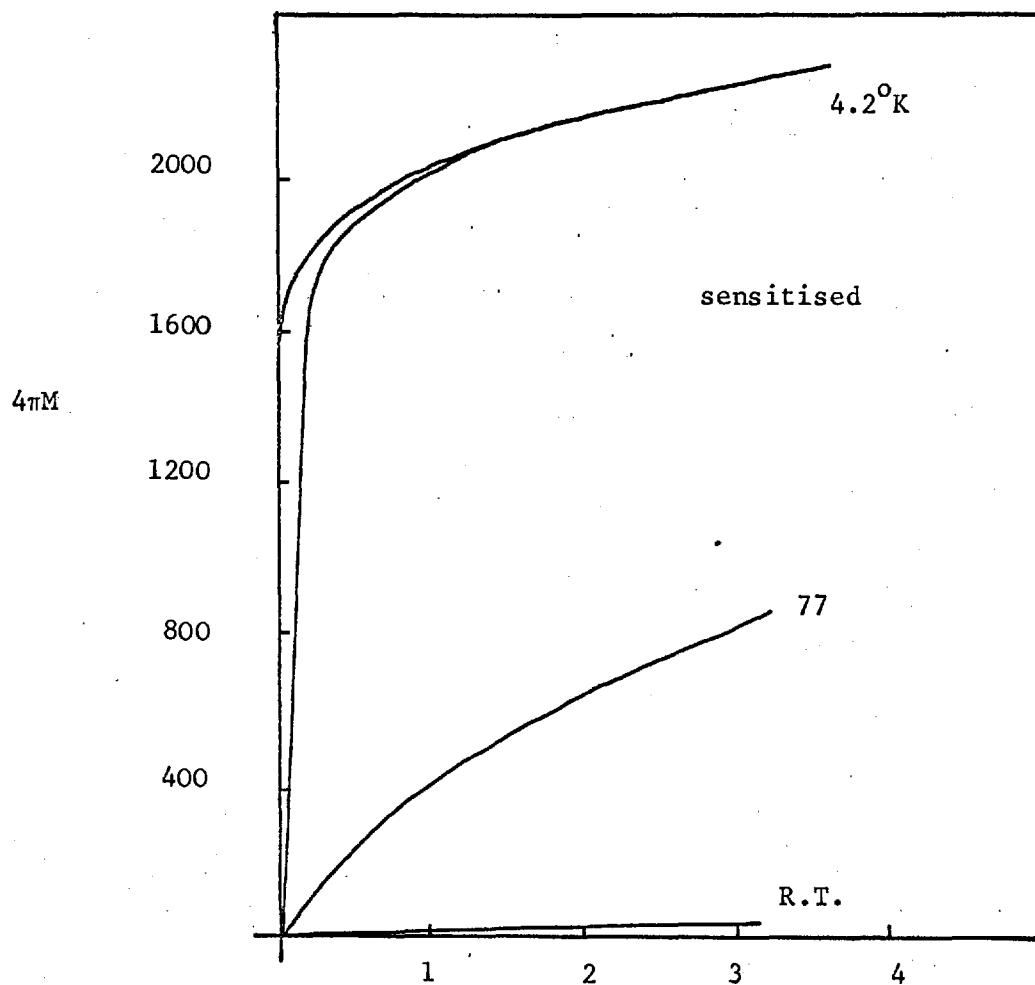
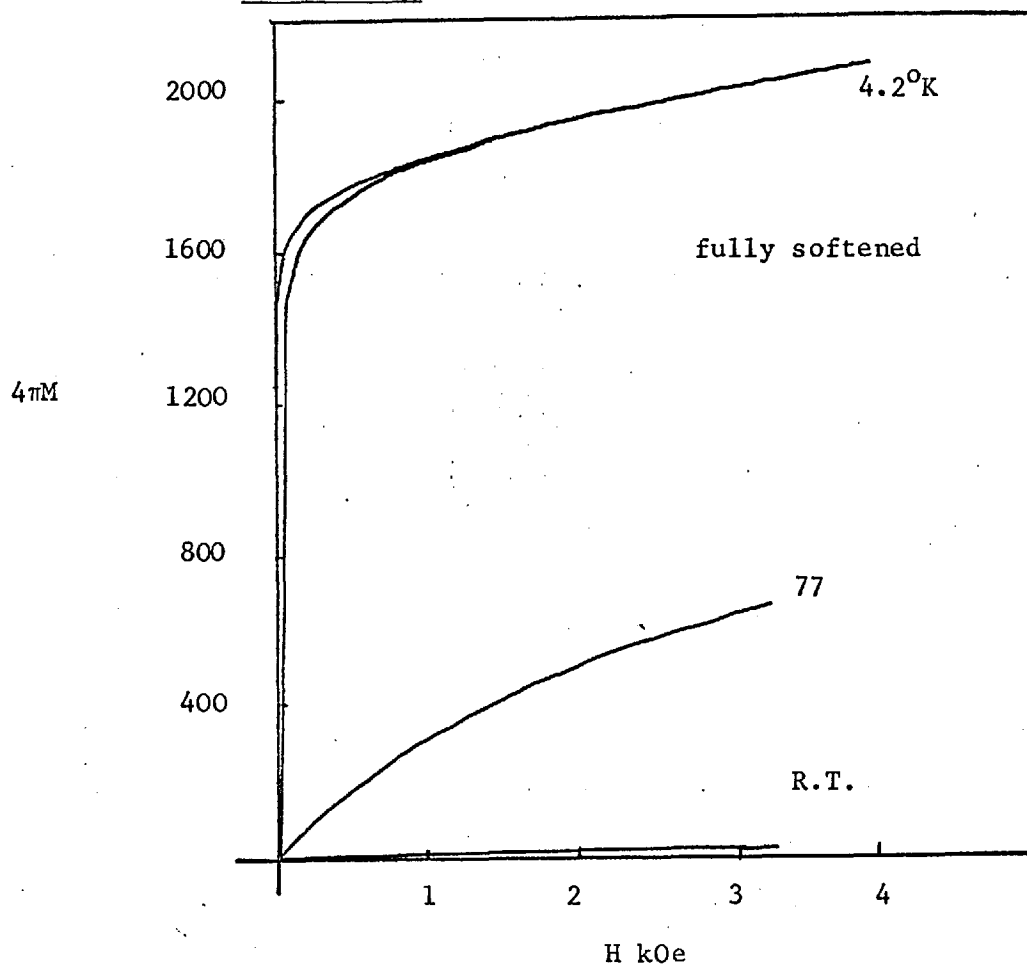


Figure 6.15 Magnetisation curves of 310.

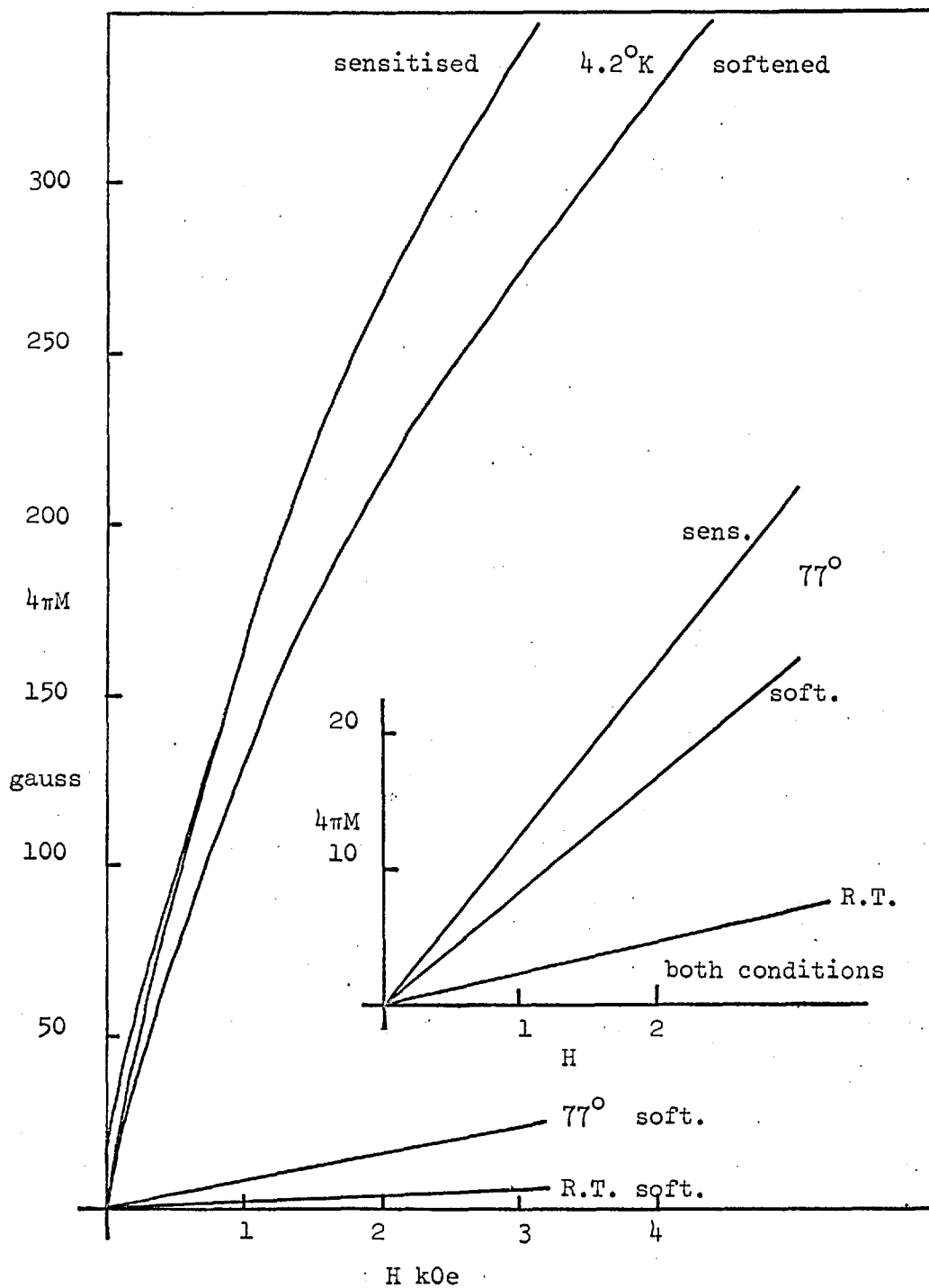
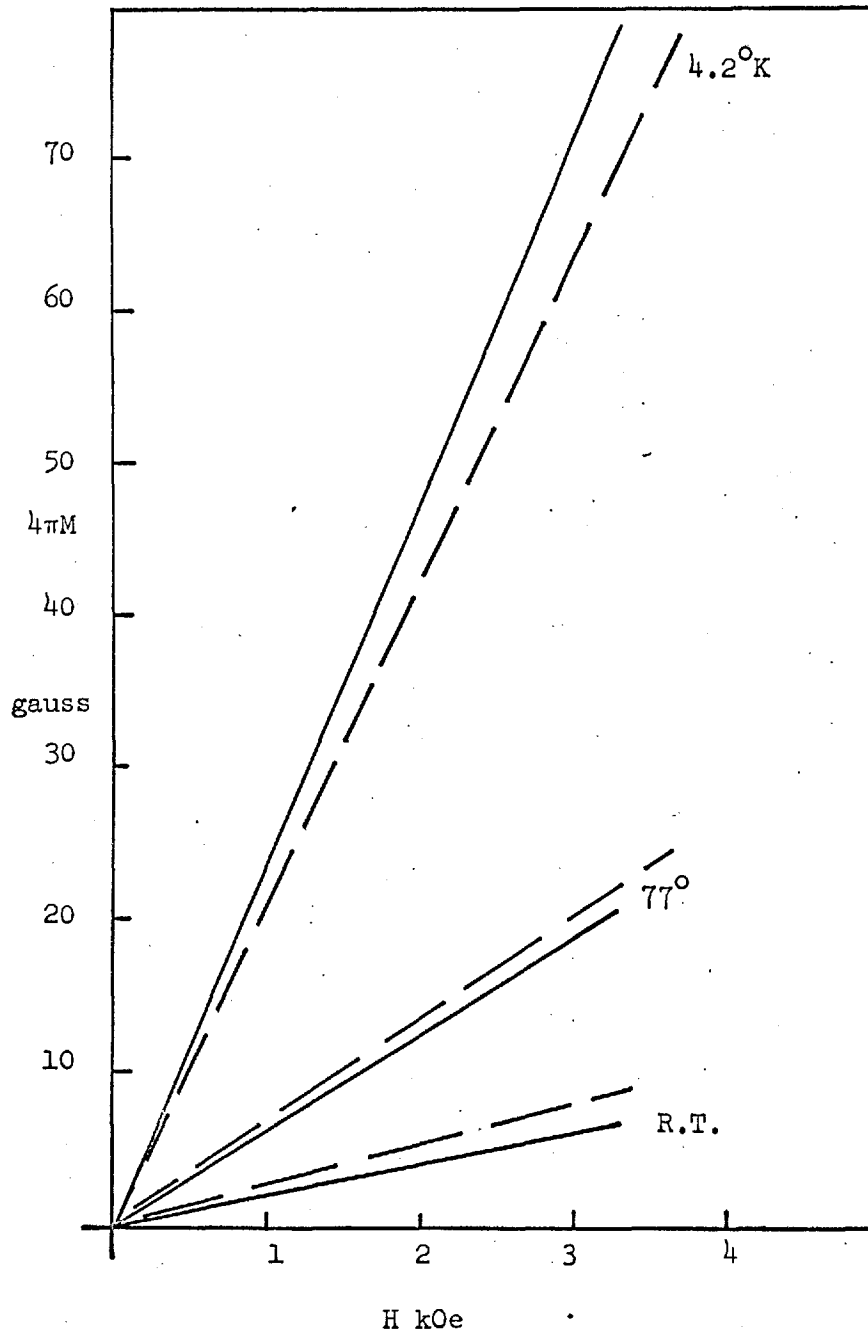


Figure 6.14 Magnetisation curves of 309.



Full line - fully softened

Broken line - sensitised

6.16. Both samples of 309 had linear magnetisation curves at all temperatures (figure 6.14) but whereas the R.T. and 77°K magnetisations were similar to those observed in the stable 18/10 steels, the 4.2°K values are approximately twice as large. The susceptibilities derived from these curves are also included in table 6.13.

Steel 310 was found to be paramagnetic at R.T. and 77°K but ferromagnetic with a remanent induction at 4.2°K, as shown by figure 6.15. This remanence is very small for the annealed sample (2 gauss) but somewhat larger for the sensitised sample (14 gauss). The general form of the magnetisation curves at 4.2°K is similar to that obtained for the steels containing martensites (321 and 347) and the magnetisation shows no sign of saturating at the maximum applied field of 4 kOe.

Incoloy 800 shows a most interesting sequence of magnetisation curves (figure 6.16). A normal paramagnetic curve was obtained at room temperature, while a smoothly increasing ferromagnetic curve, similar to those obtained for 321 and 347 was observed at 77°K. The remanent induction at this temperature was ~ 4 gauss. On cooling to 4.2°K, however, not only was the magnetisation the largest measured in any of the present steels, but a striking change was observed in the shape of the curve. As may be seen from figure 6.16 the initial permeability is high (~ 16 at 100 Oe for the softened sample) and a characteristic knee appears in the curve at low fields. The remanent induction of 1250 gauss is also much greater than that in any of the other steels. The significance of these findings is discussed in the following section.

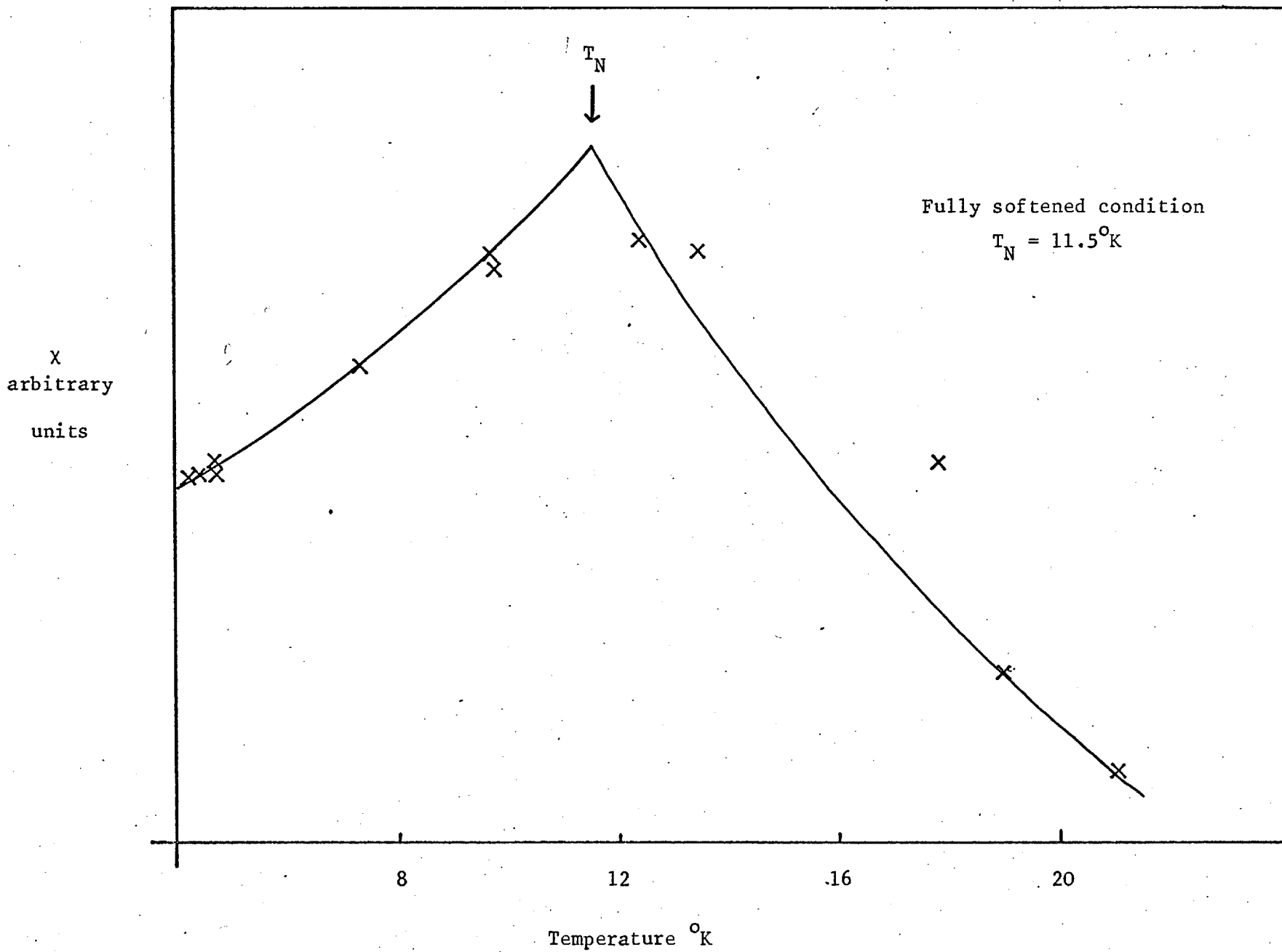
6.42b Paramagnetic and anti-ferromagnetic behaviour

According to both a classical and a quantum mechanical view (18) the paramagnetic susceptibility of a metal is expected to increase rapidly as the temperature is lowered, following the Curie law :

$$\chi = C/T \quad \text{where} \quad C = Np\mu_B^2/k_B$$

where C is the Curie constant, N is the number of atoms/unit volume, p the number of effective Bohr magnetons μ_B associated with each electron

Figure 6.22 The Néel temperature of steel 309



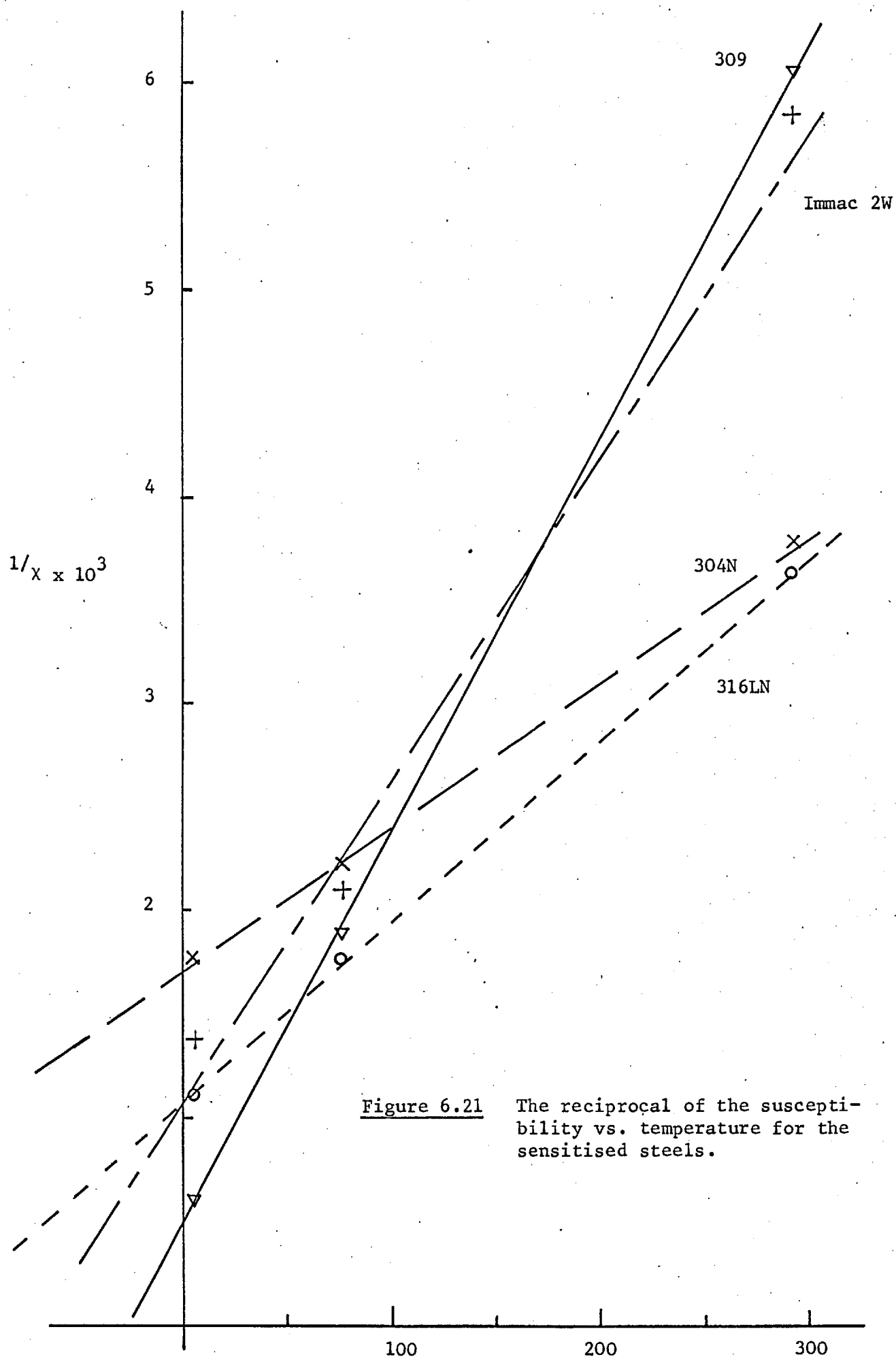


Figure 6.21

The reciprocal of the susceptibility vs. temperature for the sensitised steels.

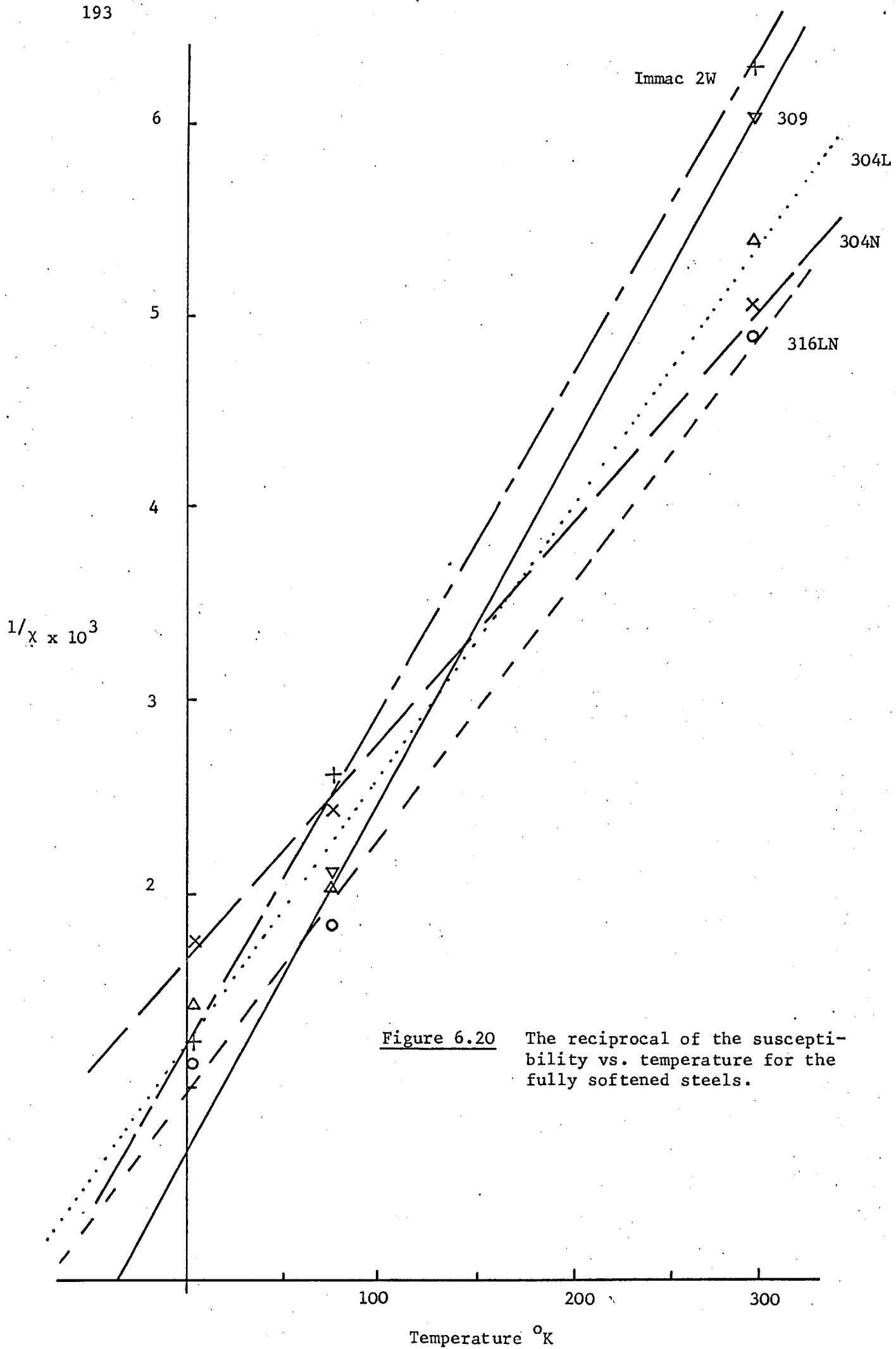


Figure 6.20

The reciprocal of the susceptibility vs. temperature for the fully softened steels.

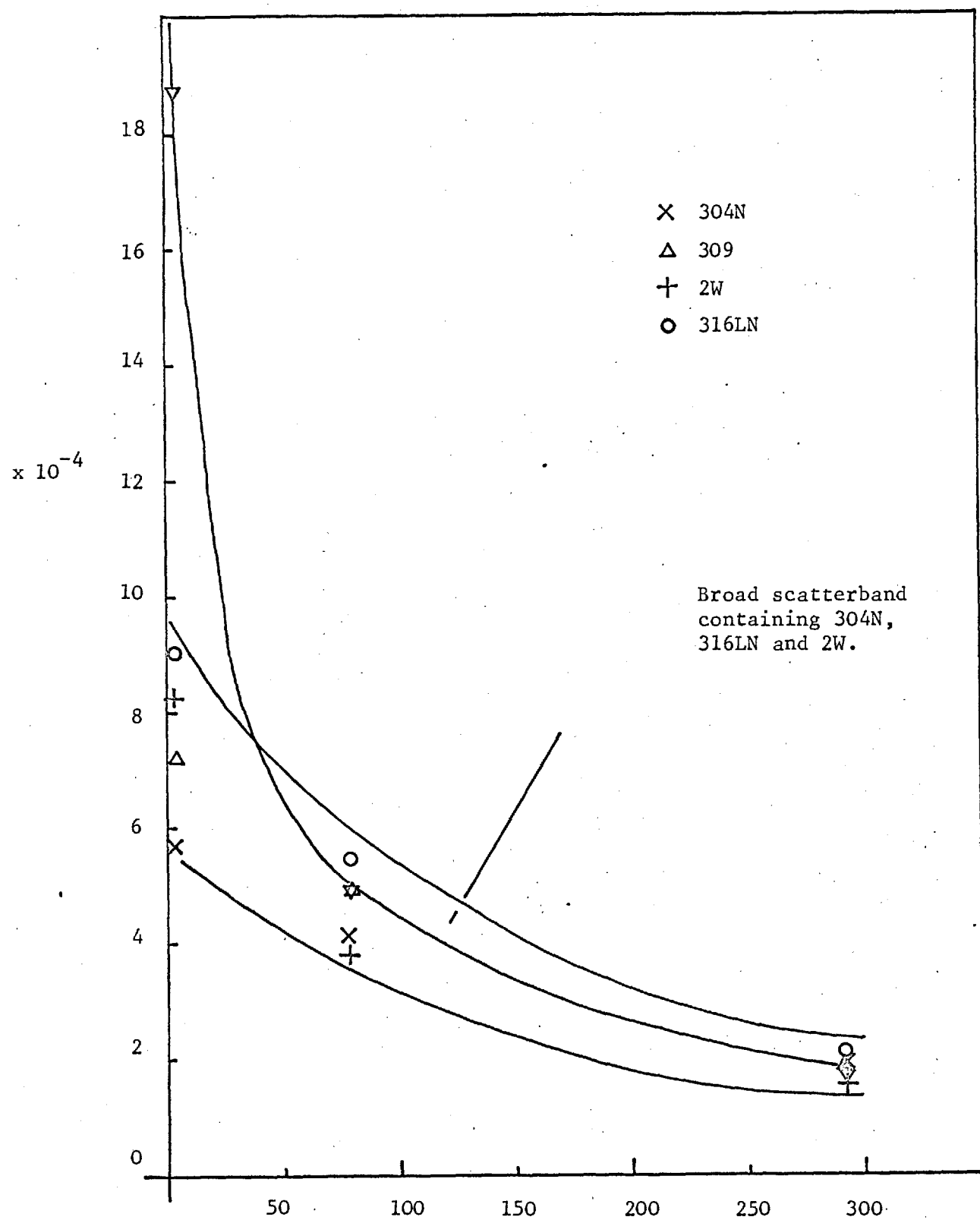


Figure 6.19 Susceptibility vs. temperature for the sensitised steels.

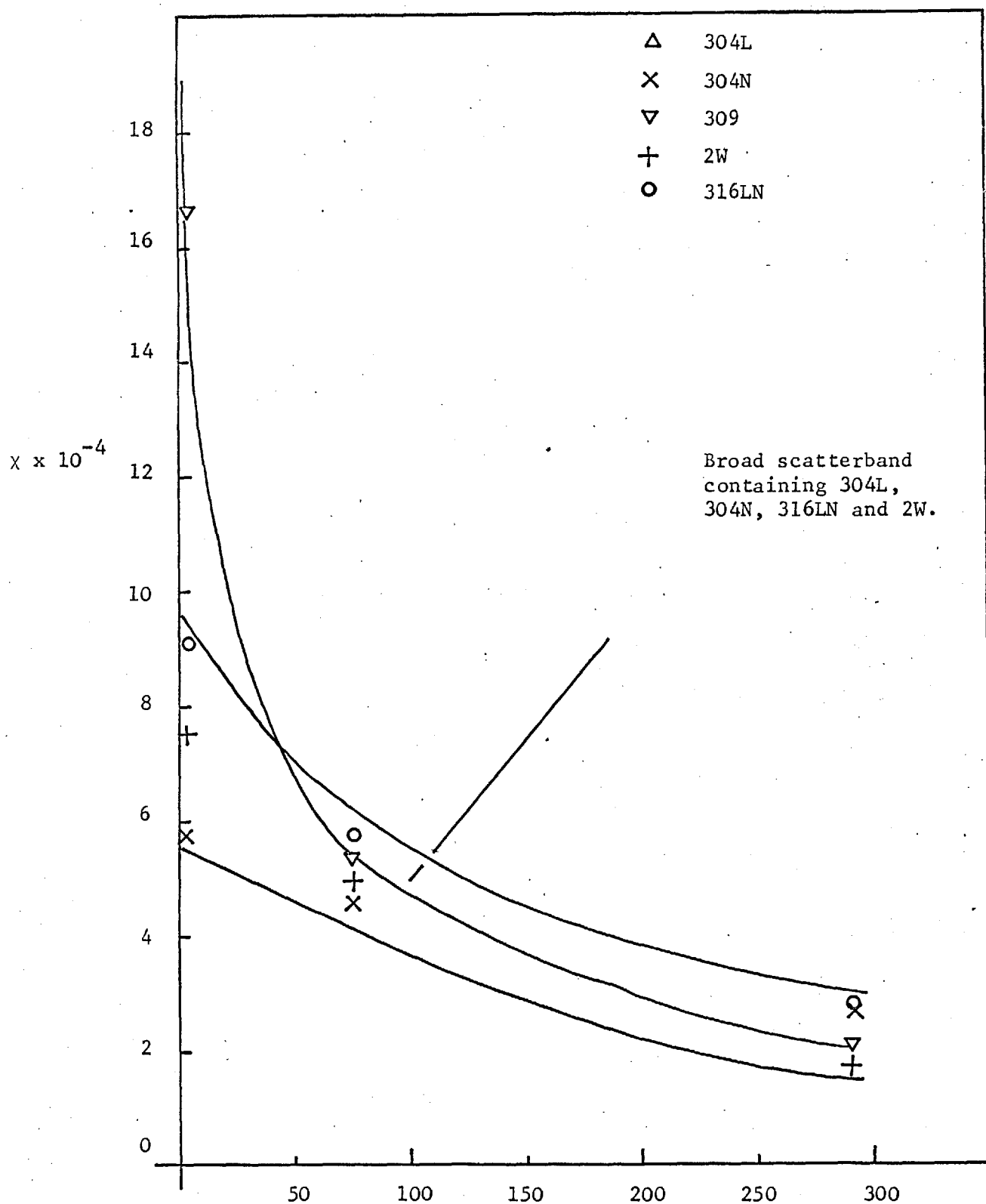


Figure 6.18

Susceptibility vs. temperature for the fully softened steels.

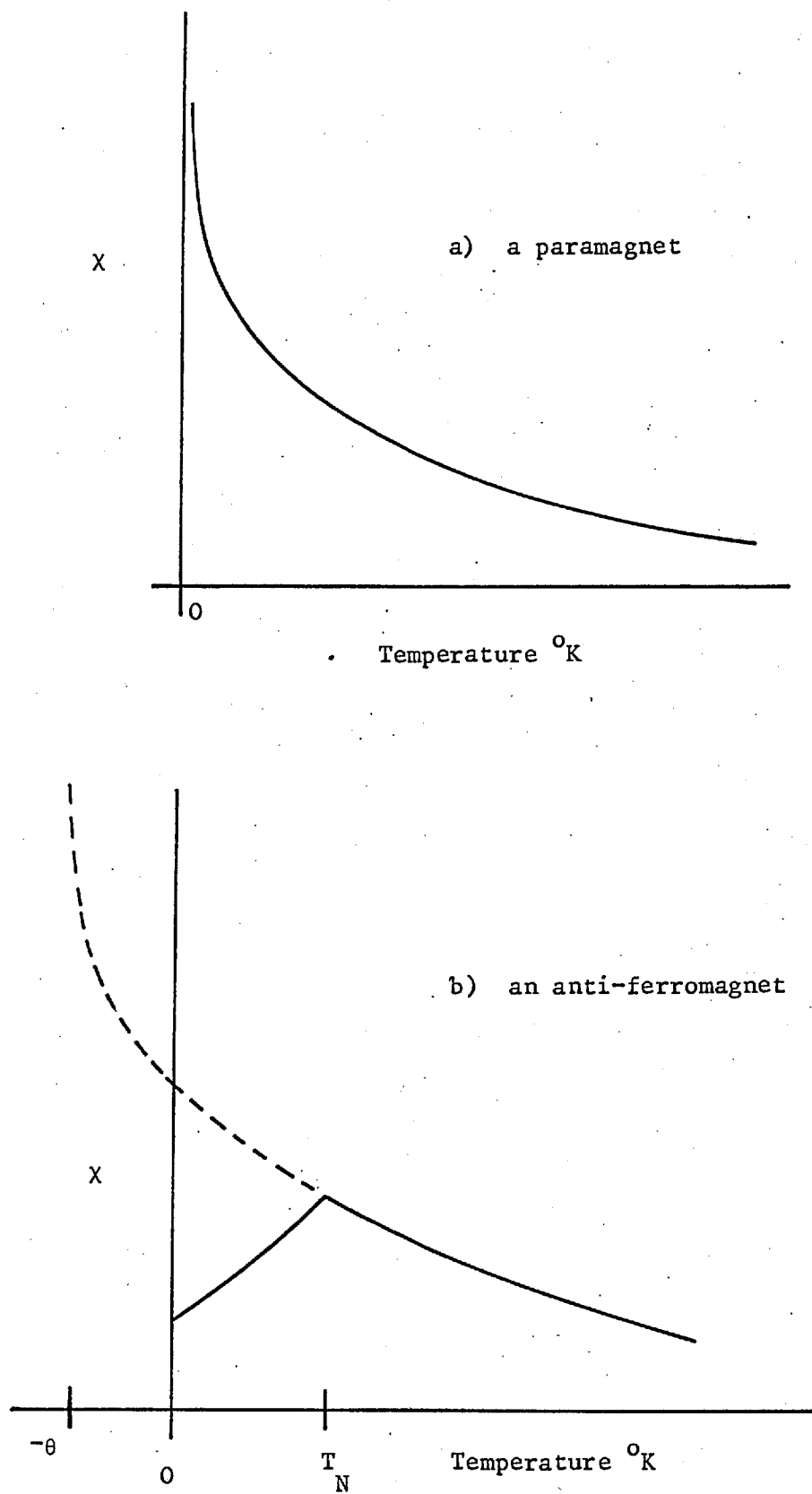


Figure 6.17 Susceptibility vs. temperature curves for ferromagnets and paramagnets.

and k_B is Boltzmann's constant. This behaviour is illustrated in figure 6.17a.

Materials which become anti-ferromagnetic below a Néel temperature, T_N , show a similar behaviour above T_N and the susceptibility is now given by a Curie-Weiss law :

$$\chi = C/T + \theta$$

where θ is the negative temperature intercept at which the extrapolated susceptibility becomes infinite, as shown in figure 6.17b. This figure also shows the characteristic χ/T curve expected of a paramagnetic/anti-ferromagnetic transition. On entering the anti-ferromagnetic state at T_N an antiparallel alignment of electron spins now becomes favourable, resulting in a lower net magnetic moment. As the temperature is further reduced this state of magnetic order becomes more perfect and the susceptibility progressively declines.

The susceptibility values of table 6.13 for the non-ferromagnetic steels are plotted against temperature in figures 6.18 and 6.19. It can be seen that the 18/10 steels lie within a broad band, while 309 although having similar values of χ at R.T. and 77°K has a value $\sim$ twice as large at 4.2°K. Such behaviour is qualitatively explicable by assuming that the 18/10 steels are anti-ferromagnetic at 4.2°K while 309 is still paramagnetic. Evidence for anti-ferromagnetic behaviour in 304 and 347 has been previously reported by Kondorsky and Sedov (19), Gonser et al (20) and Meiklejohn (21). When, however, $1/\chi$ is plotted against T , as in figures 6.20 and 6.21, negative intercepts are obtained for not only the 18/10 steels but also 309, suggesting that this steel also is anti-ferromagnetic above 0°K.

In order to test this supposition, the fully softened specimen of 309 was cooled from 77° to 4.2°K over a period of about 30 minutes and its temperature monitored to $\pm 1^\circ\text{K}$ with a germanium thermometer. At selected temperatures, the magnetisation of the sample was measured in a fixed field of $\sim 3 \text{ kOe}$. When these results are plotted against temperature as in figure 6.22, a clear peak in the magnetisation was obtained in the vicinity of 11.5°K. Cycling between 8 and 16°K gave reproducible values of the magnetisation and it was thus concluded

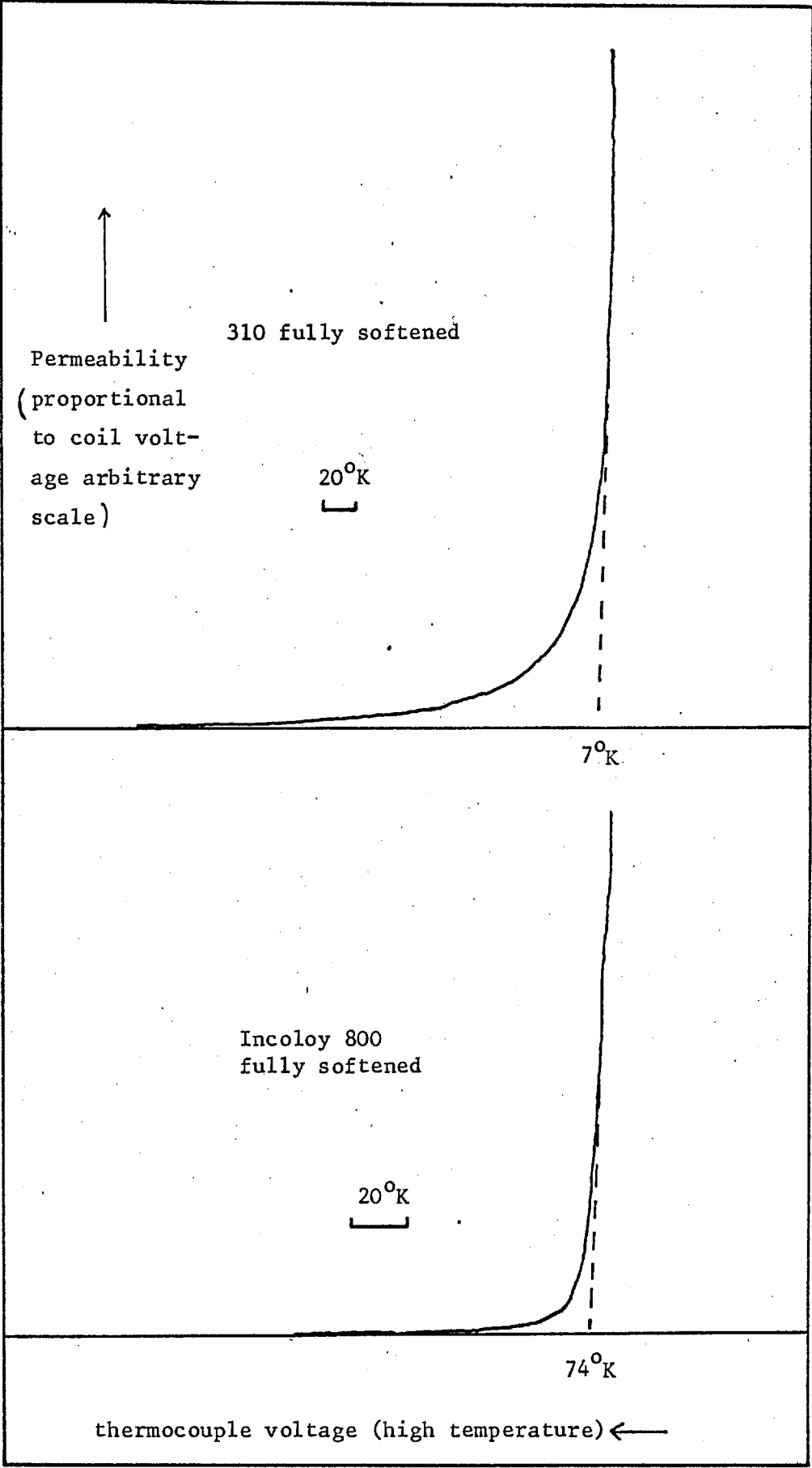


Figure 6.23 Traces of A.C. susceptibility curves for 310 and Incoloy 800.

that 309 was anti-ferromagnetic at 4.2°K and had a Néel temperature of $11.5 \pm 1^{\circ}\text{K}$. Although this experiment was not repeated for the remaining 18/10 steels, it was concluded that the data shown in figures 6.20 and 6.21 are consistent with a paramagnetic/anti-ferromagnetic transition between 77° and 4.2°K .

6.42c Ferromagnetic behaviour

Using the apparatus described in section 4.42, the low field A.C. susceptibility of the fully softened specimens of 310 and Incoloy 800 was followed on cooling from R.T. to 4.2°K . The curves obtained in this way are shown in figure 6.23.

According to Bozorth (22), the low field permeability of a ferromagnet falls off steeply near the Curie point before changing more gradually to a value characteristic of the paramagnetic state. A linear extrapolation of the steep portion of the curve gives the Curie point, as in figure 6.23.

Using a copper constantan thermocouple, for which fixed point calibrations had been obtained at 4.2° and 77°K , the extrapolated Curie points derived from the plots in figure 6.23 were found to be $7^{\circ} \pm 2^{\circ}\text{K}$ for 310 and $74^{\circ} \pm 1^{\circ}\text{K}$ for Incoloy 800. This latter value is surprising in view of the ferromagnetic magnetisation observed in this alloy at 77°K (figure 6.16) and is discussed further in section 6.52.

6.5 Discussion

6.51 The occurrence of martensite in the 18/10 steels

6.51a Discrepancies with previous work

The finding of α' martensite in the fully softened specimens of steels 321 and 347 but not in 304L is in direct disagreement with the previous findings of Reed and Mikesell (1) who reported martensite in steels 303 and 304 but not 316, 321 and 347 even after extended cycling to 77° and 20°K . The analyses of their steels and the cast

analyses supplied with the present ones show that all the above steels fall within the relevant AISI 300 specification (table 3.1). Although the specimen analyses performed at Imperial College indicate carbon contents considerably higher than specification, equation 3.3 shows that an increased carbon content will tend to stabilise the austenite and thus the present disagreement cannot be explained in this way. A review of the literature shows that essentially stable samples of 304 and 347 have been obtained by Gonser et al (20) and Meiklejohn (21) who were able to measure Néel temperatures in their samples. Guntner and Reed (15) found, also, that, of five samples of 304 and 304L, two transformed and three did not. It must therefore be concluded that the individual AISI specifications are sufficiently broad that very significant differences exist in the low temperature magnetic properties of different casts of the same grade. The results obtained in the present study must therefore be closely examined with this in mind.

6.51b The prediction of low temperature instability

The quantitative approach to the prediction of the M_s temperature in the austenitic stainless steels, proposed by Eichelmann and Hull (6), has already been discussed in section 3.14c, together with the objections that carbon and nitrogen do not necessarily act linearly with composition as is proposed by these workers. Nevertheless, this analysis is the only quantitative approach available and it has been applied both to the present steels and to previous alloys whose chemical composition is known in sufficient detail to make meaningful calculations of M_s . Because of the pronounced influence of nitrogen a value of 0.02% has been assumed in the absence of an analysis, while the effects of free niobium and titanium have been ignored as no data on their behaviour is available. The effect of molybdenum was also not considered by Eichelmann and Hull but since all the elements considered were found to depress the M_s , it is likely that molybdenum, titanium and niobium do also and that subsequent calculations for steels containing these elements may underestimate their low temperature stability.

The M_s is then given by

TABLE 6.14 Calculated M_s temperatures for 18/8 - 18/10 steels
using equation 3.3.

Steel and Source	Heat analysis	Specimen analysis	
	M_s	M_s	Corrected M_s^*
a) from Reed & Mikesell(1)			
302		-16°K	
303		<u>149</u>	
304		<u>50</u>	
316		-143	
321		-38	52
347		-141	-58
b) from Guntner & Reed(15)			
304	155°K		
304	<u>83</u>		
304	54		
304L	<u>171</u>		
304L	122		
c) present work			
304L	53°K	0	
304N	-233	-291	
316LN	-210	-291	
321	<u>90</u>	<u>31</u>	<u>181</u>
347	<u>-22</u>	<u>-4</u>	<u>138</u>

Notes :

Steels underlined contained α' martensite.

* The stabilised steels have been corrected for free carbon,
see text.

$$M_s (^{\circ}\text{K}) = 41.7 (14.6 - \text{Cr}) + 61.1 (8.9 - \text{Ni}) + 33.3 (1.33 - \text{Mn}) \\ + 27.8 (0.47 - \text{Si}) + 1667 (0.068 - (\text{C} + \text{N})) + 255 \quad 3.3$$

Applying this equation to the sample analyses of the six steels studied by Reed and Mikesell (1), it is found that the predicted M_s temperatures of steels 303 and 304 lie above 0°K , while those for 302, 316, 321 and 347 have negative values, as shown in table 6.14. This finding is in complete agreement with the magnetic studies of these authors which showed that, of their samples, only 303 and 304 became unstable at low temperatures.

A similar calculation, using the heat analyses of a series of 304 and 304L steels studied by Guntner and Reed (15), shows that the predicted M_s temperatures within the two compositions can vary over a range $54 - 155^{\circ}\text{K}$ and $122 - 171^{\circ}\text{K}$ respectively. The samples of 304 and 304L with predicted M_s temperatures of 83° and 171°K were reported to decompose spontaneously to martensite on cyclic cooling to 4.2°K , while the remaining samples, all with M_s temperatures above 0°K , remained stable. This sharp contrast to the apparent success of the equation in predicting the M_s temperatures of Reed and Mikesell's steels can be attributed to the use of the heat analyses instead of repeating the analysis on the particular samples under test.

To test this hypothesis, the predicted M_s temperatures of the present steels have been calculated using both the heat and actual sample analyses. The results, also included in table 6.14, show that in general the M_s calculated from a sample analysis lies some $50 - 120^{\circ}\text{K}$ below that from the respective heat analysis, the difference being almost entirely due to the variation in carbon composition. Neither of these calculated M_s sequences really fits the magnetisation results, however, for if the consideration is restricted to fully softened steels, for example, 321 contained approximately 3 times the quantity of α' as 347 (3.7% vs 1.3%) whereas the sample analysis indicates that only 321 has an M_s above 0°K . Experiments indicated that quenching to 77°K was quite adequate to produce α' martensite in both 321 and 347 but these results may be explained if the free carbon and nitrogen contents are considered.

According to a simple point of view titanium and niobium remove carbon from solid solution in the weight ratios of 4 : 1 and 8 : 1. As discussed by Keating (9) and by Pryce and Andrews (23) some carbon may be left in solution, particularly by titanium which also has a strong affinity for nitrogen. Following Pryce and Andrews, 0.03%C has been assumed to be present in solution in both 321 and 347 even in the presence of excess Ti and Nb and the nitrogen in the presence of titanium has been assumed to be fixed as TiN before the carbon. This is not true in 347 where niobium is not appreciably affected by nitrogen. Thus, in the present samples of 321 and 347, sufficient titanium and niobium was present to remove 0.09% C + N from 321 and 0.085% C from 347 which results in increases in the M_s of 150° and 142°K , respectively. The present steels are now found to lie in the M_s sequence 321 (181°K), 347 (138°K), 304L (0°K), 304N and 316LN (-291°K) which corresponds exactly to the order of martensite contents of these steels after cryogenic cycling. It is also of interest to compare the predicted M_s of 0°K for the fully softened sample of steel 304L with the value of 117°K derived for the sensitised sample after the extensive chromium carbide precipitation shown in figure 6.8a. The similarity of the M_s temperature of 347 (138°K) which contained 1.3% α' to this sample which contained 1.4% α' is striking.

When a similar procedure is applied to Reed and Mikesell's specimens of 321 and 347, the M_s temperatures are found to have increased to 52°K (321) and -58°K (347) by the removal of 0.054% C + N and 0.05% C, respectively. Since both these steels were found to be stable and samples were cycled to 20°K the result for 321 is not at first in accord with the preceding analysis. Two factors, however, must be taken into account. The first of these is that equation 3.3 produced an average deviation of 20°C between the measured and calculated M_s temperatures of Eichelmann and Hull. The second factor is that it is difficult to allow precisely for the effect of titanium because it is partially soluble in austenite at temperatures above 1000°C and therefore unavailable for combination with carbon or nitrogen. When subsequent fully softening treatments at $1050^\circ - 1100^\circ\text{C}$ are short (as in Reed and Mikesell's case, where $\frac{1}{2}$ hour at 1065°C W.Q. was given) excess titanium may remain in solution. Evidently this was not the case for the present work as the magnetic evidence shows that there was little difference in the amount of α' martensite formed after fully

TABLE 6.15 The variation of M_s within permitted compositional tolerances according to equation 3.3

The maximum and minimum compositions are those from table 3.1, together with likely lower limits of 0.5 % Mn and 0.25 % Si. 0.02 % N has also been included. In the plain carbon grades the likely carbon variation is 0.01 - 0.03 % (304L & 316L) and 0.04 - 0.08 % (304 & 316). In the stabilised grades a constant 0.03 % C has been assumed, but in 321 the nitrogen will be present as TiN and not available for stabilisation. No factor is known for molybdenum but if it is assumed that it behaves like silicon, the weakest depressant of the M_s , 2.5 % Mo in the 316 grades would result in a further depression of 72°K to the figures in the table.

Steel	Calculated M_s	
	Upper limit	Lower limit
304	215°K	-251°K
304L	265	-167
316	176	-292
316L	226	-209
321	258	- 80
347	225	-175

softening or on sensitising. Since Reed and Mikesell did not sensitise their samples this hypothesis cannot be checked but it is noteworthy that this problem is not expected to occur for 347 as niobium is not soluble to the same extent (9).

The predictions of M_s in the preceding discussion, although based on a limited amount of data, are very encouraging because they suggest that equation 3.3 does allow a quantitative approach to the occurrence or non-occurrence of martensite in the stainless steels. It is interesting therefore to apply equation 3.3 to estimate the maximum and minimum values of M_s which can be expected from typical commercial samples of these steels. The results of this calculation together with the likely lower limits of carbon, manganese and silicon on which the calculation is based are shown in figure 6.15 and indicate that a wide range of M_s temperatures is possible in these steels. The 304 and 316 grades are seen to be the most stable with the low carbon versions about 50°K less stable, as would be expected from general considerations. 347 is similar to the low carbon grades but the strong affinity of titanium for nitrogen as well as carbon ensures that 321 will in general be the least stable of all these steels. Since, according to Keating (9), the stabilised steels are also the most likely to contain δ -ferrite they should perhaps be avoided for low temperature use where non-magnetic properties are required.

How then can this analysis be applied to the original problem which was to obtain a structurally stable non-ferromagnetic stainless steel ?

1) The preceding discussion suggests that a quantitative approach may be possible using equation 3.3 but only if the exact chemical composition of the particular specimen is known. This would be a costly exercise for a small scale user since current commercial analysis costs are of the order of £3 - 5 per element (24). Some relief from this problem would be gained by raising the nickel content to the maximum in each specification. As may be seen from table 6.16 the principal variations in the calculated M_s temperatures of table 6.15 are due to the wide range of nickel content possible and in the

TABLE 77—STAINLESS AND HEAT RESISTING STEEL PRODUCTION
BY TYPE NUMBERS

(Net tons)

Type Number	1968	1967	1966	1965	1964
201.....	85,836	29,295	23,955	23,818	44,895
202.....	2,354	474	942	1,772	1,631
301.....	120,882	107,919	107,805	105,135	116,620
302.....	30,478	29,234	36,178	35,744	38,295
302B.....		99		118	623
303.....	39,261	41,064	51,947	42,109	35,636
303Se.....	1,953	3,813	3,070	2,390	1,791
304.....	463,862	484,586	577,076	466,373	473,615
304L.....	38,722	38,545	56,194	52,890	50,270
305.....	14,633	15,446	21,601	13,629	11,327
308.....	2,042	4,731	4,688	4,970	3,178
309.....	8,308	8,548	7,888	6,836	6,818
309S.....	1,976	2,211	3,951	3,914	2,154
310.....	5,292	5,745	7,207	6,513	7,069
310S.....	209	273	572	983	1,218
314.....	132	46	218	220	309
316.....	66,103	76,169	93,854	84,810	69,776
316L.....	26,470	27,913	39,214	36,683	31,160
317.....	1,866	883	3,036	1,330	1,812
321.....	24,105	24,258	37,486	33,214	30,925
347.....	8,843	9,333	13,553	11,512	12,186
348.....	2,299	1,507	2,523	2,880	1,026
Other chromium nickel stainless steels with:					
Nickel under 8%, other alloys under 10%.....	16,526	21,445	22,039	13,211	16,858
under 8%, over 10%.....	24,540	24,154	24,225	17,410	14,570
8% to 16%, under 10%.....	416	1,082	1,383	1,217	3,093
8% to 16%, over 10%.....	7,242	8,362	13,389	9,085	12,125
16% to 24%, under 10%.....	94	378	590	1,402	2,668
16% to 24%, over 10%.....	3,005	4,900	5,249	2,866	
over 24%, under 10%.....	22,979	2,211	5,234	7,771	6,347
over 24%, over 10%.....		22,201	28,938	17,226	14,039
Total.....	970,428	996,825	1,194,005	1,008,031	1,011,034
403.....	20,325	26,151	19,971	19,935	17,043
405.....	4,058	3,315	4,240	3,334	2,589
406.....				1,589	2,192
410.....	53,772	55,035	64,041	63,472	48,012
414.....	228	417	501	462	338
416.....	45,439	45,758	48,823	35,820	31,405
416Se.....			1,056	200	116
420.....	6,950	6,284	8,169	8,277	6,658
430.....	135,858	134,912	146,408	178,293	178,030
430F.....	4,494	2,919	4,531	3,701	3,247
430F Se.....		421			578
431.....	2,356	3,917	4,684	3,690	2,900
440A.....	4,120	3,164	4,601	5,003	4,379
440B.....	185	218	111	186	184
440C.....	7,305	9,411	10,913	6,676	6,128
442.....	1,467	596	1,164	376	1,313
443.....		360	419	319	319
446.....	2,202	1,986	2,863	3,540	2,654
All other.....	133,659	123,496	97,893	111,985	97,635
Total.....	421,418	418,360	420,388	446,858	405,170
501 and 502.....	13,919	11,299	11,051	13,265	6,642
All other high cr. heat resisting.....	24,171	23,285	23,715	23,318	18,335
Total.....	38,090	34,584	34,766	36,583	24,977
TOTAL ALL TYPES.....	1,429,936	1,449,769	1,649,159	1,491,472	1,441,181

Excludes stainless steel for castings.

Similar data not available prior to 1942.

Table 6.17 American production of stainless steels.

TABLE 6.16 The influence of individual elements within the
permitted composition ranges on the M_s
according to equation 3.3

Steel	Variation of M_s possible from the lower and upper limits of the AISI specifications					
	Ni	Cr	C+N	Mn	Si	Total
304	245 ^{°K}	84	67	50	21	466
304L	245	84	33	50	21	433
316	245	84	67	50	21	468
316L	245	84	33	50	21	433
321	183	84	0*	50	21	338
347	245	84	0*	50	21	400

* at constant 0.03 % C - see table 6.15

composition ranges are from table 6.15

cases of 304, 316 and 316L the M_s would then lie below 0°K even if the remaining elements were at their lower limits. The original problem of significant variations of composition within the one cast and the possibility of significant "leanness" in some of the resulting stock produced from the cast remains, however, and it is unlikely furthermore that such high nickel casts would be made without a significant cost premium.

2) A second approach to the problem is to reject the conventional 18/10 steels in favour of a more highly alloyed steel. Equation 3.3 shows that the high nitrogen versions of the 18/10 steels should be considerably more stable than the conventional grades and this was amply confirmed in the present experiments. Assuming an average increase of 0.15 % in the nitrogen content this should lead to a reduction of 250°K in the M_s and would be sufficient to give 304, 316, 316L and 347 an M_s below 0°K for all ranges of composition. This stability could also be obtained by increasing the chromium and nickel content, as in AISI 305 and 308. As however, it proved impossible to obtain samples of both these steels for the present study, the practical problem of availability would seem to rule out their use except perhaps for a large project warranting a special cast. The latter problem may also occur for the small scale user with respect to the high nitrogen steels. Tonnage figures for the various grades of stainless steel are not released in this country, as they are regarded as a commercial secret (25), but the published American figures (table 6.17) show clearly that production is concentrated in the 18/10 grades, 304(L), 316(L) and 321 and, to a lesser extent, 347 (26).

3) This concentration of production within the conventional 304(L), 316(L), 321 and 347 specifications means that it would be extremely useful if a simple, cheap, room temperature test were available which would enable the cryogenic properties of particular samples of these grades to be assessed without recourse to wet chemical analysis. Such a test may be possible using the general observations of Eichelmann and Hull that steels with an M_s in the region of room temperature have their M_d around 300°C higher. If this observation is equally applicable to steels with an M_s near 0°K , a room temperature deformation test can

then be used to predict the cryogenic behaviour of the steel.

This possibility was therefore investigated by rolling one set of as-machined specimens at room temperature, using about 15 passes through a two high mill. The heating induced by the deformation was minimised by giving small reductions in each pass and allowing the steel to come back to thermal equilibrium before the next pass. As in no case was any specimen more than warm to the touch after rolling, the deformation induced was accepted as being typical of room temperature ($\sim 20^{\circ}\text{C}$). The final thickness of the foils varied between 0.014" and 0.017", representing a 10 - 12 fold reduction in thickness.

After rolling, specimens were cut from the foils with shears and drilled with a 10 BA hole for mounting in the Sucksmith balance so that their martensite content could be determined.

The results of these measurements, after correction for the paramagnetic susceptibility of austenite, are shown in table 6.18.

TABLE 6.18 Martensite content of steels after cold rolling at R.T.

Steel	$4\pi M$ at 12 kOe	% α' martensite
304L	525 gauss	3.1 %
304N	393	2.2
316LN	47	0
321	15,820	~ 100
347	17,100	~ 100

It is evident that 316LN has an M_d below room temperature, while those for 321 and 347 lie considerably above room temperature. Since the rolling procedure produced only 3.1 and 2.2 % α' in 304L and 304N their M_d must lie in the vicinity of room temperature. This qualitative agreement

between the stability of these steels when subjected to room temperature deformation and when subjected to cryogenic cycling (table 6.11) suggests that a comprehensive study of a wide range of heats in these steels would be advantageous. If a definite general relationship can be established between M_s and M_d this will enable a simple, cheap and routine method of selection amongst different batches of the same general specification to be made. It would also incidentally ensure that the problems encountered with the solenoid system, which were responsible in the first place for this study, do not again arise.

6.52 The magnetic properties of austenite

The magnetisation studies at 4.2°K described in section 6.42 have indicated the existence of anti-ferromagnetic behaviour in steels 304L, 304N, 309, 316LN and Immac 2W and ferromagnetic behaviour in 310 and Incoloy 800. In addition, the weldable steels 321 and 347, which have essentially the same Fe - Cr - Ni composition as the remaining 18/10 steels, are also expected to have an anti-ferromagnetic austenite matrix at 4.2°K , but this is obscured by the ferromagnetic behaviour of α' martensite.

The anti-ferromagnetic behaviour is in full agreement with previous reported work in the 18/8 - 10 steels (302 and 303 (27), 304 (19,20) and 347 (21)) but the evidence for ferromagnetism in 310 is apparently contradictory to the work of Mikesell and Reed (27) and Kohlhas et al (28), Mikesell and Reed report that 310 is paramagnetic down to 4.2°K but a close analysis of their results reveals a fall in the slope of the M vs T curve at temperatures below 10°K . This effect is discussed later. Kohlhas et al report no anti-ferromagnetism in a 23.5 Cr/22 Ni alloy, which, however, also contained 2.4 % Si, 0.9 % higher than the permitted limit of 1.5 % in 310. Silicon is known to be a powerful depressant of the Curie point (29) and thus the high silicon content of this alloy (more than three times that of the sample used in the present study) could be sufficient to depress the Curie point below 4.2°K .

The general conclusion to emerge from the study of austenite is that all the steels investigated were either ferromagnetic or antiferromagnetic at 4.2°K. Gonser et al (20) have reviewed the evidence for suggesting that, in contrast to b.c.c. iron which is ferromagnetic, f.c.c. iron is anti-ferromagnetic at low temperatures. From their own Mössbauer measurements, they obtained Néel temperatures of 55° and 67°K for different sizes of γ -iron precipitates, coherent with an f.c.c. copper matrix. The higher value was obtained for the larger precipitate. They also consider, as do Kondorsky and Sedov (19), that the existence of a Néel temperature in the 18/10 steels is evidence of the basic anti-ferromagnetic nature of γ -iron at low temperatures. Further evidence for the anti-ferromagnetic behaviour of γ -iron in 17/13 and 16/16 steels is given by Kohlhaas et al (28). Using the analysis of Danielan (30), they conclude that the basic magnetisation of these austenitic steels is characteristic of nearest neighbour anti-ferromagnetic iron interactions and second nearest neighbour ferromagnetic nickel interactions.

Kaufmann, Clougherty and Weiss (31), however, in an extensive review of the thermodynamic properties of pure iron, conclude that f.c.c. γ -iron can exist in two different electronic states. Some of the physical properties of these two states, as derived from the behaviour of iron in various alloy systems by Weiss (32), are shown in table 6.19. The important difference for the present discussion,

TABLE 6.19 Physical properties of the two γ states in iron
(after Weiss, 32)

	<u>MAGNETIC STATE</u>	<u>CRITICAL TEMPERATURE</u>
γ_1	antiferromagnetic $\sim 0.5 \mu_B$	$\sim 80^\circ\text{K}$
γ_2	ferromagnetic $\sim 2.8 \mu_B$	$\sim 1800^\circ\text{K}$

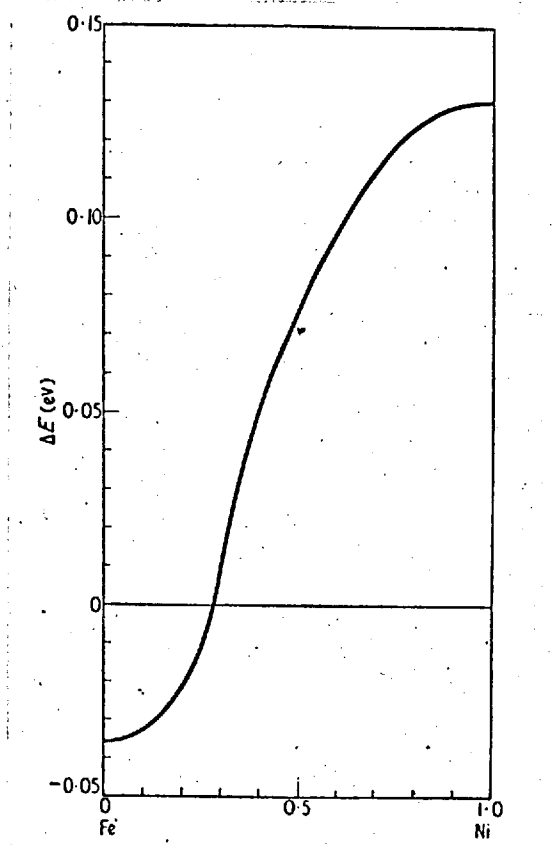


Fig. 6.24 The energy gap between the two γ states of Fe in the Fe-Ni system. (Weiss, 32)

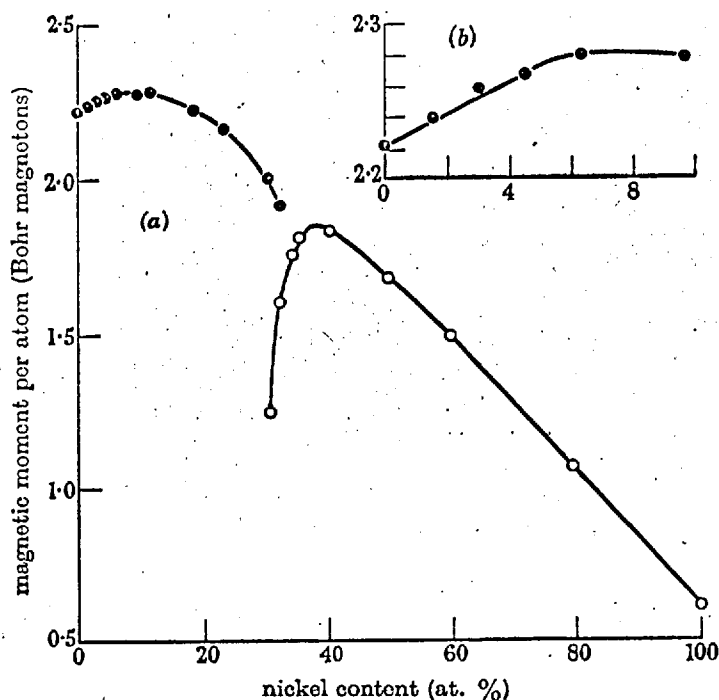


FIGURE 7. (a) The variation of the magneton number of b.c.c. (solid points) and f.c.c. (open points) with composition for iron + nickel alloys, according to the present measurements. (b) The initial part of figure 7 (a) for low nickel contents drawn on a magnified scale.

Fig. 6.25 The variation of Bohr magneton number with composition for Fe-Ni alloys. (Crangle and Hallam, 35)

is that the ground state γ_1 is indeed anti-ferromagnetic with $\sim 0.5\mu_B$ /atom but that the higher energy state is ferromagnetic with $\sim 2.8\mu_B$ /atom, that is with a larger moment than that possessed by α -iron. While thermal energy can cause transitions from the γ_1 to the γ_2 state, these transitions are never sufficient in number to give macroscopic ferromagnetism in pure γ -iron.

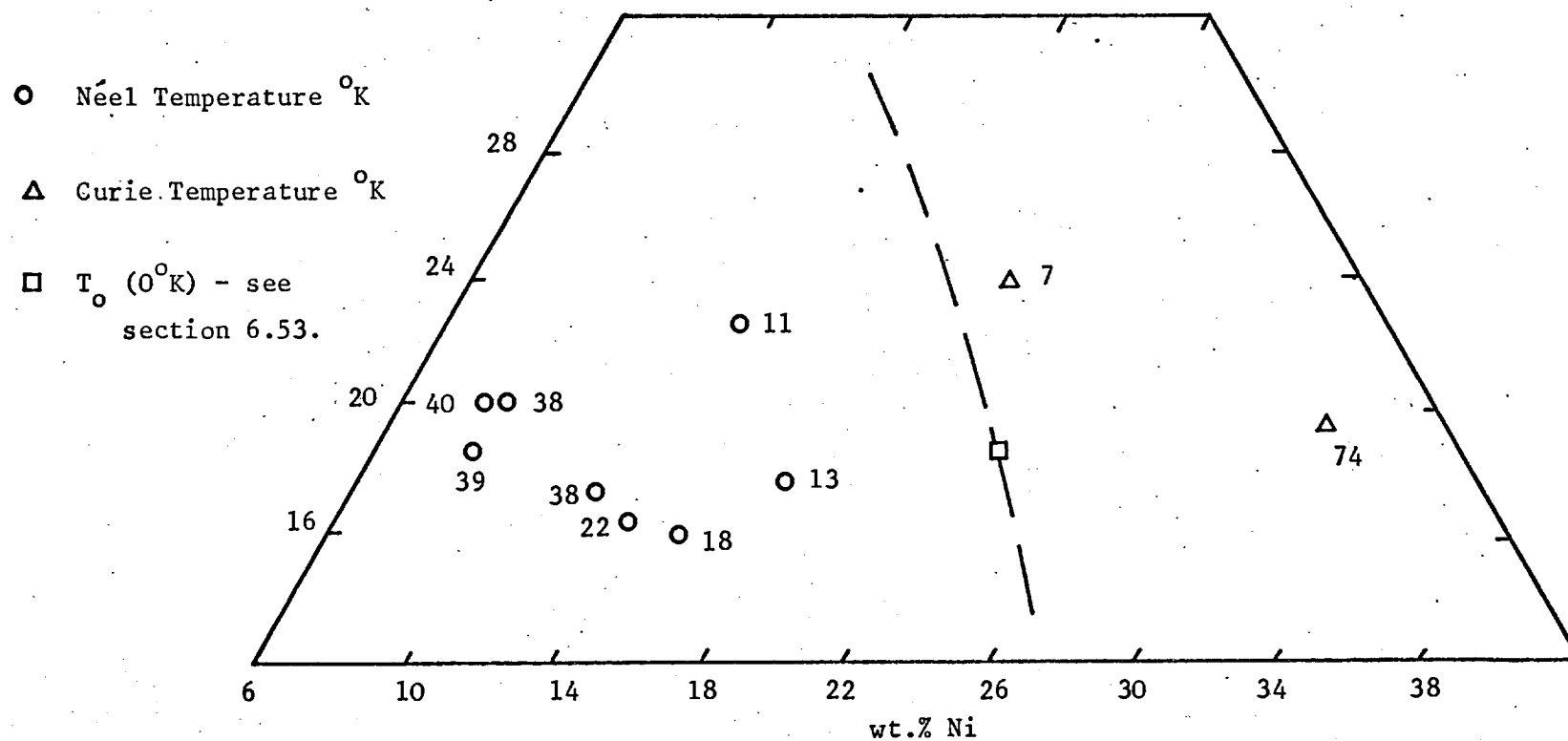
Weiss (32) has extended this concept to the binary iron-nickel alloys and postulated that the addition of nickel reverses the relative stability of the two states so that at nickel contents greater than Fe/29 at.% Ni macroscopic ferromagnetism of the f.c.c. phase is observed. By assuming that the magnetic moments of the two γ states are those given in table 6.19, and that the moment of Ni remains constant at $0.6\mu_B$ /atom, he is able to account for the thermal expansion anomalies in the Invar alloys (Fe/30 - 35 at.% Ni) and the anomalous variation of Curie temperature and magnetic moment. Miodownik* (33) has recently extended this analysis to some thermodynamic properties of Fe-Cr-Ni alloys. Using the previous Curie point and saturation magnetisation data of Jackson and Russell (34) for alloys containing 5 and 10 wt.% Cr, Miodownik calculates the difference in energy between the two states and shows that chromium stabilises the ferromagnetic γ_2 state, while at the same time depressing the Curie temperature. By generalising the effect of Cr on the energy gap, it was found possible to obtain satisfactory agreement with the experimentally measured excess entropies in alloys with up to 20% Cr and enthalpies of formation for compositions up to 40% Cr.

While this approach has been successful, particularly when applied to the peculiar properties of the Invar alloys in the Fe-Ni system, it should be realised that the energy variation given by Weiss (figure 6.24), and used by Miodownik, is in the nature of a working hypothesis rather than an established experimental fact.

* I am grateful to Dr. A.P. Miodownik for kindly providing me with a preprint of his paper.

Figure 6.26 Néel and Curie temperatures in austenitic stainless steels

Data from Kondorsky and Sedov (19), Meiklejohn (20), Gonser et al (21), Mikesell and Reed (27), Kohlhaas et al (28) and present work.



For example, Weiss uses the magnetisation data of Crangle and Hallam (35) (figure 6.25) and arbitrarily takes the lowest composition Fe/29 at.% Ni, for which these authors could retain the f.c.c. phase without martensitic decomposition, as that composition at which the energy difference between the two states goes to zero. It is seen from figure 6.25, however, that at this composition the average atomic moment for this alloy is still greater than $1\mu_B$ and the Curie temperature about 350°K . More recently, Bolling, Arrott and Richman (36) have measured Curie points in Fe-Ni-C alloys containing up to 2 at.% C. They find that carbon stabilises the austenite at compositions down to below Fe/25 at.% Ni and that a linear dependence of T_θ^2 on carbon content is obtained. In this way, the composition for which T_θ goes to 0°K in a binary Fe-Ni alloy is determined as Fe/25 at.% Ni, rather than Fe/29 at.% Ni. Nevertheless, the concept of two γ states appears to be well-founded and the calculations of Weiss for Fe-Ni are a considerable improvement on the previous classical calculation of Kondorsky and Sedov (19), who considered only anti-ferromagnetic Fe atoms with $0.5\mu_B$ and ferromagnetic Ni atoms with $0.6\mu_B$, obtaining a balance between the two in the region of Fe/33 at.% Ni.

It thus seems reasonable to explain the present low temperature magnetic behaviour in terms of a balance between states of anti-ferromagnetic γ -iron on the one hand and states of ferromagnetic iron and ferromagnetic nickel on the other. This leads naturally to the concept of a critical composition line at which the overall magnetic behaviour changes smoothly from anti-ferromagnetic to ferromagnetic as Cr and Ni are substituted for Fe. This interpretation is supported by the collation of all the presently available Curie points and Néel temperatures in figure 6.26 which shows just such a variation but, unfortunately, the data points are rather sparse in the vicinity of the presumed critical compositions.

An interesting feature of the Curie point determinations for Incoloy 800 was that the extrapolated value of T_θ was 74°K , 3° below that at which a characteristically curved and ferromagnetic magnetisation curve had previously been obtained (figure 6.16) and some 80°K

below the figure of 158°K quoted as the Curie point of a compositionally unknown specimen in the commercial specification handbook (37). It is also of interest to note the striking change in the shape of the magnetisation curve observed on cooling this alloy from 77°K to 4.2°K and the similarity of the 77°K curve to that obtained for 310 at 4.2°K (figure 6.15). High field measurements up to 100 k Oe^* at 77°K on Incoloy 800 and on 310 at 4.2°K have shown that ferromagnetic saturation does not occur for either alloy. At 4.2°K , however, Incoloy 800 saturates as would be expected from normal ferromagnetic behaviour.

The gradual approach to saturation is similar to Langevin paramagnetic behaviour (18) in the limit of low temperatures and/or high fields, with the exception that the total magnetic moment is very much larger. The effective absence of remanent inductions for the fully softened specimens (it was less than 1 gauss in both cases) is consistent with this approach and suggests that this is a super-paramagnetic phenomenon similar to that observed in very small, single domain particles ($150\text{ \AA}$ dia.) of the ferromagnetic elements (38, 39). The fully softened specimens of these steels, though nominally homogeneous, could well contain local inhomogeneities of this size where the dominant interaction is ferromagnetic.

This interpretation is given added weight by the marked increase (<1 to 14 gauss) of the remanent induction of 310 at 4.2°K after sensitising. During this treatment precipitation of chromium carbide occurs resulting in considerable local inhomogeneities, so that, if such regions have an overall ferromagnetic interaction, a multidomain structure will form. The application of an external field to this structure will cause domain boundary movement and a consequent hysteresis.

Comparison of the chemical analyses of Mikesell and Reed's (27) sample of 310 and that used in the present study shows that they were very close, the present sample containing slightly more iron (0.7%) and nickel (0.3%). The M vs. T curve of their sample is reproduced

* Measurements made at the High Field Magnet Laboratory, R.R.E., Great Malvern, after the main work of this thesis was completed.

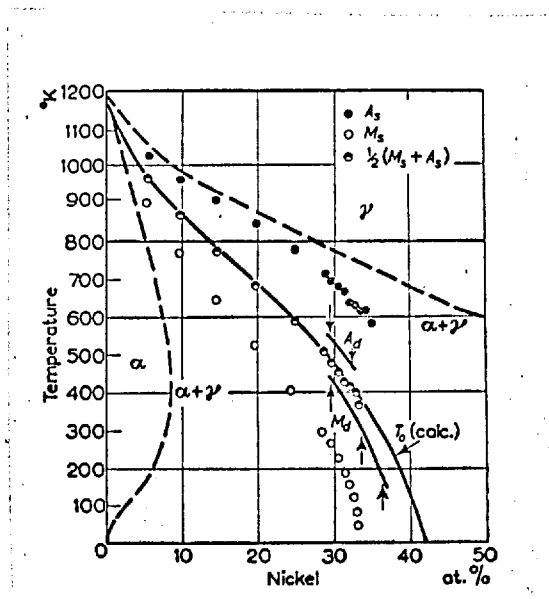


Figure 6.27 T_0 as a function of composition in Fe-Ni (Kaufman and Cohen, 43).

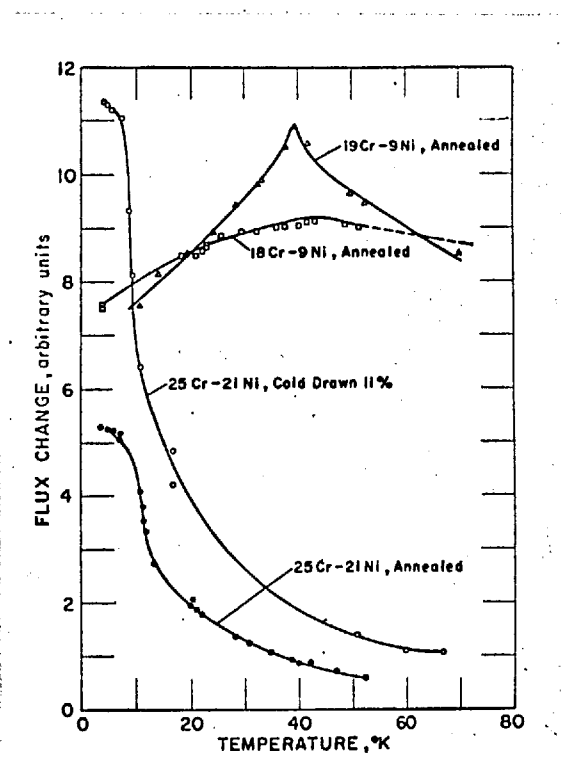


Figure 6.28 The low temperature magnetisation of a type 310 (25/21) steel after Mikesell and Reed (27).

in figure 6.27 and the reduction in the slope of the curve below about 10°K can be interpreted in terms of the onset of local anti-ferromagnetic interactions. Evidently other regions are still paramagnetic (or perhaps superparamagnetic), as the magnetisation continues to increase as the temperature is lowered to 4.2°K . In contrast to this, our specimen contains a dominant ferromagnetic interaction. The fact of this different magnetic behaviour in the presence of only very small composition differences thus suggests very strongly that the composition 25 Cr/21 Ni lies very close to the critical composition line between the anti-ferromagnetic and ferromagnetic γ states.

6.53 The deformation behaviour and the magnetic properties of austenite

The review of the published literature on the low temperature mechanical properties of the austenitic stainless steels in section 3.15a has shown that tensile destruction of the 18/10 steels down to 4.2°K produces α' martensite. It is clear, therefore, that while the M_s may lie below 0°K , as discussed in section 6.51, these steels do have a finite M_d temperature.

Examination of the fracture surfaces of samples of the higher alloy steels after deformation at 4.2°K^* shows that the fracture neck of 309 contains more than 50% α' martensite, but, in agreement with previous investigations (15, 40), no martensite was found in 310. A general conclusion can thus be drawn that all the AISI 300 stainless steels, with the exception of 310, are structurally unstable at 4.2°K .

If these observations are related to their magnetic properties, two patterns of behaviour are found:

- (i) At low temperatures the austenite phase in the 18/10 steels and 309 is anti-ferromagnetic and structurally unstable with respect to cooling and/or deformation, decomposing to a ferromagnetic martensite.

* I am grateful to Mr. P.T. Clee of the Rutherford High Energy Laboratory for supplying these broken tensile bars.

- (ii) The high alloy steels 310 and Incoloy 800 are ferromagnetic at 4.2°K and remain structurally stable when deformed at these temperatures.

An important feature of both these situations is that in each case the structurally stable state is ferromagnetic, which implies that the contribution of the magnetic energy of the ferromagnetic state is important in stabilising the structure. Kaufman (41) has shown that this factor is indeed important for the structural changes observed in pure iron, since at low temperatures the h.c.p. form of iron would exist in preference to the b.c.c., were the latter not ferromagnetic. The breakdown of α -iron at higher temperatures (31) is also determined by magnetic factors, since thermal excitation to the ferromagnetic γ_2 state results in an increased entropy which stabilises γ -iron. The reversion to the b.c.c. structure at higher temperatures is again determined by factors as in this case the magnetic entropy of b.c.c. Fe increases rapidly above the Curie point and eventually over-rides the two spin entropy of γ -iron.

We should like to propose the following hypothesis based on the properties of pure iron outlined above:

Under conditions where macroscopic regions of both magnetic states can be retained, alloys based on the anti-ferromagnetic γ_1 state are structurally unstable while those based on the ferromagnetic γ_2 state retain the f.c.c. structure.

In pure iron, of course, neither macroscopic magnetic state is observed for bulk samples, but, as stated above, it is the partial excitation to the γ_2 state which results in the stability of γ iron between 1183°K and 1665°K (31). The generalisation of the two γ states to some of the physical properties of f.c.c. Fe-Ni alloys has already been referred to, but this concept does not appear to have been applied to the structural transformation of γ to α .

We believe, however, that there is good evidence for such a correlation. Figure 6.25 shows the magnetic moments of binary Fe-Ni alloys as a function of composition, while figure 6.28 shows the

observed M_s , A_s , M_d and A_d temperatures in the same system. Also shown in the latter figure, are the values calculated by Kaufman and Cohen (43), for T_0 , the temperature at which the free energy difference between the two phases α and γ is zero. It can be seen that T_0 is bracketed well by $\frac{1}{2}(M_s + A_s)$. The interesting feature of this curve of T_0 is that the intercept at 0°K occurs at Fe/42 at.% Ni which is almost identical with the position of the peak in the curve of μ_B vs. composition (figure 6.25).

As already described, Weiss (32) has explained the compositional variation of μ_B in the γ phase by invoking a change in the ground state of γ iron (figure 6.24) and the anomalous properties of the Invar alloys (i.e. those alloys between 30 and 40 at.% Ni where μ_B is sharply increasing) are well explained by thermal excitation of the low volume anti-ferromagnetic γ_1 state above the ferromagnetic γ_2 ground state. Since at Ni contents higher than 42 at.% Ni the curve of μ_B vs. composition is approximately linear (with a slope which extrapolates to the Fe axis to give an atomic moment of $\sim 2.8\mu_B$; i.e. that characteristic of the γ_2 state) it is evident that beyond this composition the γ_1 state can no longer be thermally excited in appreciable quantities before macroscopic ferromagnetism is destroyed at the Curie point ($\sim 600^\circ\text{K}$). The hypothesis advanced above is consistent with this behaviour because a comparison of figures 6.25 and 6.28 shows that it is only when appreciable anti-ferromagnetic γ_1 is present that the alloy can be decomposed to the b.c.c. phase.

Macroscopic anti-ferromagnetism is never observed in the Fe-Ni system since the γ phase cannot be stabilised at sufficiently low Ni contents. In the Fe-Cr-Ni system, however, Cr stabilises the f.c.c. lattice, so that both anti-ferromagnetic and ferromagnetic austenites can exist but unfortunately no extensive structural and magnetic studies have been made on these alloys. It is possible, however, to derive the composition at which M_d goes to 0°K , from the recent tensile measurements of Sanderson and Llewellyn (5) on a series of steels with constant 18.5% Cr. As may be seen from figure 6.29, a smooth extrapolation to 0°K gives $M_d(0^\circ\text{K})$ for 18.5 Cr at 21 wt.% Ni. A_d points were not determined for these steels.

Figure 6.29 Variation of M_d with composition on a pseudo-binary based on 18.5 wt.% Cr.

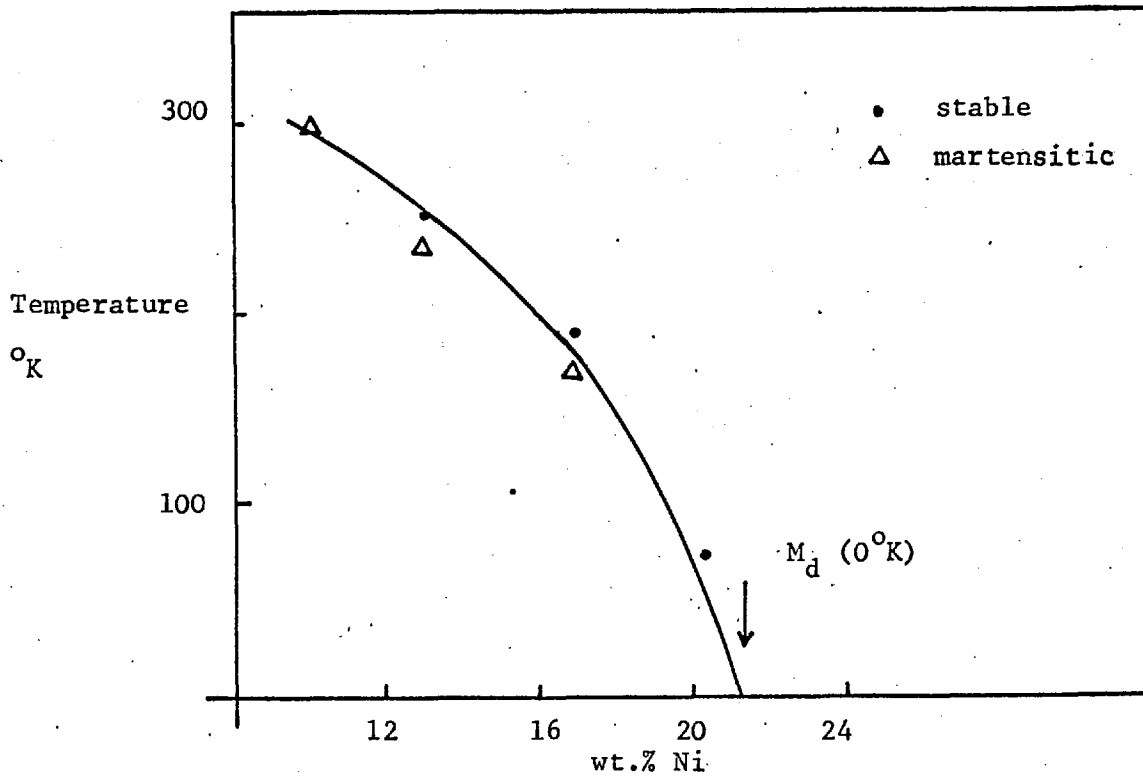
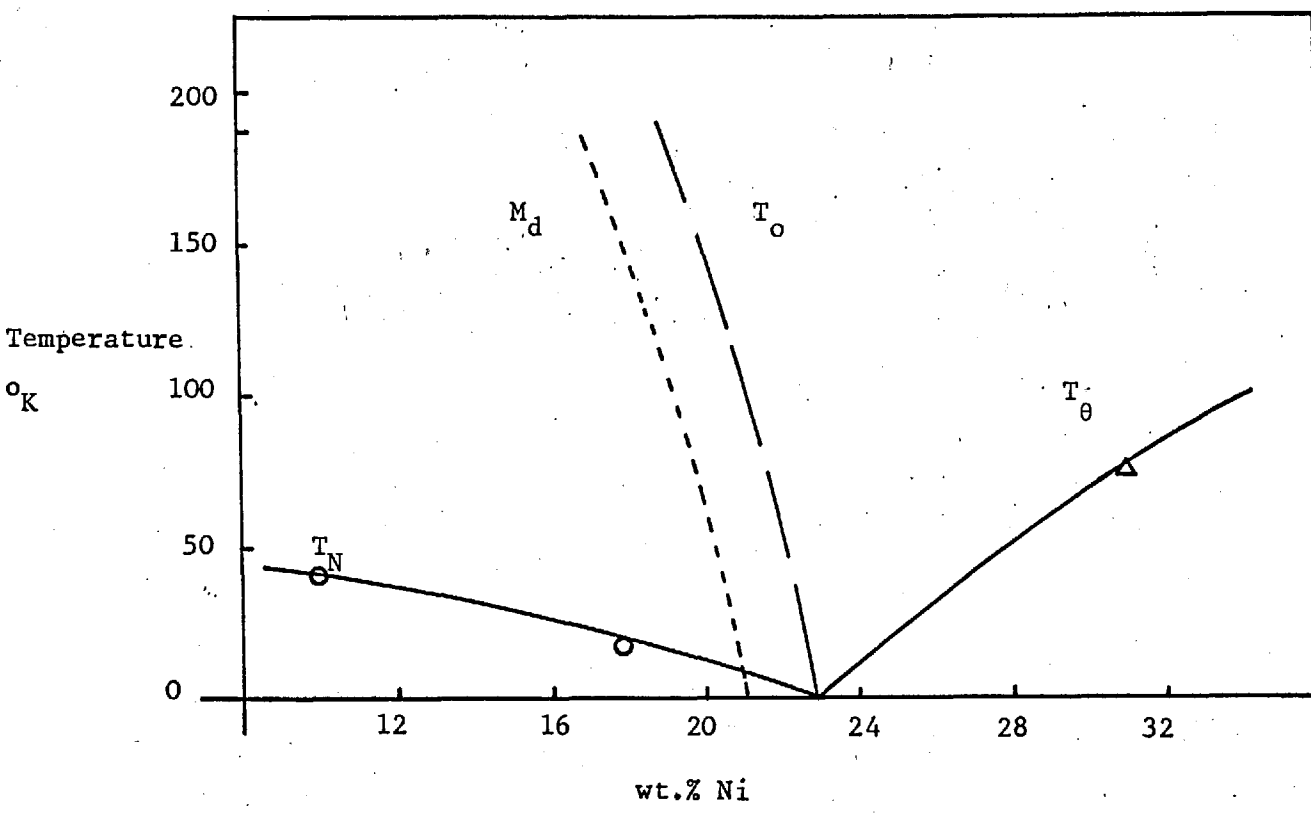


Figure 6.30 The relation between magnetic and deformation properties across a pseudobinary based on ~20 wt.% Cr



so that $T_o = (A_d + M_d)/2$ cannot be explicitly identified but, assuming a similar separation between T_o and M_d as in the Fe-Ni system (figure 6.28), we suggest that T_o (0°K) lies at a Ni composition ~ 2 wt.% higher than M_d (0°K). When this value of T_o (0°K) is included on the ternary diagram relating T_θ and T_N to composition (figure 6.26) it can be seen to fall very close to the curve of critical composition where the changeover from anti-ferromagnetic to ferromagnetic behaviour occurs.

We may now construct a pseudo-binary section through this ternary for a constant Cr content in the region of 18.5 - 20%, as shown in figure 6.30.. It can now be seen that the curve of T_N extrapolates smoothly to ~ 23 Ni. Independent evidence for this particular composition from the extrapolation of T_θ is not available, however, since only one alloy on this pseudo-binary has been investigated but the curves of T_θ and T_N are made to intersect at 0°K in line with the arguments of section 6.52. The composition at this intersection is seen to be identical with the derived value of T_o (0°K) for this Cr composition. A T_o curve has therefore been constructed from this point with a slope similar to that of the M_d curve, figure 6.29.

Assuming that the particular pseudo-binary section in figure 6.30 is typical of the general behaviour of steels within the composition range studied it may be concluded that:

- (i) All steels which have an anti-ferromagnetic austenite matrix above 0°K must be considered to be structurally unstable on being deformed at sufficiently low temperatures.
- (ii) Steels with a ferromagnetic austenite matrix above 0°K are structurally stable.

It will thus be possible to assess the probability of a low temperature martensitic transformation on the basis of a simple non-destructive magnetic test at 4.2°K .

6.6 Conclusions and Suggestions for Future Work

6.61 Conclusions

- (i) All the standard 18/10 grades of stainless steel (AISI 304(L), 316(L), 321 and 347) must be considered liable to undergo a martensitic transformation on cryogenic cycling between room temperature and 77° or 4.2°K. Since the product of this transformation (α') is ferromagnetic, severe problems may be encountered with the use of these steels as constructional members in the vicinity of magnetic fields.
- (ii) Within each 18/10 grade both stable and unstable steels may be found. The occurrence of such instability was found to be well described by an empirical equation for M_s , in terms of the C, N, Cr, Ni, Si and Mn contents, originally proposed by Eichelman and Hull for lower alloy steels. This good agreement was, however, only obtained when the actual specimen analyses were used, the use of a heat analysis being inadequate.

The Eichelman and Hull equation has been applied to the compositional variations possible within the 18/10 grades and it is found that the weldable quality steels 304L, 321 and 347 are the least stable, mainly on account of their lower free carbon contents. If, however, the Ni content of the remaining steels, 304, 316 and 316L is held always at its maximum limit it is shown that these compositions can then be considered unconditionally stable for all other permitted composition variations. The disadvantage of such steels is, however, their considerably higher cost but this can be overcome by using the Hi-proof varieties of the standard grades for which it has been shown that a minimum of 0.17% N results in an unconditionally stable steel.

Since, however, production is concentrated within the standard 18/10 grades an alternative test for predicting the low temperature stability has been devised, based on the resistance of the steel to stress induced transformation at R.T.

- (iii) All alloys were found to be strongly paramagnetic at R.T. On cooling to 4.2°K the austenitic phase in the 18/10 steels and AISI 309 (23/14) becomes antiferromagnetic, while the steel 310 (25/20) is super-paramagnetic and Incoloy 800 (20/32) ferromagnetic. This magnetic behaviour is described in terms of a balance between anti-ferromagnetic and ferromagnetic states of γ -Fe with additional ferromagnetic contributions from Ni.
- (iv) Steels which become anti-ferromagnetic at low temperatures also become structurally unstable, decomposing to the b.c.c. phase martensitically. Steels which become ferromagnetic, however, retain the f.c.c. structure under all normal deformation conditions. The possibility of α' formation under stress at low temperatures may thus be assessed by a simple non-destructive magnetic measurement.

6.62 Suggestions for Future Work

The present work opens up a number of possibilities for future research which may be conveniently summarised in three groups:

- (i) Further work on the commercially important 18/10 steels is desirable to check the validity of the deformation test proposed. For this purpose a survey of a wide variety of different heats from the various grades will enable the test to be definitely established. Since the validity of the test depends on identifying the separation between M_d and M_s precisely, these deformation tests might also need to be carried out at temperatures other than R.T. These investigations should also be applied to the high nitrogen steels, with a particular attention being paid to the behaviour of nitrogen in quantities up to 0.2 wt.%.
- (ii) Since steel 310 has been shown to be close to the critical composition at which the magnetic state changes from anti-ferromagnetic to ferromagnetic, correlation of the low temperature magnetic and mechanical properties of different

heats of this steel would be extremely interesting from a practical viewpoint, steel 310 being the "standard" high alloy grade of austenitic stainless steel.

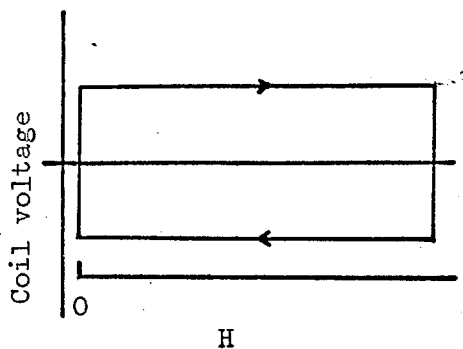
- (iii) From a more fundamental point of view, the hypothesis of the relative structural stability of two γ states of Fe needs to be investigated further. A detailed study of the magnetic properties of pure Fe-Cr-Ni austenites both before and after low temperature deformation would eliminate the unknown effects of the additional alloying elements present in the steels and allow detailed comparison between theory and experiment. These studies could also be generalised to other systems based on Fe-Ni where the austenite phase can be stabilised by elements such as C, N, Mn or Co.

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Figure A.1 Ideal coil imbalance loop.



A.2 Loop obtained in practice.

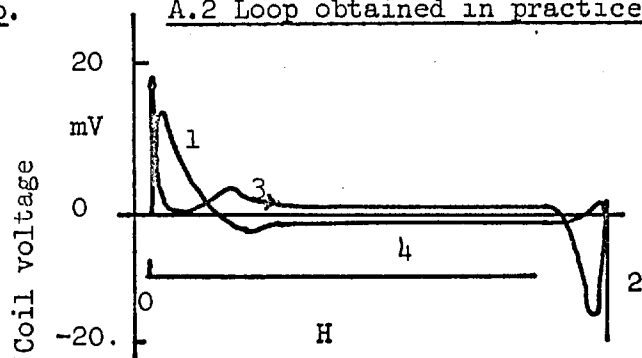
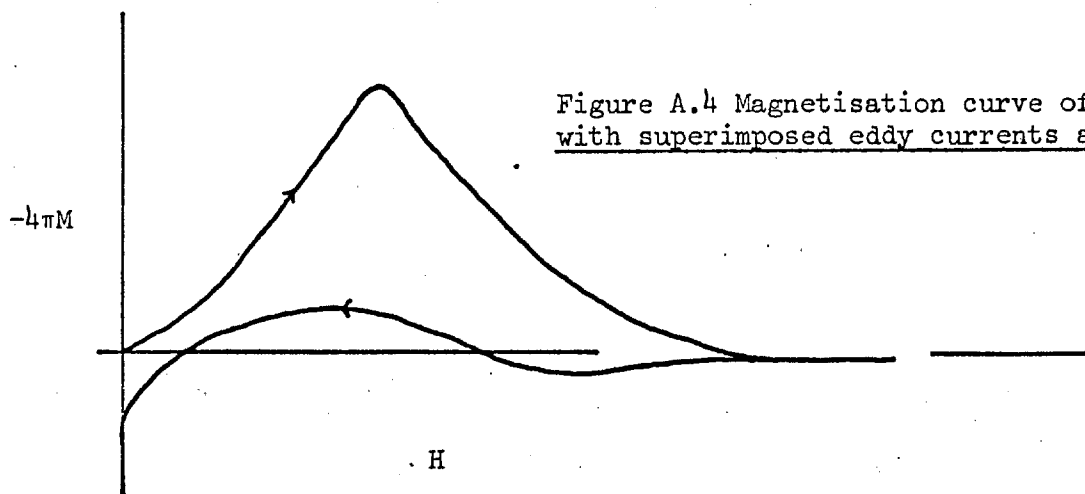
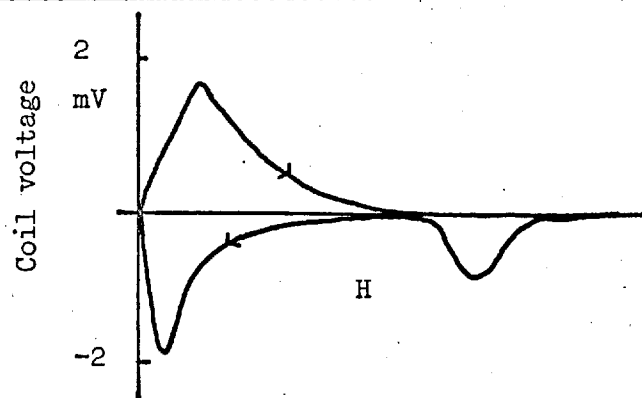
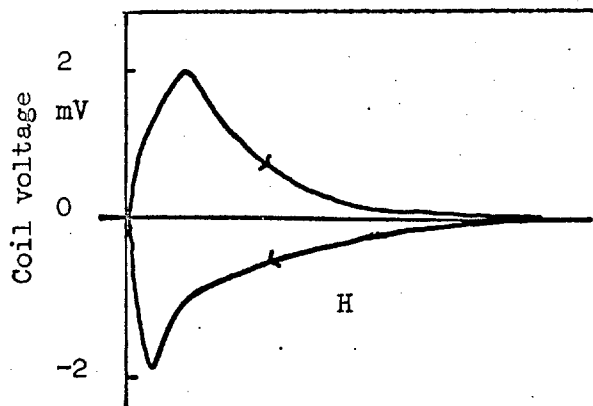


Figure A.4 Magnetisation curve of In/29 Tl with superimposed eddy currents at low fields.



Figures A.6 and A.7 Coil balance curves obtained with the split-former solenoid.



Appendix 1

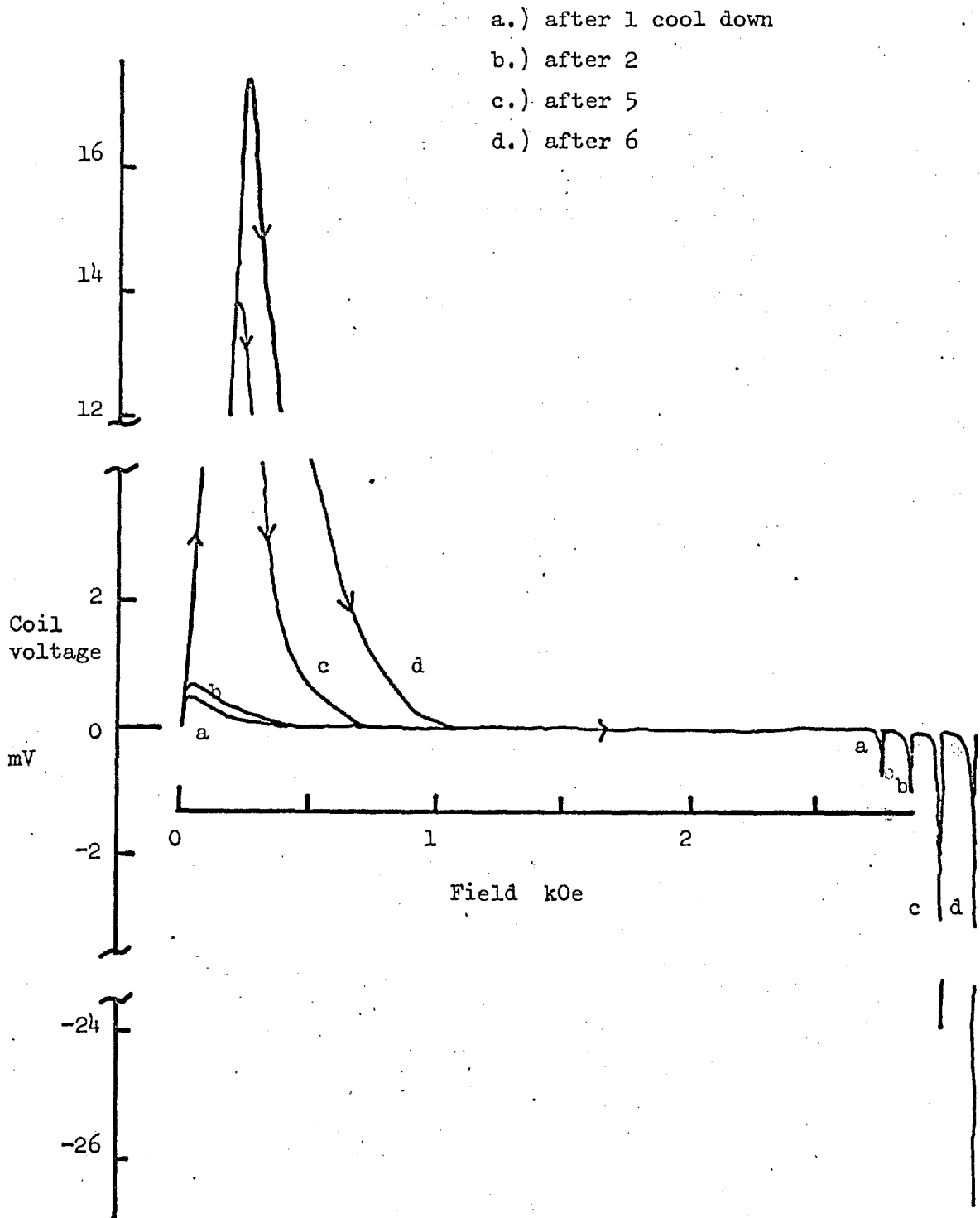
Problems with the superconducting solenoid

As originally supplied by its makers, the 4 k Oe superconducting solenoid was wound on an unsplit copper former. This has the important advantage that the superconducting windings are in good thermal contact with the helium bath so that when flux jumps occur the heat liberated may be dissipated within the bath instead of causing the magnet to go normal by a run-away instability in the solenoid windings.

During the coil balancing experiments described in 4.33 the coil voltage, proportional to dB/dt , was plotted against field on the X - Y recorder. A curve of the form shown in figure A.1 was expected, with the separation between the sweep up and sweep down curves being constant and proportional to sweep rate and the total imbalance of the coils. By removing excess turns from one of the coils or by adjusting the series trim coil the imbalance is reduced to zero and the coils are balanced.

In fact the curve obtained was quite different and is shown in figure A.2. This has large peaks (1 and 2) at the beginning and end of each sweep and a distinctive inflection in the curve (3) at about 500 Oe. Only the separation distance (4) corresponds to the expected curve. The inflection (3) was traced to precipitated lead in the brass can of the magnetisation probe and is discussed later in Appendix 2 and was eliminated by choosing a different material for the can but the large peaks remained essentially unchanged as the coil imbalance was reduced to zero. In figure A.2, and subsequent figures, the coil voltage has been normalised to a sweep rate of 10 Oe/sec. As the analysis of section 4.33 gives an upper limit of 10 μ V for a constant coil imbalance signal it is obvious that these peaks, which are of the order of 15 mV, cannot be tolerated.

Figure A.3 Eddy current effects in a stainless steel former



These peaks were attributed to the rise and decay of eddy currents generated in the solenoid former by the field sweep. Since the manufacturers considered that the copper former would be insufficiently strong to withstand the magnetic and mechanical forces on it if it was split axially to remove the eddy currents, it was decided to rewind the coil on an unsplit austenitic stainless steel former. As the residual resistivity of these steels is $\sim 60 \mu\Omega \text{ cm}$ at 4.2°K as against $1.7 \times 10^{-2} \mu\Omega \text{ cm}$ for high conductivity copper, eddy currents should become quite negligible.

On first cooling the magnet after rewinding, the curve shown in figure A.3(a) was obtained, from which it can be seen that the eddy currents were not negligible and peaks of $\sim 0.5 \text{ mV}$ were obtained. Although this represented a reduction of some thirty times on the copper former it was still some fifty times the tolerable limit of $10 \mu\text{V}$.

When the solenoid was cooled for a second time the peaks were slightly larger and broader than before, as may be seen from trace b of figure A.3, but on a third cool down with a pair of side by side coils, which are subject to the same eddy current distribution, an ideal curve of the form shown in figure A.1 was obtained. Some magnetisation curves were plotted with these coils but it was not really convenient as the magnetisation probe had been designed for axial exchange of specimens and it was necessary to remove the whole probe from liquid helium in order to exchange specimens with this coil pair. On the fourth cool-down, still using the side by side coil pair, small eddy current peaks of $\sim 0.5 \text{ mV}$ appeared and the effect of this on a magnetisation curve of some superconducting In/Tl alloys is shown in figure A.4 where a pronounced deviation from the perfect diamagnet in the Meissner state is seen.

For the fifth cool down the original vertical coil pair was fitted and the eddy current peaks were now found to be $\sim 14 \text{ mV}$ (figure A.3(c)), i.e. as great as those obtained with the copper former. On a further cool-down (figure A.3(d)) the peaks had

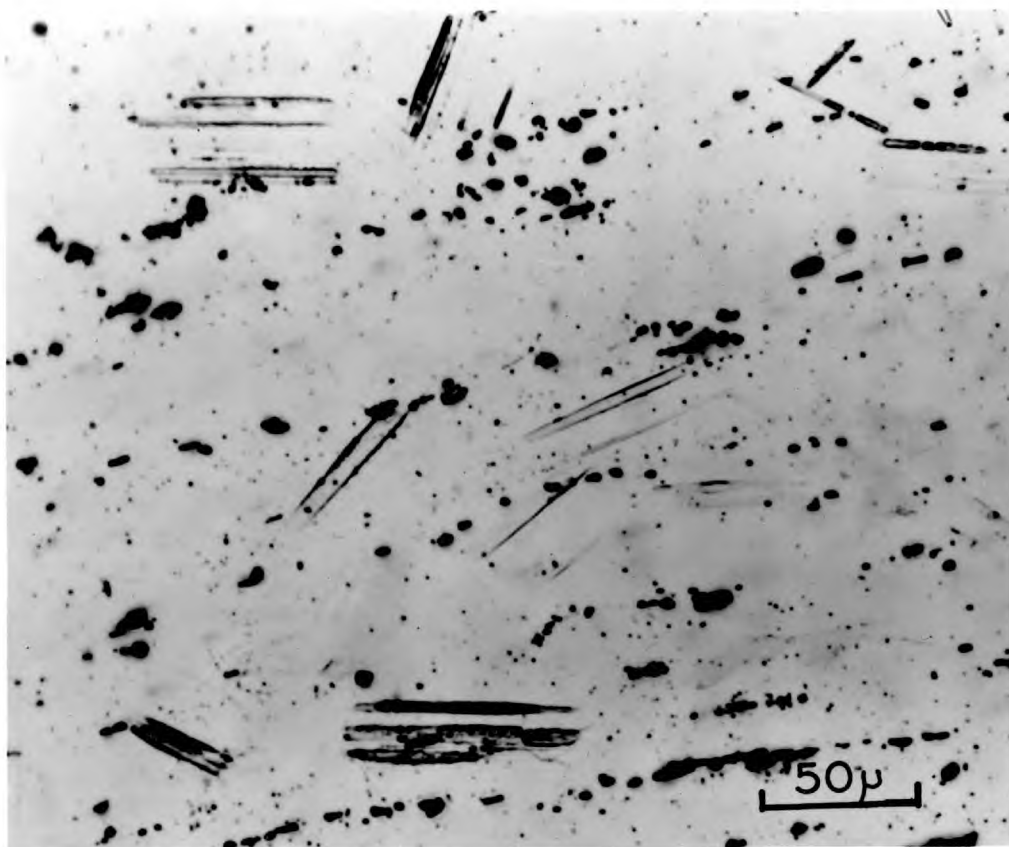
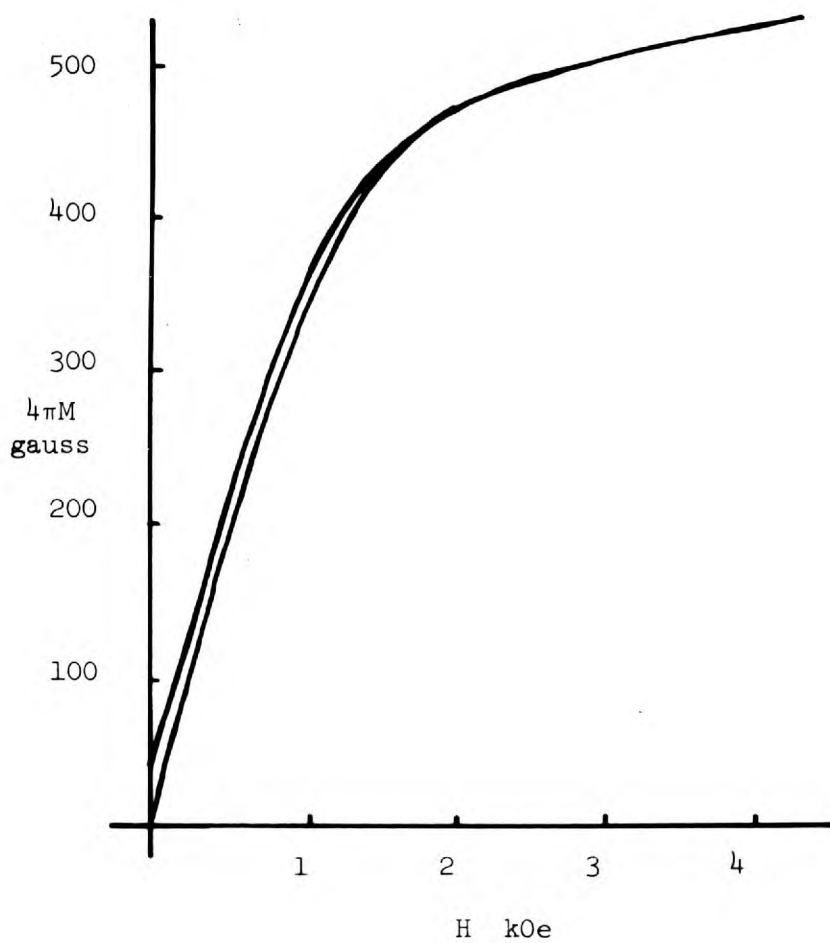


Figure A.5 Microstructure of magnet former

Figure A.8 Magnetisation of magnet former



increased again to approximately 17 mV and under these circumstances the system was clearly unusable.

At this point a thorough consideration of possible co-operative electronic effects between the solenoid and magnetometer circuits was made before further attention was paid to the material of the solenoid former. A study of the literature revealed a number of references to the partial martensitic decomposition of 18/8 - 18/10 stainless steels on cooling to cryogenic temperatures. The effect of such a transformation was at first considered solely in terms of an increased resistivity which should lead to smaller eddy currents, but the correct explanation is obtained when the ferromagnetic nature of the martensitic product is considered. The eddy current power loss in a cylinder in axial field is given by

$$\text{Power loss} \propto \frac{r^2}{\rho} \left(\frac{dB}{dt} \right)^2 \quad \text{A.1}$$

where r is the radius of the cylinder, ρ its resistivity and dB/dt the rate of change of induction within the cylinder (1). It is evident that as the induction appears as a square term and the resistivity only linearly, the local increases in induction due to ferromagnetic martensite needles or plates are extremely potent in increasing the total loss. Microscopic examination of a specimen cut from the same barstock as the material of the solenoid former showed the presence of both ϵ and α' martensite (figure A.5).

These conclusions were confirmed by tests made in a similar solenoid, loaned by the Oxford Instrument Co. Ltd. This solenoid was also wound on a stainless steel former which was, however, axially split to eliminate eddy currents. The loop obtained with this (figure A.6) shows a peak only at low field values and the curves of sweep up and sweep down are now approximate mirror images of each other. This loop is in fact the incremental susceptibility $4\pi \frac{dM}{dH}$ vs H of the former as measured at the coil pair, and if integrated the curves will yield the normal magnetisation curve of the material ($4\pi M$ vs H). Thus it may be seen that the curves shown in figure A.3 are a composite of strong eddy current effects and a

former magnetisation signal of about one tenth of the magnitude.

An interesting curve obtained from a later sweep during the same cool down of the split former solenoid is shown in figure A.7. On the sweep up a large susceptibility was obtained in the vicinity of 2.5 k Oe which was not obtained on the sweep down. This feature could not be duplicated in any subsequent experiments but, in view of the irreversibility of the effect, it is tentatively explained in terms of the isothermal nucleation of α' martensite in the presence of a magnetic field.

The manufacturers were of the opinion that the magnet former steel was supplied to EN58BM or AISI 321 (i.e. 18/10/Titanium stabilised) but insufficient material was available to confirm this by chemical analysis. A sample cut from the bar stock was later cycled twice to 77°K and then tested at 4.2°K after the solenoid had been rewound on a tufnol former. The magnetisation curve of this material is shown in figure A.8, from which it may be seen that its magnetisation is ~ 500 gauss at 3 k Oe which corresponds to $\sim 4\%$ α' martensite. Thus the experiences with this solenoid indicate that very careful control of the composition of the austenitic stainless steels is necessary if they are to be used in low temperature magnetic environments and that the presence of 1% of ferromagnetic martensite can seriously interfere with magnetisation measurements.

In the light of these difficulties and the expectation that the amount of α' martensite would continue to increase on further cooling between R.T. and 4.2°K, it was decided that the solenoid must be rewound yet again on another former. As demonstrated in the second appendix a number of brasses were considered and found to possess significant magnetic moments at 4.2°K. Aluminium alloys were avoided because of the possibility of corrosion couples with the copper sheathing of the superconducting wire in the presence of moisture. It was therefore decided to rewind the solenoid on a former made from tufnol, a cloth reinforced plastic. The disadvantages of this material are its low stiffness, its high thermal contraction and its low thermal conductivity (2). Thus the former must be increased in thickness and the serious possibility exists that, on cooling, the super-

conducting windings may become loose. In more than twenty cool-downs to 4.2°K no evidence of movement has been obtained in returning to room temperature but the frequency with which the magnet goes normal was much increased with the tufnol former. To some extent this can be attributed to microdamage in the superconducting wire caused during the two rewinds but the large differential thermal contraction of the former may lead to winding movement in an applied field with consequent mechanical shock and local flux jumping. The low thermal conductivity of tufnol means that the heat liberated by these flux jumps cannot be readily dissipated in the liquid helium bath and a runaway instability in the windings results. This was often a very serious limitation on the useful sweep rate and the number of magnetisation loops which could be measure in any given cool-down.

TABLE A.1 Structure and composition of brasses

Alloy	Structure	Cu wt %	Specified additions	Impurities
Hard drawn tube (CZ 105)	α	70 - 73	0.02 - 0.06 As	0.3 max incl. 0.075 Pb, 0.06 Fe
Admiralty brass (CZ 111)	α	70 - 73	1 - 1.5 Sn	———— " ————
Free machining brass (CZ 121)	α/β	56 - 60	2 - 3.5 Pb	0.75 max incl. 0.35 Fe
Naval brass (CZ 112)	α/β	61 - 64	1 - 1.5 Sn	———— " ————

All compositions in wt % - Zn the balance.

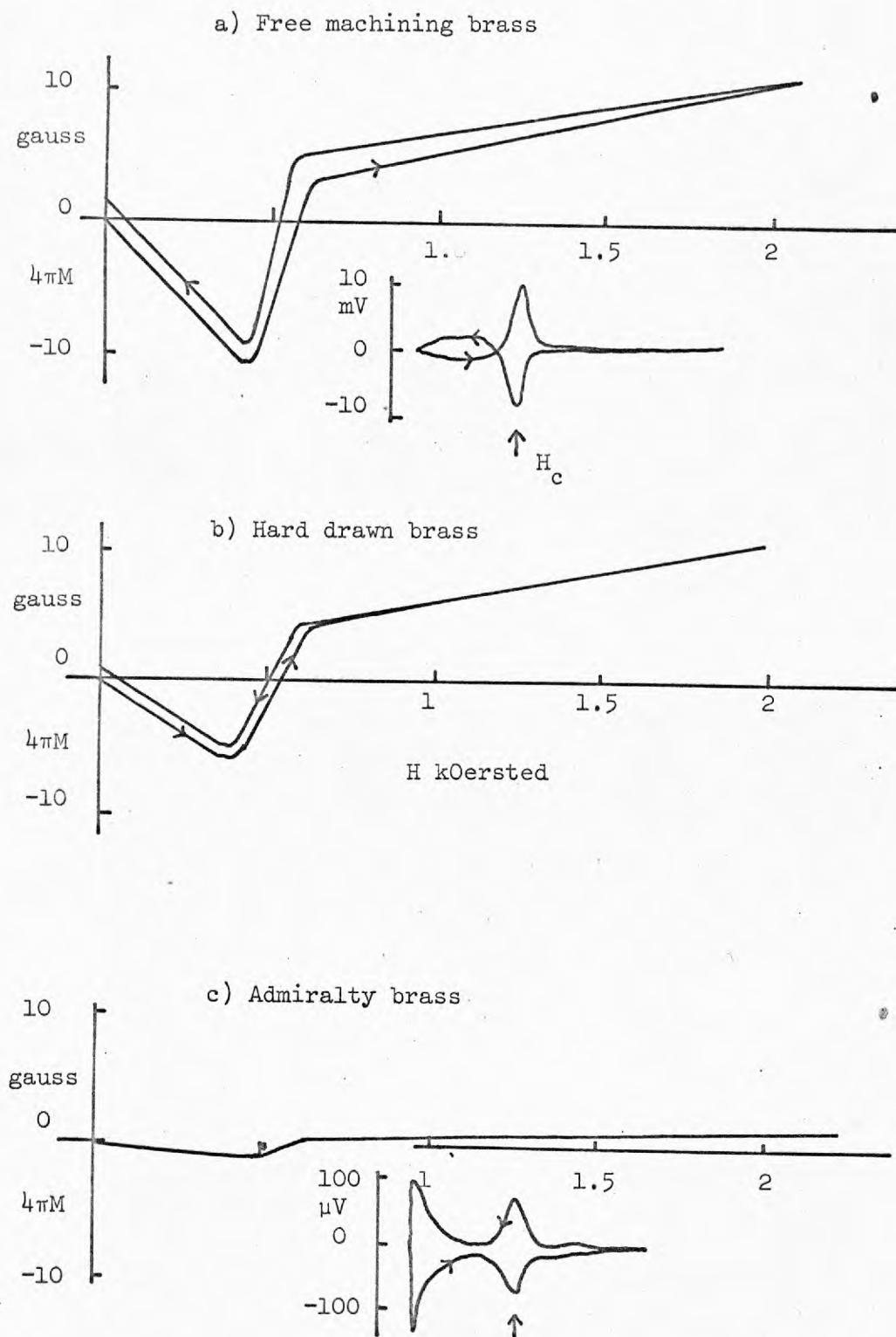
Appendix 2

Magnetic properties of some copper and aluminium based alloys at 4.2°K

Materials for use in the vicinity of solenoids and magnetometers need to have negligible magnetisations. Appendix 1 has shown that, in addition, a high electrical resistivity is desirable in swept field situations. While in theory a number of materials can be found to meet these conditions, in practice, only a limited number of alloys are commercially available in the size and quantity required by the small scale user. The behaviour of a number of austenitic stainless steels has been discussed in Chapter 6 and thus the present section is limited to the presentation of studies made on certain brasses and an aluminium alloy.

The chemical composition and structural constituents of four commercially available brasses which conform to B.S. 2871 (tubes) and B.S. 2874 (rods and bars) (3) are listed in table A.1. Of these, the free machining brass (CZ 121) is the most commonly available material in rod form, while hard drawn brass (CZ 105) is the most common material for tube. In view of the high iron contents permitted in naval brass, this material was dismissed from further consideration. Magnetisation curves for the remaining materials are shown in figure A.9 from which it may be seen that each curve shows a distinctive diamagnetic magnetisation superimposed on a general paramagnetic magnetisation. As the susceptibility of 70/30 brass is $\sim 10^{-6}$ (4) both of these effects must be attributed to other elements within the alloy. The initial diamagnetic magnetisation is due to free particles of lead which become superconducting below $\sim 7^{\circ}\text{K}$ and whose bulk critical field is ~ 450 Oe at 4.2°K . The critical fields shown here are somewhat higher (~ 550 Oe) and reflect the normal increase of H_c as the dimensions of a superconductor are decreased. The paramagnetic moment is in fact ferromagnetic and due to free iron impurities within the alloys. Using a saturation magnetisation of ~ 20 KG for pure iron and assuming that the magnetisations at 2k Oe

Figure A.9 Magnetisation curves of Brasses at 4.2°K .



are approximately three quarters of saturation, the amount of iron impurity in the brasses was calculated to be 0.065, 0.06 and 0.006 wt % respectively for the free cutting, hard drawn and admiralty brasses. The hard drawn brass was thus found to be right on specification while the iron content of the free machining brass was well within the maximum limit of 0.35 wt %. The admiralty brass had an exceptionally low iron content and as its free lead content was an order of magnitude smaller than the other two alloys, it was therefore used for the flanges on the double-walled can. The tin present in this alloy is in a solid solution in the α -brass and although no magnetisation measurements were made on this sample below 4.2°K no spurious magnetisations due to the can have been detected in the course of many subsequent experiments down to 2°K.

When the diamagnetic moments are similarly converted to give the free lead content, values of 2, 1.2 and ~0.15 wt % for free cutting, hard drawn and admiralty brass, respectively, were obtained. Lead is intentionally added to free cutting brass, where it is present as a fine dispersion of insoluble lead particles but it is present only as an impurity in the other two brasses. It can be seen that while the free cutting content is well within specifications, both the remaining brasses are outside their maximum limits of 0.075 wt % Pb. For admiralty brass the content is twice too high but still small; for the hard drawn brass, however, the content is some sixteen times that permitted and clearly unacceptable. It is not known whether this content would seriously impair the corrosion resistant properties of this alloy but it is clear that stock material needs to be treated with some suspicion in critical applications.

The magnetisation curve shown in figure A.9c for admiralty brass is close to the limits of sensitivity of the instrument. The sensitivity of the magnetometer to free lead (or any other free superconductor with a known H_c) can be considerably increased by measuring the change of susceptibility in the region of H_c and this is shown in inset to figure A.9, for the free machining and admiralty brasses. These curves were taken by simply amplifying the detector coil voltage as in the coil balancing experiments; they were also taken in the

presence of the germanium thermometer which, as described in section 4.33, has a ferromagnetic moment, most likely due to free iron within its brass case. It is the high initial permeability of this thermometer which is detected at low fields in the curve for admiralty brass but the sharp change of signal at H_c is not obscured. It is not known whether superconductivity has hitherto been applied to chemical analysis but these experiments show that the technique may be a promising one for the detection of free lead.

Aluminium alloys were not extensively investigated because of their tendency to form a corrosion couple with copper when moisture is present. As superconducting windings are usually sheathed with copper, the use of an aluminium former for a solenoid is not to be recommended. However, one specimen of duralumin (H 30) was tested at 4.2°K . This alloy had a very low magnetic moment which was, within the limits of measurement, directly proportional to field, with a paramagnetic susceptibility of 2×10^{-5} . Although a maximum of 0.5 wt % of iron is permitted in H 30, it is present as an iron/manganese/silicon intermetallic. The limits for lead in this alloy are below 0.5 wt % and thus, apart from its corrosion properties, this material would otherwise be quite satisfactory for use as a split former for a superconducting solenoid.

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