

STRUCTURAL AND MAGNETIC  
PROPERTIES OF TERNARY ALLOYS  
NEAR MnAs

by  
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## ABSTRACT

Measurements have been made of the magnetic and structural properties of MnAs and ternary alloys formed by substituting small amounts of V, Cr, Fe, Co, or Ni. Lattice spacing measurements in MnAs have been extended down to liquid nitrogen temperature, and in the ternary alloys the general range from  $-120^{\circ}\text{C}$  to the first-order transformation at  $\approx 40^{\circ}\text{C}$  has been covered.

The relative magnetization of the alloys has been measured in the ferromagnetic region and in the neighborhood of the first-order transformation. The magnetic susceptibility has been measured for each alloy in the range of  $\approx 40^{\circ}\text{C} \longrightarrow \approx 360^{\circ}\text{C}$ . Special attention was paid to the intermediate region between  $40^{\circ}\text{C}$  and  $120^{\circ}\text{C}$  where X-ray diffractometer measurements were done. The results have indicated that MnAs in this region has the orthorhombic MnP structure.

In the discussion, a model is proposed for the electronic state of MnAs and two possible interpretations of its unusual properties are given. The relationship between the properties of the ternary alloys and the model is discussed.

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STRUCTURAL AND MAGNETIC  
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## CHAPTER I

### 1. Introduction

A considerable number of compounds containing transition metal elements crystallize with the NiAs structure. The presence of the transition metal ions with partly filled d-shells leads to a variety of magnetic properties including ferromagnetism, antiferromagnetism, paramagnetism and ferrimagnetism. There is a correspondingly wide variety in the electrical properties which include, metallic conductivity, semiconductivity and superconductivity. Many of these compounds undergo phase transformations during which the changes in electrical or magnetic properties are accompanied by dimensional changes. A study of the magnetic and structural properties through such a transformation can be expected to give information about the electronic structure and chemical bonding of the transition metal ions, about how magnetic interactions between ions depend on structure, and about the nature of the transition itself.

MnAs undergoes a first-order transformation at about 40°C and a further (probably second-order) transformation at about 120°C. At each of these transformations a marked change in magnetic properties occurs. Below 40°C MnAs is ferromagnetic, while above 120°C it is clearly paramagnetic. Between 40° and 120° the susceptibility rises with increasing temperature. This behavior has been described as antiferromagnetism by Guillaud (1951). Neutron diffraction work by Bacon and Street (1955) and by Kasper (1961), and electron spin resonance measurements by Rodbell (1957), however, have failed to show

any evidence for antiferromagnetism. The exact nature of the magnetic behavior in this temperature region is of great interest.

Willis and Rooksby (1954) measured the lattice parameters over a wide temperature range and ascribed to them the NiAs (B8) structure, shown in Fig. 1-1. Their results show a discontinuous change in the  $a$ -parameter and in the volume at the lower transformation, with thermal hysteresis. At about 120°C there is a change of slope of the  $a$  - vs. - temperature curve, suggesting a second order transformation.

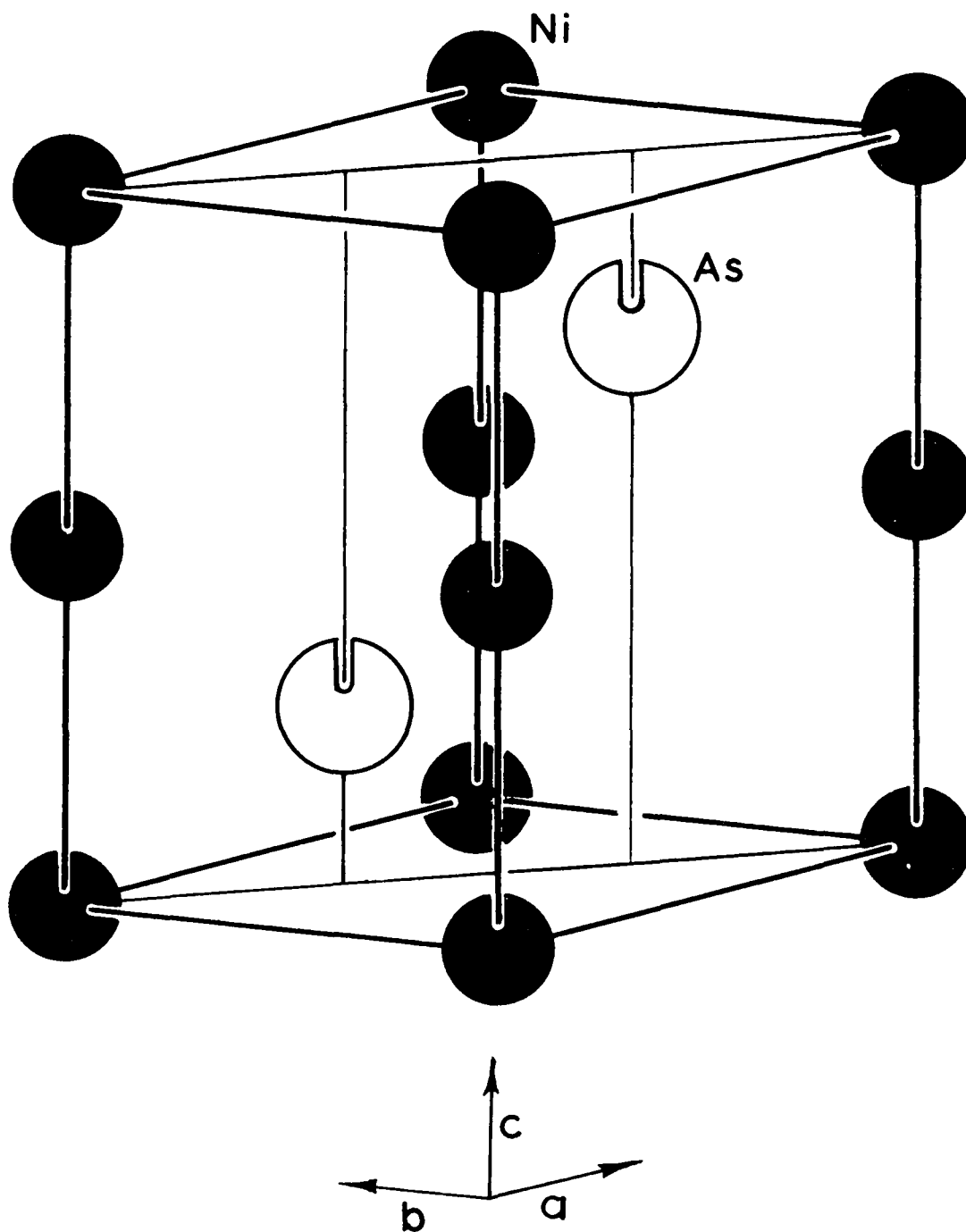
The mechanism of the first-order transformation has been described in detail by Basinski and Pearson (1958). More recent work by Wilson and Kasper (1961) and by Kornelsen (1961) has shown that in the intermediate region (40°C - 120°C) MnAs does not have the exactly hexagonal NiAs structure, but probably the orthorhombic MnP (B31) structure. Some of this work will be described in detail later. It was recently noticed, that in the appendix of a book by Taylor (1952) the structure of MnAs is listed as "orthorhombic, pseudo-NiAs". Unfortunately no reference is made to the source of this information.

The work reported in this thesis consists of measurements of the lattice spacings and magnetic properties of a number of ternary compounds obtained by replacing some of the manganese atoms in MnAs by other transition metals (V, Cr, Fe, Co, Ni).

## 2. Magnetic Theory

### A. Atomic magnetic moments.

The magnetic moment associated with an atom depends on the orbital and spin angular momenta of the electrons in the atom and on



**FIG 1.1**  
The unit cell of the NiAs (B8) structure.

the way in which they combine to form a resultant. Each electron in an atom is characterized by four quantum numbers,  $n$ ,  $\ell$ ,  $m_\ell$ , and  $m_s$ . According to the Pauli exclusion principle, no two electrons are allowed to have all four quantum numbers the same. The principle quantum number,  $n$ , denotes the shell which the electron occupies and is the major factor in determining its energy. The orbital angular momentum quantum number,  $\ell$ , may take integral values from 0 to  $(n - 1)$  and is related to the orbital angular momentum vector  $\vec{\ell}$  by

$$|\vec{\ell}|^2 = \ell(\ell + 1) \hbar^2 \text{ ----- ( 1 - 1)}$$

The projection of  $\ell$  along the magnetic axis is determined by  $m_\ell$  :

$$\vec{\ell}_z = m_\ell \hbar \text{ ----- ( 1 - 2)}$$

where  $m_\ell$  can take integral values between

-  $\ell$  and +  $\ell$

The spin vector  $\vec{s}$  is related to the quantum numbers  $s$  and  $m_s$  by

$$|\vec{s}|^2 = s(s + 1) \hbar^2 \text{ ----- ( 1 - 3)}$$

and  $s_z = m_s \hbar$  where  $m_s = \pm \frac{1}{2}$ .

For an atom containing a number of electrons, the total angular momentum is obtained by adding the momenta of the individual electrons according to certain rules. For most atoms it is valid to assume "Russell-Saunders" or L-S coupling. The  $\ell$ 's of the individual electrons are added vectorially to give a resultant  $L$  for the whole atom, where

$$L = \sum m_\ell \text{ ----- ( 1 - 4)}$$

and

$$|\vec{L}|^2 = L(L + 1) \hbar^2 \text{ ----- ( 1 - 5)}$$

Similarly, for the spin component

$$S = \sum m_s \text{ -----( 1 - 6)}$$

$$\text{and } |\vec{S}|^2 = S(S + 1) \hbar^2 \text{ -----( 1 - 7)}$$

The two vectors  $\vec{L}$  and  $\vec{S}$  then combine to form a resultant  $\vec{J}$  for which

$$|\vec{J}|^2 = J(J + 1) \hbar^2 \text{ -----( 1 - 8)}$$

There are, in general, a number of possible values of  $J$  from  $|L - S|$  to  $|L + S|$ , and the particular value of  $J$  which corresponds to the lowest energy state of the atom must be obtained from spectroscopic data. However, Hund's rules \* are a valuable guide in most cases.

The component of  $\vec{J}$  along the magnetic axis is quantized with

$$\vec{J}_z = M \hbar \text{ -----( 1 - 9)}$$

where  $M$  can change by integers from  $-J$  to  $+J$ .

Information about  $L$ ,  $S$ , and  $J$  is condensed in the spectroscopic term, the general form of which is

$$^{2S+1}X_J, \text{ where } X = S, P, D, F, \text{ -----}$$

when  $L = 0, 1, 2, 3, \text{ -----}$ .

---

#### \*Hund's rules

1. Maximize  $S$ , subject to Pauli principle.
2. Maximize  $L$ , subject to Pauli principle.
3. If the subshell is half-full or less,  $J = |L - S|$  ;  
more than half-full,  $J = |L + S|$  .

From classical theory, an electron moving in a circular orbit has an associated magnetic dipole moment given by

$$\mu_l = \frac{e}{2mc} |\vec{L}| \quad \text{-----} (1 - 10)$$

Substituting for  $\vec{L}$  we get

$$\mu_l = \frac{e}{2mc} \sqrt{l(l+1)} \hbar = \sqrt{l(l+1)} \beta \quad \text{-----} (1 - 11)$$

where  $\beta = \frac{e\hbar}{2mc}$  is a unit of magnetic moment called the "Bohr magneton".

Unfortunately, this simple relationship does not hold for the spin angular momentum. According to the Dirac theory of the electron, the ratio of magnetic moment to angular momentum for electron spin is exactly twice that for the orbital motion. For an electron with spin quantum number  $s$ ,

$\mu_s = 2 \beta \sqrt{s(s+1)}$ , and for an atom with total spin quantum number  $S$ ,

$$\begin{aligned} \mu_S &= 2 \beta \sqrt{S(S+1)} \\ &= g_s \beta \sqrt{S(S+1)} \end{aligned}$$

where  $g_s = 2$ .

The equation for the orbital moment may be put into the same form;

$$\mu_L = g_L \beta \sqrt{L(L+1)}, \quad \text{where } g_L = 1$$

For the total moment of the atom,

$\mu_J = g \beta \sqrt{J(J+1)}$ , where  $g$  is now a function of  $L$ ,  $S$ , and  $J$ .

To calculate  $g$  let us refer to Fig. 1 . 2

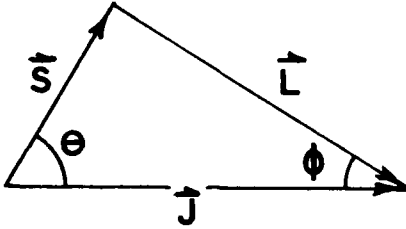


Fig. 1.2 a.

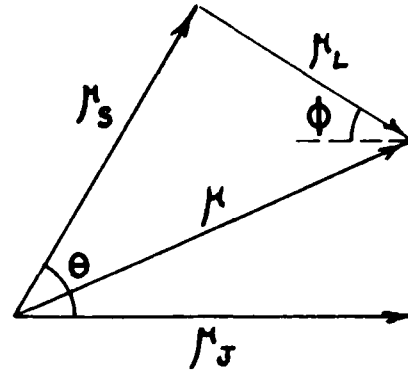


Fig. 1.2 b.

The projection of the total magnetic moment along the J-direction can be obtained from Fig. 1 - 2(b).

$$\begin{aligned}
 \mu_J &= \mu_S \cos \theta + \mu_L \cos \phi \\
 &= g_s \beta \sqrt{S(S+1)} \cos \theta + g_L \beta \sqrt{L(L+1)} \cos \phi \\
 &= \frac{2e}{\hbar} |\vec{S}| \cos \theta + \frac{e}{\hbar} |\vec{L}| \cos \phi \text{ ----- (1 - 12)}
 \end{aligned}$$

From Fig. 1 - 2 (a),

$$\begin{aligned}
 \cos \theta &= \frac{|\vec{S}|^2 + |\vec{J}|^2 - |\vec{L}|^2}{2 |\vec{S}| |\vec{J}|} \\
 \cos \phi &= \frac{|\vec{L}|^2 + |\vec{J}|^2 - |\vec{S}|^2}{2 |\vec{L}| |\vec{J}|}
 \end{aligned}$$

Substituting these values into equation (1 - 12) we get

$$\mu_J = \frac{e}{\hbar} |\vec{J}| \left[ 1 + \frac{|\vec{S}|^2 + |\vec{J}|^2 - |\vec{L}|^2}{2 |\vec{J}|^2} \right]$$

In terms of the quantum numbers S, L and J,

$$\mu_J = \beta \sqrt{J(J+1)} \left[ 1 + \frac{S(S+1) + J(J+1) - L(L+1)}{2J(J+1)} \right]$$

$$= \beta \sqrt{J(J+1)} \quad g. \quad \text{-----}(1 - 13)$$

where g is the semi-empirical Lande g-factor from spectroscopy.

The resultant magnetic moment  $\mu$  does not lie along J. However, since the atom is spinning about the J - direction, the time-average of any component of  $\mu$  perpendicular to J, is zero. For this reason we are justified in choosing  $\mu_J$  as the magnetic moment of the atom, which will be referred to hereafter simply as  $\mu$ .

#### B. Behavior in a magnetic field.

The energy of a magnetic dipole in a magnetic field is given by

$$E = -\mu H \cos \theta \quad \text{-----}(1 - 14)$$

In the quantum case of an atom with total angular momentum  $\vec{J}$ , the component of  $\mu$  in the direction of H,  $\mu \cos \theta$ , is just  $M g \beta$  and we obtain

$$E = -M g \beta H \quad \text{-----}(1 - 15)$$

where M can take values J, (J - 1), -----, -J.

The behavior of N such independent dipoles in a magnetic field H can be described by statistical mechanics. The net moment in the direction of H is given by

$$\sigma = N \bar{\mu} = N \frac{\sum_M g \beta M e^{-\frac{g \beta H M}{kT}}}{\sum_M e^{-\frac{g \beta H M}{kT}}} \quad \text{-----}(1 - 16)$$

summed over M from -J to +J.

This expression, with considerable algebra, can be reduced to

$$\sigma = N g \beta J \left[ \frac{2J+1}{J} \coth \left( \frac{2J+1}{2J} a \right) - \frac{1}{2J} \coth \frac{a}{2J} \right]$$

$$= N g J \beta B_J(a) \quad \text{-----}(1 - 17)$$

where  $B_J(a)$  is the "Brillouin function" and

$$a = \frac{g \beta J H}{k T}$$

When  $a \ll 1$  the expression reduces to

$$= \frac{N g^2 \beta^2 J(J+1)}{3 k T} H \quad \text{-----} (1 - 18)$$

The magnetic susceptibility, defined as  $\frac{\sigma}{H}$ ,  
 becomes  $\chi = \frac{\sigma}{H} = \frac{N g^2 \beta^2 J(J+1)}{3 k T}$ ,  $= \frac{N \mu^2}{3 k T}$   
 ----- (1 - 19)

This is the well-known Curie law,

$$\chi = \frac{C}{T} \quad \text{with} \quad C = \frac{N \mu^2}{3 k} \quad \text{-----} (1 - 20)$$

This simple formulation ignores any interaction between magnetic ions, which was first taken into account by Weiss. He replaced  $H$  in the Curie Law by an effective field,  $H_{\text{eff}} = H + H_i$ , where  $H_i$  was called the "molecular field" and was assumed to be proportional to the magnetization,  $\sigma$ . By rewriting the Curie Law in the form

$$\frac{\sigma}{H_{\text{eff}}} = \frac{C}{T} \quad \text{and putting } H_{\text{eff}} = H + \lambda \sigma$$

it is easily shown that  $\chi = \frac{C}{T - \theta}$  ----- (1 - 21)

where  $C$  has the same meaning as before

and  $\theta = \lambda C$  is called the "paramagnetic Curie temperature".

The strength of the interaction between a magnetic ion and its neighbors is thus measured by  $\theta$  (or  $\lambda$ ) which can be either positive or negative. A positive  $\theta$  indicates a tendency for a magnetic ion to line up parallel to its neighbors; a negative  $\theta$ , antiparallel. Despite the general crudity of these assumptions, a surprisingly large number of substances obey equation (1 - 21), which is known as the Curie-

Weiss law. If the customary plot of  $\frac{1}{\chi}$  vs. T is made, a straight line indicates the Curie-Weiss law is obeyed. The intercept on the T axis gives  $\theta$  and the slope is equal to  $C^{-1}$ . It has been pointed out by Van Vleck (1932) that when the intercept is small ( a few degrees ) it is risky to identify it with a molecular field, since other effects can produce intercepts. However, when  $\theta$  is large (10's or 100's of degrees) it is usually interpreted as evidence of a molecular field.

The foregoing discussion has been based on the assumption that the atom remains in a single J- state which is independent of temperature. This is true if the energy difference between the lowest and next J- state is much larger than kT and the "wide multiplet" condition is said to exist. At the other extreme, when the energy differences between possible J- states are very small compared to kT the susceptibility can also be calculated; however, when the energy is of the order of kT the Curie-Weiss law no longer holds (since  $\mu$  is a function of T) and the mathematics becomes very complicated.

Experimentally, there is a tendency for compounds containing transition metal ions of the first series to behave as though the L- component of angular moment were inoperative. Thus, if we put  $L = 0$  and  $S = J$ , g takes the value 2 and we obtain the "spin only" form of equation (1 - 13).

$$\mu = 2 \sqrt{4S(S + 1)} \text{ -----(1 - 22)}$$

This "quenching" of the L-component of the magnetic moment is due to the effect of the crystalline electric field of the surrounding ions. In compounds with a high degree of symmetry the interactions between ions

must be directional. Since the spatial charge distribution of an ion depends on the orbital quantum number  $L$ , these interactions involve the  $L$ -component of angular momentum. The electric field then creates an energy difference between electron states formerly having the same energy, i.e. it removes the degeneracy associated with the  $L$ -momentum. As a result it is no longer possible for the magnetic field to raise an ion from one  $L$ -state to another. The  $S$ -component of magnetic moment which is due to the spin of the electrons remains unaffected by the electric field and is free to behave as expected in a magnetic field.

### C. Effective Bohr magneton number.

It is customary to express the effective magnetic moment of an ion as,  $\mu = p_{\text{eff}} \beta$  where  $p_{\text{eff}}$  is called the "effective Bohr magneton number".  $p_{\text{eff}}$  is an experimentally determined quantity which is derived from the paramagnetic Curie constant. From equation (1 - 20)

$$\mu^2 = \frac{3kC}{N}$$

$$p_{\text{eff}}^2 \beta^2 = \frac{3kC}{N} = \frac{3kCM}{n}$$

where,  $C$  is the Curie constant per gram,

$M$  is the molecular weight,

and  $n$  is Avogadro's number.

$$\text{Then } p_{\text{eff}} = \frac{1}{\beta} \sqrt{\frac{3k}{n}} \sqrt{CM}$$

$$= 2.828 \sqrt{CM} \text{ ----- (1 - 23)}$$

If we retain the assumptions of Russell-Saunders coupling and the wide multiplet condition,

$$\begin{aligned} p_{\text{eff}} \beta &= \mu = \beta g \sqrt{J(J+1)} \\ p_{\text{eff}} &= g \sqrt{J(J+1)} \text{-----}(1.24) \end{aligned}$$

Under the added condition of complete quenching of the orbital magnetic moment we obtain

$$p_{\text{eff}} = \sqrt{4S(S+1)} \text{-----}(1.25)$$

In the limit of very large H and low T, one might expect complete alignment of atomic moments leading to a saturation magnetization,'

$$\sigma_s = N \mu = N g \beta \sqrt{J(J+1)}$$

However, this is not the case since the Brillouin function does not approach 1 in the limit but a value such that

$$N \mu = N g \beta J$$

Hence, measurement of the saturation magnetization yields an effective Bohr magneton number, which we will denote by  $f_{\text{eff}}$ , where

$$f_{\text{eff}} = \frac{\mu}{\beta} = g J \text{-----}(1.26)$$

This situation sometimes leads to confusion because the effective Bohr magneton number for a particular ion deduced from magnetic susceptibility measurements in the paramagnetic region is different from that deduced from magnetization measurements. Consider an assembly of magnetic ions each having a net moment due to a single electron spin ( $J = S = \frac{1}{2}$ ;  $g = 2$ ). The effective Bohr magneton number from paramagnetic measurements will be

$$p_{\text{eff}} = \sqrt{4S(S+1)} = 1.73,$$

while from magnetization measurements the results will be

$$f_{\text{eff}} = g S = 1.$$

Experimentally the value of  $f_{\text{eff}}$  can be obtained from the formula

$$f_{\text{eff}} = \frac{\sigma_s M}{5585} \text{-----}(1 \cdot 27)$$

where,  $\sigma_s$  is the saturation magnetization per gram;

M is the gram molecular weight.

Table I. shows the spin only values of  $p_{\text{eff}}$  and  $f_{\text{eff}}$  for ions having from 1 to 5 unpaired electrons.

TABLE I.

| No. of unpaired electrons | $p_{\text{eff}}$ | $f_{\text{eff}}$ |
|---------------------------|------------------|------------------|
| 1                         | 1.73             | 1                |
| 2                         | 2.82             | 2                |
| 3                         | 3.88             | 3                |
| 4                         | 4.90             | 4                |
| 5                         | 5.92             | 5                |

#### D. Spontaneous magnetization.

There are a few elements and a large number of compounds which can possess a large magnetic moment in the absence of a magnetic field. This spontaneous magnetization is evidence of long range order of the magnetic moments (ferromagnetism) due to the exchange interactions between them, and can be explained on the basis of the simple Weiss model. If we consider an assembly of atoms with  $J = S = \frac{1}{2}$ , the equation for the magnetization can be written,

$$\frac{\sigma}{\sigma_s} = \tanh \frac{\mu H}{kT} \text{-----}(1 \cdot 28)$$

Replacing, as before,  $H$  by  $H_{\text{eff}} = H + \lambda \sigma$

it can be shown that below some critical temperature,

$$T_c = \frac{\lambda N \mu^2}{3k}, \text{ in the absence of a magnetic field,}$$

$$\frac{\sigma}{\sigma_s} = \tanh \left( \frac{\sigma/\sigma_s}{T/T_c} \right) \text{ -----(1 . 29)}$$

Thus, the relative magnetization  $\sigma/\sigma_s$  can be represented by a single function of  $T/T_c$ , for a given  $J$  value. Referring to equations (1 . 20) and (1 . 21), it can be seen that  $T_c$ , the ferromagnetic Curie temperature is exactly equal to  $\theta$ , the paramagnetic Curie temperature, on this simple model.

Experimental results for Ni, Co, and Fe, (Fig.1 . 3) agree quite well with equation (1 . 29). The limitations of the equation are those inherent in the Weiss molecular field approximation. It is of particular interest to note that the use of a constant field coefficient,  $\lambda$ , which is independent of temperature, implies the assumption of either a rigid lattice or an exchange interaction which does not depend on interatomic distance.

#### E. Theories of magnetic exchange interactions.

Most theoretical discussions of the properties of solids use one of two different approaches. The Heitler-London approach is based on one-electron wave-functions localized at the atomic sites. The wave-functions are assumed to be nearly the same as in the free atom. The collective electron or Bloch approach begins with the behavior of a gas of free electrons. The application of Fermi-Dirac statistics and of a periodic potential leads to non-localized wave functions and to the concepts of energy bands, Brillouin zones, and Fermi surfaces. The Bloch

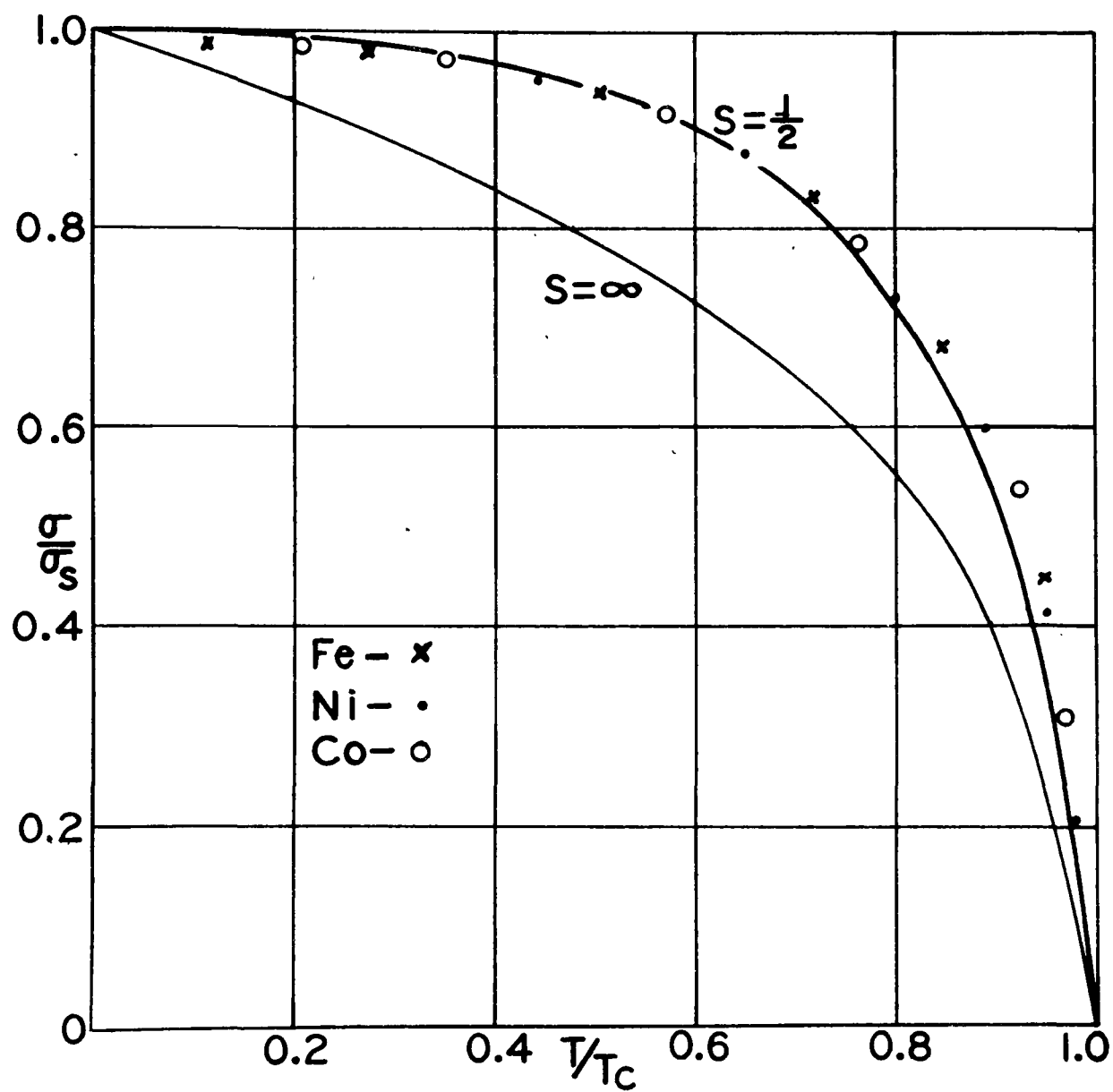


FIG 1.3

Magnetization vs. temperature based on molecular field model.

approach has been used with great success in the description of the outer valence electrons of a metal. Most attempts to explain cooperative magnetic phenomena such as ferromagnetism and antiferromagnetism have been based on the localized electron model, the magnetic moment of each carrier being accounted for by the structure of the free atom. Heisenberg's early theory of ferromagnetism was the first application of the Heitler-London method to magnetic phenomena.

(i) Heisenberg theory of ferromagnetism.

To account for the behavior of a strongly paramagnetic substance, the molecular field coefficient,  $\lambda$ , must be of the order of  $10^5$ . It can be shown that if the molecular field is due to magnetic dipole-dipole interactions, it cannot exceed  $\frac{8\pi}{3}$ . Hence the origin of the field must be electrostatic or electrodynamic.

In 1928, Heisenberg showed that an exchange interaction could be expected as a consequence of quantum-mechanical ideas (the indistinguishability of electrons and the Pauli exclusion principle). He suggested that the exchange forces in ferromagnetism are similar in origin to the exchange forces in a hydrogen molecule which keep the spins of the two electrons antiparallel. The effect in hydrogen can be visualized in the following way. If a second electron enters a hydrogen atom already containing one s-electron, by the Pauli exclusion principle it must go in antiparallel to the first. In a hydrogen molecule, since the two electrons spend at least some of the time together on a given atom, it is not unreasonable to expect a net tendency toward antiparallel

spins.

If the energy of a system with spins parallel is lower than that for spins antiparallel by an amount  $2J$ , the exchange energy is said to be  $+2J$  where  $J$  is the "exchange integral". For ferromagnetism to exist,  $J$  must be positive. The magnitude of  $J$  as calculated by Heisenberg was of the right order to account for the molecular field. The sign of  $J$ , however, was much less certain. One weakness of the Heisenberg theory was the necessity of assuming  $J$  to be positive for Fe, Co, and Ni. Another weakness lay in the values of the magnetic moments predicted for the ferromagnetic metals. On the localized electron model the magnetic moments should correspond to values predictable from atomic theory, (integral numbers of electron spins). Experimentally they do not, the moments being 2.2, 1.7 and 0.6 electron spins per atom for Fe, Co, and Ni, respectively.

#### (ii) Stoner theory

Stoner resolved the latter difficulty by presenting a collective electron theory of ferromagnetism in which the d-electrons are considered as existing in a band. The magnetization is a result of unequal population of the band by electrons of opposite spins due to their mutual exchange interaction. Although this theory readily accounts for the non-integral moments, it introduces other difficulties.

#### (iii) Zener theory.

In a third model, presented by Zener (1952) and Zener and Heikes (1953), the magnetic moments are provided by localized electrons. The direct exchange interaction, however, is always negative as it is in the hydrogen molecule. Metals which show ferromagnetism do so inspite of the

negative exchange interaction, the aligning forces being transmitted via the conduction electrons. In the original Zener theory these forces were thought to be always positive and to have a long range. More refined calculations by Yoshida (1957) showed that the interactions have a relatively short range and are not necessarily positive at all distances. There is considerable doubt whether interactions of this kind play a significant role in the ferromagnetism of Fe, Co, or Ni. In the rare earth metals, however, and in some dilute alloys of transition metals it is believed that interaction via conduction electrons is very important. It has been given the name "pseudo-exchange" interaction, and since it may have either sign it can, theoretically, give rise to ferromagnetism or antiferromagnetism in metals.

Although the division of problems in solid state physics into "localized" and "collective" is one of convenience, there is increasing support for the idea first advanced by Mott that there is a critical interatomic distance,  $R_c$ , at which the behavior of electrons changes sharply from collective to localized. For electrons with quantum numbers  $n, l$ , the critical distance  $R_c^{n,l} \approx 2R_0^{n,l}$  where  $R_0^{n,l}$  is the interatomic distance for optimum bonding via these electrons. When the only unfilled shell is the outermost one, we always have the condition  $R \approx R_0^{n,l} < R_c^{n,l}$ . However, for the first series transition metals and their compounds the interatomic spacing is determined primarily by the  $4s$ - or  $4p$ - electrons, which means that the  $3d$ -electrons may be separated by distances comparable to  $R_c$ .

Using hydrogen atom equations, Goodenough has derived an approximate expression for the interatomic as determined by the s-electrons:

$$R \approx R_0^{n,l} \left( \frac{n}{n'} \right)^{\frac{3n' (3n' + 1)}{(3n - l)(3n - l + 1)}} \text{-----}(1 \cdot 30)$$

where,  $n'$  refers to the outer electrons (4s for example),  $n$  and  $l$  refer to the inner electrons (3d), and  $R_0^{n,l}$  is the equilibrium separation for bonding via the inner (3d) electrons. Consideration of the rare earth metals, and of the behavior of dilute alloys of iron in palladium has led Goodenough to conclude that for 3d-electrons the critical distance  $R_c(n,l) \approx 2.5 R_0^{n,l}$  -----(1 · 31) In transition metal compounds, equation 1 · 31 is a guide for deciding whether particular d-electrons should be treated as localized or collective.

#### F. Antiferromagnetism.

Neel (1936) using a Heitler-London approach, put forward a theory of antiferromagnetism to explain the fact that the transition metals Ti, V, Cr and Mn are not ferromagnetic. His simplest assumption was to consider the lattice of magnetic ions to be divided into two sub-lattices such that all the nearest neighbors of any ion on one sub-lattice (A) lie on the second sub-lattice (B). (This is not possible if the number of nearest neighbors exceeds 8).

The molecular field experienced by an ion on the A- sub-lattice was assumed negative and proportional to the magnetization of the B-sub-lattice, and vice versa. By replacing  $H$  in the Curie Law by  $H_{\text{eff}} = H - \lambda \sigma$  for each sub-lattice, it is easily shown that above a critical temperature,  $T_c$ , the susceptibility follows a Curie-Weiss law;

$$\chi = \frac{C}{T + \theta} \text{ -----(1 . 30)}$$

$$\text{where } \theta = |\lambda c|$$

At the critical temperature  $T_c$ , which on this model is equal to  $\theta$  the magnetic moments of the two sub-lattices start to align themselves antiparallel, producing a sharp peak in the plot of  $\chi$  against  $T$ . In the ordered state there is no spontaneous magnetism since the moments of the two lattices exactly cancel.

Although Néel's theory met with little success in accounting for the non-ferromagnetic transition metals, it turned out to be a good description of the behavior of a number of antiferromagnetic compounds, (MnO, NiO, CrSb, etc.) with one important modification. The strongest negative interactions in, say, MnO are between next - nearest - neighboring Mn ions instead of nearest neighbors as assumed. Experimental data demonstrate strikingly the sharp peak in susceptibility and obedience to the Curie-Weiss law. However,  $T_c$ , is seldom equal to  $\theta$ , or anything near it. This is hardly unexpected since the theory takes into account only a single exchange interaction, while ignoring others which are certainly present.

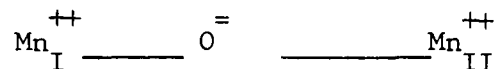
It is not surprising that a theory based on the localized electron (Heitler-London) approach proved successful in describing antiferromagnetic compounds which tend to be ionic, yet failed in the case of metals where some of the electrons must certainly be non-localized.

Mention should be made of a situation akin to antiferromagnetism which occurs when the moments on two opposed sub-lattices are different. The resulting magnetic behavior is known as "ferrimagnetism".

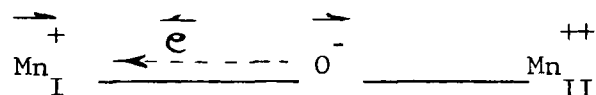
### G. Super-exchange interaction.

The mechanism for the required strong negative interaction between two magnetic ions separated by a non-magnetic ion, is provided by the "super-exchange" interaction predicted by Kramers (1934) and Anderson (1950).

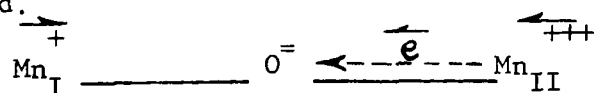
Let us consider  $\text{MnO}$ , which is an antiferromagnet with Na Cl structure. Each  $\text{Mn}^{++}$ -ion is separated from its next-nearest-neighbor  $\text{Mn}^{++}$ -ion by an  $\text{O}^{=}$ -ion. The ordered magnetic structure can be completely accounted for by a single negative interaction through the oxygen ion between next-nearest-neighbors. The super-exchange mechanism can be demonstrated by the following crude picture. The divalent ionic description of  $\text{MnO}$ ,



is not completely adequate. There is a finite probability that an electron will leave the oxygen ion and go to one of the Mn ions:



Since the  $\text{Mn}_I^{++}$  ion has a half-full d-shell of 5 electrons, it can accept only an electron of opposite spin. The spin of  $\text{Mn}_I^{+}$  ion is now parallel to that of the  $\text{O}^{-}$  ion which originally had a full p-shell. An electron going from the  $\text{Mn}_{II}^{++}$  ion to the oxygen ion can only do so if their spins are opposed.



The net result of the two electron transfers is a tendency for the two Mn atoms to have antiparallel spins. Because of the directional proper-

ties of the p-wave-function in oxygen, the super-exchange interaction is very sensitive to direction being a maximum when the Mn — O — Mn angle is  $180^\circ$ . The super-exchange interaction described above has been called "delocalization" super-exchange. It can be shown that by considering electron correlations on either side of the anion the same conclusions can be arrived at. The mechanism is given the name "correlation" super-exchange. The conditions under which a super-exchange interaction is positive or negative will be discussed in section K.

#### H. Competition between positive and negative interaction.

In general, in a magnetic solid, there is a competition between direct, indirect, and pseudo-exchange, each of which can be either positive or negative. As a result few substances obey in detail the simple equations derived on the basis of a single exchange interaction. Even the seemingly obvious conclusion that the order associated with a predominantly positive interaction must be ferromagnetic has been shown to be false. Yoshimori (1959) has shown that a situation is possible in which the main interaction is positive and yet the long range order is antiferromagnetic. For certain ratios of the first -, second -, and third - neighbor interactions the configuration of lowest energy is a helical spin arrangement in which each plane of magnetic ions perpendicular to a certain lattice direction has all spins parallel. The magnetization of each successive plane, however, is rotated at some angle with respect to its neighbors. A total rotation of  $360^\circ$  results in a net magnetization of zero. Antiferromagnetism of the helical type has been verified in  $\text{MnF}_2$ , Dy, Ho, and a number of other substances. Another possible configuration is the linear spin wave pre-

dicted by Overhauser (1959). This structure has been verified for dilute Cu(Mn) alloys and has been suggested as a probable structure for Cr.

### I. The Effect of Collective Electrons on the Magnetic Moment.

When the magnetic electrons of an atom are strictly localized (Heitler-London treatment) and when orbital quenching is complete, the moment per atom should correspond to an integral number of electron spins. Failure of a particular material to conform to this rule is often caused by the presence of collective electrons. The effect of collective electrons on the magnetic moment can be considered under different conditions:

#### (i) Broad Band.

Nearly free electrons such as occur in an s - band are well described by Fermi-Dirac statistics, the criterion being that  $kT \ll E_F(0)$  the Fermi energy. The application of a magnetic field results in a weak paramagnetism which is almost independent of temperature. The susceptibility is given by

$$\chi_{mp} \approx \frac{3N z_e \beta^2}{2E_F(0)}$$

where  $z_e$  is the number of electrons per atom.

Since there is no mechanism for the generation of a strong internal magnetic field, no spontaneous magnetism is possible.

#### (ii) Narrow Bands.

It is believed that as the interatomic separation reaches the critical value,  $R_c$ , the change from collective to localized electron behavior is abrupt, accompanied by a discontinuity in the electrical conductivity.

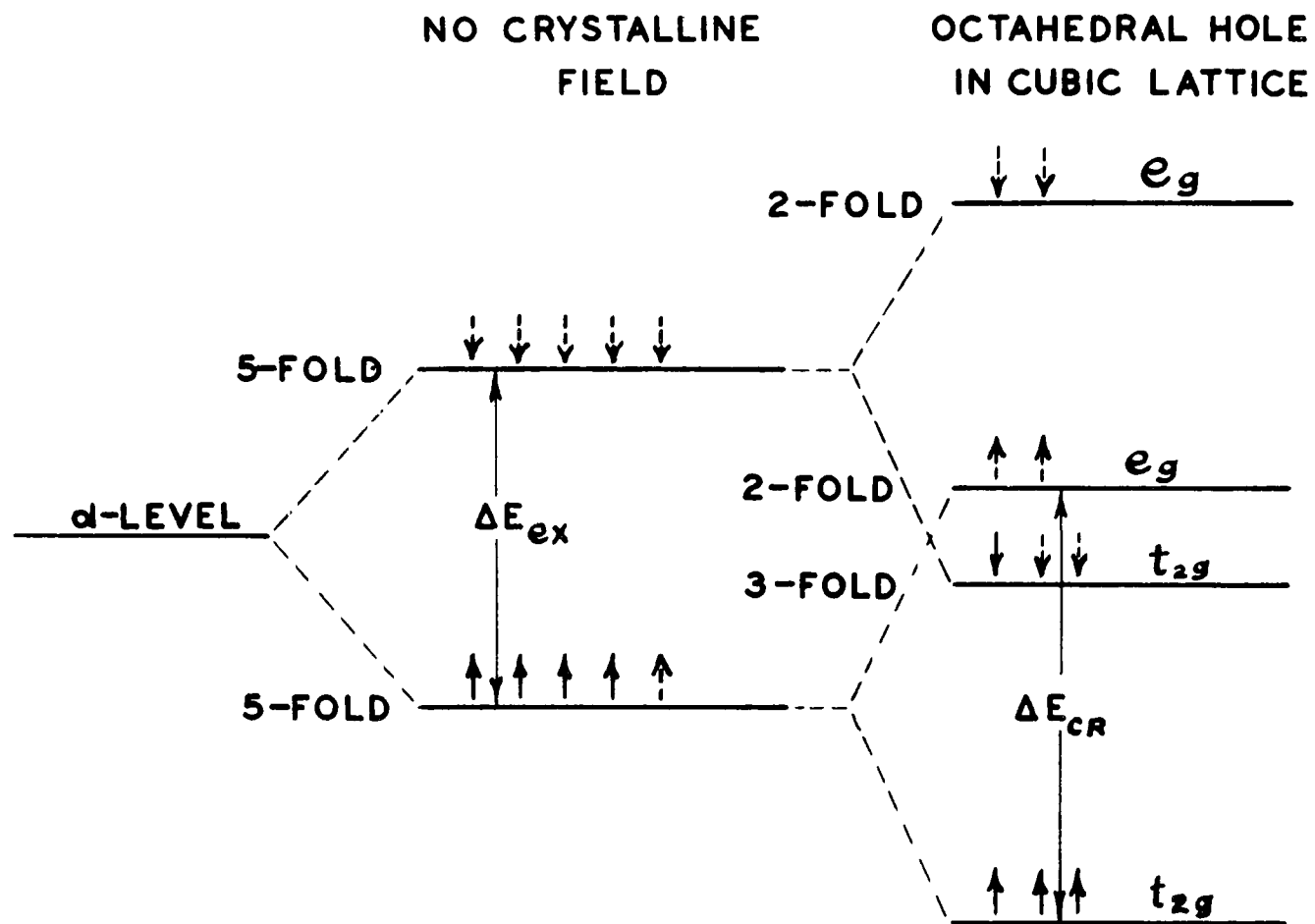
It can be shown, however, that magnetic behavior of electrons in an increasingly narrow band must approach the localized electron limit. As the width of the band increases the average magnetic moment per atom falls. Typically, a substance with magnetic electrons in a narrow band has a spontaneous moment corresponding to a non-integral number of spins, and a paramagnetic moment which approaches the integral, localized value at very high temperatures.

(iii) Simultaneous Localized and Collective Electrons.

Collective electrons moving in a lattice of atoms with localized, aligned magnetic moments, experience a strong effective field which tends to align their spins parallel to the spins of the atoms. Even in broad s- bands the collective electron contribution to the magnetic moment might be  $.1 \text{ to } .2 \mu_B$ , where  $z$  is the number of collective electrons per atom. For narrow bands values of  $.5 \text{ to } .7 \mu_B$  are not uncommon and even the maximum value  $z \mu_B$  is sometimes approached.

J. Effect of the Crystalline field.

We have referred earlier to the quenching of orbital magnetic moment by the crystalline field. This, however, is only one manifestation of the dependence of the 3d energy levels on the field of the lattice. In the absence of a field the 3d- level can be considered as two five-fold degenerate levels one each for electrons with spin up and with spin down, separated by the intra-atomic exchange energy  $\Delta E_{ex}$  (see Fig. 1 .4). In an atom containing four 3d- electrons the spins will be parallel as required by Hund's rule. A crystalline field can remove some or all of the degeneracy depending on its symmetry. Since the surroundings of



**FIG 1.4**

Splitting of d-level in an octahedral field.

an atom in a solid often have cubic symmetry, let us consider the splitting of a d-level in the octahedral interstice\* of a cubic lattice. In many non-cubic situations the major splitting can be derived from the cubic case, with smaller additional splittings due to deviation from cubic symmetry.

The directional properties of the d sub-levels or d-orbitals are assumed to be those given by the quantum-mechanical solution of the hydrogen atom. Linear combinations of the original functions can be made to give five functions which are related to a Cartesian system as follows:

1. The two  $e_g$  -orbitals are considered to have 6- maxima along the  $\langle 100 \rangle$  - directions.

2. The remaining three orbitals, following Goodenough (1960), can be thought of either as "unmixed"  $t_{2g}$  -orbitals having 12 maxima in the  $\langle 110 \rangle$  -directions or as "hybridized"  $t_{2g}$  -orbitals having 8 maxima in the  $\langle 111 \rangle$  -directions. The appropriate choice in a particular case usually depends on the positions of next-nearest-neighbor atoms. In an octahedral interstice the  $e_g$  -orbitals point at the 6 nearest neighbors located at the corners, while the  $t_{2g}$  orbitals point at the 12 edges (unmixed) or at the 8 faces (hybridized). The energy of the

$e_g$ -level is raised with respect to the  $t_{2g}$  -level. In the extreme case, when the crystal field splitting exceeds  $\Delta E_{ex}$ , Hund's rule will be

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\*An octahedral interstice is formed by 6 atoms at equal distances along the 3 Cartesian axes.

violated and the net moment of an atom with four d-electrons will be reduced to two spins. (see again Fig. 1 · 4).

In MnAs, the Mn ions occupy irregular octahedral holes, with nearest Mn neighbors at  $\approx 2.86\text{\AA}$  and next-nearest-neighbors at  $\approx 3.7\text{\AA}$ . Any description of the 3d- electrons in MnAs must take account of the crystalline field and of the probability that both localized and non-localized d-electrons occur on the same atom. Such a model for MnAs will be proposed in Chapter IV.

#### K. Relation between Structural and Magnetic Properties.

We have seen that the magnetic moment of an atom with a partly filled 3d-shell, when it is placed in a solid, can be greatly affected by the crystalline field. Also any chemical bonding involving d-electrons would have a profound effect. Since the magnetic properties are a function of the 3d- electrons, while the interatomic distances are determined primarily by the outer 4s electrons it may be anticipated that the relationship between magnetic and structural properties can become extremely complex.

Following Heisenberg, early attempts to relate the exchange interaction,  $J$ , to the interatomic distance were made by Bethe and Slater. Bethe suggested a probable shape for the interaction curve, from theoretical arguments. Slater attempted to fit the first series transition metals to such a curve by plotting values of  $J$  obtained from Curie temperatures against  $D/d$ , the ratio of the interatomic distance to the diameter of the d-shell of the ion. The resultant variation of  $J$ , given approximately in Fig. 1 · 5, is usually referred to as the Bethe-Slater curve. Subsequent attempts to calculate  $J$  for a par-

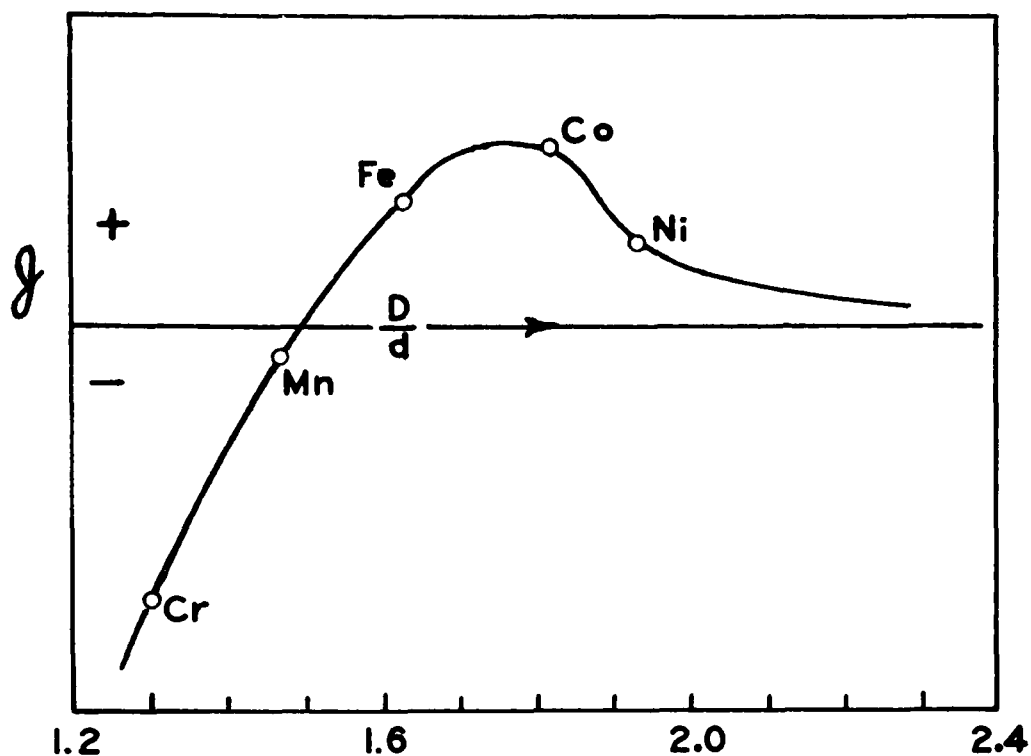


FIG. 1 · 5

ticular situation have met with a notable lack of success, different methods producing widely different values for the magnitude and the sign of  $J$ . It is safe to say that we have not yet reached the stage when a numerical value for  $J$  can be calculated, even approximately, for a given case. It is necessary therefore to adopt a more empirical approach to exchange interactions. The tremendous interest in "ferrite" compounds in recent years and the extensive investigation of their properties by a large number of workers, especially Goodenough (1960) has led to the establishment of semi-empirical rules for estimating the sign and approximate strength of the exchange interaction. For convenience we will discuss direct cation - cation interactions

separately from indirect ones.

(i) Direct Interactions.

The Bethe-Slater expression of  $J$  as a function of distance only is a serious over-simplification. In a particular case it is necessary to consider the direction properties of the d-orbitals in the crystalline field. Attention must be paid as to whether the particular orbitals participating in the interaction are full, half-full or empty. The rules for direct cation-cation interactions can be summarized as follows:

(a) Two half-filled orbitals.

If two half-filled orbitals overlap there is a possibility for electron transfer from one atom to the other. This exchange can take place only if the spins of the two electrons are opposed, according to the Pauli principle. The result is a negative exchange such as occurs in the hydrogen molecule.

(b) One half-filled and one empty orbital.

By reasoning similar to that in part (a) it can be shown that the interaction is positive, though probably weaker than in (a).

(c) One half-filled and one filled orbital.

The interaction is positive as in (b). If both orbitals are either full or empty there can be no electron transfer. It is still possible to have an exchange interaction through spin polarization but this is usually much smaller than those described above.

(ii) Indirect interactions.

By reasoning similar to that used above rules can be formulated

to predict the sign of the interaction for various combinations of empty, half-filled and full orbitals. For a complete list, see pp.174 - 178 in "Magnetism and the Chemical Bond" by J.B.Goodenough, 1963.

It should be pointed out that although the mechanism for the interactions was described in terms of electron transfer, exactly the same conclusions can be reached by considering electron correlations on either side of the intervening anion. Interactions at angles approaching  $90^\circ$  can also be important but will not be discussed here.

#### L. Lattice distortion associated with magnetic ordering.

In early treatments of magnetic ordering it was assumed that the lattice was rigid. If, however, the lattice is assumed to be compressible, a transition from a paramagnetic (disordered) to a ferromagnetic or antiferromagnetic (ordered) state, is in general accompanied by a distortion of the crystal lattice. This will be true if there is some dependence of the exchange interaction on inter-atomic distance or angle. The distortion is in such a direction as to lower the free energy of the crystal. The contribution of the exchange interaction to the free energy may be written  $E_{ex} = -J \cos \theta$ . For ferromagnetic ordering,  $J$  is positive and  $\cos \theta$  is positive; for antiferromagnetism  $J$  and  $\cos \theta$  are both negative. Hence  $E_{ex}$  always makes a negative contribution to the free energy.

Taking the derivative with respect to some suitable co-ordinate,  $x$ , we get

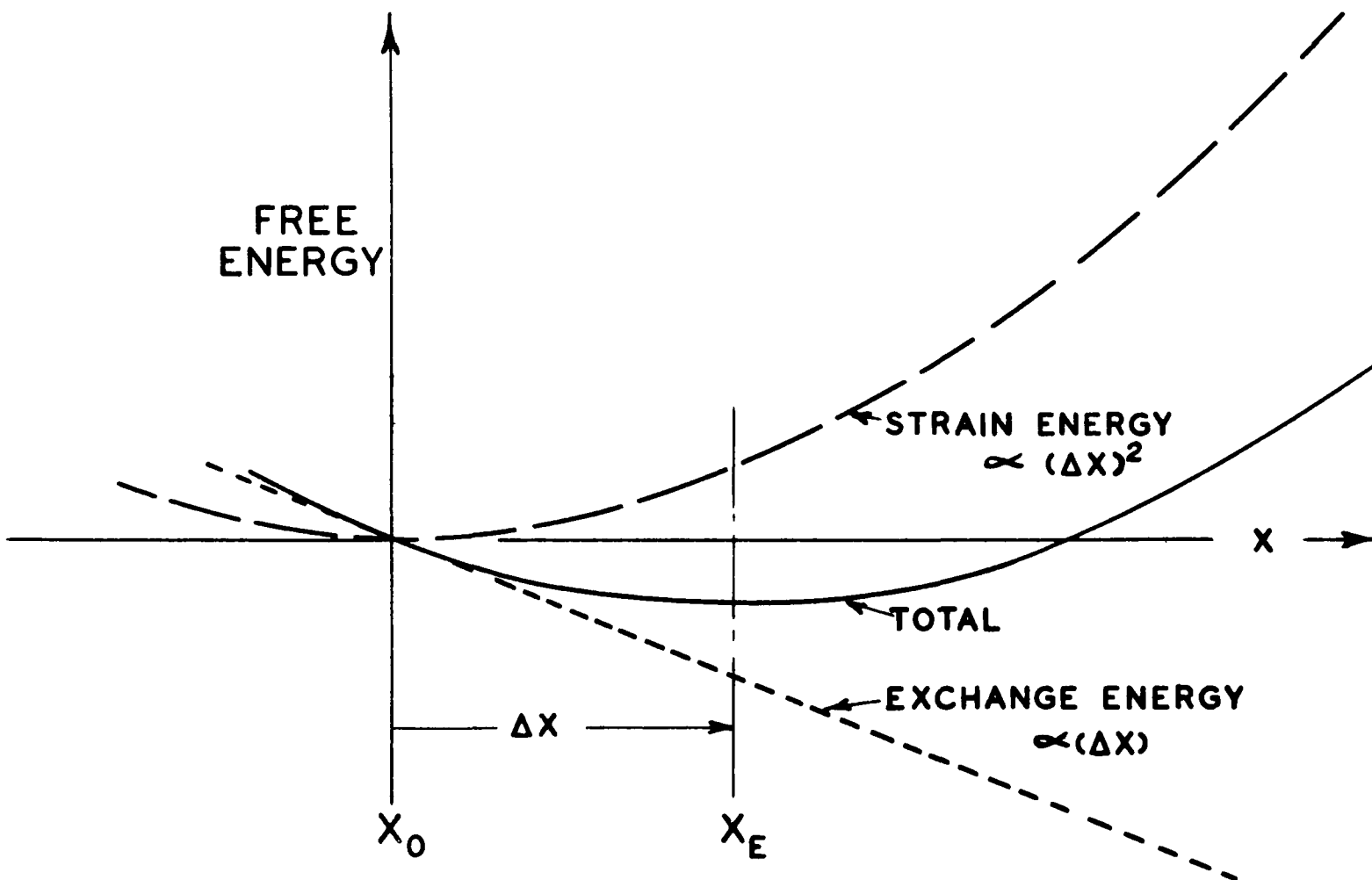
$$\frac{d E_{ex}}{d x} = - \frac{d J}{d x} \cos \theta$$

If we assume ferromagnetic ordering ( $\cos \theta$ , positive) and further assume  $\frac{d J}{d x}$  positive,  $\frac{d E_{ex}}{d x}$  must be negative, and the free

energy is lowered by an expansion of the lattice. Considering the three other possible combinations of signs of  $\cos \theta$  and  $\frac{d J}{d x}$ , it is easily shown that the distortion is always in such a direction as to increase  $|J|$ , the absolute value of  $J$ .

For small distortions,  $\frac{d J}{d x}$  can be considered constant and the decrease in exchange energy on ordering, proportional to the distortion  $\Delta x$ . This decrease in free energy is opposed by an increase in the strain energy of the lattice which varies, for small distortions, as  $(\Delta x)^2$ . These approximate relationships are shown in Fig.(1 · 6). The equilibrium lattice spacing for the dis-ordered lattice is given by  $x_0$ . It can be seen that the energy minimum for the ordered lattice occurs at a new value  $x_e$ , in this case greater than  $x_0$ . The co-ordinate,  $x$ , need not be restricted to an interatomic spacing but may represent an angle or other suitable parameter.

From this point of view it is profitable to examine the observed distortion in the antiferromagnet, CrSb which has the nickel arsenide structure, with the spin arrangement shown in Fig.(1 · 7), below its Neel point. (Snow, 1953). This magnetic structure can be accounted for by a single negative super-exchange interaction, Cr - Sb - Cr, through an angle  $\alpha$  ( $\approx 139^\circ$ ), as indicated. Since the super-exchange interaction becomes stronger as  $\alpha$  approaches  $180^\circ$ ,  $\alpha$  might be expected to increase on ordering, since this would increase  $|J|$ .



**FIG 1.6**

Free energy relationships for a substance which distorts on magnetic ordering.

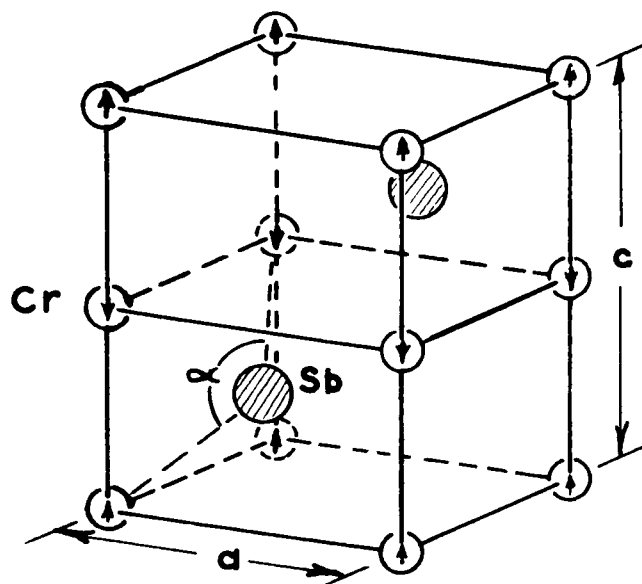


FIG. 1 . 7

The path A - X in Fig.(1 . 8), represents an increase in  $\alpha$  ,

keeping the Cr - Sb distance ,  $s = \sqrt{\frac{c^2}{16} + \frac{a^2}{3}}$  ,

constant. This same path also represents an increase in  $c$  keeping  $s$  constant. Points "A", "B" and "C" on the diagram are the experimental values of Snow (1953) measured at 500°C (just above the transition), at 400°C, and at 300°C (just below the transition), respectively. It can be seen that the experimental points nearly follow the line A - Z which represents not an increase but a decrease in  $\alpha$  , and  $c$ , with  $s = \text{constant}$ . It must be concluded that the distortion is caused by some other mechanism, most likely the direct Cr-Cr interaction along the  $c$ -axis. Although the Cr - Sb - Cr interaction is sufficient to account for the magnetic structure, a negative direct Cr-Cr interaction is also compatible with it. Since each Cr-atom has

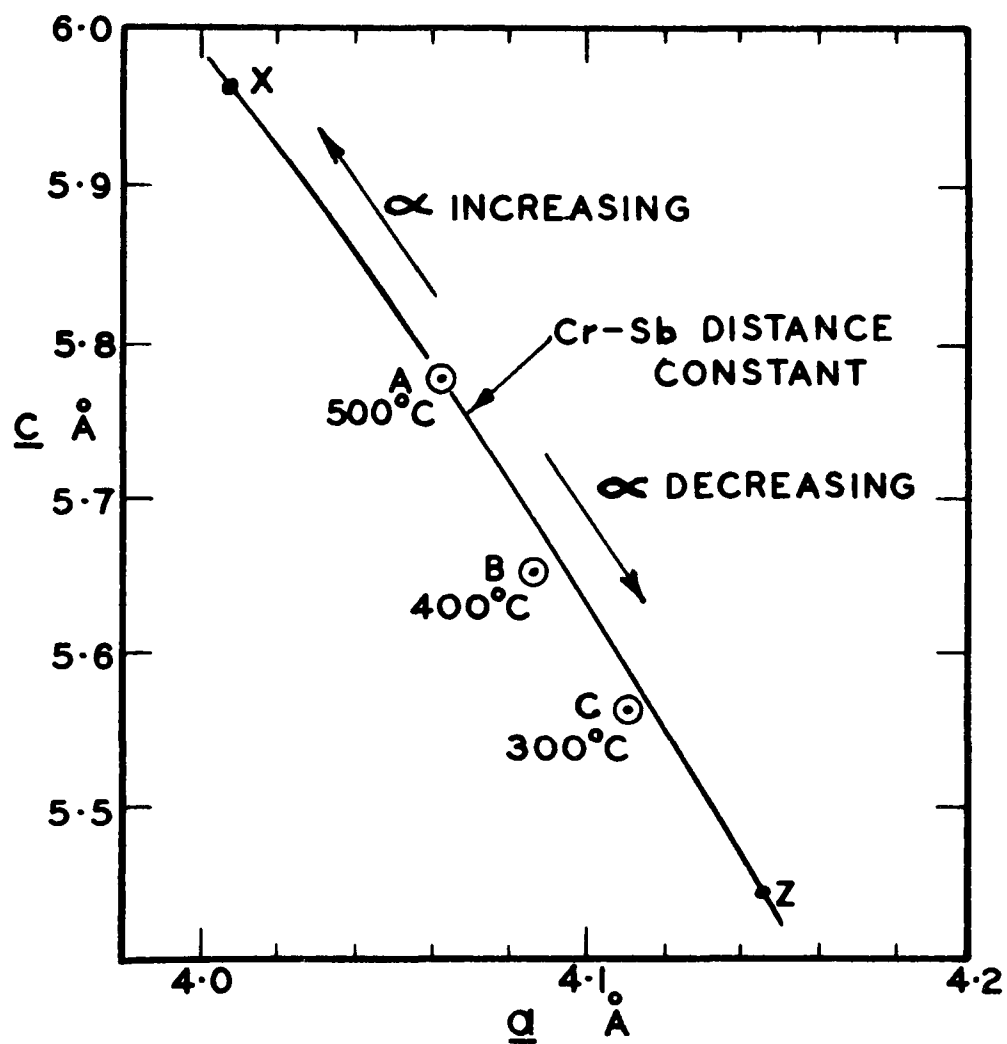


FIG 1.8

Structural distortion in CrSb near the Neel point.

three d-electrons, they will occupy  $t_{2g}$  -orbitals, and two half-filled orbitals will overlap along the c-axis providing negative interaction. The contraction along the c-axis on ordering is evidence of a negative value for  $\frac{d}{d} \frac{181}{x}$  as would be expected. It is interesting to note that even though the indirect interaction may be the dominant one, the direct interaction because of its strong dependence on distance could well be responsible for the observed distortion.

There are other possible mechanisms which may contribute to distortion on ordering. The two most important are dipole-dipole interactions and spin-orbit effects. Consideration of the distortions in MnO, FeO, CoO and NiO quickly leads to the realization that all three effects may be important.

We must also conclude that although the distant-dependent exchange interaction gives a plausible explanation for CrSb, it is not the only possibility.

## CHAPTER II - APPARATUS AND EXPERIMENTAL PROCEDURE.

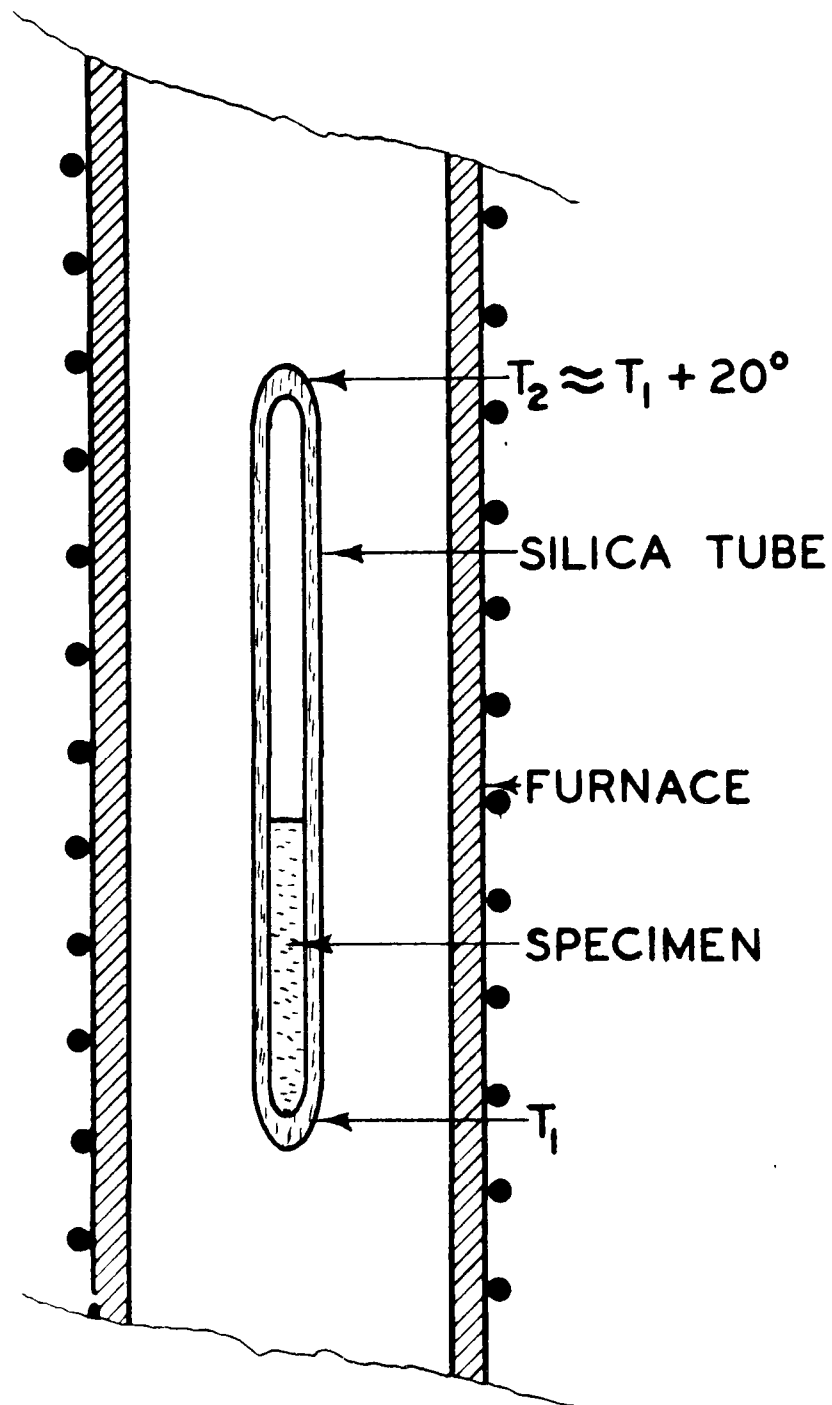
### 1. Preparation of Specimens.

All specimens used in these experiments were prepared from the following constituents:

- Manganese, electrolytically refined by A.D. MacKay and Co., New York.
- Arsenic, "resublimed under nitrogen" by A.D. MacKay and Co., New York.
- Minor constituents - (V, Cr, Fe, Co, Ni), in the form of powders all better than 99.8% pure.

Specimens weighing 3 grams were made by heating together appropriate weights of the constituents in an evacuated, sealed silica tube, 3 or 4 samples being prepared at the same time. The manganese was received in the form of lumps covered with a dull brown film of oxide which could be removed by etching in dilute nitric acid and rinsing in distilled water, alcohol, and ether in succession, thus leaving the manganese metal bright and shiny in appearance. Since arsenic oxidizes rather rapidly in air, it was kept in evacuated glass ampoules until time of use. The manganese, arsenic, and minor constituents were powdered and weighed into a 5 mm. bore silica tube which was then rapidly flushed with helium and evacuated and sealed.

The sealed tubes were placed in a vertical furnace (see Fig. 2 · 1) in a temperature gradient, the upper end of the tube being about 20° C hotter than the lower end. Because arsenic vaporizes at 410° C and because the reaction between manganese and arsenic is exothermic, some precautions had to be taken to prevent explosions on



**FIG 2.1**

Position of specimen in the furnace.

heating the mixture. The contents of the silica tubes were mixed thoroughly to ensure good contact between manganese and arsenic, and the temperature of the furnace was raised slowly to allow the reaction to proceed without producing too large a vapor pressure of arsenic. Heating to  $800^{\circ}\text{C}$  over a period of about 8 hours proved satisfactory. Thereafter the temperature was rapidly increased to  $960^{\circ}\text{C}$  so that the sample melted. (Melting point of  $\text{MnAs} = 890^{\circ}\text{C}$ ). The temperature was maintained for 10 to 15 minutes while the tubes were shaken vigorously at intervals, and then the furnace was allowed to cool slowly to room temperature. The higher temperature at the top of the specimen tube prevented distillation of the arsenic from the melt.

A. Specimens for magnetic measurements.

After removal from the furnace the specimens were inspected for signs of oxidation or obvious inhomogeneity. Usually a small amount of fine black powder was seen at the top surface. This was removed and if they appeared otherwise satisfactory they were resealed in evacuated silica tubes and given a homogenizing anneal at  $670^{\circ}\text{C}$  to  $690^{\circ}\text{C}$  for four or five days, before being quenched into ice-water.

B. Specimens for X-ray diffraction studies.

A portion of each homogenized specimen was ground in an agate mortar until all of it would pass through a No. 230 wire mesh. The powder was then resealed into very thin-walled silica tubing, annealed at about  $670^{\circ}\text{C}$  for three or four days and again quenched into ice-water.

C. Composition of specimens.

The composition of any sample depends on the weight loss

(presumed arsenic) during melting and annealing treatments and on the overall macroscopic homogeneity. Since melting and annealing was conducted with the whole sealed silica tube in the furnaces and as visual inspection of the opened tubes revealed little separation of arsenic, the assumption that the overall composition differed little from the nominal weighed-out composition seems justified. Further justification of this assumption was obtained on two occasions when it was possible to remove the whole specimen from the silica tube in one piece. On weighing, these specimens showed weight losses of approximately 20 and 30 mg. from the nominal 3 gram weight, (i.e. only 1%), indicating that the loss of ingredients during weighing, pumping, sealing and melting was small. The actual homogeneity of the specimens will be discussed later in context with the magnetic and X-ray data.

## 2. Magnetic Measurements.

### A. Magnetic Apparatus.

#### (i) Choice of apparatus.

The magnetic susceptibility of the various specimens was determined by measuring the force exerted on the sample in a magnetic field gradient using a modified Sucksmith ring balance. The force on an element of matter with mass  $\Delta m$  and magnetization  $\sigma$  per unit mass is given by,

$$\Delta f_y = \frac{dH}{dy} \sigma \Delta m \text{ -----(2 \cdot 1)}$$

If the magnetization is proportional to the magnetic field we may put  $\sigma = \chi H$ , where  $\chi$  is the magnetic susceptibility per unit mass.

$$\text{Then, } \Delta f_y = \Delta m \chi H \frac{dH}{dy} \text{ -----(2 \cdot 2)}$$

$$\text{or } \frac{\Delta f_y}{\Delta_m} = \chi H \frac{dH}{dy} \text{ -----}(2 \cdot 3)$$

If a specimen is placed in a region of the magnetic field where  $H \frac{dH}{dy}$  is constant,  $\frac{\Delta f}{\Delta_m}$  will be the same for each part of the specimen and it is permissible to write

$$\frac{f}{m} = \chi H \frac{dH}{dy} \text{ -----}(2 \cdot 4)$$

The force on a sample is then dependent only on its mass, its susceptibility and on  $H \frac{dH}{dy}$ , a constant of the magnetic field. It does not depend on the shape of the sample, which allows sample of irregular shape to be compared accurately. This method has been given the name of the short sample or Curie method to differentiate it from the long sample or Gouy method. The Curie method was chosen for the following reasons:

1. The Gouy method demands that the specimen be of uniform cross-section over its whole length. When using powdered specimens uneven packing can lead to errors.
2. It is easier to keep the temperature uniform over a short specimen than a long one.
3. In the short sample method the magnetic field is fairly high over the whole specimen, which simplifies the method of correcting for ferromagnetic impurities.

The only advantage of the long sample method is the larger force obtainable for a sample of given cross-section, that is, for a given pole-tip spacing. Since all the alloys measured here were strongly paramagnetic, the magnitude of the force obtainable was not a factor in making the choice.

For a ferromagnetic sample at high fields the magnetization

can be considered nearly independent of H.

$$\text{Then } \frac{\Delta f}{\Delta m} = \sigma \frac{dH}{dy} \text{-----}(2 \cdot 5)$$

If  $\frac{f}{m}$  is to be a constant over the whole sample,  $\frac{dH}{dy}$  should be a constant. The construction of a pair of pole-tips to give a region of constant  $H \frac{dH}{dy}$  and of a pair to give a constant  $\frac{dH}{dy}$ , will be discussed later.

#### (ii) Description of the balance.

The balance used to make the magnetic measurements, which is based on a design originally described by Sucksmith (1929), (1938), is illustrated in Fig. 2 · 2. The essential parts of the balance are a flexible beryllium-copper ring and two front-surface mirrors attached to the ring in such a way that a beam of light entering one window of the balance case reflects from each mirror in turn and leaves by the other window. When a vertical force is applied to the lowest point of the ring, the distortion produced, changes the angles of the mirrors and deflects the light beam. For small deflections it can be shown that the angle of deflection is proportional to the applied force. In the original design by Sucksmith the deflection of the light spot was measured with a travelling microscope. This design was modified and improved by using the optical system only as a null indicator. The null position of the light spot was detected with a split cadmium sulphide photoconductive cell. A restoring force could be applied to the suspension of the balance by passing a current through a fine copper wire coil in the field of an "Alnico" permanent magnet, thus any magnetic force on the specimen could be balanced out. This method has a particular advantage. Whenever the system is brought into balance

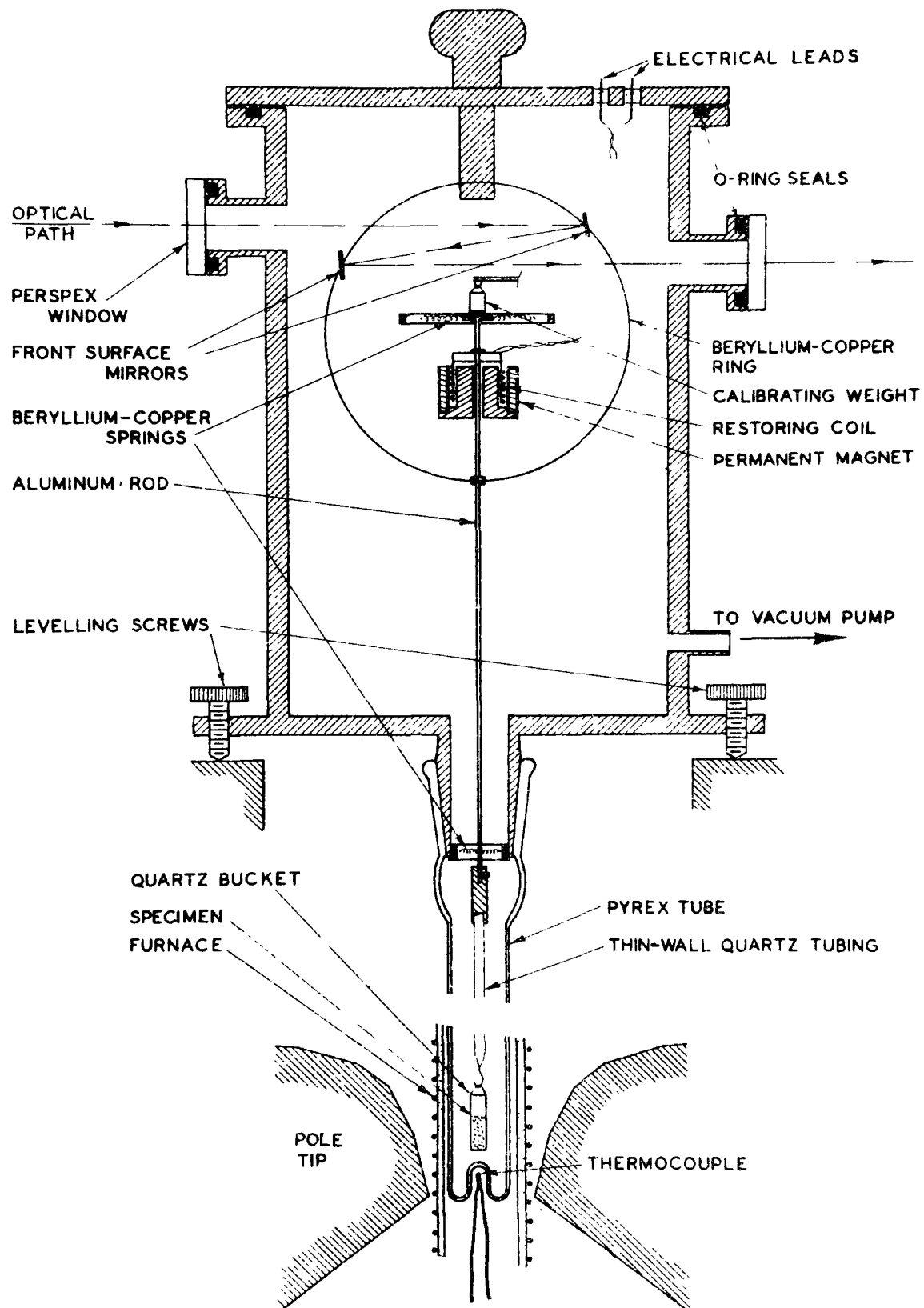
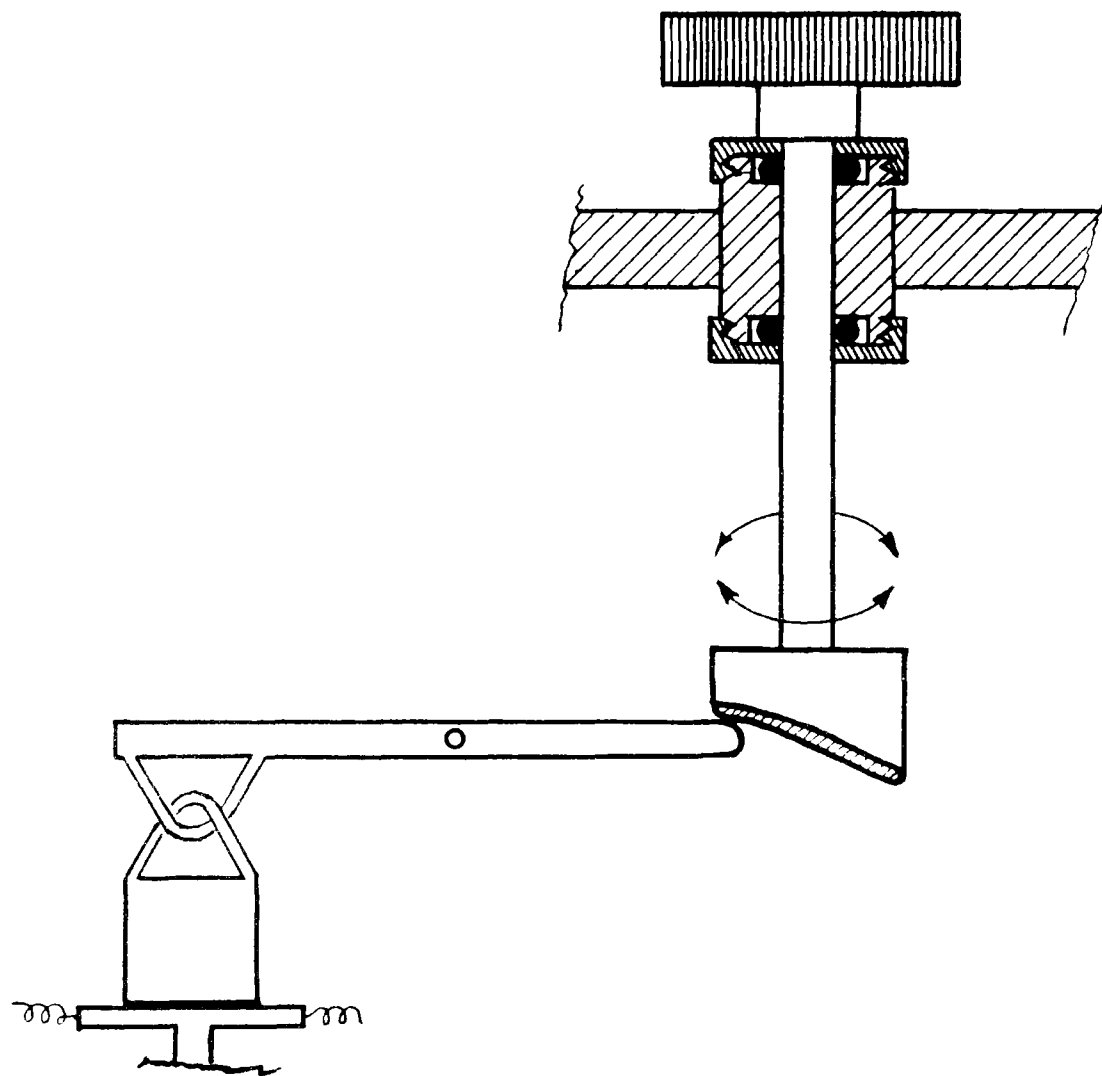


FIG. 2.2 The magnetic balance.

under the influence of the magnetic force on the specimen and the restoring force on the coil, the exact geometries of the specimen with respect to the electromagnet and of the coil with respect to the permanent magnet are re-established, and the current through the coil is directly proportional to the magnetic force on the specimen.

The large susceptibilities of the alloys studied resulted in magnetic forces on specimens which were of the same order as their weight. By symmetry, the direction of the magnetic force should be exactly vertical. However, a slight displacement of the specimen from the mid-point between the pole-tips would result in an appreciable lateral component of force. A hanging suspension was therefore not feasible, as the specimen would swing toward one of the pole-tips, and in order to overcome this difficulty, the suspension was designed in such a way as to constrain the displacement along the axis of the balance. The moving part of the suspension was made completely rigid and the constraint was provided by two assemblies of three beryllium-copper springs as shown in Fig. 2 · 2.

Although the coil-magnet geometry remained constant throughout a run on a particular specimen, this was not the case when one specimen was compared with another. It was therefore necessary to have some means of calibrating the restoring coil under any given load conditions. Thus a cam and lever system (Fig. 2 · 3) was arranged so that a known weight could be added to the suspension of the balance and removed from it. In this way it was possible to calibrate the current in the restoring coil against the known weight for each run and, therefore, to measure the absolute value of the force on the specimen.



**FIG 2.3**

Cam and lever system for applying a known force to the balance.

The restoring coil located in a cylindrical Alnico magnet, consisted of a thin-walled Perspex former on which was wound about 100 turns of #40 enamelled copper wire. The resistance of the coil was approximately 30 ohms.

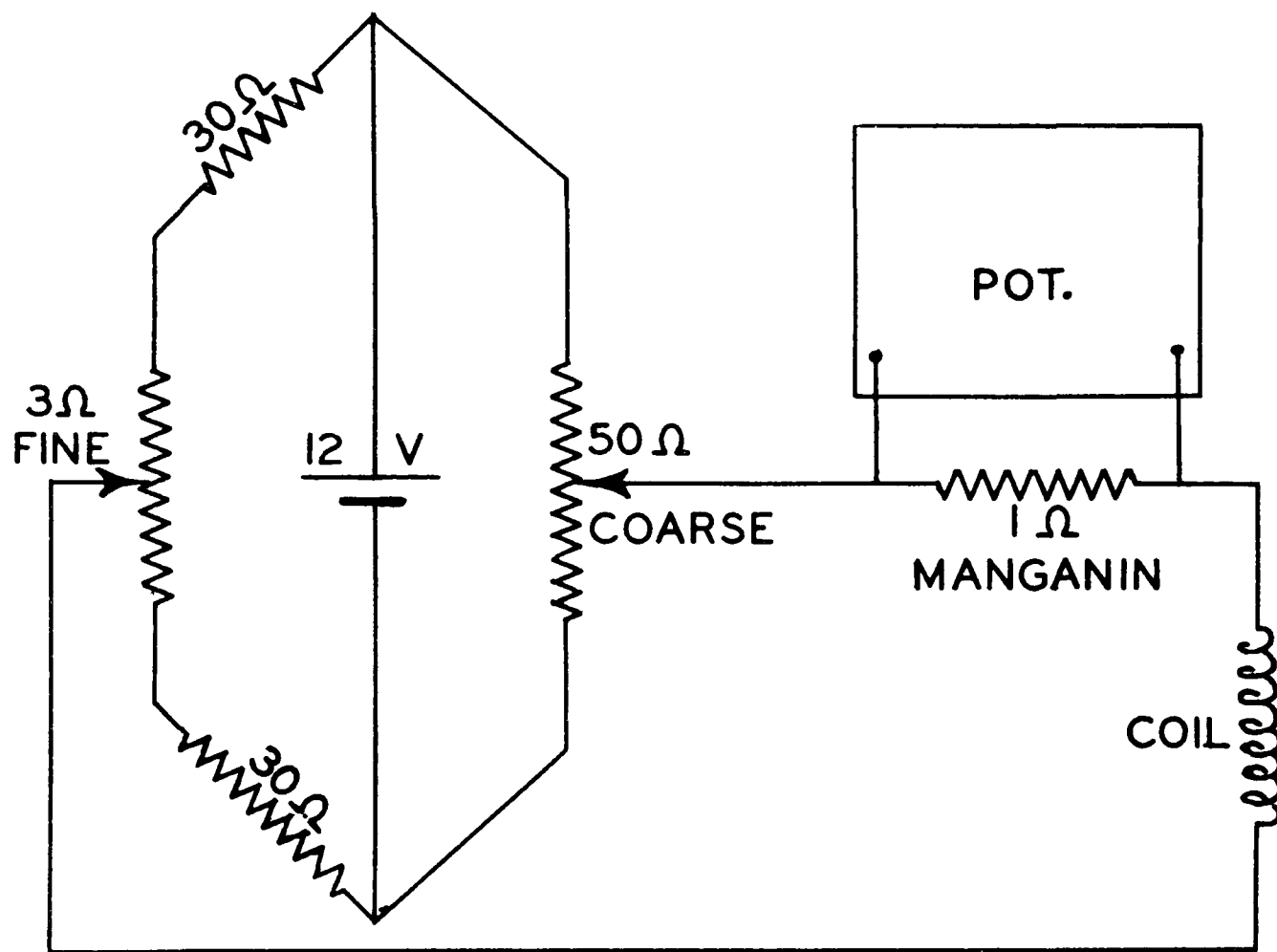
The current through the restoring coil was applied by the circuit shown in Fig. 2 · 4 which has several desirable features:

1. The battery is under a more or less constant current load of approximately 0.5 amps which minimizes fluctuation in battery voltage.
2. The current in the coil can be varied continuously from plus to minus.
3. The coarse current control is quite linear over the range used (0 - 60 ma).

The coil current was determined by putting a 1 ohm manganin resistor in series with the coil and measuring the voltage drop across it with a potentiometer.

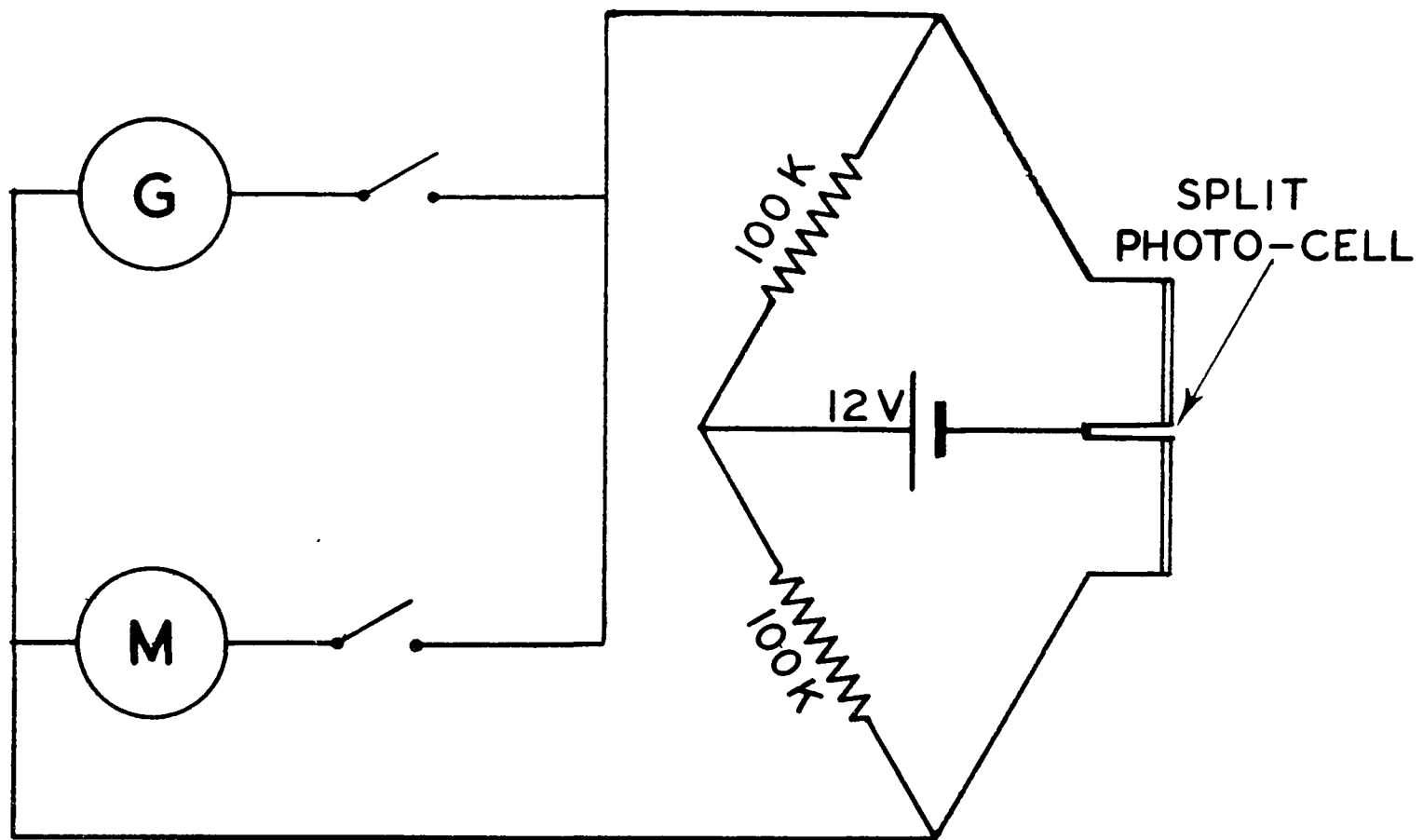
The split Cd S photo-conductive cell was connected into a bridge-type circuit shown in Fig. 2 · 5. Each side of the photo-cell had a resistance of about 100,000 ohms, when the light spot was centered. For maximum sensitivity the two fixed resistors were chosen to have this value. A -50, 0, 50  $\mu$ a ammeter, (M), was used for rough balancing, and a Tinsley box galvanometer, (G) with a sensitivity of approximately 50 mm per  $\mu$ a, was used for fine balancing.

The balance rested on a heavy (200 pounds) slate slab to which was bolted an aluminum framework which supported the light source, split photo-cell and any necessary lenses. (See Fig. 2 · 6). The slab



**FIG 2.4**

Circuit to control and measure restoring coil current.



**FIG 2.5**

Balance circuit for split photo-cell.

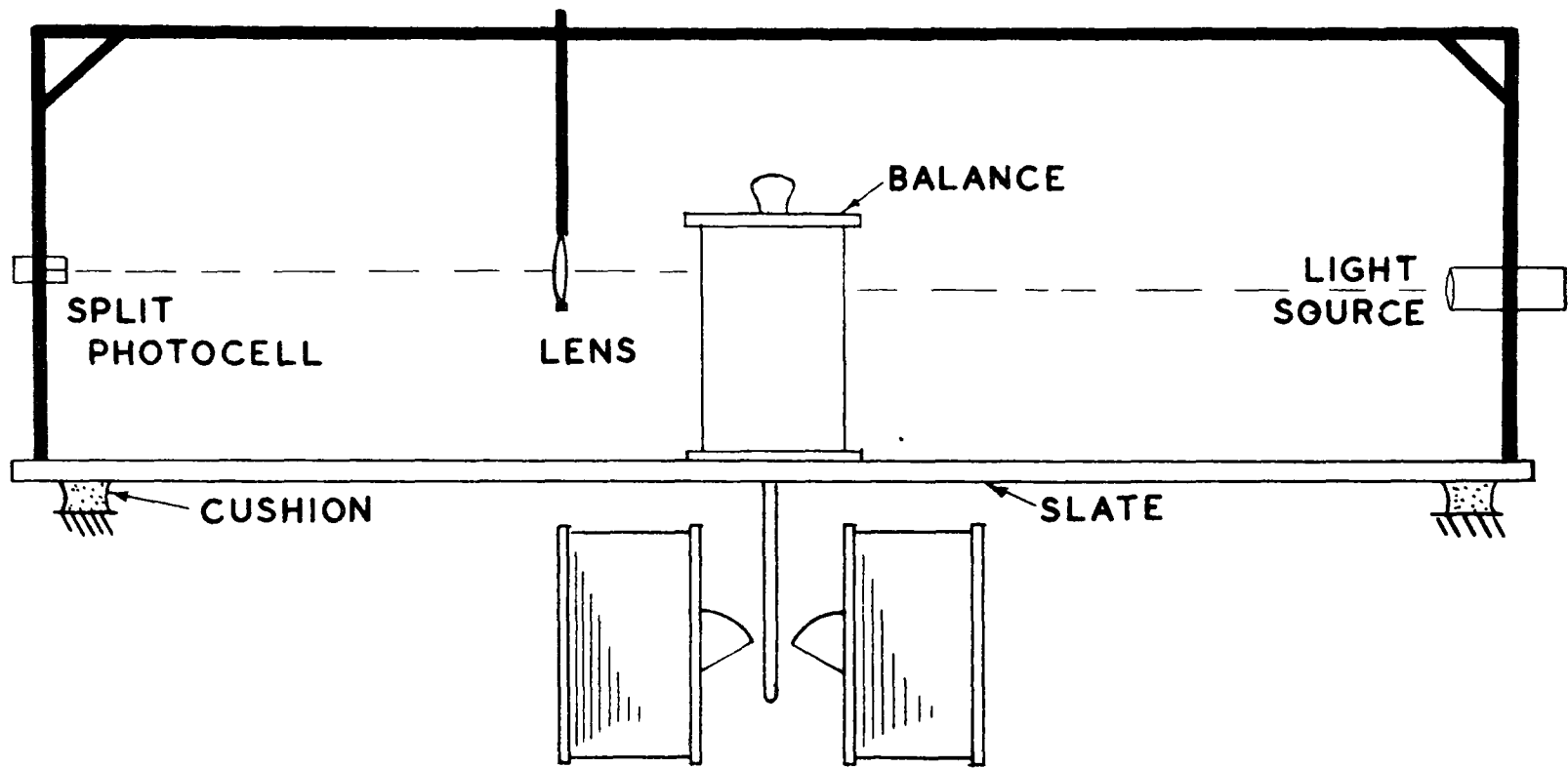


FIG 2.6

was separated from its supporting table by compressible pads which reduced the transmission of vibrations from the surroundings to a satisfactory level. The magnetic field was applied to the specimen by a 4-inch electromagnet which ran on floor rails so that it could be positioned under the balance or removed for assembly of the apparatus.

(iii) Control of magnet current.

The current through the coils of the electromagnet was supplied by a D.C. generator driven by an A.C. motor. The output of the generator was controlled by varying the current in the field winding. An electronic servo-system, described by Hedgcock and Hunt (1956), made it possible to select and keep the current at any value between 0 and 5 amp to within .01 amp on the scale of a 7-inch ammeter. The reproducibility of the magnet current settings was checked with a potentiometer which measured the voltage drop across a manganin resistor in series with the magnet coils. It was found that current values could be repeated to within .01 amp of a given setting by observing the ammeter, and since the regulation of the current controller was also about .01 amp, there was little to be gained by more elaborate means to measure the magnet current.

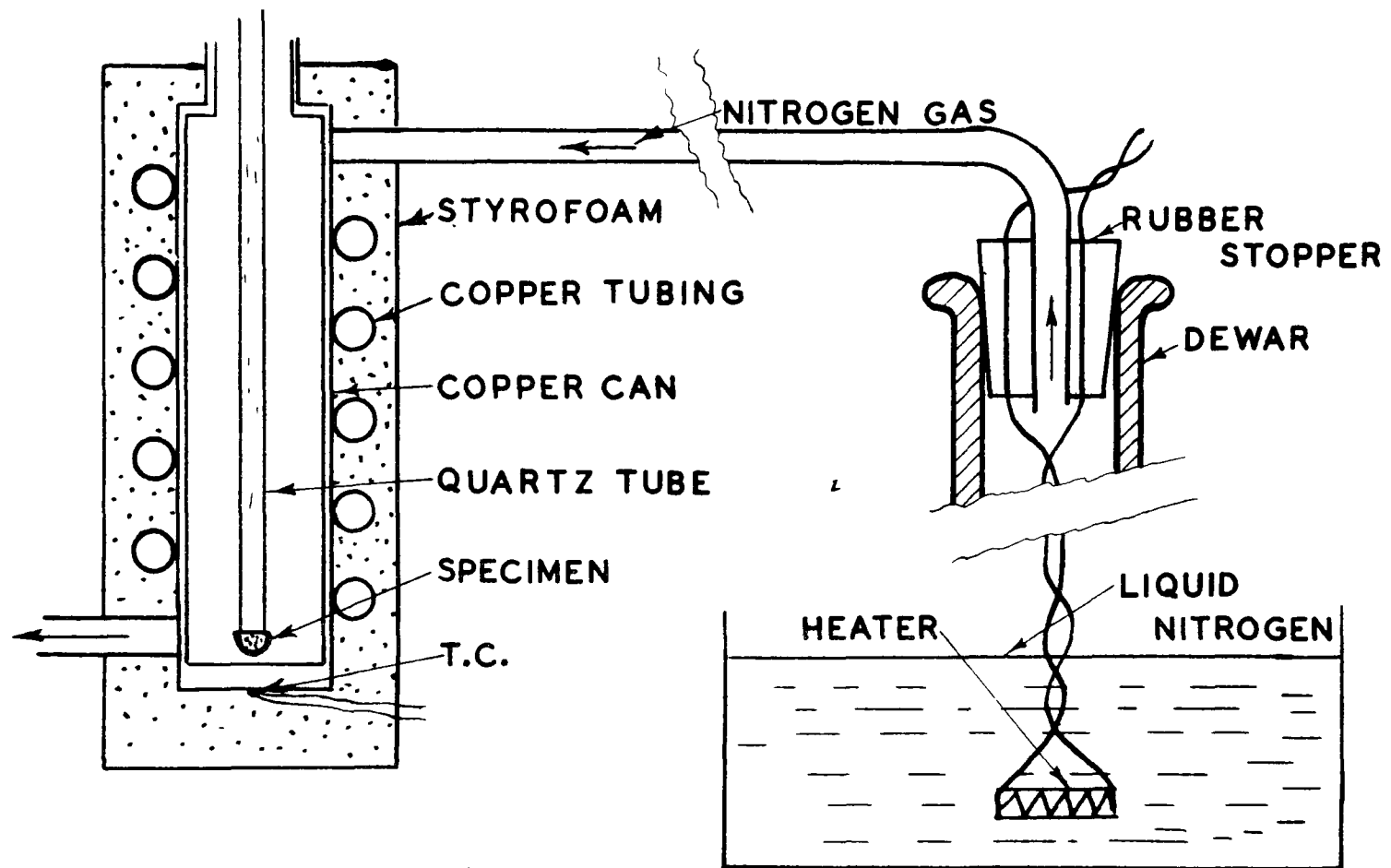
(iv) Control and measurement of temperature.

Specimen temperatures above room temperature were obtained with an externally water-cooled resistance furnace which fitted around the Pyrex specimen tube between the pole-tips. The heating element of the furnace was wound non-inductively with two layers each having the same number of turns, one clockwise and the other anti-clockwise. This method of winding minimized the effects of the current in the heater

on the magnetic field. The temperature of the furnace was controlled manually by adjusting the input voltage with a "Variac" autotransformer. The time constant of the furnace was such that the temperature reached equilibrium in about 20 to 30 minutes after a major change of input voltage. Short-term line voltage variations thus had little effect on furnace temperature and over the period of 15 or 20 minutes required to complete the measurements at a given temperature, it was seldom necessary to adjust the voltage input to the furnace.

The temperature of the specimen was measured with a Chromel P — Alumel thermocouple placed in relation to the specimen as shown in Fig.2 · 2. During an experiment the space inside the balance case was filled with dry helium gas at a pressure of approximately one-half of an atmosphere, which assured good thermal contact between the specimen and its surroundings. The convection currents produced did not appreciably affect the operation of the balance. To test whether the thermocouple temperature was a good measure of the specimen temperature, a second thermocouple was placed in contact with the specimen. At times more than ten minutes after a major change in input voltage, the temperature of the two thermocouples never differed by more than  $\frac{1}{2}$  of a degree.

The apparatus shown in Fig.2 · 8 was employed to obtain temperatures lower than room temperature. The Pyrex tube was replaced by a copper can attached to a Pyrex tube at a glass-to-metal seal. A coil of copper tubing was soldered around the outside of the can and cooled by gas boiled off from a large metal dewar of liquid nitrogen. The rate of boil-off from the nitrogen was controlled with a Variac across a 50-ohm 20-watt wire-wound resistor immersed in the nitrogen.



**FIG 2.8**  
Apparatus to go below room temperature.

By varying the voltage across the resistor, temperatures down to  $-140^{\circ}\text{C}$  could be obtained easily. Equilibrium temperature was reached about 30 minutes after a major change in input voltage.

The specimen temperature was measured with a copper-constantan thermocouple soldered to the bottom of the copper can. The relation between the thermocouple and specimen temperatures was again determined. Fig. 2 · 9 shows how the temperatures of the two thermocouples varied with time after a very large change in input voltage. It is seen that there is a lag of specimen temperature at first. At equilibrium, however, the agreement is quite good.

In all experiments the "room temperature and" of the thermocouple was immersed in a dewar of water together with a mercury thermometer. All thermocouple voltages were measured on a Tinsley potentiometer and converted to temperatures with National Bureau of Standards tables, each thermocouple having been checked against the tables at one point by immersing it in fresh liquid nitrogen. The agreements were excellent and no corrections were applied.

(v) Construction of pole-tips to give a constant  $H \frac{dH}{dy}$  .

The design of the magnet pole-tips to give a constant value of  $H \frac{dH}{dy}$  has been discussed by Davy (1942). The pole-tips described here which were milled from a four-inch diameter bar of mild steel, were adapted from a design due to Henry (1957). The cross-section through one of the tips is shown in Fig. 2 · 10, the shape being constant in the direction perpendicular to the page. The gap between the tips at the narrowest point was kept constant at 34 mm.

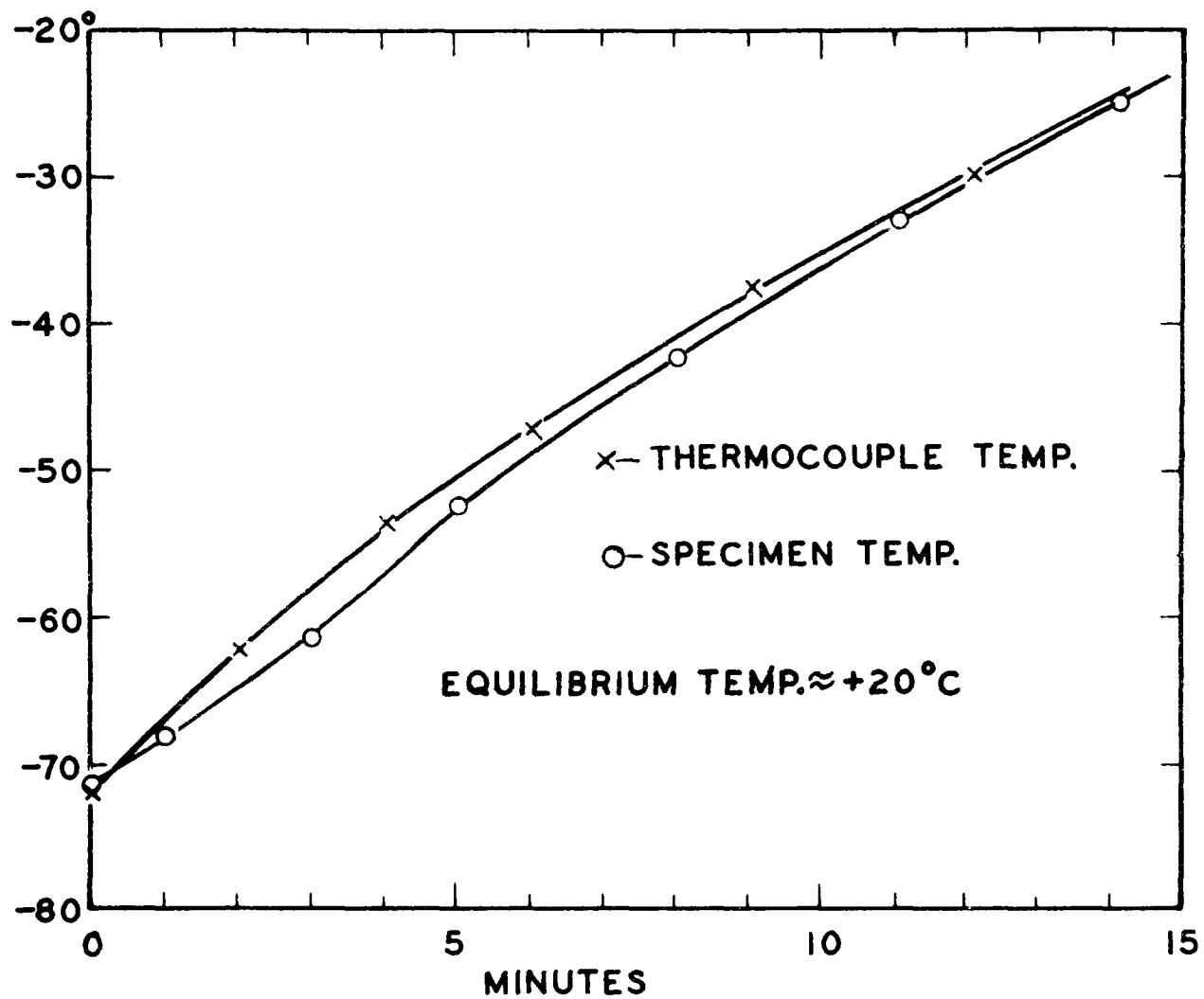
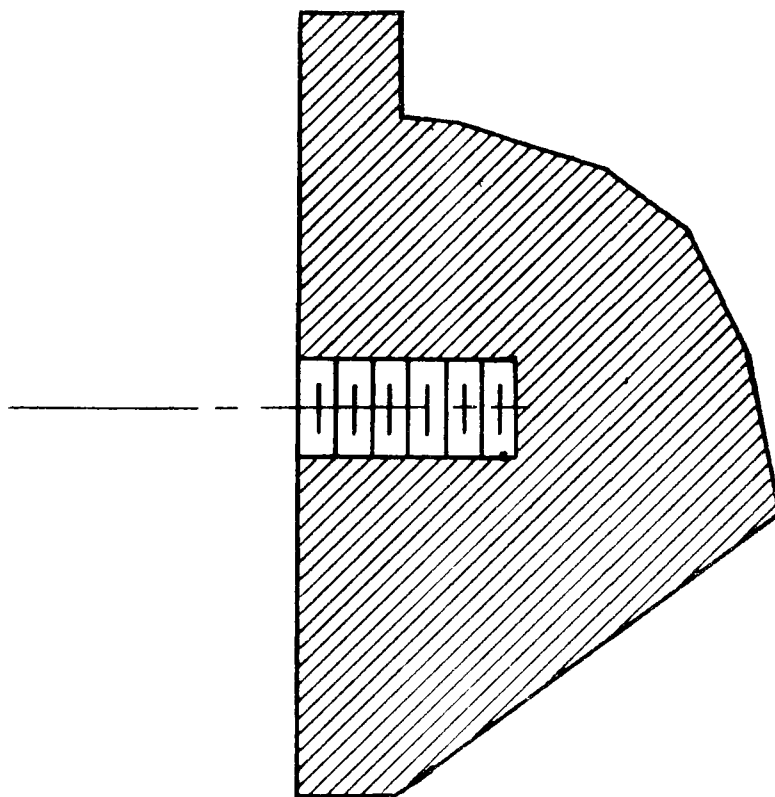


FIG 2.9

Specimen and thermocouple temperatures during  
a very rapid temperature change.

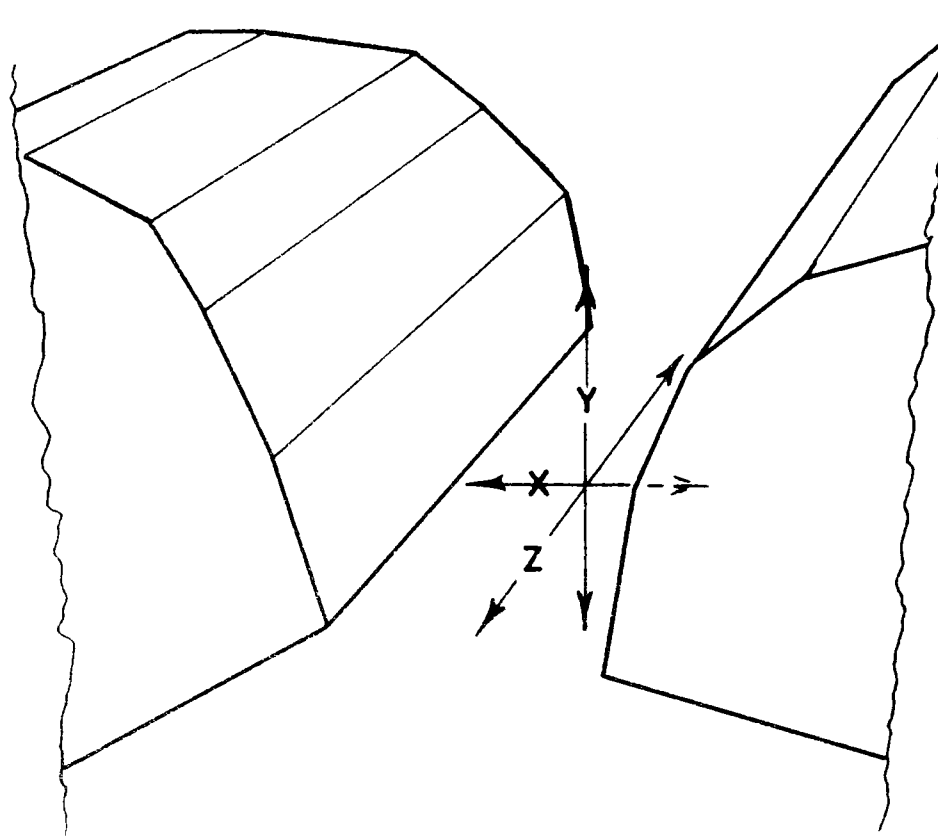


**FIG 2.10**

Cross-section through pole-tip to give a constant  $H \frac{dH}{dy}$ .

The field between the pole-tips was explored with a specimen which was known to be paramagnetic at room temperature. A coarse powder of the specimen was contained in a thin-walled quartz bucket, whose contribution to the force was not detectable with the balance. The specimen occupied a cylindrical volume about 4.5 mm in diameter and 10 mm long and weighed about 800 mg. The x- y- and z- directions were chosen as shown in Fig.2 · 11. By varying the specimen position in the y- direction it was found that the force did in fact show a maximum, as indicated in Fig.2 · 12, which occurred when the center of the specimen was 21 mm above the sharp point of the pole-tip. Since the force on the specimen is proportional to an average  $H \frac{dH}{dy}$  over the whole specimen, the effective value of  $H \frac{dH}{dy}$  from one specimen to another should be closely reproducible, if all specimens have the same length (10 mm), especially as the overall variation of  $H \frac{dH}{dy}$  in the y- direction is not large. The variation of force in the z- direction is shown in Fig.2 · 13, and as expected it is independent of position over a wide range.

The variation in the x- direction showed an unexpected behavior. By symmetry, one would expect a maximum or minimum of force at the mid-point. However, it was found that the variation was asymmetrical having a gradient of about 2% per mm. This can be accounted for in the following way. Although the force on a perfectly centered specimen should be exactly in the y- direction, any slight deviation from the central position leads to a lateral component of force toward the nearest pole-tip. Since the ring and mirrors are in the x-y plane the ring is distorted by the lateral force and it is easy to see that this



**FIG 2.11**  
Selection of axes.

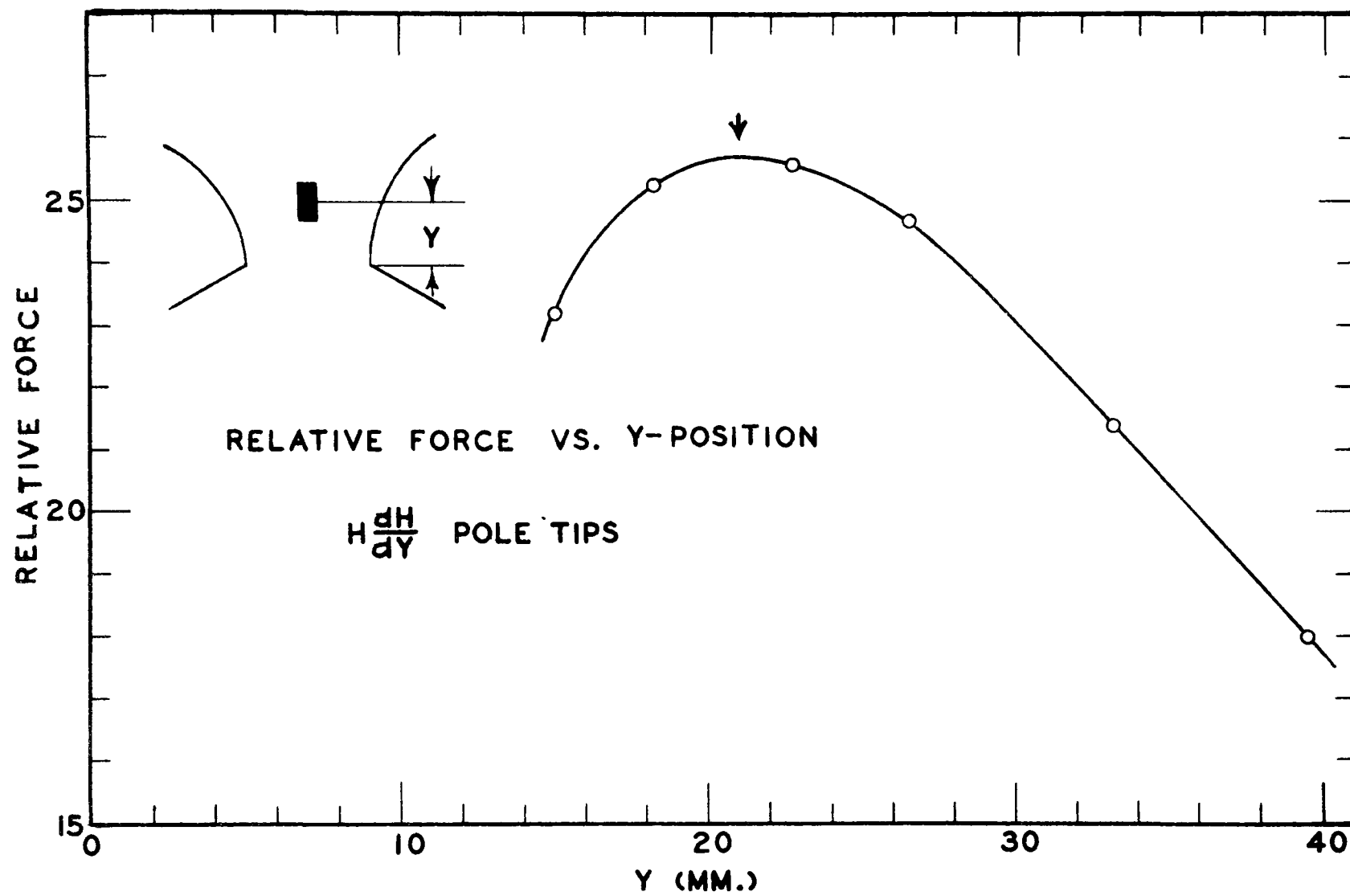


FIG 2.12

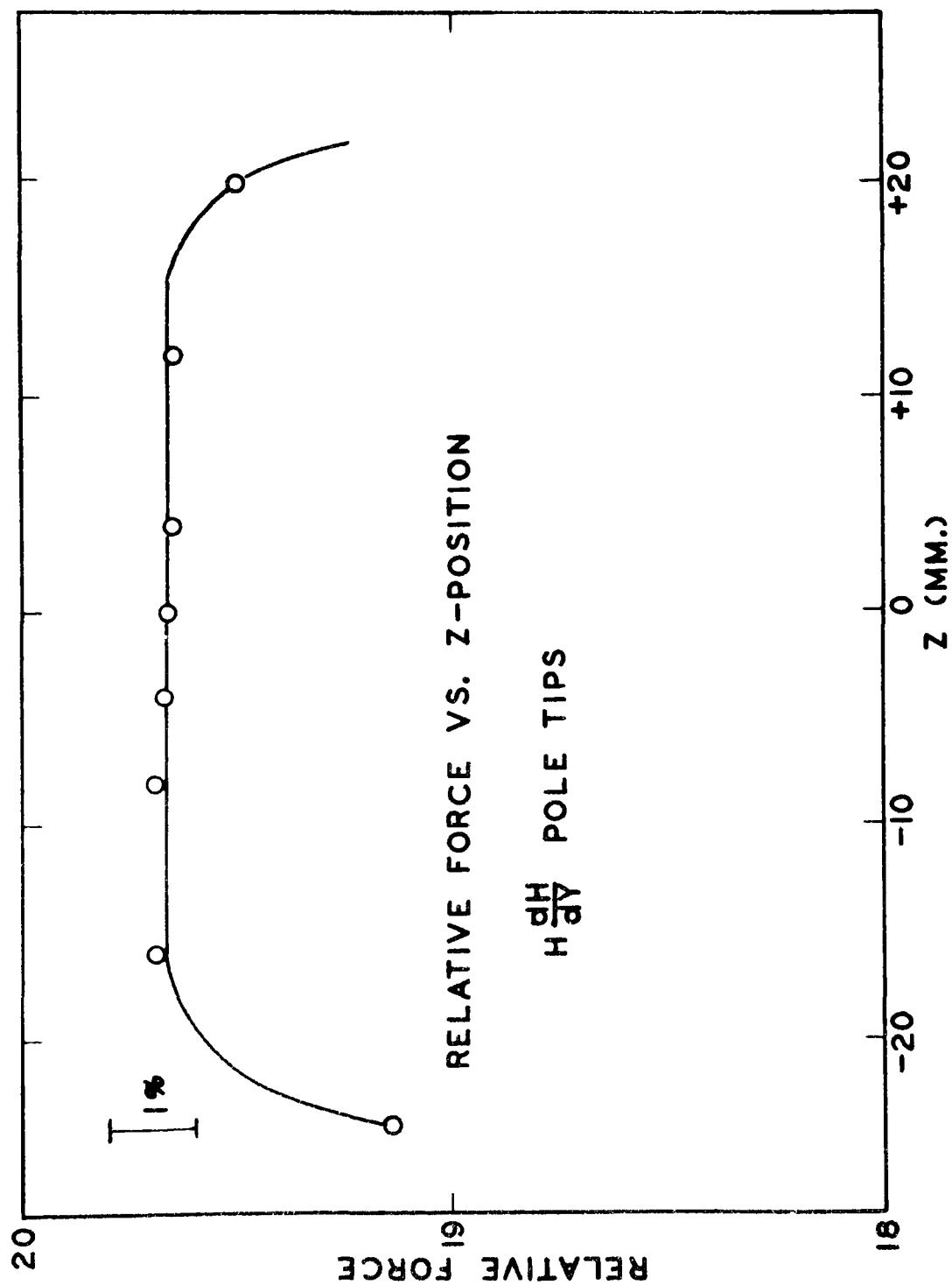


FIG 2.13

could give rise to a spurious deflection of the light beam. To remedy the situation the whole balance was rotated through  $90^\circ$ , putting the ring in the y-z plane perpendicular to the lateral force. As there was no provision for rotating the magnet, two  $90^\circ$  prisms were added to the optical system allowing the lamp, lens and photo-cell to remain in about the same positions. The asymmetry effect was thereby reduced to about 0.5% per mm. Since it was easy to center the sample to .25 mm the effect was, for all practical purposes, eliminated.

(vi) Estimation of  $H \frac{dH}{dy}$  .

The effective value of  $H \frac{dH}{dy}$  at the position of maximum force was estimated for five fixed magnet currents by measuring the force on specimens of pure germanium and of Mohr's salt. The measurements were made by Miss M. Treuil with a Bunge microbalance and the same electromagnet, pole-tips, current controller and magnet current ammeter. The specimens of germanium and Mohr's salt were made 10 mm long, but their cross-sectional areas were, however, quite different. The germanium sample had been loaned to this laboratory by Dr. D.K. Stevens of the Oak Ridge National Laboratory. The absolute susceptibility measured by him was given as  $-.103 \times 10^{-6}$  emu/gm. The magnetic susceptibility of Mohr's salt is given by Selwood (1956) as  $\frac{9500}{T+1} \times 10^{-6}$ . At  $26^\circ$  C this gives a value of  $31.6 \times 10^{-6}$  emu/gm. Values of  $H \frac{dH}{dy}$ , shown in Table I were computed for the five fixed magnet currents from the relation

$$f_m = \chi H \frac{dH}{dy}$$

where,  $H \frac{dH}{dy}$  is in oersteds<sup>2</sup>/cm

$\chi$  is in emu/gm.

f is in dynes

m is in grams.

The agreement between the values obtained with two specimens of quite different mass and volume and of very different susceptibility is good indeed. The average of the two sets of values of  $H \frac{dH}{dy}$ , given in the last column of Table I, were used for our experiments.

TABLE I

| Magnet<br>Current | Germanium<br>Weight = 2.098 gm.<br>$\chi = - .103 \times 10^{-6}$ |                   | Mohr's Salt<br>Weight = 0.0788 gm.<br>$\chi = +31.6 \times 10^{-6}$ |                   | (Ave)<br>$H \frac{dH}{dy}$ |
|-------------------|-------------------------------------------------------------------|-------------------|---------------------------------------------------------------------|-------------------|----------------------------|
|                   | Force                                                             | $H \frac{dH}{dy}$ | Force                                                               | $H \frac{dH}{dy}$ |                            |
| 0.9 A             | Dynes<br>.086                                                     | $.40 \times 10^6$ | Dynes<br>1.045                                                      | $.42 \times 10^6$ | $.41 \times 10^6$          |
| 1.9               | .396                                                              | 1.83              | 4.508                                                               | 1.82              | 1.82                       |
| 2.9               | .822                                                              | 3.80              | 9.380                                                               | 3.79              | 3.80                       |
| 3.9               | 1.186                                                             | 5.49              | 13.625                                                              | 5.50              | 5.50                       |
| 4.8               | 1.450                                                             | 6.71              | 16.500                                                              | 6.67              | 6.69                       |

(vii) Measurement of H.

Although the value of H does not enter the calculation of  $\chi$  directly, it is necessary to know H, at least approximately, to apply corrections for ferromagnetic impurities. The magnetic field

at the position of maximum force was measured for the five magnet currents with a rotating-coil fluxmeter which had been calibrated in an electron-spin-resonance apparatus. The results are shown in Table II

TABLE II

| Magnet Current | Field(H) |
|----------------|----------|
| 0.9 amp        | 1670 oe  |
| 1.9            | 3510     |
| 2.9            | 5070     |
| 3.9            | 6100     |
| 4.8            | 6740     |

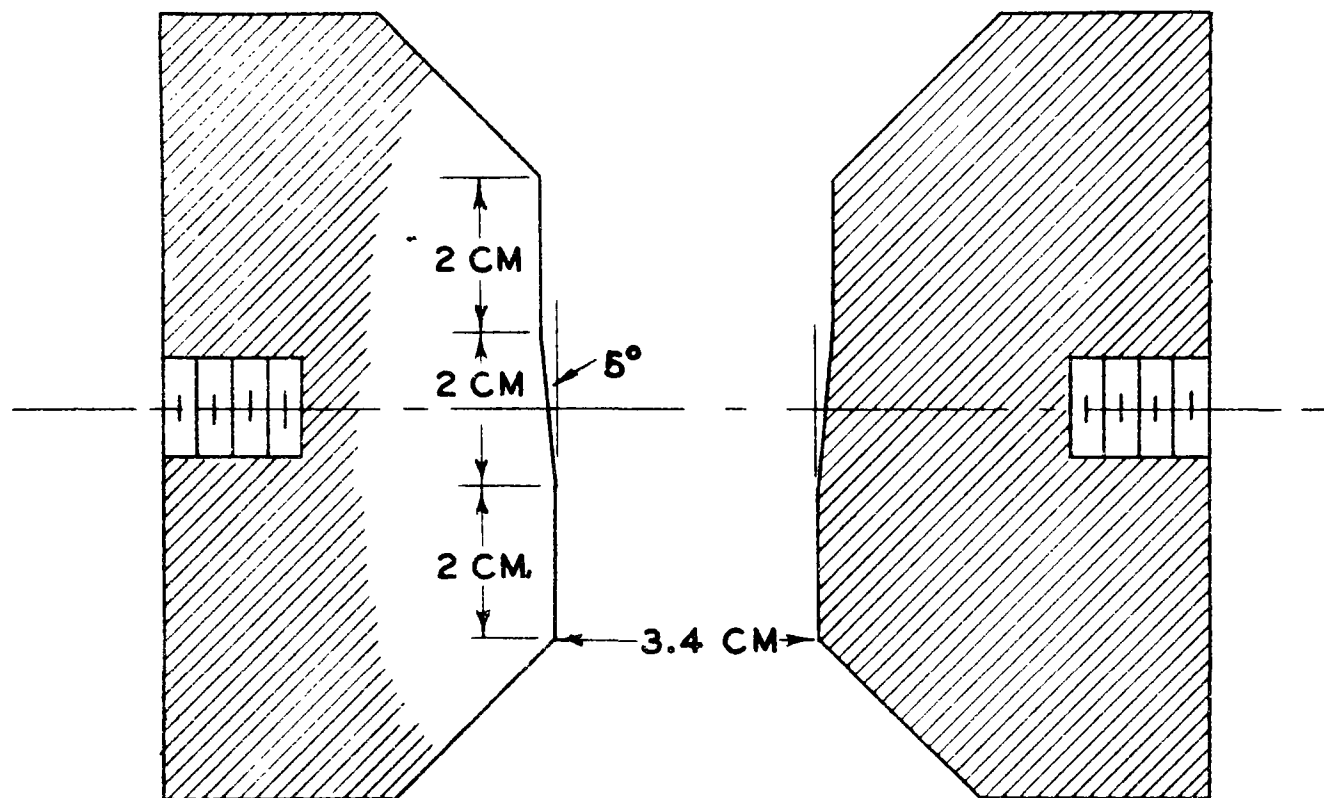
(viii) Pole-tips to give a constant  $\frac{dH}{dy}$  .

For measurements on ferromagnetic samples, a region of constant  $\frac{dH}{dy}$  is desirable. The pole-tips shown in Fig.2 · 14 were designed by trial and error to give a region of maximum force on a ferromagnetic specimen, as shown in Fig.2 · 15. Variation in the x- and z-direction was negligible within the limits to which the specimen could be centred.

(ix) Estimation of  $\frac{dH}{dy}$  .

To deduce the absolute value of the magnetization of a ferromagnetic sample it is necessary to know  $\frac{dH}{dy}$  .  $\left( \frac{f}{m} = \sigma \frac{dH}{dy} \right)$

This turned out to be a difficult quantity to measure accurately. An apparatus was built to vibrate a coil of known area at a constant frequency, through a constant amplitude about the point where  $\frac{dH}{dy}$



**FIG 2.14**

Cross-section through pole-tips to give a constant  $\frac{dH}{dy}$

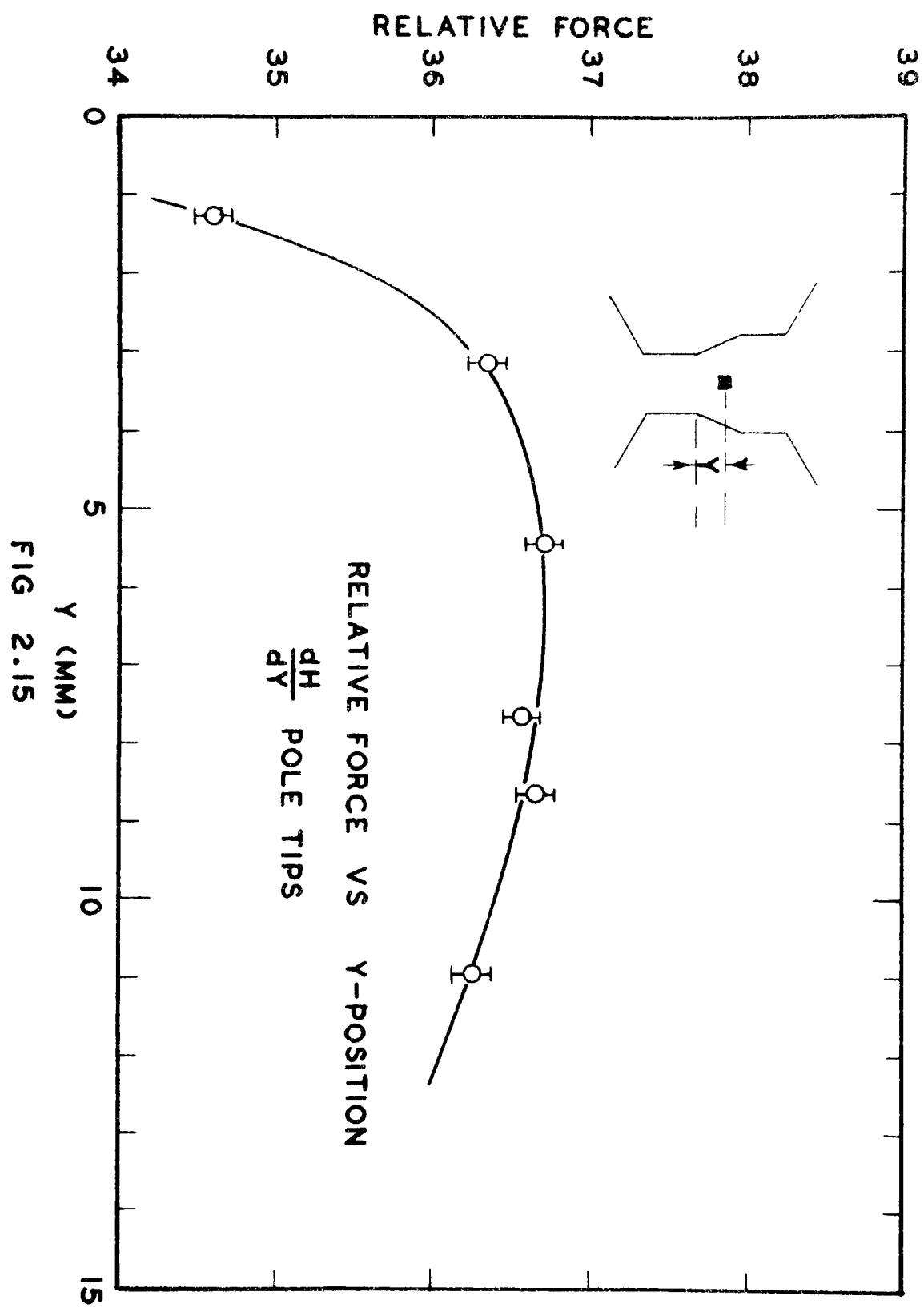


FIG 2.15

is a maximum. However, other aspects of the ferromagnetic measurements, which will be discussed later, prevented an absolute determination of

$\sigma$ . The details of the measurement of  $\frac{dH}{dy}$  will not be given, since they were not used.

The magnetic fields for these pole-tips, at the fixed magnet currents are given in Table III

TABLE III - Magnetic fields for  $\frac{dH}{dy}$  pole-tips.

| Magnet Current | Field    |
|----------------|----------|
| 0.9 amp        | 2350 oe. |
| 1.9            | 4720     |
| 2.9            | 6520     |
| 3.9            | 7630     |
| 4.8            | 8320     |

(x) Performance of the apparatus.

In the absence of an applied magnetic field it was possible to establish balance in the system within about .05 ma of current in the restoring coil. This was the amplitude of the random fluctuations on the box galvanometer. These fluctuations were attributed to the following causes:

1. Mechanical vibrations.
2. Friction in the balance suspension.
3. Fluctuations in the intensity of the light source.
4. Noise in the photo-conductive cell.

In addition to the fluctuations there was usually a steady zero drift. By putting a variable voltage across the filament of the lamp, it was found that the position of balance depended on the filament

voltage. In practice the lamp was run from a 6-volt storage battery, the zero drift usually becoming small after 30 minutes operation. It is believed that additional zero drift was caused by the thermal expansion of the aluminium structure which supported the lamp, the lens and the photo-cell. The drift became noticeably worse after a rapid change in room temperature.

With the magnetic field on a specimen, there were added fluctuations due to variations in the magnet current (about 0.2%). Some idea of the overall precision of the apparatus was obtained by noting the deviations from means in a large number of groups of readings. The root-mean-square deviation from the mean was about .06 ma of coil current. Since a typical value of the net coil current measured was 20 ma, the relative accuracy of the force measurements was about 0.3%. In view of the excellent agreement between the results from germanium and Mohr's salt, the absolute values of susceptibility are probably accurate to better than 1%.\*

#### B. Experimental Procedure.

##### (i) Susceptibility measurements.

A portion of an annealed specimen, which was brittle was crushed to a coarse powder in a percussion mortar and filled into the quartz bucket to a depth of 10 mm. The bucket and sample were weighed on an analytical balance (accuracy  $\pm .2$  mg), the average weight being about 800 mg. The bucket was then attached to the suspension of the susceptibility balance and centered between the " $H \frac{dH}{dy}$ " pole-tips at the

---

\*If no ferromagnetic corrections are necessary.

appropriate height by means of a cathetometer. Next, the Pyrex tube and furnace, (or the cryostat) were put into place. The pyrex tube was attached to the balance case at a tapered joint and the furnace was fixed to the supporting wooden table in such a way that it did not touch the balance case or Pyrex tube. After evacuating the system and flushing it with dry helium gas three or four times, it was pumped down and filled with half an atmosphere of helium.

The coil current was adjusted to a small value ( $\approx 5$  ma) and the split photo-cell was positioned mechanically to give approximate balance. Exact balance was established by fine adjustment of the coil current. To calibrate the current sensitivity of the balance, the calibrating weight was repeatedly loaded and unloaded, the sensitivity being given by

$$s = \frac{f}{i} = \frac{m \cdot g}{i} \quad \text{dynes} \quad \text{-----} (2 \cdot 6) \\ \text{ma.}$$

where, m is the mass of calibrating weight (1.543 gm),

i is the net restoring coil current.

At each desired temperature the force on the sample was measured at the five selected magnet currents. Once temperature equilibrium was established, and the zero current in the restoring coil ( $i_0$ ), readjusted, the restoring coil current ( $i_c$ ) necessary to balance the magnetic force on the sample was measured for magnet current of 4.8, 3.9, 2.9, 1.9 and 0.9 amperes in succession. The procedure was repeated with the magnet current reversed. Zero drift was corrected for by linear interpolation. The force per unit mass of the specimen was computed from the average of three readings at each magnet current

$$\text{by } \frac{f}{m} = \frac{\quad}{i_c - i_0} \quad \frac{s}{m} \quad \text{dynes/gm.} \quad \text{-----} (2 \cdot 7)$$

The magnet was carefully kept in "cyclic" condition throughout the experiment.

The susceptibility measurements generally covered the range of temperature from just above the first order transformation (at about room temperature) to about 375° C, both on warming and cooling. The upper temperature limit was imposed by the fact that at about 400° C the specimens began to decompose losing arsenic.

### (ii) Calculation of susceptibility.

In the case of a specimen whose magnetization is strictly proportional to the magnetic field (e.g. a paramagnetic substance) the evaluation of the susceptibility is straightforward.

Since  $\frac{f}{m} = \chi H \frac{dH}{dy}$ , plotting the measured values of  $f/m$  against  $H \frac{dH}{dy}$  should result in a straight line through the origin having a slope equal to the susceptibility,  $\chi$ . Typical curves at a few selected temperatures are shown in Fig. 2 · 16 for the sample MnAs (1% Co). The data measured at 198° C and 302° C are well fitted by straight lines through the origin, within experimental precision. In such cases, the slope of the line was determined by evaluating

$\frac{\sum f/m}{\sum H \frac{dH}{dy}}$  for all points. In this way each measurement was weighted according to its size.

Some of the curves, such as those measured at 29° C and 57° C showed obvious deviations from straight lines. This was assumed to be due to the presence of a ferromagnetic non-linear component. Taking account of the ferromagnetic contribution, the equation for the force on a specimen becomes

$$\frac{f}{m} = \chi H \frac{dH}{dy} + c \sigma \frac{dH}{dy} \text{ ----- (2 · 8)}$$

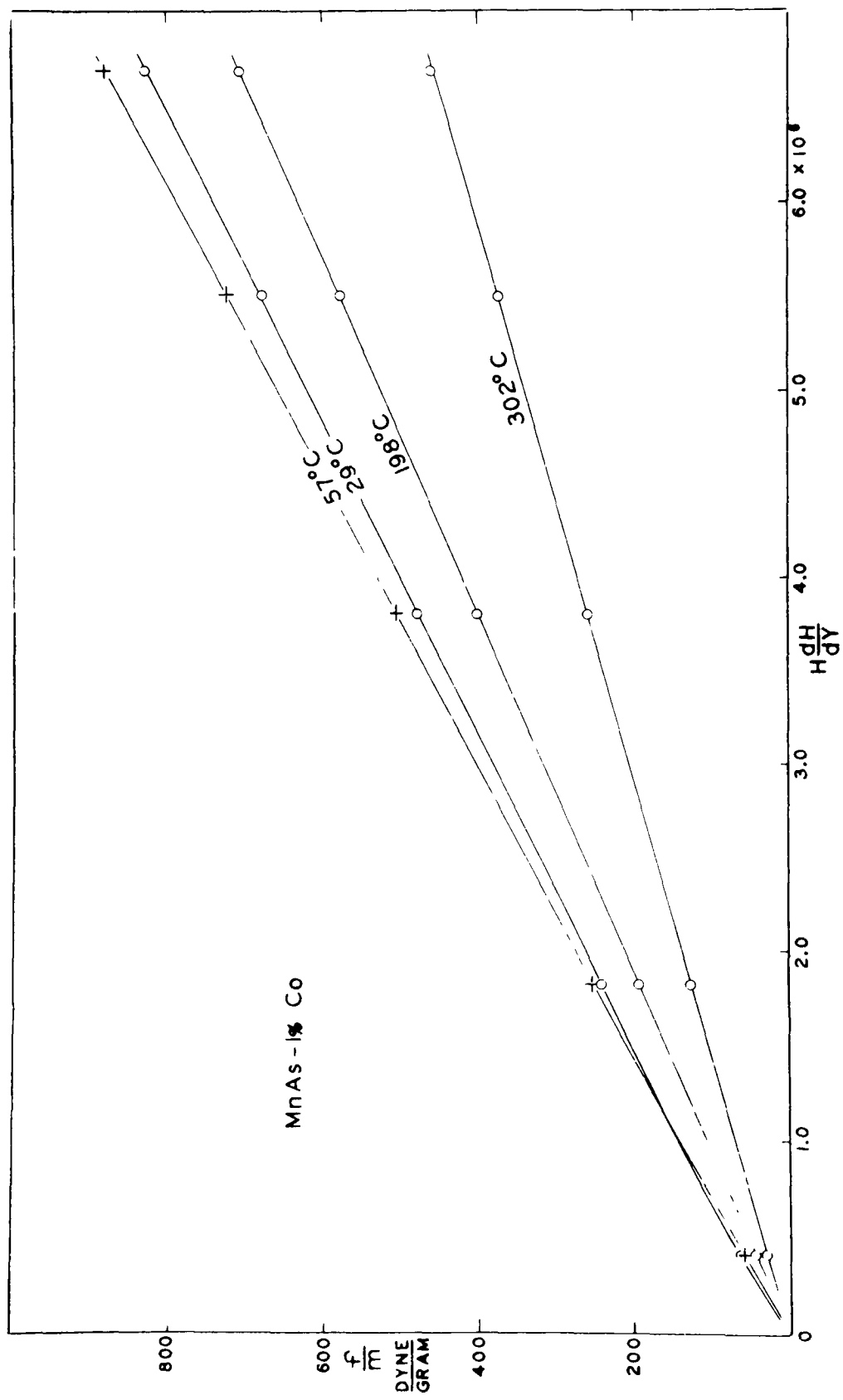


FIG. 2.16  $f_m$  versus  $H \frac{dH}{dY}$  for MnAs - 1% Co.

where  $c$  is the fraction by weight of the specimen which is ferromagnetic with magnetization,  $\sigma$ , per unit mass. The first term on the right hand side should be multiplied by  $(1 - c)$ , but since in practice  $c \ll 1$ ,  $(1 - c)$  has been replaced by 1. The ferromagnetic component could be due to a number of causes, such as free cobalt (or nickel or iron) in the sample, small amounts of other phases which might be ferromagnetic, or small amounts of the specimen which have persisted in the low temperature ferromagnetic state on warming through the first-order transformation. To evaluate the true paramagnetic susceptibility,  $\chi$ , the two contributions to the force must be separated.

(iii) Correction for ferromagnetic component.

The usual methods of correcting for ferromagnetic impurities involve plotting the apparent susceptibility determined at an interval of magnetic field around  $H$ , against some function like  $\frac{1}{H}$  and extrapolating to infinite field; the higher the maximum magnetic field the better the extrapolation. Because of the limited range of magnetic field obtainable with our apparatus, the loss of accuracy in taking a number of field intervals made a graphical extrapolation virtually useless. Therefore, an analytical method, which we believe makes better use of the experimental data, was derived by us for the " $H \frac{dH}{dy}$ " pole-tips. The values of  $H$  and  $\frac{dH}{dy}$  independently at each magnet current are required though not to the same precision as the product  $H \frac{dH}{dy}$ . In Table IV, the measured values of  $H$  and the deduced values of  $\frac{dH}{dy}$  are given for the five fixed magnet currents with the previously tabulated values of  $H \frac{dH}{dy}$ .

TABLE IV

| $I_m$ | $H \frac{dH}{dy}$ | H    | $\frac{dH}{dy}$ |
|-------|-------------------|------|-----------------|
| 0.9   | $.41 \times 10^6$ | 1670 | 246             |
| 1.9   | 1.82              | 3510 | 518             |
| 2.9   | 3.80              | 5070 | 749             |
| 3.9   | 5.50              | 6100 | 901             |
| 4.8   | 6.69              | 6740 | 993             |

A detailed description of the method follows.

Fig. 2 · 17 shows schematically an exaggerated non-linear curve of  $f/m$  against  $H \frac{dH}{dy}$ . Two magnet currents  $I_1$  and  $I_2$  were selected, usually at 1.9 and 4.8 amps. At the corresponding values of magnetic field (3510 and 6740 oe), the ferromagnetic component was assumed to be saturated. This assumption is difficult to justify further than arguing that a 10% correction computed to an accuracy of  $\pm 10\%$  is still very worthwhile.

Referring to Fig. 2 · 17, OCD is the experimental curve. OAB is the desired curve, **after** subtraction of the ferromagnetic component. At the magnet current  $I_1$ :

OX is the value of  $\left(H \frac{dH}{dy}\right)_1$

CX is the measured value of  $f/m$

CA, the portion of CX due to the ferromagnetic component

$$= c \sigma_s \left( \frac{dH}{dy} \right)_1. \quad (\text{See equation 2 · 8})$$

AX is the portion of CX due to the paramagnetic component

$$= \chi \left( H \frac{dH}{dy} \right)_1.$$

Similar interpretations can be made at  $I_2$ .

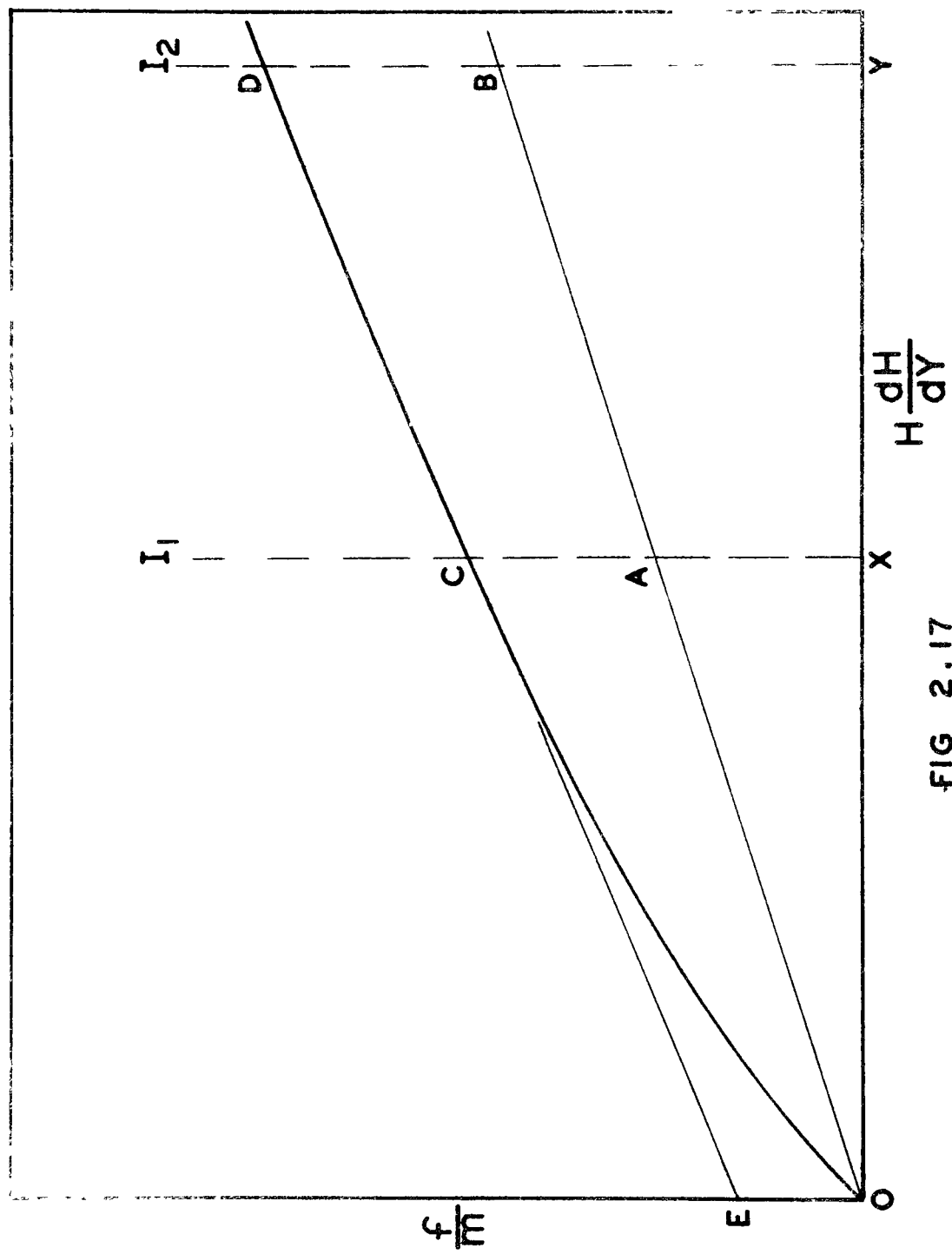


FIG 2.17

EO is the intercept on the ordinate axis of DC extrapolated. Since OAB and ECD are straight lines, on geometrical grounds we may write

$$CA = EO + k (OX) \text{ -----}(2 \cdot 9)$$

$$DB = EO + k (OY) \text{ -----}(2 \cdot 10)$$

where k is a constant.

Substituting for CA, OX, DB and OY we obtain

$$c \sigma_s \left( \frac{dH}{dy} \right)_1 = EO + k \left( H \frac{dH}{dy} \right)_1 \text{ -----}(2 \cdot 11)$$

$$\text{and } c \sigma_s \left( \frac{dH}{dy} \right)_2 = EO + k \left( H \frac{dH}{dy} \right)_2 \text{ -----}(2 \cdot 12)$$

Subtracting 2 · 11 from 2 · 12 and solving for k we get

$$k = c \sigma_s \left[ \frac{\left( \frac{dH}{dy} \right)_2}{\left( H \frac{dH}{dy} \right)_2} - \frac{\left( \frac{dH}{dy} \right)_1}{\left( H \frac{dH}{dy} \right)_1} \right] \text{ -----}(2 \cdot 13)$$

We now make a further assumption, (which is not vital to the argument, but which simplifies the arithmetic), that  $\frac{dH}{dy}$  is proportional to H. This is the same as saying that the field "shape" does not change with magnet current. From Table **IV** it can easily be verified that

this is, in fact, a good assumption. The term in brackets then reduces to  $\frac{1}{H_2 + H_1}$  and

$$k = c \sigma_s \frac{1}{H_2 + H_1} \text{ -----}(2 \cdot 14)$$

Substituting for k in equation 2 · 11

$$c \sigma_s \left( \frac{dH}{dy} \right)_1 = EO + c \sigma_s \frac{1}{H_1 + H_2} \left( H \frac{dH}{dy} \right)_1$$

from which  $EO = c \sigma_s \left( \frac{dH}{dy} \right)_1 \frac{H_2}{H_2 + H_1} \text{ -----}(2 \cdot 15)$

From the geometry of Fig.(2 · 17) it is easy to show that

$$EO = \frac{CX \cdot OY}{OY} - \frac{DY \cdot OX}{OX}$$

and since all quantities on the right hand side are known, EO can be determined, and using equation 2 · 15,  $c \sigma_s$  also.

By computing the ferromagnetic contribution to the force at each magnet current,  $\left(c \sigma_s \frac{dH}{dy}\right)$ , and subtracting it from the measured value of  $f/m$ , the corrected value,  $\left(f/m\right)'$  and the true susceptibility,  $\chi = \frac{\sum \left(f/m\right)'}{\sum \left(H \frac{dH}{dy}\right)}$ , can be determined.

Assuming an accuracy in the force measurement of 1/3 of 1% of the maximum reading, the smallest value of  $c \sigma_s$  that could be detected was about  $.007 \text{ emu/gm}$ . For a typical value of susceptibility this corresponds to a correction of approximately 1%. Hence the corrected values of susceptibility could not be determined to better than 1%. In those cases where  $c \sigma_s$  turned out to be less than  $.007$ , no correction was applied.

#### (iv) Magnetization measurements.

The procedure followed in making magnetization measurements was very similar to that described above. There were, however, some differences such as the use of the pole-tips giving a constant  $\frac{dH}{dy}$ . Because of the large force per unit mass, the specimens were considerably smaller (about 40 mg). To prevent movement of parts of the specimen during an experiment, a different method of attaching the specimen was employed. A coarse powder of the specimen was weighed into a small platinum cup about 2 mm in diameter and 3mm deep, and sealed with a drop of molten wax. By warming the cup gently the wax was made to run down, completely "wetting" the powder. After cooling, the particles were firmly imbedded preventing movement within the cup. The platinum cup was attached to the thin-walled quartz tube on the balance with rubber cement. The force per unit mass was measured at

a number of fixed temperatures for each specimen and, in addition, the region of temperature near the first-order transition was explored "on the run" by varying the temperature slowly and taking readings of force and temperature alternatively.

The main reason for measuring the magnetization in the ferromagnetic region was to establish the variation of effective Bohr magneton number with alloying. This, however, turned out to be impossible because of the difficulty in ascertaining whether all of the specimen had transformed to the low temperature state. It was discovered that the fraction of the specimen which transforms on cooling through the first-order transition depends on the thermal and magnetic history. Because of this difficulty it was possible to measure only the variation of relative magnetization with temperature for a given sample.

Fig. 2 · 18 shows the relative magnetization of a sample of MnAs. It is interesting to note that the first time the specimen was warmed through the transformation under a magnetic field of about 8 kilogauss, the magnetization actually increased with increasing temperature over a small temperature range. Well below the transformation, the magnetization seemed to follow a smooth curve suggesting that the fraction of sample which had transformed was constant. The difference between the three smooth curves in Fig. 2 · 18 is interpreted as being due to different amounts of ferromagnetic material being measured. In fact, by multiplying each curve by the appropriate constant, all points can be made to lie on a single curve.

Guillaud (1951) and Meyer and Taglang (1953) have shown that the

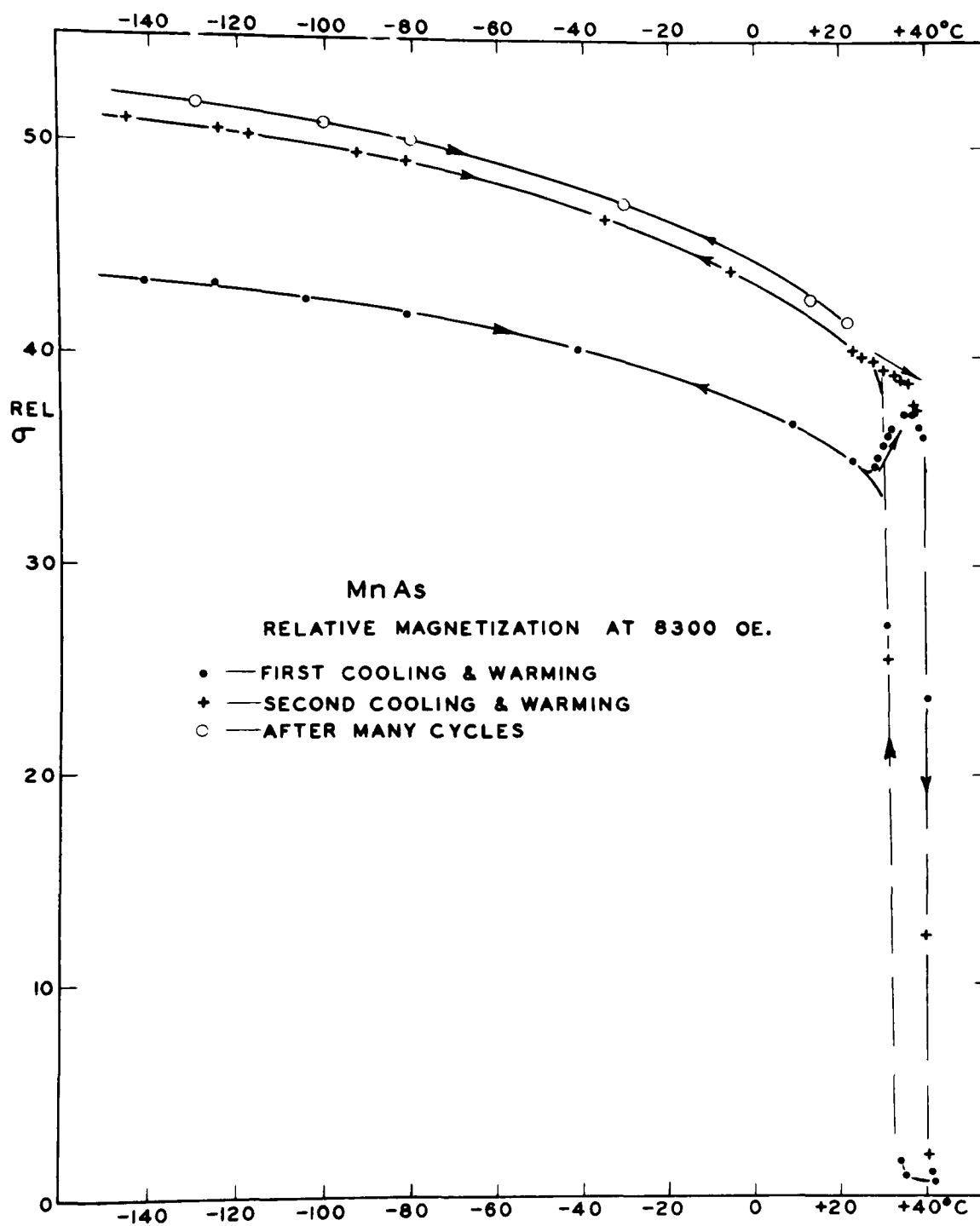


FIG. 2.18 Relative magnetization of MnAs on warming and cooling through the transformation.

temperature at which MnAs transforms can be raised by a strong magnetic field. That is, a magnetic field can keep the specimen ferromagnetic to a higher temperature on warming and cause the specimen to become ferromagnetic at a higher temperature on cooling. At the maximum fields used in these experiments this effect would change the transformation temperature by about  $1.5^{\circ}$  C.

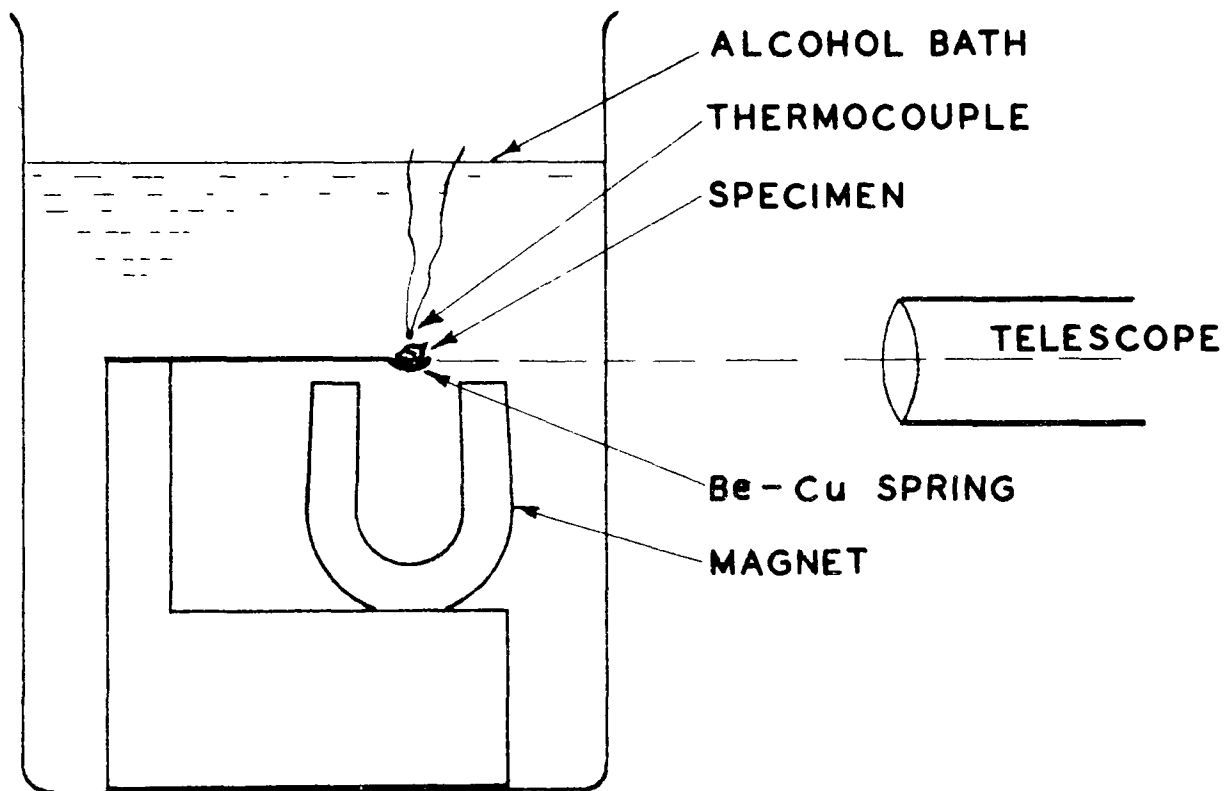
(v) Note on homogeneity of the alloys.

To determine the approximate transformation temperature quickly without mounting the sample in the balance, the simple apparatus in Fig. 2 . 19 was constructed. A small portion (about 50 mg.) of the specimen was supported on a flexible beryllium-copper strip above a small permanent magnet. The whole apparatus was immersed in a beaker of alcohol. The temperature of the bath, which was measured with a thermocouple a few millimetres from the sample, could be raised with an electric heater or lowered by the addition of liquid nitrogen. By observing the deflection of the strip with a travelling telescope the onset and departure of ferromagnetism was easily detected. Since the addition of impurities lowers the transformation temperature (see next chapter), this proved to be valuable in testing the homogeneity of the alloys. Samples were taken from different parts of several alloys and measured in this way. The results tabulated in Table V indicate that the homogeneity was generally good. This is taken as added justification for using the nominal alloy compositions.

3. X-ray Diffraction Measurements.

A. Theory.

A crystal consists of a three-dimensional array of atoms whose



**FIG 2.19**

Apparatus for checking homogeneity of alloys.

TABLE V

| Specimen                  | 1    | 2    | 3    | $T_c / \frac{*}{\% \text{ solute}}$ |
|---------------------------|------|------|------|-------------------------------------|
| MnAs upper $T_c$          | 42   | 40.5 |      |                                     |
| lower $T_c$               | 35   | 34.5 |      |                                     |
| $\frac{1}{2}\% \text{Co}$ | 35   | 34.8 | 35   | $14^\circ / \% \text{ solute}$      |
|                           | 26.8 | 25.7 | 25.8 |                                     |
| 1%Co                      | 31.6 | 31.2 | 30.5 | $14^\circ / \% \text{ solute}$      |
|                           | 21.2 | 22   | 19   |                                     |
| $\frac{1}{2}\% \text{Fe}$ | 32   | 32   | 32.5 | $35^\circ / \% \text{ solute}$      |
|                           | 13.5 | 14   | 14.5 |                                     |
| $\frac{1}{2}\% \text{Cr}$ | 42   | 42   | 42   | $6^\circ / \% \text{ solute}$       |
|                           | 32.5 | 32   | 31   |                                     |
| 1%Cr                      | 39.5 | 41.5 |      | $6^\circ / \% \text{ solute}$       |
|                           | 28   | 29   |      |                                     |

\*  $\frac{T_c}{\% \text{ solute}}$  is the approximate rate of change of the lower

transformation temperature with alloyings.

Columns 1, 2 and 3 represent small portions taken from different parts of the same specimen.

positions are periodic in space. Consider three vectors  $\vec{a}$ ,  $\vec{b}$ , and  $\vec{c}$ . From some point with co-ordinates ( x, y, z) in the crystal, let us perform the translation operation which brings us to the point (x + p  $\vec{a}$ , y + q  $\vec{b}$ , z + r  $\vec{c}$ ), where p, q, and r, are integers. If the surroundings of the new point are identical to the surroundings of ( x, y, z), we say that the vectors  $\vec{a}$ ,  $\vec{b}$ ,  $\vec{c}$ , define a unit cell of the crystal. If  $\vec{a}$ ,  $\vec{b}$  and  $\vec{c}$  enclose the smallest volume that will satisfy these conditions, they are said to define the primitive unit cell. Sometimes it is convenient to choose a unit cell which is not the primitive one, if it shows the symmetry of the crystal better. The three vectors  $\vec{a}$ ,  $\vec{b}$ , and  $\vec{c}$ , are called the unit cell edges, the axial lengths, the lattice parameters or the primitive translations. (Hereafter they will be denoted by  $\underline{a}$ ,  $\underline{b}$  and  $\underline{c}$  ). The whole array of points obtained by performing the above operation is called the space lattice. For any crystal structure, if  $\underline{a}$ ,  $\underline{b}$  and  $\underline{c}$  are known, and if the positions of the atoms within the unit cell are known, the structure is determined. The lattice spacings can be determined by measuring the angles at which X-rays are reflected from powder specimens. To find the positions of the atoms within the unit cell is much more difficult and, except in simple cases, requires single-crystal measurements.

#### (i) Miller indices.

Any set of equidistant parallel planes drawn through the crystal in such a way that they pass through all points of the space lattice, is called a set of "lattice planes". Each set of such planes is described by its Miller indices. Since all points of the space lattice lie on any particular set of lattice planes and since the planes are

parallel and equidistant, they must divide each unit cell edge into an integral number of equal parts. If  $\underline{a}$  is divided into  $h$  parts of length  $\underline{a}/h$ ,  $\underline{b}$  into  $k$  parts of length  $\underline{b}/k$  and  $\underline{c}$  into parts of length  $\underline{c}/\ell$ , the Miller indices are  $(h, k, \ell)$ . It is customary to write the Miller indices of a plane in parentheses, for example  $(1, 1, 0)$ . The X-ray reflections from this set of planes will be referred to simply as the  $110$  or  $220$  (second-order) reflections.

#### (ii) Diffraction of X-rays by a crystal.

The diffraction of X-rays by a crystal lattice is governed by the Laue equations. When working with powder pictures it is simpler and more descriptive to use the Bragg equation,  $2d \sin \theta = n\lambda$  where,  $d$  is the interplanar spacing,

$\theta$  is the angle between the incident beam and the planes,

$n$  is an integer,

$\lambda$  is the wave length of the radiation.

The spacing,  $d$ , is determined by the unit cell edges  $\underline{a}$ ,  $\underline{b}$  and  $\underline{c}$  and the indices  $h$ ,  $k$ , and  $\ell$ . If the crystal contains one atom per unit cell, reflections corresponding to all combinations of  $h$ ,  $k$ , and  $\ell$  are possible. If there is more than one atom per unit cell, the contribution of scatter from each atom must be added vectorially to obtain the total scatter. Usually some combinations of  $h$ ,  $k$  and  $\ell$  lead to total cancellation of the X-ray reflection. The presence or absence of particular reflections for the NiAs structure is tabulated in Appendix I, with the structure factor.

### (iii) Debye-Scherrer powder pictures.

A Debye-Scherrer powder picture is obtained by placing a powder specimen in the shape of a thin rod at the center of a cylindrical film. The specimen is exposed to a narrow beam of nearly monochromatic X-rays, (e.g. copper characteristic radiation). If the sample is stationary, reflections occur only from crystallites which happen to be so oriented that they satisfy the Bragg conditions of angle and wave-length, so that the resulting film shows a number of spots. By rotating the specimen about its axis normal to the beam, many particles are permitted to contribute to the diffraction pattern, producing smooth lines on the film. Lines occur wherever a cone of diffracted radiation of half-angle  $2\theta$  intercepts the cylindrical surface of the film. (See Fig. 2 · 20). A typical diffraction pattern obtained for pure aluminum is shown in Fig. 2 · 21.

### B. Description of X-ray diffraction apparatus.

In the diffraction experiments, X-radiation was obtained from a Phillips X-ray diffraction unit with a copper target. The Cu-radiation was filtered through approximately .02 mm of nickel to absorb the Cu  $K\beta$ -radiation so that the transmitted beam was composed almost entirely of Cu  $K\alpha_1$  ( $1.54050 \text{ \AA}$ ) and Cu  $K\alpha_2$  ( $1.54433 \text{ \AA}$ ).

In the Bradley-type 19 cm diameter "Unicam" camera used, the film is placed in the camera in two parts as shown in Fig. 2 · 20. Sharp knife edges at the high ( $\approx 85^\circ$ ) and low angle ( $\approx 5^\circ$ ) limits, served as reference marks for the accurate determination of reflection angles. The specimen was mounted on a nylon support which

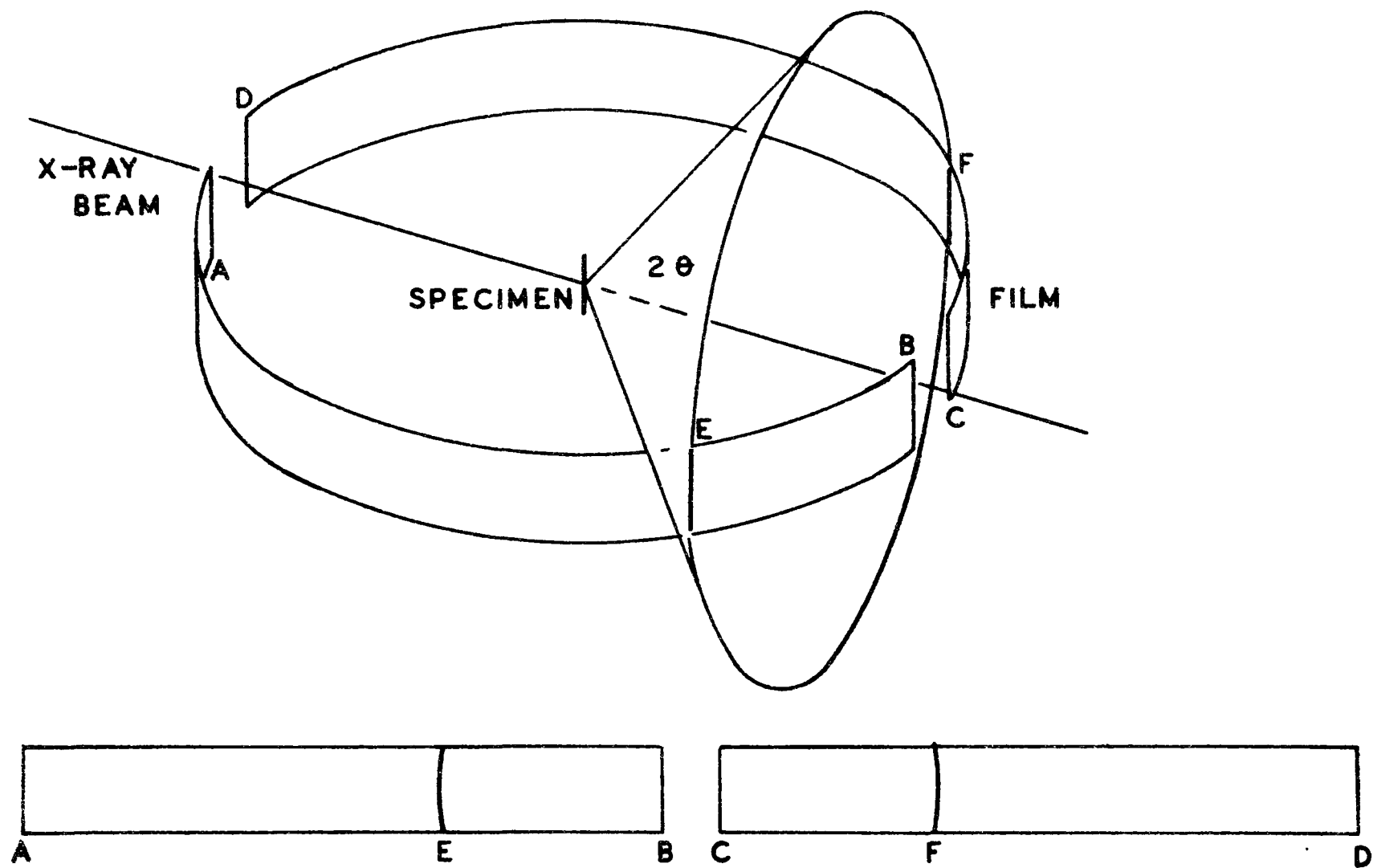


FIG 2.20

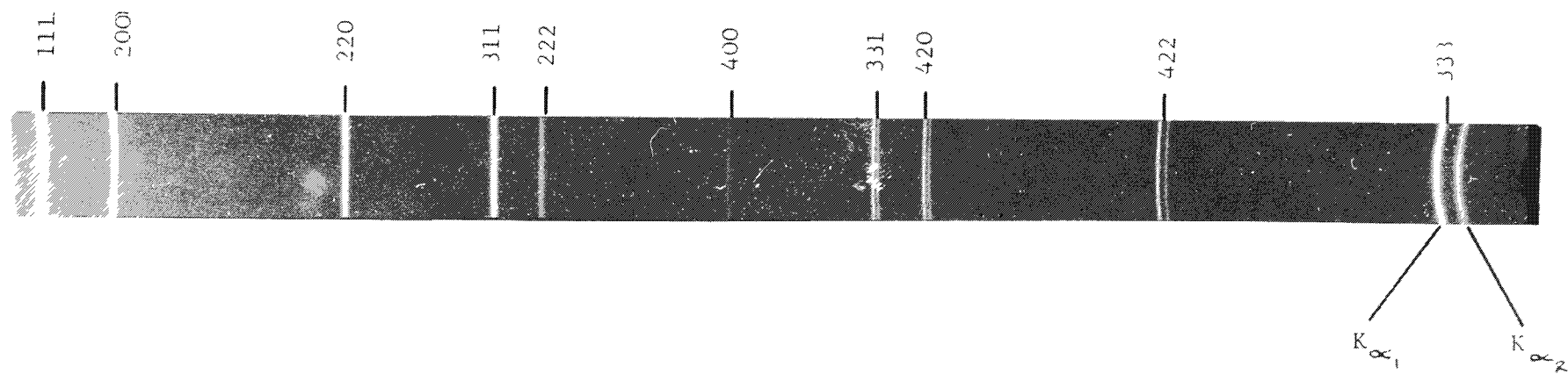


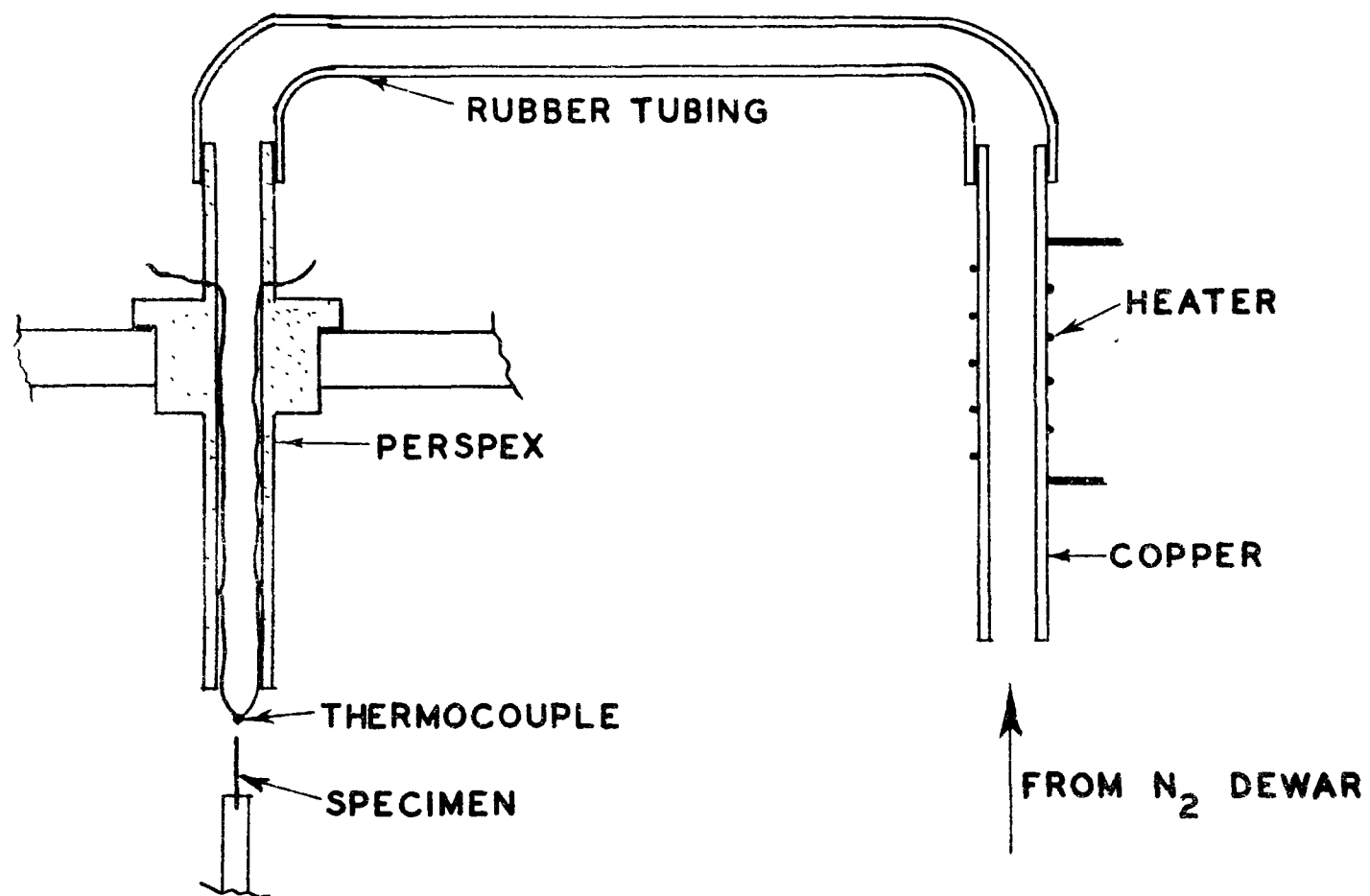
FIG. 2.21 Diffraction pattern for aluminum at 20°C.

could be centered on a rotating platform by two adjusting screws. The axis of rotation of the platform was very nearly the axis of the cylindrical film.

#### C. Control and measurement of temperature.

The specimen temperature was controlled by blowing over it a cold (or warm) nitrogen gas stream, obtained by boiling liquid nitrogen from a dewar as shown in Fig. 2 · 22. For temperatures above room temperature a wire-wound heater was incorporated into the nitrogen line; thus temperatures from  $-120^{\circ}\text{C}$  to  $+80^{\circ}\text{C}$  could be obtained. A copper-constantan thermocouple, positioned just above the specimen at the opening of the tube, recorded, the temperature. However, early results indicated that temperatures measured in this way were unreliable, and in subsequent experiments the temperature of the specimens was determined with pure aluminum powder as an internal standard. The lattice spacings of aluminum as determined from the films were converted to temperatures using data of Nix and McNair (1941). To prevent interference by condensation of water vapor, the whole camera was enclosed in a large copper can. The steady release of dry nitrogen in the can satisfactorily excluded the moist room air.

Some difficulty was experienced in obtaining the best mixture of aluminum and sample powders to get both sets of diffraction lines with reasonable intensity. On damp days the aluminum tended to cling to the sides of the 0.3 mm Lindeman glass capillary into which it was loaded resulting in a concentration gradient from top to bottom. The suitability of any given mixture had to be tested by a trial X-ray exposure and the procedure repeated until a satisfactory mixture was



**FIG 2.22**

Apparatus to control temperature of diffraction specimens.

obtained.

#### D. Procedure.

The specimen was first centered on the rotating platform of the camera; then after the desired temperature was reached the X-ray exposure was started. Temperature was controlled manually during the exposure. Generally, 1 hour at 45 Kv, 15 ma with a Cu target was sufficient to obtain a good X-ray film. After developing, the films were dried for at least 24 hours before measurement, in order to stabilize the film-shrinkage.

#### E. Measurement of film and determination of $\theta$ .

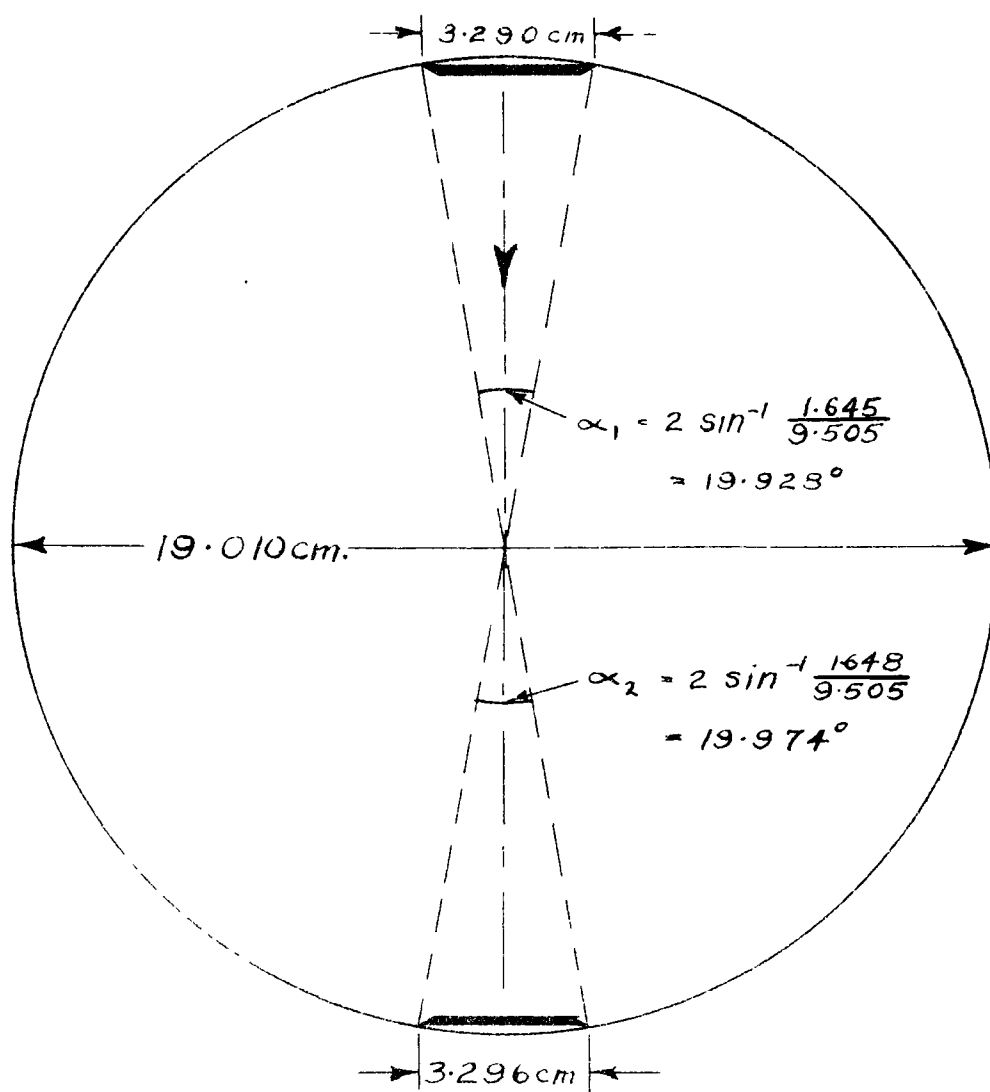
The angular positions of the knife edges were determined by direct measurement of the camera diameter and the linear distances between the knife edges, with the results shown in Fig. 2 · 23. The total Bragg angle included between the high angle edges is  $85.018^\circ$ ; between the low angle edges  $4.994^\circ$ .

The positions of diffraction lines and of the knife edges on the film were measured with a Cambridge Universal Measuring Instrument. By arranging the films as shown in Fig. 2 · 24 the computations were simplified. Thus the total film length  $S_k$  corresponding to the Bragg angle  $\theta_k = 85.018^\circ$  is given by

$$\begin{aligned} S_k &= b - a + d - c + l'_L \\ &= (d - a) + (b - c + l'_L), \end{aligned}$$

where  $l'_L$  is the effective length of film between the low angle knife edges. The film length  $S_\theta$  corresponding to an angle of reflection  $\theta$  is given by

$$\begin{aligned} S_\theta &= b - e + f - c + l'_L \\ &= (f - e) + (b - c + l'_L) \end{aligned}$$

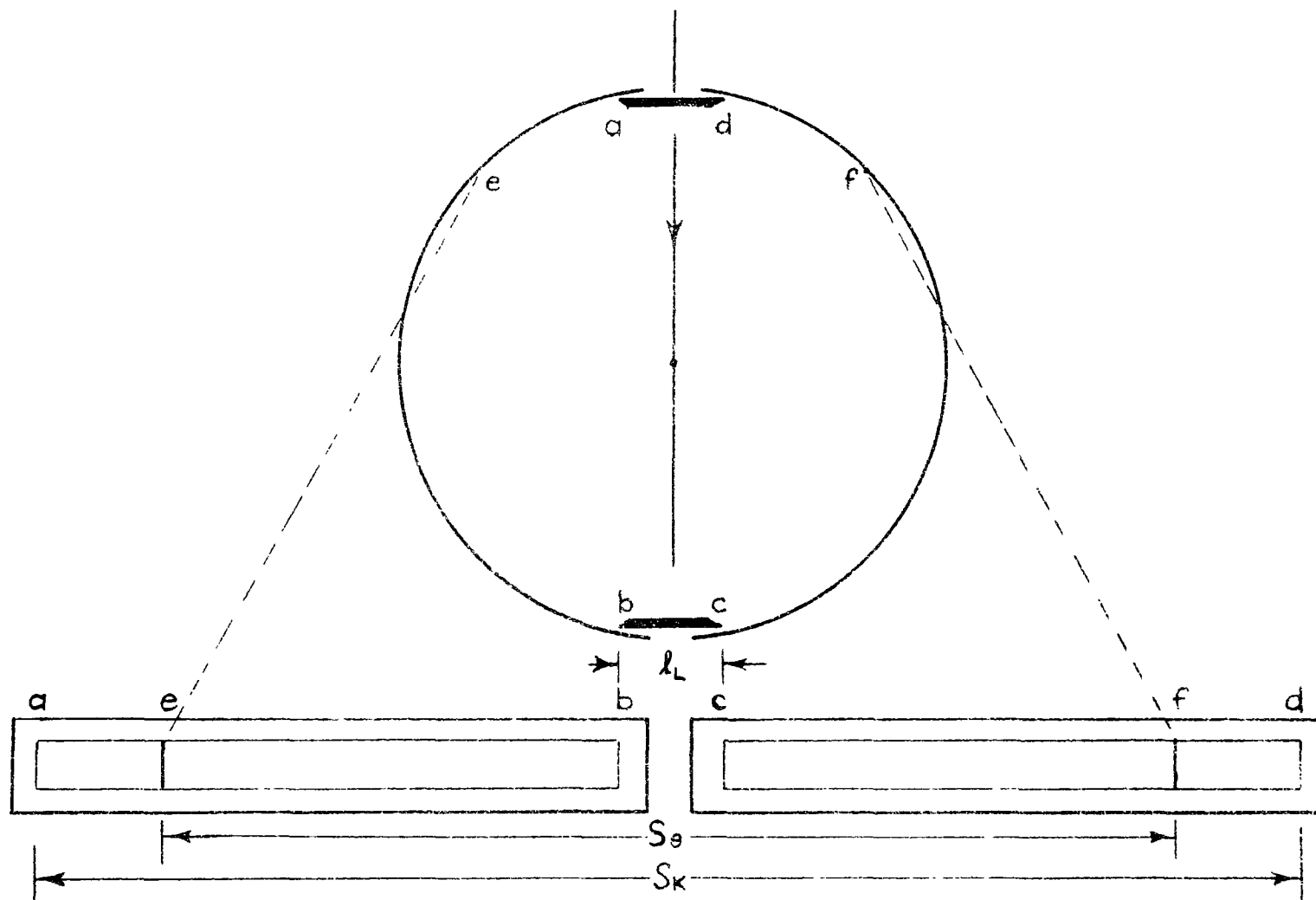


$$\text{LOW BRAGG ANGLE LIMIT} = \frac{1}{4} (19.974) = 4.994^\circ$$

$$\begin{aligned} \text{HIGH BRAGG ANGLE LIMIT} &= \frac{1}{4} (360^\circ - 19.928^\circ) \\ &= 85.018^\circ \end{aligned}$$

**FIG 2.23**

Constants of the X-ray camera.



**FIG 2.24**

Placement of film for measurement of line positions.

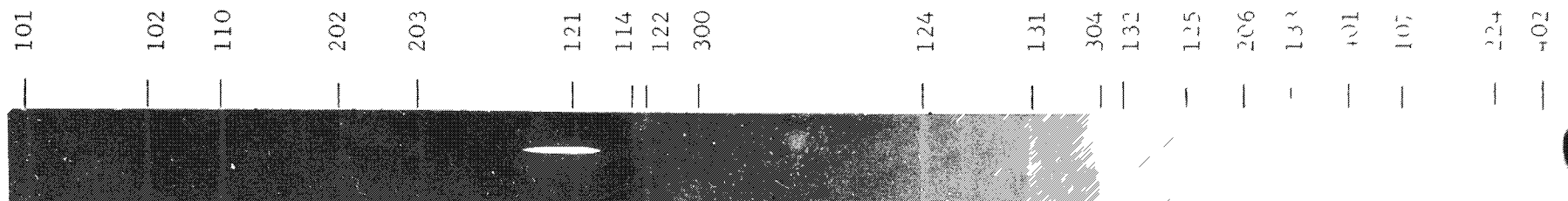


FIG. 2 25 Diffraction pattern for MnAs at 20°C.

If we assume linear film shrinkage, the angle  $\theta$  is given by

$$\theta = \theta_k \frac{s_{\theta}}{s_k} = 85.018 \frac{(f - e) + (b - c + \ell'_k)}{(d - a) + (b - c + \ell'_k)}$$

Since the nature of this relationship indicates that the lattice parameters, determined essentially by the high angle lines, depend very little on  $\ell'_k$ , the uncorrected value,  $\ell_k$ , taken directly from the camera can be used. The position of each line was measured three times and the average taken. Typical values of agreement were  $\pm .03$  mm from the mean.

#### F. Identification of reflections.

Once the Bragg angle,  $\theta$ , and the corresponding interplanar spacing,  $d$ , have been computed, the next step is to assign the appropriate Miller indices ( $h$ ,  $k$  and  $\ell$ ) to each reflection. For a crystal with cubic symmetry, ( $a = d \sqrt{h^2 + k^2 + \ell^2}$ ), identification is easily made. If the crystal structure is known to be of a lower symmetry (tetragonal or hexagonal) lines may often be identified using a Hull-Davey chart. In the low temperature region all specimens studied were found to have the hexagonal NiAs structure (as reported by Willis and Rooksby, 1954), and the Hull-Davey chart proved adequate. Fig. 2 · 25 shows a typical diffraction pattern for MnAs with the reflections labelled.

#### G. Precise determination of lattice parameters.

A number of effects can lead to a systematic error in the position of a line on the film. The more important ones are listed here:

1. Film shrinkage.
2. Refractive index of the specimen.

3. Eccentricity of the specimen in the camera.
4. X-ray absorption in the specimen.
5. Distribution of X-ray intensity across the focal spot of the X-ray tube.

The effect of uniform film shrinkage can be eliminated completely by using a camera equipped with calibrated knife edges, such as that described previously. Non-uniform shrinkage is difficult to correct for except by the use of an internal standard.

The refractive index of the specimen for X-rays leads to a small error in the lattice parameter. When the lattice parameters are extrapolated to  $\theta = 90^\circ$  (as described below) the only correction necessary is that due to the difference in wave-length of X-rays in air and in the crystal. For copper  $K_{\alpha}$ - radiation and an aluminum specimen the correction is less than 1 part in 100,000. Since the deviation of the refractive index from unity is approximately proportional to the density of the specimen, the correction for MnAs has been estimated to be 1 in 60,000 and, as is usual, it has been ignored.

Absorption within the specimen displaces the effective center of reflected rays toward the incident beam. This, together with the eccentricity and the variation of the intensity in the focal spot produces an error which approaches zero as the Bragg angle,  $\theta$ , approaches  $90^\circ$ . Analytical methods to eliminate this effect in both Cubic and non-cubic crystals have been derived by Cohen (1935,1936) and by Taylor and Floyd (1950). However, we found it quite satisfactory to extrapolate graphically the apparent lattice parameters against the function  $f(\theta) = \frac{1}{2} \left[ \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right]$  which was found, em-

pirically by Nelson and Riley (1945), and theoretically by Taylor and Sinclair (1945), to give the best linearity. For the reflections from face-centered cubic aluminum, (which was added to each X-ray specimen as an internal thermometer), the extrapolation was straightforward since

$$\underline{a} = d \sqrt{h^2 + k^2 + l^2}$$

and hence  $\underline{a}$  is uniquely related to  $d$ . Using the four highest angle lines (333, 422, 420 and 311) a reasonably accurate determination of  $\underline{a}$  could be made.

The case of the hexagonal structure is complicated by the fact that  $\underline{a}$  and  $\underline{c}$  may vary independently. For a given reflection the relationship between  $\underline{a}$ ,  $\underline{c}$  and  $d$  is given by

$$\underline{a} = d \sqrt{\frac{4}{3} (h^2 + hk + k^2) + \frac{l^2}{(\underline{c}/\underline{a})^2}}$$

The value of  $\underline{c}/\underline{a}$  giving the best extrapolation was selected by trial and error. When using this method it is desirable to have high angle reflections both of the type  $h k 0$ , (dependent only on the  $\underline{a}$ -parameter), and of the type  $00l$ , (dependent only on  $\underline{c}$ ). In practice one is seldom so fortunate and use must be made of the high angle reflections available, weighting each according to its intensity and sharpness. The most useful reflections in determining the parameters of the hexagonal structure were, in order of descending Bragg angle, 402, 224, 401, 133, 206, 125, 132 and 304. The  $\underline{a}$ -parameter was determined primarily by the 402 and 401 lines while  $\underline{c}$  was determined primarily by the 224, 206 and 125 reflections.

#### H. Estimation of error.

Under favourable conditions the position of a line on the film could be measured to about  $\pm .03$  mm. In a 19 cm camera, at a Bragg

angle of  $80^\circ$ , this corresponds to a lattice-spacing error of about 1 in 35,000. Making allowance for uncertainty introduced by the extrapolation procedure, the values reported for the a-parameters are probably valid to 1 part in 20,000. The c-parameters, since they were determined by lines occurring at lower angles, are probably good to only 1 part in 10,000.

For each film, the specimen temperature was estimated from the lattice spacing obtained for the aluminum additive, using thermal expansion data due to Nix and McNair (1941). Temperatures measured in this way are probably accurate to  $\pm 2^\circ\text{C}$ , corresponding to an error of 1 in 20,000, for the a-parameter of aluminum.

Less favourable conditions existed when overlap of lines occurred on the film. Since a  $K_{\alpha_1}$ - and a  $K_{\alpha_2}$ - line were present for each aluminum and each MnAs reflection, the probability of an overlap was appreciable. When this happened it was sometimes necessary to discard important high angle lines resulting in reduced accuracy in the determination of the lattice constants.

1. Introduction.

Before presentation of the experimental results it would seem appropriate to review the information available about MnAs when the problem was undertaken and to indicate clearly the areas in which further investigations were carried out. Table VI summarizes the structural and magnetic properties of MnAs in the three temperature regions and the changes that take place at each of the transformations.

The measurements that were made and the reasons for making them are set out below:

(a)     MnAs

(i) The lattice parameters were measured by Willis and Rooksby down to only 20°C, at which temperature the co-efficient of thermal expansion (in the a-direction) is still large and negative. To explore this unusual situation, the measurements were extended down liquid nitrogen temperature for samples taken from two separate melts.

(ii) The magnetic susceptibility of MnAs, on cooling, undergoes a sharp change in slope at about 120°C and begins to decrease, a behavior characteristic of antiferromagnetism. In fact, MnAs in the intermediate region was reported as antiferromagnetic by Guillaud (1951) and others. Neutron diffraction work by Bacon and Street (1953), however, showed no evidence of antiferromagnetism. Furthermore, there was the difficulty, but not impossibility, (see page 21), of reconciling a large positive Curie temperature ( $\Theta = 290^\circ\text{K}$ ) with antiferromagnetism. There was also the possibility that the strange magnetic behavior was due to a non-equilibrium effect,

TABLE VI

|                                                                                                                                                                                                     | STRUCTURAL PROPERTIES                                                                                                              | MAGNETIC PROPERTIES                                                                        |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|
| Low Temperature region (below 30°C)                                                                                                                                                                 | Hexagonal NiAs structure (a)                                                                                                       | Ferromagnetic, $f_{\text{eff}} = 3.4$ (b)<br>3.34 (e)                                      |
| First-order transition (30° - 40°)                                                                                                                                                                  | Discontinuous decrease in volume of 2% on warming.<br>Thermal hysteresis, (a)<br>Diffusionless, non-martensitic transformation (c) | Loss of ferromagnetism on warming. (b)                                                     |
| Intermediate temperature region (40° - 125°C).                                                                                                                                                      | Reported NiAs (a)                                                                                                                  | Reported antiferromagnetic (b)<br>Neutron diffraction negative for antiferromagnetism. (d) |
| Second-order transition (125°C)                                                                                                                                                                     | Change in slope of $\underline{a}$ vs. T<br>and $\underline{c}$ vs. T                                                              | Marked change in slope of<br>vs. T (e)                                                     |
| High temperature region (Above 125°C)                                                                                                                                                               | Hexagonal NiAs structure (a)                                                                                                       | Paramagnetic obeying Curie-Weiss Law. (e)                                                  |
| <div> <div>(a) Willis and Rooksby (1954)</div> <div>(b) Guillaud (1951)</div> <div>(c) Basinski and Pearson (1958)</div> <div>(d) Bacon and Street (1955)</div> <div>(e) Present Work.</div> </div> |                                                                                                                                    |                                                                                            |

which might disappear by diffusion at higher temperatures. For these reasons it was decided to measure carefully the susceptibility of MnAs between 40°C and 375°C both on warming and cooling.

(iii) Attempts to measure the lattice spacings in the intermediate region produced results suggesting that the structure was probably not hexagonal. This led to measurements with a high-temperature camera and to investigations of some reflections with a Geiger-counter type diffractometer.

(b) Ternary Alloys.

Ternary alloys of the type  $(\text{Mn}_{1-x}, \text{M}_x)\text{As}$  were studied, where **M** represents one of the transition metals, V, Cr, Fe, Co or Ni. MnAs, 1% Fe refers to the alloy  $(\text{Mn}_{.99} \text{Fe}_{.01})\text{As}$ . The effects of alloying on the properties of MnAs were investigated through the following measurements:

(i) Lattice parameters in the low-temperature region.

(ii) Approximate lattice parameters in the intermediate region.

(iii) Magnetic susceptibility from just above the first-order transformation to about 375°C from which  $\mu_{\text{eff}}$  and the Curie temperature,  $\theta$ , were determined.

(iv) Relative magnetization in the low temperature region including the first-order transformation.

It was expected that these experiments would yield information about the electronic structure and chemical bonding of the manganese atoms, about the exchange interactions which are responsible for the magnetic properties and about the nature of the first and

second order transformations themselves.

## 2. Lattice Spacings of MnAs.

The lattice parameters measured for the two samples of MnAs are compared with the results of Willis and Rooksby in Fig. 3 . 1, showing good agreement between 20° and 40°C. The extended measurements down to liquid nitrogen temperature show the disappearance of the negative thermal expansion of the a-parameter with the suggestion of normal behavior at lower temperatures.

The points in the intermediate region were derived on the basis of a hexagonal approximation to the true unit cell described later (See Section 4). The change in unit cell volume at the first order transformation is found to be approximately 2.7% compared with a value of 1.8% from the data of Willis and Rooksby.

## 3. Magnetic susceptibility of MnAs.

The results of susceptibility measurements on MnAs are presented in Fig. 3 . 2 in the form of the usual plot of against T. The straight line behavior above 121°C is well described by a Curie-Weiss law,  $\chi = \frac{C}{T - \theta}$ , with  $\theta = 290^\circ\text{K}$  and with C corresponding to a value of  $p_{\text{eff}} = 4.59$ . Assuming complete quenching of the orbital moment, slightly less than 4 unpaired electrons per manganese atom are indicated. At 121°C there is a sharp change of slope, reminiscent of the Neel point in an antiferromagnetic followed by a steady increase in  $\frac{1}{\chi}$  on cooling, right down to the temperature of the first-order transformation. The data on warming and cooling agree extremely well, indicating that the magnetic behavior is a real equilibrium effect.

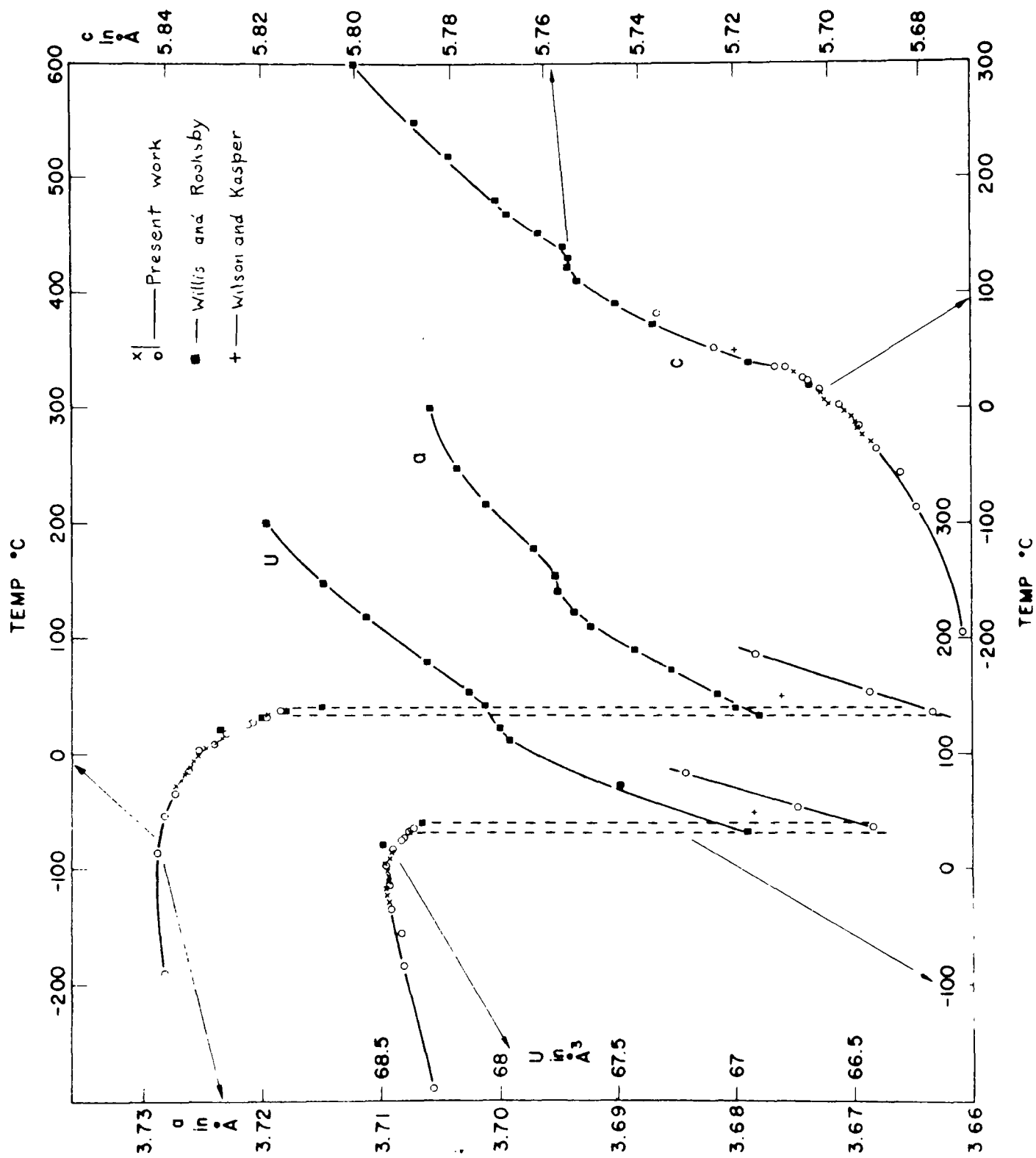


FIG. 3.1 Summary of lattice spacing data on MnAs.

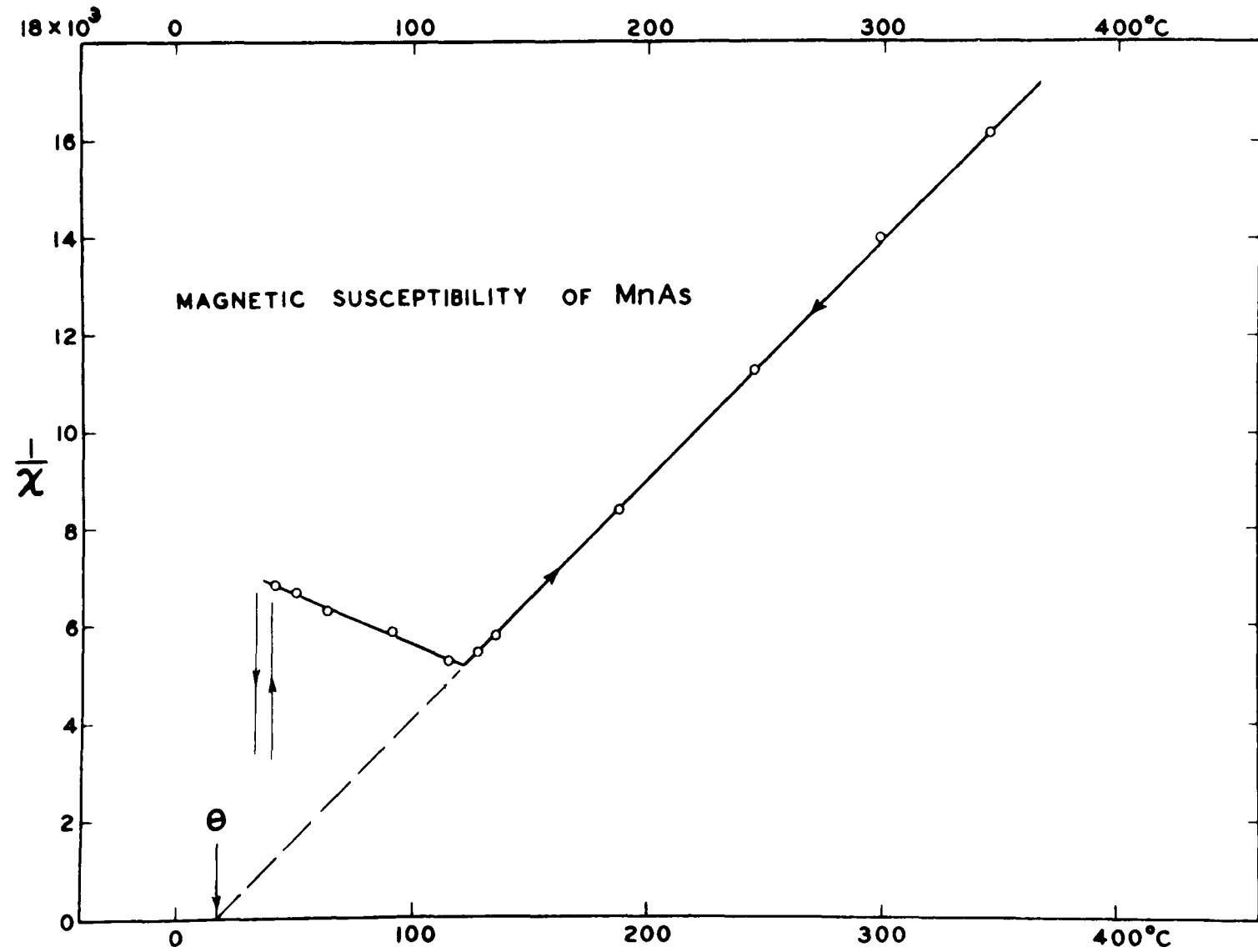
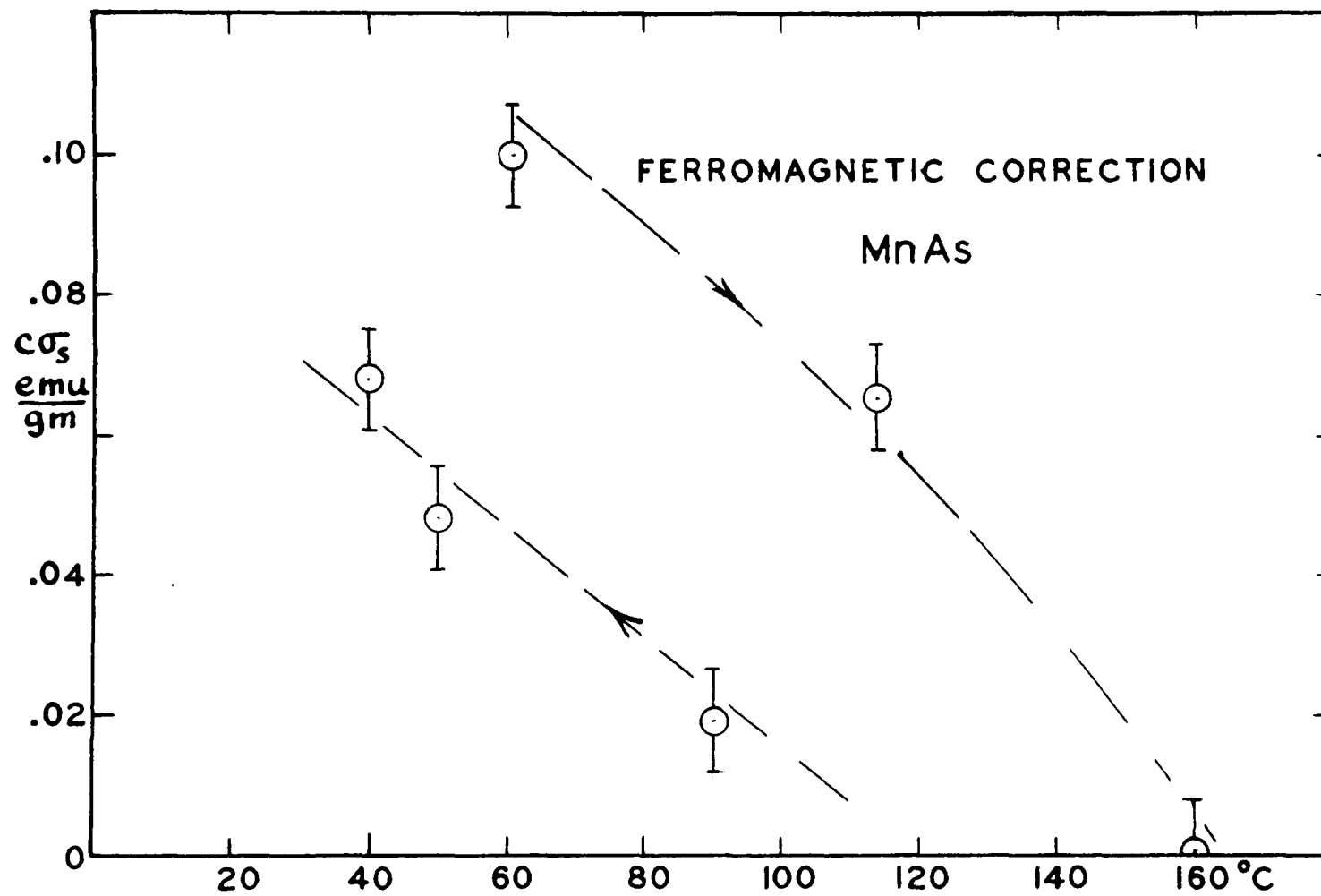


FIG. 3.2 Inverse magnetic susceptibility of MnAs against temperature.

It is interesting to note that the necessary ferromagnetic corrections, (see Fig.3 · 3) were greatest just above the first-order transformation, and decreased with increasing temperature. Furthermore, after warming to 375°C and cooling, the correction at a given temperature was significantly reduced. This suggests that the ferromagnetic component is due not to free iron, cobalt or nickel or to some compound different from MnAs, but to small amounts of the specimen which transform at a higher temperature than the bulk of the specimen. The reasons for such behavior are not understood, but it is believed that very small crystallites, for which surface effects become important, may be involved.

#### 4. The Structure of MnAs in the Intermediate Region:

Attempts to determine lattice constants in the intermediate temperature region on the basis of a hexagonal cell met with poor success. The most noticeable characteristics of the diffraction patterns was a consistently "poor quality". The lines were fuzzy and poorly resolved, making measurement of their positions, and even identification extremely difficult. Closer inspection of the best-resolved films gave the impression that reflections of the type  $h, k, \ell$  were split into three, while those of the type  $h, 0, \ell$  seemed to be made up of two lines, one stronger than the other. It was very difficult to be sure because of the presence of the  $K\alpha$ -doublet which almost always caused some overlap of lines. Nevertheless, the presence of line splitting suggested a deviation of the symmetry from hexagonal. It seemed plausible that the structural distortion was closely related to the unusual magnetic properties.



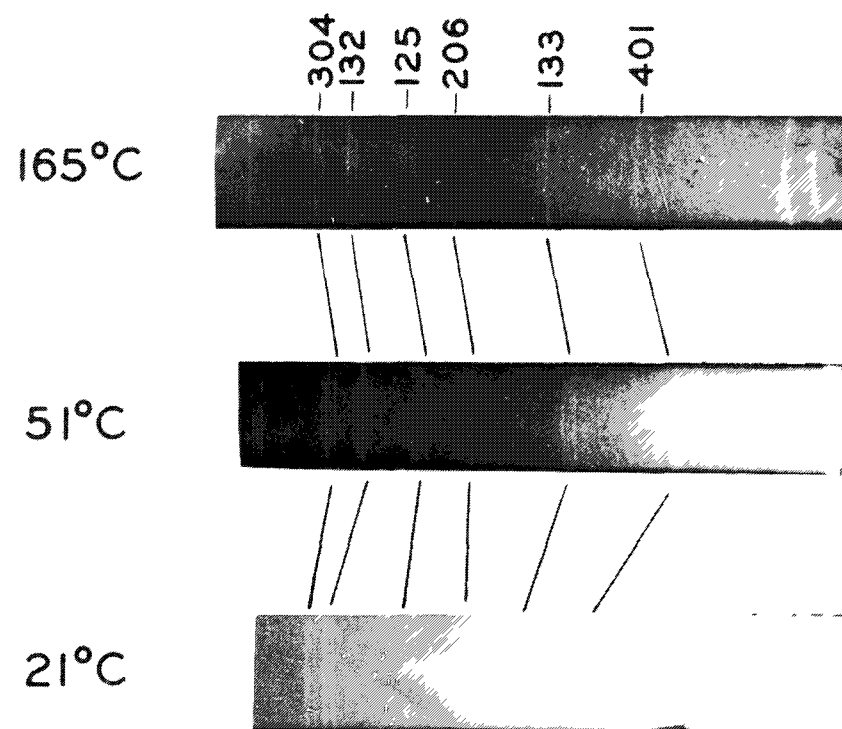
**FIG 3.3**

Ferromagnetic corrections in MnAs on warming and cooling.

A possible explanation of both the structural and the magnetic properties presented itself in the helical spin structure predicted by Yoshimori (1959), (see also Chapter I, page 21) which has been shown to exist in  $\text{MnF}_2$ , Ho and some other substances. In the presence of such a magnetic structure it is possible for a large positive Curie temperature to co-exist with antiferromagnetism. Also, it is possible that this type of spin arrangement might escape detection by neutron diffraction if only simpler magnetic structures were being looked for.

A lattice, on ordering in a helical spin arrangement, would be expected to undergo an expansion or a contraction between planes of aligned spins. If this situation were true for MnAs, the distortion should be absent in the low-temperature ferromagnetic region, (all spins aligned), present in the intermediate region, and should disappear again in the paramagnetic region above  $125^\circ\text{C}$ .

To test this possibility, X-ray powder pictures were taken with a high-temperature camera, incorporating an arrangement of thermocouples and heaters which made it unnecessary to dilute the specimen with aluminum powder. In this way the relative intensity of the diffraction lines above background was greatly improved. Well-resolved diffraction patterns were obtained in the low temperature ( $+21^\circ\text{C}$ ), the intermediate temperature ( $+51^\circ\text{C}$ ) and the high temperature ( $+165^\circ\text{C}$ ) regions. These films, shown in Fig.3 - 4, display strikingly the change from the hexagonal to the distorted structure and back to the hexagonal again as the temperature is increased.



**FIG 3.4**

Diffraction patterns for MnAs in the low, intermediate and high temperature regions.

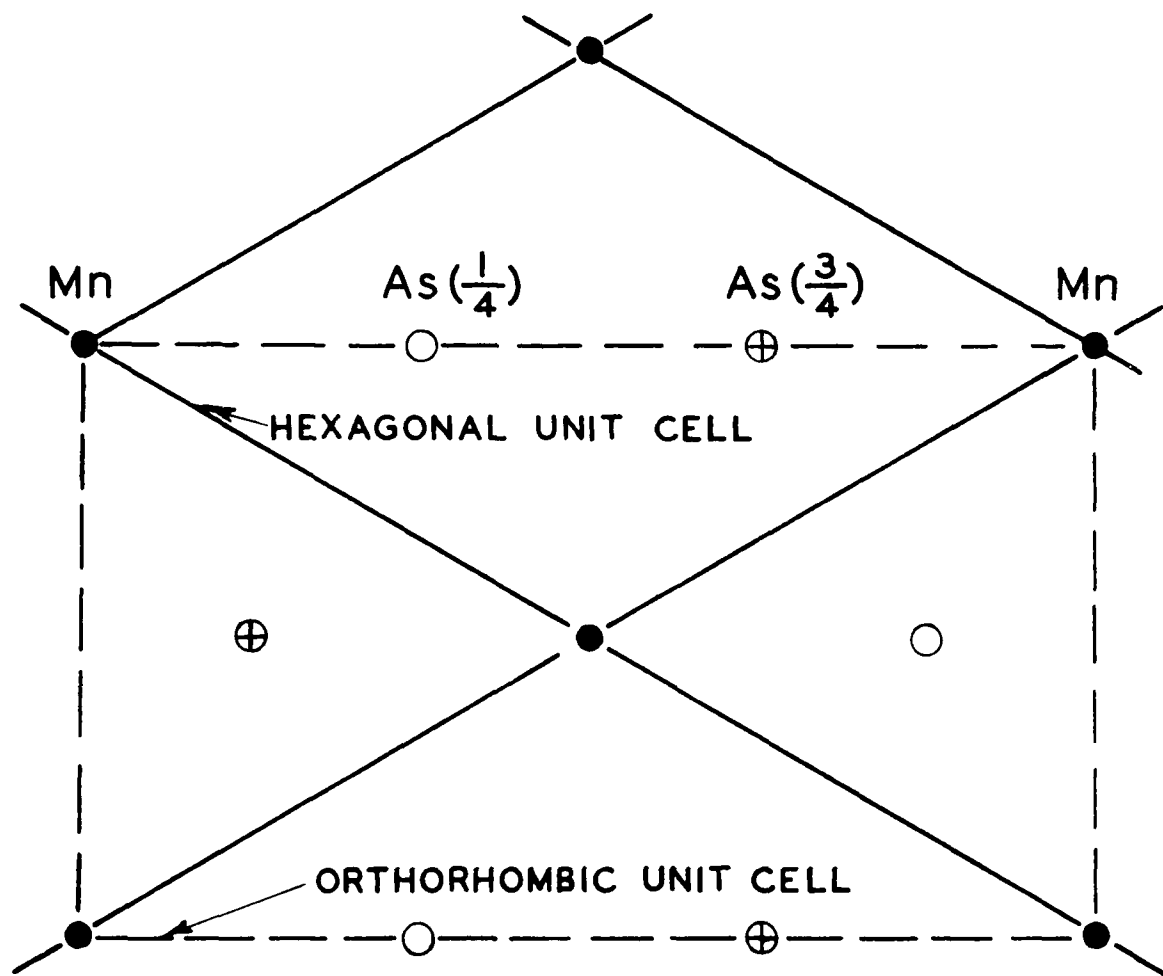
An attempt was made to account for the splitting of the lines by assuming that the lattice was distorted by an expansion or a contraction between (100) planes. Any hexagonal lattice can also be described by a larger orthorhombic cell, as shown in Fig.3 · 5. The axes of the orthorhombic cell were chosen in such a way as to give the following relationship between the two unit cells:

| (orthorhombic)   |   | (hexagonal)              |         |
|------------------|---|--------------------------|---------|
| $\underline{a'}$ | = | $\underline{c}$          |         |
| $\underline{b'}$ | = | $\underline{a}$          |         |
| $\underline{c'}$ | = | $\underline{a} \sqrt{3}$ |         |
| $\underline{h'}$ | = | $\underline{l}$          | (3 · 1) |
| $\underline{k'}$ | = | $\underline{h}$          |         |
| $\underline{l'}$ | = | $2k + h$                 |         |

When there is no distortion from hexagonal,  $\frac{c'}{b'} = \sqrt{3}$ , as expected. The distortion is introduced by letting  $\frac{c'}{b'} = y\sqrt{3}$ , where  $y$  is a number slightly different from 1.

In the basal plane of a hexagonal structure there are three equivalent but not independent axes with associated Miller indices  $h$ ,  $k$ , and  $i$ , where  $i = -(k + h)$ . To obtain all equivalent indices for any given hexagonal reflection it is necessary to take for  $h$  and  $k$ , all possible pairs of  $h$ ,  $k$ , and  $i$ . The corresponding orthorhombic indices can be obtained from equations 3 · 1.

Three distinct types of splitting can take place. An example of each is shown in Table VII, which gives the hexagonal indices,



**FIG 3.5**

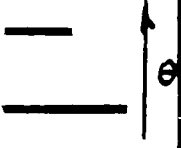
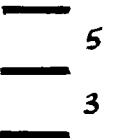
Relationship between the hexagonal and orthorhombic cell in MnAs.

the orthorhombic indices, the relative splitting,  $\frac{\Delta d}{d}$ , for the particular case of  $y = 1.002$ , and the expected splitting pattern.

The angular splitting on the film  $\Delta\theta$ , is given by

$$\Delta\theta = - \frac{\Delta d}{d} \tan \theta .$$

Table VII

| Case                                   | Hexagonal Indices                                                              | Orthorhombic Indices                                                            | $\frac{\Delta d}{d}$<br>( $y = 1.002$ )        | Pattern                                                                               |
|----------------------------------------|--------------------------------------------------------------------------------|---------------------------------------------------------------------------------|------------------------------------------------|---------------------------------------------------------------------------------------|
| $h = 0$<br>or<br>$k = 0$               | $4\ 0\ 1$<br>$0\ 4\ 1$<br>$-4\ 0\ 1$<br>$0\ -4\ 1$<br>$4\ -4\ 1$<br>$-4\ 4\ 1$ | $1, 4, 4$<br>$1, 0, 8$<br>$1, -4, -4$<br>$1, 0, -8$<br>$1, -4, 4$<br>$1, 4, -4$ | $1.96 \times 10^{-3}$                          |    |
| $h = k \neq 0$                         | $1\ 1\ 0$<br>$1\ -2\ 0$<br>$-2\ 1\ 0$                                          | $0\ 1\ 3$<br>$0\ 1\ -3$<br>$0\ -2\ 0$                                           | $2.00 \times 10^{-3}$                          |   |
| $h \neq k$<br>$h \neq 0$<br>$k \neq 0$ | $1\ 2\ 1$<br>$2\ 1\ 1$<br>$1\ 3\ 1$<br>$-3\ 1\ 1$<br>$-3\ 2\ 1$<br>$2\ -3\ 1$  | $1\ 2\ 4$<br>$1\ 1\ 5$<br>$1\ 1\ -5$<br>$1\ -3\ -1$<br>$1\ -3\ 1$<br>$1\ 2\ -4$ | $1.37 \times 10^{-3}$<br>$0.82 \times 10^{-3}$ |  |

At  $51^\circ\text{C}$ , the splitting of the  $401$  hexagonal line was measured to be  $0.595^\circ$  from which,  $\frac{c'}{b'} = 1.0022 \sqrt{3} = 1.7358$ . The structural splitting was of the same order as the  $K\alpha$  - splitting making it difficult to index many of the lines. However the observed pattern was consistent with an orthorhombic cell with edges,

$$\underline{a} = 5.724\text{\AA}, \quad \underline{b} = 3.668\text{\AA}, \quad \underline{c} = 6.367\text{\AA}, \quad \text{at } 51^\circ\text{C}.$$

Consideration of line splitting, line overlap, and  $K\alpha$ -doublet separation indicated that diffractometer data collected for the 121 hexagonal reflection would provide the most satisfactory test of these conclusions. In Fig. 3 · 6, the diffractometer trace is compared with the splitting calculated from the above orthorhombic cell. The number of peaks and their positions are in good agreement with the calculation. However, the intensities of the three peaks should be equal. That they are not suggests there is also some displacement of the atoms from their positions in the unit cell. On the basis of this it was suggested (Kornelsen, 1961) that MnAs in the intermediate region has the MnP (B31) structure which CrAs and FeAs also have.

Parallel work by Kasper and Wilson (1961) on a single crystal of MnAs showed that the Mn-atoms are indeed displaced from the positions which they occupy in the nickel arsenide structure, resulting in the MnP structure. Kasper (1961) also repeated the neutron diffraction measurements on MnAs, particularly looking for a long range magnetic structure. The result was completely negative.

The magnetic and structural properties of MnAs in the intermediate region are, then, not a result of a helical spin arrangement but are due to a change in crystal structure probably arising from changes in chemical bonding.

#### 5. Lattice Spacings of the Ternary Alloys.

The low temperature  $a$ - and  $c$ - spacings for the alloys with Ni, Co, Fe, Cr, and V are shown in Figures 3 · 7 to 3 · 11 with the MnAs curve included each time for comparison. The general features

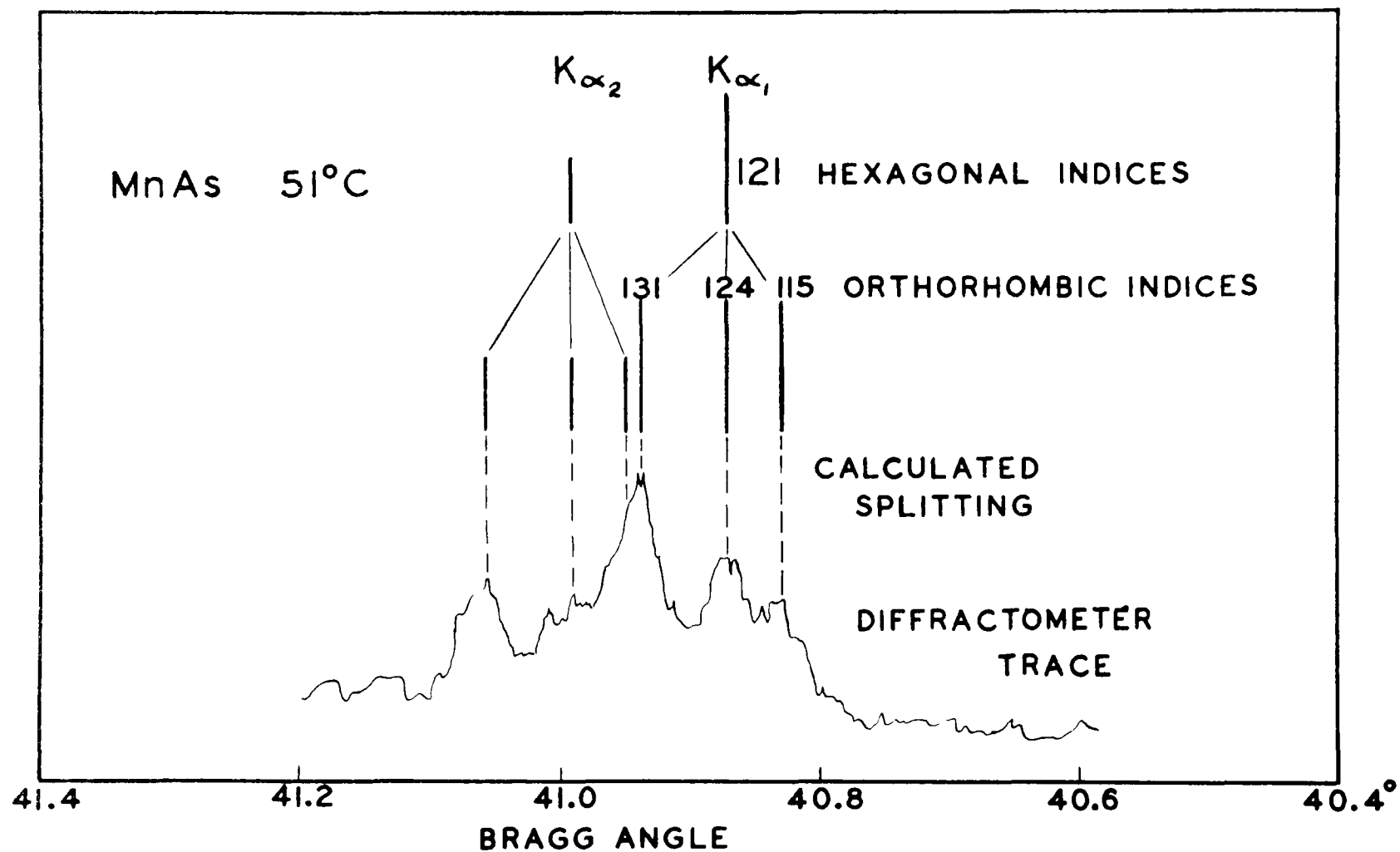


FIG 3.6

Comparison of the diffractometer trace with the calculated splitting of the 121 reflection.

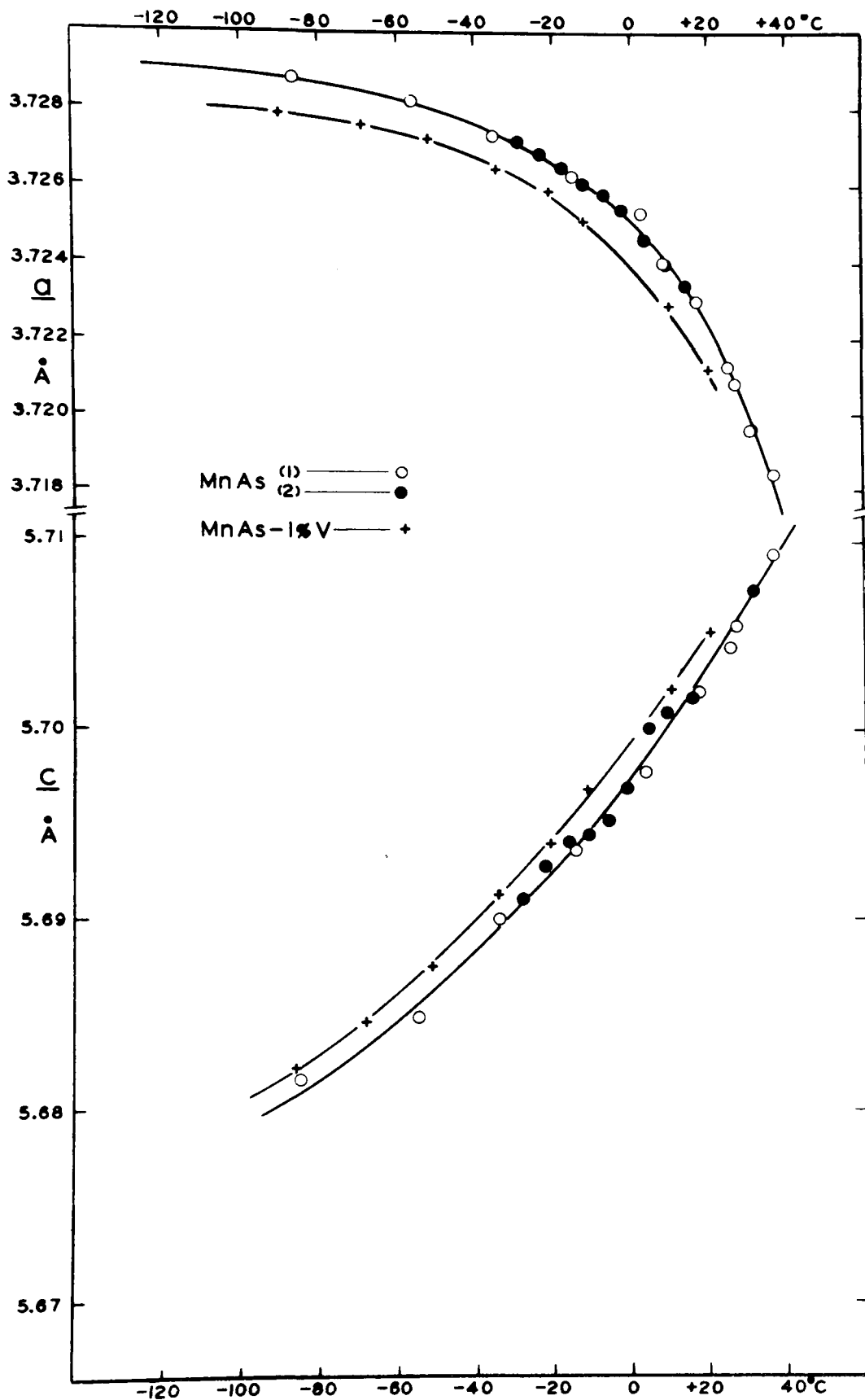


FIG. 3.7 Lattice spacings of V alloys.

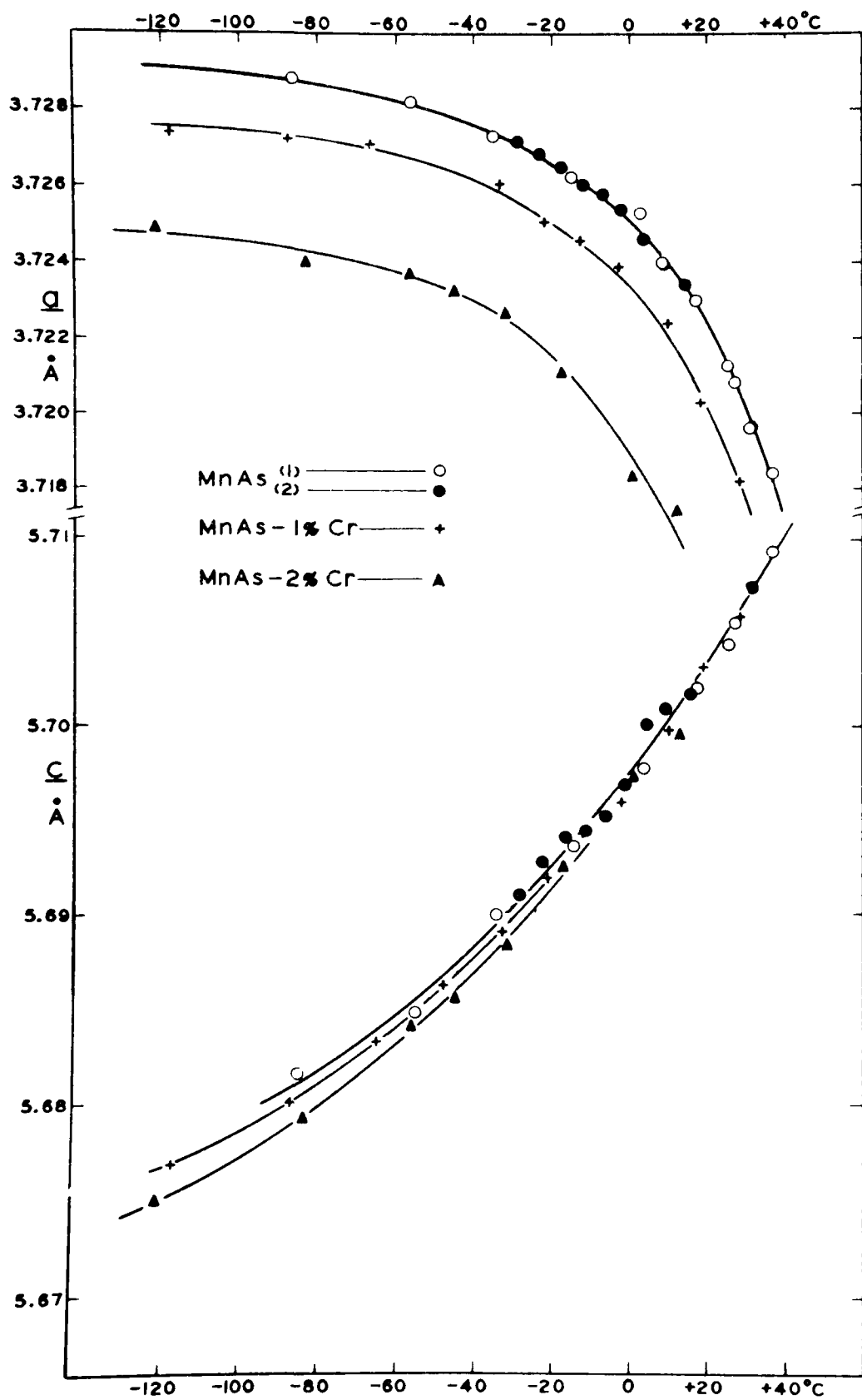


FIG. 3.8 Lattice spacings of Cr alloys.

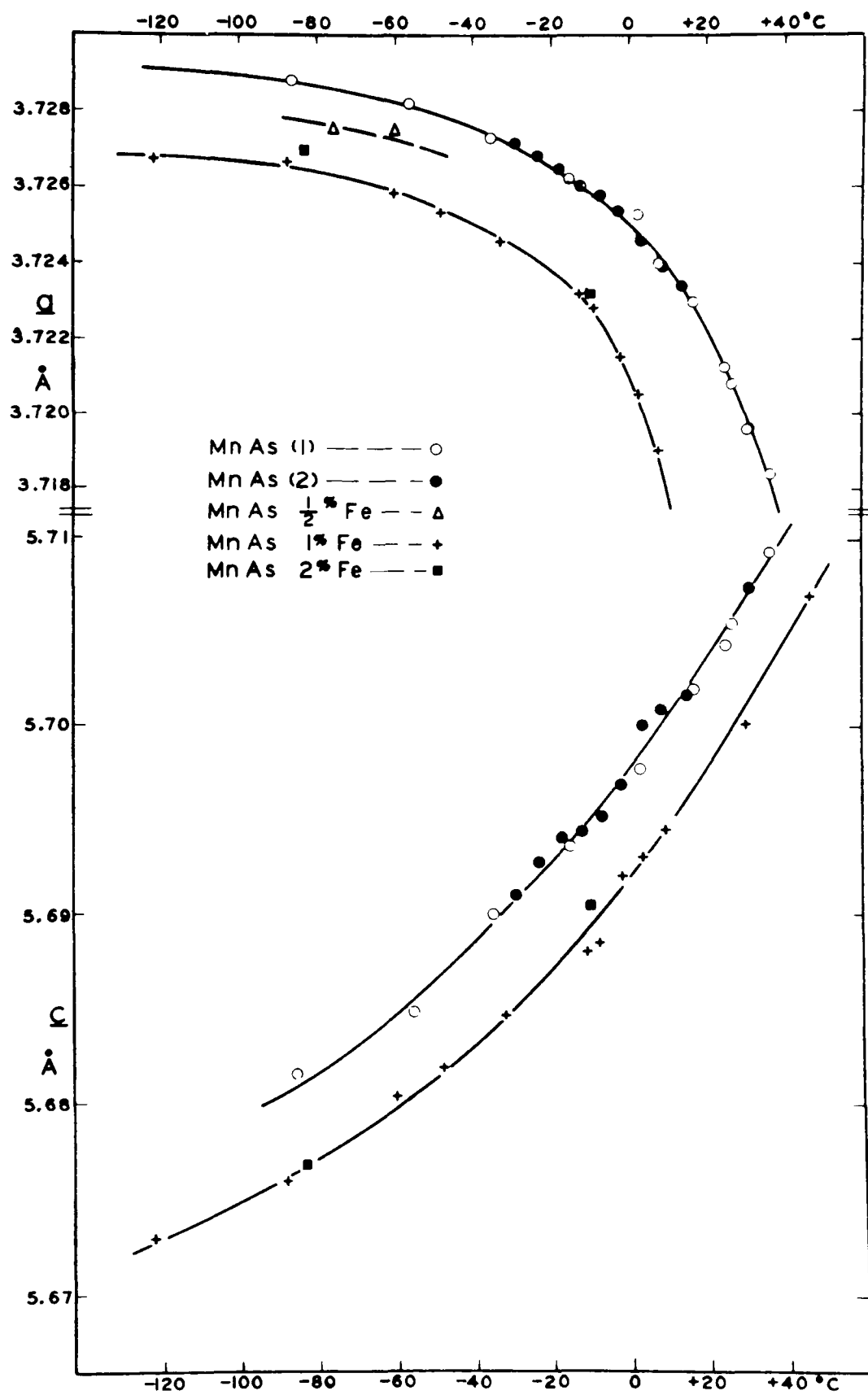


FIG. 3.9 Lattice spacings of Fe alloys.

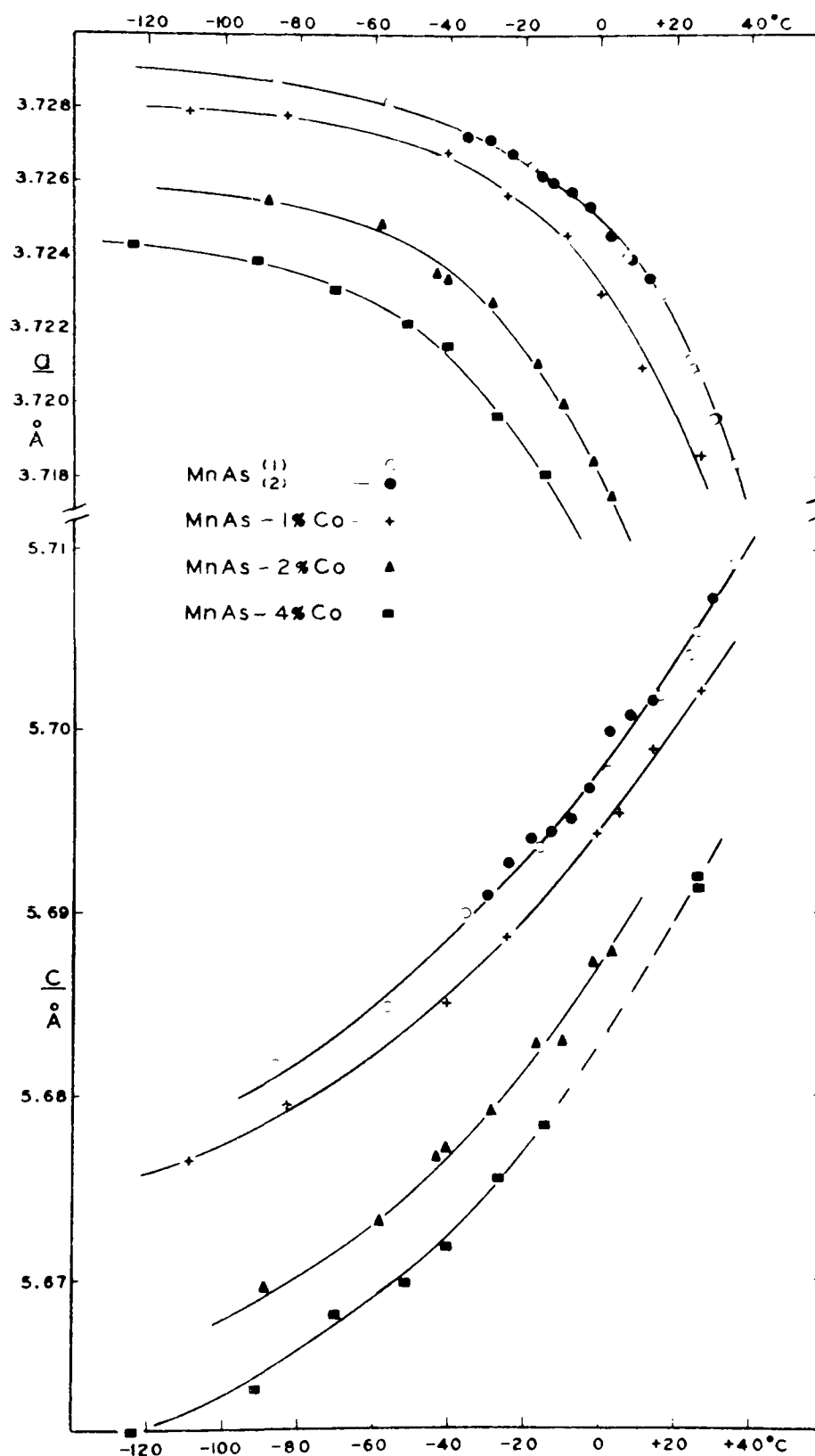


FIG. 3.10 Lattice spacings of Co alloys.

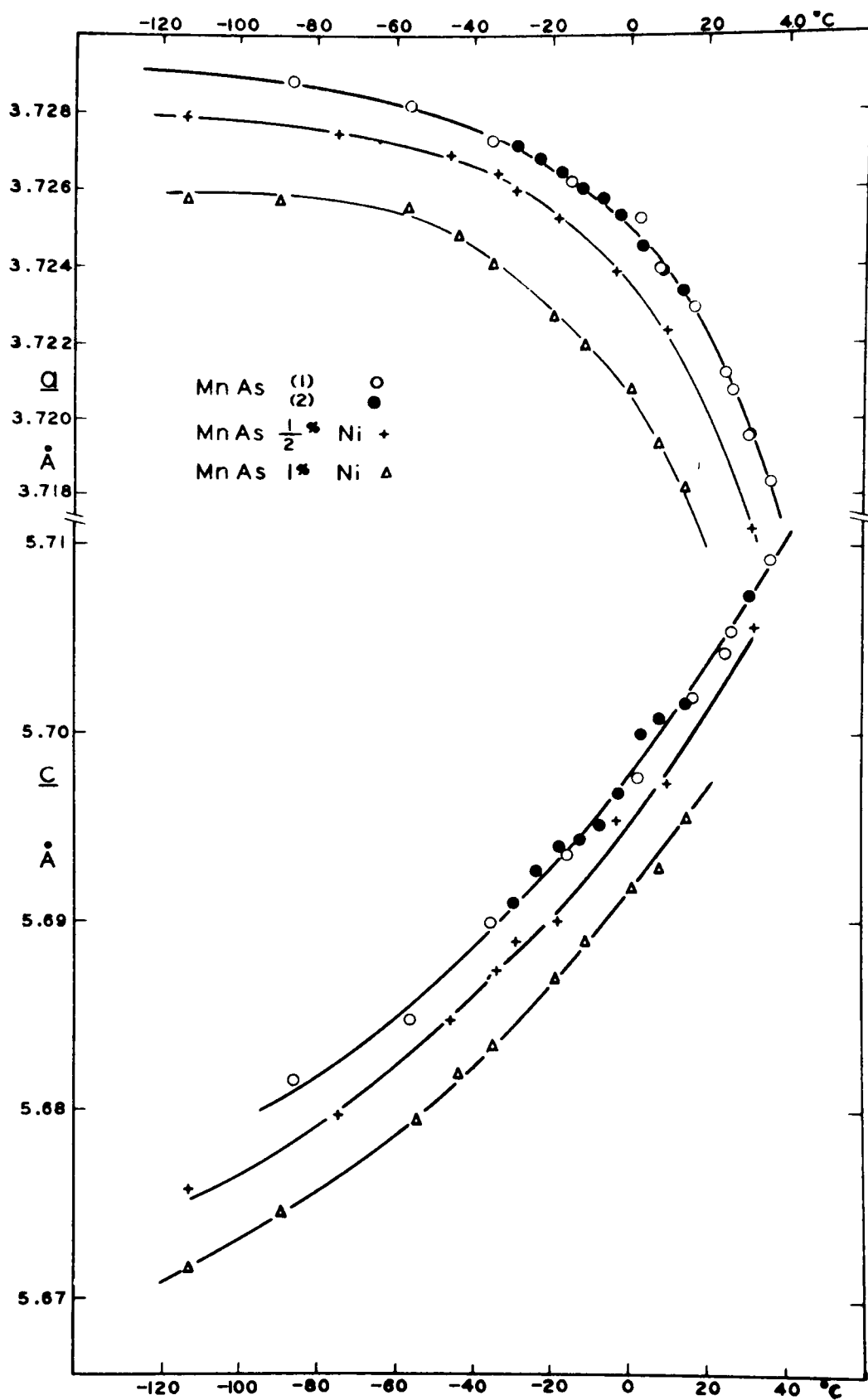


FIG. 3.11 Lattice spacings of Ni alloys.

of the curves are similar, each solute producing a decrease in the a-parameter, a decrease or increase in the c-parameter, and a lowering of the first order transformation temperature. Although the transformation temperatures are not indicated, they were consistent with the data obtained from magnetization measurements, except for the 4% Co alloy.

The effect of alloying on the a-parameter at a particular temperature, ( $-70^{\circ}\text{C}$ ), is shown in Fig. 3 . 12. This temperature was chosen because the variation of a has levelled off making the temperature values less critical.

The different effects of the various solute atoms are better pointed out by plotting the results on a single graph of a against c. In Fig. 3 . 13 the broken line, representing an isotropic contraction, divides the V and Cr data from the Fe, Co and Ni data.

The approximate lattice spacings obtained in the intermediate region are of insufficient accuracy to provide detailed information about the distortions produced by the solute atoms. However, they do confirm that all the alloys measured undergo a discontinuous volume change as MnAs does.

#### 6. Magnetic Susceptibilities of the Ternary Alloys.

The magnetic susceptibilities of the ternary alloys are presented as the usual graphs of  $\frac{1}{\chi}$  against T in Figures 3 . 14 to 3 . 18. Above the second-order transformation, in all cases the data are fitted by a Curie-Weiss law, from which  $\theta$ , the Curie temperature, and  $p_{\text{eff}}$  have been calculated. The results are summarized in Figures 3 . 19 and 3 . 20.

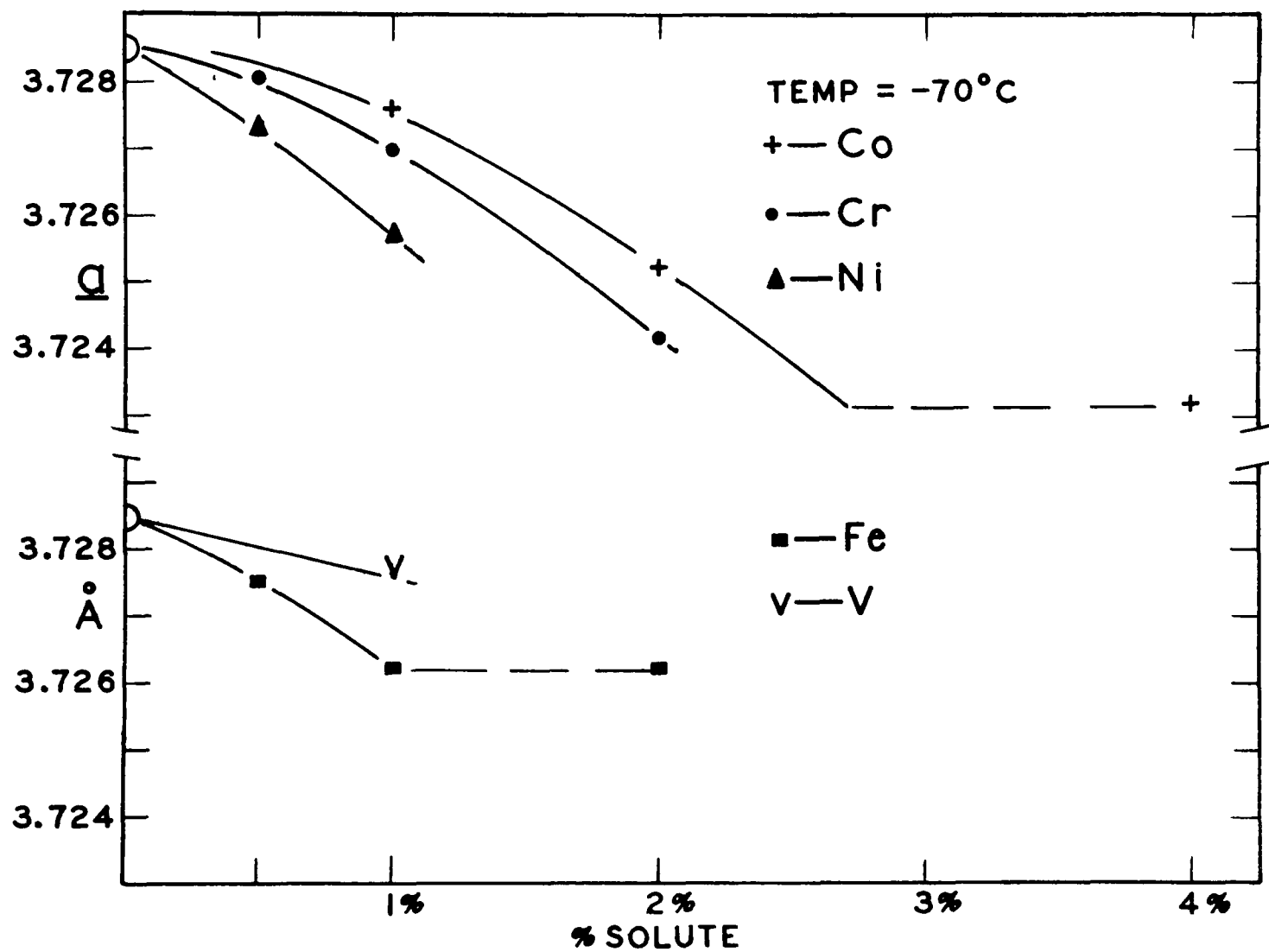


FIG 3.12

a-parameter versus solute concentration at -70°C.

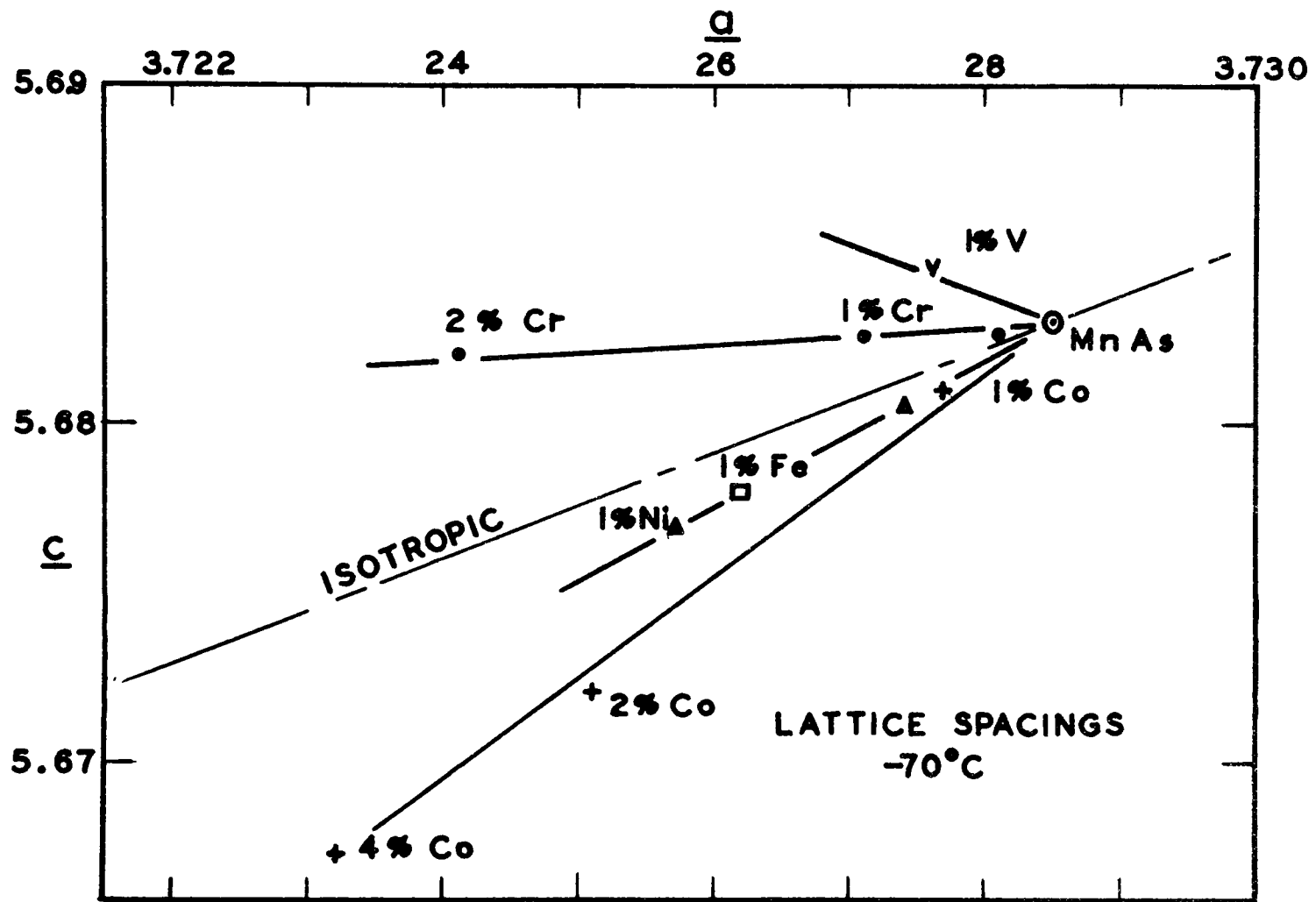


FIG 3.13

$c$  versus  $a$  at  $-70^{\circ}\text{C}$  for all alloys.

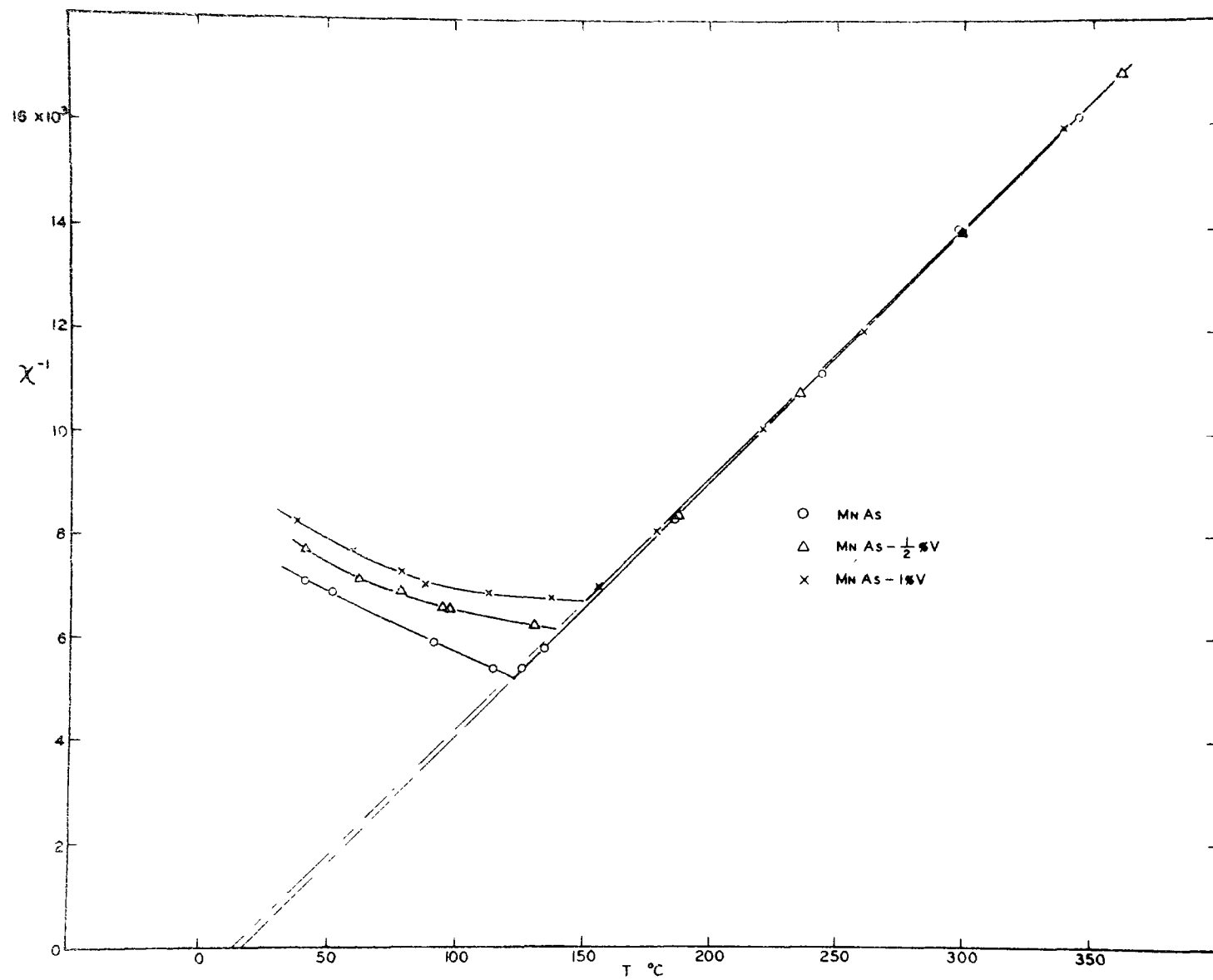


FIG. 3.14 Susceptibility of V alloys.

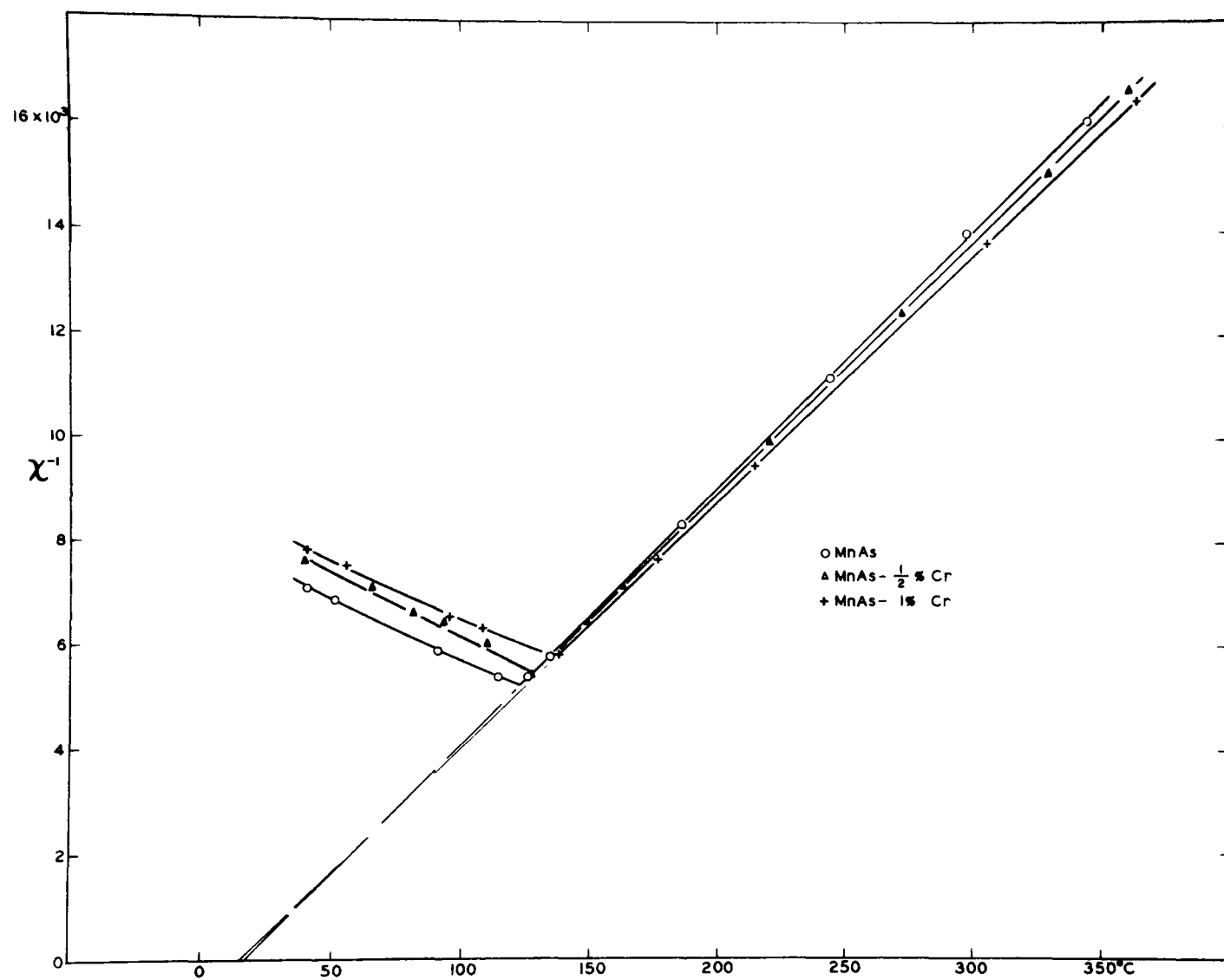


FIG. 3.15 Susceptibility of Cr alloys.

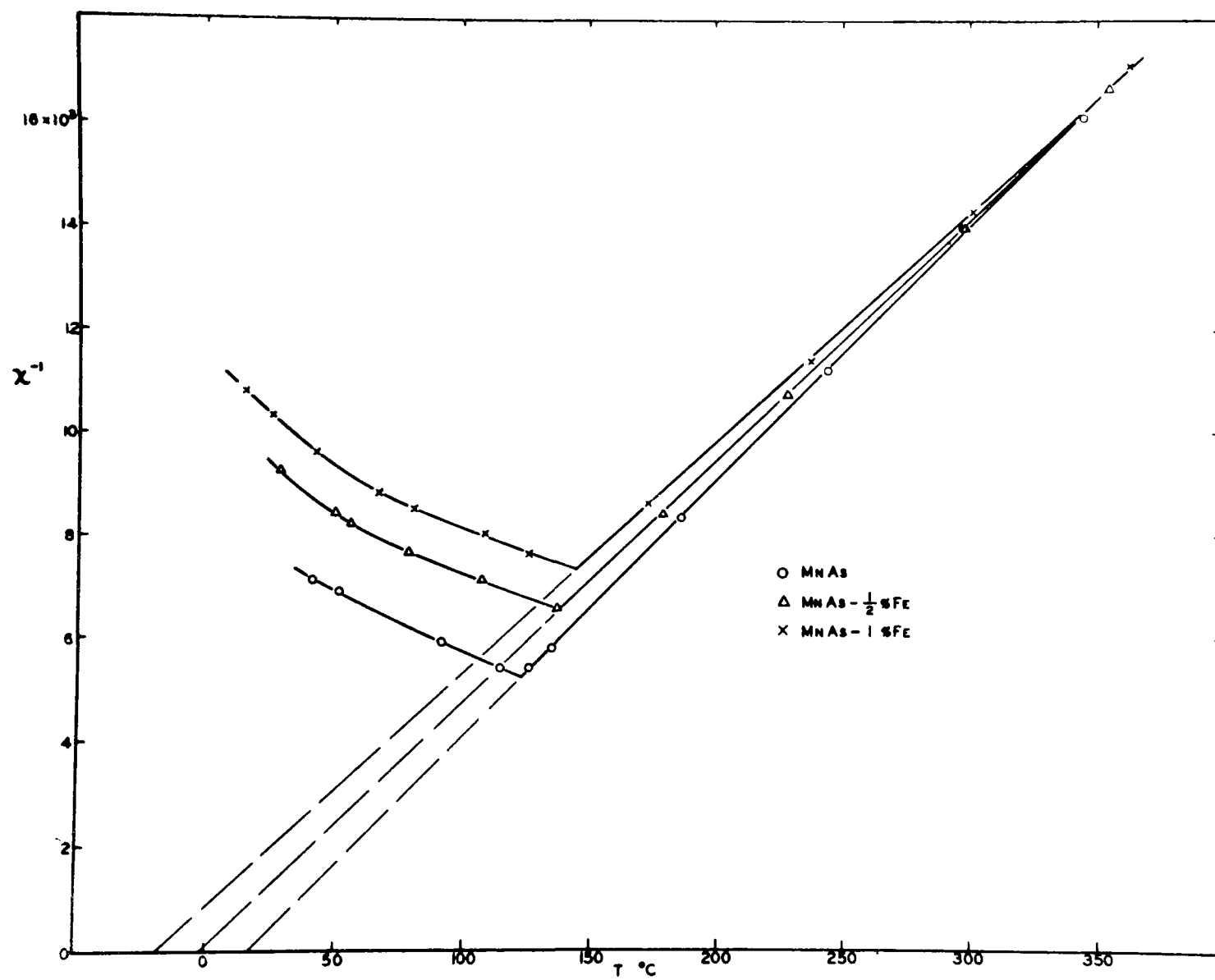


FIG. 3.16 Susceptibility of Fe alloys.

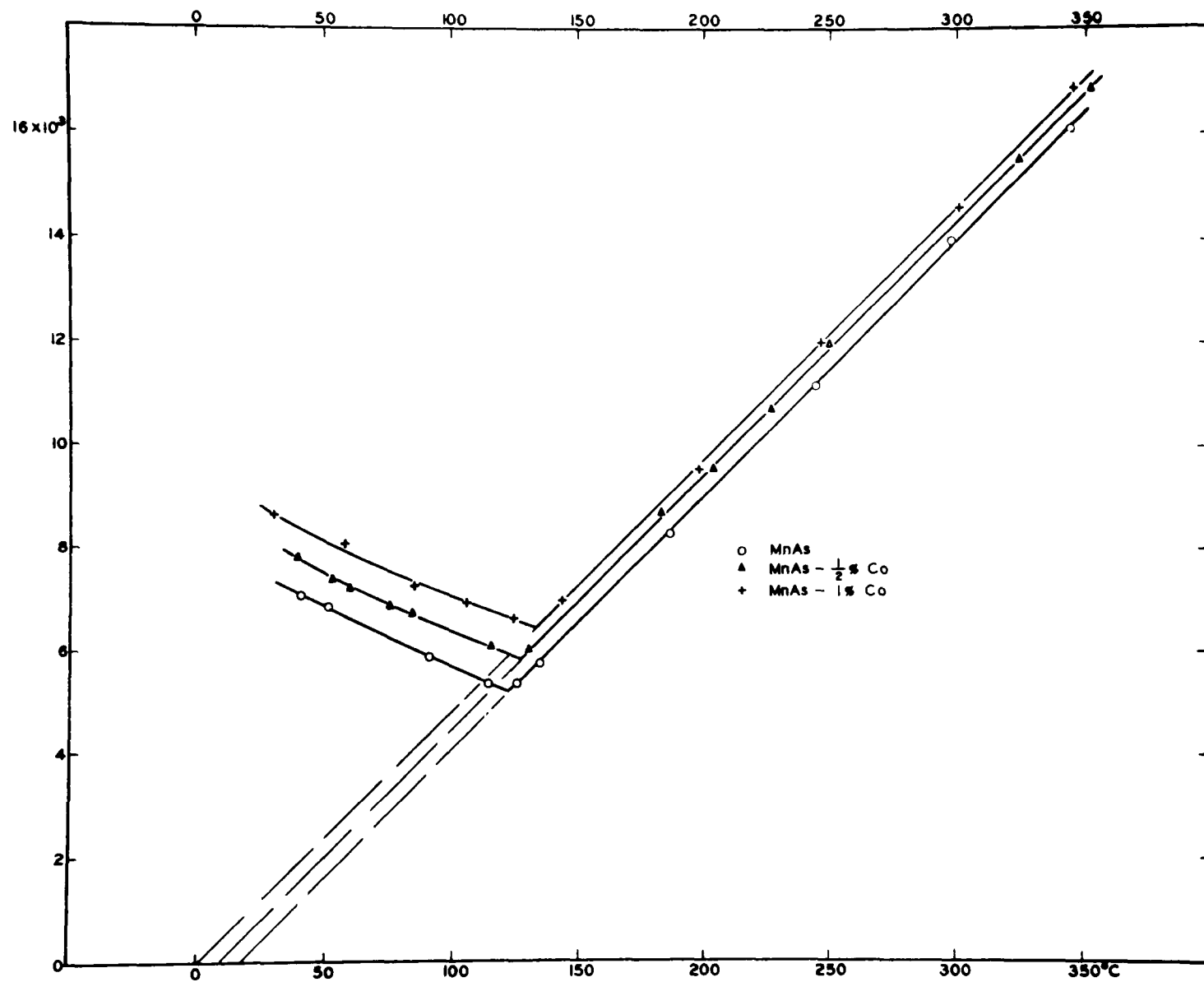


FIG. 3.17 Susceptibility of Co alloys.

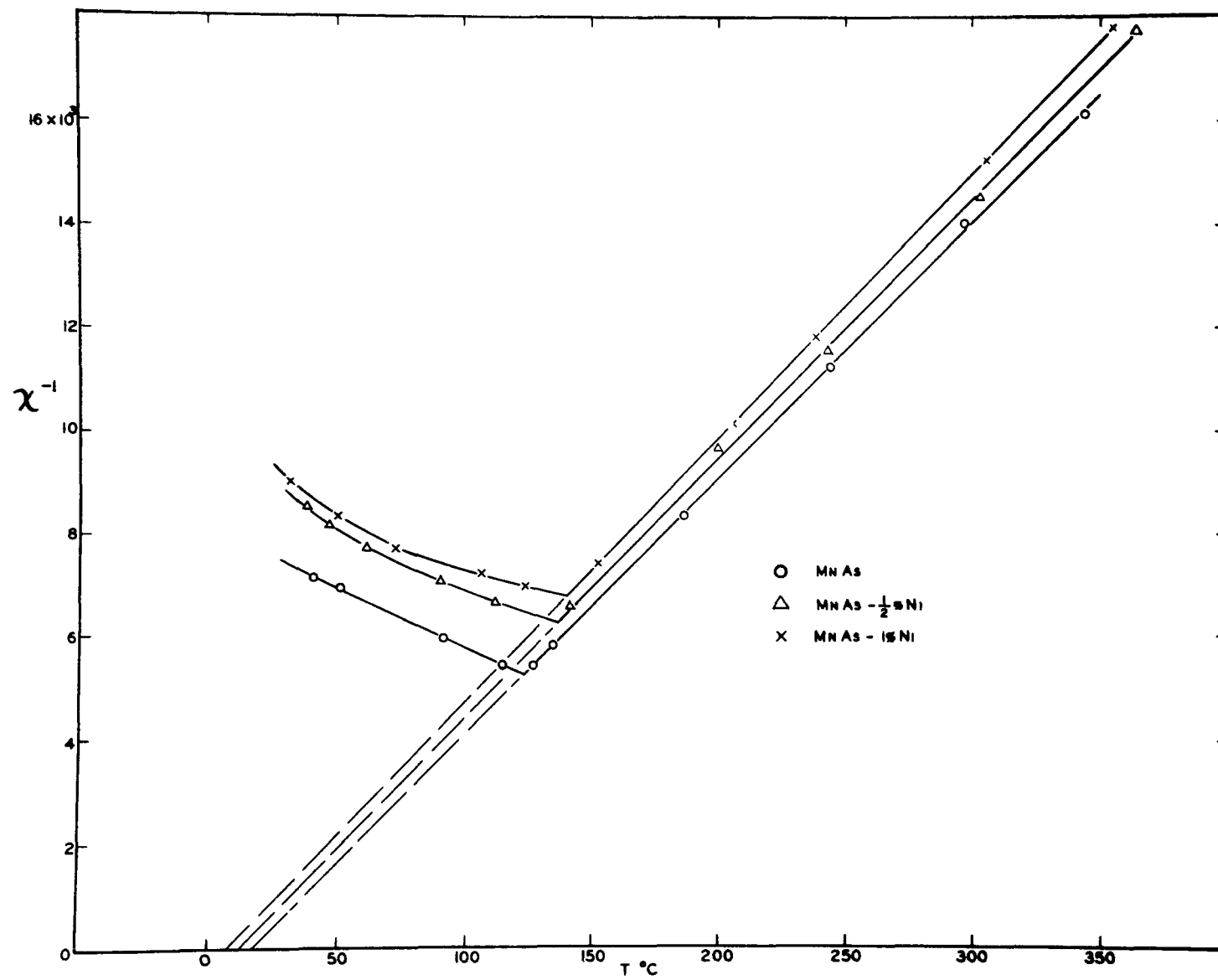


FIG. 3.18 Susceptibility of Ni alloys.

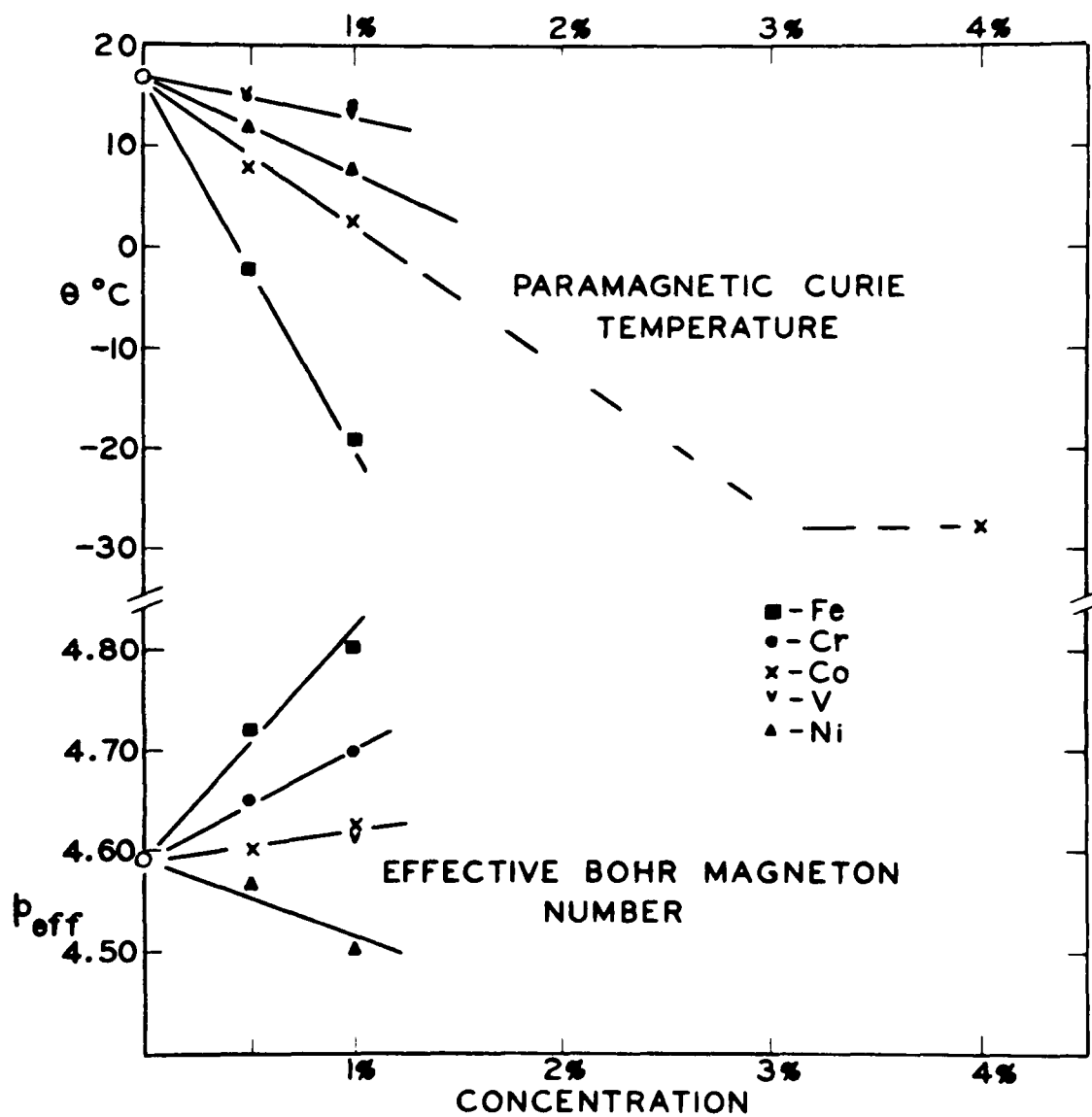


FIG. 3.19 and FIG. 3.20

One particular sample, MnAs (4%Co), Fig. 3 · 21 gave quite unexpected results. Measurements were taken down to the temperature of liquid nitrogen without any sign of ferromagnetism. Since the X-diffraction specimen did transform to the low temperature structure, at about 0°C, this is taken as evidence that the first order transformation is not necessarily to a ferromagnetic state.

#### 7. Magnetization of Ternary Alloys.

As it was previously noted, absolute measurement of the magnetization was impossible. Indeed, even after a large number of thermal cycles through the first-order transformation in zero magnetic field, it was still possible to increase the magnetization by thermal cycling in a strong magnetic field.\* This is not too surprising, since incomplete transformation is the rule rather than the exception for diffusionless transformation.

It was possible, however, to determine with reasonable precision, the temperature at which each alloy transforms. Although the measured transformation temperature depended markedly on the sample history, after several thermal cycles with a strong magnetic field a stable value was obtained, as shown in Fig.3 · 22 for MnAs (1%Fe). Values for the upper (warming) and lower (cooling) transformation temperatures, measured in this way for each alloy, are shown in Fig.3 · 23. The effect of alloying is generally to lower the transformation temperature and to increase the width of the thermal hysteresis.

---

\*In two specimens of pure MnAs, however, it is believed that almost complete transformation was attained. These gave values of  $f_{\text{eff}} = 3.32$  and  $3.36$  as compared to Guillaud's value of  $3.40$ .

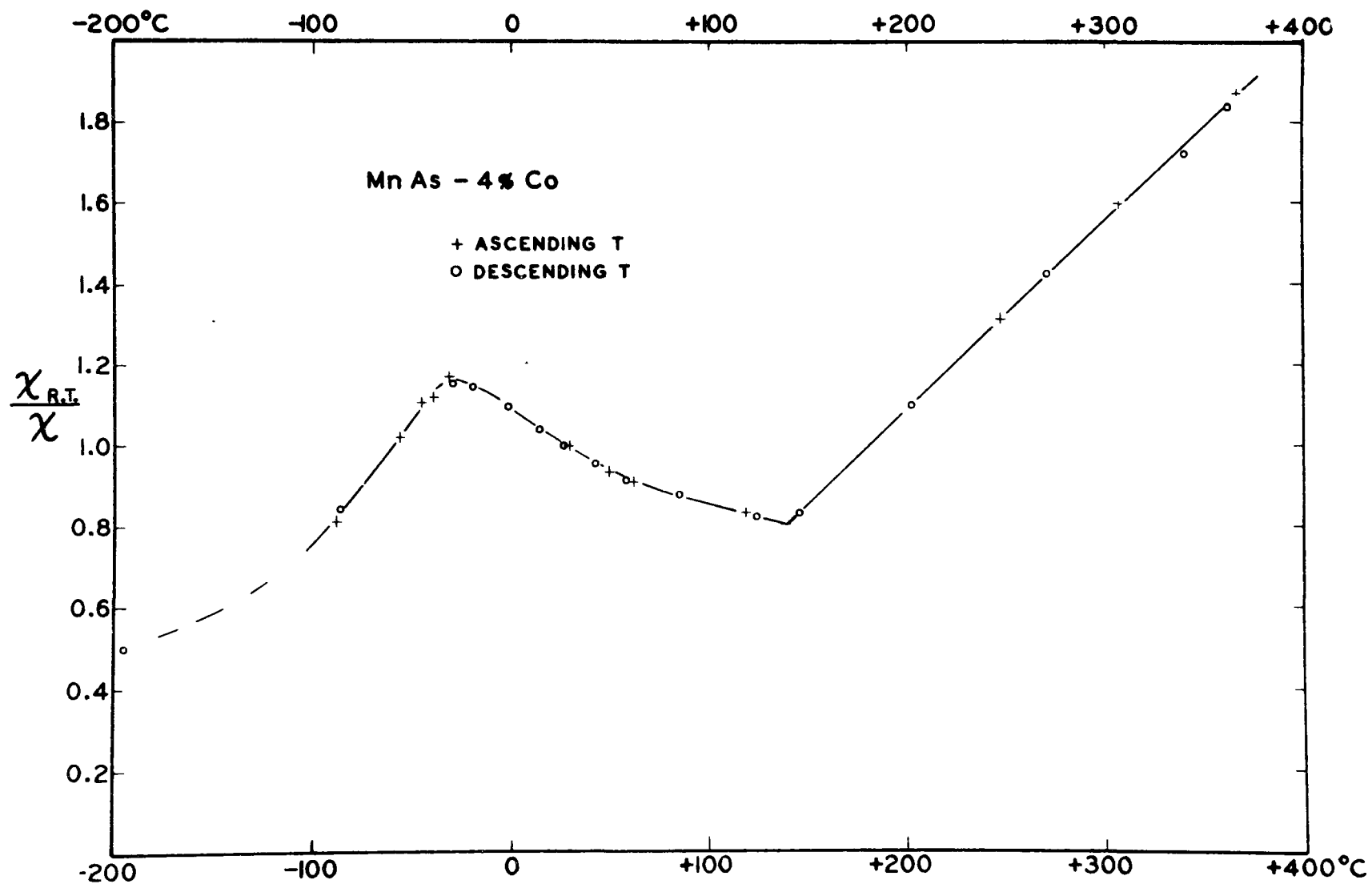


FIG. 3.21 Relative susceptibility of MnAs -4% Co versus temperature.

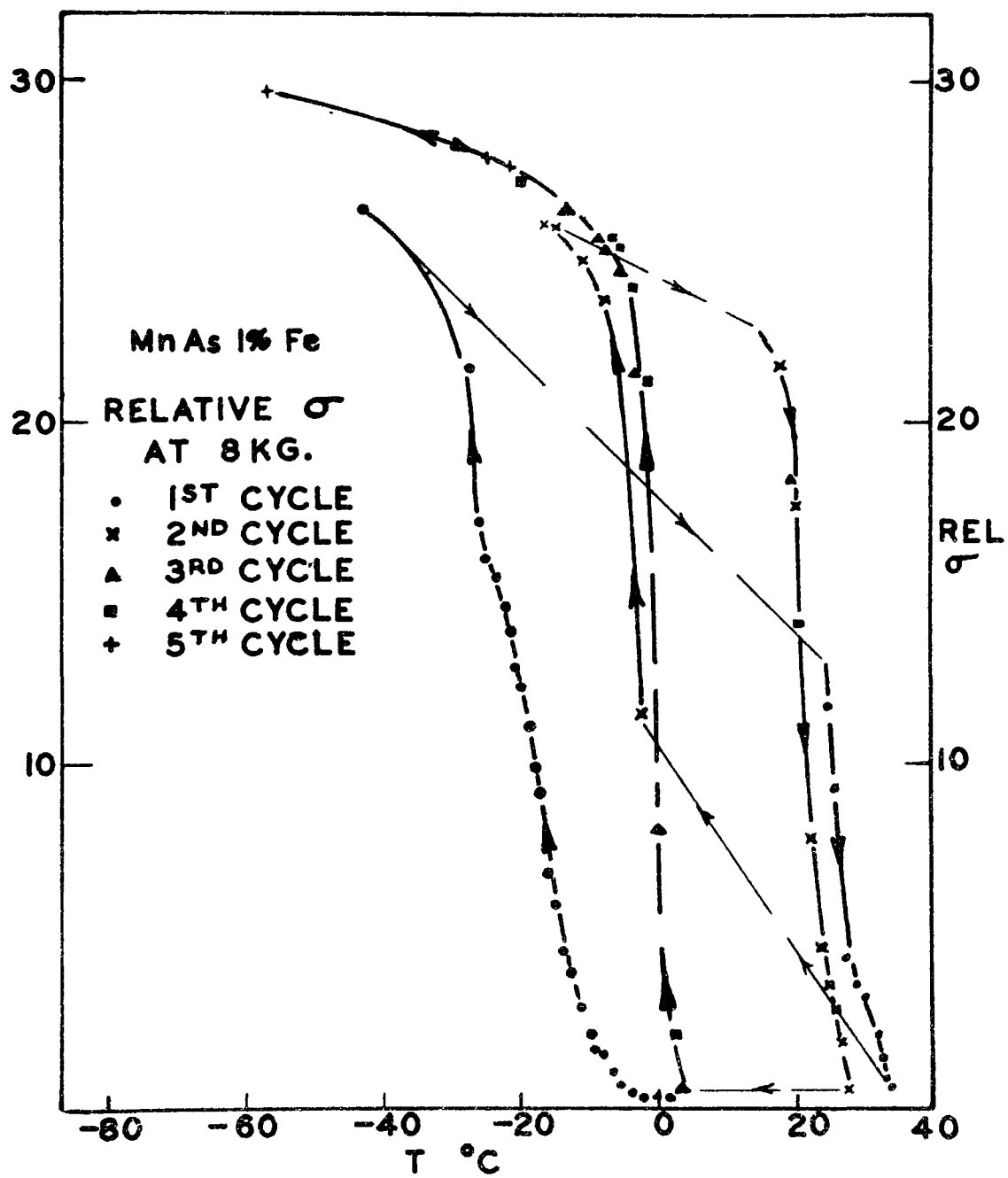


FIG. 3.22

Relative magnetization on warming and cooling through the transformation, MnAs 1% Fe.

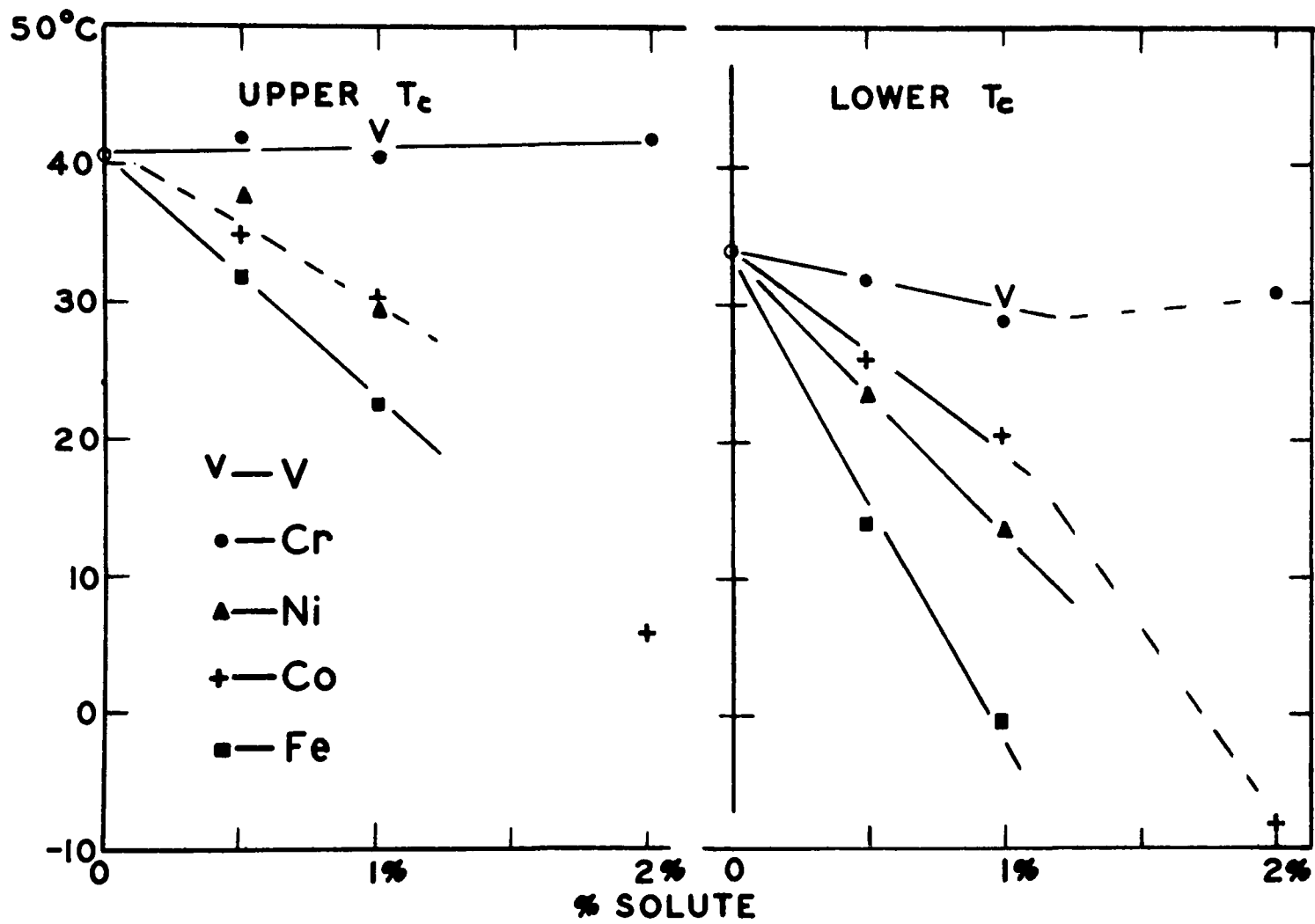


FIG 3.23

Upper and lower transformation temperature versus solute concentration.

## CHAPTER IV - DISCUSSION OF RESULTS AND CONCLUSIONS

In order to discuss the wide variety of effects which must be correlated to give an adequate explanation of the behavior of MnAs and its alloys, we will first develop a model for the electronic state of the Mn atom and its relationship to the crystalline field of the lattice. Some reference will of course be made to experimental data which have a direct bearing on the choice of the model. There will follow a discussion of the results given in Chapter III, and any other available data to see if they support the model and to discover to what extent it may be useful in accounting for the complex phenomena observed.

### 1. Model for MnAs

#### A. General

Although the general appearance of MnAs does not suggest that it has an ionic constitution there are certain advantages (as with any other similar transition metal compounds) in considering it initially from the standpoint of an ionic model. To a first approximation we can consider that  $\text{Mn}^{+++}$  ions occupy the octahedral holes in a close-packed-hexagonal array of  $\text{As}^{---}$  ions in the NiAs (B8) structure. The magnetic moments measured in the ferromagnetic region ( $f_{\text{eff}} = 3.34$ ) and in the paramagnetic region ( $p_{\text{eff}} = 4.59$ ) are less than the expected values for a  $\text{Mn}^{+++}$  ion in a high-spin state which should have four unpaired electrons with  $f_{\text{eff}} = 4$  and  $p_{\text{eff}} = 4.90$ . In the case of  $p_{\text{eff}}$ , at least, this can be interpreted as evidence

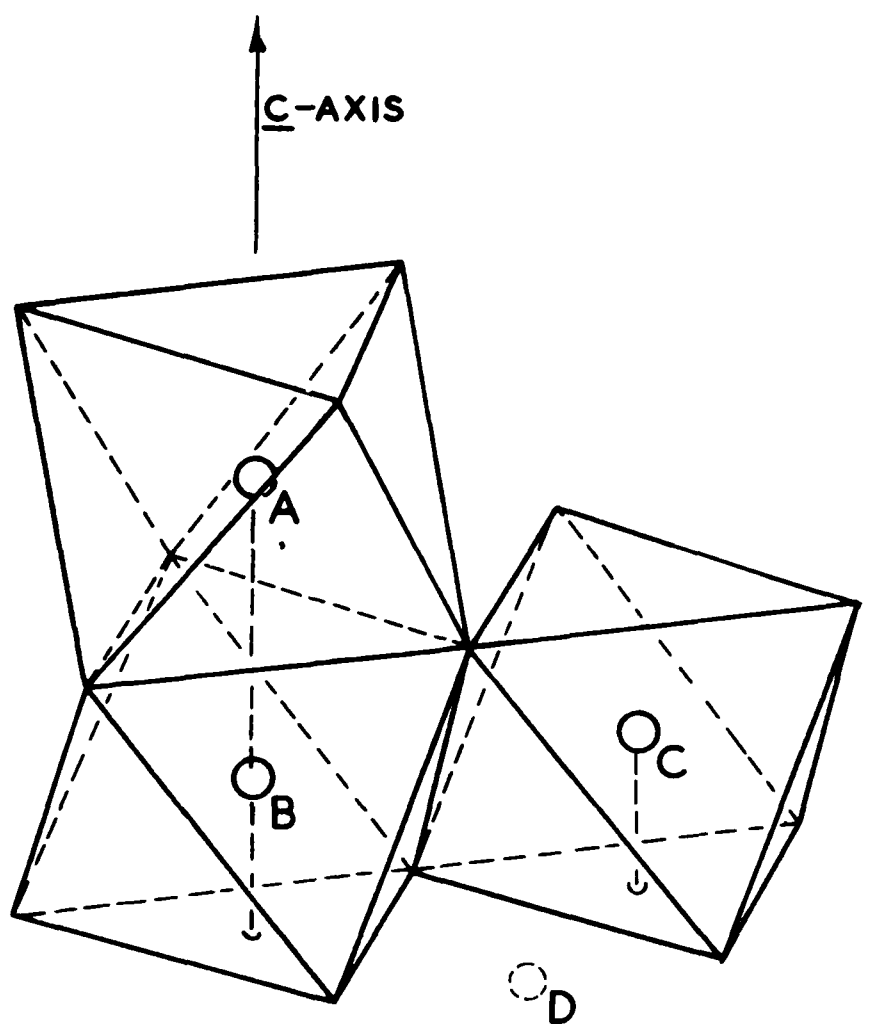
of some delocalization of Mn d-electrons, as described in Section 2 - I of Chapter I, and measurements of the electrical conductivity of MnAs by Fischer and Pearson (1958) have indeed confirmed its metallic conduction.

### B. Structural

The spatial relationship between Mn atoms can best be visualized by considering the octahedra which contain them. (See Fig. 4 · 1) Along the  $\underline{c}$ -axis the octahedra share common faces and each Mn atom has two neighbors of the type AB at a distance  $\frac{c}{2} \approx 2.86 \text{ \AA}$ . In the basal plane the octahedra share common edges and each Mn atom has 6 neighbors of the type BC at a distance,  $\underline{a} \approx 3.7 \text{ \AA}$ . Also each octahedron shares a corner with twelve others to give twelve neighbors of the type AC. On the basis of equation (1 · 31) and on the consideration of the properties of a large number of transition metal compounds, Goodenough has estimated that the critical distance for the delocalization of d-electrons in Mn lies in the range

$2.93 \text{ \AA} \leq R_c \leq 3.13 \text{ \AA}$ , where the lower limit holds true for oxides and the upper limit is applicable in metals. Accepting  $R_c = 3.05 \text{ \AA}$  for MnAs as reasonable, the presence of both localized and collective d-electrons is indicated.

A complicating factor in the NiAs-type structure is the presence of trigonal-bipyramidal holes (i.e. pairs of tetrahedral interstices joined on a face) in the anion array. These holes, with a co-ordination number of five, are large enough to accept cations fairly easily. This fact makes it difficult to ensure that



A,B,C – OCTAHEDRAL SITES  
 D – TRIGONAL-BIPYRAMIDAL  
 SITE

**FIG. 4.1**

Stacking of octahedra in the NiAs structure.

all the cations are ordered into the octahedral sites. Their presence also permits, rather readily, deviations from stoichiometry. The distance between an octahedral and a trigonal-bipyramidal cation is even less than that along the  $c$ -axis, so that the presence of trigonal-bipyramidal atoms could be a very important factor in determining the properties of MnAs.

#### C. d-Levels in the Crystalline Field

In a close-packed hexagonal array with  $c/a = 1.63$  the octahedral holes are regular (cubic) and the d-level is split into a 2-fold  $e_g$ -level and a 3-fold  $t_{2g}$ -level (See Fig. 4 · 2).

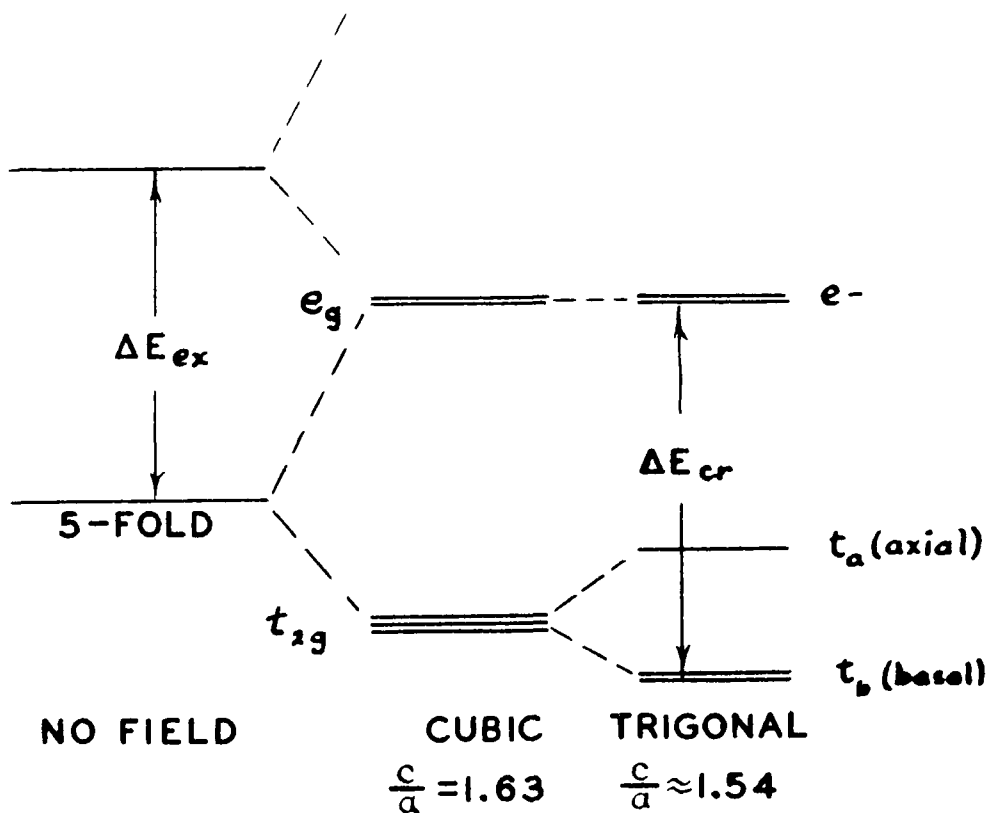


FIG. 4 · 2

In MnAs the axial ratio,  $c/a \approx 1.54$ , corresponds to a compression of the regular octahedron along the  $c$ -axis, resulting in a change from cubic to trigonal symmetry. The  $e_g$ -level will remain degenerate since the  $e_g$ -orbitals have trigonal symmetry about the  $c$ -axis. The  $t_{2g}$ -levels, however, will be split into a higher energy single level arising from the  $t_{2g}$ -orbital pointing in the  $c$ -direction, and a 2-fold level corresponding to orbitals in the basal plane. In the following discussion these will be referred to simply as  $e$ -,  $t_a$ - and  $t_b$ - levels.

The way in which the levels will be occupied depends on the relative size of intra-atomic splitting  $\Delta E_{ex}$  and the crystalline field splitting  $\Delta E_{cr}$ . If  $\Delta E_{ex} > \Delta E_{cr}$ , the ion will be in the high spin state,  $(t_b^2 t_a^1 e^1)$ . If  $\Delta E_{cr} > \Delta E_{ex}$ , Hund's rule will be violated and the ion will take on the low-spin state  $(t_b^3 t_a^1)$ . The experimental data for MnAs indicate that at least below  $40^\circ\text{C}$  and above  $120^\circ\text{C}$  the Mn ion is in the high-spin state. However, let us consider the series MnP, MnAs, MnSb and MnBi. There is strong evidence that MnP is in the low-spin state ( $f_{eff} = 1.3$ ), while MnSb and MnBi are almost certainly in the high-spin configuration. Although MnAs seems to favor the high-spin state, it is probably "just barely" so (i.e.  $\Delta E_{cr} \lesssim \Delta E_{ex}$ ) and transitions from high-spin to low-spin must be considered a distinct possibility.

#### D. Magnetic Exchange Interactions

The exchange interaction between neighbors along the c-axis takes place via half-filled  $t_a$ -orbitals and hence must be negative. Similarly, in the basal plane, if any appreciable interaction exists, it is through half-filled  $t_b$ -orbitals and must also be negative. The strong positive interaction necessary for ferromagnetism is provided by the indirect super-exchange between Mn atoms in octahedra sharing a common corner. This interaction involves half-filled and empty  $e$ -orbitals and is strongly positive. Provided that the positive interaction outweighs the negative ones, it is sufficient to account for the spread of ferromagnetism throughout the lattice since each Mn atom has twelve such neighbors. Mn atoms in trigonal-bipyramidal sites will align themselves antiparallel to the ferromagnetic matrix, (interaction via half-filled orbitals) and their presence will enhance the positive molecular field experienced by octahedral site atoms.

#### 2. Discussion of the Behavior of MnAs

##### A. At the First-order Transition

There is no doubt that the transformation in MnAs at  $\approx 40^\circ\text{C}$  is of the first-order as evidenced by the specific heat and by the discontinuous changes in cell volume and in electrical and magnetic properties. The view, previously held by some, that the transition is from a ferromagnetic state to an antiferromagnetic one, must be rejected because of the neutron diffraction work by Kasper (1961) who established conclusively the absence of antiferromagnetism in

the intermediate temperature region. It should be pointed out that the common assumption that a transition from ferromagnetism to anti-ferromagnetism is necessarily of the first-order is probably wrong. Adachi (1961) has indicated how a f.m.  $\longrightarrow$  a.f.m. transformation can be of the second-order and indeed that this is the rule rather than the exception.

Bean and Rodbell (1962) have given an elegant theoretical treatment of the magnetization of an isotropic, compressible lattice in which the exchange interaction is a strong function of atomic spacing. Using a molecular field approximation, the exchange interaction (as represented by the Curie temperature) was assumed to vary linearly with volume, expressed as

$$T_c = T_0 \left( 1 + \beta \frac{\Delta v}{v} \right)$$

where,  $T_0$  is the Curie temperature of the rigid lattice,

$T_c$  is the Curie temperature of the compressible lattice,

$\beta$  is the slope of the variation of exchange interaction with volume.

On the basis of these assumptions, Bean and Rodbell have predicted the possibility of a first-order transformation from the f.m. to a paramagnetic state, accompanied by a discontinuous volume change and by thermal hysteresis. Extension of the equations to include the effects of pressure and magnetic field had led to the prediction that the transformation temperature should be sensitive to applied pressure and magnetic field. As an example of a substance that obeys their theory they cite MnAs, and indeed, the

experimental data (magnetization vs temperature, size of the volume change and shift of transition temperature with pressure) can be brought into excellent agreement with the theory. However, a theory based on an isotropic exchange interaction and on isotropic elastic constants cannot be expected to give detailed information about MnAs whose structural change is decidedly anisotropic. Furthermore, the unusual behavior of the ternary alloy MnAs - 4% Co leads us to reject the applicability of the Bean and Rodbell theory to MnAs. Although this alloy exhibits the discontinuous volume change (Fig. 4 · 3) much like MnAs, it shows no sign of ferromagnetism below the transformation even down to the temperature of liquid nitrogen (see Fig. 3 · 22). Therefore, at least in the 4% Co alloy, and probably in MnAs itself, the first-order volume change is not a direct result of the magnetic exchange energy, contrary to Bean and Rodbell.

#### B. In the Intermediate Temperature Region

No explanation of the unusual magnetic properties of MnAs between 40°C and 120°C was possible before the discovery (described in Chapter III) of the structural distortion to orthorhombic symmetry with displacement of the Mn atoms from the centers of their interstices, thus giving the MnP-type structure. Although Bean and Rodbell attributed this to a Jahn-Teller effect, it is now known that this is not the case since Jahn-Teller distortions are symmetrical and produce no displacement of the cation from the center of the octahedron in these transition metal compounds. A more attractive explanation for the distortion would be the forma-

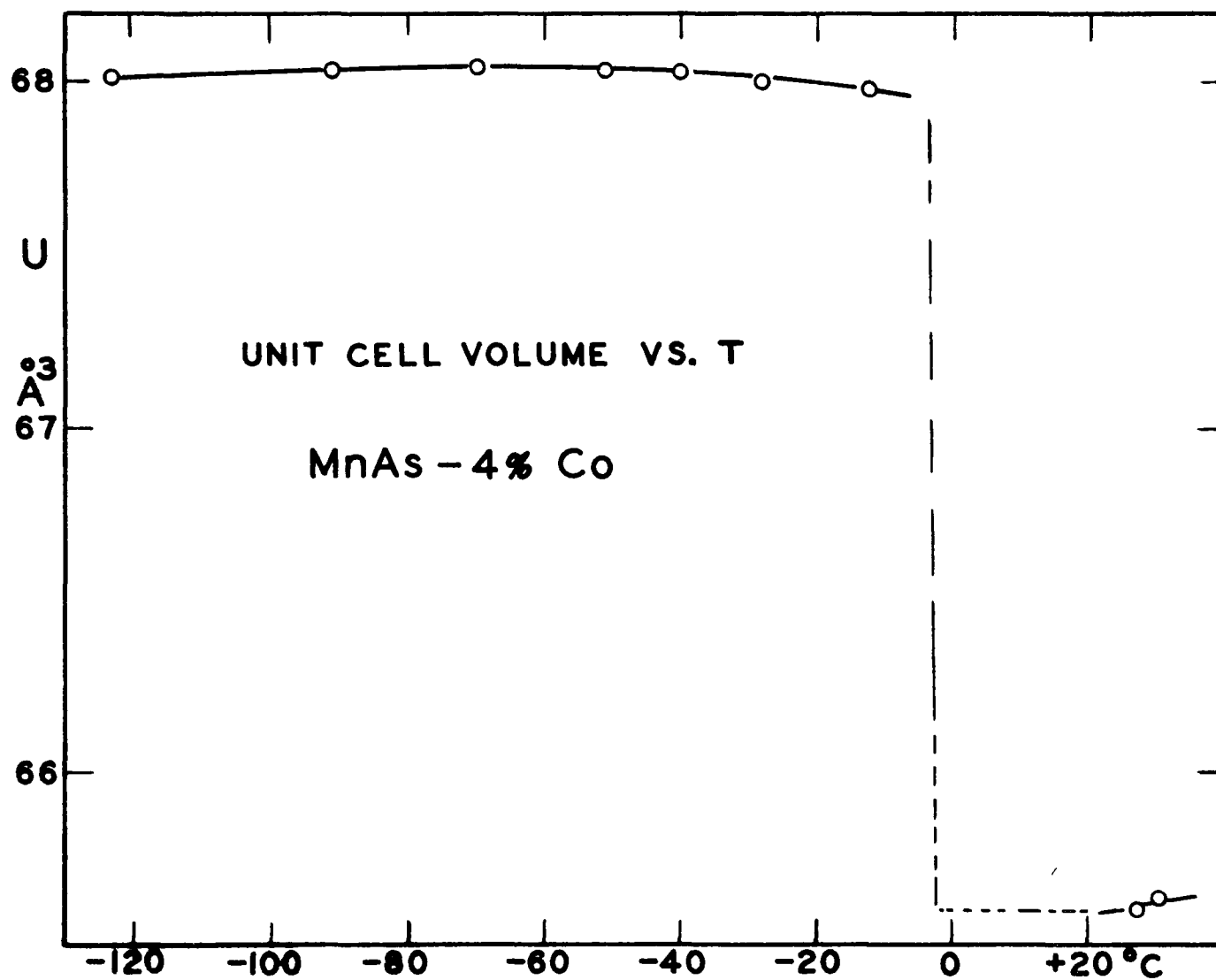


FIG 4.3

tion of covalent bonds between Mn atoms, each Mn atom forming bonds to two neighbors in the basal plane so that chains of Mn atoms are established as required by the MnP structure. Hulliger (1963) has used the concept of covalent cation-cation bonds to account for the magnetic properties of a group of compounds with the  $\text{CoSb}_2$  structure. The compounds described are characterized by a much smaller  $p_{\text{eff}}$  than a purely ionic model would predict, and a displacement of the cations from the centers of their interstices. Goodenough (1963) has assumed the formation of a "bonding band" in the basal plane to account for both the distortion from hexagonal and the displacement of the Mn atoms in MnP itself. In order that covalent bonds or bonding band formation be possible the intercation distance must be shorter than the critical distance  $R_c \approx 3.05 \text{ \AA}$ . Both in MnP and in the  $\text{CoSb}_2$  compounds, cation-cation distances of  $\approx 3 \text{ \AA}$  occur. In undistorted MnAs (above  $120^\circ\text{C}$ ) the separation between atoms in the basal plane is about  $3.7 \text{ \AA}$ . In the distorted structure the distances are not known exactly. However, using the lattice parameters measured at  $51^\circ\text{C}$ , and taking atomic positions commonly found in compounds with the MnP structure, (CrAs, FeAs and CoAs), the distances between Mn atoms in the basal plane become; two neighbors at  $3.02 \text{ \AA}$ , two neighbors at  $3.67 \text{ \AA}$  and two neighbors at  $4.36 \text{ \AA}$ . Thus, at least two neighbors in the basal plane are at a distance comparable with  $R_c$  and band formation would seem possible. The presence of Mn atoms in the trigonal-bipyramidal sites, or "interstitial" sites as we shall call them, would change the argument. The distance

between an octahedral and an interstitial cation is given by

$$s = \sqrt{\frac{c^2}{16} + \frac{a^2}{3}} \approx 2.6 \text{ \AA}^o, \text{ a distance which also makes covalent bonding attractive.}$$

In this connection it would be of interest to make an estimate of the fraction of Mn atoms, if any, which occupy interstitial sites. According to Roberts (1956), the low ferromagnetic moments (below  $4 \mu_B$ ), reported for MnBi, MnSb and MnAs are almost certainly due to interstitial Mn atoms. Since, in the paramagnetic region, the interstitial ions would contribute positively to  $p_{\text{eff}}$ , while in the ferromagnetic region they would align antiparallel to the ferromagnetic matrix, the difference in the effective number of spins could be used as a measure of the fraction of Mn atoms in interstitial sites. Let  $f$  be the fraction of interstitial atoms. The ratio of unpaired spins per atom in the ferromagnetic state to that in the paramagnetic is given by

$$\frac{N_f}{N_p} = 1 - 2f \text{ ----- (4 . 1)}$$

Using the values measured in this work;

$$f_{\text{eff}} = 3.34 = N_f, \text{ and } p_{\text{eff}} = 4.59 = \sqrt{N_p (N_p + 2)}$$

from which  $N_p = 3.71$ . (The difference between  $N_p$  and 4 is attributed to delocalized electrons and is assumed not to change.)

Substituting into 4 . 1, we get

$$1 - 2f = \frac{3.34}{3.71}, \text{ from which the fraction of interstitial Mn atoms is } f = .05. \text{ Each interstitial atom has four d-electrons permitting the formation of covalent bonds with a maximum of four of its six neighbors. If the bonds are formed in such a way as to leave two of the four adjacent atoms parallel to the other two,}$$

each interstitial atom could result in the removal of 5 atomic moments, since the moment of the interstitial atom is lost in the bonding. Thus, the sharp change in slope of the magnetic susceptibility on cooling through 120°C could be interpreted as the onset of covalent bond formation. The expected decrease in unpaired spins would be of the order of  $5 \times .05 = .25$ , leaving 75% of the spins unpaired.

The actual decrease in the number of spins on going down from 120°C to 40°C can be calculated from the magnetic susceptibility as given in Fig. 3 · 2. Above 120°C MnAs obeys equation 1 · 21:

$$\chi = \frac{C}{T - \theta} \quad \text{where } \theta = 290^\circ\text{K}$$

$$\text{and } C = .0201 \text{ emu/gm.}$$

If we substitute into equation (1 · 21),  $\theta = C \lambda$ , where  $\lambda$  is the molecular field constant, and solve for C, we get

$$C = \frac{\chi T}{1 + \chi \lambda} \text{ ----- } 4 \cdot 2$$

Assuming  $\lambda$  to be constant in the range 120°C  $\rightarrow$  40°C, the Curie constant can be evaluated at each temperature in the intermediate region with the result shown in Fig. 4 · 4. At 40°C about 73% of the spins remain unpaired. This value may be compared with the estimate of 75% made on the basis of four covalent bonds about each interstitial atom. Although there seems to be good agreement, there are reasons for suspecting that the above argument is not correct:

(i) The formation of bonds about interstitial atoms could account for the distortion from the hexagonal structure, but it is

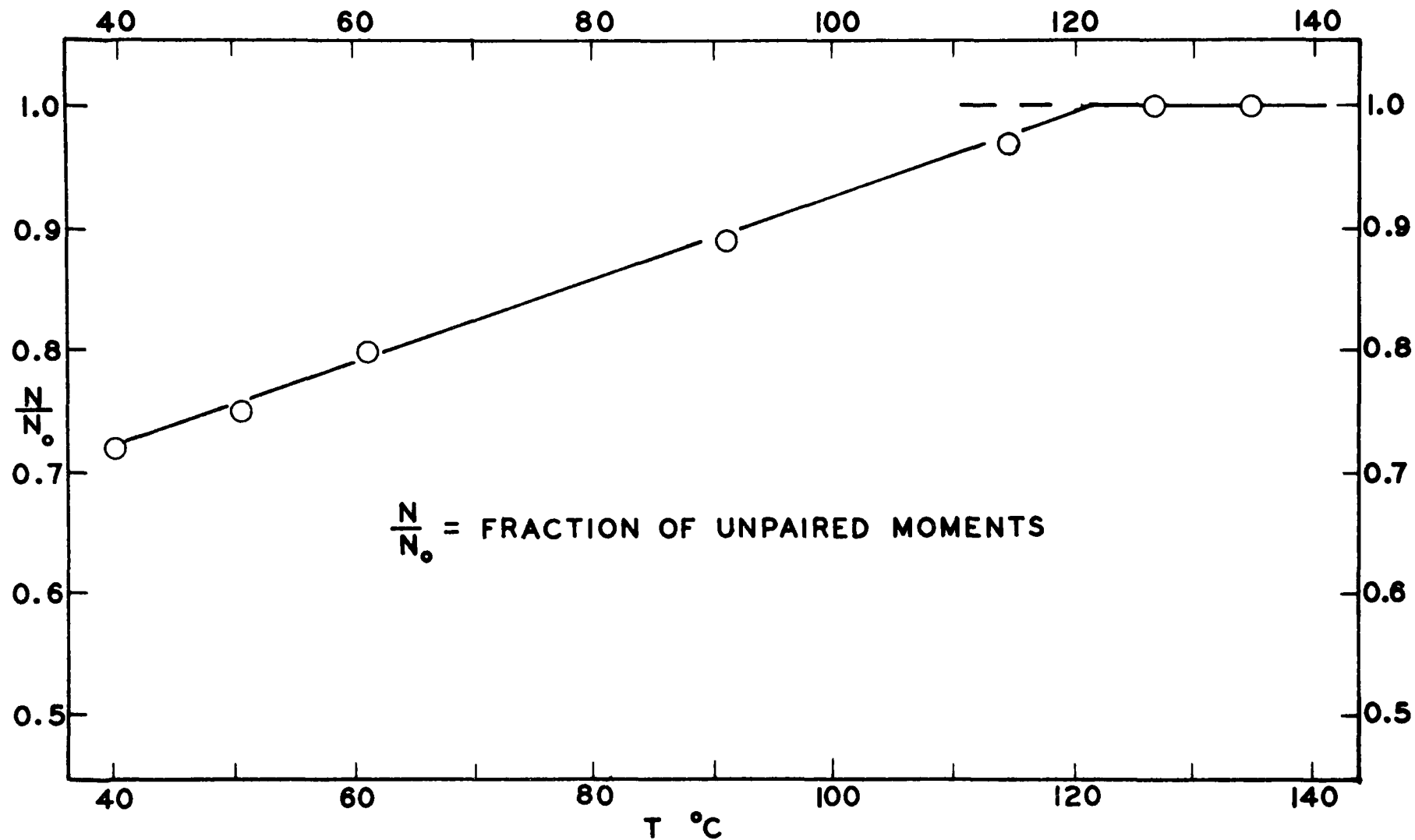


FIG 4.4

Reduction of unpaired moment in MnAs in the intermediate region.

more difficult, if not impossible, to demonstrate how such bonds can be arranged to displace the Mn atoms into "zig-zag" chains as required by the MnP structure.

(ii) Since the distance between octahedral and trigonal-bipyramidal atoms is  $\approx 2.64 \text{ \AA} < R_C^o$  even in the paramagnetic region, it could be argued that the covalent bonds should always be there, whereas the experimental evidence requires that they start forming below  $120^\circ\text{C}$ . However, this objection may not be as serious as it seems, since  $R_C^o \approx 3.05 \text{ \AA}$  is the critical distance for electron delocalization. The distance at which covalent bonds can form, is most likely shorter than  $R_C$  and could quite conceivably be  $\approx 2.64 \text{ \AA}$ .

An alternative explanation for the behavior of MnAs can be given without resorting to the supposition of interstitial atoms. The difference in effective number of spins between the ferromagnetic and the paramagnetic region could be attributed to a difference in the number of collective electrons. Because of the appreciable difference in unit cell size this may not be unreasonable. Since MnAs is near the border between the high-spin and low-spin state, the onset of reducing moment on cooling through  $120^\circ\text{C}$ , could be taken as evidence of either a transition from a high-spin ( $t_b^2 t_a^1 e^1$ ) to a low-spin ( $t_b^3 t_a^1 e^0$ ) state, or sufficient delocalization of the  $t_b$ -electrons to seriously alter the effective moment. In the first case, the structural distortion could be attributed to the formation of covalent bonds or directional bonding bands with the atoms at a distance of  $3.02 \text{ \AA}^o$ . In the

second case only bonding bands would be allowed. It is difficult to visualize exactly how, at 120°C either covalent bonds or a bonding band set in sharply between ions  $\approx 3.7 \overset{\circ}{\text{A}}$  apart. Perhaps the high-spin, low-spin explanation is more attractive from this point of view. It is even more difficult to visualize how they disappear precipitously at the first-order transformation.

It remains to explain the absence of ferromagnetism in the 4% Co alloy. According to the proposed d-level scheme, a  $\text{Co}^{+++}$  ion with six d-electrons when placed in an octahedral interstice will assume the structure  $t_b^3 t_a^1 e^2$ . The exchange interaction between  $d^4(\text{Mn}^{+++})$  ion and a  $d^6(\text{Co}^{+++})$  ion is more likely to be negative. If the net positive molecular field in MnAs is the result of highly competitive positive and negative interactions, it is quite conceivable that replacing a relatively small number of the positive interactions by negative ones could drastically reduce the positive surplus. Although, any numerical estimate is impossible, it seems reasonable that the temperature at which ferromagnetism would set in, could be lowered below the temperature of liquid nitrogen by a substitution of 4% Co ions.

In the foregoing discussion, two possible explanations have been given for the structural and magnetic phenomena occurring in MnAs, neither of which is entirely satisfactory. No attempt has been made to present a mechanism by which the first-order transformation occurs, or to explain the large negative thermal expansion coefficients encountered just below the first-order transformation. Although we rejected the model of Bean and Rodbell as applying to MnAs, there is no doubt that it gives an

extremely good account of the variation of cell volume with temperature in the low temperature region. Perhaps the reason for its failure, is that it is an isotropic model applied to an anisotropic substance, and were it possible to generalize it to this situation, it would prove entirely satisfactory.

### 3. Discussion of the Effects of Alloying on the Lattice Spacings

The results of Chapter III show that the substitution of solute atoms into the MnAs lattice produces little effect on the general features of the variation of lattice constants with temperature. To bring out any systematic variation, the results at a fixed temperature,  $-70^{\circ}\text{C}$ , were displayed on a graph of  $\underline{c}$  vs.  $\underline{a}$  in Fig. 3 · 13. Although a contraction of the lattice is found for each type of solute atom, in no case is it isotropic. The distance,  $\Delta c'$ , by which the points fall above or below the isotropic line is a measure of the anisotropic part of the distortion, favoring either  $\underline{c}$  or  $\underline{a}$ , which should be related to the way in which the d-levels of the solute atoms are occupied. The deviation from isotropic,  $\Delta c'$ , per % of solute atom, has been estimated from Fig. 3 · 13, and plotted in Fig. 4 · 5. A definite trend is observed. With the help of Table VIII we can explain, at least qualitatively the observed behavior. The d-level occupancy follows simply from the level scheme proposed in section 1 - B of this chapter.

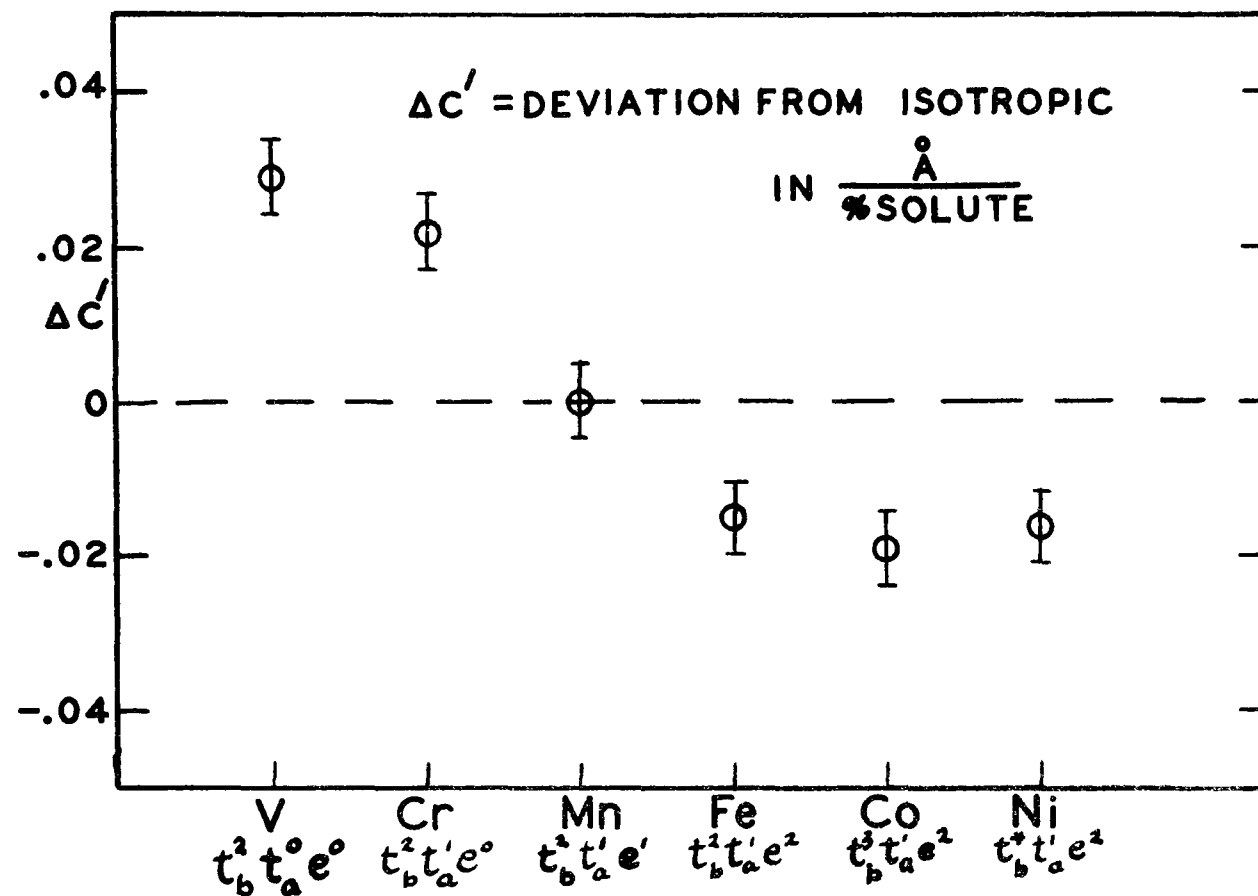


FIG 4.5

The deviation from isotropic distortion in MnAs at  $-70^\circ\text{C}$  for various solutes.

TABLE VIII

| Cation     | Occupancy of d-levels* |         |       |                                |
|------------|------------------------|---------|-------|--------------------------------|
| $V^{+++}$  | $t_b^2$                | $t_a^0$ | $e^0$ | d-level half-filled or less    |
| $Cr^{+++}$ | $t_b^2$                | $t_a^1$ | $e^0$ |                                |
| $Mn^{+++}$ | $t_b^2$                | $t_a^1$ | $e^1$ |                                |
| $Fe^{+++}$ | $t_b^2$                | $t_a^1$ | $e^2$ |                                |
| $Co^{+++}$ | $t_b^3$                | $t_a^1$ | $e^2$ | d-level more than half-filled. |
| $Ni^{+++}$ | $t_b^4$                | $t_a^1$ | $e^2$ |                                |

\*assuming high-spin state

Let us consider each solute atom in turn:

(i) Cr. The Cr ion has one less e-electron than Mn. In a regular octahedron the  $e_g$ -orbitals point directly at the anions. In MnAs, however, with  $c/a \approx 1.54$  the three  $e_g$  maxima project partly through the common face along the  $c$ -axis. Assuming there is some bonding due to the  $e_g$ -orbitals the removal of an e-electron would decrease the bonding causing a relative increase in  $c$ , as observed.

(ii) V. In going from Cr to V, a  $t_a$ -electron is lost. Presumably, there is bonding along the  $c$ -axis which is a maximum when there is exactly one  $t_a$ -electron per atom. Therefore the removal of a  $t_a$ -electron reduces the bonding strength leading to the observed further increase in  $\Delta c$ .

(iii) Fe. In going from Mn to Fe one e-electron is added. Since maximum strength occurs when there are 2 e-electron per atom, an increase in bonding along the c-axis is expected with a decrease in  $\Delta c'$  as observed.

(iv) Co. With Fe, the d-level is half-filled. In Co the extra electron goes to the  $t_b$ -orbital. The bonding in the basal plane must be small to begin with and the addition of a  $t_b$ -electron if it produces any effect at all, might lead to a decrease in bonding with an accompanying relative increase in a or a decrease in  $\Delta c'$ .

(v) Ni. Another  $t_b$ -electron is added and as described in the case of Co little change is expected.

Qualitatively, at least, the observed behavior of the distortions of the octahedral interstice in the ternary alloys is in accord with the d-level scheme proposed. The absolute variation of a and c independently is much more complex.

#### 4. The Effect of Alloying on the Paramagnetic Curie Temperature

The Curie temperature,  $\theta$ , is a measure of the sum of the various contributions to the molecular field influencing a particular ion. In MnAs the main contribution is the positive Mn - As - Mn interaction. Of lesser importance are the direct axial cation-cation interaction and possibly the direct basal cation-cation interaction both of which are negative. Any contribution due to interstitial ions is positive.

Indirect interactions between Mn and either Fe, Co or Ni are

believed to be negative and of the same order as Mn - As - Mn interactions. As was pointed out in the previous section, in the presence of highly competitive positive and negative interactions a relatively small concentration of negatively interacting solute could change the Curie point drastically. This seems to be born out in the results of Fig. 4 · 6 for Co, Ni and especially for Fe, where a 1% concentration of solute changes  $\theta$  by about 12%.

When V or Cr cations are substituted into the lattice their interactions are still positive but weaker because they have no e-electrons. In Fig. 4 · 6 the values for V and Cr may be compared with the dotted line which is calculated for simple dilution,  $\theta_x = \theta_0 (1 - x)$ , where  $x$  is the % solute.

#### 5. The Effect of Alloying on $p_{eff}$

The variation of  $p_{eff}$  with solute concentration is shown in Fig. 4 · 7 (Fig. 3 · 20 repeated). No obvious systematic behavior is observed. However, the change of  $p_{eff}$  with added Fe, for example, is many times greater than can be accounted for by simple substitutional considerations. Let us assume that the deviation of  $p_{eff}$  from 4.90 (4 spins), is due to delocalization of electrons. The strong dependence of  $p_{eff}$  on concentration can then be interpreted as a variation in the number of collective electrons. It is not too surprising that the number of collective electrons should depend in a complex way on the type of solute atom, especially if interstitial atoms are present.

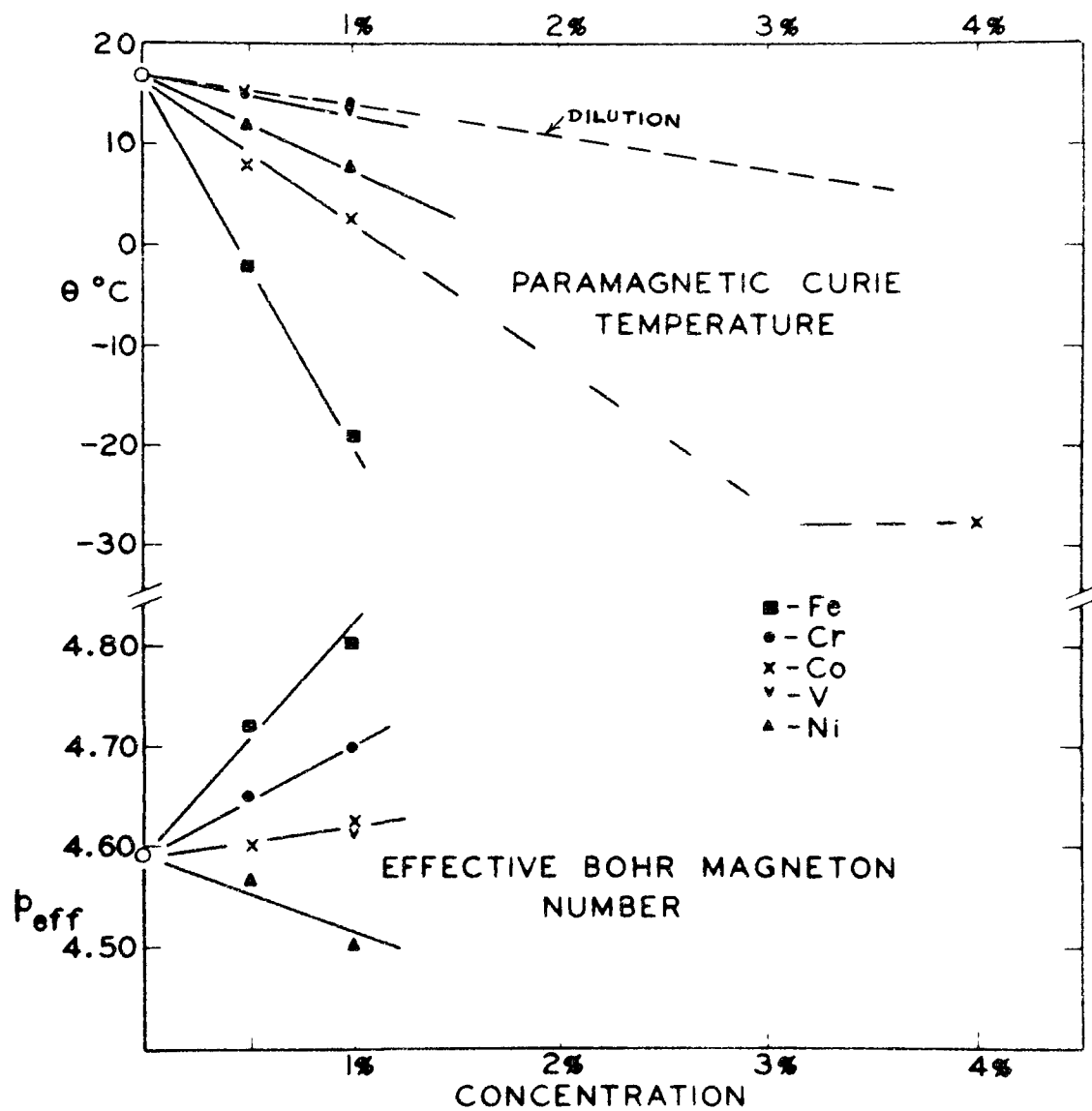


FIG. 4.6 and FIG. 4.7

## 6. The Effect of Alloying on the First-order Transformation Temperature

The addition of solutes to MnAs was found to generally lower the transformation temperature. In the cases of V and Cr the effect was small, whereas Fe, Co and Ni had a very marked effect. (See Fig. 3 · 23). However, since little is known about the means by which the covalent bonds, or bonding bands could disappear precipitously at the first-order transformation, it has been impossible to obtain any basic information from these data. Perhaps the only value of these measurements has been as a check on the homogeneity of some of the alloys. (See Table V, Chapter II).

## 7. Conclusions

Two possible explanations have been presented to account for some of the unusual properties of MnAs, in the process of which a number of conclusions were reached. A summary of the major points follows:-

- (i) The first-order transformation at  $\approx 40^{\circ}\text{C}$  is not necessarily associated with a change to ferromagnetism.
- (ii) In the region between  $40^{\circ}\text{C}$  and  $120^{\circ}\text{C}$  it was discovered that MnAs does not have the NiAs structure, but an orthorhombic distortion of it compatible with the MnP structure. Without this discovery, no explanation of the unusual magnetic behavior would have been possible.
- (iii) Two mechanisms have been suggested for the connection

between the structural distortion and the magnetic properties in the intermediate region. One depends on the formation of covalent bonds about interstitial (trigonal-bipyramidal) atoms. The other depends on the transition of Mn atoms from the high-spin to the low-spin state, or rapid delocalization of d-electrons accompanied by the formation of covalent bonds or bonding bands in the basal plane. Weaknesses in both arguments have been pointed out.

(iv) A number of the properties of ternary alloys were shown to be consistent with the d-level splitting proposed in the model, assuming that the Mn atoms are in the high-spin state (below 40°C and above 120°C) and provided that some collective electrons are present.

(v) The concept of a critical distance in determining whether electrons should be considered localized or collective, was found to be of great value in understanding the properties of MnAs and its ternary alloys.

APPENDIX I - STRUCTURE FACTORS FOR  
REFLECTIONS FROM HEXAGONAL MnAs.

| REFLECTION | STRUCTURE FACTOR                  |
|------------|-----------------------------------|
| 001        | 0 (ABSENT)                        |
| 002        | $2 f(\text{Mn}) - 2 f(\text{As})$ |
| 003        | 0                                 |
| 004        | $2 f(\text{Mn}) + 2 f(\text{As})$ |
| 005        | 0                                 |
| 006        | $2 f(\text{Mn}) - 2 f(\text{As})$ |
| 007        | 0                                 |
| 100        | $2 f(\text{Mn}) - f(\text{As})$   |
| 101        | $0 - \sqrt{3} f(\text{As})$       |
| 102        | $2 f(\text{Mn}) + f(\text{As})$   |
| 103        | $0 + \sqrt{3} f(\text{As})$       |
| 104        | $2 f(\text{Mn}) - f(\text{As})$   |
| 105        | $0 - \sqrt{3} f(\text{As})$       |
| 106        | $2 f(\text{Mn}) + f(\text{As})$   |
| 107        | $0 + \sqrt{3} f(\text{As})$       |
| 110        | $2 f(\text{Mn}) + 2 f(\text{As})$ |
| 111        | 0                                 |
| 112        | $2 f(\text{Mn}) - 2 f(\text{As})$ |
| 113        | 0                                 |
| 114        | $2 f(\text{Mn}) + 2 f(\text{As})$ |
| 115        | 0                                 |
| 116        | $2 f(\text{Mn}) - 2 f(\text{As})$ |

| REFLECTION | STRUCTURE FACTOR                  |
|------------|-----------------------------------|
| 117        | 0                                 |
| 200        | $2 f(\text{Mn}) - f(\text{As})$   |
| 201        | $0 + \sqrt{3} f(\text{As})$       |
| 202        | $2 f(\text{Mn}) + f(\text{As})$   |
| 203        | $0 - \sqrt{3} f(\text{As})$       |
| 204        | $2 f(\text{Mn}) - f(\text{As})$   |
| 205        | $0 + \sqrt{3} f(\text{As})$       |
| 206        | $2 f(\text{Mn}) + f(\text{As})$   |
| 207        | $0 - \sqrt{3} f(\text{As})$       |
| 120        | $2 f(\text{Mn}) - f(\text{As})$   |
| 121        | $0 + \sqrt{3} f(\text{As})$       |
| 122        | $2 f(\text{Mn}) + f(\text{As})$   |
| 123        | $0 - \sqrt{3} f(\text{As})$       |
| 124        | $2 f(\text{Mn}) - f(\text{As})$   |
| 125        | $0 + \sqrt{3} f(\text{As})$       |
| 126        | $2 f(\text{Mn}) + f(\text{As})$   |
| 127        | $0 - \sqrt{3} f(\text{As})$       |
| 220        | $2 f(\text{Mn}) + 2 f(\text{As})$ |
| 221        | 0                                 |
| 222        | $2 f(\text{Mn}) - 2 f(\text{As})$ |
| 223        | 0                                 |
| 224        | $2 f(\text{Mn}) + 2 f(\text{As})$ |
| 225        | 0                                 |
| 226        | $2 f(\text{Mn}) - 2 f(\text{As})$ |
| 227        | 0                                 |

| REFLECTION | STRUCTURE FACTOR                  |
|------------|-----------------------------------|
| 300        | $2 f(\text{Mn}) + 2 f(\text{As})$ |
| 301        | 0                                 |
| 302        | $2 f(\text{Mn}) - 2 f(\text{As})$ |
| 303        | 0                                 |
| 304        | $2 f(\text{Mn}) + 2 f(\text{As})$ |
| 305        | 0                                 |
| 306        | $2 f(\text{Mn}) - 2 f(\text{As})$ |
| 307        | 0                                 |
| 130        | $2 f(\text{Mn}) - f(\text{As})$   |
| 131        | $0 + \sqrt{3} f(\text{As})$       |
| 132        | $2 f(\text{Mn}) + f(\text{As})$   |
| 133        | $0 + \sqrt{3} f(\text{As})$       |
| 134        | $2 f(\text{Mn}) - f(\text{As})$   |
| 135        | $0 - \sqrt{3} f(\text{As})$       |
| 136        | $2 f(\text{Mn}) + f(\text{As})$   |
| 137        | $0 + \sqrt{3} f(\text{As})$       |
| 400        | $2 f(\text{Mn}) - f(\text{As})$   |
| 401        | $0 - \sqrt{3} f(\text{As})$       |
| 402        | $2 f(\text{Mn}) + f(\text{As})$   |
| 403        | $0 + \sqrt{3} f(\text{As})$       |
| 404        | $2 f(\text{Mn}) - f(\text{As})$   |
| 405        | $0 - \sqrt{3} f(\text{As})$       |

## REFERENCES

- ADACHI, K. 1961. J. Phys. Soc. Japan, 16, 2187.
- ANDERSON, P.W. 1950. Phys. Rev. 79, 350.
- BACON, G.E. and STREET, R. 1955. Nature, 175, 518.
- BASINSKI, Z.S. and PEARSON, W.B. 1958. Can. J. Phys. 36, 1017.
- BEAN, C.P. and RODBELL, D.S. 1962. Phys. Rev. 126, 104.
- COHEN, M.U. 1935. Rev. Sci. Instrum. 6, 68.
- COHEN, M.U. 1936. Rev. Sci. Instrum. 7, 155.
- COHEN, M.U. 1936. Z. Krist. A94, 288.
- DAVY, N. 1942. Phil. Mag. 33, 575.
- FISCHER, G. and PEARSON, W.B. 1958. Can. J. Phys. 36, 1010.
- GOODENOUGH, J.B. 1960. J. Appl. Phys. Supp. to Vol. 31.
- GOODENOUGH, J.B. 1960. Phys. Rev. 117, 1442.
- GOODENOUGH, J.B. 1963. Magnetism and the Chemical Bond  
(Interscience).
- GUILLAUD, C. 1951. J. Phys. Rad. 12, 223.
- HEDGCOCK, F.T. and HUNT, F. 1956. Rev. Sci. Instr. 27, 970.
- HENRY, W.G. 1957. Private communication.
- HULLIGER, F. 1963. Phys. Letters, 4, 282.
- KASPER, J.S. 1961. Private communication.
- KORNELSEN, R.O. 1961. Can. J. Phys. 39, 1728.
- KRAMERS, H.A. 1934. Physica, 1, 182.
- MEYER, A.J.P. and TAGLIANG, P. 1953. J. Phys. Radium, 14, 82.
- NEEL, L. 1936. C.R. Acad. Sci. Paris, 203, 304.
- NELSON, J.B. and RILEY, D.P. 1945. Proc. Phys. Soc. 57, 160.

- NIX, F.C. and MacNAIR, D. 1941. Phys. Rev. 60, 597.
- OVERHAUSER, A.W. 1959. Phys. Rev. Let. 3, 414.
- ROBERTS, B.W. 1956. J. Metals, 8, 1407.
- ROBERTS, B.W. 1956. Phys. Rev. 104, 607.
- RODBELL, D.S. 1957. Private communication.
- SELWOOD, P.W. 1956. Magnetochemistry,  
(Interscience Publishers Inc., New York)
- SNOW, A.I. 1953. Rev. Mod. Phys. 25, 127.
- SUCKSMITH, W. 1929. Phil Mag. 8, 158.
- SUCKSMITH, W. and PEARSE, R.R. 1938. Proc. Roy. Soc. A176, 189.
- TAYLOR, A. and SINCLAIR, H. 1945. Proc. Phys. Soc. 57, 108.
- TAYLOR, A. and FLOYD, R.W. 1950. Acta Cryst. 3, 285.
- TAYLOR, A. 1952. Introduction to X-ray Metallography.  
(Chapman and Hall) p.374.
- VAN VLECK, J.H. Electric and Magnetic Susceptibilities.  
(Oxford University Press) p.303.
- WILLIS, B.T.M. and ROOKSBY, H.P. 1954. Proc. Phys. Soc. B, 67, 290.
- WILSON, R.H. and KASPER, J.S. 1961. American Crystallographic  
Assoc. 1961 Annual Meeting. Abstract M8.
- YOSHIDA, K. 1957 Phys. Rev. 106, 893.
- YOSHIMORI, A. 1959. J. Phys. Soc. Japan, 14, 807
- ZENER, C. 1952. Phys. Rev. 85, 324.
- ZENER, C. and HEIKES, R.R. 1953. Rev. Mod. Phys. 25, 191.

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2. The Physical Aspects of Treatment of Cancer by 22 MeV X-rays.  
H.E. JOHNS, E.K. DARBY and R.O. KORNELSEN, 1951.  
Brit. Journ. Rad. 24, 355.
3. Depth Dose Data, 150 kVp to 400 kVp. H.E. JOHNS, S.O. FEDORUK,  
R.O. KORNELSEN, E.R. EPP and E.K. DARBY, 1952.  
Brit. Journ. Rad. 25, 542.
4. A Method to Determine the Shielding Effect in Multiple Radium  
Sources. R.O. KORNELSEN, 1952. Journ. Can. Assoc. Rad. 3, 67.

5. Tumour Dose in the Chest Cavity. R.O. KORNELSEN, 1954.  
Brit. Journ. Rad. 27, 289.
6. Predetermined Dose Distribution for Cobalt <sup>60</sup> Circumaxial  
Rotation. R.O. KORNELSEN, 1957. Journ. Can. Assoc. Rad. 8, 42.
7. Radioactive Gold Grains Replacing Radon Seeds in Radiation  
Therapy. T.G. STODDART and R.O. KORNELSEN.  
The Ontario Medical Review, November 1959.
8. The Structure of Manganese Arsenide between 40°C and 120°C.  
R.O. KORNELSEN, 1961. Can. J. Phys. 39, 1728.