TEMPERATURE AND FIELD DEPENDENCE OF THE WEAK FERROMAGNETIC MOMENT OF HEMATITE

A Thesis
Submitted to
the Faculty of Graduate Studies
University of Manitoba

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Geoffrey W. Dean
May, 1970

THE UNIVERSITY OF MANITOBA
LIBRARY

ACKNOWLEDGEMENTS

The author wishes to thank his supervisor, Dr. C. W. Searle for his continuous advice and encouragement.

He wishes to thank his fellow graduate student, John Eaton, for many rewarding discussions and helpful comments.

The support of the National Research Council of Canada is gratefully acknowledged.

TABLE OF CONTENTS

LIST OF FIGURES

INTRODUCTION

Hematite (α-Fe_2O_3) is basically a uniaxial antiferromagnet with interesting and unusual properties. At temperatures below 262.7°K the antiferromagnetic axis is parallel to the [111] direction (Shull et al., 1951). At this temperature a transformation occurs whereupon the antiferromagnetic axis rotates into the (111) plane. This transition is known as the Morin transition and the temperature at which it occurs is referred to as T_M (Honda and Sone, 1914; Charlesworth and Long, 1938; Morin, 1950).

It has been shown as a result of many measurements on hematite that there is a weak spontaneous moment within the basal plane (Smith, 1916; Chevallier, 1951; Guillaud, 1951; Neel and Pauthenet, 1952; Neel, 1953; Lin, 1959, 1960, 1961, 1962; Tasaki et al., 1962; Iwata et al., 1962; Tasaki and Iida, 1963). This is now known to be due to a canting of the antiferromagnetic sublattices arising from a term $\beta(l_x m_y - l_y m_x)$, in the expression for the free energy where

$\bar{m} = \bar{s}_1 + \bar{s}_2 + \bar{s}_3 + \bar{s}_4$,

$\bar{l} = \bar{s}_1 - \bar{s}_2 - \bar{s}_3 + \bar{s}_4$,

β is a constant,

$\bar{s}_1$, $\bar{s}_2$, $\bar{s}_3$ and $\bar{s}_4$ are the average values of the spins of the four magnetic ions (Dzialoshinskii, 1957; Aharoni et al., 1962).

This transition from the purely antiferromagnetic state to the weak ferromagnetic state is field dependent. A magnetic field applied along the [111] direction induces the well known "spin-flop" transition (Néel, 1936; Nagamiya et al., 1955; Morrish, 1965) which has been experimentally verified (Poulis et al., 1951; Gorter, 1953; Besser and Morrish, 1964; Foner and Williamson, 1965; Hirone, 1965). A field applied in the (111) plane will also induce the Morin transition (Kaczér and Shalnikova, 1964; Flanders and Shtrikman, 1965).

In both cases as the field increases the temperature of the Morin transition decreases, though there is a difference in the temperature dependence (Foner and Shapira, 1969).

Microscopically the Dzialoshinskii canting term was expressed by Moriya (1960) in the free energy expression as

$$\bar{d} \cdot (\bar{s}_1 \times \bar{s}_2)$$

where $\bar{d}$ is a vector parallel to the [111] direction and $\bar{s}_1$ and $\bar{s}_2$ are the spin angular momenta of the two ions under consideration. It has been postulated by Searle (1968) that $\bar{d}$ is allowed to point in either direction along the [111] axis; i.e. the expression should be

$$\pm \bar{d} \cdot (\bar{s}_1 \times \bar{s}_2).$$

In that case the macroscopic $\bar{D}$ vector must be a combination of the microscopic $\bar{d}$ vectors and would then exist because of a long range cooperative effect between the vectors leading to a spontaneous alignment of the microscopic $\bar{d}$ vectors.

$\bar{D}$ would therefore be replaced by $\langle \bar{D} \rangle = \bar{D}f$, f being an appropriate statistical distribution function.

Using this assumption it was attempted, using molecular field theory, to describe theoretically the Morin transition when a field is applied in the (111) plane.

The field induced transition was experimentally studied and the results compared with theory.

The temperature dependence of the weak spontaneous moment in the range of room temperature to T_N was also studied in an effort to elucidate the nature of the vector $\bar{D}$. (T_N is the temperature at which the weak moment disappears, see Conclusions).

CHAPTER I

Crystal and Magnetic Structure of Hematite

The crystal structure of hematite was established from X-ray data on natural single crystals (Pauling and Hendricks, 1925) and has been refined slightly by Blake et al. (1965). Hematite is the stable rhombohedral form of ferric sesquioxide but there is also a cubic spinel form, γ-Fe_2O_3 which transforms irreversibly to the α-phase at high temperatures (Mason, 1943). The unit cell of hematite is a rhombohedron with edge length 5.4243 A.U. and rhombohedral angle $55^{\circ}17.5'$. There are two molecules and hence four magnetic ions in each unit cell. The iron ions lie along the [111] direction, i.e. the trigonal axis of the crystal. Each iron ion is surrounded by six oxygen ions, one at each corner of a distorted octahedron. Three of the oxygen ions are slightly nearer to the central iron ion than the other three.

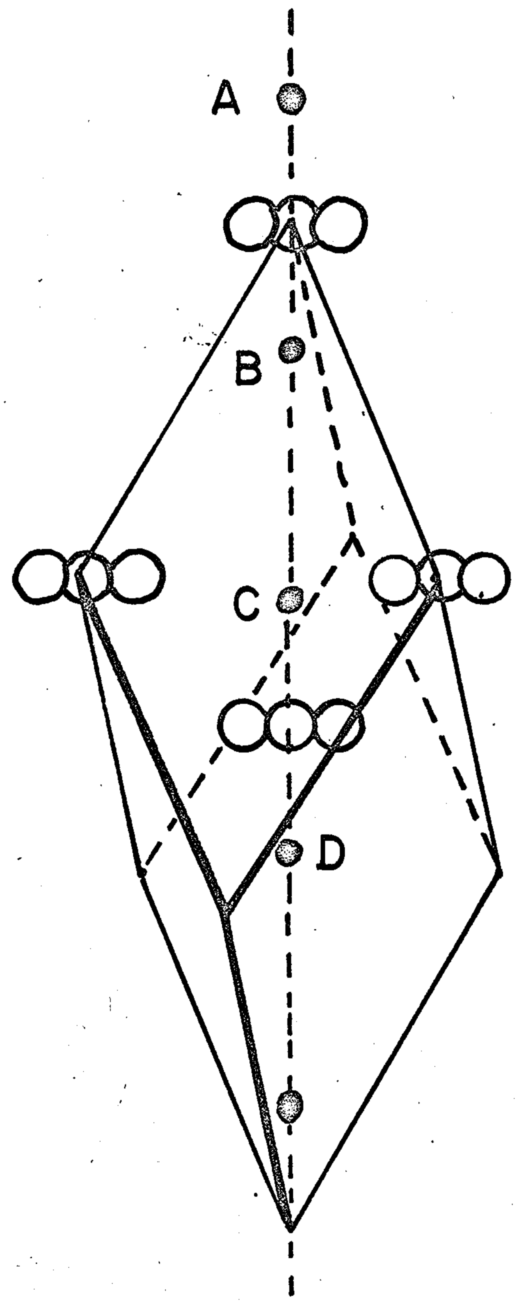
The structure is shown in Figure 1.

The disposition of the spin system was resolved by Shull et al. (1951). Neutron diffraction patterns of a powdered sample were taken over a range of temperatures from $80^{\circ}K$ to $1000^{\circ}K$ and indicated a basic antiferromagnetic structure. However there was some difference with temperature in structural detail. Shull also demonstrated that the magnetic unit cell is the same size as the chemical unit cell and that there are four

Fig. 1

Crystal Structure of Hematite.

Dark circles are iron ions and open circles are oxygen ions.


A
B
C
D

uniquely positioned Fe ions in the cell, shown as A, B, C and D in Fig. 1.

There are three possible antiferromagnetic arrangements of relative spin orientations for these four atoms. They are as follows:-

a) + - - +
b) + + - -
c) + - + -

Here a) indicates that ions A and D have parallel orientation, say upwards, while B and C both have antiparallel arrangements with respect to A and D and therefore downwards. The magnetic structure factor for c) vanishes in the (111) and (100) reflections and hence is immediately excluded since they were seen. Finite intensities however are predicted for a) and b). The observed intensities depend not only on the model but also on the orientation of the moments in the model with respect to the diffracting planes. For the orientation within the unit cell, the three most reasonable possibilities are

I) the moments directed along the unit cell edges.

II) the moments directed along the space diagonal of the unit cell and are thus perpendicular to the (111) sheets in the lattice.

III) the moments are in the (111) sheets and directed towards one of the three nearest neighbours in the sheet.

From the results of Shull's neutron diffraction data, i.e. by comparing data obtained in experiment with calculated structure factors, it was seen that the room temperature data suggested a) with orientation III as being correct, while at low temperatures the suggested structure is that of a) with orientation II.

Shull therefore proposed that the low temperature data could be accounted for as a reorientation of the magnetic moment alignment from within the (111) sheets to one perpendicular to these sheets when the temperature is lowered.

This structure has since been confirmed by further neutron diffraction experiments (Nathans et al., 1964).

Theories of the Origin of Weak Ferromagnetism

Neel (1949, 1953) attempted to explain the phenomenon of weak ferromagnetism in hematite as a "parasitic" ferromagnetism due to inclusions of magnetite (Fe_3O_4) lying in (111) sheets so that the resultant moment was in the (111) plane. However this model could not account for the disappearance of the weak moment below the Morin temperature. Li (1956) ascribed the moment to the presence of antiferromagnetic domain walls which were stabilized by inhomogeneities and imperfections. However it has been well established that the moment is insensitive to doping (Tasaki and Iida, 1961; Flanders and Remerka, 1965) and this would rule out Li's hypothesis.

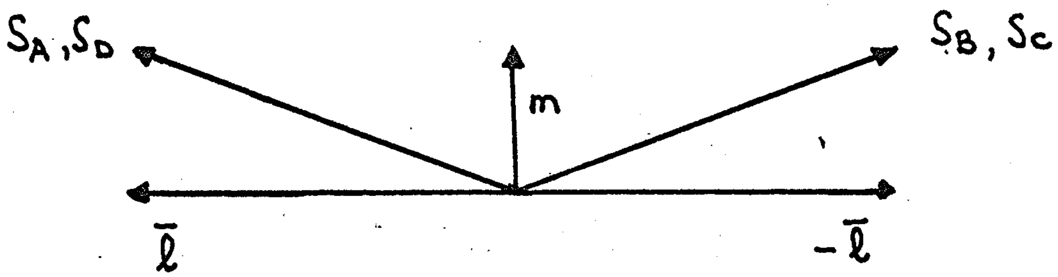
In a series of experiments Tasaki and his coworkers showed that weak ferromagnetism is most likely an intrinsic property of the crystal (Tasaki et al., 1960; Tasaki and Iida, 1961, 1963). A systematic study was made of the influence of oxidation and reduction on the "parasitic" moment of pure and doped hematite. They were always able to analyse their results in terms of an isotropic part and an anisotropic part (after Néel, 1953). The isotropic part remained after cooling below -15°C whereas the anisotropic part disappeared. Since the isotropic part largely changed with the process of oxidation or reduction and became almost zero by proper heat treatment this part was almost certainly due to the non stoichiometry of the Fe_2O_3. The anisotropic part did not change by these treatments and therefore it would seem to be an intrinsic property of the material.

Furthermore Aharoni et al. (1962) using differential thermal analysis measurements found that of all the theories for the existence of the weak moment only that of Dzialoshinskii would fit the experimental data.

Dzialoshinskii's explanation (1957) was proposed on the basis of symmetry arguments (Birss, 1964; Tavger and Zaitsev, 1956) and on the use of the theory of phase transitions (Landau, 1937; Belov, 1965; Sirota et al., 1966). He suggests that weak ferromagnetism can arise in an antiferromagnetic lattice by a canting of the spins towards one another (illustrated in Fig. 2), whenever the canting does not change the symmetry. In other

Fig. 2

Canting of the sublattices producing weak moment



S_A, S_D
m
S_B, S_C
$\bar{l}$
$-\bar{l}$

words, a spontaneous magnetic moment may exist only when it is invariant under the action of all of the symmetry transformations of the corresponding group (Tinkham, 1965). In hematite, besides the paramagnetic phase above T_N, there are two states. State 1 has the spins along the [111] direction whilst in state 2 the spins are perpendicular to it. Dzialoshinskii showed that the weak moment is allowed in state 2 and that it is not allowed in state 1.

The next step was to write down the free energy of the system in terms of the spin variables, i.e.

$$\bar{m} = \bar{s}_1 + \bar{s}_2 + \bar{s}_3 + \bar{s}_4$$
$$\bar{l}_1 = \bar{s}_1 - \bar{s}_2 - \bar{s}_3 + \bar{s}_4$$
$$\bar{l}_2 = \bar{s}_1 - \bar{s}_2 + \bar{s}_3 - \bar{s}_4$$
$$\bar{l}_3 = \bar{s}_1 + \bar{s}_2 - \bar{s}_3 - \bar{s}_4$$

$\bar{s}_1$, $\bar{s}_2$, $\bar{s}_3$, $\bar{s}_4$ are the average values of the spins of the four magnetic ions and $\bar{m}$ is the average magnetic moment of the unit cell. Dzialoshinskii showed that the free energy of the system was lower when a canted arrangement was considered than for a purely colinear antiferromagnetic arrangement of the sublattice moments.

This term is expressed by Dzialoshinskii as

$$\beta(l_{1x}m_y - l_{1y}m_x),$$

Where β is a constant and the coordinates refer to a rectangular system with the z axis along the trigonal axis.

The theory of Dzialoshinskii is however phenomenological.

It was not shown how the interaction causing the weak moment arose or how the magnitude of the weak moment could be calculated. Moriya (1960a, 1960b, 1963) demonstrated that the interaction is due to an anisotropic super exchange interaction. He extended the formalism developed by Anderson (1950) in a theory of super exchange to include the effects of spin orbit coupling.

The mechanism of super exchange was first proposed by Kramers (1934) in an effort to explain the magnetic behaviour of paramagnetic salts. Bizette (1946) and Néel (1948) emphasized the importance of this mechanism by which magnetic ions interact via a non magnetic ion in antiferromagnetic substances. Anderson (1950) presented a detailed treatment and clarified the mechanism. He considered one oxygen ion and two adjacent magnetic ions. Also two electrons occupy the same p-orbital of the O^{--} ion and one electron is in each d-orbital of the magnetic ions. The two electrons in O^{--} form a singlet state so that there will be no exchange coupling between magnetic ions M_1 and M_2. However the possibility exists of one of the two electrons of the O^{--} ion being transferred to one of the two magnetic ions, say M_1, and occupying its s- or d-orbital. In this excited state, the unpaired electron left in O^{--} can couple with the electron of the other magnetic ion M_2. There should also be a strong coupling between the electron transferred to M_1 and the original electron in M_1. The two electrons originally belonging to the oxygen ion have opposite spins, so that there will appear an indirect spin coupling between M_1 and M_2 through this excited state. Gilleo (1957) applied the super exchange mechanism to account for a calculation of the exchange energy in hematite.

In Moriya's development the most general form of the spin-spin coupling between two spins $\bar{s}_1$ and $\bar{s}_2$ is written as

$$V_{12} = \bar{s}_1 \cdot k_s \cdot \bar{s}_2 + \bar{s}_1 \cdot k_A \cdot \bar{s}_2$$

k_s and k_A represent symmetrical and antisymmetrical tensors respectively. Thus the first term is invariant under the interchange of the two spins, while the second term changes sign. The symmetrical part of the spin coupling determines the most favorable orientation of the ordered spins, but does not give rise to the canting of the spins in two sublattice antiferromagnetic materials. The antisymmetrical part of the spin coupling is given by an expression of the form

$\bar{d} \cdot (\bar{s}_1 \times \bar{s}_2)$, $\bar{d}$ is a vector and $\bar{s}_1$ and $\bar{s}_2$ are the spin angular momenta of the ions on the two sublattices. It will be shown below that $\bar{d}$ is parallel to the [111] direction. This type of coupling can give rise to canting of the spins because the coupling energy is at a minimum when the two spins are perpendicular to each other. (It is this term which corresponds to the one developed by Dzialoshinskii, i.e. $\beta(l_{1x}m_y - l_{1y}m_x)$.)

Furthermore Moriya showed that the magnitude of $\bar{d}$ is $\approx \frac{\Delta g}{g} J$ where g is the gyromagnetic tensor and Δg is the deviation from the value for a free electron (Bogle and Symmons, 1959). J is the isotropic super exchange coupling constant.

The coupling between two ions 1 and 2 located at the points A and B in a crystal is considered. The following rules are used to determine the direction of $\bar{d}$ (Birss, 1964; van der Lugt, 1965):

(i) When a centre of inversion is located at a point halfway between A and B,

$$\bar{d} = 0.$$

(ii) When a mirror plane perpendicular to AB bisects AB,

$\bar{d} \parallel$ mirror plane.

(iii) When there is a mirror plane including A and B,

$d \perp$ mirror plane.

(iv) When a twofold rotation axis perpendicular to AB passes through the midpoint of AB,

$d \perp$ two fold axis.

(v) When there is an n-fold axis ($n \geqslant 2$) along AB,

$d \parallel AB$.

α-Fe_2O_3 has a corundum type crystal structure and the space group is D_{3d}^6 (Bertaut, 1958). The symmetry elements of the group are E, $2C_3$, $3U_2$, I, $2S_6$, $3\sigma_d$, C_3 denotes a vertical threefold axis, U_2 a horizontal twofold axis, σ_d a vertical symmetry plane, S_6 a sixfold rotation-reflection axis and I the operation of inversion. Because of the threefold rotation axis C_3, $\bar{d}$ must be parallel to the trigonal axis ([111]) for any pair of ions, i.e. in α-Fe_2O_3 an Fe^{3+}-Fe^{3+} pair. As there are inversion centres at the midpoints on the lines containing ions A and D and B and C, there is no antisymmetrical coupling between ions A and D or B and C. The couplings between A and B and A and C must be equal but of the opposite sign to those between C and D and B and D, respectively, because of the glide plane.

Since the spin arrangements in α-Fe_2O_3 are such that $\bar{s}_1 \parallel \bar{s}_4$ and $\bar{s}_2 \parallel \bar{s}_3$ $\bar{d} \ddagger 0$ for these pairs and lies along the [111] direction.

Thus a firm ground has been given to the mechanism of weak ferromagnetism first proposed by Dzialoshinskii. It is no longer a phenomenological model but is a real effect established theoretically. Though there may be effects contributed by chemical impurities or structural defects, this mechanism always exists as an intrinsic property of the crystal.

CHAPTER II

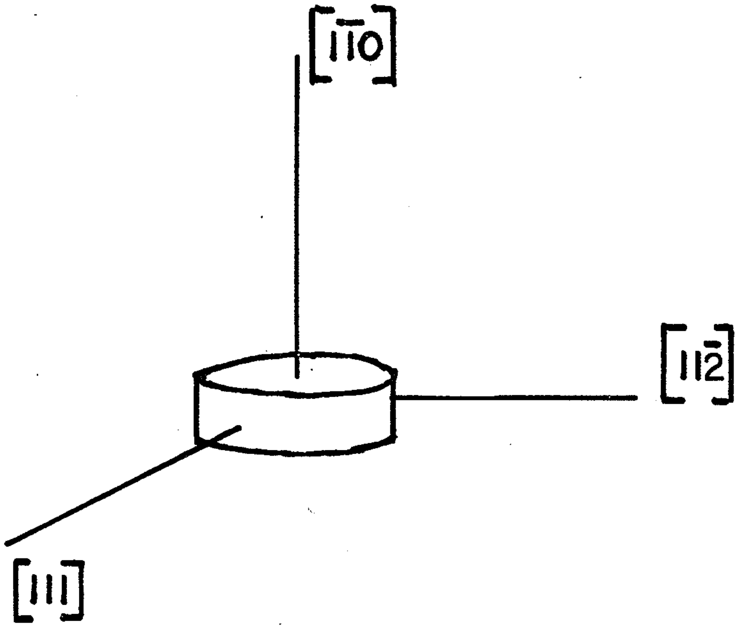
EXPERIMENTAL TECHNIQUE

The crystal on which the measurements were made was prepared in the laboratory by the Bi_2O_3 flux technique (Curry et al., 1965). 240 gm of Bi_2O_3 and 140 gm of Fe_2O_3 were loaded into a 220 cc platinum crucible. This was heated for two hours at 1320°C. It was then cooled at an average rate of 1°/hour between 1320°C and 900°C. The power was then turned off and the furnace left to cool overnight.

The crystal was further prepared by means of an ultrasonic grinder (Raytheon) and a diamond saw (Micro-Matic). After orienting the crystal by X-rays, using the back reflection technique (Besser, 1965), the crystal was cut into a disc 3 mm thick with principal axis perpendicular to the $(1\bar{1}0)$ plane. The section was then made into a disc with $(1\bar{1}0)$ faces by means of an ultrasonic grinding apparatus. The diameter of the disc was 4.5 mm and the final mass was approximately 200 mg. The $(1\bar{1}0)$ face was chosen so that measurements could be made along the $[111]$ direction and also in the (111) plane by rotating about the $[1\bar{1}0]$ direction. The $[11\bar{1}]$ direction is a direction within the basal plane (Fig. 3). It was not important which direction in the basal plane was chosen because the in plane anisotropies were neglected. The effective field due to magneto crystalline anisotropy is of the order of 10 Oe compared

Fig. 3

Relation of sample to crystal directions.


[1̄1̄0]
[112̄]
[111]

to the weak moment (Besser et al., 1967). The sample was also annealed so that anisotropies due to random strains could be neglected.

Measurements of the magnetization were made using a vibrating sample magnetometer designed by Foner (1959) and manufactured commercially (P.A.R. Ltd.).

The sample is fastened to a vibrating sample holder which moves sinusoidally along the z direction (Fig. 4) with a frequency of 82 cps. This motion induces a current in two pickup coils attached to the magnet pole faces. The current induced is proportional to the magnetization of the sample and also on the mass of the sample. The current is amplified and compared with a reference signal derived from the sample holders motion. The measurements are thus made insensitive to changes of vibration amplitude, vibration frequency, amplifier gain or amplifier linearity. The measurements are made insensitive to the exact sample position by suitable positioning of the coils and of the sample holder. The sample is first centrally positioned between the coils by visual inspection. The sample is then moved along the z axis for maximum output, it is then translated along the x direction for a minimum output and then along the y direction for maximum output. This procedure is then repeated until the three signals agree. The sample is then located at a saddle point and the output signal is independent of small displacements of

Fig. 4a

Relation of coordinate system to magnet pole faces. Origin is at the centroid.

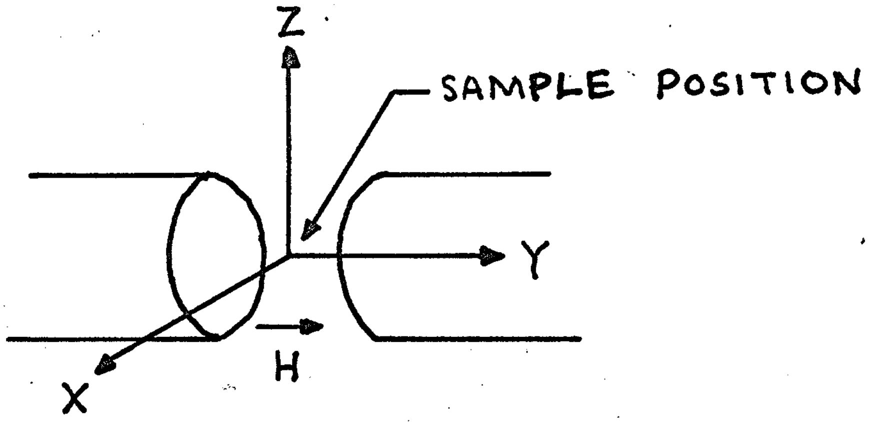
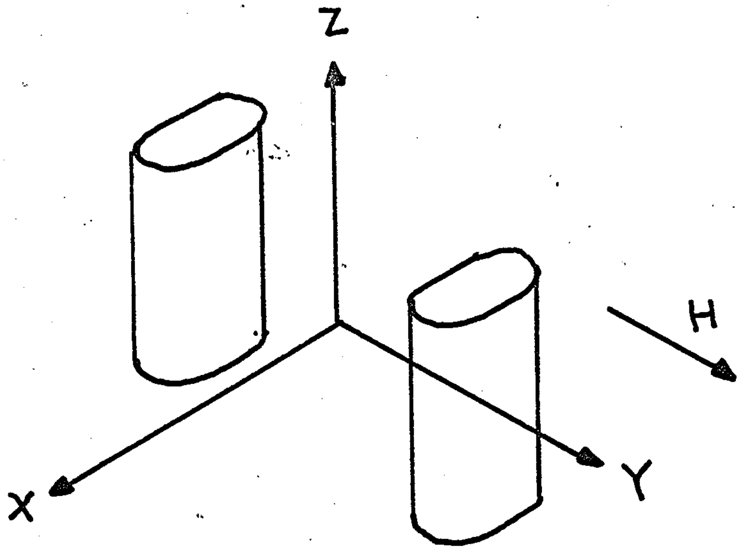

Z
SAMPLE POSITION
Y
H
X

Fig. 4b

Relation of coordinate system to pick up coils.


Z
H
X
Y

Leaf 15 omitted in page numbering.

the sample in any direction.

The system was calibrated by taking measurements of the magnetization of a sphere of spectroscopically pure nickel. The magnetization of which is known to be 55.07 emu/g (Arajs and Dummyre, 1967). The demagnetizing field of the hematite sample was approximately 10 Oe. It was therefore neglected as was the demagnetizing field of the nickel sample. The error introduced was less than ½%.

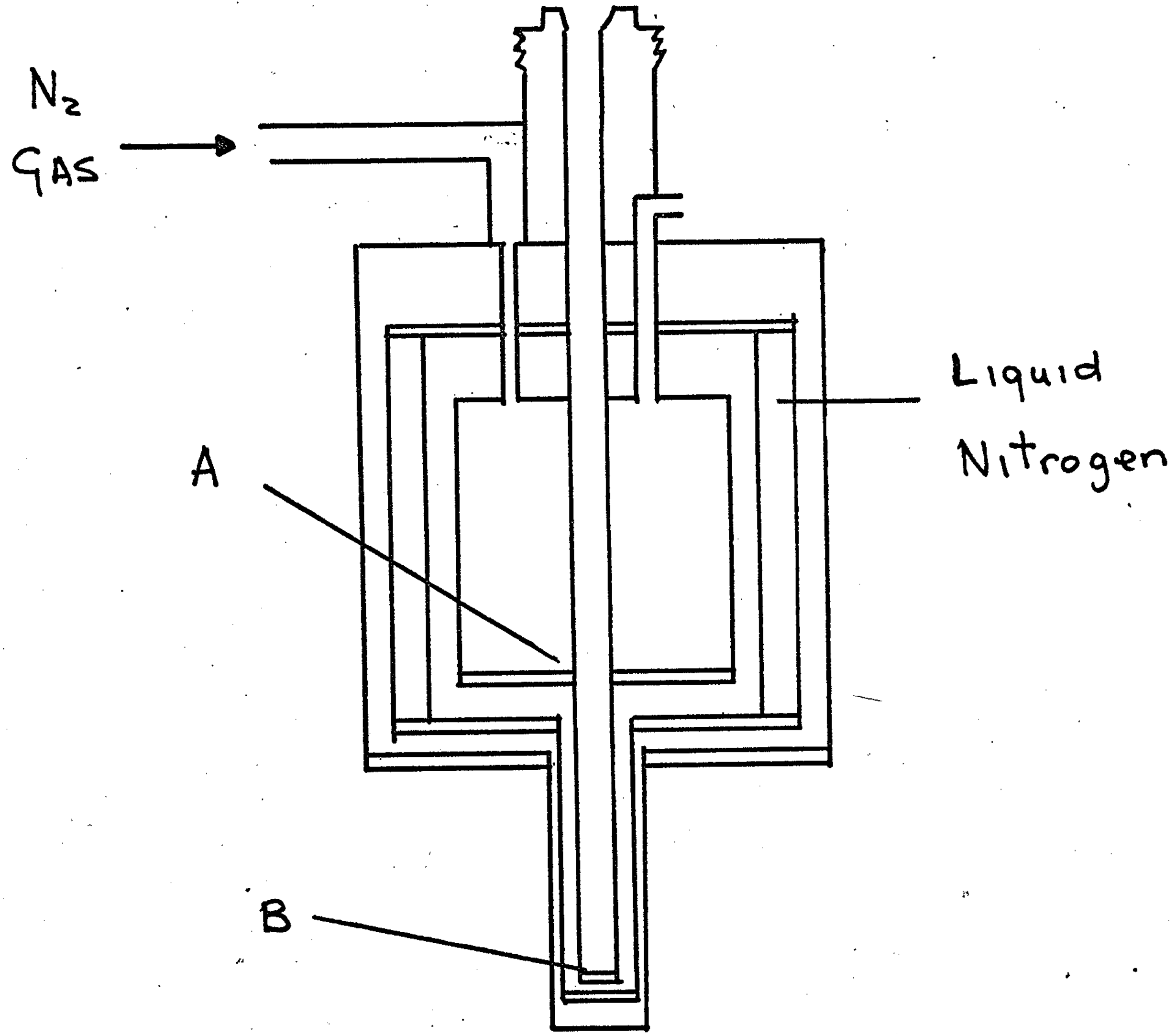
During the course of the experiments the whole calibration procedure was repeated several times to eliminate any systematic error.

The magnetic field was supplied by an electromagnet (Magnion). The measurements were made with a rotating coil gauss meter giving a reading accurate to ± 1%.

The low temperature measurements were made using a liquid helium dewar (Andonian). The coolant used throughout was liquid nitrogen. A technique was developed by means of which the temperature was stabilized to less than 1/5°C. This involved passing nitrogen gas through the inner chamber and adjusting the flow rate via a valve at the point A and through valve near B past the sample, whilst keeping the outer chamber full of liquid nitrogen (Fig. 5). The temperature was measured by a copper-constantan thermocouple directly in contact with the sample. The cold junction of the thermocouple was attached to a block of copper frozen in ice.

Fig. 5

Schematic of Dewar


N_2
GAS
Liquid
Nitrogen
A
B

The ice was then immersed in a freezing mixture of ice and water. The cold junction was thus constant at 0 + 0.1°C.

The high temperature measurements were made using a furnace manufactured to be compatible with the magnetometer facility (P.A.R.). A sample holder was made out of a quartz tube. The sample was affixed by using a boron nitride paste. The moisture evaporated and left a fragile joint which withstood the required temperatures.

The thermocouple for the high temperature measurements was a chromel-alumel one. There was no insulation on the wire due to the high temperatures to be considered and it was thus impossible to mount the thermocouple junction on the sample. However the furnace was provided with a thermocouple embedded in the jacket. This was the thermocouple used in the experiments. It was calibrated by a chromel-alumel thermocouple made in the laboratory which itself was calibrated using the fixed points of ice and molten zinc. Again the cold junction was a freezing mixture of ice and water.

The calibrated thermocouple was then placed in exactly the same position the sample was to occupy and the furnace then runs slowly up through the temperature range several times. The thermocouples were then compared and thus the furnace thermocouple was calibrated.

During the time that was necessary for the magnetization to be measured as a function of field at a particular temperature the temperature remained constant to within 1/3°C.

CHAPTER III

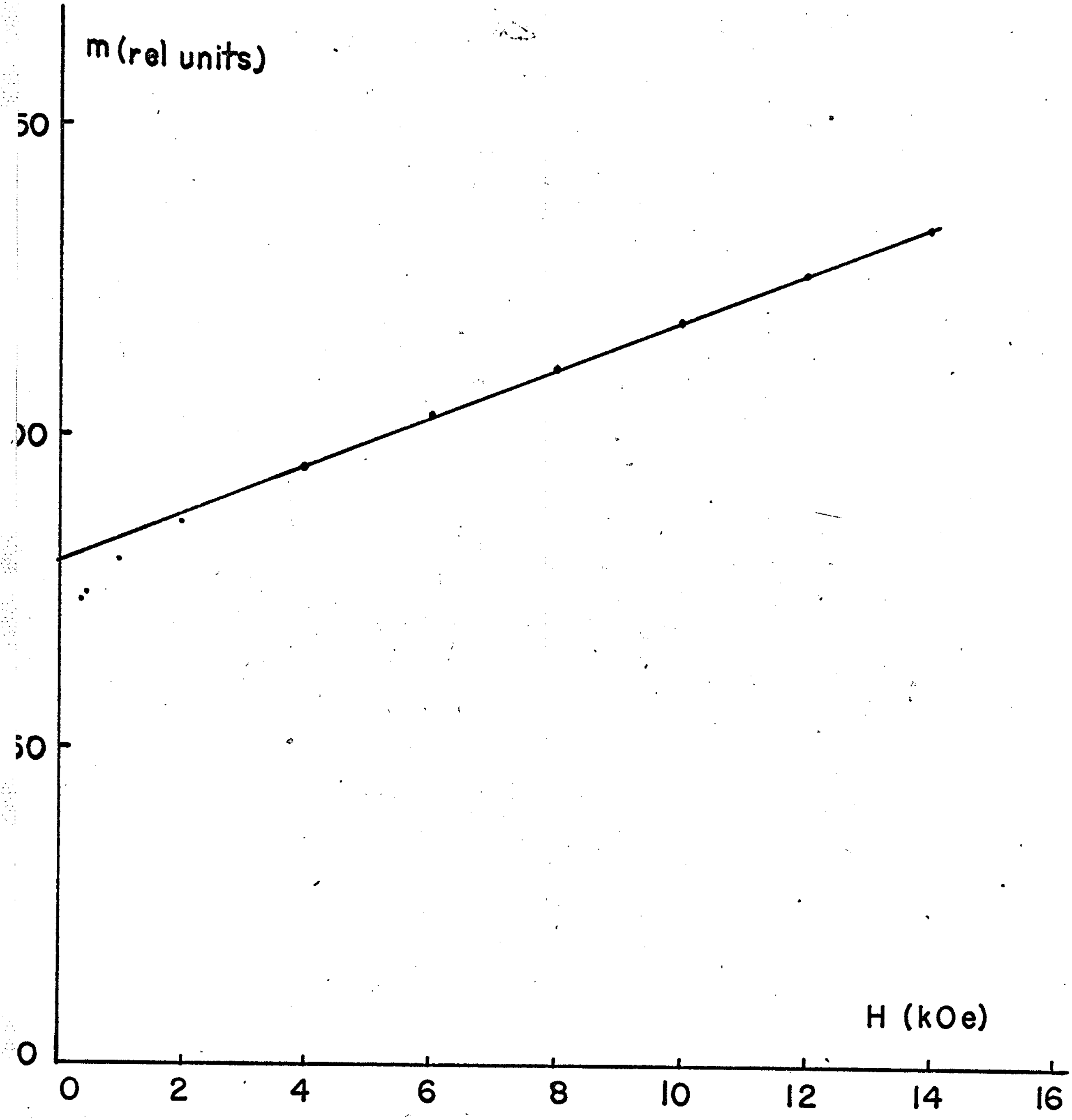
EXPERIMENTAL RESULTS

A typical magnetization curve is shown in Fig. 6 for temperatures above the Morin transition temperature. A curve such as this was taken for the whole range of temperatures from room temperature ($\approx 294^{o}$K) up to 970^{o}K. The spontaneous magnetization for each temperature was obtained by extrapolating a straight line from the high field points ($>$ 10 kOe) back to the point H=0. In purely ferromagnetic materials this method can only be used at temperatures that are low compared to the Curie temperature (Belov, 1965). This is because of the non-linearity of the magnetization curve in the region of the Curie point. The Curie temperature is the temperature at which the energy due to thermal agitation is sufficient to destroy the spontaneous magnetization, i.e. the point at which the material becomes disordered. However if the material is in a magnetic field below the Curie point the ferromagnetic axis will be aligned parallel to the field. Thus, when the material reaches the "ordering" temperature it will have an induced magnetic moment because of the applied field. This in turn induces a non zero molecular field which leads to a discontinuity in the susceptibility at the ordering temperature. One of the methods given by Belov (1965) must be used to determine the Curie temperature.

It has been seen above that hematite is a weak ferromagnet.

Fig. 6

Typical magnetization Curve.

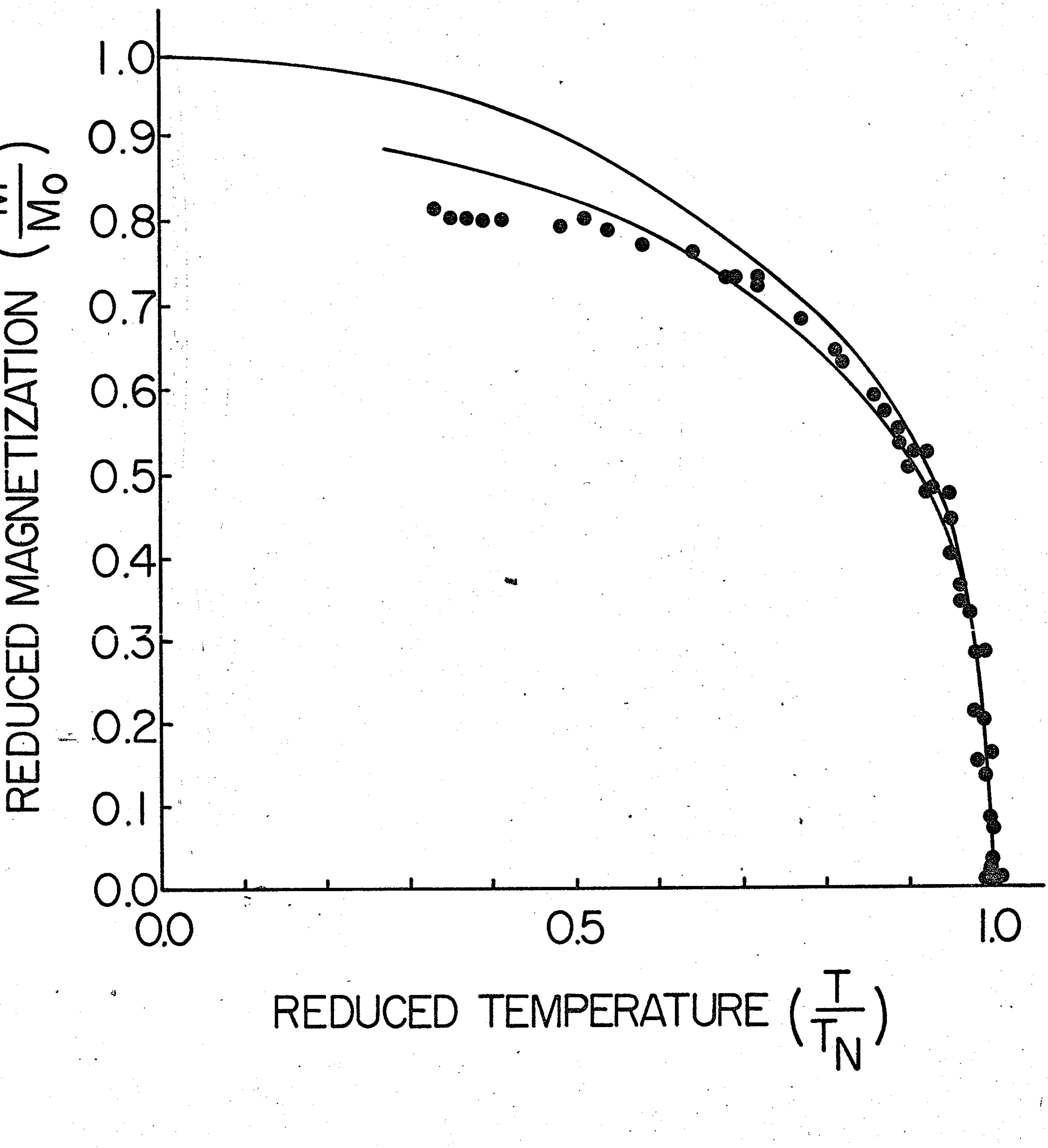

m (rel units)
50
00
50
0
H (kOe)
0
2
4
6
8
10
12
14
16

Thus when a magnetic field is applied it has been assumed that because any effective anisotropy fields are negligible the weak moment is colinear with the field and thus the field is perpendicular to the antiferromagnetic axis. Thus unlike the case of a ferromagnetic material the susceptibility perpendicular to the antiferromagnetic axis is constant up to the Néel temperature (i.e. the disappearance of antiferromagnetic order) and then decreases rather sharply (Nagamiya et al., 1955; Moriya, 1960; Smart, 1966). In a ferromagnetic material the susceptibility diverges which is the reason for the non-linearity. Hence it is assumed that the spontaneous magnetization can be found in the manner described above. Any error arising from this procedure would tend to overestimate the ordering temperature yet the ordering temperature determined in this fashion is, experimentally, always less than methods using other effects such as the Mossbauer or N.M.R.

The Néel point determined by noting when the weak spontaneous moment became zero was 938 ± 3°K. A curve of reduced temperature against reduced magnetization was then obtained. It is shown by the dots in Fig. 7. The curve is normalized to the sublattice magnetization curve, obtained from hyperfine field data (van der Woude, 1966), at $\frac{T}{T_N} = 0.95$. The susceptibility was also measured as a function of temperature both within the (111) plane and along the [111] axis for temperatures between room temperature and T_N. It was found

Fig. 7

Temperature dependence of the weak ferromagnetic moment of hematite. The upper curve represents the normalized temperature dependence of the sublattice magnetization, the dots are experimental data, while the lower curve is calculated from equation (32). The experimental data has been fitted to the lower curve by choosing an appropriate normalization constant.



REDUCED MAGNETIZATION $\left(\frac{M}{M_0}\right)$
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
0.5
1.0
REDUCED TEMPERATURE $\left(\frac{T}{T_N}\right)$

that they were constant and the values are

$$\chi_{(111)} = 21.0 \pm 1.0 \times 10^{-6} \text{ emu/gOe}$$

$$\chi_{[111]} = 19.5 \pm 1.0 \times 10^{-6} \text{ emu/gOe}$$

The moment in the basal plane was measured for several temperatures below T_M. Some of the results are shown in Fig. 8. It is seen that at a critical field H_c there is a transition from the purely antiferromagnetic state to the weak ferromagnetic one. The field H_c increases for decreasing temperature. At -10.5°C the transition occurs at zero field. The transition was studied using both increasing field and a decreasing field. The transition occurred at the same value of H_c in both directions. In Fig. 9 the crosses are points for the field decreasing and the dots are for an increasing magnetic field.

Fig. 8

Field induced transitions where the external magnetic field is applied in the (111)

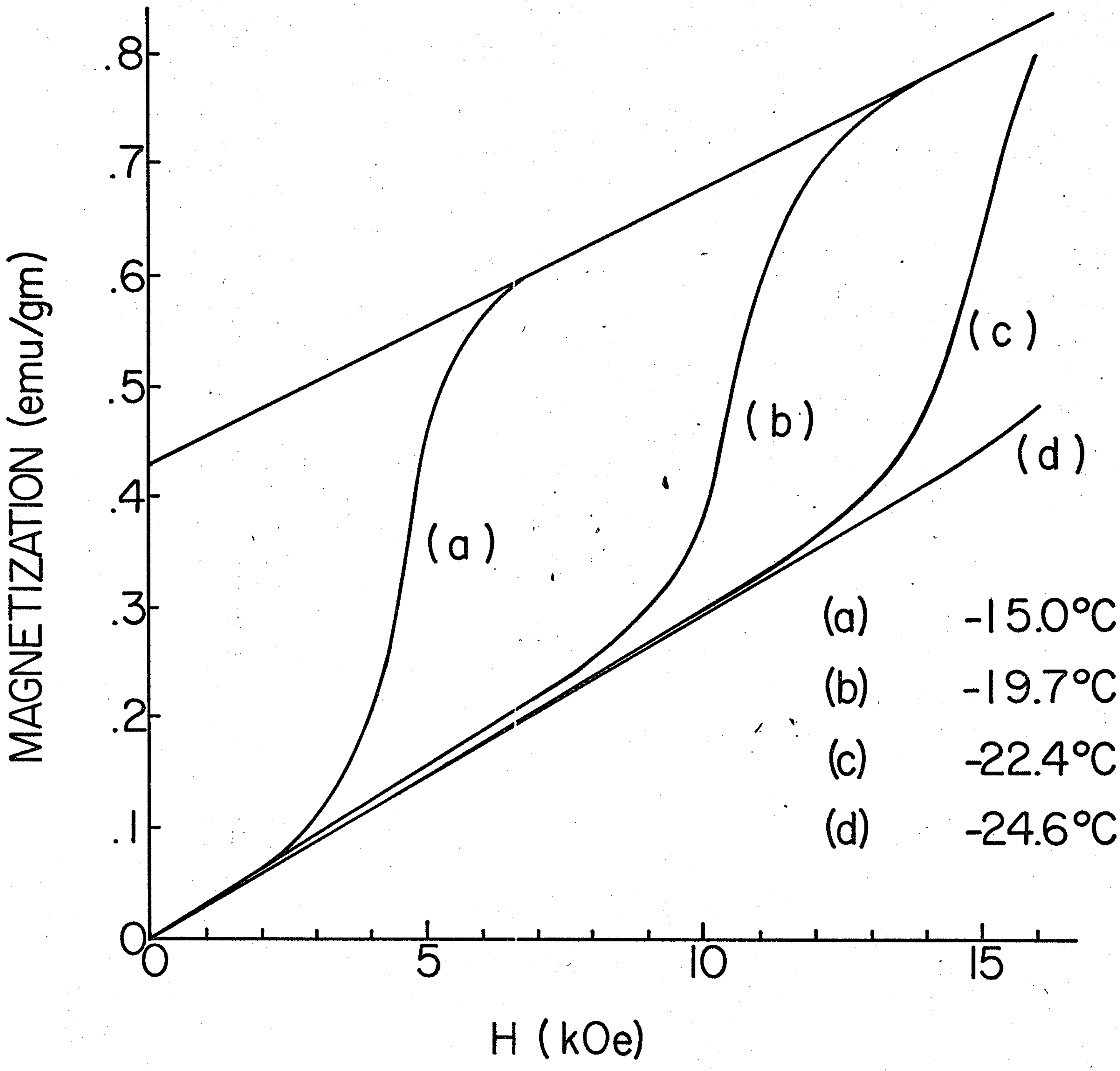
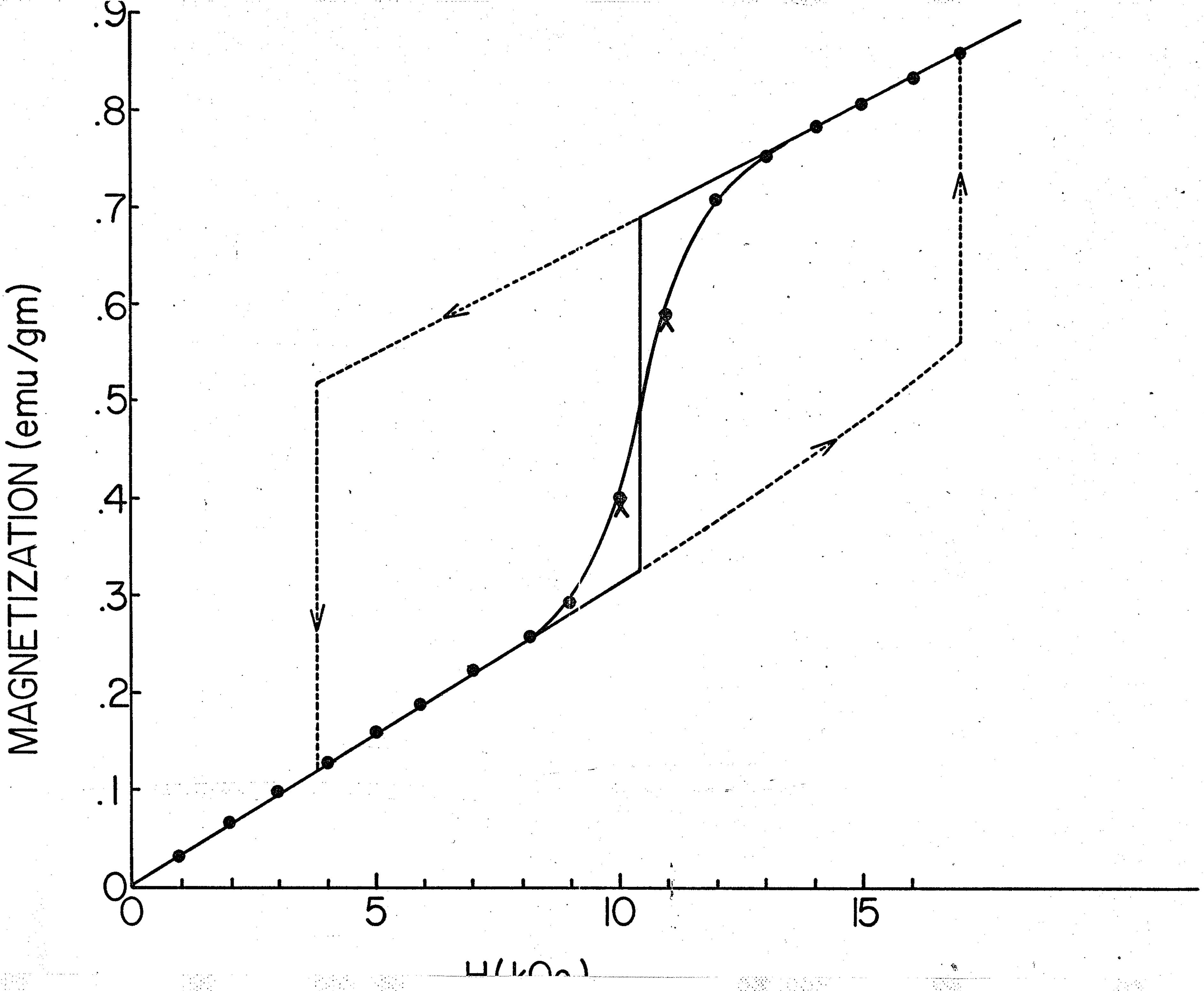

MAGNETIZATION (emu/gm)
.8
.7
.6
.5
.4
.3
.2
.1
0
0
5
10
15
H (kOe)
(a)
(b)
(c)
(d)
(a) -15.0°C
(b) -19.7°C
(c) -22.4°C
(d) -24.6°C

Fig. 9

Comparison of the data obtained in the field induced transition experiment with a molecular field calculation


MAGNETIZATION (emu/gm)
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
0
5
10
15
H(kOe)

CHAPTER IV

DISCUSSION OF RESULTS

The free energy for the system shown in Fig. 10 is

$$E = \lambda \bar{M}_1 \cdot \bar{M}_2 - \bar{D}\cdot(\bar{M}_1 x \bar{M}_2) - \bar{H}\cdot(\bar{M}_1 + \bar{M}_2) - \frac{K}{2M_0^2}(\bar{M}_{1z}^2 + \bar{M}_{2z}^2) \qquad (1)$$

(Cinader and Shtrikman, 1966; Cinader et al., 1967). The first term is the exchange energy, the second the Dzialoshinskii-Moriya canting term, the third term is the Zeeman energy where $\bar{H}$ is the field applied in the basal plane and the last term is the anisotropy energy. $\bar{M}_1$ and $\bar{M}_2$ are the sublattice magnetizations, $M_0 = |\bar{M}_1| = |\bar{M}_2|$.

The free energy is expressed in terms of the components along the axes and it is noted that

$$M_1^x = -M_2^x, \; M_1^y = M_2^y, \; M_1^z = -M_2^z$$

$$\text{and} \quad M_0^2 = M_1^{x^2} + M_1^{y^2} + M_1^{z^2}$$

Therefore

$$E = \lambda[-M_1^{x^2} + M_1^{y^2} - M_1^{z^2}] - 2DM_1^xM_1^y - 2HM_1^y - \frac{K}{M_0^2} M_1^{z^2} \qquad (2)$$

Now at equilibrium the torque must be zero and so

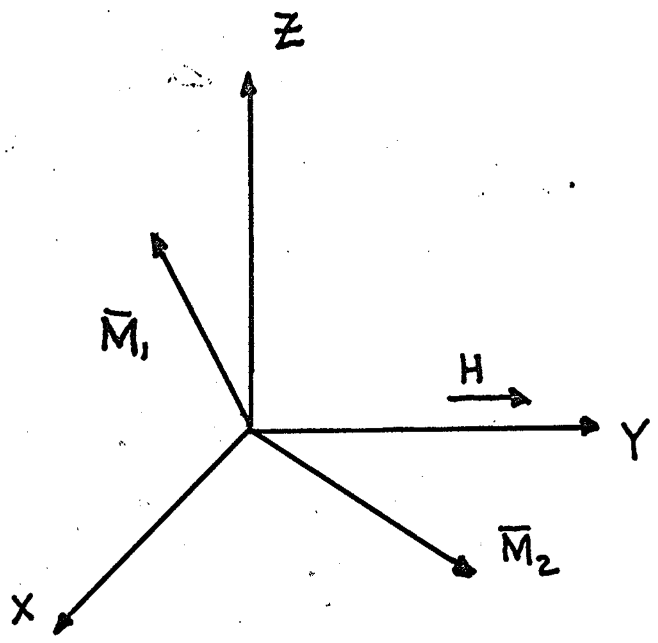
$$\frac{\partial E}{\partial M_1^y} = \frac{\partial E}{\partial M_1^x} = 0,$$

solving the equations for M_1^y it is found that

$$M_1^y = \frac{KH}{2K\lambda - D^2M_0^2 + \frac{K^2}{M_0^2}} \qquad (3)$$

Fig. 10

System during transition from [111] to (111)



Z
$\overline{M}_1$
$\underline{H}$
Y
$\overline{M}_2$
X

which is

$$= \frac{H_eH_K}{2H_eH_K+H_K{}^2-H_D{}^2} \chi H \qquad (4)$$

H_e, is the exchange field ($= \lambda M_0$), H_K the effective anisotropy field ($= \frac{K}{M_0}$) and H_D the effective Dzialoshinskii field ($= DM_0$). χ is the susceptibility in the basal plane.

The measured magnetic moment, m, is of course equal to $2M_1{}^y$, i.e.

$$\bar{m} = \frac{2H_eH_K}{H_{11}{}^2} \chi H \qquad (5)$$

Since $H_{11}{}^2 = 2H_eH_K + H_K{}^2 - H_D{}^2$,

H_{11} is the "spin-flop"field (Cinader and Shtrikman, 1966).

As is quite easily seen, the calculated magnetization curve is linear. However since some experimental data had indicated that there was definite curvature (Flanders and Shtrikman, 1965) it was concluded that the simple molecular field calculation was inadequate. This discrepancy was thought to be essentially due to statistical effects (Searle, 1968).

(a) $\bar{D}$ should therefore be replaced by $\langle\bar{D}\rangle$. $\langle\bar{D}\rangle$, which is equal to $\bar{D}f$, f being an appropriate statistical function, is a function of temperature and magnetization in the y direction.

The free energy expression becomes

$$E = -\lambda M_0{}^2 + 2\lambda M_1{}^{y2} - 2\langle D\rangle M_1{}^x M_1{}^y - 2HM_1{}^y - \frac{K}{M_0{}^2}\left[M_0{}^2 - M_1{}^{x2} - M_1{}^{y2}\right] \qquad (6)$$

At constant temperature

$$\frac{\partial E}{\partial M_1{}^y} = 4\lambda M_1{}^y - 2\langle D\rangle M_1{}^x - 2M_1{}^x M_1{}^y \frac{\partial\langle D\rangle}{\partial M_1{}^y} - 2H + \frac{2K}{M_0{}^2} M_1{}^y \qquad (7)$$

$$\frac{\partial E}{\partial M_1{}^x} = -2\langle D\rangle\ M_1{}^y + \frac{2KM_1{}^x}{M_0{}^2} \qquad (8)$$

which are equal to zero.

Solving for $M_1{}^y$

$$m = 2M_1{}^y = \frac{2K\lambda}{H_{11}{}^2+H_D{}^2-\langle H_D\rangle^2-\langle H_D\rangle}\ M_1{}^y \frac{\partial\langle H_D\rangle}{\partial M_1{}^y}$$

$$\text{i.e. } m = \frac{(H_{11}{}^2+H_D{}^2)\,\chi H}{H_{11}{}^2+H_D{}^2-\langle H_D\rangle^2-\langle H_D\rangle\ m\frac{\partial\langle H_D\rangle}{\partial m}} \qquad (9)$$

Since $M_1{}^y \dfrac{\partial\langle H_D\rangle}{\partial M_1{}^y} = \dfrac{m}{2}\dfrac{\partial\langle H_D\rangle}{\partial m}\dfrac{\partial m}{\partial M_1{}^y}$

It remains to find an appropriate expression for $\langle\bar{D}\rangle$. The individual microscopic $\bar{d}$ vectors from which the macroscopic $\langle\bar{D}\rangle$ vector is composed can be considered as quasi-spins which are either parallel or antiparallel to the [111] direction. The function f was then taken to be of the form which is often found in the mechanics of spin systems. Thus the following expression was tried

$$\langle D\rangle = D\,\frac{1-e^{-\Delta m/kT}}{1+e^{-\Delta m/kT}} \qquad (10)$$

where Δ is a variable parameter and m is the magnetization.

The low temperature experiments described earlier were performed in order to see if the statistical model was satisfactory. However no correlation could be found consistently over the entire temperature range between experiment and the statistical theory.

Another difficulty that became apparent was the size of the "interaction energy" between the $\bar{d}$ vectors. If they are to be considered as quasi-spins then the system is quantized. The interaction energy necessary to reverse the direction of a spin has to come from a large number of spins. This number is so large that the energy is of the order of the exchange energy. It was difficult to envisage any mechanism responsible for this interaction and so it was concluded that this model was not correct.

(b) The free energy expression in this model is similar to that of the simple molecular field model with the exception that a second order anisotropy term is added.

i.e. $$E = \lambda \bar{M}_1 \cdot M_2 - \bar{D} \cdot (\bar{M}_1 x \bar{M}_2) - \bar{H} \cdot (\bar{M}_1 + \bar{M}_2) - \frac{K_1}{2M_0^2} (\bar{M}_{1z}{}^2 + \bar{M}_{2z}{}^2) + \frac{K_2}{2M_0^4} (\bar{M}_{1z}{}^2 + M_{2z}{}^2)^2 \qquad (11)$$

Again the energy is expressed in terms of the components,

$$E = 2\lambda M^{y2} - 2DM_xM_y + \frac{K_1{}^1}{M_0^2} [M_y{}^2 + M_x{}^2] - \frac{K_2}{M_0^4} M_x{}^4 - 2HM_y \qquad (12)$$

The x and y axes are two mutually orthogonal axes in the (111) plane. It has been mentioned above that the basal plane ((111)) anisotropy was neglected and therefore this co-ordinate system is independent of the direction within the plane, i.e. the weak moment is along the y-axis and so this axis coincides with the direction of the field in the (111) plane. Also due to the fact that the energy has been re-expressed in terms of the magnetization components the first order anisotropy in this formalism has to be expressed as $K_1^1 = K_1 + 2K_2$. K_1 and K_2 are the values of the anisotropy energies when expressed in terms of direction cosines as is usually the case (Morrish, 1965), K_2 has the same value in both formalisms.

At a particular temperature and applied field the x and y components are in equilibrium, therefore $\frac{\partial E}{\partial M_1{}^x} = 0 = \frac{\partial E}{\partial M_1{}^y}$.

$$\frac{\partial E}{\partial M_1{}^y} = 4\lambda M_y - 2DM_x + \frac{2K_1{}^1 M_y}{M_0{}^2} - 2H = 0 \qquad (13)$$

$$\frac{\partial E}{\partial M_1{}^x} = -2DM_y + \frac{2K_1{}^1 M_x}{M_0{}^2} - \frac{4K_2 M_x{}^3}{M_0{}^4} = 0 \qquad (14)$$

$$2\lambda M_y - DM_x + \frac{K_1{}^1 M_y}{M_0{}^2} - H = 0 \qquad (15)$$

$$-DM_y + \frac{K_1{}^1 M_x}{M_0{}^2} - \frac{2K_2 M_x{}^3}{M_0{}^4} = 0 \qquad (16)$$

These equations are too difficult to solve analytically and it was necessary to use a numerical method. The value of M_x obtained from (15) was substituted into (16) to obtain

$$-DM_y + \frac{K_1{}^1}{M_0{}^2}\left\{\frac{M_y}{D}\left(2\lambda + \frac{K_1{}^1}{M_0{}^2}\right) - \frac{H}{D}\right\} - \frac{2K_2}{M_0{}^4}\left\{\frac{M_y}{D}\left(2\lambda + \frac{K_1{}^1}{M_0{}^2}\right) - \frac{H}{D}\right\}^3 = 0 \qquad (17)$$

The exchange energy is much greater than the anisotropy energy (Tasaki and Iida, 1963) and so $2\lambda \gg \frac{K_1{}^1}{M_0{}^2}$. It is seen that a solution exists when the straight line represented by

$x = \frac{2\lambda M_y}{D} - \frac{H}{D}$ intersects with the cubic

$$-DM_y + \frac{K_1{}^1}{M_0{}^2} x - \frac{2K_2}{M_0{}^4} x^3 = 0 \qquad (18)$$

Thus (18) is plotted as M_y vs. x for different temperatures represented by different values of $K_1{}^1$. Straight lines are drawn of M_y vs. x for different values of H. The value of M_y at the intersection of a straight line with the cubic is the magnetization at the field represented by coefficients of the straight line at the temperature represented by the coefficients of the cubic.

It is necessary to calculate the field at which the transition from the antiferromagnetic state to the weak ferromagnetic state occurs. This is done by expanding the free energy in a Taylor series about a minimum point.

Using (13) and (14)

$$\frac{\partial^2 E}{\partial M_x{}^2} = \frac{2K_1}{M_0{}^2} - \frac{12K_2}{M_0{}^4} M_x{}^2 \qquad (19)$$

$$\frac{\partial^2 E}{\partial M_y{}^2} = 4\lambda + \frac{2K_1{}^1}{M_0{}^2} \qquad (20)$$

and $\frac{\partial^2 E}{\partial M_x \partial M_y} = \frac{\partial^2 E}{\partial M_y \partial M_x} = -2D,$

therefore around E_{min}

$$E = \tfrac{1}{2}\left(4\lambda + \frac{2K_1{}^1}{M_0{}^2}\right)(M_y - M_y{}^m)^2 + \tfrac{1}{2}\left(\frac{2K_1{}^1}{M_0{}^2} - \frac{12K_2}{M_0{}^4} M_x{}^{m^2}\right)(M_x - M_x{}^m)^2$$
$$- 2D\,(M_x - M_x{}^m)(M_y - M_y{}^m) \qquad (21)$$

In the $M_x - M_y$ plane the solution will move along a line of constant H until $M_x = M_0$. Now

$$M_y = \frac{2H + 2DM_x}{4\lambda + \frac{2K_1{}^1}{M_0{}^2}}$$

and so $$M_y - M_y{}^m = \frac{2D[M_x - M_x{}^m]}{4\lambda + \frac{2K_1{}^1}{M_0{}^2}} \qquad (22)$$

Thus

$$E = \left\{ \frac{\frac{1}{2}(4\lambda + \frac{2K_1{}^1}{M_0{}^2})\ (2D)^2}{(4\lambda + \frac{2K_1{}^1}{M_0{}^2})^2} + \frac{1}{2}\left(\frac{2K_1{}^1}{M_0{}^2} - \frac{12K_2}{M_0{}^4}\ M_x{}^{m2}\right) \frac{-(2D)^2}{4\lambda + \frac{2K_1{}^1}{M_0{}^2}} \right\} [M_x - M_x{}^m]^2 \qquad (23)$$

This becomes unstable when the coefficient of $[M_x - M_x{}^m]^2$ becomes 0.

i.e. $$\frac{K_1{}^1}{M_0{}^2} - \frac{6K_2}{M_0{}^4} M_x{}^{m2} - \frac{D^2}{2\lambda + \frac{K_1{}^1}{M_0{}^2}} = 0,$$

$$M_x{}^{m2} = \left(\frac{K_1{}^1}{M_0{}^2} - \frac{D^2}{2\lambda + \frac{K_1{}^1}{M_0{}^2}}\right) \frac{M_0{}^4}{6K_2} \qquad (24)$$

The value of M_y is obtained by substituting for $M_x{}^m$ into (13).

The downward transition occurs when (14) evaluated at $M_x = M_0$ becomes positive.

i.e. $$-2DM_y + \frac{2K_1{}^1}{M_0} - \frac{4K_2}{M_0} = 0$$

$$M_y = \frac{1}{2D}\left\{\frac{2K_1{}^1}{M_0} - \frac{4K_2}{M_0}\right\} \qquad (25)$$

It is seen that this theory predicts a hysteresis effect for the transition. The transition from the purely antiferromagnetic state to the weak ferromagnetic one occurs at a higher field than the transition the other way, as indicated by the dashed curves in Fig. 9. The fact that no hysteresis is found is probably due to the presence of imperfections in the form of impurities and dislocations. Obviously with any dislocation there will be regions of effective positive and negative pressures. It is known that positive pressures shift T_M up and negative pressures shift T_M down (Umebayashi et al., 1966; Searle, 1967; Worlton et al., 1967). Because of this effect when the equal energy point is approached, for H decreasing or increasing, some regions will already have gone through the transition and thus will act as nucleating centres for the remainder of the crystal. Therefore the bulk transition will most likely take place at a point where the energies of the two phases are equal.

The energy of the weak ferromagnetic phase is

$$E^f = 2\lambda M_y^2 - 2H_D M_y + K_1^1 - K_2 - 2HM_y$$

and $M_y = \frac{H_D + H}{2\lambda}$

and so $$E^f = K_1^1 - K_2 - \left(\frac{H_D^2 + 2HH_D + H^2}{2\lambda}\right) \qquad (26)$$

The energy of the antiferromagnetic phase is

$$E^{af} = 2\lambda M_y^2 - 2DM_xM_y + \frac{K_1^1}{M_0^2} M_K^2 - \frac{K_2}{M_0^4} M_x^4 - 2HM_y$$

and $M_y = \frac{DM_x + H}{2\lambda}$

$$E^{af} = K_1^1 \frac{M_x^2}{M_0^2} - K_2 \frac{M_x^4}{M_0^4} - \frac{1}{2\lambda} (DM_x + H)^2 \qquad (27)$$

Thus putting $r = \frac{M_x}{M_0}$,

$$E^f - E^{af} = \frac{H_D^2}{2\lambda}(1-r^2) + \frac{H_D H}{\lambda}(1-r^2) - K_1^{1}(1-r^2) + K_2(1-r^4)$$

which at the point of transition is zero.

$$\frac{H_D H}{\lambda} - K_1^{11}(1+r) + K_2(1+r)(1+r^2) = 0 \qquad (28)$$

K_1^{11} is equal to $K_1^{1} - \frac{H_D^2}{2\lambda}$

This equation is solved by iteration. The field at which the transition took place was determined experimentally. This was taken to be the equal energy point and values of K_1 and K_2 were found.

For the curve shown in Fig. 9, i.e. at a temperature of -19.7°C, the values were

$K_1 = 5623$ erg/gm

$K_2 = 4226$ erg/gm

According to the theory of Levitin and Schurov (1968), these values indicate that the transition is of first order in agreement with Dzialoshinskii (1957) and with Foner and Shapira (1969).

(c) The upper curve in Fig. 7 is the sublattice magnetization curve taken from hyperfine field data obtained by van der Woude (1966). It is assumed that the temperature dependence of the measured hyperfine field and the sublattice magnetization M are the same (Sawatzky, 1969). The magnetization m was fitted to the sublattice magnetization at $T/T_N = 0.95$. It is apparent that m/M increases with temperature for a considerable range. If there was any statistical effect present it would be expected to decrease with increasing temperature. Therefore it would appear that the statistical effect is absent or is masked to such an extent that it cannot be seen by some other effect.

The experimental results can be ascribed to the effect of microscopic differences between single ion and dipole-dipole contributions to the anisotropy energy. The problem is very complicated and it is necessary to make simplifying assumptions.

The spin hamiltonian for hematite is written to second order in the spin components as follows

$$\mathcal{H} = \sum_{j > k} \left\{ J_{jk} (\bar{S}_j \cdot \bar{S}_k) + \bar{d}_{jk} \cdot (\bar{S}_j \times \bar{S}_k) + \bar{S}_j \cdot K_{jk} \cdot \bar{S}_k \right\} - \sum_j D_1 \, S_{jx}^2 \tag{29}$$

The first term is the isotropic super exchange interaction, the second is the antisymmetrical spin coupling, the third term is the magnetic dipole interaction and the fourth term is the single ion anisotropy. The equation is expressed in terms of the molecular field approximation and only the jth term is considered. The antisymmetrical spin coupling is considered later.

$$\mathcal{H}_j = -g\mu_B \, S_{jz} \, H_{ex} - D_1 S_{jx}^2 + D_2 \langle S_x \rangle S_{jx} \tag{30}$$

H_{ex} is the effective molecular field, the second term is the single ion anisotropy energy and the last term is the magnetic dipole interaction. The notation is similar to that of Artman et al. (1965). $\langle S_x \rangle$ is the average spin polarizatio per ion of one sublattice in the x direction.

The relation of the spin coordinate system to the crystal structure is shown in Fig. 11.

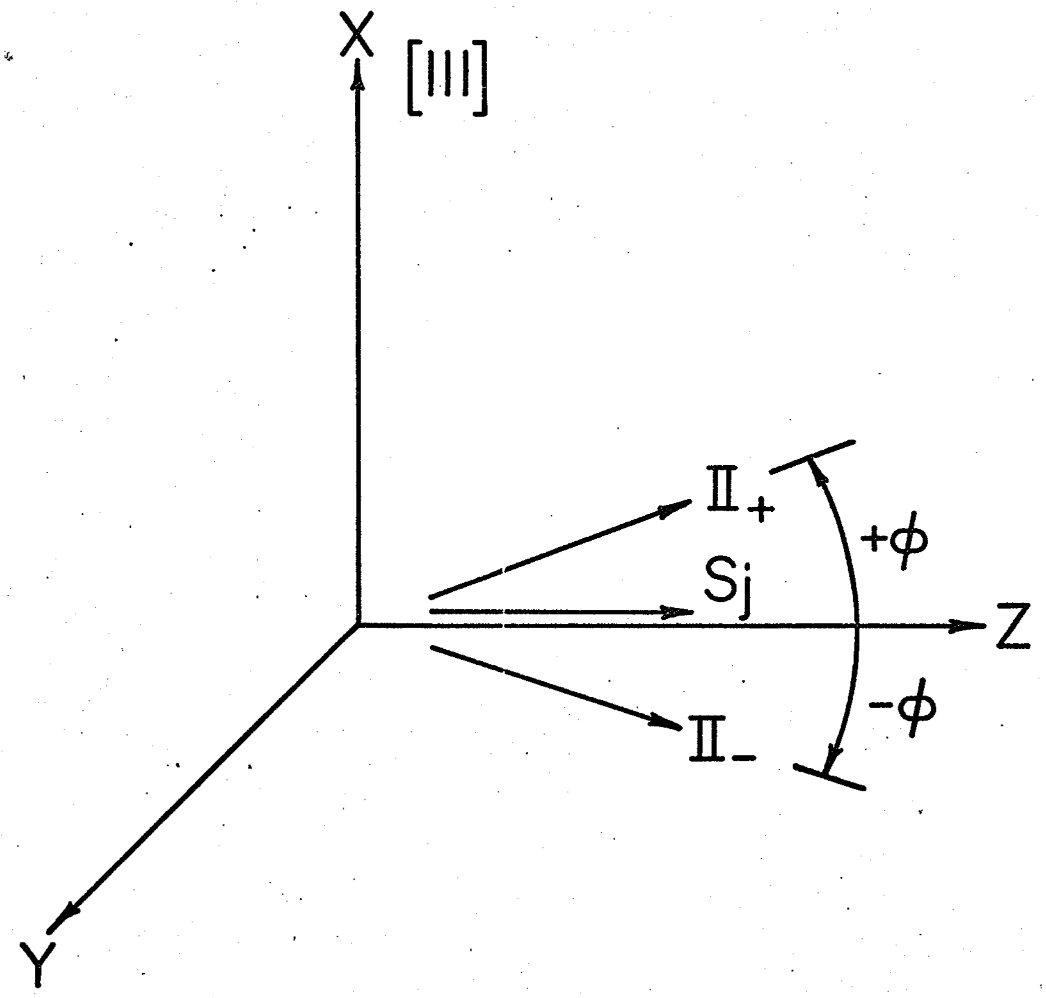
Furthermore it is assumed that the temperature variation of the anisotropy energy can be taken into account by allowing D_1 and D_2 to be temperature dependent. D_2 is greater than D_1 in the temperature range to be considered, i.e. for $T_M < T < T_N$. According to the molecular field approximation the antiferromagnetic axis lies in the (111) plane and it is assumed that it is stabilized along the z direction by a very small anisotropy field. Equation (30) is expressed in terms of raising and lowering operators as follows

$$\mathcal{H}_j = -g\mu_B S_{jz} H_{ex} - \frac{D_1}{4}\left[S_{j+}^2 + S_{j+}S_{j-} + S_{j-}S_{j+} + S_{j-}^2\right] + \frac{D_2}{2}\langle S_x\rangle\left[S_{j+} + S_{j-}\right] \qquad (31)$$

where $S_{j\pm} = S_{jx} \pm i\, S_{jy}$. It is apparent that $|S_{jz}\rangle = |5/2\rangle$ is not the correct ground state. If it is the correct ground state then $\langle S_x\rangle$ must be zero, however the second term in (31) mixes in some of the excited states $|\tfrac{1}{2}\rangle$. Now the "quantization" axis of the state $|\tfrac{1}{2}\rangle$ is at an angle to that of the system where $|5/2\rangle$ is the ground state, therefore due to exchange the actual mixed state will lie between these two. The single ion energy would then be reduced. Although neither ± x direction is favoured each sublattice will rotate to minimize the exchange energy. In this situation then it is obvious that $\langle S_x\rangle =$

Fig. 11

The relation of the spin coordinate system to the crystal structure


X
[111]
Π_+
$+\phi$
S_j
Z
$-\phi$
Π_-
Y

$\pm|\langle S_x\rangle| \neq 0$. The third term is no longer zero and it now mixes in some of the excited state $|3/2\rangle$. Again the result is a rotation of the quantization axis, this time towards the (111) plane reducing the dipole energy. Thus there are two possible values for $\langle S_x\rangle$, i.e. $\pm|\langle S_x\rangle|$.

The hamiltonian is invariant with respect to a change of sign of $|\langle S_x\rangle|$ and therefore there are two antiferromagnetic states, II_+ and II_- (Fig. 11). The state represented by II_- is obtained from II_+ by a rotation of the spin coordinates of 180^o around the z axis whilst leaving the crystal coordinates unchanged. In a single domain the configuration is either II_+ or II_- with no statistical mixing between them since they originate because of a long range cooperative effect. An excitation from II_+ to II_- involves a large number of spins and thus corresponds to the creation of a macroscopic domain. There is no reason why adjacent domains cannot be simultaneously in the two different states (Searle, 1968).

ϕ is estimated within the limits imposed by the approximation and thus m can be calculated.

$$m = X_{\perp}H_D$$

$X_{\perp}$ is the susceptibility perpendicular to the antiferromagnetic axis and is equal to $\frac{1}{\lambda}$ where λ is the exchange constant. H_D is the Dzialoshinskii field, which is DM_z.

Therefore

$$m = \frac{1}{\lambda} DM_z$$

$$= \frac{D}{\lambda} M \cos \phi \qquad (32)$$

The value of $\langle S_x \rangle$ required to produce no rotation of the antiferromagnetic axis is calculated to first order in the perturbed spin functions. This occurs when the gain of spin deviation associated with a rotation towards the [111] direction is equal to the loss of spin deviation associated with a rotation back towards the (111) plane.

The state formed by a rotation towards the ± x direction is

$$|S\rangle = \frac{|5/2\rangle + a|\tfrac{1}{2}\rangle}{\sqrt{1 + a^2}}$$

where $a = \dfrac{\langle \tfrac{1}{2}|\mathcal{H}_j|5/2\rangle}{\langle 5/2|\mathcal{H}_j|5/2\rangle - \langle \tfrac{1}{2}|\mathcal{H}_j|\tfrac{1}{2}\rangle}$,

and $\sqrt{1+a^2}$ is a normalizing factor. When operated on by S_z the state becomes

$$S_z|S_z\rangle = \frac{5/2|5/2\rangle + \tfrac{1}{2}a|\tfrac{1}{2}\rangle}{\sqrt{1 + a^2}}$$

The magnitude of the spin is thus $\langle S|S_z|S\rangle$,

i.e. $5/2 - (5/2 - 1/2)a^2$ (to 2nd order)

Similarly a rotation towards the (111) plane will change the spin magnitude to

$$5/2 - (5/2 - 3/2)b^2,$$

where $b = \dfrac{\langle 3/2|\mathcal{H}_j|5/2\rangle}{\langle 5/2|\mathcal{H}_j|5/2\rangle - \langle 3/2|\mathcal{H}_j|3/2\rangle}$

The new state will thus be at an angle such that the gains of spin deviation are equal

i.e. $(5/2 - 3/2)b^2 = (5/2 - 1/2)a^2$

thus $2a^2 = b^2$ (33)

From equation (31)

$$\langle 1/2|\mathcal{H}_j|5/2\rangle = -\frac{D_1}{4}\sqrt{40},\ \langle 3/2|\mathcal{H}_j|5/2\rangle = \frac{D_2}{2}\langle S_x\rangle\sqrt{5},$$

$$\langle 5/2|\mathcal{H}_j|5/2\rangle = g\mu_B\ 5/2\ H_{ex},\ \langle 3/2|\mathcal{H}_j|3/2\rangle = -g\mu_B\ 3/2\ H_{ex},$$

and $\langle 1/2|\mathcal{H}_j|1/2\rangle = -g\mu_B\ 1/2\ H_{ex}$.

This yields

$$a^2 = \frac{D_1{}^2\ 5}{8g^2\mu_B{}^2\ H_{ex}{}^2} \quad \text{and} \quad b^2 = \frac{D_2{}^2\langle S_x\rangle^2\ 5}{4\ g^2\mu_B{}^2\ H_{ex}{}^2}$$

Substitution in (33) results in

$$\langle S_x\rangle^2 = \left(\frac{D_1}{D_2}\right)^2$$

Therefore $\sin^2\phi = \dfrac{\langle S_x\rangle^2}{(5/2)^2} = 0.16\left(\dfrac{D_1}{D_2}\right)^2$

This procedure was used to calculate the lower curve in Fig. 7. $\frac{D_1}{D_2}$ is the ratio of the anisotropy energies (Artman et al., 1965; Worlton, 1967).

The states II+ and II- are related by a rotation of the angular momentum coordinate system through 180° around the z axis.

i.e.

$$\begin{array}{ccc} \text{II}_+ & & \text{II}_- \\ \langle S_z\rangle & = & \langle S_z\rangle \\ \langle S_x\rangle & = & -\langle S_x\rangle \\ \langle S_y\rangle & = & -\langle S_y\rangle \\ S_{jz} & = & S_{jz} \end{array}$$

$$\begin{array}{lcl} S_{jx} & = & -S_{jx} \\ S_{jy} & = & -S_{jy} \end{array}$$

The ground orbital state is assumed to be non-degenerate (Moriya, 1963) and therefore because of the spin orbit coupling

$$\begin{array}{lcl} II_+ & & II_- \\ L_{jz} & = & L_{jz} \\ L_{jx} & = & -L_{jx} \\ L_{jy} & = & -L_{jy} \end{array} \qquad (34)$$

The spin hamiltonian for the state II_- is obtained from that of II_+ by replacing the operators and average values for state $II+$ by those of II_- in the hamiltonian. The average value of the energy associated with an individual ionic spin is

$$\left\langle E_j \right\rangle_+ = \left\langle E_j \right\rangle_- = - g\mu_B \left\langle S_{jz} \right\rangle H_{ex} - D_1 \left\langle S_{jx}{}^2 \right\rangle + D_2 \left\langle S_x \right\rangle \left\langle S_{jx} \right\rangle$$

It is necessary to show that $\bar{d}_{12(+)} = -\bar{d}_{12(-)}$, where 1 and 2 designate two ionic positions and $\bar{d}_{12}$ is a vector leading to the antisymmetric interaction between them. The second order perturbation energy which is bilinear in the spin orbit coupling and the exchange interaction is written as

$$\begin{aligned} E_2 = & \sum_m \left\{ \frac{\langle n|\lambda \bar{L}_1 \circ \bar{S}_1 | m\rangle \; 2J(mn^1nn^1)\; \bar{S}_1 \cdot \bar{S}_2}{E_n - E_m} \right. \\ & \left. + \frac{2J(nn^1mn^1)\; \bar{S}_1 \cdot \bar{S}_2 \langle m|\lambda \bar{L}_1 \cdot \bar{S}_1 | n\rangle}{E_n - E_m} \right\} \\ & + \sum_{m^1} \left\{ \frac{\langle n^1|\lambda \bar{L}_2 \cdot \bar{S}_2 | m^1\rangle \; 2J(m^1nn^1n)\; \bar{S}_1 \cdot \bar{S}_2}{E_n{}^1 - E_m{}^1} \right. \\ & \left. + \frac{2J(n^1nm^1n)\; \bar{S}_1 \cdot \bar{S}_2 \langle m^1|\lambda \bar{L}_2 \cdot \bar{S}_2 | n^1\rangle}{E_n{}^1 - E_m{}^1} \right\} \end{aligned}$$

where n, n^1 represent the ground orbital states, m, m^1 the excited orbital states of the two ions 1 and 2, and $J(nn^1mm^1)$ is an exchange integral. According to Moriya's calculation (1963)

$$\bar{d}_{12} = 2i\lambda\left\{\sum_{m}\frac{J(nn^1mn^1)}{E_n - E_m}\left\langle n\middle|\bar{L}_1\middle|m\right\rangle - \sum_{m^1}\frac{J(nn^1nm^1)}{E_{n^1} - E_{m^1}}\left\langle n^1\middle|\bar{L}_2\middle|m^1\right\rangle\right\}$$

It has been shown above that $\bar{d}_{12}$ is required to be parallel to the [111] direction, therefore $\bar{d}_{12}$ is rewritten as

$$\bar{d}_{12} = 2i\lambda\left\{\sum_{m}\frac{J(nn^1mn^1)}{E_n - E_m}\left\langle n\middle|L_{1x}\middle|m\right\rangle - \sum_{m^1}\frac{J(nn^1nm^1)}{E_{n^1} - E_{m^1}}\left\langle n^1\middle|L_{2x}\middle|m^1\right\rangle\right\} i_x \tag{35}$$

This immediately leads to the conclusion that $\bar{d}_{12(+)} = - \bar{d}_{12(-)}$ using (34) and (35).

CONCLUSIONS

In order to account for the data near T_M a second order term was included in the phenomenological expansion for the anisotropy energy. (Flanders, (1969) has recently added a third order term).

The experimental results for the magnetization above T_M are accounted for by the microscopic differences between the single ion and the dipole-dipole contributions to the anisotropy energy. These differences also account for the higher order terms in the phenomenological expression for the anisotropy energy below T_M (Kanamori and Minatono, 1962).

It is also pointed out that the model is consistent with a recent observation by Ozhogin et al. (1968). They found that the sign of $\bar{D}\cdot\bar{l}$ was conserved, $\bar{l}(=\bar{S}_1 - \bar{S}_2)$ describes the direction of the antiferromagnetic axis, after labelling the spins. The sign of $\bar{D}\cdot\bar{l}$ is not conserved when $\bar{D}$ is required to be uniquely determined in direction and magnitude.

The susceptibility was found to be higher in the direction of the basal plane than along the [111] direction. This could also indicate that the antiferromagnetic axis is not completely in the plane. This follows because the susceptibility would then be a combination of the antiferromagnetic susceptibility plus a contribution from the rotation of the antiferromagnetic axis towards the (111) plane.

It has been proposed that α-Fe_2O_3 is actually a four sublattice antiferromagnet (Herbert, 1968). At temperatures $T > T_M$ the pairs of sublattices which tend to be parallel may separate into two distinct sublattices each canting slightly towards the [111] direction with opposite senses. This would also be consistent with the argument presented above based on the microscopic differences between the dipole-dipole and single ion anisotropy, and thus might also explain the experimental results.

It is therefore suggested that a precise experiment is needed which would show whether the magnetization results obtained indicate a slight inclination of the antiferromagnetic axis with respect to the (111) plane or indicates four distinct sublattices.

A possible experiment is to study the $\Delta m = 0$ transition in the Mossbauer spectrum of α-Fe_2O_3 (van der Woude, 1966). When the γ-rays propagate parallel to the antiferromagnetic axis this should be zero. If the spectra are recorded with the basal plane perpendicular to this direction and also at an angle it might be possible to reach some conclusion.

It has been found that the Néel point is 938 ± 3°K. This was measured by noting the disappearance of the weak moment. There is doubt as to whether this temperature actually corresponds to the temperature at which the antiferromagnetic order disappears (Aharoni et al., 1962; Freier et al., 1962;

Robbrecht and Doclo, 1962; Gilad et al., 1963; Iserentant et al., 1964).

Although 938°K was assumed to be the Néel temperature, published values range from 946°K to 960°K. These depend on Mossbauer effect measurements and N.M.R. measurements which will obviously indicate when disorder is reached. Since more information might be obtained on the differences between the components of the anisotropy it is suggested that an experiment be done in which the weak moment and the sublattice magnetizations are somehow observed simultaneously.

REFERENCES

Aharoni, A., Frei, E. H. and Schieber, M., Phys. Rev. 127, 439 (1962).

Anderson, P. W., Phys. Rev. 79, 350 (1950).

Andonian, Manufactured by Andonian Associates Inc., Waltham, Mass.

Arajs, S. and Dummyre, G. R., Phys. Stat. Sol. 21, 191 (1967).

Artman, J. O., Murphy, J. C. and Foner, S., Phys. Rev. 138, A912 (1965).

Belov, K. P., "Magnetic Transitions", Boston Technical Publishers Inc. (1965).

Bertaut, F., Compt. rend. acad. Sci. 246, 3335 (1958).

Besser, P. J. and Morrish, A. H., Phys. Letters 13, 289 (1964).

Besser, P. J., Ph.D. Thesis, University of Minnesota (1965) (unpublished)

Besser, P. J., Morrish, A. H. and Searle, C. W., Phys. Rev. 153, 632 (1967).

Birss, R. R., "Symmetry and Magnetism", North-Holland Publishing Company, Amsterdam (1964).

Bizette, H., Ann. de Phys. 1, 87 (1946).

Blake, R. L. and Zoltai, T. Z., Report, Bureau of Mines, Minneapolis, Minn. (1965).

Bogle, G. S. and Symmons, H. F., Proc. Phys. Soc. 73, 531 (1959).

Charlesworth, G. and Long, F. A., Proc. Leeds phil. lit. Soc. 3, 515 (1938).

Chevallier, R., J. Phys. Radium 12, 172 (1951).

Cinader, G. and Shtrikman, S., Solid State Commun. 4, 459 (1966).

Cinader, G., Flanders, P. J. and Shtrikman, S., Phys. Rev. 162, 419 (1967).

Curry, N. A., Johnston, G. B., Besser, P. J. and Morrish, A. H., Phil. Mag. 12, 221 (1965).

Dzialoshinskii, I. E., J. Exptl. Theoret. Phys. (U.S.S.R.) 32, 1547 (1957). [JEPT 5, 1259 (1957)].

Flanders, P. J. and Remeika, J. P., Phil. Mag. 11, 1271 (1965).

Flanders, P. J. and Shtrikman, S., Solid State Commun. 3, 285 (1965).

Flanders, P. J., J. Appl. Phys. 40, 1247 (1969).

Foner, S., Rev. Sci. Ins. 30, 548 (1959).

Foner, S. and Williamson, S. J., J. Appl. Phys. 36, 1154 (1965).

Foner, S. and Shapira, Y., Phys. Letters 29A, 276 (1969).

Freier, S., Greensphan, M., Hillman, P. and Shecter, H., Phys. Letters 2, 191 (1962).

Gilad, P., Greensphan, M., Hillman, P., and Shecter, H., Phys. Letters 7, 239 (1963).

Gilleo, M. A., Phys. Rev. 109, 777 (1958).

Gorter, C. J., Revs. Mod. Phys. 25, 277 (1953).

Guillaud, G., J. Phys. Radium 12, 489 (1951).

Herbert, D. C., Ph.D. Thesis, University of London (1968).

Hirone, T., J. Appl. Phys. 36, 988 (1965).

Honda, K. and Soné, T., Sci. Rep. Tôhoku Univ. 3, 223 (1914).

Iserentant, C. M., Robbrecht, G. G. and Doclo, R. J., Phys. Letters 11, 14 (1964).

Iwata, M., Iwata, T. and Yamamoto, M., J. Phys. Soc. Japan 17 Suppl. B-1, 231 (1962).

Kaczér, J. and Shalnikova, T., Proceedings of the International Conference on Magnetism, Nottingham (1964) (Institute of Physics and Physical Society, London, 1965).

Kanamori, J. and Minatono, H., J. Phys. Soc. Japan 17, 1759 (1962).

Kramers, H., Physica 1, 182 (1934).

Landau, L., J. Exptl. Theoret. Phys. (U.S.S.R.) 7, 19 (1937).

Levitin, R. Z. and Shchurov, V. A., ZhETF Pis'ma 7, 142 (1968) [JEPT Letters 7, 110 (1968)].

Li, Y. Y., Phys. Rev. 101, 1450 (1956).

Lin, S. T., Phys. Rev. 116, 1447 (1959).

Lin, S. T., J. Appl. Phys. 31, 2735 (1960).

Lin, S. T., J. Appl. Phys. 32, 3945 (1961).

Lin, S. T., J. Phys. Soc. Japan 17 Suppl. B-1, 226 (1962).

Magnion. Manufactured by Magnion, Middlesex Turnpike, Burlington, Mass.

Mason, B., Geol. Foren. Forhandl. 65, 95 (1943).

Micro-Matic. Manufactured by Micromech Mfg. Corp., Union, N.J.

Morin, F. J., Phys. Rev. 78, 819 (1950).

Moriya, T., Phys. Rev. 117, 635 (1960).

Moriya, T., Phys. Rev. 120, 91 (1960).

Moriya, T. in Magnetism I, edited by G. T. Rado and H. Suhl, Academic Press, New York-London, (1963) Chapter 3.

Morrish, A. H., "The Physical Principles of Magnetism", John Wiley and Sons, New York (1965).

Nagamiya, T., Yosida, K. and Kubo, R., Advan. Phys. 4, 1 (1955).

Nathans, R., Pickart, S. J., Alperin, H. A. and Brown, P. J., Phys. Rev. 136, A1641 (1964).

Néel, L., Ann. de Phys. (Paris) 5, 232 (1936).

Néel, L., Ann. de Phys. 3, 137 (1948).

Néel, L., Ann. de Phys. 4, 249 (1949).

Néel, L. and Pauthenet, R., Compt. rend. acad. Sci. 234, 2172 (1952).

Néel, L., Revs. Modern Physics 25, 58 (1953).

Ozhogin, V. I., Yakimov, S. S., Voskanyan, R. A. and Gamlickii, V. Ya., Report Institute of Atomic Energy, Moscow (IAE 1674) (1968).

Pauling, L. and Hendricks, S. B., J. Am. Chem. Soc. 47, 781 (1925).

P.A.R. Manufactured by Princeton Applied Research, Princeton, N. J.

Poulis, N. J., van der Handel, J., Ubbink, J., Poulis, J. A. and Gorter, C. J., Phys. Rev. 82, 552 (1951).

Raytheon. Manufactured by Raytheon Mfg. Co., Waltham, Mass.

Robbrecht, G. G. and Doclo, R. J., Phys. Letters 3, 85 (1962).

Sawatzky, G. A., Ph.D. Thesis, University of Manitoba (1969).

Searle, C. W., Phys. Letters 25A, 256 (1967).

Searle, C. W., Phys. Rev. Letters 21, 741 (1968).

Shull, C. G., Strauser, W. A. and Wollan, E. O., Phys. Rev. 83, 333 (1951).

Sirota, N. N., Gorskii, F. K. and Varikash, V. M., (Editors), "Solid State Transformations" Consultants Bureau, New York (1966).

Smart, J. S., "Effective Field Theories of Magnetism", W. B. Saunders Company, Philadelphia and London (1966).

Smith, T., Phys. Rev. 8, 721 (1916).

Tasaki, A., Siratori, K. and Iida, S., J. Phys. Soc. Japan 17 Suppl. B-1, 235 (1962).

Tasaki, A., Siratori, K. and Iida, S., J. Phys. Soc. Japan 15, 1535 (1960).

Tasaki, A. and Iida, S., J. Phys. Soc. Japan 16, 1697 (1961).

Tasaki, A. and Iida, S., J. Phys. Soc. Japan 18, 1148 (1963).

Tavger, B. A. and Zaitsev, V. M., J. Exptl. Theoret. Phys. (U.S.S.R.) 30, 564 (1956) [JEPT 3, 430 (1956)].

Tinkham, M., "Group Theory and Quantum Mechanics", McGraw-Hill Book Company, New York (1964).

Umebayashi, H., Frager, B. C. and Shirane, G., Phys. Letters <u>22</u>, 407 (1966).

van der Lugt, W., Ned. T. Natuurk. <u>31</u>, 402 (1965).

van der Woude, F., Ph.D. Thesis, University of Groningen (1966) (unpublished).

Worlton, T. G., Bennion, R. B. and Brugger, R. M., Phys. Letters <u>24A</u>, 653 (1967).

Worlton, T. G., Ph.D. Thesis, Brigham Young University (1967) (unpublished).