A thesis

entitled

A DOMAIN STUDY OF THE MAGNETIC TRANSFORMATION IN HEMATITE

by

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Abstract

This thesis includes a review of the ferromagnetic and the antiferromagnetic properties of hematite (α-Fe_2O_3). In the review a special reference is made to the magnetic transformation and the large variation of the magnetic parameters of natural and synthetic crystals.

Details are given of a Kerr effect apparatus and an electron beam method which were used to study the domain structure of hematite. A sensitive magnetic colloid which functioned down to $-30^{\circ}C$ was developed to produce cine films of domain wall motion at the low temperature transformation. The colloid sensitivity was increased to permit the study of the variation of the magnetic leakage field across the domain surface. Using the Kerr effect and Bitter technique the domain walls often appear discontinuous on natural and synthetic crystals. The magnetisation was seen to exhibit a variation of direction within an individual domain.

In synthetic crystals the weak ferromagnetism reduces considerably on cooling through the transformation temperature by a domain denucleation mechanism. A natural crystal showed no domain wall movement at

the transformation but the remanent magnetisation had decreased. For at least 15°C below the denucleation temperature of a synthetic crystal the high sensitivity colloid indicates patterns reminiscent of iron filings around a bar magnet. Hence this crystal is still ferromagnetic at these temperatures. This additional pattern which is also present on natural crystals is unchanged above the transformation temperature except for the addition of the domain walls.

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Chapter One

INTRODUCTION

The thesis contains a review of the magnetic properties of hematite followed by an investigation of the low temperature transformation of natural and synthetic hematite crystals. It concludes with a discussion of the results obtained and suggestions for further experiments.

A detailed study of magnetic materials at temperatures in the neighbourhood of a magnetic transformation permits a more comprehensive interpretation of magnetic phenomena. For this reason magnetic transformations have recently received increased attention both theoretically and practically.

At this stage a brief introduction to hematite will facilitate understanding of the results described in the review.

Hematite, α -Fe_2O_3 has a rhombohedral structure which was first identified with the use of X-rays by Pauling & Hendricks (1925). The disposition of the oxygen ions, which are denoted by open circles, is indicated in fig. 1(a) relative to a rhombohedral unit cell with centre at O. The Fe^{3+} ions are situated along the [111] axis (ternary axis), AB, at the points a, b, c and d (so that Aa = Ob = Oc = Bd).

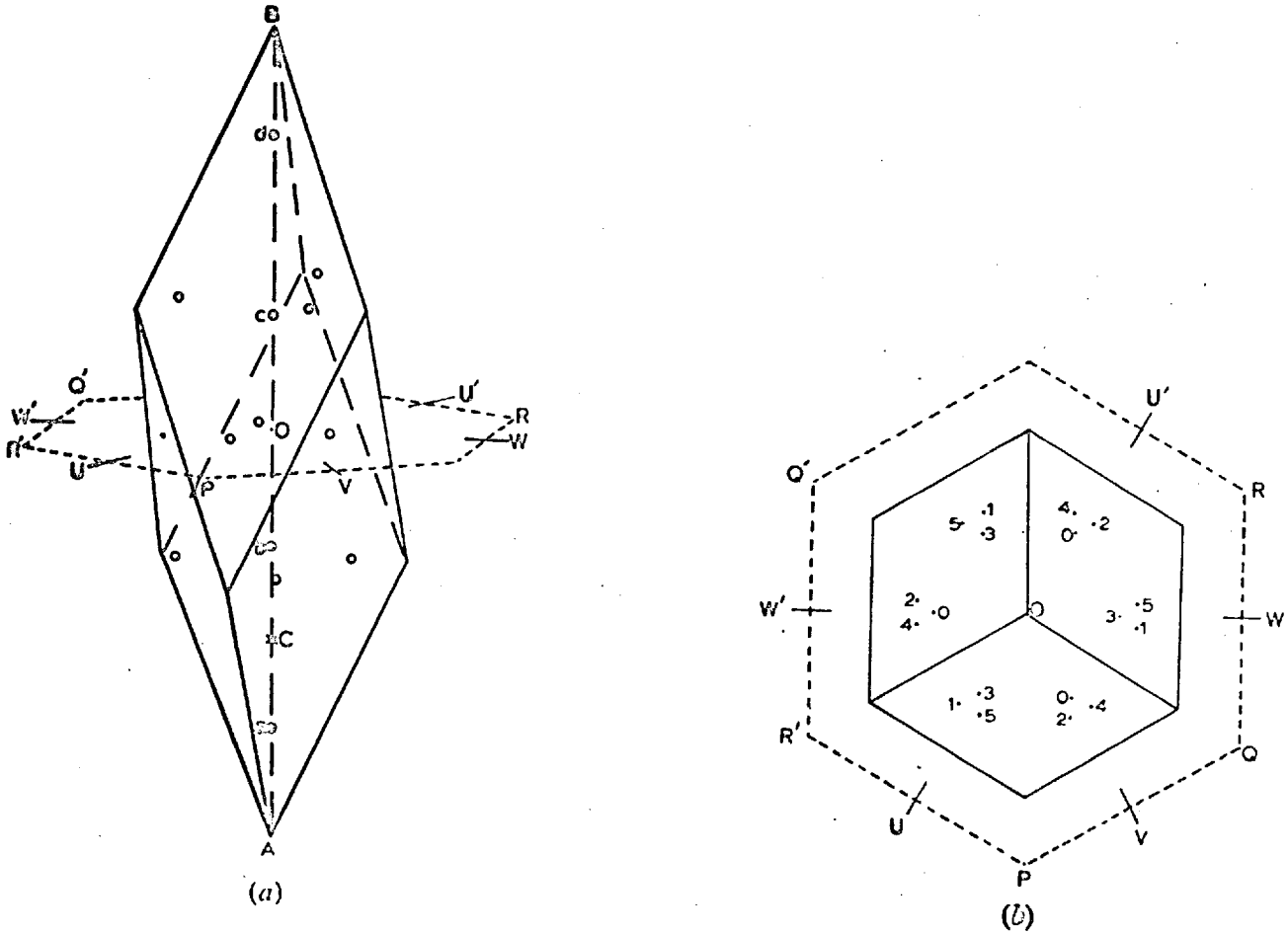


Fig. 1. Position of oxygen and iron ions in hematite relative to a rhombohedral unit cell.

The exact location of the O^{2-} ions may be more readily appreciated by referring to fig. 1(b) which shows their positions relative to a succession of equally spaced (111) planes, the basal planes. The numbers indicate the perpendicular distance of the planes from A (towards B) in units of one-sixth of the distance AB. Classically, the crystal possesses a threefold axis AB, and three twofold axes, OU, OV, OW.

Neutron diffraction shows hematite to be basically antiferromagnetic (Shull, Strauser & Wollan, 1951). At room temperature the spins of the Fe^{3+} ions are in ferromagnetic sheets perpendicular to the ternary axis. Neighbouring basal plane sheets are coupled antiferromagnetically in the following sequence + - - + . At room temperature the spins in the sheets are directed in the basal plane towards one of the three nearest neighbour Fe^{3+} ions e.g. RR′ in fig. 1. This results in trigonal symmetry.

The low temperature transformation of hematite occurs on cooling to about $-11^{\circ}C$. At this temperature the spins change their orientation from the basal plane to along the ternary axis.

Besides being antiferromagnetic, hematite exhibits a weak ferromagnetism. The value of the saturation magnetisation is at least five hundred

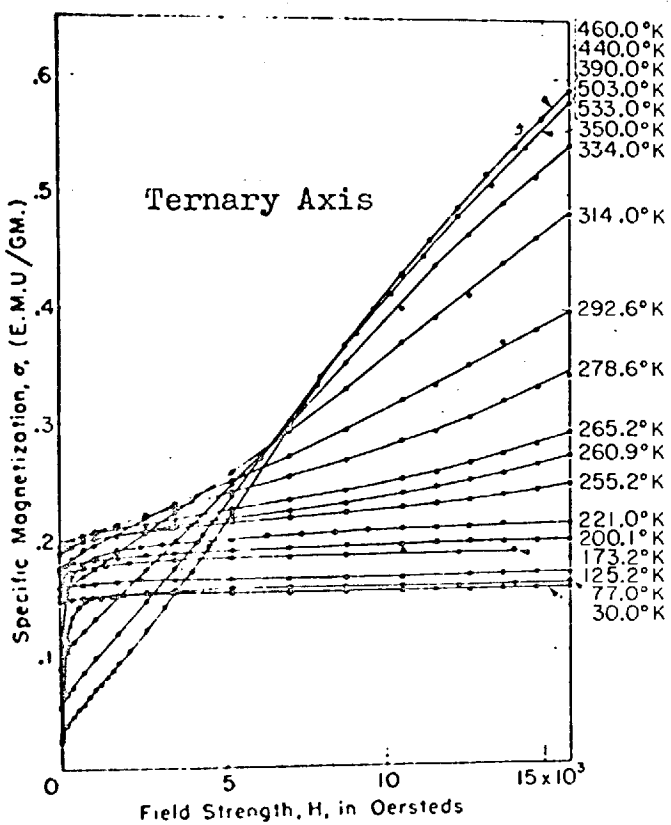
times weaker than iron, ranging from 0·5 to 0·15 e.m.u./g. Below the transformation the ferromagnetism is considerably reduced or is seen to disappear completely.

There are several theories of the origin of the weak ferromagnetism. The theory of Dzialoshinskii (1957) which uses the crystal symmetry of hematite and Landau's phase transitions of the second kind fits the experimental data most satisfactorily. He shows that the crystal symmetry properties above the transformation permit the antiferromagnetically coupled spins to be slightly tilted or canted towards each other. This canting of the spins produces a resultant magnetic moment directed in the basal plane (e.g. along OV in fig. 1). Using the thermodynamic theory he postulates that the spin canting is caused by relativistic spin lattice interaction and magnetic dipole interaction.

The Curie and Néel point of hematite has received little attention from research workers. However, allowing for the difference in sensitivity of the experimental methods, the ferromagnetic and antiferromagnetic ordering seems to disappear at the same temperature, 675°C. This has yet to be checked conclusively by work on the same synthetic crystal.

N.B. The low temperature transformation is studied by measuring the variation of a magnetic parameter with temperature. The resulting curve usually takes the form of a steady high temperature value and a steady low temperature value with a smooth change at the transformation. In order to compare the behaviour of different parameters in the transformation region I have arbitrarily defined the endpoints of the transformation. These endpoints are the temperatures at which tangents to the curve drawn from the high temperature region and the low temperature region intersect with the tangent drawn to the curve in the transformation region.

1.1 Hematite Crystals. The natural specimens are often found in the form of single crystals with well developed faces. Kaye (1960) gives a spectrochemical analysis of the major impurities in many natural crystals from different origins. These range from an immeasurable impurity content in his natural hematites from Elba and Etna to a maximum of 5% Ti (origin - St. Gothard), 0·35% Al (Japan), 0·75% Sn (Japan) and 0·5% V (St. Gothard). Of the eight areas from which he had hematite specimens, six areas had Ti impurities, five had Al, two had Sn and one area had V.



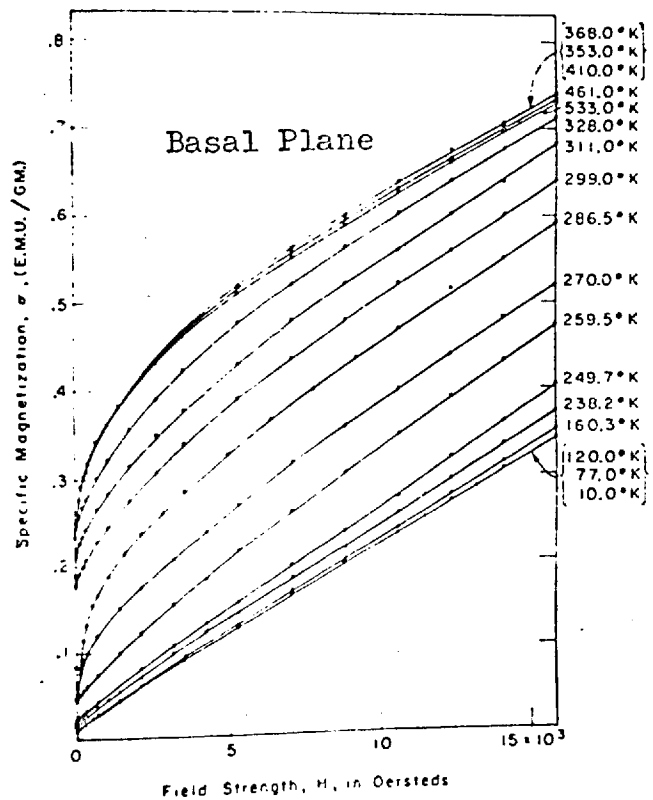


Fig. 2. Magnetisation isotherms in the basal plane and along the ternary axis of an Elba hematite crystal (Lin, 1959).

1.2 The Effect of Temperature on the Antiferromagnetic Susceptibility and the Saturation Magnetisation of Hematite Crystals. Of the few papers on the basic magnetic properties of hematite there are two on the variation of antiferromagnetic susceptibility and saturation magnetisation with temperature (Néel, 1953, and Lin, 1959). They experimented on natural single crystals from Elba and obtained different results. Pauthenet who made the measurements for Néel ground his specimen into a 4 mm. sphere whereas Lin's was a $3 \times 3 \times 6$ mm.^{3} rectangular prism (there is no appreciable demagnetising effect as hematite has a very low permeability).

Both experimenters used the Curie method to find the variation of specific magnetisation with magnetic field at different temperatures in the basal plane and along the ternary axis. Lin's magnetisation isotherms are shown in fig. 2. Like Townsend-Smith (1916), Néel and Lin represented the specific magnetisation, σ, as

$$\sigma = \sigma_f + \sigma_a$$

where σ_f is a ferromagnetic and σ_a an antiferromagnetic contribution (Townsend-Smith termed this a paramagnetic contribution, of course). Above a certain magnetic field, 5 KOe. in Néel's case, any further increase of

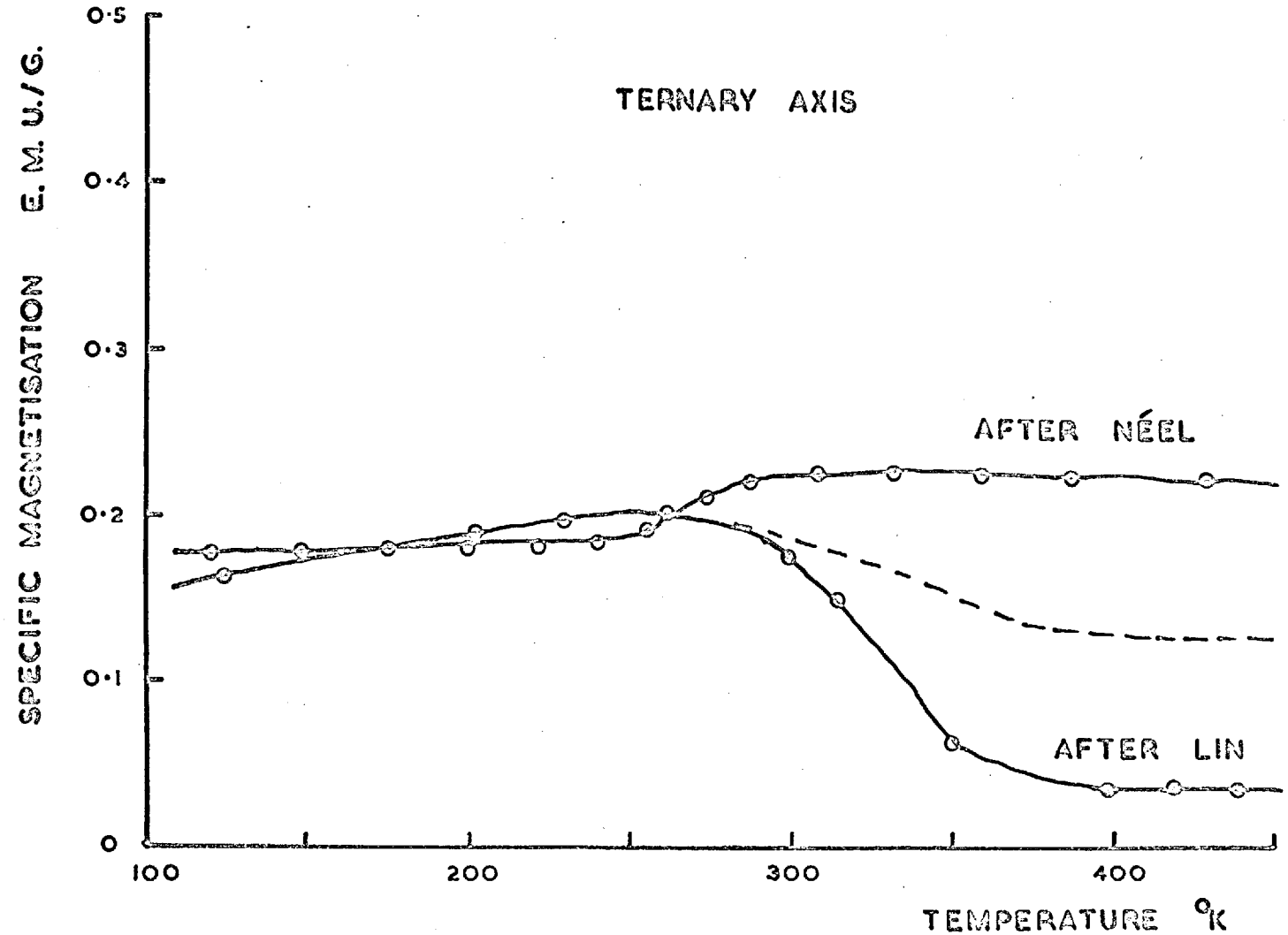


Fig. 3a. Specific magnetisation as a function of temperature along the ternary axis of two Elba hematite crystals (Néel, 1953 and Lin, 1959). The dashed curve is the author's interpretation of Lin's isotherms.

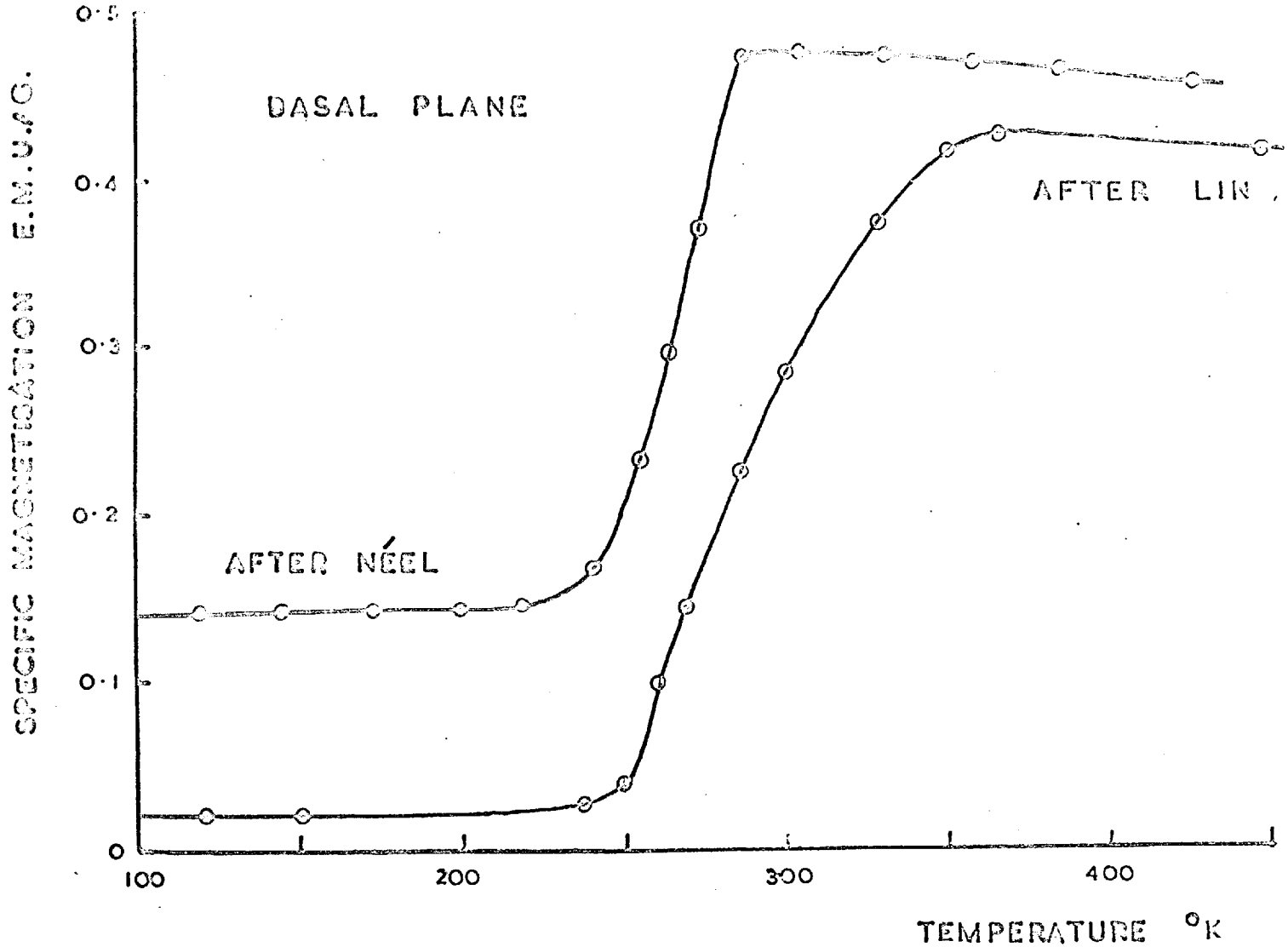


Fig. 3b. Specific magnetisation as a function of temperature in the basal plane of two Elba hematite crystals (Néel, 1953 and Lin, 1959).

field resulted in a linear increase of specific magnetisation. They concluded that the ferromagnetic component was saturated and that the specific magnetisation could now be represented by

$$\sigma = \sigma_s + \chi H$$

where σ_s is the saturation magnetisation of the ferromagnetic component and χ the antiferromagnetic susceptibility either parallel or perpendicular to the theoretical spin direction. Hence the antiferromagnetic susceptibility was found at each temperature measurement by the slope of the straight line portion of the σ/H graph. The saturation magnetisation could be obtained by subtracting the antiferromagnetic contribution, replotting the remaining ferromagnetic portion of the isotherm and noting the saturation value.

Néel and Lin found that unlike normal ferromagnetic materials the ferromagnetism in Elba hematite crystals did not saturate to the same value in different directions, see fig. 3a-b. The dashed portion of Lin's ternary axis curve is a modification derived from his isotherms. In the high temperature region he appears to have extrapolated the isotherms to zero field rather than using the method described above. His results are more like Néel's after

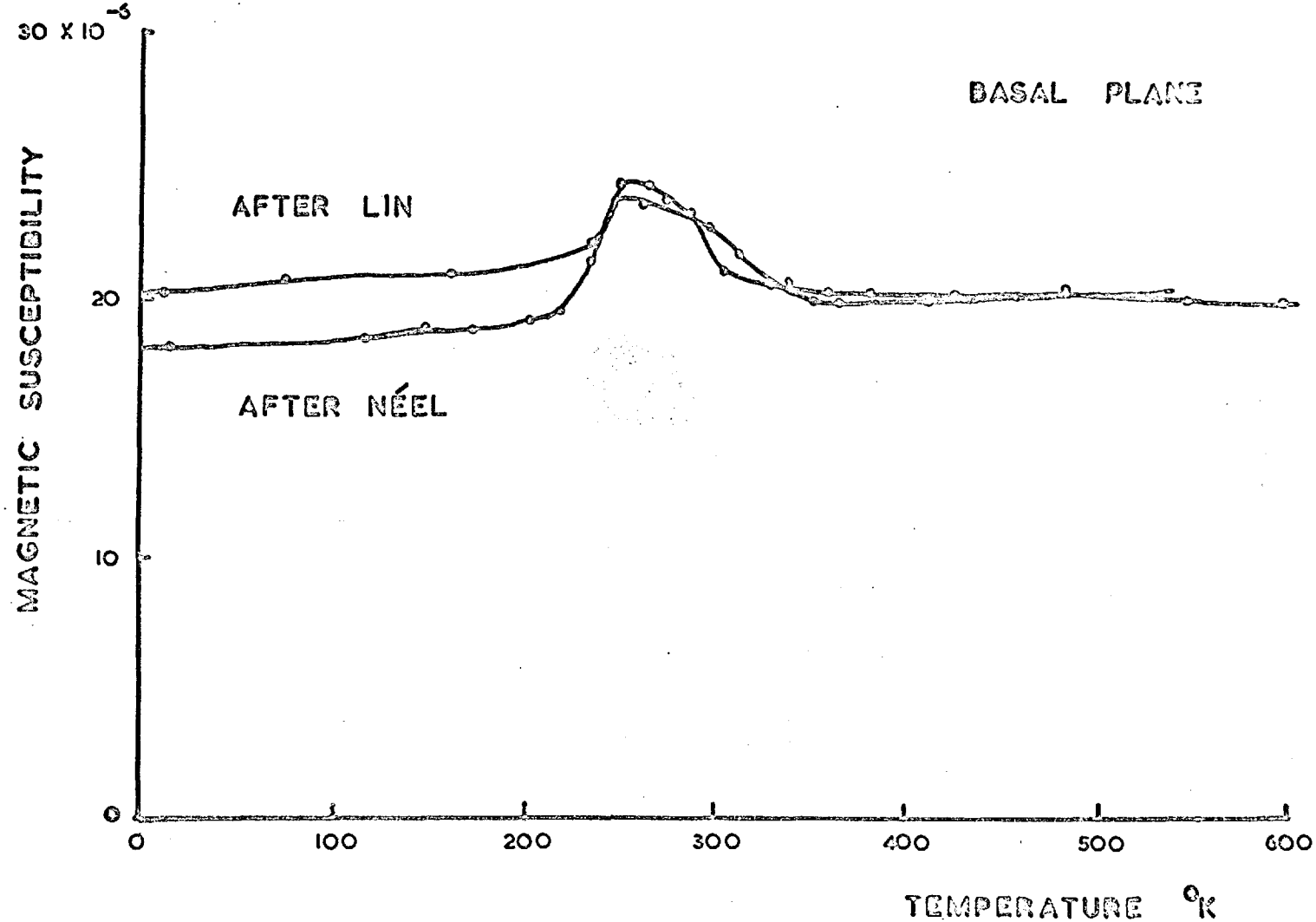


Fig. 4a. Antiferromagnetic susceptibility as a function of temperature in the basal plane of two Elba hematite crystals (Néel, 1953 and Lin, 1959).

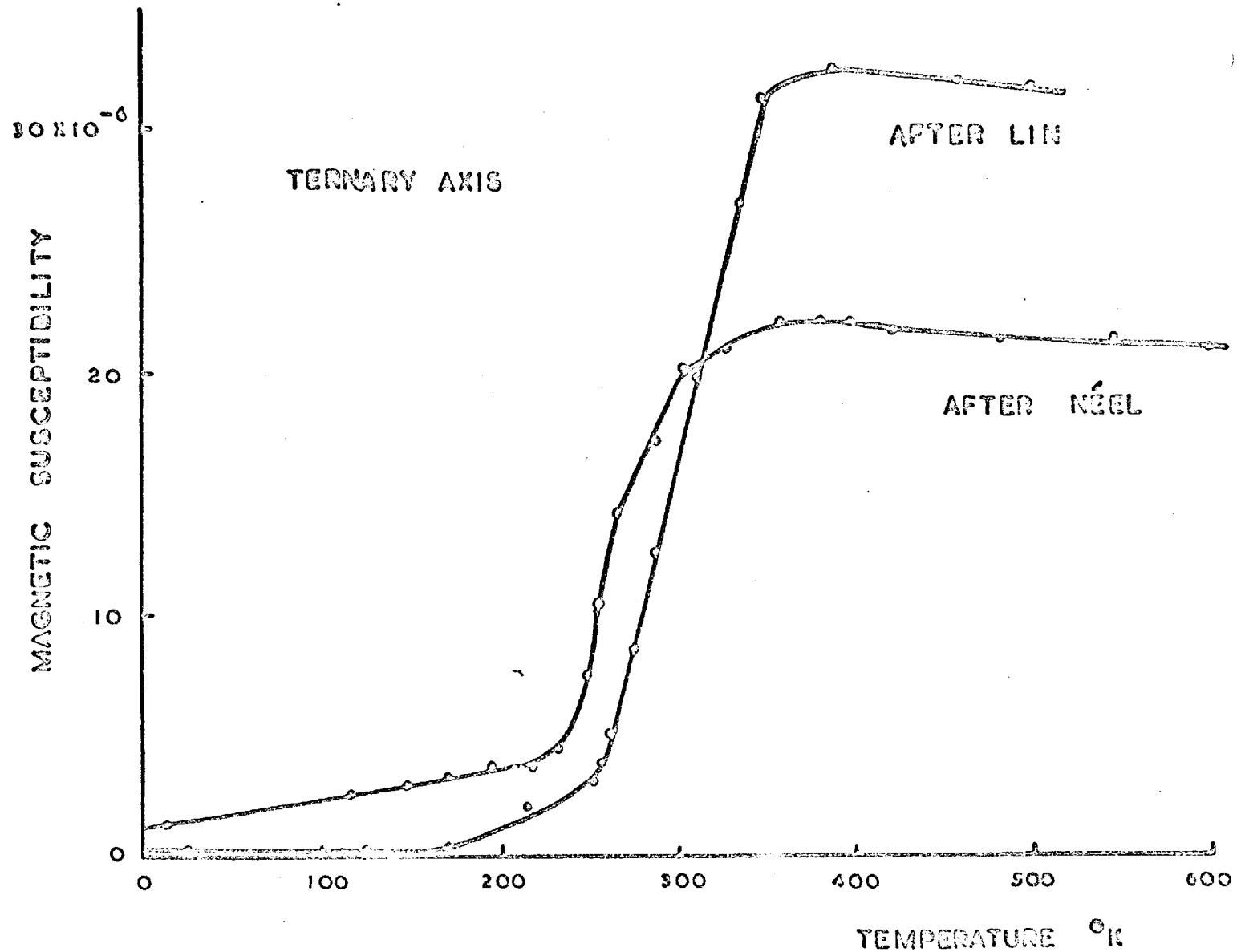


Fig. 4b. Antiferromagnetic susceptibility as a function of temperature along the ternary axis of two Elba hematite crystals (Néel, 1953 and [illegible]).

modification.

Above the transformation the ferromagnetism of Néel's Elba saturates at 0.47 e.m.u./g. in the basal plane and 0.225 e.m.u./g. along the ternary axis compared with 0.425 and 0.13 e.m.u./g. in Lin's crystal. Below the transformation the basal plane and ternary axis show saturation magnetisations of 0.15 and 0.175 e.m.u./g. whereas Lin obtained corresponding values of 0.02 and 0.16 e.m.u./g. Néel's transformation occurred between + 77 and - 48°C and Lin's between + 87 and - 23°C.

Lin and Néel found that the antiferromagnetic susceptibility in the basal plane was constant with temperature except for a 20 % increase at the transformation. Parallel to the ternary axis Néel's crystal had an antiferromagnetic susceptibility changing from 22×10^{-6} above the transformation to 2×10^{-6} below compared with Lin's changing from 32×10^{-6} to 0.05×10^{-6} (see fig. 4a & b).

These authors each have a different interpretation of their results. Néel, who published his paper six years before Dzialoshinskii's theoretical work (see 1.10), resolves his ferromagnetism into an isotropic component present at all temperatures and a highly anisotropic component present in the basal

plane above the transformation. He assumes that it disappears below the transformation because there are two domain orientations parallel to the ternary axis producing the same magnetisation in opposite directions. As this ferromagnetism is highly anisotropic it is impossible to saturate even with 20 KOe. The ferromagnetism is attributed to incomplete compensation of the antiferromagnetic sublattices originating from local fluctuations of composition. Lin's interpretation of the ferromagnetism is again incomplete compensation of sublattices but with very slight canting of one spin lattice with respect to the other. The latter contribution originates from Dzialoshinskii's relativistic spin interaction which exists only above the transformation.

Analysing Lin's isotherms further, one finds that the ferromagnetism saturates at 8 KOe. in the basal plane (at all temperatures) and 12 KOe. in the ternary axis above the transformation. Below the transformation some saturation seems to take place by domain wall motion up to 500 Oe. (although Lin states his results are unreliable in the low field region). Any further increase of field has no effect whatsoever, the ferromagnetism remaining at the low field value. The magnetisation is no smaller than the high

temperature state. Hence there is not a reduced couple on the ferromagnetism. We conclude that the magnetisation remaining below the transformation along the ternary axis seems extremely anisotropic, to the extent of preventing rotation of the magnetisation within a domain.

The most important points arising from these two papers are the antiferromagnetic susceptibility results. These show good qualitative agreement with the neutron diffraction work of Shull, Strauser & Wollan (1951) on a natural specimén. Below the transformation the susceptibility along the ternary axis is the lowest measured and is temperature dependent i.e. it is a susceptibility parallel to the spin system. The susceptibility in the basal plane is constant at 20×10^{-6} above and below the transformation i.e. it is a susceptibility perpendicular to the spin system. As Néel points out, the susceptibility in the basal plane is isotropic. Hence we are forced to the unusual conclusion that for this particular antiferromagnetic material the spin system always sets itself orthogonal to a magnetic field applied anywhere in the basal plane i.e. the antiferromagnetic spin system is isotropic in the basal plane.

Bizette, Chevalier & Tsai (1953) made measurements

		σ_s E.M.U./G. BELOW TRANS.	σ_s E.M.U./G. ABOVE TRANS.	$\chi \times 10^6$ BELOW TRANS.	$\chi \times 10^6$ ABOVE TRANS.	TRANS. RANGE °C
NEEL 1953	BASAL PLANE	0·15	0·47	17·5	20	+77 TO -48
ELBA	TERNARY AXIS	0·175	0·225	2·0	22	
LIN 1959	BASAL PLANE	0·02	0·425	21	20	+87 TO -23
ELBA	TERNARY AXIS	0·16	0·13	0·05	32	
BIZETTE ET AL.	BASAL PLANE	0	0·42	23·5	23·5	-20 TO -100
1953 ETNA (1)	TERNARY AXIS	0	0	0	19·3	
BIZETTE ET AL.	BASAL PLANE	0	0·36	20·6	20·6	-20 TO -100
1953 ETNA (2)	TERNARY AXIS	0	0	0	21·2	
TASAKI ET AL.	BASAL PLANE	0	0 36	17·5	16	-9 TO -12·5
SYNTHETIC (A) 1963	TERNARY AXIS					

Fig. 5. Table of magnetic results obtained from five natural hematite crystals.

of the specific magnetisation versus temperature on two Etna crystals. They applied fields of up to 21,750 Oe. at six different temperatures but only noted the magnetisation at four field values. Even in a field of 21,750 Oe. they found no ferromagnetism along the ternary axis above the transformation. There was no ferromagnetism anywhere below the transformation. The results were analysed in terms of a ferromagnetic and antiferromagnetic component. The results are summarised in fig. 5 but because of the small number of measurements their values, especially the transformation range, are not as reliable as Néel's and Lin's.

Tasaki & Iida (1963) measured the variation of saturation magnetisation and susceptibility of a synthetic hematite crystal with temperature. The crystal, grown by the flux melt method, was rather small (about 1 $mm.^3$). A magnetic balance was used to measure the magnetisation in a field. In the same way as Néel and Lin they expressed the magnetisation in a field as an antiferromagnetic component and a saturated ferromagnetic component. The values of these contributions were obtained from isotherms of specific magnetisation plotted against only three field values (4.8, 8.8 & 13.36 KOe.).

The magnetic parameters were measured only in the basal plane between -40 and 20°C. The magnetic balance had no facility for preventing rotation of a suspended crystal hence it was impossible to make measurements along the ternary axis. Their results are tabulated in fig. 5. In the basal plane the antiferromagnetic susceptibility increased from 16.0×10^{-6} above the transformation to 17.5×10^{-6} below. The characteristic peak in susceptibility is present at the transformation. The saturation magnetisation was 0.36 e.m.u./g. above and undetectable below the transformation. After 2.5 KOe. had been applied throughout the cooling the remanence magnetisation was measured and found to be 3.0×10^{-4} e.m.u./g. at -50°C.

The transformation occurred between -9 and -12.5°C.

The crystal exhibited a uniaxial anisotropy in the basal plane at room temperature (from torque measurements).

1.3 The Effect of Temperature on the Remanent Magnetisation of Synthetic and Natural Crystals. The only quantitative measurements of remanent magnetisation are on a synthetic and an Elba crystal by Lin (1961), (1960). The synthetic crystal, supplied

by Bell Telephone Laboratories was $3x3x4.5\,mm.^3$. The natural crystal was ground into a 4.5 mm. diameter sphere.

The remanent magnetisation was obtained from the vertical component of force on a crystal suspended in a vertical field gradient of several Oe./cm. To obtain repeatable results both virgin crystals had to be cycled through the transformation prior to measurement.

Lin measured the remanent magnetisation of the Elba crystal in two orthogonal directions in the basal plane and then along the ternary axis in the temperature range -196 to $+215^{\circ}C$. From these values he computed the direction and magnitude of the resultant remanent magnetisation. He checked the validity of this computation by actually measuring the remanent in a plane containing the ternary axis and the direction of the maximum component in the basal plane (found by the previous method). This was done at three temperatures and in each case the resultant by calculation agreed in magnitude and direction with the measured maximum remanent magnetisation. Hence the field gradient which he had applied in three orthogonal directions was not affecting the magnetisation. The remanent magnetisation of the synthetic crystal was

measured in a direction in the basal plane and along the ternary axis.

In the Elba crystal the remanent magnetisation turned completely from the basal plane into the ternary axis after cooling through the transformation. The remanent decreased from 0.049 to 0.014 e.m.u./g. The transformation occurred between +87 and -53°C (i.e. midpoint of +13°C) which he compared with the spontaneous magnetisation changing between +87 and -23°C (see 1.2). Presumably his Elba specimens were cut from the same mother crystal.

As with the Elba, the remanent magnetisation is a maximum in the basal plane of the synthetic crystal above the transformation. On cooling it changed from 0.015 e.m.u./g. above the transformation to zero below. The remanent magnetisation had disappeared completely. The transformation range was 1 or 2°C. This crystal showed a temperature hysteresis at the transformation of 10°C. Averaging the hysteresis effect the mid-point of the transformation was -10°C. The Elba also exhibited a hysteresis effect but the beginning and end of the transformation was independent of whether the crystal was being heated or cooled.. It was only during the transformation that the remanent magnet-isation had two different values at a finite temp-

erature. However Lin's saturation magnetisation results showed no temperature hysteresis.

Lin obtained some additional results on his synthetic crystal. He applied a field to compensate for the earth's field. If this field was adjusted correctly and he cycled the crystal through the transformation he found that after removing the field the crystal possessed no remanent magnetisation at room temperature. Hence, he concluded, the earth's field is a directive field producing the remanent magnetisation. He applied directive fields from 0 to 100 Oe. in the basal plane and cycled the crystal through the transformation. The field was removed and the remanence measured. The remanence increased with directive field, tending to saturate at a value of 0.12 e.m.u./g. at 30 Oe. Note that the magnetisation processes in these small fields are irreversible, i.e. when he removes the field at room temperature the crystal does not assume its 'earth's field' remanence value.

1.4 The Low Temperature Transformation in Synthetic Hematite Powders. Honda & Soné (1914), Charlesworth & Long (1939) and Morin (1950) measured the susceptibility of synthetic powders by noting the force on

	PURITY	CURIE POINT	PARAMETER	FIELD APPLIED	TRANS. MID-POINT	TRANS. RANGE	$\chi \times 10^6$ ABOVE TRANS.	$\chi \times 10^6$ BELOW TRANS.	NOTES
HONDA & SONE 1914	–	682 – 692 °C	χ	–	-25 °C	-18 TO -32 °C	40	15·5	–
CHARLESWORTH & LONG 1939	–	–	χ	–	-23·5 °C	-17 TO -30 °C	37·5	20·5	10 °C HYSTERESIS
MORIN 1950	99·1 %	690 °C	χ	2 KOE.	-22·5 °C	-9 TO -36 °C	132	16	NOT SATURATED
GUILLAUD 1951	–	674 – 688 °C	σ_S	33 KOE.	-42 °C	-29 TO -54 °C	16·6	16·6	SATURATED AT 23 KOE.
HAIGH 1957	99·9 %	–	σ_R	–	-19·5 °C	-7 TO -32 °C	–		–
HAIGH 1957	99·9 %	–	σ_R	–	-11·5 °C	-7 TO -16 °C	–		HEAT TREATED

Fig. 6. Table of magnetic results obtained from synthetic hematite powders.

a specimen in an inhomogeneous field at different temperatures. Haigh (1957) subjected his specimens to 17 KOe. at room temperature and noted the remanent magnetisation on cooling through the transformation. Guillaud (1951) plotted the variation in specific magnetisation with temperature at constant fields.

Unfortunately quantitative comparision of the magnetic susceptibility results is almost impossible. Morin found that the susceptibility varied with particle size; after he had ground a powder specimen the room temperature susceptibility changed from 127×10^{-6} to 20×10^{-6}. In addition Morin and Charlesworth et al. found a field dependent susceptibility. Morin found a value of 14.8×10^{-6} in a field of 5 KOe. compared with 16.7×10^{-6} in 2 KOe. The variation can be attributed to an unsaturated ferromagnetic component.

Most specimens contain some impurities which have an effect on the susceptibility and the transformation temperature (see 1.6). The purity of some specimens has been included in the table of results (see fig. 6). The Curie temperatures of the powders give an additional indication of purity (the Curie point for pure hematite is $675^{\circ}C$).

The powder work serves the purpose of showing the

large variation of results in hematite which is due to the specimen purity and/or the impossibility of direct comparision of the measurements. For example the mid-points of the low temperature transformation vary from -42 to -11.5°C. Charlesworth & Long (1939) found a 10°C temperature hysteresis which could not be ascribed to their apparatus.

It should be noted that after heating his specimen in air (1100°C for 16 hours) Haigh (1957) found that the temperature range of the transformation had decreased by a factor of two, and that the mid-point had increased from -19.5 to -11.5°C.

Contrary to other measurements, Guillaud's (1951) susceptibility results showed no difference above and below the transformation, but his susceptibility measurements were made in a field of 33 KOe. compared with other measurements which were made in fields of not more than 10 KOe. His plot of σ/H at room temperature only begins to saturate at 23 KOe. but in spite of this it is not comletely saturated in 33 KOe. Guillaud found that for a field increase of 28 KOe. the mid-point of the transformation was depressed by 6°C. He detected no latent heat effect at the transformation. On cooling he finds a gradual decrease of the linear expansion coefficient of the powder specimen

from -46 to -52°C followed by a sudden increase and a continued decrease down to -63°C at which it remains constant. This compares with the specific magnetisation changing between -29 and -54°C.

1.5 Domains and Domain Effects in Hematite. Magnetic domain effects were first found by Blackman, Haigh & Lisgarten (1957) using the electron beam method (see 2.8) on natural single crystals. The cycloid-like magnetic shadow pattern of the crystal decreased in amplitude on cooling through the transformation, and on heating to room temperature the pattern reappeared exactly as before.

The domains themselves were observed by Williams, Sherwood & Remeika (1958) in thin synthetic crystals with polarised light using the Faraday effect. The crystals were transparent plates 25 microns thick which had grown parallel to the (111) plane. As the magnetisation vectors lie in the basal plane at room temperature the specimens had to be tilted to obtain any appreciable magneto-optic rotation. The domain structure could be changed by the application of a magnetic field of 10 Oe. The domain boundaries sometimes came together without annihilating each other

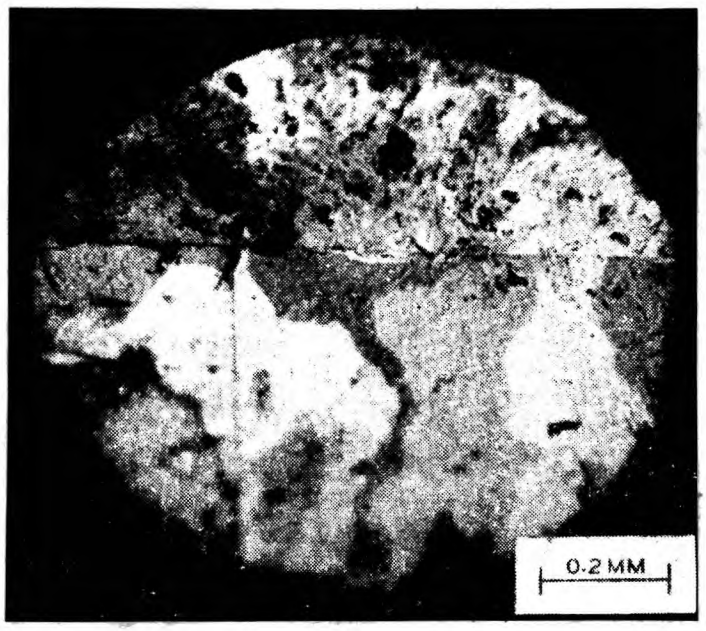


Fig. 7. Magnetic domains seen in a synthetic hematite crystal by means of the Faraday effect (Williams, Sherwood & Remeika 1958).

to form pairs of boundaries. Frequently domains of three different intensities were present (see fig. 7).

When the specimen was cooled through the transformation the domains disappeared. Then as the specimen warmed up they reappeared in a different pattern. The mechanism by which the domains moved at the transformation was a nucleation process in which a small region formed and then grew rapidly by the propogation of a sharp boundary until it spread over the entire crystal. Domains of high contrast were seen on one side of the boundary while the other side appeared uniform in intensity.

The electron beam work has been reported by Blackman, Haigh & Lisgarten (1959), Kaye (1961), (1960). The electron shadow pattern (see 2·8) of many natural hematite crystals generally exhibits the same cusp size and amplitude above the transformation no matter which crystal face is being studied. It is possible to change these patterns by applying a magnetic field. A domain size of approximately 250 microns was calculated from the width of the cusp patterns. Considering the difficulty of defining the size of these irregular domains this result shows good agreement with the photographs of Williams, Sherwood & Remeika (1958).

On cooling a number of natural crystals of different origin through the low temperature transformation about two thirds of them exhibited a cusp pattern which decreased in amplitude to form a geometrical shadow of the crystal. The shadow pattern of the remaining third of the crystals decreased a fifth to a tenth of their room temperature amplitudes and remained at this value with only slight changes on cooling down to - 180°C. Hematite crystals from St. Gothard which had been cooled to this same temperature exhibited no low temperature transformation except for a slight rearrangement of the cusp pattern.

After one or two temperature cycles practically all the crystals had developed a 'memory' in the sense that the electron beam patterns at room temperature were nearly identical after successive transformations.

Kaye (1960) did a preliminary heat treatment experiment to investigate its effect on the low temperature transformation. He heated three crystals from Elba, the Ascension Islands and Brazil to 1100°C in air for a day and then quenched them in air. There was no change in the transformation as seen by the electron beam method in the crystal from the Ascension Islands. The Elba had the same transformation temperature but below the transformation there

was no usual cusp pattern, only a geometrical shadow of the crystal. Instead of transforming between - 75 and - 95°C the crystal from Brazil transformed between - 57 and - 105°C.

It is interesting to examine Kaye's (1962) results on the Curie point of hematite as this is another magnetic transformation. On heating his natural crystal to 600°C there were very few additional features to the electron beam pattern. Between 600 and 688°C (the highest Curie point he measured) there was a rapid decrease in amplitude of the cusps giving rise to a geometrical shadow at 688°C. On any one crystal he found no local variation of Curie temperature. If a crystal was cycled through the Curie point several times the cusp pattern indicated a memory effect but not as perfect as at the low temperature transformation.

1.6 Effect of Impurities on the Low Temperature Transformation. In recent years impurity effects have been invoked more and more as an interpretation for some of the ferromagnetic properties of hematite. For this reason it will be useful to summarise the experimental results obtained in this field.

This work has taken on at least two distinct

forms. One has been to dope synthetic hematite powders with known amounts of impurity and to measure the variation of spontaneous magnetisation, susceptibiliy or remanent magnetisation with temperature at the transformation. Another has been to study the transformation by measuring the change in leakage field at the surface of natural analysed crystals using the electron beam method at different temperatures (see 2.8). The natural crystals have certain impurities already substituted in them.

Morin (1950) and Haigh (1957) used the first approach and chose to dope their synthetic powders with titanium. They prepared their specimens in exactly the same way except that Haigh started with 99.9% and Morin with 99.1% pure α-Fe_2O_3 powder. The hematite powder was doped by adding known amounts of TiO_2 and grinding the mixture. The powders were next pressed together, using 18,000 p.s.i. in Haigh's case, and sintered at 1100^{o}C for 16 hours. Haigh's specimens were sealed previously at room temperature in one atmosphere of oxygen whereas Morin sintered his in oxygen at atmospheric pressure. The pellets were ground into a powder and the variation of magnetic properties with temperature noted.

Morin measured the magnetic susceptibility of

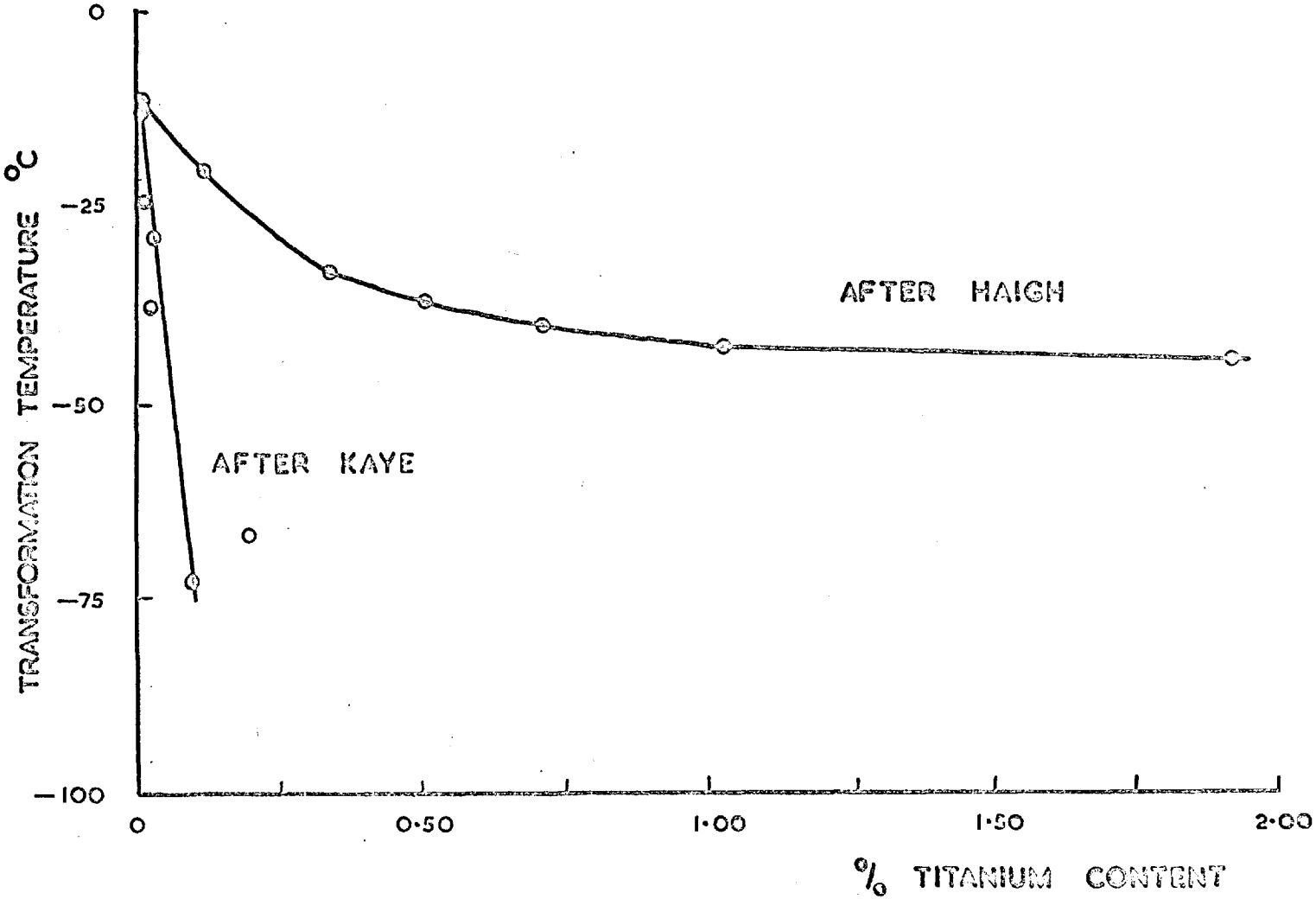


Fig. 8. The transformation temperature of hematite as a function of Ti ion content (Haigh, 1957 and Kaye, 1961).

his specimens at different temperatures by the Gouy method. On heating a pure specimen from below the transformation the susceptibility changed from 16.7×10^{-6} to 132.0×10^{-6}, the main changes occurring between -18 and -28°C. The addition of 0.05% Ti and 0.2% Ti (by weight) had no effect on these results but 1.0% Ti suppressed the transformation to at least -170°C, the magnetic susceptibility retaining its room temperature value even at -170°C.

Haigh (1957) magnetised his synthetic powder specimens in 6 KOe. at room temperature and plotted how the saturation remanence varied on cooling. He defined the transformation temperature as the temperature at which the saturation remanence was midway between the high temperature and the low temperature states. This temperature was plotted against percentage titanium impurity by weight. Haigh did the same experiments on aluminium impurity introduced in the form of Al_2O_3 (see fig. 8).

Morin was able to depress the transformation down to at least -170°C with only 1% titanium but Haigh's work still shows a transformation with 1.92% titanium present.

The decrease in the transformation temperature on adding titanium reached a saturation value at

about 1.5% titanium impurity. When Haigh tried to substitute 5% and 10% titanium into the hematite lattice he obtained additional X-ray rings not associated with the hematite lattice. Hence it appears that above 1.5% titanium he was unable to substitute any more into the lattice.

It is interesting to note that 0.17% titanium lowered the transformation by the same amount as 10% aluminium.

The differences in Morin and Haigh's results will be examined in the light of Kaye's (1961) work which will be discussed next.

Kaye's paper is essentially a continuation of the work of Blackman, Haigh & Lisgarten (1959). Kaye had many natural crystals from different sources spectrochemically analysed. Crystals from the same source were shown to have about the same transformation temperature measured by the electron beam method (see 2.8). From the spectroscopic analysis and the following deduction Kaye arrived at an upper limit of the titanium accomodated in the lattice. If a number of specimens from the same source have the same transformation temperature then the titanium content in the lattice ought to be the same. If the spectrochemical analysis of these specimens gives different titanium

contents, then the lowest value found should be an upper limit to the actual titanium content in the lattice. His results are plotted with Haigh's in fig. 8.

Both Haigh's and Kaye's work shows an increase in the temperature range of the transformation as well as a decrease in the transformation temperature with increase of titanium in the lattice. Haigh found that below the transformation the remanent magnetisation of the specimen containing 0.98% Ti was two and a half times greater than the pure hematite powder.

Examining the results of the three workers together one concludes from Kaye's work that the titanium in Morin's and Haigh's powders was not completely substituted into the lattice, even below 1% Ti. This is because the transformation temperature of Kaye's natural specimens was depressed to $-80^{\circ}C$ with as little as 0.1% Ti. Although Haigh used X-rays to look for unaccommodated impurity this was only indicated as extra rings after as much as 5% titanium impurity was added. Assuming that 2.5% titanium is needed to make X-ray rings of the other material visible, then according to Kaye's results nearly 2.5% is present in a manner which does not effect the transformation temperature as drastically as direct

substitution of titanium. The only other way of accommodating titanium ions is as interstitials in the hematite lattice.

Morin's results can be interpreted in the same way except that he obtained very sudden changes in the effect of titanium, viz. no change in transformation temperature for 0·2% titanium and complete suppression down to at least $-173^{\circ}C$ for 1·0% titanium. The differences between Morin's and Haigh's results can perhaps be attributed to Morin sintering his specimens in an atmosphere of oxygen whereas Haigh sealed his in one atmosphere of oxygen so the resultant pressure at $1100^{\circ}C$ was nearer four atmospheres.

Tasaki, Siratori & Iida (1962) doped synthetic polycrystals with different trivalent metal ions to the extent of 2% (atomic). The method of doing this was not described. They obtained curves of spontaneous magnetisation versus temperature for the substitution of different elements. Their results show general agreement with Kaye's and Haigh's work in that the impurities lowered the transformation temperature and decreased the temperature range of the transformation. The mid-points of the transformation were $-15^{\circ}C$ for no substitution, $-25^{\circ}C$ (Al), $-50^{\circ}C$ (Ga), $-65^{\circ}C$ (Mn) and $-100^{\circ}C$ (Cr). Haigh

used 7% aluminium impurity to lower the transformation temperature to the $-25^{\circ}C$ obtained by Tasaki's 1.25% aluminium.

Morrish, Johnston & Curry (1963) studied the direct effects of impurities on the antiferromagnetic ordering at the transformation. They grew hematite crystals from spectroscopically pure powders by the flux melt method. Some crystals were grown with Ga^{3+} ions incorporated. Gallium is diamagnetic and has virtually the same ionic radius as Fe^{3+}. The variation of the intensity of the (111) magnetic reflections were measured using neutron diffraction.

The pure hematite crystals exhibited a sharp transformation between -10 and $-11.6^{\circ}C$, being almost identical for several crystals from different melts. The form of the intensity curve is compared with other neutron results in fig. 9. The most interesting fact is that they found a residual reflection of 3% of the room temperature intensity at $-25^{\circ}C$, and 1.5% at $-140^{\circ}C$. The background scattering was only one quarter of the last value.

The mid-points of the doped specimens were

Trans. mid-point $^{\circ}C$	Mole % of Ga^{3+}
-10.8	0
-15.0	0.30
-21.5	0.60
-30.5	1.38

The addition of impurities lowered, and produced a longer 'tail' to the transformation. The 1·38% crystal was unlike the other specimens. It showed a gradual decrease of intensity from $-8^{\circ}C$ down to the main part of the transformation starting at $-30^{\circ}C$.

Ogilvie (1963) irradiated a natural crystal (having a temperature hysteresis of $10^{\circ}C$ at the transformation) with neutrons. The integrated fast flux was 5×10^{17} n.v.t. Irradiation produced a general increase of spontaneous magnetisation both above and below the transformation. Essentially the transformation temperature was unchanged.

Kaye found that the transformation was depressed to at least $-180^{\circ}C$ in specular hematites from St. Gothard containing 1% titanium. Morin's synthetic powder doped with 1% titanium exhibited at least the same depression. His specimen showed the same magnetic susceptibility, and Kaye's the same magnetic leakage field and domain size, as the room temperature state of hematite. Curzon (1963) has cooled a St. Gothard hematite to liquid helium temperatures, and still no transformation has been found using the electron beam method. It seems that the turning of the spins is completely suppressed in some natural hematites.

The ferromagnetism of hematite specimens exhibiting

no transformation has the characteristics of the state above the transformation. Presumably the magnetisation is directed in the basal plane or at an angle to it rather than lying along the ternary axis.

Consider the effect of cooling a normal hematite from above the transformation. The reduction of temperature tends to force the spins to turn from the basal plane into the ternary axis. This tendency increases with decrease of temperature, and at the transformation temperature the spins are turned into the ternary axis. The addition of impurities to pure hematites maintains the high temperature state and hence the transformation does not occur until a still lower temperature is reached.

The addition of impurities to hematite broadens the transformation as well as lowering the transformation temperature. This effect can be interpreted in terms of very localised differences in the amount of substituted impurity. Suppose that the impurity is titanium, the local transformation temperature will be some function of the amount of substituted titanium. Hence there is a local variation of transformation temperature. Considering the magnetic changes with temperature over the whole of the crystal this results in a broadened transformation due to the

substituted titanium. The broadening of the transformation could be interpreted in exactly the same way using interstitial impurity atoms intead of substituted impurity atoms. It would probably need larger percentages of titanium to have the same effect as the substituted atoms.

Summarising the effect of impurities, we note that Haigh (1957) found a 10 % increase in the saturation remanence (based on the room temperature value) below the transformation for the addition of 0·68% titanium. The large amount of titanium needed to displace the transformation temperature in Morin's and Haigh's synthetic powders compared with Kaye's natural specimens could be caused by the titanium being absorbed in the lattice as interstitial atoms rather than by complete substitution.

The differences in Morin's and Haigh's results could be attributed to the use of hematite powders of different purity or to the different oxygen pressures used when sintering the specimens. However, the most important results are that the transformation was always depressed by the addition of metal impurities. The impurities preserved the high temperature state rather than the low. The impurities expressed in order of their effectiveness at depressing the transformation are

Ti, Cr, Mn. Ga and Al.

Haigh and Kaye found that the transformation becomes broader with successive additions of impurities. This could be due to local variations in the percentage of substituted or interstitial atoms resulting in a local variation of transformation temperature.

1.7 Anisotropy Measurements in Hematite Crystals. Work has been reported recently on the direct measurements of the anisotropy properties of hematite crystals. Flanders & Schuele (1963) examined some 40 single crystals, both natural and synthetic (from Bell Telephone Laboratories), at room temperature. The anisotropy was measured in the basal plane at 10 KOe. using a torque magnetometer. Due to the crystal structure of hematite a triaxial anisotropy is to be expected in the basal plane. If the energy density in the basal plane is assumed to be

$$E = K \sin^2 3\vartheta$$

where K is the crystalline anisotropy constant (ergs./cc.), then a torque

$$L = 3K \sin 6\vartheta$$

must be applied to the crystal to maintain the saturation magnetisation at an angle ϑ to the easy

direction of magnetisation.

Of the 40 specimens studied only 6 natural specimens displayed a 6θ behaviour. No substantial number of the remaining crystals possessed any singular angular dependence on torque similar to the 6θ behaviour. These results are similar to those of Kaczér (1963) except that he had a higher proportion of crystals exhibiting a triaxial anisotropy.

Banerjee (1963) obtained torque curves at 12 KOe. from three Naples crystals. He found a mixture of 2θ, 4θ and 6θ terms in the basal plane of all his specimens (the 2θ could be attributed to incorrect setting of the crystal).

The value of K obtained by Flanders & Schuele ranged from 7 to 188 ergs./cc. The magnetic susceptibility varied from 19×10^{-6} to 26×10^{-6} and the specific magnetisation from 0.40 to 0.49 e.m.u./g. in the basal plane.

Magnetic resonance gives some indication of the anisotropy properties of hematite. Anderson, Merritt, Remeika & Yager (1954) used magnetic resonance at 1.25 cm. wavelength to study the anisotropy properties of a synthetic hematite crystal. This early crystal (volume 73 $mm.^3$) grown at Bell Telephone Laboratories had 3% Fe^{2+} impurity present. They found a small

trigonal dependence of ferromagnetic anisotropy in the basal plane. There was strong resonance in a field of 2·3 KOe. when the D. C. and R. F. fields were both perpendicular to the ternary axis. From this they deduced that the anisotropy field out of the basal plane was 30 KOe.

From -50°C to room temperature, and at fields up to a maximum of 19 KOe., no resonance peak was detected with the D. C. field along the ternary axis. As the crystal was cooled through the transformation there was no shift or broadening of the basal plane resonance peak. At -13·5°C the peak began to decrease in intensity. The resonance is half of the room temperature intensity at -14·5°C. At -17°C there was no measurable resonance. They concluded from these results that the ferromagnetism does not change its direction with the antiferromagnetism. Corliss, Hastings & Goldman (1954) examined the transformation of this synthetic crystal using neutron diffraction. With a temperature control of 0·2°C they noted the change of intensity of the (111) scattering which originates entirely from the magnetic ordering in the basal plane. The intensity begins to decrease rapidly at -10°C reaching a third of its room temperature value at -13·5°C (the beginning of the transformation

in terms of a change of the intensity of resonance). The magnetic neutron scattering peak disappears at about the same temperature, $-17{\cdot}5^{\circ}C$, as the resonance peak.

Tasaki & Iida (1963) measured the magnetic anisotropy in two synthetic crystals. They used a different method on each crystal. The crystals which were grown by the flux melt method were rather small having a volume of about 1 $mm.^3$ Torque measurements on crystal A in the basal plane above the transformation temperature indicated a uniaxial form to the anisotropy.

Magnetic resonance was used at room temperature on crystal B ($2x2x0{\cdot}3$ $mm.^3$). A resonance peak for 0·8 cm. wavelength was found at a D. C. field of 5·55 KOe. compared with Anderson's value of 2·27 KOe. for microwaves of 1·25 cm. wavelength. Tasaki & Iida found a trigonal anisotropy in the basal plane of crystal B. If pressures of 2 $Kg./cm.^2$ were applied to the basal plane, the resonance peak was broadened and reduced in intensity. In addition, the peak was shifted to give a resonance at 100 Oe. lower than the original 5·55 KOe.

1.8 The Effect of Strain on the Low Temperature Transformation. Makkay, Geiger & Fine (1962) measured

the variation of Young's modulus with temperature of two natural crystals from Congonhas, Brazil. They employed a resonant longitudinal vibration method using piezoelectric 5° X-cut quartz crystals at 125 and 150 Kc/s.

Crystal A was $3{\cdot}4 \times 1{\cdot}5 \times 26{\cdot}1$ mm.^{3} in size. The long direction was the $[2\bar{1}\bar{1}0]$ direction, i.e. parallel to one of the theoretical directions for the spin system in the basal plane. The crystal was heated from -173°C. Young's modulus decreased gradually from $26{\cdot}0 \times 10^{11}$ to $25{\cdot}0 \times 10^{11}$ dynes/cm.^{2} at -13°C. Between -13 and -8°C there was a sudden decrease to $22{\cdot}2 \times 10^{11}$ dynes/cm.^{2} The modulus remained constant with any further increase in temperature. When a field of 1·57 KOe. was applied in the basal plane perpendicular to the direction of measurement there was no change in the transformation temperature but the sudden decrease in Young's modulus did not appear and the value remained at $25{\cdot}0 \times 10^{11}$ dynes/cm.^{2}

In crystal B, $2{\cdot}5 \times 4{\cdot}2 \times 21{\cdot}2$ mm.^{3}, Young's modulus was measured along the ternary axis and a magnetic field was applied along one of the preferred spin directions in the basal plane. Under these conditions Young's modulus was $41{\cdot}3 \times 10^{11}$ dynes/cm.^{2} at -170°C. This crystal exhibited the same characteristic changes

of modulus with temperature and magnetic field as crystal A.

Urquhart & Goldman (1956) measured the strain in a natural hematite crystal as a function of applied magnetic field and temperature. Above the transformation temperature the spin systems are directed towards one of the three nearest neighbours in the basal plane. The strain was measured with a strain gauge along one of these directions.

In an applied field of 3·7 KOe. the strain could be expressed as

$$\frac{\Delta l}{l} = (8\times10^{-6})\sin^2\vartheta .$$

ϑ is the angle between the direction of strain measurement and the field applied in the basal plane. Hence the strain was a maximum (8×10^{-6}) when the magn magnetic field was perpendicular to the preferred spin direction. The crystal was longest with the field parallel to this direction and shortest with the field orthogonal to it.

Detailed values of strain were obtained between -12 and $-38^{\circ}C$ with the gauge and applied field oriented to give maximum strain. The resulting strain-temperature curve is similar to Guillaud's expansion coefficient-temperature curve. The strain was zero

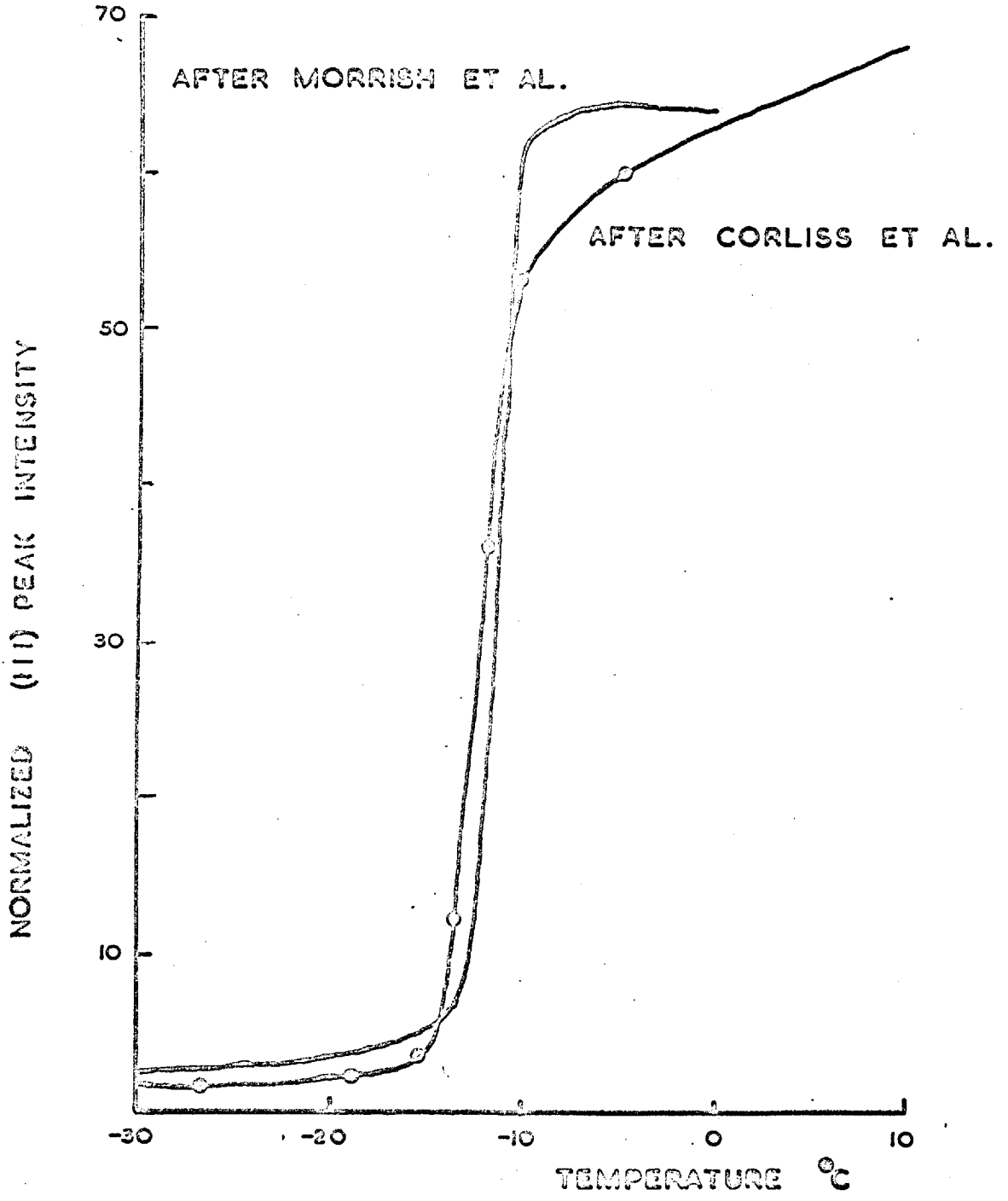


Fig. 9. The peak height of neutron scattering from the (111) plane of two synthetic crystals as a function of temperature (Corliss et al., 1954 and Morrish et al., 1963).

at $-141^{\circ}C$. The range of the transformation was $1^{\circ}C$.

The strain-temperature relationship retained the same form in different applied fields between 1·2 KOe. and the maximum which was applied, 6·5 KOe. An increase of 6 KOe. in magnetic field lowered the mid-point of the transformation temperature by $3·5^{\circ}C$. The reduction of the transformation temperature was a linear function of magnetic field. Extrapolating to zero applied field, the mid-point of the transformation would be $-26·5^{\circ}C$. However, Corliss, Hastings & Goldman (1954) carried out a neutron diffraction study of this same crystal and found that the intensity of the (111) magnetic reflection and the transformation temperature was unaffected by magnetic fields up to 6 KOe. The transformation, in terms of a change of the intensity of the magnetic reflection, occurred between -23 and $-24^{\circ}C$ (see fig. 9). The field was applied in one direction only.

1.9 The Curie Point of Hematite. The Curie temperature and the Néel temperature are both given as $675^{\circ}C$ in a review by Nicholls (1955) of the magnetic, thermal expansion and specific heat measurements on hematite specimens from different origins. This figure must be subjected to a range of at least $15^{\circ}C$

because the change of a magnetic parameter with temperature does not exhibit a sharp discontinuity in the neighbourhood of the Curie point.

The only work using neutron diffraction at high temperatures (Shull, Strauser & Wollan, 1951) indicates antiferromagnetic ordering above 725°C. As this paper is a report of the first neutron diffraction work on antiferromagnetics it is important to have confirmation of the result by measurements on good synthetic crystals.

Willis & Rooksby (1952) tried to establish a discontinuity in the linear expansion coefficient at the Curie or Néel point using X-ray diffraction. From powder patterns photographed between 20 and 950°C they were able to plot the c/a ratio of hematite as a function of temperature. They computed the expansion coefficient along the ternary axis. The change of ordering could have occurred anywhere between 650°C and 710°C as the results do not indicate a well defined discontinuity. The c/a ratio gradually decreases with increase of temperature, the decrease being less marked above the Néel point. The expansion coefficient decreases from $1{\cdot}0\times10^{-5}$ to $0{\cdot}77\times10^{-5}$ between 200°C and 650°C. This is followed by a rapid increase to a maximum of $1{\cdot}35\times10^{-5}$ at 710°C. At higher temperatures, the decrease of the expansion coefficient is more

marked than those between 200 and 650°C.

Kaye (1962) measured the Curie point by extrapolating the curve of the relative values of the domain leakage field at different temperatures onto the temperature axis. The curve was obtained by measuring the amplitude of the electron cusp pattern of hematite crystals at different temperatures. For an Elba crystal, which contains impurities smaller than 0·01%, Kaye obtained a Curie point of 688°C (± 3°C), and found that 1% titanium impurity in hematite, all of which is not necessarily accomodated in the lattice, depressed the Curie point to 643°C.

1.10 Theories on the Ferromagnetism of Hematite. In 1956, Li advanced a theory that the ferromagnetism of hematite is produced by ferromagnetic ordering at antiferromagnetic domain walls. He calculated the domain size that was needed to produce the ferromagnetism measured in hematite. Experimental results have shown that the domains in hematite are a factor of 50 larger than Li's theoretical value, and the domains have the characteristics of ferromagnetic domains when a magnetic field is applied (see 1.5). If polarised light is passed through a hematite crystal the plane of polarisation is rotated by each

domain.

Néel (1953) has proposed that the ferromagnetism originates from the two antiferromagnetic sublattices of hematite. Néel suggests that they are not equivalent and that this is due to local fluctuations of composition producing an excess of iron ions in one of the sublattices. However, chemical examination of recent synthetic specimens from the Bell Telephone Laboratories shows them to be stoichiometric crystals, and using electron diffraction no local variation of structure is found. These crystals possess a magnetic moment comparable with that of the natural crystals.

The work of Dzialoshinskii (1957) is the most comprehensive theoretical treatment of the ferromagnetism of hematite. He postulates that above the transformation temperature the ferromagnetism of hematite is an intrinsic phenomenon. This is based partly on the fact that in this temperature region the ferromagnetism does not vary appreciably from one crystal to another. Using the neutron diffraction results, Dzialoshinskii writes down the symmetry of the antiferromagnetic distribution of spins. He shows that this symmetry permits ferromagnetism, i.e. it is possible to change the directions or magnitudes of the spins without disturbing the symmetry of their original

distribution, in such a way as to make the sum of the spins over the unit cell different from zero. The magnetic symmetry of hematite below the transformation temperature makes it impossible for ferromagnetism to exist in an ideal crystal. The ferromagnetism present above the transformation temperature is directed either along one of the two-fold axes or it is in one of the symmetry planes. Dzialoshinskii uses Landau's theory of phase transitions of a second kind to chose between these two possibilities.

He states that hematite exhibits a phase transition of the second kind in which the magnitude and orientation of the spins in the crystal change in a continuous manner with temperature, but the symmetry changes discontinuously. At the transformation point itself, the symmetries of the two phases coincide. The thermodynamic potential is expanded in terms of a series of powers of the components of the mean spin of each of the four iron ions in the unit cell. The expansion is made to be invarient under the action of all the symmetry transformations of the ordinary space group of the crystal. The terms in the expansion are classed into three types of spin interaction, exchange interaction, relativistic spin lattice interaction and

magnetic dipole interaction. The equation for the thermodynamic potential is minimised in the neighbourhood of the transformation temperature. This produces two possible states. State 1: The antiferromagnetic spins are directed along the ternary axis and no ferromagnetism is present. State 2: The antiferromagnetic spins lie in the basal plane along one of the two-fold axes or in one of the symmetry planes. The second state produces a spontaneous magnetic moment of $1x10^{-2}$ to $1x10^{-5}$ e.m.u./g. due to the antiferromagnetic spin systems being tilted or canted at an angle of $1x10^{-4}$ radians with respect to one another. By minimising the expression for thermodynamic potential at a temperature well above the transformation temperature he obtains additional information on the position of the antiferromagnetic spins. The two sets of spins are retained in a plane, a plane which is not the basal plane but is less than $1x10^{-2}$ radians to it. It will be remembered that above the transformation temperature the antiferromagnetic spins were directed along one of the two-fold axes or they were in one of the symmetry planes. Dzialoshinskii choses between these two possibilities by considering the situation at the transformation. From Landau's theory it follows that a transition of the second kind is possible only between

two states such that the symmetry of one state is a subgroup of the symmetry group of the other. From the magnetic symmetry of the two possible directions it is only possible for the antiferromagnetic spins to be directed along one of the two-fold axes.

1.11 A Summary of the Magnetic Properties of Hematite.

The papers reviewed in this introduction do not include all the work that has been done on hematite. They have been selected because they describe the behaviour of the basic magnetic parameters of hematite. This behaviour has yet to be interpreted before more complicated experiments can be undertaken.

Hematite is essentially an antiferromagnetic material. This has been established by neutron diffraction and susceptibility measurements in magnetic fields greater than 10 KOe. Using neutron diffraction, the antiferromagnetic ordering is seen to disappear at about 675°C. In order to be more specific about this temperature a further study of the Néel point is needed.

At approximately -12°C, the magnetic properties of hematite undergo a transformation. The antiferromagnetic spin system changes its direction. Above the transformation temperature the spin moments lie in ferromagnetic sheets parallel to the basal plane with

neighbouring sheets coupled antiferromagnetically. The spin moments are directed towards one of the three nearest neighbours in the sheet. Below the transformation temperature the method of coupling is the same but the moments are now directed perpendicular to the sheets, i.e. along the ternary axis. This arrangement of the spin moments was derived from neutron diffraction measurements. However, Morrish, Johnston & Curry (1963) found that in their synthetic crystals the (111) magnetic neutron diffraction peak was still present at $-140^{\circ}C$ to the extent of 1·5% of its room temperature intensity. Hence, not all the spin moments were directed along the ternary axis below the transformation temperature.

The antiferromagnetic susceptibility of synthetic and natural crystals shows a constant value for all directions in the basal plane above and below the transformation temperature. The variation between crystals is $17{\cdot}5\times10^{-6}$ to $23{\cdot}5\times10^{-6}$. The susceptibility of the natural specimens along the ternary axis has this same range of values above the transformation temperature but below the transformation it decreases to between 2×10^{-6} and zero. Allowing for some anomolously high values above the transformation temperature due to the use of non-saturating magnetic fields,

the powder work shows good agreement with these results.

In addition to its antiferromagnetic properties hematite is weakly ferromagnetic. The ferromagnetism varies considerably from one crystal to another. The ferromagnetic ordering disappears at 680 ± 10°C, depending on the method of measurement and the interpretation of the results. The Curie point is depressed to 643°C in natural crystals containing 1% Ti impurity. Kaye (1962) found no local variations of Curie point across a crystal surface.

In hematite the ferromagnetism undergoes a low temperature transformation with the antiferromagnetism. Below the transformation temperature the saturation magnetisation is much reduced in natural crystals and is immeasurable in some synthetic crystals. The ferromagnetism of hematite is unusual in that it saturates at different values depending on the direction of measurement. The saturation magnetisation (σ_s) of several Elba crystals has been measured in two specified directions above and below the transformation temperature. The results are tabulated overleaf. The field necessary for saturation was obtained by analysing Lin's (1959) magnetisation isotherms. Below the transformation temperature his Elba crystal appeared to saturate along the ternary axis and in the basal

plane in a magnetic field of less than 500 Oe. Above the transformation the same crystal saturated along the ternary axis and in the basal plane at field values of 12 and 8 KOe. respectively. The magnetisation was not equivalent, even in a field of 15 KOe. The range of values depicts the differences between crystals.

	Basal Plane σ_s (e.m.u./g.)	Ternary Axis σ_s (e.m.u./g.)
Above Transformation Temperature	0·36 - 0·47	0 - 0·225
Below Transformation Temperature	0 - 0·15	0 - 0·175

The remanent magnetisation shows a considerable reduction on cooling hematite below the transformation temperature. A synthetic crystal exhibited a remanent magnetisation of 0·014 e.m.u./g. directed in the basal plane at room temperature. The remanent magnetisation disappeared on cooling through the transformation temperature. An Elba crystal had a remanent magnetisation which turned from the basal plane to the ternary axis while the magnitude changed from 0·049 to 0·014 e.m.u./g. on cooling below the transformation temperature. These

measurements were made in a field gradient of several Oe./cm. The value of the remanent magnetisation of the synthetic crystal indicates that the domain structure reduces the saturation magnetisation at room temperature by a factor of 25 compared with the natural crystal's factor of 8.

The domains in hematite are approximately 250 microns across. In synthetic crystals, they are moved by magnetic fields of less than 10 Oe. Williams, Sherwood & Remeika (1958) found that the domain pattern on a synthetic crystal, seen by the Faraday effect, disappeared on cooling through the transformation temperature. Kaye (1960) reported that domain effects in a third of his natural crystals were still present well below the transformation temperature.

The anisotropy of the ferromagnetism has been investigated at room temperature. In fields of 10 KOe., only a small proportion of the synthetic and natural crystals had the triaxial anisotropy predicted by theory. In these crystals the anisotropy constant, K in the equation

$$E = K \sin^2 3\theta$$

varied from 7 to 188 ergs/cc. The remaining crystals showed complicated torque curves.

Having summarised the magnetic properties of hematite

we are now able to examine the low temperature transformation. In a good synthetic crystal, 80% of the (111) neutron diffraction peak produced by the antiferromagnetic arrangement of the spin moments disappeared between -10 and -11·6°C. Measurement of the saturation magnetisation and the antiferromagnetic susceptibility of a hematite crystal yields the same transformation temperature. Hence the ferromagnetism transforms with the antiferromagnetism. However, neutron diffraction and resonance experiments on a synthetic crystal (containing 3% Fe^{2+} impurity) indicated that the antiferromagnetic spin system begins to turn at a temperature 3·5°C higher than that of the first ferromagnetic changes. No ferromagnetic resonance was observed out of the basal plane at any temperature.

A discontinuity has been found in the linear coefficient of expansion of synthetic powders at the low temperature transformation. No latent heat effect has been observed. Again in synthetic powders, the transformation temperature was lowered by magnetic fields greater than 20 KOe.

The variation of strain with temperature in a natural crystal showed a discontinuity at a temperature 2·5°C lower than the antiferromagnetic transformation temperature. The temperature of the discontinuity

was depressed in a linear fashion by applying a magnetic field ($0{\cdot}6^{\circ}C$ / KOe.). Neutron diffraction results on the same crystal showed that the antiferromagnetic transformation temperature was independent of the applied field.

The addition of very small amounts of impurities to hematite broadens and lowers the transformation temperature range. The impurities preserve the high temperature state rather than the low. 1% Ti in natural crystals suppresses the transformation completely. The production of physical defects in an Elba hematite by neutron irradiation increased the saturation magnetisation but did not effect the temperature of the transformation.

Heat treatment experiments on a synthetic powder produced a transformation characteristic of a synthetic crystal (Haigh,1957). The transformation temperature range was decreased, and the remanent magnetisation of the low temperature state was reduced.

A domain memory effect is present in most natural crystals (kaye,1960). After one or two transformation cycles, subsequent cycles produced identical leakage fields at room temperature.

At the transformation temperature, a hysteresis of $10^{\circ}C$ has been found in the value of the

susceptibility of a synthetic powder and in the remanent magnetisation of a synthetic crystal. The equipment used to measure the remanent magnetisation also indicated a temperature hysteresis in an Elba crystal.

Chapter Two

Details of Experimental Techniques

2.1 Introduction to the Magnetic Colloid Technique.

The principle of the magnetic colloid technique was discovered independently by Bitter (1931) and Hámos & Thiessen (1931). They were looking for magnetic inhomogeneities on the surface of ferromagnetic specimens by coating the surface with a thin film of water containing magnetic particles. Unexpectedly they found a pattern indicating the boundaries between magnetic domains. The existence of magnetic domains had been predicted earlier by Weiss (1907).

Kittel (1956) has produced a quantitative theory of the relative intensities of magnetic colloid in regions of differing magnetic field. He assumes that the particles are in thermal equilibrium; therefore the density distribution of the particles in the liquid is a Boltzmann function. That is, the particle density p(H) at a point where the field intensity is H is related to the density p(0) where the field is zero by the relation

$$p(H,\vartheta) = p(0)\exp(\mu H\cos\vartheta/kT)$$

where ϑ is the angle between the magnetic moment μ of the particle and the field H. He has assumed that

the particle has a permanent magnetic moment, and has neglected particle-particle interactions. On averaging $p(H,\vartheta)$ over all angles, ϑ, he obtained the mean value

$$p(H) = \sinh(\mu H/kT) / (\mu H/kT).$$

As this is a sharply increasing function with H, the density of the colloid where the field is 3×10^{-4} Oe. is nearly four times greater than where the field is zero. Hence more magnetic particles are attracted to the domain boundaries where the magnetic leakage field is relatively higher.

Normal magnetic colloids give a poor indication of the domain walls on hematite because the saturation magnetisation is only 0·5 e.m.u./g. In the next section details are given of a colloid which was developed to indicate these boundaries on hematite. The working temperature of this colloid was extended in order to study the low temperature transformation.

2.2 Preparation of a Low Temperature Colloid. The colloidal magnetite particles were prepared by precipitation using essentially the same method as Elmore (1938). The sensitivity of the colloid was increased by boiling the precipitate in a magnetic field of 1600 Oe. The working range of the colloid was extended

to $-30^{\circ}C$ by suspending the particles in acetone.

The method of preparation was as follows: The magnetite was precipitated in a 30 cc. beaker located between the pole pieces of a permanent magnet having a field strength of 1600 Oe. 20 cc. of distilled water and 5 cc. of NaOH (5 gm. per 50 cc.) were boiled together in the beaker. An electrical stirrer prevented the liquid from boiling over. 2·5 cc. of $FeCl_3.6H_2O$ (5·40 gm. per 50 cc.) and 2·5 cc. of $FeSO_4.7H_2O$ (2·78 gm. per 50 cc.) were mixed together and the precipitate formed when this was added slowly to the boiling liquid. The stirrer was still in operation. The precipitate was boiled for 30 minutes to increase the particle size Garrood (1962). Provided the stirrer touched the walls of the beaker near the pole pieces most of the magnetic particles were kept in motion. The liquid level was maintained by periodically adding distilled water. To ensure that a large percentage of the particles were of maximum colloidal size the field was removed and boiling continued for 30 minutes. The precipitate was boiled for a further 5 minutes in the magnetic field.

The precipitate had now to be transferred to an acetone medium. The magnetic aggregate was filtered off and washed for 60 minutes in distilled water to

remove the unwanted chemicals adhering to the particles. The washing consisted of filling the filter-funnel with distilled water and decanting it off. After the liquid had been decanted off three times distilled water was poured through the filter paper for 60 minutes. Next the precipitate was washed with ethyl alcohol and acetone for 60 minutes using the same technique. The precipitate was never allowed to become dry as the magnetic particles might have aggregated together. Even though acetone is miscible in water, ethyl alcohol was used as an intermediate stage in the washing process. The impurities ought to dissociate more easily in alcohol and hence be removed from the surface of the precipitate.

Ethyl cellulose was found to be a successful stabiliser for the acetone colloid. The precipitate was added to 10 cc. of a saturated solution of ethyl cellulose. The particles were dispersed by subjecting them to ultrasonic cavitation for 5 minutes. The colloid was sealed in a specimen tube partially immersed in a water bath connected to an ultrasonic generator (Ultrasonic Industries Inc., New York). The heavy non-colloidal aggregate was allowed to settle out for two hours before using the colloid at low temperatures.

Unfortunately the preparation of a good colloid owes more to chance than to scientific effort. In colloid preparation as with the study of hematite there are rather too many uncontrollable parameters. To minimise this difficulty any new colloid was prepared identically to a successful one except for changing one variable.

The successful colloids functioned down to $-30^{\circ}C$, with any further decrease of temperature they flocculated or became attached to a particular domain wall which had since moved. These colloids exhibited their normal properties when reheated to $-30^{\circ}C$.

A few days after preparation the $FeCl_3.6H_2O$ formed a hydroxide precipitate due to hydrolysis. Before pouring out the 2·5 cc. for colloid preparation, the precipitate was dispersed into the liquid by shaking.

Acetone was chosen as a medium for the low temperature colloid because, unlike alcohol, its viscosity increases only slightly in the temperature range down to $-30^{\circ}C$. Hence, given the same magnetic conditions, the colloid particles formed domain patterns in the same time as at room temperature.

The acetone colloid could be applied to the crystal at low temperatures. If, for example, a particular colloid application ceased to function, and the

crystal was at -20°C, the sealing ring was carefully removed and the crystal surface quickly cleaned with acetone. Fresh colloid was applied and the crystal resealed before too much water was absorbed.

2.3 Details of Other Colloids. Colloid patterns were first observed on hematite using the water-based colloid of Elmore (1938). The particle sensitivity was not as good as the acetone-based colloid developed from it. A 'Celacol' stabilised colloid made by Craik & Griffiths (1958) indicated no domain walls on hematite.

The acetone-based colloid described in 2.2 was increased in sensitivity by subjecting the settled aggregate to ultrasonic cavitation for 5 minutes. Provided the liquid was used immediately there was a large number of non-colloidal particles in temporary suspension. These particles had a higher magnetic moment than the colloidal particles. When used on a hematite crystal this colloid produced, in addition to weaker domain walls, an extra pattern (reminiscent of the behaviour of iron filings in a magnetic field). This extra pattern indicated the direction of magnetic field on the crystal surface. By low temperature application or continual tapping of the sealing ring

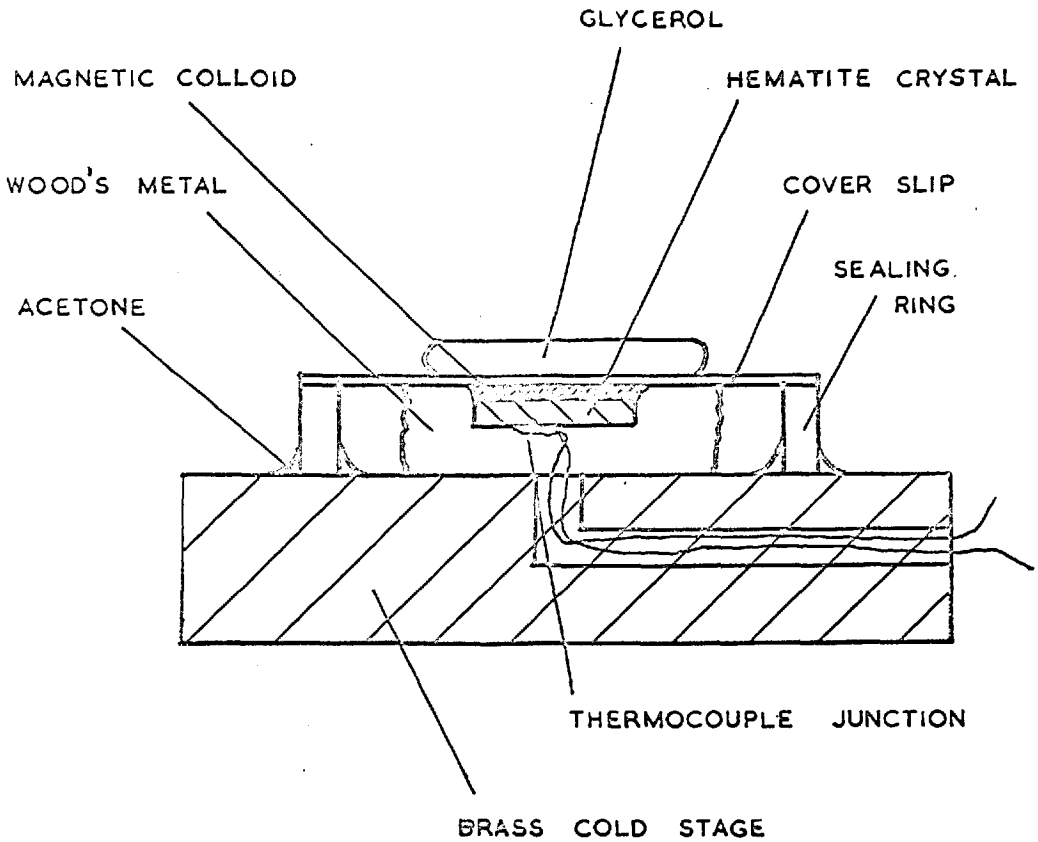


Fig. 10. Apparatus used for observing colloid patterns on hematite crystals at low temperatures.

this 'iron filing' colloid operated down to $-30^{\circ}C$.

2.4 Microscope Cold Stage. A microscope cold stage was designed which was capable of cooling hematite crystals to below $-40^{\circ}C$. Hence it was possible to view the domain structure of all the synthetic and some of the natural hematite specimens at and below their low temperature transformation. The cold stage was a brass conduction bar cooled by a dewar of liquid oxygen. The bar was mounted on a quarter inch plate of glass which was gripped by the jaws of the movable microscope stage. The glass insulated the cold metal from the body of the microscope.

Certain precautions had to be observed during the mounting of the crystal specimens. A uniform critical thickness of colloid was required on the crystal face under investigation. The whole of this face had to be in focus. The thermocouple needed to be in intimate contact with the crystal.

Fig. 10 shows how a hematite crystal was mounted on the cold stage. A one inch square microscope cover slip was cemented with Araldite to a brass sealing ring which was deeper than the crystal under examination. A metal jig was made to accommodate the thermocouple junction through a hole of equivalent diameter

to the one in the cold stage. The jig was heated above 60°C. The bottom of the hole was blocked with plasticine. Wood's metal (alloy of cadmium, zinc and lead melting at 60°C) was made to form a globule which plugged the hole. The hematite crystal was made to float on the molten alloy and then pressed into it by placing the sealing ring on top of the crystal. The colloid thickness could be varied by putting paper slips onto the crystal surface. The Wood's metal never 'wets' the hematite but spreads around the crystal forming a well for the colloid. Due to its resilience the copper/constantan thermocouple pressed against the underside of the crystal. When cool the plug of Wood's metal containing the crystal and thermocouple was pressed into the hole in the cold stage. Provided the lower surface of the sealing ring and cover slip were parallel, the hematite crystal face remained in focus when the crystal was moved across the field of view. The seal between the ring and the cold stage was made by flooding the base with acetone approximately every 15 minutes.

At low temperatures the condensation of water vapour on the cover slip obscured the field of view. This was prevented by coating the cover slip with a pool of glycerol which dissolved the condensing vapour

to form a low freezing point mixture. Provided the pool was larger than the crystal there was no distortion of the image seen in the microscope. Even after a two hour cine-film experiment the concentration of condensed water was never enough to form solid crystals on the cover slip.

2.5 Temperature Measurements and Control. Copper/constantan thermocouples with liquid oxygen as the cold junction were used in all the experiments. A calibration curve for the microvoltmeter and each thermocouple was obtained by noting the arrest points of melting mercury, water and benzene.

A constant temperature/time gradient of 0·01°C/min. had to be produced in the hematite crystal for the colloid to track any domain wall movement caused by temperature changes. Temperature differences of 0·01°C were measured by backing off 98% of the thermocouple output and amplifying the remainder. The backing off voltage was provided by a Mallory cell (a secondary standard cell) controlled by a potentiometer. Voltage amplification and continuous recording of temperature was obtained with a Keithley 149 D.C. microvoltmeter and a Honeywell-Brown continuous recorder. The thermocouple leads were lagged; and twisted together to

prevent a change of the D.C. level caused by alternating currents in other parts of the apparatus. The oxygen level in the dewar provided a coarse control of temperature. Immediate and small changes of temperature were produced by using a 'Variac' transformer to alter the intensity of illumination from a conventional 150 watt lamp three or four inches from the crystal. By controlling the lamp intensity in relation to the temperature on the recorder the required temperature/time gradient was obtained.

2.6 Temperature Gradients in the Hematite Crystals.

Due to the method of cooling it was possible that temperature gradients would be produced in the hematite crystals. Parts of the crystal would then be at different stages in the magnetic transformation and hence produce considerable difficulty in the interpretation of results. Two types of experiment were designed to find the temperature gradient, with the proviso that they must disturb the thermal conditions as little as possible. As these experiments were done at $-40^{\circ}C$ any lags measured were larger than those produced in normal transformation experiments.

The temperature gradients across the surface of hematite were measured by noting the apparent

difference in the melting point of mercury drops on the crystal face. The five smallest globules that could be made by sucessively dividing a pool of mercury were spaced as far apart as possible on the crystal surface. Acetone was added instead of the normal colloid and the cold stage set for a normal transformation experiment except that it was cooled down to $-40^{\circ}C$. The mercury drops became discs under the weight of the cover slip. The transition from solid to liquid could be seen by continually pressing the cover slip with a cooled probe. When the solid mercury became liquid the disc diameter could be seen to fluctuate. The experiments showed that the mercury discs all melted at the same instant i.e. there were no temperature gradients greater than $0.01^{\circ}C$ for a heating rate of $0.025^{\circ}C/min$.

A value for the temperature gradient between the crystal surface and the thermocouple was found by another experiment on the melting of mercury drops. The voltage produced by a thermocouple at the melting point of bulk mercury was noted, and compared with the temperature at which a mercury drop melted on the crystal surface. This gave the temperature gradient. The same thermocouple was used throughout. The experiment was identical to a normal transformation run except

that acetone was used instead of colloid and the very small mercury drop was on the surface. The same technique as the previous experiment was used for noting when the mercury drop became molten. No gradient could be measured on cooling as there was a supercooling effect of 2·3°C. The temperature gradient on warming at 0·25°C per minute was 0·6 °C.

2.7 Photographic Recording of Domain Patterns. The fine detail of domain patterns was recorded with an Exakta reflex camera with its lens removed. The camera was supported on the barrel of the microscope with the aid of extension tubes. The eyepiece of the microscope was removed and the times 2·5 or times 10 objective was used as a camera lens. The image was focussed on the camera's ground glass screen by using the microscope focussing controls. Ilford F P 3 '127' film was used most extensively and the prints were produced on grade 4 photographic paper. The negatives were processed with Ilford Microphen fine grain developer, and the prints with Ilford I D 2 to produce maximum constrast.

The cine recording was done with a Vinten Mark 1 cine camera using either Ilford Pan F or Ilford F P 3 film. The negatives were processed for maximum

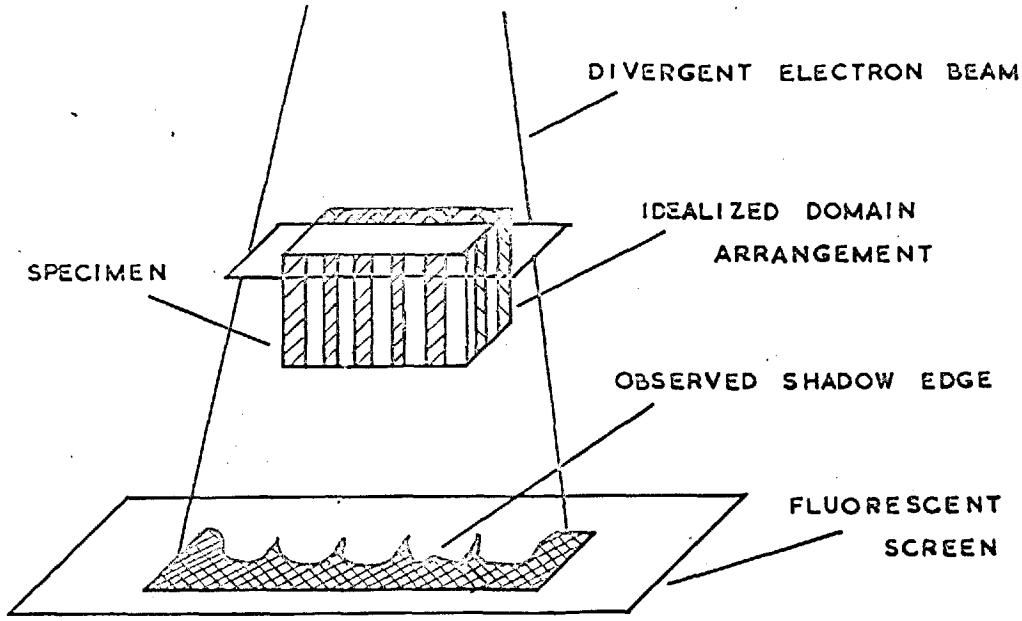
contrast. The camera received the domain pattern image in the same way as the Exakta. A Watson 'Watching Eyepiece' was clamped in the camera lens position. This reflected 20 % of the light through an eyepiece allowing the operator to focus and track whilst filming.

The colloid patterns were illuminated by a Baker 30 watt source reflected through the objective by a half-silvered mirror. The exposure times were one twentieth of a second with the cine-camera and one tenth of a second with the Exakta. The cine film exposures were made once every two seconds throughout the two and a half hours of an experiment in which the cooling rate was $0.025^{\circ}C$/min. The resulting cine film lasted 5 minutes when projected at 16 f.p.s.

A Bell & Howell 613 16 mm. projector was used for examining the film. This had continuously variable projection speeds from 24 to 10 f.p.s., forward or reverse, and allowed projection of a single frame.

2.8 Introduction to the Electron Beam Method.

A scanning electron beam method was first used by Blackman, Haigh & Lisgarten (1957) to study magnetic domain effects in cobalt. Germer (1942) had previously seen a complex pattern of curves and arcs produced on a



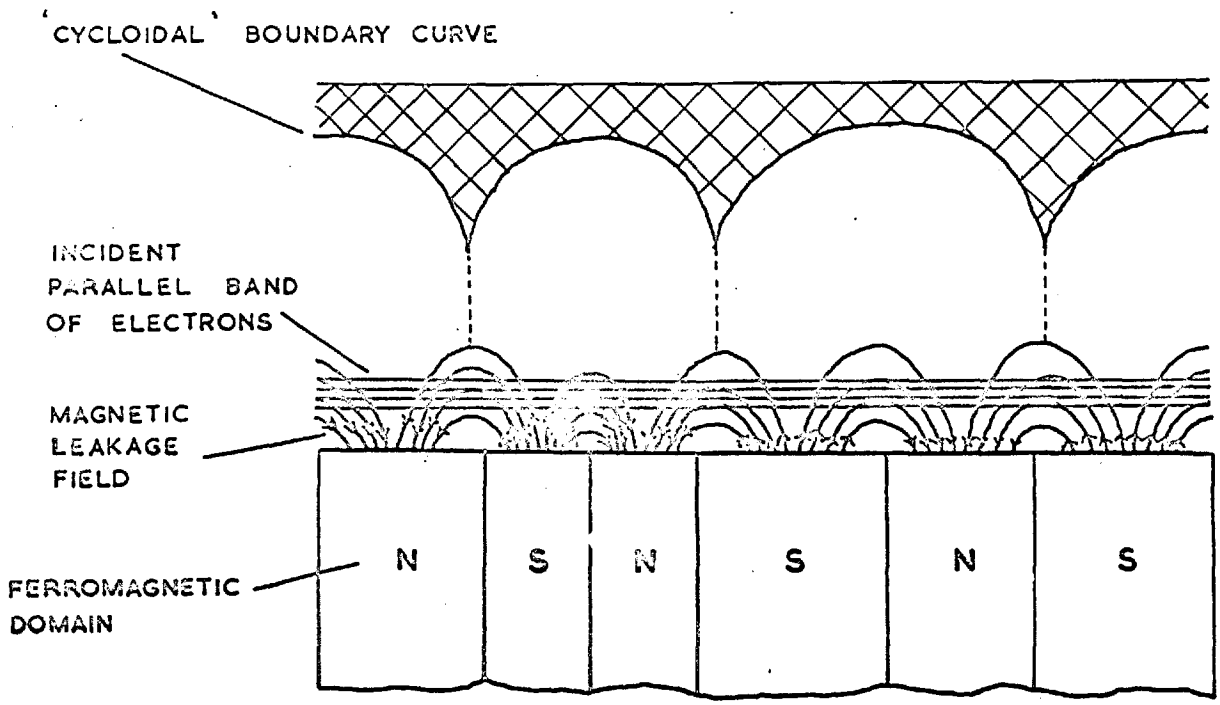


Fig. 11. The principle of the electron beam method used for observing ferromagnetic domain effects.

photographic plate by an electron beam deflected in the magnetic leakage field from a cobalt crystal. The method of Blackman & Grünbaum was developed further by Blackman & Lisgarten (1958) and was used in this research to study the domain effects at the low temperature transformation.

A divergent electron beam is made to oscillate parallel to the surface of a hematite crystal. The profile is observed on an electron sensitive screen (see fig. 11). A domain model of a magnetic crystal constructed by Blackman & Lisgarten (1958) reproduced nearly all the characteristics of the shadow patterns obtained from hematite. Blackman & Grünbaum (1957) have made a mathematical analysis of the pattern formed by an electron beam passing above an ideal arrangement of domains. Their results indicate that the electrons are deflected by the leakage field from the domain surfaces rather than the walls; and that the magnitude of the cusps is an indication of the local magnetic leakage field above a crystal. An estimate of the domain size can be made from the periodicity of the cusp pattern.

2.9 Experimental Details of the Electron Beam Method.

The electron beam is produced in a vertical

electron diffraction camera designed by Kehoe & Newman (see Kehoe 1956). A conventional type of hot filament gun was used to produce a beam of electrons which could be accelerated to 45 Kv. Using the method of Blackman, Haigh & Lisgarten (1957), the beam was focussed at the axis of a pair of coils 10 cm. from the specimen. Due to the 50 c.p.s. alternating current in these coils, the beam oscillated parallel to the surface of the crystal. The profile of the hematite crystal distorted by the magnetic leakage field from the crystal was observed on the fluorescent screen.

The low temperature unit used in the diffraction camera has been generally described by Blackman & Lisgarten (1957) and in more detail by Lisgarten (1957). It incorporates a control for tilting the specimen ± 5 degrees with respect to the beam. In the original design cooling and heating was by conduction from a liquid oxygen container and a resistance heating unit to a brass end-plate on which the specimen and thermocouple were mounted. In the work reported here the liquid oxygen was used as a coarse temperature control and the fine control was obtained by the method described in 2.5. By varying the radiation from the 150 watt lamp, directed through a glass port in the camera, there was an immediate and controllable change

in the temperature.

Colloidal graphite was used to seal the specimen to a brass mounting-cap. A thin layer was applied to the surfaces of the crystal to prevent electrical charging. The thermocouple was clamped in a hole in the mounting-cap.

Photographs of the shadow pattern on the fluorescent screen were recorded in the cine-camera by tilting the screen at 45° to the electron beam. The cine-camera, viewing through an inspection port, was mounted with its lens 50 cm. from the screen. A cine-film of the low temperature transformation was recorded in the same way as described in 2.7 except that the temperature cooling rates were larger. In some experiments photographs were taken at 8 f.p.s. with large cooling rates. When doing experiments on the memory effect the shadow patterns were photographed directly on film from a cassette below the screen. Exposures were of the order of 4 seconds.

2.10 Introduction to the Kerr Effect Technique. The Faraday effect, i.e. the rotation of the plane of polarisation of electromagnetic radiation passing through a material placed in a magnetic field, gives rise to a similar rotation for radiation reflected

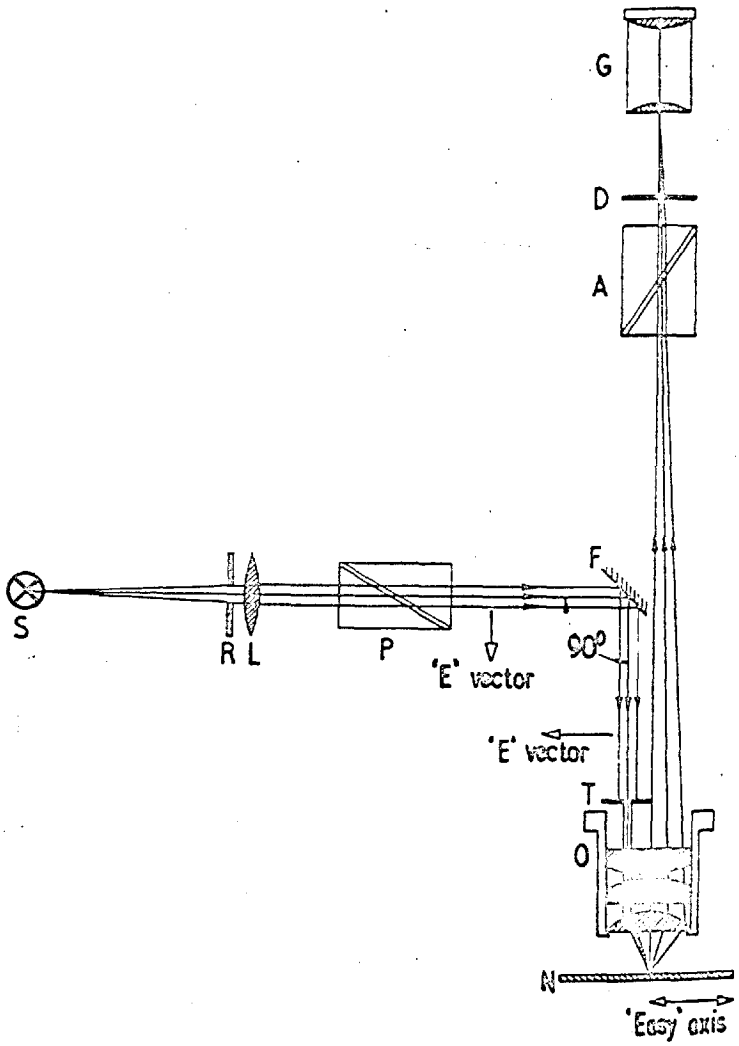


Fig. 12. Diagram of the Kerr effect microscope (Green & Prutton, 1962).

from the surface of a ferromagnetic material. In the reflection case, the effect is called the Kerr magneto-optic effect, and it has been used in this work to observe domain patterns on hematite crystals.

The experimental arrangement consists essentially of a polariser and analyser with the sample placed between them in such a way that light which passes through the first prism is reflected from the sample and then passes through the second. The plane of polarisation of the light is rotated upon reflection from the sample. It is rotated by different amounts by neighbouring domains, corresponding to the differences in the direction of the magnetisation. Consequently, the polariser and analyser may be rotated so as to extinguish the light reflected from certain domains and an observer may adjust them in order to obtain maximum visibility of the domains.

2.11 Kerr Effect Microscope. The Kerr effect microscope of Green & Prutton (1962) at I.C.T. Ltd., Stevenage, Herts. was used for most of the magneto-optical work on hematite crystals. A diagram of the apparatus is shown in fig. 12. Light from a high pressure mercury lamp S (Philips CS 90 W) was collimated by a lens L (75 mm. Swift microscope objective) and

passed through a polariser P (12 mm. Glan Thompson prism) so that the plane of polarisation was parallel to the plane of the diagram. The aluminised glass plate F was adjusted so that its normal was in this same plane. An off-centred stop T was mounted behind the objective O (x 14 Swift, strain free) so that the mean angle of incidence was about 16°. On reflection from the hematite crystal the cone of light was collected by half the objective and passes through an analyser A (12 mm. Glan-Thompson) and a stop D which served to reduce glare and scattered light in the primary image plane. The final image was viewed by the eyepiece C. The iris R was placed at the working distance from the objective O, consequently it was in focus at the image plane.

It was easy to transfer the cold stage (described in 2.4) to the Kerr effect microscope at I.C.T. as the same Baker microscope was used in the colloid studies at Imperial College. In the low temperature experiments one difficulty was encountered. The water-absorbing pool of glycerol on the crystal produced an undesirable reflection from its top surface. This was eliminated by turning the sealing ring upside down, placing it on the liquid pool and filing it with glycerine. The depth of glycerine was now at least 5 mm. This

was sufficient to reflect the light from the top surface onto the off-centred stop instead of into the field of view.

Ilford Pan F film was used for recording the domain patterns. This was developed for maximum contrast. The exposure time for the negative was about three minutes.

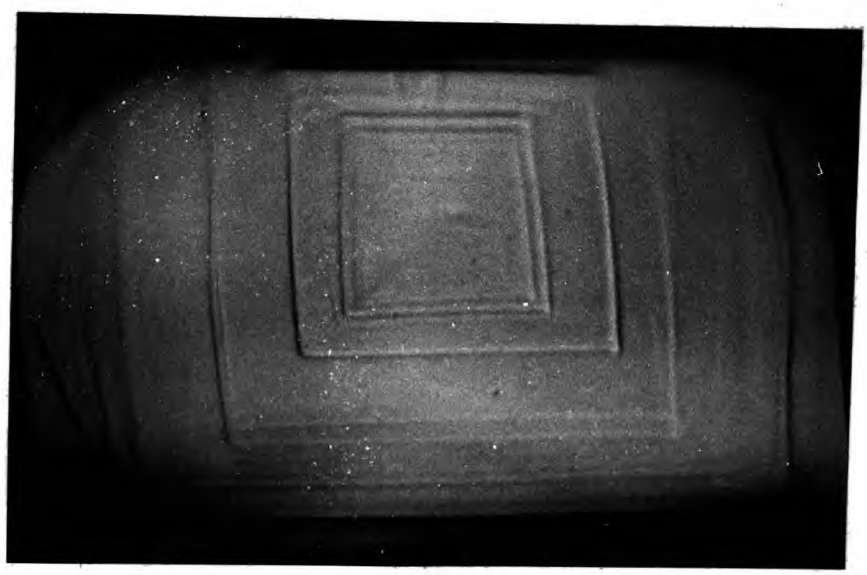


Fig. 13. The (110) face of the synthetic hematite crystal, A G 1, indicating rectangular zone growth steps (x 28).

Chapter Three

A Domain Study of A G 1, Synthetic Hematite Crystal

3.1 The Crystal. The hematite specimen was kindly provided by Dr. J.P. Remeika of the Bell Telephone Laboratories. Such single crystals were made by the flux-melt method in which hematite powder was heated with a PbO_2 flux to 1250°C. If the mixture was cooled at 1°C per hour good crystals were formed on the melt at 950°C. The flux was removed from the crystal surface by washing in dilute HNO_3.

The crystals prepared by this method grew in rectangular plates. The large face parallel to the melt was well developed and the remaining faces were much cruder. Bell Telephones made tests on samples from the melt and found them to be stoichiometric. X-ray and electron diffraction patterns of the A G 1 specimen showed it to be a single crystal.

Magnetic effects were studied on the one good face. This was indexed with X-rays as the (110) face (in the rhombohedral system) by Dr. D. Rogers of the Chemistry Dept., Imperial College. The face itself was composed of rectangular zone growth steps, indicating that the crystal had grown from two contra-rotating spiral dislocations (see fig. 13). A large

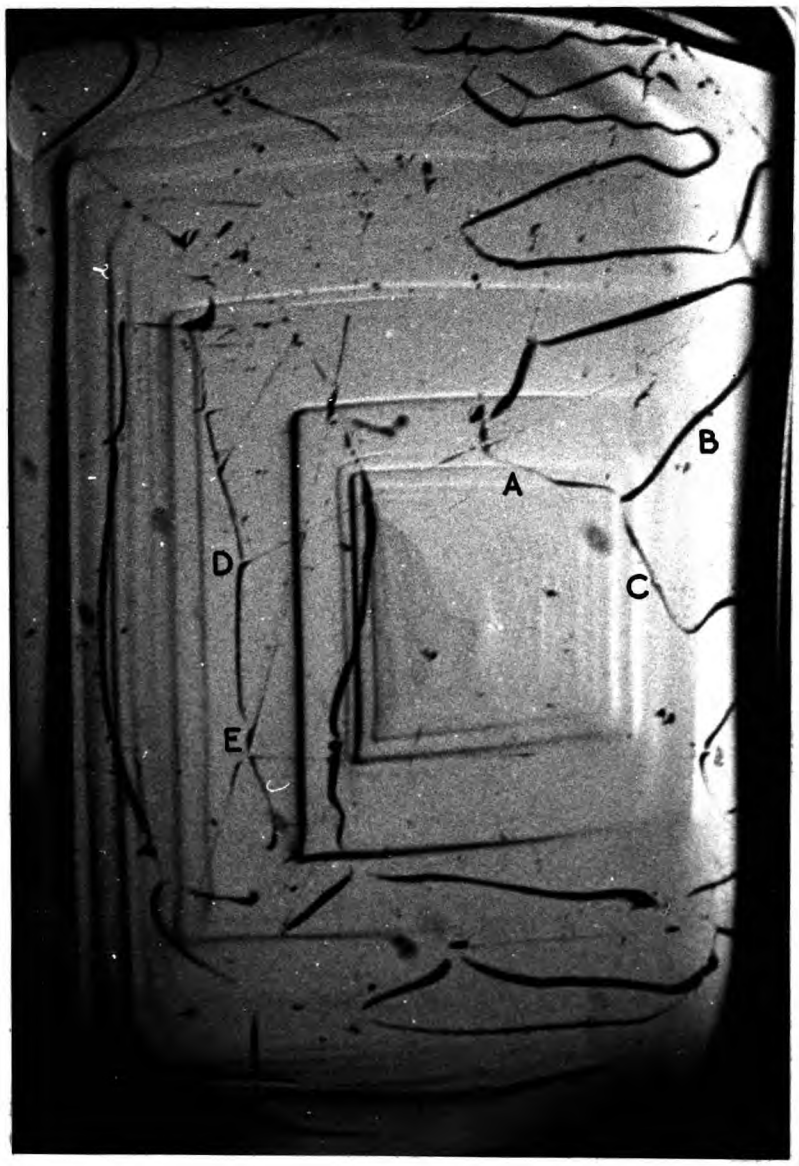


Fig. 14. Normal sensitivity colloid indicating domain walls on, A G 1, synthetic crystal. A,B and C indicate differing amounts of colloid attracted to the domain walls. Note the discontinuities in the colloid boundaries at D and E (x 40).



No magnetic field applied



Magnetic field applied

Fig. 15. Application of a magnetic field of approximately 30e. to A G 1, synthetic hematite crystal (x 40).

crystal fault on this face was found to be lying in the (111) basal plane of hematite.

3.2 Domains in A G 1 at Room Temperature. The crystal ($4 \times 3 \times 1.5\ mm.^3$) was mounted for colloid, electron beam and Kerr effect observations using the method described in 2.4.

A normal acetone colloid was applied to the synthetic crystal, and the pattern produced on the surface is shown in fig. 14. It was found that the patterns which were not obviously associated with faults in the crystal could be moved by fields of approximately 3 Oe. (see fig. 15). Because of this and other reasons it is concluded in 7.1 that the normal acetone colloid generally indicated the position of domain walls in hematite.

Unlike most 'Bitter' figures of single crystals there is no obvious symmetry in the patterns. This lack of symmetry occurred in all the synthetic and natural hematites described in this thesis. In A G 1 the only tendency is for the pattern to be elongated in a direction parallel to the nearest crystal edge. As seen in fig. 14 at A, B and C, the domain wall attracts different amounts of colloid. In addition the colloid pattern becomes discontinuous where domain



Fig. 16. Increased sensitivity colloid indicating direction of magnetic leakage field on A G 1, synthetic hematite crystal (x 40).

walls cross a crystal fault (see D and E in fig. 14). Some of the domains on A G 1 were found to be very soft magnetically; they altered their shape when the field applied to the crystal was varied by less than 0·35 Oe. This was discovered when changing from a x 10 to a x 40 microscope objective. Some of the domain walls had moved due to the variation of the magnetic field from the mild steel sealing rings in each of the objectives.

The increased sensitivity colloid (iron filing colloid) described in 2.3 was applied to the A G 1 crystal (see fig. 16). In addition to showing more detail of 'weaker' domain walls this colloid produced an extra pattern (reminiscent of the behaviour of iron filings in a magnetic field) which indicated the direction of the magnetic leakage field just above the crystal surface. In section 7.1 the extra pattern is shown to originate from the unusual situation of localised variation of magnetisation in direction and/or magnitude within individual domains.

3.3 Domain Wall Patterns on A G 1 at the Transformation.

This crystal has been cycled through the low temperature transformation over a hundred times. After the first dozen coolings subsequent transformations gave identical colloid patterns at and above the

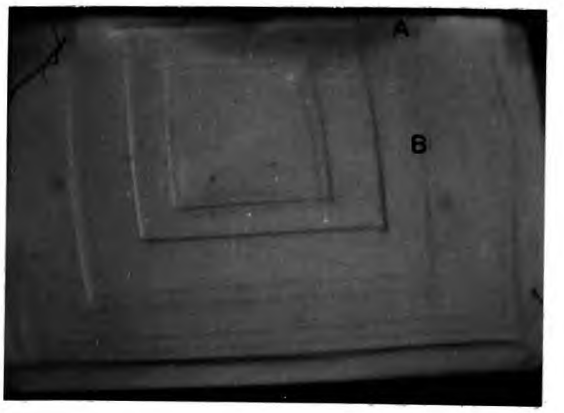


Fig. 17 a.



Fig. 17 b.

Fig. 17. Patterns formed by two colloids of different sensitivity applied to A G 1, synthetic hematite crystal below the transformation temperature. Colloid is attracted only to crystal faults at A. and B in fig. 17 a. Four additional patches of colloid are seen in fig. 17 b (x 21).

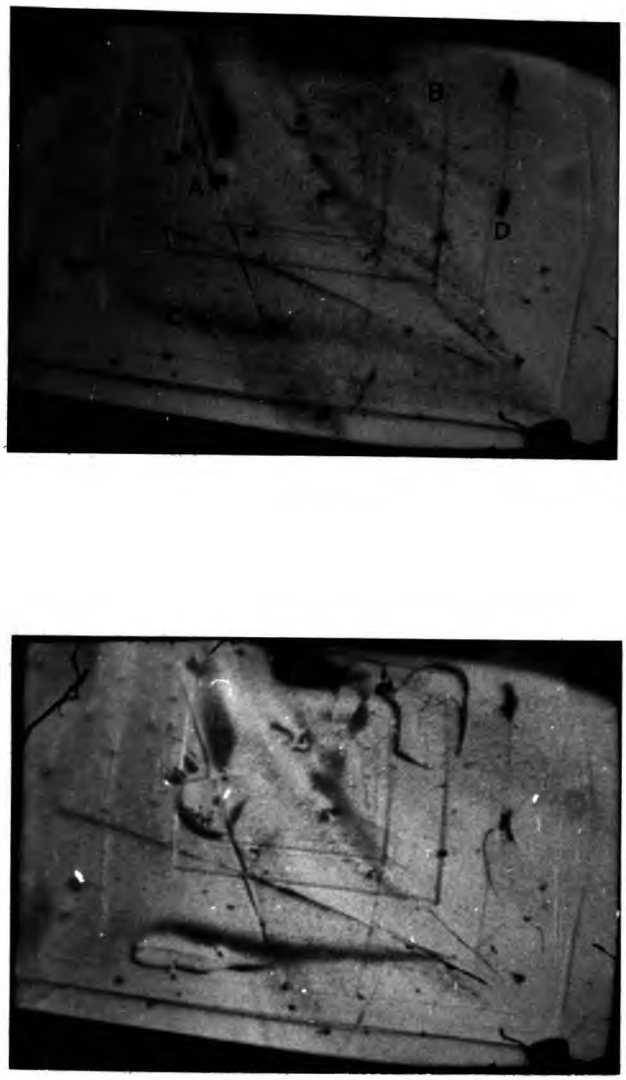


Fig. 18. Colloid pattern on A G 1, synthetic hematite crystal, just below and above the domain nucleation temperature (x 23).

transformation. This occurred provided no magnetic field had permanently altered the domain pattern. If such an alteration had occurred the crystal stabilised into its original domain configuration after a few coolings. This memory effect will be discussed in more detail in 3.8.

The low temperature transformation was studied in terms of domain wall motion from cine-film photography of the patterns formed by normal sensitivity colloid applied at $-18.6^{\circ}C$. From -18.6 to $-14.5^{\circ}C$, the strongest magnetic effect was the attraction of colloid to imperfections seen on the crystal surface. These were crystal faults ('cracks') and local discontinuities ('knots') which were the result of large dislocations (A and B respectvely in fig. 17a).

Some normal colloids had a higher sensitivity than that shown in fig. 17a. In this same temperature range these showed four additional areas of colloid about 150 microns across (see fig. 17b).

At $-14.5^{\circ}C$ domain wall nucleation was seen at area A in fig. 18. This was followed by further domain wall nucleation in areas B,C and D at temperature intervals of 0.27, 0.27 and $0.11^{\circ}C$ respectively.

Nucleation occurred in A by a redistribution of colloid to form a smaller patch which was bounded on

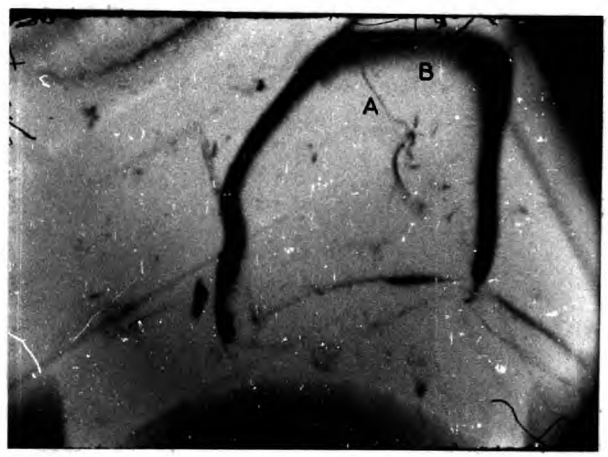


Fig. 19. Colloid pattern on A G 1, synthetic hematite crystal, indicating a lighter domain wall (A) which follows the same path as the heavier domain wall (B) on heating through the transformation temperature (x 70).

half the circumference by a large amount of colloid in the shape of a broad cusp (see fig. 18). A further increase of temperature expanded the circumference and the patch of colloid also formed into a boundary to complete a circular domain.

The second nucleating area, B, which was rectangular in shape, formed a rectangular expanding domain. This particular nucleation was a two stage process in which a 'heavier' wall was followed in exactly the same way by a 'lighter' wall. The same thing happened to the domain which had formed at A but at a later stage of the transformation. This occurred when the single circular domain met a long crack and crossed it by expanding from a patch of accumulated colloid on the other side in a two stage process (see fig. 19). Consequently it was impossible to follow each wall throughout the transformation.

The long area of colloid, C, formed a straight line wall along its length which split into two parallel walls expanding apart from each other.

Area D was very similar in its nucleation of a wall to area A.

All of these domains continued to expand with temperature until at $-10{\cdot}8^{\circ}C$ the domain wall movement ceased by two pairs of walls closing together.



Fig. 20. Colloid pattern on A G 1, synthetic hematite crystal, showing two pairs of domain walls closing together at the final stage of heating through the transformation temperature (x 36).



Fig. 21 a.



Fig. 21 b.

Fig. 21. Comparison of iron filing colloid patterns on A G 1, synthetic hematite crystal, below and above the transformation temperature (x 25).



Fig. 22 a.



Fig. 22 b.

Fig. 22. Comparison of the nucleated domains in A G 1, synthetic hematite crystal, with the iron filing pattern below the transformation temperature (x 23).

As can be seen from fig. 20 this occurred very near the original nucleation areas.

3.4 Iron Filing Colloid Patterns at the Transformation.

The transformation in A G 1 was studied with the iron filing colloid as well as the normal colloid. Fig. 21a is a photograph of the iron filing colloid applied to the crystal at $-16^{\circ}C$. The crystal is below the transformation temperature in the sense that all the domain walls have denucleated. Comparing fig. 21a with fig. 21b taken at room temperature, the iron filing patterns are seen to be identical except for the superposition of conventional domain walls in the latter. In fact this underlying pattern does not change throughout the transformation.

It is interesting to note that the four nucleating areas marked in fig. 18 are regions which appear to indicate magnetic discontinuities not associated with cracks or knots on the surface.

The manner in which a domain wall expanded after nucleation has already been described. However it should be noted that the domain shapes taken during the expansion can be seen to correspond with the iron filing pattern by comparing fig. 22a with fig. 22b.

The crystal was softest magnetically, and the

domain walls moved into their stable positions in the smallest temperature range in the area where the iron filing colloid indicated homogeneous leakage fields.

The iron filing colloids were incapable of recording magnetic changes in fields greater than 100 Oe. due to the polarising effect of the field on the colloid. Above the transformation temperature the distribution of the iron filing pattern could be changed by applying a field of 15 Oe. in comparision with the 3 Oe. necessary to move the domain walls. Fields of up to 300 Oe. were applied below the transformation temperature but they had had no effect on the iron filing pattern once the field was removed. By applying 15 Oe. above the transformation temperature area A in fig. 22b. was twice converted into what appeared to be a domain wall. The long rectangle of colloid collapsed into a narrow line along the length of the rectangle taking all the colloid with it. After the formation of this new wall no iron filing pattern remained in the region. Even though the crystal was cooled to $-29{\cdot}5^{\circ}C$, the new wall did not move at the transformation, except for a slight rearrangement. However application of a magnetic field of approximately 300 Oe. below the transformation temperature did move the wall. It was found that when the crystal was heated to room temperature



Fig. 23. Stage at which domains on A G 1, synthetic hematite crystal, were first indicated with the Kerr effect on heating through the transformation temperature (x 36).

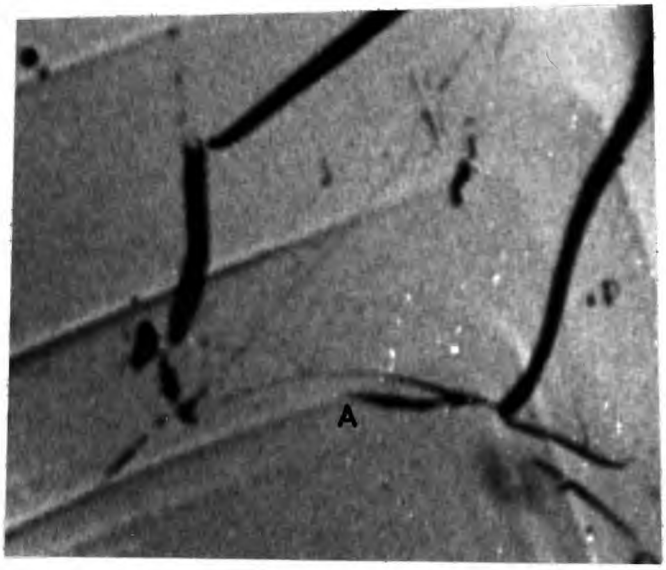


Fig. 24 a.

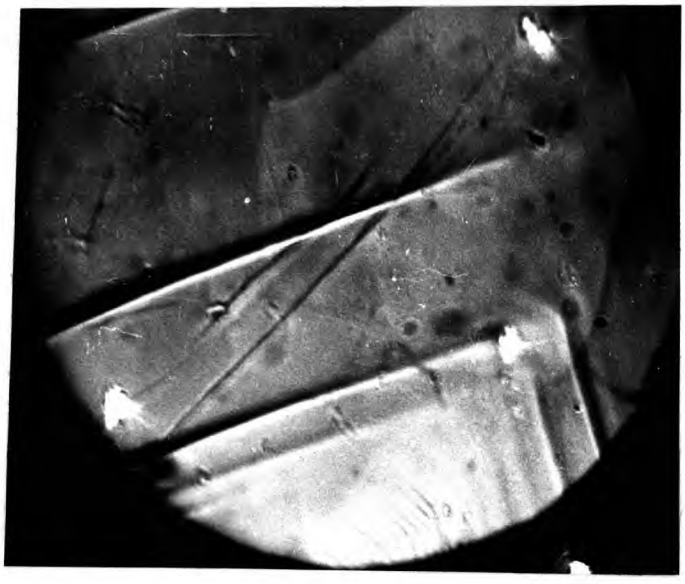


Fig. 24 b.

Fig. 24. Showing how the Kerr effect does not indicate the domain boundary at which the transformation finishes in A G 1, synthetic hematite crystal (x.100).

the wall had disappeared. In these experiments the crystal did not exhibit its normal memory but regained it after a few more coolings.

3.5 Kerr Effect on A G 1 at the Transformation. The A G 1 crystal was viewed below the transformation temperature using the Kerr effect. The polariser and analyser were set at the optimum orientation for domain observation but no magnetic effects were seen. In fact the domains were indicated only at the stage shown in fig. 23. The Kerr effect patterns were identical to the colloid patterns throughout the transformation. However, one new feature was observed on heating the crystal through the high temperature region of the transformation. After the two walls at A in fig. 24a closed together, there was a gradual decrease in contrast between the two domains. The contrast became so poor that the boundary separating them was no longer visible with the Kerr effect (see fig. 24b).

3.6 Electron Shadow Method on A G 1 at the Transformation.

This method was the most insensitive to the magnetisation of the crystal. When warming A G 1 from temperatures below the transformation the magnetic shadow pattern formed at $-9.9^{\circ}C$, i.e. $0.9^{\circ}C$ after the domain



No magnetic field applied



Magnetic field applied

Fig. 25. Application of a magnetic field of approximately 20 Oe. to A G 1, synthetic hematite crystal at - 12·9°C (x 19).



No magnetic field applied



Magnetic field applied

Fig. 26. Application of a magnetic field of approximately 100 Oe. to A G 1, synthetic hematite crystal at $-13{\cdot}6^{\circ}C$ (x 19).

walls had nucleated. The cine-film of the transformation showed that there was no sideways movement of the cusps with increase of temperature but simply an increase in their amplitude which stopped at $-8{\cdot}1^{\circ}C$

There was no domain wall movement seen by the colloid technique during the electron beam changes.

3.7 Application of a Magnetic Field to A G 1 Crystal.

The average magnetic field needed to move the domain walls at room temperature and down to the beginning of the transformation at $-10{\cdot}8^{\circ}C$ was about 3 Oe.

At $-12{\cdot}9^{\circ}C$, fields of the order of 20 Oe. had to be applied to make any change in the domain wall pattern. As can be seen in fig. 25 these fields had an exactly similar effect to changing the temperature of the crystal. If 20 Oe. was applied with opposite senses at $-13^{\circ}C$ there was an effective increase or decrease in the temperature of $0{\cdot}05^{\circ}C$.

The same effect is recorded in fig. 26 near the denucleation temperature. In this case 100 Oe. was equivalent to a temperature change of $0{\cdot}02^{\circ}C$.

It was possible to cause a complete denucleation by applying the appropriate magnetic field just above

the denucleation temperature. The reverse was never achieved even with a field of 100 Oe. applied immediately below the nucleation temperature. However, new walls might not be indicated by the colloid due to its decreased mobility in the polarising field.

3.8 The Memory Effect in A G 1. In an earlier section it was mentioned that the A G 1 crystal had a magnetic memory after its first few coolings. A crystal will be said to have a magnetic memory if on cycling the crystal through its low temperature transformation the domain wall pattern at any specific temperature is identical with the pattern at that same temperature in previous cycles.

The virgin A G 1 synthetic crystal had to be cooled 12 times before it developed a magnetic memory. In these first coolings the wall movements could not be recorded as the colloid technique had not been developed sufficiently. However, it was noticed that there were some slight rearrangements of domain walls above the normal temperature range of the transformation.

If the domain pattern was changed by momentarily applying a magnetic field, within a few cycles the memory was restored. During these cycles the

transformation still took the form of a denucleation phenomenon, starting and finishing at the same temperature and in the same place as the normal transformations.



Fig. 27. Normal sensitivity colloid indicating domain walls on an Elba (A 1) natural hematite crystal at room temperature (x 25).

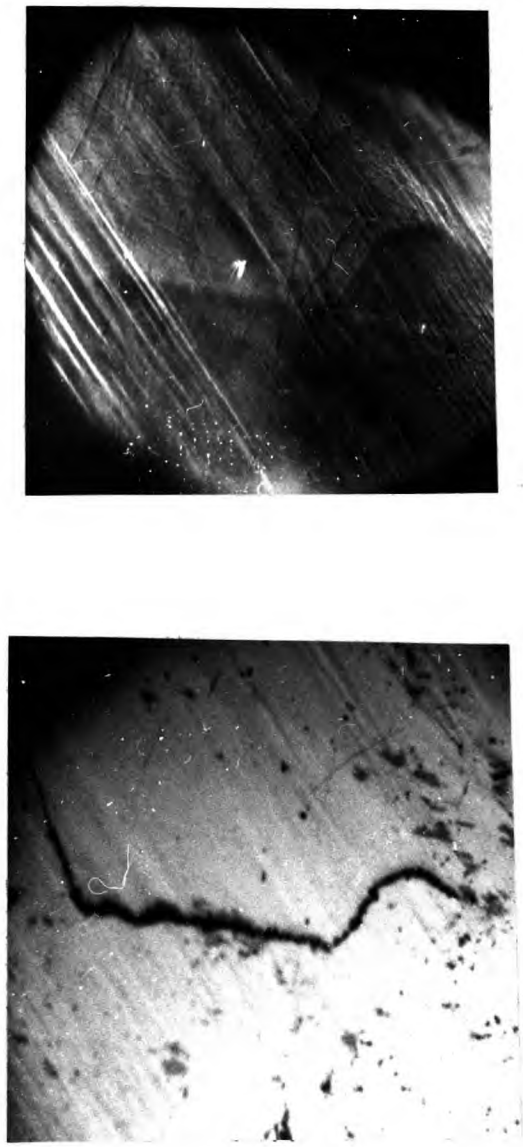


Fig. 28. A domain wall on Elba (A 1) natural hematite crystal shown by the Kerr effect and with a normal sensitivity colloid (x 70).

Chapter Four

A Domain Study of a Natural Hematite Crystal, Elba (A 1)

4.1 Domain Patterns on Elba (A 1) at Room Temperature.

The domain patterns were studied on the (110) face of this natural crystal of hematite from Elba. The face was identified by X-ray diffraction. The crystal was a large plate 6 mm. across and 2 mm. thick. From fig. 27 it can be seen that the natural face had a slightly corrugated surface.

Comparision of the normal colloid pattern on Elba A 1, (fig. 27), with the results of the same colloid on the synthetic crystal, A G 1, (fig. 14) produced the following differences:

a) The domains on the Elba crystal were generally smaller than those on the synthetic crystals.

b) The domain wall patterns were more discontinuous and irregular in shape.

c) For the same colloid the pattern along a domain wall on the Elba specimen was less intense but more uniform.

The Kerr effect indicated domains on the Elba crystal. The visibility of domains was better than on A G 1. One of the domains is shown in fig. 28 , and can be compared with the pattern of the normal colloid.



Fig. 29. Iron filing colloid pattern on Elba (A 1) natural hematite crystal (x 60).



Fig. 30 a.

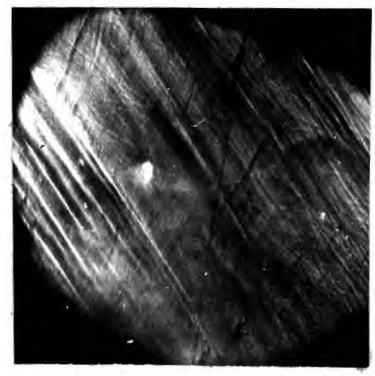


Fig. 30 b.

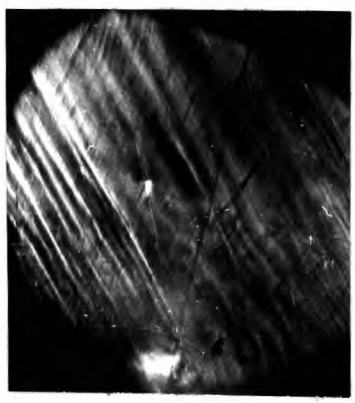


Fig. 30 c.

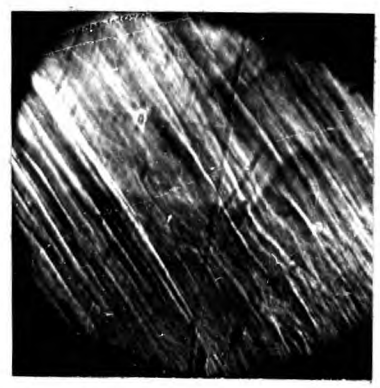


Fig. 30 d.

Fig. 30. b & c indicate the gradual loss of visibility of domains seen with the Kerr effect at the transformation temperature (- 11 to - 12·5°C) in Elba (A 1) natural crystal. a & d are room temperature photographs taken before and after a transformation (x 50).

The optical rotation within a domain appeared to be uniform.

It was possible to move the domain walls with a field of 5 Oe.

Fig. 29 shows the iron filing colloid applied to Elba, A 1. Comparing this with the same colloid on A G 1, (see fig. 21), one finds that despite the lack of knots and cracks the leakage fields are much more irregular. In addition an increased number of 'weaker' domain walls are indicated.

4.2 Domain Patterns on Elba (A 1) at the Transformation.

Using the electron beam method, the transformation occurred between - 11 and - 21°C. Photographs taken at room temperature after subsequent transformations were found to be identical; i.e. the crystal had a memory.

Normal colloid was applied well above or below the electron beam transformation temperatures. No change of pattern was observed on heating or cooling the crystal through the transformation, except for a slight rearrangement during the first 4 cycles.

The Kerr effect work confirmed these results (see figs. 30 a - d). At - 11°C the domains shown in the photograph began to lose their visibility in some areas.

The constrast between the two domains continued to decrease with further cooling until at $-12.5^{\circ}C$ they were no longer visible. The reverse effect occurred on reheating the crystal.

A cine-film was made of the transformation as indicated by the electron beam method on Elba B 6. This specimen came from the same mother crystal as Elba A 1. The shadow pattern cusps continuously decreased their amplitude without the sideways displacement seen in the transformation of Art. 100.



Fig. 31. Iron filing colloid pattern on Art. 100, synthetic hematite crystal (x 40).

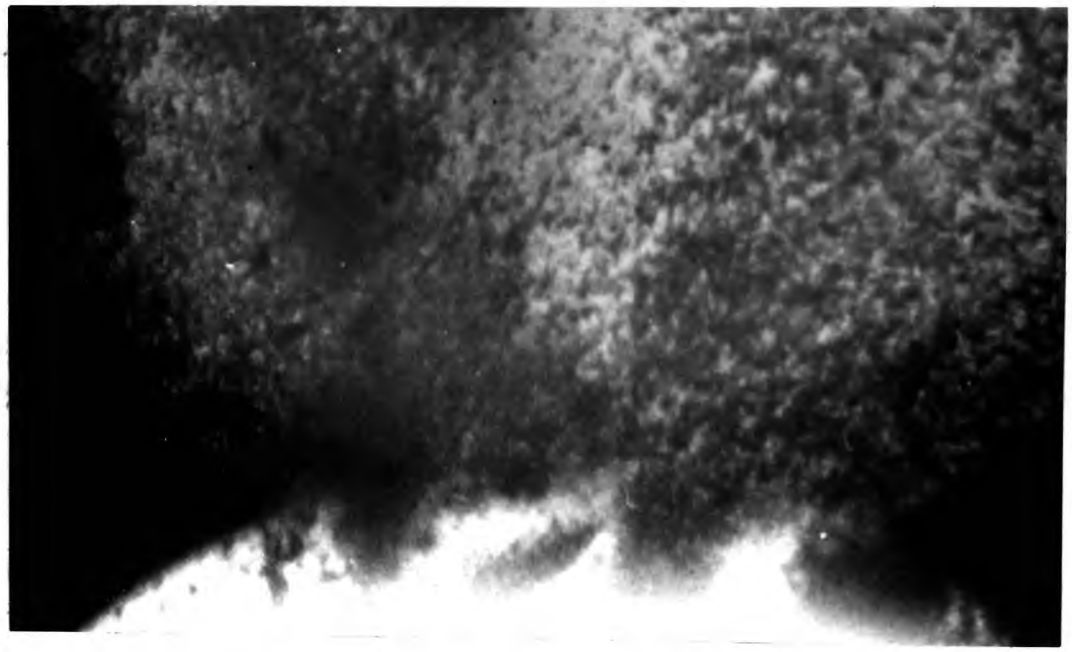


Fig. 32 a. Below $-26{\cdot}7^{\circ}C$ no magnetic effects indicated by the iron filing colloid (x 100).

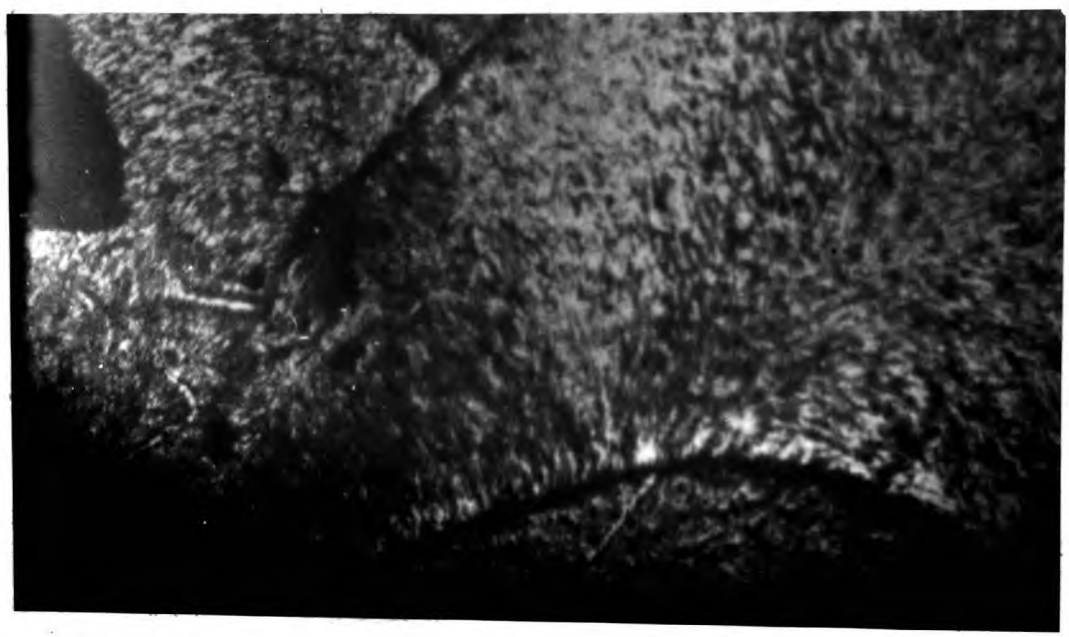


Fig. 32 b. At $-24{\cdot}8^{\circ}C$ a domain wall is seen as a 'line' of colloid which suddenly accumulates on Art. 100, synthetic hematite crystal (x 100).



Fig. 33. On heating through the transformation, domain A changes its shape from a serrated to a rectangular form. Art. 100, synthetic hematite crystal (x 40).

Chapter Five

A Domain Study of Art. 100, Synthetic Hematite Crystal

5.1 Domains at Room Temperature. This Bell Telephone Laboratories' synthetic hematite crystal was a large rectangular plate ($11 \times 12 \times 2.5$ mm.^{3}). The normal colloid and the iron filing colloid indicated domains which were about the same size and exhibited the same leakage field patterns as on A G 1 (see fig. 31).

5.2 Domain Patterns at the Transformation. Fig. 32 shows some of the stages in the transformation as the crystal is heated from -29.3°C. Between -29.3°C and -26.7°C the iron filing colloid indicated no magnetic effects from the crystal. Above -26.7°C the same colloid mapped out a magnetic field produced at the crystal surface. Next, at -24.8°C, a domain wall nucleation process started which occurred in different ways throughout the transformation. For example in fig. 32, the field distribution pattern suddenly accumulated a 'line' of colloid without the rest of the pattern being modified. In fig. 33, the colloid accumulated around area A, where the leakage field was parallel to the surface, to form an area of serrated domain walls. The number of serrations

decreased on warming the crystal, and finally the colloid formed a rectangular domain wall. There were several of these serrated walls on the crystal, and the serrations were all in the same direction. If the specimen was set at a different orientation to the earth's field the serrated walls continued to remain in their original position. The final stage of the transformation consisted of a discontinuous rearrangement of the domain wall pattern finishing at 3·8°C.

It should be noted that in some areas at room temperature the iron filing pattern was different between successive transformations. The temperatures of different stages of the transformation and the domain nucleation areas were approximately constant in successive transformations.

The electron beam method was used to study the transformation. Cine-films showed the cusps of the electron shadow to disappear between -12.5 and -14.1°C. Besides the cusps decreasing in amplitude, a certain amount of sideways motion occurred.

5.3 The Memory Effect in Art. 100, Synthetic Hematite Crystal. In spite of the fact that this crystal had been transformed 113 times it did not develop a

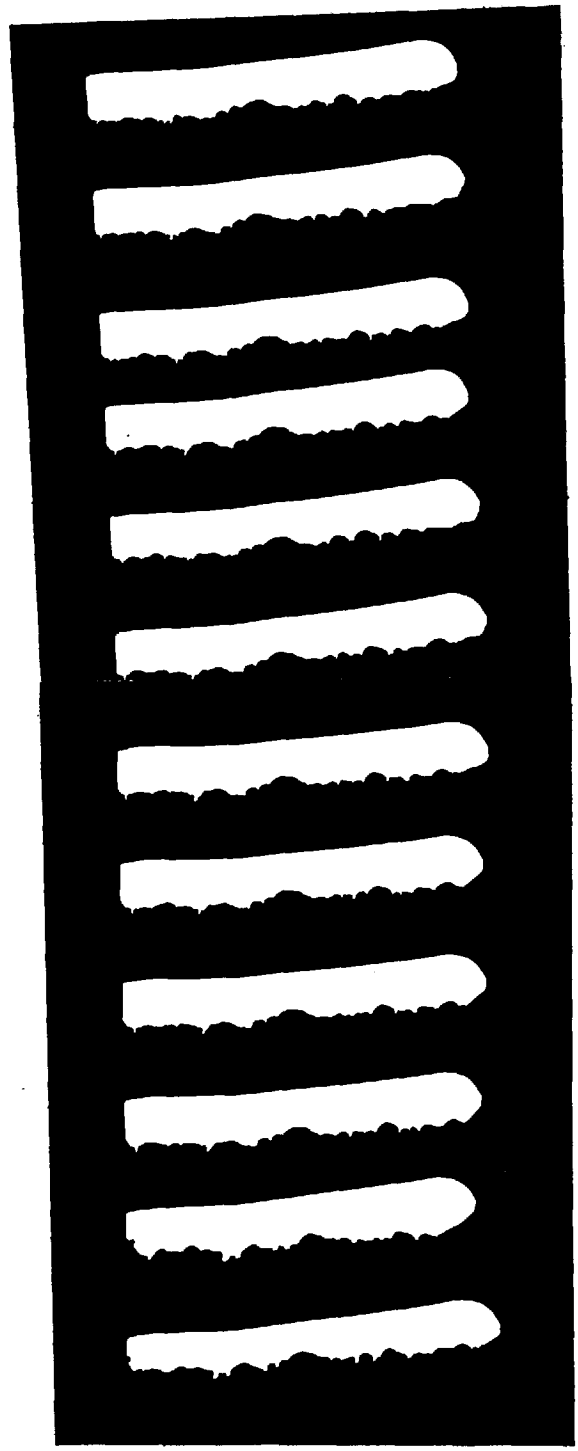


Fig. 34. Electron beam patterns at room temperature after successive transformations indicate that there is only a general tendency towards repeating the same pattern on Art. 100, synthetic hematite crystal. Trans. 32 - 43.

complete magnetic memory as seen by the colloid and the electron beam method. The crystal was transformed 68 times in the diffraction camera. Throughout these transformations the magnetic field imposed on the crystal remained at a constant value. From the photographs (fig. 34) of the electron shadow pattern taken after cycling through the transformation it is obvious that only a general trend towards repeating the same pattern developed. The next 45 transformations were studied with the colloid technique. The crystal did not produce identical patterns at room temperature, the domains tended to form only in the same areas between temperature cycles.

Chapter Six

A Domain Study of Several Hematite Crystals

6.1 The Transformation in Two Synthetic Hematite Flakes, J A H 1 & J A H 2. These flakes were kindly supplied by Dr. Y. Iida of Tokyo University. None of the specimens have been examined to the same extent as the synthetic crystals from Bell Telephone Laboratories. J A H 1 and J A H 2 were 0·1x2x2 mm.^{3} in size. These crystals are so thin that it ought to be possible to examine their magnetic properties by the Faraday effect.

The normal colloid indicated only a few domain walls on these specimens (the faces were not basal planes). The attraction of colloid to the domain walls was weaker than on the Bell Telephone specimens. A serrated domain wall like those seen on Art. 100 was found on J A H 1.

The low temperature transformation was studied with a normal colloid on J A H 1. After 10 transformations the crystal did not exhibit a domain wall memory. On cooling, the transformation consisted of a rearrangement of domain walls starting at -13·5°C. No denucleation of domain walls was seen. At -19·5°C, the lowest temperature at which the crystal was examined, there was still a domain pattern present.



Fig. 35. Iron filing colloid pattern on Gihiofuji, (J 2 B) natural hematite crystal (x 80).

Only the first two transformations of the J A H 2 crystal were studied with the electron beam method. The shadow pattern had cusps of small amplitude compared with the American synthetic crystals. The cusps disappeared at temperatures between -11.5 and -16.0°C.

6.2 The Transformation in a Natural Hematite Crystal, Gihiofuji (J 2 B). The transformation of this natural crystal (6x3x1.5 mm.^{3}) was studied with normal colloid. The domain walls at room temperature were similar to those on the Elba crystal (compare fig. 35 with fig. 29).

The transformation took the form of a discontinuous rearrangement of the domain wall pattern which started at -23·0°C and was still proceeding at -30·6°C. The walls appeared to attract less colloid at the lower temperature either because the intensity of magnetisation was smaller or because the colloid was tending to flocculate. After 12 transformations the domain pattern did not repeat at room temperature.

Kaye (1960) reports that the transformation as measured with the electron beam method occurs between -25 and -35°C for a crystal from the same origin as the Japanese J 2 B crystal.

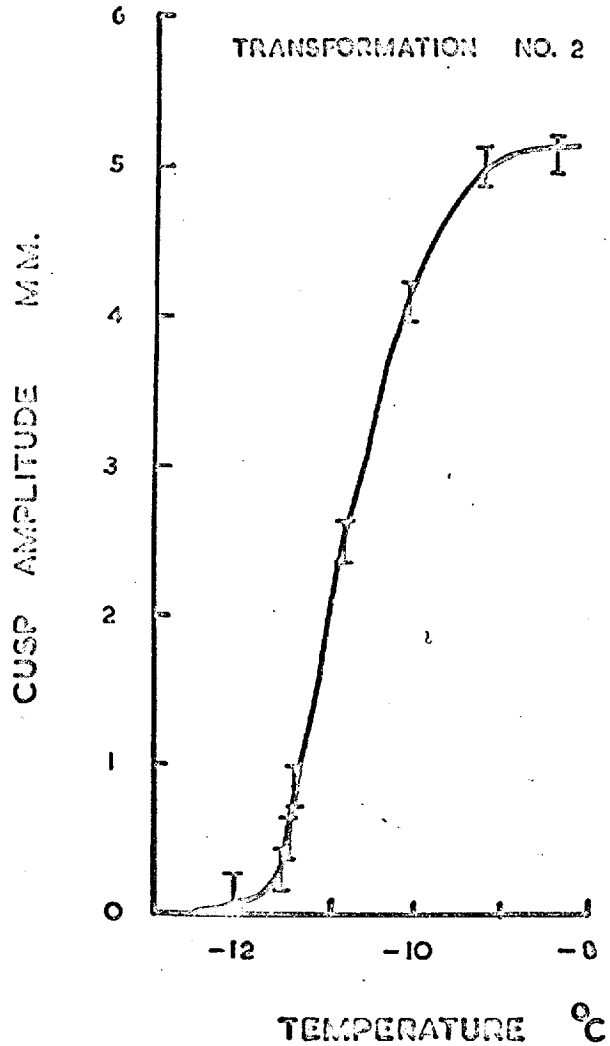
6.3 The Transformation in a Synthetic Hematite Crystal, Art. 101. This circular crystal (2 mm. thick, 8 mm. diameter) of synthetic hematite from Bell Telephone Laboratories was given only a cursory investigation with the colloid technique. The crystal was transformed 6 times.

The domain pattern at room temperature was similar to the pattern on the Art. 100 synthetic crytsal which was grown from the same melt.

The transformation occurred in three stages. Between $-3{\cdot}5$ and $-7{\cdot}5^{\circ}C$ there was a discontinuous rearrangement of the domain pattern. Next a needle structure formed in some areas. At $-16{\cdot}8^{\circ}C$ the walls disappeared by a dispersion of colloid rather than a denucleation process. It was not established whether the iron filing pattern that still remained disappeared with additional cooling.

After 6 transformations no exact domain wall memory had developed.

6.4 The Transformation in a Synthetic Hematite Crystal, Art. 3. As in the previous section this Bell Telephone Laboratories' synthetic specimen was subjected only to a preliminary examination. The crystal ($5 \times 5 \times 5$ mm.^{3}) was transformed 13 times, transformations



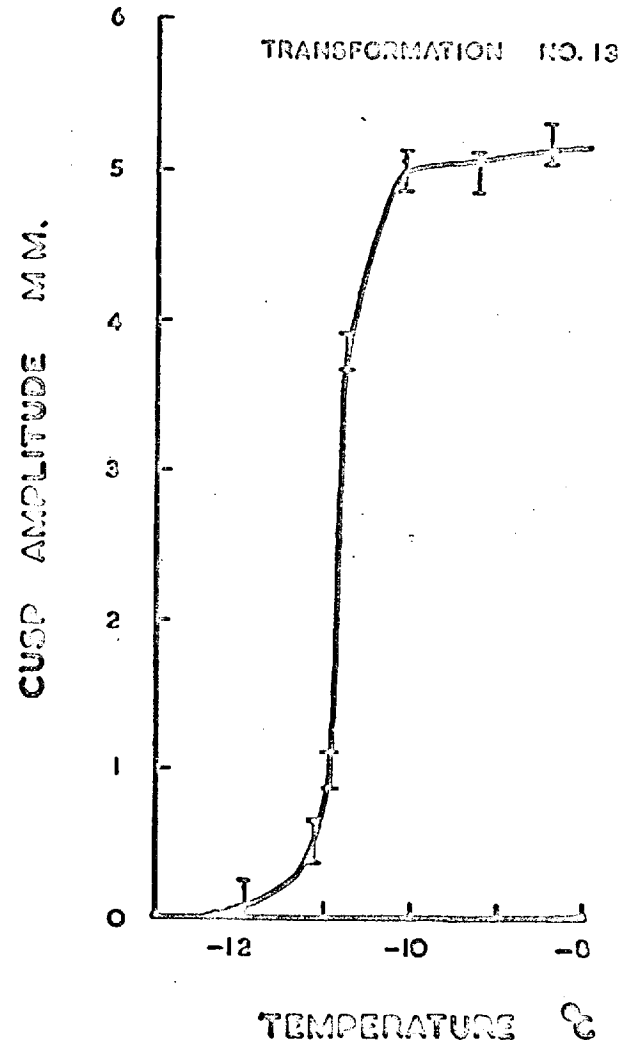


Fig. 36. Cusp amplitude of the electron beam pattern as a function of temperature for Art. 3, synthetic hematite crystal.

4 to 12 being examined with the colloid technique and the remainder with the electron beam method.

This crystal was grown from the same melt as the A G 1, synthetic hematite specimen. In the 8 transformations examined by the colloid technique there was a discontinuous rearrangement of the domain walls between -0.5 and $-12.3^{\circ}C$. Between -12.3 and $-12.5^{\circ}C$ the walls disappeared by the colloid dispersing. These experiments were done before the tracking of domain wall movements had been perfected. Hence these results could be masking a denucleation phenomenon. The domain patterns of subsequent transformations at room temperature showed that the crystal had not developed a memory. The crystal was not examined at the transformation with the iron filing colloid.

Transformations 1 to 3 and transformation number 13 were studied with the electron beam method. The amplitudes of the cusps of the shadow pattern were plotted against temperature for transformations 2 and 13 (see fig. 36). Even though the crystal had no domain memory the transformation finished at the same temperature in both experiments. The range was $-8.9^{\circ}C$ to $-11.4^{\circ}C$ in transformation 2. Single shot photographs of these two transformations were taken. Careful inspection showed that the electron beam

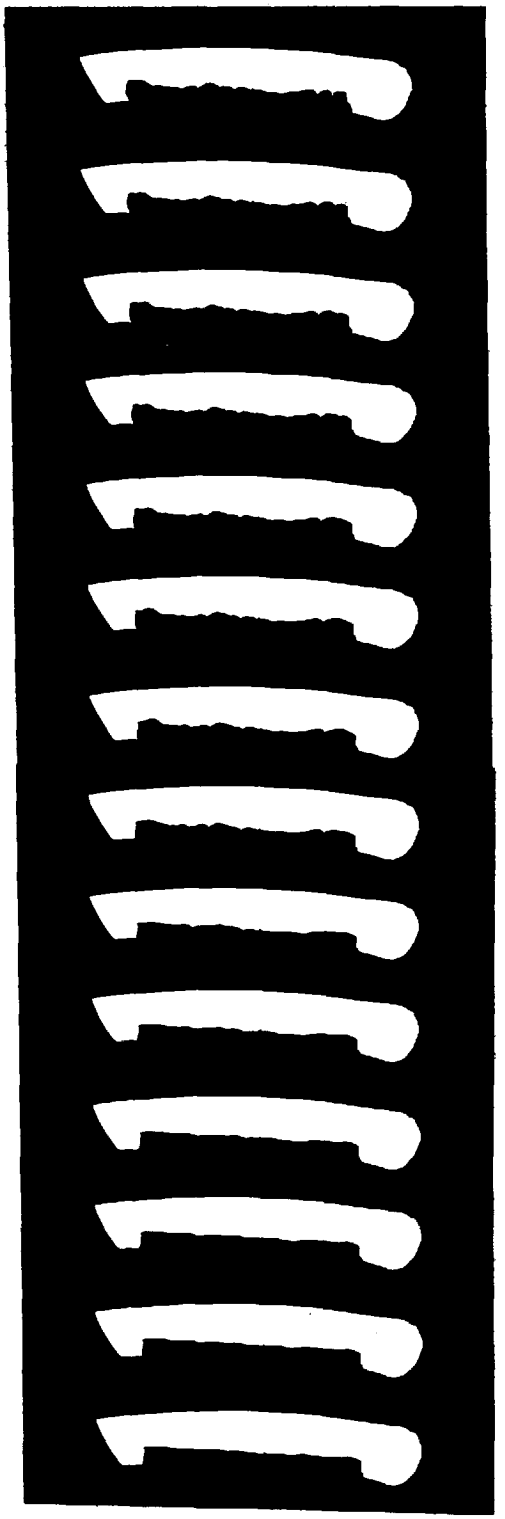


Fig. 37. Electron beam pattern obtained from cooling Art. 3, synthetic hematite crystal through its transformation temperature (-8·9 to -11·4°C).

pattern just decreased in amplitude. There was no sideways movement of the cusps (see fig. 37).

6.5 A Summary of the Experimental Results. It is possible to group the hematite specimens into crystals exhibiting three types of domain behaviour at the low temperature transformation. The first group includes the natural crystals of which Elba A 1 was most extensively studied. The synthetic crystals from Bell Telephone Laboratories form two groups characterised by the behaviours of A G 1 and of Art. 100.

On cooling Elba A 1 through the transformation there is no change of the domain pattern or of the iron filing colloid pattern, yet the Kerr effect and the electron beam method both indicate a reduction of the remanent magnetisation. We will group the Japanese natural crystal (J 2 B) and the Japanese synthetic crystal (J A H 1) with the Elba crystal as their domain patterns did not disappear below the transformation temperature. There was some rearrangement of the domain patterns and a domain memory had not developed in the Japanese specimens. These crystals had however been transformed only about a dozen times.

The domains disappeared by a continuous denucleation phenomenon in A G 1, the crystal which

characterises one group of synthetic crystals. The iron filing pattern still remained after cooling at least 15°C below the temperature of the disappearence of the last domain wall. The electron beam method showed a steady decrease of the amplitude of the cusp pattern with no sideways displacement on lowering the temperature.

The final group includes Art. 100, Art. 101 & Art. 3 of which Art. 100 was studied most extensively. On cooling, Art. 100 exhibits discontinuous rearrangements of domain patterns over a temperature range of 21°C followed by a sudden dispersal of the pattern. The iron filing pattern disappeared 1·0°C below the temperature at which the dispersal occurred. The electron beam method exhibits sideways movement of the cusp pattern together with a decrease in amplitude of the cusps when used on Art. 100. This crystal did not develop a domain memory after over 100 transformations. The two remaining crystals in this group showed the same lack of memory and the same rearrangement-dispersal phenomenon. The iron filing pattern was not studied on them. When the electron beam method was used on Art. 3 it gradually decreased in cusp amplitude with no sideways movement on cooling the crystal. After more transformations it is possible that Art. 3 might develop the memory characteristics of A G 1.

Chapter Seven

A Discussion of the Experimental Results

7.1 Hematite Domains above the Transformation Temperature. In hematite the Kerr effect indicates areas of different magneto-optic rotation. The boundaries of these regions are in the same positions as the patterns obtained with the normal acetone colloid, and can be moved by magnetic fields of less than 10 Oe. Hence we may term these regions magnetic domains. The domains in hematite have rather different properties compared with those in normal ferromagnetic and ferrimagnetic materials. The interpretation of these unusual properties follows naturally from the shape of the domain boundaries and the iron filing effect seen with the high sensitivity colloid.

Normal strain-free magnetic crystals exhibit domains with well defined geometrical shapes. To some extent, the shapes are determined by the arrangement of the easy directions of magnetisation within a particular crystal. In zero applied field the magnetisation in the domains is oriented along easy directions of magnetisation. The domain walls are arranged to maintain a constant component of magnetisation normal to the domain wall.

In hematite the domains possess no obvious symmetry and are irregular in appearence. For the normal component condition to apply, the magnetisation must be parallel to the domain wall surface, i.e. the magnetisation must be antiparallel either side of the wall. Hence, as in cobalt, all the remaining crystal faces, except one, would exhibit straight line domain walls. This does not occur in hematite; all the natural faces exhibit an irregular domain pattern. There must therefore be another explanation for the shape of the domain pattern in hematite.

The additional patterns obtained using the iron filing colloid are due to a variation of leakage field above the surface of individual domains. This leakage field cannot be attributed to the domain walls because it is still present in the same form after they have disappeared at the transformation temperature. It must therefore originate from the domain itself and indicates a variation of direction and/or magnitude of magnetisation within individual domains. This effect was present on all the single crystals examined with the high sensitivity colloid. A variation of magneto-optic rotation within some domains confirms this conclusion.

This unusual result can be used to interpret the

shape of the domains if we accept the principle that generally the component of magnetisation normal to the domain wall is constant. The local variation of direction of magnetisation within a domain produces the unusual domain shapes seen on the surface of hematite crystals.

It seems improbable that the domains reported here are characteristic only of the surface of hematite. Williams, Sherwood & Remeika (1958) obtained domains of a very similar size using the magneto-optic effect in transmission through a synthetic crystal 25 microns thick.

Many domains are surrounded by colloid patterns of varying intensity. The Kerr effect shows the same variations at these domain walls. Sometimes these methods give the impression that the domains are not completely surrounded by domain walls but appear to merge into one another.

Studying the domain structure on hematite in relation to the leakage field pattern below the transformation, one is given the impression that besides the domain walls being complete boundaries between domains they have a more important role of reducing high local leakage fields by substituting this boundary. The walls often end at major imperfections in

the crystal.

The leakage field pattern below the transformation temperature governs the possible directions which domain walls will take above the transformation. The walls set themselves with the plane of the wall normal to the external lines of flux indicated by the colloid.

7.2 The Magnetic Transformation. The results reported here emphasise the wide variation of the magnetic properties from one hematite crystal to another. The magnetic transformation occurs at considerably different temperatures for crystals from the same melt. Of crystals prepared in the same laboratory, one exhibits a magnetic domain memory whereas others do not.

Generally speaking the remanent magnetisation of the synthetic crystals from Bell Telephone Laboratories decreases by a factor of 30 at the transformation temperature (Gallon, 1963), and in natural crystals the reduction is much less. The results of the colloid experiments described above and those of other workers are different from the earlier results in which the remanent magnetisation was observed to disappear completely in synthetic crystals.

The results reported here show that in terms of

the micromagnetic structure the transformation is found to occur by three distinct mechanisms. These mechanisms will be interpreted by considering the relative number of physical defects in the crystals.

The room temperature magnetisation is the same for all mechanisms whereas below the transformation temperature the micromagnetic properties are all different. The first mechanism occurs in the crystals which are the least perfect, the natural crystals, and is seen in the crystal from Elba. On cooling well below the transformation temperature there is no change in domain pattern nor in the local direction of the leakage field. However, the Kerr effect and the electron beam method show that the remanent magnetisation has decreased. This effect occurred in both the Elba crystal and the A G 1 synthetic crystal, i.e. the magnitude of the leakage field was shown to vary with temperature by the electron beam method whilst the colloid patterns showed no change. This could occur only if the leakage field retained the same relative intensities in different areas at specific temperatures whilst decreasing in magnitude. This would be an ideal situation especially for hematite. Although the electron beam pattern is an average effect of several domains, the electron beam

method did seem to indicate that the same relative intensities were being maintained throughout the transformation.

The second mechanism indicates a more perfect crystal. This is found in the synthetic specimen A G 1. No change of the local direction of the leakage field is found after cooling at least 15°C below the transformation temperature. The domain walls disappear by a denucleation mechanism. The direction of motion of the domain walls is determined to some extent by the local directions of magnetisation within the crystal. It is possible that some denucleating domain walls are phase boundaries separating two different magnitudes of magnetisation (see 7.3).

The third mechanism is perhaps indicative of the most perfect synthetic crystals. This is found in Art. 100. On cooling, this specimen exhibits a rearrangement and a sudden weakening of the domain walls rather than a denucleation phenomenon. 1·9°C below the temperature at which the final domain wall disappears, the high sensitivity colloid shows no magnetic effects whatsoever, just a random distribution of colloid. We should note that this crystal did not develop a domain memory even after 100 transformations.

To interpret the three different transformation mechanisms we need to examine the origin of the local variations of magnetisation within a hematite domain. The variations are independent of the domain wall structure. Hence the patterns must be dependent on some crystal property. One property which could have local variations throughout a crystal and affect the magnetisation is strain.

It is reasonable to assume that the natural crystals are more strained than the synthetic crystals, and that the A G 1 crystal has more strains in it than Art. 100. Comparing a strained volume of a crystal with an unstrained volume, we find slightly different lattice parameters in the two regions. Due to the changes of spacing the strained volume is essentially a different crystal. This would manifest itself magnetically by a change of saturation magnetisation and anisotropy compared with the ideal crystal. Using Dzialoshinskii's postulate that an ideal hematite should be non-ferromagnetic below the transformation temperature we see that the low temperature ferromagnetism is not an intrinsic ferromagnetism but originates from the strain produced by the imperfections in the crystal. This low temperature magnetisation is forced into certain directions by the local

strain. It is interesting that the A G 1 crystal is essentially a single domain below the transformation.

At room temperature the effects of strain are shown by a greater number of variations of magnetisation within the same area on the Elba crystal compared with A G 1 and especially when compared with Art. 100.

In these crystals we have regions of ideal hematite and regions which have slightly different properties. The properties differ enough to affect the second order magnetism of hematite, i.e. the ferromagnetism. The regions are extensive enough in A G 1 to impose certain local directions on the magnetisation, but there is still sufficient 'ideal' hematite to produce domain wall movement and to reduce the magnetisation considerably at the transformation. In the Elba crystal there are more strains distributed throughout the crystal and these prevent the magnetic spins from moving the domain walls at the transformation. In spite of this the magnetisation is reduced slightly on cooling the crystal.

With this strain model a crystal should have a domain memory if it possesses a sufficient number of dislocations.

This interpretation is completely qualitative and

relies on some of the ferromagnetism being maintained in fixed directions by the local effect of strain independently of temperature. The strains originate from the large numbers of dislocations present in any crystal grown by either natural or experimental methods. In order to give a more precise model we need to know the origin of anisotropy and possibly magnetostriction in hematite.

7.3 Discussion of a Possible Two Phase System at the Transformation in A G 1. It is interesting to consider whether the transformation in A G 1 is a more stable form of the domain wall rearrangement and disappearance phenomenon seen in Art. 100 or whether it is a radically different process in which two distinct magnetic phases are separated by the denucleating domain walls. In this context one phase is defined as a ferromagnetism having a certain magnitude of magnetisation within a domain and the other phase as a ferromagnetism having a different magnitude of magnetisation.

When the A G 1 crystal is cooled, examination by the electron beam method and the Kerr effect indicates that the remanent magnetisation first changes without any movement of the domains. With further cooling, the crystal forms new domains by splitting existing walls

in two and expanding the new region. The domain movement occurs first in areas having the least magnetic inhomogeneity. The new domains could be formed because the decrease in temperature produces new easy directions of magnetisation or a new magnetic phase with a lower intensity of magnetisation. When the denucleating domain boundaries move across the magnetically homogeneous regions their movement shows no dependence on the existing domain structure. One boundary, almost a straight line, advances continuously, leaving behind considerable areas with no domain structure. The lack of dependence of the moving boundary on the stationary domain structure is more easily explained by assuming that the new region is one of local anisotropy change rather than of a new phase of much reduced magnetisation. The latter would be more likely to produce additional rearrangement due to the greater change of leakage field. During later stages, some of the denucleating walls are not complete, so that it is difficult to imagine them as phase boundaries. There is no difference in the amount of colloid or the way in which it is attracted to the moving domain boundaries compared with the room temperature domain walls.

On heating the A G 1 crystal from below the denucleation temperature an increased accumulation of

colloid occurs in some areas. This is then surrounded by a domain wall due to the local increase of magnetisation. Some of the areas behave like the domain walls in Art. 100 by forming a straight line in the middle of a patch of colloid. Hence, if two phases do exist at the transformation in A G 1, it is only in certain regions, and it occurs more by accident than as an intrinsic phenomenon.

On warming any synthetic crystal through the transformation temperature the domain walls are created in the same region even if there is no magnetic memory. From this we can infer that these areas have the lowest transformation temperature due to some local change of crystal property, i.e. strain.

7.4 Discussion - The Effect of a Magnetic Field on the Transformation in A G 1. The application of a magnetic field to the A G 1 crystal while the domain walls were denucleating produced an apparent increase or decrease in the temperature of the crystal. Like the domain changes caused by a temperature change, the pattern of movement of domain walls in a magnetic field is governed by the local variation of direction of magnetisation.

In this crystal, the minimum field needed to move

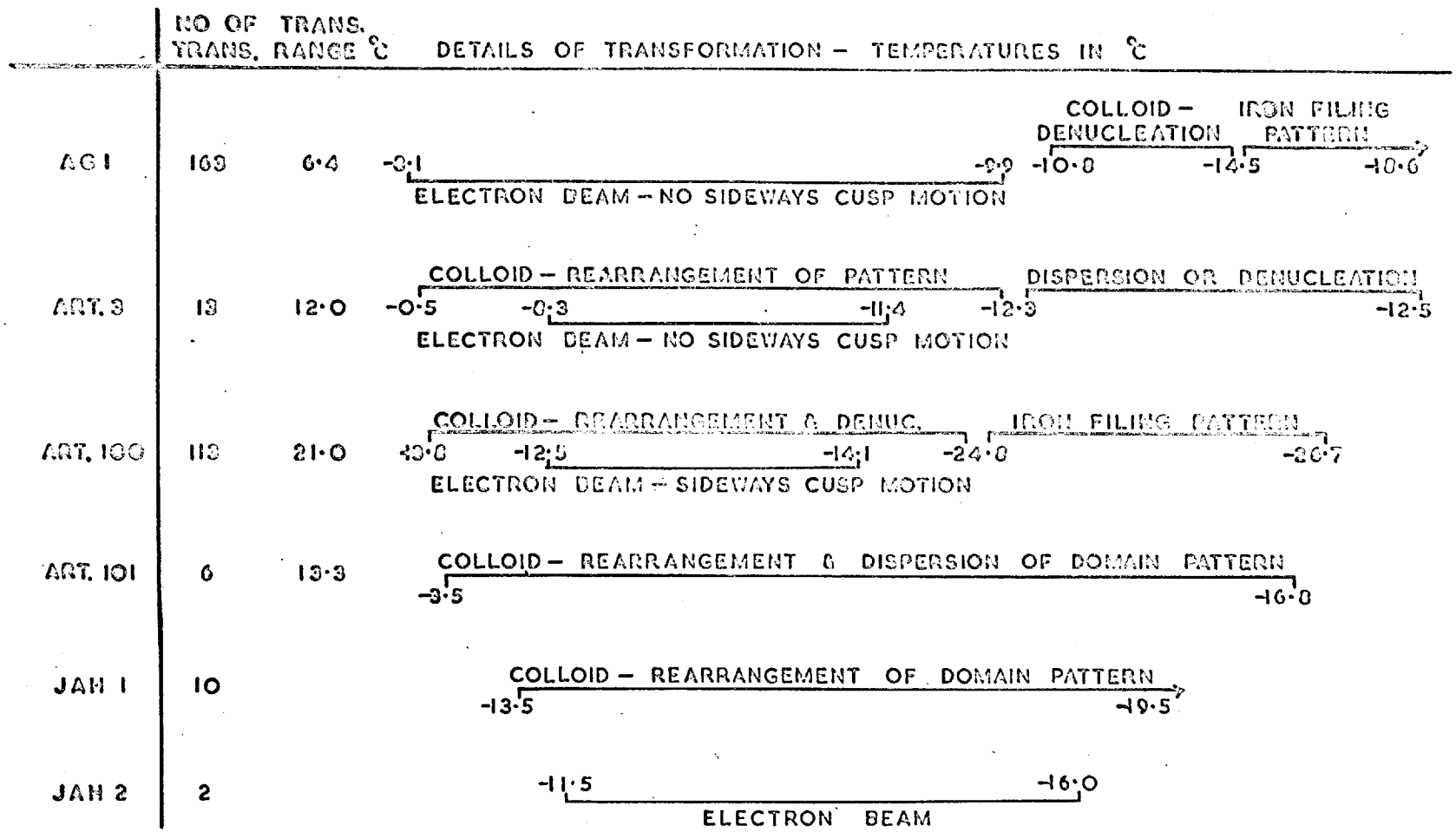


Fig. 38. A table of the transformation temperatures for synthetic crystals using the colloid technique and the electron beam method.

a domain wall during denucleation increases from 20 Oe. half way through the denucleation stage to 100 Oe. just as the final domain denucleates. This can be interpreted as being due to the weakening of the couple on the spin system as the magnetisation decreases and possibly a gradual increase of the anisotropy energy as the crystal transforms.

The domains could not be nucleated by applying a 100 Oe. magnetic field immediately below the transformation temperature, either because the field was not sufficient or the colloid would not settle on domain walls in the high polarising field.

The iron filing pattern was modified by a magnetic field of only 15 Oe. at room temperature and yet 300 Oe. had no effect when applied below the transformation temperature. Presumably this is again due to weakening of the couple on the spin system or perhaps the anisotropy energy of the crystal is increased.

7.5 General Discussion. The transformation temperatures for synthetic crystals using the colloid technique and the electron beam method are tabulated in fig. 38. There is an alarming variation in transformation temperature from one pure crystal to another. The electron beam method shows transformation mid-points

ranging from $-9{\cdot}9^{\circ}C$ in Art. 3 to $-13{\cdot}7^{\circ}C$ in J A H 2. The transformation mid-point, in terms of the mid-point between temperatures at which any method detected magnetic changes, ranges from $-6{\cdot}5^{\circ}C$ in Art. 3 to $-16{\cdot}5^{\circ}C$ in J A H 1. The most perfect crystal, Art. 100, exhibits domain wall changes over a temperature range of $28{\cdot}6^{\circ}C$ compared with $6{\cdot}4^{\circ}C$ for the less perfect crystal, A G 1. It is difficult to determine whether the wall movement at higher temperatures in a sensitive crystal is part of the transformation or due to the normal variation of magnetisation with temperature.

The changes in domain structure serve to illustrate, more than any other method, how variable a phenomenon the transformation can be.

In the interpretation of the present work on hematite it has been found unnecessary to introduce the concept of antiferromagnetic domains. However, these have been found in NiO crystals. In an abstract of an unpublished paper, Pickart, Nathans, Brown & Alperin (1963) claim to have found regions in a Bell Telephone Laboratories' synthetic crystal in which the arrangement of the magnetic spins with respect to the oxygen ions is different. The volume of these arrangements could be varied by applying a field of 50 Oe. It is difficult to discuss the relationship between

ferromagnetic and antiferromagnetic domains until a study has been made of the two forms of domains on the same crystal. This is even more necessary as the neutron diffraction work indicated antiferromagnetic domains below the transformation.

7.6 General Conclusions and Future Experiments on Hematite. Physicists experimenting on the magnetic properties of natural hematites must have felt that when synthetic crystals were made available the variation in magnetic properties from one crystal to another might disappear. Unfortunately the recent literature and the results reported here have shown quite the reverse, especially with regard to the ferromagnetic properties. It is impossible to compare the results of different techniques on synthetic specimens obtained not only from the same laboratory but from the same melt. In order to appreciate the relationship between the antiferromagnetic and the ferromagnetic parameters different techniques must be used on the same crystal.

The low temperature transformation, in the sense of any change of remanent magnetisation below room temperature, has been found to occur by three domain mechanisms depending on the micromagnetic arrangement

of the ferromagnetism below the transformation. The three mechanisms caused by a reduction in temperature are: -

1) A rearrangement of the domain pattern over a range of 21°C followed by a sudden dispersal of the colloid pattern leaving the crystal as a single ferromagnetic domain exhibiting local variations in direction and/or magnitude of magnetisation. The magnetisation in this domain no longer attracted iron filing colloid when the crystal was cooled 1·9°C below the temperature at which the domain wall pattern dispersed.

2) A denucleation of domain walls over a range of 3·7°C leaving a single domain exhibiting local variations in direction and/or magnitude of magnetisation. The magnetisation in this domain does not weaken for at least an additional 15°C cooling below the denucleation temperature. The remanent magnetisation is 30 times lower at these temperatures compared with room temperature. The crystal with this form of transformation possesses a domain memory in that successive transformations are identical at all temperatures.

3) A change of the remanent magnetisation occurs without any domain wall movement or change in the

direction of the magnetic leakage field on the surface of the crystal. This behaviour is found in a natural crystal from Elba.

Below the transformation temperature the ferromagnetism has been interpreted as a defect property in all the hematites. The ferromagnetism has not disappeared completely on cooling because local strains (produced by the defects) have prevented the spins in certain areas from aligning themselves completely along the ternary axis. The first mechanism occurs in crystals having the least number of defects, and the third mechanism in those having the greatest number. Using this interpretation, below the transformation temperature, the remanent magnetisation of crystals transforming by the first mechanism should be lower than those crystals transforming by the second. The strain affects the ferromagnetism above the transformation temperature by causing local inhomogeneities in the leakage field from domains.

The strain interpretation can be tested by annealing synthetic crystals. The transformation mechanism should then be of a rearrangement-dispersion type rather than a denucleation phenomenon. The remanent magnetisation below the transformation should decrease with annealing. It might be possible to do

the reverse, i.e. to make synthetic specimens more like natural crystals by quenching them. The majority of crystals do not exhibit any well defined anisotropy properties in the basal plane above the transformation temperature and if the strains are annealed out the theoretical three-fold anisotropy may well appear.

It seems that the ferromagnetism present below the transformation temperature will be found to originate from defects rather than an intrinsic ferromagnetism. Research using neutron diffraction is needed to establish the manner in which the ferromagnetic domains interact with antiferromagnetic domains and to establish the origin of the ferromagnetism. An interpretation must be given to explain why the ferromagnetism does not saturate to the same value in different directions in a crystal, and how it is possible to turn the antiferromagnetic spin system in the basal plane with small magnetic fields.

N O T E

The University of London Board of Studies recommended that the spelling of the title should read hæmatite and not hematite. This recommendation has not been adopted in the main body of the thesis for three reasons. The Shorter Oxford Dictionary (published 1956) gives two possible spellings for α-Fe_2O_3 they are 'hematite' or 'hæmatite'. Since it is difficult for most typewriters to produce a dipthong, and because the vast majority of modern scientific journals use the spelling, hematite, this has been maintained throughout.

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