An investigation of the magnetic fractionation of ilmenite.

Author:
Parry, Lindsay George

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<u>AN INVESTIGATION OF THE MAGNETIC FRACTIONATION</u>

<u>OF ILMENITE</u>

This thesis is submitted for examination for the award of Degree of Master of Science in Applied Physics.

I hereby certify that the work embodied in this thesis has not previously been submitted elsewhere for a higher degree.

Submitted by:-

L. G. PARRY
School of Applied Physics
N.S.W. University of Technology

AN INVESTIGATION OF THE MAGNETIC FRACTIONATION

OF ILMENITE

Abstract.   This investigation was undertaken with two
objects in mind. Firstly to obtain a chrome-free ilmenite
from the deposits of ilmenite available in the New South
Wales Beach Sand deposits and secondly to investigate the
possibilities of concentrating an economically useful chrome
ore. Methods of magnetically fractionating the raw ilmenite
are discussed together with a description of the chemical,
magnetic and X-ray properties of the various fractions. The
effects of heat treatment on the natural ores are discussed
together with an enumeration of the properties of these
secondary products. It has been found possible to obtain
an 80% recovery of ilmenite with a chromic oxide content
of 0.1-0.2% which may be treated further to yield 65% of
ilmenite with 0.05% chromic oxide. The residual chromic
oxide impurity depends on the amount in the original sample.
Limited success is achieved in concentrating the chromium
bearing grains. Finally a brief survey is made of the
possible mechanism by which the magnetic properties of the
ilmenite varies.

INTRODUCTION

Ilmenite is one of several minerals occurring in the
black beach sand deposits which are found along the Australian
eastern coast from Newcastle northwards, at least to Stradbroke
Island. Over this region many commercial enterprises are
exploiting these deposits for rutile, zircon, monazite and,
to a minor extent, ilmenite.

These heavy sands are naturally concentrated by wave
action along the beaches which are gradually sloping with a
gradient of 1 in 8 to 1 in 20 having a margin of sand dunes
10ft-20ft high along the landward side. During normal wave
activity the seaward margin of the dunes is built up and the

silica is selectively removed by the winds leaving thin
layers of concentrates. The heavy south-east gales which
seasonally prevail are particularly effective in building up
mineral deposits and layers several feet thick with small
silica content are found. These bands are thickest near the
dunes and taper to the seaward side. In some areas (Evans
Head) appreciable deposits are located several miles from
the present sea coast.

The principal components of the beach sands are listed
in table 1 W.R. Poole (1939) with slight modifications.

TABLE 1. Heavy Beach Sand Constituents and
Physical Properties

Mineral	Zircon	Rutile	Ilmenite	Monazite	Garnet
Colour in bulk	Cream to Greyish	Reddish Grey Lustrous	Lustrous Black	Yellowish Green	Brown, pink,red
Size (Standard Mesh)	56%120-150 15%150-200	60%120-150 10%150-200	15%48-65 80%65-100	Above 100	93%150-200
Specific Gravity	4.66	4.24	4.56	5.07	3.70
Composit-ion	$ZrO_2 SiO_2$	TiO_2	$FeO TiO_2$	Phosph-ates of rare earths, e.g.cerium	Mixture of Silicates
Shape	sub-cryst-alline	sub-spherical	sub-spherical	sub-spherical	angular
Colour under micro-scope Transmitted light)	whitish trans-lucent to transpar-ent	amber to red to almost (black)	black opaque	yellowish green to colourless	amethyst or rose to colourless
Purity	High	At least 99% TiO_2 Iron colours grains	43-44% FeO & Fe_2O_3 48-49% TiO_2 1-3% Cr_2O_3		

Mineral	Zircon	Rutile	Ilmenite	Monazite	Garnet
Magnetic Properties	"Non Magnetic"	Non Magnetic	Weakly Magnetic	Very weakly magnetic	Very weakly magnetic
Electro-static activity	Not attracted	attracted	attracted	not attracted	not attracted

X Varies considerably along coast.

Rutile and zircon are readily saleable, monazite is valuable but is present in very small amounts (less than 1%). Generally the ilmenite is regarded as unsaleable and is dumped. The separation of these minerals is simply accomplished by a battery of electrostatic and magnetic separators and in some cases flotation methods are adopted.

A typical flow sheet is gravitational separation on Wilfley tables or by spiral separators to remove the silica and wash the grains, the mineral is then dried in a drier and passed through screens to a rough electrostatic separator, thence to a battery of magnetic separators and a final cleaning electrostatic separator. The middlings are fed back at appropriate stages. Sometimes a magnetic rougher is used prior to the first electrostatic separator.

The subject of the series of experiments, reported here, was a detailed study of the magnetic properties of the ilmenite fraction which contains certain impurities. This work was undertaken with aim of developing a separating technique which would produce a more useful grade of ilmenite with an enhanced commercial value.

Several industrial processes make use of ilmenite and the chief source at present is the Travancore (India) deposits worked by primitive methods but using native labour and hence available at low prices. In Australia some ilmenite is saleable to manufacturers of electric arc welding rods but a possible market lies in the paint industry. A very common constituent of high grade paints is the titanium white base which is used extensively in place of lead oxide where the poisonous nature of lead oxide is dangerous. Most manufacturers produce titanium white from ilmenite by a process involving digestion in sulphuric acid. One notable objection to the use of Australian ilmenite is that there is always present from 1% to 3% of chromic oxide. This contaminent causes discolouration of the titanium white. By physically reducing this chromium content from the ilmenite concentrate prior to chemical processing, it may be possible to increase its commercial value.

A second possible line of approach is to obtain a chromium enriched concentrate from the ilmenite which may be commercially useful. This is possible because it has been found by Stillwell and Baker (1948) (and confirmed in these laboratories) that a large proportion, at least, of the chromic oxide is present in grains of "chromite". Many of these grains are identifiable by residual rhombohedral crystal structure.

The practical questions involved then become:-

1. Is it possible by simple physical means to separate the chrome bearing fraction?

2. Are these processes readily adaptable to the industry
as constituted at the present time, bearing in mind the
ready source of cheap ilmenite from Travancore?

In an attempt to answer these questions a set of
experiments described below were designed, concentrating on
magnetic methods.

This thesis is chiefly concerned with the magnetic
analysis of the problem; however there are many additional
problems beside the magnetic studies.   In general, the results
of these other investigations will be summarised but the
details will not be discussed except where they directly bear
on the propositions stated above.

In outline the report is divided into chapters
(I, II, III, IV and V) followed by an appendix.   Chapter 1
deals with the physical, magnetic and chemical properties
of ilmenite.   Chapter II discusses the magnetic product
obtained from ilmenite by roasting.   Chapter III outlines
the properties of a nonmagnetic compound obtained by further
heat treatment.   In chapter IV comparable properties of
chromite are assembled for study and Chapter V deals with the
author's discussion of the questions posed above.   In the
appendix a survey of a theoretical nature is made of the
iron-titanium oxides and a brief statement is made of some
of the possible theories covering the magnetic properties of
ilmenite.

CHAPTER 1

THE MAGNETIC AND PHYSICAL PROPERTIES OF NATURAL ILMENITE

1.1 Magnetic Fractionation

It is possible to separate a component from the beach sand minerals by magnetic means; which is rather loosely spoken of as ilmenite. However this material consists of grains for which the magnetic and other physical and chemical properties vary over a very wide range. Included with grains that are ilmenite there will generally be small quantities of chromite, garnet and monazite, with relatively small magnetic susceptibility, and also highly magnetic magnetite or titanomagnetite.

Preparatory to a full investigation of the ilmenite it was found necessary to select samples with a much narrower range of magnetic properties. A laboratory gravitational-magnetic method, in which a stream of particles was dropped vertically in a region of inhomogeneous magnetic field, proved inadequate since the division was insufficiently defined for experimental purposes. Finally a method was adopted in which the grains were attracted vertically through a distance of at least on centimetre.

In this latter method an electro-magnet was fitted with wedge and groove pole pieces (see fig.1.1) (4) represents the slotted yokes.

The grains were held in a grooved nonmagnetic carried (R)

and were spread in a shallow
layer.   During separation the
carrier was oscillated slowly
in a horizontal direction to allow
all grains freedom to be lifted
in the inhomogeneous magnetic
field.   Using this arrangement
it proved possible to divide the
concentrate into a large number

FIG. I.I   Diagram of the
magnetic separator.

of different magnetic fractions; sixteen were chosen and were
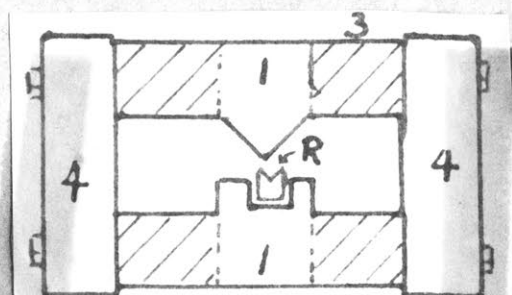labelled A to P.

Separation by this method yields a series of fractions
each covering a rather narrow range of magnetic properties and
any one sample contains but few grains which should fall into
adjacent fractions.   However the process is tedious except for
obtaining small samples and consequently a second method
was used later in which the carrier was replaced by a nonmagnetic
disc rotating in a horizontal plane.   Under these circumstances
the separation was rapid but the spread of magnetic properties
of the grains in any one magnetic fraction was much wider and
for most investigations each fraction was further refined by
the first method.

The following discussion applies generally to the
magnetic fractions D to N inclusive and these fractions are
considered to be very closely related substances which can be
classed as ilmenite but fractions A,B,C,O and P contain many
grains of other material.

1.2 Physical Properties

a. In Bulk. Each of the magnetic fractions has similar physical appearance. The grains are opaque, black, lustrous and rather uniform in size. The size of the grains was determined for fractions G, K, N and O and the results are tabulated below (Table 1.1). This experiment was performed in one case with a "rotap" machine and the second case with a vibrator. From these results it is apparent that there is no significant correlation between grain size and magnetic susceptibility.

TABLE 1.1   Percentage of Fractions in Various Screen Sizes

Fraction	Mesh sizes of Screens (B.S.S.)				Percentage of Fraction Pass 115
	35-48	48-65	65-100	100-115	
G		12.4	81.8	5.8	Small amount passed 150
K		19.3	77.6	3.1	1%
N		11.7	83.6	4.3	0.4
O	2.1	14.1	75.4	6.6	1.6

b. Microscopic Examination. Grains from different fractions were observed externally but no significant differences could be seen. In all cases the grains exhibited metallic lustre, rounded subspherical form and pitted surfaces. Many of the grains showed the presence of a surface decomposition product in the surface pits. The marginal materials were dull yellow to orange in colour and were assumed to be haematite and leucoxene-limonite.

In addition, in about 1% of the grains there are traces

of white, dull mineral deposits, probably leucoxene which is a common decomposition product of ilmenite. The ilmenite is hard and brittle showing no regular cleavage and occasionally conchoidal fracture.

c. Polished section. Further studies were made of polished sections of representative samples. Again no significant variation was noticeable under either ordinary or polarised light. The best results were obtained by mounting the grains in a bakelite mould. The temperature of the mould was approximately 130°C and high pressure was used.

The polishing proved to be difficult but some specimens were obtained with a sufficient polish. Best results were had by hand polishing on a lead lap using fine grade metallurgical polishing agent. Some samples were prepared on a "Gratten-Vanderbilt" polishing machine.

Examination under ordinary reflected light did not reveal any variation between the grains and so most of the observations were made between slightly uncrossed nicols. Under these circumstances the grains were steel greyish colour and showed anisotropy, with a constant position of extinction for the whole grain. Twenty percent of the grains show a marginal decomposition material and occasionally the ilmenite had intergrown with an isotropic brownish mineral which was probably haematite. These investigations showed that there was no gross inclusion of a second phase which could account for a variation in magnetic properties.

Most grains showed a noticeably pitted character.
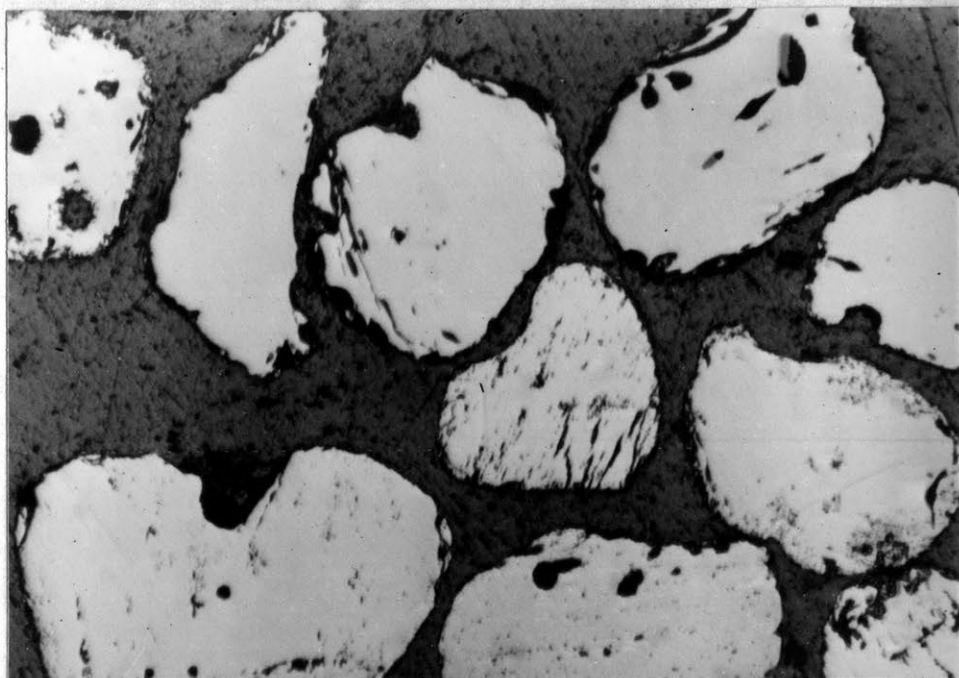
a.
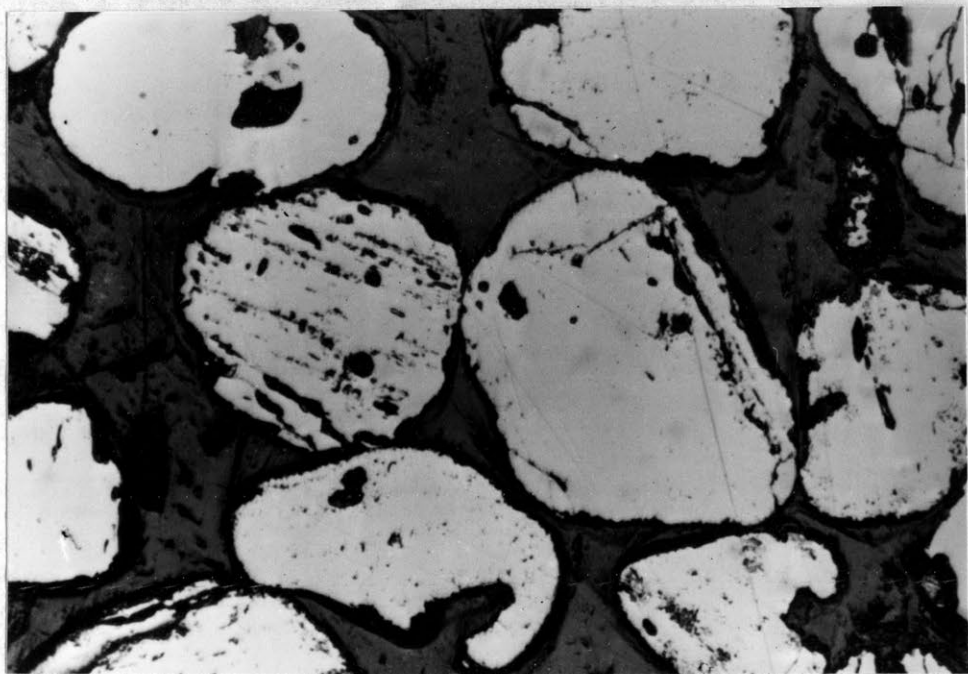
b.

PLATE 1.1 Microphotographs of samples of material considered
          in the text (magnification X212).

    a. Fraction L showing apparently homogeneous grains,
        in most cases weathering and pitting are evident.

    b. Fraction G – indistinguishable at this
        magnification from fraction L.

    c. Magnetic ilmenite (GX2) indistinguishable from
        fraction G at this magnification.
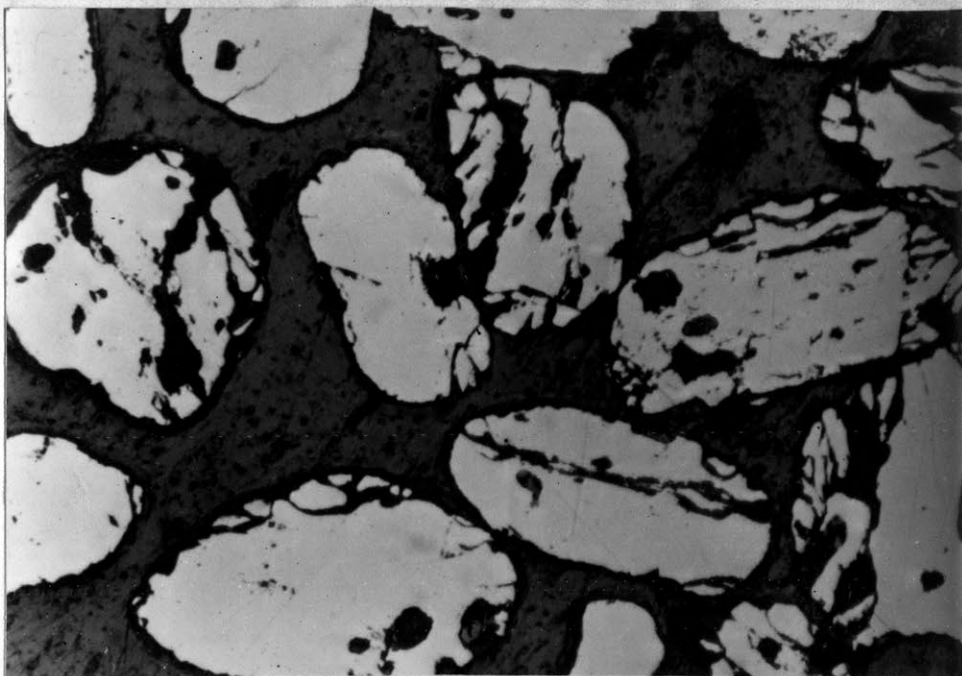
c.
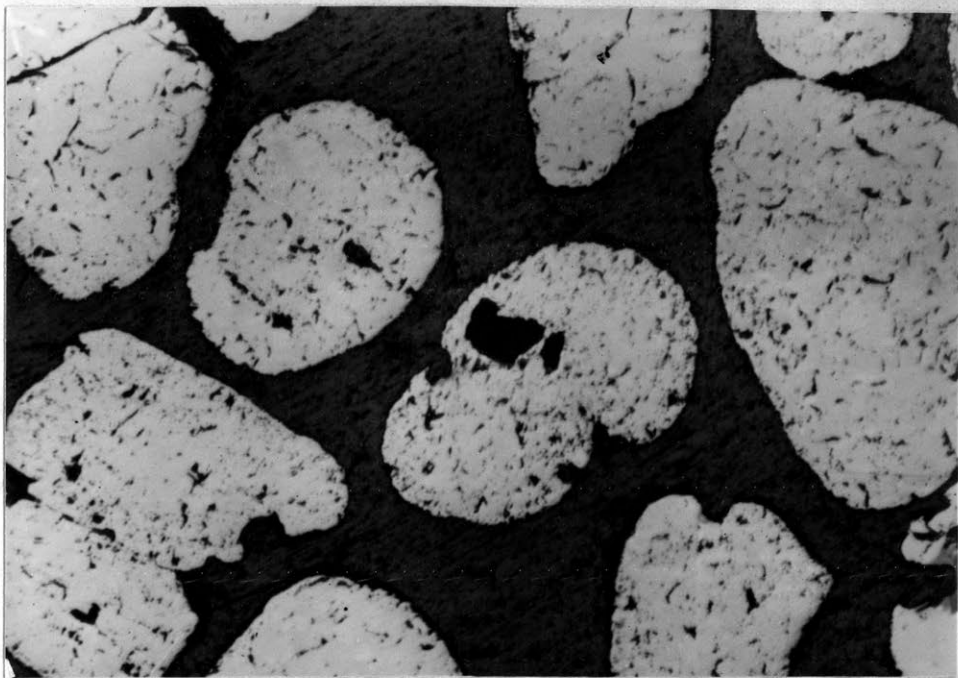
d.

d. Iron titanate GX1 readily distinguished by the
   network of irregular lines bordering twinned
   crystals.

   This set of microphotographs are made available
   through the kind co-operation of Mr. R.L.Stanton,
   Department of Geology, University of Sydney.

In less than one percent of the grains there were inclusions of rutile. The nature of the surface may be seen from plates 1.1 which are microphotographs of several grains. The isotropic basal sections are generally more polished.

Since it is difficult to distinguish between minerals such as haematite, ilmenite, titanomagnetite, etch tests were performed using acids. Hydrochloric acid, nitric acid, aqua regia were all found to give inconclusive results with the grain surfaces tested. Prolonged treatment with hydrofluoric acid led to discolouration but the effects again did not appear to be sufficiently definite to draw unambiguous conclusions.

These mineragraphic experiments were not exhaustive but from the observations made it is possible to conclude that there is no obvious systematic variation in appearance from one fraction to another *for magnifications up to 200 Diameters.* In addition both X-ray and mineragraphic evidence lead to the conclusion that any included phase must be present in very small amounts and, or finely divided. In the few cases where definite phases were present the technique was quite adequate to detect this fact. It is not claimed, however, that a further systematic and careful examination would not be profitable from a mineragraphic point of view. **※**

1.3 <u>X-ray Diffraction Investigations</u>

The X-ray data are listed below Table 1.2 and are compared directly with the pattern quoted by Posnjak and Barth (1934). The material studied by these authors was obtained from Egersund, Norway and is listed in the literature

※ Private communication with Mr. R.L. Stanton, School of Geology, University of Sydney, who kindly prepared and studied some samples, is in accord with these conclusions.

Interplanar spacings, d, (in angstrom units) for various samples of Ilmenite

Norwegian Ilmenite d (Rel.Int)	FRACTION*				Rhombohedral Miller, Indices (h k ℓ)	Posnjak and Barth (Corrected values quoted)
	N d(Int)	K d(Int)	G d(Int)	D d(Int)		
—	—	—	—	—	—	4.5 (1)
3.697(4)	3.697(3)	3.700(3)	3.684(4)	3.693(2)	110	3.70 (4)
2.729(10)	2.728(10)	2.721(10)	2.720(10)	2.727(10)	211	2.74 (10)
2.513(7)	2.525(8)	2.522(8)	2.521(7)	2.526(7)	X̄,110	2.54 (9)
2.218(4)	2.223(3)	2.220(5)	2.211(4)	2.221(3)	210,120	2.23 (2)
1.857(6)	1.856(5)	1.858(5)	1.857(5)	1.857(4)	220	1.865 (6)
1.717(8)	1.715(8)	1.717(8)	1.715(8)	1.714(6)	_321	1.720(8)
1.629(2)	1.624(1)				211,632	1.630 (3)
1.501(6)	1.500(5)	1.501(7)	1.499(6)	1.498(3)	310	1.504 (7)
1.463(7)	1.465(5)	1.463(7)	1.462(6)	1.462(4)	211	1.465(7)
						1.375 (2)
1.338(1)	1.337(2)	1.340(1)	1.333(2)	1.332(<1)	432,342	1.347 (1)
1.266(6)		1.304(1)	1.267(2)		220	1.270 (3)
						1.242 (1)
						1.205 (2)
1.188(1)	1.198(1)	1.198(1)	1.183(2)	1.181(1)	442	1.185 (2)
1.166(2)	1.152(1)	1.146(1)	1.148(2)	1.131(1)	32Ī	1.147 (2)
1.115(2)	1.115(2)	1.116(6)	1.112(3)	1.109(1)	420	1.111 (2)
1.071(3)	1.074(2)	1.073(1)	1.070(2)	1.055(1)	522,532	1.069 (7)
1.049(1)				1.020(1)	Not	1.050(1)
						1.000 (2)
0.978(9)					Indexed	0.98 (1)
0.970(4)	0.970(<1)	0.971(<1)	0.973(1)			
0.961	0.960(<1)	0.961(<1)	0.965(1)	0.964(1)		
0.921(1)						

* d values are uncorrected except for film distortion.

Dana (System of Minerals), Barksdale (Titanium) as having a very small amount of Fe_2O_3 and other impurities. In this laboratory X-ray diffraction photographs were also taken of some Norwegian ilmenite.

Posnjak and Barth give the following data:-
The unit cell is a rhombohedron containing two molecules of $FeTiO_3$, with two atoms of titanium at the points (u, u, u,) and (ū, ū, ū,) where u = 0.142Å and with two atoms of iron at the points (v, v, v) and (v̄, v̄, v̄) where v = 0.358Å and six oxygen atoms at (xyz),(yzx),(zxy) (x̄, ȳ, z̄)(ȳ, z̄, x̄)(z̄, x̄, ȳ) where x = 0.555Å, y = -0.055Å, z = 0.250Å. The unit cell dimensions are a_R = 5.52Å, ⍺ = 54.83 deg.

This lattice (Bunn: Chemical Crystallography) may be expressed in terms of hexagonal parameters a, c where

$$a2 = 4a^2_R \sin^2 \frac{⍺}{2}$$

$$c^2 = 9a^2_R - 3a^2$$

where a = 5.08Å, c = 14.03Å, $\frac{c}{a}$ = 2.761;

Thus it is possible to index natural ilmenite on a hexagonal chart for which the interplanar spacings (d) are given by

$$\frac{1}{d2} = \frac{4(h^2+hk+k^2)}{3a^2} + \frac{l^2}{c^2}$$

where h, k, l are the Miller indices. However only those indices are allowable for which the corresponding rhombohedral indices (H, K, L) are integral, that is

$$H = \frac{1}{3}(h - k + 1)$$

$$K = \frac{1}{3}(h + 2k + 1)$$

$$L = \frac{1}{3}(-2h - k + 1)$$

An indexing chart with axes plotted logarithmically was available, drawn for a hexagonal structure but omitting the indices which are forbidden by these above requirements and was used to index the ilmenite.

X-ray powder photographs[I] were exposed to cobalt $K\alpha$ radiation (iron filter) in a 11.46cm. Debye-Scherrer Camera. From the measured lines, the Bragg angle and the inter-planar spacing (d) were determined using the Bragg relation

$$n\lambda = 2d \sin\theta$$

The intensities quoted are visual estimates and are very approximate since in all films considerable fogging occurred at high angles.   The data are assembled in Table 1.2.

From a close study of these data it is apparent:-

(1) That the material is composed of a single phase within the limits of resolution of the technique which even in unfavourable circumstances should reveal any phase present in greater than 5 per cent concentration.

(2) There is no significant variation of the lattice dimensions from fraction to fraction

(3) Within the limit of visual estimate, the relative line intensities are constant.

[I]   Exposed and processed by Messrs. Hansen and Schwartz using Phillips X-ray set.

(4) The values compare equally closely to the photographs
taken of Norwegian ilmenite but unfortunately insufficient
material was available to check the Fe_2O_3 content of the
crystal from which the powder was obtained.

(5) The notable discrepancy between the Norwegian ilmenite,
Barth and Posnjak's results, and those for beach sand
ilmenite fractions, except N, is the absence of the line
corresponding to d = 1.630Å. This may be due to
distortion of the crystals or slight change in crystal
parameters.

The accuracy of measurement of the interplanar spacings
was limited by the background fogging, which increases as the
angle of diffraction increases. The higher intensity cobalt
tubes on a Geiger Counter unit allowed much clearer films.

An estimate of the probable error of the interplanar
spacing (d value) was made by applying a t - test to
measurements taken on four films, three of which were made
using one specimen. The lines examined were those due to the
(211) and (310) reflections and the respective d values were
(2.720 ± 0.005)Å and (1.497 ± 0.001)Å. Both these lines were
strong lines and in general the probable error of other
d values would be greater than for the line due to the
(310) reflection.

1.4 Magnetic Properties at Room Temperature

Pouillard (1950), Chevallier (1953) state that ilmenite
is a paramagnetic material with probable ferromagnetic
inclusions or contaminations. Consequently it was considered

sufficient to measure the magnetic susceptibility by the Gouy Method in preliminary investigations.

In the experimental arrangement the left hand scale pan of chemical balance was replaced by a special counterpoised pan which had similar dimensions to the original pan. A light aluminium chain passed from the balance stirrup hook through a hole in the base of the case. This modified balance was capable of giving reproduceable weighings to better than 0.2mgm.

The magnetic field was provided by the electro-magnet discussed above (see fig. 1.1), the wedge and groove pole pieces being replaced by cylindrical pole pieces (fig. 1.2) with flat faces. These faces were aligned parallel with an air gap of approximately 1.5 cm. Under these circumstances the magnetic field remained constant to within 1 per cent over 4 cm. from the centre of the pole piece.

The magnetic field intensity was measured by a calibrated search coil and fluxmeter. Since a relative method was used the significant factor is the precision with which readings of the fluxmeter may be reproduced. A set of observations

Fig. 1.2 Diagram of pole piece (elevation).

showed that for a deflection of 12 fluxmeter divisions the probable error of an observation is 0.2 divs. At higher

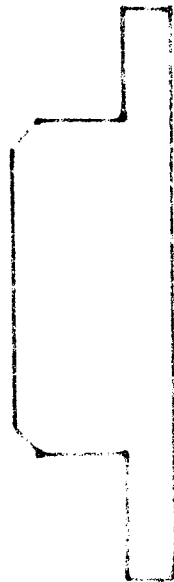deflections the probable error would be of similar magnitude.

The sample was contained in a glass tube made of pyrex glass. Blank runs showed that the effect due to the glass tube in this field was negligibly small. The sample packed in this tube was equivalent to a cylinder of mean radius 0.4 cm. and height 9.0 c.m. but in each case corrections had to be made for the packing of the sample, and the cylinder of ilmenite had to be replaced by an equivalent solid cylinder. This required that the effective area should be determined.

The standard reference material chosen was ferrous ammonium sulphate ($FeSO_4(NH_4)_2SO_46H_2O$) of A.R. purity. For this material the volume susceptibility k is equal to 60.49×10^{-6} e.m.u.

During measurements the sample tube was enclosed in a glass fronted chamber fitted over the poles in order to overcome the effects due to draughts.

This experimental arrangement was capable of producing results which are accurate to better than 1 per cent, but such precision is not attained in this work for the following reasons:-

(1) The packing fraction cannot be completely corrected because of uneven packing, uncertain values of density and stray magnetic fields.

(2) Graphs of many of the samples showed definite curvature proving that a ferro- magnetic impurity is present.
In this work graphical extrapolation methods were used to determine the value of susceptibility at zero magnetic field. However the presence of the ferromagnetic effects

cause considerable uncertainties.

1.5 Theory of the Method.

The potential energy of a sample of material of permeability μ when placed in a magnetic field H in a medium of permeability $\mu_0 \doteqdot 1$ is given by

$$P = \frac{(\mu - \mu_0)vH^2}{8\pi}$$

where v is the volume.

For air $\mu_0 = 1$ within the accuracy of these experiments when measuring large values of magnetic susceptibility Therefore

$$P = \frac{1}{2} kvH^2 \qquad \dots\dots\dots\dots(1)$$

where $k = \frac{\mu - 1}{4\pi} =$ volume susceptibility.

In the Gouy method, a solid cylinder of material is suspended with one end in a region where the magnetic field is H and at the other end the magnetic field is H_0. Choose axes x, y, z such that z is parallel to the axis of the cylinder and x, y are mutually perpendicular such that $\frac{\partial H}{\partial x} = \frac{\partial H}{\partial y} = 0$ thence the force on the sample will be parallel to z.

Let df_z be the force in the vertical direction on a volume $dv = Adz$ where A is the cross-sectional area therefore

$$df_z = \frac{d}{dz}(P) = \frac{d}{dz}(\tfrac{1}{2}kAdzH^2) \qquad \dots\dots\dots(2)$$

therefore integrating for the cylinder

$$f_z = \tfrac{1}{2}kA(H^2 - H_0^2) \qquad \dots\dots\dots(3)$$

In the samples studied here in many cases k is a
function of the magnetising field and consequently equation (3)
is approximate only.   Since the magnitude of k is of chief
interest and the departure of k from a constant value is small
the results are taken by using the modified form of equation (3)

A relative method was used, and since the sample
comprises solid grains, a correction must be made for packing.
It is assumed that H_0 is negligible; indeed H_0^2 is never greater
than 1 per cent of H^2.

Let the apparent length and radius of the sample be
h and r respectively.   Let the mass of sample be m and the
density of the material be d.

Therefore the actual volume of solid material $= \dfrac{m}{d}$
and the apparent volume $= h\pi r^2$.

To correct for packing the porous cylinder is replaced
by a solid cylinder of the same length with an effective
area A_e and then

$$hA_e = \frac{m}{d} \qquad \ldots \ldots (4)$$

therefore

$$A_e = \frac{m}{hd} \qquad \ldots \ldots (5)$$

From equation (5) and equation (3)

$$k = 2\frac{hd}{m} \cdot \frac{f}{H^2 H_0^2} \qquad \ldots \ldots (6)$$

In using the relative method, H is measured in terms of a
fluxmeter deflection which is readily reproducible there being
no need to determine H absolutely.

Suppose the sample tube is filled with material of magnetic susceptibility k_s, let d_s, h_s, m_s, f_s be the density, length, mass and force on the standard sample.
Therefore

$$k_s = 2(\frac{d_s h_s}{m_s}) \frac{f_s}{H_s^2 - H_{so}^2} \quad \ldots \ldots (7)$$

Therefore

$$k = k_s \times (\frac{dh}{m})(\frac{m_s}{d_s h_s}) (\frac{H_s^2 - H_{so}^2}{f_s})(\frac{f}{H^2 - H_o^2}) \ldots (8)$$

All the quantities with subscripts s are experimentally determined and are constant throughout the experiments therefore

$$k = C(\frac{dh}{m}) \frac{f}{H^2 - H_o^2} \quad \ldots \ldots (9)$$

When f is measured in g.wt. and H in divisions deflection on the fluxmeter with standard coil

$$C = 33.44 \text{ units}$$

giving k in e.m.u.

In a few cases further dilution was used and the method adopted was to dilute the magnetic material with non-magnetic zircon and pack as uniformly as possible in the carrier. Formula (9) still applies but considerable loss in accuracy occurs because of aggregation of the grains with consequent non uniform vertical distribution.

1.6 Experimental Results

The relative method outlined above was used in all cases and the grains were tamped to a constant height in the specimen tube so that packing was constant throughout one experiment. In

each case a series of observations was made with increasing
magnetic field.   In this way several experimental points
were obtained and plotted on a graph in which the force was
plotted against H^2 (since H_0^2 was less than 1% of H^2).   The
graphs were reproducible if the sample was emptied and repacked
but with the higher fractions the sample became permanently
magnetised with consequent variations in the force on the sample
when a repeat observation was taken without repacking.   Care
had to be taken to demagnetise the magnet between experiments
because appreciable residual field was present.

In all cases the volume magnetic susceptibility was
measured by obtaining f/H^2 from the graph extrapolated to zero H,
hence the values quoted in the tables refer to the magnetic
susceptibility at zero field.   Under these circumstances any
ferromagnetic impurity exhibits its maximum effects and a second
value is obtained at a magnetic field of 500 oersteds.   This
value of magnetic susceptibility has little significance except
as a guide to the field dependence.   If sufficiently high fields
had been used it may have been possible to obtain an estimate
of the paramagnetic contribution but the field was not
sufficiently uniform in the horizontal direction and caused by
lateral movement of the specimen thus preventing accurate
measurements.

Table 1.3 records the information obtained on the
susceptibility at zero field.   A few values of the effective
susceptibility at 500 oersteds are also quoted.   Table 1.3 also
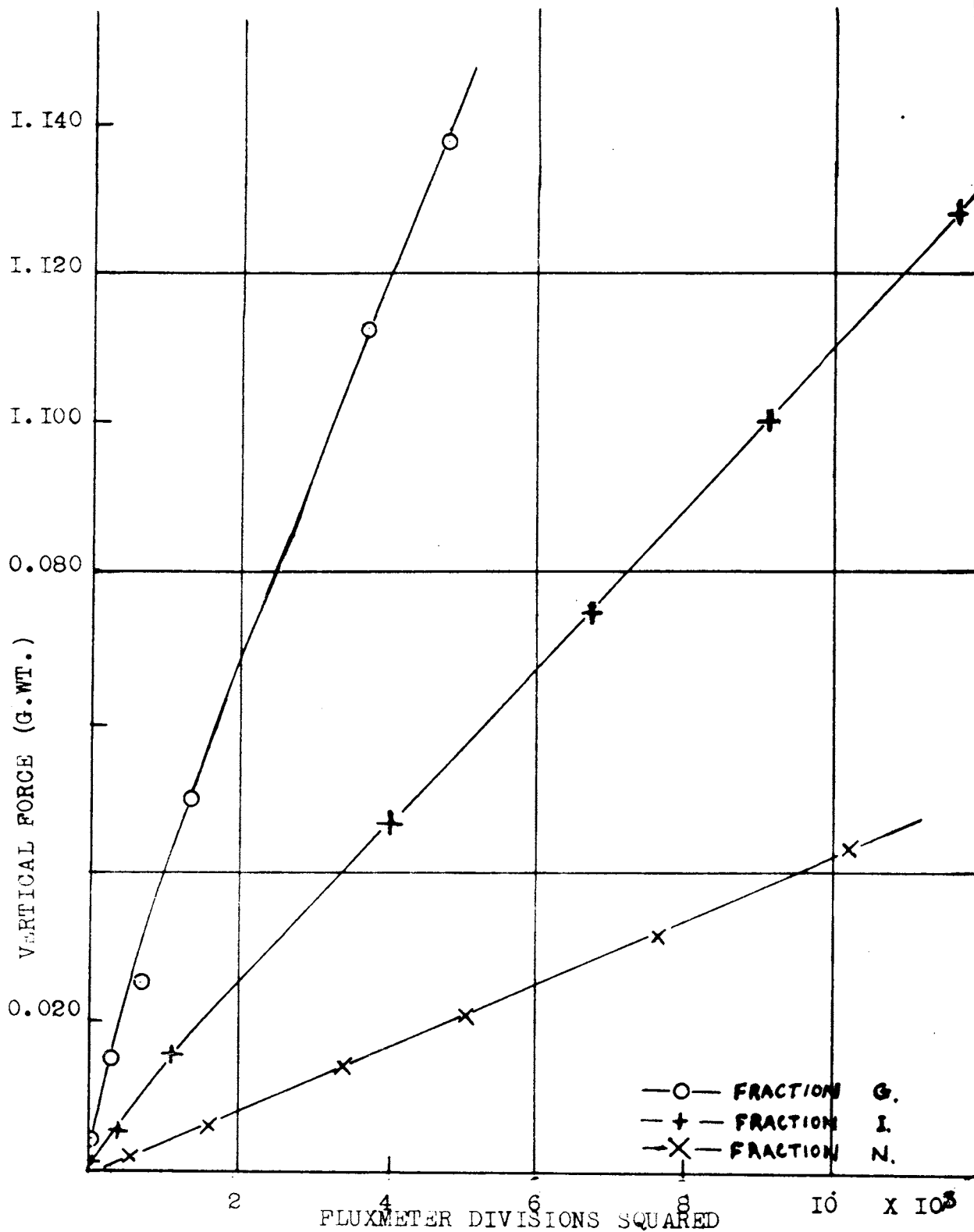shows the relative abundance of each fraction.

FIG I.3 Three sample curves from which the magnetic susceptibility was estimated.

Representative graphs from which these results were obtained are shown in fig. 1.3. The increasing curvature of the graphs for higher magnetic fractions is evident.

Examination of these results shows that there is a well defined variation in the value of k as the various fractions are taken so that the value for fraction D is more than twenty times greater than that for fraction N. It is apparent also that L

TABLE 1.3 - <u>Abundance and Magnetic Susceptibility at Zero Field and a Field of 500 oc.</u>

Fraction	k (e.m.u. x 10^{-3})	k_{500} (e.m.u. x 10^{-3})	Mass of Fraction as % of Total Raw Ilmenite
A,B,C	100		2
D	1.1^x		2
E	8.7^x		12
F	4.3	2.9	16
G	3.83	2.3	7
H	2.32	1.9	13
I	1.43^x		10
J	1.29		4
K	0.65	0.55	5
L	0.62^x		6
M	0.52	0.52	11
N	0.467	0.467	5
O	0.32		6

x Obtained by dilution methods and hence less accurate.

and M and I and J are very similar in these magnetic properties. Also there is field dependence of the susceptibility in fractions from A at least as far down as K.

It is common in natural minerals, that impurity may very markedly change the magnetic properties of a substance and consequently further investigations were made with the aim of

discovering the reason for such a variation. X-ray investigations did not show any marked variations. Similarly chemical evidence is negative except for the variation in the Fe^{+3}/Fe^{+2} ratio. The high values of magnetic susceptibility suggest that there must be either a second phase present or that the lattice itself shows magnetic interactions and the material is weakly ferromagnetic.

1.7   The Accuracy of the Measurements.

The accuracy of these results, as mentioned above, is not high and in addition it is difficult to arrive at an estimate of the probable error because of the following factors:-
Packing effect, imperfect separation, the possible effects of previous magnetic history. An estimate could be made of greatest significance, if the experiment was repeated several times from the beginning and independent determinations of the susceptibility were made. Such a procedure was impracticable and so the same fraction from one separation was examined several times and the value of the susceptibility determined independently several times.

Examination of equation (9) shows that with the exception of the determination of $f/H^2-H_0^2$ all observations have a total percentage probable error approximately 1%. The probable error of value of $f/H^2-H_0^2$ varied considerably depending on the curvature of the graph. By taking a series of determinations of the slope it was possible to estimate a percentage probable error of approximately 3% in most cases.

Superimposed on the above errors could be an uncertainty

in the temperature of approximately two degrees which more
recent experiments suggest could, in unfavourable cases, cause
an additional uncertainty of approximately 1 percent.

In conclusion, then, it seems possible to assess the
percentage probable error at 5% in the most unfavourable cases
while for a fraction such as N there is no reason why a result
with a probable error of 1% could not be attained by this
technique.

2. HEAT TREATMENT OF ILMENITE

2.1 Effects of Heating Ilmenite in Air

The magnetic properties of ilmenite are changed only
very slightly by heating in air below 600°C. However above
600°C several remarkable changes occur; these changes have been
shown to be due to oxidation and no appreciable effects were
noted on samples heated over the same temperature range in an
evacuated silica tube for the same time intervals. Chemical
assays show appreciable increase in the ferric to ferrous ion
ratio.

The following experiments were carried out in an open
crucible heated in an electric muffle furnace. The temperature
was measured by a chromel-alumel couple embedded in the sample
and confirmed by observations with a disappearing-filament
radiation pyrometer.

In excess of 600°C oxidation may occur more or less
rapidly, depending on the temperature and to some extent on the
initial magnetic fraction of the ilmenite used.

Two oxidation products which are different from the
original ilmenite were prepared:-

1. A partial oxidation product which is readily obtained by
    carefully heating ilmenite in the temperature range
    $650^{\circ}C$-$800^{\circ}C$. The reaction proceeds more rapidly at higher
    temperatures and at $800^{\circ}C$. requires a few minutes only.
    The oxidised material is similar in appearance, chemical
    composition and X-ray patterns regardless of the magnetic
    fraction which was heated.

2. A fully oxidised compound which is obtained by heating in
    excess of $850^{\circ}C$, or for very prolonged periods at lower
    temperatures. This material similarly has properties
    which are independent of the original fraction used in its
    preparation.

The magnetic properties of these materials are discussed
elsewhere (Chapters ll and lll).

The preliminary tests were performed on a sample of
ilmenite. This material was split into four magnetic
fractions α, β, γ, δ in the magnetic separator using wedge
and groove pole faces. The field current was set at 0.5A, 1.5A,
3.5A. α was the fraction raised through 1 cm distance when the
current was set at 0.5A. β was the fraction left when the
current was 0.5A but lifted when the current was 1.5A.

γ was left when the current was 1.5A and lifted when the
current was 3.5A. δ was left when the current was 3.5A.

At the outset any material in the fractions α and δ
was rejected and the remaining fractions where heated for

The numbers represent the mass of Sample in each category.

FURNACE TEMPERATURE (C)

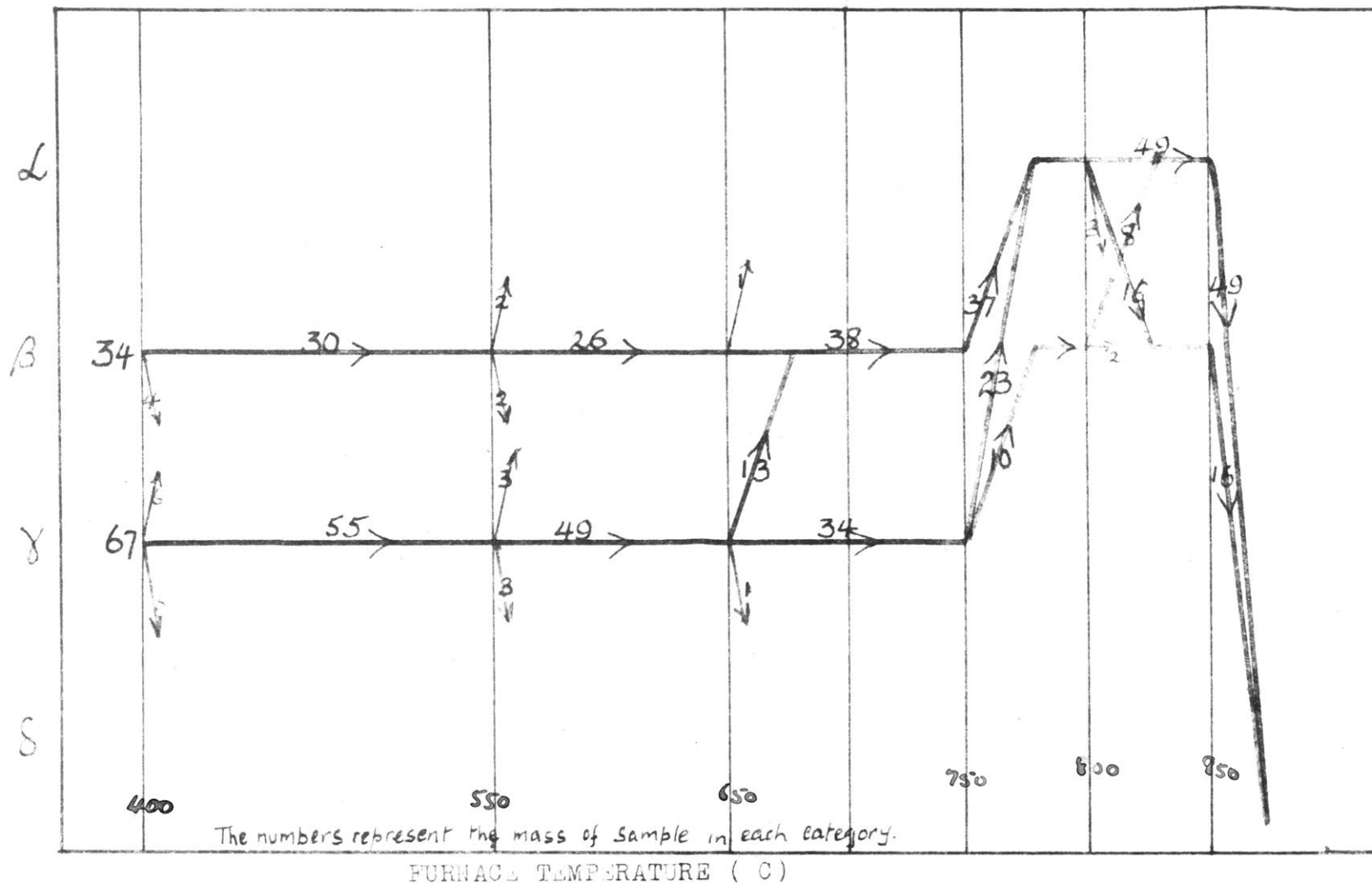FIG.2.I FRACTIONS β,γ were heated for approximately half an hour at the temperatures quoted. The ordinates represent the magnetic fractions. The solid lines show the magnetic properties of the grains after cooling.

approximately 30 minutes at each of the temperatures 400°, 550°, 650°, 750°, 800°, 850° and then cooled. Between each heating, the material was re-separated into the four fractions α, β, γ, δ . Usually all material in each category was combined regardless of origin. More than 90% of the material was raised at some stage to a higher magnetic category and at least 70% reached the category α .

The general results of this investigation are summarised in fig. 2.1

Some small samples behaved in an irregular fashion but this was probably due to borderline grains which were incorrectly sorted in some separation.

Two conclusions emerge:-

a. Two stable oxidation products are formed from all original magnetic fractions of the ilmenite. This suggests that there might be a process to allow differential magnetic separation of ilmenite from other magnetic minerals such as chromite.

b. The more magnetic fractions are oxidised at somewhat lower temperatures.

It would be interesting to check whether there is a phase change in the ilmenite crystal at elevated temperature which allows of more ready oxidation.

In view of these preliminary results it was thought desirable to investigate these changes more carefully and so that the progress of the reaction could be checked more readily by magnetic means the least magnetic fraction, N, which could

reasonably be assumed to be representative of ilmenite was chosen.

During this experiment the time of heating and the temperature were carefully noted and the mass increase was measured. No account was taken of slight dehydration losses since these appeared to be small but difficult to determine accurately.

The results are summarised in Table 2.1

TABLE 2.1 - HEAT TREATMENT OF FRACTION N

Temperature ($^{\circ}$C)	Time of Heating (mins.)	Progressive Total Mass % increase	Magnetic Activity	Remarks
778	2	0.1	-	-
800	2.5	0.4	Enhanced slightly	
822	5	1.1	Highly magnetic	slight sintering
800-820	15	1.6	Highly magnetic	slight sintering
810-820	90	2.6	Non-magnetic	slight sintered

Approximately 10% of this sample showed no appreciable change. Test showed that this residue was largely comprised of tailings.

A further check was then made using fraction L which contains no impurity as non-magnetic tailings. The results are summarised in Table 2.2.

TABLE 2.2 - BEHAVIOUR OF FRACTION L WHEN HEATED IN AIR

Temperature (°C)	Time of heating (mins.)	Progressive Total % Mass Increase	Magnetic Activity	Remarks
740-745	15	0.3	Few magnetic grains	
760	23	1.0	Most grains magnetically active	slight sintering
760	40	1.5	Highly magnetic	slight sintering
760	50	2.0	Decreased Magnetic activity	slight sintering
950	30	2.8	Non-magnetic	slight sintering

The lower temperatures were chosen here in order to give better control of the oxidation process. Rough calculation based on the increase in mass due to oxidation gives a ratio Fe^{+3}/Fe^{+2} of 1.3 in place of the unoxidised ratio approximately 0.42.

These results were not intended to be highly accurate since the inhomogeneity of the original material did no warrant it. It is also of importance to note that when total oxidation occurs the mass increase is 2.8% which does not agree well with the theoretically required increase of 3.2% (see section 3). It may be that this discrepancy is due to the loss of water but an alternative explanation could be that the estimated Fe^{+3} content is too low.

Summarising, then, we note that a rapid partial oxidation occurs between 600°C and 800°C which is accompanied by very

enhanced magnetic susceptibility. This product is fairly stable at temperatures, in air or vacuum, below 750°C. The X-ray powder pattern shows some similar and some different features from the pattern for ilmenite.

Above 850°C the oxidation proceeds rapidly to the complete stage and a new compound is formed with much lower magnetic susceptibility and a different crystal structure.

2.2 Differential Thermal Analysis

This series of experiments was performed with a view to clarifying the mechanism of formation of the oxidation products. Since oxidation suggests heat transfer, the optimum temperature for oxidation may be revealed by differential thermal analysis.

The experimental arrangement was a three junction, differential thermocouple using chromel-alumel junctions. The location of the junctions was varied but in the test from which fig. 2.3 is taken the arrangement used in fig. 2.2 was adopted. The ilmenite was contained in a nickel crucible and this crucible was placed in alundum contained in an open porcelain dish.

Considerable temperature gradients existed between the surface and embedded junctions and hence the three junctions were found necessary.
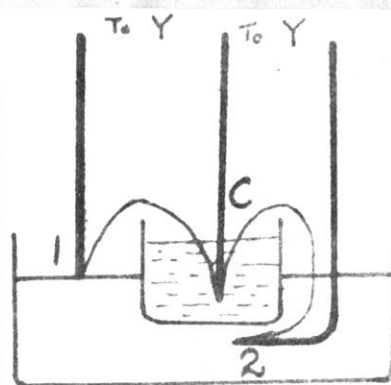

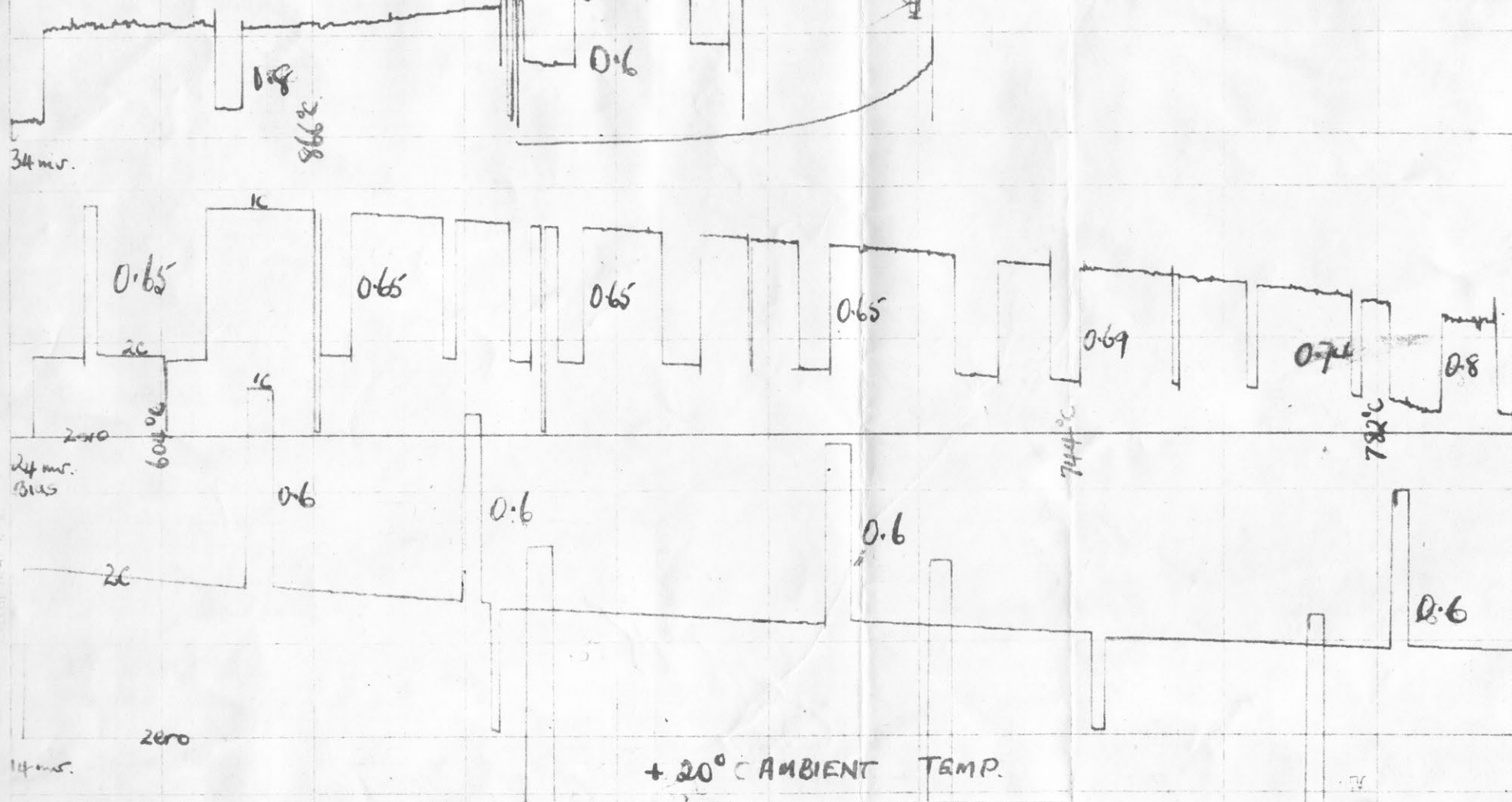FIG. 2.2 Arrangement of the differential thermocouples.

Fig. 2.3 Horizontal Axis - e.m.f. of Temperature Measuring Couple. Basis is shown on Axis. Vertical Axis. Shows partial trace for e.m.f. of Differential 1C, 2C (Fig. 2.2). The figures are the ratio e.m.f. 2C/e.m.f. 1C.

The absolute temperature was recorded by a chromel-alumel thermo-couple applied to the X drive of a Leeds and Northrup X-Y recorder with a back bias when necessary. The differential emf was applied to the Y drive of the recorder.

Heating was carried out in an electric muffle furnace which was fed from a manually operated "auto-volt" transformer. The arrangement suffered somewhat from spurious gradients but gave adequate sensitivity for this experiment.

Fig 2.3 is the reproduction of a trace obtained from one run with the above apparatus using fraction M, the rate of heating being approximately 10 deg. per minute. From the lower trace it can be seen that when the furnace is heating up the gradients gradually decrease while, however, the ratio of the emf of the junctions 1C to 2C (see fig. 2.2) remains constant up to 600°C. Above this temperature there is slight change in this ratio but although this is suggestive of slight reaction, it is not until 760°C that definite thermal activity is recorded. This activity continues until almost 900°C.

These results are in good accord with the results given above but indicate a gradual oxidation rather than a sudden transition, the apparent increased thermal flow at higher temperatures does confirm the previous conclusions that the rate of oxidation is very dependent on the temperature and the optimum temperature is from 700°C to 800°C for the formation of the partial oxidation product.

2.3 Reduction of Ilmenite by Hydrogen

The primary aim of this series of experiments was to

produce a meterial with low or zero ferric iron content since
such material should provide valuable information on both magnetic
and crystallographic properties of an ideal natural ilmenite.

Although it was shown that oxidised ilmenite could be
reduced at high temperature ($\sim$ 1200°C) when mixed with powdered
graphite it was decided to use hydrogen at lower temperatures to
give a greater degree of control. Since the higher oxides of
iron are reduced to a ferrous state at about 450°C a preliminary
trial was made at this temperature but proved inadequate. The
success of the reaction was gauged only by the magnetic suscept-
ibility determination made at room temperature by the Gouy
method after highly magnetic grains were removed.

The reduction vessel was a silica U tube heated in an
electric muffle furnace. The hydrogen was passed at a slow rate
over the ilmenite. The temperature of the sample was measured
by means of a chromel-alumel thermocouple bound to the silica
tubing with asbestos tape.

In the first case, fraction G was chosen, being one of the
more highly oxidised samples of the original ilmenite. The
results of a series of experiments can be seen most
conveniently by tabulation (see table 2.3).

In reviewing this table it should be noted that:-
a. there was always a small yield of very highly magnetic grains
    possibly due to over reduction to small fragments of iron.
    The highly magnetic grains showed a tendency to rust in
    water indicating the presence of free iron.
b. In each case the reduced grains showed a wide range of

susceptibility and magnetic separation was necessary to
yield the final material of low susceptibility denoted
by G.R.

TABLE 2.3 - <u>EFFECTS OF HEATING FRACTION G IN HYDROGEN</u>

Temperature $^\circ$C	Duration of Heating Minutes	Observations
430 $\pm$ 20	60	No bulk change. A few grains highly magnetic.
520 $\pm$ 20	60	No appreciable change, few highly magnetic grains evidence of exothermic reaction; some H_2S evolved
800 $\pm$ 20	60	Decrease in magnetic susceptibility
900 $\pm$ 20	70	Further decrease in magnetic susceptibility
900 $\pm$ 20	150	Little change in magnetic properties (G.R.)

Since it was found very difficult to produce an
appreciable yield of G.R. with a susceptibility less than that
for naturally occurring N another run was performed commencing
with N.   This sample was roasted for 50 minutes at 850 $\pm$ 30°C.
As before evidence of an exothermic reaction and the evolution of
traces of hydrogen sulphide were noted.   When the reduced
material was separated magnetically a material N.R. was obtained
having susceptibility approximately 80% of that for unheated N.

The Chemical assay shows the FeO content for N.R. as
37.5%/but the reduced material is readily reoxidised and this
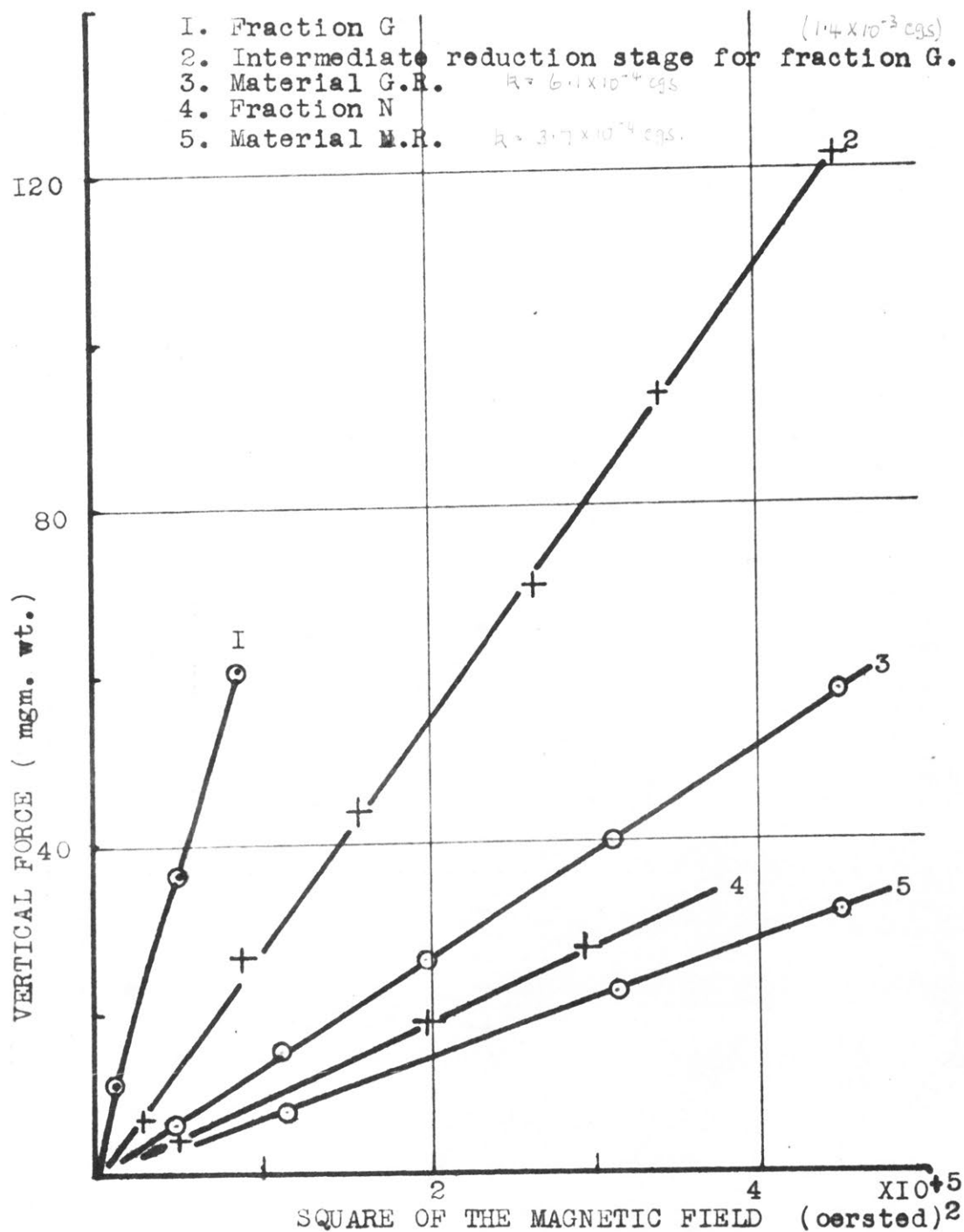(Fe^{+3}/Fe^{+2} = 0.15)
figure may be low.

FIG.2.4 Curves for reduced Ilmenite.

Fig 2.4 reproduces some curves obtained by the Gouy method for G.R. and N.R. In these graphs the force on a sample of the material is plotted against the square of the magnetic field. These curves yield values of susceptibility immediately by using the method discussed earlier. Mean values of the volume susceptibility are shown near the curves. It is interesting to note that the materials obtained by reducing G have a constant susceptibility, which may be due to the reduction of Fe^{+3} ions giving ferromagnetic interactions.

Further experiments were performed with the oxidation products obtained by heating the original ilmenite in air. In each case the materials obtained after reduction had a wide range of susceptibility similar to unheated ilmenite.

From the preceeding series of experiments three important facts emerge:-

1. The ilmenite and oxidation products of the ilmenite show a surprisingly high stability to heating in hydrogen atmosphere and very little of the materialis reduced to iron.

2. It is possible to obtain from one magnetic fraction a set of grains with widely varying volume susceptibility, the mean value for G.R. being comparable with that for naturally occurring N.

3. The X-ray powder photographs for G.R. are somewhat sharper and show clearer high angle lines than G itself. This suggests some relief of crystal strains.

In conclusion we find that heat treatment in a hydrogen atmosphere gives rise to material with a wide range of magnetic

susceptibility and presumably to an equally wide range of Fe^{+3}/Fe^{+2} ratio. Thermomagnetic observations, however, which are discussed elsewhere (section 6.1) point strongly to a fundamental difference between the reduced material and the original ilmenite. This difference is not distinguished by magnetic measurements at room temperature.

3. CHEMICAL ASSAYS

The stoichiometric composition of ilmenite is Fe Ti O_3, the iron is divalent and the titanium quadrivalent so the formula may be written $FeO.TiO_2$. One obvious source of variations in the magnetic properties of ilmenite would be a varying chemical constitution. It is also desirable, from a commercial point of view to find how the chromium occurs in the ilmenite. The results of this may suggest a differential magnetic separation.

Accordingly systematic assays were made on the magnetic fractions which had been separated from the bulk ilmenite. Representative fractions D, G, K, N which were spaced at approximately regular intervals of susceptibility were chosen. Preliminary spectrographic investigations established the presence of manganese, chromium, silicon, vanadium in addition to iron and titanium. Silicon and vanadium were present as traces only but chromium and manganese were analysed chemically. Magnesium which interferes with several of the chemical tests was shown to be present in minute amounts only and could safely be neglected.

Since the initial separation into fractions was imperfect and since for the purposes of this work, the highest precision was not deemed necessary, in most cases colorimetric methods were adopted when possible, being more rapid and simpler.

One very significant feature of the assay was the determination of the ferrous, ferric state of the iron, since experiments showed that oxidation did probably affect the magnetic properties. However this problem is difficult and it is not possible to say with certainty that such an assay will be reliable because regardless of the charge on the titanium atom in the compound it will register as Ti^{+4} in the solution with the result that in the molecule we could have Ti^{+3} which would reduce the Fe^{+3} and assay as Ti^{+4}. Extensive work has been done on the possibility of titanium changing its charge on additional ions being added to ilmenite. Pouillard (1950) investigated the solid solution of Fe_2O_3 in $FeTiO_3$ advances fairly satisfying arguments based on experiments on the reduction of TiO_2 that the titanium preserves its four charges and the substitution mechanism is

$$2Fe^{+3} \rightleftharpoons Fe^{+2} + Ti^{+4}$$
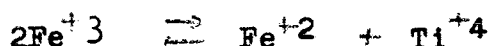
It is believed that the assay gives a relatively correct view of the ferrous, ferric state of the iron in the molecule.

3.1 Methods of Analysis

Titanium. Briggs W. (Private communication). The mineral was ground finely with an agate mortar and pestle and approximately 0.1 g of powdered material was fused with pyrosulphate, and then leached in 5% w/v sulphuric acid and made to 500ml with 5%

sulphuric acid. The coloured pertitanic complex formed in sulphuric acid solution between titantium and hydrogen peroxide was used to compare the titanium dioxide content of this unknown sample with the concentration in a standard solution prepared from rutile of known purity.

A volume of each solution containing approximately 5mg per 100 millilitres was taken, 10 ml of 3% hydrogen peroxide was added and made to 100 ml with 5% sulphuric acid. Portion of these test solutions were transferred to absorption cells in a Unicam spectrophotometer set at a wavelength of 4100Å and suitable slit width.

The colour was shown to be permanent within the sensitivity limits of the instrument after a short stabilising interval of about two minutes.

Test solutions were prepared to verify that the presence of iron did not upset the colorimetric determinations and within the accuracy of these determinations concentrations of ferric iron equal to those of the titanium had no effect.

A second possible interfering element is vanadium which was known to be present to a very minor extent, less than 1%. The colouration produced by vanadium is less intense than that for titanium and hence within the accuracy of these determinations, the error introduced could safely be ignored.

Total Iron. (Vogel p 701.) The mineral was brought into solution as for titanium and oxidised with 3% hydrogen peroxide. The solution was boiled to remove excess hydrogen peroxide and after cooling the iron was precipitated with excess

ammonium hydroxide. The filtrate was tested and shown to be
free of iron and the residue was brought into solution in 5N
hydrochloric acid. The iron content of the solution was
determined colorimetrically in the Unicam spectrophotometer
using the colour produced by excess potassium thiocyanate.
The absorption being measured at 4750Å. The test solutions
were made as follows:-

10 ml of a solution containing approximately 0.1g of
mineral per litre was added to 5 ml of 4N potassium thiocyanate
and 5 ml of 5N hydrochloric acid and made up to 100 ml. This
solution was compared with a standard solution made by oxidising
ferrous ammonium sulphate.

Fading of the colour did occur and it was necessary to
allow a standard time for the colour to develop.

Ferrous Iron. (Ref. Thornton "Titanium" p.172)
Approximately 0.2g of the unpowdered specimen was taken in a
platinum crucible and moistened with 2 ml of water. 8 ml of 1:1
sulphuric acid were added and the liquid was covered by a close
fitting crucible lid, carbon dioxide was passed into the crucible
from a fine bore tube and the liquid was brought to the boil.
At this stage the lid was moved slightly and 5 to 10 ml of 40%
hydrofluoric acid solution was added, the lid was replaced and
gentle boiling was maintained for 5 to 10 minutes. At the end
of this interval the crucible was quickly plunged into 500 ml of
recently boiled water containing 10 ml 1:1 sulphuric acid and
5g boric acid. The solution was immediately titrated with
standardised potassium permanganate and the mass of ferrous iron

present was determined.

Manganese (Haywood F.W. and Wood[A] 1944). The manganese present was estimated by the persulphate method. Approximately 0.1g of the original powdered sample was fused with pyrosulphate and taken up in 5% sulphuric acid. The titanium hydrolysed in some trials so the concentration was kept as low as possible. 3ml of phosphoric acid and 5 ml nitric acid (s.g. 1.2) were added and the solution boiled. After cooling 10 ml silver nitrate solution and 2.5 g ammonium persulphate were added and the solution was again boiled and cooled, 0.5g of urea being then added and the solution compared colorimetrically in a "Spekker" photoelectric colorimeter against a standard manganese solution (MW 223.06) taken through the same oxidation procedure. The absorption band used in this work was defined by a heat filter and filter number 604.

Chromium (Vogel p.709) The crushed mineral was brought into solution by fusion by a mixture of sodium peroxide and potassium nitrate in an iron crucible. When the fusion had cooled approximately 100ml of water was added very carefully to wash the fusion vessel. The resultant solution and precipitate was boiled for 30 minutes to drive off the oxygen and the volume was then made up to 200ml. The filtrate contained chromium which had been oxidised to the chromate.

A suitable aliquot of the chromate solution was measured into a 50 ml flask this solution was made 0.2N with sulphuric acid, 20 ml diphenylcarbazide solution (1.0 g. in 100 ml. alcohol) was added and the solution finally made to 50 ml. The colour was

compared after a standard time interval with the colour of a standard chromate solution in a colorimeter using filter 624.

The standard chromate solution was made by dissolving 0.2555 g of potassium chromate and 0.100 g sodium carbonate in 1 litre of distilled water.

Vanadium, Silica,present as traces only and were not suspected of affecting the magnetic properties.

3.2 Results

The results of these chemical assays are summarised in Table 3.1. Several interesting factors emerge from this analysis.

a. The chromium distribution is very dependent on the magnetic properties of the samples, being principally confined to the most magnetic fraction and the lowest magnetic fraction. The latter fraction contains approximately 80% of the total chromium present.

b. The most significant variation in chemical properties that may correlate with variation of magnetic properties is the ratio of the Fe^{+3}/Fe^{+2} ions.

TABLE 3.1   -   <u>THE CHEMICAL COMPOSITION OF THE MAGNETIC</u>

<u>FRACTIONS.   THE COMPOSITION IS EXPRESSED</u>

<u>AS A MASS % OF THE SAMPLE</u>

Fraction	A	D	G	K	N	O	Stoichiometric
TiO_2		46.9	49.7	51.8	50.1		52.6
Fe_2O_3	Total Fe −45%	20.6	17.8	15.0	13.8	Total Fe 22%	0
FeO		29.1	31.2	31.8	31.6		47.4
MnO		2.2	2.3	2.6	1.6		
Cr_2O_3	1	0.36	0.09	0.09	0.24	13.0	
Total %		99.2	101.1	101.3	97.3		100

TABLE 3.2   -   <u>THE RATIO OF FERRIC TO FERROUS IRON</u>

Fraction	D	G	K	N
Fe^{+3}/Fe^{+2}	0.64	0.51	0.44	0.39

     To confirm these results of the chromium distribution and
to test the practical possibility of readily obtaining a low
chromium ilmenite two samples were taken one from Swansea and
one from Stradbroke Island. Each of these samples was split
into three fractions by the magnetic separator. The results
are tabulated, but these should be regarded as very approximate.

TABLE 3.3 - <u>THE PRACTICAL SEPARATION OF A CHROME FREE</u>

<u>SAMPLE OF ILMENITE</u>

	FRACTION		
	Highly Magnetic	Middling	Low Magnetic
National Minerals Mass % Cr_2O_3	0.26	0.09	6.0
Mass of Fraction as % of Sample	20	70	10
Stradbroke Is Cr_2O_3	0.37	0.16	6.0
Mass of Fraction as % of Sample	10	70	20

3.3 Precision of Results

The accuracy of the above results was not high but there were several unknown factors in these determinations and it was not considered necessary to attempt a more precise assay. Following is table 3.4 which gives the percentage probable error of the estimation of the ions in solution. These errors were arrived at by comparing the results of several independent determinations and applying Student t-test.

TABLE 3.4 - <u>PERCENTAGE PROBABLE ERRORS OF THE ANALYSES</u>

Element	Titanium	Total Iron	Ferrous Iron	Ferric Iron	Manganese	Chromium
P.P.E.	0.6	0.4	1.0	1.5	4.0	4.0

Sources of Error

The following considerations must be taken in conjunction with the above estimate of the errors of the determination of the ions in solution.

a.   It is a well-known fact (Hillebrand and Lundell P.907) that prolonged grinding of many minerals results in partial oxidation of the components and in this case such grinding was necessary to ensure complete fusion.   A check was made in this case and it appears that the oxidation is not very great. Certainly less than 5% of the ~~original~~ ferrous iron originally present is oxidised by grinding.

b.   Oxidation of the ferrous iron by an unknown amount will have occurred during the sulphuric acid, hydrofluoric acid digestion.   Several determinations indicated that this amount of oxidation was at least consistent.

4 - DETAILED STUDY OF MAGNETIC PROPERTIES OF ILMENITE

4.1 Magnetisation Curves

Since the magnetic fractions K to D show noticeable field dependence for susceptibility, it was necessary to investigate the magnetisation curves by a different method.   The high value of saturation field and the low effective permeability preclude the use of the usual toroidal solenoid technique.

The method adopted was to use a sample of material as the core of one of two otherwise matched coils connected in series opposition.   Under these circumstances the deflection obtained on a fluxmeter can be directly related to the intensity

of magnetisation for the sample. The magnetising field was provided by a small electromagnet but the pole gap had to be large and the field varied by no more than 5% along the length of the specimen. The sample was tamped into the coil which was wound on a thin walled glass former with inside diameter of (0.31 $\pm$ 0.01) in and carried approximately 1500 turns. The turns area for each coil was determined by direct comparison with a standard coil using a fluxmeter. Initially the two coils were slightly unmatched but matching was achieved by shunting the coil of slightly higher inductance with a fixed resistance.

The circuit used in these determinations was the conventional circuit (fig.4.1) where G was a Cambridge ballistic galvanometer S a 30 ohm shunt, M a standard 10 millihenry inductor, A an Avo ammeter, R and P variable resistors and C the special search coils one of which is shunted with X, a resistor, adjusted to a value of 850 ohms.

The magnetising field was determined in each case by means of a calibrated search coil and fluxmeter with a standard certificate showing $\pm$ 2% accuracy.

The procedure was to place the two coils rigidly in the air gap with the axis of the coil parallel to the magnetic field. The deflection of the galvanometer was recorded when the magnetising field was reversed. The method gave quite reproducible results and the shape of the curve is reliable; however the absolute accuracy of the intensity of magnetisation is not high and the percentage probable error is approximately 10% as determined by repeated observations and there are

considerable systematic errors
due to non-uniformity of the
magnetising field.

It was not possible to
correct for the presence of
air gaps between the grains and
it was impossible to consolidat
the material.   Pressures up to
10,000 pounds/sq.in. did not
appreciably improve the porous
nature of the material and
negligible bonding occurred.
Slugs bonded with gum
tragacanth were used in some
cases without altering the
results.

FIG. 4.I Circuit used in
determing the magnetisation
curves.

The observed deflection
when the field was reversed was
readily related to the intensity of
magnetisation 1.   In this case, when the appropriate constants
were inserted the relationship was:-

$$I = 2.9 \, \Theta \qquad \ldots \ldots \ldots \ldots 4.1$$

Θ being the scale deflection in centimetres at a fixed scale
distance and I the intensity of magnetisation.

The results are recorded graphically in fig. 4.2.   The
values of specimen K are less reliable since the throws had to be
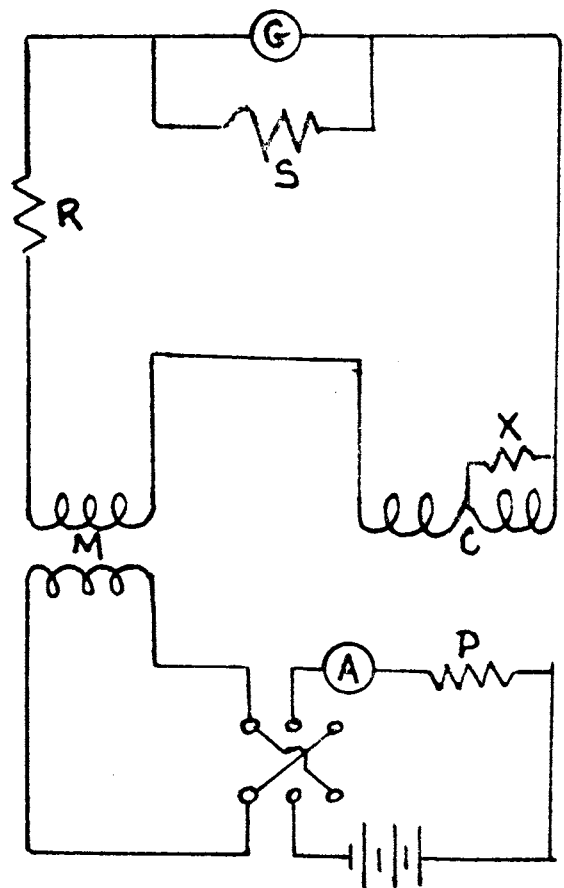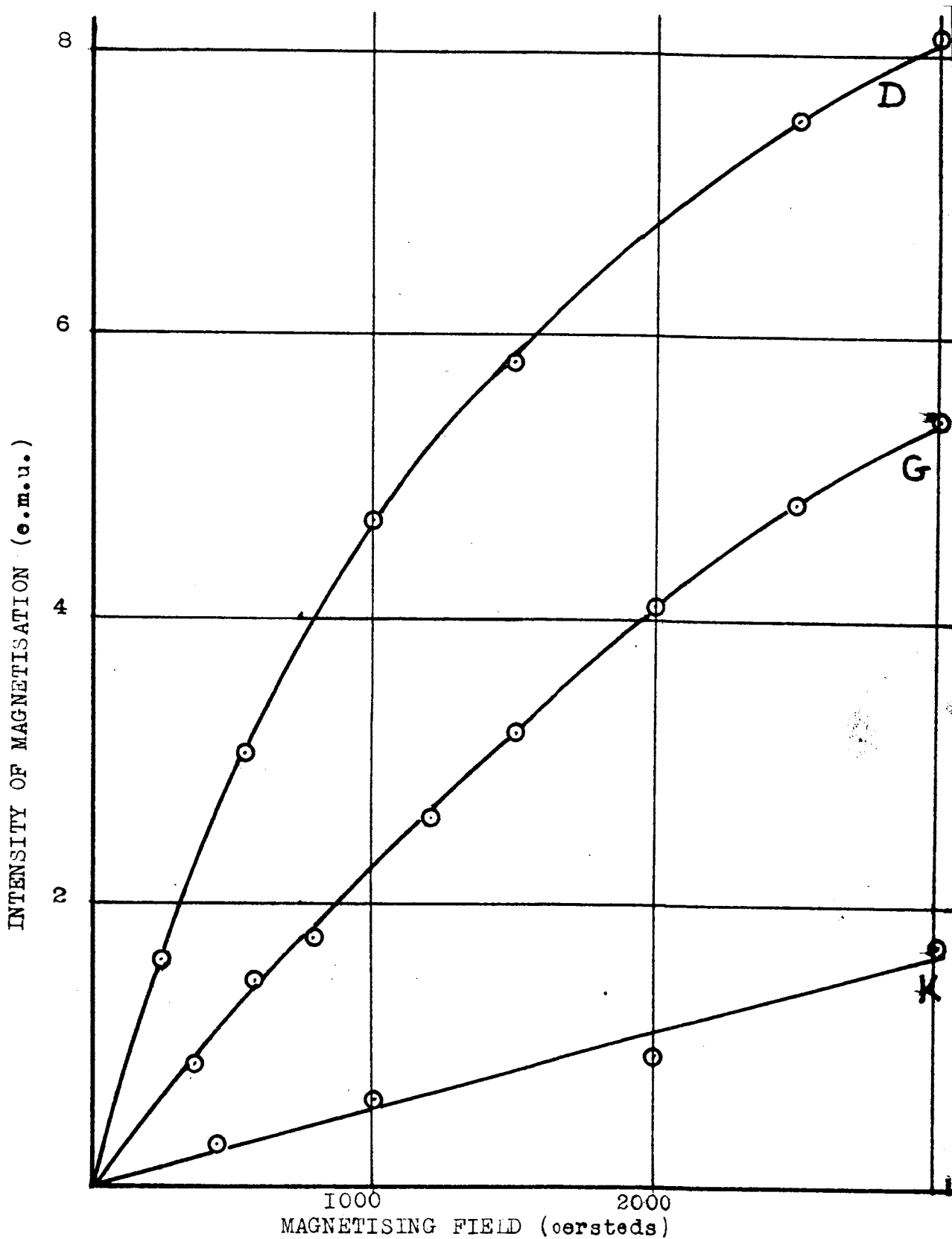corrected by 50 per cent, however the method is quite applicable

FIG. 4.2   Magnetisation curves for fractions D,G,and K.

to fractions more magnetic than K and could be refined by using
a more homogeneous magnetic field.   Cylindrical slugs can be
used here since the magnetic moment per unit volume is very
small and consequently the mean demagnetisation field probably
is negligible compared with the unknown demagnetisation field
of individual grains.

From the slopes of the magnetisation curves it is
possible to obtain an estimate of the effective initial
susceptibility.   These results are listed in Table 4.1.

TABLE 4.1 - INITIAL SUSCEPTIBILITY

Fraction	D	G	K
Initial susceptibility (e.m.u.)	7.3×10^{-3}	2.4×10^{-3}	5.7×10^{-4}

It is noted that the results in table 4.1 compare quite
favourably with the results from the Gouy Method when it is
recalled that here no packing correction has been made.   From
the curves it is seen that the saturation magnetic field, is
very high.   This is at least partly due to the air gaps and
even for fraction D is well in excess of 5,000 oersteds.

Further experiments were performed to obtain a hysteresis
loop and hence an estimate of the coercive force.

The procedure adopted in this experiment was to replace
the variable resistor P (fig.4.1) by a set of three rheostats
individually fitted with shorting switches.   In this circuit
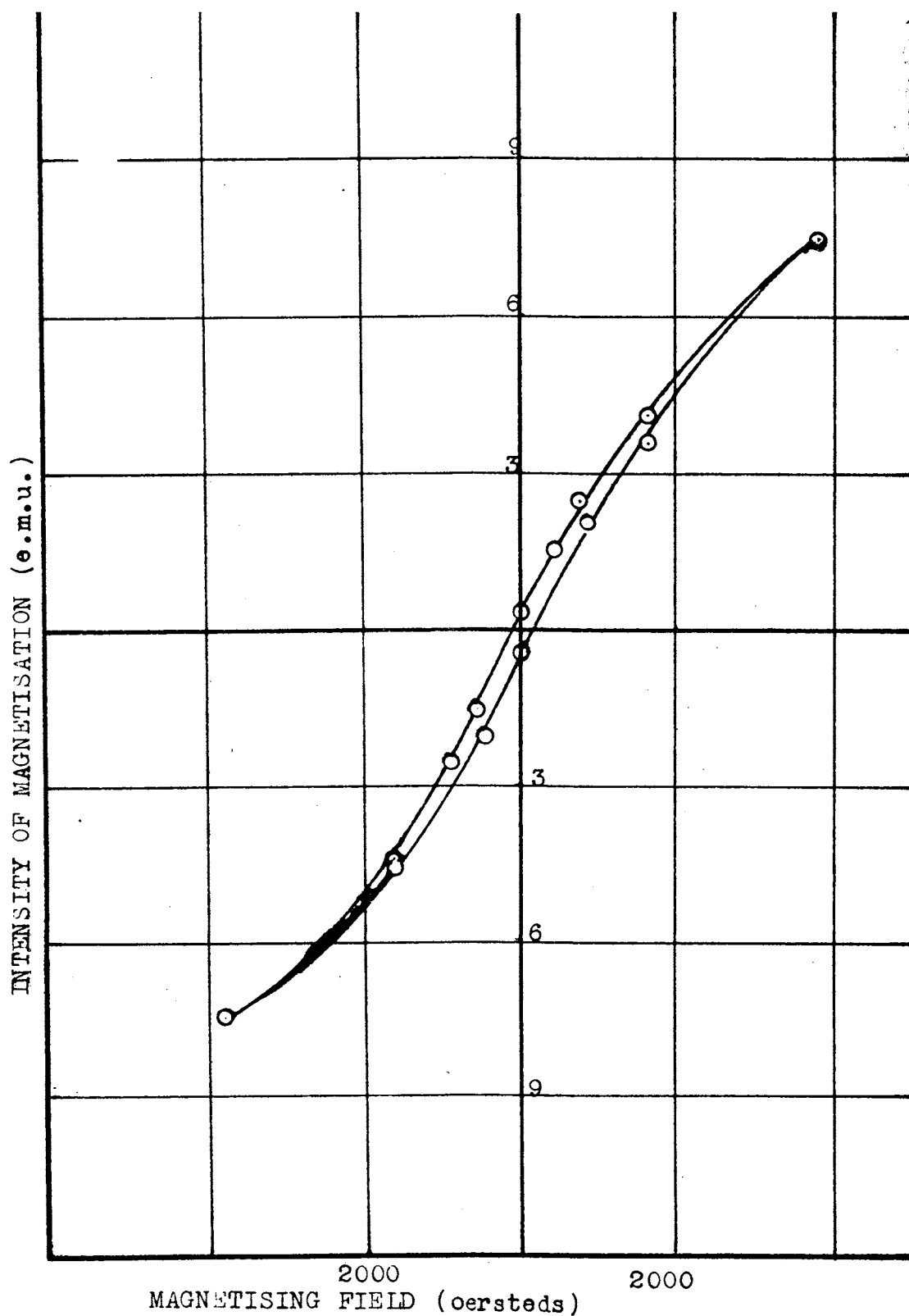it was then possible to vary the electromagnet current and hence

FIG. 4.3 Approximate hysteresis loop for G.

obtain the deflection due to the change in magnetisation for the sample in the coil. In this way sixteen points on the loop were obtained. However, the technique was inadequate for these fractions since the method of varying the magnetic field was subject to uncertainties and also the saturation field could not be attained. However the results obtained for fraction G are given in fig. 4.3 but it must be emphasised that at best only the order of magnitude of the coercive force can be inferred.

From fig. 4.3 it can be seen that the coercive force for sample G is quite low being of the order of 100 oersteds while the remanent magnetic intensity is of the order of 0.3 e.m.u. The relatively low value for the coercive force for ilmenite has been suggested (Report of Investigations 3223 American Bureau of Mines) as the reason for the small activity of ilmenite on the A.C. type of magnetic separator.

4.2 Thermomagnetic Studies

The Ring Balance

The ring balance is a convenient apparatus for use in high temperature magnetic investigations. It was first designed by Sucksmith. The chief attraction of the ring balance is its compact size and the ease with which it can be totally enclosed in an evacuated chamber. Since it measures the force on a sample placed in a nonuniform magnetic field it is not well suited to the investigations of ferromagnetic materials except for measurements in saturation fields.

In this case, the design used was a slight variation of that described by van Oort, (1951) and the following is a brief statement of the experimental arrangement.
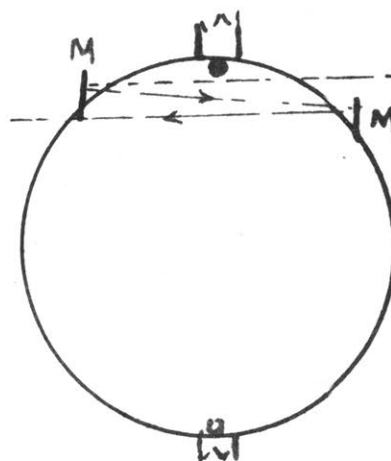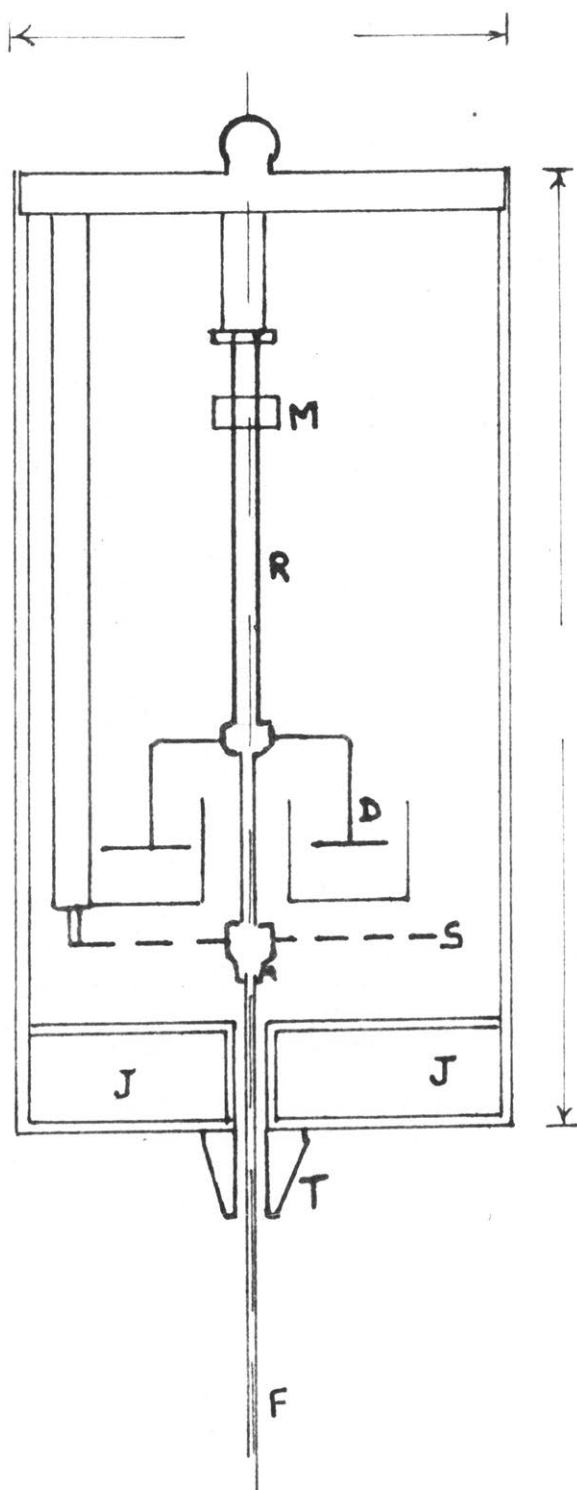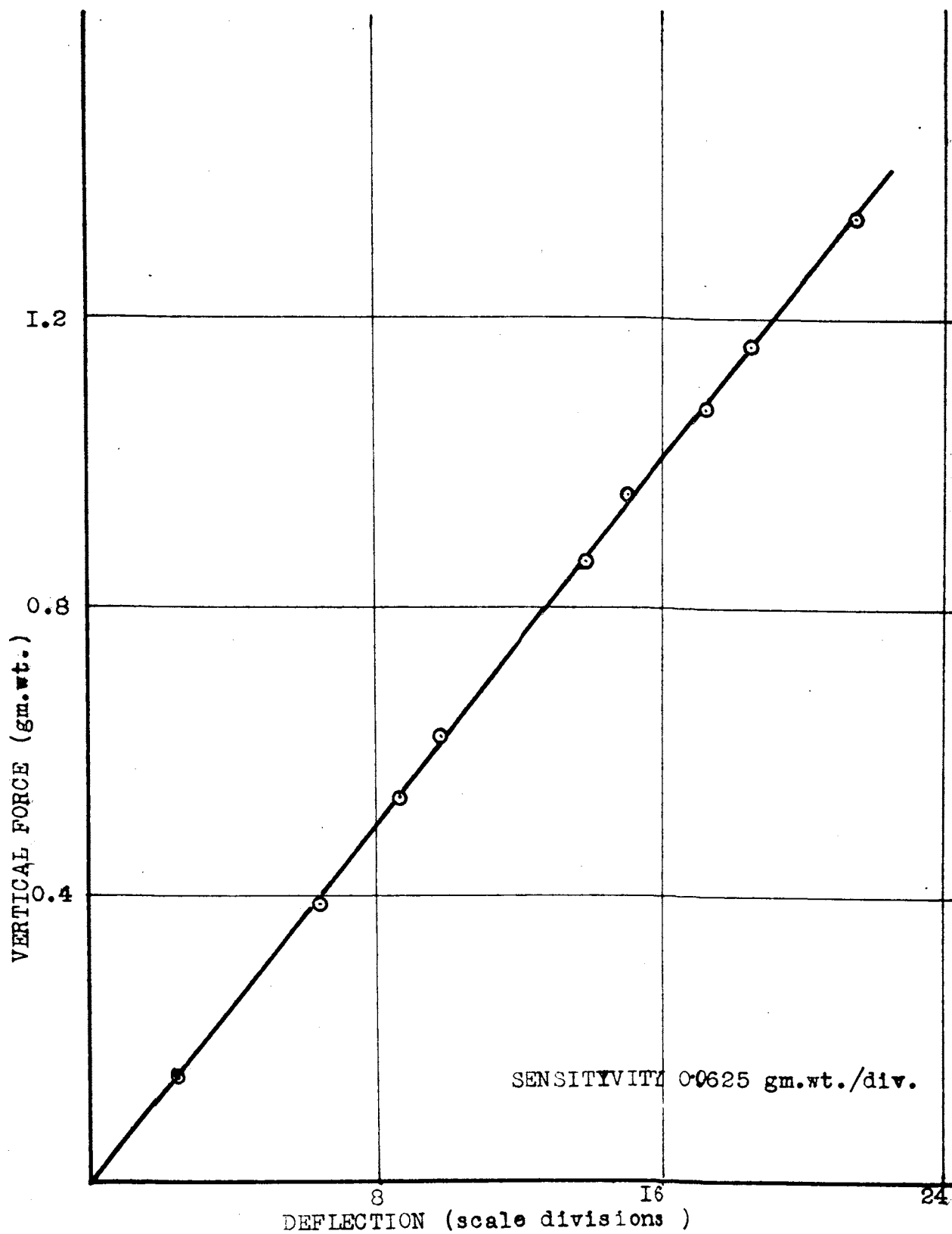
FIG. 4.4   Diagram of the Ring Balance.

FIG. 4.5   Calibration curve for the Ring Balance.

The principle of the ring balance is to use the distortion of a phosphor bronze ring to measure the displacement of a sample container. This distortion is linearly related to the displacement and hence to the applied force and is magnified by an optical lever device consisting of two critically located mirrors clamped to the ring.

Fig. 4.4 is a sketch of the apparatus, most dimensions are not critical but in this case the ring is approximately three inches in diameter formed from phosphor bronze strip 0.005 in. thick which is approximately one eighth of an inch wide. The jacket is vacuum tight and provided with two windows. The jacket is also provided with a cooling chamber through which water is circulated.

M represents the approximate position of the mirrors, R is the ring to which is attached the damping ring D which moves in "apiezon B" oil. S is a flat spiral spring to minimise lateral movement of the quartz suspension F. J is the cooling jacket which thermally isolates the ring from the heated sample below. T is a tapered plug which allows the connection of a furnace or cryostat.

In figure 4.5 is given a calibration curve of deflection against load for the present arrangement. The sensitivity was adjusted to be suitable for this problem but for weakly paramagnetic materials further refinements would be necessary. For example the spring S could be detached from the duralumin attachment for the suspension.

Various methods were tried to detect the distortion of the ring and a very satisfactory method is adopted in which

a microscope giving an overall magnification of approximately
ten times is mounted so that the objective lens is near one
window and the beam of light is reflected from both mirrors on
the ring and then received on the eyepiece.   The objective is
focussed on an engraved graticule carrying very fine graduations.
A similar graticule is situated in the eyepiece.   The system
could be refined by using a micrometer eyepiece, however the
above arrangement has proved compact and of convenient
sensitivity.

The furnace is enclosed in a clear silica tube of outside
diameter 16.5 mm which is flanged so that it fits the taper T
in fig. 4.4.   The furnace is wound noninductively on a second
clear silica tube, the windings being held in place by a heat
resistant cement.   The lower end of the quartz tube is cemented
to a pyrex bulb using "Araldite" cement and waxed to ensure
that the join is vacuum tight.   The general form of the furnace
is shown in fig. 4.6.

In diagram fig. 4.6, O is the outer silica sheath I the
inner silica core.   F represents the furnace which is wound
from 28 gauge platinum wire.   P is the "pyrex" base into which
the tungsten leads of the furnace windings are sealed.   These
tungsten leads H were made sufficiently robust to hold the
furnace in place with the support from a tube projecting from
the base of the bulb.   T.C. represents the thermocouple which
is made of matched chromel-alumel wires.   The thermocouple leads
pass down the central tube and are waxed into the pyrex base with
the junction close to the sample.   A radiation shield

surrounding the furnace is necessary,
brass shim can be used but the ideal
shield would be platinum foil   An imput
of 200 watts gives a temperature of
approximately 900°C and for small changes
in power the equilibrium temperature is
reached in less than 15 minutes.

T   The magnet used in this series
of experiments is a simple electromagnet
(see fig. 1.1) except that the poles are
cylindrical with bevelled inner faces
(fig. 1.2).   These two poles are set
so that the pole faces are inclined at an
angle of 40 degrees to one another.   The
winding resistance is approximately
25 ohms and it is desirable to cool the
magnet.   This arrangement gives a value
of dH^2/dz in the vertical direction of
up to $(1.2 \pm 0.1) \times 10^7$ oersteds^2 cm^{-1}.

In general the design is quite
satisfactory but there are two factors
that should be recorded.   Firstly the
sensitivity which is suitable for most
of the investigation does not allow of
a high accuracy for paramagnetic materials.
This sensitivity could be achieved by
using a finger ring and by detaching the
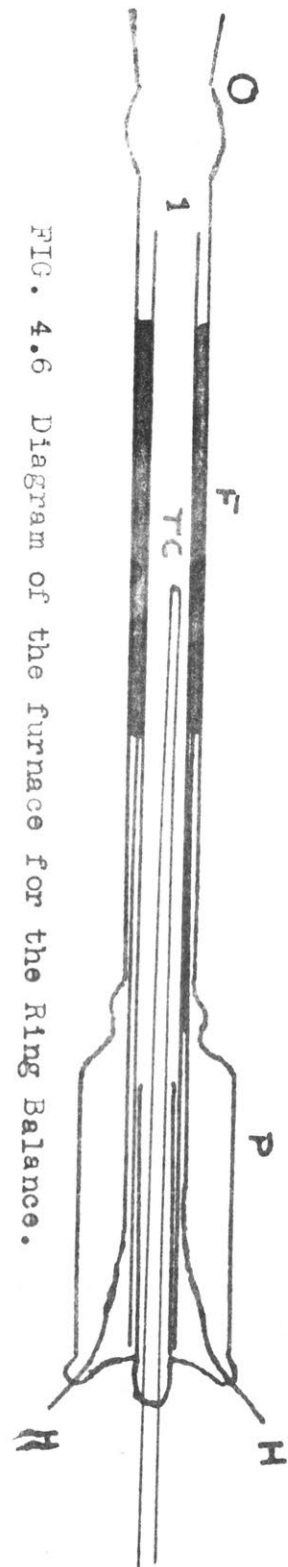connection to the spiral spring but

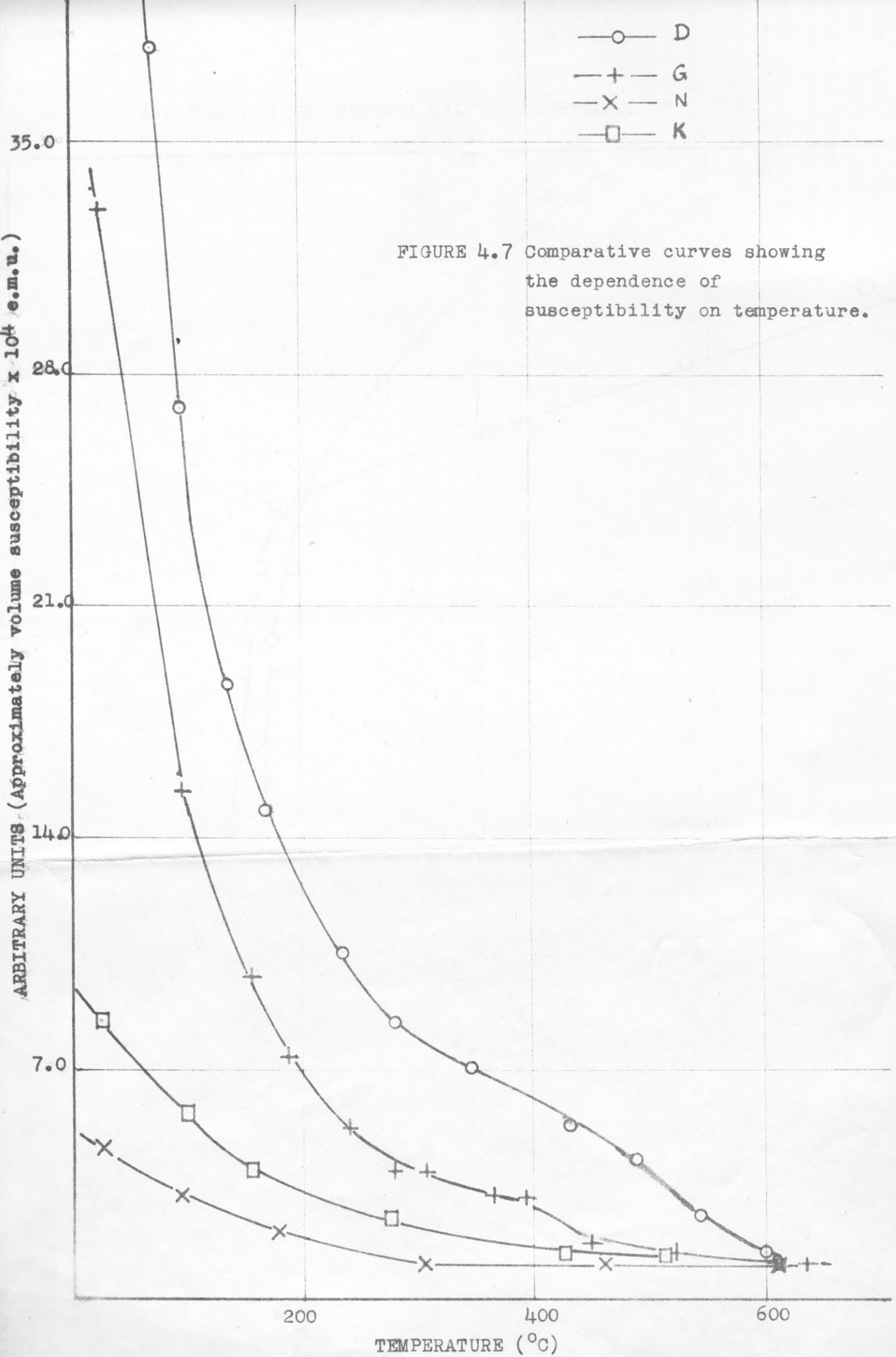FIG. 4.6 Diagram of the furnace for the Ring Balance.

could not be done until this work was completed. Secondly
the zero tends to drift slightly (discontinuously). This
drift has been of no consequence in the observations taken
to date but frequent checks have to be made. All results
have been quite reproducible to a few percent when repeat
readings have been taken.

Results

The variation of magnetic susceptibility with temperature
was a useful guide in interpreting the magnetic properties of
the different magnetic fractions, especially in identifying
possible ferromagnetic contaminations, inclusions or phases
which may be too minute to be visible under the microscope or
detectable by X-ray methods or chemical assay.

Measurements were made using the ring balance described
above and several sets of curves have been obtained.
Unfortunately it is impossible to make any allowance for field
dependence of susceptibility in these measurements however,
the experiments are only required to show the form of the
susceptibility-temperature relation, and it has been possible
to get reproducible relative curves without carrying through
the elaborate corrections necessary to arrive at a reliable
estimate of the susceptibility of the ilmenite in bulk.

A small sample, approximately 0.5 gm. of the material
was placed in a cylindrical copper crucible and suspended from
the ring balance. The deflection of the balance was
linearly related to the force on the ring over the range of
forces used. Observations were made using magnetic fractions
D, G, K and N. The results of these measurements are given in

FIGURE 4.7 Comparative curves showing the dependence of susceptibility on temperature.

FIG. 4.8 Details of the susceptibility v. temperature curves for D and N (ordinate scale is approximately I unit = 5×10^5 e.m.u.). The discrepancy between the curves above 600 °C is not significant.
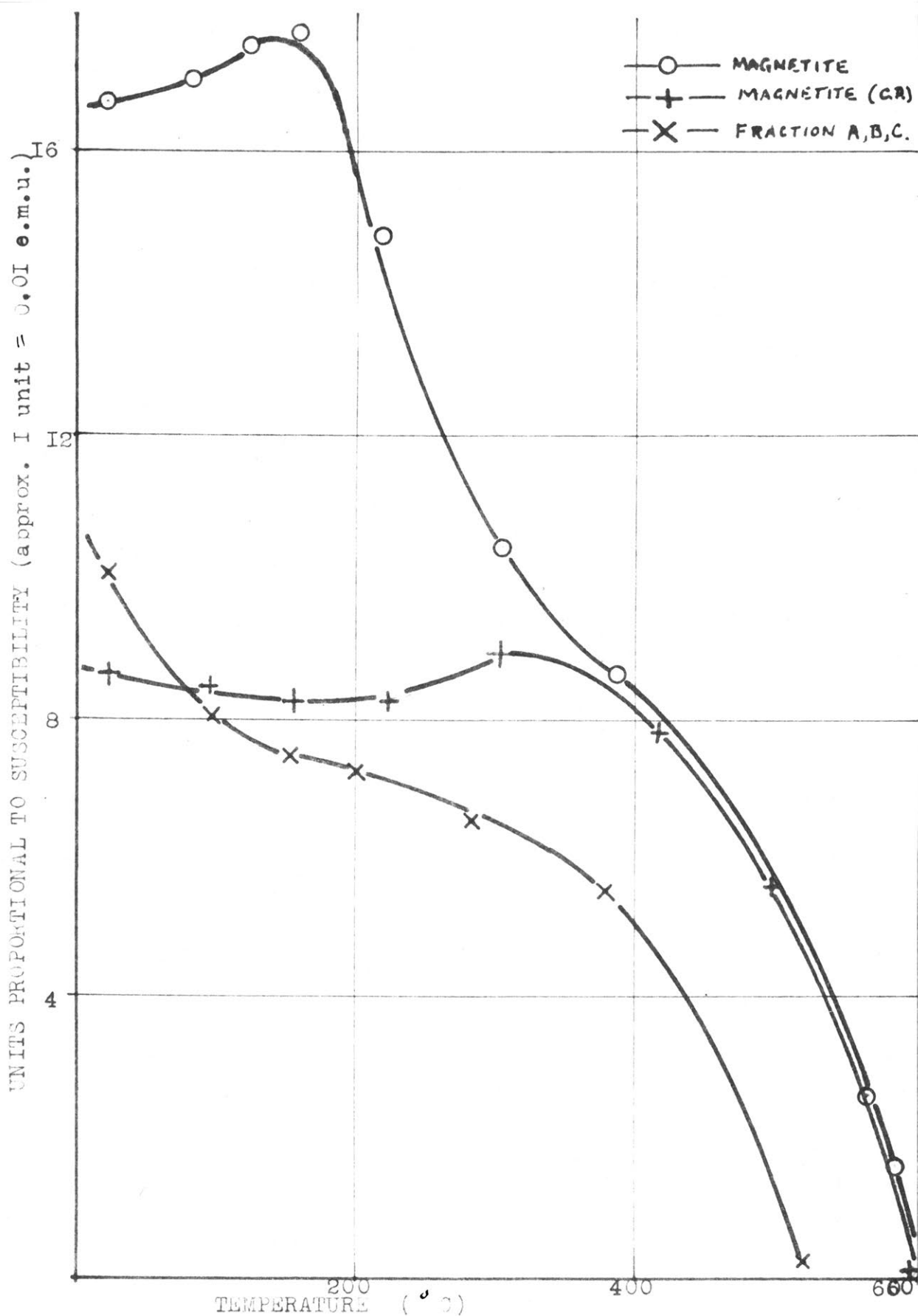
FIG. 4.9 Comparative curves for magnetite and fraction
A B C (magnetic field approx. 1000 oersteds)

Fig. 4.10. Comparative curves
showing the effect of
adding free magnetite
and "magnetic ilmenite".
(Ordinate scale approx.
1 division = 10^{-4} e.m.u.)

ARBITRARY UNITS PROPORTIONAL TO SUSCEPTIBILITY

TEMPERATURE °C.

—O— FRACTION K

—X— FRACTION N

—+— FRACTION N +10% by Mass

NX2 + 1% by Mass of

MAGNETITE.
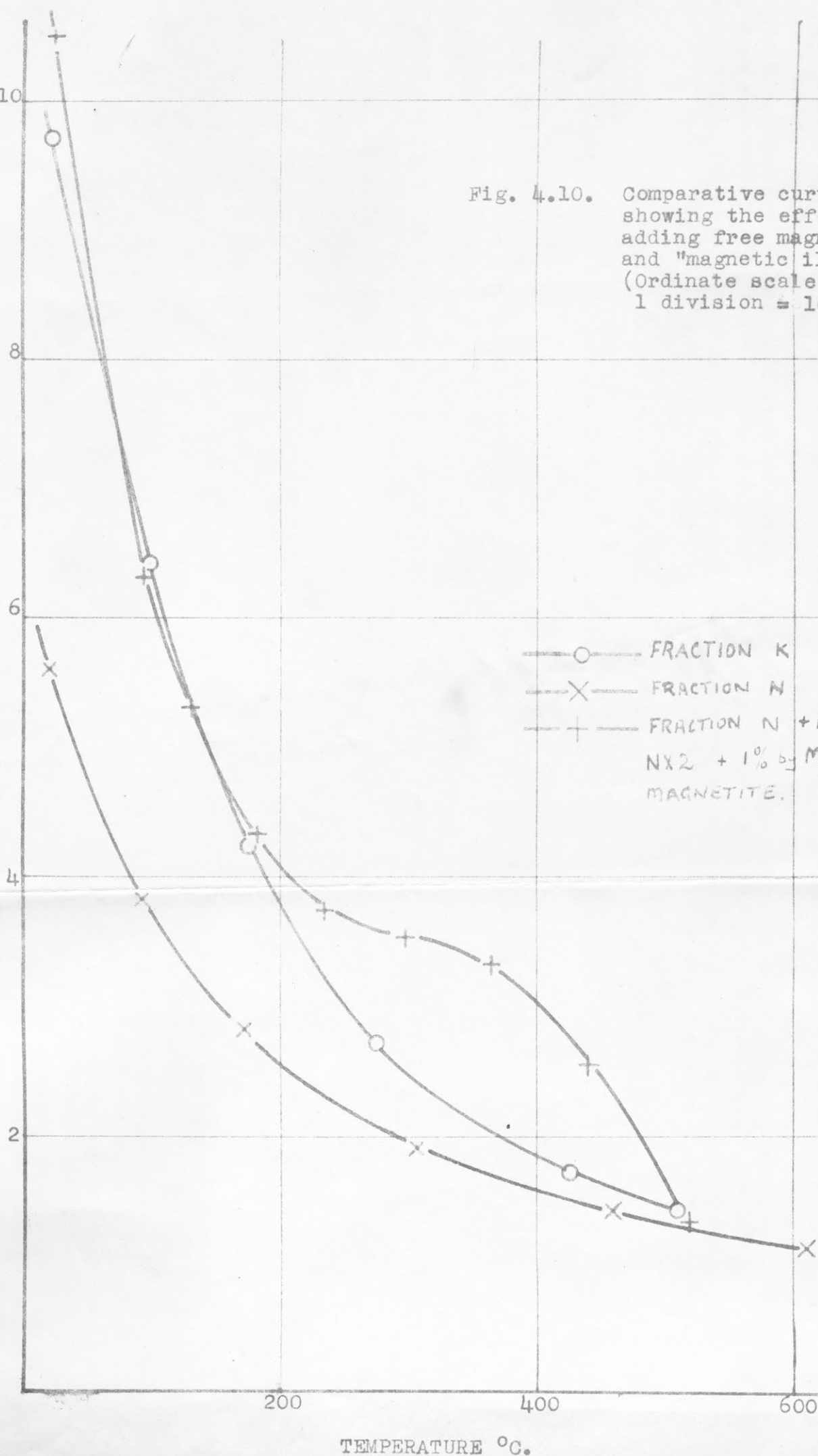
graphical form in figs. 4.7, 4.8, while 4.9 gives comparative curves for a sample of magnetite and a sample of A, B, C combined in the original proportions. In one case the sample was sealed in an evacuated silica capsule but no significant difference was noted between this experiment and the others performed with an open crucible. In all cases the pressure of air in the system has been low, generally less than a few tenths of a millimetre of mercury.

The fields chosen in this work are lower than that considered necessary to ensure complete saturation of the samples, but to attain such fields a magnet with cooling would be necessary. However, since comparative data only are required this is not considered to lead to seriously ambiguous results.

All the curves discussed in this section are obtained as heating curves but it is invariably the case that the cooling curve is not coincident with the heating curve. This factor is probably due to oxidation and to the effects due to cooling the sample in a strong magnetic field. The initial heating curves fig. 4.7 are obtained by plotting the ring balance deflection, which is proportional to the susceptibility, against the temperature.

The first point of interest is that the curves show that all samples behave similarly with possibly slight variation in the apparent Curie temperature. It is strong evidence for the assumption that all fractions are very closely related.

Secondly, the curves show that at approximately 600°C all the samples have the same magnetic susceptibility being $(1.1 \pm 0.3) \times 10^{-4}$ e.m.u. This suggests that basically all

fractions have the same magnetic lattice which gives a para-magnetic mass susceptibility of 24 x 10^{-6} e.m.u./gm. at 600°C.

Thirdly, it is seen that in all fractions the susceptibility varies rapidly at room temperature suggesting that supplementary measurements below room temperature would be useful. The Curie temperature for all samples is estimated to be between 150° to 200°C.

Fourthly, the curves in fig. 4.9 suggest that the main magnetic carrier is not free magnetite which has an accepted Curie temperature at 575°C [X] and a temperature-susceptibility curve which is quite different to that encountered in the ilmenite. However it is evident that sample A B C, shows considerable proportion of magnetite as well as another material having a steeply sloping susceptibility temperature relation between 0°C and 100°C. In addition it is almost certain that the somewhat larger susceptibility of D at high temperature see fig 4.7 is due to the presence of free magnetite in small quantities.

It appears safe to assert that the principal variation of the magnetic properties of fractions N to D is not due to submicroscopical inclusions of free magnetite. Three possible causes remain and this method cannot give further information about the relative merits of the three.

a. Pouillard (1950) claims to have synthesised materials of a spinel type which may be regarded as solid solutions between magnetite and iron titanium oxide (Fe_2TiO_4). These substances form unlimited solid solutions and the Curie

[X] It is of course well known that the magnetite minerals may have Curie temperatures much less than this value (Nature, 1954, Pouillard, 1950)

temperature falls from 575°C for magnetite to below room temperature as the proportion of iron-titanium spinel (ulvo-spinel) is increased. A conceiv^ble mechanism is that such a solid solution exists as a second phase with the ilmenite. It should however be possible to identify the phase by X-ray method but there is no evidence for this even in fraction D.

b. The second phase is present similar to that which is obtained by oxidising the ilmenite ("magnetic ilmenite") the properties of which are discussed in detail in Chapter II.

c. There are two sublattices in the ilmenite and it is possible for interactions between the atoms in these sublattices as occur in "ferrites" (Neel, 1948).

Returning now to the detailed experimental curves (fig. 4.8) which are obtained for samples D and K using higher temperatures and greater fields, it is seen that at above 600°C the two curves are very similar; however the measurements are not sufficiently accurate to allow of the determination of the laws of paramagnetism for these samples and accurate inter-comparison of the susceptibility of each sample at high temperature.

In conclusion, it is possible to eliminate free magnetite as an important source of the ferromagnetism of the samples but for the remainder it is only possible to suggest several possible mechanisms.

From the point of view of practical separation of the ilmenite from impurities, it is seen that at elevated temperatures the ratio of the volume susceptibility of different components

is no greater than the corresponding ratio at room temperature
and hence no advantage is to be had from separation at
elevated temperatures.

CHAPTER II

5. ## THE FIRST OXIDATION PRODUCT

As discussed earlier in Section 3, when any of the
magnetic fractions of the natural ilmenite are heated in air
at temperatures in excess of 650°C, a rapid oxidation occurs
during which the Fe^{+3}/Fe^{+2} ratio changes to approximately 1.3.
The rapidity of this oxidation depends on the temperature
and on the magnetic fraction which is heated. To obtain a
large yield of this oxidised form of the ilmenite it is found
necessary to work at 750 $\pm$ 50°C and to continue the roasting
for from 10 minutes to half an hour. Although the product
formed by this treatment appears to be stable, prolonged roasting
for intervals of several hours causes the FeO content of the
material to drop still lower. Also roasting in air at
temperatures above 850°C results in the rapid formation of
the second oxidation product which has less than 2% FeO by mass.

The first oxidation product which may be referred to
as "magnetic ilmenite" has very similar properties when produced
from different magnetic fractions of the original ilmenite,
consequently only two materials were studied in detail GX2, NX2,
that is the highly magnetic modification of ilmenite derived
by heat treatment of G fraction and N fraction respectively. As
the name suggests, it is found on cooling to room temperature
that the first oxidation product has greatly enhanced

magnetic properties (activity).

From an examination of the magnetic properties of fraction A, B and C it can be concluded that portion of the highly magnetic rejects consist of impure forms of "magnetic ilmenite".

5.1 X-ray Investigations

X-ray powder photographs were taken of both NX2 and GX2 and a chart was taken by the Geiger Counter X-ray Spectrometer, in all cases great difficulty was experienced in resolving any high angle lines and consequently highly accurate measurements were impossible. The resulting interplanar spacings are given in Table 5.1

The X-ray pattern may be resolved into two patterns. A weak set of lines which matches closely the published information for rutile and the remaining interplanar spacings are not significantly different from those of the fraction of the ilmenite from which the magnetic material was prepared. In GX2 the line corresponding to d = 1.621 comes up strongly as in the case given by Barth and Posnjak. This is not so in any other film, as this line is usually absent appearing only in films of N and then at low intensity.

5.2 Mineragraphic Studies

In bulk the grains appear grey and much duller than the unheated grains but they form small aggregates of crumbs during the heating and partial sintering is a guide to the completion of the reaction. This sintering appears to occur at the temperatures at which rapid oxidation takes place and may be indicative of an increased atomic or ionic mobility and

TABLE 5.1 - INTERPLANAR SPACINGS FOR NX2 AND GX2

d values in Angstrom Units

Rutile	G	GX2	N	NX2 [film heavily fogged]
	3.684 (4)	3.690 (4)	3.697 (4)	3.76 (3)
				3.56 (2)
3.24 (10)		3.236 (3)		3.27 (3)
	2.720 (10)	2.721 (10)	2.728 (10)	2.75 (10)
	2.521 (7)	2.530 (7)	2.525 (8)	2.56 (9)
2.49 (7)		2.478 (1)		2.52 (2)
	2.211 (4)	2.221 (3)	2.223 (3)	2.25 (2)
2.19 (4)		2.181 (3)		2.21 (1)
	1.857 (5)	1.856 (6)	1.857 (5)	1.87 (6)
	1.715 (8)	1.712 (6)	1.715 (8)	1.73 (6)
1.682 (10)		1.684 (6)		1.71 (4)
		1.621 (5)	1.624 (1)	
	1.499 (5)	1.499 (5)	1.500 (5)	1.506 (4)
	1.462 (6)	1.461 (6)	1.465 (5)	1.468 (4)
1.357 (8)		1.357 (1)		
	1.333 (2)	1.330 (1)	1.337 (2)	
	1.267 (2)	1.268 (1)		
	1.205	1.198 (1)	1.198 (1)	1.205 (1)
	1.184 (2)	1.180 (1)		
	1.148 (2)	1.151 (2)	1.152 (1)	1.157 (1)
1.141 (4)		1.134 (1)		1.135 (1)
	1.113 (2)	1.115 (2)	1.115 (2)	
1.103 (2)		1.100 (1)		
1.095 (4)		1.083 (1)		
1.077 (5)	1.070 (2)	1.069 (2)	1.074 (2)	
	1.000 (nor)	1.005 (1)		
	0.973 (2)	0.974 (2)	0.970 (1)	0.968
	0.965 (1)	0.960 (1)	0.960 (1)	0.959

Film heavily fogged.

(nor) Appears in Norwegian ilmenite but not in G

diffusion occurs where mechanical contact takes place between the grains.

Under reflected light, at a magnification of approximately 100 times, the grains show the same subspherical form, metallic lustre but appear to have a more pitted surface. The inclusions of decomposition mineral are converted from a

yellowish or brick red to an orange colour. The increased pittedness of the surface accounts for the duller macroscopic appearance.

In section, under reflected light, the grains of GX2 are very similar to the grains of G and using polarised light it is not possible to distinguish between G and GX2 grains. *for magnification to 200 diameters.* Both show anisotropy but it is not possible to distinguish any difference in degree of anisotropy. (Private communication with Mr. R.L. Stanton, Department of Geology, Sydney University, who is an experienced mineragrapher confirms this opinion).

5.3 Chemical Assay

The chemical assay of these products is not of interest except as a guide to the state of oxidation of the iron in the compound. An apparent Fe^{+3}/Fe^{+2} ratio may be obtained but there is no way in which the valency of the titanium can be checked. However since the crystal structure (see Table 5.1) is very similar to that for the unheated ilmenite it is reasonable to assume that the valency of the titanium is unaffected by heat treatment. On this assumption the chemical composition of the two compounds GX2, NX2 is shown in table 5.2.

TABLE 5.2 - CHEMICAL COMPOSITION OF GX2, NX2 EXPRESSED
IN MASS PERCENTAGES

Sample	FeO	Fe_2O_3	TiO_2	MnO	Cr_2O_3
GX2	20.1%	29.7%	49.0%	2.1%	0.09%
NX2	17.6%	29.3%	49.5%	1.6%	0.2%

From this table it is apparent that the ferric ion content of the material correlates well with the increased magnetic susceptibility and that the composition represented here is typical of a stable oxidation product.   In addition to this end product it is possible to oxidise the grains so the effective magnetic susceptibility lies between that for the unheated material and that for the end product.

5.4   The Amount of Free TiO_2

The rutile line (Bragg angle 15.9 degrees) which occurs in the spectrum of magnetic ilmenite was the most prominent rutile line and a series of tests were made in which the ratio of the intensity of this line to the intensity of the ilmenite line at the Bragg angle 18.9 degrees was compared with ratios of the intensities of the same lines in prepared mixtures of ilmenite and rutile.   The intensities were measured, using the Geiger Counter X-ray Spectrometer[x] and the samples irradiated were powdered and passed through a 200 mesh screen.

In each case four scannings were made across the line and the total count taken.   The background count was determined at either limit of traverse and subtracted from the total giving four times the intensity of the line.   The series of tests gave a mean value for the mass percentage of rutile in magnetic ilmenite of (10 ± 1) per cent.

The principal sources of error are:-

[x]   Operated by Mr. A Schwartz

a. The intensity of the rutile line is small compared with the
    background and hence it is difficult to arrive at an
    accurate estimate of its value.

b. The sampling of the comparison mixtures is difficult and
    there are considerable difference between estimates of
    the intensity of the rutile when the sample holder is
    emptied and repacked.   The effect of both these sources of
    errors may be minimised by repeated observations.

5.5 Magnetic Properties at Ambient Temperatures

        Preliminary experiments using the Gouy method showed
that the susceptibility of the magnetic ilmenite was large and
field dependent and consequently little information could be
gained from such experiments.   The technique finally adopted
was that outlined in section 4.1 by which both magnetisation
curves and hysteresis loops were obtained.   However at the outset
it must be emphasised that the experiments left considerable
uncertainty as to the properties of a solid sample of "magnetic
ilmenite" because it was possible only to form porous slugs of
the material with very large intergranular air spaces, resulting
in two complicating factors.   Firstly, each grain gave rise
to its own local demagnetising field with consequent variation
of the magnetising field and secondly, the local air gaps
introduced a large effective air gap in the magnetic circuit so
that the actual magnetic moment per unit volume of a grain
could not be calculated.

        One way of overcoming such difficulties would be to
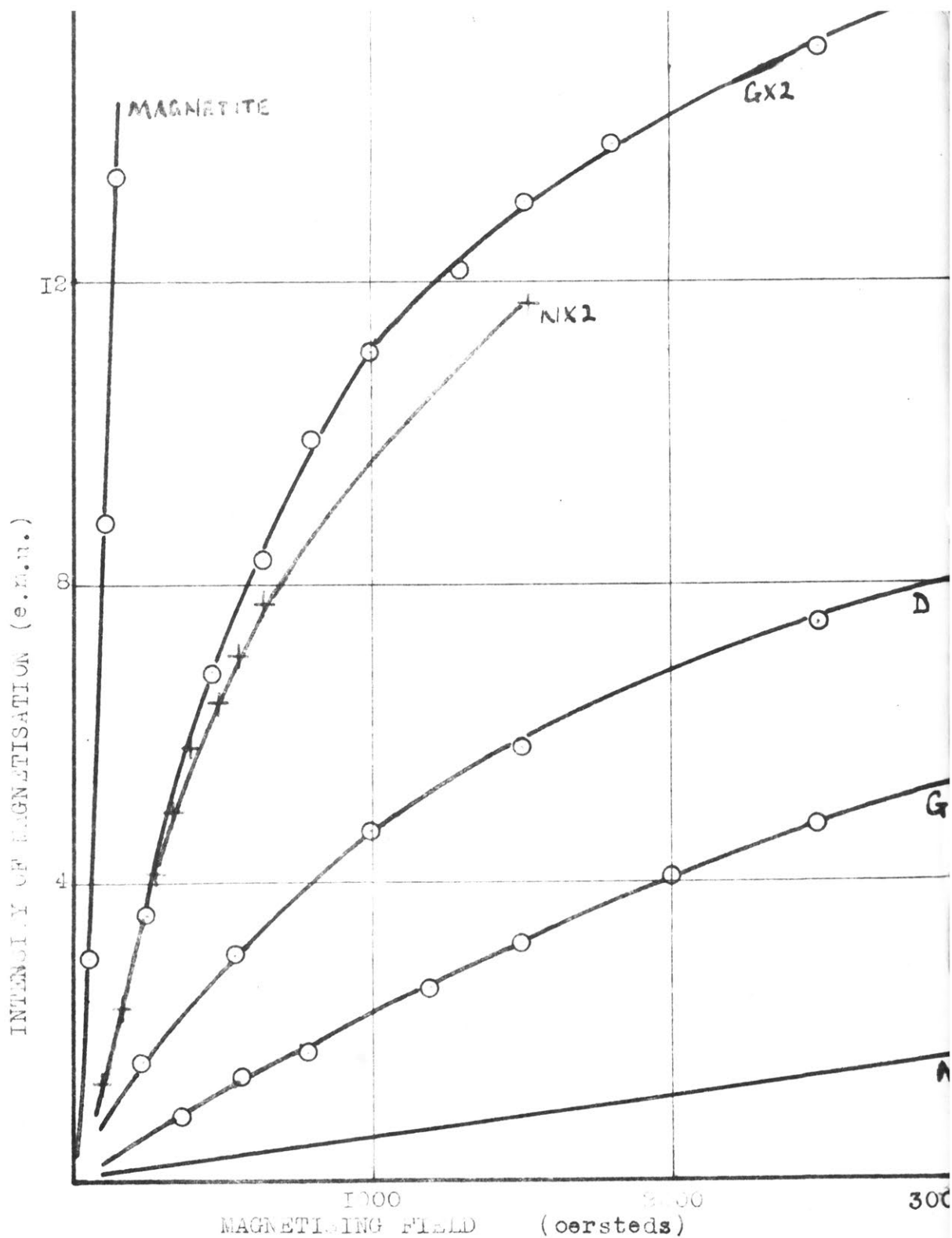compress the material but despite considerable fracturing

FIG.5.I. Magnetisation curves for magnetite, GX2, NX2, D, G, and N.

of the grains, no appreciable improvement was possible under
pressures as high as 10,000 p.s.i. At these pressures,
the bonding between grains was negligible.

However, not withstanding the above limitations it was
considered that valuable information of a comparative nature
could be obtained by studying the effective variation of
intensity of magnetisation and apparent magnetising field.

Fig. 5.1 presents the results obtained from an
investigation of magnetite, GX2, NX2, D and G under comparable
conditions, tamped into the glass tube forming the core of one
of the balanced search coils (see Section 4.1).   The curve for
N is sketched roughly from the data available from the Gouy Method.

The values of the bulk magnetic susceptibility at zero
field obtained from such curves is listed for comparison purposes
in Table 5.3.

TABLE 5.3 - <u>COMPARATIVE FIGURES FOR THE INITIAL MAGNETIC
SUSCEPTIBILITY</u>

Name	Magnetite	GX2	NX2	G	N
Initial susceptibility	85×10^{-3}	15×10^{-3}	15×10^{-3}	2.4×10^{-3}	5.0×10^{-4}
Permeability	2.1	1.2	1.2	1.04	1.008

From these results can be seen the large range of
magnetic susceptibility which can be achieved by suitable heat
treatment.   The permeability of the "magnetic ilmenite" however
is not very high and it is not a source of technical magnetic
material in its granulated form.

FIG. 5.2. Hysteresis loops .
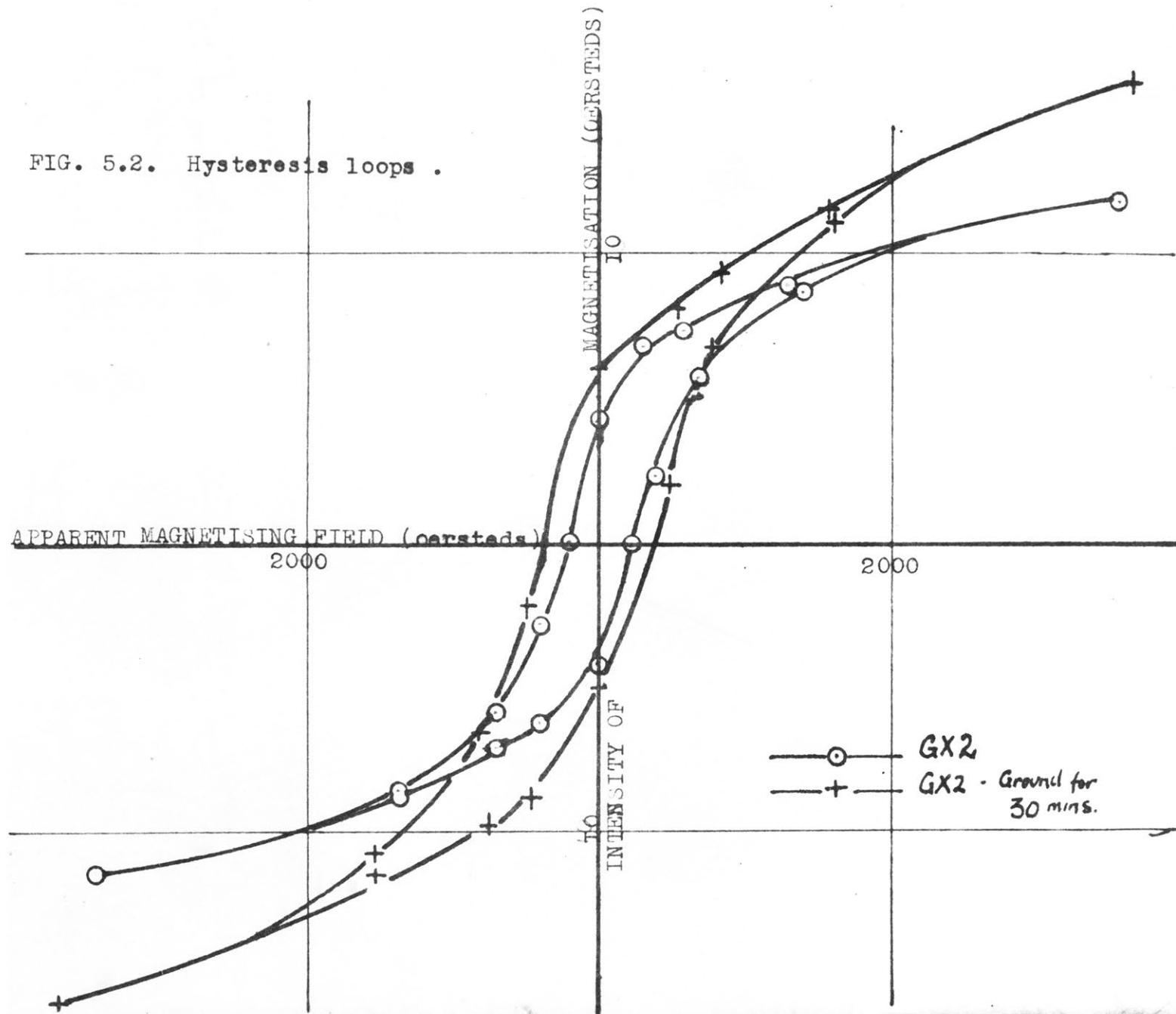
The determination of the coercive force of the "magnetic ilmenite" presented difficulties due to the problem of packing so that the individual grains preserved their initial alighment. However it was possible by carefully packing the sample to minimise this effect and several hysteresis loops were obtained using the technique outlined earlier in Section 4.1.

In fig. 5.2 are presented the results of several experiments on samples of material GX2.   Since the magnetisation curve for NX2 is similar to that for GX2 the experiments were not repeated.

From fig. 5.2 it is apparent that the coercive force for "magnetic ilmenite" is large and for the slug made of uncrushed grains the value is approximately 200 oersteds which is to be compared with a value of the order of 50 to 100 oersteds for a sample of G which had no heat treatment.

The second loop shows
(a)   the effects of closer packing on the residual or remanent intensity of magnetisation and
(b)   the effect of smaller particle size on the coercive force which is increased to approximately 400 oersteds.

It is usual to quote the coercive force for material which has been subjected to a saturation magnetising field but unfortunately such fields could not be realised with the magnet used.   However it is reasonable to assume that the values quoted above are of the correct order and, indeed that is as much as can be attained using this technique.

Concluding, then, not only is the bulk susceptibility of the natural ilmenite greatly increased varying from 6 times for
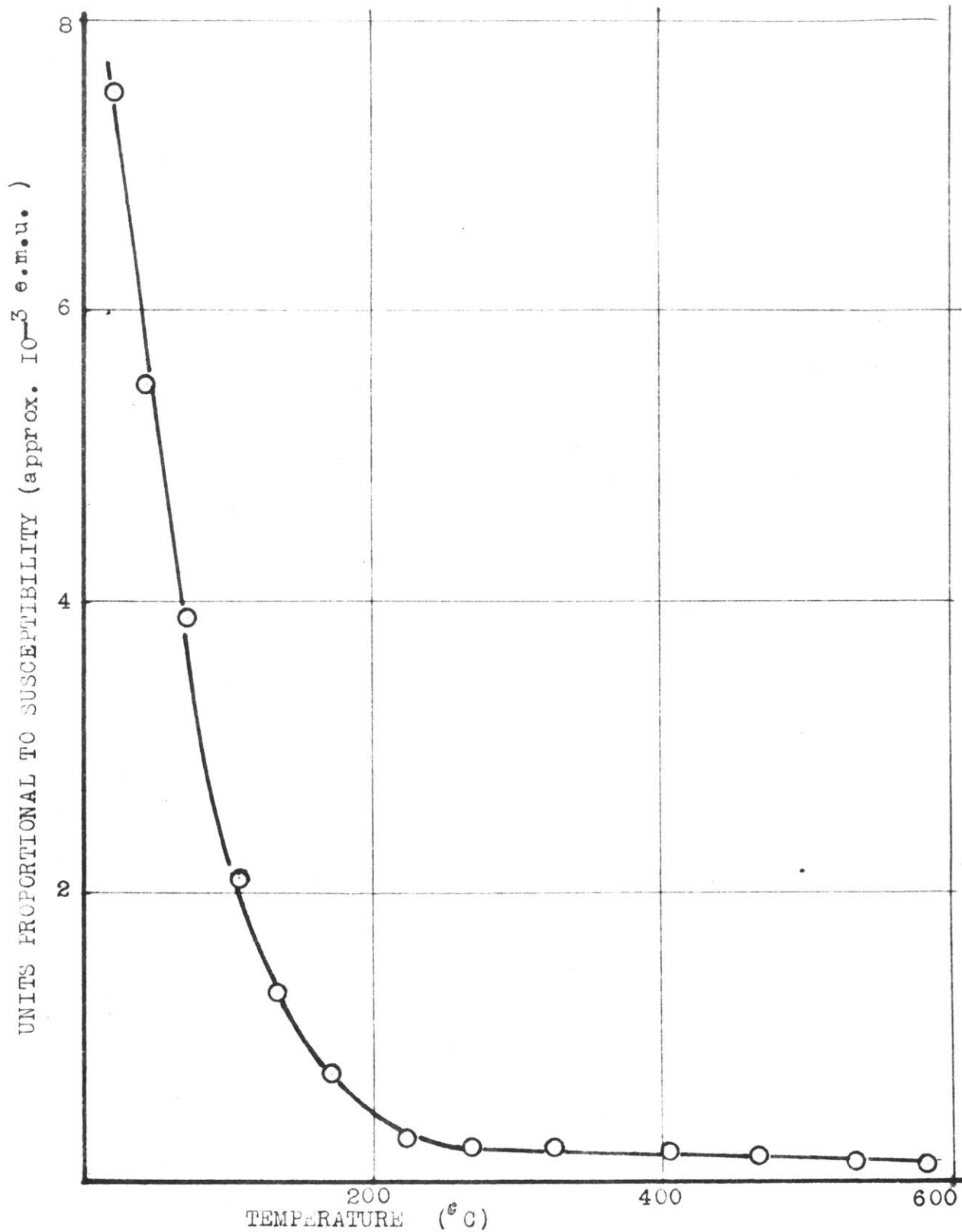
FIG. 5.3.   Variation of the magnetic properties of GX2
with temperature (magnetising field I250 oersteds).

G to 30 times for N but in addition the coercive force is
considerably increased, the increase for G being of the order
of two.

These two factors, then must be considered when studying
any differential separation of ilmenite from other magnetic
components, naturally bearing in mind the added expense of
heat treatment in the final separation.

5.6 Thermo-magnetic Properties

It is possible that the thermo-magnetic relations for
the "magnetic ilmenite" could elucidate the reason for the
variation of the magnetic properties of the ilmenite and
accordingly, a series of experiments were undertaken to obtain
such information.

For material with such high values of magnetic
susceptibility the intergranular demagnetising field is large
and the Ring Balance provides information that is very difficult
to interpret and consequently it is possible to use the results
only on a comparative basis.   In the case of "magnetic ilmenite"
the applied field was 1250 oersteds figs. 5.3 and 4.9 present
the results of the series of experiments made on magnetic
ilmenite, magnetite and the magnetic rejects of the natural
ilmenite.   A study of these curves shows that the variation
of magnetic susceptibility of the ilmenite fractions is
intimately related to the presence of magnetic ilmenite as
a separate phase or in the lattice of the ilmenite.   There
is slight contamination by magnetite.

"Magnetic ilmenite" is ferromagnetic or ferrimagnetic ▓
with a Curie temperature of 120 ± 50°C at room temperature, the
permeability is small but is varying very rapidly.   There is no
detectable difference between the thermo-magnetic curves for
GX2 and NX2 and so only one curve is presented in fig. 5.3.

The law of paramagnetism above the Curie temperature was
not obtained, because the sensitivity of the Ring Balance was
not sufficiently great.   The approximate plot of $\frac{1}{k}$ vT showed
a curvature which may have been fitted to a law of the type
proposed by Neel (equation 11.17) but further study is necessary
before such a law could be determined.

CHAPTER 111

THE SECOND OXIDATION PRODUCT

6.   Ilmenite when heated for a prolonged period at temperatures
greater than 850°C is converted to a new material in which there
is no more than 1-2% of ferrous iron and it is probable that
the ideal end point contains no ferrous iron at all.   This
material possesses magnetic properties such that it would be
difficult to separate from chromite if present in appreciable
quantities in the original ore.   Its properties are described
briefly.   The symbol X1 is applied after the letter denoting
the original ilmenite fraction which was roasted.

The chemical properties are similar to the parent

▓   Nagata (1953) reports the presence of a B component in
    the lavas from Haruna which appears to be very similar
    to "magnetic ilmenite".   A private communication between
    Nagata and Neel is quoted in which the saturation
    magnetisation is said to increase linearly with temperature
    to very low temperatures which suggests a ferrimagnetic
    origin of the magnetism.

ilmenite except that all the ferrous iron has been oxidised and also, probably, the manganese is oxidised because in normal ilmenite it is usually assumed to occupy the ferrous ion lattice points.

In bulk this material is dull, dark grey, it has a relative density of 4.271 $\pm$ 0.005 and during the heat treatment it exhibits some sintering but the sintered mass is friable and requires light grinding to separate it again into a granular form.

X-ray powder photographs show that a new crystal structure has been formed showing many more lines than the ilmenite and also giving a much clearer pattern which is the same regardless of the initial fraction used in the preparation. Table 6.1 records the available information obtained from mean Bragg angle values from several powder photographs for GX1 and NX1 taken with the 11.46 cm Debye-Scherrer camera.

The pattern of lines may be resolved into two patterns one of which is in good agreement with the published data for rutile while the remaining lines were indexed on a tetragonal Hull-Davies Chart. This strongly suggests that there are two phases present.

In a tetragonal structure the interplanar spacings d are given by the formula

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{1^2}{c^2}$$

Where h, k, 1 are Miller indices, d the interplanar spacing, a and c the tetragonal parameters.

From the indexed lines in Table 6.1 it is possible to

TABLE 6.1   INTERPLANAR SPACINGS FOR THE OXIDISED ILMENITE

Complete Pattern GX1		Rutile *		Residual Pattern d	Tetragonal Indices h, k, l	NX1	
d	(int)	d	(int)			d	(int)
		d in angstom units					
4.73	(3)			4.73	100	4.77	(1)
3.425	(8)			3.425	110	3.44	(10)
3.192	(3)	3.24	(8)			3.21	(1)
2.722	(10)			2.722	102	2.724	(9)
2.49	(1)	2.49	(7)			2.451	(1)
2.427	(2)			2.427	200	2.422	(1)
2.371	(2)			2.371	112		
2.197	(2)	2.19	(4)			2.201	(1)
2.170	(2)			2.170	210	2.170	(1)
1.957	(7)			1.957	202	1.958	(8)
		1.877	(4)				
1.851	(7)			1.851	113	1.848	(8)
1.734	(4)			1.734	220	1.739	(1)
1.673	(4)	1.69	(10)			1.683	(1)
1.652	(4)			1.652	(004)(221)	1.656	(1)
1.626	(4)			1.626	(203)(300)	1.628	(1)
1.534	(10)			1.534	310	1.534	(6)
1.495	(<1)	1.495	(2)				
1.490	(<1)			1.490	(311)(114)		
1.415	(6)			1.415	312	1.418	(1)
1.374	(1)			1.374	204		
1.353	(5)	1.357	(8)	1.353	223	1.351	(1)
1.309	(<1)	1.309	(2)				
1.291	(<1)			1.291	303		
1.260	(1)			1.260	313	1.261	(1)
1.235	(1)	1.238	(2)			1.238	(1)
1.215	(1)			1.215	400		
		1.141	(4)				
1.093	(2)	1.095	(4)	1.093	332		
1.080	(4)	1.077	(5)	1.080	420		
1.036	(3)	1.041	(5)	1.036	413		
1.027	(3)	1.031	(6)	1.027	422		
1.011	(2)	1.022	(5)	1.011	333	1.012	(1)
1.000	(4)			1.000	(206)(315)	0.999	(1)
0.954	(3)			0.954	510		
0.925	(8)			0.925	(432)(502)		

* ASTM Crystallographic Index, 1945

calculate the $\overset{v}{b}$alues of a, c.   This was done in the case of a number of pairs of lines which allowed of accurate computation and the resultant mean values for the parameters were

$$a = 4.861 \text{ Å}, \quad c = 6.625 \text{ Å}, \quad {}^c/a = 1.363$$

The only other tetragonal iron - titanium oxide recorded in the literature (Pouillard 1950) was made synthetically by fusing measured proportions of Fe_2O_3 and TiO_2.   This material had parameters

$$a = 9.30\text{Å}, \quad c = 9.50\text{Å}, \quad {}^c/a = 1.02$$

and its probable formula is $Fe4(TiO4)_3$; the titanium ions behave as non-metallic ions.   The plot of this substance on an isothermal section of a ternary diagram locates it in a position similar to that for GX1 and it appears probable that they are related materials.   The synthetic material known as ferric titanate is "weakly ferromagnetic" but the only information given is that the Curie temperature is 240°C.

6.1 Magnetic Properties

The magnetic susceptibility has been examined and it is field dependent but small compared with that of ilmenite, being lower than that for fraction N.   The volume magnetic susceptibility was determined by the Gouy method as described above and is $(3.36 \pm 0.08) \times 10^{-4}$ e.m.u.   The value determined varies from sample to sample probably due to the small quantity of ferrous iron present.

Thermomagnetic investigations showed that there was a ferromagnetic contamination, or the material itself has very
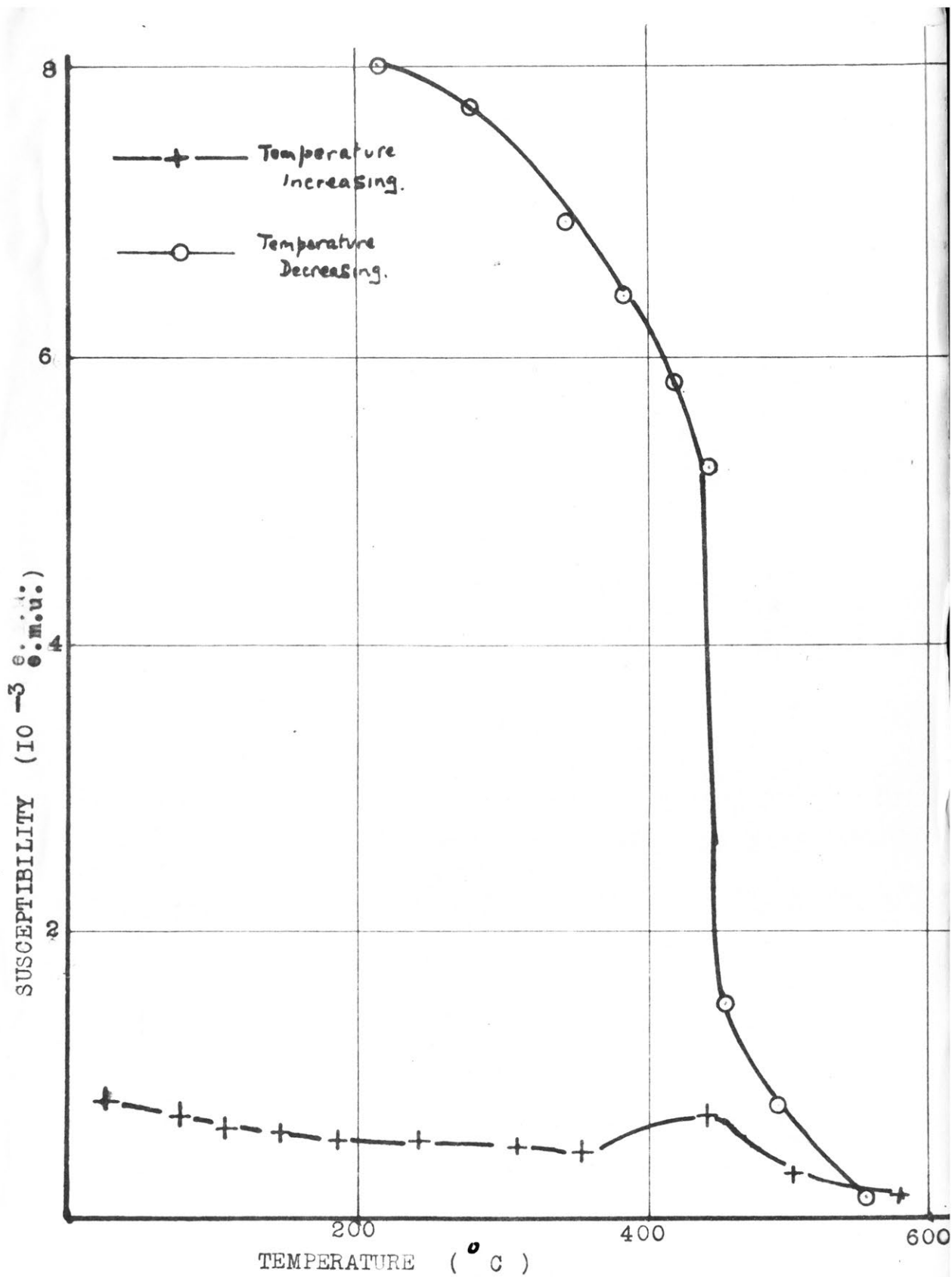
FIG. 6.I. Temperature _susceptibility curves for reduced
ilmenite showing the formation of magnetite.

weak ferromagnetic properties because the magnetic susceptibility falls rapidly to a temperature of $200^{\circ}C$ at which point there is a change in slope of the thermomagnetic curve and thereafter the susceptibility falls approximately linearly with increasing temperature to a value of 1.6×10^{-4} e.m.u. at $500^{\circ}C$. If the ferromagnetism is inherent in this new compound it shows a Curie temperature of $(200 \pm 50^{\circ}C)$ but the shape of the curve suggests that the effect is probably due to traces of the agent which causes the ferromagnetic properties of the ilmenite itself.

This oxidation product may be reduced quite readily by heating with powdered carbon or in a hydrogen atmosphere to give material with possible values of magnetic susceptibility in the ranges considered. A sample of NX1 was reduced in hydrogen and a thermomagnetic study made and the results of the initial heating and cooling curve are given in fig. 6.1. In considering this pair of curves it must be realised that although pressure of air in the ring balance during heating is less than 1mm of mercury yet in this atmosphere the compound formed by the reduction of NX1 undergoes oxidation or a rearrangement of the crystal lattice at temperatures in excess of $400^{\circ}C$. The shape of the cooling curve suggests that an appreciable quantity of magnetite has been formed in the lattice, as may be seen from figs. 4.9 and 6.1.

In concluding then, it may be assumed that this final oxidation material represents a new compound not found in appreciable quantities in the natural ilmenite. It is quite near in chemical composition to the titanate $Fe4(TiO4)_3$ in which

according to Pouillard the titanium behaves as does Si^{+4}
and not as a metallic ion as it does in the mixed oxides known
as ilmenite.   Pouillard states that the iron titanate is
weakly ferromagnetic but does not give any numerical values.
The reduction - oxidation results are not unique to the Xl
category of substances and reduced ilmenite, fraction F, shows
a similar reoxidation involving the probable formation of
magnetite.   Further investigations in this reoxidation may help
to elucidate the basic cause of ferromagnetism in the
ilmenite-like lattice.

<div align="center">

CHAPTER IV

THE PROPERTIES OF FRACTION O AND CHROMITE

</div>

7.1   Fraction O obtained by magnetic separation was
heterogeneous, there being appreciable numbers of grains of
garnet, ilmenite and occasional monazite grains.   A considerable
number of these grains showed a residual crystalline form which
is attributed to the "chromite" grains but there is too much
uncertainty for useful grain counts to be attempted.

In polished section under reflected light the grains
again did not offer definite characteristics to allow of a
useful grain count.   Under crossed nicols the grains showed
quite definite reddish colouration, however no detailed counting
was undertaken but (Stillwell and Baker 1948) have undertaken
an exhaustive investigation on similar sands.

The distribution of the chromium amongst the different
grains was investigated in order to check the maximum possible
separation.   From the assays of Cr_2O_3 and assuming chromite present,

a number of grains was determined which had a good chance of
including a chromite grain. Sets of this number of grains
were burned to completion in an arc. The resulting spectrum
was photographed and the position of certain strong chromium
lines was studied carefully against a "raies ultime" spectrum.
In all samples examined it was found that the chromium occurred
in a few rich grains and was present to < 0.01% in other cases.
The exposure of sample G choosing 200 grains resulted in two
exposures out of twelve showing strong chromium lines absent
in the other ten.

7.2 X-ray Studies

X-ray powder photographs were made using fraction O and
natural chromite ore (obtained from the School of Mining,
N.S.W.U.T.). The patterns did not agree. The interplanar
spacings for fraction O are presented in table 7.1 with those
given in the A.S.T.M. index and there is little similarity.
It appears certain that the Chromium rich grains occurring in
these beach sands is not a simple chromite ore.

The results of this investigation are in agreement with
the minergraphic findings of Stillwell and Baker (1948).
Stillwell suggests that the grains are a low grade chromium-
bearing mineral and are similar to the magneso-chromite of
County Liebig, Queensland. The assay quotes is SiO_2 1.50%,
FeO 25.13%, Al_2O_3 27.93%, Cr_2O_3 35.03%, MgO 17.97% for the
mineral from Liebig.

TABLE 7.1

| Fraction O | | Chromite (ASTM index) | | Ilmenite |
d	intensity	d	intensity	
3.634	(1)			3.74
3.229	(1)			
2.890	(1)	2.84	(9)	
2.720	(10)			2.74
2.676	(4)			
2.510	(8)			2.53
2.457	(8)	2.42	(10)	
		2.32		
2.218	( )			2.23
2.175	(1)			
2.046	(4)			
1.851	(7)	2.01	(9)	1.865
		1.85	(8)	
1.828	(1)			
1.712	(10)			1.720
1.686	(10)			
1.621	(1)	1.64	(9)	1.630
1.581	(2)			
1.499	(4)			1.504
1.481	(1)			1.465
1.459	(6)			
1.450	(6)			
Other lines.		1.42	(10)	

7.3 Magnetic Properties

Since the fraction O was so impure it was not used in magnetic studies except in the initial measurements which gave the mean volume magnetic susceptibility of fraction O to be 3.21×10^{-4} e.m.u. The chromite (Mining Department) which was crushed and measured gave a value of 1.4×10^{-3} e.m.u. but this may have been due to impurity beyond the range detected by X-ray methods.

The thermomagnetic curve showed a general decrease of

susceptibility with increasing temperature.   The graph obtained
by plotting ## the reciprocal of susceptibility against
temperature suggests two straight lines intersecting at
approximately 360°C.

It appears that the chromium rich grains in the ilmenite
concentrate are different both in magnetic behaviour and crystal
structure from natural chromite mineral.

CHAPTER V

THE SEPARATION OF CHROMIC OXIDE FREE ILMENITE

8.1   From the foregoing analysis it is evident that a grade
of ilmenite containing approximately 0.1 per cent by mass of
chromic oxide can readily be attained, commencing with raw
ilmenite as found at Swansea in N.S.W.   Using raw ilmenite
with a higher chrome content the residual chromic oxide content
will be generally higher due to the greater probability of
mechanical occlusion of Chromium rich grains.

An economic separation could be achieved by taking three
magnetic fractions from the natural concentrate. The first
fraction necessary should remove between 2 and 3 per cent of the
ore comprising highly magnetic materials such as magnetite
and magnetic ilmenite carrying a chromic oxide contamination
of from 0.5 - 1.0 per cent.   This fraction has no commercial
value.   The second fraction is taken so that approximately
75 - 80 per cent of the most magnetic material remaining is
removed.   This fraction consists of ilmenite of very low
chromium content.   The residue will consist of impure chromite

grains, some ilmenite, garnet and monazite but, if the ilmenite
has previously passed through an electrostatic separator, the
garnet and monazite will be present in small amount only.

In this section the composition of the second fraction
is of interest and the material concentrated in this fashion
appears to be of closely related form and contains 49 per cent
TiO_2 and 0.1 per cent Cr_2O_3. The magnetic properties of the
grains vary over a wide range and the Fe^{+3}/Fe^{+2} ratio is
related to the increase in magnetic properties. In addition
approximately 2 per cent manganese oxide is present and there
are very slight amounts of vanadium and silicon. From the
published assays of Indian ilmenite (Barke "Chemistry of Titanium")
the chromium content of this ilmenite is of the same order
varying from 0.07 to 0.09 per cent while the reseparated fraction
above contains from 0.1 to 0.2 per cent. Further separation
of chromium rich grains is very difficult by magnetic methods
alone. Evidence of spectroscopic investigations shows that the
chromium in this fraction occurs almost entirely as relatively
few chromium rich grains and the chromic oxide content of most
of the grains is less than 0.01 per cent.

It is suggested that the most satisfactory separation
would be achieved by a separator employing a vertical lift of the
more highly magnetic grains preferably from a single layer
feeding system. Thus either a McLean Separator or a Rapid
Separator would be most satisfactory.

Several tests on varying scales have been made. The
first two experiments were reported in section 3.2 and confirm

the conclusions above.   The third test was made on a Rapid
type separator[*] using Swansea ilmenite.   It was not possible
to spend sufficient time to obtain the optimum setting of the
three rotating poles but further adjustment was practicable and
finer grades of concentrate might be attained.   In this machine
a vibrating hopper feeds a thin layer of grains onto a moving
belt which passes under three poles.

A division was made in which 9 per cent of the ore was
taken at the first pole, 75 per cent was taken at the second
pole, 11 per cent at the third pole and 6 per cent was left as a
low magnetic residue.   The 6 per cent tailing consisted princip-
ally of monazite and garnet.

The ilmenite or second pole concentrate showed a chromic
oxide content of 0.2 per cent.   Unfortunately the adjustment
had been made so that too much concentrate was taken in the
first fraction and too much of the tailing was taken in the
second fraction.(see table 3.3).   The concentrates used in these
former separations were free of monazite and garnet hence there
was a much smaller proportion of tailing.

Thus a satisfactory separation of a concentrate containing
at most from 0.2 per cent but probably less than 0.1 per cent
Cr_2O_3 may be achieved by a Rapid type three pole separator.
This work is confirmed by the findings of the C.S.I.R.O. Ore
Dressing Laboratory (Research Report 461, 1953).

If economically desirable however, a further refinement
is possible which reduces the chromic oxide content to much less
than 0.1 per cent.   The second pole fraction above (assaying

[*]   Used by kind permission of Lemprieres Ltd.

0.2 per cent Cr_2O_3) was roasted at 720 $\pm$ 20°C for a period
of 15 minutes and then after cooling, was separated by means
of a hand magent.

The more magnetic material from this separation comprised
84 per cent of the Rapid second pole concentrate and assayed
0.06 per cent Cr_2O_3 while the less magnetic material comprising
16 per cent of the second pole concentrate contained 0.65 per cent
Cr_2O_3. A separation in which the forces were more closely
controlled would probably reduce the Cr_2O_3 content of the more
magnetic component to lower values.

Two aspects of this separation must be considered.

1. The economic desirability of roasting for the period
   suggested above. The period suggested is sufficiently
   prolonged to convert most of the ilmenite to "magnetic
   ilmenite" however it may be desirable to heat for a shorter
   period and only partially convert the ilmenite to magnetic
   ilmenite, while still allowing of more effective separation.

2. The exsolution of the rutile discussed above, Chapter DI,
   may have disadvantages as far as the solubility of the
   ilmenite is concerned. This question has not been studied
   carefully.

In conclusion, it is possible to separate an ore
containing 65% of the original ilmenite assaying as low as
0.06 per cent Cr_2O_3 but the product obtained before heating
appears to be more satisfactory.

8.2 <u>Chromium Ore Concentration</u>

Before proceeding with the discussion of the concentration

of the chrome bearing fractions of the ilmenite it is useful
to consider Table 8.1

TABLE 8.1 - <u>CHROMIC OXIDE DISTRIBUTION IN MAGNETIC</u>

<u>FRACTIONS</u>

Magnetic Fraction	% Mass Distribution	Chromic Oxide Content of Fraction As Mass % of Fraction	Chromic Oxide Content of Fraction As % of Total Chromic Oxide
A) B) C)	2		1.4
D	1.8	0.36	0.66
E	12.0	0.15	1.7
F	15.9	0.09	1.4
G	14.6	0.09	1.4
H	5.8	0.097	0.6
I	9.8	0.093	0.9
J	4.2	0.11	0.5
K	5.9	0.09	0.5
L	4.6	0.09	0.4
M	11.3	0.09	1.0
N	5.0	0.24	1.2
O	6.2	13.0	80
P	1.0	0.1	
Original		0.72	

An examination of this table shows that at least 80% of
the chromic oxide content of the ilmenite may be removed by
taking the least magnetic 10% of the ilmenite. With the less
sensitive control available on a commercial separator a fraction
of 15-20% might be better.

The concentrate left after most of the ilmenite is
removed contains approximately 10 per cent chomic oxide as can
be seen from the tests reported in Table 8.2. Further attempt
at magnetic concentration of this material involves separation
of grains of only slightly different magnetic susceptibility

and consequently is not recommended.   However it has been shown that the magnetic properties of the ilmenite grains may be changed by roasting and so the difference in the magnetic properties of the chromium rich grains and the ilmenite grains may be increased.

Two possible techniques suggest themselves:-
a. Partial oxidation to "magnetic ilmenite" by heating in air at temperatures between 700°C to 800°C for 10 minutes.
b. Total oxidation of the ilmenite to the weakly magnetic form which has been discussed above.   The difference of magnetic susceptibility for the unheated chromite bearing grains and the "ferric titanate" is small and the success of this method would be due to a shift in the magnetic susceptibility of the "chromite".   Unfortunately it has not been possible to concentrate a pure specimen of these grains and the effect of heat treatment is not known.   The natural chromite ores studied are more highly magnetic than this chrome ore.

In table 8.2 the distribution of the chromic oxide amongst the fractions separated on the Rapid separator is shown.

TABLE 8.2 -   COMMERCIAL SEPARATION

Sample	Head	Middling	Third Pole Concentrate	Tailing
Mass % Distribution	9	75	11	6
% Cr_2O_3 of fraction of cut	1.8	0.2	10	1.6
% Cr_2O_3 of Total Cr_2O_3	11	9	73	6

In assessing the results of Table 8.2 it is to be emphasised that the results given in Table 8.1 applied to concentrates in which the monazite and garnet has been removed by prior electrostatic separation.   Should the raw ilmenite contain monazite and garnet it is probable that the least magnetic cut should be approximately 30% and then it will contain a large amount of unwanted tailing.

In the trial on the Rapid separator the recovery of the chromic oxide in the third pole concentrate was approximately 73 per cent and the concentrate assayed 10 per cent Cr_2O_3.

In order to obtain a higher grade concentrate the third pole concentrate was then submitted to the two methods of heat treatment suggested above.

a.   The third pole concentrate was heated in an electric muffle furnace in an open crucible at ($750^o \pm 20^oC$) for 15 minutes, and after rapid cooling the sample was separated by a hand magnet.

Using this technique it is possible to concentrate more than 60 per cent of the chromic oxide into a sample consisting of approximately 6 per cent by mass of the original raw ilmenite and assaying 18 per cent Cr_2O_3.   Further concentration by these means is difficult.   This is in accord with the suggestion that the chromium rich grains are not true chromite but are a low grade chromium bearing crystal.

b.   A sample taken from the third pole concentrate was heated for 15 minutes in an open crucible in an electric muffle furnace at temperatures in excess of 900^oC.   Partial

separation was achieved but the results were not conclusive and a large loss of chrome rich grains occurred in the less magnetic fraction.

In conclusion, it may be stated that from the evidence obtained in these experiments it is not possible to concentrate a chrome ore containing more than about 20 per cent Cr_2O_3 by heat treatment and magnetic separation without an appreciable loss of chromium bearing grains. It would however, be possible to concentrate a fraction with up to 18 per cent Cr_2O_3 and which contained up to 75 per cent of the chromium content of the original raw ilmenite.

APPENDIX

9. The Constitution of the Mixed Oxides of Iron.

Much work has been done on the constitution and magnetic properties of the mixed oxides of iron, rhombohedal iron oxide and magnetite but little has been published on the family of substances known as ilmenite. In all cases extensive solid solution of one oxide in another causes complex behaviour both chemically and magnetically. On the chemical side a work has been published by Pouillard (1950) in which he makes an attempt to systematise the behaviour of the mixed aluminium-iron oxides and the titanium-iron oxides. It is possible to summarise many of the conclusions which he makes. However at the outset it should be emphasised that there are certain objections to the work which detracts somewhat from the reliability of the conclusions.

(1)   Pouillard bases much of his argument on the occurrence of
certain zones in an isothermal section of a ternary diagram and
the accuracy of the diagram is open to some doubt particularly
in the cases of the limited solid solution between Fe_2O_3 and
ilmenite $FeTiO_3$.

(2)   Insufficient data are given regarding the heat treatment
of the synthetic materials and it is doubtful if these results
of laboratory experiments may be made the basis of an argument
on the constitution of minerals which have cooled at the rates
encountered in geological deposition of minerals.   Certainly
the possible limits of solid solution quoted by Pouillard are
much greater than is considered possible by Edwards (1948) where
the limit is regarded as being of the order of 10 per cent of
ilmenite in Fe_2O_3 or vice versa.

(3)   The generalisations appear to be made on the basis of
too few synthetic samples.

        Nevertheless, it appears that there is considerable
merit in many of the results which are quoted and Pouillard has
used magnetic and X-ray analysis which should supplement the
data from the mineragraphic methods employed by Rhamdor and
Edwards for the investigation of solid solutions and phases of
similar constitution.

        Pouillard claims that the iron-titanium oxides which
have been synthesised consist of four basic compounds besides
the three pure oxides FeO, TiO_2, Fe_2O_3 .   He succeeded in
synthesising one compound which is not reported as a natural
mineral and has been unable to form pseudo Brookite (Fe_2TiO_5).

These basic compounds are ilmenite ($FeTiO_3$), iron titanate
$Fe4(TiO4)_3$ and a spinel type material Fe_2TiO_4
all these materials are weakly ferro-magnetic or paramagnetic
and their properties are listed below in Table 9.1 together with
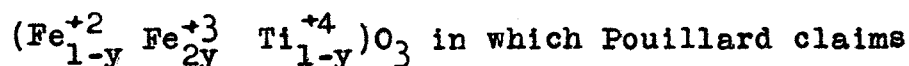those of other important oxides.

TABLE 9.1 - <u>MAGNETIC AND CRYSTAL DATA FOR SOME</u>
<u>OF THE IRON AND IRON-TITANIUM OXIDES</u>

Chemical Composition	Structure	Crystal Parameters	Magnetic Props.	Curie Temp. ^oC
FeO	Cubic	4.28 Å	Non Magnetic	
Fe_2O_3	Rhombohedral	a= 5.413Å = 55°17'	Complex, Ferro magnetic (very weak)	675
TiO_2	f.c.Tetragonal		non magnetic	
$FeTiO_3$	Rhombohedral	a= 5.52 Å = 54.53^o	Paramagnetic	
$Fe4(TiO4)_3$	f.c. tetragonal	a=9.30Å c=9.50Å c/a=1.02	Feebly Ferro magnetic	240
Fe_3O_4	b.c. cubic Spinel	a= 8.41Å	Ferromagnetic	575
Fe_2TiO_4	f.c. cubic	a= 8.534Å	Not Ferro-magnetic at room temp.	
Fe_2O_3 𝕩	cubic (spinel)	a= 8.32Å	Ferromagnetic	675 (by extra-polation)

𝕩 Michel (1951)

In addition to these components, it is possible to
synthesise materials which show a single phase and which have
the following compositions:-

(1) Solid solution of Fe_2O_3 in $FeTiO_3$ probably by the mechanism $2Fe^{+3} \rightleftarrows Fe^{+2} + Ti^{+4}$ since all the iron in $FeTiO_3$ is in Fe^{+2} state. This solid solution is limited and may be represented by the equation $(Fe^{+2}_{1-y} Fe^{+3}_{2y} Ti^{+4}_{1-y})O_3$ in which Pouillard claims $0 \not\leqslant y \leq \frac{1}{3}$ but apparently this limit should be greater $(y = \frac{1}{2})$ to give consistent interpretation of his diagram The rhombohedral crystal parameters are $a = 5.47Å$, $\alpha = 54°38'$.

(2) Solid solution of $FeTiO_3$ in Fe_2O_3 in which a single phase is represented by the equation

$$(Fe^{+2}_x \ Ti^{+4}_x \ Fe^{+3}_{(2-2x)})O_3 \text{ where } 0 \leqslant x \leq \frac{1}{3}$$
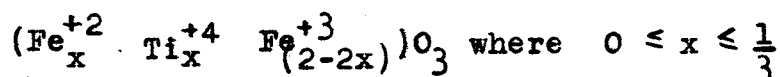
In this case the parameters change to the limiting value of $a = 5.46Å$, $\alpha = 55°7'$ while the Curie temperature falls to $160°C$.

(3) Solid solutions of iron titanium spinel in magnetite ~~ion~~ for which all molar proportions give a single phase with a gradual change of Curie temperature from $575°C$ to $215°C$ as the molar proportion of Fe_2TiO_4 rises from 0 to 42 per cent. At the same time the crystal parameter changes from $8.413Å$ to $8.46Å$. These materials are represented by the equation

$$(Fe^{+2}_{1+x} \ Ti^{+4}_x \ Fe^{+3}_{2-2x})O_4$$
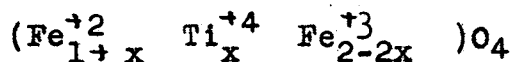
In addition to these solid solutions in Nature (1954) it is reported that solid solutions may exist between magnetite and an ilmenite like material. This is in agreement with Edwards statements.

FIG. 9.I. Ternary diagram (isothermal section).
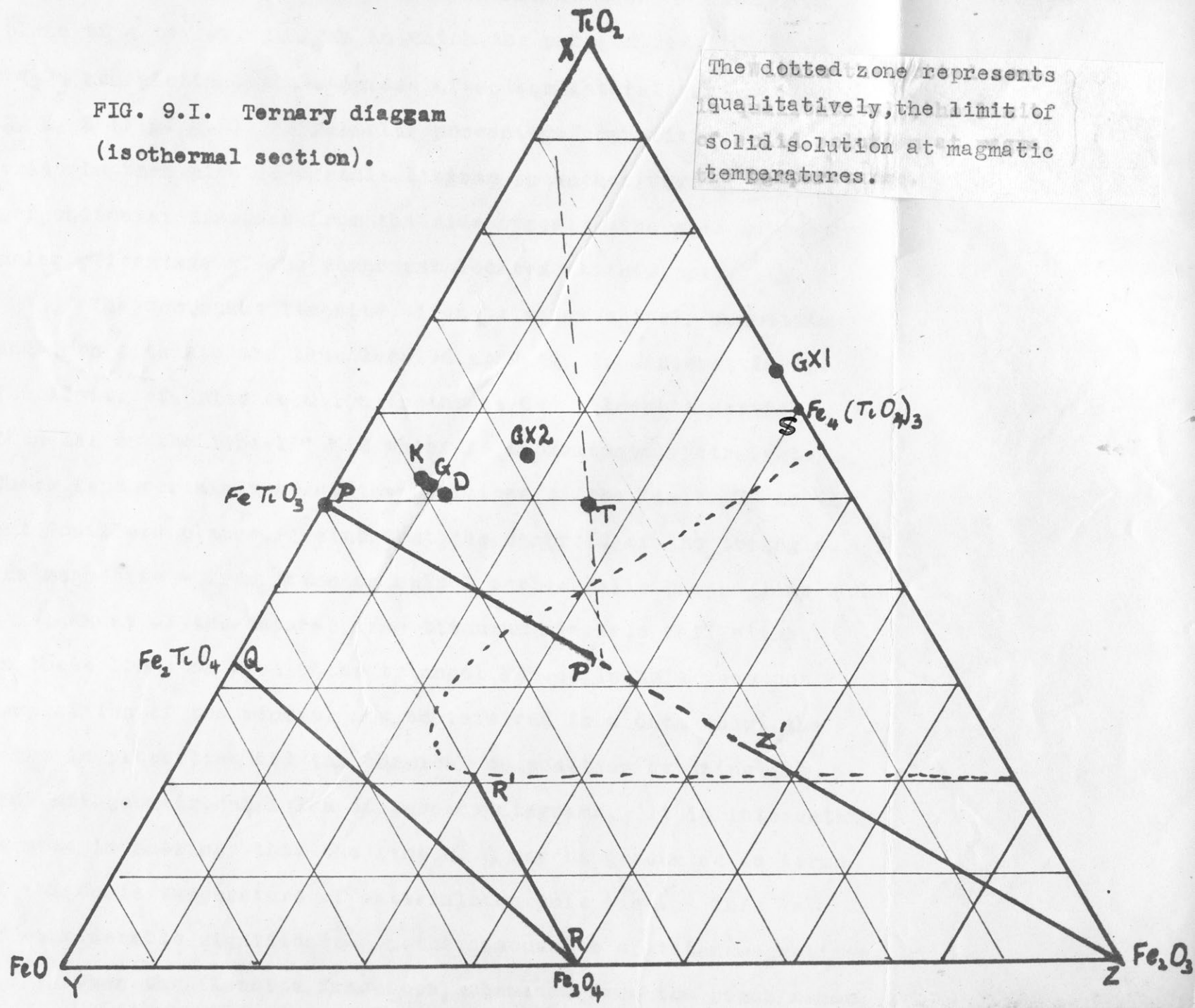
The dotted zone represents qualitatively, the limit of solid solution at magmatic temperatures.

These data are conveniently summarised on an isothermal plane of a ternary diagram in which the pure oxides TiO_2, FeO, Fe_2O_3 are plotted at the apices of an equilateral triangle X, Y, Z (Fig. 9.1). The molar percentage composition of any oxide is then plotted on this diagram in such a way that the perpendicular distance from the side opposite the apex gives the molar percentage of the component located at this apex.

The compounds ilmenite, iron-titanium spinel, magnetite and iron titanate are thus located at P, Q, R, S respectively. The limits of solid solution in the Fe_2O_3 - ilmenite series then lie on the line PP' Z'Z which is approximately straight. There is uncertainty about the positions of the limits P' and Z' but Pouillard places P' almost at the centroid of the triangle. The magnetite - iron titanium spinel series falls on the line Q R.
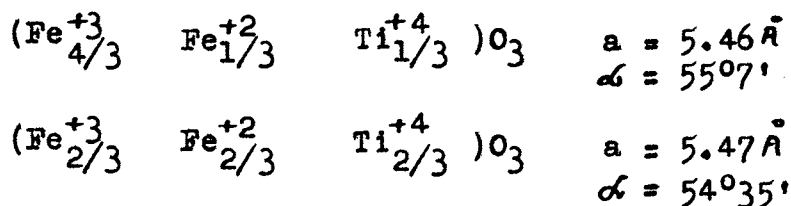
Most of the natural iron titanium minerals fall either on these lines or within the triangel PZY. In this case the composition of the mineral may be inferred from data about the magnetic properties and the chemical composition by using the ordinary geometrical rules of ternary diagrams, It is interesting to note in passing, that the line R, Q may be graduated in terms of the Curie temperature of materials on this line. This is of considerable significance in the discussion of titanomagnetites.

When the ilmenite fractions, obtained from the beach sands, are plotted on this diagram it is found that these compounds lie in the triangle XPZ about which Pouillard has given little information. The reasons for neglecting this zone are three fold.

(a)   It is not of great concern in the study of the
        titanomagnetites.

(b)   The X-ray data is difficult to obtain because of fogging and broadening of lines.

(c)   There is great uncertainty of the behaviour of TiO_2 in the presence of small amounts of FeO ~~and~~ ~~TiO_2~~; it appears that limited solid solution is possible with a single phase of doubtful composition.

In order to test his hypotheses Pouillard has prepared a number of compounds comprising Fe_3O_4 and TiO_2 prepared by reducing precipitated Fe_2O_3 and TiO_2.   The amount of TiO_2 is uncertain in some cases.   The compound of interest in this discussion was prepared from Fe_3O_4 $2TiO_2$ and is represented on the diagram by the point T lying on the line XR and consequently in fairly close proximity to the "magnetic ilmenite".   This synthetic material had a Curie point of $160°C$ and X-ray data showed the presence of three phases which Pouillard states are:-

$$(Fe^{+3}_{4/3} \quad Fe^{+2}_{1/3} \quad Ti^{+4}_{1/3})O_3 \qquad a = 5.46 Å$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad \alpha = 55°7'$$

$$(Fe^{+3}_{2/3} \quad Fe^{+2}_{2/3} \quad Ti^{+4}_{2/3})O_3 \qquad a = 5.47 Å$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad \alpha = 54°35'$$

TiO_2

The "line of correspondence" indicates that the phase listed as TiO_2 is a solid solution of uncertain composition and the films were too difficult to interpret due to fogging.

Unfortunately the magnetic properties are not given but since a Curie temperature is quoted the material must be ferromagnetic.   It would be expected that the properties would be those of the first phase mentioned modified by the fact that it is dispersed in non-magnetic ilmenite-like and rutile-like phases.

In fig. 9.1 are plotted the approximate positions representing the composition D, G, K, GX2, GX1 and it is seen that all fractions lie in the triangle PZX and consequently the magnetic properties are difficult to explain on the bases of Pouillard's work. - If it is valid to use Pouillard's results, the beach sand ilmenites should be complex materials comprising a solid solution of Fe_2O_3 in ilmenite and a free rutile-like second phase. The solid solution would be approximately $(Fe^{+3}_{0.2} \quad Fe^{+2}_{0.9} \quad Ti^{+4}_{0.9}) O_3$ (i.e. in general formula $y = 0.1$) and the approximate molecular proportions would be

rutile$/$solid solution $= \frac{6}{35}$ i.e. by mass approximately 8 per cent rutile and 92 per cent solid solution. It is difficult to understand the apparent ferromagnetism with a Curie temperature at approximately $120 - 150^oC$ which is not in accord with the report of Pouillard who presumably finds these solid solutions to be paramagnetic except for a spurious ferromagnetism due to magnetite contamination. In addition, tests show that the Geiger Counter X-ray spectrometer will certainly detect the presence of as little as 5% of crushed rutile mixed with ilmenite. Thus either the exsolved rutile is extremely finely divided or the estimate above is too large.

Considering now the compound GX2 it is seen that here we would expect two phases to be present. On an ilmenite substituted by Fe_2O_3 and the second a rutile like substance. The substituted ilmenite has the approximate formula

$$(Fe^{+3}_{.48} \quad Fe^{+2}_{.76} \quad Ti^{+4}_{.76}) O_3 \quad \text{i.e.} \quad y \doteq 0.24$$
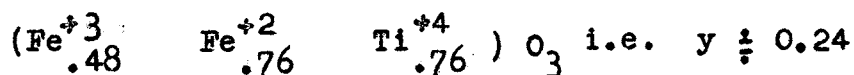
and the molecular proportion is rutile/substituted ilmenite 12/31 i.e. approximately 17 per cent rutile to 83 per cent substituted ilmenite by mass. According to Pouillard these phases should not be ferromagnetic.

This estimate of the amount of rutile present in magnetic ilmenite does not compare well with the estimate made by X-ray methods (See Section 5.4) but the semi width of the rutile line in magnetic ilmenite is 0.36 ± 0.04 units while in the reference mixtures is 0.21 ± 0.01. This indicates that either the rutile is present in smaller aggregates in magnetic ilmenite or it is under strain. In both cases it is possible that examination of the intensity of the rutile line would lead to a low value for the estimate of the amount of free rutile.

Thirdly considering GX1 there would again be two phases present, namely rutile and ferric titanate present in the molecular ratio 1/8 which represents a mass ratio of 2/98.

Although the results of the X-ray determination are in broad qualitative agreement with these results there are certain reasons which suggest that the picture presented here is too simple.

1. The rutile phase in the "ilmenite" fractions should be detected by X-rays unless extremely finely divided.

2. There is a discrepancy between the measured mass increase on oxidation and the calculated increase required to convert all the FeO to Fe_2O_3

3. It is difficult to imagine a change which does not cause a large rearrangement of the crystal lattice when the $Fe^{+2} \rightarrow Fe^{+3}$ and the Ti^{+4} exsolves

4.   The parameters obtained for the iron titanate (tetragonal phase) are not in agreement with Pouillard's values.

It would appear that the assumption that all the titanium is present as Ti^{+4} is open to some doubt.   It should be possible if there is some Ti^{+3} present to substitute Fe^{+3} ions for Ti^{+3} ions by simple heating and the Ti^{+3} ions then could move to form an exsolution body.   If this were so the Fe^{+3} content of the lattice would be higher than the assays suggested which in turn would mean that less oxygen would be required to convert all the Fe^{+2} to Fe^{+3} on the assumption that the Ti^{+3} is not oxidised during heating and conversion to iron titanate.

In conclusion then it would seem that the general deductions from the ternary diagram are valid but it is not possible to draw quantitative conclusions from the results of such a diagram without further information on the synthetic materials which would be formed in the triangle PZX.

10   The Magnetic Properties of Iron Oxides

10.1   Ilmenite

Pure ilmenite which may be synthesised (Pouillard (1950) Chevallier (1953)) is regarded as paramagnetic but often shows ferromagnetic/contamination.   The most useful summary of the magnetic properties is given by Chevallier who has prepared very pure synthetic crystals of ilmenite.   The aim was to use a detailed investigation of the magnetic properties to supplement the conclusions of Hamos and Stscherbina (1933) who deduced that the correct formula, at room temperature, was ($Fe^{+2} Ti^{+4} O_3$) from X-ray absorption-edge measurements on ilmenite

and on materials with titanium of known valency.

The ilmenite examined by Chevallier had an Fe_2O_3 content of less than 0.5 per cent and the magnetic susceptibility was proportional to the field between 0 and 6500 oersteds and the value of specific susceptibility (χ) determined for a randomly oriented powder made from the crystals was 96×10^{-6} e.m.u. at 20°C i.e. $k = 4.5 \times 10^{-4}$ e.m.u. which compares with the value of fraction $N = 4.67 \times 10^{-4}$ e.m.u. The temperature variation of χ followed the Curie-Weiss Law from the temperature of liquid oxygen to room temperature the relation being

$$(T - 23) = 0.0260$$

This leads to an estimate of 5.49 Bohr magnetons per ion in the molecule if it is assumed that there is one paramagnetic ion per molecule as is the case in (Fe^{+2} Ti^{+4} O_3). This is in good accord with the reported values for Fe^{+2} which range from 5.25 to 5.53.

When Chevallier calculates the value assuming Fe^{+3} and Ti^{+3} he estimates that the magnetic moment per molecule will be 6.13 Bohr magnetons if there is no orbital interaction. Thus the results of the magnetic measurements are in accord with the assumed formula:

$$Fe^{+2} \quad Ti^{+4} \quad O_3$$
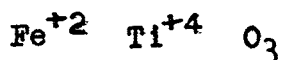
Sample N does not show a linear relation between $\frac{1}{k}$ and T above room temperature probably because of ferromagnetic interactions.

10.2 <u>Rhombohedral Sesquioxide of Iron (α Fe$_2$O$_3$)</u>

A great deal of work has been done with this material

and many slightly different magnetic modifications have been
reported, however, it appears fairly clear that one reason for
the numerous modifications reported is that α Fe_2O_3 and γ Fe_2O_3
may exist in an apparently homogeneous crystal and the γ Fe_2O_3
introduces a strong ferromagnetic contamination.

Michel, Chandron and Benard (1951) give a review
of the non-metallic ferromagnetic compounds and Chevallier (1951)
gives a detailed discussion of the magnetic properties of
α Fe_2O_3 derived from a number of sources.   Neel (1953) describes
some results derived from the study of a single crystal also
discussed by Neel and Pauthenet (1952).

The general conclusion one can draw is that α Fe_2O_3
behaves in a very complex fashion depending on its origin and
in general the magnetic properties are characterised by a
ferromagnetism superimposed on a paramagnetism, so that in high
fields (5,000 - 20,000 oersteds) the specific magnetisation is
given by the relation

$$\sigma = \sigma_0 + \chi H$$

where σ_0 is the spontaneous magnetisation of the ferromagnetic
portion of the magnetisation and χ is the antiferromagnetic
susceptibility.   Above 260°K the value of χ is almost independent
of temperature up to 950°K at which there is an antiferromagnetic
transition and the material becomes paramagnetic following a
Curie-Weiss Law

$$\chi (T + 3727) = 0.085$$

In the interval 260°K - 950°K the values of χ parallel
and perpendicular to the ternary axis are approximately equal.

Superimposed on this paramagnetism there is a
ferromagnetism of uncertain origin which has a Curie point at
approximately $1000^\circ K$ while Neel (1953) requires two
ferromagnetic mechanisms.

(a)   An isotropic ferromagnetism for which $\sigma_0 \doteq 0.2$ e.m.u.
        in the interval $0^\circ K$ to $600^\circ K$ after which it vanishes at
        the Curie Temperature.

(b)   An anisotropic ferromagnetism appearing at $260^\circ K$ and
        disappearing at approximately $1000^\circ K$

Neel regards these as parasitic magnetisation which is
associated with the presence of ferrous ions in the lattice.
This is equivalent to an oxygen deficit.   If the stoichiometric
deficiency were associated with one or other of an antiferromagnet
ic sub-lattice there would arise slightly different magnetisation
in these sub-lattices with the result that the antiferromagnetism
would not be perfectly compensated.   This explanation is
similar in essence to postulating the formation of small
deformed magnetic crystallites oriented by epitaxy on one of
the crystal faces.

Alternatively, there could exist a local domain structure
with a nett magnetic moment due to local variations on
composition.   In the case of pyrrhotite (FeS_{1+x} where x is
small) the magnetic properties appear to be associated with an
ordered pattern of vacant iron sites in one sub-lattice of the
crystal while the other sub-lattice is filled.   There is some
evidence from X-ray study that such a state exists.

The magnetic behaviour of monocrystalline powders
of $\mathscr{L}$ Fe_2O_3 has been described by Chevallier (1951) and his

results are summarised briefly as follows:

As the crystals are pulverised the magnetic properties gradually

decrease while the coercive force increases.   For grains of

comparable dimensions to those encountered in the beach sands

the following approximate data apply

$$\chi_i \doteqdot 2.5 \times 10^{-4} \text{ e.m.u.} \qquad \sigma_o \doteqdot 0.4 \text{ e.m.u.}$$

$$k_i \doteqdot 1.2 \times 10^{-3} \text{ e.m.u.}$$

(χ_i and k_i being initial values of specific and volume

susceptibilities)   while the coercive force is of the order of

a few hundred oersteds.

These figures compare with some of the values obtained

for the "ilmenite".

The magnetisation curves for the monocrystalline powders

all lie between the curves giving the magnetisation parallel

to the ternary axis and perpendicular to the ternary axis.

Considering fig. 4.2 and 4.3 it is seen that for ilmenite,

fraction G, $k_i = 2.4 \times 10^{-3}$ e.m.u. when no correction is made

for packing and $k_i = 3.8 \times 10^{-3}$ when corrected;   further the

remanent magnetic moment is of the order of 1 e.m.u.

Thus the behaviour of fraction G is of similar order to that

for haematite.   However the value of the reversible magnetic

susceptibility $\chi_r = 400 \times 10^{-6}$ e.m.u. which is much greater

than that for α Fe_2O_3 which gives $\chi_r = 20 \times 10^{-6}$ e.m.u. and

in most cases the magnetism of α Fe_2O_3 is characterised by a

constant value of χ_r.

Unfortunately these values are obtained from relatively

loosely packed grains and are not very useful for comparison

purposes because Chevallier does not give the state of compactness of the specimen when the observations were made. However it appears that the significantly higher values for χ_r reported here preclude an interpretation based on a simple picture where the structure giving ferromagnetism in haematite is responsible for the ferromagnetism in the solid solution found in ilmenite.

10.3 γFe_2O_3

The γFe_2O_3 is formed by the careful oxidation of Fe_3O_4 at low temperatures and in its purest form is very unstable, changing at slightly over 300^oC to αFe_2O_3. The Curie Temperature of γFe_2O_3 is found by examining the oxide when stabilised by the presence of other ions. Much work (Haggett (1924), Michel (1937)) has been done on this property of the Fe_2O_3 and by extrapolation it is found that the Curie point is near 675^oC. The crystal structure is cubic with a lattice parameter of $8.32\overset{o}{A}$, however there is some doubt as to the type of lattice existing and the mechanism by which magnetite is oxidised. Some authors (Verwey, 1935) favouring a migration of Fe^{+2} ions while Michel (1937) suggests that oxygen enters the lattice. Neither of these suggestions are entirely satisfactory according to dilation experiments.

The chief interest in the cubic sesquioxide lies in the fact that this oxide is able to enter into stabilised solid solution in a great number of oxides and in many cases in a fashion in which it is very difficult to detect by X-ray or magnetic means, since the Curie point is varied from 675^oC to 150^oC by the state of solid solution.

There are cases where γ Fe_2O_3 (Michel 1951) has been
the cause of magnetic anomalies in what is apparently α Fe_2O_3.
Weak ferromagnetic effects could then be the result of γ Fe_2O_3,
in the ilmenite, a few percent of the material would not be
detected by X-ray techniques and could account for the magnetic
properties of the natural fractions.   It is considered that
the presence of sufficient γ Fe_2O_3 to account for the magnetism
of magnetic ilmenite would be detected by X-ray methods.

10.4   Magnetite (Fe_3O_4)

Magnetite is one of the simplest of the magnetic iron
oxides.   It is a cubic spinel type crystal of parameter 8.41Å
and shows a complex magnetic behaviour and a Curie temperature
of 575°C.   An extensive range of substitutions are possible
by mono-valent, divalent and trivalent ions.   These
substitutions are accompanied by change of parameters up to
approximately one per cent and a change of the Curie temperature
which generally decreases but may increase. (e.g. Michel, 1951
states ($Fe^{+3}_{2.5}$ $Na^{+1}_{0.5}$)O_4 has a parameter 8.31Å and Θ_c = 620°C).

Of more interest is the work reported by Pouillard (1950)
in which he is able to relate the magnetic iron-titanium oxides
of many natural minerals to the complex solid solution which
occurs between iron-titanium spinel and Fe_3O_4.   Unlimited
solid solution is possible with a change of lattice parameter
and Curie temperature down to room temperatures.   However, in the
case of these materials there has been no evidence of a spinel-
like phase and this should have been detected at any rate in the
case of "magnetic ilmenite" by X-ray means.   If free magnetite

were present the Curie temperature of the materials should have
been much higher.

10. 5 Conclusion

From this brief review of the properties, it is apparent,
that with the data available it is impossible to give a
categorical statement of the reasons for the ferromagnetism
of ilmenite and magnetic ilmenite.   It appears that three
possible explanations need experimental and theoretical
examination

(a)   The possibility of substituted magnetite being present
        with l/ow Curie temperature.   This alternative is unlikely
        because:- (i) it has not been detected by X-ray
        investigation and (ii) from Pouillard's work it is
        unlikely that such a compound could be in equilibrium
        with the ilmenite and rutile phases.

(b)   The presence of γ Fe_2O_3 in a stabilised form with a much
        reduced Curie temperature.   This oxide should be detected
        by X-ray techniques at least in the magnetic ilmenite but
        it appears that this is not certain because many cases
        have been reported in which masked forms of γ Fe_2O_3 are
        the ferromagnetic agent.

(c)   The magnetism of ilmenite is similar to that of Fe_2O_3 which
        is due probably to some variation in the localised
        crystal pattern or to an ordered variation between the
        antiferromagnetic sub-lattices.   This is an effect which
        has not been satisfactorily decided.

At this stage of the knowledge of the magnetic behaviour
of ilmenite it is impossible to decide between the latter two

alternatives or to make a satisfactory explanation of the change of magnetic properties with heat treatment.

11   Summary of Theory of Magnetisation

11.1   Paramagnetism

It is proposed in this section to outline briefly some of the theoretical considerations which apply to the study of paramagnetism following in general the methods of L.F.Bates (1949)

It is assumed that the paramagnetic material is comprised of an assemblage of atoms between which there is negligible magnetic interaction.   Under these circumstances in the presence of an applied field $\underline{H}$ an effective field $\underline{F}$ ≈ $\underline{H}$ acts on each of the particles.   (At low temperatures in solids and liquids $\underline{F}$ may not be sufficiently near to the value $\underline{H}$).

The potential energy of a particle is

$$V = -\underline{\mathcal{M}} \cdot \underline{F} \qquad \ldots \ldots \ldots \ldots (11.1)$$

where $\underline{\mathcal{M}}$ is the magnetic moment per atom and each atom will tend to align itself parallel to $\underline{F}$ however this alignment is upset by the thermal agitation of the assemblage.

It is necessary to make use of information which was initially devised to account for the spectroscopic data of atoms and in magnetic deflection experiments of atomic beams in order to decide which directions of orientation of magnetic moment are allowed, relative to the impressed magnetic field. The vector models of spectroscopy give some information and a detailed quantum mechanical treatment has been followed by Van Vleck.   Following the simpler theory it may be shown that the magnetic moment of an assemblage of electrons in an atom

may be written in terms of a basic quantity, the Bohr magneton

$$\mu_B \;=\; \frac{eh}{4\pi m} \;=\; 0.92712 \times 10^{-20} \text{ e.m.u.}$$

(e = electronic charge, m electron mass, h = Plancks' constant)
Two cases are distinguished on the simple vector theory of
spectroscopic multiplets.

(a) Where the applied field is small the coupling is such
     that the quantum numbers L and S combine to give a
     resultant J. (which is equivalent to a wide multiplet).
     The possible orientations of the atoms relative to the
     magnetic field being measured by M_J = -J, -J + 1, ...,
     J + 1, J.   Under these circumstances it follows that the
     magnetic moment is $J_g \mu_B$ (g being the Lande splitting
     factor).

$$g = 1 + \frac{J(J + 1) + L(L + 1) - S(S + 1)}{2J\,(J + 1)} \quad \dots \; (11.2)$$

while the magnetic potential energy is $-M_J g \mu_B H$.

   If we assume that the atoms in the assemblage are
divided among the possible potential energy values
according to the Maxwell-Boltzmann statistics the number
of atoms possessing a given quantum number M_J will be
proportional to exp $(M_J g \mu_B H/k_T)$ where k = Boltzmann's
constant and T is the absolute temperature.

   Considering an assemblage of N atoms there will be no
resultant magnetic moment perpendicular to the magnetic
field but parallel to the field the moment will be I_H
where

$$\underline{I}_H = N \frac{\text{sum of the moments of all the atoms}}{\text{total number of atoms}}$$

$$\underline{I}_H = N \frac{\sum\limits_{-J}^{+J} M_J g \mu_B \exp(M_J g \mu_B / kT)}{\sum\limits_{-J} \exp(M_J g \mu_B / kT)} \quad \dots 11.3$$

$$+ \frac{N g \mu_B \sum\limits_{-J}^{+J} M_J (1 + M_J g \mu_B / kT)}{\sum\limits_{-J}(1 + M_J g \mu_B / kT)} \quad \dots 11.4$$

Where the second term is small, which will be the case

at ambient temperatures for fields normally encountered

in these experiments. The denominator reduces to $2J + 1$

while the summed term in the numerator reduces to

$$0 + \frac{2 g \mu_B H}{kT} \cdot (J^2 + (J-1)^2 + (J-2)^2 + \quad - \quad)$$

$$= 0 + \frac{g \mu_B H}{kT} \cdot \frac{J(J + 1)(2J + 1)}{3}$$

$$\therefore \underline{I}_H = \frac{N g^2 \mu_B^2 H \, J(J+1)}{3kT} \quad \dots 11.5$$

But by definition $\underline{I}_N / \underline{H} = \chi_m$

hence $\chi_m = \dfrac{N g^2 \mu_B^2 \, J(J+1)}{3kT}$

$$= \frac{N^2 p_{eff}^2 \mu_B^2}{3RT} \quad \dots 11.6$$

where p_{eff} = effective magneton number of the system

and $p_{eff} = g\sqrt{J(J+1)}$

These conditions are fulfilled in some rare earth atoms

and 11.6 holds accurately and the Curie Law applies.

In this case the multiplet separation is large and there

is relatively low population of atoms in the higher energy

states.

(b)　　　When the multiplet separation is small and the energy

to cause atoms to change to higher state is small

i,e, the L & S coupling is small which is equivalent to

the strong field Zeeman splitting, the two magnetic

quantum Nos. M_L and M_S must be used i.e. orbital and spin

moments are separately quantised and $g_L = 1$, $g_S = 2$.

$$I_H = N\mu \left\{ \frac{\sum_{-L}^{L} M_L \exp M_L \mu_B H/kT}{\sum_{-L}^{L} \exp M_L \mu_B H/kT} + \frac{\sum_{-S}^{S} 2 m_S \exp 2m_S \mu_B H/kT}{\sum_{-S}^{S} \exp 2m_S \mu_B H/kT} \right\}$$

Assuming again $m_L \mu_B H << kT$

$$I_H = \frac{N\mu_B}{kT} \left\{ \frac{1}{3} L(L+1) \mu_B H + \frac{4}{3} S(S+1) \mu_B H \right\}$$

$$\therefore \chi_m = \frac{N^2 \mu_B^2}{3kT} \left\{ L(L+1) + 4 S(S+1) \right\} \quad \ldots \ldots 11.7$$

This again gives a Curie Law with a different value

of p_{eff} which applies in some cases to the iron group

of transition metals in ionic state.

There are intermediate cases which have been calculated

e.g. by Van Vleck (1932) in which the Curie Law does not

apply.

When the temperature is reduced to very low values and

strong magnetic fields are used, the approximation used

above is inadmissable and saturation effects are observed.

Let $a = Jg\mu_B H/kT$ and $x = a/J$.

Then equation 11.3 goes into the form

$$I_H = Ng\mu_B \sum_{-J}^{J} m_J \exp m_J x \bigg/ \sum_{-J}^{J} \exp m_J x$$

$$= Ng\mu_B \frac{d}{dx} \cdot \ln \sum_{-J}^{J} \exp m_J x$$

$$= Ng\mu_B \frac{d}{dx} \cdot \ln \left\{ \frac{\exp Jx \cdot (1 - \exp[-(2J+1)x])}{1 - \exp(-x)} \right\}$$

$$= Ng\mu_B \frac{d}{dx} \cdot \ln \left\{ \frac{\exp[(J+\frac{1}{2})x] - \exp[-(J+\frac{1}{2})x]}{\exp x/2 - \exp(-x/2)} \right\}$$

$$= Ng\mu_B \frac{d}{dx} \cdot \ln \frac{\sinh(J+\frac{1}{2})x}{\sinh x/2}$$

$$= Ng\mu_B \frac{\sinh\frac{x}{2}}{\sinh\frac{2J+1}{2}x} \cdot \left[\frac{2J+1}{2}\cdot\frac{\cosh\frac{2J+1}{2}x}{\sinh\frac{x}{2}} - \frac{1}{2}\frac{\sinh\frac{2J+1}{2}x\,\cosh\frac{x}{2}}{\sinh^2\frac{x}{2}}\right]$$

$$= Ng\mu_B J\left[\frac{2J+1}{2J}\coth\frac{2J+1}{2J}a - \frac{1}{2J}\coth\frac{a}{2J}\right]$$

$$\therefore \frac{I_M}{Ng J\mu_0} = \frac{2J+1}{2J}\coth\frac{2J+1}{2J}a - \frac{1}{2J}\coth\frac{a}{2J}$$

$$= \frac{\bar{\mu}}{\mu} = B_J(a) \qquad\qquad \ldots\ldots 11.8$$

which results in a saturation effect. e.g. μ v H/T
curves obtained by Henry (1952) are in good agreement
with equation 11.8 and at 40,000 oersteds the saturation
is higher than 99.5%

$B_J(a)$ is referred to as Brillouin function.

When $J \to \infty$, $\frac{\bar{\mu}}{\mu} = \coth a - \frac{1}{a}$ which is in agreement
with classical results.

In the case of the iron group ions it is found that
equation 11.7 does not apply as it stands but that

$$P_{eff} = \sqrt{4S(S+1)} \qquad \ldots\ldots 11.9$$

more nearly fits the experimental data.

This requires that the orbital motion make no contribution
to the magnetic moment of the atom. In this case the orbital
motion is said to be quenched. This situation may arise when a
perturbing electrostatic field is superimposed on the central
field of the atom. However it is seldom that the orbital
motion is completely quenched e.g. in case of Mn^{+3}, Cr^{+2}, Fe^{+3},
Mn^{+2}.

In the case of ilmenite the following data are useful.

TABLE 11.1 - DATA TAKEN FROM KITTEL "INTRODUCTION TO SOLID STATE PHYSICS"

Ion	Configuration	Basic Level	P_{eff} $g\sqrt{J(J+1)}$	P_{eff} $g\sqrt{S(S+1)}$	P_{eff} (Exptl.)	g (Exptl)
Ti^{+3}	$3d^1$	$^2D_{3/2}$	1.55	1.73	1.8	-
Mn^{+3}	$3d^4$	$^5D_0$	0	4.90	4.9	2.0
Fe^{+3}, Mn^{+4}	$3d^5$	$^6S_{5/2}$	5.92	5.92	5.9	2.0
Fe^{+2}	$3d^6$	$^5D_4$	6.70	4.90	5.4	2.2
Ti^{+4}	Non Magnetic					

As mentioned above 10.1 pure synthetic crystals give magnetic susceptibility-temperature curves consistent with the assumption that the iron is Fe^{+2} while the titantium is present as Ti^{+4} and the equation χvT is given above following a Curie-Weiss Law and not the simple Curie Law as predicted by the theories above. The restricted nature of the assumptions are such that many exceptions must be expected. However the simple theory as outlined has many useful applications and many materials follow the Curie Law as derived.

11.2 Molecular Fields

The theory of ferromagnetism is as yet in a somewhat uncertain position and although more or less rigorous quantum mechanical theories exist which explain the possible existence of ferro-magnetic phenomena, it is necessary in any complex crystalline system as the iron oxides and the ferrites to rely on a phemonological approach similar to that adopted by Weiss.

In these circumstances it is assumed that within a crystal the atoms are located in regions of intense localised magnetic fields.   Associating a spin $\underline{S}$ with the atom, the interaction energy between the atom and the local field $\underline{h}_m$ given an interaction energy of $gS\mu_B h_m$ which at the Curie point must be of the order of kT since the thermal agitation is then sufficient to overcome the magnetic interaction.

That is $gS\mu_B h_m \approx kT_c$

and for iron

$$T_c \approx 1000^0K, \ g \approx 2, \ S \approx 1$$

Therefore

$$h_m \approx \frac{k \ T_c}{gS\mu_B} \approx 5 \times 10^6 \text{ e.m.u.} \quad \ldots \ldots \ 11.10$$

This effective field has its origin in the exchange coupling between the electrons and the quantum mechanical explanation was first suggested by Heisenberg and is a result of the interaction of the coulomb field when electron orbits overlap and has no classical analogue.   As van Vleck states:-
"The exchange effect, though entirely orbital in nature, is, because of the exclusion principle, very sensitive to the way the spin is aligned, and is formally equivalent to cosine coupling between the spin magnets of the various atoms."

Several approaches have been developed in an attempt to obtain satisfactory theoretical interpretation of the exchange integral which usually gives rise to antiparallel arrangement of spins.   These include the band theory developed largely by Slater, collective electron theory of Stoner, the theory of superexchange due to Zener, Kramer etc.   These theories are

discussed at some length in Reviews of Modern Physics 1953, 25 191-227.

The potential energy term due to the spin interaction in ferromagnets is shown (Van Vleck, 1931) to be

$$V_i = -2 J_{ae} \, S_e \, S_a \qquad \ldots \ldots 11.12$$

where J_{ae} is the exchange integral.

In the case where J_{ae} is positive the spin alignment is parallel and spontaneous magnetisation results in ferro-magnetism. When J_{ae} is negative there may still be strong antiparallel spin alignments which will sometimes give rise effectively to two sub-lattices, magnetised to saturation in antiparallel directions, and resulting in no nett spontaneous magnetic moment and the anti-ferromagnetic state.

Occasionally it may happen that periodic fluctuations in the crystal lattice due to vacant ion sites or aggregates of ions may cause uncompensated antiferromagnetism which may be a partial explanation of weak ferromagnetism in some of the iron oxides. This alternative is as yet a tentative explanation and the rigorous treatment is very difficult.

Consequently, it appears that with such materials as ilmenite the approach devised by Neel for ferrites would be the most satisfactory. Hence a brief outline of the Neel approach is given.

11.3 Neel's Theory of Magnetism in Ferrites

In a theoretical discussion Neel (1948) has developed a comprehensive treatment of the magnetisation of ferrites which may be extended to other materials in which there exists a

crystallographic sub-lattice as for example may exist in
ilmenite where the titanium and iron ions occupy definite
crystallographic sites.

Neel postulates a gram molecular moment $\underline{M}_a$ and $\underline{M}_b$
associated with atoms on A sites and on B sites respectively.
The A sites refer to positions where ions are surrounded by
4 oxygen atoms and the B sites are surrounded by 6 oxygen atoms.
Neel assumes, in agreement with experiment, that ions which
act as carriers of magnetic moment may exist on both sites.
Let λ be the fraction of magnetic ions on A sites and μ the
fraction of these ions on B sites.   Thus $\lambda + \mu = 1$
Suppose the constants α, β are constants of interaction between
ions within the A sites or B sites respectively. α, β are
positive for ferromagnetic coupling and negative for anti-
ferromagnetic coupling.   Let ϵ be the coupling constant
between the A and B groups of ions. ϵ also will be positive
for ferromagnetic and negative for antiferromagnetic coupling
being $= 1$.   Also let $\underline{I}_a$ and $\underline{I}_b$ be the gram ion magnetisation
for atoms on A site and B sites respectively.

Then the equivalent molecular field $\underline{h}_a$ acting on an
ion on an A site is assumed to be given by

$$\underline{h}_a = n\left(\alpha\lambda\underline{I}_a + \epsilon\mu\underline{I}_b\right)$$

and

$$\underline{h}_b = n\left(\beta\mu\underline{I}_b + \epsilon\lambda\underline{I}_a\right)$$

.... 11.13

The A and B sites have different magnetisations in
general and consequently the average gram-ion magnetisation $\underline{I}$
is given by

$$\underline{I} = \lambda\underline{I}_a + \mu\underline{I}_b \qquad \ldots\ldots 11.14$$

Now if $\underline{h}_a$ is proportional to $\underline{I}_a$ in accord with Weiss' assumption and a Curie law applies above the Curie temperature we have an effective magnetic field for the A site atoms

$$\underline{I}_a = \frac{C_a}{T}\left[\underline{H} + \underline{h}_a\right]$$

$$\underline{I}_b = \frac{C_b}{T}\left[\underline{H} + \underline{h}_b\right] \qquad \ldots \ldots 11.15$$

where $\underline{H}$ is the external applied magnetic field. That is

$$\underline{I} = \frac{\lambda C_a}{T}\left(\underline{H} + \underline{h}_a\right) + \frac{\mu C_b}{T}\left(\underline{H} + \underline{h}_b\right)$$

hence from equations 11.13, 11.14, 11.15 and putting $C_a = C_b = T$
$\epsilon = \pm 1$ and $\lambda + \mu = 1$

$$\underline{I} = \frac{T(\lambda + \mu) - nC\lambda\mu(2 + \alpha + \beta)}{T^2 - nC(\lambda\alpha + \mu\beta)T + n^2 C^2 \lambda\mu(\alpha\beta - 1)} \cdot \underline{H} \ldots \ldots 11.16$$

which may be rewritten in the form

$$\frac{1}{\chi} = \frac{H}{I} = \frac{T}{C} + \frac{1}{\chi_0} - \frac{\sigma}{T - \theta} \qquad \ldots \ldots 11.17$$

$$\frac{1}{\chi_0} = n(2\lambda\mu - \lambda^2\alpha - \mu^2\beta)$$

$$\sigma = n^2 C \lambda\mu \left[\lambda(1+\alpha) - \mu(1+\beta)\right]^2$$

$$\theta = nC\lambda\mu\left[2 + \alpha + \beta\right]$$

$$\ldots \ldots 11.18$$

which represents a law of paramagnetism in which the third term represents a departure from the Curie-Weiss law resulting in a concave curve to the temperature axis.

This curve meets the axis at the value of $\theta = \theta_p$ where θ_p = paramagnetic Curie Temperature. If this temperature is positive, spontaneous magnetisation results. If ϵ is negative there is a special type of magnetisation referred to as "ferrimagnetism" for which a number of variations may be

distinguished giving rise to different laws of variation of saturation magnetisation with temperature below the Curie Temperature (Neel, 1948; fig. 7).

In the region of spontaneous magnetisation the Weiss Theory adopts the expression 11.8 to give saturation magnetisation

$$I_s = M B_J \left(\frac{MH}{RT} \right)$$

where $\underline{M}$ is the saturation gram-ion magnetisation and $\underline{H}$ is the effective field, B_J = Brillouin Function. Hence in this case the magnetising fields are $\underline{h}_a$ and $\underline{h}_b$ for the ions on two types of sub lattices and hence

$$I_{as} = M B_J \left(\frac{Mh_a}{RT} \right) \quad \text{and} \quad I_{bs} = M B_J \left(\frac{Mh_b}{RT} \right). \quad \ldots \ldots 11.19$$

where the values of $\underline{h}_a$ and $\underline{h}_b$ are determined above and depending on the parameters, Neel is able to distinguish the various type of ferrimagnet.

This treatment is also applicable directly to the discussion of antiferromagnetism and this state arises naturally when $\lambda = \mu = 0.5$, $\epsilon = -1$ and it is necessary only to have atoms situated on different sites magnetically, the sites being arranged in an ordered fashion.

Here $\underline{I}_a = \underline{I}_b$, $\lambda = \mu = 0.5$, $\epsilon = -1$ $C_a = C_b$

and hence we have from 11.13, 11.15

$$I_a = \frac{C}{T} \left[H + \frac{n}{2} I_a (\lambda - 1) \right]$$

$$I_b = \frac{C}{T} \left[H + \frac{n}{2} I_b (\lambda - 1) \right] \quad \ldots \ldots 11.20$$

remembering that at high temperatures that the magnetic field tends to line the magnetic moments parallel to the field and

hence $\underline{I}_a$, $\underline{I}_b$ and $\underline{H}$ are all parallel and simple addition applies

Let $\underline{I} = I_a + I_b = 2I_a$

$$\therefore \frac{T}{C}\underline{I} = 2\underline{H} + \frac{\nu}{2}\underline{I}(\alpha-1)$$

$$\underline{I}\left[\frac{T}{C} - \frac{\nu}{2}(\alpha-1)\right] = 2H.$$

$$\therefore \chi_m = \frac{C/2}{T+\theta} \qquad\qquad \cdots\cdots 11.21$$

where $\theta = \frac{1}{2}\nu\, C\,(1-\alpha)$ $\qquad\qquad \cdots\cdots 11.22$

Thus the asymptotic Curie Temperature will be negative

so long as $\alpha < 1$ i.e. so long as the interaction between atoms

on the A sites are small compared with the A - B interactions.

Below the Curie Temperature there will exist spontaneous

magnetisation of both lattices and $\underline{I}_{as} = \underline{I}_{bs}$ at all temperatures

and hence at $T=0$ this requires that $T = \frac{\nu C}{2}(\alpha-1)$ which is known

as the transition temperature. However in practice this is not

found to be true and other than nearest neighbour interactions

have been considered by Anderson (1950) and better agreement is

reached.

Below the transition temperature it is possible to

calculate the values of the susceptibility parallel to and

perpendicular to the applied field. The presence of interaction

between the atoms in an antiferromagnet lead to the presence of

specific heat and expansion anomalies at the transition

temperature.

Further experimental data must be sought before these

theories could find application to the ilmenite crystals, however

the tendency for the paramagnetic curves of these materials to

show non linear relationships at high temperatures indicates

that a type of magnetisation as outlined above could apply.
Unfortunately the data is sparce at elevated temperature and
curvature of the $\frac{1}{\chi} \backsim$ Temperature relation could indicate the
presence of some magnetite. It is necessary to convert the
ring balance for paramagnetic observations and to carry out
careful high field measurements before the evidence could be
evaluated. The iron titanate shows a similar non linear
$\frac{1}{\chi} \backsim T$ curve which also may be attributable to ferrous ions.

11.4 The Curie Temperature

Incidental to the investigations described above   4.4
designed to test the desirability of separation of the minerals
in beach sand ilmenite at other than room temperatures, the
thermomagnetic curves revealed certain well defined Curie Points
which suggest the cause for the magnetic interactions.

It is a well known fact that the determination of the
Curie Temperature is a valuable guide in magnetic analysis
but it is well to enumerate some of the difficulties arising in
the interpretation of the curves.

The shape of the magnetisation
and temperature curves depend markedly
on the magnitude of the field in which
the determination is made and figure 11.2
gives the general behaviour of these
curves for various values of magnetising
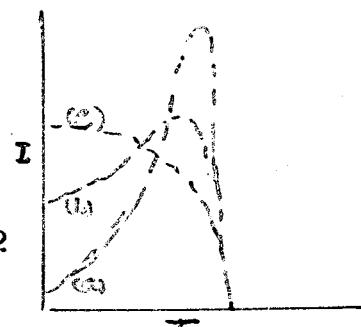field (H) relative to the coercive force
(H_c).

Fig 11.2 Shape of I~T curves

(a) $H \ll H_c$
(b) $H < H_c$
(c) $H > H_c$

There have been determinations of thermomagnetic curves
by methods employing both high and low field.   Hoselitz

"Ferromagnetic Properties of Metals and Alloys" favours using high fields in which there can be no doubt that the specimen is saturated while Chevallier and Nagata have used low fields in work on magnetisation of rocks.

Although these methods allow an approximate location of the point at which I_s reaches low values it must be remembered that theoretically it is desirable to locate three Curie temperatures which seldom agree. There is the ferromagnetic Curie Temperature at which $I_s \to 0$, the Curie temperature at which $\eta_c \to 0$ and finally the paramagnetic Curie Temperature at which $\frac{1}{\chi} \to 0$. In the case of magnetic analysis the former is usually adopted and is characteristic of pure phases or compounds. The solution of other atoms in compounds however has a very noticeable effect on the Curie point and it is possible to find substituted magnetites with Curie points from room temperature to 675°C. Also γ Fe_2O_3 shows extremely complex behaviour.

Nevertheless as a preliminary investigation much may be gained from thermomagnetic analysis, particularly if a complete pattern $\sigma \sim H$ is obtained for a series of temperatures see Bates p.261. In addition, if the curve $\frac{d\sigma}{dH} \sim T$ is obtained the location of small amounts of ferromagnetic phase is improved. For the purpose of this survey such elaborate investigation is not necessary but if a complete analysis of the magnetic properties of ilmenite were undertaken such measurements would be valuable.

$\sigma = \frac{I}{\rho}$ where ρ= density.

Conclusion

From the point of view of mineral ore dressing the experiments have proved very satisfactory providing a method by which adequate separation may be achieved of:-

(a)   An ilmenite fraction containing much less than 0.1 per cent chromic oxide which is the allowable upper limit for pigment manufacture.

(b)   An enriched ore containing approximately 18 per cent chromic oxide.

This work has not entailed a thorough study of the economic situation and several points require consideration by plant operators.

(a)   Is the ilmenite saleable with 0.2 per cent chromic oxide contamination or must the rather costly roasting process be used?

(b)   Is the roasting contributing to the insolubility of the ore?

(c)   Is the chromic oxide enriched ore marketable?

If both components are marketable a small subsidiary ore dressing plant involving a McLean or Rapid type separator and possibly a furnace should be a sound investment.   It must be recalled that the full 15 minutes roasting is probably unnecessary.

The theoretical side of the problem is at this stage in an unsatisfactory state.   Further studies could profitably be made on compacted samples at high temperatures and at low temperatures.   In addition it is necessary to perform measurements on single crystals of ilmenite and ilmenite which

has been converted to "magnetic ilmenite" It has been shown
that such conversion occurs in natural ilmenite from Egersund
when roasted for prolonged periods in air at temperatures in
excess of $900^{\circ}C$. Such data may allow of an interpretation
of the magnetic properties of the ilmenite. Further X-ray
studies could profitably be made in order to establish the
crystal structure with greater precision.

The other puzzling feature of the problem which needs
further investigation is why the ilmenite lattice is so readily
oxidised and what is the mechanism of the oxidation.

These investigations proposed are essentially of a
theoretical interest and it is unlikely that they would contribute
additional information on the technical problems facing the
Beach Sand Industry.

Reference should be made to the work on similar lines
which has been undertaken at the C.S.I.R.O. Ore Dressing Section
in Melbourne, more or less simultaneously with this work. In
general the conclusions are in agreement and investigations into
the effects of roasting ilmenite in atmospheres other than air
and hydrogen are being considered in detail. These experiments
may contribute to the knowledge of the problem of high temperature
transitions. Details of the preliminary investigations are
contained in the Progress Report 461.

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