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TECHNICAL NOTE 5.

Preparation of Single Crystals of Yttrium Gallium Garnet and Yttrium Aluminium Garnet, and Investigation of Paramagnetic Resonance Spectra of four Rare Earth ions in these Garnets.

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** Work carried out as a partial requirement for the degree of Bachelor of Science, Oxford University, November 1960.

ABSTRACT

This report summarizes the first results of an extensive survey of the magnetic properties of rare earth ions in crystals with the garnet structure. Methods of preparing suitable samples are described, and results of low temperature microwave resonance experiments with Yb^{3+}, Dy^{3+}, Er^{3+}, and Nd^{3+} ions are given. For each of these ions, the ground state is a doublet which can be characterized by three principal values of a g tensor, and with one exception, all the principal values have been determined for these ions in both yttrium aluminium and yttrium gallium garnet.

Comparison of the two sets of results shows that great care must be exercized in applying the results of resonance experiments for one kind of garnet to a seemingly similar case, but some general conclusions can be drawn, even without the necessary detailed analysis. The main result is that the local environment of the rare-earth ions is far from being spherically or cubically symmetrical, so that the individual rare earth ions have magnetic properties which are very anisotropic. The relation of these results to the observed anisotropies in rare earth iron garnets and rare earth doped YIG are discussed.

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1. Introduction

1.1. The general programme.

This report describes the successful completion of the first two phases of an extensive programme of research into the properties of rare earth ions in garnet crystals. The first of these was the preparation of single crystals of diamagnetic yttrium aluminium and yttrium gallium garnets, for use as hosts in the study of the magnetic rare earth ions. Under conditions of high magnetic dilution the properties of the magnetic ions depend only on their electrostatic environment, and this should be very similar in garnets all having the same structure, even if they contain ions of different types. If this is so, any information about the electronic states obtained in "dilute" crystals should also apply when the ions are part of a magnetically concentrated assembly, so that data obtained on lightly "doped" diamagnetic garnets may be used to explain the properties of ferrimagnetic rare earth iron garnets. The particular properties of the ferrimagnetic garnets which one may hope to account for in this way are the spontaneous magnetization, the anisotropy, and possibly also some of the relaxation processes which control microwave resonance line widths. The importance of rare earths, even if present only in minute quantities (of the order of a few parts per million), has recently been demonstrated empirically by Dillon and Nielsen (1959, 1960).

There are several ways in which the properties of magneti-

cally dilute ions can be investigated. In this report we describe the first set of results which we have obtained using microwave paramagnetic resonance, while later reports will deal with the results obtained from susceptibility and specific heat measurements. Ultimately, all these data will be combined in terms of a unified theoretical model, but even before this is complete we can draw several interesting conclusions from the resonance measurements alone. We therefore present these here in the form of an interim report.

1.2. Paramagnetic resonance in rare earth ions

The theory of the magnetic properties of rare earth ions in crystals has been dealt with at length by various authors, notably by Elliot and Stevens (1953). In rare earth compounds the effect of the electric field due to the neighbouring ions is in general small compared with the spin-orbit coupling, because of the shielding of the magnetic electrons by outer closed shells of 5s and 5p electrons. The states of an ion are then characterized by quantum numbers $J(= L \pm S)$ and M, where in general M is an admixture of several states of J_z depending on the crystal symmetry. If the point symmetry is low, as it is in the case of the garnets, the $2J + 1$ fold degeneracy of the free ion ground state is removed to the maximum extent allowed. In the case of ions with an even number of electrons, (integral J), this leads to $2J + 1$ singlet states separated by energies of the order of 10 to 100 cm^{-1}, for which no paramagnetic resonance can therefore be observed at

microwave frequencies.

For ions with an odd number of electrons, on the other hand, Kramers' theorem (reflecting time reversal symmetry) predicts that in the absence of a magnetic field all states will be at least two-fold degenerate. When a magnetic field is applied, these doublet states are split, and for fields of the order of a few Kilōoersted resonance may be observed at microwave frequencies. The splitting ΔE is directly proportional to the field H, and may be characterised by an "effective spectroscopic splitting factor" g, defined by

$$\Delta E = g\beta H,$$

where β is the Bohr magneton, g is *in* general anisotropic, reflecting the point symmetry at the rare earth site, and values ranging from zero to about 18 have been observed. Defined in this way, g is therefore a very different quantity from the free electron spin g value, which is close to 2. The large range of values, which are frequently observed even in a single ion, arise from the strong admixtures of different J_z states produced by the crystal field, and they indicate how intimately the properties of any particular ion depend on the nature of the environment in which it is situated.

In making measurements on 'dilute' compounds, with a view to applying the results to 'concentrated' compounds with a somewhat different composition, it is necessary therefore to investigate how critically the magnetic properties depend on small changes of environment. This we have done in the present case by measuring

each ion in both an aluminium and a gallium garnet, and comparing the principal values of the observed g tensor. In two cases (Yb and Nd) very similar results were found, but in two other cases (Dy, Er) very marked differences were observed. The nature of the differences will be described below, but even from the qualitative result one can conclude immediately that the electronic states of Yb^{3+} and Nd^{3+} * will probably be very similar in the iron garnet to those measured in the diamagnetic garnets, while those of the two other ions will require careful interpretation. The full significance of the Yb results will be discussed in a later theoretical report, of which a brief, preliminary version has already been published. (Wolf, 1959).

1.3 Experimental Method.

The equipment used in this work was almost entirely constructed in this laboratory. The spectrometer was of the standard transmission type operating at a frequency of 9.7 Gc/s. The cavity was cylindrical, resonating in the TE111 mode. The steady magnetic field was variable from 0 to 6Kgauss and was modulated at 50 c/s. The spectrometer could be used at temperatures between room temperature and $2^{\circ}K$. Detection was by a rectifying crystal whose output was displayed on an oscilloscope after passing through a

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* Although 100% Nd iron garnet does not form, garnets with composition of up to 50% Nd in yttrium iron garnet have been made. (Bertaut and Forrat, 1956).

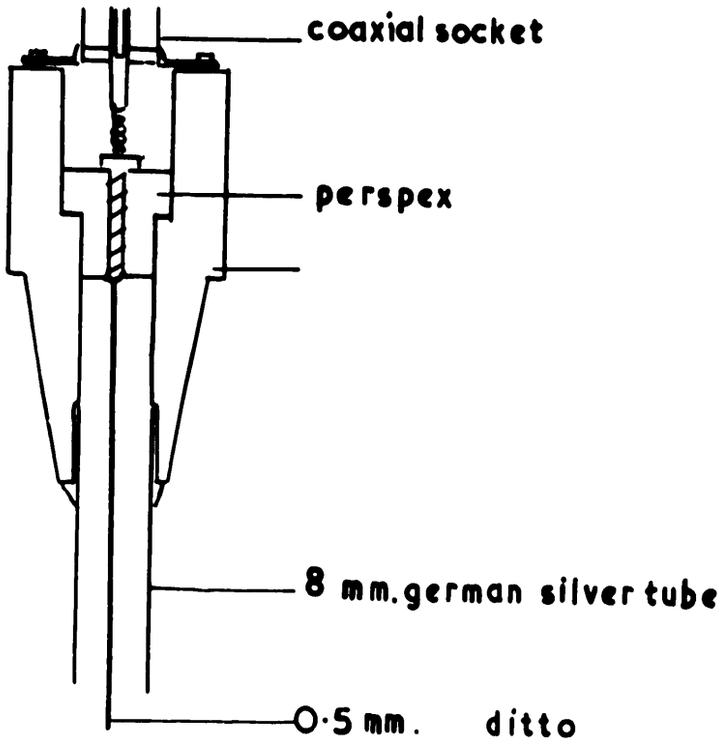

coaxial socket
perspex
8 mm. german silver tube
0·5 mm. ditto

FIG. 1

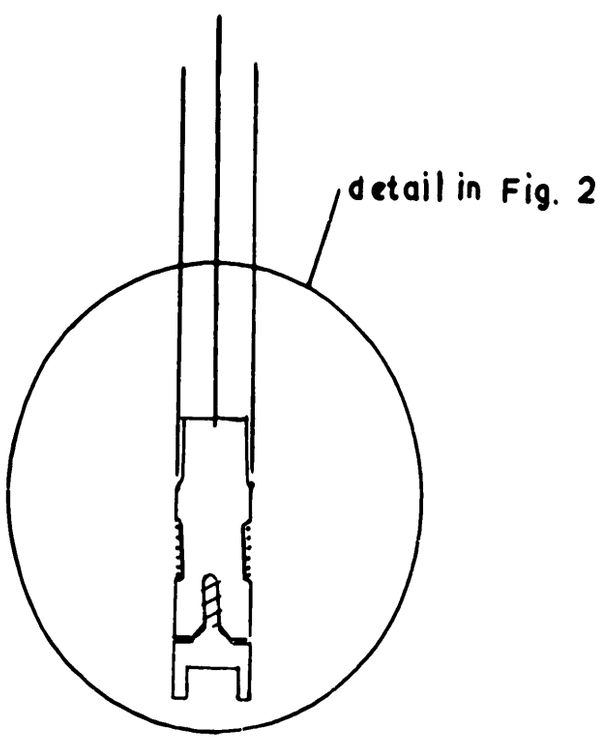
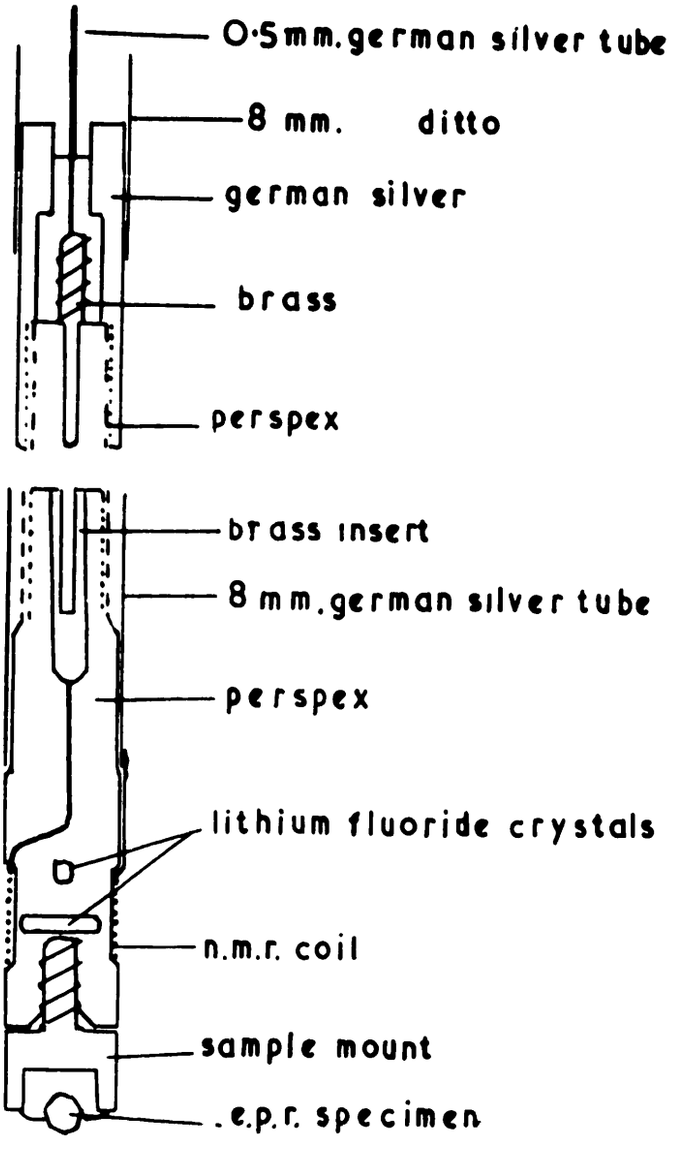

detail in Fig. 2

FIG.2


0·5mm. german silver tube
8 mm. ditto
german silver
brass
perspex
brass insert
8 mm. german silver tube
perspex
lithium fluoride crystals
n.m.r. coil
sample mount
e.p.r. specimen

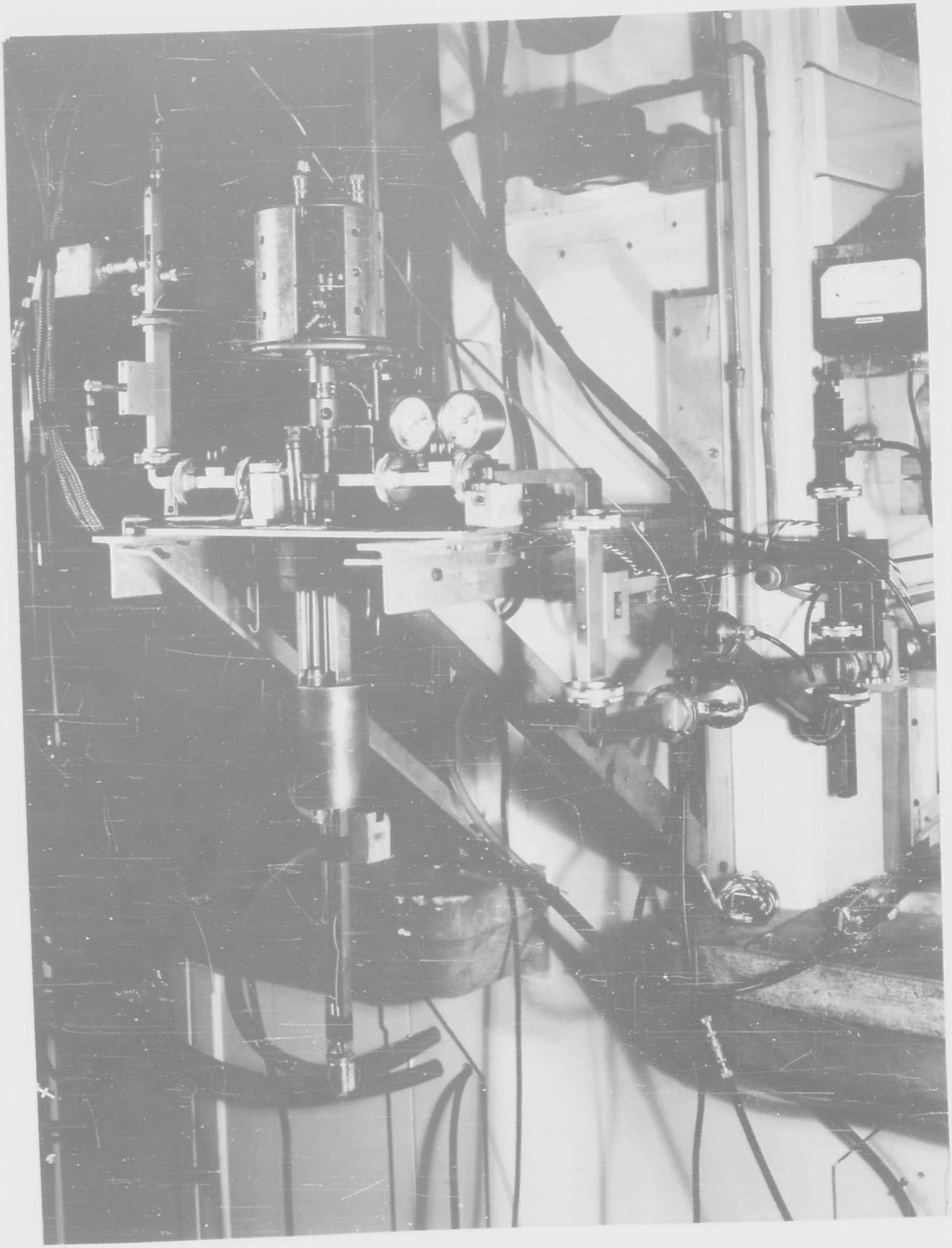
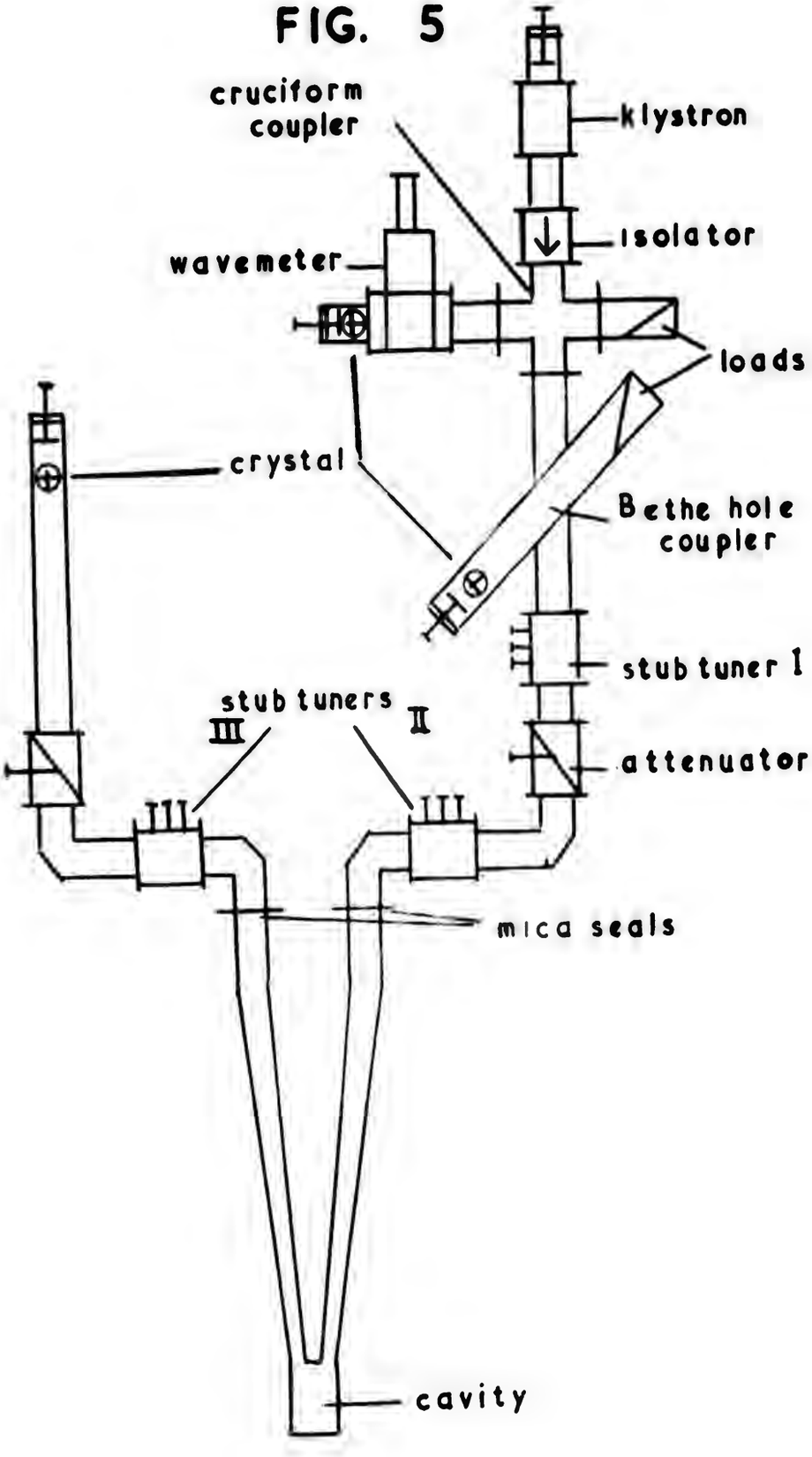


FIG. 5


cruciform coupler
klystron
isolator
wavemeter
loads
crystal
Bethe hole coupler
stub tuner I
stub tuners
III
II
attenuator
mica seals
cavity

video-amplifier. The magnetic field at the sample was measured by nuclear magnetic resonance techniques, using a circuit developed in this laboratory by Robinson (1959).

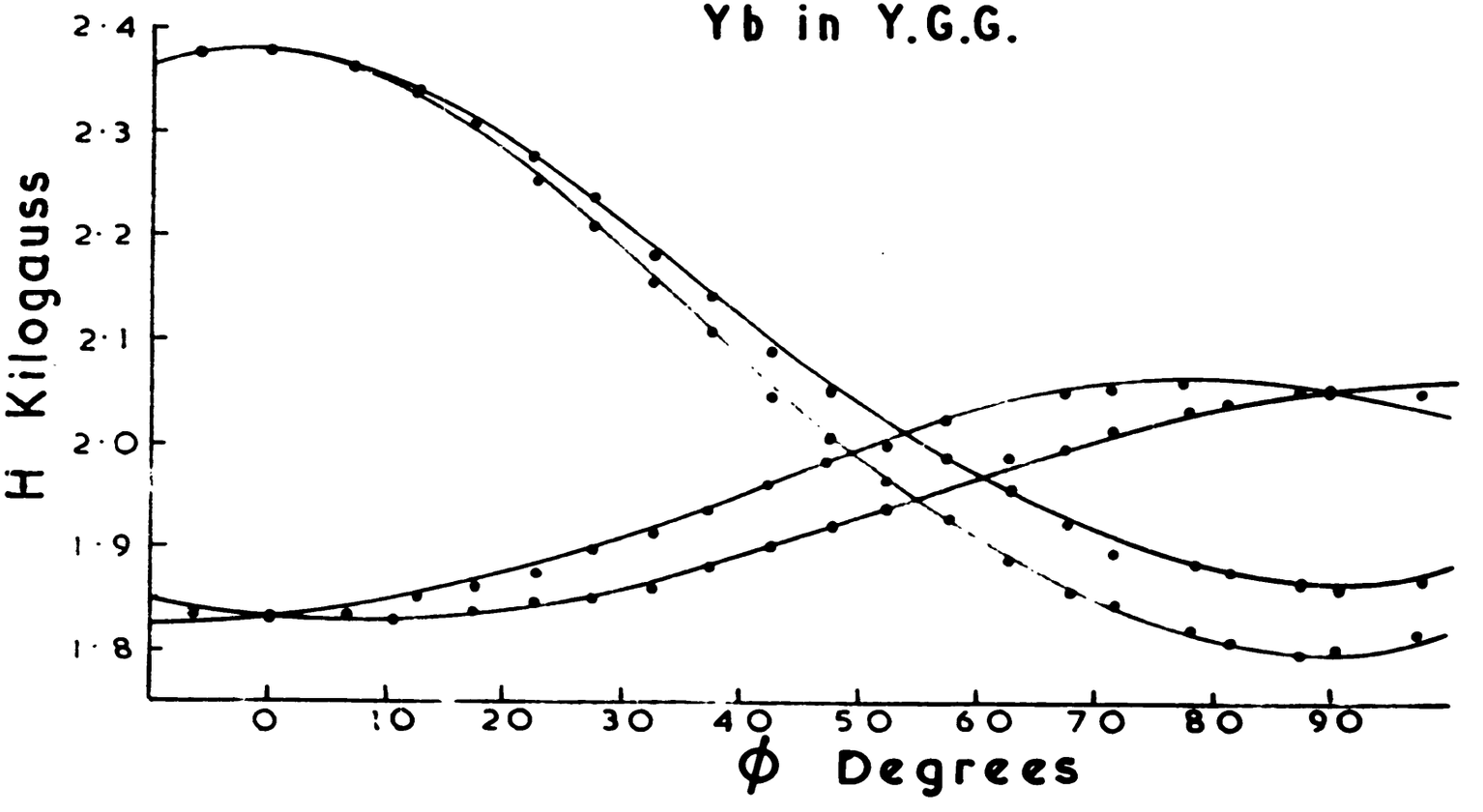
Great care had to be exercised in the orientation and mounting of the samples. In order to preserve this orientation it was necessary to design and construct a rod on which the oriented and mounted sample could be inserted into the cryostat. This was finally achieved by the design illustrated in Figs. 1 and 2. As these drawings show this rod also served as a coaxial lead to the probe coil used on the nuclear magnetic resonance field meter. The samples used for the magnetic field measurement were protons, present in the perspex (lucite) former and Li^7 nuclei present in single crystals of lithium fluoride.

Figs. 3 and 4 show photographs of the apparatus, as used in an experiment at room temperature and with the two dewar vessels necessary for an experiment at liquid helium temperatures. Fig. 5 is a block diagram of the microwave equipment used.

To plot out the anisotropic spectrum of an oriented sample - that is the variation of resonant field with the angle between the field and the crystal axes - the following steps were followed. The oriented specimen was inserted into the cryostat and this was cooled to the required temperature using the standard cryogenic techniques. Starting at one of the important crystal axes the resonant field for each line in the spectrum was measured. The magnet was then turned through an angle of 5° and the fields

measured again. This was repeated until sufficient measurements had been obtained for the anisotropy of the spectrum to be deduced. The garnet structure is cubic and the spectra of crystals oriented so that the magnetic field was always in the [110] plane were investigated. In such a situation it is necessary only to take measurements over a range of about 100^{o}, since the spectrum is repeated every 90^{o}. This is illustrated by a typical set of results, as shown in Fig. 6.

FIG. 6


Yb in Y.G.G.
H Kilogauss
2·4
2·3
2·2
2·1
2·0
1·9
1·8
0
10
20
30
40
50
60
70
80
90
φ Degrees

2. Sample Preparation.

2.1 Method of growing the crystals.

Single crystals of yttrium gallium ($Y_3Ga_5O_{12}$) and yttrium aluminium garnet ($Y_3Al_5O_{12}$) were grown by an adaptation of the method described by Nielsen (1959).

Nielsen's method for growing single crystals is to cool slowly a solution of the constituent oxides in a fused mixture of lead oxide and lead fluoride in an atmosphere of oxygen. For growing yttrium gallium garnets, the recommended composition of the melt is:-

PbO	39.4 mole%
PbF_2	40.8 mole%
Ga_2O_3	14.8 " "
Y_2O_3	5.8 " "

The crystals used in the resonance studies had a small percentage of rare earth oxide substituted for the yttrium oxide. Ball (1960) found that similar molar proportions, substituting aluminium oxide for gallium oxide, gave reasonable yields of yttrium aluminium garnet. These yields were in general lower than for the gallium garnets, and some experiments were performed to try to improve the yield. The composition of the melt was changed in various ways, and cooling was commenced 75° higher than usual, but in none of these experiments was there any improvement in yield. It is possible that the lower yields are associated with the greater stability of aluminium oxide compared with gallium oxide, and the

lower stability of yttrium aluminium garnets, caused by the smaller ionic radius of aluminium.

Charges of between 150 and 300 grams were packed into 50ml or 100 ml platinum crucibles with tightly fitting lids. The crucibles were then set in holes in refractory bricks by means of an air-setting aluminous refractory cement, as shown in Fig. 7. This proceedure was intended to: -

i) facilitate removal of the crucibles from the furnace;

ii) smooth out temperature fluctuations by providing a large thermal capacity;

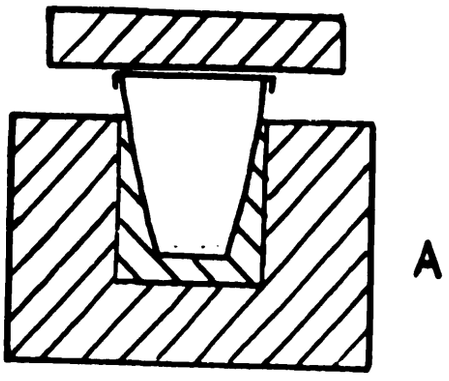
iii) protect the furnace fabric and elements from the flux in case of crucible failure;

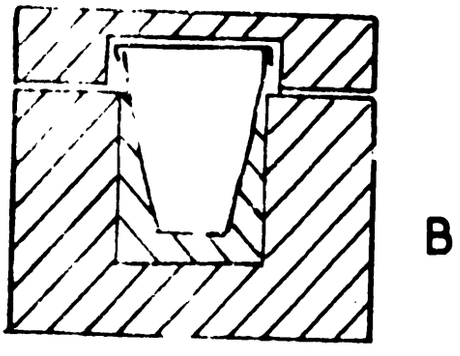
iv) provide adequate support for the platinum crucibles, which are subjected to considerable mechanical strain, and have little mechanical strength under the experimental conditions.

Firebrick lids were placed over the crucibles to prevent flakes of silicon carbide from the elements coming into contact with the flux or crucible, and to absorb lead compounds which volatilised during the experiment.

In earlier experiments (Boakes, 1959), the crystal growing programme was considerably delayed by repeated failure of the platinum crucibles, resulting in complete loss of charge in many cases. The possibility of physical failure was removed as described above, the other possibility being chemical attack.

The mechanism of chemical attack was probably alloying of





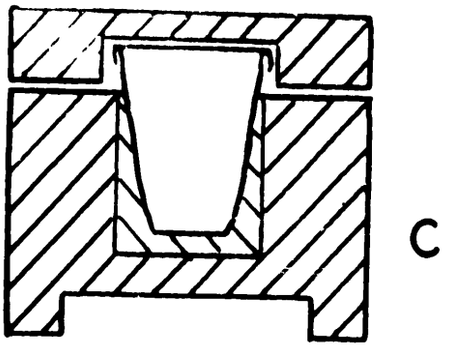


FIG. 7

the platinum with free lead in the melt. Any carbonaceous matter in the charge would reduce lead oxide to lead. Filter paper fibres, for example, might be present from previous processing of the charge. An oxygen atmosphere in the furnace was apparently insufficient to prevent reduction of the litharge to lead. The difficulty was overcome by maintaining the crucibles at about 460° for 10 hours in oxygen. This provided an opportunity for oxidation of any carbon present, and also partially converted the litharge to red lead. When the charge was heated further, the red lead decomposed to litharge and oxygen, providing an atmosphere of oxygen within the crucible from the start of the high temperature operations.

$$3PbO + \tfrac{1}{2}O_2 \rightleftharpoons Pb_3O_4$$

Platinum crucibles with twice normal wall thickness, i.e. 0.30 mm. instead of 0.15 mm. were used, as these were found to have a longer useful life.

The crucibles were heated to 1250°C for between 4 and 12 hours, and finally cooled to between 950 and 1000°C at a rate of approximately 3°C per hour. They were then allowed to cool naturally to room temperature.

The garnets were freed from the matrix mechanically, and were cleaned by boiling with 50% HNO_3.

From gallium experiments, the yields were of the order of 40 grams from a 475gm melt. Crystals weighing up to 5gm were obtained, but large crystals were almost invariably twinned, included some of

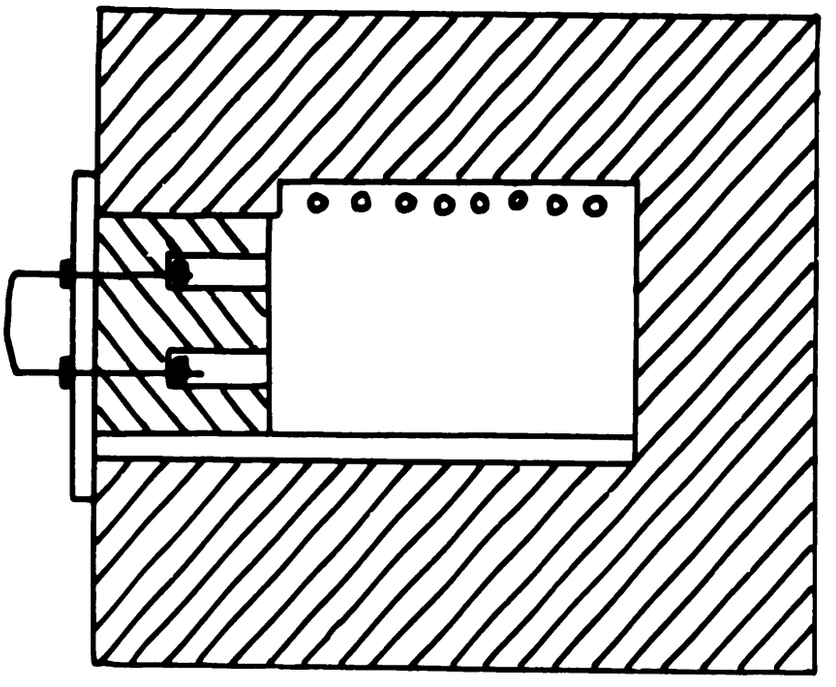
the melt, or were defective in some other way. There usually appeared to be three sites in the melt at which crystallisation took place. The largest crystals grew on the surface of the melt, and were generally pale brown and imperfect. The best crystals, few in number, grew in the body of the melt, and were often colourless. A large number of smaller crystals grew on the sides and bottom of the crucible, and apart from the face in contact with the metal, were generally well-formed. Their colour varied from pink to violet.

In one experiment, the crystals grew in a horizontal layer in the melt. Vertical and horizontal sections through the melt matrix in this case are shown in Fig. 8. Some experiments were carried out to determine whether the crystallisation sites were caused by temperature gradients between the atmosphere and floor of the furnace. These were, however, inconclusive. Details of these experiments may be found in Ball, 1960.

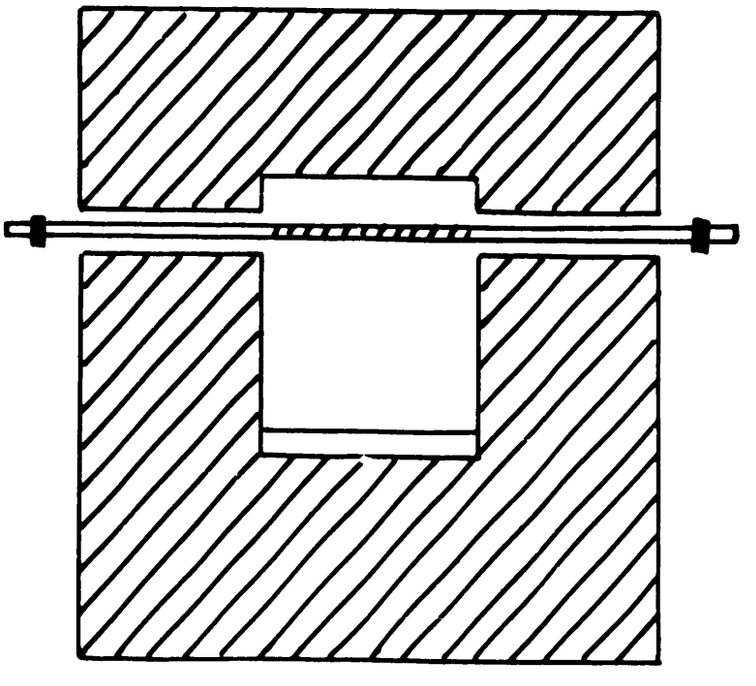
The yields from the aluminium melts were of the order of 8gm from a 300gm melt, the largest crystals being at least 5 times smaller than in the case of the gallium runs. The crystals grew in the same sites in the melts as the gallium compound, though relatively less surface crystallisation occurred. These crystals were usually colourless, and were morphologically more perfect than the gallium garnets.

In the case of the gallium garnets, the different sites for crystallisation in the melt produced different crystal habits.

FURNACE



sectional side elevation



sectional end elevation

FIG. 9

Crystals growing on the surface usually had some well-formed $\{110\}$ faces, but with mainly $\{211\}$ faces. Crystals growing in the body of the melt had almost exclusively $\{211\}$ faces with occasional small $\{110\}$ faces. Crystals growing on the crucible surfaces were never found with $\{110\}$ faces. The aluminium garnets on the other hand, grow almost entirely with $\{110\}$ faces; only occasional $\{211\}$ faces were observed.

2.2 Furnace and Control Equipment.

The success of the method described in producing good crystals of a suitable size for the resonance work was in no small measure due to the furnace and its control equipment, and these are described briefly below.

The furnace used was an experimental chamber furnace, heated by Crusilite ("Globar") silicon carbide elements. Basically, the furnace consisted of a box of refractory alumina bricks, cemented together. There were eight transverse heating elements, and there were two holes in the back of the furnace, one to admit a Pt/13% Pt,Rh thermocouple, and the other, an oxygen inlet tube. Sintered alumina hearth plates were used to minimise damage in case of crucible failure. There was a working space of 9" by 6" by 4". A diagram of this furnace is given in Fig. 9.

The elements were wired in two parallel series of four elements. Power was supplied from the control equipment (see below) via a 50B "Variac" variable auto transformer. This was adjusted to give maximum permissible current through the elements,

whose resistance slowly changes with age.

Power supply and temperature control were obtained from a "West Instruments" stepless temperature controller actuated by a cam-operated programme controller. This system eliminates temperature irregularities inherent in on-off type controllers, and containing no electronic devices apart from a photo-electric cell, was very reliable.

The control equipment was composed of three units:

a) Instrument

b) Driver unit

c) Reactor

a) In the instrument unit, the main device was an indicating millivoltmeter, calibrated in degrees Centigrade, which registered the output voltage from the furnace thermocouple. The cold junction was in an electrically heated thermostatic bath. A setting arm carrying a pointer was positioned on the temperature scale, either manually or by means of the movement of the programme cam. On this arm were a light source and a photocell, arranged so that the light fell on the sensitised surface of the cell. When the temperature, as registered by the thermocouple output on the millivoltmeter, approached the value shown by the set pointer, the light beam was interrupted by a vane attached to the meter needle, and the photocell current was reduced. The instrument also contained a slow-speed motor and gear system to drive the programme cam, and a primary magnetic amplifier for the photocell current.

The driver unit (b) provided a second stage of magnetic amplification, and suppled a D.C. current to the control winding of the saturable-core magnetic reactor (c). The magnitude of this current governed the output of the reactor to the Variac and elements. The input of the reactor came from the mains.

Thus the power input to the elements was governed by the current flowing through the photocell, and hence by the difference between the actual and desired furnace temperatures.

Excluding accidental mechanical damage to the furnace elements, which are very fragile, this system has now given almost trouble-free service for over one year.

2.3 Purity of the Crystals.

All the chemicals used were the purest readily obtainable. Yttrium and rare earth oxides were supplied by the Lindsay Chemical Division of the American Potash and Chemical Corporation (99.99% and 99.9% pure respectively). Gallium metal used to prepare gallium oxide was supplied by Johnson Matthey and Company Ltd. (99.9 + % pure). Other reagents and raw materials were supplied by B.D.H. Ltd. in Analar grade or highest obtainable purity.

Magnetic susceptibility measurements were made at 4° K by Dr. Leask of this laboratory on PbO, PbF_2, Al_2O_3 and Y_2O_3. The results for the Y_2O_3 and the Al_2O_3 showed a slight deviation from the diamagnetism expected. The concentration of rare earth impurities (the most likely) required to cause such a deviation was found to be less than 30 parts per million. The PbO and

PbF_2 were both found to be completely free (i.e. less than a few parts per million) from any paramagnetic contaminants. Similar experiments on single crystals of yttrium aluminium garnet showed that these could have no more than 10 parts per million of rare earths. Any iron ions present as impurities in these substances would be about twice as effective magnetically as rare earth ions. The above limits of impurity concentration of rare earths could therefore be halved to give the concentration of iron present.

Despite the established purity of the constituents, and of the product in the case of yttrium aluminium garnet, a most puzzling feature has been the wide variation in colour of the single crystal garnets. Colours are particularly striking in the yttrium gallium garnets, ranging from colourless through yellow and pink to deep mauve among crystals of the same batch.

The concentration of iron in the crystals required to produce these colours need not be high. Because of the similarity in size of the Fe^{3+} ion (0.60 Å) and the Ga^{3+} ion (0.62 Å) there could be selective incorporation of any iron present in the charge, so requiring even lower concentrations in the constituents of the charge. Spectrographic analysis, by Dr. D.F. Evans of the Department of Mineralogy of this University, of some yttrium gallium garnets showed that any iron present must be less than the detection limit of 100 parts per million. Variations of concentration within this limit could produce the variations of colour observed.

A further possible cause of the colouring was the presence of

varying concentrations of Pb^{2+} ions which would give rise to colouring because of the defects associated with a divalent ion in a trivalent site.

The lack of colouring in the yttrium aluminium garnets is consistent with both of these hypotheses because the size of the Al^{3+} ion (0.50 Å.) is sufficiently small compared with Ga^{3+} (0.62 Å.) to make the lattice dimensions too small to accomodate Pb^{2+} or Fe^{3+} ions in either Y^{3+} or Al^{3+} sites.

In this context, it is interesting to note that J.A. Bruce and F.K. Euler of the Structure Unit of the Properties and Phenomena Section of the Electronic Material Sciences Laboratory, U.S.A.F., Bedford, Massachussets, have analysed by X-ray fluorescence, single crystals of yttrium iron garnet grown by the Nielsen method. They found that up to ½ mole percent of lead replaces yttrium in this compound. (Status Report, June 1960).

2.4 Crystal Orientation.

The crystals to be used in the experiments were carefully chosen to be free from any large inclusions of lead oxide and to be as well formed as possible. The two methods of orientation that were used were optical and X-ray. In the optical method the crystal was mounted on a Technico two circle goniometer, and a stereogram of the reflections from all visible faces plotted. Since the crystals showed faces of only two types (the (110) and the (211) types) it was then only necessary to measure the angles between a few faces to find the orientation of the crystal. Once the crystal had been

oriented thus an X-ray photograph of the Laue back reflection type was taken in order to complete the orientation to the desired accuracy. The X-ray equipment used was a Newton Victor 'RayMax 60' set with continuosly pumped tube. The Laue camera was supplied by the Cambridge Instrument Company.

The transfer of the crystal from the mount used on the X-ray equipment to that used in the spectrometer was carried out on a lathe so as not to loose any of the alignment. The adhesive used was an Epoxy Resin of the Araldite group, (X83/4, by CIBA (A.R.L.) Ltd., Duxford, Cambridge, England. A finely powdered form of silica was added to the resin in order to improve its elasticity at low temperatures. The amount of silica added was adjusted until the adhesive was of the required consistency, which was that of a very viscous paste. This combination was found to be very effective and in no case did the adhesive suffer fracture because of thermal shock.

The type of sample mount used is shown in Fig. 2 where the method of attaching it to the long rod is obvious. This method ensured that the axes of the holder, that is of the crystal, and of the rod were well aligned with one another.

3. Structure of the Garnet and its effect on the Spectra.

3.1 Crystallography.

Extensive investigations into the structure and the possible compositions of garnet type compounds have been carried out by Geller and Gilleo (1959) and by Bertaut and Forrat (1956). The garnets lend themselves to a very wide range of substitutions - the limit being set by the ionic size of the constituents and by the total charge balance. An excellent list of the substitutions that are known to be possible has been given by Geller (1960) who also gives the cation site preferences.

The space group of the garnets is O_{10}^{h} - Ia3d, number 230. There are eight formula units per unit cell, in total 160 ions. The general formula is $P_3\ Q_2\ R_3\ O_{12}$ where:-

P is Ca^{2+}, Fe^{2+}, or Mn^{2+}

Q is Al^{3+}, Fe^{3+}, or Ga^{3+}

R is Si^{4+}, or Ti^{4+},

in the naturally occuring garnets. The crystallography of this very complex structure is well understood and the positions of the various sites known except those of the oxygen ions. These occupy non-parameter positions and are difficult to place accurately by X-ray methods because they are very weak reflectors compared with the much more dense rare earths. However the positions of these oxygen ions are very important because it is these that give rise to the electrostatic field at the rare earth sites. The oxygen ion neighbours of each rare earth are eight in number and they

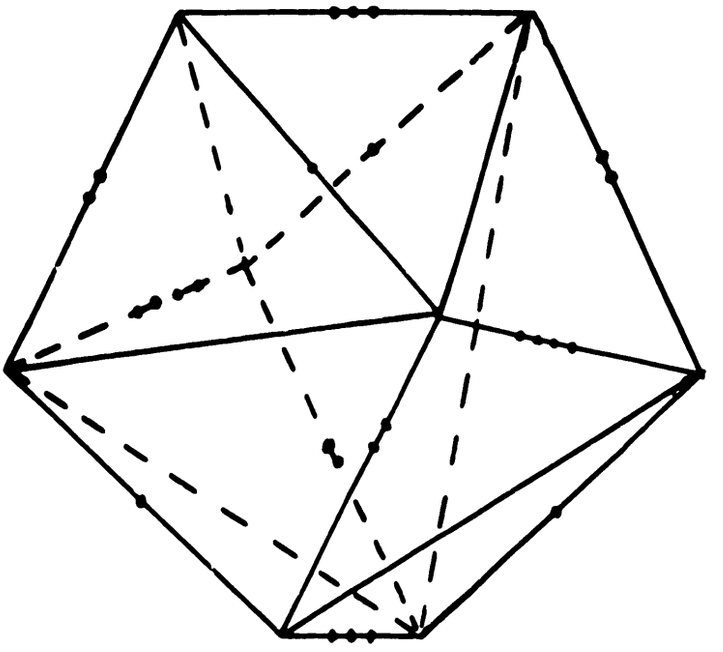
form a polyhedron which is a cube with distortions. It is the symmetry of this electrostatic field which decides the energy level scheme of the rare earth ion in the crystal. Work has been done in the determination of these oxygen parameters using the techniques of X-ray diffraction and of neutron diffraction. The results published are by Prince (1957) on YIG and YALG, and by Geller and Gilleo (1959) and Bertaut et al. (1956) on YIG. Czerlinsky and Euler (AFCRL, unpubl.) are now actively engaged in a complete survey and have already announced results for these parameters in YIG, LuIG, GdIG, YGaG, YbGaG and YALG.

In the report of Geller and Gilleo (1957) a scale drawing is given of the eight cornered twelve sided polyhedron formed by the oxygen ions about a rare earth site. The values given in this drawing (which is reproduced in Fig. 10) are those quoted by these authors for the case of yttrium iron garnet.

The twenty four possible sites for the rare earth ions in each unit cell are all identical except for the orientation of this coordination polyhedron of oxygen ions with respect to the cell axes. The rare earth ions at these sites will have the same g tensor with principal values g_x, g_y, and g_z. The symmetry axes of the g tensor for any ion must be identical to those of the coordination polyhedron for that ion in order that the tensor transform correctly under the various operations detailed below.

The unit cell of the garnet structure is composed of two identical sets each of four octants; the four in each set being

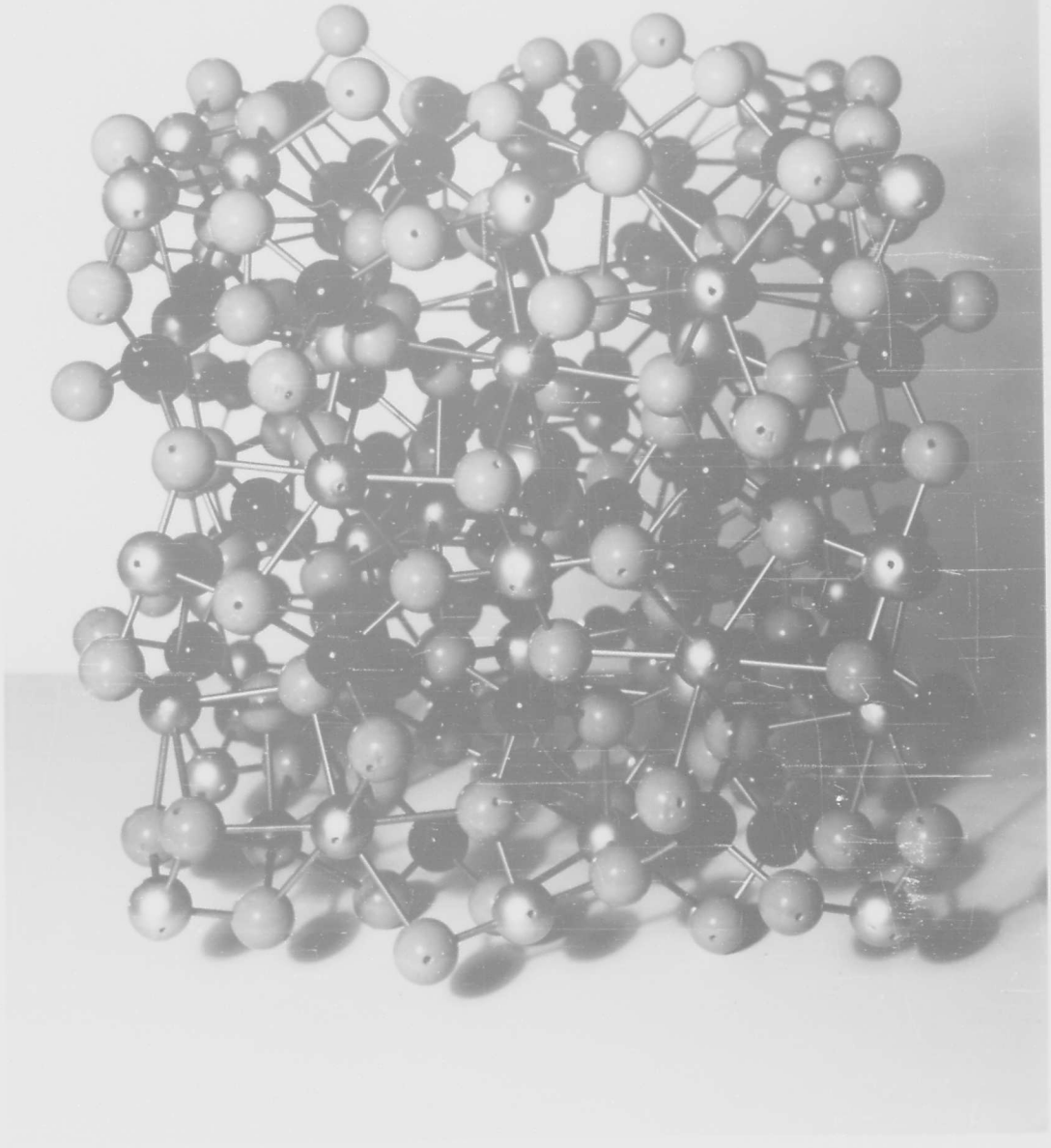
FIG. 10



• 2·68 , •• 2·81 ,

Å . in YIG,

••• 2·87 , •••• 2·96 ,



related to one another by 180° rotations about cell axes. In each octant there are three rare earth ions, each surrounded by its coordination polyhedron of oxygen ions, and related to one another by 120° rotations about a body diagonal. Using these two operations there are only six inequivalent transformations which can be performed on a vector or set of vectors. Examination of the crystal structure shows that the 24c ions all lie in inter-octant planes. This implies that the axis of the polyhedron of the ion common to two octants must be invariant under the operation which transforms one octant into its neighbour. Since this operation is a 180° rotation about a cell axis it follows that one of the axes of the g tensor must be parallel to this cube axis. The other two g values must be in the plane perpendicular to this and can be in, and perpendicular, to the inter-octant plane or both at 45° to it. This pictorial type of argument is incapable of deciding which of these must be the case. The above argument was developed by lengthy study of a scale model of the garnet structure of which a photograph is given in Fig. 11.

Another method which can be used to derive the number of inequivalent sites for the rare earth ion was developed by making direct use of the symmetry elements of the crystal.

The space group number 230, that of the garnets, is represented by the symbol O_h^{10} - Ia3d. The latter part is a shortened version of the Herman-Maugin notation which in full is:

$$I\left(\frac{4_1}{a}\right)\bar{3}\left(\frac{2}{d}\right)$$

This defines the full complement of symmetry elements possessed by the structure of which four are of interest here. They are:-

1. a glide plane of $\frac{a}{2}$ along the (001) axis
2. a three-fold axis of rotation-inversion along the (111) axis
3. a two-fold axis of rotation along the (110) axis
4. a body centre.

These symmetry elements must apply also to the polyhedron of oxygen ions about the 24c sites. Let us represent the three mutually orthogonal two-fold axes defined by 2. and 3. by the symbols 2A, 2B and 2C. Let us also define g_x, g_y, and g_z as the principal values of the g tensor of the rare earth ion and note that they can be regarded as the principal axes of an ellipsoid centered on the ion. There are twenty four polyhedra in the unit cell all alike but for orientation. By element 4. above the number is reduced to twelve identically oriented pairs. The cubic symmetry reduces this to six sets each of four identically oriented polyhedra, because of the inherent centre of symmetry. These six possible orientations of the axes 2A, 2B, 2C (or g_z, g_x, g_y) are shown in Fig. 12 where the axes XYZ are the axes of the cubic unit cell. With reference to these diagrams the orientations can be listed thus

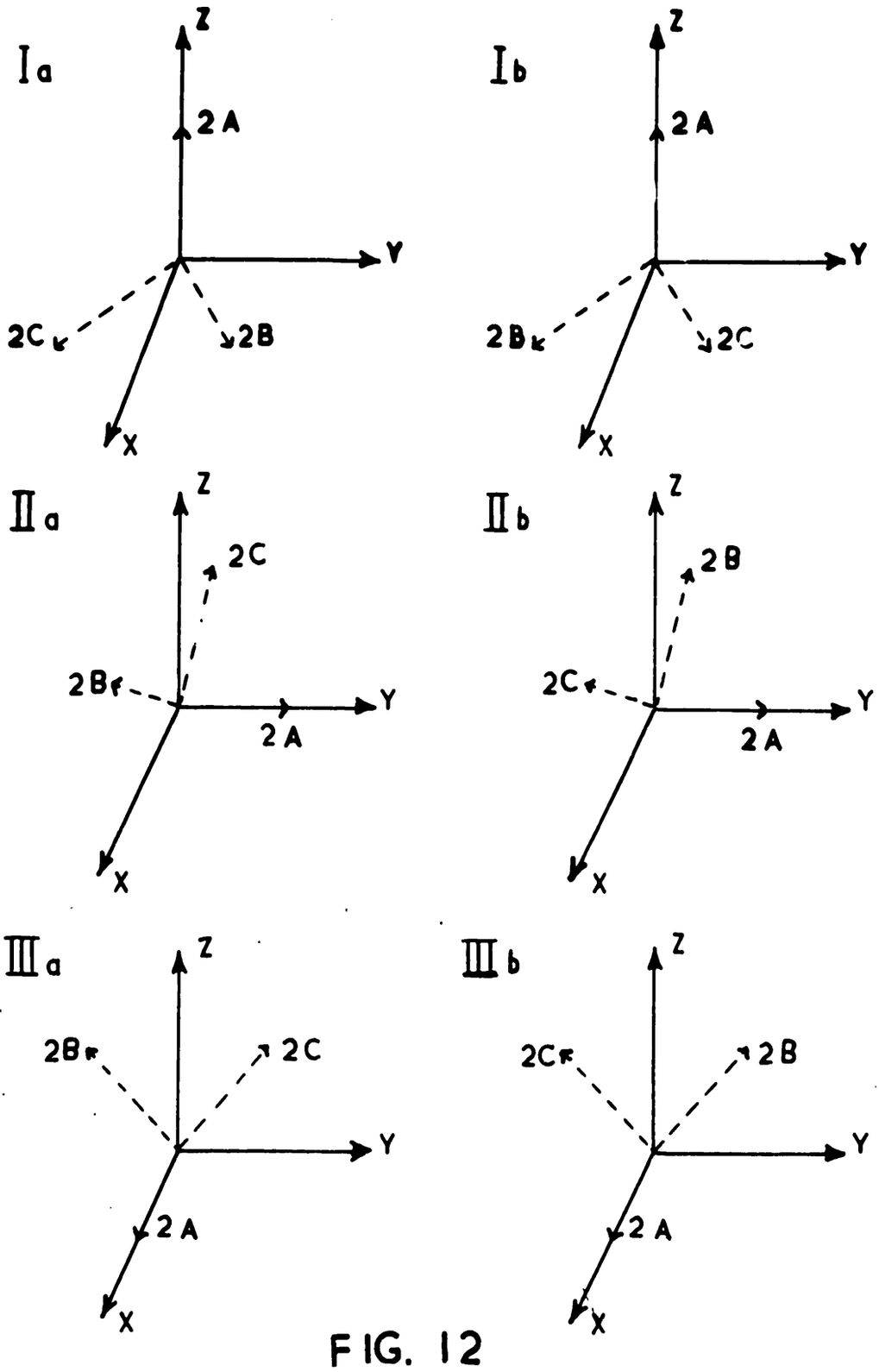

Ia
Z
2A
Y
2C
2B
X
Ib
Z
2A
Y
2B
2C
X
IIa
Z
2C
2B
Y
2A
X
IIb
Z
2B
2C
Y
2A
X
IIIa
Z
2B
2C
Y
2A
X
IIIb
Z
2C
2B
Y
2A
X

FIG. 12

2A, g_z	2B, g_x	2C, g_y
X	$\bar{Y}\bar{Z}$	YZ
X	YZ	$\bar{Y}Z$
Y	XZ	$\bar{X}Z$
Y	$\bar{X}Z$	XZ
Z	XY	$X\bar{Y}$
Z	$\bar{X}\bar{Y}$	XY

As a result of the above discussion the number of inequivalent sites for a rare earth ion has been reduced to six. As a result of this it is to be expected that ions of effective spin $S^1 = \frac{1}{2}$ in these sites would produce a spectrum containing six lines. It should now be possible to calculate the anisotropy of these lines as a function of the direction of the steady magnetic field and of the direction cosines of the g value axes at these six sites.

3.2 Character of the Spectrum.

Let us now define the direction cosines of the g value axes (i.e. of the principal axes of the ellipsoid of the g tensor) as:-

$$g_x \quad (l_x, m_x, n_x)$$
$$g_y \quad (l_y, m_y, n_y)$$
$$g_z \quad (l_z, m_z, n_z)$$

The result of the arguments above is that the six sets of these sets of direction cosines can be written down immediately.

g_x	g_y	g_z
(l_x, m_x, n_x)	(l_y, m_y, n_y)	(l_z, m_z, n_z)
$1/\sqrt{2}(1, 1, 0)$	$1/\sqrt{2}(1, 1, 0)$	$(0, 0, 1)$
$1/\sqrt{2}(1,-1, 0)$	$1/\sqrt{2}(1, 1, 0)$	$(0, 0, 1)$
$1/\sqrt{2}(1, 0, 1)$	$1/\sqrt{2}(-1, 0, 1)$	$(0, 1, 0)$
$1/\sqrt{2}(-1, 0, 1)$	$1/\sqrt{2}(1, 0, 1)$	$(0, 1, 0)$
$1/\sqrt{2}(0,-1, 1)$	$1/\sqrt{2}(0, 1, 1)$	$(1, 0, 0)$
$1/\sqrt{2}(0, 1, 1)$	$1/\sqrt{2}(0,-1, 1)$	$(1, 0, 0)$

The direction cosines of the steady field must now be defined as (l_f, m_f, n_f) [illegible] making (l_i, m_i, n_i) as the direction cosines of g_i where i can be x, y, or z, we can now write the equation for the effective g value of any ion with a Kramers' doublet ground state (see Sect. 1.2) as:-

$$g_e^2 = \sum_{i=x,y,z,} g_i^2 (l_i l_f + m_i m_i + n_i n_f)^2 \qquad \ldots\ldots\ldots 3.2.1$$

Direct substitution of the six sets of (l_i, m_i, n_i) in Eqt. 3.2.1 will give six effective g values and on substituting for (l_f, m_f, n_f) the equations describing the spectrum are obtained. By careful choice of the plane of rotation of the field, however, a considerable simplification can be achieved. Reference to the diagrams in Fig. 12 will make clear the reasons for the choice of the [110] plane as the plane of rotation of the field. With H confined to this plane ions Ia and Ib will give rise to two lines whose turning points will give g_z - when H is along the Z axis, and and g_x and g_y - when H is along the (110) line. Ions IIa and IIIb

will be equivalent with respect to the [110] plane and so will give rise to one compound line; as will ions IIIa and IIb. The spectrum has thus been reduced to four lines of which two are capable of simple analysis for the three g values.

The restriction of the field to the [110] plane enables its direction cosines to be expressed in a particularly convenient form as a function of θ, the angle between the direction of H and the Z axis. The direction cosines are then ($1/\sqrt{2} \sin\theta$, $1/\sqrt{2} \sin\theta$, $\cos\theta$) and when substituted in Eqt. 3.2.1 they give

$$g_e^2 = \sum_{i=x,y,z} g_i^2 \left(1/\sqrt{2} \sin\theta . l_i + 1/\sqrt{2} \sin\theta . m_i + \cos\theta . n_i\right) \quad \ldots\ldots 3.2.2$$

Direct substitution of the six sets of (l_i, m_i, n_i) gives the equations for the four lines of the spectrum.

$$g_e^2 = g_x^2 \sin^2\theta + g_z^2 \cos^2\theta \quad \ldots\ldots 3.2.3$$

$$g_e^2 = g_y^2 \sin^2\theta + g_z^2 \cos^2\theta \quad \ldots\ldots 3.2.4$$

$$g_e^2 = \tfrac{1}{4} g_x^2 (\sin\theta + \sqrt{2}\cos\theta)^2 + \tfrac{1}{4} g_y^2 (\sin\theta - \sqrt{2}\cos\theta)^2 + \tfrac{1}{2} g_z^2 \sin^2\theta \quad \ldots\ldots 3.2.5$$

$$g_e^2 = \tfrac{1}{4} g_x^2 (\sin\theta - \sqrt{2}\cos\theta)^2 + \tfrac{1}{4} g_y^2 (\sin\theta + \sqrt{2}\cos\theta)^2 + \tfrac{1}{2} g_z^2 \sin^2\theta \quad \ldots\ldots 3.2.6$$

From inspection these reduce in the special cases of $\theta = 0^\circ$ and $\theta = 90^\circ$ to

$\underline{\theta = 0}$ $\quad g_e^2 = g_z^2$ from Eqts. 3.2.3 and 3.2.4

$\quad g_e^2 = \tfrac{1}{2} g_x^2 + \tfrac{1}{2} g_y^2$ from Eqts. 3.2.5 and 3.2.6

$\underline{\theta = 90^\circ}$ $g_e^2 = g_x^2$ from Eqt. 3.2.3

$g_e^2 = g_y^2$ from Eqt. 3.2.4

$g_e^2 = \frac{1}{4}\left(g_x^2 + g_y^2\right) + \frac{1}{2} g_z^2$ from Eqts. 3.2.5 and 3.2.6

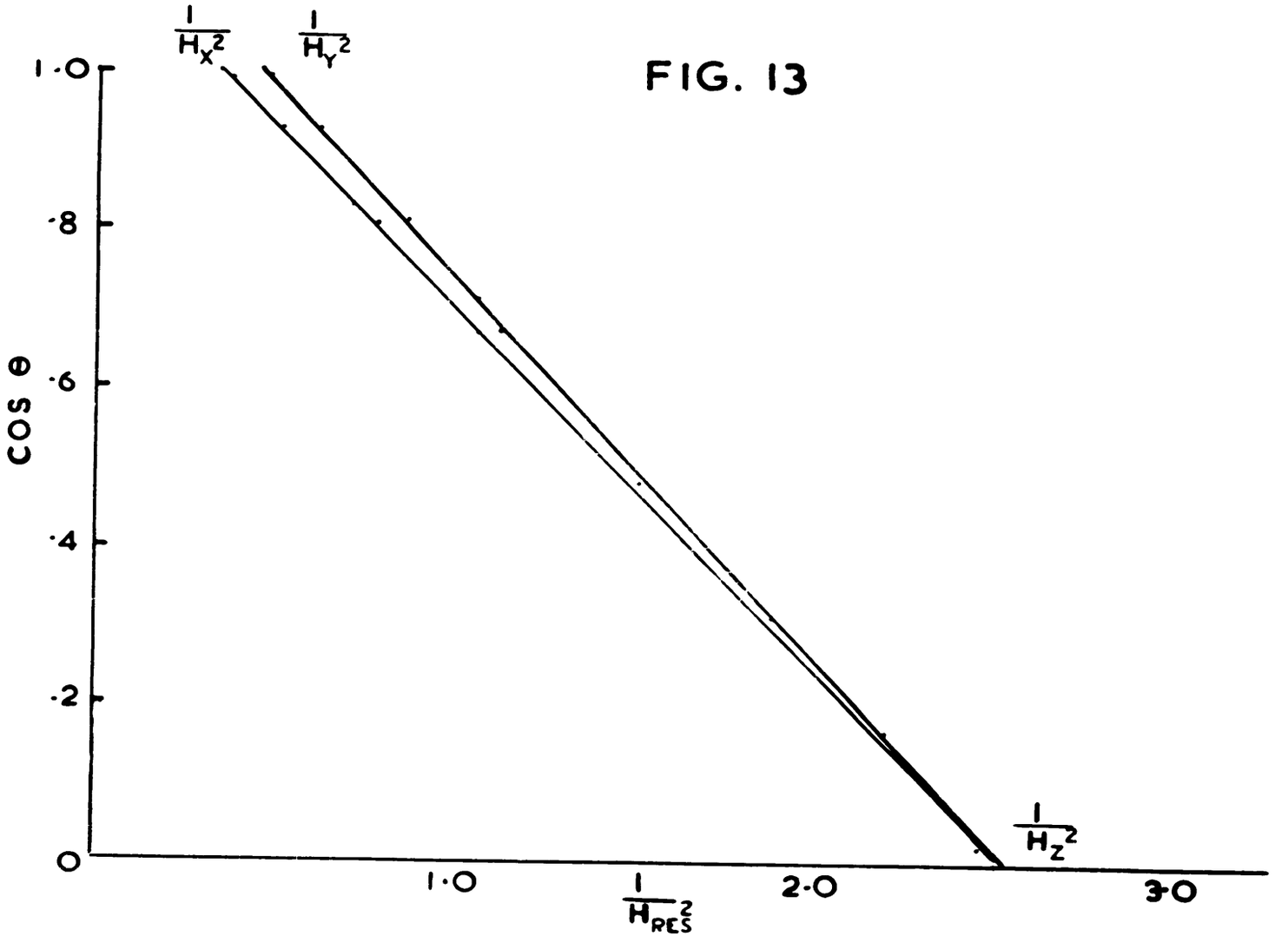
We will now show how these formulae can be used in the processing of the results of measurements of the resonant field as a function of the angle θ.

3.3 Analysis of Experimental Data.

In Sect. 1.3 a description was given of how in a typical experiment a plot of the four lines in the (110) plane was made over a region from 10° before the (001) axis to 10° after the (110) axis. A preliminary assessment of the g values could be made from these curves by observing the turning values at the (001) and (110) axes. This however was not the method used for the calculation of the values quoted here.

From the experimental values of resonance field given by the two curves with simple turning points at $\theta = 0^\circ$ and $\theta = 90^\circ$ a plot of $\frac{1}{H_{res}^2}$ v. $\cos^2\theta$ was made. Since these curves of H_{res} v. θ are principal conic sections and θ is measured from a principal axis this plot should be a straight line. A typical example is reproduced in Fig. 13 and on it are marked $\frac{1}{H_x^2}$, $\frac{1}{H_y^2}$ and $\frac{1}{H_z^2}$ which are the values of $\frac{1}{H_{res}^2}$ when the field is parallel to g_x, g_y and g_z respectively. These three values of $\frac{1}{H_{res}^2}$ gave

FIG. 13



the g values by substitution in the equation $h\nu = g\beta H$. (Standard notation). The three g values thus derived were substituted in Eqts. 3.2.3 - 3.2.6 and the values of g_e^2 computed at 5° or 10° intervals of θ. g_e^2 was then converted to H by the equation given above and the values of H v. θ plotted on the same graph as the experimental results. The fit of the computed and experimental curves was then carefully examined. Any deviation could be attributed to an error in the choice of g_x, g_y, or g_z. When it had been decided which of the three was wrong the necessary correction was made and the new curves computed using the new g values. There was this slight uncertainty in the g values from the $\frac{1}{H_{res}^2}$ v. $\cos^2\theta$ lines because of the nature of the scales of such a plot involving squares. The second choice of g values was in all cases sufficient to give a fit of experimental and computed curves that was within the scatter of the experimental points. The g values which gave such a fit are those quoted in later Sections of this report.

3.4 Errors due to Misalignment.

The above method of extracting a set of g values from the experimental data assumes that the equations used for computed curves actually relate to the experimental conditions. This will be so only if the crystal is oriented so that its (110) plane coincides with the plane of rotation of the steady magnetic field. The purpose of the considerations that follow is to investigate the effect of any misalignment of the specimen.

Since the analysis required for the case of a completely general misalignment is unnecessarily long, the effects of two different types of misalignment will be considered. Each of these will be further simplified to the situation of $\theta = 0^{\circ}$ or 90°. The two cases to be treated are:-

a. the field rotating in a plane containing the Z axis and cutting the XY plane in a line with direction cosines ($\sin\alpha$, $\cos\alpha$, 0) where α is defined as the angle between this line and the Y axis, nearly 45°.

b. the field rotating in a plane containing the line (110) and cutting the plane $\overline{1}10$, not in the Z axis, but in a line at an angle to this - i.e. in the line with direction cosines ($1/\sqrt{2}\sin\beta$, $-1/\sqrt{2}\sin\beta$, $\cos\beta$).

These two cases are illustrated in Fig. 14.

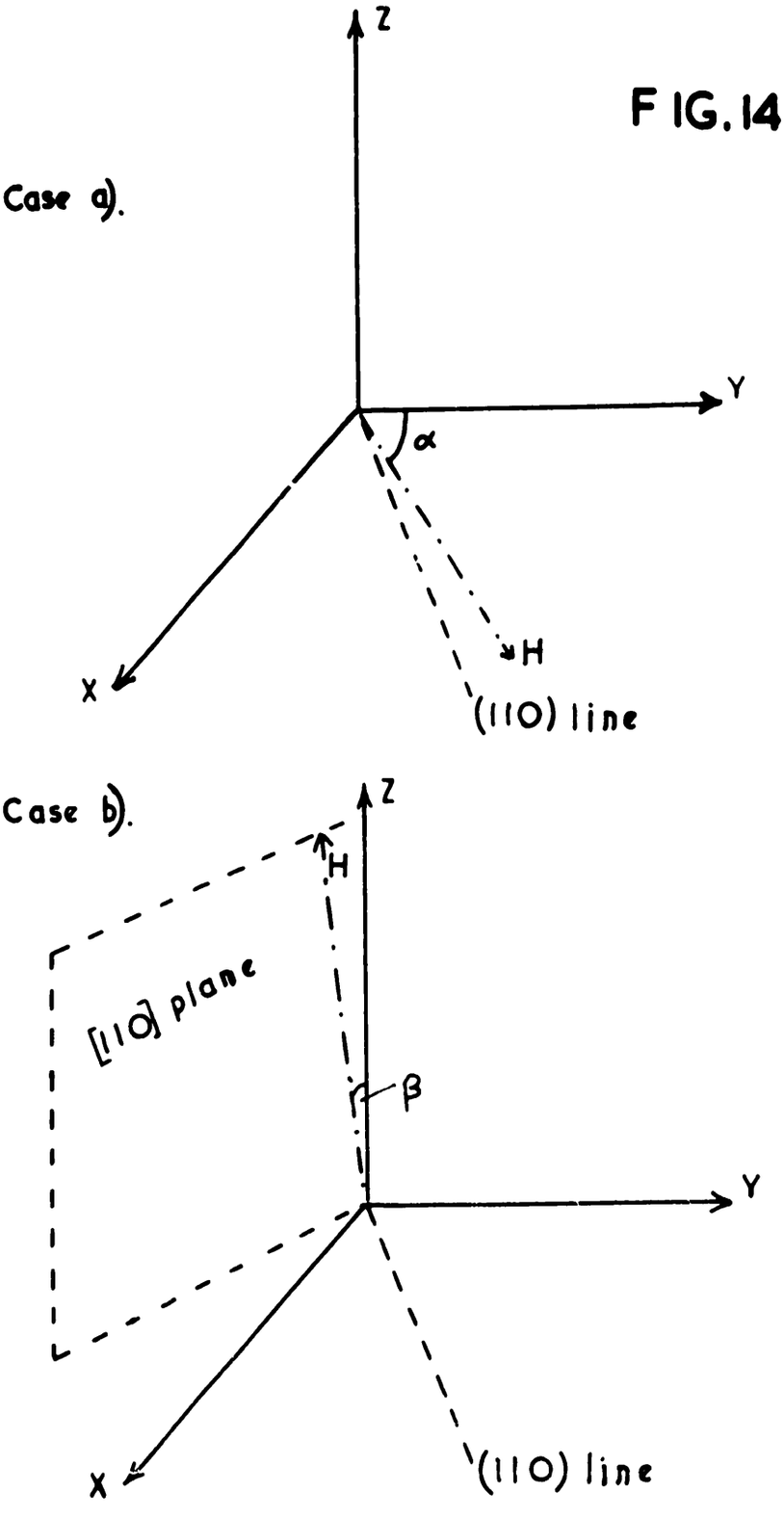
Considering case a.

$\underline{\theta = 0^{\circ}}$ When the field is in the YZ plane it is along the Z axis and there is no deviation from the ideal (properly oriented specimen) case.

$\underline{\theta = 90^{\circ}}$ When the field is in the XY plane it is along the line with direction cosines ($\sin\alpha$, $\cos\alpha$, 0) and as a result it is not parallel to g_x or g_y for ions Ia and b. Though ion IIa is equivalent to IIIb and ion IIIa is equivalent to IIb the two pairs are no longer identical and the single crossing point of four lines becomes two crossing points.

Direct substitution of $\theta = 90^{\circ}$ and $(l_\rho, m_\rho, n_\rho) = (\sin\alpha,$

FIG. 14



cosα,0) in Eqt. 3.2.1 gives the effective g values and these can be used to find the spacing of the two crossing points and the shift of the two turning points.

The spacing is:

$$\Delta g_e = \sin 2\gamma \frac{g_z^2 - g_e^2}{g_e} \qquad \ldots\ldots 3.4.1$$

where $g_e^2 = \frac{1}{4}(g_x^2 + g_y^2) + \frac{1}{2} g_z^2$

and $\gamma = 45^\circ - \alpha$

γ therefore is the actual angular deviation from the ideal case.

The shifts are given by

$$\delta g_x = \tfrac{1}{2} \frac{g_y^2 - g_x^2}{g_x} \sin^2 \gamma \qquad \ldots\ldots 3.4.2$$

$$\delta g_y = \tfrac{1}{2} \frac{g_y^2 - g_x^2}{g_y} \sin^2 \gamma \qquad \ldots\ldots 3.4.3$$

These expressions will be used in Section 4 to estimate the errors on our results due to misalignment but a typical case will be treated here both to illustrate the method and to give some numbers. Let us consider the case of neodymium in yttrium gallium garnet with approximate g values.

$$g_x = 1 \qquad g_y = 2 \qquad g_z = 4$$

On inserting these in Eqt. 3.4.1 we find

$$\Delta g_e = 8.5 \sin 2\gamma$$

Now $\frac{\Delta g}{g} = \frac{\Delta H}{H}$

$$\Delta g = \frac{\Delta H}{H} g \approx \frac{\Delta H}{7} g^2$$

because $H = \frac{21.4178}{g\lambda}$ is approximately equivalent to

$H = \frac{1}{g}$ for a typical value of λ.

From this we can say

$$\sin 2\gamma = \frac{\Delta H \times g_e^2}{7 \times 8.5}$$

$$= \frac{2.5}{7 \times 8.5} \times \Delta H$$

ΔH must now be put equal to the maximum spacing of the two compound lines which would not be observable. This can generally be said to be a spacing of one line width, which in this case was about 40 gauss.

Then

$$\sin 2\gamma = 0.0017$$

$$= 0^\circ\ 03^1$$

Putting this value of γ in Eqts. 3.4.2 and 3.4.3 gives errors in g_x and g_y of less than 0.001%.

Considering case b.

<u>$\theta = 90^\circ$</u> With the field in the XY plane the spectrum does not differ from the ideal case.

<u>$\theta = 0^\circ$</u> The field is now along the line in the $[\bar{1}\bar{1}0]$ plane with direction cosines $(1/\sqrt{2}\ \sin\beta,\ -1/\sqrt{2}\ \sin\beta,\ \cos\beta)$. Eqt. 3.2.1 then yields Δg_e for the splitting of the compound line, where

$$\Delta g_e = \frac{1}{2\sqrt{2}} \frac{g_x^2 - g_y^2}{g_e} \sin 2\beta \qquad \ldots\ldots\ldots 3.4.4$$

In this case $g_e^2 = \frac{1}{2}(g_x^2 + g_y^2)$

Using the g values of neodymium in yttrium gallium garnet once

more shows that, for a splitting of the compound lines of 40 gauss, $\beta = 4\frac{1}{2}^{\circ}$. The effect of this type of misalignment on the coalesced lines which have a single turning point at $\theta = 0$ is to split them slightly and to move them both up in field. The amounts of these shifts in g value are

$$\delta g_1 = \tfrac{1}{2} \sin^2\beta \, \frac{g_x^2 - g_z^2}{g_z} \qquad \ldots 3.4.5$$

$$\delta g_2 = \tfrac{1}{2} \sin^2\beta \, \frac{g_y^2 - g_z^2}{g_z} \qquad \ldots 3.4.6$$

These are equivalent to shifts in field of 7 gauss and 5 gauss respectively - a splitting of 2 gauss which is of course, not observable. The percentage error in g_z is however of the order of 0.5% due to this effect.

The above analysis, as stated at the beginning, has rested on the assumption that the two very special cases treated are sufficient. This assumption can be seen to be reasonable by consideration of the fact that all of the curves of H_{res} v. θ, whether for a properly oriented specimen or not, are sections of an ellipsoid. If the specimen is properly aligned the two curves used to find g_x, g_y and g_z are the ellipses resulting from intersections of the ellipsoid with two orthogonal planes each containing two of its principal axes. For a misaligned specimen the planes may not contain one or more of these axes. In this case the maximum difference between the two ellipses will be at their axes that are at $\theta = 0$ and $\theta = 90^{\circ}$ - the cases considered.

3.5 Other Errors.

Errors might arise in the measurement of the resonant field, the angular setting of the magnet, and the microwave wavelength.

The technique of setting the signal from the nuclear magnetic resonance field meter exactly at the centre of the electron resonance signal on the other oscilloscope trace is one which requires a measure of experimental skill. If we take typical values of the widths of the nuclear and of the electron resonance lines as 20 gauss and 60 gauss respectively it will be seen to be that an error of 10 gauss be attributed to the setting of the two signals to coincidence. The rather large value for the nuclear resonance line width was caused by the inhomogeneity of the magnetic field at the sample. This would introduce an error of 1% in a g value of 7 or an error of 0.3% for a g value of 2. In fact a sufficiently accurate measure of the percentage error is given by

$$\text{Percentage error in } g = \frac{\delta g}{g}$$

$$\text{Because } \frac{\delta g}{g} = \frac{\delta H}{H} \approx \frac{\delta H}{7} \qquad g \text{ in kgauss}$$

$$\text{So for } \delta H \text{ in gauss } \frac{\delta g}{g} \times 100 = \frac{\delta}{7}$$

The frequency meter used for measuring the frequency of oscillation of the field probe unit was checked against broadcast frequency standards and found to be correct to within 1 part in 10^5 and so introduced negligible error into the measurement of field.

Since the magnet scale was easily readable to 0.1° there was no appreciable error from this source. The wavemeter accuracy

was checked against a laboratory substandard and was certainly better than 0.1% which is the smallest that the field measuring error could be.

The only error therefore that is comparable with the possible errors due to misalignment is that of setting the two resonance signals to coincide on the oscilloscope. It has not been assumed that the nuclei which are resonating are in the same magnetic field as the paramagnetic material because the linear spacing of 1 cm. between the two made this unlikely. To overcome this effect the nuclear magnetic resonance signal was always used to measure the resonant field for a sample of free radical actually fixed to a face of the paramagnetic crystal. It was assumed that the ratio between the field at these two points - the free radical and the nuclear coil - was the same at all fields. Assuming this to be so all g values measured were corrected by a factor equal to the ratio of the true g value for the free radical to its apparent g value as then measured. This factor was usually of the order of 0.1% but was on a few occasions as high as 1% because of movement of the magnet which was necessary for other reasons.

4. Results.

4.1 Introduction.

In this chapter the results of paramagnetic resonance experiments performed on rare earth-yttrium aluminates and gallates, in a range of temperatures from 80°K to 2°K., are given. These results embrace:- a detailed investigation of the relationship between the resonant field magnitude and direction (with respect to the unit cell axes) for each type of magnetically inequivalent rare earth ion; a measurement of the range of temperature over which resonance can be observed; an approximate measurement of the line width. In some cases the variation of line width with rare earth concentration and with temperature was noted. These measurements of line width were carried out by setting the signal from the nuclear resonance spectrometer directly above the half power point of the electronic absorption signal on the double beam oscilloscope and measuring the separation in field of these half power points. This method is not at all accurate because it takes no account of the effect on the line shape of the various amplifying stages through which the signal passes. Further the half power level was found by measurement of the signal height on the oscilloscope and so was subject to error. However for the purpose of checking on which was the best concentration of rare earth ions and which was the best working temperature this method was quite satisfactory. The question of line widths will be returned to in Section 5. Fuller experimental results are given by Ryan (1960).

4.2a Yb^{3+} Ion in Yttrium Gallium Garnet.

The spectrum of the Yb^{3+} ion was observed from single crystals of gallium garnet containing 1% of ytterbium. Measurements were made at 20°K. and it was observed that no change occurred on lowering the temperature to 2°K. The line width was effectively constant at 35 gauss over this range of temperature.

The method of analysis described in Sect. 3.3 was applied to the data from these experiments. The g values finally assigned to the Yb^{3+} ion in yttrium gallium garnet were

$$g_x = 3.73 \pm 0.02$$

$$g_y = 3.60 \pm 0.02$$

$$g_z = 2.85 \pm 0.02$$

The errors due to misalignment were calculated by the method developed in Section 3. This showed that for this spectrum an error of $1\frac{1}{2}^{c}$ in the XY plane would be detectable but would give rise to errors in g_x and g_y of less than 0.01%. A similar misalignment of the second type would be detectable at $\theta = 0$ and would give rise to an error of 0.03% in g_z. So in this case the significant error is that in setting the field measuring signal on the paramagnetic signal. Fig. 6 shows the experimental values of H_{res} as points against the full line curve which is that computed using the above values of g_x, g_y and g_z. A comparison of these results with those of a group of workers who carried out essentially the same investigation independently of and simultaneously with our

work is possible. White and Carson (1960) using different samples found the following values for Yb^{3+} in yttrium gallium garnet.

$$g_x = 3.74$$

$$g_y = 3.60$$

$$g_z = 2.85$$

These are in excellent agreement with our values and are interesting also because they were measured at 8 mm. wavelengths instead of 3 cm. as ours were, so showing that the higher frequency does not introduce any other effects.

4. 2b Yb^{3+} Ion in Yttrium Aluminium Garnet.

No investigation was entered into on this ion because White and Carson (1960 a) had already obtained the full spectrum before samples were available for our use. The results quoted by these authors were:-

$$g_x = 3.87$$

$$g_y = 3.78$$

$$g_z = 2.47$$

4.3a Er^{3+} in Yttrium Gallium Garnet.

Resonance experiments were carried out on crystals containing 1% erbium but the line width was very great - about 100 gauss - and the signals very intense. Crystals containing 0.3% of erbium were then prepared and found to be suitable for study. The lines were still wide - about 60 gauss - but this was a more suitable width to work with. The temperature at which these crystals were

studied was 4°K. because the spectrum was only just visible at 20°K.

It was observed that at 4°K. it was possible to saturate the resonance signal from these 0.3% erbium samples with less than the 60 milliwats of microwave power that was the maximum available. For this reason these experiments were carried out with a very low power level.

In Fig. 15 are plotted values of H_{res} from experiment and from computation - as a function of θ the angle between H and the (001) axis of the crystal. The larger differences here can be attributed to the greater line width of this spectrum and to the fact that the lines A and B are close together over so much of the range. Experimental values of H_{res} are not given for $\theta = 54^{\circ}$ because it is at about this angle that the lines are crossing and so pulling effects are maximum.

On the basis of this fit the g values for the Er^{3+} ion in yttrium gallium garnet were taken to be

$$g_x = 4.03 \pm 0.03$$

$$g_y = 4.69 \pm 0.04$$

$$g_z = 10.73 \pm 0.21$$

The misalignment errors were decided upon by the use of the equations and criteria of Sect. 3, which showed that in g_x and g_y they were less than 0.01%, and in g_z they were 0.5%. The large difference between the possible errors is caused by the similarity of the values of g_x and g_y which results in the possibility of a relatively large misalignment of the sort referred to as case b in Sect. 3. In fact at $\theta = 0^{\circ}$ the field could be at an angle of 6° to the (001) axis before the splitting of the compound lines would become visible (i.e

FIG. 15

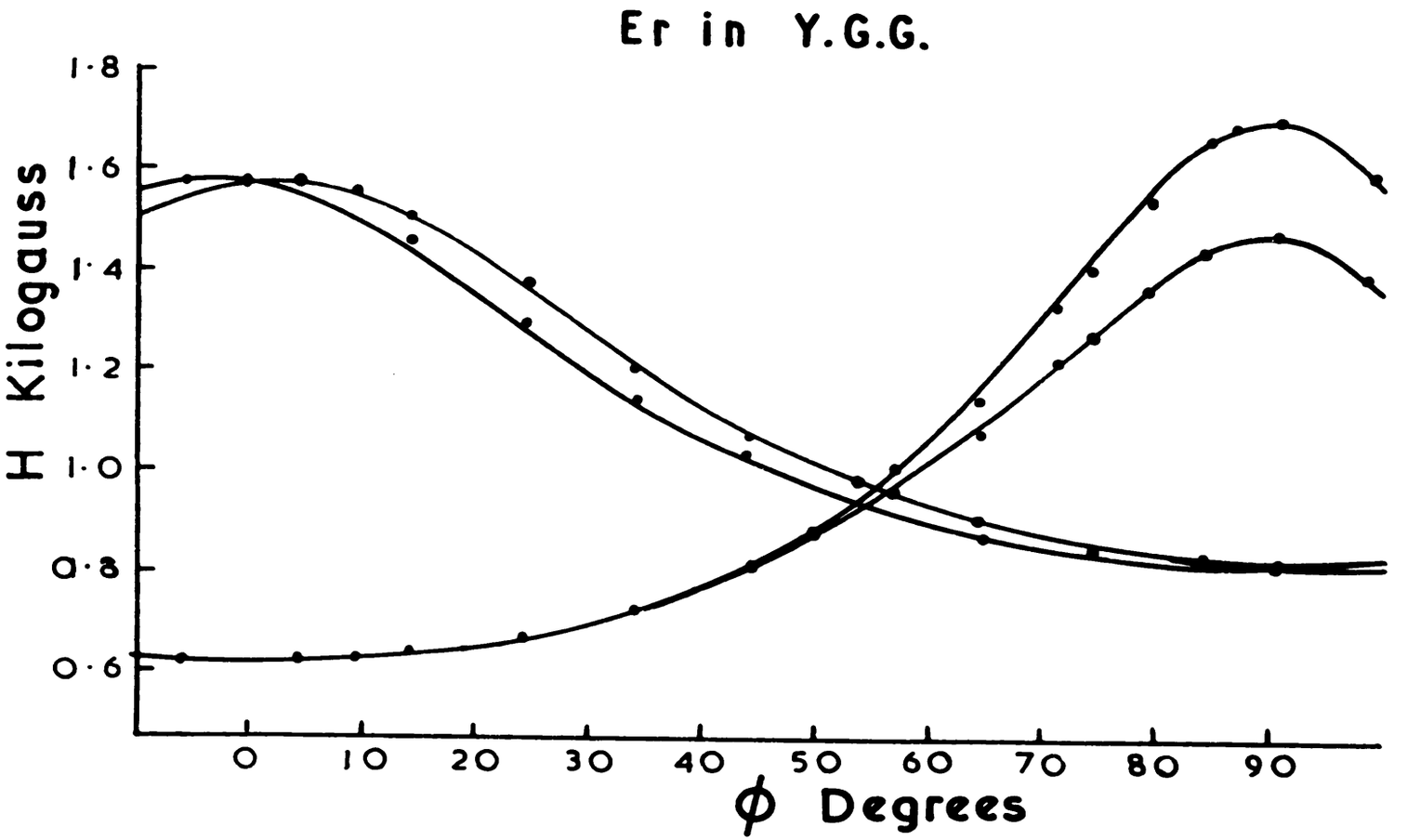
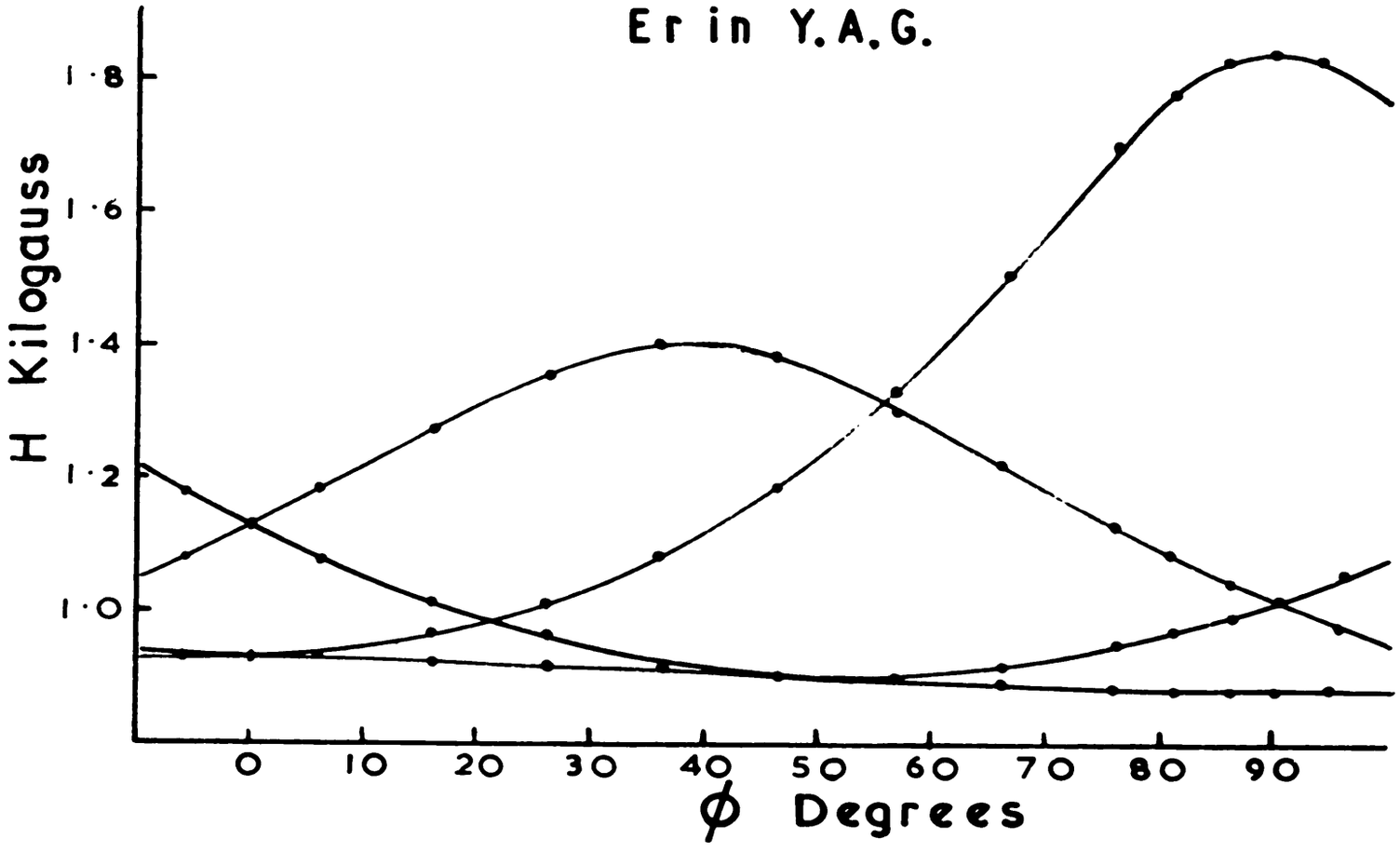

Er in Y.G.G.
H Kilogauss
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0
10
20
30
40
50
60
70
80
90
φ Degrees

FIG. 16


Er in Y.A.G.
H Kilogauss
1·8
1·6
1·4
1·2
1·0
0
10
20
30
40
50
60
70
80
90
φ Degrees

of the order of the linewidth). However since g_x and g_y are considerably smaller than g_z this results in an error of only 0.5% in g_z. In Case a. however the possible angle of misalignment is much smaller and since its effect is to admix g_x and g_y at $\theta = 90^\circ$ it is quite small owing to the value of these two being so close.

On investigating the possible error in measurement of the centre of the resonance line we find an error of 0.6% i.e. $\pm$ 0.02 in g_x; of 0.7% i.e. $\pm$ 0.03 in g ; 1.5% i.e. $\pm$ 0.16 in g_z.

4.3b Er^{3+} in Yttrium Aluminium Garnet.

The spectrum from single crystals of aluminium garnet containing 0.1% of erbium was visible at 20°K. but the experiments were carried out at 4°K. because of the superior signal to noise ratio at the lower temperature. The line width was of the order of 40 gauss with little temperature variation and no saturation effects were observed.

The experimental and computed values of H_{res} are plotted against θ in the graph of Fig. 16 for Er^{3+} in the aluminium garnet.

The g values used were

$$g_x = 7.75 \pm 0.09$$

$$g_y = 3.71 \pm 0.02$$

$$g_z = 7.35 \pm 0.08$$

The errors here are mainly due to the difficulty of accurate measurement of the resonant field. The maximum possible misalignment errors are 0.1% in g_x and g_z and 0.5% in g_y. The setting errors however are 1.1% in g_x, 0.53% in g_y and 1.05% in g_z.

4.4a Nd^{3+} Ion in Yttrium Gallium Garnet.

The intensity of the spectrum from 1% neodymium-yttrium gallium garnet single crystals was sufficient at 20°K. for this work to be carried out. The line width was about 50 gauss and showed no variation with temperature. The spectrum was well spaced out (as can be seen from the graph in Fig. 17) so an excellent fit of calculated and experimental values of H_{res} was obtained. From this fit the g values chosen were

$$g_x = 1.251 \pm 0.007$$

$$g_y = 2.027 \pm 0.008$$

$$g_z = 3.667 \pm 0.018$$

The errors quoted are a combination of those caused by alignment faults and setting difficulties. The maximum possible misorientation in the XY plane is $3\frac{1}{2}^\circ$ and in the [110] is 1°. These could give rise to errors of 0.3% in g_x, 0.1% in g_y and 0.01% in g_z. The maximum possible percentage errors due to setting are 0.2%, 0.3% and 0.5% in g_x, g_y and g_z respectively.

4.4b Nd^{3+} In Yttrium Aluminium Garnet.

In the single crystals of yttrium aluminium garnet containing 1% of neodymium resonance was detected at 20°K. and below. At helium temperatures it was observed that there were three complete spectra of the type common to the other rare earths. Two of these spectra were fully investigated and graphs of H v. θ plotted. (See Fig. 18 and 19). The larger of these spectra was found to have associated g values:

FIG. 17

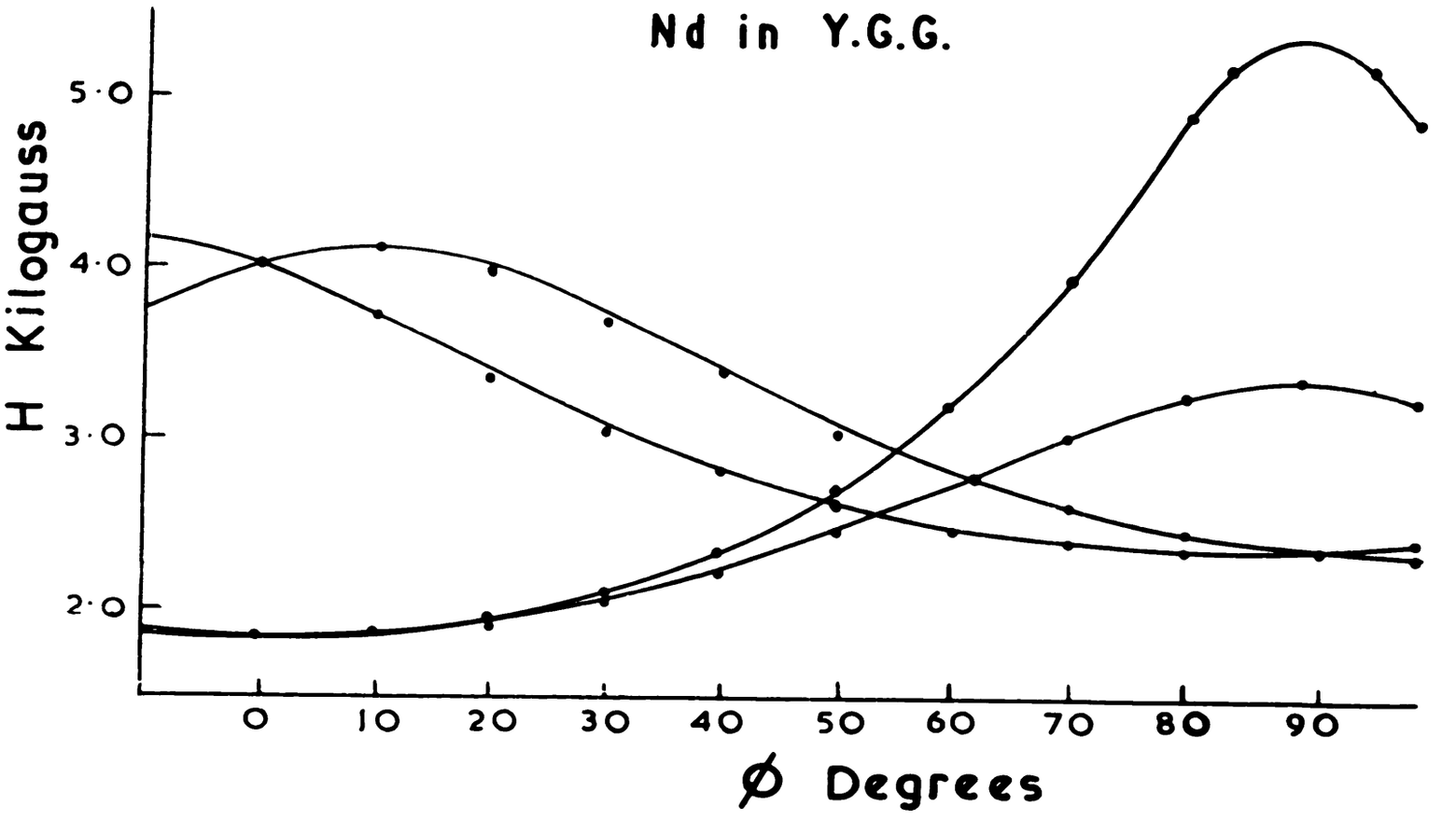

Nd in Y.G.G.
H Kilogauss
5·0
4·0
3·0
2·0
0
10
20
30
40
50
60
70
80
90
Ø Degrees

FIG. 18

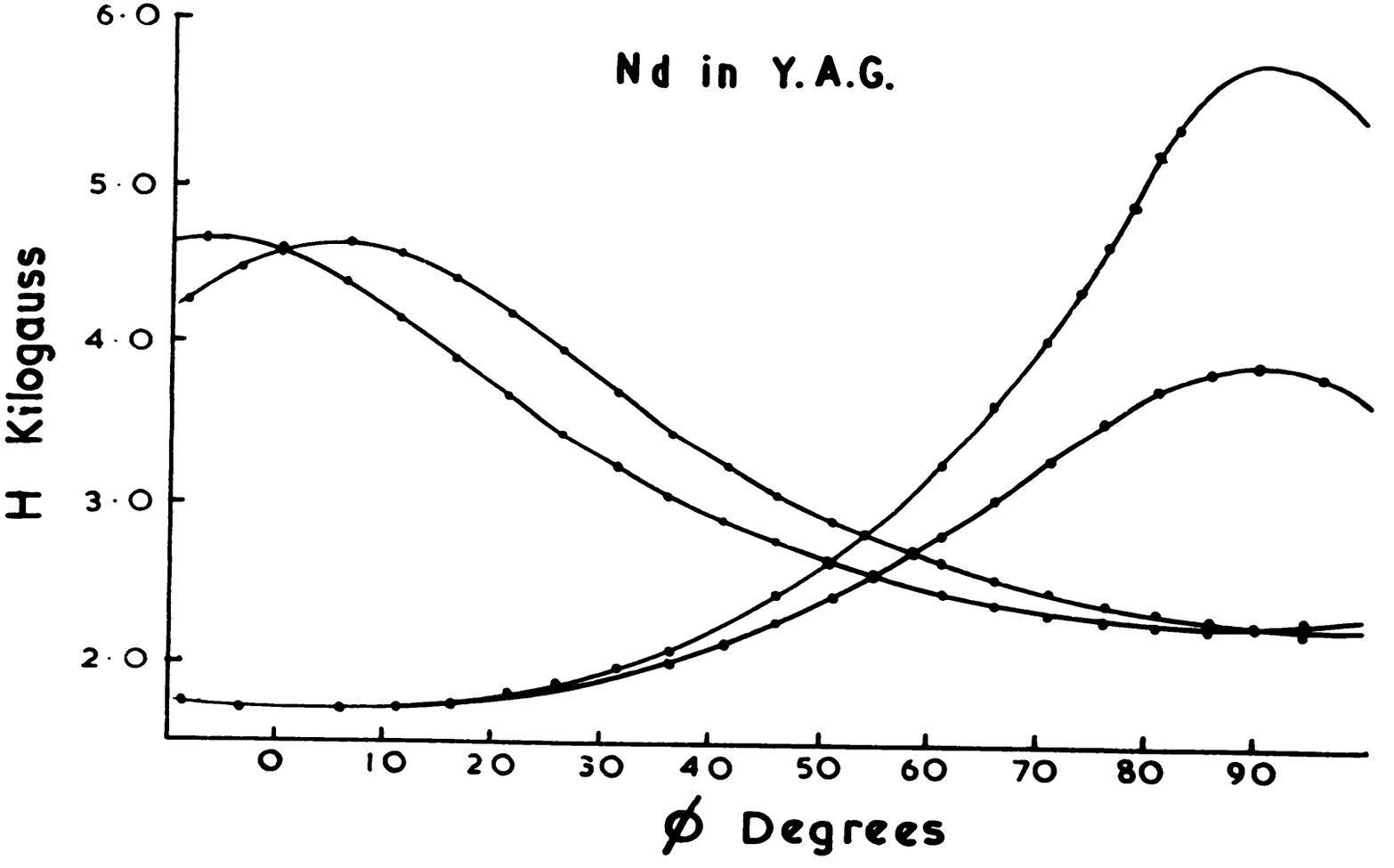
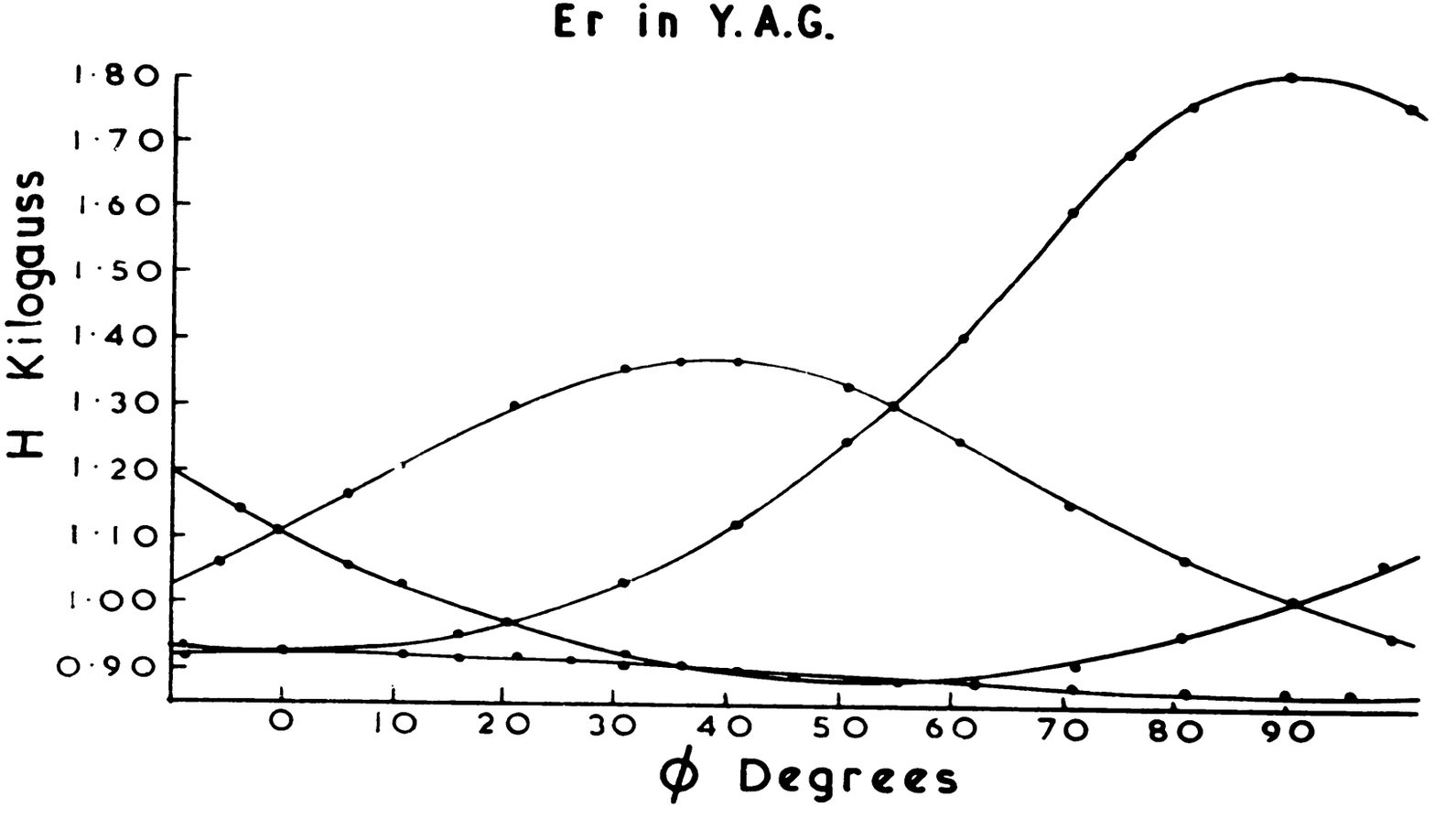

Nd in Y.A.G.
H Kilogauss
6·0
5·0
4·0
3·0
2·0
0
10
20
30
40
50
60
70
80
90
Ø Degrees

FIG. 19


Er in Y.A.G.
H Kilogauss
1·80
1·70
1·60
1·50
1·40
1·30
1·20
1·10
1·00
0·90
0
10
20
30
40
50
60
70
80
90
φ Degrees

$$g_x = 1.179 \pm .002$$

$$g_y = 1.733 \pm .004$$

$$g_z = 3.915 \pm .026$$

The errors in these g values due to setting were 0.1% in g_x i.e. $\pm$ 0.002; 0.25% in g_y, i.e. $\pm$ 0.004; 0.56% in g_z i.e. $\pm$ 0.02. The maximum angular error in the XY plane is $\frac{1}{2}^\circ$ which introduces negligible error into g_x and g_y. That in the [110] plane is $2\frac{1}{2}^\circ$ resulting in a 0.1% error in g_z

The other two spectra were very puzzling because the relative intensity of the three remained unchanged on lowering the temperature to 2°K. This suggested that if the spectra were due to the population of other levels they must be very close to the main one. The third spectrum could not be investigated very fully because it was several orders of magnitude smaller than the other two and being very anisotropic overlapped both. The secondary spectrum was of a similar intensity to the main one. On fitting g values to this spectrum it was found that it was almost identical with that of the Er^{3+} ion in yttrium aluminium garnet. The small differences were shown to be entirely due to effects such as difference in wavelength of the microwave radiation at the times of the two experiments and a small difference in the apparent g value of d.p.p.h. On taking these into account the g values for this spectrum agreed with those of the Er^{3+} spectrum to within our errors. The most likely explanation of this phenomenon is that at some stage of the preparation of these crystals the charge

became contaminated by erbium. The result of this unintentional check on our accuracy by measuring the same spectra under different conditions was very reassuring.

4.5a Dy^{3+} Ion in Yttrium Gallium Garnet.

This spectrum, observed in single crystals containing 1% of dysprosium, was visible only at temperatures of 4°K. and below. The line width, of the order of 60 gauss, was constant with temperature from 4°K. to 2°K. The anisotropy of this spectrum was greater than that of any of the other rare earths investigated. One of the g values was so low that the appropriate turning point (extremum of field as a function of angle) could not be seen because it was outside the range of the magnet used. To find this turning point values of H_{res} near the top of the range of magnetic field were measured at very close intervals and then used on a $\frac{1}{H_{res}^2}$ v. $\cos^2\theta$ plot which was extrapolated to give the turning value. (See Fig. 20).

Using the experimental results as detailed elsewhere the g values decided upon for the Dy^{3+} ion in yttrium gallium garnet were

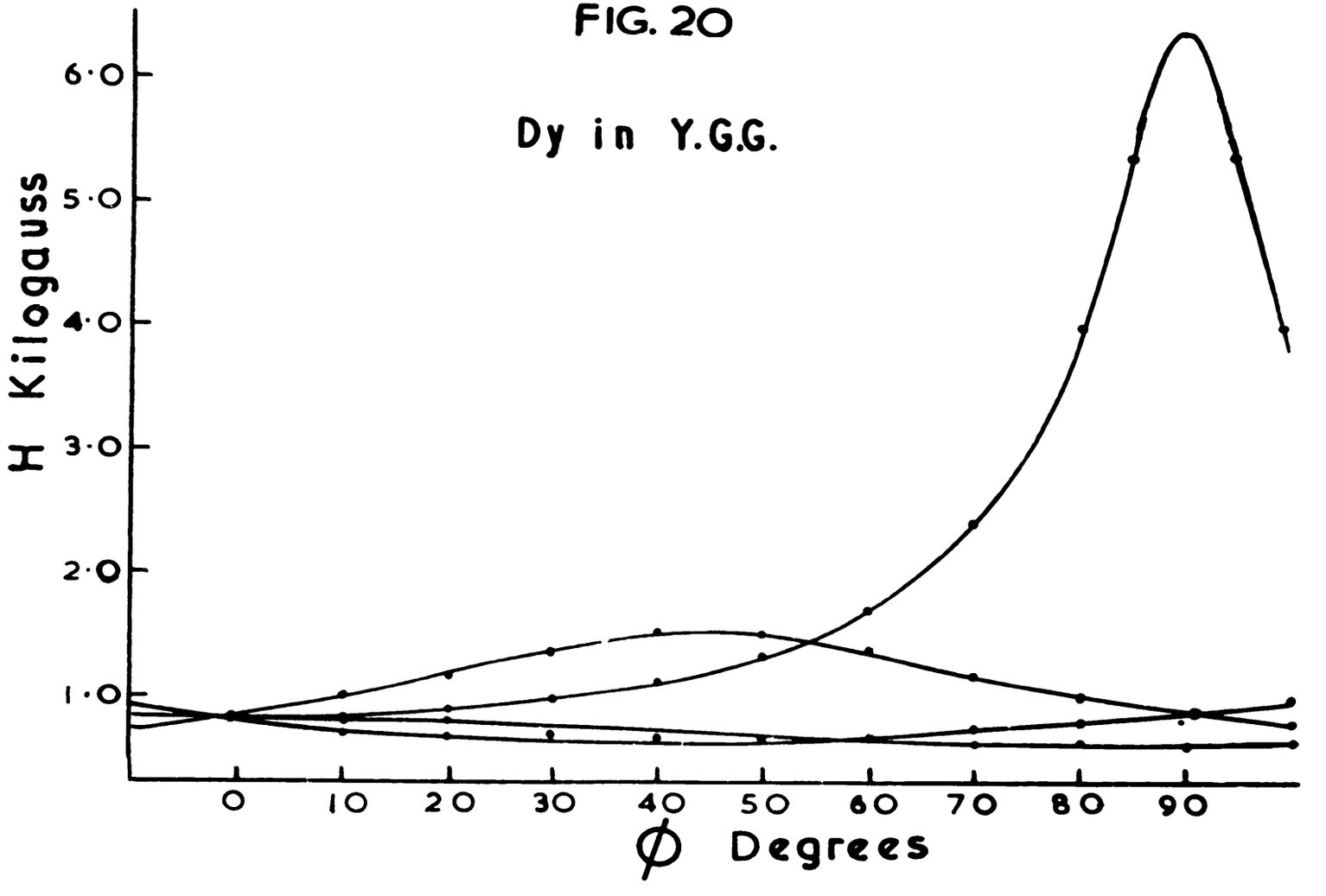
$$g_x = 1.07 \pm 0.14$$

$$g_y = 11.07 \pm 0.20$$

$$g_z = 7.85 \pm 0.10$$

The setting errors in g_y and g_z here are ± 0.11 and ± 0.08 respectively. To estimate the maximum possible errors due to misalignment the criteria of Section 3 could not be used.

FIG. 20


Dy in Y.G.G.
H Kilogauss
6·0
5·0
4·0
3·0
2·0
1·0
0
10
20
30
40
50
60
70
80
90
φ Degrees

Since in this spectrum g_x is so small compared with g_y and g_z it is possible for very large misalignments, which would affect g_y and g_z little and g_x a great deal, to be unnoticed. Since none of the other specimens showed signs of misorientation, and because particular care was taken in this case, it was assumed that the maximum possible angular error was not larger than the largest possible in the other cases. Angles of 4° were therefore taken for angles α and β of Cases a and b in Section 3. These give errors of 13% in g_x and 0.25% in g_y and g_z. It is reasonable that the error for g_x should be so large for the reasons given above.

White and Carson (1960b) have also measured this spectrum and quote their results as

$$g_x = 1.07$$

$$g_y = 11.07$$

$$g_z = 7.78$$

which are in excellent agreement with ours.

4.5b Dy^{3+} Ion in Yttrium Aluminium Garnet.

Experiments were carried out at temperatures from 80°K. to 2°K. on several different samples of yttrium aluminium garnet containing 0.1%, 0.3%, 0.5%, 1.0%, 5% and 100% of dysprosium. No resonance was observed in any of these crystals at 3 cm. wavelength and within our field range of 0-5.5 kgauss approximately. The crystals used were well formed, of reasonable size and in most cases showed a slight yellow colouring typical of dysprosium (though colour is not a good guide to the

contents of the garnets). However Dr. Leask of this laboratory has performed susceptibility measurements at helium temperatures on these crystals and found them to be quite strongly paramagnetic, so proving that the dysprosium has been incorporated into the crystals. Some very small lines at very low temperatures were seen at some angles but these were visible over only a very small range of angle and were not reproducible from one specimen to another.

In the case of the crystals containing 1% of dysprosium an extensive and extremely complex spectrum was visible from liquid air temperatures down. Because this spectrum was so complex and because it was visible at such high temperatures it was thought to be due to an abnormally high concentration in these crystals of impurities belonging to the iron group. On investigating the history of these crystals it was found that at one stage of the crystal growing procedure the crucible lid had fallen off so exposing the charge, at a very high temperature, to the atmosphere in the furnace. It was therefore not surprising that there was so high a level of impurity concentrations in these crystals and for this reason they were discarded.

A more intensive search for resonance was then carried out in the other samples but none was found.

5. Discussion.

5.1 Significance of the observed g values.

The experimental results, summarized in Table, show several interesting and unexpected features. Comparison of corresponding g-values in the gallium and aluminium compounds shows a clear difference between Yb on the one hand, and Er, Dy, and Nd on the other. For Yb, the g tensor is not very anisotropic, and its principal values are very similar for the two different host lattices. As discussed in the introduction this indicates that the electronic states are not critically sensitive to small changes of environment, so that it is very likely that the same g-values will apply also in the iron garnet. The relatively small anisotropy of g indicates that Yb^{+3} ions present in a ferrimagnetic iron garnet should not contribute very much to the total magneto-crystalline anisotropy, compared with the other rare earth ions. This is in agreement with the empirical results of Dillon and Nielsen (1959, 1960), who found that Yb was about 10 times less effective than, say, Dy in influencing the low temperature anisotropy of slightly doped yttrium iron garnet. It is difficult to make an exact quantitative estimate of the anisotropy to be expected on the basis of the measured g-values alone, but an order of magnitude calculation (Wolf, 1959) shows that the observed magnitudes are quite reasonable. The value of the spontaneous magnetization can be estimated with much greater certainty, and for this very good quantitative agreement is obtained (Wolf l.c).

For the three other ions, Er, Dy, and Nd the situation is more

difficult. For all three ions the g values show considerable anisotropy, so that one may expect also large effects on the ferrimagnetic anisotropy. In the case of Nd^{+3} the values are again fairly similar in the YGG and YAG host lattices so that they should also apply in an iron garnet. Unfortunately, pure neodymium iron garnet can not be prepared (because of ionic sizes), so that one can not compare the predicted and calculated spontaneous moments, but it would be possible to do this for mixed (Nd-Y)IG which can be made. So far there are no reported moment measurements for these garnets.

The results for Er^{+3} show the most unexpected effect. In both the Al and Ga hosts the spectrum has approximately axial symmetry, but whereas the axis in the Ga host is parallel to the (001) direction it has changed to the (110) direction in the Al case. Moreover, in one case $g_z \gg g_x, g_y$, while in the other the situation is reversed. This shows that the electronic states are extremely sensitive to small changes of environment, and it illustrates rather dramatically how important it is to use more than one type of host lattice for paramagnetic investigations of this kind. The two main conclusions which can immediately be drawn from the observed values are (i) that Er iron garnets will be very anisotropic, and (ii) that the anisotropy may be strongly strain dependent. This would imply large magnetostrictive effects at low temperatures. So far no such measurements have been reported.

The results for Dy^{+3} are even more mysterious. In this case no resonance of any kind could be found in the Al compound, though the Ga crystals had shown a very strong absorbtion spectrum. One possible explanation for this might be that the g values in the Al compound are even more anisotropic than in the Ga compound, so that either the transition probabilities are very much reduced, or the resonances all occur at magnetic fields beyond the range of our magnet. Another possible explanation would be an extremely short relaxation time, broadening the lines beyond detection. This might somehow be related to the fact that the Dy ions interact with one another unusually strongly, as indicated by the fact that pure Dy aluminium garnet becomes ordered at about 2°K (Ball, Leask and Wolf, to be published). At present, however, the absence of resonance for Dy in YAG must be regarded as unexplained and requires further investigation.

5.2 Line Width Anomalies.

In Section 4 approximate values were given for the width of the observed resonance lines. The unpredictable variations of these was puzzling and on the whole they were remarkably large. Since the crystals contained no more than 1% of rare earth the width was unlikely to be caused by interaction breadening. The lines were not observed to decrease greatly in width on lowering the temperature and so spin-lattice relaxation was an unlikely cause. The line width in rare earth compounds is often due to the broadening produced by the protons of the surrounding water molecules e.g.

in the ethyl-sulphates. However, no such broadening will take place in the garnets because nearly all the oxygen ions have zero nuclear magnetic moment.

It was also observed that the line width was not constant but varied with the angle between the magnetic field and the crystal. This effect was particularly noticeable in the Nd^{3+} in yttrium aluminium spectrum where at certain angles, the turning points of resonant field with respect to angle, the lines were 5 to 10 gauss wide. These turning points occur at positions where the magnetic field is along an edge of the cubic unit cell or along a face diagonal. A likely cause of this anomalous line width is the presence of lattice imperfections or inhomogeneities. If there were any microcrystalline structure in the specimens the interfacial boundaries would, because of the morphology of the garnets, contain $\{110\}$ faces. If the microcrystals were slightly misaligned relatively then one of the positions in which the angle between the component crystal axes and the magnetic field would be the same would be when the field was in an interfacial plane. In other positions the angle between the crystal axes and the field would be different in the different microcrystals - resulting in a smearing out of the resonance field. This, therefore, is a cause of broadening which would exhibit the required minima at turning points. The techniques of micro-beam X-ray analysis are suitable for detecting such micro-mosaic structure of crystals. The equipment at our disposal was not suitable for this work because of the relatively

large size of its beam which could not be reduced below 1mm. radius.

5.3 Conclusion.

The results presented in this report clearly constitute only the first stage of a very extensive investigation. As such they can only lead to rather general conclusions, some of which however turn out to be very significant. As might have been expected, all the rare earth ions have been found to exhibit very appreciable anisotropies, emphasizing again their importance in connection with the anisotropy of ferrimagnetic garnets. The wide range of g values found (1.07 to 11.07) shows clearly that a considerable amount of experimental and theoretical information is essential for the understanding of these rare earth compounds, which may in general be expected to have properties very different from ferrimagnetic materials containing only 3d ions with "spin-only" paramagnetism. The marked differences found in several cases between apparently very similar compounds stress the need for great care in applying some of the paramagnetic results to ferrimagnetism, a point which has until now not been appreciated generally. The observed structure sensitivity also suggests that some marked magneto-elastic effects might be found in certain of the rare earth garnets. Further experiments on some of the problems related to these conclusions are now in progress, and it is hoped to present the results in the near future.

TABLE

Summary of Experimental Results.

	In Y.G.G.	In Y.A.G.
Yb^{3+}	g_x 3.73 ± 0.02	g_x = 3.87 ± *
	g_y 3.60 ± 0.07	g_y = 3.78 ±
	g_z 2.85 ± 0.02	g_z = 2.47 ±
Er^{3+}	g_x 4.03 ± 0.02	7.75 ± 0.09
	g_y 4.69 ± 0.03	3.71 ± 0.02
	g_z 10.73 ± 0.05	7.35 ± 0.08
Nd^{3+}	g_x = 1.25 ± .007	1.179 ± .002
	g_y = 2.027 ± .008	1.733 ± .004
	g_z = 3.667 ± .018	3.915 ± .026
Dy^{3+}	g_x = 1.070 ± 0.14	
	g_y = 11.07 ± 0.20	No resonance observed
	g_z = 7.85 ± 0.10	

* Measured by Carson and White (1960).

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PREPARATION OF SINGLE CRYSTALS OF YTTRIUM GALLIUM GARNET AND YTTRIUM ALUMINIUM GARNET, AND INVESTIGATION OF PARAMAGNETIC RESONANCE SPECTRA OF FOUR RARE EARTH IONS IN THESE GARNETS.

M. Ball, G. Garton, D. Ryan, and W. P. Wolf

May 1961

46 pages and 20 illustrations

Clarendon Laboratory, Oxford.

ABSTRACT:

This report summarizes the first results of an extensive survey of the magnetic properties of rare earth ions in crystals with the garnet structure. Methods of preparing suitable samples are described, and results of low temperature microwave resonance experiments with Yb^{3+}, Dy^{3+}, Er^{3+} and Nd^{3+} ions are given. For each of these ions, the ground state is a doublet which can be characterized by three principal values of a g tensor, and with one exception, all the principal values have been determined for these ions in both yttrium aluminium and yttrium gallium garnet.

Comparison of the two sets of results shows that great care must be exercized in applying the results of resonance experiments for one kind of garnet to a seemingly similar case, but some general conclusions can be drawn, even without the necessary detailed analysis. The main result is that the local environment of the rare-earth ions is far from being spherically or cubically symmetrical, so that the individual rare earth ions have magnetic properties which are very anisotropic. The relation of these results to the observed anisotropies in rare earth iron garnets and rare earth doped YIG are discussed.

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