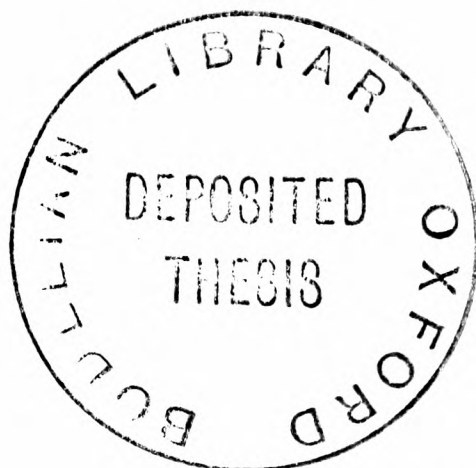


AN EXPERIMENTAL STUDY
OF PARAMAGNETIC SUSCEPTIBILITY
AT LOW TEMPERATURES

A THESIS SUBMITTED FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY
AT OXFORD UNIVERSITY

BY

H. J. DUFFUS



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PREFACE

The work described in this thesis was carried out at the Clarendon Laboratory, Oxford, under the supervision of Dr. A. H. Cooke.

I am indebted to Professor Lord Cherwell for extending the facilities of the laboratory. Dr. K. W. H. Stevens, Dr. B. Bleaney and Dr. R. J. Elliott have generously given advice upon theoretical aspects of the work. Dr. H. Meyer and Mr. W. P. Wolf have been of great assistance during experiments. I wish to express my thanks to them, and especially to Dr. Cooke for his active but gentle supervision.

The work was supported by two Special Overseas Fellowships from the National Research Council of Canada, and a grant from the Carnegie Trust.

ABSTRACT

An Experimental Study of Paramagnetic
Susceptibility at Low Temperatures

We have investigated the microwave absorption spectra of cerium, praseodymium, neodymium and samarium in magnesium double nitrate at 4.2°K . We have also measured the bulk susceptibility of a nitric oxide clathrate and of potassium manganicyanide from 4.2°K to 300°K .

I. APPARATUS:

We used a 3 cm reflex klystron microwave spectrometer, obtaining temperatures down to 1.5°K by the use of free liquid helium. A large water-cooled electromagnet produced homogeneous fields of up to 15 kilogauss which were usually measured by an ammeter showing the current through the coils. In order to measure the field accurately very close to the specimen at 4.2°K we used proton resonance in perspex. Lithium fluoride which had been bombarded with neutrons also gave a nuclear resonance signal at 4.2°K , but it was too broad to be very useful.

The bulk susceptibilities were measured by means of a Sucksmith ring balance which covered the temperature range from 2°K to 300°K by use of the free liquid helium,

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hydrogen and oxygen. The ring deflections were measured by means of two opposing selenium photocells in series with a sensitive galvanometer used as a null detector. The force on the specimen was produced by the inhomogeneous field of an air-cooled electromagnet. We were unable to obtain a field of suitable symmetry to measure highly anisotropic crystals.

II. RESULTS:

1. THE DOUBLE NITRATES:

a. Cerium:

An absorption line was observed with

$g_{\perp} = 1.82 \pm 0.02$ and $g_{\parallel} = 0.25 \pm 0.05$, and interpreted as a single electronic transition between the states

$$\begin{aligned} & \cos \theta |1, -\rangle - \sin \theta |0, +\rangle \\ & - \cos \theta |1, +\rangle + \sin \theta |0, -\rangle \end{aligned}$$

in $^{4,5}L_3$ quantization where $\theta = 17\frac{1}{2}^\circ$.

The line width at half intensity of 120 gauss is wider than theory predicts, and it is not caused by a short spin lattice relaxation time.

b. Praseodymium:

Six absorption lines were observed with the r.f. and d.c. fields parallel. They are interpreted as resulting from a single electronic transition having

3.

$g_{\parallel} = 1.55 \pm 0.02$ split by the nuclear spin of $\frac{5}{2}$ into six hyperfine lines. The transition is not between the states of a Kramers' doublet. A crystal field of C_{3h} symmetry will give a singlet and J doublets, which will be split by the Jahn Teller effect. We propose that the transition occurs between states described by J_z quantization as

$$\cos \theta | \pm 2 \rangle + \sin \theta | \mp 4 \rangle$$

with $\theta = 22^\circ$.

The hyperfine parameters are interpreted in terms of the spin Hamiltonian

$$\mathcal{H} = \beta g_{\parallel} H_z S_z + A I_z S_z$$

giving $A = \frac{0.078 \pm 0.001}{0.100 \pm 0.002} \text{ cm}^{-1}$.

c. Neodymium:

A main line flanked by 15 resolved hyperfine lines was observed. They are interpreted as resulting from a single electronic transition having $g_{\perp} = 2.72 \pm 0.02$ and $g_{\parallel} = 0.45 \pm 0.05$ split by the nuclear spins of $\frac{7}{2}$ of two odd isotopes, Nd^{143} and Nd^{145} , into sixteen hyperfine lines, one of which was not resolved from the main line. The hyperfine parameters are interpreted in terms of the usual spin

Hamiltonian

$$\mathcal{H} = (\beta [g_{\parallel} H_z S_z + g_{\perp} (H_x S_x + H_y S_y)]) + A I_z S_z + B(I_x S_x + I_y S_y)$$

giving $B^{143} = 0.0372 \text{ cm}^{-1}$

~~$A^{143} = 0.0037 \text{ cm}^{-1}$~~

$B^{145} = 0.0194 \text{ cm}^{-1}$

~~$A^{145} = 0.0034 \text{ cm}^{-1}$~~

The ratio of the nuclear magnetic moment of Nd^{143} to that of Nd^{145} is 1.61.

The transition is proposed to occur within the Kramers' doublet in J_z quantization of

$$\cos \theta \left| \pm \frac{7}{2} \right\rangle + \sin \theta \left| \mp \frac{5}{2} \right\rangle$$

where $\theta = 47^\circ$

The line width of the main line was 170 gauss which is wider than theory predicts.

Several weak unidentified lines were observed.

d. Samarium:

A main line flanked by 16 fully resolved hyperfine lines was observed. They are interpreted as resulting from a single electronic transition having $g_{\perp} = 0.40 \pm 0.05$, $g_{\parallel} = 0.76 \pm 0.01$ split by the nuclear spins of $\frac{7}{2}$ of two odd isotopes, Sm^{147} and Sm^{149} . The hyperfine parameters are interpreted from the same spin Hamiltonian as (c) to be

5.

$$|A|^{147} = 0.0316 \pm 0.0005 \text{ cm}^{-1} \quad |A|^{149} = 0.0287 \pm 0.0005 \text{ cm}^{-1}$$

$$B \leq 0.009 \text{ cm}^{-1} \text{ for both isotopes}$$

$$\frac{\mu_N^{147}}{\mu_N^{149}} = 1.22$$

The transition is proposed to occur within the Kramers' doublet in JJ_z quantization of

$$\cos \theta \left| \frac{5}{2} \pm \frac{1}{2} \right\rangle + \sin \theta \left| \frac{7}{2} \pm \frac{1}{2} \right\rangle$$

where $\theta \sim 6^\circ$.

The observed line width of 75 gauss is very much wider than theory predicts, but this may be due to a short spin lattice relaxation time.

2. POTASSIUM MANGANICYANIDE:

$$\text{The effective magnetic moment, } n = \sqrt{\frac{3 \chi_K T}{N \beta^2}}$$

approaches zero as the temperature is decreased, showing that the ground level is diamagnetic. From the temperature variation of n we conclude that the covalent forces upon the Mn^{+++} ion cannot be accurately represented by an electrostatic crystal field of cubic symmetry.

At 293°K the effective magnetic moment of

$$n = 3.6.$$

3. NITRIC OXIDE CLATHRATE:

The effective magnetic moment of nitric oxide molecules trapped in the quinol lattice approaches zero as the temperature is decreased, showing that the ground level is diamagnetic.

The first excited level is not as far above the ground level as it is in the free molecule, and we conclude that there is a small interaction between the NO molecules and the quinol lattice. At 293°K, however, the susceptibility of the NO in the clathrate is that of free NO within the experimental error, viz. 47×10^{-6} emu per gram.

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CHAPTER I

INTRODUCTION

The post-war development of microwave spectroscopy has greatly stimulated interest in paramagnetism, and has added enormously to our understanding of the interaction between a paramagnetic ion and its surroundings in a crystal.

A good deal of work has been done upon the bulk susceptibilities of solids by means of various balance and optical techniques. However powders have often been used rather than single crystals, and observations have been made over limited ranges of high temperatures. More recently the development of the theory of the electric fields in crystals has led to measurements upon single crystals over larger temperature ranges.

The work at high temperatures has been carried out principally by Krishnan, Banerjee, Bhatnagar, Mathur and Mookherji in India: and the work at low temperatures on single crystals by Jackson in England, and by the Leiden school.

Measurements of the bulk properties are difficult to interpret in terms of the energy levels of the individual ions when more than one doublet is occupied. Furthermore in the case of rare earth elements, which are difficult to obtain pure, the effect of impurities may be large. These difficulties underline some advantages of microwave spectroscopy.

I.2

This technique clearly separates the effect of different doublets, different elements and different ions within a unit cell. Indeed, the spectra of different isotopes may be resolved. In addition to the sort of information comparable to that obtained from bulk susceptibility measurements, we may also obtain information about the nuclear spin and electric quadrupole moment. Furthermore the line width and shape give information about the interaction between the paramagnetic ions and the lattice, and between the paramagnetic ions themselves.

Unfortunately the conditions under which we can expect to observe microwave absorption are rather stringent. The electrons must not be in a homopolar valence bond. There must be an interaction between the electron and the lattice such that the time required for energy to be transferred from the spin system to the lattice is neither so short that the uncertainty in the electron's energy becomes large, nor so long that equipartition of energy occurs among the levels, causing saturation. Finally, the energy levels of the electron must be such that magnetically degenerate doublets are occupied, and available magnetic fields must be able to split these doublets by an amount equal to the quantum of energy associated with microwave radiation.

Our microwave apparatus was designed to operate at or below 4.2°K because the spin-lattice relaxation time in

1.3

the rare earths is usually short, due to the presence of low-lying excited electronic energy levels. The spin-lattice relaxation time increases as between T^{-2} and T^{-10} , and therefore some spectra which are invisible at 20°K are visible at 4.2°K.

There is no way of overcoming the other difficulties mentioned except to try different kinds of crystals, and herein lies one of the disadvantages of our apparatus. It is obviously a much slower process to perform experiments requiring liquid helium ... experiments requiring not only that the apparatus itself function, but also that supplies of liquid oxygen, liquid hydrogen and liquid helium be simultaneously provided.... than it is to work at higher temperatures. Our apparatus was therefore designed to maintain a temperature of 4.2°K for as long as the experimenter could take observations, and provision was made to change the specimen during the course of the experiment.

As we have said, the observation of microwave resonance in any given paramagnetic substance is unlikely. However measurements of bulk susceptibility can be made upon any chemically stable paramagnetic substance, with a sufficiently sensitive balance. Although it is usually impossible to reach a definite conclusion about the properties of a substance by failing to observe microwave absorption, one can rule

I.4

out the possibility of such absorption from measurements of the bulk susceptibility if they show the ground state to be a singlet energy level with no nearby excited levels.

We therefore built a Sucksmith ring balance in order to measure bulk susceptibilities over a large range of temperatures, not only to rule out certain microwave absorption experiments, but also to provide information about the energy level structures where no resonance is observed.

The following considerations governed the choice of the substances which we investigated.

Extensive measurements have been made upon the ethyl sulphate salts of the rare earths. Bulk susceptibility and optical rotation measurements over a large range of temperatures were performed at Leiden, and paramagnetic resonance experiments over a range of temperatures and frequencies were performed at Oxford. The detailed theory of these measurements was in good agreement with the measurements. It was therefore desirable to measure another isomorphous series of rare earth salts to see if the parameters established for the ethylsulphates could be logically extrapolated to agree with the new observations.

A suitable salt must give a resonance spectrum and form as complete an isomorphous series with the rare earths as possible. In addition it should have a large lattice struc-

1.5

ture in order that the interactions between neighbouring ions should be small. (This condition implies a salt that might be useful for work below 1°K using adiabatic demagnetization.) Finally, the salt should form large single crystals easily so that its specific heat and susceptibility could be measured by the mutual inductance technique. Such measurements, as well as providing new information, would offer an independent check upon the resonance measurements.

Dr. Bleaney pointed out the advantage of the large lattice structure in the double nitrates. He had observed resonance in the cerium double nitrate while investigating its suitability for nuclear alignment work. Since the strong absorption line seen at 4°K was invisible at 20°K we deduced that we might be able to see the spectra of other rare earths at 4°K , which were unobservable at higher temperatures. This proved to be the case for neodymium, samarium and praseodymium. Unfortunately the whole series of rare earths will not form crystals of double nitrate, so that although we could probably introduce them as small impurities in the lanthanum double nitrate there was no hope of making specific heat or bulk susceptibility measurements.

The Physical Chemistry Laboratory supplied us with oxygen and nitric oxide clathrates. These new compounds contain the paramagnetic oxygen and nitric oxide molecules en-

closed in holes in the quinol lattice. It was hoped that this might provide a field-free space in which to observe the properties of paramagnetic "gases" below their liquefaction temperatures.

Our attention was drawn to the problem of the temperature variation of the susceptibility of $K_3Mn(CN)_6$ by the current interest in the resonance spectra of the complex cyanides. We wished to discover whether or not resonance was ruled out by a diamagnetic level being lowest, and to obtain information about the covalent binding of the Mn^{+++} ion.

CHAPTER II

APPARATUS AND TECHNIQUE

I. THE SUCKSMITH BALANCE:

A ring balance (figure 1) was constructed like that of W. Sucksmith (1929). The force exerted on a paramagnetic specimen by an inhomogeneous magnetic field is proportional to the displacement of the bottom of a phosphor bronze ring (B) to which the specimen is attached. The displacement of the ring is measured by the displacement of a beam of light reflected from mirrors (C) mounted on its edge. This balance was designed to measure susceptibilities over a range of temperatures from 300°K down to 1.5°K.

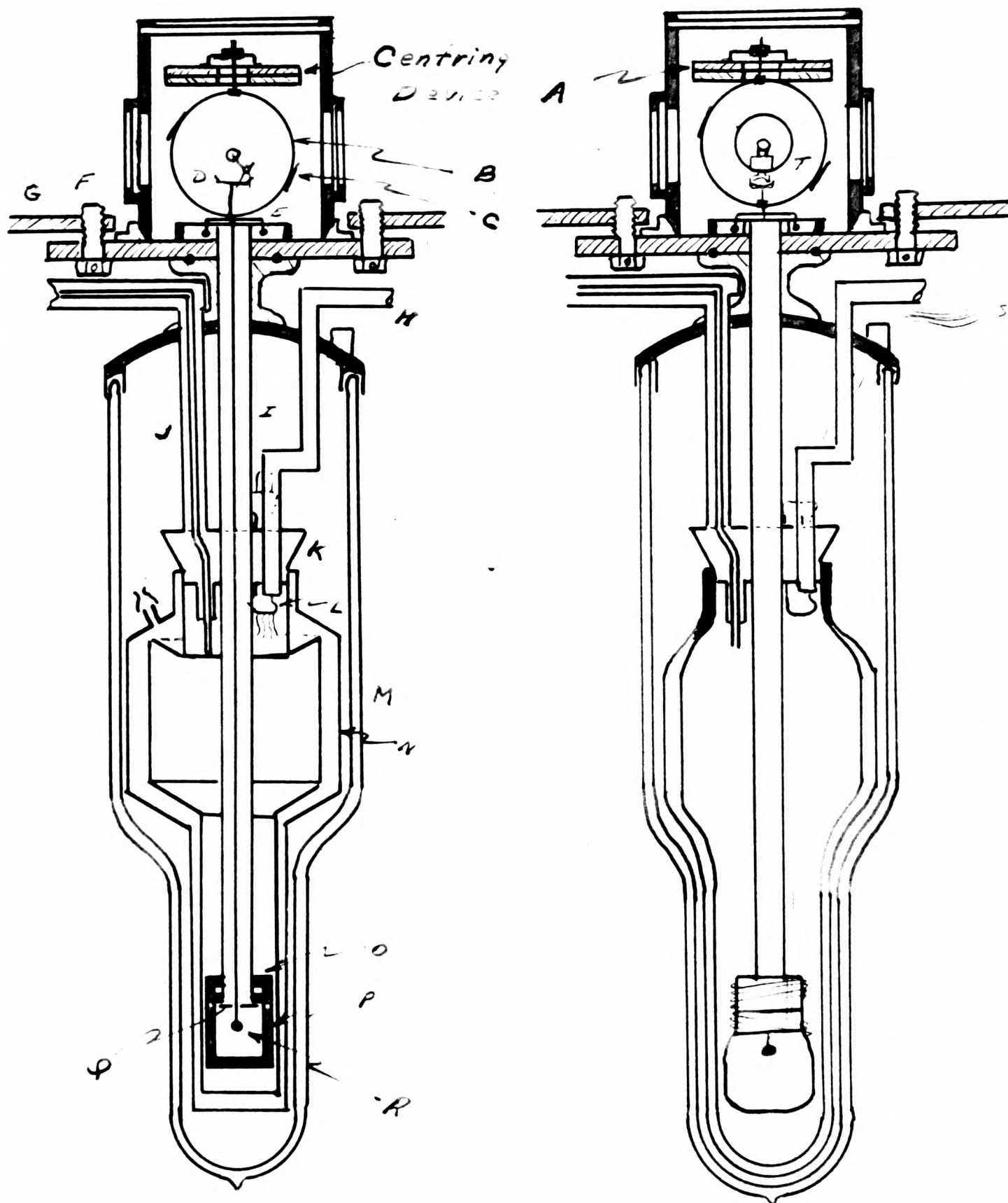
We shall first describe the details of construction of the balance, then some of the problems which arose, and finally the resulting alterations. The major difficulties were to measure the deflection of the beam of light, to measure and maintain the temperature of the specimen, and to obtain an inhomogeneous magnetic field of the desired symmetry. We believe we have successfully overcome the first two difficulties, but we did not obtain a suitable magnetic field for measuring large anisotropies or absolute susceptibilities.

1. THEORY OF THE SUCKSMITH BALANCE:

a. The Faraday Method;

If $\bar{I}$ is the dipole moment per unit volume of

Figure 1



FIRST AND SECOND
ARRANGEMENTS OF
SUCKSMITH BALANCE

II.2

a paramagnetic substance in a magnetic field $\underline{H}$, then the internal energy is $U = \int \underline{I} \cdot \underline{H} d\tau$ where the integral is taken over the volume of the specimen.

The force on the specimen $\underline{F} = -\nabla U$

$$\begin{aligned}\therefore \underline{F} &= -\nabla \int \underline{I} \cdot \underline{H} d\tau \\ &= -\nabla (\underline{M} \cdot \underline{H})\end{aligned}$$

where $\underline{M}$ is the effective (average) magnetic moment of the specimen. We may let $M_x = \chi_x H_x$ $M_y = \chi_y H_y$ $M_z = \chi_z H_z$ because it is always possible to choose axes X, Y, Z so that the susceptibility tensor has its principal values along them.

Then:

$$F_z = -\frac{1}{2} \frac{\partial}{\partial z} (\chi_x H_x^2 + \chi_y H_y^2 + \chi_z H_z^2) \quad 1.1$$

Consider the force on a crystal whose axes are ξ, η and z . Let the angle between the ξ and x axes be θ , and H_η and H_ξ be the components of magnetic field along the η and ξ directions.

It may be shown that for an arbitrary θ

$$\begin{aligned}F_z &= -\left[\chi_x \left(H_\xi \frac{\partial H_\xi}{\partial z} \cos^2 \theta + H_\eta \frac{\partial H_\eta}{\partial z} \sin^2 \theta \right. \right. \\ &\quad \left. \left. - H_\xi \frac{\partial H_\eta}{\partial z} \cos \theta \sin \theta - H_\eta \frac{\partial H_\xi}{\partial z} \cos \theta \sin \theta \right) \right. \\ &\quad \left. + \chi_y \left(H_\xi \frac{\partial H_\xi}{\partial z} \sin^2 \theta + H_\eta \frac{\partial H_\eta}{\partial z} \cos^2 \theta \right. \right. \\ &\quad \left. \left. + H_\xi \frac{\partial H_\eta}{\partial z} \sin \theta \cos \theta + H_\eta \frac{\partial H_\xi}{\partial z} \sin \theta \cos \theta \right) \right. \\ &\quad \left. + \chi_z H_z \frac{\partial H_z}{\partial z} \right] \quad 1.2\end{aligned}$$

$$F_z = (\chi_x - \chi_y)(a \cos^2 \theta + b \sin^2 \theta) + c$$

II.3

at $\theta = 0$

$$F_z = - \left[X_x H_x \frac{\partial H_x}{\partial z} + X_y H_y \frac{\partial H_y}{\partial z} + X_z H_z \frac{\partial H_z}{\partial z} \right] \quad 2.3$$

b. The Ring Deflection:

According to Sucksmith (1929), the force F applied downward to the bottom of a ring whose top is fixed produced a radial displacement U at any point

$$U = \frac{Fr^3}{4EI} \left\{ \theta \sin \theta + \cos \theta - \frac{4}{\pi} \right\} \quad 2.4$$

where r is the radius of the ring, E = Young's modulus, and θ the angle between the radius through the point considered and the horizontal.

When $\theta = 90^\circ$, the displacement of the lowest point relative to the point of support is

$$U = \frac{Fr^3}{2EI} \left(\frac{\pi}{2} - \frac{4}{\pi} \right) = \frac{0.298}{2EI} Fr^3 \quad 2.5$$

The angle turned through by the tangent to the ring is to the first approximation

$$\phi = \frac{1}{r} \frac{dU}{d\theta} = \frac{Fr^2}{4EI} \theta \cos \theta \quad 2.6$$

This is maximum at about 49° , whence

$$\phi_{\max} = \frac{0.561}{4EI} Fr^2 \quad 2.7$$

Thus we see that the deflection of the beam of light from the two mirrors (4ϕ) is linear with the force F .

II.4

We verified that the deflection of the beam of light was linear in the force and hence in

$$H_z \frac{\partial H_z}{\partial z} = \frac{1}{2} \left(\frac{\partial H_z^2}{\partial z} \right)$$

by plotting the deflection caused by a specimen of $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ as a function of H^2 . We were then able to check for ferromagnetic impurities in an unknown specimen by a similar experiment, since $\chi = \chi(H)$ for such a substance, and the deflection is no longer linear in H^2 .

To measure H^2 we calibrated the homogeneous part of the magnetic field by proton resonance (Chapter II,32) as a function of current. The linearity of $\left(\frac{\partial H_z^2}{\partial z} \right)$ with H^2 was also verified by the experiment with the $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

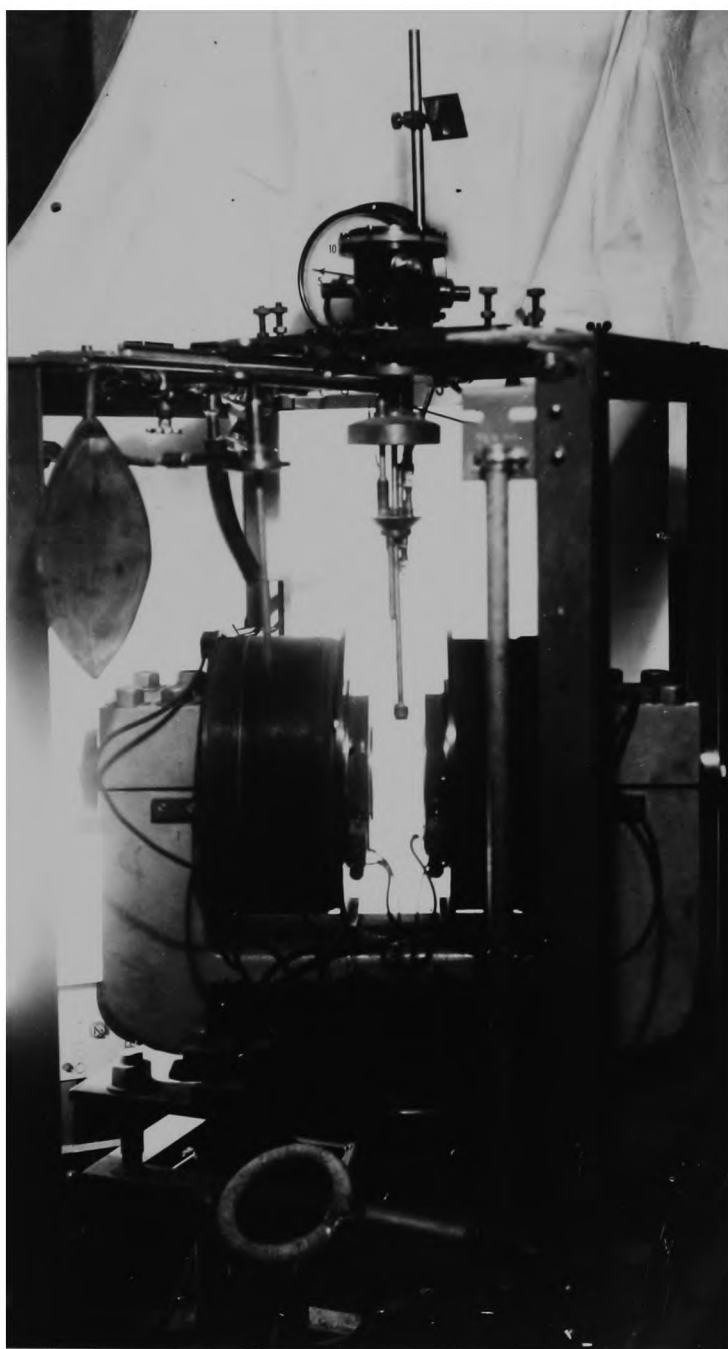
2. THE ORIGINAL CONSTRUCTION:

a. Optics:

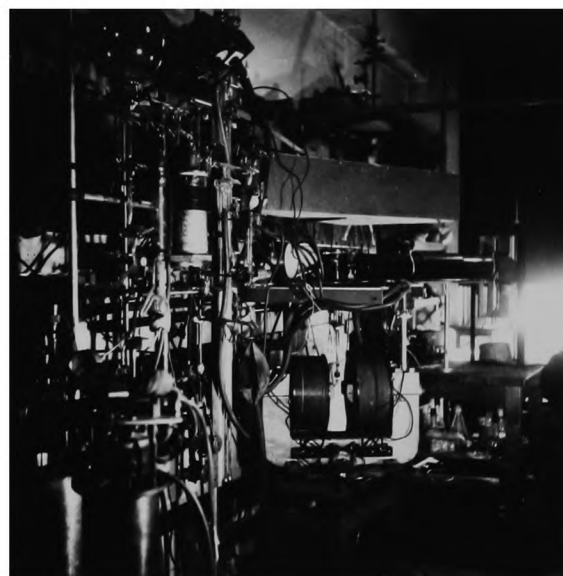
The displacement of the specimen is measured by the deflection of a beam of light. In the original apparatus a lamp and condensing lens were mounted on the same rigid frame as a travelling microscope (figure 2). The light was brought to a focus at the nearer ring mirror after being collimated by an adjustable slit and reflected through about 180° by two adjustable plane mirrors as shown. The light beam was then reflected onto the farther ring mirror and from it back towards

Chapter II

Photographs 1 and 2



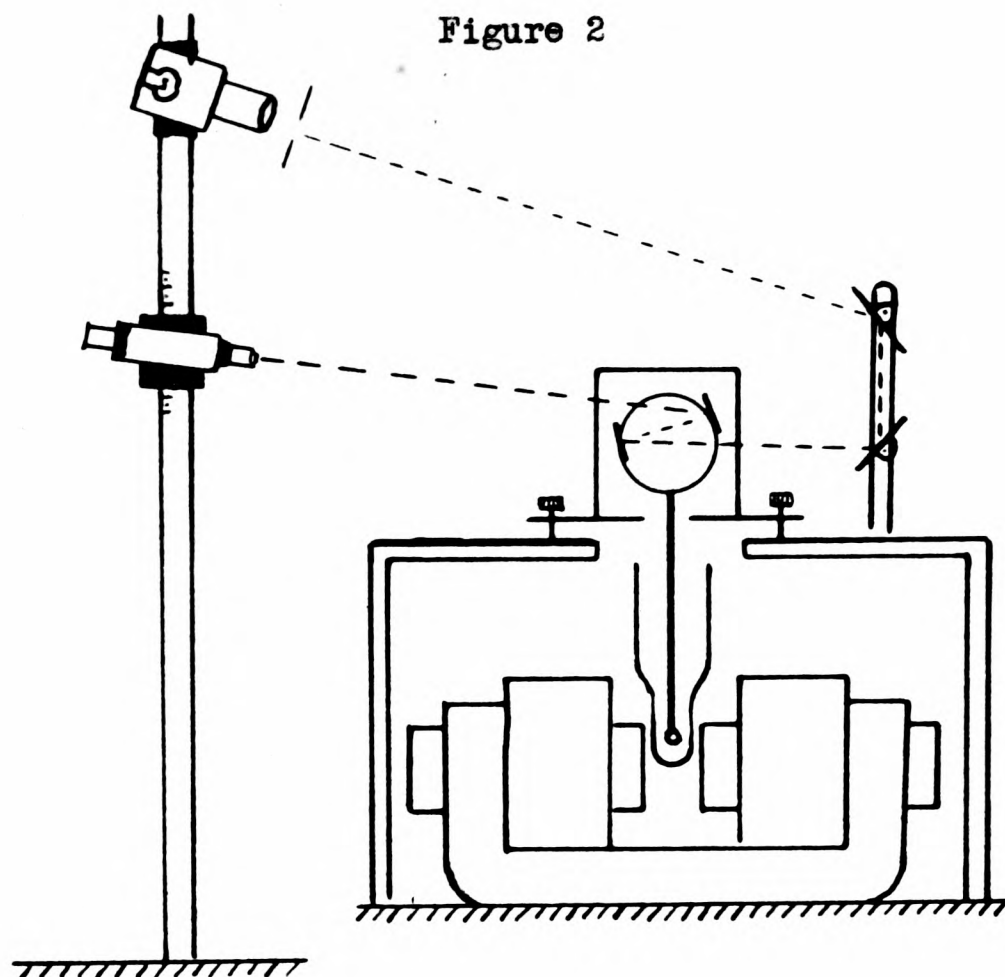
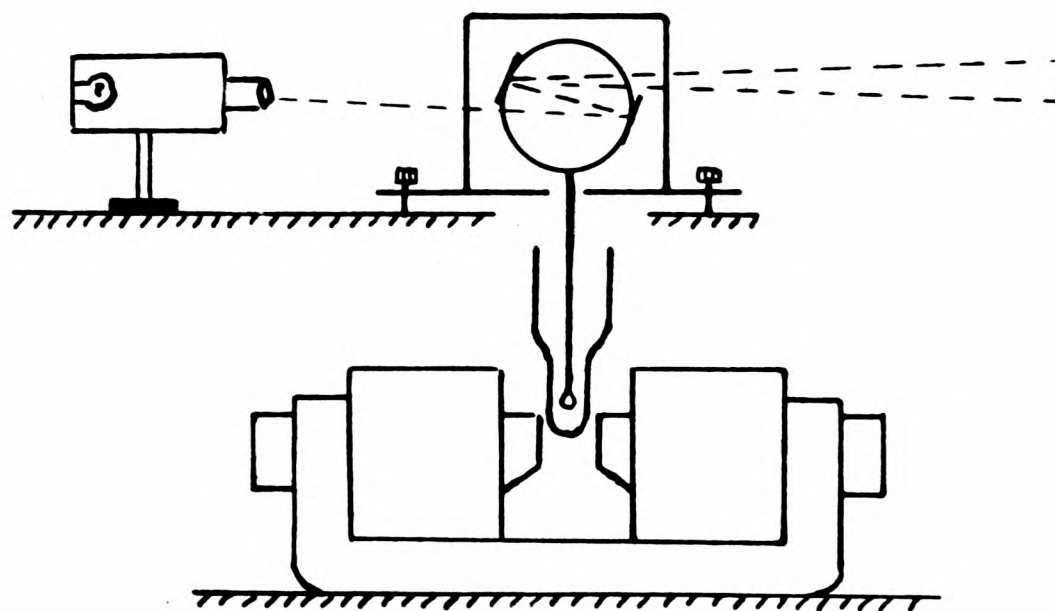
1



2

1. Sucksmith balance mounted upon the magnet.
2. Sucksmith balance mounted permanently on the wall.

Figure 2

*FIRST BALANCE ARRANGEMENT**SECOND ARRANGEMENT*

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the lamp. An image of the slit, formed about 90 cm from the balance by a convex-concave lens, was observed through a travelling microscope.

To avoid moving the microscope a microscope eyepiece graduated into 100 divisions was used occasionally. Although it is difficult to produce an image of the slit which can be read to 0.01 m.m., a diffraction pattern can be formed (with practice) which is very crisp.

The plane mirrors were supplied by H. Tinsley & Co. Ltd. from their stock of galvanometer mirrors.

The whole apparatus was originally mounted on an adjustable frame on the Tickford magnet as shown in the photograph, and the optical system arranged as shown in figure 2. The measurements of χ_1 of $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ from 4°K to 1.5°K were made with this arrangement.

b. Balance:

The ring, 2m.m. wide, 0.09 m.m. thick and 6cm in diameter, was turned from a piece of phosphor bronze. The quartz rod (R), 1 m.m. in diameter, hung on a pivoted mount and supported a specimen in an inhomogeneous magnetic field. This rod was enclosed by an 8m.m. German silver tube (I) which terminated in a larger copper container (P). The bottom of the copper container unscrewed so that a centering spring (Q)

II.6

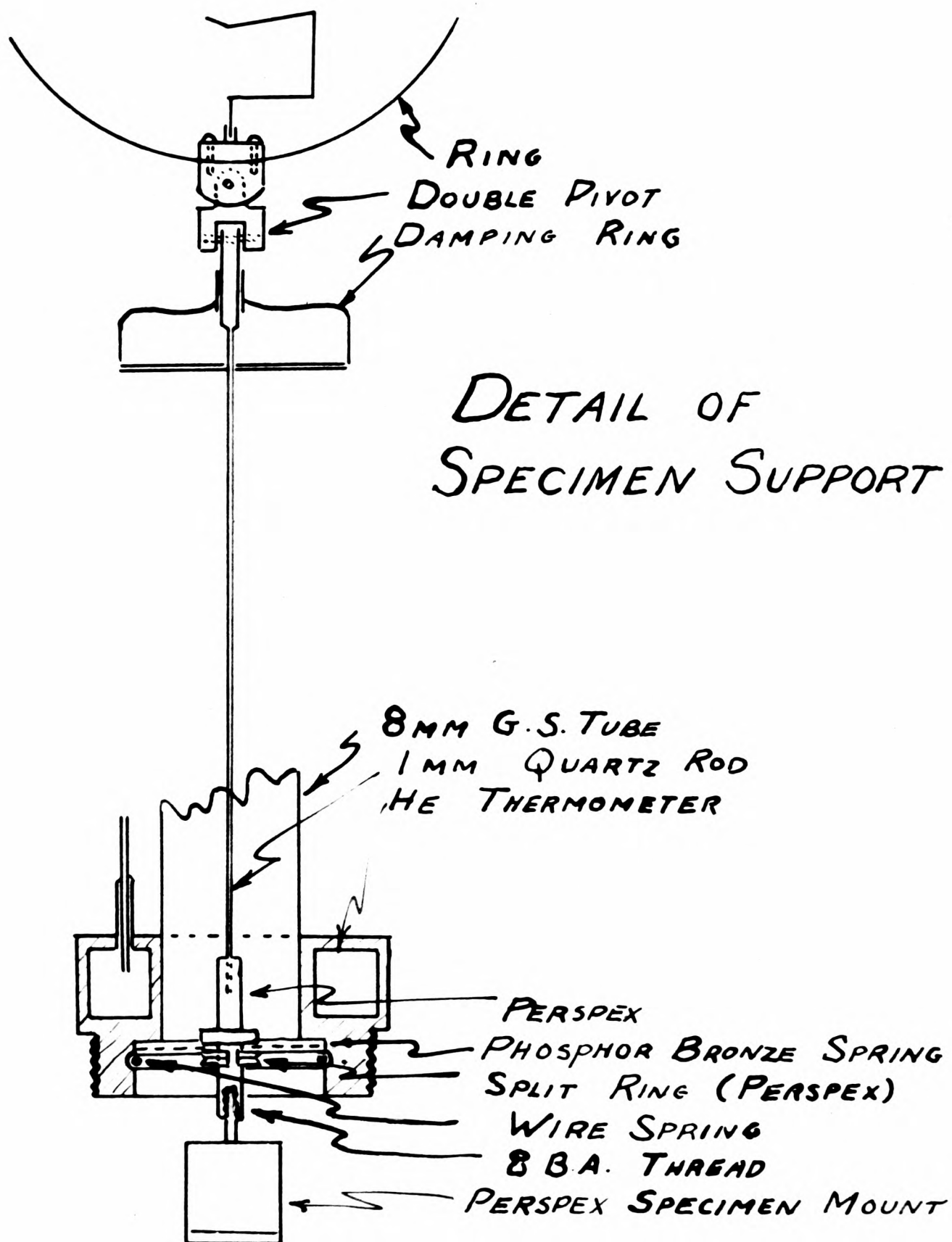
and specimen could be inserted. A rubber gasket lubricated with tap grease and glycerol was used to make a vacuum seal between the bottom and top of the copper container. The centering spring was cut as a flat spiral from a thin sheet of phosphor bronze by soft soldering it on a backing, cutting the spiral on a lathe, and slicing off the resulting spring with a razor blade. It was held in place in the container by a wire spring which fitted in a groove. A split sleeve pushed the spiral spring against a collar on a "spec pure" copper fitting durofixed to the end of the quartz rod (see figure 3). The specimen was mounted on a piece of perspex which also screwed into the copper fitting.

The temperature of the specimen was shown by a helium gas thermometer built into the copper container, and provision was made to attach a resistance thermometer to wires (L) passing through the siphon vacuum case (K).

c. Balance Case:

The upper case (figures 1 and 4) contained a screw and slide arrangement (A) for holding and centering the ring; a damping bath; an arm for placing a known rider weight on the ring; the rider support (D); and three perspex windows. Together with the eight m.m. tube and copper can, it formed one unit of the vacuum system. This unit could be evacuated,

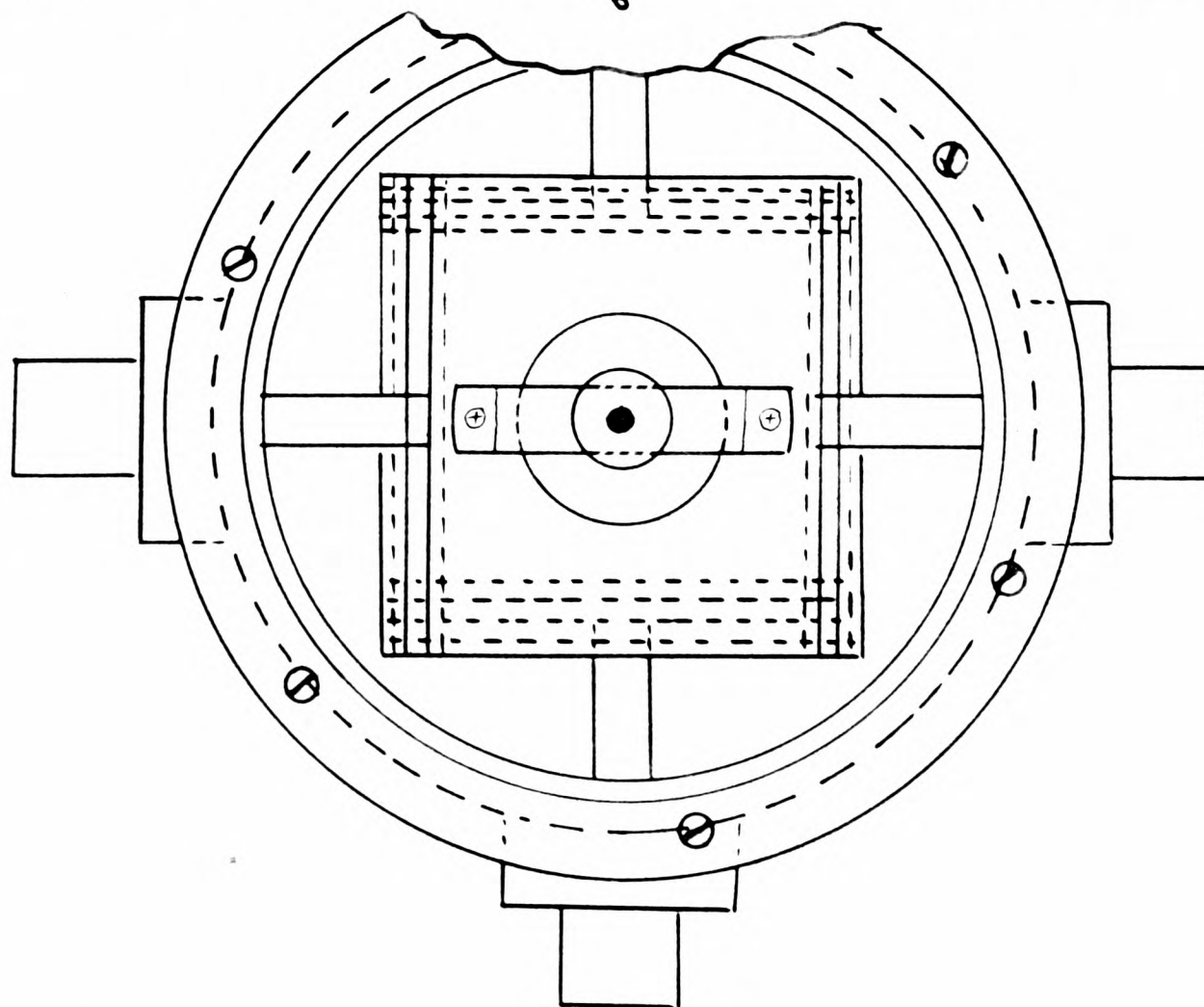
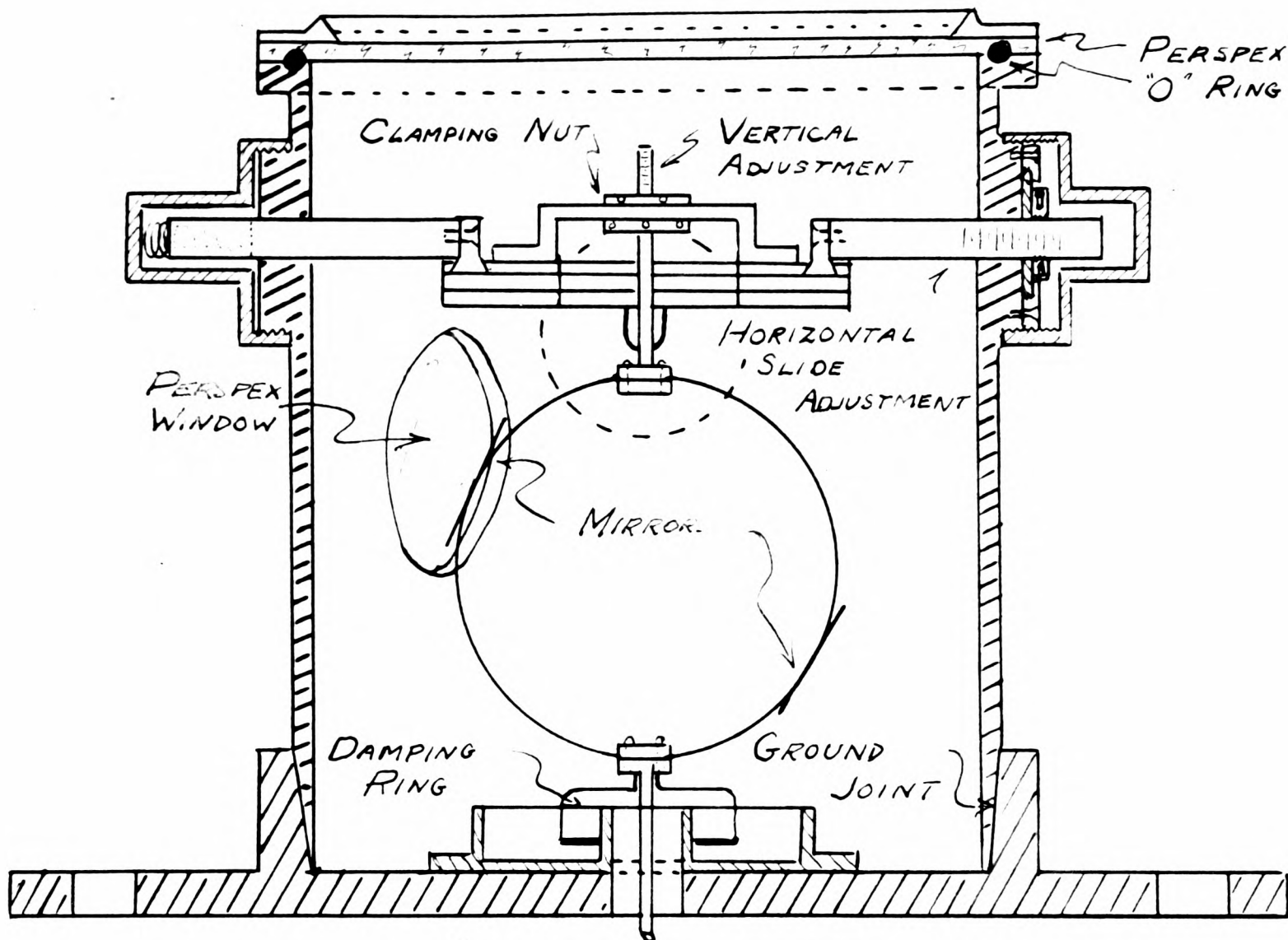
Figure 3



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DETAIL OF BALANCE HEAD & CENTRING

Figure 4



II.7

or used as a vapour pressure thermometer by filling it with helium and connecting it to a mercury manometer. All the perspex windows were sealed with rubber gaskets, and the case was sealed to the levelling table (G) by a ground joint (F).

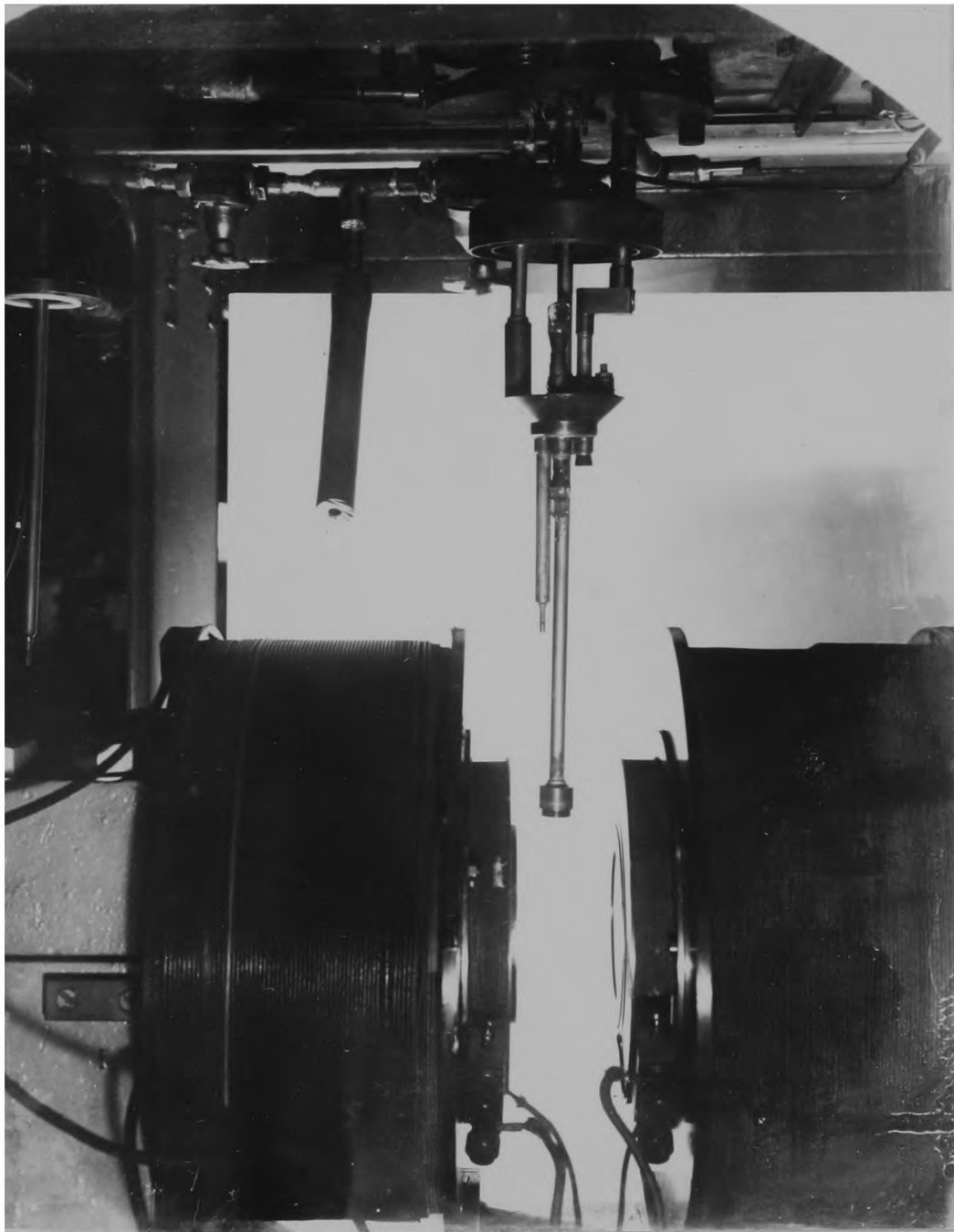
Some trouble was experienced in finding a suitable damping bath (E), which is very close to the liquid hydrogen bath. Its equilibrium temperature is about 0°C . Ordinary "Apiezon" oils were too viscous at this temperature. However, butyl phthalate is suitable as it has a low viscosity and a fairly low vapour pressure. Unfortunately it condenses on the cooler parts of the system and eventually dissolves the black wax and durofix joints holding the quartz rod to the ring and to the specimen holder.

d. Cryostat;

Outside the lower part of the 8 m.m. German silver tube was a double-walled metal cryostat (H) into which 200 c.c. of liquid helium could be siphoned. This metal cryostat was made of brass except for a two-inch length of thin stainless steel tube supporting and thermally insulating the inner wall from the top. The space between the inner and outer walls was evacuated and closed off by an ordinary pinch clamp on a short length of soft rubber tubing covered with glycerol. The cryostat was sealed to the ground joint (K) with

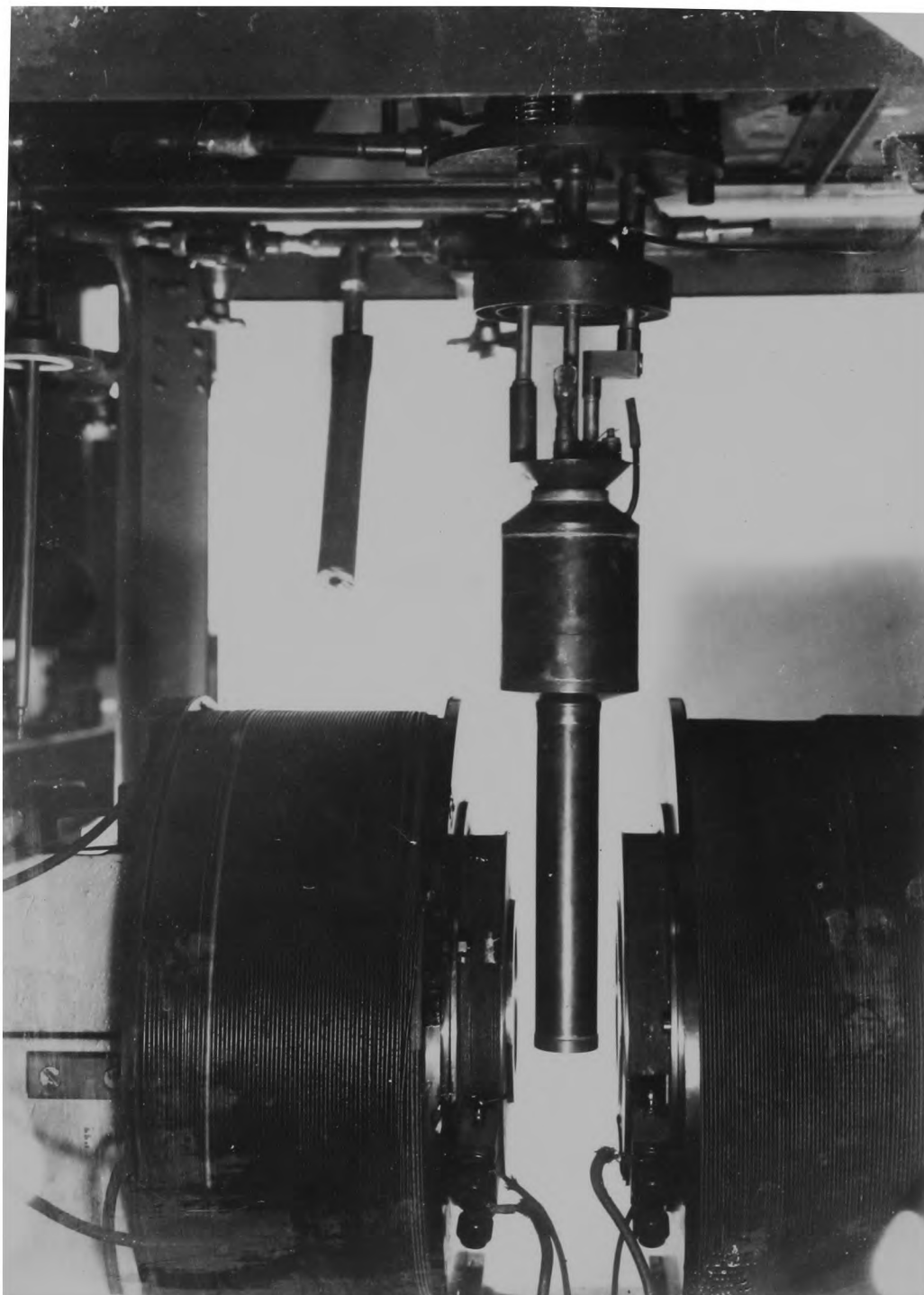
Chapter II

Photograph 3



Sucksmith balance mounted on the magnet
(without specimen)

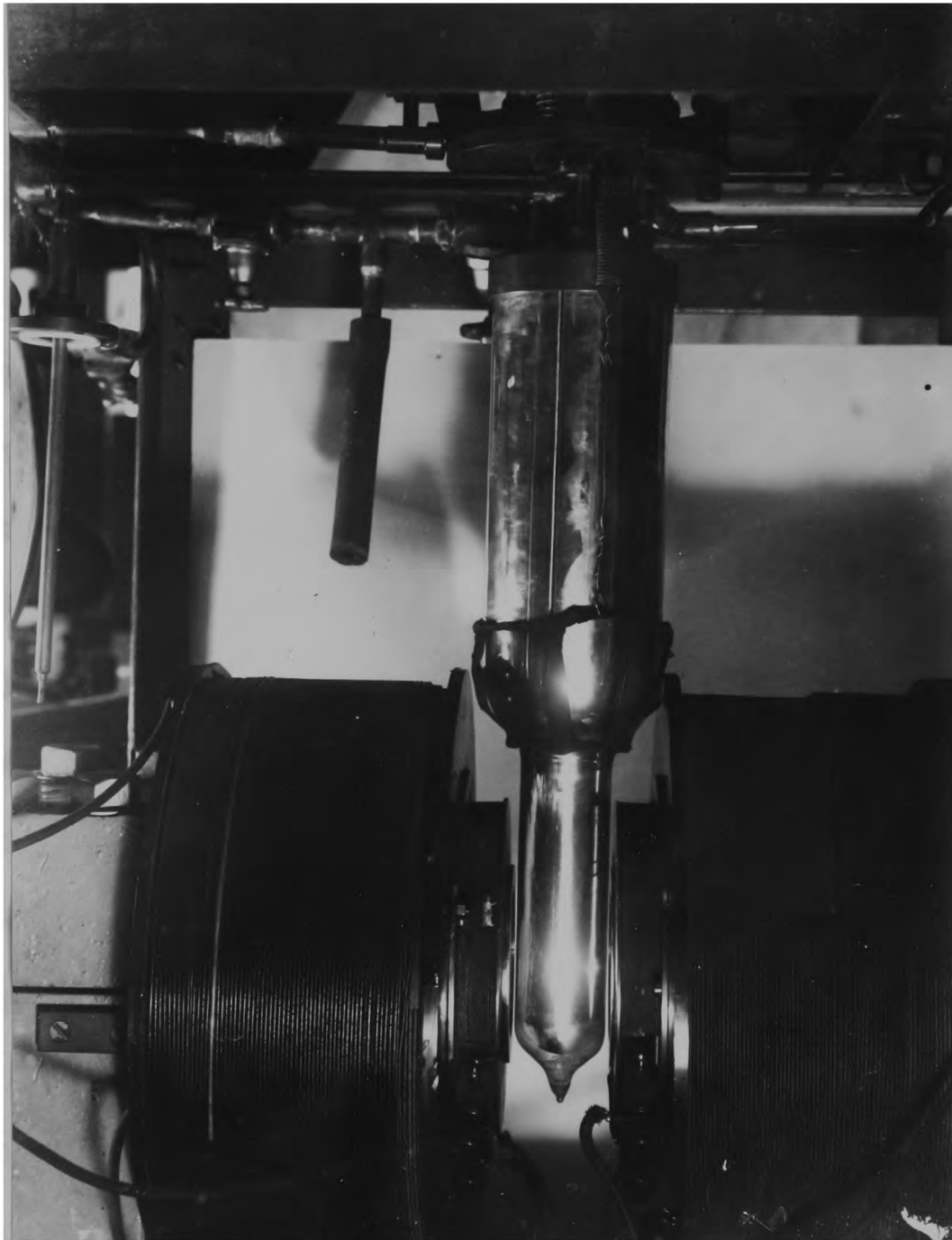
Chapter II
Photograph 4



Sucksmith balance with metal cryostat in place.

Chapter 11

Photograph 5



Sucksmith balance with outer dewar in place.

II.8

glycerol and a thin layer of apiezon grease. The ground joint was part of the vacuum case (K) of the helium siphon (J).

The cryostat and upper part of the eight m.m. tube were surrounded by a bath of liquid hydrogen in an open dewar.

There is a strong horizontal force on the specimen if it is not at the centre of symmetry of the inhomogeneous magnetic field. The centering spring was therefore placed very near to the specimen, and the whole apparatus was made as short as possible to facilitate centering the quartz rod, and to lessen the chance of it sticking to the side of the tube. In this respect the apparatus is successful, for it has frozen only when gases other than helium leaked in. Any air entering the upper case after the liquid hydrogen is put on will condense in the eight m.m. tube where it passes through the hydrogen bath, well above the centering spring.

3. MODIFICATIONS:

a. Magnet:

When we tried to measure $\chi_{//}$ of $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ at 4°K , a deflection in the diamagnetic direction was observed. This was attributed to the interaction of the larger $\chi_{\perp}$ with an off-axial component of magnetic field having a gradient of the opposite sign to that acting on the smaller $\chi_{//}$.

That is, if we write equation (3), Chapter II, as

II.9

$$F_z = - \left[X_{//} H_{//} \frac{\partial H_{//}}{\partial z} + X_{\perp} \left(H_y \frac{\partial H_y}{\partial z} + H_z \frac{\partial H_z}{\partial z} \right) \right]$$

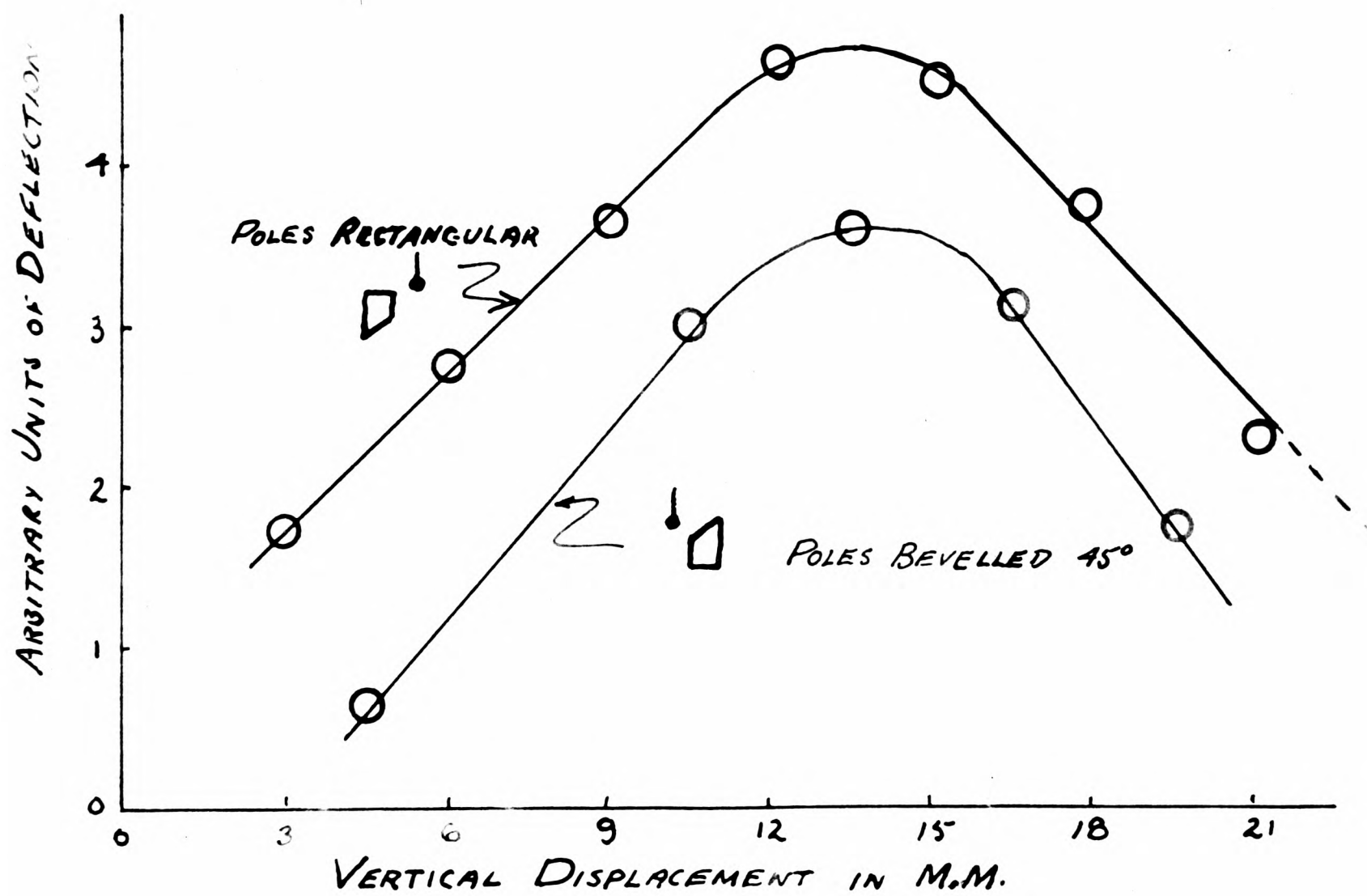
where H_x is parallel to the principal axis of susceptibility $X_{//}$, we have finite $H_y \frac{\partial H_y}{\partial z}$ and/or $H_z \frac{\partial H_z}{\partial z}$.

Rectangular pole pieces with sloping faces were therefore made to replace the round ones used in resonance work. Shims were milled on the sides from data given by Rose (1938). The problem of computing the optimum face angle and length proved intractable. Although a similar problem which involves maximizing the function $H_x \frac{\partial H_x}{\partial x}$ over a volume has been solved for a torsion balance, it is difficult to treat $H_x \frac{\partial H_x}{\partial z}$ similarly. We therefore decided to try rectangular poles and poles bevelled at 45° as shown in figure 5.

The pole pieces were tested by measuring the deflection caused by a fixed current as the magnet was raised or lowered relative to a specimen of $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. Figure 5 shows that the rectangular edge has a greater $H_x \frac{\partial H_x}{\partial z}$ than has the bevelled edge. It will be noted that the gradient of the forces is about 3% per m.m. in the linear regions above or below the maximum. If the specimen has a volume comparable to the region where the force is constant, i.e. three m.m. long, the gradient of the force is about 1% per m.m.

The off axial components $\left[H_y \frac{\partial H_y}{\partial z} + H_z \frac{\partial H_z}{\partial z} \right]$ were estimated by comparing the measured principal suscep-

Figure 5



II.10

tibilities of $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ at 4°K with those calculated from the microwave resonance data. The results indicated that $\left[H_y \frac{\partial H_y}{\partial z} + H_z \frac{\partial H_z}{\partial z} \right]$ was 2% of $H_x \frac{\partial H_x}{\partial z}$ at the particular position of the specimen.

It was therefore impossible to measure the $\chi_{//}$ of the cerium, neodymium and samarium double nitrates because below 20°K it contributed less than one quarter of the observed deflection, which was itself very small.

b. Cryostat:

It was not possible to calibrate the balance very accurately by means of a specimen of $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, presumably because we never managed to replace the specimen in exactly the same field as the standard. Although the balance could be centered at room temperature, the double walled metal cryostat, when it was put on, would bend the eight m.m. tube and move the specimen.

For this reason a glass inner dewar with a copper-glass seal was made, and the copper specimen container replaced by one of soft glass with a copper-glass seal by which it was screwed on. Thus the position of the specimen could be observed directly.

II.11

c. Mounting:

As the damping was satisfactory we were encouraged to mount the balance permanently on the wall, as shown in photograph . Although there was more vibration, we could adjust the optical system more conveniently.

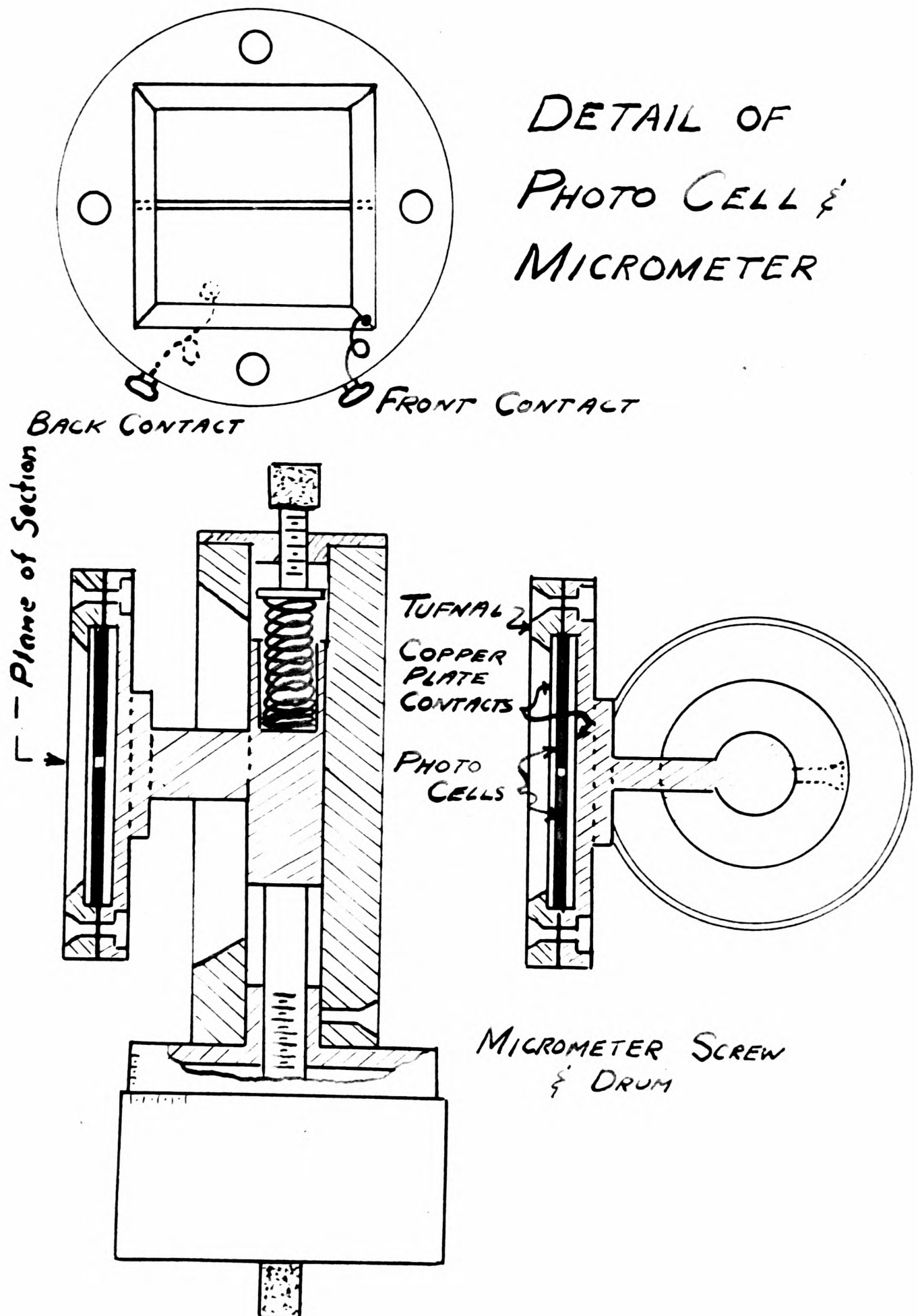
d. Sensitivity:

When we attempted to measure the susceptibility of a nitric oxide clathrate the balance was not sufficiently sensitive, so we constructed the photocell detector shown in figure 6.

Two selenium photocells from Evans Electro-selenium Co. were used. Their silvered backs were joined together, and their front contacts were connected through a Tinsley taut suspension galvanometer of sensitivity $1450 \text{ m.m./}\mu\text{a}$ at one meter. Several cells were tested in order to obtain a pair with matched internal resistances.

Unfortunately the deflection of the galvanometer is not always linear in the deflection of the light beam because of stray light falling on the photocells, water drops condensing on the balance windows, and changes in the internal resistance of the cells. When liquid hydrogen is in the outer dewar the water vapour condensed in the air by the rising hydrogen gas produces fluctuations in the intensity of the light beam which seriously effect the galvanometer.

Figure 6



II.12

The sensitivity is a function of the intensity of illumination, and seems to increase faster than random fluctuations due to the instability of the internal resistance and/or e.m.f. of the photocell up to the intensity supplied by a 12V, 84 watt clear lamp with the filament focussed on the cells. This lamp was run from the 12V output of a 250 V transformer on the mains, as the laboratory 12V d.c. supply was unstable. If accumulators were used the sensitivity fell noticeably during an experiment as they discharged.

There are four ways of measuring the deflection of the light beam.

1. Microscope and eyepiece scale:

This method is rapid (once a clear diffraction pattern of the slit has been obtained) and speed is important because the zero drifts and the liquid helium evaporates fairly quickly in the metal cryostat.

One hundred scale divisions correspond to a movement of about $2\frac{3}{4}$ m.m. of the light beam one meter from the mirrors, and it is possible to read to ± 1 scale division. Hence the precision is 0.01m.m., but the percentage error is large for small deflections. The zero position is unlikely to be changed during the reading by moving the microscope

ii. Microscope Vernier:

The diffraction pattern can only be set to $\pm 0.01\text{m.m.}$, so that even by reading the vernier to within 0.01m.m. we only get a precision of $\pm 0.02\text{m.m.}$ Furthermore it is necessary to touch the microscope in order to change the setting, possibly altering the position of its scale slightly relative to the mirror system. Again, if there is a slow drift of the rest position of the balance the longer time required to make these two vernier readings increases the total uncertainty.

While in principle it is possible to increase the sensitivity by increasing the length of the optical lever, in practice only a factor of 2x or 3x can be conveniently gained.

iii. Photocell and micrometer:

By using a galvanometer as a null detector and reading the deflections by means of a micrometer drum, an accuracy of $\pm 0.002\text{m.m.}$ can be obtained. Because of the inherent instability of the photocell e.m.f. or internal resistance, a precision of only about $\pm 0.003\text{m.m.}$ was achieved. This may be worsened by any fluctuations in the light source intensity or changes in the relative positions of the light, balance and photocell. If the latter effects are small drifts

II.14

they can be accounted for in the final calculation. Again, the necessity of touching the micrometer screw can introduce error, and the longer time required to make an observation increases the uncertainty due to drift.

iv. Photocell and galvanometer;

The highest sensitivity results if the micrometer is used only to balance the two opposing photo e.m.f.'s so that the galvanometer initially reads zero, and the galvanometer reading is taken as a measure of the deflection. However as we have noted, the galvanometer deflection is not consistently proportional to the light beam deflection for large deflections. For this reason the procedure we adopted was to lift a rider off the ring. The magnet current was read when the specimen had been pulled down by the increasing magnetic field and the galvanometer had returned to its original position. The rider was then dropped back on the ring and the magnetic field turned down. The final position of the galvanometer showed the drift, half of which was assumed to take place during the reading.

In the case of the nitric oxide clathrate, at 20°K the deflection of the beam of light was 14 eyepiece divisions, = 0.37m.m., and could thus be measured by the travelling microscope to only $\pm 10\%$. By using the photocell

II.15

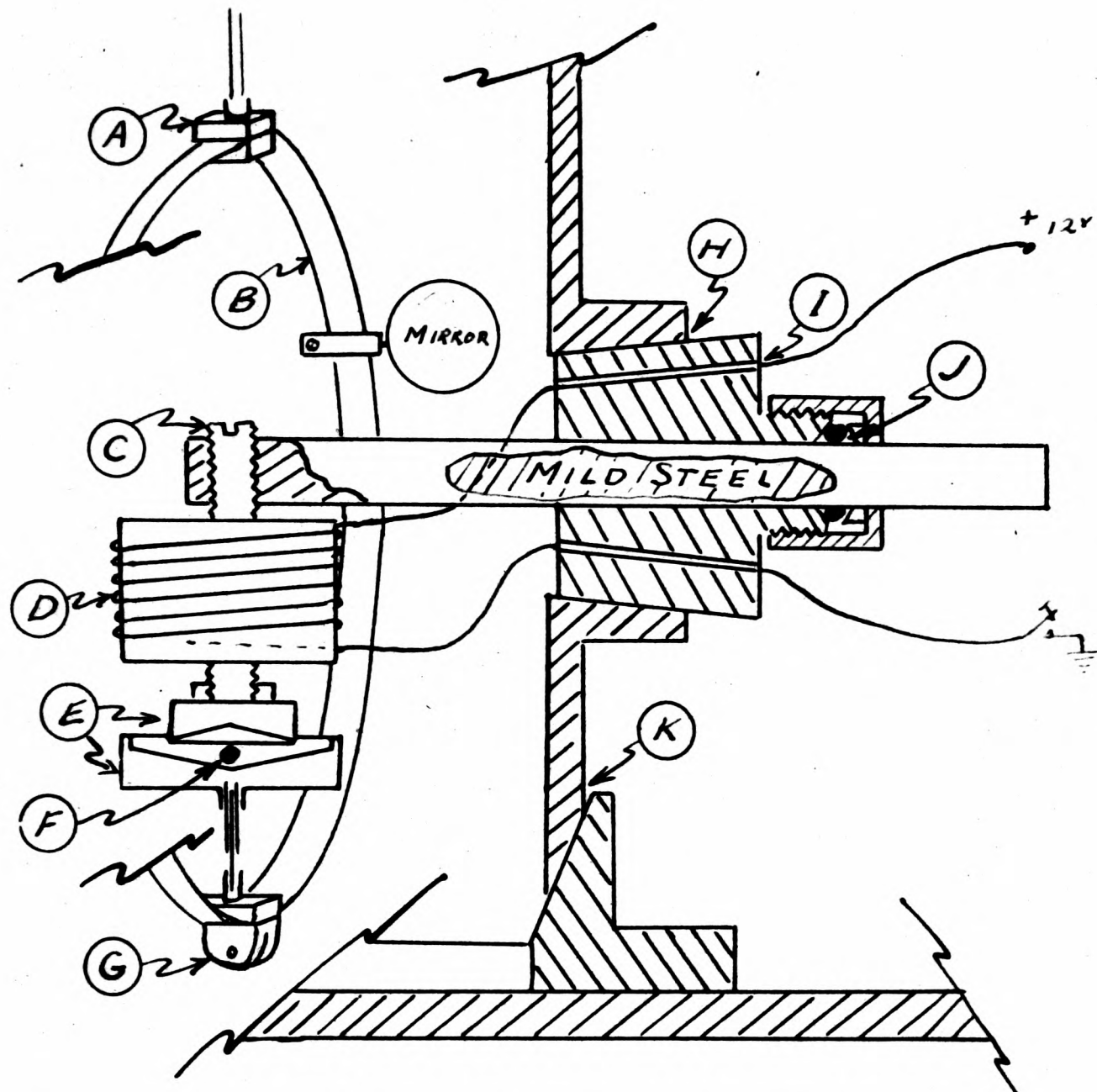
and galvanometer as above, the deflection of the galvanometer was easily 250m.m., and the accuracy limited by the accuracy of the square of the magnet current measurement, i.e. $\pm 2\%$. This is of course worsened by drifts.

The procedure followed with the rider avoids the effects of any changes in the elastic modulus of the system due to change in temperature of the phosphor bronze centering spring which may be as much as 5% between 300° and 20° K.

In measuring the diamagnetic susceptibilities of the specimen holders, i.e. forces much less than the weight of the practical rider, it is necessary to rely upon the approximate linearity of the galvanometer deflection with small light beam deflections. In this case we can obtain a greater sensitivity by using the galvanometer deflection (method iv) than by using the null method (iii) and reading the micrometer drum.

Lifting off the rider manually often introduced changes in the rest position during a reading. For this reason we made a magnetic pickup of 60 Ω of #46 s.w.g. copper wire wound upon a "Tufnol" former over a soft iron core, as shown in figure 7. The riders are steel ball bearings weighing from four to 32 milligrams. The ball bearing rests in the bottom of a conical perspex bowl attached to the ring. The perspex cone is

Figure 7



DETAIL OF BALL BEARING RIDER PICKUP

- A RING SUPPORT
- B RING
- C 2 B.A. MILD STEEL SCREW
- D 60 Ω , 40 S.W.G. COIL ON TUFNAL FORM
- E PERSPEX CONICAL CUPS
- F STEEL BALL BEARING RIDER
- G PIVOT FOR QUARTZ ROD
- H GROUND JOINT
- I WAX SEAL OF LEAD TO COIL
- J GACO "O" RING SEAL
- K GROUND JOINT

II.16

durofixed to the bottom of the magnet (C) in order to keep the rider so far away that the residual magnetism will not support it.

Several other arrangements were tried for picking up iron wire rings, but the ball bearings proved the only reliable device having a stable rest position on the ring or against the magnetic pickup.

e. Thermometry:

The interesting regions of temperatures for the clathrates were between room temperature and 20°K . In this range the helium gas thermometer is not as sensitive as a resistance thermometer or a thermocouple. Because only platinum wires went into the inner dewar it was necessary to use a resistance thermometer. Thus $70\ \Omega$ (at 300°K) of #47 s.w.g. platinum wire was annealed at a dull red heat for three minutes in air, and wound on a former.

The final coil was wound over a sheet of cigarette paper, on a copper former, bakelite varnished and baked one hour at 80° and two hours at 100° . After half a dozen immersions in liquid air its calibration was stable.

If the wire was bakelite varnished to perspex it was torn when the perspex cracked at low temperatures. If it was not varnished it sagged and short circuited when the

II.17

perspex contracted on cooling. A coil wound on soapstone did not crack but had too poor a thermal conductivity to be in equilibrium with the specimen case at liquid oxygen temperatures.

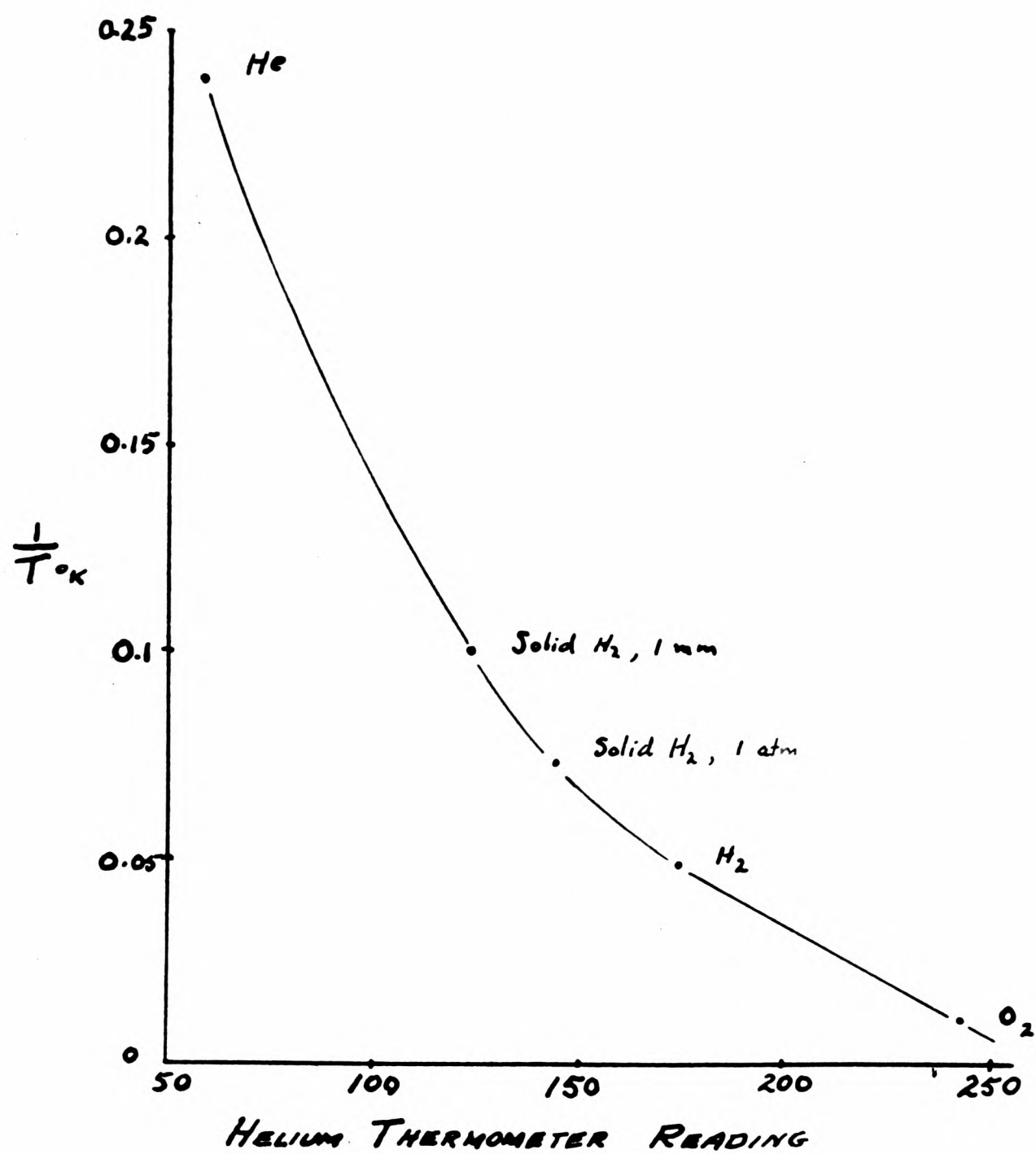
The resistance was read to $\pm 1\%$ between 300°K and about 45°K on a Pontavi Wheatstone bridge.

Fixed points were obtained at 0°C in an ice bath, at -78°C with dry ice in an atmosphere of CO_2 , at -183°C in a bath of liquid oxygen, and at 20.4°K in a bath of liquid hydrogen. The usual precautions were taken of allowing the solid CO_2 to come to thermal equilibrium by heating it sufficiently to generate an atmosphere of pure CO_2 , and of bubbling oxygen gas through the liquid oxygen bath for several hours. The dry ice mixture may be 8 to 10°K above the equilibrium point at first, and the oxygen may supercool several degrees. (Temperature, 1941)

The helium constant volume gas thermometer was calibrated in a liquid oxygen bath, in a liquid hydrogen bath, at the triple point of liquid hydrogen (14°K), at the temperature of solid hydrogen at less than 1 m.m. pressure (10°K), and at the liquid helium point (4.2°K). Figure 8 shows the calibration curves of the helium gas thermometer.

As an independent check, the measured

Figure 8



II.18

susceptibility of $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was plotted assuming it to be a function of $\frac{C}{T}$ and the appropriate helium gas thermometer readings were also plotted versus $\frac{1}{T}$. They fall on a straight line as shown in figure 9.

The resistance thermometer is useful from 300°K to about 50°K, and the helium gas thermometer from 90°K to 4.2°K. As noted on page 3 of this chapter, the balance case can be used as a vapour pressure thermometer below 4.2°K. The expected linear behaviour of X_1 of $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ as a function of $\frac{1}{T}$ indicated by the vapour pressure thermometer is a self-consistent check on the validity of this method of thermometry.

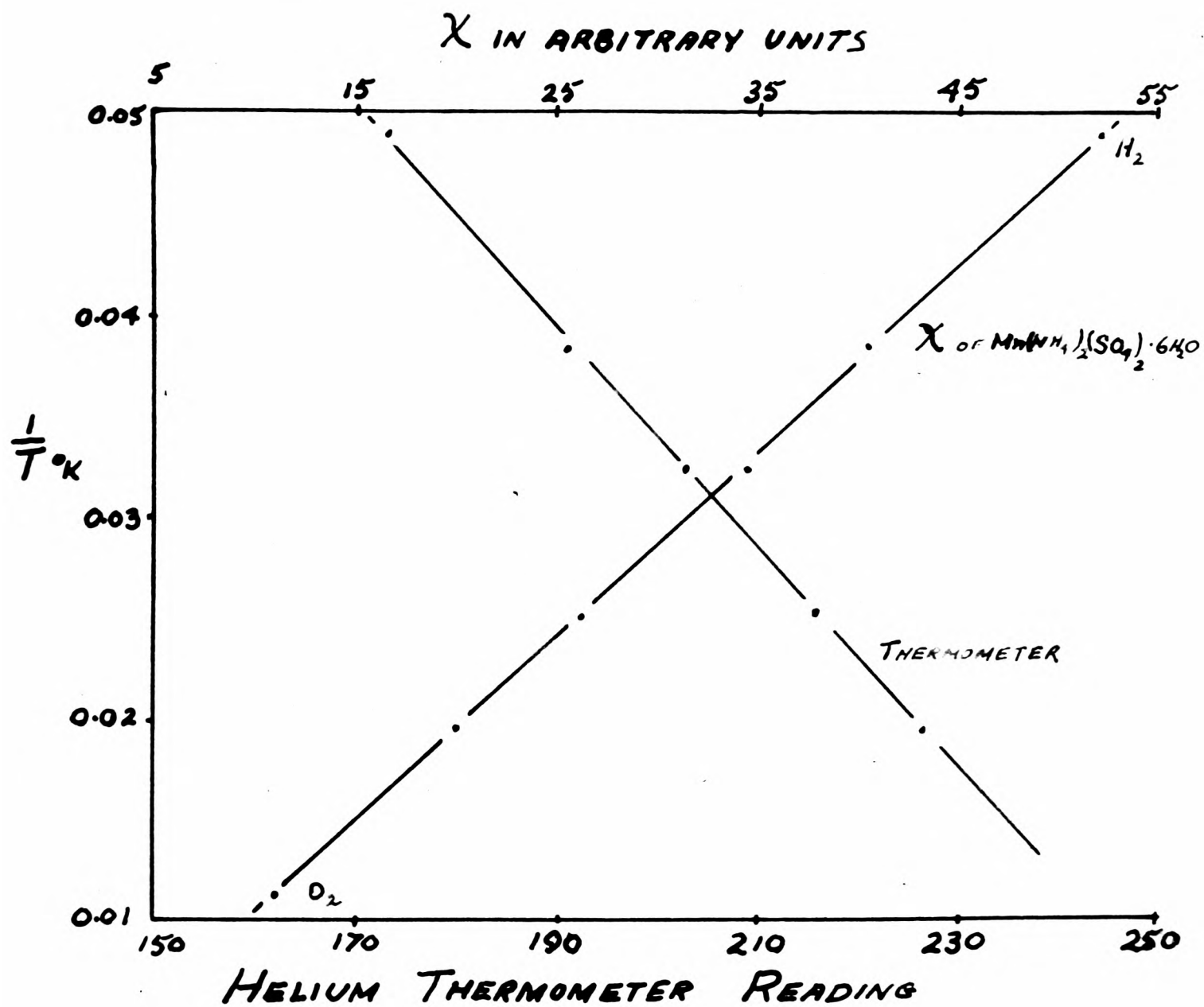
In order to vary the temperature of the specimen continuously we made a heating coil of 45 Ω of constantan wire wound like the thermometer.

Thermal equilibrium could be obtained by:

- i. Immersing the specimen chamber in a bath, or,
- ii. Establishing a thermal gradient from the heater to a cold bath in contact with the top of the inner dewar.

Thus it was possible to obtain any temperature from 300°K to 90°K by filling the outer dewar with liquid oxygen; and from 90°K to 20°K, with liquid hydrogen. Equilibrium could be obtained from 20° to 10° by filling

Figure 9



II.19

the inner dewar with liquid hydrogen and pumping it. To obtain temperatures below 4.2°K we pumped liquid helium in the inner dewar.

We were unable to establish thermal equilibrium between 10°K and 4.2°K .

4. COOLING DOWN:

The cooling procedure is as follows:

- a. Set up balance at room temperature with the optical system working properly, and the specimen centered and moving freely.
- b. Blow out any water which may be in the siphon, and pump the siphon case.
- c. Seal the bottom on to the copper container with tap grease and pump down the balance case to test for leaks.
- d. Remove the perspex top of the balance case and fill the damping bath with butyl phthalate which has been kept in a vacuum for some hours to remove any dissolved air. If this precaution is not taken the air will form bubbles when the balance case is evacuated, and the butyl phthalate will spatter onto the centering spring and later freeze.
- e. Again evacuate the balance case having sealed off the copper container with glycerol.

II.20

- f. Evacuate the space between the walls of the metal cryostat and seal it off with a pinch clamp on a bit of rubber lubricated with glycerol.
- g. Seal the cryostat onto the ground joint with glycerol and freeze it with liquid air, or Wood's metal it. Pump down the cryostat and test for leaks, first closing off the outside end of the siphon with a pinch clamp.
- h. Fill the cryostat and balance case with helium gas.
- i. Pre-cool the outer dewar and the apparatus with liquid oxygen. Empty and replace the outer dewar.
- j. Siphon liquid hydrogen into the outer dewar and wait for the specimen to come to the temperature of the liquid hydrogen.
- k. Siphon in liquid helium from the transport dewar by pumping on the cryostat. After the transfer, close off the outer end of the siphon.

One dewar (four litres) of liquid hydrogen is sufficient to cool the apparatus and keep it cold while a single fill of liquid helium (about three cylinder atmospheres) lasts ... about two hours in the metal cryostat. Using the glass inner dewar Wood's metal~~l~~ed onto the siphon case a single fill of liquid helium (three cylinder atmospheres) lasts about six hours.

II.21

II. MICROWAVE RESONANCE APPARATUS:

Most of the work in the field of radio frequency spectroscopy has been done at or above 20°K . However there are a number of substances which have a suitable relaxation time to give a narrow absorption line at 4°K , although they have a short spin lattice relaxation time at high temperatures. For this reason we wished to adapt the conventional spectrometer equipment for use at very low temperatures.

Dr. G. S. Bogle developed a microwave spectrometer used at liquid helium temperatures in this laboratory. His first apparatus consisted of a cylindrical resonant cavity immersed in liquid helium. The dewar containing the liquid helium was enclosed in another dewar filled with liquid hydrogen or oxygen. The specimen was introduced into the top of the cavity on the end of a long rod. In order to increase the sensitivity and convenience of the apparatus he then made a second model using a more sensitive rectangular resonant cavity and a brass can of liquid hydrogen above the resonant cavity to cut down the influx of heat. Although the dewar containing the liquid helium was only surrounded by liquid oxygen, the time 750 c.c. of liquid helium would last was increased from three hours to more than 12 hours.

II.22

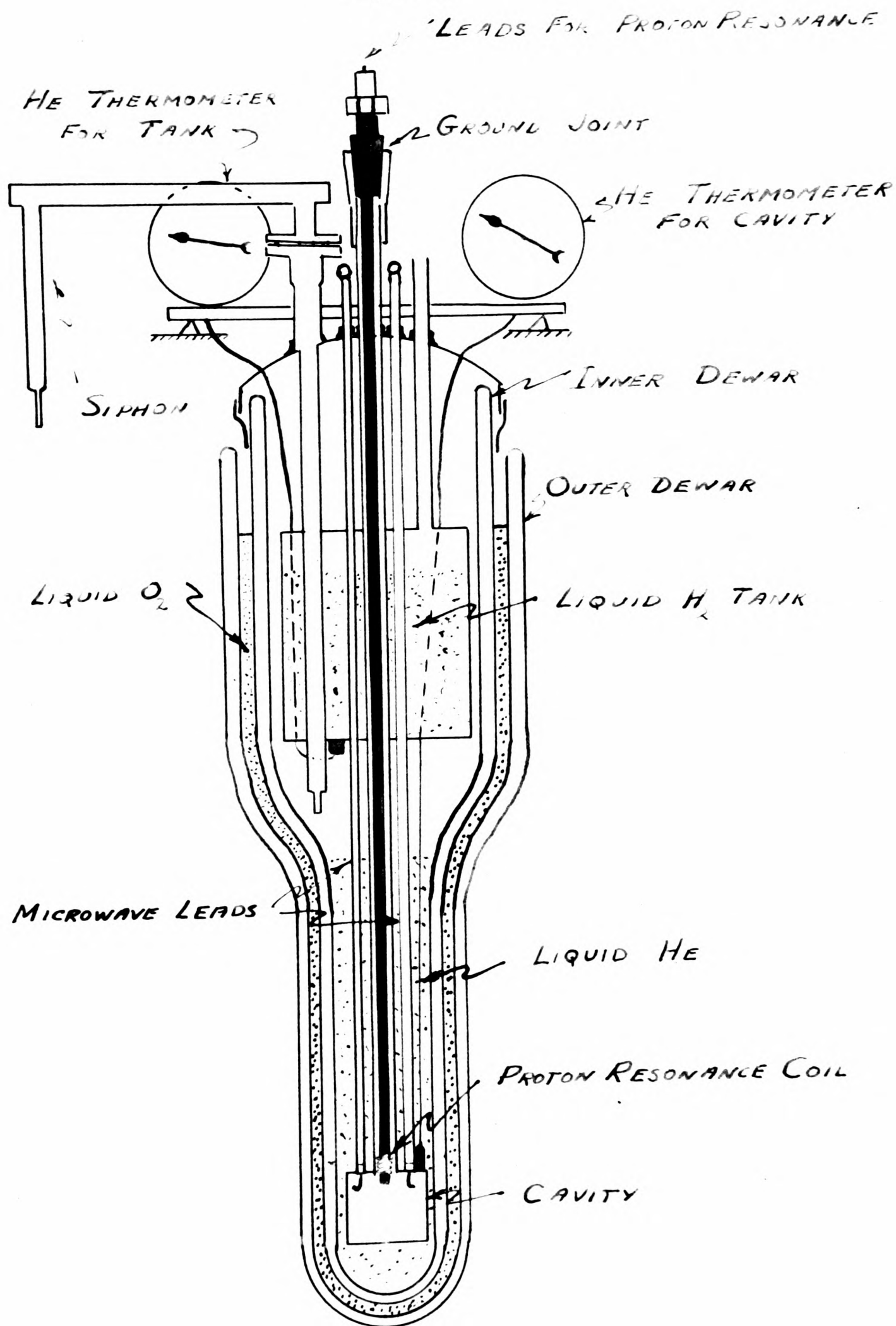
We were unable to remove the specimen from the apparatus during the course of many an unsuccessful experiment, and therefore constructed an apparatus in which we could change the specimen. (Figure 10) It is cooled in the same way as Dr. Bogle's apparatus.

The electronic part of the apparatus consists of a stabilized power pack whose circuit is shown in figure 11. A reflex klystron oscillator feeds three c.m. microwave power through a variable attenuator down a wave guide with an adjustable termination. Power is picked up from the wave guide by an adjustable probe and carried by a coaxial line to the rectangular cavity to which it is loosely coupled by a probe. The cavity is excited in the H_{011} mode, and power taken from it by another loosely coupled probe as shown in figure 12.

This power is then brought to a crystal detector and rectified. The rectified output is fed into a shielded microphone transformer. The output of the transformer is amplified by a conventional two-stage amplifier and fed onto the vertical amplifier of a C.R.O.

When a suitable paramagnetic crystal is placed at the top of the cavity in a steady magnetic field, if the Zeeman splitting is equal to a quantum of radiation

Figure 10



MICROWAVE SPECTROMETER

Figure 11

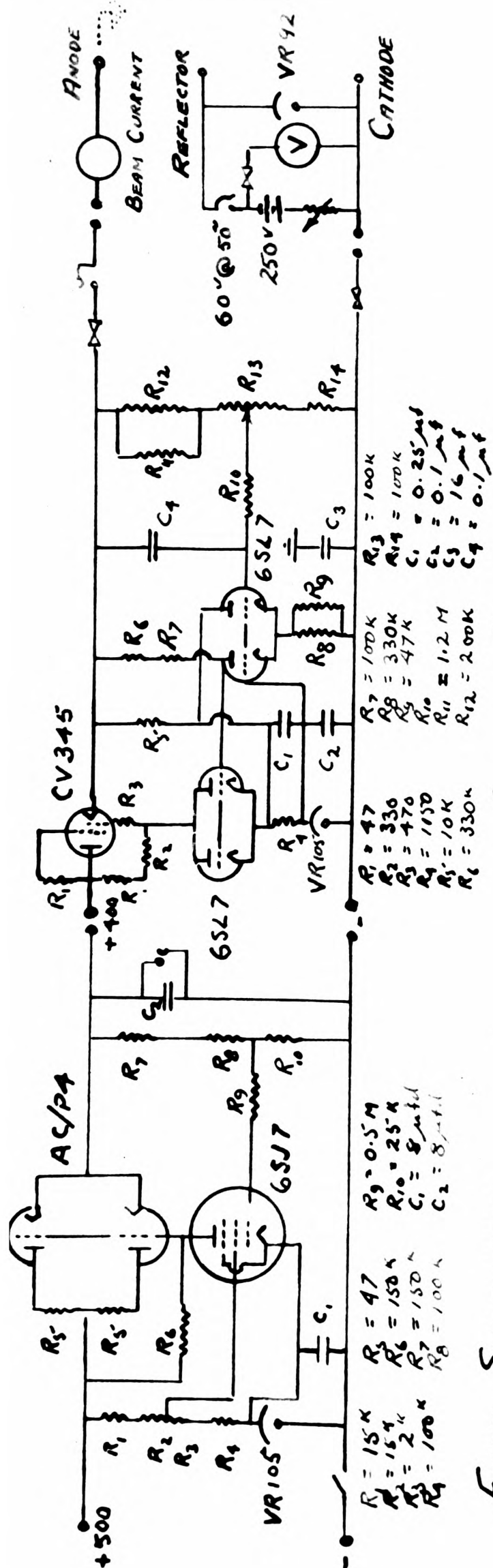
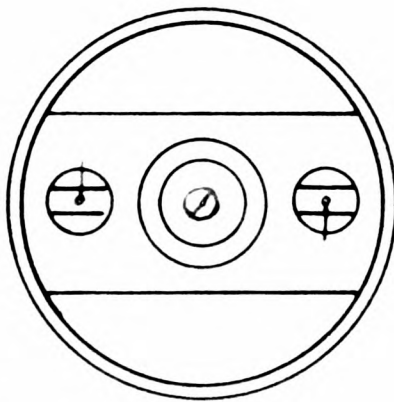
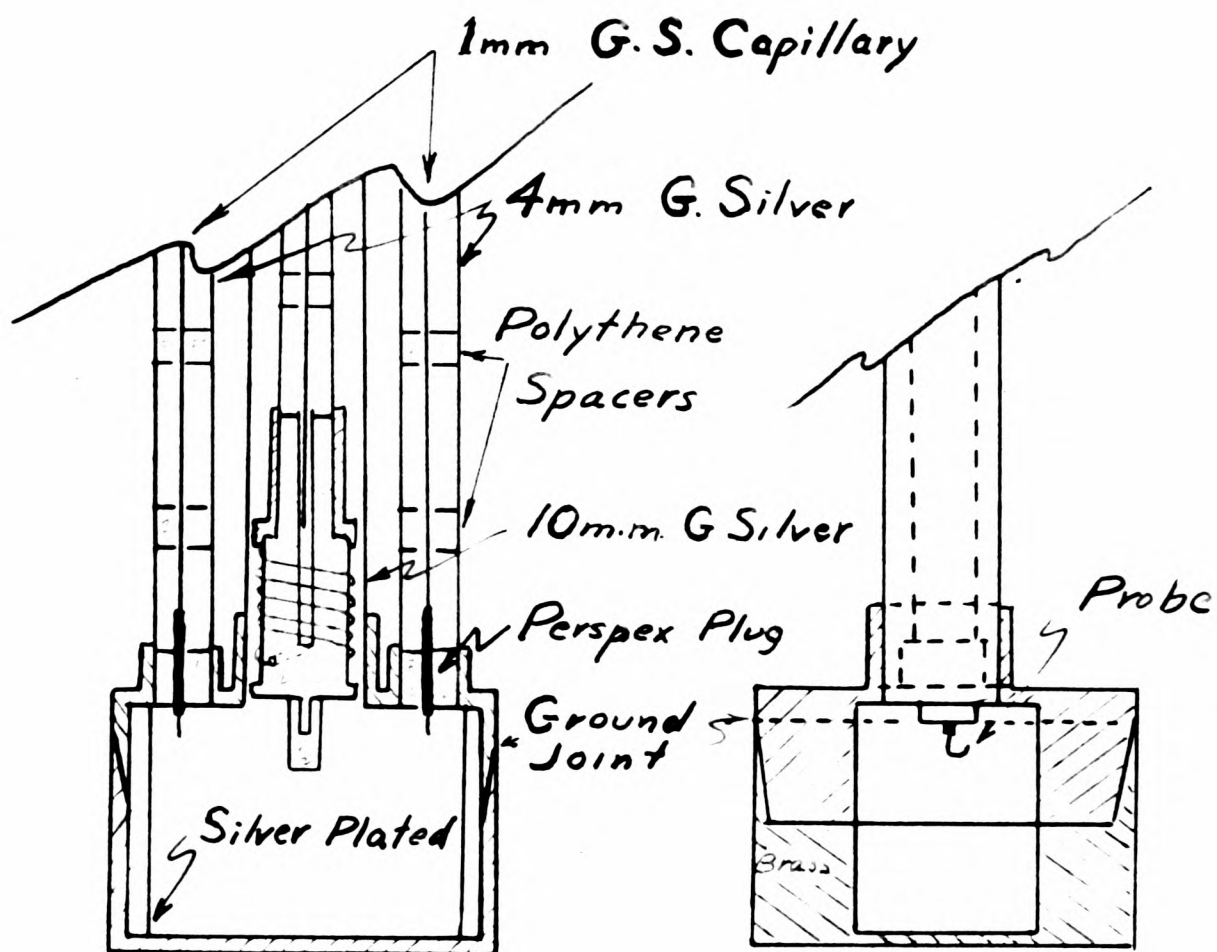


Figure 12



3cm RESONANT
CAVITY WITH PROBES
& PROTON COIL

Plan of Top Half of Cavity

II.23

in the resonant field, the crystal will absorb energy. If the steady field is modulated to a depth of a few hundred gauss at the same frequency as the C.R.O. horizontal sweep, a stationary trace of the absorption (as a function of H) may be obtained.

The apparatus was made to be used with a rotatable magnet. A disadvantage of rotating the magnet is that the microwave field component parallel the steady magnetic field varies sinusoidally with the direction, and hence the intensity of the spectrum usually vanishes when the r.f. and d.c. fields are parallel. However the error in marking the scale of the Royal Society magnet is only 0.1° in 180° , and we cannot measure the rotation of the specimen equally accurately. Therefore we measure angles by moving the magnet after a suitable starting position has been found by rotating the specimen.

1. DETAILS OF APPARATUS:

a. The cavity:

A diagram of the cavity is given in figure 12. The rectangular box is chosen instead of a cylinder so that a greater proportion of the magnetic flux in the resonator will be intercepted by the paramagnetic specimen. The specimen is introduced into the top of the cavity glued to a perspex

II.24

mount on the end of a long German silver rod. There was no appreciable gain in sensitivity when a $\frac{1}{4} \lambda$ choke was used in place of the dielectric mount, and we conclude that very little r.f. power is dissipated up the central tube.

For the H_{011} mode, if the horizontal and vertical dimensions of the cavity are a and b , the magnetic field at the centre of a horizontal face is a/b times the field at a vertical face. As the square of the magnetic field enters in the intensity of a paramagnetic absorption, the cavity is made as wide and as shallow as possible. The inner dewar limits the breadth to 25.0 m.m. The height is made 22.6 m.m. and the width 11.0 m.m.

The cavity is made of brass, and is silver plated to give a higher Q for testing at room temperature. The calculated Q of this cavity without the hole in the top is 5,500.

Bogle (1952) has experimentally examined the variation of the sensitivity of this type of cavity with the Q , and finds 3,000 at 290°K to be a good loaded Q for working. We have chosen a slightly higher $Q = 4,000$ to utilize the better frequency stability of a high voltage klystron supply.

The power absorbed by a paramagnetic sample

II.25

in an oscillating magnetic field $H \cos \omega t$ is $\frac{1}{2} \omega X'' H^2$ where X'' is the imaginary part of the susceptibility of the sample. If V is the effective volume of the resonant cavity, the microwave energy stored in the cavity is $\frac{H^2 V}{8 \pi}$ and hence the power absorbed by the cavity is $\frac{H^2 V}{8 \pi} \frac{1}{Q_0} \omega$ where Q_0 is the ratio of the power stored to the power dissipated per cycle of the unloaded cavity. As far as detection is concerned the important quantity is the ratio of the power dissipated in the cavity to that dissipated in the cavity plus the sample, defined as the loaded $Q = Q_L$.

$$\therefore \frac{1}{Q_L} \omega \frac{H^2 V}{8 \pi} = \frac{1}{Q_0} \omega \frac{H^2 V}{8 \pi} + \frac{1}{2} \omega X'' H^2$$

Hence
$$\frac{1}{Q_L} = \frac{1}{Q_0} + \frac{4 \pi X''}{V}$$

The minimum detectable X'' may be calculated from the dimensions of the cavity, the wavelength, the noise factor and the band width of the final amplifier, to be $X_{\min} \sim 10^{-11}$ c.g.s. units.

However Trenam (1953) and others have found that the experimental sensitivity is about 10^{-3} times that calculated.

We have never made an absolute calibration of the sensitivity of the apparatus. However we have established that it is quite high by noting that the signal of a

II.26

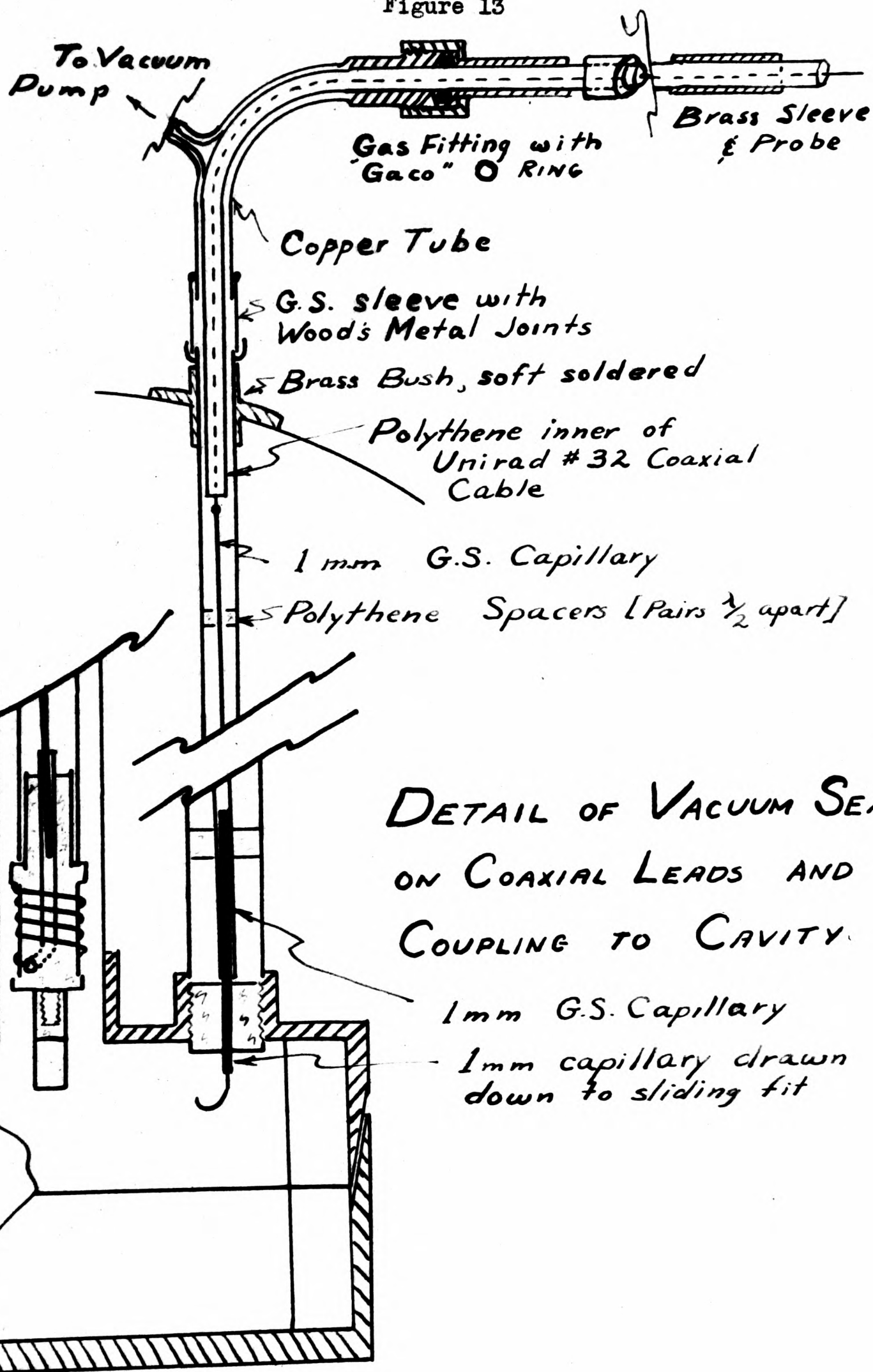
piece of di-phenyl-tri-nitro-phenyl-hydrazyl, which we could just distinguish from noise at 20°K was 4x noise at 20°K in the apparatus of Mr. I. Ward, employing heterodyne detection. The limitation of our working sensitivity at 4°K seems to be caused by microphonics and the frequency instability of the low voltage klystron.

b. The coaxial leads:

The resonator is connected with the wave guide and detector by coaxial lines of which the outer conductors are 4 m.m. German silver tubes which change to 1/8" Yorkshire copper tubing on emerging from the cap as shown in figure 13. The polythene and inner conductor of Uniradio 32 cable are continuous from the waveguide coupling probe to a point several centimeters inside the apparatus, where the copper inner wire is replaced by a 1 m.m. German silver capillary. Thus even if the polythene has not adhered to the copper inner, the leakage path is long.

The great length of coaxial line between the cap and the cavity is very susceptible to microphonics which, as we have noted, appear to be the major shortcoming of this design of apparatus. These are caused not only by the boiling liquid helium jarring the coaxial leads, but also by the 50 c.p.s. field modulation shaking the magnet. As the inertia

Figure 13



II.27

of the magnet is large, this effect can be very disturbing.

A difficulty encountered in bringing a coaxial line down to liquid helium temperatures is that the differential contraction will pull the cavity probes loose, and thus change the coupling. The German silver capillary is superior to the constantan wire previously used on two counts. It eliminates most of the differential contraction because the inner and outer tubes will have nearly the same temperature gradient. Furthermore, we can use drawn-down German silver tubes to make sliding expansion contacts as shown in figure 13. The probes, whose adjustment is extremely critical, consist of short loops of copper wire soldered into the ends of bits of drawn-down 1 m.m. German silver capillary which slide into the main 1 m.m. capillaries. The probes are insulated from the cavity by threaded perspex plugs which screw into the ends of the 4 m.m. outer tubes. It is easy to replace the probes or to adjust them, but this arrangement has worked satisfactorily for six months without any adjustment.

They are originally adjusted for optimum coupling by starting with overcoupling and gradually snipping off the ends of the probes until a suitable Q is obtained. The Q is measured at room temperature by observing the change in

II.28

frequency for a given reflector voltage when the dielectric constant of the cavity is altered by pumping out the air.

It is common for this type of apparatus used at 20°K to be troubled by water condensing in the coaxial leads where it absorbs a great deal of microwave power. This does not bother us for the coaxial lines are easily pumped out before an experiment.

c. The klystron:

The input coaxial line of the resonator receives power from a waveguide by means of a probe and plunger matching device. The source of power is either a 723A/B or a CV149 reflex klystron isolated from the resonator by a variable attenuator.

The 723A/B operates with 300 volts negative on the reflector. The beam current is 20 - 30 m.a. A stabilized power pack (figure 11) is used for the beam, and batteries are used to give the extra -200 volts required for the reflector. The tube is designed to allow frequency control by means of the reflector voltage. In paramagnetic resonance work frequency modulation must be kept very low as there is a frequency discriminating element in the microwave circuit, i.e., the cavity.

II.29

Provision is made to apply a 50 c.p.s. sweep of 60 volts peak to peak to the reflector. The whole klystron mode, of width about 50 volts, can then be scanned, corresponding to a range of 0.3% in wave length.

The wavelength was measured with a direct reading coaxial plunger absorption wavemeter. Four readings could be obtained spaced at $\frac{\lambda}{2}$. The points can be read to ± 0.05 m.m. Because of the very high Q of the cavity, we should not expect the resonant frequency to vary during an experiment on a given crystal whose position is fixed. It may vary from one experiment to the next because the lower part of the cavity may not seat at exactly the same place on the ground joint, and the amount of dielectric in the cavity may vary. For this reason all results are related to the line of g-marker, di-phenyl-tri-nitro-phenyl-hydrazyl.

d. Detection and display:

The coaxial line bringing microwave power from the resonator is coupled by a probe to a short section of waveguide which carries a crystal detector lying parallel to the electric field and is terminated by a matching plunger. The crystal detectors used are type CS3B made by British Thompson Houston Ltd. They are not manufactured for d.c. applications where audio-frequency noise is required to be a

II.30

minimum, and it is necessary to make a selection from a number of detectors whose outputs may vary by as much as 80%. The detector cartridge takes the form of a quarter wave coaxial resonator with the crystal rectifier included in the inner conductor. The CS3B gives about three times as much current for the same microwave power as the unshielded types such as the CV119.

Current from the detector passes through a 4 : 1 microphone transformer of low input impedance to match the detector.

The output voltage from the transformer is amplified by a two stage amplifier with negative feedback and a high frequency cutoff.

e. Magnetic field:

For fields up to 6.5 kilogauss at a gap of 50m.m. an air-cooled Tickford electromagnet is used. A current of up to 10 amperes at 100 volts is obtained from the 230 volt mains through a variac and step down autotransformer followed by a full wave rectifier circuit employing iron-selenium rectifiers. Smoothing is performed by a conventional π filter with $C_1 = 600 \mu\text{fd}$, $L = 0.08$ henry and $C_2 = 500 \mu\text{fd}$. The ripple at a field of 4 kilogauss is 0.15 gauss peak to peak.

II.31

The pole pieces are shimmed slightly to give a homogeneous region at the centre according to the calculations of Rose (op.cit.)

A water-cooled magnet made by Savage and Parsons of Watford gave fields up to 16 Kilogauss at a gap of 56 m.m. with tapered poles at 100 amperes and 200 volts. It was purchased with funds made available by the Royal Society, and will be referred to as the Royal Society magnet.

Some convenient features of the magnet are that it can be rotated about a vertical axis on a ball ring thrust bearing; each pole can be moved in and out by a micrometer screw gauge; and ordinary tap water is all that is required to cool it. Power is supplied by a 25 K.W. generator which is controlled by a potentiometer system in the excitation circuit of the generator. This is not too stable, however, and has a time constant of several seconds. Furthermore the minimum field is about three Kilogauss. However as the resistance of the magnet is only two ohms we can easily obtain 10 Kilogauss by a few six-volt accumulators.

f. Measurement of Magnetic field:

The magnetic fields are measured by a proton resonance machine similar to that described by H.E.D. Scovil (1951). The principle of the measurements is similar to that

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of the paramagnetic resonance experiments, with the difference that the resonant circuit is a coil and condenser combination, and the frequency is variable.

The coil surrounds a proton rich substance, and the whole is placed in the field to be measured. The frequency of the r.f. oscillator is now varied until it equals the Larmor precession frequency of the protons in the field. An absorption of energy then occurs which is displayed on an oscilloscope in the same manner as in the paramagnetic resonance experiments. The frequency is then compared with two or more harmonics of a crystal controlled wavemeter. Beats between the two frequencies are displayed on the oscilloscope.

The relation between the magnetic field H (in oersteds) and the proton precession frequency f (in megacycles per second) is $H = 234.86 f$, according to the work of the U.S. Bureau of Standards.

Our preliminary procedure in correlating the paramagnetic spectral lines with fields measured in the above way was to construct calibration curves for the magnets giving the relation between the readings of an ammeter and the magnetic fields measured in a standard hysteresis cycle. Ammeter readings were again taken during the experiment and converted to magnetic fields via the calibration curve. A Cambridge

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unipivot 150 millivolt meter was used with the Tickford magnet. It was sluggish, and liable to changes in the zero error. Furthermore the dipole field of the magnet influenced the meter by $\pm 1\%$ and varied with the angle of the magnet.

A sub-standard meter made by Ernest Turner & Co., High Wycombe, was used with the Royal Society magnet. This meter was intrinsically more accurate, and seemed little affected by the external field of the magnet.

In both cases, however, the double reading of the meters introduced the principal error in the final result.

We therefore made some measurements of spectral lines with the coil of the proton apparatus (containing liquid paraffin as a source of protons) inserted between the pole of the magnet and the paramagnetic resonance apparatus dewar. We could thus measure the field about four c.m. from the paramagnetic specimen, and Dr. Bogle has shown that this introduced an error of only $\frac{1}{4}\%$. The proton resonance signal at room temperature is rather small, however, and the vibration from the sweep coils of the Royal Society magnet made it difficult to observe.

We therefore decided to introduce a proton

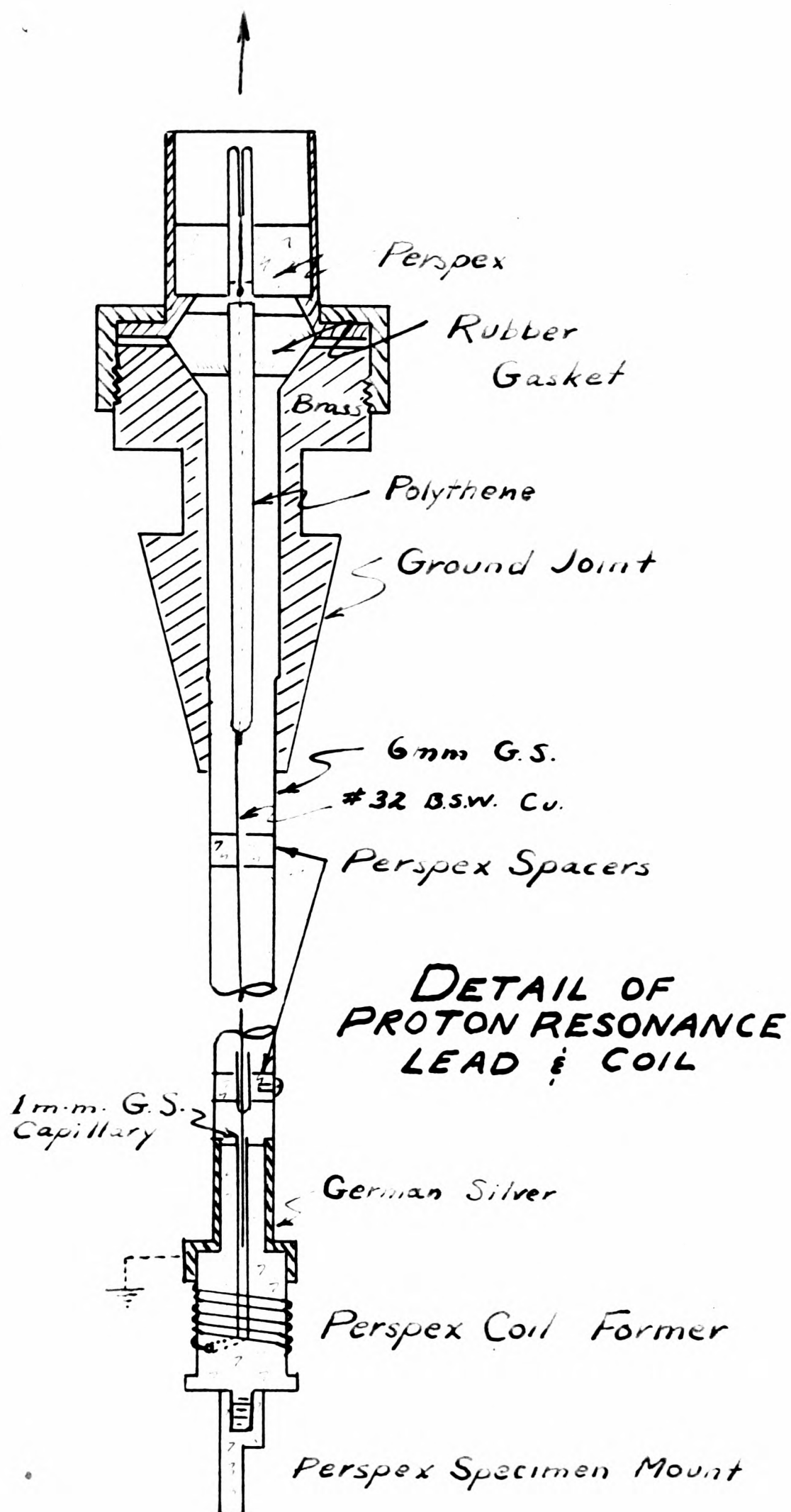
II.34

coil just above the specimen at liquid helium temperatures as Dr. Scovil had done at 20°K . There were some difficulties in doing this, as the coil had to be placed about one meter from the rest of the r.f. oscillator (figure 14). Furthermore the line width of many nuclear resonance signals at 4°K is very great because of long nuclear spin-lattice relaxation times. Our first attempt to use LiF nuclear resonance failed on this account. We observed a strong signal from the F^{-} and, at about twice the field, from the Li^{+} . At 4° they saturated and disappeared in about one second. However we obtained a strong resonance from the coil's perspex container, some 15 gauss in half width, and therefore made a series of coils wound on perspex formers.

g. Mounting:

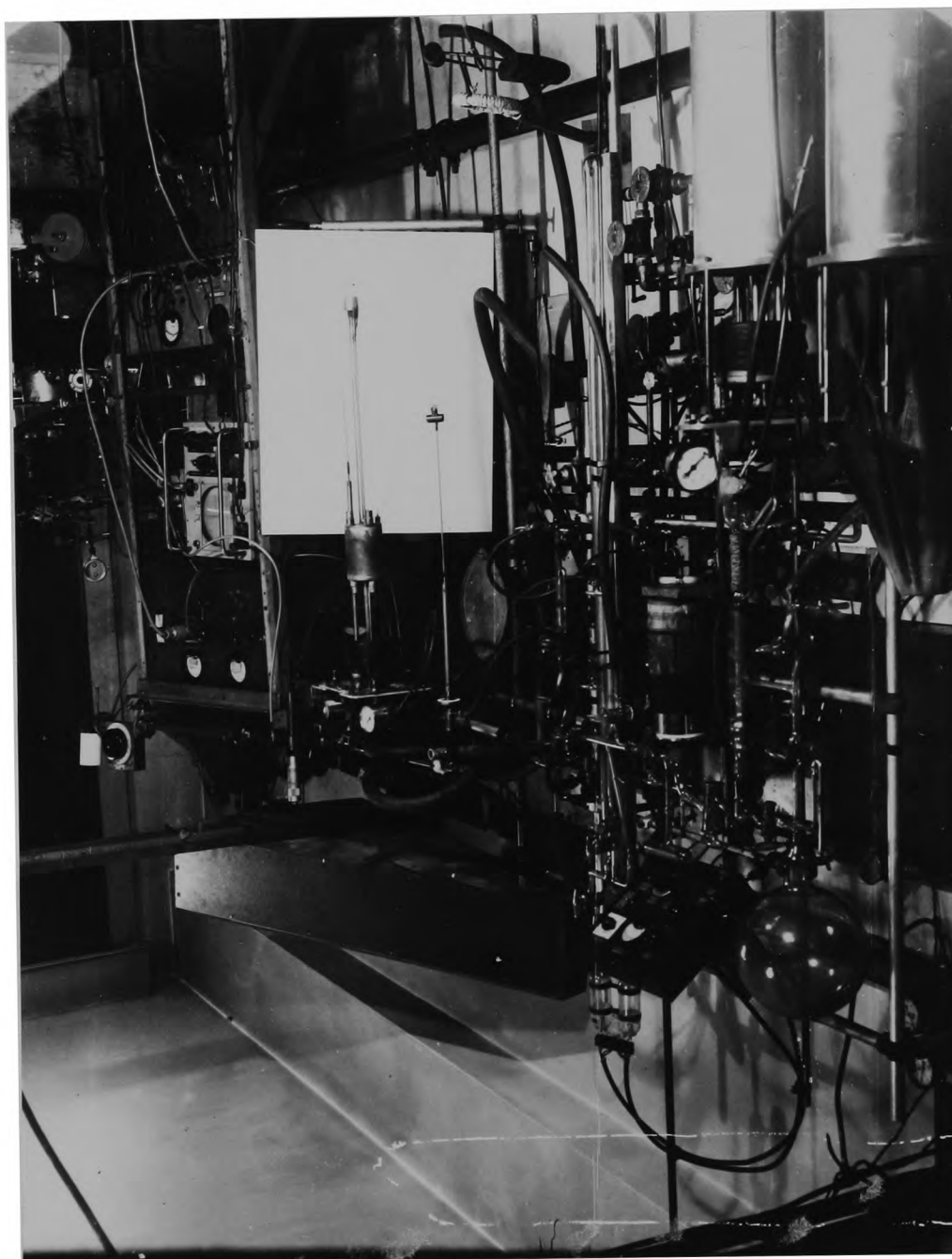
There was not enough space available in the laboratory to mount both the Sucksmith balance and the resonance apparatus permanently on the wall. As the resonance apparatus had to be moved to the Royal Society magnet, it was decided to mount it in the Tickford magnet in the same way that it was mounted on the larger magnet. A container was made as shown in photograph 7, which fitted between the pole pieces of the Tickford magnet and was supported in a tapered joint by the fixed base plate.

RF Oscillator



Chapter 11

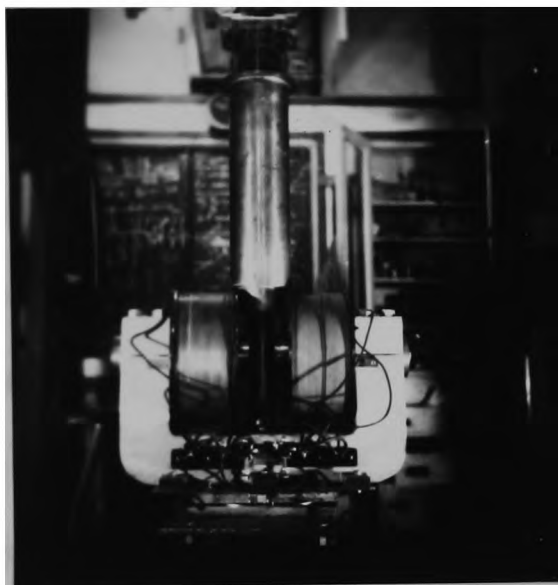
Photograph 6



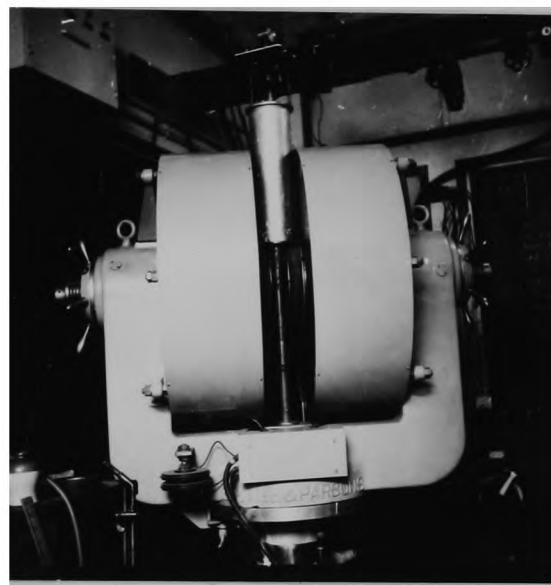
microwave spectrometer mounted upon the wall

Chapter II

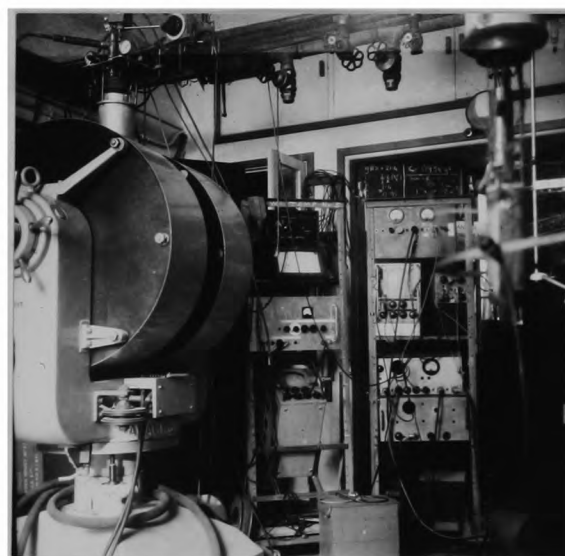
Photographs 7, 8 and 9



7



8



9

7. Microwave Spectrometer mounted in the Tickford magnet.
8. Microwave spectrometer mounted in the Royal Society magnet.
9. Apparatus arranged for an experiment.

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h. Cooling down;

The cooling procedure is as follows:

- a. Pump the siphon jacket.
- b. Seal the ground joint on the bottom of the cavity with glycerol and the ground joint at the top of the specimen holder with light tap grease.
- c. Blow any water out of the siphon with a stream of hydrogen gas.
- d. While bubbling hydrogen through the siphon raise the inner dewar full of liquid air until the hydrogen can is covered by the liquid.
- e. Pump the cavity and coaxial leads and check for leaks.
- f. After about five minutes remove the dewar and empty the liquid air into the large outer dewar.
- g. Quickly raise the inner dewar again, cut off the hydrogen flow through the siphon and close the outside end with a pinch clamp. Seal the inner dewar to the metal top by glycerol and a tight turn of wire about the rubber tubing.
- h. Pump the inner dewar to see there are no leaks from the outside through the rubber on the metal top, or more important, that the hydrogen can does not leak.
- i. Siphon liquid hydrogen into the can as quickly as possible.
- j. Keep pumping on the inner dewar to see that no hydrogen leaks from the can into the helium space.
- k. Fill the inner dewar with helium exchange gas to cool

II.36

the resonant cavity.

- l. Put on the outer dewar of liquid oxygen.
- m. Test that the siphon is not blocked by letting some of the exchange gas bubble out into a beaker of water.
- n. When the resonant cavity has reached liquid hydrogen temperature, raise the transport dewar of liquid helium and clamp it to the siphon. Suck over the liquid helium by pumping the inner dewar. When the liquid has been transferred allow the pressure in the transport dewar and the inner dewar to reach atmospheric; then remove the transport dewar and close off the outer end of the siphon.

CHAPTER III

THEORY

We have performed our experiments upon paramagnetic ions and molecules which were surrounded by the diamagnetic constituents of the rest of the crystal. Therefore we shall describe the theory of the energy states of a free ion as a first approximation. Then we shall go on to include the effect of the electric field produced by the paramagnetic ions' nearest neighbours (which we shall refer to as the crystal field.) Proceeding in the order of their magnitudes, we shall discuss the Zeeman effect; the effect of nuclear magnetic and electric moments; and finally, the magnetic interactions between nearest magnetic neighbours. All these effects will be related to the observed resonance spectra.

As we are also interested in the bulk susceptibility we shall derive Van Vleck's (1932) useful expressions for it. But we shall derive it in terms of the Spin Hamiltonian because this form can express very concisely the information obtained not only from the resonance measurements but also from bulk susceptibility and specific heat measurements.

III.2

I. QUANTUM NUMBERS:

Neglecting for the moment the effect of nearest magnetic neighbours, the crystal field, etc., consider the ion in a crystal as a free ion.

We wish to classify the energy states of this "free" ion in terms of quantum numbers, and eventually to classify the perturbed energy states of the "quasi free" ion whose properties we observe in terms of these same quantum numbers.

We can classify the state of a single electron in a central field by two quantum numbers, n and l ; hence the state of an N -electronic system is determined by a set of N pairs (n_1, l_1) .

A physical picture of the atom as having so many electrons of type (n_1, l_1) , so many of type (n_2, l_1) , so many of type (n_2, l_2) , etc., may now be drawn. This is called an electronic configuration. The configuration having the lowest energy is called the ground configuration.

The quantum numbers l, m , have a range of values restricted by $n > l \geq |m|$ and we shall require a two-valued quantum number s . According to the Pauli exclusion principle only one electron in the ion may have a given set (n, l, m, s) , of quantum numbers. Hence the number of elec-

III.3

trons which can have a given (n_1, l_1) is limited. If in a configuration electrons with all the possible m_1, s_1 are present, they are said to form a closed shell, (and contribute nothing to the ion's paramagnetism).

Generally there will be a number of possible values of m_1, s_1 associated with the electrons outside the closed shell. Although the calculated energy of the free ion with a central field does not depend upon m_1, s_1 the energy calculated by a field including interactions between electrons does. Therefore the electronic configuration has degeneracy which depends upon the values of m_1, s_1 .

We can apply the interaction energy as a perturbation if it is small compared with that of the central field. The degeneracy of the configurations will be at least partly removed, and the "terms," (states arising from one configuration) may not have values near the terms arising from any other configuration.

II. THE FREE HAMILTONIAN:

Consider an electron of charge e moving in the coulomb field of a nucleus of charge Ze a distance r_i from it. If there are other electrons in closed shells of radii r_i less than r_j , then the free ion Hamiltonian operator may be written down as:

III.4

$$\mathcal{H} = \sum_i \nabla_i^2 - \frac{Ze^2}{r_i} + \sum_{i>j}^j \frac{e^2}{r_{ij}} \quad 3.1$$

where we sum over all electrons, and where r_{ij} is the mean separation between the i th and j th electrons. ∇_i^2 is the linear momentum operator. $-\frac{Ze^2}{r_i} + \sum_{i>j}^j \frac{e^2}{r_{ij}}$ is the coulomb potential which takes account of the shielding due to the inner electrons.

Solution of the eigenvalue problem $\mathcal{H}\psi = E\psi$ is complicated by the quantity r_{ij} , and the Hartree central field approximation (or some equivalent approximation) is used.

The total Hamiltonian for the configuration using the Hartree central field approximation is usually written:

$$\begin{aligned} \mathcal{H} &= \left[\sum_i \left(\nabla_i^2 - \frac{Ze^2}{r_i} + V(r_i) \right) \right] + \left[\sum_{i>j}^j \frac{e^2}{r_{ij}} - \sum_i V(r_i) \right] + \left[\sum_i f(r_i) \underline{l}_i \cdot \underline{s}_i \right] \\ &= \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2 \end{aligned} \quad 3.2$$

where the Hartree potential $V(r_i)$ is chosen so that $\mathcal{H}_1 + \mathcal{H}_2 < \mathcal{H}_0$ in order that perturbation theory may apply.

It is in general possible that

$$\mathcal{H}_1 \gg \mathcal{H}_2, \quad \mathcal{H}_1 \div \mathcal{H}_2, \quad \mathcal{H}_1 \ll \mathcal{H}_2 \quad 3.4$$

The iron group fall under the case $\mathcal{H}_1 \gg \mathcal{H}_2$ called Russell-Saunders coupling; and the rare earths under $\mathcal{H}_1 \div \mathcal{H}_2$ called intermediate coupling.

III.5

H_2 has been written as $\sum_i f(r_i) \underline{l}_i \cdot \underline{s}_i$

called the spin-orbit coupling. This is the simplest mathematical assumption we can make in order to consider the dependence of an electron's energy upon the magnitude of its own orbital angular momentum and spin.

We could also consider the interactions between the spin of the i^{th} electron and those of the others guessing this to be $\sum_{i \neq j}^j A \underline{s}_i \cdot \underline{s}_j$; but this is only about 1 cm^{-1} whereas the spin-orbit coupling is about $10^2 - 10^3 \text{ cm}^{-1}$.

The interaction of the orbital magnetic moment of the i^{th} electron, with the spins of the other electrons, i.e. $\sum_{i \neq j}^j B \underline{l}_j \cdot \underline{s}_j$; and the interaction of the spin of the i^{th} electron with the orbital magnetic moments of the others, i.e. $\sum_{i \neq j}^j B \underline{l}_j \cdot \underline{s}_i$, are experimentally negligible as noted in the next section.

We postpone discussion of the effect of the crystal field, nuclear magnetic moment and nearest neighbours until later.

If we neglect the spin orbit coupling then the total spin and total orbital momentum of a configuration are constant in time, and are hence good quantum numbers. Therefore each free ion term is characterized by a value of

$\underline{L} = \sum_i \underline{L}_i$ and $\underline{S} = \sum_i \underline{s}_i$. The term described by $\underline{L}$ and $\underline{S}$ is $(2L+1)(2S+1)$ degenerate.

III.6

If H_2 is not neglected the sum of orbital and spin momenta may be shown to be constant, but not their individual values, i.e. $J = L + S$ is a good quantum number. The term described by J is $(2J + 1)$ fold degenerate and is called a multiplet.

If $H_0 \gg H_1 \gg H_2$ each multiplet will belong to a definite term of a definite configuration. We may then write the spin orbit coupling $\sum_i f(r_i) \underline{L}_i \cdot \underline{S}_i = f' \underline{L} \cdot \underline{S}$ where f' is a constant.

III. THE GROUND STATE:

Denote the r^{th} free ion configuration as X_r and the levels into which it is split as M_r^a ($a = 0, 1, 2 \dots n$). X_r is spanned by manifold of states denoted by $|X_r, M_r^a\rangle$.

If X_0 is the ground configuration we may write the ground state, i.e. that having the lowest energy level, as:

$$|X_0, M_0^0\rangle + \sum_{r,a} \frac{|X_r, M_r^a\rangle \langle X_r, M_r^a | H_1 | X_0, M_0^0 \rangle}{E(X_0) - E(X_r)}$$

3.5

from first order perturbation theory, where $E(X_r)$ is the eigenvalue of configuration X_r .

This has admixed configurations to predict the lowest level and the right hand fraction is therefore called the configurational interaction. Unless it is small, first order perturbation theory does not apply and we cannot accurately

III.7

describe an atom in terms of a configuration. We shall see in Chapter V how the resonance experiments offer a sensitive test of this interaction.

From susceptibility measurements Van Vleck (1932) showed that the rare earth ions have ground states predicted by Hund's Rule, i.e.:

"The ground level has maximum spin (S) and then maximum orbital momentum (L) and these are coupled by the spin-orbit interaction to give levels of minimum total angular momentum (J) lowest when the 4f shell is less than half full, and maximum (J) lowest when it is more than half full."

The fact that at room temperatures the susceptibilities are near those expected for free ions shows that the splittings produced by the crystal fields (to be considered later) are less than kT and less than the effect of spin-orbit coupling in the case of the rare earths.

We have now at least touched on those parts of the theory of the free ion to which we shall later refer, and conclude by tabulating data for Ce^{+++} , Nd^{+++} , Pr^{+++} and Sm^{+++} .

In the following table the quantity n_{eff}^2 is defined by the equation:
$$n_{eff}^2 = \frac{3 \times kT}{N\beta^2}$$

III.8

(Van Vleck, 1932), where χ is the molar susceptibility, k is Boltzmann's constant, T the absolute temperature, N Avogadro's number, and β the Bohr magneton. χ is given by:

$$\chi = \frac{N \bar{\mu}^2}{3 k T} + N \alpha^2 \quad 3.7$$

The column headed "Hund" is calculated from only the unperturbed part of equation 3.7, i.e.

$$\chi = \frac{N \bar{\mu}^2}{3 k T} \quad 3.8$$

The experimental values identify the ground level term and hence act as a starting point for the more precise calculations (given in the next section) which include the effect of the crystal field.

Ion (X)	Z	Ground State	Excited State	Theory (cm^{-1})	Exp't. (cm^{-1})	Method	Source	n_{eff} Hund	n_{eff} Van Vleck and Frank
Ce	58	$4f^1 2F_{5/2}$	$2F_{17/2}$	2100	2240	Spectra	Lang (1936)	2.54	2.56
Pr	59	$4f^2 3H_4$	$3H_2$ $3H_6$	2000 4480	5200	"	Spedding (1940)	3.58	3.62
Nd	60	$4f^3 4I_{9/2}$	$4I_{11/2}$ $4I_{15/2}$ $6H_{7/2}$	1800 6500 980	5200 1100	"	Gobrecht (1938) Van Vleck (1932)	3.62	3.68
Sm	62	$4f^5 6H_{5/2}$				Suscep- tibility		0.84	1.55 1.65

Table I Chapter 3.

III.9

IV. THE ION IN THE CRYSTAL:

The preceding section has dealt with the problem of the energy states of the free ion. However our experimental work has been done on "quasi free" ions in the electrical fields of the other particles forming crystals. As we have seen, the effect of crystal fields on rare earth ions is small, and we can apply it as a perturbation on the free ion multiplet structure. The symmetry of these fields greatly limits the type of mathematical function which describes them. The function must be a solution of Laplace's equation and hence can be expanded in spherical harmonics, i.e.:

$$V_c = \sum_l \sum_{|m| \leq l} A_l^m \sum_{i=1}^N r_i^l Y_l^m(\theta_i, \phi_i) = \sum_l \sum_{|m| \leq l} A_l^m V_l^m \quad 3.9$$

Here, $Y_l^m(\theta, \phi)$ denotes a surface harmonic and A_l^m is a coefficient depending on the nature of the surroundings. We would like to be able to calculate the A_l^m from our experimental data.

In the rare earths we deal with 4f electrons. Any matrix element arising from the perturbation due to the electric field will have the form $\int \psi^* X \psi d\tau$, where ψ and ψ both refer to the f electrons. If the charge density of $\psi^* \psi$ is expanded in spherical harmonics it will not contain terms beyond the sixth degree, and any integral in which X is

III.10

higher than the sixth degree will vanish by the orthogonality relations of spherical harmonics. Hence we can terminate the series at $n=6$, for the matrix elements of all higher terms are zero. We can also drop all terms which reverse sign under $x \rightarrow -x$, $y \rightarrow -y$, $z \rightarrow -z$ (odd parity), for $u^* v$ does not change sign under this transformation and it readily follows that $\int u^* x v d\tau$ is then zero. (Stevens and Elliott, 1952.)

In referring to types of symmetry we shall use the notation of Eyring, Walter and Kimball, (1944). Thus C_3 means that there is a vertical three-fold axis of symmetry. The subscript v is added if there is also a vertical reflection plane (C_{3v}), and h is added if there is a horizontal plane (C_{3h}). If both these additional symmetries are present the total symmetry is denoted by D_{3h} . Any surface harmonic $Y_n^m(\theta, \phi)$ for which m is zero shows no dependence on ϕ and is said to have an axial symmetry. If $m = \pm 4$ it is said to have tetragonal symmetry, $m = \pm 3$ trigonal symmetry, and $m = \pm 2$ rhombic symmetry. Any form which contains terms of different symmetry is said to have overall symmetry which is the greatest symmetry common to all terms.

Helmholtz (1939) showed that the rare earth ethylsulphates and bromates have C_{3h} symmetry, and Elliott

III.11

and Stevens (1952) have worked out the crystal field potentials for D_{3h} and C_{3h} symmetries.

The following theory has been worked out for ions having an odd number of electrons and hence having Kramers' degeneracy (Kramers, 1930), i.e. at least a single degeneracy which cannot be removed by an electric field.

V. THE HAMILTONIAN:

The Hamiltonian for the quasi-free ion can be written

$$H = H_0 + H_1 + H_2 + V_c \quad 3.10$$

where V_c is of the form $-\sum_i e_i \nabla_c$.

For the rare earth group, usually

$$H_0 \gg H_1 + H_2 \gg V_c \quad 3.11$$

If 3.11 is true any crystal level will arise primarily from the splitting of one multiplet and be slightly perturbed by an admixture of other J multiplets.

Various ways of finding the splittings caused by the crystal field have been used, e.g. Bethe (1929), Becquerel and Opechowski (1939), Abragam and Pryce (1950).

We shall describe the method used by Stevens and Elliott (1952), which sets up the secular equation in the usual way for degenerate systems. The polar axis is

III.12

chosen as axis of quantization with wave functions ψ_m where m denotes the component of angular momentum in the direction of the axis, and the elements in the secular determinant are the integrals:

$$\int \psi_m^* \left\{ \frac{\epsilon}{i} - eV(x_i, y_i, z_i) \right\} \psi_m d\tau \quad 3.12$$

If U_N^M is any function which has the same angular variation as $Y_N^M(\Theta, \phi)$, the integral $\int \psi_m^* U_N^M \psi_n d\tau$ vanishes unless $m = n + M$ (Stevens and Bleaney, 1953). If $\int \psi_m^* U_N^M \psi_n d\tau$ does not vanish, all the other non-vanishing elements for the same N can be found from it by symmetry arguments as we shall now show.

IN EFFECT, ANY NON-ZERO ELEMENT $\int \psi_m^* U_N^M \psi_n d\tau$
CAN, BY SUITABLE CHANGES OF AXES, BE
TRANSFORMED INTO A MULTIPLE OF SOME KNOWN
MATRIX ELEMENT $\int \psi_m^* U_N^M \psi_n d\tau$.

The process of replacing operators by multiples of other simpler operators, which we shall use to derive the Spin Hamiltonian, is based on this result.

We wish to find the matrix elements of

$$\sum_i r_i^\rho Y_\rho^n(\Theta_i, \phi_i), \quad (1) \text{ inside a } J \text{ manifold, and } (2)$$

between manifolds of different J .

III.13

VI. OPERATOR EQUIVALENTS:

A theorem in group theory states that if D_1 is spanned by two different bases of irreducible representations $\phi_\ell^r(1)$ and $\phi_\ell^r(2)$ ($r = 1, 2, \dots$) where there is a correspondence between $\phi_\ell^r(1)$ and $\phi_\ell^r(2)$; and D_j is spanned by $\phi_j^s(1)$ and $\phi_j^s(2)$ ($s = 1, 2, \dots$), then

$$\phi_\ell^r(1) \times \phi_j^s(1) = \sum_{k=|\ell-j|}^{\ell+j} B_k^1 \sum_i a_{rs}^i \phi_k^i(1) \quad 3.13$$

$$\phi_\ell^r(2) \times \phi_j^s(2) = \sum_{k=|\ell-j|}^{\ell+j} B_k^2 \sum_i a_{rs}^i \phi_k^i(2) \quad 3.14$$

where the constants on the right multiplying each ϕ_k^i are the same except for the multiplicative constants B^1 , and these B^1 are the same for all i with a given k . In our case $\sum_i r_i^\ell Y_\ell^m(\theta_i \phi_i)$ transforms like D_ℓ and is $\phi_\ell^r(1)$, say, while the wave functions of the lowest multiplet transform like D_j and are the $\phi_j^s(1)$. The quantities required are the $B_k^1 a_{rs}^i$ and if the problem can be formulated more simply in a different representation and $B_k^2 a_{rs}^i$ found, the original problem is solved except for a constant factor.

Therefore consider the states $\langle J, J_z |$ as the $\phi_j^s(2)$ and discover by some means what function of the operators J_x, J_y, J_z (called $Y_\ell^m(J)$) is the $\phi_\ell^r(2)$ required. In this case all the $B_k = 0$ ($k \neq j$) since $\phi_j \times \theta_j = \sum_{i < j} \phi_i$.

III.14

Stevens (1952) has tabulated some functions of J_x, J_y, J_z which transform like $\sum_i r_i^\ell Y_\ell^m(\theta_i, \phi_i)$. They are obtained by replacing x, y, z by J_x, J_y, J_z and allowing for the commutation properties of the J 's by replacing any product x, y and z by $\frac{1}{n} (P_{xyz})$ where n is the number of permutations of P_{xyz} of the variables.

To evaluate the B_j^2 we must find some particular matrix element by integrating over the wave functions. The simplest approach is to consider the $|J, J_z\rangle$ as built from one Russel-Saunders term of one configuration for we can now find $|J, J_z\rangle$ in terms of $|LL_z, SS_z\rangle$. V_0 commutes with the spin variables, hence within a manifold of total L the $\sum_i r_i^\ell Y_\ell^m(\theta_i, \phi_i)$ can be replaced by a similar operator to that for J in terms of L_x, L_y, L_z ; $Y_\ell^m(L)$ say, and the actual matrix elements will be some constant C times the numerical factors for the elements tabulated by Stevens. Thus when one expansion of $|J, J_z\rangle$ in terms of $|LL_z, SS_z\rangle$ is known, a proportionality can be obtained between B and C .

The $|LL_z, SS_z\rangle$ for which $L_z = L$ and $S_z = S$ can be expressed as a single Slater determinant because the $p = 2s$ electrons outside the closed shells will have

$$(m_\ell)_\alpha = \ell_\alpha, \ell_\alpha - 1, \dots, (\ell_\alpha - p - 1) \text{ and } (m_s)_\alpha = \frac{1}{2}$$

III.15

The matrix element is a sum of matrix elements of one electron functions like

$$\langle n_{\alpha} l_{\alpha} (m_l)_{\alpha} (m_s)_{\alpha} | r^l Y_l^m(\theta, \phi) | n_{\alpha} l_{\alpha} (m_l)_{\alpha} (m_s)_{\alpha} \rangle$$

and within the manifold l_{α} is constant, so $r^l Y_l^m(\theta, \phi) = D Y_l^m(l_{\alpha})$ and we need integrate over only one element. These integrals are given by Elliott (1952) in terms of $\bar{r}^2$, the square of the average value of the electron over a 4f orbit.

Our procedure in finding the matrix elements for the crystal field perturbation now reduces to replacing the Cartesian coordinate operators with their operator equivalents and multiplying the resulting operator by the appropriate constants tabulated by Stevens.

Table 2 gives the operator equivalents and proportionality constants which we shall use.

VII. THE ZEEMAN EFFECT:

If we are to consider perturbations in the order of the magnitude of their effect we should next consider the Zeeman effect. By Kramers' theorem the energy levels of an ion having an odd number of electrons are at least doubly degenerate in the absence of a magnetic field. Dirac (1936) shows that the perturbation W caused by the application of a magnetic field is $W = \frac{eh}{4\pi mc} (\underline{L} + 2 \underline{S}) \cdot \underline{H}$.

CHAPTER III Table 2

Operator equivalents inside a manifold for which J is constant

$$\sum (3z^2 - r^2) \equiv \langle J || \alpha || J \rangle \bar{r}^2 \{ 3J_z^2 - J(J+1) \}$$

$$\begin{aligned} \sum (35z^4 - 30r^2 z^2 + 3r^4) &\equiv \langle J || \beta || J \rangle \bar{r}^4 [35J_z^4 - 30J(J+1)J_z^2 \\ &+ 25J_z^2 - 6J(J+1) + 3J^2(J+1)^2] \end{aligned}$$

$$\begin{aligned} \sum (231z^6 - 315r^2 z^4 + 105r^4 z^2 - 5r^6) &\equiv \langle J || \gamma || J \rangle \bar{r}^6 [231J_z^6 \\ &- 315J(J+1)J_z^4 + 735J_z^4 + 105J^2(J+1)^2J_z^2 - 525J(J+1)J_z^2 \\ &+ 294J_z^2 - 5J^3(J+1)^3 + 40J^2(J+1)^2 - 60J(J+1)] \end{aligned}$$

	Ce ⁺⁺⁺	Pr ⁺⁺⁺	Nd ⁺⁺⁺	Sm ⁺⁺⁺
$\langle J \Delta J \rangle$	$\frac{6}{7}$	$\frac{4}{5}$	$\frac{8}{11}$	$\frac{2}{7}$
$\langle J \alpha J \rangle$	$\frac{-2}{5.7}$	$\frac{-2^2.13}{3^2.5^2.11}$	$\frac{-7}{3^2.11^2}$	$\frac{13}{3^2.5.7}$
$\langle J \beta J \rangle$	$\frac{2}{3^2.5.7}$	$\frac{-2^2}{3^2.5.11^2}$	$\frac{-2^2.17}{3^3.11^3.13}$	$\frac{2.13}{3^3.5.7.11}$
$\langle J \gamma J \rangle$	0	$\frac{2^4.17}{3^4.5.7.11^2.13}$	$\frac{-5.17.19}{3^5.7.11^3.13^2}$	0

(Values for ground state)

$\langle J || \alpha || J \rangle$, $\langle J || \beta || J \rangle$ etc. correspond to the different B_J^1 of 3.14 in Stevens' notation.

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where $\underline{H}$ is the magnetic field. The associated energy is of the order of 1 cm^{-1} . There is an associated diamagnetic term which we shall neglect here as it does not occur in the resonance work, although we shall have occasion to mention it in Section XII, 2.

In Stevens' notation

$$\langle J | \underline{L} + 2 \underline{S} | J \rangle = \langle J || \underline{L} || J \rangle \langle J \dots | \underline{J} | J \dots \rangle$$

and he has tabulated these elements, some of which are shown in Table 2. We have already defined the spectroscopic splitting factor g from $g\beta H = 2\Delta$ where Δ is the energy shift caused by the magnetic field. Hence the problem of finding g theoretically reduces ultimately to finding the matrix elements of

$$\langle J | \underline{L} + 2 \underline{S} | J \rangle = \langle J || \underline{L} || J \rangle \langle J | \underline{J} | J \rangle$$

and applying first order perturbation theory. We shall note some properties of the g tensor in the section on the theory of measurements, and show their detailed calculation in Chapter IV.

VIII. NUCLEAR HYPERFINE STRUCTURE:

A nuclear magnetic moment, $\underline{I}$, will interact with the spin and orbital magnetic moments, and the electric quadrupole moment of the nucleus will interact with the crystal field to give an axis of quantization relative to which the

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magnetic moment can have $2I+1$ values. Hence each level resulting from the previously discussed perturbations will have a $2I+1$ degeneracy.

The nucleus is in the strong magnetic field (100KG) of the electron spins. When an electron goes from $l+>$ to $l->$ the change in energy of the ion results not only from the difference in energy of the $l+>$ and $l->$ states, but also from their shift in energy caused by the reversal of the field at the nucleus. The nucleus itself does not change its orientation during an electronic transition, hence $\Delta m = 0$ is a good selection rule.

The interaction between the electrons and the nucleus arises from two causes:

- a. The magnetic interaction between the electron spin magnetic moment and the magnetic moment of the nucleus (linear in the nuclear spin vector, $\underline{I}$).
- b. The electrostatic interaction between the electric quadrupole moment of the nucleus (quadratic in $\underline{I}$) and the electrostatic field caused by the electrons at the nucleus.

We shall neglect the small interaction of the nuclear moment with the magnetic field $\equiv \int \underline{T} \cdot \underline{H}$.

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We shall use cosine coupling as in the spin orbit interaction. Higher electric and magnetic poles need not be considered, their effects being negligibly small (Abragam and Pryce, 1951). The nuclear contribution to the Hamiltonian can therefore be written:

$$W_n = 2\mu_N\beta\beta_N \sum_k \left\{ \frac{(\mathbf{l}_k - \mathbf{s}_k) \cdot \mathbf{I}}{r_k^3} + 3 \frac{(\mathbf{r}_k \cdot \mathbf{s}_k)(\mathbf{r}_k \cdot \mathbf{I})}{r_k^5} \right. \\ \left. + \frac{8\pi}{3} \delta(r_k) \mathbf{s}_k \cdot \mathbf{I} \right\} + \frac{e^2 Q}{2I(2I-1)} \sum_k \frac{I(I+1)}{r_k^3} - 3 \frac{(\mathbf{r}_k \cdot \mathbf{I})^2}{r_k^5} \quad 3.15$$

where the first bracket is from (a) and the second from (b); $\mathbf{l}$ stands for the orbital angular momentum of the k^{th} electron, $\mathbf{s}$ its spin, β the Bohr magneton, β_N the nuclear magneton, I the nuclear spin, μ_N the nuclear gyromagnetic factor in units of $\frac{e}{2} mc$, and Q the quadrupole moment as usually defined (Kopfermann, 1940).

The experiments of Bleaney, Elliott, Scovil and Trenam (1951) on gadolinium with $L=0$ show that it has no hyperfine structure in any of several complexes, including particular crystals we have investigated. This indicates that we may neglect the Fermi term (Fermi, 1930), $\frac{8\pi}{3} \delta(r) \mathbf{s}_k \cdot \mathbf{I}$

Like Stevens (1953) let us define N by

$$N = \sum_i (\mathbf{l}_i \cdot \mathbf{s}_i) + 3 \frac{(\mathbf{r}_i \cdot \mathbf{s}_i)(\mathbf{r}_i \cdot \mathbf{I})}{r_i^5} \quad 3.16$$

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Then the magnetic interaction term becomes

$$\frac{2\beta\beta_N}{I^2} \sim \left(\frac{I}{r^3} \right) N \cdot I$$

A very useful method of carrying out the perturbation calculation has been given by Pryce (1950). The method, which is only applied when the lowest orbital state is a singlet, consists of carrying out a formal perturbation treatment in which the operators referring to spin and nuclear variables are treated as non-commuting algebraic quantities. That is, no representation is chosen for either S or I . The result is that instead of obtaining the perturbed energy as usual, an expression is obtained which involves the components of S and I . This is the so-called Spin Hamiltonian, and the actual energies are the eigenvalues of this new operator.

Thus finding the matrix elements of N is similar to the problem of finding the elements of $(L+2S)$ already considered, i.e., one of finding the multiplicative factors $\langle J \| N \| J \rangle$ and $\langle J+1 \| N \| J \rangle$ defined by:

$$\langle J \dots | N | J \dots \rangle = \langle J \| N \| J \rangle \langle J \dots | J | J \dots \rangle \quad 3.17$$

and

$$\langle J+1, J_z | N | J J_z \rangle = \langle J+1 \| N \| J \rangle \sqrt{(J+1)^2 - J_z^2} \quad 3.18$$

though we will not need the latter.

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Elliott and Stevens (1953) list formulae and tables for these.

The 2 x 2 matrix which is obtained for $2\beta\beta_N \frac{\mu_N}{I} \overline{\left(\frac{1}{r^3}\right)} N \cdot \underline{I}$ can be written as $\underline{S} \cdot \underline{T} \cdot \underline{I}$ where $\underline{T}$ is a tensor with principal values A, B and B. Thus

$$A = 4\beta\beta_N \frac{\mu_N}{I} \overline{\left(\frac{1}{r^3}\right)} \langle +1 N_z | + \rangle \quad 3.19$$

$$B = 4\beta\beta_N \frac{\mu_N}{I} \overline{\left(\frac{1}{r^3}\right)} \langle +1 N_x | - \rangle \quad 3.20$$

The matrix elements of

$$\frac{e^2\varphi}{2I(2I-1)} \sum_K \left\{ \frac{I(I+1)}{r_K^3} - \frac{3(\underline{r}_K \cdot \underline{I})^2}{r_K^5} \right\}$$

can be obtained using operator equivalents (replacing r by J and performing some simple operator algebra), thus:

$$\begin{aligned} \langle J J_z | \sum_K \left\{ \frac{I(I+1)}{r_K^3} - \frac{3(\underline{r}_K \cdot \underline{I})^2}{r_K^5} \right\} | J J_z \rangle \\ = -\frac{9}{2} \langle J || \alpha || J \rangle \overline{\left(\frac{1}{r^3}\right)} \left\{ J_z^2 - \frac{1}{3} J(J+1) \right\} \left\{ I_z^2 - \frac{1}{3} I(I+1) \right\} \end{aligned} \quad 3.21$$

where $\langle J || \alpha || J \rangle$ is tabulated by Stevens.

IX. THE SPIN HAMILTONIAN:

We have shown the nuclear part of the spin Hamiltonian to be of the form $W = \underline{S} \cdot \underline{T} \cdot \underline{I} + Q' \left\{ I_z^2 - \frac{1}{3} I(I+1) \right\}$. When $\underline{T}$ has its principal values this may be written as

$$W = AS_z + B(S_x I_x + S_y I_y) + Q' \left\{ I_z^2 - \frac{1}{3} I(I+1) \right\} \quad 3.22$$

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if there is at least tetragonal symmetry.

For the case of the lowest orbital singlet, then, we may write the total spin Hamiltonian in the most general form:

$$\begin{aligned} \mathcal{H}_s = & \underline{S} \cdot \underline{D} \cdot \underline{S} + \beta \underline{H} \cdot \underline{g} \cdot \underline{S} + \underline{S} \cdot \underline{T} \cdot \underline{I} + \underline{I} \cdot \underline{P} \cdot \underline{I} \\ & - \chi \beta_N \underline{H} \cdot \underline{I} - \beta^2 \underline{H} \cdot \underline{\Lambda} \cdot \underline{H} \end{aligned} \quad 3.23$$

However the spin Hamiltonian must show the same symmetry as the crystal field, and hence for trigonal or tetragonal symmetry we may write:

$$\begin{aligned} \mathcal{H}_s = & D S_z^2 + \beta [g_{\parallel} H_z S_z + g_{\perp} (H_x S_x + H_y S_y)] \\ & + A I_z S_z + B (I_x S_x + I_y S_y) + P I_z^2 \\ & - \chi \beta_N \underline{H} \cdot \underline{I} - \beta^2 \underline{H} \cdot \underline{\Lambda} \cdot \underline{H} \end{aligned} \quad 3.24$$

The various terms can be interpreted as follows:

The terms in $\underline{H}$ and $\underline{S}$ show that the spin is no longer completely free because of the crystal field, but can either be regarded as free and precessing about the magnetic field ($g_{\perp} H_x$, $g_{\perp} H_y$, $g_{\parallel} H_z$) or as having an anisotropic magnetic moment ($g_{\perp} S_x$, $g_{\perp} S_y$, $g_{\parallel} S_z$). The term DS_z^2 describes how the levels behave in zero magnetic field in the absence of the nuclear interaction and comes from the second order effects of the crystal field, the spin orbit coupling, and from the spin-spin interaction.

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The terms in S and I come from the magnetic interactions between the electrons and the nucleus and are anisotropic in the same way as the electronic moment is anisotropic. The term PI_z^2 comes from the quadrupole interactions. The direct interaction between the magnetic field and the nuclear moment takes the usual form $-\gamma \beta_N \underline{H} \cdot \underline{I}$ and the final term $-\beta^2 \underline{H} \cdot \underline{A} \cdot \underline{H}$ does not depend on either $\underline{S}$ or $\underline{I}$, and can be neglected in resonance work although it appears in the susceptibility as an additive temperature-independent constant.

As this spin Hamiltonian has complete axial symmetry, there is no way of deducing from it whether the crystal field is trigonal or tetragonal.

Using the spin Hamiltonian we are now able to describe the magnetic properties of a crystal in terms of a relatively small number of constants.

X. THE KRAMERS DOUBLET:

We shall now calculate the energy levels and the magnetic fields at which absorption lines occur for a Kramers doublet.

The simple Hamiltonian

$$W = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + A S_z I_z \\ + B (S_x I_x + S_y I_y) + P \left[I_z^2 - \frac{1}{3} I(I+1) \right]$$

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which includes only the effect of the magnetic field, the nuclear interaction with the spin and the quadrupole effect, may be broken up into two parts when $\underline{H}$ is parallel the z-axis.

$$W_1 = g_{\parallel} (\beta H S_z + A S_z I_z + P (I_z^2 - \frac{1}{3} I(I+1)))$$

$$W_2 = B (S_x I_x + S_y I_y) = \frac{1}{2} B (S_+ I_- + S_- I_+)$$

(The symbol $S_{\pm} = S_x \pm i S_y$; $I_{\pm} = I_x \pm i I_y$; etc.)

We shall apply W_1 and W_2 as successive perturbations - a procedure justifiable only when W_1 is large, i.e. the high field spectrum.

1. APPLICATION OF W_1 :

W_1 is diagonal with respect to S_z and I_z and the typical matrix element is

$$\begin{aligned} \langle S_z = M, I_z = m | W_1 | M m \rangle &= g_{\parallel} (\beta H M + A m M \\ &+ P (m^2 - \frac{1}{3} I(I+1))) \end{aligned} \quad 3.25$$

Thus the state $|M, m\rangle$ is a zero order eigenstate of the perturbation with the energy (3.25). Let $g\beta H = G$. The states fall into two groups $|\frac{1}{2}m\rangle$ with energies $\frac{1}{2}G + \frac{1}{2}Am + P(m^2 - \text{const})$ and $|\frac{1}{2}m\rangle$ with energies $-\frac{1}{2}G - \frac{1}{2}Am + P(m^2 - \text{const})$.

Ignoring the effect of W_2 , an oscillating magnetic field h can produce transitions between the groups

$$\text{if } \langle \frac{1}{2}, m | g_{\parallel} h_z S_z + g_{\perp} (h_x S_x + h_y S_y) | -\frac{1}{2}, m' \rangle$$

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is not zero. This only happens for $m = m^1$, and the effective component of the oscillating field is that perpendicular to $\underline{H}$. Transitions occur when $\hbar \nu = G + Am$. It will be noted that P does not enter into the relation.

2. APPLICATION OF W_2 :

The first order effect of W_2 on the energy levels is zero since

$$\langle M, m | S_+ I_- + S_- I_+ | M, m \rangle = 0 \quad 3.26$$

In fact the only non-zero matrix elements of W_2 are those of the type

$$\langle M \pm 1, m \mp 1 | W_2 | M, m \rangle \quad 3.27$$

Therefore the second order effect on the energy of the state $|\frac{1}{2}m\rangle$, which is

$$\sum_{\text{other states}} \frac{|\langle \text{other state} | W_2 | \frac{1}{2}m \rangle|^2}{E_{\frac{1}{2}m} - E_{\text{other state}}}$$

consists solely of the term

$$\frac{|\langle -\frac{1}{2}, m+1 | \frac{1}{2} B S_- I_+ | \frac{1}{2}, m \rangle|^2}{\frac{1}{2} G + \frac{1}{2} Am + Pm^2 - (-\frac{1}{2} G - \frac{1}{2} Am - \frac{1}{2} A + P(m+1)^2)} \quad 3.28$$

Since we are getting merely a correction, the denominator may with sufficient accuracy be put equal to $G + Am$. The correction to the energy of the $|\frac{1}{2}m\rangle$ state, in this approximation is

$$\frac{\frac{1}{4} B^2 [I(I+1) - m(m+1)]}{G + Am}$$

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In the same way the correction to the $|\frac{1}{2}m\rangle$ state is found to be

$$\frac{-\frac{1}{4} B^2 [I(I+1) - m(m+1)]}{G + Am}$$

The energy difference between the states $|\frac{1}{2}m\rangle$ and $|\frac{1}{2}m+1\rangle$ is then

$$G + Am + \frac{\frac{1}{2} B^2 [I(I+1) - m^2]}{G + Am} \quad \text{and absorption occurs}$$

when $h\nu$ equals one of the $2I+1$ values of this expression.

Since $g\beta H_0 = h\nu$ where H_0 is the field at which resonance would occur in the absence of hyperfine structure, then

$$g\beta H_0 = g\beta H + Am + \frac{\frac{1}{2} B^2 [I(I+1) - m^2]}{g\beta H + Am}$$

$$\div g\beta H + Am + \frac{B^2 [I(I+1) - m^2]}{2 g\beta H_0}$$

Put $g_{\parallel} \beta A' = A$ $g_{\perp} \beta B' = B$

then $H = H_0 - A'm - \frac{1}{2} \frac{B'^2 g_{\perp}^2 [I(I+1) - m^2]}{H_0 g_{\parallel}}$

The effect of W_2 is that the eigenstates of the energy are no longer pure eigenstates of s_z and I_z , i.e. to $|\frac{1}{2}m\rangle$ is admixed $|\frac{1}{2}, m+1\rangle$ in amount proportional to $\frac{B}{g\beta H}$. The selection rule $m=m'$ then breaks down although at 3 cm microwave frequencies the intensity of the forbidden transitions is low. When m changes during a transition the energy difference contains first order terms in P from which P can be deduced. This will be discussed further in connection with erbium ethyl sulphate and neodymium double nitrate.

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In conclusion we will list some useful formulae given by Bleaney and Ingram (1951) and Bleaney (1951).

a. H parallel Z-axis:

$$H = H_0 - A_m - \frac{1}{2} \frac{B^2}{H_0} \{I(I+1) - m^2\} \quad 3.29$$

b. H perpendicular Z-axis:

$$H = H_0 - B_m - \frac{1}{4} \frac{(A^2 + B^2)}{H_0} \{I(I+1) - m^2\} \quad 3.30$$

c. H at θ to Z axis; transition $(M, m) \rightarrow (M-1, m)$:

$$\begin{aligned} \hbar\nu = & g\beta H + Km + \frac{B^2}{4g\beta H_0} \left(\frac{A^2 + K^2}{K^2} \right) \{I(I+1) - m^2\} \\ & + \frac{B^2}{2g\beta H_0} \frac{A_m(2M-1)}{K} + \frac{1}{2g\beta H_0} \left(\frac{A^2 + B^2}{K^2} \right) \left(\frac{g_{\parallel} g_{\perp}}{g^2} \right)^2 \sin^2 \theta \cos^2 \theta m^2 \\ & + \frac{\varphi^2 \cos^2 \theta \sin^2 \theta}{2KM(M-1)} \left(\frac{AB g_{\parallel} g_{\perp}}{K^2 g^2} \right)^2 m \{4I(I+1) - 8m^2 - 1\} \\ & - \frac{\varphi^2 \sin^4 \theta}{8KM(M-1)} \left(\frac{B g_{\perp}}{K g} \right)^4 m \{2I(I+1) - 2m^2 - 1\} \end{aligned}$$

where $K^2 g^2 = A^2 g_{\parallel}^2 \cos^2 \theta + B^2 g_{\perp}^2 \sin^2 \theta$
 $\varphi \equiv \varphi' \text{ (of 3.22)} \equiv P$

XI. APPLICATION TO OTHER SUBSTANCES:

The preceding theory has been derived for the case of the rare earths where $H_0 \gg H_1 + H_2 \gg V_c$. In the case of the iron group cyanides, however, $H_0 \gg V_c \gg H_1 + H_2$ and the perturbations must be applied in a different order.

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The free ion electronic wave functions of the magnetic carriers are 3d rather than 4f, but there is evidence of some chemical bonding. We shall develop these differences more explicitly in the chapter on the experimental results.

Some work was done on paramagnetic molecules viz. O_2 and NO, and although the theory has the same structure as for ions, there are differences in nomenclature which we shall note in the chapter on experimental results.

XII. THEORY OF OBSERVATIONS:

1. PARAMAGNETIC RESONANCE:

a. g Values:

In paramagnetic resonance a large (1-20 Kilogauss) steady homogeneous magnetic field is applied to a crystal. The large magnetic field separates a Kramers doublet according to the Zeeman effect. If a small a.c. field of high frequency ν is applied perpendicular to the steady field, it may induce transitions between the separated levels when the quantum energy $h\nu$ is equal to the Zeeman splitting $g\beta H$.

As we have already noted, g is a tensor of rank 2 and if l, m, n , are the direction cosines of the magnetic field relative to the coordinate system where g has its principal values g_{11}, g_{22}, g_{33} (usually coincident with

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the crystallographic axes) then

$$g^2 = l^2 g_{11}^2 + m^2 g_{22}^2 + n^2 g_{33}^2 \quad 3.31$$

If the Z-axis is an axis of rotational symmetry, in the $x - y$ plane

$$\begin{aligned} g^2(\phi) &= g_{//}^2 \cos^2 \phi + g_{\perp}^2 \sin^2 \phi \\ &= g_{//}^2 + (g_{22}^2 - g_{//}^2) \sin^2 \phi \end{aligned} \quad 3.32$$

3.33

If the crystal field has an r -fold symmetry the field must be the same at $\phi = \phi_0 + \frac{2\pi}{r}$ as it is at ϕ_0 . If $r = 2$ (rhombic) this is compatible with 3.33. But if $r > 2$, then $g_{22}^2 - g_{11}^2 = 0$. Hence we have the important result that $g_{22} = g_{11}$, called $g_{\perp}$. Now put $g_{33} = g_{//}$. Then at an angle θ to the Z-axis

$$g^2 = g_{//}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta \quad 3.34$$

Equation 3.34 is particularly useful if the minimum g value lies beyond the range of the magnetic field as $g_{\text{obs}}^2 \text{ vs. } \sin^2 \theta$ can be extrapolated linearly to get the minimum g . The derivation of 3.34 is based upon the first order approximation that the Zeeman splitting $= g\beta H$. It may be shown from perturbation theory that the two energy levels will never cross over due to the effect of the magnetic field, so that at huge fields we expect an effect in H^2 . This would

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lead to departures from linearity in $g_{\text{obs}} \text{ vs } \sin^2 \theta$ which we have never observed.

b. Line Width:

In microwave spectroscopy the resolution of the spectrum is generally limited by line width rather than instrumental effects. The two major causes of line width are the interaction between the paramagnetic ions and the lattice, and the interaction between the various paramagnetic ions themselves.

These interactions have often been treated in terms of two relaxation times - the spin lattice relaxation time (τ) and the spin-spin relaxation time. The latter is not as successfully described by a single parameter as the former.

i. The Spin Lattice Interaction: The inverse of τ is a measure of the rate at which a spin reverses direction and either gives to or takes from the lattice a quantum of energy.

Van Vleck's theory (1940) was given with particular reference to non absorption, and Bagguley and Griffiths (1952) report that the line widths do not follow exactly the expressions given by the theory.

The mechanism considered is one in which the

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thermal vibrations of the lattice give a fluctuating crystalline electric field. This effects the spin (upon which the magnetic effects depend) via the spin orbit coupling. The development shows that τ depends very markedly upon the separation between the ground state and the first excited state; if Δ is large, τ is large; if Δ is small, τ is small. Other effects of thermal vibrations, such as modulation of the dipole-dipole interaction between the spins appear to give negligible widths.

It is usual in resonance work to increase spin-lattice relaxation times by working at low temperatures. This indeed is the reason why our apparatus was designed to be used at liquid helium temperatures. As we have noted, τ is short when there is a low-lying excited level, and this is the case for several of the rare earths because the 4f electrons are so well shielded from the crystalline electric field.

If $\tau > 10^{-5}$ sec. we should expect the absorption line to be weakened because of the inability of the spins to transfer the energy received from the radiation field to the lattice quickly enough. This is the case for gadolinium in the ethylsulphates and double nitrates, for its spectrum is not observed at 4°K, although it is visible at and above 20°K.

The long spin-lattice relaxation time of the nuclei of Li^+ and F^- prevented us from using them as reference lines for measuring the magnetic field. The slightly larger

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interaction provided by dislocations formed by bombarding the LiF with neutrons was sufficient to prevent the signal from saturating at 4°K, but the line width is still very large.

ii. Spin-Spin Interaction: The second broadening process arises from the interactions between the dipoles regarded as situated in a rigid lattice. This broadening shows no dependence on temperature (above the Curie point) and can only be reduced by separating the magnetic carriers.

Two main types of interaction between the ions have been recognized; the dipole-dipole and the exchange interactions.

The dipole-dipole interaction is due to the magnetic moments of the ions, which can be regarded as rather like bar magnets. A picture of the broadening process can be obtained as follows.

Each bar magnet is regarded as precessing about the external magnetic field. Its magnetic field can be resolved into a component which is steady and directed along the field, and a rotating component at right angles to the field. The steady component sets up a steady field at any other magnet, which then behaves as if it is in a field which is slightly different from the external field. The rotating component sets up a rotating field, and if this rotating field has the same frequency as the frequency of precession of some other magnet

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there will be a couple acting on this second magnet tending to change its direction. The first process gives a broadening which is rather like that which arises from using an inhomogeneous magnetic field, and the second process gives resonance broadening because it tends to reduce the lifetime of an ion in a given state.

Free Spins: Van Vleck (1948) gives the following formula for the mean square width of a line for free spins using dipole-dipole interactions only (assuming cosine coupling):

$$\hbar^2 \overline{\Delta \nu^2} = \frac{3}{4} S(S+1) g^4 \beta^4 \sum_K \left(\frac{1 - 3 \cos^2 \theta}{r^3} \right)_{jk}^2 + \frac{1}{3} S'(S'+1) g'^4 \beta^4 \sum_{K'} \left(\frac{1 - 3 \cos^2 \theta}{r^3} \right)_{jk'}^2 \quad 3.35$$

where the resonance is from ions of type J, where dissimilar ions are of type K^1 , S^1 , g^1 , and where θ denotes the angle between the line joining two ions and the direction of the external field. It will be noticed that similar ions are $1\frac{1}{2}$ times as effective as dissimilar ions in broadening the line.

Kittel and Abraham (1953) have calculated the line shapes to be expected from various concentrations assuming randomly filled lattice sites. They conclude that if less than 0.01 of the lattice sites are filled with paramagnetic ions the line width will vary linearly with the concentration,

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that the fourth moment of the width will be large, and hence the tail of the line will be wide and the half width narrowed as it is in exchange narrowing. If more than 0.1 of the lattice sites are filled the width will vary roughly as the square root of the concentration, and the line shape will be Gaussian.

The above considerations refer only to isotropic g values. Stevens and Pryce (1950) have developed a more general theory of line widths and Elliott (1952) has applied it to the case of anisotropic g 's for dipole-dipole broadening in the ethyl sulphates as follows.

Let us consider only the dipole-dipole interaction of the ions.

The mean square width of the resonance line corresponding to the transition between the states $|1\rangle$ and

$|2\rangle$ of the i^{th} ion surrounded by j neighbours is

$$(\overline{\Delta h^2})^2 = \frac{1}{2} \sum_j [| \langle 1; i, j | W_{ij} | 1; i, j \rangle - \langle 2; i, j | W_{ij} | 2; i, j \rangle - \langle 2; i, j | W_{ij} | 1; i, 2j \rangle |^2 + | \langle 1; i, 2j | W_{ij} | 1; i, 2j \rangle - \langle 2; i, 2j | W_{ij} | 2; i, 2j \rangle + \langle 2; i, j | W_{ij} | 1; i, 2j \rangle |^2] \quad 3.26$$

where $\sum_j$ is taken over all atoms except the i^{th} .

Now the dipole-dipole interaction between two ions i, j , whose relative positions are given by $\underline{R}_{ij}$, is

$$W_{ij} = \frac{1}{R_{ij}^3} \left[\underline{\mu}_i \cdot \underline{\mu}_j - 3 \frac{(\underline{R}_{ij} \cdot \underline{\mu}_i)(\underline{R}_{ij} \cdot \underline{\mu}_j)}{R_{ij}^2} \right] \quad 3.27$$

III.34

where μ_i is the magnetic moment, $\beta (\underline{L}_i + 2\underline{S}_i)$. But we have shown that this can be written $g \cdot \underline{S}$ when the lowest level is a Kramers' doublet. If the ions i, j , have the same principal axes x, y, z , and the principal g values are $g_{\parallel(i)} : g_{\perp(i)} : g_{\parallel(j)} : g_{\perp(j)}$ and referred to those axes $\underline{R}_{ij}$ is $\underline{R}_{ij}(\ell_{ij}, m_{ij}, n_{ij})$ where ℓ_{ij}, m_{ij} , and n_{ij} are direction cosines. As we shall have occasion to calculate the line widths due to dipole-dipole interactions of the rare earth double nitrates a table of the direction cosines of the 26 nearest neighbours will be given at the end of this section.

Then W_{ij} becomes:

$$W_{ij} = \frac{\beta^2}{R_{ij}^3} \left\{ \frac{1}{3} [g_{\parallel(i)} g_{\parallel(j)} - g_{\perp(i)} g_{\perp(j)}] (1 - 3n_{ij}^2) S_i \cdot S_j \right. \\ + \frac{1}{6} [2g_{\parallel(i)} g_{\parallel(j)} + g_{\perp(i)} g_{\perp(j)}] (1 - 3n_{ij}^2) (2S_{iz} S_{jz} - S_{ix} S_{jx} - S_{iy} S_{jy}) \\ - \frac{3}{2} (\ell_{ij}^2 - m_{ij}^2) g_{\perp(i)} g_{\perp(j)} (S_{ix} S_{jx} - S_{iy} S_{jy}) \\ - 3\ell_{ij} m_{ij} g_{\perp(i)} g_{\perp(j)} (S_{ix} S_{jy} + S_{iy} S_{jx}) \\ - 3n_{ij} \ell_{ij} g_{\parallel(i)} g_{\perp(j)} S_{iz} S_{jz} - 3n_{ij} \ell_{ij} g_{\perp(i)} g_{\parallel(j)} S_{ix} S_{jz} \\ \left. - 3n_{ij} m_{ij} g_{\parallel(i)} g_{\perp(j)} S_{iz} S_{jy} - 3n_{ij} m_{ij} g_{\perp(i)} g_{\parallel(j)} S_{iy} S_{jz} \right\}$$

$$W_{ij} = A^{ij} S_i \cdot S_j + B^{ij} (2S_{iz} S_{jz} - S_{ix} S_{jx} - S_{iy} S_{jy}) \\ + C^{ij} (S_{iz} S_{jx} + S_{ix} S_{jz}) \\ + D^{ij} (S_{iz} S_{jy} + S_{iy} S_{jz}) \\ + E^{ij} (S_{ix} S_{jx} - S_{iy} S_{jy}) \\ + F^{ij} (S_{ix} S_{jy} + S_{iy} S_{jx})$$

III.35

If we are considering a transition where the external field is put in the XZ plane at θ to the Z-axis, the states $|1\rangle$ and $|2\rangle$ are given by

$$a|+\rangle + b|-\rangle ; \quad b|+\rangle - a|-\rangle$$

where

$$a = \frac{g_{\perp} \sin \theta}{[2g(g - g_{\parallel} \cos \theta)]^{\frac{1}{2}}} \quad b = \frac{g - g_{\parallel} \cos \theta}{[2g(g - g_{\parallel} \cos \theta)]^{\frac{1}{2}}}$$

Hence it may be shown where i, j are identical ions

$$\hbar^2 \Delta \bar{\nu}^2 = \frac{g}{16} \sum_j \left| B^{ij} (2g_{\parallel}^2 \cos^2 \theta - g_{\perp}^2 \sin^2 \theta) + 2C^{ij} g_{\parallel} g_{\perp} \sin \theta \cos \theta + E^{ij} g_{\perp}^2 \sin^2 \theta \right|^2 \frac{1}{g^4} \quad 3.39$$

where

$$B^{ij} = \frac{\beta^2}{R_{ij}^3} \frac{1}{6} [2g_{\parallel}^2 + g_{\perp}^2] (1 - 3n_{ij}^2) \quad 3.40$$

$$C^{ij} = -\frac{\beta^2}{R_{ij}^3} 3n_{ij} l_{ij} g_{\parallel} g_{\perp} \quad 3.41$$

$$E^{ij} = -\frac{\beta^2}{R_{ij}^3} \left(-\frac{3}{2}\right) (l_{ij}^2 - m_{ij}^2) g_{\perp}^2 \quad 3.42$$

Dirac (1947) showed that when all spin orbit couplings are neglected the coulomb interactions between electrons can be replaced by an interaction between their spins of the form $\frac{1}{4}J(1 + 4\mathbf{S}_1 \cdot \mathbf{S}_2)$ where J depends upon the overlap of the orbital wave functions and $\mathbf{S}_1$ and $\mathbf{S}_2$ are the spins of the ions ... not necessarily $\frac{1}{2}$. No detailed treatment of

III.36

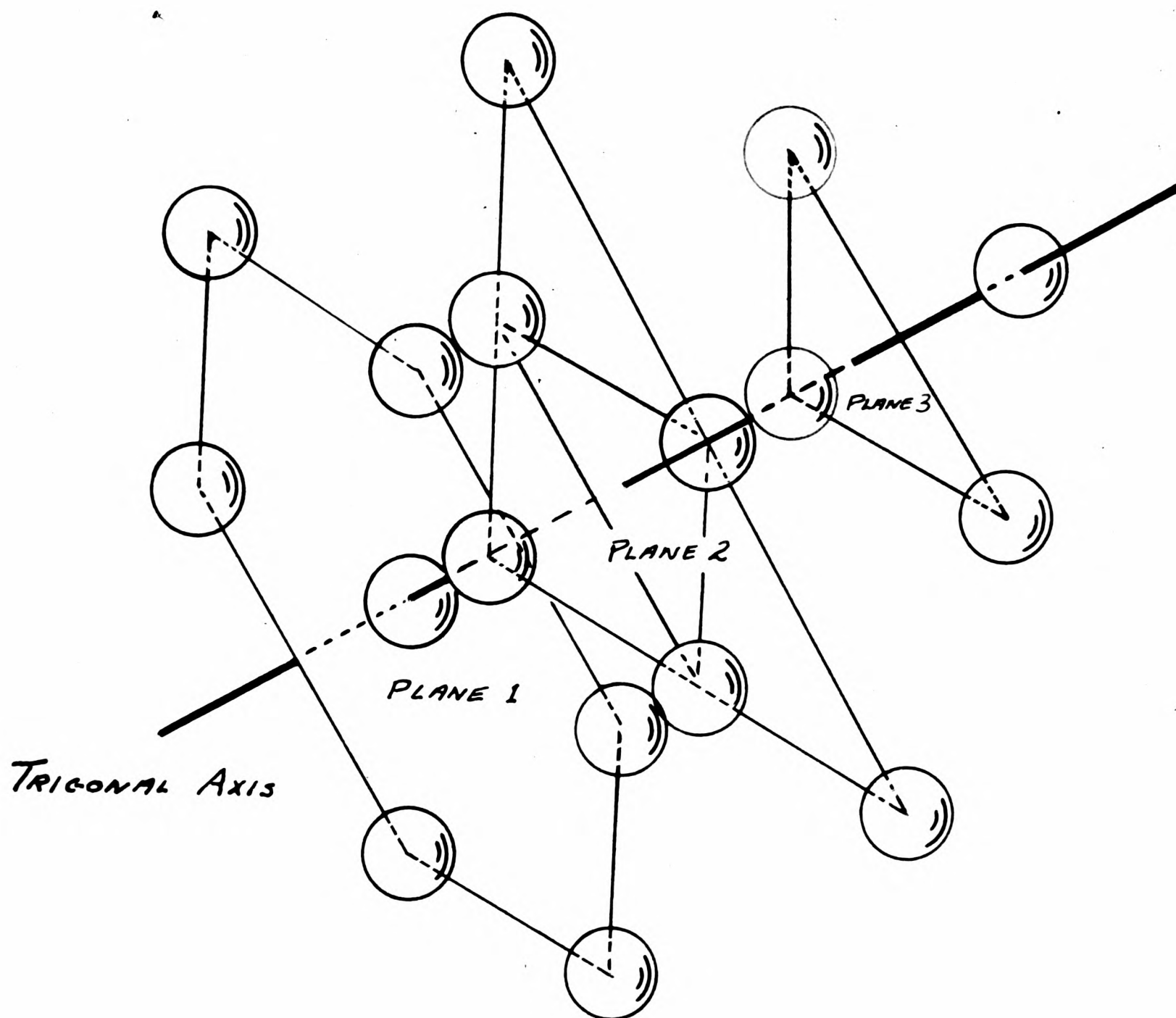
the effect on the exchange of spin orbit coupling seems to have been published. This interaction is said to be isotropic because it depends only on the relative orientations of the spins. However the value of J will probably depend upon the separation and position of the ions because the charge densities are not spherically symmetrical in a crystal field.

Any interaction which is not of the form $J(\underline{S}_1 \cdot \underline{S}_2)$ is called anisotropic exchange. Thus far in paramagnetic resonance work the exchange has usually been assumed purely isotropic.

Van Vleck's free spin treatment shows that there is no contribution to the second moment from isotropic exchange between similar ions, but there is a contribution to the fourth moment. If in the absence of exchange a line shape is gaussian, with exchange the shape will alter so that its area and second moment are unchanged, while its fourth moment is increased. This suggests that the centre part of the line will be peaked, i.e. exchange narrowing, and the excess distributed to the wings.

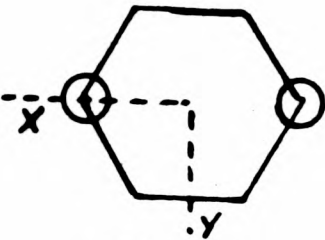
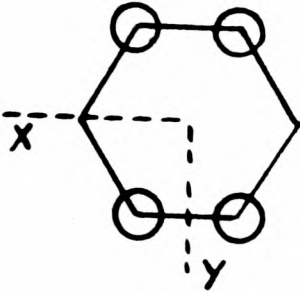
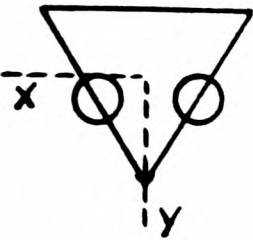
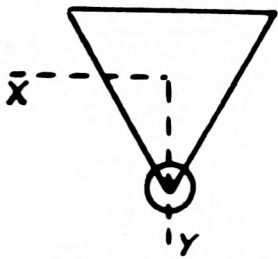
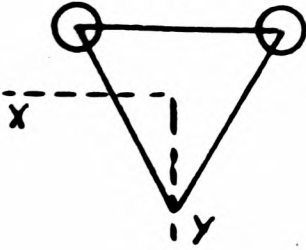
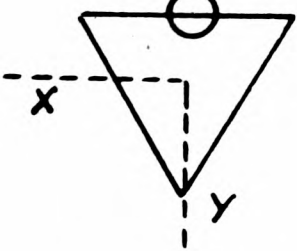
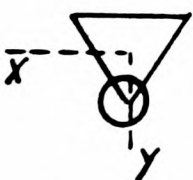
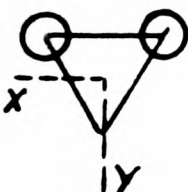
Bleaney and Stevens (1953) have pointed out that Van Vleck's free spin theory does not predict an exchange contribution to the second moment from similar ions, whereas Pryce and Stevens (1950) theory indicates that in general there

Figure 1



LATTICE OF MAGNETIC IONS
IN THE DOUBLE NITRATES

CHAPTER III Table 3

	PLANE	l_{ij}^2	m_{ij}^2	n_{ij}^2	$\frac{1}{R_{ij}^3} \text{ cm}^{-3}$
	1	1	0	0	0.772×10^{21}
	1	0.250	0.749	0	0.772×10^{21}
	2	0.412	0.135	0.451	1.62×10^{21}
	2	0	0.832	0.170	0.381×10^{21}
	2	0.625	0.206	0.170	0.381×10^{21}
	2	0	0.575	0.450	1.62×10^{21}
	3	0	0.241	0.811	0.455×10^{21}
	3	0.176	0.058	0.775	0.455×10^{21}

III.37

is a contribution. They found that the formulae for second moments reduce to summations of the form $(W_{ij})^2$ where W_{ij} denotes an interaction between ions i and j . This means we need consider only the two body problem. Stephens and Bleaney conclude that in nearly all cases exchange does contribute to the second moment except in Van Vleck's case where the ions are regarded as similar and precessing about parallel axes.

Thus it is possible that there may be either exchange narrowing or exchange broadening of the lines, and as yet there is no a priori way of predicting the effect in a given substance.

2. BULK SUSCEPTIBILITY:

Thus far the theory has been developed for the individual ion, and we must now deduce the microscopic behaviour in terms of this ionic theory.

a. First Approximation:

The partition function of an assembly can be written in terms of the spur of the spin Hamiltonian if it is expressed in a representation in which it is diagonal, as each element then represents an energy level. Hence

$$Z = \text{Spur} \left\{ e^{-\frac{(W_0 + HW_m)}{KT}} \right\} \quad 3.43$$

III.38

We shall assume at first that the Hamiltonian W may be accurately enough expressed in terms of a magnetic field dependent and field independent part, and further, that the field dependent part is of the first degree in H .

We shall neglect the H^2 term which gives rise to a diamagnetic effect in the usual magnetic Hamiltonian ...

$$W = \sum_{i=1}^N \left\{ -\frac{\hbar^2}{8\pi^2 m_i} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) - \frac{H e_i \hbar}{4\pi m_i c} \left(x_i \frac{\partial}{\partial y_i} - y_i \frac{\partial}{\partial x_i} \right) + \frac{H^2 e_i^2}{8 m_i c^2} (x_i^2 + y_i^2) \right\} \quad 3.44$$

where the magnetic field H is directed along the z -axis, or the term $-\beta^2 H \cdot \mathbf{L} \cdot H$ in the spin Hamiltonian (equation 3.24).

Now the free energy $F = kT \ln Z$

$$= -kT \ln \text{spur} \left\{ e^{-\frac{(W_0 + H W_m)}{kT}} \right\}$$

and the magnetic moment per ionic volume

$$M = \frac{\partial F}{\partial H} = \frac{-\text{spur} \left\{ W_m e^{-\frac{(W_0 + H W_m)}{kT}} \right\}}{\text{spur} e^{-\frac{(W_0 + H W_m)}{kT}}} \quad 3.45$$

where k is Boltzman's constant, T is the absolute temperature.

This can be expanded in a series form to give

$$M = \frac{-\text{spur} \left[W_m \left\{ 1 - \frac{(W_0 + H W_m)}{kT} + \frac{(W_0 + H W_m)^2}{2 k^2 T^2} + \dots \right\} \right]}{\left[1 - \frac{(W_0 + H W_m)}{kT} + \dots \right]} \quad 3.46$$

III.39

Define the susceptibility per ionic volume as

$$\chi = \lim_{H \rightarrow 0} \frac{M}{H}$$

We can now take only terms linear in H in 3.46 and if we put $H=0$ in 3.46 we get

$$M=0 = \frac{-\text{Spur} \left[W_m \left(1 - \frac{W_0}{KT} + \frac{W_0}{2K^2T^2} + \dots \right) \right]}{\text{Spur} \left[1 - \frac{W_0}{KT} + \dots \right]} \quad 3.47$$

and assuming the numerator is zero

$$\chi = \frac{-\text{Spur} W_m \left(-\frac{W_m}{KT} + \frac{W_m W_0 + W_0 W_m}{2! K^2 T^2} + \frac{(W_m W_0^2 + W_0 W_m W_0 + W_0^2 W_m)}{3 K^3 T^3} + \dots \right)}{\text{Spur} \left[1 - \frac{W_0}{KT} + \frac{W_0^2}{2K^2T^2} + \dots \right]}$$

Now by the principle of spectroscopic stability $\text{Spur } W_m^2 = \frac{1}{3} \text{spur } W_m^{02}$ where W_m^0 is the magnetic moment of the m^{th} state in the absence of a magnetic field.

Thus, following Van Vleck (1932) we may conclude:

$$\begin{aligned} \chi &= \frac{\frac{1}{3} \text{Spur} \frac{W_m^{02}}{KT} - \frac{2}{3} \text{Spur} f\left(\frac{1}{T^3}\right)}{\text{Spur} \left[1 + \frac{W_0}{KT} + \dots \right]} \\ &= \frac{N \bar{\mu}^2}{3 KT} \end{aligned} \quad 3.48$$

where $\bar{\mu}^2$ is the statistical mean square of the magnetic moment.

III.40

We have neglected second order terms in H which would have arisen from a second order perturbation calculation of the diagonal representation of the Hamiltonian. We shall now indicate the results of performing the same calculation including the second order perturbation effect.

b. Second Approximation:

Now let

$$W_{n_j m} = W_{n_j m}^0 + W_{n_j m}^{(1)} H + W_{n_j m}^{(2)} H^2 + \dots \quad 3.49$$

$$= (W_0 + W_m H \text{ of 3.43})$$

where $n_j m$ are the quantum numbers which distinguish a particular state. The time average of the magnetic moment of an ionic or molecular state in the direction of H is

$$\langle n_j m | P_H | n_j m \rangle = \frac{\partial W_{n_j m}}{\partial H} = -W_{n_j m}^{(1)} - 2H W_{n_j m}^{(2)} + \dots$$

The total magnetization

$$M = \frac{N \sum_{n_j m} \langle n_j m | P_H | n_j m \rangle e^{-\frac{W_{n_j m}}{kT}}}{\sum_{n_j m} e^{-\frac{W_{n_j m}}{kT}}}$$

(we are regarding $\langle n_j m |$ states as distinct, although they may indeed be degenerate)

$$\text{and } \chi = \left(\frac{\partial M}{\partial H} \right) \doteq \frac{N \sum_{n_j m} \left[W_{n_j m}^{(1)} / kT - 2 W_{n_j m}^{(2)} \right] e^{-\frac{W_{n_j m}^0}{kT}}}{\sum_{n_j m} e^{-\frac{W_{n_j m}^0}{kT}}}$$

where the numerator is developed to include only the first power of H , and the denominator to be independent of H .

III.41

We have also assumed that part of

$$\sum \langle njm | P_H | njm \rangle e^{-\frac{W_{njm}^0}{KT}} \quad \text{which is equal to}$$

$$\sum -W_{njm}^{(1)} e^{-\frac{W_{njm}^0}{KT}} \quad \text{equals zero, i.e. there is no residual magnetic moment.}$$

Now when W_{njm} is an energy level,

$$W_{njm}^{(1)} = \langle njm | P_H^0 | njm \rangle$$

and

$$W_{njm}^{(2)} = \sum_{n'j'm'} \frac{\langle njm | P_H^0 | n'j'm' \rangle \langle n'j'm' | P_H^0 | njm \rangle}{\hbar \Delta \nu_{njm, n'j'm'}}$$

from second order perturbation theory where $\hbar \Delta \nu_{njm, n'j'm'}$ is the energy separation $[W_{njm} - W_{n'j'm'}]$. We have still neglected the diamagnetic contribution to the term in H^2 .

Thus

$$X = \frac{N}{\sum_{njm} e^{-\frac{W_{njm}^0}{KT}}} \sum_{njm} \left[\frac{\langle njm | P_H^0 | njm \rangle^2}{KT} - 2 \sum_{n'j'm'} \frac{\langle njm | P_H^0 | n'j'm' \rangle \langle n'j'm' | P_H^0 | njm \rangle}{\hbar \Delta \nu_{njm, n'j'm'}} \right] e^{-\frac{W_{njm}^0}{KT}}$$

$$= B \sum_{jm} \left\{ \left[\frac{\langle njm | P_H^0 | njm \rangle^2}{KT} - 2 \sum_{n'j'm'} \frac{|\langle njm | P_H^0 | n'j'm' \rangle|^2}{\hbar \Delta \nu_{njm, n'j'm'}} \right] e^{-\frac{W_{njm}^0}{KT}} \right\}$$

where $B = \frac{N}{\sum_{njm} e^{-\frac{W_{njm}^0}{KT}}}$

where we assume that only levels of a given n are populated,

while j and m are quantum numbers whose effect on the energy

is $\leq KT$. ($\sum_{n'j'm'}$ means $n = n'$, $j = j'$, $m = m'$ excluded from summation.)

III.42

But:

$$\sum \langle n_{jm} | P_z^0 | n_{jm} \rangle^2 = \frac{1}{3} \sum \langle n_{jm} | P^0 | n_{jm} \rangle^2.$$

where $\langle n_{jm} | P^0 | n_{jm} \rangle$ is the unperturbed moment of a state $| n_{jm} \rangle$ in the absence of a field.

$$\begin{aligned} \therefore X &= \frac{1}{3} B \sum_{jm} \left\{ \left[\frac{\langle n_{jm} | P^0 | n_{jm} \rangle^2}{kT} \right. \right. \\ &\quad \left. \left. - \frac{2}{3} \sum_{n'j'm'} \frac{|\langle n_{jm} | P^0 | n'j'm' \rangle|^2}{\hbar \Delta v} \right] e^{-\frac{W_{n_{jm}}}{kT}} \right\} \\ X &= \frac{N \bar{\mu}^2}{3kT} + N \bar{\alpha} \end{aligned} \quad 3.53$$

where $\bar{\mu}^2$ is the statistical mean square of the magnetic moment, and $\bar{\alpha}$ is a temperature independent term which we may now choose to include a correction for the diamagnetism of the ions.

In the case of the clathrates (Chapter II) and in crystals where the paramagnetic ions are very dilute, this term must include the diamagnetism of the majority of non-magnetic atoms, and is thus not dependent on N , i.e.

$$X \doteq \frac{N_{\text{magnetic}} \bar{\mu}^2}{3kT} + N_{\text{non-magnetic}} \bar{\alpha}' \quad 3.54$$

CHAPTER IV

CERIUM MAGNESIUM DOUBLE NITRATE

I. BACKGROUND:

This salt, $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$, is one of the isomorphous series of rare earth double nitrates which have the formula $\text{A}_2\text{B}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ where A is the trivalent rare earth ion and B is a divalent metal, e.g. Mg or Zn. They are very soluble in water, from which they crystallize readily in thick plates of trigonal symmetry. Although the external morphology has been described by Groth (1908) the detailed crystal structure is not known. Powell (unpublished) has determined the structure of the lattice formed by the cerium ions in cerium magnesium double nitrate. These lie on rhombohedral lattice with a unit cell of side 8.51Å and interaxial angle $79\frac{1}{2}^\circ$ (figure 1.IV).

Krishnan and Mookerji (1938) measured the susceptibility and magnetic anisotropy at room temperature of several salts in double nitrate series. Becquerel et alia (1931) measured the Faraday effect at helium range temperatures with a magnetic field along the trigonal axis. They found the effect too small to allow an accurate estimate of the magnetic susceptibility to be made; they concluded that the effective magnetic moment of the cerium ion in the direction of measurement was not greater than 0.2 Bohr magnetons, i.e. $g < 0.27$

IV.2

A. Mookherji (1949) measured the principal susceptibilities of this salt from 300°K to 80°K and interpreted his results in terms of a cubic field.

Cooke and Wolf (Cooke, Duffus and Wolf, 1953) measured the specific heat between 1° and 4.2°K by the paramagnetic relaxation method of Casimir, Bijl and DuPre (1941) obtaining $C_I = 7.5 \times 10^{-6} \text{ K/T}^2$, and showed that it can be accounted for almost entirely by dipole-dipole interaction. The relaxation time varied at T^{-9} or T^{-10} in this range, and at 2.14°K it was $4 \times 10^{-4} \text{ sec}$. Daniels and Robinson (1953) showed that the susceptibility obeys Curie's law within 2% between 1°K and 0.006°K.

The experiments we shall now describe were performed in conjunction with those just mentioned in order to determine the suitability of the salt for nuclear alignment experiments and for adiabatic demagnetization.

At low temperatures this salt is a magnetic plate, having a large susceptibility in a plane, and a very small susceptibility perpendicular to this plane. This is the reverse of the ethyl sulphate, which has a plane of small susceptibility and a large susceptibility along the normal to it. The geometry of the double nitrate allows it to be cooled simply by rotating a magnetic field from perpendicular

IV.3

to the trigonal axis to parallel to it. The specific heat is extremely low because the cerium has no hyperfine structure and is in an open lattice. Hence very low temperatures, viz. $T^* = 3$ millidegrees, have been obtained. The heating-up rate is correspondingly large, however, for a small influx of energy.

The salt has been used successfully for nuclear alignment by both the Bleaney method and the Gorter method. In the latter, however, the calculated degree of alignment has not been achieved. For this reason we measured the line width in order to find the size of the interactions between the cerium and cobalt ions.

In order to measure the specific heat of helium II below 1°K Kurti and MacIntosh are attempting to cool it by adiabatically demagnetizing a large quantity (75 grams) of cerium double nitrate.

II. RESULTS:

1. g-VALUES:

Paramagnetic resonance measurements were made on a small single crystal at a wavelength of 3.33 cm. This wavelength was measured by the standard type of cavity wave meter with a micrometer screw head. It was checked by making measurements with two different wave meters, and by calculating

IV.4

λ from the value of the magnetic field, measured by proton resonance, at which the resonance line of di-phenyl-tri-nitro-phenyl-hydrazyl ("g-marker") appears using the relation

$$\begin{aligned} h\nu &= g\beta H \\ \therefore \lambda &= \frac{hc}{2.001\beta H} \end{aligned} \quad 4.1$$

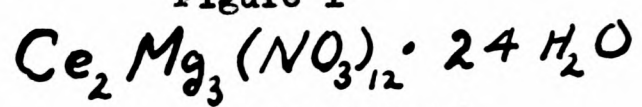
Resonance was observable only at temperatures below about 10°K. This shows that at higher temperatures the spin lattice relaxation time was so short as to broaden the line beyond the possibility of detection, and indicates the presence of a low-lying excited level.

Measurements at 4.2°K gave a single resonance line, indicating that as in the case of gadolinium magnesium double nitrate (Trenam, 1953) all the rare earth ions occupy equivalent positions in the unit cell. (There are two un-equivalent Mg^{++} ions per unit cell.

The first measurements were made with the crystal mounted with its trigonal axis horizontal in a magnetic field whose direction could be rotated about a vertical axis. The magnetic field at which resonance occurred was strongly dependent on the angle ϕ between the direction of the field and the crystal axis, and was given by the relations

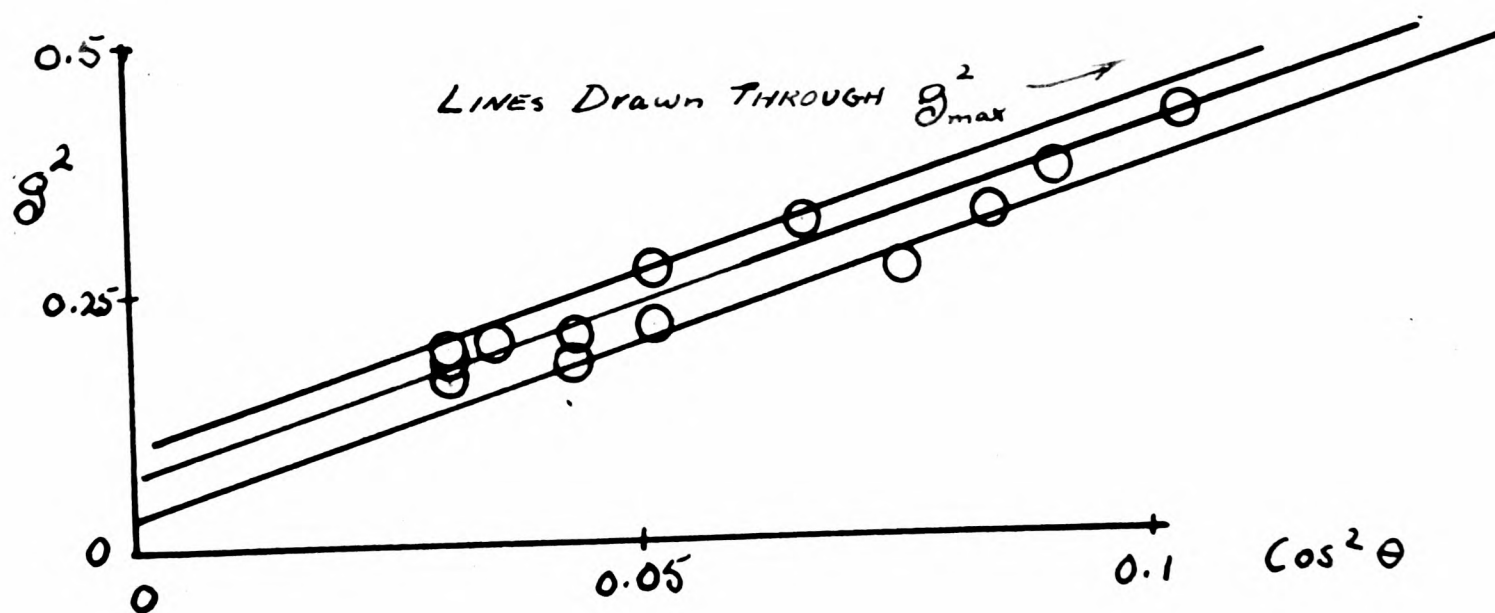
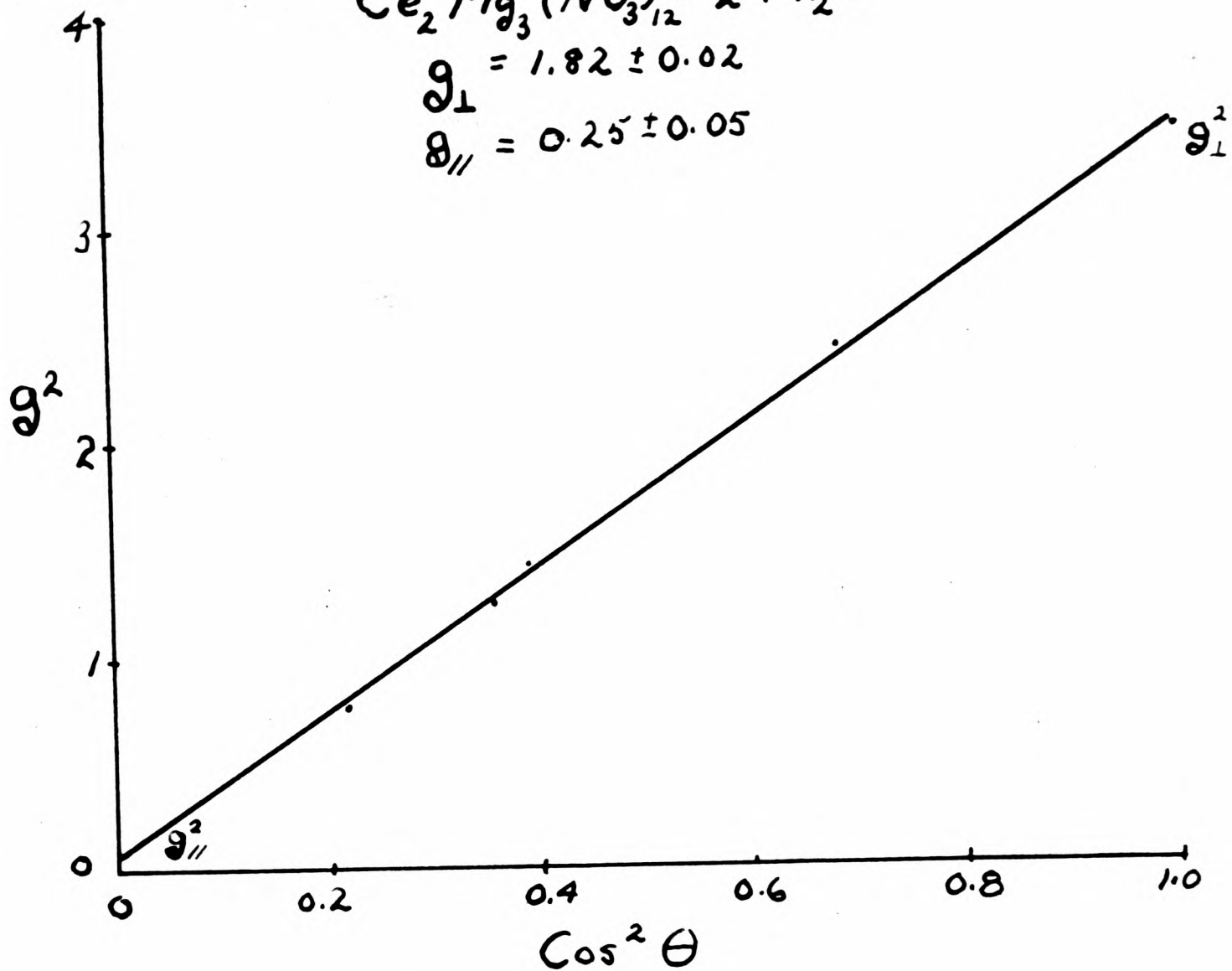
$$\begin{aligned} h\nu &= g\beta H \\ g^2 &= g_{\parallel}^2 \cos^2 \phi + g_{\perp}^2 \sin^2 \phi \end{aligned} \quad 4.2$$

Figure 1



$$g_{\perp} = 1.82 \pm 0.02$$

$$g_{\parallel} = 0.25 \pm 0.05$$



1.(a)

IV.5

The experimental points showing this relationship are given in figure 1.

If the trigonal axis does not lie parallel to the field it will be impossible to make $g = g_{//}$. Since $g_{\perp} > g_{//}$ in this salt it means the observed $g_{\min} \geq g_{//}$. In order to make the trigonal axis lie as near parallel to the magnetic field as possible the crystal was mounted with its (001) plane cemented to a piece of perspex which had been accurately milled flat.

In order to obtain points as near as possible to $g_{//}$ we used the Royal Society magnet (a field of up to 15 Kilogauss) and measured the field during the experiment by means of the Turner sub-standard meter mentioned in Chapter II. The meter readings were later compared with ballistic galvanometer throws from a search coil. Knowing the current at which g -marker appears, and λ , we can calibrate the search coil readings absolutely. The largest source of error was the accuracy with which the rather broad (60 gauss) resonance line could be centered on the C.R.O.

The results of this experiment are shown in figures 1 and 1(a), which are extrapolated to give

$$g_{//} = 0.25 \pm 0.05; \quad g_{\perp} = 1.84 \pm 0.02.$$

IV.6

2. LINE WIDTH

The line width was measured by photographing the C.R.O. trace and measuring the width of the trace in gauss by proton resonance. Knowing the width of the trace, the half width at half height of the absorption line was easily found to be 60 gauss. As the absorption was very strong we measured the width in the $g_{\perp}$ direction with the r.f. and d.c. fields very loosely coupled, i.e. nearly parallel. There was apparently no appreciable dispersion, for the line width was the same as when the r.f. and d.c. fields were perpendicular. The specimen used for this experiment was the size of a pinhead.

III. THEORY:

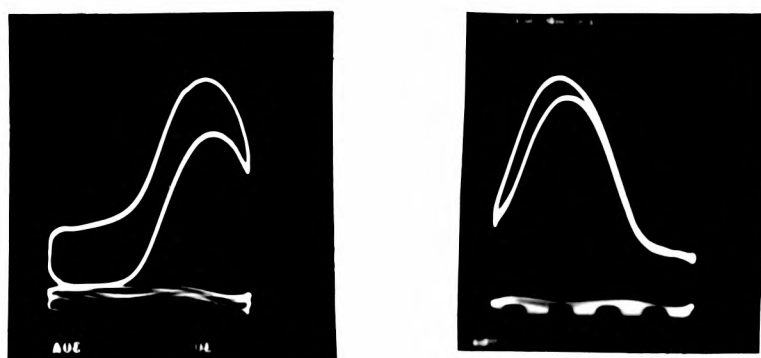
1. THE FREE ION:

As was mentioned in Chapter III, it was shown by room temperature experiments that Hund's rule is obeyed. We shall assume that the lowest configuration of a free Ce^{+++} ion is adequately described by a system of electrons moving in closed shells and a single 4f electron moving in a central field. The natural isotopes of cerium (i.e. Ce^{140} 89%, Ce^{142} 11%) have no magnetic moments, and hence no hyperfine structure is observed.

The 4f electron has one Russell-Saunders term, 2F , which is split by the spin orbit coupling into two levels,

Chapter IV

Photograph 1.



Concentrated cerium magnesium double
nitrate. The width of the C.R.O trace
is 220 gauss.

$J = \frac{7}{2}$ and $J = \frac{5}{2}$. The separation of these is known to be 2250cm^{-1} with $J = \frac{5}{2}$ lower (Lang, 1936). The susceptibility of cerium salts at room temperatures agrees well with that expected for the $J = \frac{7}{2}$ level of the free ion, so it seems that any splitting of the energy levels arising from the crystal fields are smaller than kT and also smaller than the doublet spacing (2250cm^{-1}).

2. THE ION IN THE CRYSTAL:

Assuming that the crystal field perturbs a 4f electron and that its effect is smaller than that of the spin orbit coupling the problem becomes that of a single 4f electron moving in accordance with a Hamiltonian:

$$\mathcal{H} = \int \underline{L} \cdot \underline{S} + V \quad 4.3$$

By Van Vleck's (1932) formula for the position of the components of a multiplet,

$$E = \frac{1}{2} \mathcal{F} [J(J+1) - L(L+1) - S(S+1)] \quad 4.4$$

$$\begin{aligned} \therefore \Delta = 2250 &= \frac{1}{2} \mathcal{F} \left[\frac{5}{2} \times \frac{7}{2} - 3 \times 4 - \frac{1}{2} \times \frac{3}{2} \right] \\ &\quad - \left[\frac{7}{2} \times \frac{9}{2} - 3 \times 4 - \frac{1}{2} \times \frac{3}{2} \right] \end{aligned} \quad 4.5$$

$$\therefore \mathcal{F} = 643 \text{ cm}^{-1}$$

Assuming that the electron does not overlap the charge clouds of the surrounding ions, V can be expanded in spherical harmonics in ascending powers of V , using polar coordinates with the nucleus as origin. Then:

$$V = \sum_{nm} A_n^m r^n Y_n^m(\theta, \phi), \quad n \leq 6 \quad 4.6$$

IV.8

(See Chapter III, equation 9.)

For either C_{3h} or D_{3h} symmetry V can be readily reduced, according to Elliott and Stevens (1952) to:

$$V = A_0^0 + A_2^0(3z^2 - r^2) + A_4^0(35z^4 - 30r^2z^2 + 3r^4) \\ + A_6^0(231z^6 - 315r^2z^4 + 105r^4z^2 - 5r^6) \\ + A_6^6(x^6 - 15x^4y^2 + 15x^2y^4 - y^6) \quad 4.7$$

A_6^6 here is a combination of A_6^6 and A_6^{-6} chosen to give V this form.

a. First Order Theory:

If we regard V as a perturbation on $\mathcal{Y}(\underline{L}, \underline{S})$ then for the lowest group of states this is equivalent to V acting within the manifold of states spanned by the lower level $J = \frac{5}{2}$.

The terms in A_6^0 and A_6^6 have zero matrix elements,

$$\therefore V_1 = A_2^0(3z^2 - r^2) + A_4^0(35z^4 + 30r^2z^2 + 3r^4) \quad 4.8$$

is now the perturbation (we have dropped the constant A_0^0).

As V_1 involves only z and r , it commutes with J_z and the multiplet is split into three Kramers doublets, each spanned by $\pm J_z$.

When a magnetic field is applied the doublets are split by an amount proportional to H . The term in the

IV.9

Hamiltonian which gives the splitting is $\beta \underline{H} \cdot (\underline{L} + 2\underline{S})$
or $\beta \underline{H} \cdot (\underline{J} - \underline{S})$.

Elliott and Stevens (1952) give the following table:

<u>State</u>	<u>Energy</u>	$\epsilon_{\parallel}$	$\epsilon_{\perp}$
$\pm \frac{1}{2}$	$-7\lambda + 2\mu$	$\frac{6}{7}$	$\frac{18}{7}$
$\pm \frac{3}{2}$	$-\lambda - 3\mu$	$\frac{18}{7}$	0
$\pm \frac{5}{2}$	$5\lambda + \mu$	$\frac{30}{7}$	0

$\lambda = -\frac{4}{35} A_2^0 \bar{r}^2$
 $\mu = \frac{8}{105} A_4^0 \bar{r}^4$

Magnetic resonance would occur within the $J_2 = \pm \frac{1}{2}$ doublet as the selection rule $\Delta J_2 = \pm 1$ forbids transitions between the other two.

Because the $J = \frac{7}{2}$ level is only 2250cm^{-1} away we will not get g values as tabulated, however we can now identify a level whose g's are observed with the level whose theoretical g's are nearest. We shall call doublets by their states in the first order theory, although this is not an accurate description.

IV.10

b. Second Approximation:

Following Stevens and Elliott (1952) we shall solve the eigenvalue problem of $H = \mathcal{P}(\underline{L} \cdot \underline{S}) + V$ completely where V has the form 4.7.

The secular determinant breaks down into four quadratics and two cubics, which, by Kramers' theorem are identical in pairs.

The only non-zero matrix elements of V in

ℓ_z, s_z quantization are:

$$\langle 0 | V | 0 \rangle = a = -4X + 6Y - 10Z$$

$$\langle 1 | V | 1 \rangle = \langle -1 | V | -1 \rangle = b = -3X + Y + 15Z$$

$$\langle 2 | V | 2 \rangle = \langle -2 | V | -2 \rangle = c = -7Y - 6Z$$

$$\langle 3 | V | 3 \rangle = \langle -3 | V | -3 \rangle = -\frac{1}{2}a - b - c$$

$$\langle 3 | V | -3 \rangle = \langle -3 | V | 3 \rangle = d = \frac{-320}{429} A_6^0 r^6$$

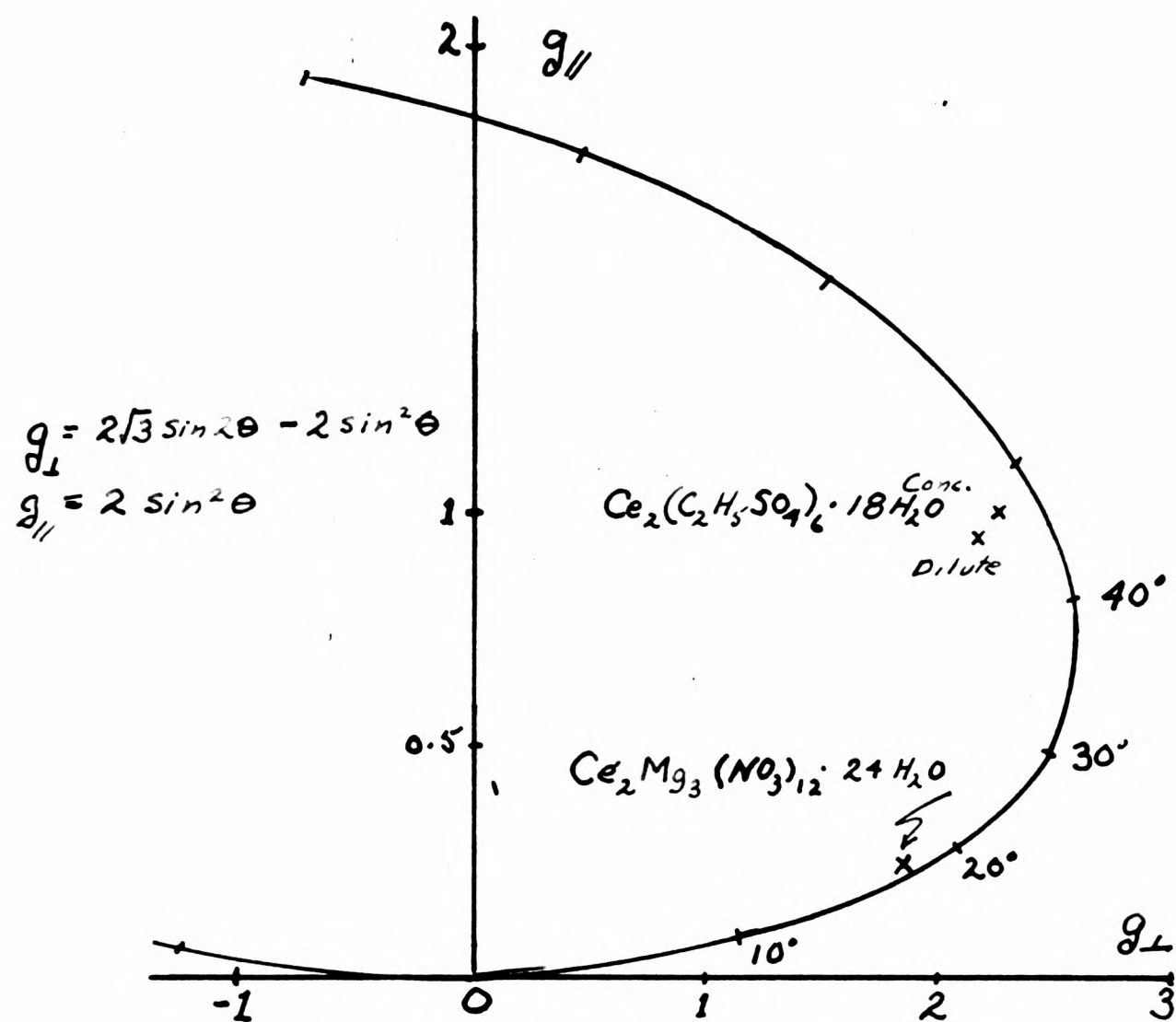
$$\text{where } X = \frac{-2}{15} A_2^0 r^2, \quad Y = \frac{8}{33} A_4^0 r^4 \quad \text{and} \quad Z = \frac{-80}{429} A_6^0 r^6$$

Values of s_z have been omitted since V is independent of spin, and hence diagonal in s_z .

Consider now the manifold of $J_z = \pm \frac{1}{2}$. We can form a state of $J_z = \frac{1}{2}$ by linear combination of $|\underline{L}_z, \underline{S}_z\rangle$ states $|0, +\rangle$ and $|1, -\rangle$, hence the sub matrix is of the form

$$\begin{vmatrix} \langle 1, - | \mathcal{P} \underline{L} \cdot \underline{S} + V | 1, - \rangle & \langle 1, - | \mathcal{P} \underline{L} \cdot \underline{S} + V | 0, + \rangle \\ \langle 0, + | \mathcal{P} \underline{L} \cdot \underline{S} + V | 1, - \rangle & \langle 0, + | \mathcal{P} \underline{L} \cdot \underline{S} + V | 0, + \rangle \end{vmatrix} \quad 4.9$$

Figure 2



IV.11

Stevens gives this as

$$\begin{vmatrix} b + \frac{3}{2}\gamma & \gamma\sqrt{3} \\ \gamma\sqrt{3} & a + 2\gamma \end{vmatrix} \quad 4.10$$

It is obtained from the matrix elements of Appendix 1 with $L=3$; and 2γ added to the diagonal terms.

An eigenstate is

$$\begin{aligned} |\frac{1}{2}\rangle &\equiv \cos\theta |1-\rangle - \sin\theta |0+\rangle \\ \therefore \cos\theta \{ (b + \frac{3}{2}\gamma) |1-\rangle + \gamma\sqrt{3} |0+\rangle \} \\ &\quad - \sin\theta \{ \gamma\sqrt{3} |1-\rangle + (a + 2\gamma) |0+\rangle \} \\ &= E \{ \cos\theta |1-\rangle - \sin\theta |0+\rangle \} \end{aligned} \quad 4.11$$

where E is the eigenvalue.

$$\begin{aligned} \therefore E &= b + \frac{3}{2}\gamma - \gamma\sqrt{3} \tan\theta \\ &= -\gamma\sqrt{3} \cot\theta + (a + 2\gamma) \\ \therefore b + \frac{3}{2}\gamma - a - 2\gamma &= \gamma\sqrt{3} (\tan\theta - \cot\theta) \\ &= \frac{\gamma\sqrt{3} (\sin^2\theta - \cos^2\theta)}{\cos\theta \sin\theta} \\ &= -\gamma\sqrt{3} \frac{\cos 2\theta}{\frac{1}{2} \sin 2\theta} \\ \therefore \tan 2\theta &= \frac{2\gamma\sqrt{3}}{a + 2\gamma - b - \frac{3}{2}\gamma} \\ &= \frac{4\sqrt{3}\gamma}{2a - 2b + \gamma} \end{aligned} \quad 4.12$$

The two values of θ which differ by π

correspond to the two eigenstates. We choose the value of θ which makes $|\frac{1}{2}\rangle$ the lower energy state. Its Kramers' conjugate is

$$|-\frac{1}{2}\rangle \equiv -\cos\theta |-1+\rangle + \sin\theta |0,-\rangle \quad 4.13$$

IV.12

We choose the unimodular phase factor so that

$$\langle +\frac{1}{2} | l_z + 2s_z | +\frac{1}{2} \rangle = \sin^2 \theta$$

$$\langle +\frac{1}{2} | l_x + 2s_x | -\frac{1}{2} \rangle = \sqrt{3} \sin 2\theta - \sin^2 \theta$$

Then

$$g_{\parallel} = 2 \sin^2 \theta \quad g_{\perp} = 2 | \sqrt{3} \sin 2\theta - \sin^2 \theta | \quad 4.14$$

(Figure 2 shows this function plotted for a range of θ .)

The energy of the lower level is

$$b + \frac{3}{2} \varphi - \sqrt{3} \rho \tan \theta$$

and of the higher

$$a + 2 \varphi + \sqrt{3} \rho \tan \theta$$

We now have a range of values of a single parameter within which to fit the observed g values, but the $g_{\parallel}$ and $g_{\perp}$ are not independent.

By similar arguments, in the case of $J_z = \pm \frac{3}{2}$ there are two eigenstates of $J_z = \frac{3}{2}$ consisting of linear combinations of $|2, -\rangle$ and $|1, +\rangle$ which give rise to $g_{\parallel} = 2(1 + \sin^2 \theta)$ and $g_{\perp} = 0$.

Condon and Shortley (1951) show by the use of Wigner coefficients that if U_N^M is any function which has the same angular variation as $Y_N^M(\theta, \phi)$, the integral

$$\int \psi_m^* U_N^M \psi_n d\tau \equiv \langle m | U | n \rangle \text{ vanishes unless } m = n + M$$

In the crystal field with C_{3h} symmetry

$M = 0$ or ± 6 , and with $L = |m|$ there are no pairs of states

IV.13

with $n - m = \pm 6$, so ψ_{J_z} has matrix elements only with itself for $J_z \leq \frac{3}{2}$. But for $J_z = \frac{5}{2}$ the crystal field perturbation will have elements admixing the two levels $J_z = \frac{5}{2}$ and $J_z = \frac{7}{2}$.

Although states with $J_z = \pm \frac{7}{2}$ are admixed we shall still label them $J_z = \pm \frac{5}{2}$.

If an eigenstate is $|\frac{5}{2}\rangle = p|2+\rangle + q|3-\rangle + r|-3-\rangle$ with $p^2 + q^2 + r^2 = 1$, then it may be shown that

$$g_{\parallel} = 2/3 p^2 + 2g^2 - 4r^2 \quad 4.15$$

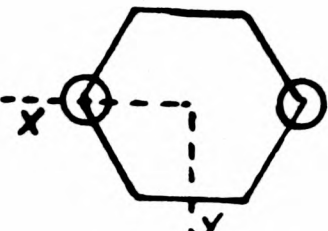
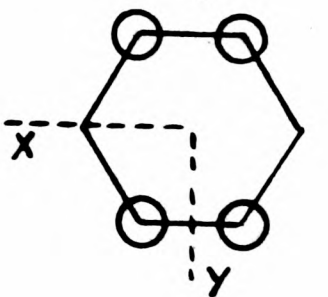
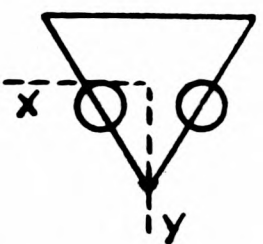
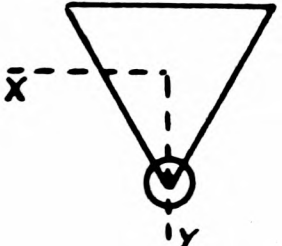
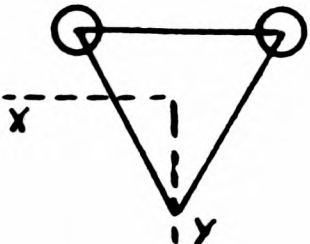
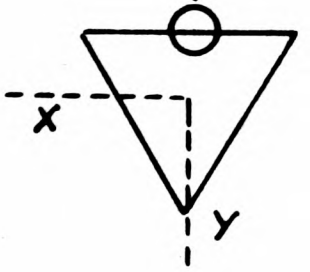
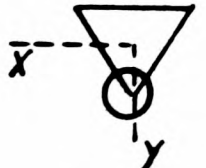
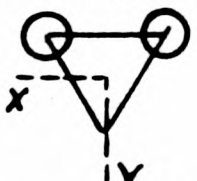
and

$$g_{\perp} = 2|r(2g + \sqrt{6}p)| \quad 4.16$$

In the case of $J_z = \frac{3}{2}$ since $g_{\perp}$ still equals zero we will not expect resonance, for the intensity $I \sim \frac{g_{\parallel}^2 g_{\perp}^2}{g^2}$. The more accurate calculation for $J_z = \frac{5}{2}$ shows we might observe resonance, and this was the case in the ethylsulphate.

Unfortunately we did not observe resonance from this $\frac{5}{2}$ level, and we are unable to interpret our g values in terms of the A_j^1 's from the single resonance. However our g values fall quite near the values predicted by the $J_z = \pm \frac{1}{2}$ states (figure 2), with $\Theta = 17\frac{1}{2}^\circ$.

CHAPTER IV Table 1

	PLANE	No of similar ions	Total Contribution (H^2)		
			Ce ⁺⁺⁺	Nd ⁺⁺⁺	Sm ⁺⁺⁺
	1	2	572	1240	24.8 18.5
	1	4	124	288	37.6
	2	4	203	485	20.0
	2	2	59	146	0.1
	2	4	45	109	1.9
	2	2	565*	1080*	10.2
	3	2	22	55	13.2
	3	4	8	1	22.8
Total			1538	3404	
$\Delta H_{\frac{1}{2}} = 2.35 (H^2)^{\frac{1}{2}}$			92.5 gauss	137 gauss	

IV.14

c. Line Width:

Table 1 shows the dipole dipole interactions between the various nearest neighbours shown in figure 1 of Chapter III. They are calculated from Elliott's formula 3.39 with $\Theta = 90^\circ$. The larger interactions have been starred and it will be seen that only a few neighbours are important. The values are very sensitive to the lattice dimensions which are $10.9 \text{ \AA}$ for the hexagonal separation and $17.2 \text{ \AA}$ for the separation of nearest neighbours along the trigonal axis. These values are given by Powell (unpublished) for the cerium double nitrate. We have assumed that they are the same for Nd^{+++} and Sm^{+++} double nitrates.

In order to compare the calculated width $(\hbar^2 \Delta \nu^2)$ with the observed resonance line it is necessary to express it in terms of the width of the line at half intensity in gauss. According to Van Vleck (1948) the usual assumption is that the frequencies have a Gaussian distribution. Then the full half width, i.e. twice the deviation from the central value at which the intensity has dropped to half its maximum, is

$$\begin{aligned} \hbar \Delta \nu_{\frac{1}{2}} &= 2 (\log \sqrt{2})^{\frac{1}{2}} \sqrt{2} (\Delta \nu^2)^{\frac{1}{2}} \\ &= 2.35 (\hbar^2 \Delta \nu^2)^{\frac{1}{2}} \end{aligned}$$

and we can express this in terms of magnetic field by the

IV.15

relationship

$$h \Delta \nu_{\frac{1}{2}} = g \beta \Delta H_{\frac{1}{2}}$$

It is the factor 2.35 to which we wish to draw attention, for it is not mentioned by either Elliott (1952) or Pryce and Stevens (1950). It restricts the use of their formulae in practice to Gaussian line shapes, the occurrence of which we have discussed in Chapter III.

The calculated values for the half width are given at the bottom of table 1 as

$$2.35 [\Delta H^2]^{\frac{1}{2}}$$

For cerium this is 92.5 gauss.

But the observed width is 120 gauss, and we did not observe any narrowing when it was cooled to below 4.2°K by pumping the helium. Despite Cooke and Wolf's observation that the specific heat was fully accounted for by dipole dipole interactions, we suspect that there may be some exchange. The failure of the Corter method to produce the expected degree of nuclear alignment lends support to this theory. When we tried to measure the hyperfine splitting of cobalt in cerium magnesium double nitrate we discovered that the hyperfine structure was broadened into a single wide line below about 8°K. Above 8°K we observed the same resolved spectrum reported by Trenas (1953)

The discrepancy in the nuclear alignment

IV.16

work below 1°K might be caused by a change of the double nitrate lattice parameters ... but we could detect no change between 20°K and 4°K. However, our accuracy was poor because of the broadening.

When on cooling the spin lattice relaxation time of the cerium becomes nearly as long as that of the cobalt, the relaxation time of the cobalt may become shorter through resonance. (See Chapter III, page 31) This would cause broadening. On the other hand it may be caused by exchange.

IV. BULK SUSCEPTIBILITY:

As noted in Chapter II our attempts to measure $\chi_{\parallel}$ were unsuccessful because of the symmetry of the magnetic field. The observations of the susceptibility perpendicular to the trigonal axis below 4°K illustrate that Curie's law is obeyed in this region, and that the balance case can be used as an effective vapour pressure thermometer.

By extrapolating the line to $\frac{1}{T} = 0$ we obtain a "temperature independent" term, and can describe the susceptibility per gram of double nitrate as

$$\chi = \frac{4.1 \times 10^{-4}}{T} + 3.2 \times 10^{-5} \text{ emu}$$

IV.17

However the susceptibility at room temperature is very much less than 3.2×10^{-5} emu. The temperature independent term is only a convenient description of the low temperature results, and is not to be compared with the $N\bar{\alpha}$ of equation 3.53

Our knowledge of the temperature variation of the principal susceptibilities of cerium double nitrate is very unsatisfactory. Mookherji (1949) has measured the anisotropy and $\chi_{\perp}$ down to 80°K, and Becquerel et al. measured the optical rotation along the trigonal axis in the helium range.

We obtain the same anisotropy as Mookherji at 300°K, and at 4°K $\chi_{\perp}$ agrees with the value of $g_{\perp}$ obtained by paramagnetic resonance. We do not obtain Mookherji's values below 300°K. Although we are satisfied that our apparatus is at fault at 4°K, the qualitative disagreement with Mookherji's results is disturbing.

We do not feel that we should present our results until further work has been done on anisotropic crystals with this balance.

CHAPTER V

PRASEODYMIUM

I. BACKGROUND:

Praseodymium ($\text{Pr}^{+++} 4f^2 \ ^3H_4$) does not have an odd number of electrons, as do the other rare earths we have investigated. It is therefore not a Kramers' degenerate ion, and the theory which we have described for the Kramers' doublet will not apply. According to Elliott and Stevens (1953), fields of C_{3h} symmetry will split each J level into a singlet and J doublets. The theorem of Jahn and Teller (1937) then states that the complex consisting of the ion and its surroundings will distort in such a way as to resolve the degeneracy of the doublets.

Using C_{3h} symmetry it may be shown that $g_1 = 0$ for each doublet, so that to a first approximation no resonance should be found. However Bleaney and Scovil (1952) observed a resonance in the ethyl sulphate, and we have observed a resonance in the double nitrate.

II. RESULTS:

A crystal of $\text{Pr}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ diluted to about one part in 50 of $\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ was placed on the bottom of the cavity in order to increase the sensitivity. At 4.2°K six asymmetrical lines were observed at equal intervals

V.2

of field when the rf and d.c. fields, and the trigonal axis were all parallel. The lines were very anisotropic, moving quickly to higher fields as the d.c. field was rotated away from the trigonal axis. We attribute them to a single electronic transition with a hyperfine structure caused by the nuclear spin.

1. g VALUES:

Calculating $g_{\parallel}$ from the centre of symmetry of the hyperfine structure we get $g_{\parallel} = 1.55 \pm 0.02$. We cannot estimate $g_{\perp}$ except to say that it is very small.

We were unable to detect the lines at high fields because of microphonics. Such observations as we did make could not be interpreted in terms of a g^2 vs $\cos^2 \theta$ law.

2. HYPERFINE PARAMETERS:

Table 1 shows the values of the magnetic field at which the hyperfine lines appear. By considering the first order part of equation 3.29, $H = H_0 - Am$, we expect them to occur at equal intervals to a first approximation. The column headed Δ shows the intervals in field between consecutive lines, and shows them to be nearly constant. We have performed this experiment more than once, and have found no consistent trend in the values of Δ , and we therefore will not use the

V.3

second order part of equation 3.29.

From Table 1, estimating the accuracy by comparing the results of two experiments, we conclude that $A = 0.078 \pm 0.001 \text{ cm}^{-1}$. B is undefined.

III. THEORY:

The ground state of the free Pr^{+++} ion is $4f^2$, 3H_4 from Table 1 of Chapter III. There is only one stable isotope, Pr^{141} , which has a nuclear spin of $\frac{5}{2}$ (Bleaney and Scovill, 1952).

1. g VALUES:

Elliott and Stevens (1955) find that the lowest doublet, under C_{3h} symmetry, has states which can be written

$$\cos \theta |J_z = +2\rangle + \sin \theta |J_z = +4\rangle$$

$$\text{Now } g = 2 \langle J || L || J \rangle \langle J... | J | J... \rangle$$

Therefore, from Table 2 of Chapter III $\langle J || L || J \rangle = \frac{4}{5}$

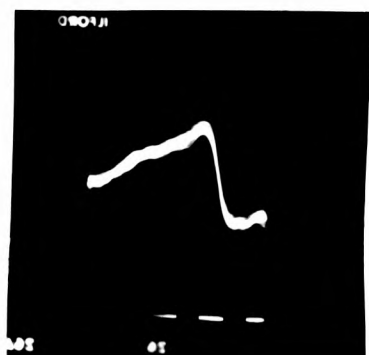
$$\text{and } g = 2 \times \frac{4}{5} \times (2\cos^2 \theta - 4 \sin^2 \theta)$$

$$= 2(1 - 3 \sin^2 \theta)$$

$$\theta \sim 22^\circ$$

Chapter V

Photograph 1.



Praseodymium magnesium double nitrate
diluted in lanthanum. The typical
asymmetry is noteworthy.

CHAPTER V Table 1

$\text{Pr}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$
 (diluted in Lanthanum)

Field in Kilogauss
 // Trigonal Axis

 Δ

1.30

1.08

2.38

3.12

g marker

1.08

3.46

4.50

1.04

5.55

1.05

6.60

1.05

$$A = 0.078 \pm 0.001 \text{ cm}^{-1}$$

B unknown

$$g_{//} = 1.55 \pm 0.02$$

 $g_{\perp}$ unknown but very small

$$\lambda = 3.42 \text{ cm}$$

V.4

2. HYPERFINE PARAMETERS:

We have used the first order part of equation 3.29 to describe the hyperfine spectrum. As Bleaney and Scovil (1952) point out, the spin Hamiltonian might be written

$$\mathcal{H} = g_{\parallel} \beta H_z S_z + A S_z I_z$$

with an effective spin of $\frac{1}{2}$. The absence of matrix elements in the magnetic field between the two states of the doublet is indicated by the absence of the usual terms $g \beta (H_x S_x + H_y S_y)$ and $B(S_x I_x + S_y I_y)$. In first order theory they have zero elements anyway, so we still get $H = H_0 - A m$ for our empirical equation.

Our theory is obviously only a very rough approximation, because the levels are separated by the Jahn Teller effect and not the usual crystal field of trigonal symmetry. However the theory of such distortions has not yet been worked out.

3. LINE WIDTH:

We have not calculated the line width because the shape is obviously not Gaussian (see photograph 1). The shape seems to be a characteristic of Pr^{+++} , however, for Bleaney and Scovil report a similar shape in the ethyl sulphate. The double nitrate line at 4.2°K is much narrower than the ethyl sulphate line at 20°K , which is several hundred gauss

V.5

broad. There is no report of the width at 4.2°K, so this large width may be due to a short spin lattice relaxation time. Bleaney and Scovill suggest that a term ΔS_z added to the spin Hamiltonian would qualitatively account for the observed asymmetry, but find that it would need to be of the order of 0.3 cm^{-1} , which seems very unlikely. Perhaps the narrower and more sharply defined line in the double nitrate will stimulate the development of the theory of these asymmetrical lines.

CHAPTER VI

NEODYMIUM DOUBLE NITRATE

I. BACKGROUND:

Bleaney and Scovil (1950) found a resonance absorption spectrum in the ethylsulphate at 20°K and obtained its g values very accurately by using proton resonance technique to measure the applied magnetic field. Earlier low temperature measurements of the Faraday effect had been made by Becquerel et al (1938) and of susceptibility by van den Handel (1942). Measurements of both magnetization and rotation, and susceptibility and Verdet constant were proportional to within a few percent showing that the states of the lowest doublet are adequately described by a single J manifold and that admixtures of other manifolds are small (Elliott, 1952).

In the ethyl sulphate Elliott is able to describe the susceptibility by

$$\chi = N \frac{(3.53)^2}{4kT} \beta^2 + 6 \times 10^{-6}$$

$$\chi_{\parallel} = N \frac{(2.07)^2}{4kT} \beta^2 + 9.3 \times 10^{-6}$$

up to oxygen temperatures where they deviate very slightly.

This indicates that only one doublet is populated up to these temperatures, and that the first excited doublet must be some 100cm^{-1} higher.

Trenam, however, was unable to detect resonance in the double nitrate down to 20°K.

VI.2

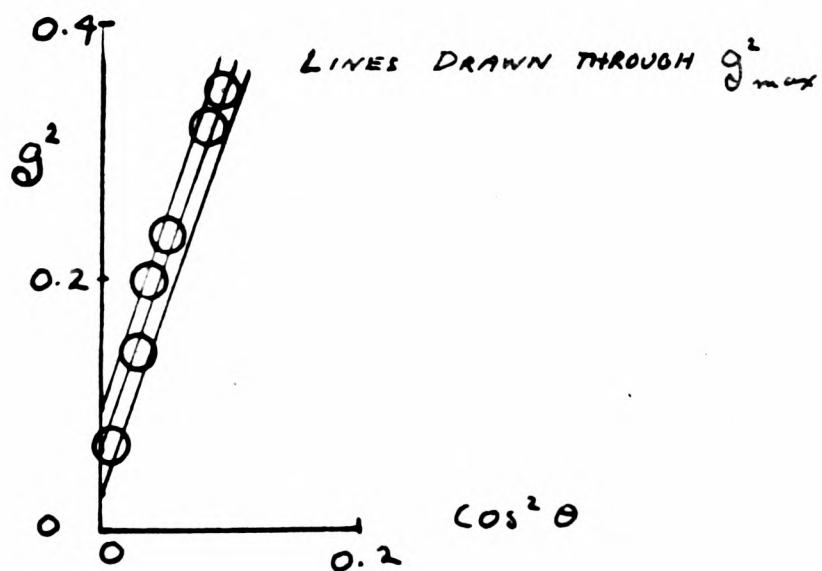
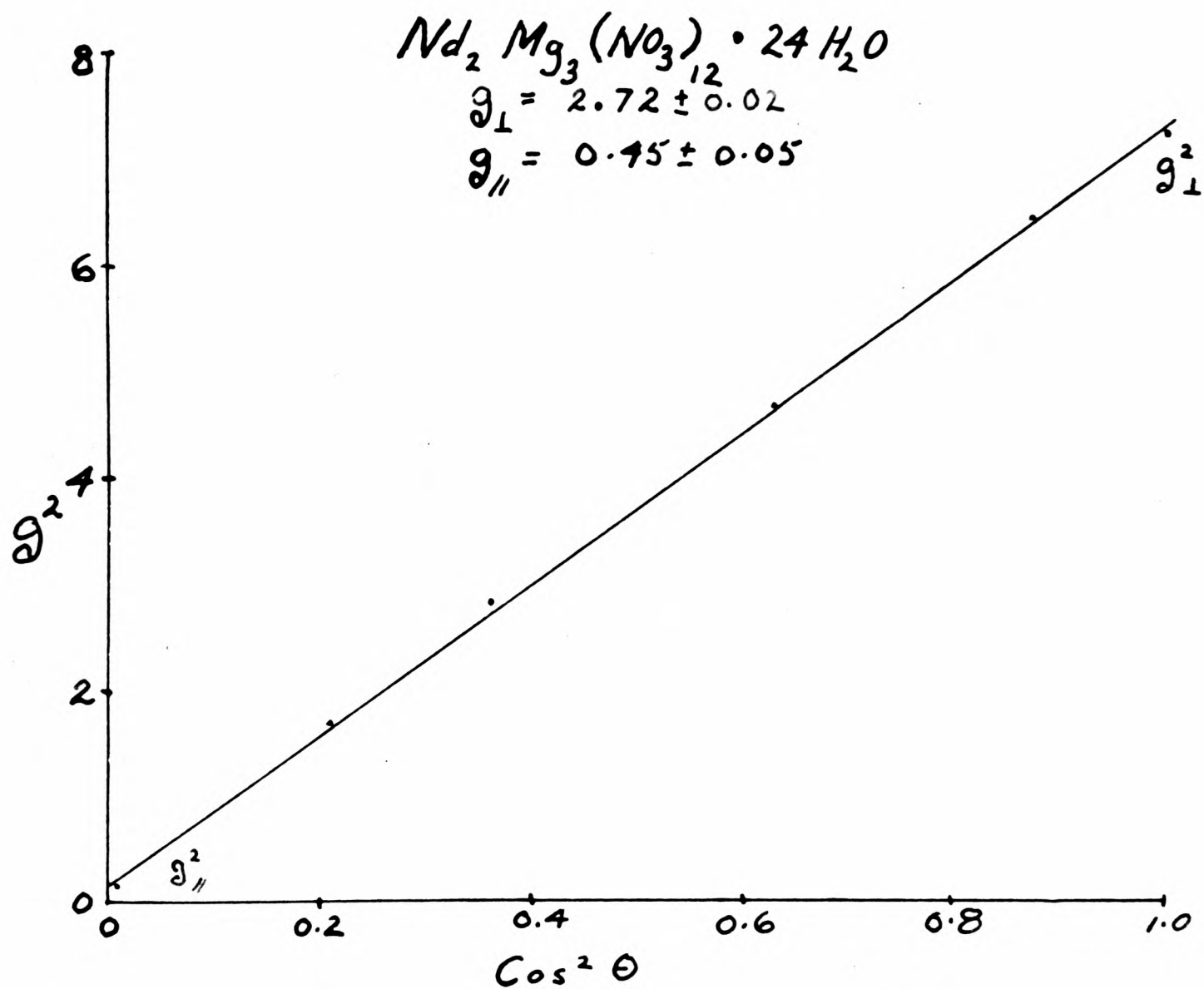
II. OBSERVATIONS:

At 4°K we observed a main line and sixteen hyperfine satellites (not all of which were resolved) in a direction perpendicular to the trigonal axis.

In order to measure the fields at which the hyperfine lines appeared we first of all used proton resonance at room temperature, inserting the resonance coil between the dewar and the magnet pole. This does not introduce an error greater than $\frac{1}{2}\%$ according to Dr. Bogle's work. However, microphonics from the vibration of the magnet make it difficult to see the rather weak proton signal. We therefore built the proton resonance coil described in Chapter II for use at 4°K, and used the signal from the protons in perspex.

The signal from the proton resonance detector was fed onto one beam of a Cossor double beam oscilloscope, while the paramagnetic absorption signal was fed onto the other. Both beams were triggered on the same time base, and therefore could not be phased independently. The proton resonance signal and paramagnetic absorption signal pass through different amplifiers before being fed on the C.R.O., and hence suffer different phase shifts. We performed our measurements by phasing the paramagnetic resonance signals to coincide, and using the intersection of the proton resonance

Figure 1



VI.3

traces as the reference point (photograph 2). Our accuracy in setting these two signals together was slightly better than 1%

1. HYPERFINE PARAMETERS:

Table 6.1 shows the observed proton resonance frequencies at which the hyperfine lines occurred together with values calculated from second order perturbation theory with $A = 0$, and with $A = 175$ Mc. using 3.30, i.e.

$$H = H_0 - Bm - \frac{1}{4} \frac{A^2 + B^2}{H_0} [I(I+1) - m^2]$$

There is no systematic variation in the difference between calculated and observed values, so we did not proceed to the third order perturbation which has been worked out by Elliott (1952).

B is given by the average separation of the hyperfine lines in the perpendicular direction and is thus well established. In principle it should be possible to calculate A from the positions of the hyperfine lines given $B, g_{\parallel}, g_{\perp}$, and neglecting the quadrupole effect. But A is very small, so it was impossible to do it this way. Elliott and Stevens (1953) however, show that if the states which describe doublets are eigenstates of the total angular momentum J, then $g_{\parallel} : g_{\perp} :: A : B$.

In a manifold where J is constant, any vector has matrix elements proportional to those of J. Hence

VI.4

$\underline{H} \cdot (\underline{L} + 2\underline{S})$ can be replaced by $\langle J \| \underline{L} \| J \rangle \underline{H} \cdot \underline{J}$, and $\underline{N} \cdot \underline{I}$ can be replaced by $\langle J \| \underline{N} \| J \rangle \underline{J} \cdot \underline{I}$ --- we do not need to know $\langle J \| \underline{L} \| J \rangle$ for this argument.

In Chapter III we have shown we can replace $\beta \underline{H} \cdot (\underline{L} + 2\underline{S})$ by $\beta \underline{H} \cdot \underline{g} \cdot \underline{S}$, and so $\langle J \| \underline{L} \| J \rangle \underline{J}$ can be replaced by $\underline{g} \cdot \underline{S}$. Similarly $\underline{N} \cdot \underline{I}$ becomes

$$\langle J \| \underline{N} \| J \rangle \underline{J} \cdot \underline{I} \cdot \underline{g} \cdot \underline{S} = \frac{\langle J \| \underline{N} \| J \rangle}{\langle J \| \underline{L} \| J \rangle} \underline{I} \cdot \underline{g} \cdot \underline{S}$$

$$\text{Hence } T = 2 \beta \beta_N \frac{\mu_N}{I} \left(\frac{1}{r^3} \right) \frac{\langle J \| \underline{N} \| J \rangle}{\langle J \| \underline{L} \| J \rangle} g$$

and the principal values of T are A, B and B, so

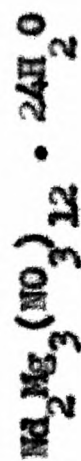
$$\frac{A}{B} = \frac{g_{\parallel}}{g_{\perp}} \quad 6.1$$

The relation is most likely to hold in the second half of the 4f shell, for the first excited level is well removed, and the admixture from it correspondingly small. In ions in the first half of the shell the departure $B_g = A_{g_{\perp}}$ from unity is roughly proportional to the separation to the first excited level. In the ethyl sulphate $\frac{B_{g_{\parallel}}}{A_{g_{\perp}}} = 0.892$

As we do not know $g_{\parallel}$ very accurately anyway, it seems the best procedure to assume $A_{g_{\perp}} = B_{g_{\parallel}}$ in order to calculate the μ 's, and $A = 173 \text{ Mc}$ is calculated this way for both isotopes.

$$\begin{aligned} B^{143} &= 1042 \pm 2 \text{ Mc.} \\ &= \cancel{0.0312} \text{ cm}^{-1} \\ &0.0312 \end{aligned}$$

$$\begin{aligned} B^{145} &= 647 \pm 2 \text{ Mc.} \\ &= \cancel{0.0194} \text{ cm}^{-1} \\ &0.0194 \end{aligned}$$



Nd¹⁴³

Nd¹⁴⁵

Observed	Calculated A = 0	A	Calculated A = 173	A	I _z	Observed	Calculated A = 0	A	Calculated A = 108	A
6110	6117	+7	6114	+4	7/2	7558	7559	+1	7558	0
6975	6993	+18	6987	+12	5/2	8132	8142	+10	8140	+8
7905	7925	+20	7916	+11	3/2	8727	8747	+20	8743	+16
8888	8912	+24	8901	+13	1/2	9369	9373	+4	9368	-1
	9954		9943		-1/2		10019		10014	
11049	11051	+2	11042	-7	-3/2	10676	10687	+11	10683	+7
12200	12203	+3	12197	-3	-5/2	11364	11376	+12	11374	+10
13383	13411	+28	13408	+25	-7/2	12075	11259	+12	12086	+11
B = 1042 ± 2			A = g _n /g _l × 10 ² B = 1.7 × 10 ²			B = 647 ± 2			A = g _n /g _l × 10 ² B = 1.1 × 10 ²	

An extra line was observed in the main line at 9742. By inspection this does not fall upon either of the calculated I_z = -1/2 lines.

Isotope ratios	± 7/2	1.610	g _n = 0.45 ± 0.05
	± 5/2	1.612	g _l = 2.72 ± 0.02
	± 3/2	1.613	

All fields quoted in Proton megacycles/second × 10³; 1 Mc = 0.0299 cm⁻¹.

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2. g VALUES:

The g values were measured in the same way as the cerium values, i.e. by extrapolating the straight line of $g^2 = g_{\perp}^2 \sin^2 \theta + g_{\parallel}^2 \cos^2 \theta$ to obtain $g_{\parallel} = 0.45 \pm 0.05$ and $g_{\perp} = 2.75 \pm 0.02$

The crystal was mounted with its trigonal axis in the plane of the applied magnetic field of the Royal Society magnet, and the field was measured by a Turner meter. Figure 1 shows the curve obtained in this way.

The line width was measured photographically as was that of cerium. As it was greater than the sweep we also estimated the points of half intensity, and measured these points by proton resonance, obtaining a width at half intensity of

$$\Delta H_{\frac{1}{2}} = 170 \pm 5 \text{ gauss.}$$

III. THEORY:

1. THE FREE ION:

The trivalent neodymium ion has three electrons in the 4f shell. Its ground state is found from the Hund rule (Chapter III, Table 1) to be $^4I_{9/2}$; the next level being 800cm^{-1} above. It has naturally abundant isotopes with atomic weights 142, 143, 144, 145, 146, 148, 150. The even isotopes account for 79.5% of the whole and are expected to have spin zero. The isotopes 143 and 145 with abundances of 12.2% and 8.3% respectively have spins 7/2 (Scovill, 1951).

VI.6

2. THE ION IN THE CRYSTAL:

A crystal field will produce a Stark splitting of the lowest level. If this field is of sufficiently low symmetry all of the degeneracy will be lifted except the Kramers' degeneracy.

To a first approximation the matrix elements coupling different J manifolds can be neglected. The states in the lower manifold can be specified as $|4f^3; J, J_z\rangle$ where $J = \frac{9}{2}$ and $J_z = \pm \frac{1}{2}; \pm \frac{3}{2}; \pm \frac{5}{2}; \pm \frac{7}{2}; \pm \frac{9}{2}$. The crystal field will, according to its symmetry, have matrix elements coupling states of different $|J_z|$ and J_z will not be a particularly good quantum number. A given state will therefore be composed of a linear combination of other states in the same J manifold; the admixture depending upon the properties of the crystal field.

a. g Values:

We wish to identify the ground state of the Nd^{+++} ion as belonging to a particular J_z by comparing the observed g values with those calculated from the various J_z states. This can be done by considering the crystal field to be a perturbation upon the levels resulting from the spin orbit coupling, rather than by considering $[\mathcal{L} \cdot \mathcal{S} + V_c]$ as a single perturbation as we did for Ce^{+++} . The procedure

VI.7

for finding the values of $\langle + | L + 2S | + \rangle$ and $\langle - | L + 2S | + \rangle$ where $\langle + |$ and $\langle - |$ represent Kramers' conjugate states formed by $a | J_z = \frac{1}{2} \rangle + b | J_z = \frac{3}{2} \rangle + \dots$ is straightforward but tedious. The operator equivalents for the crystal field have been tabulated by Stevens (1952) and the multiplying factors are also given. Elliott and Stevens (1953) have worked out the possible g values for the ethyl sulphate and find that under C_{3h} symmetry the only states which give a non zero $g_{\perp}$ are

$$| J_z = \pm \frac{1}{2} \rangle \quad 6.2$$

$$\text{and } \cos \theta | J_z = \pm \frac{3}{2} \rangle + \sin \theta | J_z = \mp \frac{5}{2} \rangle \quad 6.3$$

For the $J_z = \pm \frac{1}{2}$ states $g_{\parallel} = \frac{8}{11}$ and $g_{\perp} = \frac{32}{11}$, and these do not approximate the experimental results.

The second pair gives

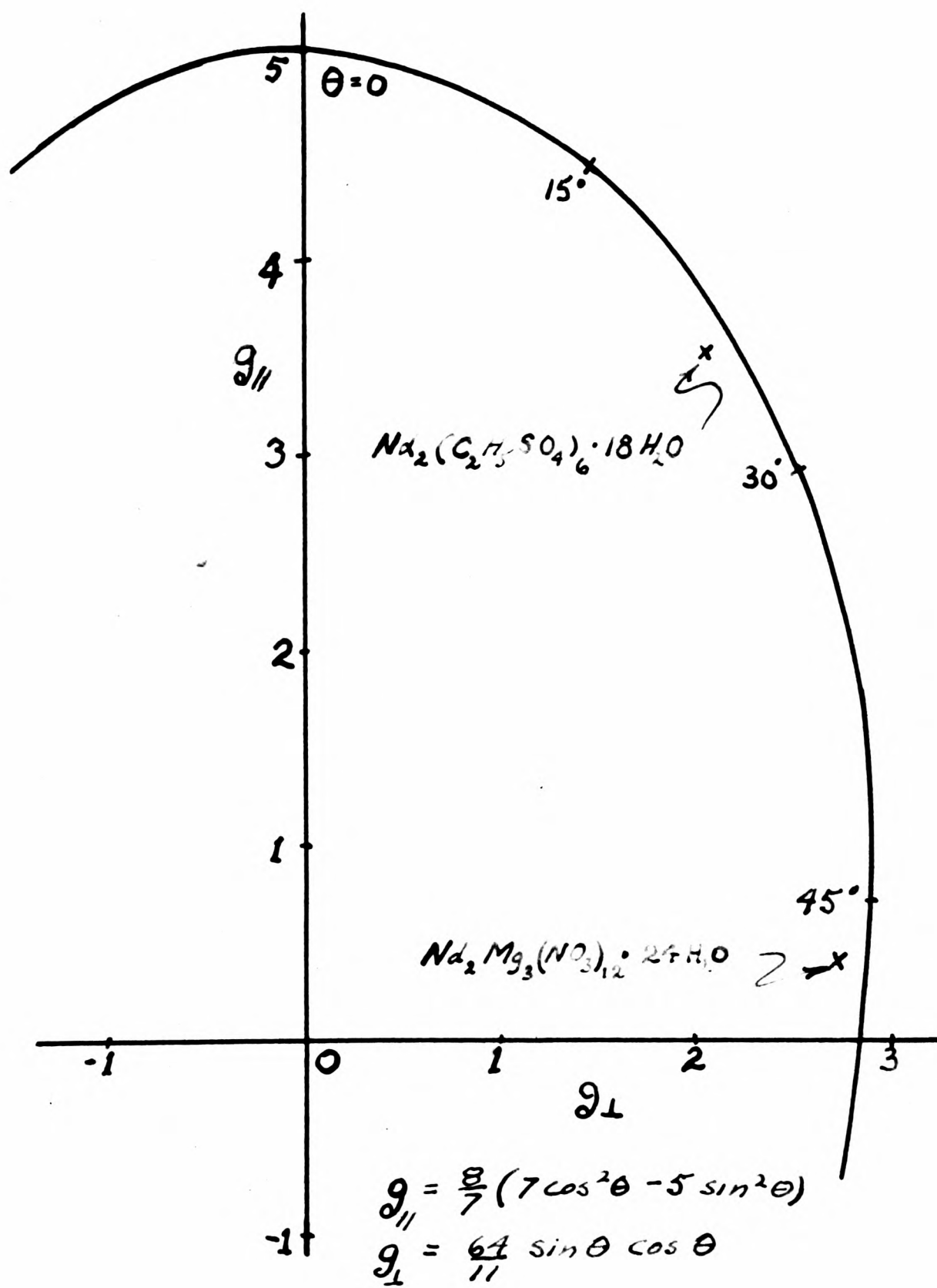
$$g_{\parallel} = \frac{8}{11} (7 \cos^2 \theta - 5 \sin^2 \theta) \quad 6.4$$

$$\text{and } g_{\perp} = \frac{64}{11} \sin \theta \cos \theta \quad 6.5$$

These are plotted in figure 2, and $\theta = 47^\circ$ fits the observed values as closely as the ethyl sulphates were approximated.

In the case of the ethyl sulphates Stevens and Elliott were then able to verify that the crystal field could give this admixture of states as the ground doublet.

Figure 2



VI.8

When the theory of the extrapolation of the ethyl sulphate parameters has been worked out this can no doubt also be done for the double nitrate. For the present all we can do is to examine the formula

$$\tan 2\theta = \frac{2 \langle \frac{7}{2} | V | -\frac{5}{2} \rangle}{\langle \frac{7}{2} | V | \frac{7}{2} \rangle - \langle \frac{5}{2} | V | \frac{5}{2} \rangle} \quad 6.6$$

which is analogous to 4.12, and is related to the crystal field parameters (4.7) $V_2^0 = A_2^0 r^2$, $V_4^0 = A_4^0 r^4$, and $V_6^0 = A_6^0 r^6$ by

$$\tan 2\theta = \frac{-0.383 V_6^0}{-0.115 V_2^0 + 0.122 V_4^0 + 4.020 V_6^0} \quad 6.7$$

It will be observed that this is strongly dependent upon

$\frac{V_6^0}{V_2^0}$. In the ethyl sulphate

$$V_6^0 \gg V_2^0, V_4^0, V_6^0$$

If this is still the case, we can approximate

$$\frac{V_6^0}{V_2^0} = \frac{-4.02}{0.383} \tan 94^\circ = 119 \quad 6.8$$

The final step in the treatment of our data might be to consider the effect of admixing the nearest excited J level which is 1800 cm^{-1} away (Chapter 3, table 1). In the case of the ethyl sulphates the ratio $\frac{B_{911}}{A_{911}} = 0.892$ indicating that there is some admixture. The resulting second order states would be of the form

$$n \left[\left| \frac{7}{2}, \pm \frac{7}{2} \right\rangle \cos \theta + \left| \frac{5}{2}, \mp \frac{5}{2} \right\rangle \sin \theta \pm x \left| \frac{11}{2}, \pm \frac{7}{2} \right\rangle \pm y \left| \frac{11}{2}, \mp \frac{5}{2} \right\rangle \right] \quad 6.9$$

VI.9

where $n^{-2} = 1 + x^2 + y^2$.

But x and y involve $V_2^0, V_4^0, V_6^0, V_6^6$,

and we do not yet know how to estimate these. Therefore we shall not carry the theoretical interpretation of the g values any further.

b. Hyperfine parameters:

Stevens and Elliott give the following expressions for $g_{\perp}$ and B in the ethyl sulphate

$$n^{-2} g_{\perp} = \frac{64}{11} \sin \theta \cos \theta - \frac{2\sqrt{14}}{11} (3\sqrt{2} x \sin \theta + \frac{\sqrt{6}}{2} y \cos \theta) - \frac{138}{143} \times 6\sqrt{3} xy \quad 6.10$$

$$n^{-2} B = \frac{2\beta_N \mu_N}{I} \left(\frac{1}{r^3} \right) \left[\frac{476}{363} \times 8 \sin \theta \cos \theta + \frac{193\sqrt{14}}{1089} (3\sqrt{2} x \sin \theta + \frac{1}{2} \sqrt{6} y \cos \theta) - \frac{14920}{14157} \times 6\sqrt{3} xy \right] \quad 6.11$$

where B is obtained by the application of 3.20 to the states 6.9. The parts of these equations not involving x and y are obtained from the first order theory states 6.3.

It will be observed that the ratio of

$$\frac{B}{g_{\perp}} = 2\beta_N \frac{\mu_N}{I} \left(\frac{1}{r^3} \right) \frac{476 \times 8 \times 11}{363 \times 64} + f(x, y)$$

and we shall expect this ratio to vary in some regular way for the rare earths in different salts to a first approximation it is independent of the ground state, and so

VI.10

should be a good check upon the theory. In the ethyl

$$\text{sulphate it is } \frac{B^{143}}{g_{\perp}} = \frac{0.0199}{2.073} = .00962 \text{ cm}^{-1}$$

$$\frac{B^{145}}{g_{\perp}} = \frac{0.0124}{2.073} = 0.00599 \text{ cm}^{-1}$$

For the double nitrates it is

$$\frac{B^{143}}{g_{\perp}} = \frac{0.0312}{2.72} = 0.0115 \text{ cm}^{-1}$$

$$\frac{B^{145}}{g_{\perp}} = \frac{0.0194}{2.72} = 0.0071 \text{ cm}^{-1}$$

The ratio of $\frac{B^{143}}{B^{145}}$ from 6.11 will be seen to be simply the ratio $\frac{\mu_{N^{143}}}{\mu_{N^{145}}}$. We can obtain three independent values of this ratio from the different lines associated with $I_z = \pm \frac{7}{2}$, $\pm \frac{5}{2}$, $\pm \frac{3}{2}$. (The $I_z = \pm \frac{1}{2}$ lines were obscured by the main line.) The ratios are:

$$\pm \frac{7}{2} \rightarrow 1.610 \pm .01$$

$$\pm \frac{5}{2} \rightarrow 1.612 \pm .01$$

$$\pm \frac{3}{2} \rightarrow 1.613 \pm .01$$

These agree with the values observed by Scovil in the ethyl sulphate, viz. 1.608 0.001.

Bleaney, Scovil and Trenam (1952) were able to estimate the nuclear quadrupole moment from forbidden transitions at zero field by using wavelengths of from 7 to 20 cm. This technique might be used on the double nitrate if the apparatus were modified. They used crystals grown in

VI.11

heavy water to reduce the proton width of the hyperfine lines. This would not increase our accuracy unless a sufficiently narrow nuclear resonance signal could be obtained at 4°K.

Photograph 1 shows quite well defined lines between the hyperfine lines. We thought that they might be forbidden transitions of $\Delta m = \pm 2$ such as are discussed by Bleaney (1951). In the case of erbium ethyl sulphate we were able to estimate the nuclear electric quadrupole moment with some accuracy (Bogle, Duffus and Scovil, 1952) by means of such transitions. However there seem to be three satellites between the outermost hyperfine lines of Nd^{143} . One of these may be due to coupling from the lower proton resonance trace to the upper trace within the C.R.O., but Bleaney's formula gives only one line between the $I_2 = \frac{7}{2}$ and $I_2 = \frac{5}{2}$ hyperfine lines, and that one line should be associated with the $\frac{5}{2}$ line. We cannot explain them as forbidden transitions then.

No satellites were observed on the low field side of the $\frac{7}{2}$ line, therefore they are not caused by dipole dipole interaction as discussed by Scovil (1951).

The lines were not due to a twinned crystal with one axis not perpendicular to the d.c. field because although the spectrum would collapse slightly it would have

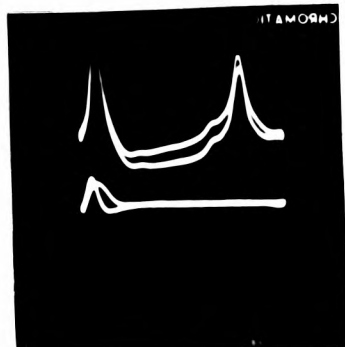
Chapter VI

Photographs 1, 2, and 3



1

2

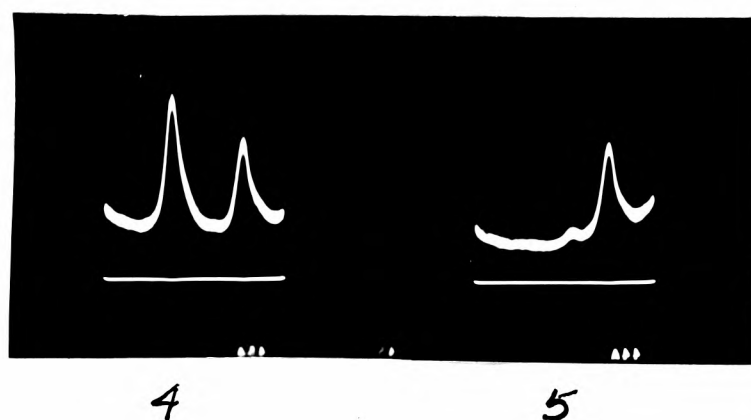


3

1. Hyperfine lines of Nd^{143} associated with $I_z = 7/2$ and $5/2$, showing three unidentified lines in between them.
2. Nd^{143} , $I_z = 5/2$ hyperfine line shown above the proton resonance signal used to measure the magnetic field.
3. A large Nd^{143} , $I_z = 5/2$ hyperfine line, a smaller Nd^{145} , $I_z = 7/2$ hyperfine line, and two unexplained lines in between.

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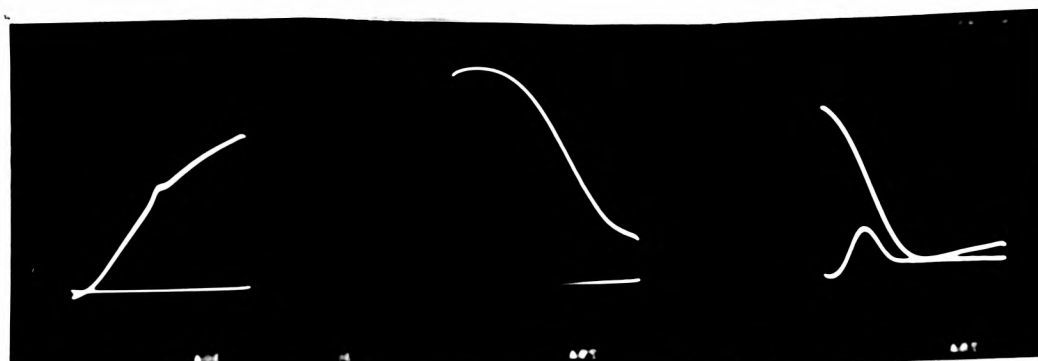
Photograph 4 and 5



4. A large Nd^{143} , I_z $3/2$ hyperfine line and a smaller Nd^{145} , I_z $5/2$ line.
5. A hyperfine line of Nd^{145} , I_z $7/2$, showing the same unidentified line on the low field side as #3, observed during a different experiment upon the same crystal.

Chapter VI

Photograph 6



Three exposures of the main line in concentrated neodymium magnesium double nitrate are shown. The smaller line on the main line in the left hand exposure is g-marker. The smaller line below the main line in the right hand exposure is the proton resonance signal set to coincide with the half intensity point on the main line in order to measure its width.

VI.12

moved to quite high fields. If there were two Nd^{+++} ions per unit cell, and if in some cells they were not equivalent ions because of local distortions ... or if there were simply a large number of lattice distortions ... we might observe such a weak spectrum. Such a hypothesis would explain the extra line observed in the main line. Unfortunately the satellites are so weak that we only observed them twice, and on several occasions we could not detect whether they were there or not. If the sensitivity of the apparatus could be increased this might be an interesting aspect of the spectra to investigate.

c. Line width:

Table 1 of Chapter IV shows the dipole contributions to the line width from the various neighbours of a Nd^{+++} ion calculated from 3.39. There was some difficulty in judging the half intensity point, but our measured width should be accurate to about ± 5 gauss. The line shown is that of concentrated neodymium magnesium double nitrate perpendicular to the trigonal axis. Because of experimental difficulties we did not cool this crystal below 4°K to see if the line became narrower due to a longer spin lattice relaxation time. We have not included the proton width due

VI.13

to the hydrogen in the water molecules, but some estimate of this can be made from the line width of the lines in a dilute salt. Trenam (1953) observed lines only 4 gauss wide in gadolinium magnesium double nitrate highly diluted with lanthanum.

CHAPTER VII

SAMARIUM MAGNESIUM DOUBLE NITRATE

I. BACKGROUND:

Samarium was the smallest ion which we managed to grow in the form of the concentrated magnesium double nitrate. The crystals were often opaque and asymmetrical, and easily dissolved in their own water of crystallization, when the room temperature rose.

As shown in table 1, Chapter III, the Sm^{+++} ion has a ground state $4f^5 \quad {}^6H_{5/2}$, and is notable for the proximity of the $J = \frac{7}{2}$ level only 1000 cm^{-1} above the ground level. This leads to the large difference between n_{eff}^2 calculated by the first and second order equations 3.7 and 3.8.

Naturally occurring samarium contains 29% of odd isotopes which we expect to produce hyperfine spectra. They occur as $15.1 \pm 0.15\% \text{ Sm}^{147}$ and $13.8 \pm 0.15\% \text{ Sm}^{149}$ (Inghram et al, 1948).

Bogle (1952) observed a resonance spectrum with $g_{\parallel} = 0.596 \pm 0.002$ and $g_{\perp} = 0.604 \pm 0.002$, and resolved the hyperfine structures of Sm^{147} and Sm^{149} . His values of $\frac{B_{g_{\parallel}}}{A_{g_{\perp}}} =$ are near 4, which suggests that there is a considerable admixture of $J = \frac{7}{2}$ to the ground level.

Trenam did not observe resonance in the double nitrate down to 20°K .

VII.2

II. RESULTS:

Experiments were performed on a crystal of $\text{Sm}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ using the Royal Society magnet in order to obtain the large fields necessary to reach the low g values.

A broad main line and sixteen fully resolved satellites were observed with the d.c. field parallel to the trigonal axis.

1. g VALUES:

Figure 1 shows the variation of g^2 with $\cos^2 \theta$.

The extrapolated values give $g_{\parallel} = 0.76 \pm 0.01$ and $g_{\perp} = 0.40 \pm 0.05$.

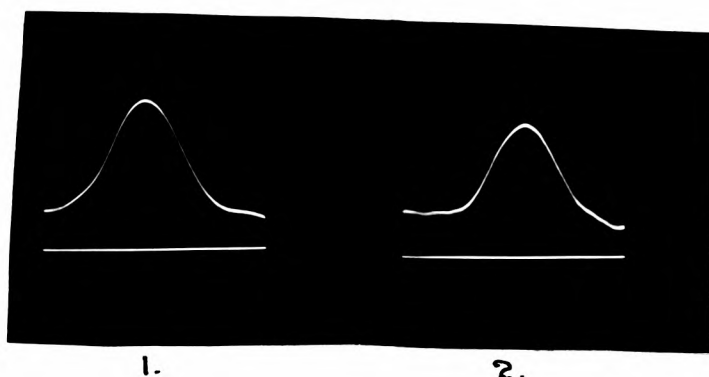
These are both inconveniently small to be measured experimentally, requiring fields greater than 10 Kilogauss at 3 cm wavelengths.

The smaller g value is beyond the maximum field obtainable. At such large fields the vibrations resulting from the interaction between the a.c. sweep field and the d.c. field produce a great many microphonics which obscure the line. Because of the difficulty in observing the line, and because of its width, we measured the magnetic field with the Turner meter rather than by proton resonance. Indeed it would be difficult to make a proton resonance coil which would cover the range from g marker to even the lowest field at which the main line occurs.

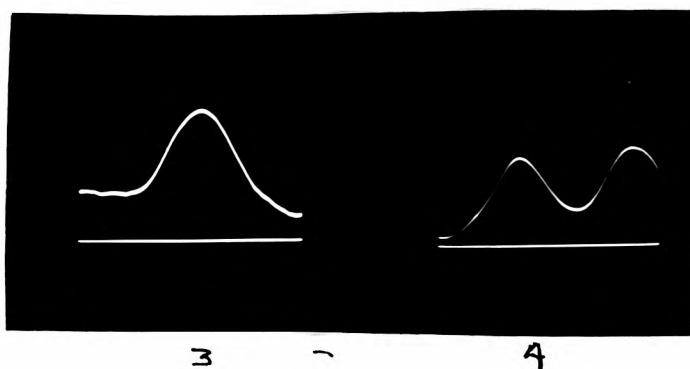
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Photographs 1, 2, 3, and 4

(The width of the C.R.O. trace is 220 Gauss)

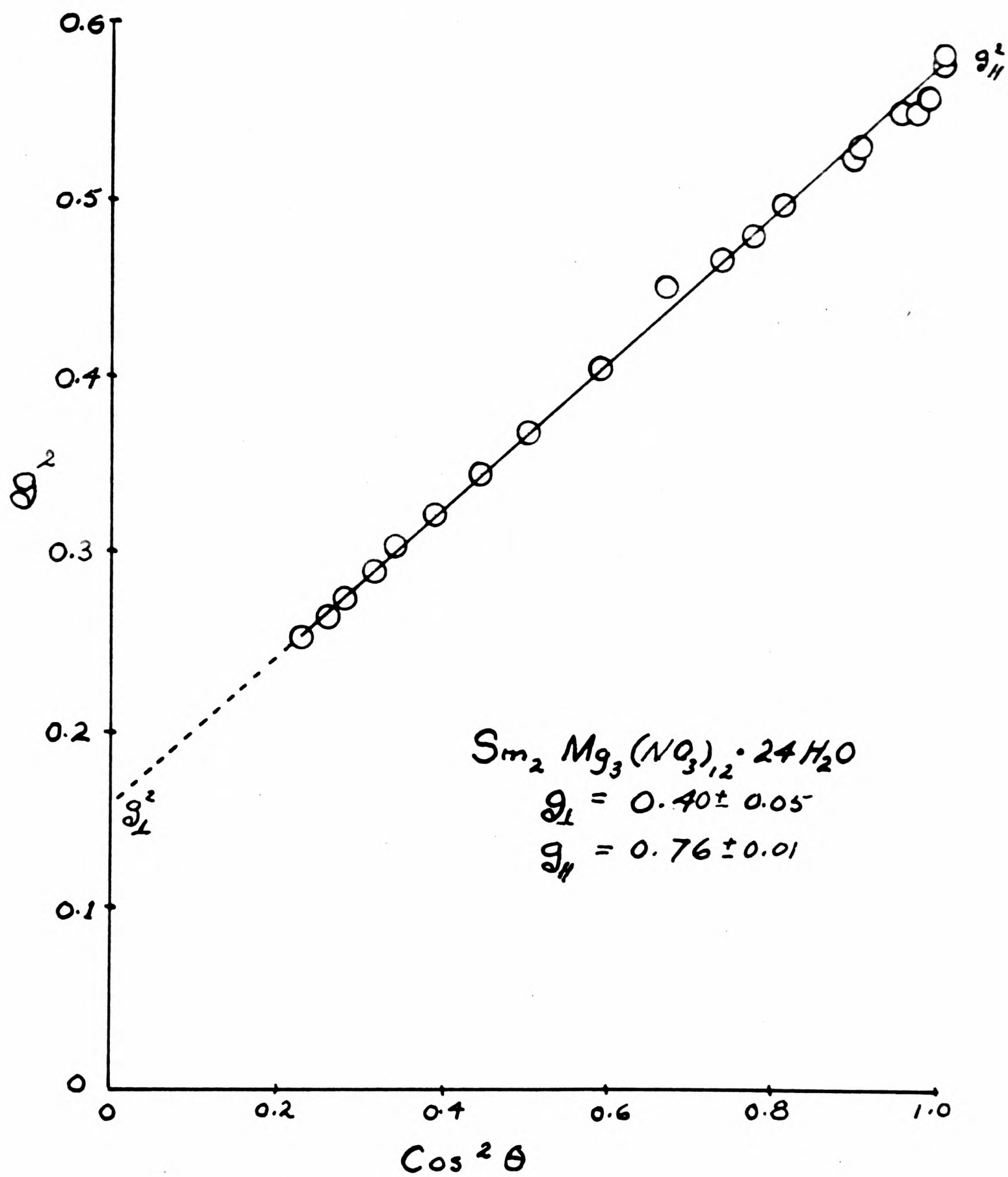


1. Main line of concentrated samarium magnesium double nitrate.
2. Hyperfine line of Sm^{147} at a higher amplification than #1.



3. Hyperfine line of Sm^{149} .
4. Hyperfine line of Sm^{147} and of Sm^{149} showing the very small difference in intensity due to the difference in their abundance.

Figure 1



VII.3

We had hoped to be able to do this by means of the resonance of the lithium nucleus in LiF. As the nuclear gyromagnetic ratios of $\text{Li} = 1.039 \times 10^4$ and $\text{F} = 2.517 \times 10^4$, the lithium line appears at about double the magnetic field at which the fluorine line is seen. When we observed these nuclear resonance signals at 4°K in a pure single crystal of LiF they saturated and disappeared in about a second. We therefore tried a piece of LiF which had been bombarded with neutrons in the Harwell pile. The bombarded specimen was black, whereas the original specimen was colourless and transparent. The extra interaction between the nuclei and the colour centres was sufficient to prevent the signal from saturating. Unfortunately the Li nucleus gave a broad line with considerable asymmetry from quadrupole interactions. We felt we would not get appreciably better accuracy from its use than we would get from ammeter readings.

2. HYPERFINE PARAMETERS:

The hyperfine structure was fitted to the first order perturbation formula appropriate for the d.c. field parallel to the trigonal axis, equation 3.29.

$$H = H_0 - Am - \frac{B^2}{2H_0} [I(I+1) - m^2]$$

We have noted in Chapter III that the last term in this formula comes from second order perturbation theory. Table 1

VII.4

shows the fields at which the lines were observed; the fields at which they are calculated to occur using the first order part of 3.29; and also including the second order part of 3.29. We are able to determine A quite accurately from the average spacing of the hyperfine lines. As in the case of neodymium we may estimate B from the relationship $\frac{A g_{\perp}}{B g_{\parallel}} = 1$

It will be observed from table 1 that the fields calculated from such a B using the second order theory are in much worse agreement with the observed values than are those calculated from first order theory. If we assume $\frac{A g_{\perp}}{B g_{\parallel}} \neq 1$ due to the admixture from the $J = \frac{7}{2}$ manifold, then we can set a limit of

$$\frac{A g_{\perp}}{B g_{\parallel}} > 1.3$$

Although our limit in the double nitrate is less than the value 4 observed in the ethyl sulphate it does not follow that there is less admixture from the $\frac{7}{2}$ level.

Unlike the neodymium hyperfine spectra there is now very little difference in intensity between the lines from the different isotopes. In the ethyl sulphate, Bogle (1952) measured the intensities of the lines very accurately by superimposing a calibrating signal on the C.R.O. trace. We have identified the spectra of the two isotopes in the

CHAPTER VII Table 1

Samarium Magnesium Double Nitrate

Isotope	Observed Field (In Kg's)	First Order Theory	Δ	I_z	Second Order Theory	Δ
Sm ¹⁴⁷	4.84	4.93	0.09	7/2	4.88	-0.04
	5.91	5.87	0.04	5/2	5.72	0.19
	6.94	6.87	0.07	3/2	6.66	0.28
	7.90	7.86	0.04	1/2	7.61	0.29
	Main Line					
	8.91	8.86	0.05	-1/2	8.61	0.30
	9.85	9.85	0	-3/2	9.64	0.21
	10.82	10.85	-0.03	-5/2	10.70	0.12
	11.82	11.79	0.03	-7/2	11.70	0.06
Sm ¹⁴⁹	5.49	5.49	0	7/2	5.45	0.04
	6.29	6.31	0.02	5/2	6.07	0.22
	7.19	7.13	-0.06	3/2	6.98	0.21
	8.04	7.95	-0.09	1/2	7.78	0.16
	Main Line					
	8.84	8.77	-0.07	-1/2	8.60	0.24
	9.53	9.57	0.04	-3/2	9.44	0.09
	10.41	10.41	0	-5/2	10.31	0.11
	11.25	11.23	-0.02	-7/2	11.19	0.06

$$A^{147} = 0.997 \text{ Kilogauss} \\ = 0.0346 \pm 0.0005 \text{ cm}^{-1}$$

$$A^{149} = 0.823 \text{ Kilogauss} \\ = 0.0287 \pm 0.0005 \text{ cm}^{-1}$$

$$B \leq 0.3 \text{ for both isotopes}$$

$$1 \text{ Kilogauss} = 0.0348 \text{ cm}^{-1}$$

$$\lambda = 3.41 \text{ cm}$$

VII.5

double nitrate by assuming Bogle's values for their nuclear moments. Photograph 4 shows a hyperfine line from each isotope on the same C.R.O. trace.

We conclude, on the basis of first order theory that $A^{147} = 0.0356 \text{ cm}^{-1}$ and $A^{149} = 0.0287 \text{ cm}^{-1}$. $|B| \leq 0.028 \text{ cm}^{-1}$ for both isotopes.

3. LINE WIDTH:

The line width was measured from photographs of the C.R.O. trace. No account was taken of the smaller a.c. field at a given a.c. current resulting from the magnet poles becoming saturated at high d.c. fields. However this effect is only a few percent.

The line width was 75 ± 5 gauss with the d.c. field parallel to the trigonal axis.

III. THEORY:

The free Sm^{+++} ion has the ground state $4f^5 \quad {}^6\text{H}_{5/2}$ (table 1, Chapter III), and hence resembles Ce^{+++} except that it has one hole instead of one 4f electron. It follows the theory worked out for Ce^{+++} having $J_z = \pm \frac{1}{2}$ for the lowest doublet with $J_z = \pm \frac{5}{2}$ for the first excited state. According to Elliott and Stevens (1953) the $\frac{5}{2}$ state is not as close to the $\frac{1}{2}$ state in Sm^{+++} as it is in Ce^{+++} .

VII.6

1. g VALUES:

If the ground states are eigenstates of a single J_z manifold the same calculation of the g values should apply as for the cerium except that the Landé factor is $\frac{2}{7}$ from $L = 5$, $S = \frac{5}{2}$, $J = \frac{5}{2}$ instead of $\frac{6}{7}$ for cerium.

(Table 2, Chapter III) Therefore, multiplying the values found on page 9 of Chapter IV by $\frac{1}{3}$ we obtain

J_z	$g_{\parallel}$	$g_{\perp}$
$\pm \frac{1}{2}$	$\frac{2}{7}$	$\frac{6}{7}$
$\pm \frac{3}{2}$	$\frac{6}{7}$	0
$\pm \frac{5}{2}$	$\frac{10}{7}$	0

Hence the $J_z = \pm \frac{1}{2}$ values are seen to most nearly approximate the observed values. Because the $J = \frac{7}{2}$ level is so near, and in view of the limit of $\frac{B_{J_1}}{B_{J_2}} \gg 1.3$ which indicates considerable admixture, we now proceed to the next order of approximation by admixing $J = \frac{7}{2}$. The Kramers' doublet becomes

$$\cos \theta \left| \frac{5}{2} \pm \frac{1}{2} \right\rangle + \sin \theta \left| \frac{7}{2} \pm \frac{1}{2} \right\rangle$$

where we have taken account of only the nearest excited J level. By performing a calculation of the g values similar to that used for cerium, Stevens and Elliott (1953) obtain

$$g_{\parallel} = \frac{2}{7} \left(\cos^2 \theta + \frac{26}{9} \sin^2 \theta + 3\sqrt{10} \sin 2\theta \right)$$

$$g_{\perp} = \frac{2}{7} \left(3 \cos^2 \theta - \frac{104}{9} \sin^2 \theta - \frac{3}{2} \sqrt{10} \sin 2\theta \right)$$

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Figure 2 shows the function of Θ plotted for a range of Θ

By extrapolating the crystal field parameters of neodymium ethyl sulphate Elliott and Stevens can show that their admixture could give the lowest doublet. We cannot yet make this test.

The approximation to the observed values is worse than for the Ce^{+++} and Nd^{+++} . In the samarium ethyl sulphate there is also greater disagreement with theory than in the cerium and neodymium, suggesting that admixtures other than $J = \frac{7}{2}$ may be important.

Stevens and Elliott give

$$\tan \Theta = \frac{0.0869V_2^0 - 0.431V_4^0 - 1.013V_6^0}{\Delta}$$

where $\Delta \doteq 1000 \text{ cm}^{-1}$ and from figure 2, $\Theta \doteq 6^\circ$

Unfortunately if $V_6^0 \doteq V_4^0 \doteq V_2^0$, as in the ethyl sulphate, we cannot estimate V_6^0 , nor the ratio $\frac{V_6^0}{V_4^0}$

The $\frac{A}{g_{||}}$ ratios are as follows:

Ethyl Sulphate

$$\frac{A^{147}}{g_{||}} = 0.0100 \text{ cm}^{-1}$$

$$\frac{A^{149}}{g_{||}} = 0.00822 \text{ cm}^{-1}$$

Double Nitrate

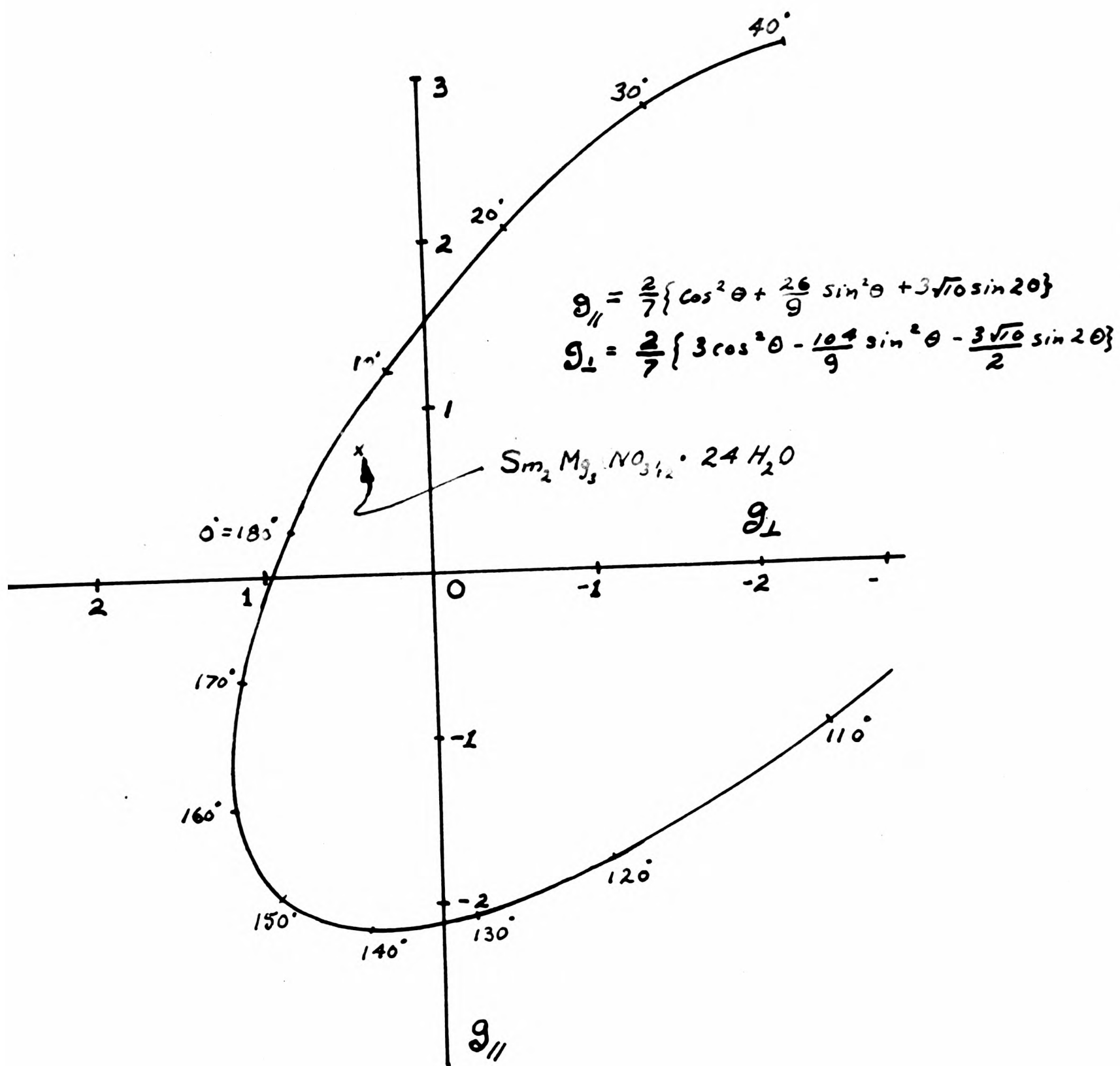
$$\frac{A^{147}}{g_{||}} = \frac{0.122}{0.046} \text{ cm}^{-1}$$

$$\frac{A^{149}}{g_{||}} = \frac{0.102}{0.038} \text{ cm}^{-1}$$

The isotope ratios are:

Doublet	$\bar{I}_2 = \pm \frac{7}{2}$	$\pm \frac{5}{2}$	$\pm \frac{3}{2}$	$\pm \frac{1}{2}$
μ^{147}				
μ^{149}	1.21	1.19	1.24	1.26

Figure 2



where the accuracy of the values decreases as we go from $\pm \frac{7}{2}$ to $\pm \frac{1}{2}$. These agree with Bogle's value of 1.222 ± 0.009

2. LINE WIDTH:

The last column in table 1 of Chapter IV gives the contributions of the various ions in the unit cell of figure 1 of Chapter III. They are calculated from equation 3.29 with $\theta = 0$, i.e.

$$\hbar^2 (\Delta v)^2 = \frac{9}{16} \frac{1}{g_{\parallel}^4} \sum_i |B_{ij}^i 2 g_{\parallel}^2 \cos^2 \theta|$$

and the data of table 3, Chapter III. The contributions from ions close to the trigonal axis are now very large, and the contribution from the nearest neighbours on the trigonal axis amounts to $\frac{57}{130}$ of the total.

Assuming a Gaussian shape, we get $2.35 \sqrt{130} = 27$ gauss for the width at half intensity. This does not agree at all well with the observed value of 75 gauss. This may well be due to a short spin lattice relaxation time caused by the proximity of the $\frac{7}{2}$ level. In the ethyl sulphate the line width decreased when the salt was cooled below 4.2°K . We did not observe the double nitrate below 4.2°K .

SUMMARY

Having presented our data and analysed it in some detail, we may now try to see the overall picture.

(a) The theory which has been derived for the ethyl sulphates gives a good explanation of the double nitrate g values. There is similarity between the ground state of a given rare earth in the ethyl sulphate and in the double nitrate, except for samarium.

(b) We do not yet understand how to predict the crystal field parameters. Judd (unpublished) is able to estimate the double nitrate crystal field parameters of certain rare earths from their ethyl sulphate parameters. He is not yet able to move along the periodic table and calculate the parameters for the different rare earths from a knowledge of the double nitrate parameters of one of them. Powell has suggested that there may be a change in lattice structure within the series, and the change in symmetry from $g_{\perp} > g_{\parallel}$ for the Ce^{+++} and Nd^{+++} to $g_{\parallel} > g_{\perp}$ in Sm^{+++} may support this.

We should mention the work of Mookherji (1949) on the bulk susceptibilities of cerium, praseodymium, neodymium and samarium in the magnesium double nitrates between 300°K and 85°K . It is difficult to compare his measurements with our results at 4°K for the following reasons.

- (i) They cover too small a range of relatively high temperatures.
- (ii) They show the effect of more than one populated energy level, as well as large temperature independent effects from the excited levels.
- (iii) They may contain quite large contributions from paramagnetic impurities, especially in the case of samarium.
- (iv) They show the same qualitative disagreement with measurements by Gorter and Jackson of the sulphate octahydrate salts as they show with our measurements of cerium double nitrate.

Mookherji observes $X_{\perp} > X_{\parallel}$ in both samarium and praseodymium. In the case of samarium this may be due to impurities. In the case of praseodymium his curves of $X_{\perp}$ and $X_{\parallel}$ could easily cross over between 85°K and 4.2°K. On the other hand we did not observe resonance in $\text{Pr}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$, except when it was diluted to about one part in ten of $\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$. There may be a different crystal field in the concentrated salt.

Although we have expressed certain reservations with respect to our Sucksmith balance measurements, we feel confident of the microwave absorption results. There was no doubt as to which ion's spectrum we were observing. Furthermore,

the crystals showed very well defined symmetry properties and we took pains to establish their orientation relative to the magnetic field. Although we used the purest rare earths supplied by Johnson, Matthey and Co., impurity spectra were always observed.

(c) The lines all seem too wide to agree with theory. Elliott considers the theory to be rather a rough approximation, however, and we have not ruled out broadening due to a short spin lattice relaxation time except for cerium. Indeed we may generalize that the spin lattice relaxation time is shorter in the double nitrate than in the ethyl sulphate because both neodymium and praseodymium can be observed at 20°K in the ethyl sulphate. Furthermore, gadolinium can be observed at 4°K whereas in the double nitrate we have never seen it at so low a temperature.

CHAPTER VIII

POTASSIUM MANGANICYANIDE

I. BACKGROUND:

It is well known that the values of the effective magnetic moments of some complex cyanides are quite different from their values in simple salts of the same metallic ions. This has been explained by Van Vleck (1935) as the result of the breakdown, by very large valence forces, of both the spin orbit coupling and the Russel Saunders coupling. This makes the deepest state that of the lowest possible spin rather than of maximum spin as given by Hund's rule. Van Vleck (1935) shows that this effect can be produced by a crystal field whose symmetry depends on the orientation of the valence bonds. As a first approximation the crystal field has been assumed cubic in the case of the six $(CN)^-$ complexes surrounding a metallic ion.

Kotani (1949) has derived susceptibility formulae using this assumption, and notes the discrepancy in the published values for $K_3Mn(CN)_6$, viz.: Goldenberg, 1940, 3.25; Blitz, 1928, 3.61; Ray, Bhar, 1928, 2.95; Szego, Ostenelli, 1930, 3.40. These observations were made at high temperatures, and there do not seem to be any published measurements of the susceptibility of this salt at low temperatures.

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Bleaney, Bowers and Baker (unpublished)

have recently investigated the paramagnetic resonance spectra in some complex cyanides, and suggested that it would be worthwhile to investigate $K_3Mn(CN)_6$ in order to verify that it has a diamagnetic level lowest as predicted by Kotani. Should this be the case it would clarify the origin of some observed spectra by ruling out resonance except from excited levels at high temperatures.

II. THE MEASUREMENTS:

We investigated a specimen of Baker's Analar $K_3Mn(CN)_6$ in the form of 0.13 grams of powder packed in a cylindrical perspex container. The susceptibility was measured by reading the magnet current required to return a light beam to its original position after a 4 mm. steel ball bearing was lifted from the ring. The light beam was observed with the travelling microscope. Readings were taken from 4°K to 300°K.

The results of χ vs. $\frac{1}{T}$ are shown in figure 1, of $\frac{1}{\chi}$ vs. T in figure 2, and of n^2 vs. T in figure 3. Although we are not certain of thermal equilibrium between 4°K and 10°K, the susceptibility is obviously not changing rapidly over this region.

The absolute calibration of the susceptibility was made at 293°K by comparing the force on a known weight of

Figure 1

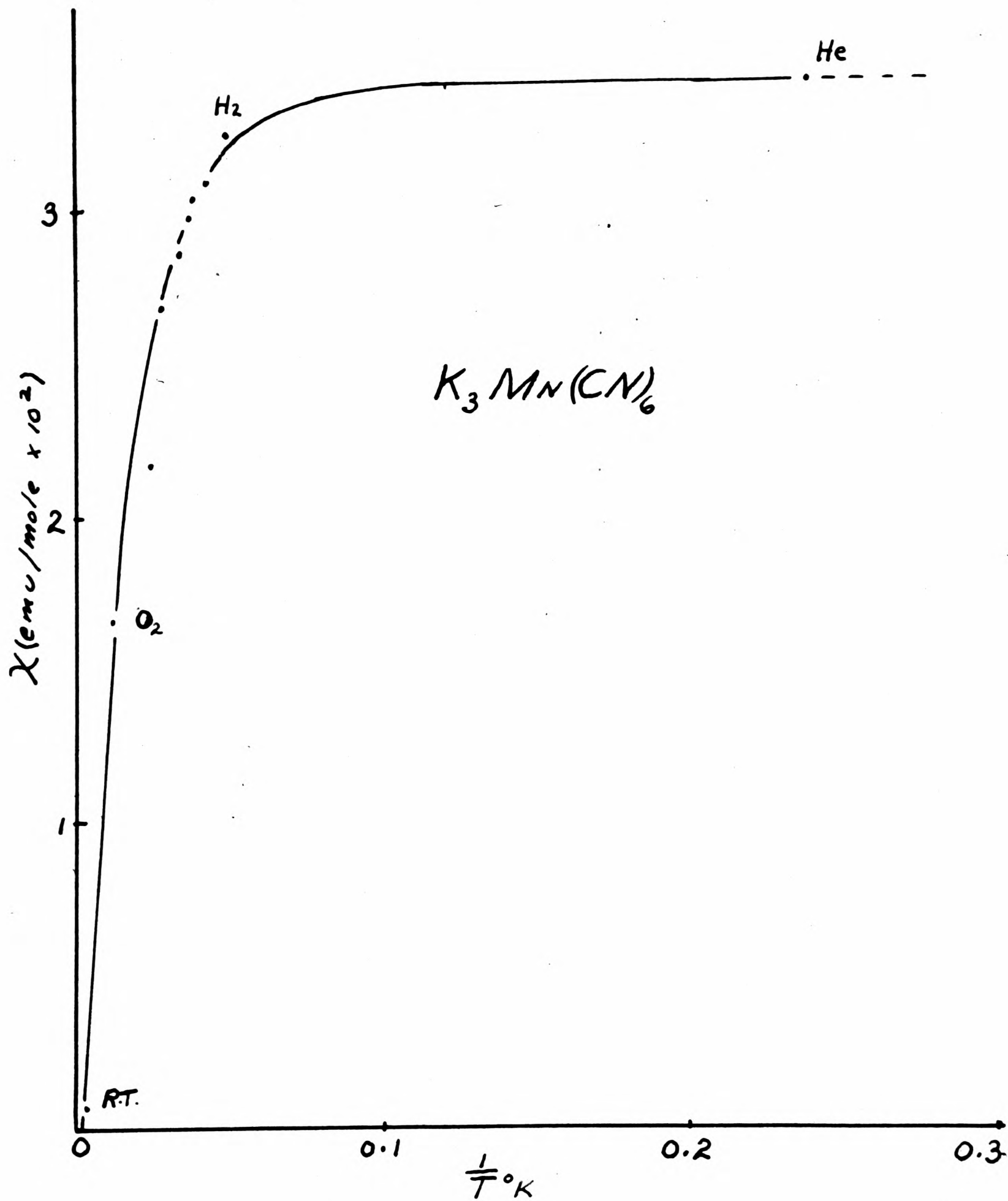


Figure 2

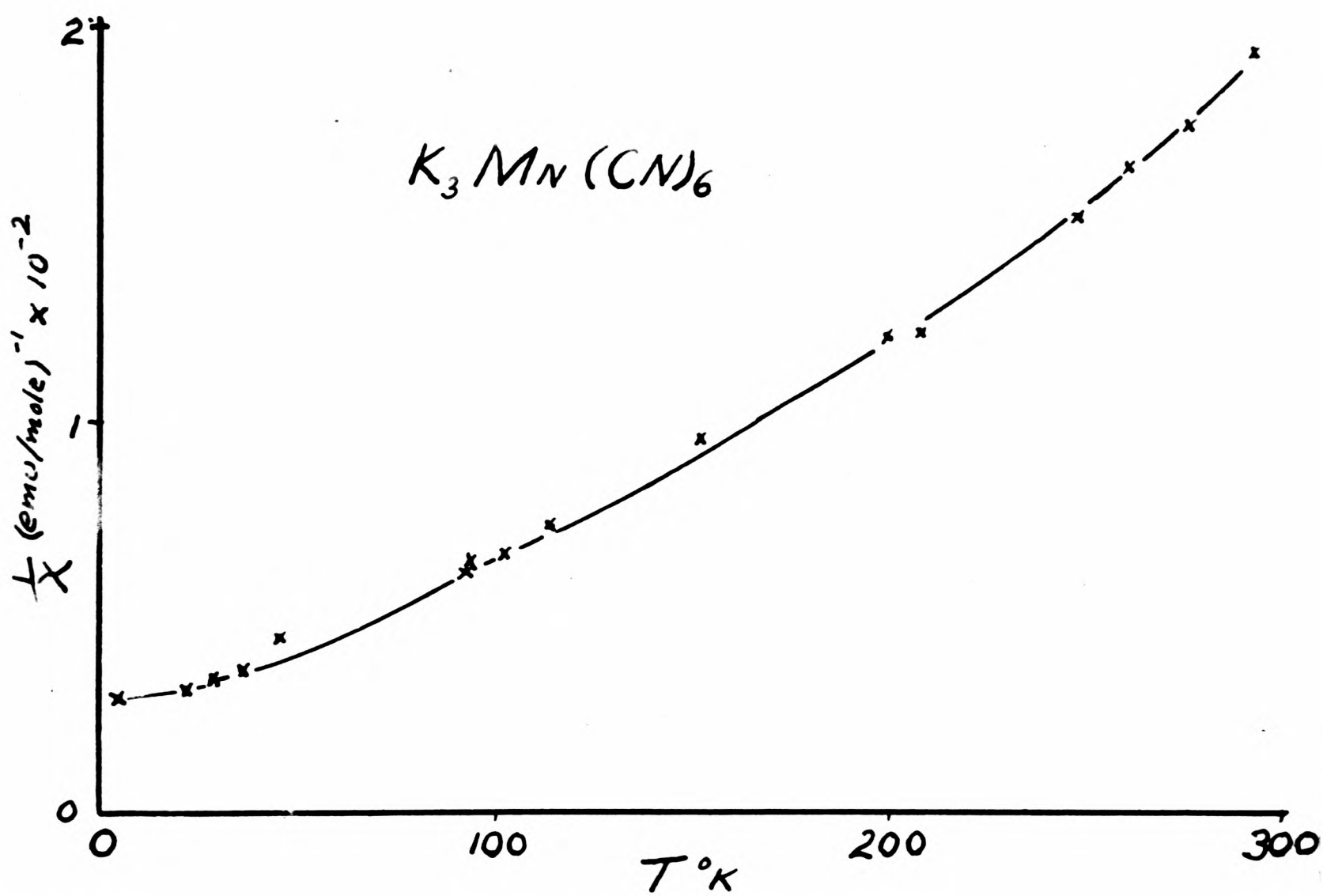


Figure 3

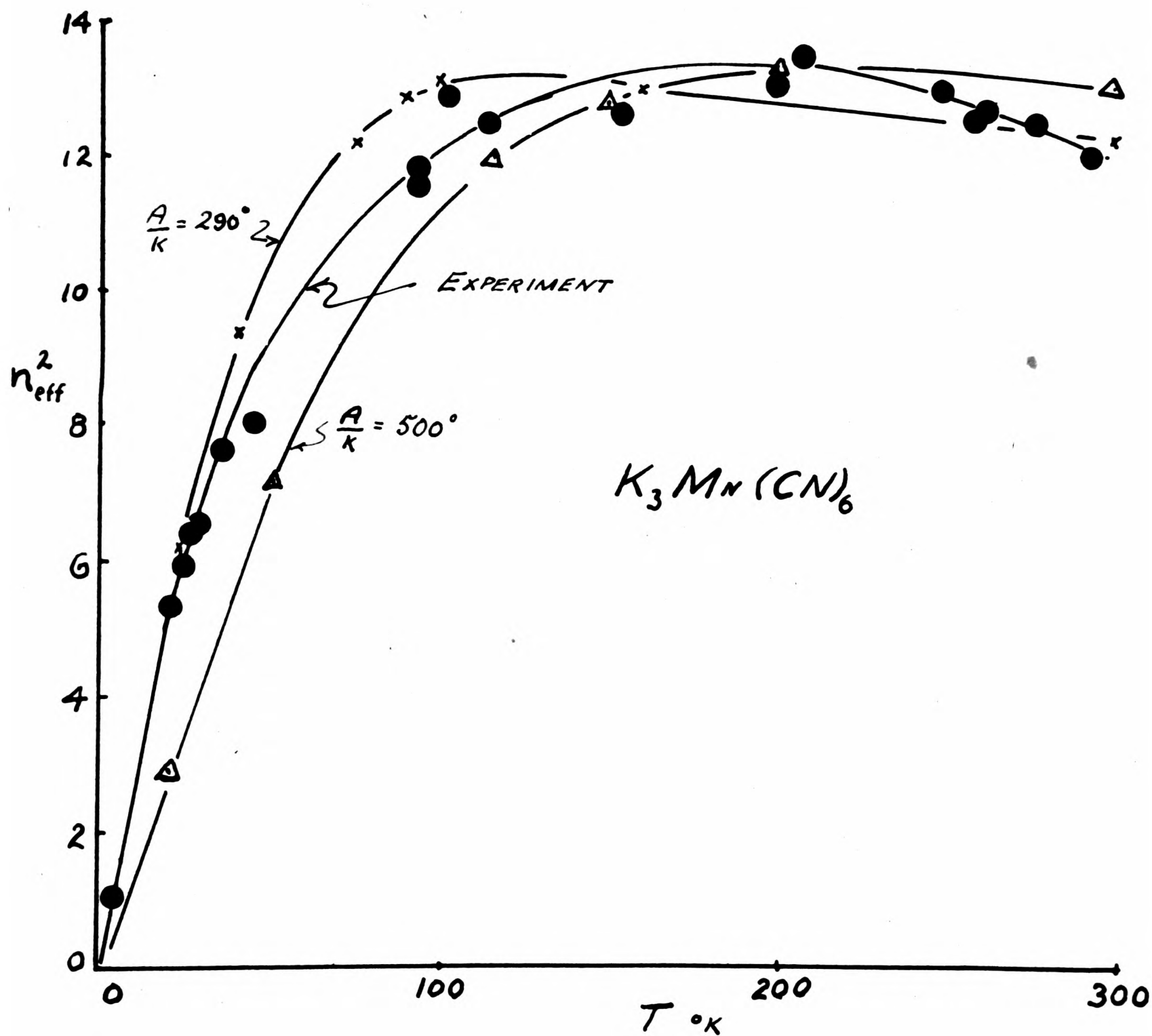
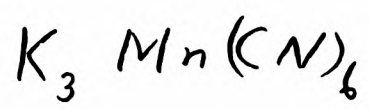
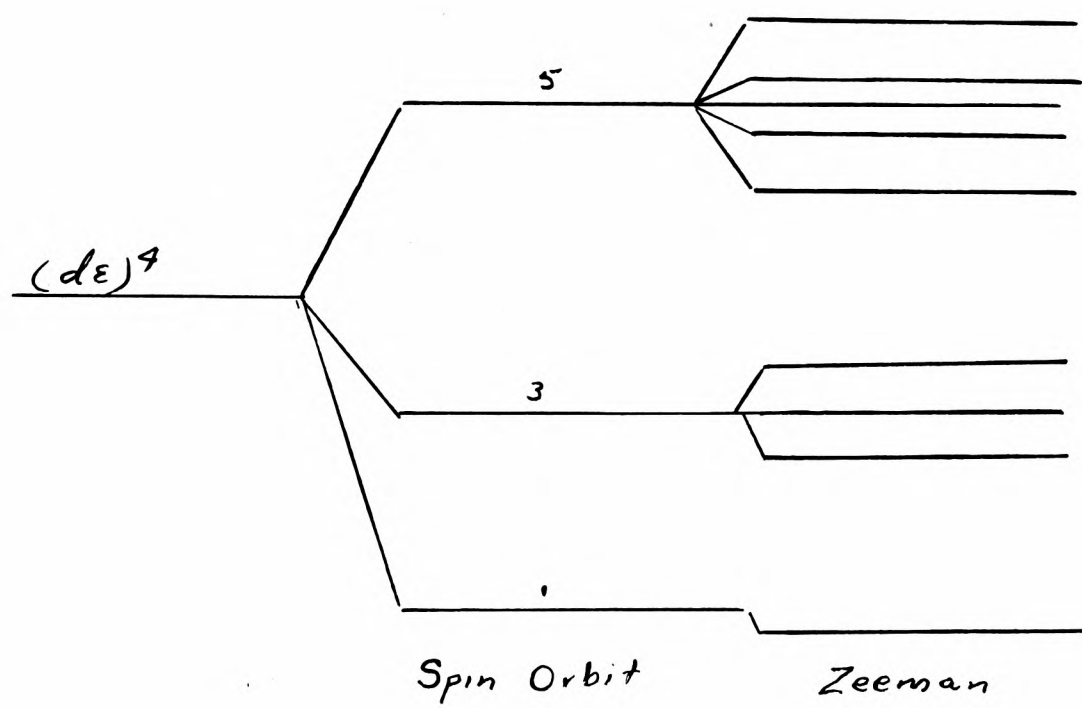


Fig. 4



VIII.3

$\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ with the force on a known weight of $\text{K}_3\text{Mn}(\text{CN})_6$ which occupied a similar volume and was enclosed in a similar amount of perspex. Intercomparison of three $\text{Mn}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ specimens showed that they could be taken out of the balance and replaced in the same effective magnetic field to within $\pm 1\%$.

The diamagnetic correction due to the empty perspex mounting was experimentally less than 1%. The diamagnetic susceptibility of $\text{K}_3\text{Mn}(\text{CN})_6$ can be estimated by adding the stoichiometric proportions of $\chi_K = -18.5 \times 10^{-6}$, $\chi_{\text{Mn}^{++}} \leq \chi_{\text{Sc}} = -10 \times 10^{-6}$, $\chi_{\text{CN}} = -10.8 \times 10^{-6}$ giving $\chi_{\text{dia}} = -125 \times 10^{-6}$ emu/mole. At 293°K the paramagnetic susceptibility is 5.15×10^{-3} emu/mole, hence the diamagnetic correction is $2\frac{1}{2}\%$; and it becomes negligible by 100°K .

As the errors in plotting the graphs are out of proportion to experimental errors, we include the following table of experimental results corrected for the diamagnetism.

The two experimental points which deviate most from the smooth curves, i.e. 45°K and 152°K , have been shown on both figure 1 and figure 2. As they both correspond to larger magnetic fields being applied than should have been necessary, they are probably caused by the balance sticking slightly. In the case of the point at 45°K however, there

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was a very large thermal gradient between the top of the ground joint at 20°K and the specimen. Thus there was the greatest chance of thermal disequilibrium. The vigorous bubbling of the hydrogen bath also made the balance unstable.

III. THEORY:

We are concerned now with an iron group element where the electrons which are magnetically important are, in the free ion picture, in the 3d orbitals rather than the 4f. As these 3d electrons are not shielded by an outer shell from the influence of the crystal field or valence forces, we find that the Hamiltonian for the central ion of a complex should be written:

$$H = H^0 + V_c + A \sum_i \underline{l}_i \cdot \underline{s}_i + \beta H \cdot (\underline{L} + 2\underline{S}) \quad 8.1$$

where $V_c \gg A \sum_i \underline{l}_i \cdot \underline{s}_i \gg \beta H \cdot (\underline{L} + 2\underline{S})$, and now includes valence forces as well as coulomb interactions. As in Chapter III, $H^0 + A \sum_i \underline{l}_i \cdot \underline{s}_i$ is the Hamiltonian of the free metallic ion; and $\beta H \cdot (\underline{L} + 2\underline{S})$ is the effect of the applied magnetic field.

Van Vleck (1935) shows that under the influence of an electric field of cubic symmetry the 3d level splits into two sub-levels ... a doubly degenerate $d_{\underline{z}}$ level, and a triply degenerate $d_{\underline{\gamma}}$ level. If the six convalent ligands coordinating the Mn^{+++} with the six $(CN)^-$ are arranged at the

VIII.5

six corners of a regular octahedron, $d\varepsilon$ is lower than $d\tilde{\varepsilon}$. If the electric field of the ligands is sufficiently strong, the $d\tilde{\varepsilon}$ level is shifted so high that the four d-electrons of Mn^{+++} are all in the $d\varepsilon$ orbitals.

Kotani (1940) shows that the two-electron $(d\varepsilon)^2$ system's nine-fold degenerate triplet ground state has its degeneracy completely removed by the action of spin-orbit coupling and the Zeeman effect. He gives the following levels shown in figure 4.

$$\begin{array}{ll} \frac{A}{2} + \frac{1}{2} \beta H + \frac{A + 12 \frac{\beta^2}{A} H^2}{4} & \frac{A}{2} - \frac{9}{A} \beta^2 H^2 \\ \frac{A}{2} - \frac{1}{2} \beta H + \frac{9}{4} \frac{\beta^2}{A} H^2 & - \frac{A}{2} + \beta H \\ - \frac{A}{2} + \frac{1}{2} \beta H - \frac{9}{4} \frac{\beta^2}{A} H^2 & - \frac{A}{2} - \frac{3\beta^2}{A} H^2 \\ - \frac{A}{2} - \frac{1}{2} \beta H - \frac{9}{4} \frac{\beta^2}{A} H^2 & - \frac{A}{2} - \beta H \end{array}$$

where $A + 12 \frac{\beta^2}{A} H^2$ is lowest for the case $(d\varepsilon)^4$, and is diamagnetic.

We have shown

$$X = \frac{1/\bar{\mu}^2}{3KT} + \alpha$$

This gives from 3.52

$$\begin{aligned} \bar{\mu}^2 = 3 & \left[\left(\beta^2 + \frac{1}{4} \beta^2 + \frac{9}{2} \frac{\beta^2}{A} KT \right) e^{-\frac{A}{2KT}} + \left(\frac{1}{4} \beta^2 + \beta^2 \right. \right. \\ & + 6 \frac{\beta^2}{A} KT + \frac{9}{2} \frac{\beta^2}{A} KT \left. \right) e^{-\frac{A}{2KT}} + \left\{ \frac{1}{4} \beta^2 + \frac{1}{4} \beta^2 \right. \\ & \left. \left. + \left(-\frac{9}{2} + 18 - \frac{9}{2} \right) \frac{\beta^2}{A} KT \right\} e^{\frac{A}{2KT}} + 24 \frac{\beta^2}{A} e^{\frac{A}{KT}} \right] \end{aligned}$$

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Putting $n^2 = \frac{\mu^2}{\beta^2}$ and $x = \frac{A}{kT}$ it can be shown

$$n^2 = \frac{3 \left\{ \left(\frac{5}{2}x + 15 \right) e^{-\frac{3x}{2}} + \left(\frac{x}{2} - 9 \right) e^{-\frac{x}{2}} + 24 \right\}}{x (5 e^{-\frac{3x}{2}} + 3 e^{-\frac{x}{2}} + 1)} \quad 8.4$$

If we consider now two positive holes instead of two electrons, i.e. consider the case of

$(d\varepsilon)^4$, we must put $x = -x$ in the above, getting

$$n^2 = \frac{3 \left\{ 24 + \left(\frac{x}{2} - 9 \right) e^{-\frac{x}{2}} + \left(\frac{5}{2}x - 15 \right) e^{-\frac{3x}{2}} \right\}}{x (1 + 3 e^{-\frac{x}{2}} + 5 e^{-\frac{3x}{2}})} \quad 8.5$$

We have now only one parameter, $\frac{A}{k}$, with which to fit this formula to our experimental results.

Kotani quotes a spectroscopic value for the free ion of

$\frac{A}{k} = 492^\circ$. We have plotted n^2 as a function of T with $\frac{A}{k} = 500^\circ$ in figure 3. As $T \rightarrow 0$, $n^2 \rightarrow \frac{72kT}{A}$ so that from our value of n^2 at $4^\circ K$ we can obtain a value of $\frac{A}{k} = 269^\circ K$. We have also plotted equation 8.5 for $\frac{A}{k} = 270^\circ K$ in figure 3.

Both theoretical curves pass through a maximum at fairly high temperatures where the accuracy of the experimental points is least. The values of n^2 plotted for different $\frac{A}{k}$ appear to straddle the experimental points at intermediate temperatures. If a value of $\frac{A}{k}$ is calculated from the measurements at $300^\circ K$ it gives a calculated curve which in no way resembles the experimental curve except that it intersects at $300^\circ K$.

While it is true that our experimental points pass through a maximum, the curvature depends very

CHAPTER VIII Table 1

Potassium Manganicyanide

T	$\frac{1}{T}$	χ emu/mole	$\frac{1}{\chi}$	$\frac{n^2}{\chi}$
293	0.00341	0.00515	194	12.0
277	361	569	176	12.5
261	383	596	165	12.65
259	386	606	165	12.55
249	402	655	153	13.0
208	480	811	123	13.5
200	500	821	122	13.1
154	657	0.0104	96.2	12.65
114	878	137	73.0	12.50
102	980	157	63.6	12.8
93	0.01075	160	62.5	11.55
90.3	111	164	61.0	11.85
45.9	218	220	45.4	8.08
35.5	281	269	37.2	7.65
28.7	348	287	34.9	6.59
27.0	370	299	33.5	6.45
26.2	381	305	32.8	6.40
24.0	417	310	32.3	5.95
20.4	490	326	30.6	5.32
4.2	0.240	343	29.1	1.15
4.2	0.240	339	29.5	1.14

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sensitively upon the diamagnetic correction and upon the absolute determination of χ at room temperature. Furthermore a large Curie-Weiss Δ would produce a curvature of n^2 at high temperatures, and alter its values.

Cooke and Wolf (unpublished) have measured the susceptibility of $K_3Fe(CN)_6$ down to $1^\circ K$. It obeys the Curie-Weiss law, and has a very small Weiss Δ . We therefore have grounds for thinking that in $K_3Mn(CN)_6$ the Weiss Δ is also very small.

The effect of a trigonal component of crystal field would be to split the levels by different amounts, so that a single parameter would no longer be sufficient to describe them. Jackson (1938) found an anisotropy of 4 : 1 in $K_3Fe(CN)_6$, which we expect to be a comparable salt. This ruled out the cubic field hypothesis, and our results indicate that the field in the $K_3Mn(CN)_6$ is probably not cubic either.

We have shown that:

- (a) A diamagnetic level lies lowest;
- (b) Its nearest neighbour must be some 100 cm^{-1} above it, and
- (c) The single parameter associated with a cubic field is insufficient to describe our results.

CHAPTER IX

CLATHRATE COMPOUNDS

The structure of a number of adducts formed by quinol with molecules or atoms of suitable dimensions have been described by Powell and his collaborators (1948). In these so-called clathrate compounds each trapped molecule is totally enclosed in a cage formed by the molecular arrangement of the β -quinol lattice. Of the common paramagnetic gases, oxygen and nitric oxide are the only ones of suitable size which do not react with quinol. Evans and Richards (1952) therefore synthesized clathrate compounds of these two gases. They suggested that these compounds offered a way of measuring the susceptibilities of "free" molecules at temperatures below their liquifaction points if the lattice holes are field free. We therefore investigated the susceptibilities of nitric oxide and oxygen clathrates over a large range of temperatures. We are indebted to Dr. Evans not only for supplying us with the clathrates but also for analysing them to find the fraction of lattice holes filled.

I. NITRIC OXIDE CLATHRATE:

A warm saturated solution of quinol in ethyl alcohol was boiled to remove dissolved air, and poured into

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a stainless steel bomb. The bomb was evacuated with a rotary pump and quickly cooled in liquid oxygen. Nitric oxide (prepared by the method of Inorg. Synth., 2, p.126,) in an evacuated vessel was passed through an evacuated train of traps containing sodium hydroxide solution to remove nitrogen peroxide, and sodium hydroxide pellets to remove water. Enough nitric oxide was condensed into the bomb this way to obtain about 40 atm. pressure at room temperature. The bomb was removed from the liquid oxygen, placed in hot water, shaken for some time to dissolve the quinol, and finally allowed to cool for 24 hours. The resulting small crystals were then washed in a saturated solution of quinol in ethyl alcohol and dried in a vacuum dessicator. The nitric oxide compound forms crystals which are unstable. They slowly turn violet and evolve NO gas even when sealed off in a glass container.

The susceptibility of this clathrate was measured by Evans and Richards (1952) at room temperature by the Gouy method. They obtained a value slightly higher than that of the free NO, but attach little significance to the discrepancy. We wished to extend their measurements to low temperatures to see if the susceptibility obeyed the theory of the free molecule below the boiling point

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of NO, and to see what effect the quinol lattice had upon the energy levels.

II. THEORY

1. SPECTRAL NOTATION FOR DIATOMIC MOLECULES:

Probably the most important distinction between quantization in atoms and in diatomic molecules is that in the latter the resultant orbital electronic angular momentum is no longer a constant of the motion, and is thus not quantized. Instead the combined field due to the two nuclear attracting centres has axial rather than spherical symmetry, and only the component of the angular momentum parallel to the axis of figure of the molecule is conserved. It can be given a quantized value Λ . A term is of the Σ, Π, Δ type according as $|\Lambda| = 0, 1, 2, 3$, etc.

We have neglected the spin orbit coupling in the above approximation. Hund (1926) distinguishes four resultant spin orbit couplings.

(a) In the first, the energy of interaction between the spin and orbital angular momenta is large compared to that between the spin and the rotational angular momentum of the molecule as a whole, J , and consequently the spin axis is firmly quantized relative to the molecular axis. The parallel component of spin angular momentum can then be

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assigned a quantized value ξ . The various values of $\xi = -S, \dots, S$ yield the different components of a multiplet. The notation $\Omega = L + \xi$ is common. Thus Ω gives the parallel component of spin and orbital angular momentum combined, and can be used to specify the multiplet component.

(b) In the second case, if $L = 0$ and $S \neq 0$ the spin vector is not coupled to the axis of figure at all and hence Ω is not defined. In this case the spin vector and the rotational angular momentum N associated with the nuclei form a resultant J .

(c) If, as in some heavy molecules, the interaction between L and S is greater than the interaction with the internuclear axis of figure, L and S are not defined. Instead L and S form a resultant J_e which is coupled to the internuclear axis with a component Ω . Again the electronic angular momentum J_e and the nuclear angular momentum N form a resultant J .

(d) If the coupling between L and the internuclear axis is very weak whereas that between L and the axis of rotation is strong, then the nuclear rotation momentum may be quantized and give the total angular momentum when its components are added vectorially to L and S .

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The normal state of the NO molecules is known to fall under Hund's case (a) as a 2π doublet of width $A = 120.9\text{cm}^{-1}$ (Jenkins, Barton and Mulliken, 1927). The lower doublet component has $\Sigma = -\frac{1}{2}$, $\Lambda = 1$, hence from equation 3.52:

$$X = \frac{N\beta^2}{3kT} \left[4 \left(\frac{1}{2} \right) \left(-\frac{1}{2} \right) + 1 \right] + \text{const}$$

$$X \rightarrow \text{const as } T \rightarrow 0$$

and the higher multiplet level becomes depopulated. At very high temperatures with $\Sigma = \frac{1}{2}$, $\Lambda = 1$, $X = \frac{N\beta^2}{3kT} [2] + \text{const.}$

In calculating X for intermediate temperatures we may neglect changes in Λ which give rise to very large energy differences. However the effect of Σ on the energy is comparable with $kT \doteq 200\text{cm}^{-1}$ at room temperature. Furthermore $\Omega = \Sigma + \Lambda$ differs from Σ only by an additive constant +1 in a π state.

Neglecting transitions to excited orbital states, all elements diagonal in Ω will involve only changes in the molecular rotation J . Since there is an appreciable Boltzmann factor for both values of Ω we must sum equation 3.52 over values of Ω in place of n . Thus:

$$X = \frac{B}{3kT} \sum_{\Omega jm; \Omega' j' m'} \left[\langle \Omega jm | P^0 | \Omega' j' m' \rangle \right]^2 e^{-\frac{W_{\Omega j}^0}{kT}} + \frac{2B}{3} \sum_{\substack{\Omega jm; \Omega' j' m' \\ (\Omega \neq \Omega')}} \frac{|\langle \Omega jm | P^0 | \Omega' j' m' \rangle|^2}{A} e^{-\frac{W_{\Omega j}^0}{kT}}$$

where now $B = \frac{N}{\sum_{\Omega jm} e^{-\frac{W_{\Omega j}^0}{kT}}}$

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But summation over Ω_{jm} and Ω' each embraces only the values $\frac{1}{2}, \frac{3}{2}$. The index j may be identified with the molecular rotational quantum number J , while m is the component of J parallel to the field.

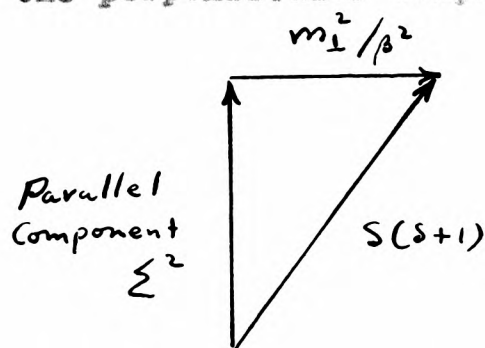
Changes in Ω are identified kinematically with precessions about the axis of figure, and so appear only as a perpendicular component of moment. Thus the first and second terms respectively refer to the parallel and perpendicular components of moment. Thus:

$$\begin{aligned} \sum_{j'm'} |\langle \Omega_{jm} | P^0 | \Omega'_{j'm'} \rangle|^2 &= m_{\parallel}^2 \\ &= (\Lambda + 2\xi)^2 \beta^2 = (1 \pm 1)^2 \beta^2 \end{aligned} \quad (a)$$

Similarly

$$\begin{aligned} \sum_{\Omega'_{j'm'}} |\langle \Omega_{jm} | P^0 | \Omega'_{j'm'} \rangle|^2 &= m_{\perp}^2 \\ &= 4 [S(S+1) - \xi^2] \beta^2 \\ &= 2\beta^2 \end{aligned} \quad (b)$$

where $m_{\perp}^2$ is the perpendicular component of purely spin moment.



$$\text{Now } W(\frac{3}{2}, j) \doteq W(\frac{1}{2}, j) + A \quad \text{and (a) and (b)}$$

are independent of j, m , so the sum over j, m , is a common factor which can be cancelled from the numerator and denominator.

Thus:

$$\chi = \frac{B}{3KT} (1+1) \beta^2 e^{-A/KT} + \frac{2B}{3} \frac{2\beta^2}{A} e^{-A/KT}$$

$$\text{Now } \eta^2 = \frac{3KT \chi}{N\beta^2}$$

$$\therefore \eta^2 = \frac{4 \left[1 - e^{-A/KT} + \frac{A}{KT} e^{-A/KT} \right]}{\frac{A}{KT} + \frac{A}{KT} e^{-A/KT}}$$

III. RESULTS:

Measurements were made of the susceptibility of this clathrate from 300°K to 10°K using the Sucksmith balance. A 1 m.m. ball bearing rider was used in conjunction with the photocell detector. Above 150°K the deflection caused by the ball bearing was greater than that which the maximum magnet current would produce. We therefore assumed that the deflection of the galvanometer was linear in the deflection of the light beam.

This was checked by observing the maximum galvanometer deflection the magnet would produce with the ball bearing lifted and with it resting on the balance. When the windows of the balance case were dried by a stream of warm air there was no difference between such readings, and we therefore assume linearity.

IX.8

The susceptibility was measured absolutely at 293°K by comparing it with two standard specimens of $\text{Mn}(\text{NH})_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. The standards were of different sizes, but both were slightly smaller than the clathrate. Their susceptibilities were 30 x greater. Because they were smaller, part of the clathrate was in a weaker field than the standard and we will obtain too small a value of the susceptibility.

The specific susceptibility of quinol has been given in emu/gram as:

0.586×10^{-6}	Palacios and Poz, Anal. fis. quim., 1935, 33, 627.
0.604×10^{-6}	French, Trans-Paraday Soc., 1945, 41, 676.
0.588×10^{-6}	Mikhail and Baddar, J. Chem. Soc., 1944, 590.

The specific susceptibility of gaseous nitric oxide has been given as

47.7×10^{-6}	Burris and Hause, J. Chem. Phys., 1943, 11, 442.
49.2×10^{-6}	Bauer, Weiss and Pickard, Compt. rend., 1918, 167, 484.
49.3×10^{-6}	Sone, Sci Rep. Tohoku Univ., 1922, 11, 139.
48.3×10^{-6}	Van Vleck (calculated) 1932.

Evans and Richards (1952) find 51.4×10^{-6} for the NO in the clathrate at 50% filling.

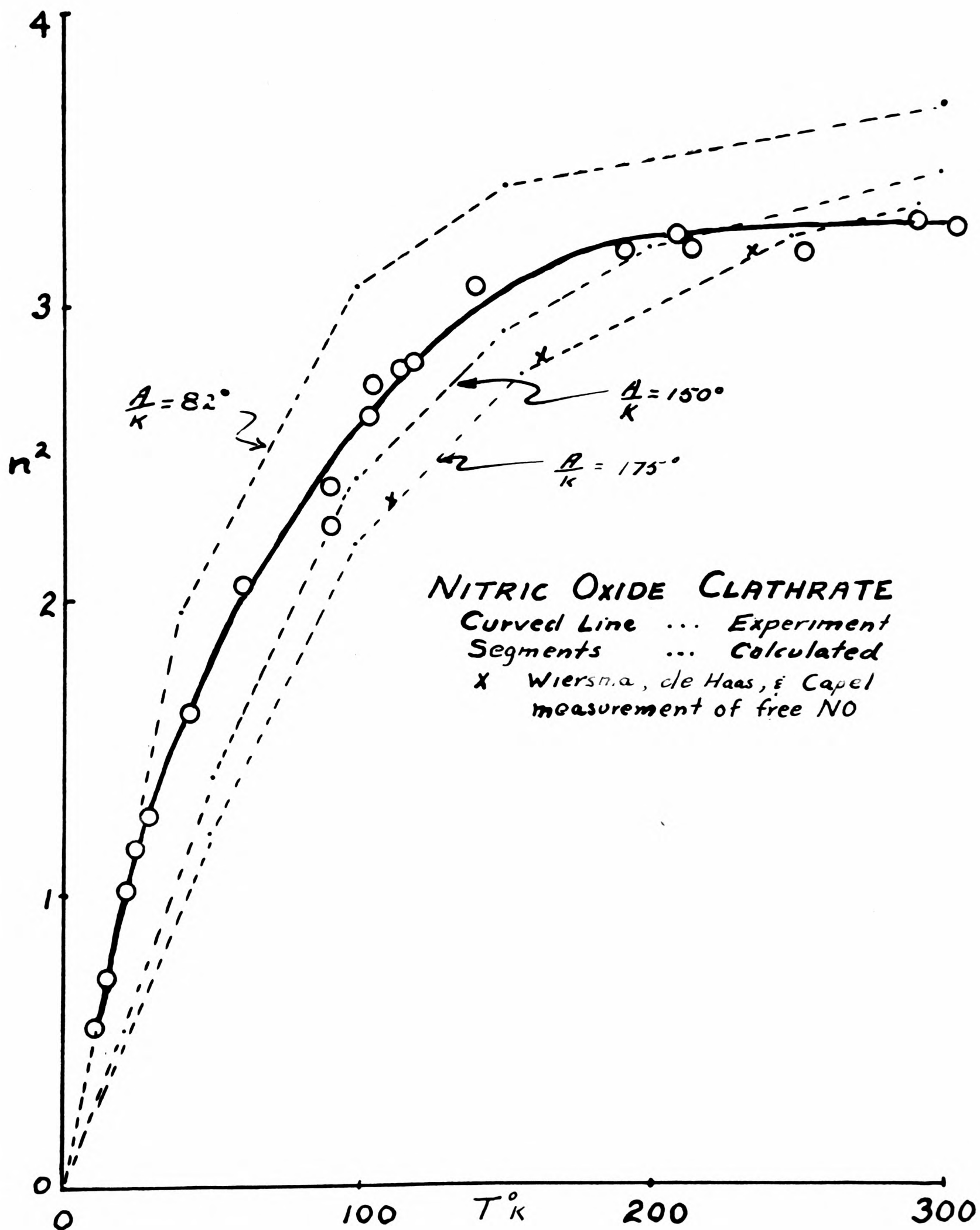
By measuring the diamagnetism of the perspex mount, calculating the diamagnetic correction for the quinol from -6.60×10^{-6} , and using the analysis made by Evans of our sample as 38.5% filled, we obtained a specific susceptibility of 45×10^{-6} and of 47×10^{-6} emu/gram from two measurements.

We may conclude that at room temperatures the susceptibility of nitric oxide in a quinol clathrate has very nearly the same value as does the free gas.

The analysis was performed by taking 0.11 grams of the 0.50 grams of clathrate and dissolving it. The gas evolved was collected and its weight calculated. As we have noted there was a pressure of NO within the sealed glass specimen container, so that some of the NO which we measured must have escaped. Nevertheless our measurement is in good agreement with theory, and in as good agreement with measured values as are those of Evans, for free NO.

In order to make a comparison with theory figure 1 has been drawn with our experimental results normalized, to a value of $X_{NO} = 47.0$ at 293° K. It includes the results of three different experiments covering overlapping ranges of temperature upon the same specimen. Experiments giving the same qualitative behaviour were also

Figure 1



IX.10.

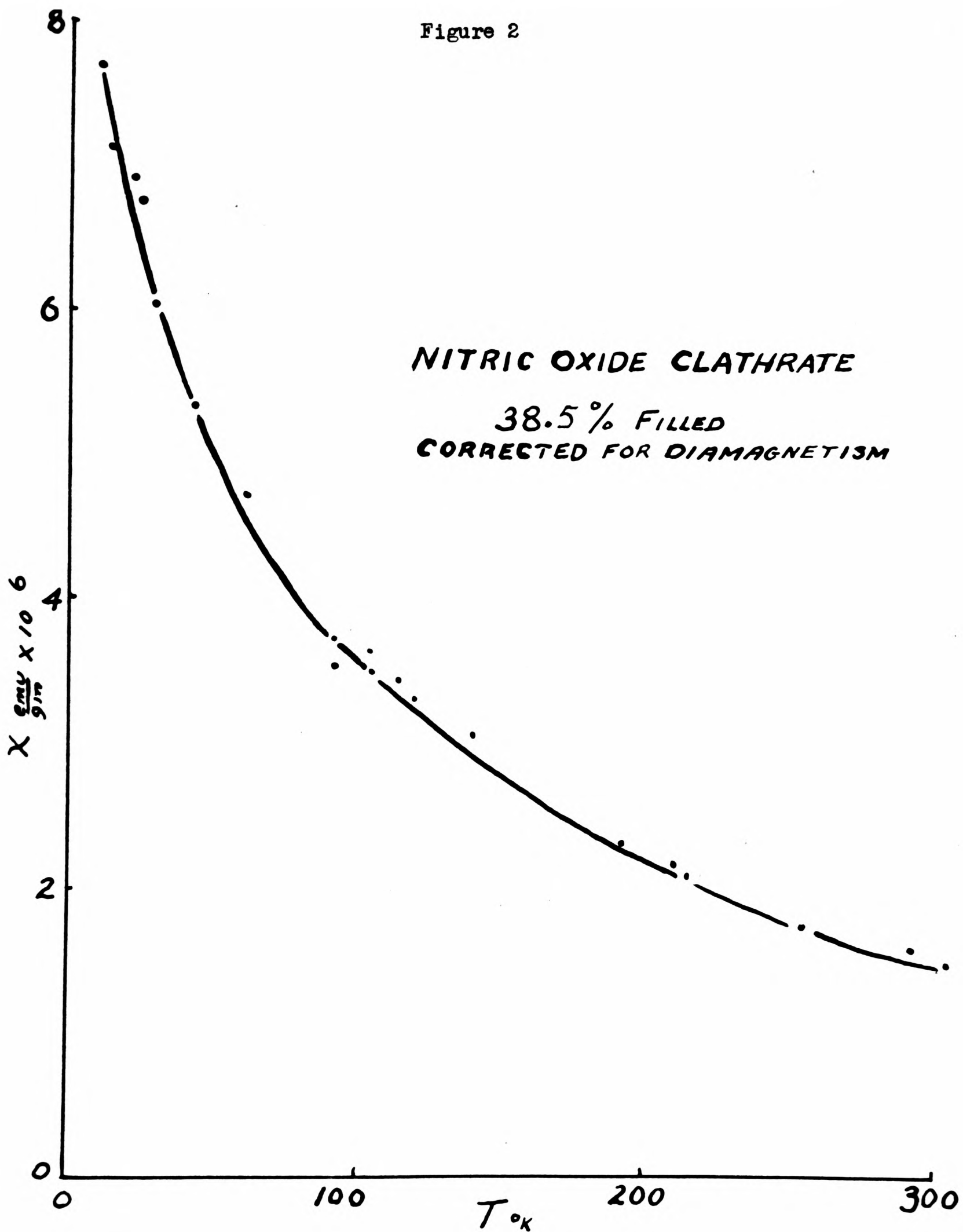
performed upon another specimen (which broke in the balance) at 293°K , 90.3°K and at 20.4°K . Unfortunately the complete experiment involves destruction of part of the specimen in the analysis and the contamination of the remainder by water vapour from the air. This liberates NO_2 which attacks the quinol lattice, and quickly destroys the specimen.

The final results are shown in figure 1 and figure 2, and are tabulated in table 1. Figure 1 shows n^2 as a function of temperature. This plot is the most sensitive way of exhibiting the departure from Curie's law. The theoretical values are plotted for different values of the doublet separation $\frac{A}{K}$. We have shown them as line segments in order to identify the experimental points more clearly. Obviously none of the calculated curves is a very good approximation at both high and low temperatures. The susceptibility is generally larger at any given temperature than theory predicts.

No simple assumption of a changed doublet splitting will fit a calculated curve to the observed curve, but relatively small changes in the diamagnetic correction would alter the shape greatly at high temperatures.

Figure 2 shows the susceptibility per gram of clathrate as a function of temperature. The curvature of the points near the oxygen and hydrogen fixed points indicates

Figure 2



IX.11

that there was some departure from thermal equilibrium. However the fixed points in Figure 1 show that n^2 is certainly falling with temperature. One of the oxygen points lies rather far off the curve, and we attribute this to the weight of the oxygen causing the whole apparatus to sag so that the specimen moved into a smaller field gradient. This points to a serious fault in the construction of the balance. The balance and magnet mounting should have been designed for much greater rigidity.

The departure from thermal equilibrium can probably be traced to the use of a glass rather than copper specimen case. On the other hand, we may simply be pushing the sensitivity of the balance too hard. The susceptibility of the 0.5 gram specimen never became greater than 7×10^6 emu/gram, and the diamagnetic susceptibility of the clathrate and perspex mount was 0.66×10^{-6} emu/gram. We were measuring only 0.02 grams of NO as compared with the 0.5 gram of paramagnetic for which the balance was designed.

The oxygen clathrate has been measured by Cooke, Wolf and Meyer (unpublished) between 20°K and 1°K , where its specific heat and susceptibility vary as would be expected from free oxygen, i.e. they become temperature

CHAPTER IX Table 1

Nitric Oxide Clathrate

38.5% Filled

X is in emu per gram of clathrate corrected for diamagnetism
is per gram molecular weight of Nitric Oxide

T	$\frac{1}{T}$	X	$\frac{1}{X}$	n^2
305	0.00333	1.49×10^{-6}	0.671×10^6	3.23
293	341	1.58	0.632	3.30
255	370	1.76	0.566	3.20
215	465	2.10	0.476	3.21
210	475	2.19	0.456	3.26
192	521	2.31	0.433	3.20
140	714	3.09	0.323	3.08
120	834	3.30	0.303	2.82
115	870	3.43	0.291	2.80
105	954	3.51	0.284	2.63
		3.66	0.273	2.74
90.3	 0.0111	3.53	0.283	2.26
		3.73	0.268	2.39
60.6	165	4.75	0.210	2.05
42.5	235	5.33	0.187	1.62
29.4	340	6.01	0.166	1.26
24.3	410	6.71	0.149	1.16
20.4	490	6.94	0.144	1.02
14	714	7.11	0.141	0.71
10	 0.1	7.75	0.129	0.55

independent at low enough temperatures. As in the nitric oxide clathrate, however, the temperature at which this occurs is associated with a smaller splitting of the energy levels than is observed spectroscopically in free O_2 . By 20°K the oxygen clathrate is obeying Curie's law very accurately. Its susceptibility has been measured at room temperature by Dr. Evans and found to be very nearly that of free oxygen. Measurements of the specific heat of an argon clathrate have been made by Poulter (unpublished) and show the argon to have the same specific heat as the free gas.

We conclude, therefore, that the available evidence points to a rather small interaction apparent only at low temperatures between the quinol lattice and the trapped molecules. It would be very helpful if paramagnetic resonance could be detected in a clathrate.

Appendix 1

Matrix Elements

$$\langle m | J_+ | m+1 \rangle = \langle m+1 | J_- | m \rangle = \sqrt{(J+1)(J+1) - m(m+1)}$$

$$\langle m | J_y | m+1 \rangle = -\langle m+1 | J_y | m \rangle = \frac{1}{2} \sqrt{(J+1)(J+1) - m(m+1)}$$

For $L = 3$ $|3\rangle$ $|2\rangle$ $|1\rangle$ $|0\rangle$ $|-1\rangle$ $|-2\rangle$ $|-3\rangle$

$$L_z = \begin{array}{c|ccccccc} \langle 3| & & & & & & & \\ \langle 2| & & & & & & & \\ \langle 1| & & & 1 & & & & \\ \langle 0| & & & & 0 & & & \\ \langle -1| & & & & & -1 & & \\ \langle -2| & & & & & & -2 & \\ \langle -3| & & & & & & & -3 \end{array}$$

$$L_x = \begin{array}{c|cccc} & & \frac{\sqrt{6}}{2} & & \\ \frac{\sqrt{6}}{2} & & & \frac{\sqrt{10}}{2} & \\ & \frac{\sqrt{10}}{2} & & & \sqrt{3} \\ & & \sqrt{3} & & 0 \end{array}$$

$$L_y = \begin{array}{c|cccc} & & -\frac{i\sqrt{6}}{2} & & \\ \frac{i\sqrt{6}}{2} & & & -\frac{i\sqrt{10}}{2} & \\ & \frac{i\sqrt{10}}{2} & & & -i\sqrt{3} \\ & & i\sqrt{3} & & 0 \end{array}$$

REFERENCES

- Abragam, A., and Pryce, M. H. L., Proc. Roy. Soc., A, 206,
173, 1951.
- Bagguley, D. M. S., and Griffiths, J. H. E., Proc. Phys. Soc.,
A, 43, 1369, 1950.
- Becquerel, J., de Haas, W. J., and van den Handel, J.,
Physica, 5, 857, 1935
5, 173, 1938
5, 753, 1938
Proc. K. A. cad. Wet. Amst., 34,
1231, 1931.
- Becquerel, J. and Opechowski, W., Physica, 6, 1039, 1939.
- Bethe, H. A., Ann. Phys. L., 133, 3, 1929.
- Bleaney, B., Phil Mag., 7, 42, 441, 1951.
- Bleaney, B., Scovil, H. E. D., Trenam, R. S., and Elliott,
R. J., Phil Mag, 42, 1068, 1951.
- Bleaney, B., and Ingram, D. J. E., Proc. Roy, Soc., A,
205, 1951.
- Bleaney, B., and Scovil, H. E. D., Proc., Phys. Soc., A, 43,
1369, 1950.
- Bleaney, B., Scovil, H. E. D., and Trenam, R. S., Phil. Mag.,
7, 43, 1952.
- Bleaney, B., and Stevens, K. W. H., Reports on Prog. Phys.,
16, 108, 1953.
- Blitz, W., Z. A norg. Allgem. Chem., 170, 161, 1928.

- Bogle, G. S., Thesis, Oxford, 1951.
- Bogle, G. S., Cooke, A. H., and Whitley, S., Proc. Phys. Soc.,
A, 64, 931, 1951.
- Bogle, G. S., Duffus, H. J., and Scovil, H. E. D., Proc. Phys.
Soc, A, 65, 760, 1952.
- Cooke, A. H., Duffus, H. J. and Wolf, W. P., Phil Mag,, 44,
623, 1953.
- Casimir, H. B. G., Bijl, D., and Du Pre, F. K., Physica,
8, 449, 1941.
- Condon, E. V., and Shortley, G. H., The Theory of Atomic
Spectra, Cambridge, 1951.
- Daniels, J. M. and Robinson, F. N. H., Phil Mag, 44, 623,
1953.
- Elliott, R. J., Thesis, Oxford, 1952.
- Elliott, R. J., and Stevens, K. W. H., Proc. Roy. Soc., A,
215, 437, 1952.
219, 387, 1953.
- Evans, D. F., and Richards, R. E., J. Chem. Soc., 631,
3295, 1952.
- Eyring, H., Walter, J., and Kimball, Quantum Chemistry,
John Wiley, New York, 1944.

Feraday, R. A., and Wiersma, E. C., *Physica*, 2, 575, 1935.

Fermi, N., *Z. S. Phys.*, 60, 320, 1930.

Groth, P., *Chemische, Krystallographie*, 2, 156, 1908.

Hemholz, J. *Amer. Chem. Soc.*, 61, 1544, 1939.

Hund, F., *Z. S. Phys.*, 36, 657, 1926.

Inghram, M. G., Hayden, R. J., and Hess, Jr., D. C., *Phys. Rev.*,
73, 180, 1948.

Jackson, L. C., *Proc. Roy. Soc., A*, 140, 695, 1933.

Jahn, H. A., and Teller, E., *Proc. Roy. Soc., A*, 161, 220, 1937.

Jenkins, Barton and Mulliken, *Phys. Rev.*, 30, 150, 1927.

Kittel, and Abraham, *Phys Rev* 1953

Kopferman, H., *Kernmomente*, Leipzig, 1940.

Kotani, M., *J. Phys. Soc., Japan*, 4, 4, 1949.

Kramers, H. A., *Proc. Amst. Acad. Sci.*, 33, 959, 1930.

Krishnan, K. S., and Mookherji, A., *Phil. Trans. Roy. Soc.*,
A, 237, 135, 1938.

Lang, R. J., *Canad. J. Res.*, 14, 127, 1936.

Mookherji, A., *Ind. J. Phys.*, 23, 5, 1949.

" 7 "

" 9 "

" 10 "

Powell, T., J. Chem. Soc., 815, 1948.

Pryce, M. H. L., Proc. Phys. Soc., A, 63, 25, 1950.

Ray, P., and Bhar, H., J. Ind. Chem. Soc., 5, 497, 1928.

Rose, M. E., Phys. Rev., 53, 392, 1938.

Satten, R. A., J. Chem. Phys., 21, 4, 1953.

Scovil, H. E. D., Thesis, Oxford, 1951.

Scovil, H. E. D., Proc. Phys. Soc., A, 64, 933, 1951.

Scovil, H. E. D., and Stevens, K. W. H., Proc. Phys. Soc.,
A, 65, 954, 1952.

Stevens, K. W. H., and Pryce, M. H. L., Proc. Phys. Soc., A,
63, 36, 1950.

Sucksmith, W., Phil. Mag., 158, 1929.

Szego, L., and Ostinelli, P., Gazz. Chim. Ital, 60, 946, 1930.

Trenam, R. S., Thesis, Oxford, 1953.

van den Handel, J., Physica, 9, 225, 1942.

Van Vleck, J. H., Theory of Electric and Magnetic Susceptibilities,

Oxford Univ. Press, 1932.

Phys. Rev., 426, 57, 1940.

74, 1168, 1948.

J. Chem. Soc., 3, 807, 1935.