

AN EXPERIMENTAL INVESTIGATION  
OF THE  
MAGNETIC PROPERTIES OF CRYSTALLINE POWDERS  
WITH REFERENCE TO THE DEPENDENCE OF SUSCEPTIBILITY  
ON CRYSTAL SIZE

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ABSTRACT

A method is described by means of which it is possible to measure the magnetic susceptibility of suspensions of finely divided graphite as single crystals. According to this method, the principal susceptibilities of graphite are

$$\chi_{\perp} \quad 0.44 \times 10^{-6}$$

$$\chi_{\parallel} \quad 13.35 \times 10^{-6}$$

As reported by other observers, the mean susceptibility is found to decrease with decreasing particle size. The decrease of susceptibility is accompanied by a proportionate decrease in the magnetic anisotropy  $\frac{\chi_{\parallel}}{\chi_{\perp}}$ . At low temperatures, the phenomenon remains qualitatively unchanged; no displacement of the critical size is observed.

Measurements on paramagnetic  $\text{MnO}_2$  show no variation of susceptibility with particle size. A slight decrease of susceptibility with decreasing particle size is found in the case of paramagnetic  $\text{Cr}_2\text{O}_3$ , although here the effect may be spurious. Experiments of a provisional nature would indicate that the susceptibilities of substances whose magnetic properties are intermediate between those of paramagnetics and ferromagnetics decrease rapidly with decreasing particle size when a critical diameter of particle of approximately  $3\mu$  is reached.

## I. Introduction.

The first successful explanation of the phenomena of paramagnetism and diamagnetism was given in 1905 by Langevin<sup>1)</sup>, on the basis of the assumption that the atoms consisted of positive and negative charges rotating in fixed orbits. These rotating charges would cause a certain permanent magnetic moment to be associated with each atom or molecule, and with the application of a magnetic field, these moments would tend to align themselves parallel to the field, being resisted only by the thermal agitation of the molecules. Since the induced field would strengthen the original field, this effect would result in the case of paramagnetism. By a statistical calculation of the equilibrium between thermal agitation and the directing tendency of the applied field, Langevin derived for the paramagnetic susceptibility

$$\chi = \frac{N\mu}{H} \left( \coth \frac{\mu H}{kT} - \frac{kT}{\mu H} \right) \quad (1)$$

where  $N$  is the number of molecules per  $\text{cm}^3$ ,  $\mu$  the magnetic moment associated with each molecule,  $T$  the absolute temperature,  $H$  the applied field, and  $k$  Boltzmann's constant. In order to obtain now the property of diamagnetism, Langevin considered the induced rather than the permanent magnetic moment of the molecule. Since the rotating charges may be considered as currents flowing in circuits undamped by resistance, an applied field will affect the motions of the charges in such a way as to induce a field opposing the applied field (Lenz's law), thus giving the property of diamagnetism. For the susceptibility, Langevin deduced the expression:

$$\chi = -\frac{Ne^2}{6mc^2} \sum \overline{r^2} \quad (2)$$

where  $N$  is the number of molecules per  $\text{cm}^3$ ,  $e$  the charge on the electron,  $c$  the velocity of light, and  $\sum \overline{r^2}$  the summation of the time average of all electron orbits for a single molecule. It is then obvious (on the basis of Langevin's theory), that diamagnetism is a property common to all substances, while paramagnetism is present only if the atom or molecule has a permanent magnetic moment (i.e. a resultant moment different from zero), in which case the diamagnetic effect is outweighed.<sup>o</sup>

Langevin's expressions for magnetic susceptibilities corresponded very well with the known experimental facts. If equation (1) is expanded for the case  $\frac{MH}{kT} \ll 1$ , there results

$$\chi = \frac{NM^2}{kT}$$

an expression which had been published by Curie<sup>4</sup> in 1895 as an experimental law governing many paramagnetic substances. From equation (2) it may be seen that  $\chi$  should be independent of temperature for diamagnetics, a fact also observed experimentally by Curie. Furthermore, the values of  $r$  derived from susceptibilities by means of equation (2) agreed nicely with such determinations by other methods.

In spite of the general success of the Langevin theory<sup>oo</sup>, exceptions are extremely numerous, particularly in the case of solids. The reason for this is apparent, however, when one considers that

<sup>o</sup>Such a result was also intimated much earlier by Weber and Maxwell, although much less precisely and without the knowledge of the electronic structure of matter which was available to Langevin.

<sup>oo</sup>Modifications of the simple Langevin theory, as introduced by quantum mechanics, need not be discussed here.

equations (1) and (2) have been derived on the basis that the atoms are completely free, and thus should be rigorously valid for gases, approximately so for liquids, while only in special cases might one assume that the forces of interaction between atoms in the solid state could be neglected. That the effect of forces of interaction between atoms in solid bodies is not necessarily of secondary importance in the determination of the magnetic properties of solids will be evident from the experimental facts presented below.

The element carbon, which in its three allotropic modifications exhibits an amazing range of physical properties, offers a striking example of the influence of configuration of the atoms in the solid state on the magnetic susceptibility. Amorphous carbon exhibits a diamagnetic susceptibility corresponding to that which would be expected from measurements on free atoms (as in gaseous compounds), diamond has a value differing only slightly from this, but graphite, in the direction parallel to its hexagonal axis (0001), is more than twenty-five times as diamagnetic as either diamond or amorphous carbon. Table 1 gives the susceptibility values for carbon in its three modifications, as well as for bismuth and antimony, which like graphite are abnormally diamagnetic. That the high susceptibilities of these substances are properties of the arrangement of their atoms in the solid state is further shown by the behaviour of bismuth and antimony at the melting point, where a sharp discontinuity of the susceptibility occurs, such that the values assumed by the liquids are those calculated from their atomic configurations. Fig. 1 represents graphically some typical measurements by Honda<sup>3)</sup>, Endo<sup>4)</sup>, and Webster<sup>5)</sup> on the susceptibilities of

\*X-ray analysis shows that "amorphous" carbon very probably has the crystal structure of graphite.

Table 1

Susceptibilities of anomalous diamagnetics

Substance	$-\chi \times 10^6$ observed	$-\chi \times 10^6$ calculated for free atoms approximately
Carbon		
amorphous	0.35-0.48 )	
diamond	0.495 )	
graphite	4.65 )	0.4
hexagonal axis	0.4 )	
hexagonal axis	13.4 )	
Bismuth	1.4	0.5
Antimony	0.6	0.1

-----

various metals above and below their melting points. One sees from this that although only in bismuth and antimony is the change at the melting point of great magnitude, it is definitely present for the other substances investigated. In the case of tin, the paramagnetism of the solid disappears at the melting point, and the liquid is diamagnetic. Although tin is the only paramagnetic substance investigated at the melting point, there are numerous examples in which paramagnetic solids may exist in various modifications possessing different magnetic properties. Thus gray tin is diamagnetic, white tin is paramagnetic, and ferric oxide ( $\text{Fe}_2\text{O}_3$ ) may exist in a ferromagnetic modification as well as in the normal paramagnetic form.

Further evidence to support the view that magnetism in the solid state is as much a crystalline property as an atomic property is furnished by the work of Lowance and Constant<sup>6)</sup> on the effect of cold working on susceptibility. For the metals investigated by them

\*Cf. also work by Bitter, Honda and Shimizu, and Banta. See Handbuch der Metallphysik, I, p. 270.

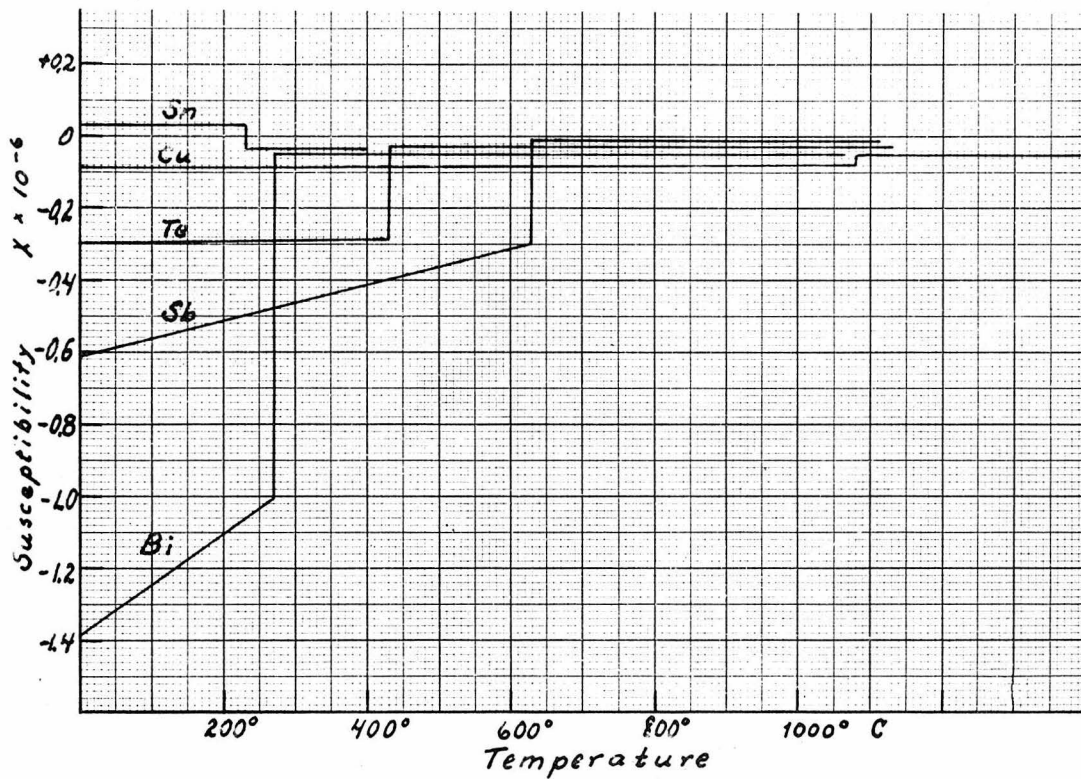


Figure 1.

Change of magnetic susceptibility at the melting point



(Pt, Ag, Bi, Cu), it was found that any form of cold working caused an increase in the permeability, that is, the susceptibility of diamagnetics was decreased, that of paramagnetics was increased. The normal value could then be restored by annealing.

Let us turn now to another set of experiments which promise to do much to clarify the problem of magnetism of solids. The investigations referred to are those of Vaidyanthan<sup>7)</sup>, Rao<sup>8,9,10)</sup>, Mathur and Varma<sup>11)</sup>, and Paramasivan<sup>12)</sup>, who found in measurements on susceptibilities of several substances in a finely divided state a critical size of particle below which the susceptibility decreased rapidly from the value for the substance in bulk, bending toward that found for the amorphous (or liquid) state. The substances first investigated were the diamagnetics of abnormally high susceptibility, graphite, bismuth, and antimony.<sup>9</sup> The results are presented graphically in fig. 2. Since such a phenomenon might easily be caused by surface effects such as the formation of the feebly diamagnetic oxides in the case of bismuth and antimony, or the adsorption of paramagnetic oxygen in the case of graphite, this point was carefully investigated. Thus measurements on bismuth were made taking special precautions to free the original material from oxide, and to prevent subsequent oxidation (cf fig. 2). With this treatment, the effect is still present; indeed, the decrease in susceptibility has become much more abrupt, so that the decrease can no longer be attributed to an increase in the ratio of surface to volume with decreasing particle size. More recent investigations on tin (paramagnetic) (fig. 2) and nickel (ferromagnetic) (table 2) show a similar behavior

<sup>9</sup>Similar results were later obtained for graphite, Bi, and Sb, by Goetz and Faessler<sup>13)</sup>.

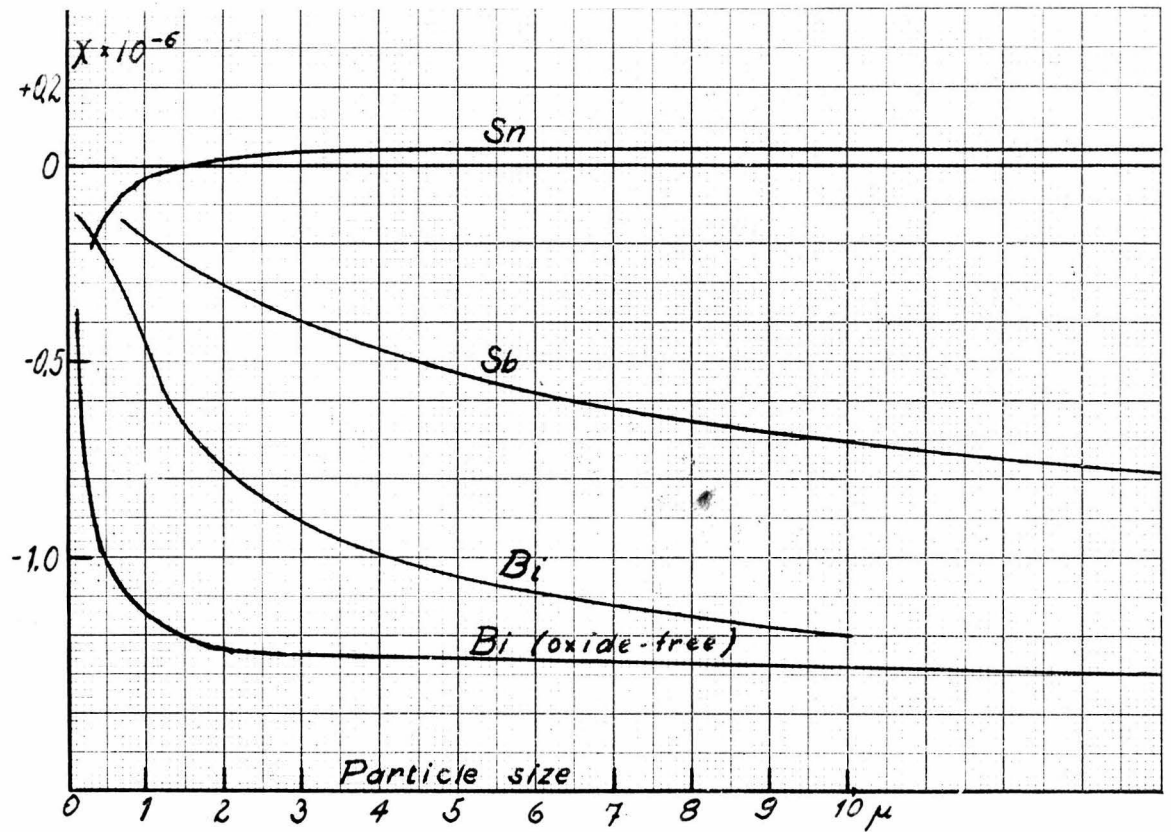


Figure 2.

Dependence of magnetic susceptibility on particle size

Table 2

Magnetisation of Ni particles

Range of diameters of the particles $\mu$		$\frac{\sigma^\circ \text{ (particles)}}{\sigma \text{ (bulk metal)}} \times 100$	
0.8-1.0	1.1-1.5	70	82
0.8-1.1	1.2-1.7	72	85
0.8-1.2	1.5-3.0	70	95
0.9-1.4	2.0-4.0	72	98
1.0-1.5	2.5-5.0	77	97

$\sigma^\circ$  - specific intensity of magnetisation

As may be seen from fig. 2, the critical diameter of particle is approximately the same for all the substances investigated, and lies in the region from 0.5 to 2 microns. It is interesting to note that this critical size is of the same order of magnitude as the "characteristic length" associated with many crystalline phenomena according to the theory of crystal structure proposed by Zwicky<sup>14)</sup>. If the observed phenomenon should be real, it should be possible by means of such measurements to gain much interesting information concerning the nature of magnetism in the solid state as well as to throw light on the nature of the solid state itself.

\*By this is meant here "large in comparison to atomic dimensions".

## II. Purpose of the Investigation

It is the purpose of the investigations described in this thesis to extend the present knowledge of the dependence of the magnetic susceptibility of crystalline powders on particle size. The investigations have been made with three distinct aims in mind:

1. To study the behavior of the phenomenon at low temperatures.
2. To study the phenomenon in connection with crystal structure and magnetic anisotropy.
3. To investigate certain typical paramagnetic substances with reference to the existence of such an effect.

For the realisation of the first two aims, graphite was chosen as the subject of investigation, for the following reasons:

1. It is easily obtained in finely divided form.
2. The formation of oxide will not affect the measurements.
3. It has an enormous magnetic anisotropy.

The paramagnetic substances chosen for investigation were metallic oxides which do not follow Curie's Law. The oxides were chosen rather than the metals themselves because they are more easily obtained in finely divided state, and because the formation of oxide on pure metals would seriously disturb any measurements.

### III. Experimental Procedure

#### 1. Preparation of specimens for measurement

In the experiments of Rao and his collaborators described in the preceding chapter, the powers were measured in compact form. In this investigation, however, the powders to be measured were suspended in a suitable medium (eg. gelatine) which becomes solid at room temperature. The reason for this is the following. If each particle of a powder is a single crystal, which is generally the case if the particles are small enough (less than  $5\mu$  in diameter), then the susceptibility of the powder can be measured with respect to the various axes of the crystal, in case that the substance investigated is magnetically anisotropic. The method for doing this, due to Faessler<sup>13)</sup>, consists in directing the particles in suspension in a magnetic field while the suspending medium is liquid, and then allowing the medium to solidify.

Graphite, which was used in this investigation, has a high diamagnetic susceptibility parallel to the hexagonal (0001) axis of the crystal, and a low susceptibility in all directions normal to this axis. If a suspension of graphite crystals is placed in a homogeneous field, the field will exert an orienting couple on the individual particles, which will direct themselves so that the hexagonal axes are directed perpendicular to the direction of the field, i.e., at random in the plane normal to the field. If the suspension is now rotated through an angle of  $90^\circ$  in a plane parallel to the direction of the field, a further orienting couple will be exerted tending to align all the hexagonal axes parallel to the axis of

rotation of the suspension and hence parallel to one another. That this process actually takes place as described, may be observed visually under the microscope, because of the flake-like shape of the graphite crystal. See fig. 6, section IV. This procedure has the effect of producing an "artificial single crystal", and the suspensions may then be measured as single crystals. Thus in the case of graphite or other anisotropic substances, the phenomenon of size dependence of susceptibility can be studied in connection with the crystal structure. In addition, this procedure provides a means whereby magnetic anisotropy may be studied in those cases where the preparation of single crystals suitable for measurement is unfeasible.

In the experiments of Faessler, gelatine was found to be the most suitable suspending medium.\* Since in the present case experiments at low temperatures were planned, gelatine could no longer be used, and after considerable experimentation the most suitable medium for this purpose was found to be a petroleum jelly composed of 75% mineral oil and 25% paraffin with a melting point of approximately 35° C.

The substances to be measured were ground together with the petroleum jelly in an agate mortar until the desired degree of fineness was attained. The resulting solid suspension was then dissolved in benzene or carbon tetrachloride, and the particles were separated according to size by means of successive settling. By evaporating the solvent, the desired suspension was obtained.

A portion of each suspension was then weighed, dissolved in benzene, and centrifuged. The sediment was carefully washed with benzene and weighed. From this data, together with the density of the petroleum jelly, the concentration of the suspended substance

\*It must be isotropic and non-crystalline.

could be determined. Those portions of the suspension to be investigated magnetically were put into brass tubes of the following dimensions.

Length	65 mm
Outside diameter	5 mm
Wall thickness	0.005 mm
Cross section	0.1925 cm <sup>2</sup>
Effective volume	1.30 cm <sup>3</sup>
Approximate weight	750 gm.

In order that the tubes be seamless, they were turned from heavy brass tubing. The ends were of brass, soldered to the cylinder.

The sizes of the particles in the suspensions was determined either by direct microscopic observation with a micrometer eyepiece, or from measurements of microphotographs.

## 2. Measurement of susceptibilities

There are two methods commonly used for measuring the small magnetic susceptibilities of diamagnetic and paramagnetic solids, the Faraday-Curie method and the Gouy method. In both methods the force experienced by a body in an inhomogeneous magnetic field is measured, and the susceptibility is determined from the following relation, valid at every point of the body

$$F_x = \kappa H \frac{\partial H}{\partial x} \circ$$

in which  $\kappa$  is the susceptibility,  $H$  the field strength,  $\frac{\partial H}{\partial x}$  the field gradient, and  $F_x$  the force in the direction of the gradient.

<sup>o</sup>This relation is given here in simplified form. A treatment of the general theory of the method is given in section 3.

The difference in the two methods lies in the placing of the sample in the field. In the Faraday-Curie method the specimen to be measured is chosen small enough so that  $H$  and  $\frac{\partial H}{\partial x}$  (or their product) may be considered constant throughout the body. The susceptibility is then determined from a measurement of  $F$ ,  $H$ , and  $\frac{\partial H}{\partial x}$ . In the Gouy method the specimen to be measured is made of uniform cross-section and is placed in the field in such a way that both ends are in known uniform fields (e.g.  $H_0$  and  $0$ ). The susceptibility is then determined from the integrated form of equation (1)<sup>o</sup>. by measuring  $F$  and  $H_0$ . The essential difference between the two methods is that the latter does not permit a quantitative investigation of the dependence of susceptibility on field strength, since it gives an average over all fields from zero to the maximum used.

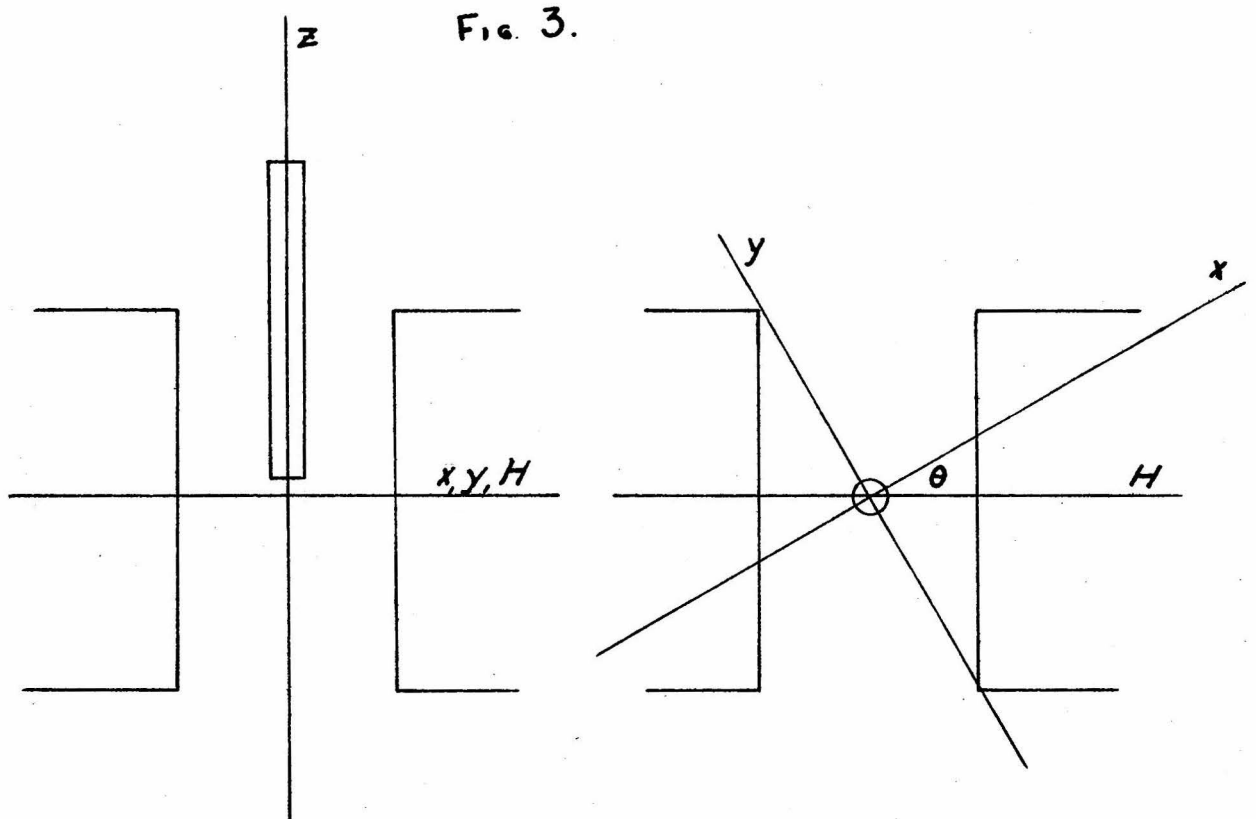
Of these two methods, that of Gouy was chosen for the present investigation for two reasons. In the first place, with the low concentration of the suspensions, the samples must be fairly large in order that the forces be large enough to be accurately measured. In the second place, the measurement of anisotropy is generally more convenient in this method than in that of Faraday-Curie. The chief requirement of the method, namely, uniform cross-section of the specimen, is sufficiently satisfied by the brass capsules described in section 1.

<sup>o</sup>See section 3.



## 2. Theory of the method.

Let a cylindrical body with principal susceptibilities  $\kappa_1, \kappa_2, \kappa_3$  be placed in a magnetic field as in fig. 3. Let the



coordinate system be chosen so that the z axis is parallel to the length of the body, and the x axis makes an angle  $\theta$  with the magnetic field. If the diameter of the body is small compared to that of the pole pieces, the following relations are valid at every point of the body:

$$H_x = H \cos \theta, H_y = H \sin \theta, H_z = 0 \quad (1)$$

also

$$\frac{\partial H_x}{\partial x} = \frac{\partial H_y}{\partial y} = \frac{\partial H_x}{\partial y} = \frac{\partial H_y}{\partial x} = \frac{\partial H_z}{\partial x} = \frac{\partial H_z}{\partial y} = \frac{\partial H_z}{\partial z} = 0 \quad (2)$$

The energy of a magnetic field in an anisotropic medium is given by

$$E = \frac{1}{8\pi} (\mu_x H_x^2 + \mu_y H_y^2 + \mu_z H_z^2) \quad (\mu = \text{permeability})$$

or

(3)

$$E = \frac{1}{8\pi} (H_x^2 + H_y^2 + H_z^2) + \frac{1}{2} (\kappa_x H_x^2 + \kappa_y H_y^2 + \kappa_z H_z^2)$$

$\kappa$ : susceptibility, since  $\mu = 1 + 4\pi\kappa$ .

If we consider that the body is suspended in a medium of susceptibility  $\kappa_0$  (for example, air) the force experienced by an element of volume  $d\tau$  of the body in the field in the directions of the coordinate axes will be

$$\begin{aligned} F_x &= \frac{\partial}{\partial x} (E - E_0) d\tau \\ F_y &= \frac{\partial}{\partial y} (E - E_0) d\tau \\ F_z &= \frac{\partial}{\partial z} (E - E_0) d\tau \end{aligned} \quad (4)$$

that is:

$$\begin{aligned} F_x &= \left\{ (\kappa_x - \kappa_0) H_x \frac{\partial H_x}{\partial x} + (\kappa_y - \kappa_0) H_y \frac{\partial H_y}{\partial x} + (\kappa_z - \kappa_0) H_z \frac{\partial H_z}{\partial x} \right\} d\tau \\ F_y &= \left\{ (\kappa_x - \kappa_0) H_x \frac{\partial H_x}{\partial y} \dots \dots \dots \right\} d\tau \quad (5) \end{aligned}$$

making use of relations 1 and 2, equations (5) reduce to

$$F_x = 0$$

$$F_y = 0 \quad (6)$$

$$F_z = \left\{ (\kappa_x - \kappa_0) H_x \frac{\partial H_x}{\partial z} + (\kappa_y - \kappa_0) H_y \frac{\partial H_y}{\partial z} \right\} d\tau$$

or

$$\begin{aligned} F_z &= \left\{ (\kappa_x - \kappa_0) \cos^2 \theta + (\kappa_y - \kappa_0) \sin^2 \theta \right\} H \frac{\partial H}{\partial z} d\tau \\ &= \left\{ (\kappa_y - \kappa_0) + (\kappa_x - \kappa_y) \cos^2 \theta \right\} H \frac{\partial H}{\partial z} d\tau \end{aligned} \quad (7)$$

Equation (7) is applicable to the Faraday-Curie method of measurement of susceptibility. In the case of the Gouy method equation (7) must be integrated over the volume of the body, i.e.

$$\begin{aligned} F &= \int_V F_z d\tau \\ &= \int_V \left\{ (\kappa_y - \kappa_0) + (\kappa_x - \kappa_y) \cos^2 \theta \right\} H \frac{\partial H}{\partial z} dx dy dz \\ &= A \int_{z_0}^z \left\{ (\kappa_y - \kappa_0) + (\kappa_x - \kappa_y) \cos^2 \theta \right\} d\left(\frac{H^2}{2}\right) \end{aligned} \quad (8)$$

in which A is the area of the cylinder. If the susceptibilities are independent of field strength (8) may be readily integrated, and the result is

$$F = \left\{ (\kappa_y - \kappa_0) + (\kappa_x - \kappa_y) \cos^2 \theta \right\} \frac{(H^2 - H_0^2) A}{2} \quad (9)$$

in which H and H<sub>0</sub> are the field strengths at the ends of the body.

For an isotropic medium, this reduces to

$$F = (\kappa - \kappa_0) \frac{(H^2 - H_0^2) A}{2} \quad (10)$$

i.e. 
$$\kappa = \kappa_0 + \frac{2F}{A(H^2 - H_0^2)} \quad (11)$$

and 
$$\chi = \frac{\kappa}{\rho} = \frac{1}{\rho} \left\{ \kappa_0 + \frac{2F}{A(H^2 - H_0^2)} \right\} \quad (12)$$

$\rho$  = density

$\chi$  = specific susceptibility.

The problem of the measurement of magnetic anisotropy is greatly simplified if there is only one principal magnetic axis. This is true of graphite, in which the principal magnetic axis is parallel to the hexagonal (0001) axis of the crystal. In all directions normal to the hexagonal axis, graphite is isotropic. In this case (cf. equation (9)) the entire measurement of anisotropy can be performed by rotating the cylindrical suspension ("crystal") about its axis, if the suspension has been prepared with the hexagonal axis perpendicular to the axis of the cylindrical sample tube. Hence the suspensions described in section III, 1, were all prepared in this fashion.

#### 4. Apparatus

The arrangement of apparatus is shown in fig. 4. An aluminum suspension S replaces one of the pans of a Sartorius microbalance (sensitivity  $1.4 \times 10^{-5}$  g./scale division) B. It is equipped with

a torsion head T, so that the specimen could be rotated about a vertical axis. In the lower end of the suspension the aluminum tube is replaced by a very fine tube of nickel silver, at the end of which is a brass cylinder over which the brass capsules described in section 1 fitted snugly. The pole pieces P of the electromagnet M are flat faced, 10 cm. in diameter, and spaced 2 cm. apart. With this arrangement, a field of 10000 gauss could be produced between the pole pieces with a current of 10 amperes, the field at the lower end of the suspension being practically zero.

In order to perform measurements at various temperatures ranging from that of liquid air to room temperature, a cryostat Cr was constructed to inclose the lower end of the suspension.

The cryostat, fig. 5, consists essentially of two concentric cylinders, forming a vacuum jacket around the suspension. The outer cylinder, 2 cm. in diameter, was made of thin nickel silver sheet (0.125 mm). The inner cylinder is composed of two parts; the lower is a thick walled (2 mm) copper tube, 1 cm. in inside diameter; the upper is a thin walled nickel silver tube 2 mm in diameter. At the bottom of the cryostat can be screwed in a copper rod 6, around which is wound a coil of copper tubing 5, which opens into the space 2 inclosed by the inner cylinder. Space 1 between the two cylinders is attached to a high vacuum system and kept evacuated during low temperature measurements. The cryostat is supported by two cylindrical grooved brass pieces 3, each held by three screws to permit vertical adjustment. The position of the pole pieces is indicated by 8. In order to measure the temperature inside the cryostat, a non inductive copper resistance thermometer 4 is placed as indicated

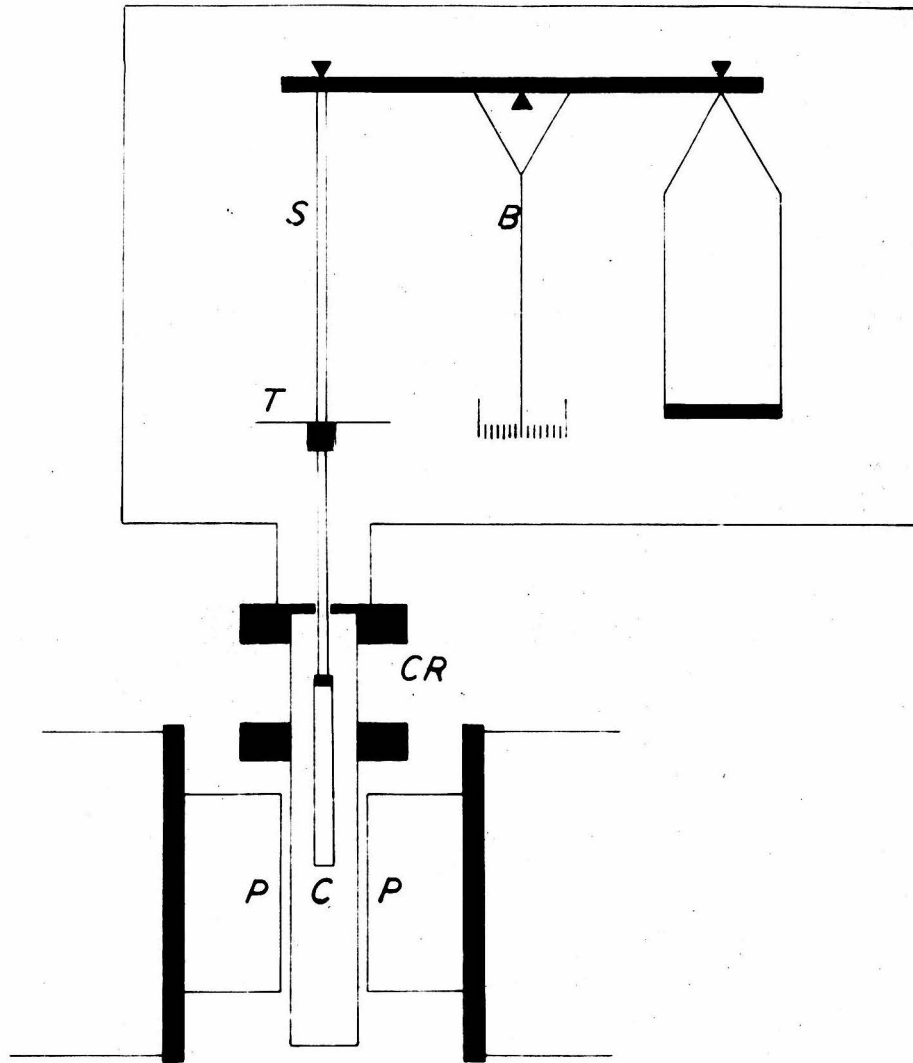


Figure 4  
Arrangement of apparatus

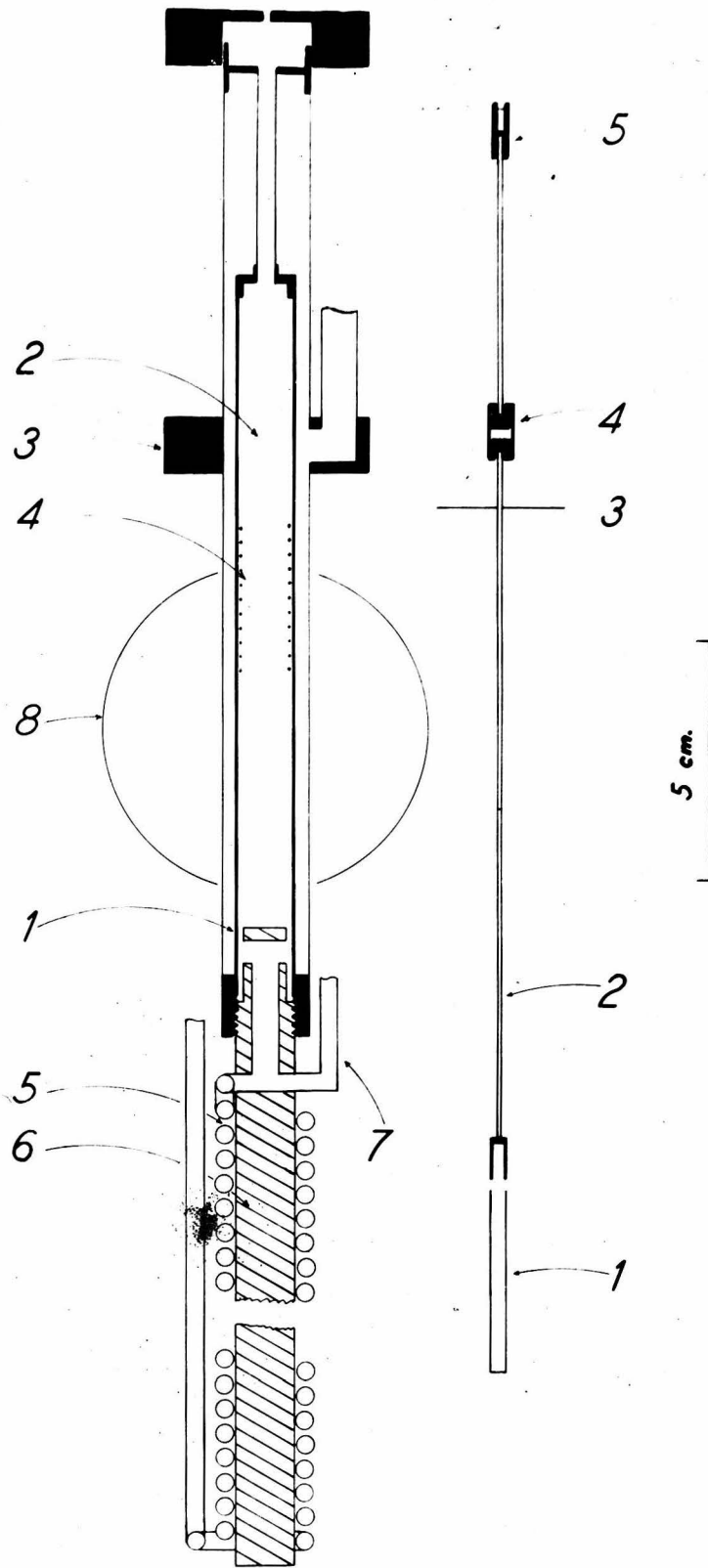


Figure 5  
Cryostat

in the figure, for which the leads are taken out through tube 7.

To cool the specimen to be measured, dry air is blown through the coil 5, which with the copper rod 6 is immersed in liquid air. When the desired temperature, as measured with the resistance thermometer, is reached, the sample is weighed with the field off. During the time of the weighing, the temperature of the sample was found to have risen by  $2^{\circ} - 3^{\circ}$ . The sample is then cooled again to the initial temperature, and weighed with the field on. In this way it was possible to make susceptibility measurements within a temperature range of approximately  $3^{\circ}$ . It was found that during the time required to make a weighing, no detectable quantity of water condensed on the suspension, although the air stream was completely stopped.

## 5. Accuracy of measurement

The method of measurement employed in the present investigation introduces numerous complications which may give rise to serious errors. A careful consideration of all sources of error is therefore essential.

### a. Measurement of force.

Since the specimens measured were suspensions of the material to be investigated in a medium of vaseline, the susceptibility must be determined from the difference of the forces exerted on the medium and on the investigated substance. Because it is usually impossible to retain a high concentration of fine particles in suspension, the



actual force to be measured was often quite small, in some cases as low as 0.1 mg. The difficulty of measuring such forces accurately has been adequately met, however, by the use of the Sartorius micro-balance. With this balance it was possible to reproduce measurements to approximately five millionths of a gram, limiting the uncertainty in the determination of the force to less than five percent. in the most unfavorable cases.

b. Measurement of density.

A reliable determination of the density of the substance in suspension is just as essential as an accurate measurement of the force. The errors which may arise in this connection are of several types. In the first place, the presence of air bubbles in the sample tube would utterly destroy the validity of any measurement. The presence of such air bubbles was easily detected, however, by a comparison of the density of the suspension in the tube with the known density. The formation of air bubbles in the process of filling the tubes was not frequent, however, because of the tendency of the oily liquid vaseline to completely moisten metal surfaces. A more serious problem is the danger of coagulation of the suspension with consequent rapid settling of the particles. In this case the susceptibility as measured would always be too low in value. It was found, however, that if a substance was once obtained completely in suspension in the liquid vaseline, there was no tendency for coagulation to occur. Furthermore, at no time was the vaseline kept liquid for more than fifteen to twenty minutes (as in filling the tubes or

or during the process of directing the particles in the field). The rate of fall of particles less than  $10\mu$  in diameter (maximum size used in this investigation) is far too slow in the highly viscous vaseline to permit appreciable settling.

## 6. Supplementary measurements

### a. Determination of field strength.

With the experimental arrangement used, it was more convenient to calibrate the magnet by means of a standard substance than to make a direct measurement of the field strength. For this purpose water, of susceptibility  $-0.72 \times 10^{-6}$  was used. One of the brass tubes was filled with water and the susceptibility was measured over the whole range of field strengths to be used in the measurements. Table 3 gives the result of this calibration.

Table 3

#### Calibration of magnet

I amp.	F <sub>c</sub> grams	$\frac{A(H_{\max}^2 - H_0^2)}{2g}$	H <sub>max</sub> gauss
1.00	-0.000213	296	1730
2.00	-0.000797	1107	3350
3.00	-0.001630	2265	4800
4.00	-0.002566	3565	6000
5.03	-0.003536	4910	7070
6.50	-0.00463	6430	8080
7.53	-0.00522	7250	8580
8.50	-0.00572	7950	8990
9.52	-0.00615	8540	9320

I - current in amperes

F<sub>c</sub> - force corrected for effect of sample tube

H<sub>max</sub> - maximum field, calculated, in gauss

b. Determination of susceptibility of petroleum jelly.

The susceptibility of the suspending medium was determined over the whole range of field strengths used. No variation of susceptibility with field strength was found.

Table 4

Susceptibility of petroleum jelly

T = 20° C

I	H	F <sub>c</sub>	$-\chi \times 10^6$
1.00	1730	-0.000213	0.718
2.00	3350	-0.000797	0.720
3.00	4800	-0.001630	0.721
4.00	6000	-0.002568	0.719
5.00	7050	-0.003523	0.720
6.00	7800	-0.004334	0.720
7.00	8360	-0.004922	0.718
8.00	8800	-0.005448	0.718
9.00	9130	-0.005917	0.719
Average susceptibility $\chi = -0.7192 \times 10^{-6}$			
T = 140° K			
6.50	8100	-0.004641	0.720
T = 105° K			
6.50	8100	-0.004643	0.721

uncorrected for susceptibility of air.

c. Correction for brass sample tubes.

The correction to be applied for the force exerted on the brass sample tubes was determined for each tube before filling with the sample. The correction to be applied did not vary greatly with the different tubes, and amounted on the average to an attraction of five hundredths of a milligram. In no case was it greater than a tenth of a milligram.

d. Measurement of temperature.

The temperature was measured with a Diesselhorst type potentiometer according to the standard procedure of the Cryogenic Laboratory of this Institute. The resistance thermometer was calibrated by measurements at  $0^{\circ}$  C,  $195^{\circ}$  K (acetone- $\text{CO}_2$ ),  $77^{\circ}$  K (boiling point of nitrogen), and  $20^{\circ}$  K (boiling point of hydrogen).

#### IV. Experimental Results

##### 1. Symbols used in tabulation of data.

H	maximum field strength in gauss.
d	diameter of particles in $\mu$ .
F	force acting on specimen in field in grams.
$\rho$	density of material in suspension in grams/cm <sup>3</sup> .
$\chi$	specific susceptibility in c.g.s. units $\times 10^6$ .
$\chi_{\perp}$	specific susceptibility perpendicular to (0001) axis in graphite.
$\chi_{\parallel}$	specific susceptibility parallel to (0001) axis in graphite.
T°K	absolute temperature.
T° C	Centigrade temperature.

##### 2. Measurements in graphite.

The graphite used in this investigation was the commercial "Aquadag", a highly concentrated aqueous suspension of finely divided graphite, manufactured by the Acheson Colloids Co. A magnetic analysis of the product showed a considerable quantity of iron to be present, which had to be removed by a thorough process of purification. In order to dissolve any silica which might inclose minute quantities of iron, the graphite was first treated for several days with cold hydrofluoric acid. The suspension, which meanwhile had coagulated from the action of the strong electrolyte, was then washed and treated with hot hydrochloric acid in a Soxhlet extraction apparatus until the washings no longer showed the presence of iron as tested by

potassium thiocyanate. The graphite was then washed, dried, and again suspended as described in section III, 1.

In connection with the preparation of "artificial single crystals" of graphite, a method has been devised whereby the orientation of the flake-like graphite crystals might be observed visually. This was done by rotating a microscope slide with a suspension of the graphite in gelatine in a magnetic field until the gelatine solidified. Fig. 6 shows a microphotograph of a slide prepared in this manner. The particle sizes represented in this figure range from  $0.4\mu$  to  $4\mu$ . In judging this photograph, it must be borne in mind that the thickness of the object is greater than the depth of focus of the microscope objective, so that only those particles which are in focus should be considered.

The measurements on the susceptibility of graphite suspensions, both directed and undirected, at various temperatures, are tabulated below. The results are summarized in graphical form in figures 7 and 8.

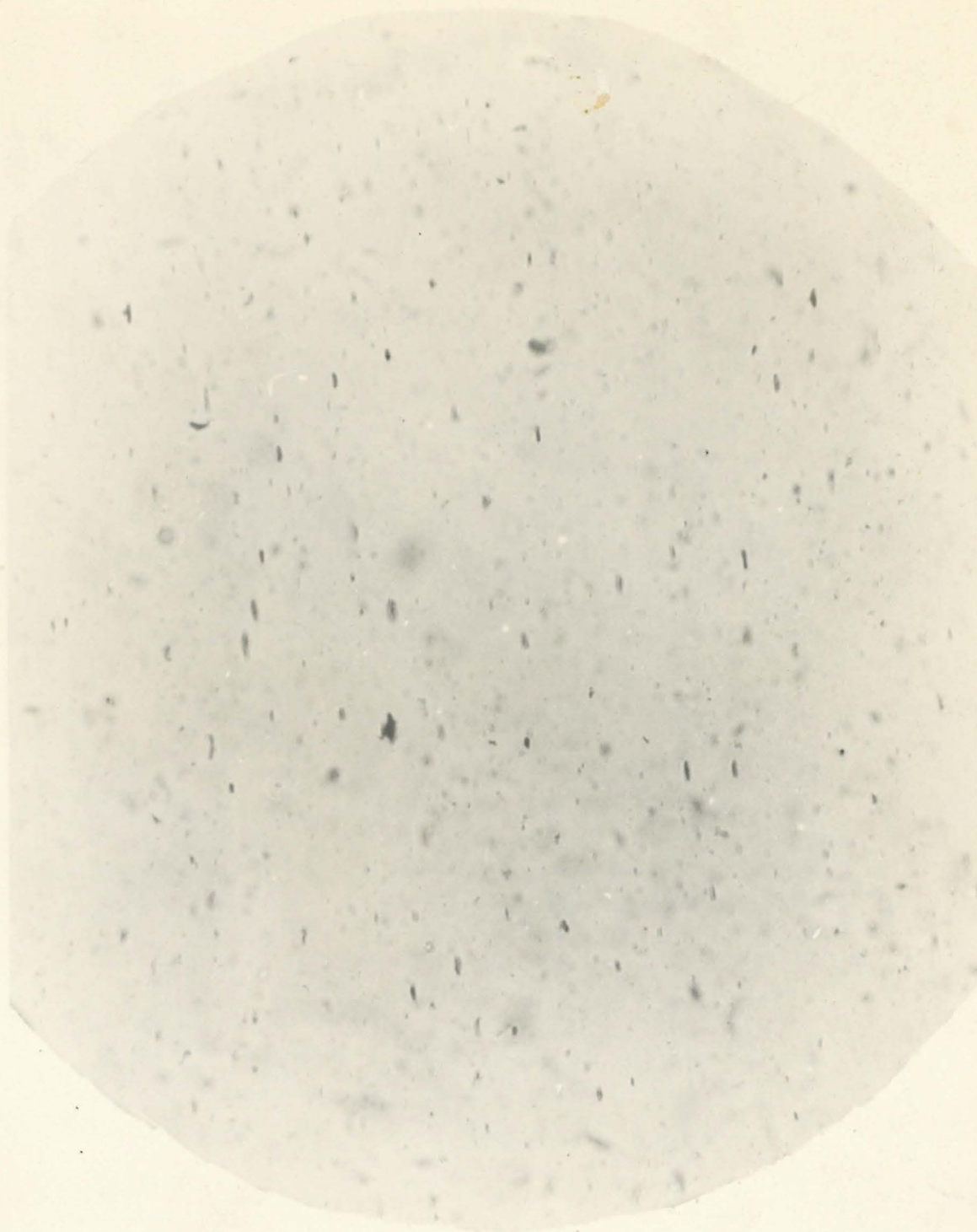


Figure 6

Graphite particles, directed in magnetic field

Oil imm. f 2mm. N.A. 1.32

1000X

Scale: 1 mm. = 1 micron

Table 5  
Graphite, undirected particles

T = 20° C

d ( $\mu$ ) <sup>o</sup>	$\rho$	H	F	$-\chi_{\text{mean}}$
0.1-0.2	0.0153	8100	-0.004739	1.03
0.3-0.6	0.0178	8100	-0.004931	2.52
0.7-1.0	0.0264	8100	-0.005318	3.96
1.8-2.2	0.0295	8100	-0.005515	4.55
2.8-3.5	0.0287	8100	-0.005509	4.70

Table 6

Graphite, directed; (0001) axis parallel to field.

T = 20° C

d ( $\mu$ )	$\rho$	H	F	$-\chi_{\parallel}$
0.1-0.2	0.0145	8100	-0.004872	2.45
0.3-0.6	0.0183	8100	-0.005441	6.77
0.7-1.0	0.0217	8100	-0.006178	11.01
1.8-2.2	0.0175	8100	-0.006035	12.31
2.8-3.3	0.0193	8100	-0.006398	13.35

Table 7

Graphite, directed; (0001) axis perpendicular to field.

T = 20° C

d ( $\mu$ )	$\rho$	H	F	$-\chi_{\perp}^*$
0.1-0.2	0.0145	8100	-0.004678	0.37
0.3-0.6	0.0183	8100	-0.004691	0.41
0.7-1.0	0.0217	8100	-0.004691	0.39
1.8-2.2	0.0175	8100	-0.004703	0.51
2.8-3.5	0.0193	8100	-0.004691	0.44

\*calculated from ( $\chi_{\parallel} - \chi_{\perp}$ ).

<sup>o</sup>In every case the diameter represents that perpendicular to the (0001) axis. The thickness of the flakes cannot be measured on the smaller particles.



Table 8

Graphite, undirected. Same specimens as in table 5.

T = 140° K

d ( $\mu$ )	$\rho$	H	F	$-\gamma_{\text{mean}}$
0.3-0.6	0.0178	8100	-0.00503	3.5
0.7-1.0	0.0764	8100	-0.00557	5.5
1.8-2.2	0.0295	8100	-0.00585	6.4
2.8-3.5	0.0287	8100	-0.00586	6.6

Table 9

Graphite, directed. Same specimens as in table 6

T = 140° K

d( $\mu$ )	$\rho$	H	F	$-\gamma_{\parallel}$
0.3-0.6	0.0183	8100	-0.00574	9.4
0.7-1.0	0.0217	8100	-0.00681	15.5
1.8-2.2	0.0175	8100	-0.00653	16.8
2.8-3.5	0.0193	8100	-0.00694	18.5

Table 10

Graphite, directed. Same specimens as in table 7

T = 140° K

d( $\mu$ )	$\rho$	H	F	$-\gamma_{\perp}^{\circ}$
0.3-0.6	0.0183	8100	-0.00468	0.4
0.7-1.0	0.0217	8100	-0.00470	0.4
1.8-2.2	0.0175	8100	-0.00466	0.4
2.8-3.5	0.0193	8100	-0.00471	0.4

°calculated from  $\gamma_{\parallel} - \gamma_{\perp}$ 

Table 11

Graphite, undirected

T = 105° K

a ( $\mu$ )	$\rho$	H	F	$-\gamma_{\text{mean}}$
0.3-0.6	0.0178	8100	-0.00509	4.0
0.7-1.0	0.0264	8100	-0.00568	6.4
1.8-2.2	0.0295	8100	-0.00598	7.1
2.8-3.5	0.0287	8100	-0.00601	7.4

Table 12

<u>Variation of <math>\chi_{  } - \chi_{\perp}</math> with size</u>					
d ( $\mu$ )	0.1-0.2	0.3-0.6	0.7-1.0	1.8-2.2	2.8-3.5
$\chi_{  } - \chi_{\perp}$ ) T = 20°C)	-2.08	-6.36	-10.62	-11.80	-12.91
$\chi_{  } - \chi_{\perp}$ ) T = 140°K)		-9.0	-15.1	-16.4	-18.1

Table 13

<u>Variation of magnetic ratio <math>\chi_{  }/\chi_{\perp}</math> with size</u>					
d ( $\mu$ )	0.1-0.2	0.3-0.6	0.7-1.0	1.8-2.2	2.8-3.5
$\chi_{  }/\chi_{\perp}$ T=20°C	6	16	26	29	31
$\chi_{  }/\chi_{\perp}$ T=140°K		20	35	45	45

From relation (9) of section III, 3, it may be seen that the susceptibility of graphite should vary as the  $\cos^2$  of the angle between the hexagonal axis and the field, i.e.,

$$\chi_{\theta} = \chi_{\perp} + (\chi_{||} - \chi_{\perp}) \cos^2 \theta$$

Fig. 9 gives curves plotted by means of this relation from the values of  $\chi_{||}$  and  $\chi_{\perp}$  given in tables 6 & 7 ~~and~~ for the largest and smallest particle sizes investigated. The circles represent intermediate points as actually measured. The agreement of the experimental points with the calculated curve gives an indication of the reliability of the anisotropy measurements.<sup>o</sup>

<sup>o</sup>It should also be noted that the determination of the quantity  $\chi_{||} - \chi_{\perp}$  is independent of the susceptibility of the suspending medium; this quantity is therefore more accurately determined than  $\chi_{\perp}$ .

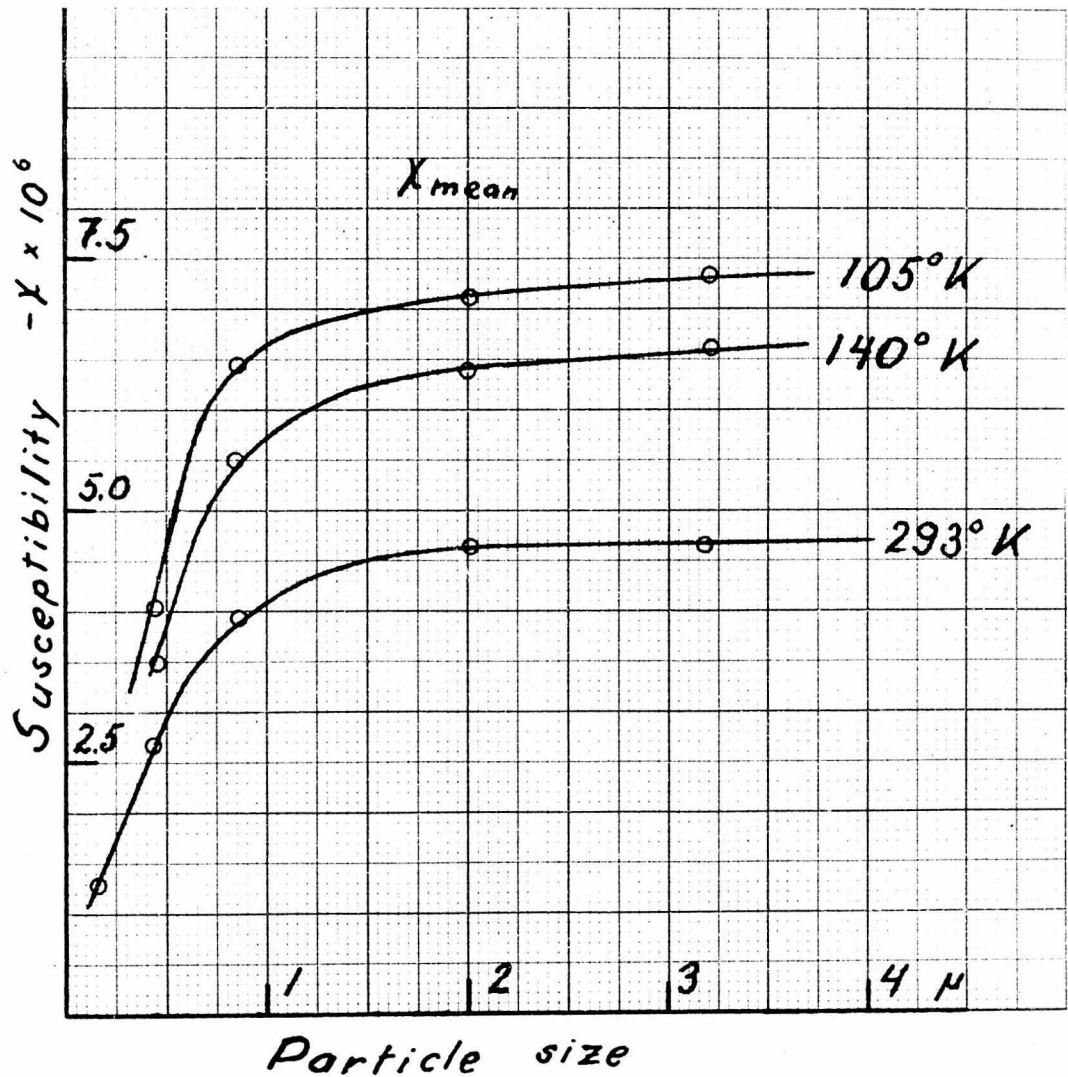


Figure 7

Dependence of the mean susceptibility of graphite on particle size at various temperatures

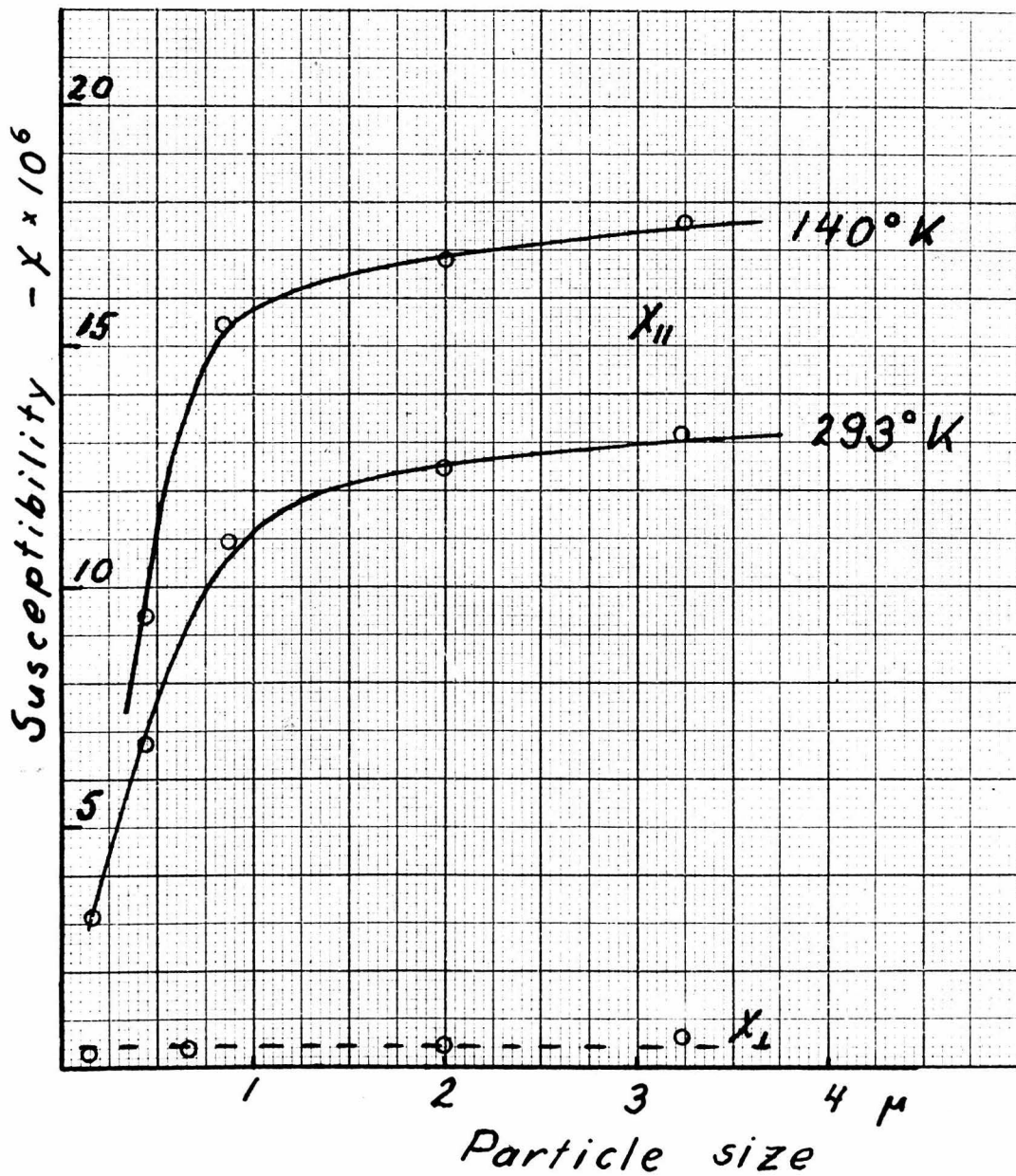


Figure 8

Dependence of the principal susceptibilities of graphite on particle size at various temperatures

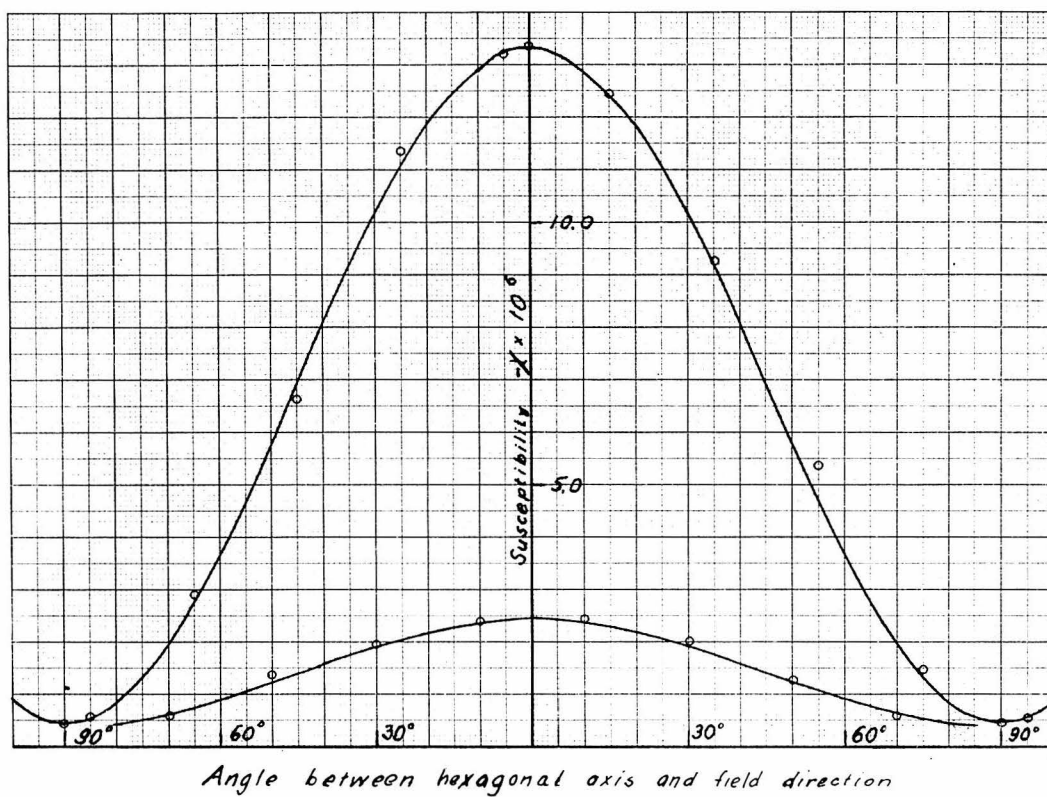


Figure 9

3. Measurements on manganese dioxide,  $MnO_2$ 

The manganese dioxide used in the investigations was a crystalline coarse grained powder, of C.P. grade, furnished by F. W. Braun Co. A chemical analysis showed no trace of iron. Honda and Soné<sup>15)</sup> give the following values for the susceptibility of  $MnO_2$

T	87°K	167°K	270°K	294°K	384°K
$\chi \times 10^6$	74.9	49.9	39.9	38.4	33.7

A preliminary measurement of the susceptibility of the powder in bulk gave the value  $33.8 \times 10^{-6}$  c.g.s. The results obtained for various sizes are given in tables 14 and 15.

Table 14

$MnO_2$   
T = 20°C

d( $\mu$ )	$\rho$	H	F	$\chi$
0.5-0.7	0.00273	8100	-0.003952	38.8
1.0-1.2	0.00615	8100	-0.003145	38.7
1.5-1.7	0.0304	8100	+0.002983	38.8
2.5-3.0	0.0362	8100	+0.004105	38.5
5.0-6.0	0.1530	8100	+0.0336	38.7

No dependence on field strength observed.

Table 15

$MnO_2$   
T = 140°K

d( $\mu$ )	$\rho$	H	F	$\chi$
0.5-0.7	0.00273	8100	-0.00364	57.2
1.0-1.2	0.00615	8100	-0.00245	55.3
1.5-1.2	0.0304	8100	+0.00640	56.2
5.0-6.0	0.1530	8100	+0.04972	55.9

Thus no change in susceptibility with decreasing particle size is observed.

The suspensions were then again melted, and allowed to solidify in a magnetic field. They remained completely isotropic, from which one may conclude that if any magnetic anisotropy is present in  $\text{MnO}_2$ , it is at least very small.

#### 4. Measurements on chromium sesquioxide, $\text{Cr}_2\text{O}_3$

The chromic oxide was a voluminous fine grained green powder of C.P. grade, supplied by the Powers Weightman Rosengarten Chemical Co. A chemical analysis showed no trace of iron. Honda gives the following values for the susceptibility of  $\text{Cr}_2\text{O}_3$

T	87°K	209°K	270°K	391°K	337°K	390°K
$\chi \times 10^6$	20.1	22.2	24.6	25.5	26.0	25.6

A preliminary measurement of the susceptibility of the powder in bulk gave the enormously high value of approximately  $250 \times 10^{-6}$ , which was strongly field dependent (no remanence). Since this high value could not possibly be due to impurities, it seemed that the only explanation was the presence of chromium trioxide ( $\text{CrO}_3$ ) in solid solution in the  $\text{Cr}_2\text{O}_3$ , since it is well known that such solutions with the definite composition  $2\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$  ( $\text{Cr}_5\text{O}_9$ ) and  $\text{Cr}_2\text{O}_3 \cdot 2\text{CrO}_3$  ( $\text{Cr}_4\text{O}_9$ ) are ferromagnetic. The powder was consequently heat-treated for 12 hours to reduce the higher oxide.

To ensure that the product be crystalline, the temperature in the heat treatment was maintained at 1000° C, since at 800° amorphous  $\text{Cr}_2\text{O}_3$  is transformed into the crystalline modification. However, after the heat treatment, the range of particle sizes was too small for a thorough investigation of the dependence of susceptibility on particle size. To obtain larger particles, a small amount of the powder was fused in a magnesia crucible by means of an oxygen torch, and then ground up to smaller sizes. It would be desirable to perform the whole investigation on the fused substance, but unfortunately no furnace was available to melt the quantity of  $\text{Cr}_2\text{O}_3$  necessary to obtain a sufficient amount of very small particles (0.5 - 2 $\mu$ ) for measurement. The results obtained are given in table 16.

Table 16

$\text{Cr}_2\text{O}_3$					
Treatment	d ( $\mu$ )	$\rho$	H	F	$\chi$
Fused, re-pulverized	5-7	0.0545	8100	+0.00510	27.7
Heat treated at 1000°C	1.0-1.5	0.0501	8100	+0.00287	23.5
Heat treated at 1000°C	0.5-1.0	0.0208	8100	-0.00161	22.5

Thus the susceptibility decreases with decreasing particle size. The data are too incomplete, however, in order to make the existence of the effect sure.

<sup>c</sup>The melting point of  $\text{Cr}_2\text{O}_3$  is 2000° C.



The original substance of high susceptibility was also investigated with respect to variation of susceptibility on particle size. (Table 17)

Table 17

T = 20°C

a ( $\mu$ )	$\rho$	H	F	$\chi$
0.5-0.7	0.0079	8100	-0.003095	30.3
0.8-1.2	0.0588	8100	+0.02415	51.7
1.2-1.5	0.1754	8100	+0.0868	93.8
1.5-2.0	0.0735	8100	+0.0770	152.5

The susceptibility decreases rapidly with decreasing particle size. Unfortunately no larger particles were present in the powder, so the measurements are limited to the range of diameters below  $2\mu$ . In this case, the decrease might easily be explained if one assumed that a greater proportion of the more or less unstable  $\text{CrO}_3$  had decomposed in the smaller particles. In view of the rapidity of the decrease, it seems likely that a process of this nature is not entirely responsible for the decrease.

A chemical analysis which might decide the question is extremely difficult in the case of chromium present in different stages of oxidation.

It must be noted that because the susceptibility is dependent on the field, the Gouy method no longer gives a definite value of the susceptibility, but rather some sort of average value over the entire range of field strengths from 0 to the maximum used.

## 5. Measurements on nickelic oxide.

The nickelic oxide was a black coarse grained crystalline powder supplied by the Powers-Weightman-Rosengarten Chemical Co. Its chemical formula was stated to be  $\text{Ni}_2\text{O}_3$ , but according to the chemical literature, such oxides are assumed to be solid solutions of  $\text{NiO}$  and  $\text{NiO}_2$ . Since the oxide seemed to be stable, i.e. lost no oxygen on heating and since no other pure oxide of nickel was available, it was prepared for measurement. No reference in the literature is made to susceptibility measurements on nickel oxides other than  $\text{NiO}$ .

Table 18  
Nickelic oxide  
T = 20°C

d ( $\mu$ )	$\rho$	H	F	$\chi$
0.5-0.7	0.0026	8100	-0.00430	19.8
1.2-1.5	0.0154	8100	-0.00253	20.9
2.2-2.5	0.0527	8100	+0.00781	23.0
3.0-4.0	0.540	8100	+0.1067	30.6

These values were dependent on the field strength. They represent, therefore, some sort of average value of the susceptibility over the range 0 to 8000 gauss. The susceptibility of the bulk material over the same range of field strengths was  $50.3 \times 10^{-6}$ . Thus a gradual decrease of susceptibility with particle size is observed. Here again the lack of any knowledge of the effect of division into small particles on the chemical constitution makes it impossible to draw any conclusions from the data.

## V. Discussion of Results

A discussion of the results presented in the preceding section is exceedingly difficult in view of our meagre knowledge of magnetic properties of the solid state, particularly from the theoretical point of view. However, a brief presentation of their possible significance in connection with certain phases of our knowledge of the solid state may be given. First, however, it should be emphasized that the effects observed may be due to disturbing circumstances of which we have no knowledge, although the shape of the curves for pure graphite and bismuth indicates that surface effects of oxidation and adsorption are not responsible.

The effect of disturbing influences must be considered very carefully, however, since all conceivable phenomena which may disguise the true state of affairs operate in the same direction, i.e. to decrease the susceptibility. As mentioned in section I, the effect of various disturbing factors of chemical nature was investigated carefully by Rao<sup>8)</sup> in the case of bismuth. The lower of the two Bi-curves in Fig. 2 was measured on bismuth powders which before measurement had been treated with tartaric acid to remove oxide, washed, then out gassed under high vacuum and sealed off in small glass bulbs. Further treatments of this nature had no further effect on the susceptibility. On the basis of this

evidence, Rao concluded that a true dependence of susceptibility on particle size was present. Evidence of an entirely different nature tending to confirm this view is furnished by our measurements on the principal susceptibilities of graphite (Fig. 8). According to these measurements, the entire decrease in susceptibility must be attributed to a decrease in  $\chi_{||}$ . This would mean, of course, that the phenomenon is characteristic of the graphite crystal, since disturbing factors of the type described above should have no directional effect if the possibility of an anisotropy of the affinity of  $O_2$  is neglected. However, another disturbing factor peculiar to these measurements may destroy the conclusiveness of these data, since the same effect could be produced by an incomplete alignment of the smaller particles in the field during the preparation of the specimens\* in combination with a spurious decrease in susceptibility due to adsorption of oxygen. Unfortunately, this question cannot be decided from visual evidence as presented in Fig. 6, because just in the case of the smaller particle sizes, the limitation in the resolving power of the microscope makes it impossible to determine

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\* The Brownian movements might easily be the cause of such an effect, especially since their influence would increase with decreasing particle size.

whether complete alignment has taken place. A comparison of the dependence of the mean susceptibility on particle size (Fig. 7) with the two Bi-curves of Rao in Fig. 2 would indicate that the spurious effects described above are partially but not wholly responsible for the results obtained, since the curves of Fig. 7 are intermediate in shape between the two Bi-curves of Fig. 2, but resemble more closely the curve of the purified material than that of the partially oxidized substance.

In the case of graphite and bismuth, no explanation of the effect may be given until the abnormal diamagnetic susceptibilities of these substances are satisfactorily explained. It is certain, however, that these anomalous diamagnetics owe their properties to the cooperative action of the atoms in the crystal lattice. The results of the experiments on size dependency would indicate that the number of atoms cooperating to give the magnetic properties is large compared to the coordination number of the lattice.

Ehrenfest<sup>16)</sup> has proposed the idea that the large diamagnetic susceptibilities of bismuth graphite and antimony might arise from electron orbits shared by two or three atoms in the lattice. However, as suggested by Raman<sup>16)</sup>, the actual values of the susceptibilities would require much larger electron orbits, shared by as many as 50 to 100 atoms. There is no conclusive

evidence that electron orbits of such large extent exist. The best evidence of the existence of such orbits is furnished by the work of Goetz and Focke<sup>18)</sup> on the effect of minimal amounts of impurity on the magnetic properties of bismuth. These authors were able to explain qualitatively the nature of their results. *on the basis of this hypothesis* They proposed in addition the suggestion that the diamagnetism is due to a few ( $1:10^5$ ) very large electron orbits (up to  $.5\mu$  in diameter) instead of many orbits shared by about 50 atoms. On the basis of the values of critical concentrations of impurities, these authors deduced a critical size characteristic of the diamagnetism of  $0.4-0.5\mu$  parallel to (111) in Bi. This value may be compared to the critical size suggested by Figs. 7 and 8, namely  $0.8-0.9\mu$ .

Rao has attempted to draw conclusions of a quantitative nature tending to support the hypothesis of large electron orbits by plotting the susceptibility against the reciprocal diameter ( $\frac{1}{d}$ ). In the case of tin, graphite, and purified bismuth, he obtains a linear relation between these two quantities.\*

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\* A similar curve for the present investigation on graphite does not give a linear relationship; the disagreement is undoubtedly due to the disturbing influences described above, which should not necessarily be the same in both cases, in view of the different source and manner of preparation of the graphite.

From this, Rao concludes that the susceptibility decreases proportionately with increasing ratio of surface to mass.\* He suggests that the increasing surface would destroy a proportionately larger number of the above mentioned orbits, causing the susceptibility to decrease. Although such a conclusion may be justified in the case of tin, whose particles may very roughly be assumed to approximate spheres, it is certainly unwarranted in the case of layer-lattices like Bi and graphite, whose particles are of flake-like shape (cf. Fig. 6). In this case one might approximate the shape of the particles by assuming them to be cylinders (discs), in which case the cylindrical surface, not the total surface, is proportional to the reciprocal diameter. It seems to the writer, however, that to draw conclusions from such manipulations of the data is unwise in the present stage of the investigations. In addition to the effect of the disturbing factors mentioned above, the effect of plastic deformation in the production of the particles must be taken into account. Furthermore, it is questionable whether the measurement of particle size is accurate enough to fix the shape of the curve. With blue light ( $\lambda = 4500 \text{ \AA}$ ) and a numerical aperture of objective of 1.4, the resolving power of the microscope is  $0.2-0.3 \mu$ . Thus measure-

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\* If a number of uniform spheres have a given total mass, it is easily shown that the surface is proportional to the reciprocal diameter.

ments on particles smaller than  $0.5 \mu$  in diameter are subject to large uncertainties which increase with decreasing particle size. In this range, the uncertainty will amount to more than 25% in the most favorable cases. The error is increased by the fact that one has to deal not with one particular size, but with a range of sizes, and further by the fact that the particles are usually very irregular in shape.

The experiments performed at low temperatures show no variation of the critical size with temperature. The range of temperature is limited, however, to the region between  $100^{\circ}\text{K}$  and  $300^{\circ}\text{K}$ . The writer feels that conclusions regarding the effect of temperature on the phenomenon of the critical size should be reserved until the behaviour has also been studied at higher temperatures. In particular the range in the neighborhood of the melting point should be significant.

The results obtained on paramagnetic substances, as mentioned in section IV, are too uncertain to permit any definite conclusions to be drawn. The results have been presented because it is believed that they are of sufficient interest to demand further investigation, particularly because the mechanism with which the forces of atomic interaction operate in paramagnetic solids is known. The mechanism of interaction is provided in quantum mechanics by the so-called "Austausch" or exchange effect, first discovered



by Heisenberg<sup>19)</sup>, which is concerned with the degeneracy associated with the possibility of two electrons (not necessarily in the same atom) trading places. Without going into detail, it may be stated that this exchange effect between electrons, because of restraints imposed by the Pauli exclusion principle, is very sensitive to the alignment of the electron spins. This has the same effect as a strong magnetic coupling between the various spin moments, and thus replaces the hypothesis of the strong inner magnetic field in the theory of Weiss<sup>20)</sup> *of ferromagnetism*. Because of this effect, large regions of the material (usually assumed to be grains) act as unit magnets and their moments are aligned under the influence of an applied field. The experiments of Rao<sup>9)</sup> on nickel colloids mentioned in sec. 1, would indicate, if correct, that the regions in which the exchange forces act may be limited by a characteristic size rather than by grain boundaries. In this connection the experiments of Bitter<sup>21)</sup> should be mentioned. Bitter found that magnetic  $\text{Fe}_2\text{O}_3$  particles were deposited from suspension on magnetized iron, nickel and cobalt in definite patterns, which indicated periodic inhomogeneities in the intensity of magnetisation. The cause of this phenomenon is not yet entirely clear, but is easily capable of interpretation on the basis of the "characteristic length" of Zwicky.

Although only in special cases do the exchange forces bring about the phenomenon of ferromagnetism, they have much to do with the properties of ordinary paramagnetic solids which do not obey Curie's law, or which in addition to this exhibit properties usually associated with ferromagnetism, such as the dependence of susceptibility on field strength. It is interesting to note that the susceptibility of manganese dioxide, which while not following Curie's law, nevertheless shows the general behavior with temperature to be expected from Curie's law, exhibits no dependence on crystal size. The susceptibility of chromic oxide, on the other hand, is nearly independent of temperature; here a variation of susceptibility with crystal size is observed. The same is true of the nickel oxide and  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$  compound investigated, which exhibit, besides a high value of susceptibility, dependence of this quantity on field strength, although no remanence was observed. While the effect may be entirely due to other circumstances, it is not in conflict with our present views on the action of the exchange forces that a true size effect should also be present.

From the discussion given, it will be evident that further experiments on the dependence of susceptibility on size are necessary. In the case of the diamagnetic substances, where the genuineness of the effect seems to be definite, experiments should be performed (a) at higher temperatures, so that the question of the dependence or independence of temperature may be decided, and (b) with particles free from plastic deformation (e.g. grown from the vapor or from solution). In the case of paramagnetics, more extensive and careful experiments should decide the question as to the existence of the effect in various substances.

Acknowledgements

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