

cies is obeyed in the majority of cases but that there are some exceptions to the rule. A survey of the available Raman data reveals only two other cases in which frequencies are increased on

the crystal-to-solution transition; in ammonium nitrate and in hydrated calcium nitrate one finds such an increase in the lower frequencies.

Thus, the results of this study and also the existing Raman data for nitrates justify the generalization based on the early infrared measurements of the high-frequency bands that the frequencies of anions are usually decreased in solutions. However, there are a few exceptions to this rule, especially in the case of low frequencies.

Summary

Early infrared measurements on bands in the 7 to 9 μ region arising from the NO₃ group showed that the frequencies were reduced when the salts were in solution. In the present work the spectra of several nitrate solutions were studied between 6 and 16 μ . The results obtained are in agreement with previous results except in the case of potassium nitrate. The infrared data are compared with the existing Raman data.

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TABLE I

THE OSCILLATION FREQUENCIES OF NITRATES			
Infrared, cm. ⁻¹ Present study	Schaefer and Schubert ^a	Raman, cm. ⁻¹ Solution	Crystal
Lithium nitrate			
			1391
1370	1069
837	..	1050	1052
683	728
Sodium nitrate			
1350	1405	1361	1389
830	831	1049	1071
678	693	721	726
Potassium nitrate			
1350	1390	1357	1351
827	816	1049	1051
673	659	730	711

^a The crystal frequencies observed by absorption would be slightly lower than those observed in reflection.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Magnetic Flux Distribution when a Cylinder of Constant Permeability Is Placed in a Homogeneous Field. The Magnetic Susceptibility of Gadolinium Oxide at Low Temperatures

BY W. F. GIAUQUE AND J. W. STOUT

The problem of the distribution of a magnetic field when a body of permeability μ is introduced into a homogeneous field has been solved accurately only for the real case of an ellipsoid and such hypothetical cases as a cylinder of infinite length or a plate of infinite extent. This well-known problem has not been solved, partly because of its mathematical complexity, and perhaps more because there has been no real incentive for obtaining an accurate solution since it would not apply to ferromagnetic substances. These substances have a variable permeability, hysteresis, and a lack of reproducibility that have made precise measurements of doubtful value. At very low temperatures many paramagnetic substances have a sufficient permeability so that Giauque and MacDougall¹ selected the convenient induction method for determining magnetic susceptibility at the very low temperatures

obtained by the adiabatic demagnetization method. Some form of the induction method is now used by all experimenters engaged in this type of investigation. The exact application of this procedure requires a solution of the magnetic distribution problem within the sample and the space enclosed by the measuring coil.

For reasons of convenience most of the existing results have been obtained with cylindrical samples, although Professor F. Simon and his collaborators recently have made use of ellipsoidal forms. In the experiments performed in this Laboratory advantage has been taken of the fact that the absolute magnetic susceptibility was known at the higher temperatures for the substances investigated. Thus a factor due to the geometry of the arrangement could be determined experimentally. Further, since the range of permeability was small the assumption was made that the factor remained constant.

Although a uniform intensity of magnetization,

(1) Giauque and MacDougall, (a) *Phys. Rev.*, **43**, 768 (1933); (b) *This Journal*, **57**, 1175 (1935).

which is obtained only with ellipsoidal samples, is very desirable for measurements in strong magnetic fields, and especially under conditions where the permeability depends appreciably on field strength, the convenience of cylindrical samples will continue to make them desirable for some types of investigation. For example, there may even be a gain in accuracy when cylinders are used for measurements in the range where permeability is independent of field strength within the limit of accuracy. However, for absolute measurements the problem of field distribution must be solved. This paper presents a report of our preliminary work on an experimental investigation of this subject.

At first it was hoped that some suitable slightly ferromagnetic material might be found with a permeability of the order of 2 or 3, so that the investigation could be undertaken at room temperature. However, a search of the literature was not encouraging and a rough experiment on a cylinder of monel metal at temperatures up to 100°C. showed that this material was not suitable. Hysteresis prevented accurate measurement when the substance was appreciably ferromagnetic.

The general plan of investigation was as follows. Coils were placed at suitable locations about a cylindrical sample and induction measurements were made at various temperatures and thus at various permeabilities. The cylindrical sample was then cut to form an ellipsoid with the same major and minor axes as those of the cylinder. Suitable coils were placed about the ellipsoid and susceptibility determinations were made at various temperatures by an induction method. The data obtained with the cylinder could then be interpreted. Gadolinium oxide was selected for investigation at the temperatures of liquid helium.

The Fluxmeter.—The flux of induction through a coil surrounding a sample may be measured by means of the deflection of a ballistic galvanometer when a known field is suddenly applied or removed. However, this method which has some usefulness for rough measurements on ferromagnetic substances is not sufficiently accurate for the present experiments. In order to increase the accuracy of measurement it was decided to use essentially a null method in which the induction through the sample coil was balanced by the induction in a suitable number of standard coils connected in opposition to it. The sample and the opposing coils could be located within the same exciting magnet provided they are sufficiently isolated from each other. There are, however, some objections to this, especially in connection with low temperature investigations where the space in and near the magnet is more valuable for other purposes. Moreover, it is desirable to keep the standard coils at a fairly constant temperature to prevent dimensional changes. The main difficulty in using

a null method lies in the necessity of having the two induced e. m. f.'s in exact phase balance as well as equal in magnitude so that a sensitive galvanometer may be used. In this work the principal phase disturbances had their origin in the induced eddy currents set up in the metal parts of the solenoid magnet used for low temperature investigations in this Laboratory. This magnet which has been described by Giauque and MacDougall^{1b} was altered by the substitution of a brass tube through the center in place of the copper tube mentioned in the earlier description. This change reduced the magnitude of the induced eddy currents.

Since we desired to develop the technique of such measurements under the conditions that exist in other magnetic experiments, and since it was not convenient to eliminate the metal shells in which the eddy currents were induced, it was decided to reproduce equal effects in opposition by constructing an instrument in which the metal parts of the magnet were duplicated in sufficient detail. This instrument which contained an exciting coil and a suitable number of standard coils will be referred to as the fluxmeter. The schematic arrangement is shown in Fig. 1. The arrows designated A and C in Fig. 1 represent the magnet field and the fluxmeter field, respectively. The exciting coils, which are not shown in Fig. 1, are connected in series during a measurement so that the same current must pass through each. The sample and its encircling coil are shown at B. Representative fluxmeter coils are

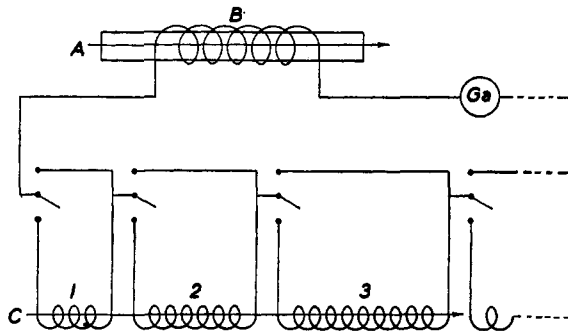


Fig. 1.—Fluxmeter arrangement.

shown at 1, 2 and 3. When any switch is down the coil is in the circuit; when a switch is up the corresponding coil circuit is open. This is necessary because the induction of a current in a closed coil circuit would produce phase irregularities in the main circuit. The fluxmeter coils were made with a suitable number of turns so that some combination would balance any e. m. f. which was induced. The lead wires from each coil were twisted together and the switches were well removed from the fluxmeter to eliminate any appreciable variation in the induced e. m. f. of any circuit.

The sensitivity of the arrangement was such that the small variations which are continually occurring in the earth's magnetic field could not be ignored. To practically eliminate this type of disturbance the field directions and coil areas in the magnet and in the fluxmeter were selected so as to cancel this external effect.

The coils were autocalibrated and the value of one fluxmeter unit was determined as follows. Coils of known

geometry and at room temperature were placed in the center of the solenoid magnet. When the permeability is unity the total flux of induction depends on the product of coil area and field strength. Since the ratio of field strengths of magnet and fluxmeter is a constant, the value of a fluxmeter unit may be determined in terms of an equivalent turn area taken in the magnet. One fluxmeter unit was found to be equivalent to 77.0 ± 0.2 cm.² of turn area located within the solenoid magnet at unit permeability. The above error, which could be reduced, affects the absolute values of susceptibility to be given later by 0.2% but it does not contribute any inaccuracy to the factors representing the field distribution about a cylindrical sample which we will tabulate.

The fluxmeter contained coils down to 0.25 unit. The galvanometer sensitivity was 60 mm. on the scale, located at the distance of 10 meters, for 0.25 fluxmeter unit. The observations could be checked repeatedly with an accuracy of 1 mm. on the scale or 0.004 fluxmeter unit.

Preparation of the Sample.—Gadolinium oxide was prepared by heating gadolinium oxalate at a temperature which was estimated very roughly to be not over 900°C. At the time the gadolinium oxide was prepared we were unaware that Goldschmidt, Ulrich and Barth² had found that a transformation from the cubic to a form of undetermined crystal structure occurs at about this temperature. It is probable that the material used here was cubic but since the properties of gadolinium oxide were only of secondary interest no crystal structure investigation was made.

The gadolinium used in the work came from the collection of the late Professor C. James. Through the courtesy of Professor H. C. Fogg of the University of New Hampshire, it was estimated to contain between 1 and 2% of terbium.

The material which was produced in the form of a powder was mixed with beeswax so that it could be molded into a definite form; 45.887 g. of beeswax was added to 192.447 g. of Gd₂O₃. The beeswax was warmed to a temperature somewhat above its melting point and thoroughly mixed with the gadolinium oxide. The stirring was continued until the mass had solidified to ensure maximum uniformity. A steel mold and plunger were constructed and the material was formed into a cylinder under high pressure. The material was molded at room temperature or slightly above due to frictional heat. No air pockets were found in material molded by this procedure.

Since it was necessary to know the dimensions of the experimental arrangement at low temperatures the expansion was measured between 80°K. and room temperature. The sample was mounted in a lathe and two fine parallel scratches were made on the surface at positions about 12 cm. apart. The cylinder was then mounted with its axis vertical in an unsilvered dewar tube and cooled very slowly by additions of liquid air to a long test-tube placed within the dewar. When the temperature reached about 100°K. filtered

(2) Goldschmidt, Ulrich and Barth, *Norske Videnskaps-akad. Skrifler Mat.-Naturv.*, 1, No. 5 (1925).

liquid air was added slowly to the dewar vessel and eventually covered the sample. Observations were made with a cathetometer accurate to 0.002 cm.

$$L \text{ at } 298.6^\circ\text{K.} = 12.322 \text{ cm.}$$

$$L \text{ at } 81^\circ\text{K.} = 12.181 \text{ cm.}$$

$$\Delta L = 0.141 \text{ cm.}$$

The expansion below 81°K. can be estimated with sufficient accuracy so that observations at lower temperatures were not made. The linear expansion of an organic solid should be roughly approximated by $\alpha = \beta T$. Then

$$\frac{\Delta L}{L} = \frac{\beta}{2} (T_2^2 - T_1^2)$$

$$\beta = 2.8 \times 10^{-7}$$

$$L = L_{0^\circ\text{K.}}(1 + 1.4 \times 10^{-7}T^2)$$

The cylinder was turned in a lathe, and at 298°K. it had a length of 12.11 cm. and a diameter of 2.522 cm. At 0°K. the values became 11.96 and 2.491 cm., respectively. These are also the dimensions for the major and minor axes of the ellipsoid which was later cut from the cylinder.

The ellipsoid was shaped with the aid of a metal template which had been cut carefully to the proper semi-elliptical shape. The ellipsoid was then examined with the aid of a comparator and minor differences from the exact ellipsoidal shape were noted but these averaged out so that the dimensions given above required no correction in considering the location of magnetic material.

The weight of the cylinder was 194.232 g.

If the ellipsoid had been perfectly shaped its weight should have been two-thirds of the weight of the cylinder from which it was cut or 129.488 g. The actual weight was in very satisfactory agreement, being 129.396 g. or 0.07% less than the theoretical amount.

The Induction Coils.—As the coil dimensions change with temperature it was necessary to investigate this effect. Not only was it necessary to know how the coil area changed with temperature but it was advantageous to have the coils located at predetermined positions of symmetry with respect to the sample after the contraction with temperature had occurred.

It was desirable to avoid the presence of conducting materials within the coils on account of phase difficulties in the measuring system which have been mentioned in connection with the fluxmeter. Accordingly, all metals were eliminated as possible supports for the coils. While

it is not an ideal material for the purpose, Bakelite impregnated molded paper (Dilecto) tubes were selected as coil and sample supports. This substance has a very low coefficient of expansion when compared to most organic materials, being comparable in this respect to metals such as copper or brass. Reference marks 12.050 cm. apart at 299°K. contracted to 12.016 cm. at about 81°K. Again assuming

$$\alpha = \beta T \quad \beta = 6.8 \times 10^{-8}$$

This equation could be used with sufficient accuracy to make the small correction necessary between 0 and 81°K. The above coefficients of expansion were used to calculate the relative coil and sample positions so that they were properly located with respect to each other at the temperatures of liquid helium.

For investigating the cylinder four Dilecto tubes were machined so that they telescoped accurately into one another. Slots 1 cm. in length were cut at three positions along each tube, to accommodate the coils as shown in Fig. 2 and presented in Table I. The coils were wound of no. 36 B. and S. gage double enameled copper wire since it has been found in other experiments that coils made of silk insulated wire are more subject to lag when the dimensions are changed by cooling to low temperatures.

In addition to the coils mentioned in Table I there was a coil which we will call "Coil 0" located with one end against the end of the sample as shown in Fig. 2. This coil was 2 mm. thick, 2 mm. in length and the inside diameter was 2 cm. At 0°K. the average root mean square diameter was 2.206 cm. The coil contained 185 turns. This coil was included in order to permit a more accurate correction to some calorimetric data previously obtained by Giauque and MacDougall³

TABLE I

DIMENSIONS OF CYLINDER AND COILS AT 0°K.

Diameter = 2a = 2.491 cm. Length = 2c = 11.96 cm. All coils were 1 cm. long.

Coils	No. layers	Coil thickness, cm.	$\sqrt{d^2}$, cm.	$\frac{1}{2a} \sqrt{d^2}$
1A, B, C	6	0.088	2.701	1.084
2A, B, C	4	.060	3.149	1.264
3A, B, C	3	.041	3.630	1.457
4A, B, C	3	.042	4.174	1.676

Mid-position of coils along cylinder

- A coils height = h = 0
- B coils h = 0.5c
- C coils h = c

(3) Giauque and MacDougall, THIS JOURNAL, 60, 376 (1938).

who made use of an induction heater located in this average position.

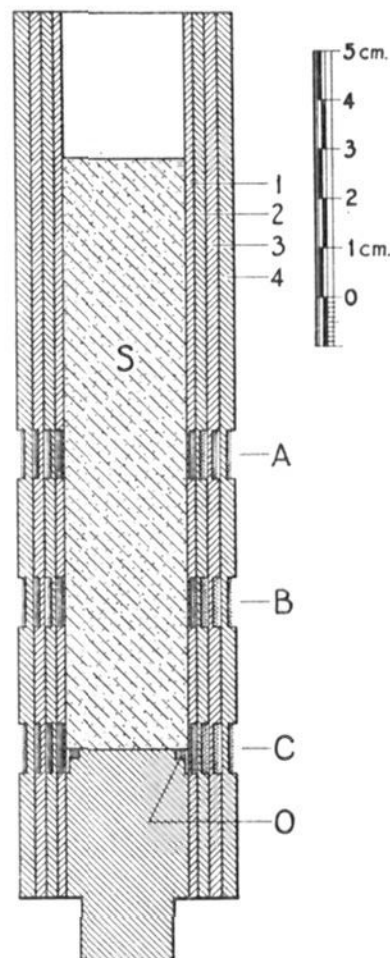


Fig. 2.—Cylindrical sample (S) and coils.

The data on the ellipsoid and the coils used are given in Table II.

TABLE II

DIMENSIONS OF THE ELLIPSOID AND COILS AT 0°K.

2a = 2.491 cm. 2c = 11.96 cm. The equatorial planes and centers of all coils coincided with those of the ellipsoid.

Coil no.	Turns	Thickness, cm.	$\sqrt{d^2}$, cm.	Layers	Width, cm.
1	1146	0.0815	3.176	6	3
2	1157	.0815	3.654	6	3
3	1158	.0815	4.228	6	3

The Flux of Induction through a Coil around an Ellipsoid.—The problem of a homogeneous ellipsoid which has been introduced into a uniform magnetic field, H_0 , has long been solved. For the case of a prolate spheroid of length 2c and diameter 2a the magnetic scalar potential outside the ellipsoid is given⁴ by

$$\Phi = z \left(-H_0 + \frac{Q}{2} \ln \frac{u + ec}{u - ec} - Q \frac{ec}{u} \right) \quad (1)$$

$$= -zH_0 + \Psi \quad (2)$$

where Ψ represents the potential due to the magnetized ellipsoid alone, r and z are cylindrical

(4) (a) Gans, "Einführung in die Theorie des Magnetismus," Leipzig und Berlin, 1908, p. 45. (b) F. Ollendorff, "Potentialfelder der Elektrotechnik," Berlin, 1932, p. 314.

coördinates, the z -axis being taken as coincident with the major axis of the ellipsoid, and the origin of coördinates at the center of the ellipsoid. The eccentricity

$$e = \sqrt{1 - \frac{a^2}{c^2}} \tag{3}$$

$$Q = 4\pi \frac{1 - e^2}{e^3} I \tag{4}$$

where I is the intensity of magnetization per cc. within the ellipsoid and directed along its major axis. H_0 is the magnetizing field applied parallel to the major axis of the ellipsoid.

u is defined by the equation

$$\frac{z^2}{u^2} + \frac{r^2}{u^2 - e^2c^2} = 1 \quad u > ec \tag{5}$$

Within the ellipsoid the field is uniform and in the direction of the major axis. The resultant field is

$$H_{(\text{inside})} = H_0 - NI \tag{6}$$

where

$$N = \frac{4\pi(1 - e^2)}{e^2} \left[\frac{1}{2e} \ln \frac{1 + e}{1 - e} - 1 \right] \tag{7}$$

= the demagnetizing factor

Consider the flux of induction through a coil, of radius b and length $2h$, surrounding the ellipsoid. The coil is concentric and coaxial with the major axis of the ellipsoid.

Outside the ellipsoid the induction in the direction of the z -axis is

$$H_z = - \frac{\partial \Phi}{\partial z} \tag{8}$$

Inside, the induction is

$$H_{(\text{inside})} + 4\pi I = H_0 + (4\pi - N)I \tag{9}$$

The flux of induction through any turn of the coil at height z , less the flux through the same coil in the absence of the sample, is designated by G .

$$G = \int_{\left(1 - \frac{z^2}{c^2}\right) a^2}^{b^2} (H_z - H_0) dr^2 + \int_0^{\left(1 - \frac{z^2}{c^2}\right) a^2} \pi(4\pi - N) I dr^2 \tag{10}$$

$$H_z - H_0 = - \frac{\partial \Psi}{\partial z} \tag{11}$$

The average additional flux of induction per turn over the coil, due to the presence of the sample is

$$= \frac{1}{h} \int_0^h G dz \tag{12}$$

$$= - \frac{\pi}{h} \int_0^h dz \int_{a^2}^{b^2} \frac{\partial \Psi}{\partial z} dr^2 -$$

$$\frac{\pi}{h} \int_c^h \sqrt{1 - \frac{r^2}{a^2}} dz \int_{\left(1 - \frac{h^2}{c^2}\right) a^2}^{a^2} \frac{\partial \Psi}{\partial z} dr^2 + \frac{\pi}{h} \int_0^h dz \int_0^{\left(1 - \frac{z^2}{c^2}\right) a^2} (4\pi - N) I dr^2 \tag{13}$$

In obtaining equation 13 the first integral of equation 10 is divided into two parts for convenience in integrating, and the order of integration changed

$$\frac{1}{h} \int_0^h G dz = - \frac{\pi}{h} \int_{a^2}^{b^2} \Psi(h, r) dr^2 - \frac{\pi}{h} \int_{\left(1 - \frac{h^2}{c^2}\right) a^2}^{a^2} \Psi(h, r) dr^2 + \frac{\pi}{h} \int_{\left(1 - \frac{h^2}{c^2}\right) a^2}^{a^2} \Psi\left(c \sqrt{1 - \frac{r^2}{a^2}}, r\right) dr^2 + \frac{\pi}{h} \int_0^h (4\pi - N) I \left(1 - \frac{z^2}{c^2}\right) a^2 dz \tag{14}$$

when

$$z = c \sqrt{1 - \frac{r^2}{a^2}}$$

$u = c$ and it may be shown from equations 1, 2, 4 and 7 that

$$\Psi\left(c \sqrt{1 - \frac{r^2}{a^2}}, r\right) = NIc \sqrt{1 - \frac{r^2}{a^2}} \tag{15}$$

then

$$\frac{1}{h} \int_0^h G dz = 4\pi^2 \frac{(e^2 - 1)}{e^3} I \left[\frac{r^2}{2} \ln \frac{u + ec}{u - ec} - ecu + \frac{h^2ec}{u} - \frac{2h^2e^3c^3}{3u^3} \right]_{r^2 = a^2 \left(1 - \frac{h^2}{c^2}\right)}^{r^2 = b^2} + \frac{2}{3} \pi NI \frac{a^2 h^2}{c^2} + \pi(4\pi - N) I \left(1 - \frac{h^2}{3c^2}\right) a^2 \tag{16}$$

Introducing the limits in the first term of equation 16, the equation can be reduced to

$$\frac{1}{h} \int_0^h G dz = 4\pi^2 \frac{(e^2 - 1)}{e^3} I \left[\frac{b^2}{2} \ln \frac{u + ec}{u - ec} - ecu + \frac{h^2ec}{u} - \frac{2}{3} \frac{h^2e^3c^3}{u^3} \right] \tag{17}$$

The volume susceptibility, χ , is defined by the expression

$$I = \chi H_{(\text{inside})} \tag{18}$$

Combining Equations 6, 7 and 18

$$I = \frac{H_0}{1 + \chi N} \tag{19}$$

The equivalent additional coil area, measured by the fluxmeter, and due to the presence of the sample is equal to

$$\frac{1}{H_0 h} \int_0^h G dz = \frac{[(A_s + A_0) - A_0] 77.0}{n} \tag{20}$$

where A_0 is the fluxmeter reading in the absence of the sample and $A_s + A_0$ is the reading when

the sample is present. n is the number of turns in the coil and the value 77.0 cm.² of the fluxmeter unit has been discussed above. Thus

$$\frac{77.0 A_s}{n} = 4\pi^2 \frac{(e^2 - 1)\chi}{e^3(1 + \chi N)} \left[\frac{b^2}{2} \ln \frac{u + ec}{u - ec} - ecu + \frac{h^2 ec}{u} - \frac{2}{3} \frac{h^2 e^3 c^3}{u^3} \right] \quad (21)$$

Measurements with the Cylinder.—In order to find the fluxmeter readings for the various coils, surrounding the cylinder, which corresponded to unit permeability and their dimensions near the absolute zero, the following procedure was adopted. Induction measurements were made at 55.6, 75.5, 88.4 and 298°K. From susceptibility measurements made with the ellipsoidal sample and values of the field distribution factors for the cylindrical sample, to be given later, the flux of induction through the coils could be corrected for the contribution of the sample. From the ellipsoid results it was concluded that the susceptibility of gadolinium oxide could be represented, in this temperature region, by the formula $\chi_M = 7.827/(T + 15.5)$ for one-half mole of Gd₂O₃. The room temperature coil values were combined with those at liquid air temperatures to give the average coefficient of expansion. It was found that the expansion corresponded closely to that of copper and therefore the small correction between the temperatures of liquid air and the absolute zero was made by using the known coefficient for copper.⁵ The above agreement was not unexpected, especially since the expansion coefficient for the Dilecto coil supports also was about the same as that of copper.

The results in terms of the linear expansion are given for each coil in Table III. The individual results are of interest because of variable properties in material such as Dilecto. Tubes 1, 2, 3 and 4 were cut from four different samples.

TABLE III

THE INFLUENCE OF TEMPERATURE ON THE COIL DIMENSIONS

$\Delta L = L_{298} - L_{0^\circ K.}$							
Coil	$\Delta L/L$	Coil	$\Delta L/L$	Coil	$\Delta L/L$	Coil	$\Delta L/L$
1A	0.0032	2A	0.0034	3A	0.0033	4A	0.0028
1B	.0030	2B	.0029	3B	.0029	4B	.0031
1C	.0029	2C	.0027	3C	.0029	4C	.0028

For copper $\Delta L/L = 0.0033$.

For Dilecto $\Delta L/L = 0.0030$.

The results given in Table III are based on the average of the observations made on each coil

(5) Keesom, van Agt and Jansen, *Comm. Phys. Lab., Univ. Leiden*, No. 182a.

at 55.6, 75.5 and 88.4°K., corrected as mentioned to 0°K. However, the individual values agreed with the average to the number of figures given.

The agreement obtained for the fluxmeter readings calculated to correspond to the coils in the absence of the sample 0°K. is shown in Table IV. The sample was not surrounded by liquid air during the measurements at liquid air temperatures since the susceptibility of the oxygen would have complicated the interpretation of the measurements.

TABLE IV

FLUXMETER READINGS FOR COILS CORRECTED FOR THE PRESENCE OF THE SAMPLE AND CALCULATED TO CORRESPOND TO 0°K.

Coil	55.6°K.	75.5°K.	88.4°K.	Average
1A	28.128	28.140	28.134	28.134
1B	27.884	27.883	27.884	27.884
1C	27.825	27.821	27.824	27.823
2A	25.105	25.108	25.107	25.107
2B	25.274	25.274	25.277	25.275
2C	25.112	25.111	25.110	25.111
3A	26.499	26.503	26.496	26.499
3B	26.147	26.148	26.149	26.148
3C	26.140	26.135	26.139	26.138
4A	34.347	34.352	34.347	34.349
4B	34.523	34.526	34.525	34.525
4C	34.166	34.164	34.165	34.165

The excellent agreement shown in Table IV confirms the expression used to represent the magnetic susceptibility at these temperatures.

The increase per unit field in the total flux of induction through an average turn of coil, when the cylindrical sample is introduced, is given in Table V. The values are expressed in terms of equivalent cm.², of turn area at unit permeability

TABLE V

FLUX OF INDUCTION, DUE TO THE CYLINDRICAL SAMPLE, PER UNIT OF APPLIED MAGNETIC FIELD

Values in cm.² are given for an average turn of each coil

Coil	n	1.508°	4.23°	13.92°	20.35°
1A	377	0.4283	0.3405	0.2341	0.1932
1B	374	.4181	.3313	.2262	.1888
1C	375	.2258	.1786	.1222	.1019
2A	248	.4247	.3360	.2316	.1925
2B	250	.4124	.3256	.2251	.1848
2C	249	.2201	.1744	.1194	.0993
3A	197	.4190	.3323	.2271	.1915
3B	194	.4045	.3199	.2179	.1814
3C	195	.2223	.1761	.1193	.0987
4A	193	.4113	.3248	.2202	.1843
4B	194	.3945	.3115	.2115	.1774
4C	193	.2210	.1739	.1169	.0962

which is equivalent to the flux of induction per unit field. The results of measurements at the susceptibilities corresponding to 1.508, 4.23, 13.92 and 20.35°K. are presented. The number of turns in each coil is also given in Table V.

Before calculating the desired flux distribution factors from the above results, it is necessary to have susceptibility values at the several temperatures. These will be given later.

The Reproducibility of the Measurements.—In order to prove that errors were not introduced due to possible lag in the coil dimensions after a change in temperature, three series of measurements were made over a considerable time interval. The coils and cylinder were cooled slowly to the boiling point of liquid helium by blowing a stream of cooled helium gas over them until a temperature of about 15°K. was reached, at which point liquid helium was added. The sample was immersed in liquid helium at 2:30 P. M. on 6-19-1937; between 3:15 and 3:45 P. M. the measurements of Series I at the boiling point of helium were taken; Series II was made between 3:45 and 3:59 P. M. Measurements were then made at 1.508°K. and the apparatus was allowed to stand in the liquid helium-bath until the next day. Series III was taken between 10:43 A. M. and 11:06 A. M. on 6-20-1937. The results are compared in Table VI. Series I and III were made with a measuring field of 26 gauss but in the case of Series II the field was 17 gauss to make sure that the susceptibility was not influenced appreciably by the field. No effect due to time or field was observed. It is also of interest to mention that the application and removal of a field of 8000 gauss left the fluxmeter reading unaltered, both at 1.508 and 4.23°K.

TABLE VI

FLUXMETER MEASUREMENTS ON THE CYLINDRICAL SAMPLE AT THE BOILING POINT OF HELIUM

Coil	Series I	Series II	Series III
1A	29.801	29.801	29.801
1B	29.493	29.490	29.493
1C	28.693	28.689	28.693
2A	26.189	26.189
2B	26.332	26.332
2C	25.675	25.671
3A	27.349	27.349
3B	26.954	26.954
3C	26.584	26.584
4A	35.163	35.163
4B	35.310	35.310
4C	34.601	34.601
0	9.391	9.391

The results recorded above were obtained by pressing the key which controlled the measuring current several times in succession and recording the average result to the nearest mm. on the scale, although the reproducibility was better than 1 mm. Since 1 mm. corresponds to about 0.004 in the fluxmeter reading, a variation of several thousandths in the above readings is possible although the fact that they were recorded only to 1 mm. makes them appear to agree within 0.001 in most cases.

The measurements at the temperatures of liquid hydrogen and liquid air were made after the above measurements and since there is little thermal expansion in the intervening region, there is no reason to believe that the coil dimensions were appreciably affected by lag effects.

Despite the good agreement of the results shown in Table IV it was decided to eliminate the uncertainty of extrapolation of the coil constants below 55°K. by mounting the ellipsoidal sample on an elevator, which moved it beyond the range of appreciable effect on the coil, so that the coil constant at unit permeability could be determined directly. It was fortunate that this was done since the coils used on the ellipsoid proved to be inferior to those used with the cylinder. This was apparently due to the fact that the longer coils were not supported as well as those of the cylinder. The ellipsoid coils definitely showed a lag in their dimensions as may be seen from the results presented in Table VII. The measurements were all made on 3-5-1938. The sample and coils were cooled to the boiling point of helium at 1:10 P. M.

TABLE VII

FLUXMETER READINGS ON ELLIPSOID AT THE BOILING POINT OF HELIUM

Time, P. M.	Coil 1	Coil 2	Coil 3	Sample
2:27	122.473	162.046	215.474	In
2:38	122.473	162.044	215.473	In
3:28	117.915	157.567	211.140	Out
3:40	122.471	162.047	215.472	In
Difference	4.556	4.480	4.332	In-out
6:59	122.462	162.032	215.459	In
7:20	117.901	157.550	211.123	Out
7:41	122.463	162.035	215.459	In
Difference	4.561	4.483	4.336	In-out

Measurements with the Ellipsoid.—As mentioned above, the cylinder used for the above measurements was cut to form an ellipsoid with the same major and minor axes. The dimensions

of the ellipsoid and coils have been given in Table II.

The volume of an ellipsoid of revolution is $2\pi a^2 c/3$. The amount of gadolinium oxide in the ellipsoid was $(192.447 \times 129.396)/(192.447 + 45.887) = 104.483$ g. The molecular weight of Gd_2O_3 was taken as 361.8. Thus the ellipsoid contained $(104.483 \times 2)/361.8 = 0.5776$ gram atoms of gadolinium.

The gram atom susceptibility of gadolinium in gadolinium oxide, χ_M , is given by the relation

$$\chi_M = \frac{2\pi a^2 c \chi}{3 \times 0.5776} \quad (22)$$

The susceptibility values obtained with coils 1, 2 and 3 are independent determinations of this quantity.

The values of Δ are calculated from the equation $\chi_M = C(T + \Delta)$, where C is the theoretical Curie constant for the trivalent gadolinium ion. $C = 21 M^2/R = 7.827$ deg. for an octet S state. M and R are the molal Bohr magneton value and gas constant, respectively.

As has been stated above the gadolinium contained from 1 to 2% of terbium and, since the susceptibility of terbium would be expected to be of the same order of magnitude as that of gadolinium, no correction was applied.

The variation of susceptibility with field strength was investigated by an induction bridge method similar to that used by Giaque and MacDougall.¹ Observations were made at 20.3, 13.92, 10.7, 4.23 and 1.48°K. At all temperatures except 1.48° the susceptibility was independent of field to 8000 gauss to within 1 or 2%. This was the limit of accuracy. At 1.48°K. the adiabatic differential susceptibility decreased by 7% at 4100 gauss and by 11% at 8200 gauss.

The susceptibility values calculated by means of Equation 21 and the values of Δ are given in Table VIII.

TABLE VIII
THE MAGNETIC SUSCEPTIBILITY OF GADOLINIUM OXIDE AT LOW TEMPERATURES

T°K.	$\chi \times 10^3$				χ_M gram atom of Gd	Δ
	Coil 1	Coil 2	Coil 3	Average		
1.406	7.183	7.197	7.196	7.192	0.4838	14.77
2.456	6.382	6.385	6.374	6.380	.4292	15.78
4.223	5.654	5.656	5.645	5.652	.3802	16.36
13.92	3.880	3.881	3.866	3.876	.2608	16.10
20.34	3.202	3.212	3.195	3.203	.2155	15.98

From these results it was estimated that the susceptibility of $1/2 Gd_2O_3$ may be represented by

the equation $\chi_M = 7.827(T + 15.5)$ at higher temperatures and this is confirmed by the results obtained with the cylindrical sample at the temperatures of liquid air.

Since the low temperature measurements on the cylinder were at temperatures that did not coincide with those of the observations on the ellipsoid, a graph of Δ vs. T was constructed and values were interpolated to correspond to the desired temperatures.

The Field Distribution Factors for a Cylinder.

—The cylindrical sample contained 194.232 g. of gadolinium oxide-beeswax mixture which corresponds to 0.8670 gram atom of gadolinium. Since the length of the cylinder was 11.96 cm., the flux of induction per unit of field due to an infinitely long cylinder of the same diameter and concentration of material would be

$$(0.8670 \times 7.827 \times 4\pi)/11.96 \times (T + \Delta)$$

The ratio of the observed induction through the various coils as given in Table V to the above quantity will be called f , the coil factor. Values of this ratio are presented in Table IX.

Measurements of the coil factors are given at susceptibilities corresponding to four temperatures. As may be seen from a rough analogy with Equation 19 for the case of an ellipsoid, there should not be any appreciable trend in the factor f , for the range of susceptibility considered here and none was observed. The values at the higher temperatures are not as reliable due to the fact that the lower susceptibility made the observed quantity smaller. The average given in column six of Table IX was obtained by weighting the several values in proportion to the corresponding susceptibility.

TABLE IX
COIL FACTORS

T, °K.	1.508	4.23	13.92	20.35		
Δ Used	14.85	16.36	16.10	15.98		
Coil	f	f	f	f	Weighted average	Calcd. from Table X
1A	0.983	0.983	0.986	0.984	0.984	0.983
1B	.959	.957	.953	.962	.958	.956
1C	.518	.516	.515	.519	.517	.513
2A	.975	.970	.975	.981	.975	.975
2B	.946	.940	.948	.942	.944	.943
2C	.505	.504	.503	.506	.504	.509
3A	.962	.960	.956	.976	.963	.960
3B	.928	.924	.918	.924	.924	.924
3C	.510	.509	.502	.503	.507	.505
4A	.944	.938	.927	.939	.938	.941
4B	.905	.900	.891	.904	.901	.901
4C	.507	.502	.492	.490	.500	.501

It was convenient to treat the results on "Coil O" in a somewhat different manner. In this case a factor was calculated which was the ratio of the actual increase in the flux of induction due to the presence of the sample to the increase if the coil were taken from a region of unit permeability and inclosed in an infinite medium of the sample material. The values of the ratio at the temperatures 1.508, 4.23, 13.92 and 20.35°K. were 0.403, 0.399, 0.398 and 0.397, respectively. The average, weighted as above, was 0.400 ± 0.005 and this value has been used³ in computing the flux of induction through the ring of no. 40 gold wire which Giauque and MacDougall used in introducing calorimetric energy.

By a graphical method corrections for the finite length of the coils were determined and factors for single turns located at simple geometrical intervals were evaluated. These results are given in Table X. b refers to the turn diameter and h is the height of its plane above the equatorial plane of the cylinder.

In drawing the curves we made use of approximate values calculated for $1.5c$ and $1.8c$ on the assumption that magnetic poles were distributed uniformly on the ends of the cylinder. The flux of induction has decreased to such an extent at the calculated points that a high accuracy is not essential.

In drawing the curve for the equatorial plane we gave some weight to data from another experiment in which a cylinder of gadolinium phosphomolybdate was enclosed by two concentric coils with $b = 1.483a$ and $1.651a$, respectively. The experiment did not give the absolute factors but did determine their ratio for the above coil positions as 1.013.

TABLE X

FACTORS FOR A SINGLE TURN AS A FUNCTION OF POSITION WITH RESPECT TO A CYLINDRICAL SAMPLE
Cylinder length/diameter = $2c/2a = 4.801$

$h/b \dots \dots a$	$1.2a$	$1.4a$	$1.6a$	$1.8a$
0	0.985	0.979	0.965	0.948
0.1c	.985	.979	.965	.947
.2c	.984	.978	.963	.944
.3c	.982	.975	.958	.938
.4c	.975	.966	.948	.927
.5c	.961	.950	.931	.910
.6c	.936	.924	.905	.886
.7c	.897	.883	.865	.846
.8c	.840	.826	.808	.790
.9c	.747	.732	.716	.700
1.0c	.527	.520	.514	.508
1.1c	.219	.250	.280	.308

The above factors are believed to be accurate to about 0.005 except at the end of the cylinder, where the error may be a little greater because the exact position of the end coils was a matter of more importance. The values appear to be a little high as an approximate calculation based on the assumption of uniform pole distribution on the ends of the cylinder leads to a maximum factor of 0.981 for the equatorial position; however, this is within the limit of error.

The factors are, of course, applicable only to the limiting case of a small susceptibility which is independent of field. For the case of a larger constant susceptibility a correction analogous to that given in Equation 19 for an ellipsoid might be made.

There are no other comparable experimental data available although several investigators have made observations corresponding to the equatorial position with iron cylinders. A comparison with the present results is of somewhat dubious value since the permeability of iron is large and variable. A summary of early results for iron cylinders has been given by Shuddemagen,⁶ and more recently Dussler⁷ has made further measurements and gives additional references to other work.

Use of the Coil Factors.—The flux of induction through an infinitely long cylinder with $\pi a^2 \rho / M$ moles per cm. of length is $4\pi^2 a^2 \chi_M H_0 \rho / M$ where ρ represents the grams of magnetic material per cc., and M the molecular weight.

$$4\pi^2 a^2 \chi_M H_0 \rho / M = (\pi / f) \int_0^b (B_z - H_0) db^2 \quad (23)$$

where B_z is the component of induction perpendicular to the plane of the turn of wire considered.

$$\chi_M = (M / 4\pi a^2 \rho f) \int_0^b [(B_z / H_0) - 1] db^2 \quad (24)$$

$\int_0^b [(B_z / H_0) - 1] db^2$ is the observed flux of induction per unit of field. For actual coils the value of f used should be a weighted average obtained by considering the length and thickness of the coil.

Summary

An experimental investigation has been made to evaluate factors, so that the magnetic susceptibility may be calculated from measurements of the flux of induction through coils located at various positions about a cylindrical sample.

The results apply to a sample with a ratio of

(6) Shuddemagen, *Proc. Am. Acad. Arts Sci.*, **43**, 185 (1907)

(7) Dussler, *Ann. Physik*, **86**, 66 (1928).

length to diameter equal to 4.8 which has been found to be a convenient size for adiabatic demagnetization experiments in this Laboratory.

The susceptibility of gadolinium oxide was determined by the induction in coils surrounding an ellipsoidal sample. These results were then used to interpret similar observations on a cylindrical sample.

The magnetic susceptibility of gadolinium oxide has been given for various temperatures in the range 1.5–88°K.

The investigation was carried out at low temperatures so that a paramagnetic substance of relatively large and field independent susceptibility could be used. Ferromagnetic materials are unsuited for this purpose because of a variable permeability and hysteresis.

An equation has been developed so that susceptibility may be deduced from induction measurements with coils located at various positions with respect to ellipsoidal samples.

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Extrapolation of the Conductivities of Strong Electrolytes of Various Valence Types

BY BENTON BROOKS OWEN

The equivalent conductivities of strong uni-univalent electrolytes in water follow the Onsager¹ equation

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{c} \quad (1)$$

so closely at high dilutions that it is possible to obtain a satisfactory extrapolation against \sqrt{c} without actually calculating the limiting slope predicted by theory. For higher valence types the region of concordance with the equation is shifted to such extreme dilutions that this simple procedure is no longer practicable. Even for such a favorable example as barium chloride, for which accurate data are available at high dilutions, the theoretical limiting slope cannot safely be ignored. The conductance of this salt has been extrapolated by five different empirical equations, which approach linearity with \sqrt{c} at the limit, and the value of Λ_0 was found² to be influenced strongly by the extrapolation function employed.

The simplest use of the limiting slope is to plot Λ against \sqrt{c} and cause the extension of a smooth curve through the lowest experimental points to merge with the limiting slope before intercepting the axis of zero concentration. A more sensitive procedure³ is based on the fact that a plot of

$$\Lambda_0' = \frac{\Lambda + \beta\sqrt{c}}{1 - \alpha\sqrt{c}} \quad (2)$$

against c is linear, or only moderately curved, for dilute solutions of simple strong electrolytes. Plots of this nature have been used widely in the estimation of Λ_0 for uni-univalent and uni-bi-

valent electrolytes, but are not well suited to the extrapolation of data for higher valence types, or incompletely dissociated electrolytes. Figure 1 shows that a fairly accurate value of Λ_0 might be derived for lanthanum chloride by producing the experimental curve horizontally⁴ but for potassium ferrocyanide and zinc sulfate it is clear that Λ_0' varies too rapidly with c to permit precise extrapolation. For convenience in comparing the

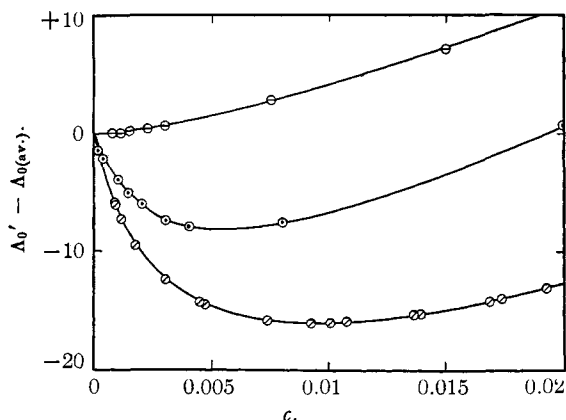


Fig. 1.—Variation of Λ_0' with C in dilute solutions at 25°. For convenience in plotting, $\Lambda_{0(av.)}$ of Table I has been subtracted from Λ_0' : \ominus , LaCl_3 ; \otimes , $\text{K}_4\text{Fe}(\text{CN})_6$; \circ , ZnSO_4 .

results for salts of different valence types in this and subsequent figures, Λ represents the equivalent conductance, and c is expressed in equivalents per liter. These units have been taken into account in evaluating the constants and empirical parameters appearing in the conductance equations and Table I. The most satisfactory methods of

(1) L. Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927).

(2) Jones and Dole, *THIS JOURNAL*, **52**, 2247 (1930).

(3) Shedlovsky, *ibid.*, **54**, 1405 (1932).

(4) Jones and Bickford, *ibid.*, **56**, 606 (1934).