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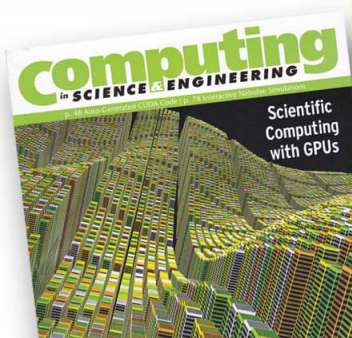
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## The Measurement of Magnetic Induction in High Magnetic Fields at Low Temperatures. $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ \*

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(Received July 24, 1962)

A discussion of the potentiometric method of measuring magnetic induction has been given for isothermal, isentropic, and isoerstedic processes. The magnetic properties of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  have been investigated over the range 1.2° to 78°K and in fields up to 93 kgauss. Values of the differential isothermal magnetic susceptibility and intensity of magnetization as a function of field have been given. Within the limits of error, the system may be considered to consist of a major component which is a function of  $H/T$ , and a small temperature independent component with a negative field dependence. The entropy of magnetization calculated from the temperature coefficient of the magnetic work has been compared with the previously published directly determined values. The saturation value of powdered  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  has been found to be 11800 gauss  $\text{cm}^3 \text{mole}^{-1}$ , and the Curie constant,  $T\chi_{\alpha,m(\text{initial})} = 1.964 \text{ deg cm}^3 \text{mole}^{-1}$ , each for the magnetic component which is a function of  $H/T$ . The temperature-independent susceptibility including diamagnetism has been represented by  $\chi_{\beta,m} = (0.011_3 - 2.5 \times 10^{-8} H_i) \text{ cm}^3 \text{mole}^{-1}$ , with  $H_i$  in gauss. A correction has been applied to the earlier initial-susceptibility measurements of Fritz and Giauque and their results are in agreement with the present data within their limit of accuracy.

ONE of the most needed types of the measurements required for a detailed understanding of magnetic substances at low temperatures and in high fields is the accurate determination of the amount of induced magnetic moment  $\mathbf{I}$ . The work done in magnetizing a substance is  $\int \mathbf{H} d\mathbf{I}$  and the free-energy change is  $-\int \mathbf{I} d\mathbf{H}$ , where  $\mathbf{H}$  represents the applied field. Usually  $\mathbf{I}$  has been determined only at small fields by means of some form of induction bridge. The principal reason for the field limitation is that accurate measurements with such a bridge involve difficulties if there are adjacent metal parts of variable temperatures and magnet circuits of variable resistance such as those of typical solenoid or iron-core magnets used in adiabatic demagnetization. Thus the sample is ordinarily removed from the primary source of magnetic field and placed in the relatively minor fields of some measuring system. What is needed are means of measurement which can be used accurately when the sample is left in the major field for measurements during frequent field and/or temperature changes, e.g., in the convenient isothermal, adiabatic, or isoerstedic processes. As is well known, equilibrium is essentially unattainable in some magnetic systems whereas others reach their final state with great rapidity and a large number of intermediate cases are within the capabilities of experimental methods which do not require an equilibrium response within excessively short time intervals. We believe that the general method which best satisfies these various requirements is what may be called the potentiometric method. This involves measuring the emf generated as changing induction cuts the turns of a coil system surrounding a spherical or ellipsoidal sample. The

integral of the emf with respect to time, adjusted by a geometrical coil factor, equals the change of magnetization within the sample. A digital integrator giving the  $\int \mathbf{E} dt$  directly or after amplification should be a very convenient and highly accurate method of determining this quantity. There are various ways in which the potentiometric method may be applied.

(1) The emf on the surrounding coil may be recorded or integrated with time as the stationary sample is warmed in a constant field. The potentiometric method was used by Giauque and MacDougall<sup>1</sup> with a very low constant field to measure the change of magnetization  $\Delta \mathbf{I}$ , as a source of information concerning possible residual magnetism. However, this technique should be generally useful at any field.

(2) The sample may be held in a fixed position with respect to a coil system and the field can be increased or decreased over an interval large enough to give an accurate measurement of the induction change in terms of  $\int \mathbf{E} dt$ .

(3) The sample may be raised or lowered within a coil system preferably consisting of upper and lower coil sections with windings in one coil arranged so that they may be connected in the reverse sense to those of the other. This coil arrangement has been used with a ballistic galvanometer by Henry<sup>2</sup> for some of the few existing measurements in high fields at low temperatures. However ballistic galvanometers are not very accurate, whereas the measurement of  $\int \mathbf{E} dt$  can give absolute values with rather high precision and accuracy, especially when digital electronic integrators or other appropriate automatic recording equipment is

\* This work was supported in part by the National Science Foundation, and by an equipment holding contract from the Office of Naval Research.

<sup>1</sup> W. F. Giauque and D. P. MacDougall, *J. Am. Chem. Soc.* **60**, 376 (1938).

<sup>2</sup> W. E. Henry, *Phys. Rev.* **88**, 559 (1952).

utilized to evaluate the integral. If necessary, the motion of an elevator may be programmed to give values of the coil emf suitable for the recording system; however, electronic digital integrators record so rapidly that any practicable elevator velocities may be used.

Method 3 appears to be the most advantageous over most of the range for isothermal or isoerstedic paths. It gives a value of the intensity of magnetization  $\mathbf{I}$  at a definite field and, if necessary for equilibrium, the sample can under many circumstances be left in a fixed field at a constant temperature for some time. At high values of  $\mathbf{I}$  it should give high accuracy. It will ordinarily require a very stable magnetic field and is one of the reasons we are now installing equipment with which it is hoped to hold fields up to 100 kgauss constant to one part in the range  $10^6$ – $10^7$ .

At low values of  $\mathbf{I}$  near the initial susceptibility region Method 2 would seem to have the advantage. The experimental results given later in this paper were obtained by the use of Method 2 as a temporary expedient at all fields because it enables the use of a coil system similar to that used by Giauque, Fritz, and Lyon<sup>3</sup> as a null-point fluxmeter. Such a coil system can largely balance out the presently existing field fluctuations which are less than 0.1%. Method 3 cannot do this. Near saturation, Method 2 gives little effect for large field changes and requires integration of data over the full field range to yield the saturation value of  $\mathbf{I}$ , whereas Method 3 gives each value directly. There are, however, situations where it would be better to use Method 2 at high values of  $\mathbf{I}$  since this could give a value of  $(\partial\mathbf{I}/\partial\mathbf{H})$  which would be more accurate than a value resulting from the subtraction of two large quantities.

The situation on an isentropic path is somewhat similar since  $\mathbf{I}$  can vary from zero to saturation, however, the over-all situation is more difficult because long experimental times and inevitable heat leak will alter the entropy. Method 3 requires less time in determining a single value of  $\mathbf{I}$ . The near impossibility of distributing heat leak uniformly throughout systems at very low temperatures makes accurate correction for heat leak impracticable. One method of avoiding the effects of heat leak would be to perform a series of demagnetizations from equilibrium conditions of known entropy and heat content to various lower fields and then use Method 3 at each terminal field before remagnetization to permit a following demagnetization from re-evaluated equilibrium conditions. On the other hand, if the magnetic system being investigated reacts rapidly, Method 2 and a recorder giving the field, and an electronic digital integrator recording  $\int \mathbf{E} dt$ , each as a function of time, could give the detailed magnetic work,  $\int \mathbf{H} d\mathbf{I}$ , during the complete demagnetization or magnetization process.

<sup>3</sup> W. F. Giauque, J. J. Fritz, and D. N. Lyon, *J. Am. Chem. Soc.* **71**, 1657 (1949).

Since a suitable coil system will permit the use of Methods 1, 2, or 3, it seems obvious that the most generally useful design will be one that will permit any of the above methods to be used when circumstances during a portion of an experiment favor its accuracy and such a system is now being constructed for work after precise field stabilization is obtained.

#### MEASUREMENT OF MAGNETIC FIELD AT THE SAMPLE POSITION

For work of moderate or low accuracy one may explore and map the field of a magnet and hope that it will continue to reproduce the field characteristics during later experimentation. For work of high accuracy it will be desirable to measure the field in the region occupied by the sample at the time of the magnetic measurements on the sample. This poses some problems since one obviously cannot have some device such as a magnetic resonance probe in the sample space during a measurement on the sample. Moreover, the field strength required is ordinarily the value which the field would have in the absence of the sample and yet the magnetized sample will necessarily alter the field in the region of interest.

A coil of wire with a high magnetoresistance, surrounding the sample position, would serve since the measured induction in the sample would enable a correction for the effect of the sample on the field in the adjacent space. We are, however, not optimistic concerning this method because a high magnetoresistance is likely to have a temperature coefficient over some of the temperature range of interest which would considerably complicate its accurate application.

The following method appears to have many advantages. The apparatus may be surrounded by a suitable coil which is connected to a digital integrator for the evaluation of

$$\int_0^H \mathbf{E} dt$$

in a manner similar to the technique to be used for measuring the magnetic induction in a sample. In the absence of a sample, the above integral is proportional to the average magnetic field within the coil and if the turn area within the coil were known the absolute value of the field could be computed. One of the difficult problems connected with the use of coils in liquid helium is that accurate knowledge of their dimensions at ordinary temperatures does not usually give with desirable accuracy the dimensions they will assume when cooled to liquid-helium temperatures, including dimensional changes with time after the initial cooling.

Since we propose to have samples mounted on an elevator it is also practicable to mount a magnetic resonance probe on the same elevator but well removed

from the sample. Thus either the sample or the probe may be moved into position within a coil.

The simultaneous use of the digital integrator and the probe in the absence of the sample should give the magnetic field and thus an accurate value of the coil-turn area at liquid-helium temperatures. This same device may be used to evaluate the average geometry of various coils used in the magnetic induction measurements after they have been stabilized at low temperatures.

The correction of the  $\int \mathbf{E} dt$  of the field-measuring coil for the effect of the magnetization of the sample will require a knowledge of  $\mathbf{I}$  at any time the field is evaluated. It will be noted that Method 3 above measures absolute values of  $\mathbf{I}$  without knowledge of the field which may have produced them and would thus permit correction. In fact, when the dimensions of the coil have been determined, the changed value of

$$\int_0^H \mathbf{E} dt$$

after the elevator separates the sample from the coil will give both the magnetization of the sample and the field which produced it. A single coil could be used for both determinations, however, it seems desirable to have separate coils for the two measurements. For example, Method 3 is best with a pair of reversed coils, whereas the  $\int \mathbf{E} dt$  for field-measuring purposes should have the simultaneous use of an entire coil wound in the same sense. Also, Method 3 with reversed coils will measure the magnetic induction  $\mathbf{I}$  with a moderate displacement of the sample. The sufficiently complete separation of a sample and coil to remove all but a negligible influence could change the temperature of the sample due to bath conditions. Also, if the sample is moved far from the very flat maximum in the "homogeneous" region there would be a change due to adiabatic demagnetization, but this should be reversed when the original position is restored, unless heat leak intervenes.

There will also be circumstances when it will be convenient to use a changing solenoid current as a measure of field change when this indicator is sufficiently interspersed by checks of the kind mentioned above.

The  $\int \mathbf{E} dt$  will include any thermoelectric effect in a coil circuit, however, experience has shown that this effect may be made very small. There are several ways of avoiding an error of this type. For example, it can be accurately measured and balanced or calculated out as such effects do not change much with time unless conditions are considerably altered, which is ordinarily inexcusable during accurate experiments. The turn area of the coil may be made large enough to make a thermoelectric contribution negligible except at very low fields. If, assuming the same time interval, the

$$\int_0^H \mathbf{E} dt$$

differs from

$$\int_H^0 \mathbf{E} dt,$$

the difference should be twice the thermoelectric effect, enabling correction.

In considering the above methods, we have been looking forward to a very well stabilized solenoid-magnet current. The ordinary generator supply of current contains a wide range of frequencies with amplitudes that make most of the methods discussed above impracticable. In the preliminary measurements given in this paper the "noise" due to magnet current has forced us to use field values obtained from measurements of current in the 4-in.-core 100 kgauss solenoid which has been described<sup>4</sup> previously. We know however from various dimensional measurements over a period of time that the solenoid coil has excellent dimensional stability. More detailed evidence was found in the fact that the product of field and turn area of a 2640-turn coil centered in the equatorial plane and balanced against two similar coils, each with about half the number of turns, and centered 10 cm above and 10 cm below the main-coil center, respectively, gave results which were reproducible to 0.001% of the total turn area over the range 0 to 100 kgauss. The measurements showed that an effect presumed to be magnetostriction gradually increased the induction in the center coil relative to the increase in the balancing coils by 0.008% when the field was increased from 0 to 20 000 gauss. Between 20 and 60 kgauss there was essentially no relative change, presumably because the warming of the magnet prevented additional axial magnetostriction of the coil. Between 60 and 100 kgauss the thermal effects gradually overcame the original effect of magnetostriction on the balance, and at the maximum field the outer balancing coils has gained 0.001% more induction relative to the center coil. Correction for these effects was taken into account by the coil calibrations used for evaluating the induction measurements. The reproducibility of the above effects during experiments extending over a period of several months demonstrates a considerable degree of stability of magnet performance.

#### EXPERIMENTAL ARRANGEMENT FOR MEASURING THE MAGNETIC INDUCTION IN $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$

During the period needed for installation of current-stabilization equipment we have been gaining experience and developing technique by an experiment on the induction in a prolate spheroid containing randomly oriented small crystals of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ . The 0.19132-mole sample and container are the same as used previously<sup>5</sup> for determinations of the entropy increase

<sup>4</sup> W. F. Giauque and D. N. Lyon, *Rev. Sci. Instr.* **31**, 374 (1960).

<sup>5</sup> W. F. Giauque, D. N. Lyon, E. W. Hornung, and T. E. Hopkins, *J. Chem. Phys.* **37**, 1446 (1962).

TABLE I. Coil data for induction measuring system of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ .

Designation	Turns	Layers	Mandrel (cm)	Coil o.d. (cm)	Position of coil from magnet center (cm)
A	1	1	4.382	4.412	+22.815
B-1=B-2	1	1	4.382		$\pm 22.457$
C-1=C-2	3	1	4.382		$\pm 22.071 \pm 22.124$
D-1=D-2	9	1	4.382		$\pm 21.614 \pm 21.766$
E-1=E-2	27	1	4.382		$\pm 20.903 \pm 21.309$
F-1=F-2	81	1	4.382		$\pm 19.338 \pm 20.598$
G-1=G-2	243	1	4.382		$\pm 15.249 \pm 19.034$
BAL-1=BAL-2	1344	4	4.318	4.425	$\pm 8.978 \pm 14.078$
MAIN	2640	4	4.318	4.425	+ 4.997— 4.997

accompanying isothermal demagnetization, except that its two outer glass jackets were removed. A schematic drawing of the method used for making the magnetic induction measurements reported here is given in Fig. 1, which is largely self-explanatory. Considering the measurement of the generator-supplied magnet current, a large share of the potential drop across the shunt is balanced by means of a potentiometer, with the amplified residual recorded on a chart, since charts are incapable of high accuracy on their total.

The glass-enclosed ellipsoidal sample is shown centered in the coil system and the equatorial plane of the solenoid. The main measuring coil was opposed by two balancing coils, Bal-1 and Bal-2, connected in series. Coils A through G contain various numbers of turns so that they may be used with Bal-1 and Bal-2 to obtain any balance within one coil turn. All coils may be reversed and connected in any order by outside switches except that G-1 and G-2 and the other balancing pairs were ordinarily connected in series. The coil data are given in Table I. The coils were made of No. 36 copper with 14 coats of Formvar insulation, making a total diameter of about 0.015 cm.

The copper coils were wound on Micarta because it has been shown<sup>6</sup> that this material has almost the same expansion coefficient as copper.

The induction per unit field in the various balancing coil was determined both at the temperatures of liquid helium and boiling nitrogen by means of the combined potentiometer and recorder after the sample had been lifted from the apparatus.

As shown in Fig. 1, the net emf was recorded by means of a decade potentiometer with a mechanically operated dial change marker and a chart recorder for the residual emf. The chart portion of the  $\int \mathcal{E} dt$  was obtained graphically from the recorded data. Although the noise in the present magnet circuit is much less than that in most such installations with a generator supply of current, it was necessary to filter the emf from the

measuring coils in order to obtain a reliable graphical record. The use of dry electrolytic capacitors, required in order to obtain the high capacitance needed, introduced a problem in that these condensers produce a small emf. In order to obtain a circuit with negligible emf, the condensers were selected from a large supply and matched in series pairs so that the emf's canceled. The whole assembly, totaling 10 000  $\mu\text{F}$ , had a residual emf of the order of one  $\mu\text{volt}$ . The inductance-capacitance filter was designed to attenuate frequencies above 1 cps.

#### MAGNETIC INDUCTION MEASUREMENTS ON $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$

Essentially, the method adopted for the present measurements is the fluxmeter method as described previously.<sup>3</sup> In the absence of a stabilized field, the use of coils within the solenoid to balance the effect of induction in the coil surrounding the sample greatly reduces the effect of "noise" in the solenoid current. In our earlier installation, however, the method was still essentially restricted to the measurement of initial susceptibility or to low fields with a battery-supplied solenoid current because of the many irregularities in a dc generator supply connected to a large number of users.

In the present situation the individual generator supply was greatly superior and the high-field magnet was of very stable construction. The greatest improvement was in the use of the filters in the measuring-coil system, which were superior to any previously available to us.

Giauque and Stout, and more recently Giauque, Fritz, and Lyon<sup>8</sup> give the basic equation (GFL 18+19+20) for relating the induction  $G$  cutting a turn in a coil near a magnetized ellipsoid of revolution. They use cylindrical coordinates  $r$  and  $z$  to refer to coil radius  $b$  and coil distance  $h$  along the direction of the coincident major axes of the ellipsoid, the measuring coils, and the solenoid. The origin is taken at the center of the ellipsoid which has a length  $2c$  and a diameter  $2a$ .

<sup>6</sup> W. F. Giauque and J. W. Stout, J. Am. Chem. Soc. **61**, 1384 (1939).

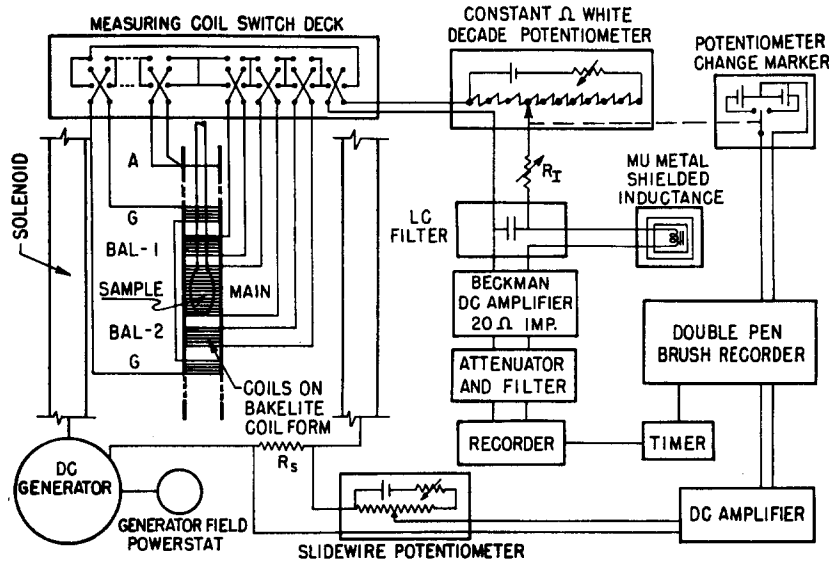


FIG. 1. Schematic diagram of induction measuring circuits.

The eccentricity of the ellipsoid is

$$e = (1 - a^2/c^2)^{1/2}. \quad (1)$$

They also use the convenient variable  $u$  as defined by the equation

$$z^2/u^2 + r^2/(u^2 - e^2c^2) = 1 \quad u > ec. \quad (2)$$

The induction per average turn in what we call the  $i$ th layer of coil  $j$ , due only to the presence of a magnetized sample, in the form of an ellipsoid of revolution is

$$\frac{1}{h_2 - h_1} \int_{h_1}^{h_2} G_{j,i} dz = \mathbf{I} \times C_{j,i}, \quad (3)$$

where

$$C_{j,i} = \frac{4\pi^2(e^2 - 1)}{(h_2 - h_1)e^3} \left[ \frac{hb^2}{2} \ln \frac{u_{(h,b)} + ec}{u_{(h,b)} - ec} - hec \left( u_{(h,b)} - \frac{h^2}{u_{(h,b)}} + \frac{2h^2e^2c^2}{3u_{(h,b)}^3} \right) \right]_{h_1}^{h_2} \text{ cm}^2, \quad (4)$$

and  $\mathbf{I}$  is the magnetization within the ellipsoid in gauss. Let  $n_{j,i}$  = total turns in the  $i$ th layer of coil  $j$  and  $n_j$  = total turns in coil  $j$ . Then the average equivalent turn area for a single turn of coil  $j$ , due to the presence of a magnetized ellipsoidal sample, is given by

$$C_j = n_j^{-1} \sum_i n_{j,i} C_{j,i} \text{ cm}^2 \text{ or } 10^{-8} \text{ volt sec gauss}^{-1}. \quad (5)$$

The total contribution to the induction cutting all of the coils used is

$$\mathbf{I} \sum_j n_j C_j \text{ gauss cm}^2 \text{ or } 10^{-8} \text{ volt sec}. \quad (6)$$

The change in induction per average turn in the absence of the sample is defined by

$$A_{j,i} (\bar{f}_{j,i} \Delta H_0) \text{ gauss cm}^2 \text{ or } 10^{-8} \text{ volt sec}, \quad (7)$$

where  $A_{j,i}$  is the area of a single turn of the  $i$ th layer of coil  $j$ ,  $\Delta H_0$  is the field change at the origin in gauss, and  $\bar{f}_{j,i}$  is a factor which would be unity in a homogeneous field. However, coils located at a considerable distance from the equatorial region will be in slightly smaller fields,  $\bar{f}_{j,i} \Delta H_0$ , where  $\bar{f}_{j,i}$  is the average factor for the  $i$ th layer of coil  $j$ . Then the average effective turn area, for a single turn of coil  $j$ , in the absence of the sample, is

$$A_j \bar{f}_j = n_j^{-1} \pi \sum_i n_{j,i} b_{j,i}^2 \bar{f}_{j,i} \text{ cm}^2 \text{ or } 10^{-8} \text{ volt sec gauss}^{-1}, \quad (8)$$

where

$$n_j = \sum_i n_{j,i}. \quad (9)$$

The total change in induction in all coils used, but in the absence of the sample and considering sign, is

$$\Delta H_0 \sum_j n_j A_j \bar{f}_j \text{ gauss cm}^2 \text{ or } 10^{-8} \text{ volt sec}. \quad (10)$$

The very small net change in induction due to the coils and sample  $\int \mathbf{E} dt$  was taken on the recorder;

$$\int \mathbf{E} dt = \Delta \mathbf{I} \sum_j n_j C_j + \Delta H_0 \sum_j n_j A_j \bar{f}_j \text{ gauss cm}^2 \text{ or } 10^{-8} \text{ volt sec}. \quad (11)$$

In an ideal case there would be enough coils in opposition to make the  $\int \mathbf{E} dt = 0$ ; however, in reality the  $\int \mathbf{E} dt$  will have some value within the effect of one coil turn.

The potentiometer plus the recorder was used only during coil calibrations in the absence of the sample.

Since the field had not been stabilized, we could not use a magnetic-resonance dimensional check as mentioned above, thus the values of  $C_j$  for each coil were calculated using room temperature coil dimensions

corrected to low temperatures by means of the coefficients of expansion<sup>6</sup> of copper for the turn area and of Micarta for the coil length. It was assumed that the coil dimensions were constant from 1°–20°K, but values at 78°K were computed for the few measurements at this temperature. The Main coil was always in opposition to coils Bal-1 and Bal-2 during the measurements and values of  $\sum n_j A_j \tilde{f}_j$  for this combination were calibrated as a unit over the entire field range.

From Eq. (11) above,

$$\Delta \mathbf{I} = \left[ \left( \int \mathbf{E} dt - \Delta H_0 \sum_j n_j A_j \tilde{f}_j \right) / \sum_j n_j C_j \right] \text{gauss}, \quad (12)$$

$$\frac{\Delta \mathbf{I}}{\Delta H_0} = \left( \Delta H_0^{-1} \int \mathbf{E} dt - \sum_j n_j A_j \tilde{f}_j \right) / \sum_j n_j C_j. \quad (13)$$

The molal intensity of magnetization,

$$\mathbf{I}_m = \mathbf{I} / \text{moles cm}^{-3} \text{ in the ellipsoid.} \quad (14)$$

The dependence of accuracy on the several terms on the right-hand side of Eq. (12) is of interest. The present method is essentially null point, with little dependence on  $\int \mathbf{E} dt$ . The summation in the denominator is obtained entirely from the geometry of the coil relative to the ellipsoidal sample which is assumed to be uniformly magnetized in the homogeneous region of the solenoid magnet. There is nothing else in the calculation of this summation which relates to the field of the solenoid. The geometry utilized involved calculated shrinkage based on coefficients of thermal expansion but the results are not as critically dependent on the dimensions as they would be if the total flux of induction through the turn area were calculated.

The summation in the numerator does involve knowing the total induction within each coil turn at their various positions in the absence of the sample, and this did not involve geometrical measurement since the value of each coil, A to G, was determined in terms of the  $\int \mathbf{E} dt$  for a measured increment of magnet current  $\mathbf{i}$ . As mentioned above, this was done with the measuring coil system at 4° and 78°K. These measurements covered the field region up to about 30 kgauss by means of the potentiometer-recorder combination shown in Fig. 1.

$$\mathbf{H}_0 = f_H \times \mathbf{i}. \quad (15)$$

Later, with a coil of large measured area at room temperature, it was found by means of some preliminary measurements with a digital electronic integrator, that  $f_H = 10.51 \pm 0.01$  gauss ampere<sup>-1</sup> over the range of field to 100 kgauss. Thus the  $\int \mathbf{E} dt$  values mentioned above applied to all field regions.

The Main coil + Bal-1 + Bal-2 was always used in this combination and thus was evaluated as a unit in terms of  $\int \mathbf{E} dt$  at 4° and 78°K, and in this case at all fields.

The most serious error in the above measurements was due to the instability of the magnet current and

there is reason to expect much more accurate measurements when construction of the current stabilization unit is completed.

The accuracy of  $\Delta \mathbf{I}$  is almost entirely dependent on  $\Delta \mathbf{i}$ , since

$$\Delta H_0 \sum_j n_j A_j \tilde{f}_j = f_H \times \Delta \mathbf{i} \sum_j n_j A_j \tilde{f}_j. \quad (16)$$

However, if the ratio  $\Delta \mathbf{I} / \Delta H_0 = \Delta \mathbf{I} / (f_H \times \Delta \mathbf{i})$  is considered, this type of error is largely canceled out in the ratio. The magnet current was recorded on a high-speed time chart, and the start and termination of the  $\int \mathbf{E} dt$  was recorded on the same chart to minimize error, especially when  $\Delta \mathbf{i}$  was small.

The observations on  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  are given in Table II. The first six columns give observations referred to calibrations made by reference to coils calibrated in the absence of the sample. The last six columns give data from earlier series in which the sample was held at 78.25°K during the coil calibrations, with the application of corrections for the portion of the intensity of magnetization which was later determined to be a function of temperature. The results of Fritz and Giauque<sup>7</sup> show that there is a substantial contribution from temperature-independent paramagnetism in  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ . We will here refer to the total magnetization as  $\mathbf{I}$ , the temperature-dependent component of magnetization as  $\mathbf{I}_\alpha$ , and the temperature-independent portion as  $\mathbf{I}_\beta$ . The procedure used in obtaining the data in the last six columns of Table II subtracts the effect of  $\mathbf{I}_\beta$  as part of the calibration.

#### TREATMENT OF THE MAGNETIZATION DATA

Table III gives integrated values of the total molal intensity of magnetization  $\mathbf{I}_m$  as a function of the internal field  $\mathbf{H}_i$  within the crystals for Series I to VII

$$\mathbf{H}_i = \mathbf{H}_0 - N\mathbf{I}. \quad (17)$$

Pending further information on the subject of demagnetization effects in powdered samples, we have used the semiempirical formula of Casimir<sup>8</sup> for a prolate ellipsoid in making this small correction. The particles are assumed to average to spheres.

$$N = 4\pi \frac{(1-e^2)}{e^2} \left[ \frac{1}{2e} \ln \frac{1+e}{1-e} - 1 \right] - \frac{4\pi(1-f_s)}{3f_s}, \quad (18)$$

where  $e$  is the eccentricity of the ellipsoid as used previously,

$$e = (1 - a^2/c^2)^{1/2}, \quad (1)$$

and  $f_s$  is the packing fraction of the sample in the ellipsoid.

<sup>7</sup> J. J. Fritz and W. F. Giauque, *J. Am. Chem. Soc.* **71**, 2168 (1949).

<sup>8</sup> H. B. G. Casimir, *Magnetism and Very Low Temperatures* (Cambridge University Press, London, 1940).



TABLE II. Change of molal magnetization of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  with field.  $\mathbf{H}$  is in gauss;  $\Delta\mathbf{I}_m$ , change in molal magnetization, in gauss  $\text{cm}^3 \text{mole}^{-1}$ .  $\Delta\mathbf{I}_{am}$ , change in temperature dependent molal magnetization, is in gauss  $\text{cm}^3 \text{mole}^{-1}$ .

$\mathbf{H}_1$	$\mathbf{H}_2$	$(\Delta\mathbf{I}_m/\Delta\mathbf{H})$	$\mathbf{H}_1$	$\mathbf{H}_2$	$(\Delta\mathbf{I}_m/\Delta\mathbf{H})$	$\mathbf{H}_1$	$\mathbf{H}_2$	$(\Delta\mathbf{I}_{am}/\Delta\mathbf{H})$	$\mathbf{H}_1$	$\mathbf{H}_2$	$(\Delta\mathbf{I}_{am}/\Delta\mathbf{H})$
Series I, $T=1.905^\circ\text{K}$			Series IIIa, $T=14.15^\circ\text{K}$			Series VIa, $T=1.237^\circ\text{K}$			7 775 10 028 0.5381		
—81	2 147	1.0201	512	8 949	0.1486	4	404	1.5429	1 194	12 007	0.4151
2 173	3 896	0.9463	8 949	20 625	0.1448	488	616	1.5373	12 015	14 119	0.3264
3 896	5 114	0.8558	20 616	29 035	0.1352	821	3 522	1.3900	14 228	18 248	0.2224
5 198	6 510	0.7565	28 999	36 122	0.1261	3 585	4 069	1.1402	18 286	21 185	0.1456
6 495	7 729	0.6698	35 969	44 296	0.1156				21 216	24 007	0.1042
7 729	8 971	0.5830	44 338	53 472	0.1051				24 049	30 908	0.0609
8 962	10 481	0.4980	53 235	59 301	0.0939				30 859	34 889	0.0324
10 525	11 826	0.4210	59 195	68 054	0.0852	Series VIb			Series VIII, $T=4.202^\circ\text{K}$		
12 000	13 935	0.3317	68 167	74 897	0.0782	5 631	6 982	0.7560	—84	823	0.4652
13 866	15 533	0.2696	64 545	73 339	0.0782	6 929	10 761	0.4657	814	1 560	0.4628
15 560	17 773	0.2105	73 348	80 988	0.0699	10 729	27 526	0.0933	1 560	3 473	0.4576
17 719	20 176	0.1596	80 970	88 320	0.0623	27 454	49 634	0.0038	3 511	5 322	0.4455
20 166	23 648	0.1142	88 320	93 569	0.0550				5 408	7 245	0.4273
23 621	26 791	0.0809	93 487	97 192	0.0514	Series VIc			7 279	8 287	0.4108
26 827	31 566	0.0560	Series IIIb			7 556	8 704	0.5265	8 287	10 408	0.3907
31 572	40 745	0.0324	552	6 311	0.1505	10 263	12 978	0.2707	10 408	12 702	0.3588
40 801	48 799	0.0178	6 311	11 848	0.1481	24 453	37 037	0.0752	12 757	15 975	0.2912
47 517	55 547	0.0149	11 848	19 360	0.1441	38 401	56 578	0.0022	15 885	17 523	0.2828
55 596	65 941	0.0111	19 360	27 721	0.1393	56 662	77 025	0.0006	15 782	17 920	0.2800
65 941	78 183	0.0096	Series IVa, $T=20.39^\circ\text{K}$			77 414	91 733	0.0007	17 926	20 813	0.2476
78 228	90 776	0.0103	—118	7 341	0.1073	91 702	85 577	—0.0004	20 829	24 816	0.2056
90 776	96 326	0.0087	7 368	16 617	0.1062	85 732	74 195	—0.0009	24 877	27 258	0.1689
Series II, $T=4.219^\circ\text{K}$			Series IVb			74 469	51 171	—0.0010	27 339	29 655	0.1450
—143	2 037	0.4730	138	7 515	0.1071	51 116	21 806	0.0115	30 096	32 727	0.1211
2 037	5 003	0.4619	7 515	16 170	0.1060	21 725	15 055	0.0876	32 775	36 126	0.1005
5 003	7 565	0.4378	16 190	25 461	0.1035	Series VIId			36 872	40 029	0.0820
7 565	9 596	0.4112	25 461	31 999	0.0997	42 323	55 006	0.0012	40 091	43 815	0.0674
9 623	11 572	0.3827	31 999	38 418	0.0957	55 008	66 194	0.0003	43 634	50 169	0.0505
11 572	14 276	0.3492	38 278	46 270	0.0938	66 194	75 684	0.0005	50 364	53 437	0.0368
14 276	15 185	0.3237	Series Va, $T=78.25^\circ\text{K}$			75 644	86 283	0.0004	Series IX, $T=4.214^\circ\text{K}$		
14 807	17 009	0.3035	343	10 012	0.0354	86 381	92 780	0.0000	—202	6 440	0.4486
17 029	20 936	0.2631	10 012	19 628	0.0348	93 170	74 886	0.0000	6 432	0	0.4483
20 981	24 110	0.2165	19 628	29 955	0.0345	74 945	51 231	—0.0010	8 416	3 646	0.4249
24 002	26 838	0.1864	Series Vb			51 104	37 161	0.0024	9 916	6 807	0.3996
27 112	29 662	0.1575	531	17 803	0.0352	Series VII, $T=1.977^\circ\text{K}$			6 807	8 669	0.4076
29 910	33 384	0.1325	17 803	27 794	0.0341	—21	997	0.9787	8 669	9 767	0.3883
33 468	36 390	0.1096	27 794	37 889	0.0341	1 039	2 318	0.9534	10 788	13 833	0.2872
36 426	42 405	0.0861	37 889	49 224	0.0337	2 318	4 063	0.8935	13 850	10 594	0.2898
42 458	51 013	0.0609				4 105	4 701	0.8262	16 016	12 544	0.3117
51 004	61 098	0.0410				4 701	6 361	0.7531	17 313	15 312	0.2843
61 098	72 831	0.0280				6 357	7 691	0.6573	19 067	21 273	0.2315
73 066	81 774	0.0202							21 273	18 597	0.2330
81 712	89 683	0.0163									
89 683	98 438	0.0131									

Descriptions of the sample of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and the Pyrex glass ellipsoid have been given previously.<sup>5</sup> At room temperature the length was 12.283 cm, diameter 2.536 cm, and volume 41.358  $\text{cm}^3$ . The volume of the 0.19132-mole sample was 27.6  $\text{cm}^3$ , thus the filling factor  $f_s=0.668$ , and  $N\mathbf{I}=0.01304\mathbf{I}_m$ .

It soon became evident that the magnetic properties could be represented within the limits of accuracy by a temperature-dependent component which was a function of  $\mathbf{H}/T$  and a temperature-independent component. These components are consistent with the  $\mathbf{H}/T$  dependence of the entropy<sup>5</sup> and the initial-susceptibility measurements of Fritz and Giauque.<sup>7</sup> The temperature-independent component has now been found to have a negative field dependence. In separating the magnetic properties into the two components we

made the provisional assumption of  $\mathbf{H}/T$  dependence for one component and then justified it graphically within the limits of accuracy.

A function

$$\Delta_{(TT')(\mathbf{H}_i/T)} \text{ was defined as}$$

$$= T(\partial\mathbf{I}/\partial\mathbf{H})_T - T'(\partial\mathbf{I}/\partial\mathbf{H})_{T'} \quad (19)$$

$$= T\chi_T - T'\chi_{T'}, \quad (20)$$

for each of a series of values of  $\mathbf{H}_i/T$ . The values of  $\chi T$  were read from a family of smoothed curves.

$$\Delta_{(TT')(\mathbf{H}_i/T)} = T(\chi_\alpha + \chi_\beta)_T - T'(\chi_\alpha + \chi_\beta)_{T'} \quad (21)$$

If the temperature-dependent component is an accurate

function of  $\mathbf{H}/T$ , and  $\chi_\beta$  is independent of  $T$  and  $\mathbf{H}$ ,

$$T(\chi_\alpha)_T = T'(\chi_\alpha)_{T'}, \quad (22)$$

and  $(\mathbf{H}_i/T)_{\text{ref}} = \text{const}$  at  $T$  and  $T'$ , from which

$$\Delta_{(TT')(\mathbf{H}_i/T)_{\text{ref}}}/(T - T') = \chi_\beta. \quad (23)$$

For the case where  $\chi_\beta$  is a linear function of  $\mathbf{H}$ , let

$$\chi_\beta = a + b\mathbf{H}_i. \quad (24)$$

It follows that

$$\Delta_{(TT')(\mathbf{H}_i/T)_{\text{ref}}}/(T - T') = a + b(T + T')(\mathbf{H}_i/T)_{\text{ref}}. \quad (25)$$

Values of  $\Delta_{(TT')(\mathbf{H}_i/T)_{\text{ref}}}/(T - T')$  were plotted against  $(\mathbf{H}_i/T)'_{\text{ref}}(T + T')$  giving  $a$  as the intercept, and  $b$  as the slope.

The equation obtained for the temperature-independent molal susceptibility is

$$\chi_{\beta,m} = (0.0113 - 2.5 \times 10^{-8} \mathbf{H}_i) \text{cm}^{-3} \text{mole}^{-1}, \quad (26)$$

with  $\mathbf{H}_i$  in gauss which has been used in the further analysis of the data. Since all of the errors are collected in the values of  $\Delta$  used,  $\chi_{\beta,m}$  may be in error by as much as 5%.

No correction has been made for the negative diamagnetic contribution which has thus reduced the positive value of  $\chi_{\beta,m}$ .

The above value of  $\chi_{\beta,m}$  is in satisfactory agreement with the corrected initial-field results of Fritz and Giauque.<sup>7</sup> We shall discuss the corrected results of Fritz and Giauque in a later section. Figure 2, curve (a), is a plot of all of the results for the  $\alpha$  component based on the measurements in Table II, except the measurements at 78°K where the percentage accuracy is too low to make them significant. The values of  $T\chi_{\alpha,m} = [\partial \mathbf{I}_{\alpha,m} / (\partial \mathbf{H}_i / T)]_T$  were obtained by subtracting  $\chi_{\beta,m}$  values as given by Eq. (26) from  $\chi_m$  for the data in the first six columns of Table II. The method used in obtaining the data in the last six columns of Table II gave  $\mathbf{I}_{\alpha,m}$  directly. However, it was necessary to use Eq. (17) in correcting  $\mathbf{H}_0$  to  $\mathbf{H}_i$  in this case since the internal field depends on the total magnetic moment  $\mathbf{I}$ . The (a) curve in Fig. 2 shows that the values of  $T\chi_{\alpha,m}$  fall on the same curve when plotted against  $\mathbf{H}_i/T$ . Table IV gives values of the temperature-dependent portion of the isothermal differential molal susceptibility of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O} \times \text{temperature}$  obtained from smoothed curves based on the values of  $\Delta \mathbf{I} / \Delta \mathbf{H}_i$ . In most cases these values could not be treated as differentials during the curve construction. Table IV also gives the corresponding value of  $\mathbf{I}_{\alpha,m}$  and the work of magnetization divided by temperature,

$$\int_0^{\mathbf{H}_i} \frac{\mathbf{H}_i}{T} d\mathbf{I}_{\alpha,m},$$

for the temperature-dependent portion of the induction. The reason for considering this work term separately is that only the temperature-dependent work contrib-

TABLE III. Magnetization of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  at various fields and temperatures.  $\mathbf{I}_m$  is in gauss  $\text{cm}^3 \text{mole}^{-1}$ .  $\mathbf{H}_0 - \mathbf{H}_i$  is the correction to internal field, in gauss.

$\mathbf{H}_0$	$\mathbf{I}_m$	$\mathbf{H}_0 - \mathbf{H}_i$	$\mathbf{H}_0$	$\mathbf{I}_m$	$\mathbf{H}_0 - \mathbf{H}_i$
$T = 1.905^\circ\text{K}$			$T = 14.15^\circ\text{K}$		
0	0	0	0	0	0
2 500	2 526	33	5 000	373	5
5 000	4 784	62	10 000	743	10
7 500	6 609	86	15 000	1 109	15
10 000	8 007	105	20 000	1 466	19
15 000	9 811	128	25 000	1 811	24
20 000	10 781	141	30 000	2 143	28
25 000	11 324	148	35 000	2 458	32
30 000	11 655	152	40 000	2 756	36
35 000	11 870	155	45 000	3 039	40
40 000	12 008	157	50 000	3 303	43
45 000	12 113	158	60 000	3 785	49
50 000	12 195	159	70 000	4 205	55
60 000	12 320	161	80 000	4 568	60
70 000	12 421	162	90 000	4 875	64
80 000	12 517	163	$T = 20.39^\circ\text{K}$		
90 000	12 608	164	0	0	0
100 000	12 699	166	5 000	268	3
			10 000	534	7
			15 000	799	11
$T = 4.219^\circ\text{K}$			20 000	1 060	14
0	0	0	25 000	1 317	17
2 500	1 177	15	30 000	1 568	21
5 000	2 326	30	35 000	1 813	24
7 500	3 421	45	40 000	2 050	27
10 000	4 443	58	45 000	2 280	30
15 000	6 222	81	50 000	2 505	33
20 000	7 639	100	$T = 78.25^\circ\text{K}$		
25 000	8 731	114	0	0	0
30 000	9 562	125	5 000	89	1
35 000	10 192	133	10 000	176	2
40 000	10 671	139	15 000	264	3
45 000	11 040	144	20 000	351	5
50 000	11 336	148	25 000	437	6
60 000	11 771	154	30 000	523	7
70 000	12 072	157	40 000	692	9
80 000	12 283	160	50 000	860	11
90 000	12 445	162			
100 000	12 568	164			

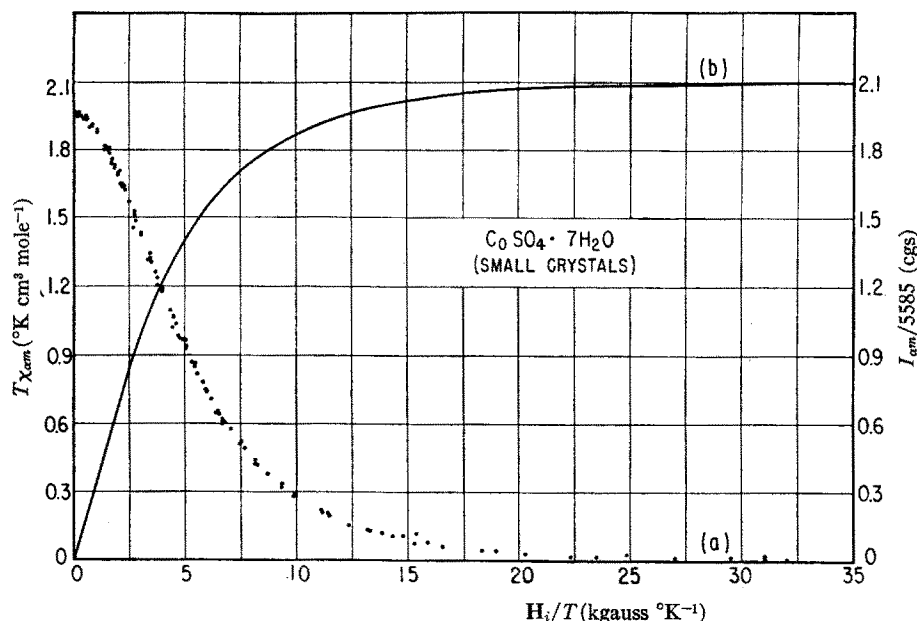


FIG. 2. (a) Temperature-dependent portion  $\chi_{am}$  of the isothermal differential magnetic susceptibility. (b) Temperature-dependent magnetic induction in molal Bohr magnetons.

utes to the entropy change. Calorimetric values of this quantity have been reported<sup>5</sup> in a separate investigation.

$$\mathbf{I}_{\alpha,m} = \mathbf{I}_m - \mathbf{I}_{\beta,m}, \quad (27)$$

$$f\left(\frac{\mathbf{H}_i}{T}\right) = \mathbf{I}_m \int -\chi_{\beta,m} d\mathbf{H}_i. \quad (28)$$

Figure 2, curve (b), shows a plots of  $\mathbf{I}_{\alpha,m}/5585$ , where 5585 gauss cm<sup>-3</sup> mole<sup>-1</sup> is the value of the molal Bohr magneton.

$$TdS = dE - \mathbf{H}_0 d\mathbf{I}, \quad (29)$$

where  $S$  and  $E$  represent the entropy and energy of the system, respectively.

$$\mathbf{H}_0 = \mathbf{H}_i - N\mathbf{I}, \quad (30)$$

$$\mathbf{I} = \mathbf{I}_{\alpha} + \mathbf{I}_{\beta}, \quad (31)$$

$$TdS = dE - N\mathbf{I}d\mathbf{I} - \mathbf{H}_i d\mathbf{I}_{\beta} - \mathbf{H}_i d\mathbf{I}_{\alpha}. \quad (32)$$

Since the temperature-dependent magnetization  $\mathbf{I}_{\alpha}$  may be separated from the temperature-independent magnetization  $\mathbf{I}_{\beta}$ , it is convenient to define the quantity  $E_{\alpha}$  as relating only to the temperature-dependent system under the influence of  $\mathbf{H}_i$ . Since the work done in producing  $\mathbf{I}_{\beta}$  is equal to an energy change,

$$dE - N\mathbf{I}d\mathbf{I} - \mathbf{H}_i d\mathbf{I}_{\beta} = dE_{\alpha}, \quad (33)$$

and

$$TdS = dE_{\alpha} - \mathbf{H}_i d\mathbf{I}_{\alpha}, \quad (34)$$

from which

$$(\partial E_{\alpha} / \partial \mathbf{I}_{\alpha})_T = -T^2 [(\partial \mathbf{H}_i / T) / \partial T]_{\mathbf{I}_{\alpha}}. \quad (35)$$

When  $\mathbf{I}_{\alpha}$  is a function of  $\mathbf{H}_i/T$ , as in the present case, the right-hand side of Eq. (29) is zero and the inference is that there is no inter-ion magnetic interference.

Since  $\Delta E_{\alpha} = 0$ ,

$$T\Delta S = - \int_0^{\mathbf{H}_i} \mathbf{H}_i d\mathbf{I}_{\alpha} \quad (36)$$

at constant  $T$ , and it is of interest to compare values of

$$\Delta S = - \int_0^{\mathbf{H}_i/T} \frac{\mathbf{H}_i}{T} d\mathbf{I}_{\alpha} \quad (37)$$

with the direct calorimetric values reported<sup>5</sup> previously. This has been done in Table IV where entropy has been given in gibbs mole<sup>-1</sup> = (cal deg<sup>-1</sup> mole<sup>-1</sup>).

The entropy change on magnetization shown in column 4 confirms the previous result, shown in column 5 of Table IV, that the *a priori* probability of cobaltous ion is  $p = 2$ .

When the 4th and 5th columns are compared it is seen that the entropy change during magnetization, as determined by direct calorimetric observation, is about one percent greater than the values calculated from the temperature coefficient of the work of magnetization. At values of  $\mathbf{H}/T$  up to about 10 000 gauss deg<sup>-1</sup>, we believe that the values obtained from the work of magnetization are to be preferred since the isothermal differential susceptibility does not change rapidly with field and may be measured with relatively good accuracy in low fields. At high values of the field the work function becomes very insensitive and the calorimetric values are preferable.

As mentioned previously<sup>5</sup> the lack of good magnetic field control has led to the suspicion that the direct calorimetric values of the entropy increase during

demagnetization are a little high. However, it is quite possible that the analysis of the data in terms of an ideal component obeying an  $\mathbf{H}/T$  function, and a temperature independent component, may be unjustified to a very small extent, which could contribute to the discrepancy. The rise in heat capacity<sup>7</sup> below 1°K cannot be overlooked as evidence that the system has a small amount of nonideality. It is evident that the ordered system at very low temperatures is lower in energy than the disordered system at higher temperatures. While this does not in itself show whether the  $\Delta E$  is positive or negative for the process of saturation ordering by isothermal magnetization above 1°K, a very small negative  $\Delta E$ , equivalent to the order of 0.01 cm<sup>-1</sup>, would explain the discrepancy between columns 4 and 5 of Table IV.

It was noted that the assumption of a larger negative field coefficient of  $\chi_s$  would increase the contribution assigned to the  $\mathbf{H}/T$  component at high fields and thus improve agreement, but the effect is well within the limit of accuracy and further adjustment of the data seems unjustified. The assumption of a component which is completely independent of temperature may also be somewhat questionable.

It is evident that better correlation of magnetic properties will require observations of very high accuracy. As has been mentioned above, there is considerable room for improvement over the accuracy of the present measurements and we regard them only as a very encouraging step in that direction.

Fritz and Giaque<sup>7</sup> (F. and G.) used the early measurements of Jackson<sup>9</sup> on  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , to correct their fluxmeter coils for the presence of the sample, which was held at 30°K to reduce the correction. The present more reliable susceptibility value, calculated to 30°K, has now been substituted. We have also found and corrected an arithmetical error in the data books of F. and G. dealing with the geometrical relationship between their measuring coils and ellipsoidal sample.

Also, F. and G. did not include the term  $\frac{4}{3}\pi[(1-f_s)/f_s]$  in the empirical demagnetizing factor given by Casimir.<sup>8</sup> Their  $f_s=0.61$ .

When these several factors are combined into a single formula the corrected values of the initial susceptibility from the work of F. and G. are given by

$$\chi_m = \frac{\chi_{m(F,G.)} - 0.001}{1.038 - 0.0113\chi_{m(F,G.)}} \quad (38)$$

The corrected results agree well with the present observations although they are of lesser accuracy due to the more difficult conditions of the earlier experiments.

Note: Our attention has been called to some initial

TABLE IV. Smoothed values of molal temperature-dependent isothermal differential magnetic susceptibility  $\times$  temperature. Magnetization. Comparison of the calorimetric and temperature coefficient of magnetic work values of the entropy change during magnetization.  $\mathbf{H}_i/T$  given in gauss deg<sup>-1</sup>,  $\mathbf{I}_{a,m}$  in gauss cm<sup>3</sup> mole<sup>-1</sup>,  $S$  in gibbs mole<sup>-1</sup>.

$\mathbf{H}_i/T$	$T\chi_{a,m}$	$\mathbf{I}_{a,m}$	$-\int_0^{\mathbf{H}_i/T} \frac{\mathbf{H}_i d\mathbf{I}_{a,m}}{T}$	$-\Delta S_{\text{calorimetric}}$
0	1.964	0	0	0
500	1.948	979	0.006	0.006
1 000	1.901	1 942	0.023	0.023
2 000	1.706	3 755	0.088	0.088
3 000	1.445	5 332	0.181	0.184
4 000	1.185	6 646	0.291	0.295
5 000	0.949	7 710	0.405	0.409
6 000	0.743	8 553	0.515	0.519
7 000	0.578	9 211	0.617	0.620
8 000	0.454	9 723	0.709	0.712
9 000	0.353	10 125	0.790	0.794
10 000	0.276	10 440	0.861	0.865
12 000	0.168	10 870	0.974	0.981
14 000	0.111	11 150	1.058	1.070
16 000	0.074	11 330	1.124	1.138
18 000	0.049	11 450	1.173	1.190
20 000	0.032	11 530	1.210	1.230
25 000	0.014	11 640	1.265	1.294
30 000	0.007	11 690	1.298	1.329
40 000	0.003	11 730	1.337	1.360
50 000	0.001	11 750	1.355	1.369
60 000	0.000	11 760	1.362	1.373
			1.377 = $R \ln 2$ =	1.377

susceptibility measurements on Pyrex-type 7740 glass ordinarily used in tubing. For this material Salinger and Wheatley<sup>10</sup> find

$$\chi(\text{initial})/\rho = [(1.6 \pm 1) + (12 \pm 3/T)^\circ\text{K}] \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$$

at the temperatures of liquid helium.

Any entropy change in the 7740 Pyrex glass ellipsoid container, which weighed about 35 g, would apply equally to the direct and indirect entropy determinations. However, in the direct calorimetric observations<sup>5</sup>

<sup>9</sup> L. C. Jackson, Commun. Phys. Lab. Univ. Leiden, No. 163 (1923).

<sup>10</sup> G. L. Salinger and J. C. Wheatley, Rev. Sci. Instr., **32**, 872 (1961).

the apparatus included an additional Pyrex jacket to enclose the helium gas thermometer. The weight of this outer jacket was about 90 g. Thus, using the value of Salinger and Wheatley as an order of magnitude for the impurity susceptibility effect, the outer glass jacket contributed an amount of about 0.005 to the Curie constant of  $1.964 \text{ deg cm}^3 \text{ mole}^{-1}$ . The effect is probably

within the limit of error of the present results, but we may note again that the direct calorimetric entropy change was a little higher than the indirect determination. Further desirable increases in accuracy will require a rather complete investigation of the magnetic properties of such containers as a function of field and temperature.

## Single-Crystal X-Ray Diffraction Study of $\beta$ Nitrogen

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Three-dimensional x-ray diffraction data have been collected from single crystals of nitrogen at  $50^\circ\text{K}$ . The observed general condition,  $l=2n$  for  $hh2hl$  reflections is in agreement with the previously assigned space group,  $P6_3/mmc$ , and there are two molecules in the unit cell. The data agree equally well with two nearly physically indistinguishable models, in each of which the molecular centers form a hexagonal closest packed (hcp) lattice. In one, the molecule is precessing about the  $z$  axis passing through its center, at an angle of  $54.5 \pm 2.5^\circ$  between  $z$  and the N—N bond, while in the other the nitrogen atoms are statistically distributed among the 24-fold positions with the molecular axis again at an angle of  $54.5^\circ$  relative to  $z$ .

### INTRODUCTION

THE  $\beta$  phase of nitrogen which exists between  $35.6^\circ$  and  $63.1^\circ\text{K}$  has been the subject of many experimental studies. An anomaly in the specific heat curve,<sup>1</sup> which precedes the transition from the low temperature  $\alpha$  phase to the  $\beta$  phase, suggests the onset of some form of rotation. X-ray diffraction studies on polycrystalline samples<sup>2-4</sup> indicate molecular rotation or disordering. On the other hand, free spherical rotation seems unlikely on the basis of molecular volume data.<sup>4</sup> There are also thermodynamic arguments<sup>5</sup> against completely free rotation. The absence of pure quadrupole resonance of the nitrogen atom ( $I=1$ ),<sup>6</sup> and the corresponding absence of a quadrupole splitting in the NMR spectrum<sup>7</sup> have led to the conclusion that the molecular motions in the  $\beta$  phase are sufficient to average the electric field gradient at the nucleus to zero. As a result of an x-ray diffraction study of oriented single crystals of  $\beta$  nitrogen we have been led, as described below, to a model which is consistent with these earlier results. This study is the first of a series of single crystal x-ray diffraction investigations at temperatures between those of liquid  $\text{N}_2$  and liquid He.

### EXPERIMENTAL

Using a liquid-helium Dewar specifically designed<sup>8</sup> for the growth and orientation of single crystals at very low temperatures, x-ray diffraction data were collected from two single crystals of  $\beta$  nitrogen at  $50^\circ\text{K}$ . Briefly, the nitrogen sample is sealed in a glass bulb which narrows to a capillary. The capillary is attached to a cold finger which extends up into the helium Dewar through a flexible copper bellows. The cold finger is oriented by manipulating wires emerging at the top of the liquid-helium container. A small heater and thermocouple provide temperature control of the crystal. The data are collected by oscillating the entire dewar.

The crystals, approximately 1 mm in diameter, were grown from the liquid phase, and oriented on the crystallographic axis nearest the camera axis, which happened to be twofold in both cases. A series of overlapping  $15^\circ$  oscillation photographs were taken using  $\text{Mo K}\alpha$  radiation, which were consistent with a reciprocal lattice symmetry of  $D_{6h}$ . The percentage standard deviation from  $D_{6h}$  symmetry for each reflection is given in Table I. The standard deviation was determined by first averaging those reflections which had identical indices (including sign) and then determining the deviations from averages of reflections whose indices were equivalent by  $D_{6h}$  reciprocal lattice symmetry. Note that this averaging process is made for

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