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Investigation of Nuclear Effects in Paramagnetic Single Crystals at Very Low Temperatures*†

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The hyperfine structure coupling of the magnetic moment of the nucleus with the magnetic moment of the electronic cloud of a paramagnetic ion gives rise to a Schottky specific heat anomaly at an appropriate temperature. For the cobaltous ion in a single crystal of cobalt ammonium sulfate this temperature is about 0.1°K. In the region where the specific heat goes as A/T^2 and where the Curie law $\chi = C/T$ holds, one can make measurements of A by means of an ac mutual inductance bridge which measures the susceptibility of the paramagnetic salt. The method of measurement consists in superposing a dc magnetic field on the salt already in the ac field of the bridge. This dc field depresses the susceptibility an amount depending on the parameter C/A which is therefore a constant of the material being investigated. If one knows the Curie constant, then one has A immediately. This measured A, however, is made up of two contributions: (a) that arising from the nuclear-electronic coupling and (b) that arising from the dipole interaction of neighboring paramagnetic ions. The (b) contribution is a function of concentration of the ions, so that by making measurements of A at various dilutions and plotting A as a function of dilution, one obtains an intercept by extrapolation to infinite dilution which is the part of A due to nuclear specific heat. The thermodynamic measurements made thus give a nuclear specific heat of $C_vT^2 = 16.1 \times 10^{-4}R$, where R is the gas constant, which is in excellent agreement with $C_vT^2 = 16 \times 10^{-4}R$ calculated from microwave data. It is observed that pure cobalt ammonium sulfate has a Curie point at ~0.125°K, while the diluted salts do not possess one in the same temperature region.

I. INTRODUCTION

THE existence of hyperfine structure coupling for paramagnetic ions in the solid state was suggested independently by Rose[1] and Gorter.[2] That this coupling should cause a splitting of the energy levels of the system and consequently give rise to a Schottky[3] specific heat anomaly was pointed out by Garrett,[4] who corroborated his interpretation with experimental work on powdered copper potassium sulfate and powdered cobalt ammonium sulfate.

Because of the paucity of information on paramagnetic single crystals and because of its importance in quantitative treatments of the solid state, our investigations on the specific heat anomaly due to the hyperfine structure coupling in cobalt ammonium sulfate were carried out on single crystals.

II. THEORY

In paramagnetic salts there are several types of interaction, any and all of which may remove degeneracies. The main interactions are (1) interaction of the paramagnetic ion with the strong crystalline electric field (Stark effect) caused by the water dipole environment, (2) exchange interactions between electrons of the paramagnetic ion and other electrons in the crystal, (3) interaction between neighboring paramagnetic ions, often called the dipole-dipole interaction, (4) hyperfine structure coupling and quadrupole coupling between the electronic "clouds" of the paramagnetic ions and their own nuclei, (5) interaction between nuclei of adjacent paramagnetic ions. The interaction (4) is the chief concern of the present paper.

Stark Effect

The effect of the crystalline field can be treated as a perturbation on the free ion. If one writes the hamiltonian of the spin system as

$$\mathcal{H} = \sum_i \mathcal{H}_i, \tag{1}$$

where $\mathcal{H}_i$ is the hamiltonian of the ith paramagnetic ion and the sum is taken over all ions, then $\mathcal{H}_i$ will have the form,

$$\mathcal{H}_i = \mathcal{H}_0 + \lambda(\mathbf{L}\cdot\mathbf{S}) + V + \beta(\mathbf{L}+2\mathbf{S})\cdot\mathbf{H}, \tag{2}$$

where $\mathcal{H}_0$ is the hamiltonian of the free ion without spin orbit coupling, $\lambda(\mathbf{L}\cdot\mathbf{S})$ is the spin-orbit interaction, V is the potential of the crystalline field, and the last term describes the influence of an external magnetic field $\mathbf{H}$; β is the Bohr magneton and $\mathbf{L}$ and $\mathbf{S}$ are the angular momenta operators for the orbital motion and spin. Higher terms proportional to $\mathbf{H}^2$ and to $(\mathbf{L}\cdot\mathbf{S})^2$ for ions which, when free, have Russell-Saunders coupling are neglected. Pryce[5] and Jauch[6] have recently given alternative approaches utilizing the eigenvalues of an observable involving only spin variables, with the energy levels correct to the second order.

In the case of ions of the iron group, the incomplete d-shell is not screened; and because of the lack of screening, the spin-orbit coupling is strongly affected by the crystalline electric field.

In cobalt ammonium sulfate $Co(NH_4)_2(SO_4)_2\cdot 6H_2O$, the waters of hydration form an octahedron around the Co^{++} ion, and one can treat the $Co^{++}\cdot 6H_2O$ unit as a

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‡ This work was performed while the author was a Graduate Fellow of the Oak Ridge Institute of Nuclear Studies.

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[1] M. E. Rose, Phys. Rev. **75**, 213 (1949).

[2] C. J. Gorter, Physica **14**, 504 (1948).

[3] W. Schottky, Z. Physik **23**, 448 (1922).

[4] C. G. B. Garrett, Nature **163** (1949); thesis, Trinity College (1949, unpublished).

[5] M. H. L. Pryce, Proc. Phys. Soc. (London) **A63**, 25 (1950).

[6] J. M. Jauch, ORNL 813 (1950), unpublished.

nonlinear "molecule." Since the "molecule" does have cubic symmetry, one must consider the Jahn-Teller effect.[7] Jahn and Teller considered a molecule in a state with a degenerate energy level as being a result of some symmetry property. Their group-theoretical arguments showed that such a state cannot be stable, and therefore a distortion will occur which will lead to a state with lower symmetry removing the original degeneracy. Van Vleck[8] applied this theorem to $Co^{++}\cdot 6H_2O$ and showed that such a deformation removes all degeneracy except the Kramers[9] degeneracy.

The configuration of Co^{++} is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^7$ and the state according to Hund's rule is $^4F_{9/2}$. It has been calculated by Laporte[10] that the parameter λ for the spin orbit coupling in the hamiltonian given by Eq. (2) is $\lambda = 180\ \text{cm}^{-1}$.

In a cubic field the orbital F level ($L=3$) is split according to $D_3 = \Gamma_2 + \Gamma_4 + \Gamma_5$ with the Γ_4-level lowest. In salts of the Tutton group where the symmetry of the field is predominantly tetragonal the lowest cubic level splits into a doublet and a singlet $\Gamma_4 = \Gamma_3 + \Gamma_5$ with the singlet lying lower. Introduction of the spins makes the degeneracy of the tetragonal levels four times as much, but the strong spin-orbit coupling splits these levels into Kramers' doublets according to $A_2 D_{\frac{3}{2}} = \Gamma_6 + \Gamma_7$ and $ED_{\frac{3}{2}} = 2\Gamma_6 + 2\Gamma_7$ giving again six doublets. Pryce[5] has shown that the tetragonal splitting is smaller than the LS coupling splitting. This is the result of the almost complete cancellation of the contributions of the second- and fourth-order terms in the series expansion of the crystalline potential. The splitting between the two lowest doublets is estimated to be about $300\ \text{cm}^{-1}$ in cobalt ammonium sulfate so that the contribution of the Stark splitting to the specific heat below 1°K is negligible. This is one reason for choosing this particular salt. The higher levels influence the properties of these paramagnetic salts only indirectly through their influence on the lower levels.

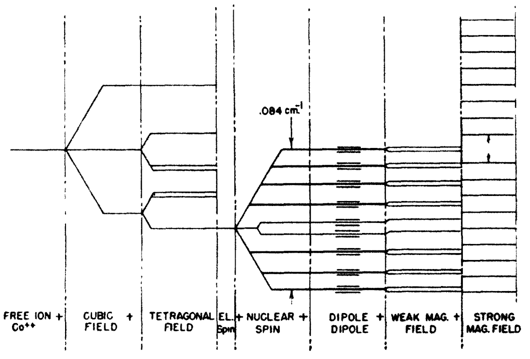

FIG. 1. Energy level scheme for Co^{++} in cobalt ammonium sulfate.

Exchange and Dipole Interactions

It is convenient to treat these two interactions simultaneously as was done by Van Vleck.[11] The results of his calculation show that the specific heat arising from these interactions is given by

$$C_v = (Nk)(Q/6)[g^2\beta^2 NJ(J+1)/k]^2/T^2, \tag{3}$$

where N is Avogadro's number, g is the splitting factor, β is the Bohr magneton, J is the total angular momentum quantum number, k is the Boltzmann constant, T is the absolute temperature, and Q is a lattice geometry factor.

As is always the case when $kT \gg$ splitting, the specific heat goes as $1/T^2$ and one can write the dipole-dipole specific heat as

$$C_v = A_{DD}/T^2, \tag{4}$$

where A_{DD} is a constant. The exchange terms are neglected here because, as will be seen later, there is experimental evidence that exchange effects in cobalt ammonium sulfate appear to be negligible.

It is interesting to consider the effect of magnetically diluting the already dilute paramagnetic salt. This dilution can be accomplished by replacing some of the paramagnetic ions by diamagnetic ions. Experimentally this can be accomplished by co-crystallizing isomorphous salts.

It can be shown that the dipole-dipole specific heat and the exchange specific heat vary linearly with random dilution. This suggests the important experimental procedure of measuring the specific heat in crystals of varying dilution and extrapolating the measured results to infinite dilution, thereby eliminating any contribution to the specific heat from phenomena which are functions of concentration.[12] The effect of the dipole-dipole coupling is not to give sharply defined lines in the energy level scheme but rather to broaden the lines because of the production of large numbers of levels of the order 2^N which form a band of width approximated by β^2/N, where β is the Bohr magneton. This is indicated in the energy level scheme shown in Fig. 1, by placing dashes above and below the sharp lines in the spectrum.

Interaction between the Nucleus and Electron Cloud

The interaction between the nucleus and electrons can be broken down into at least three parts: (*a*) magnetic interaction of the nuclear magnetic moment with the moment due to electron spin and unquenched residual orbital angular momentum of the electron, (*b*) nuclear quadrupole interaction with the gradient of the electric field in the electron cloud, and (*c*) coulombic interaction.

We consider here only the interaction given by (*a*). Assuming that both the nuclear spin and electron spin

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[7] H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) **A161**, 220 (1937).

[8] J. Van Vleck, J. Chem. Phys. **7**, 72 (1939).

[9] H. A. Kramers, Proc. Acad. Amsterdam **32**, 1176 (1929); **33**, 959 (1930).

[10] O. Laporte, Z. Physik **47**, 76 (1928).

[11] J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937).

[12] R. Benzie and J. Cooke, Nature **164**, 837 (1949).

magnetic moments can be treated as dipoles, one can write down immediately the interaction energy as

$$W_{I,J}=-(\beta\mu_I/r^3)[\mathbf{I}\cdot\mathbf{S}-(3(\mathbf{I}\cdot\mathbf{r})(\mathbf{S}\cdot\mathbf{r})/r^2)-\mathbf{I}\cdot\mathbf{L}],\quad(5)$$

where μ_I is the nuclear magnetic moment, **I**, **S**, and **L** are the usual angular momentum operators, and **r** is the radius vector with modulus r. A simple calculation shows that the $\mathbf{I}\cdot\mathbf{L}$ term in cobalt ammonium sulfate is negligible, the splitting being of the order 10^{-8} cm^{-1}.

If one now assumes that the electric field surrounding the ion is cylindrical in symmetry about the z axis (it is actually tetragonal in cobalt ammonium sulfate), one can integrate (5) over space in cylindrical coordinates, getting[13]

$$\mathcal{H}_{\mathrm{hfs}}=A^*I_zS_z+B(S_xI_x+S_yI_y),\quad(6)$$

where A^* and B are determinable from microwave measurements.

If quadrupole terms are included, the hyperfine structure hamiltonian given by (6) must include another term given by

$$\mathcal{H}_{\mathrm{quad}}=Q\{I_z^2-\tfrac{1}{3}I(I+1)\}.\quad(7)$$

Indications are that Q is very small in cobalt ammonium sulfate.

Setting up the energy matrix by means of Eq. (6) shows, from symmetry considerations of the diagonal elements, that the hyperfine structure in cobalt ammonium sulfate is composed of 7 doublets and 2 singlets. (See Fig. 1.) The off-diagonal elements given by the second member of the hamiltonian of (6) produce such a small perturbation for cobalt ammonium sulfate that the energy level system may be considered at eight equally spaced doublets with an over-all splitting of 0.084 cm^{-1}. The values of A^* and B are 0.024 cm^{-1} and 0.0028 cm^{-1}, respectively.[13]

On the high temperature side of the Schottky anomaly the hyperfine structure contribution to the specific heat is given by[13]

$$C_N=R(hc/kT)^2[\tfrac{1}{9}(A^{*2}+2B^2)S(S+1)I(I+1)],\quad(8)$$

where h = Planck's constant and c = velocity of light. The specific heat calculated from Eq. (8) is given by[13]

$$C_NT^2/R=16\times10^{-4}=A_N.\quad(9)$$

One could, in principle, measure this specific heat by making measurements on crystals possessing an ion having a nuclear spin, repeating the measurements using an isotope of the ion without nuclear spin, and taking the difference as the nuclear specific heat. The present measurements have been made using the random dilution technique. Cobalt is monoisotopic and is an excellent ion for the present purposes.

III. ENTROPY CONSIDERATIONS

There are several advantages to using a single crystal in measurements at low temperatures, among which one of the most important is the fact that the entropy is known very accurately. In addition, in the case of a magnetically anisotropic crystal like cobalt ammonium sulfate, the crystal can be so oriented that a larger portion of the entropy can be removed along one axis than another. In cobalt ammonium sulfate[13] with its g-factors‖ of 6.2, 3.0, and 3.0 along the K_1, K_2, and K_3 magnetic axes, respectively, the entropy removal is considerably greater along the K_1 axis.

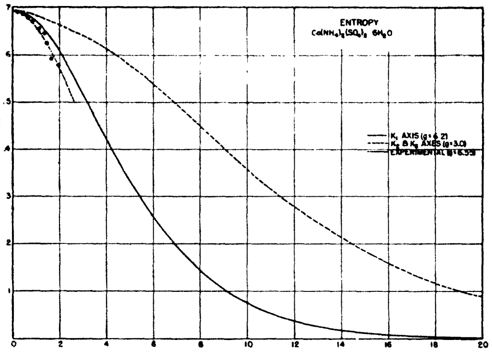

FIG. 2. Entropy removal upon magnetization along various magnetic axes.

From microwave measurements it is known that the ground state of the Co^{++} ion in cobalt ammonium sulfate is a Kramers' degeneracy doublet which is tractable as an $S=\frac{1}{2}$ system and which can be split by means of a small magnetic field.

Since the crystal is magnetically anisotropic, the energy is given by

$$W=\pm\tfrac{1}{2}\beta\theta,\quad(10)$$

where

$$\theta=[\sum(g_{ik}H_k)^2]^{\frac{1}{2}},\quad(11)$$

in which g_{ik} is the tensorial g-factor, H_k the applied field in the kth direction, and β the Bohr magneton.

From this it follows that the entropy is given by

$$S/R=[\ln\{2\cosh(\beta\theta/2kT)\}-(\beta\theta/2kT)\tanh(\beta\theta/2kT)].\quad(12)$$

The calculated electronic entropy removal upon magnetization at ~1°K along the principal magnetic axes is shown in Fig. 2, from which it is evident that a much greater entropy removal for a given H/T can be effected along the K_1 axis. The present experiment was performed by suspending the crystal with the K_2 axis vertical and the K_1 axis in the horizontal plane free to rotate so that it would be parallel to the applied magnetizing field. It is interesting to note that a directional magnetic specific heat may exist in an anisotropic crystal, and it is hoped to pursue this point experimentally at a later date.

As usual in measurements below 1°K, the temperature $T+$ was obtained by extrapolation of the Curie law.

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[13] B. Bleaney, Phys. Rev. **78**, 214 (1950).

‖ *Note added in proof:*—The g-values of 6.2 and 3.0 are ionic values; the crystalline g-values are $g_1=5.71$, $g_2=3.00$, and $g_3=4.34$.

Assuming, as previously mentioned, that the ground electronic state is $S=\frac{1}{2}$, one can write the Curie constant along a principal axis as

$$C_i = Ng_i^2S(S+1)\beta^2/3k, \tag{13}$$

where g_i is the g-factor along a principal axis i. From Eq. (13) with $S=\frac{1}{2}$, $g_i=3.0$, the calculated Curie constant C_2 is 0.852 for a mole of cobalt ammonium sulfate along the K_2 axis.

The Curie constant was checked experimentally by obtaining susceptibility-temperature calibration curves for a single crystal of chrome potassium alum whose Curie constant per mole is well known (1.760) and for the pure cobalt ammonium sulfate crystals along their K_2 axis. Knowing the ratio of the slopes of these curves and making appropriate mass corrections, we have determined the Curie constant C_2 of the cobalt ammonium sulfate to be 0.858. This figure has been used in the calculations throughout this paper. The single crystals of cobalt ammonium sulfate were ground to spherical form (~13.5-mm diameter). They were the best of the crystals left after continuous culling from several hundred seed crystals.

IV. METHOD OF MEASUREMENT

Consider now a paramagnetic salt at liquid helium temperatures. In the salt there are three separate statistical systems, with separate temperatures, namely, the lattice and the electronic and nuclear spins. Since an alternating current mutual inductance bridge is the actual measuring device, the observed susceptibility is frequency dependent. At low frequencies, the observable is the isothermal susceptibility χ_0 because heat transfer between the lattice and spin can take place. At high frequencies the adiabatic susceptibility χ_s is the observable, considering the spin system along and assuming the nuclear electronic spin relaxation time to be small compared with the period of the measuring field. The dispersion at intermediate frequencies can be explained in terms of a relaxation time of the spin-lattice system.[14]

The present experiment, however, below 1°K is such that both the lattice and spin can oscillate at the same frequency. As the temperature is decreased below 1°K, the ratio of C_L/C_S, where C_L is the lattice and C_S the spin specific heat, respectively, becomes very small; i.e., the lattice thermal capacity is negligible. Thus the observable susceptibility will be the adiabatic susceptibility χ_s, and dispersion phenomena completely irrelevant to the measurements.

If one assumes that the Curie law is valid ($\chi=C/T$) and that the specific heat is given by A/T^2, it can be shown that[4]

$$\chi_{SH} = \chi_{00}(1-\tfrac{3}{2}\Xi H^2), \tag{14}$$

where χ_{SH} is the adiabatic susceptibility in a field H, χ_{00} is the isothermal susceptibility in zero magnetic field, H is a superposed constant magnetic field and Ξ is defined by

$$\Xi = -\frac{1}{\chi}\frac{d\chi}{dT}\frac{d\chi}{dS} = \frac{C}{A}, \tag{15}$$

in which S is the entropy, T is the temperature, and χ is the susceptibility.

The application of the steady field has two effects, namely, (1) decreasing the isothermal susceptibility by production of reversible warming effects, and (2) depressing χ_S below χ_0. The two susceptibilities would be equal only in zero field but at the temperature T_H.

In terms of the measured quantities Eq. (14) can be rewritten as

$$\Xi = \frac{2}{3H^2}\left(\frac{\mathfrak{M}_S-\mathfrak{M}_0}{\mathfrak{M}_0}\right) = \frac{C}{A}, \tag{16}$$

where $\mathfrak{M}$ is the mutual inductance due to the salt, so that if one knows the Curie constant, a measurement of Ξ gives A immediately. Thus, the superposition of a steady magnetic field of proper magnitude on the ac magnetic field of the bridge enables one to measure the tail of the Schottky specific heat anomaly without recourse to calorimetry.

V. CRYSTALLOGRAPHY OF HEXAHYDRATED COBALT AMMONIUM SULFATE

The crystal structure of cobalt ammonium sulfate hexahydrate has been studied by Halla,[15] and in greater detail several isomorphic salts have been studied by Hofmann.[16] Detailed analysis of x-ray data has enabled one to draw a fair picture of the unit cell. In Fig. 3 is shown a view of the unit crystal structure, the b axis being normal to the plane of the paper. It might be pointed out here that the legend of Fig. 63 in Strukturbericht[17] is incorrect in that the **a** and **c** vectors have been interchanged. This projection demonstrates what Hofmann calls the pseudocubic structure of the salt.

These isomorphic salts are monoclinic, contain two molecules in the unit cell, and have arrangements developed from the space group C_{2h}.[5] All atoms, except Co^{++}, are located in the general position $[\pm(x, y, z); \pm(x+\frac{1}{2}, \frac{1}{2}-y, z)]$. The Co^{++} atoms are located at $(000; \frac{1}{2}\,\frac{1}{2}\,0)$. As pointed out by Wyckoff,[18] however, this arrangement cannot be correct because although the NH_4-O and $Co^{++}-H_2O$ separations are satisfactory, the sulfate oxygens belonging to the different SO_4 groups are much too close together. The given values of the $O-O$ distance are about 2.1A, while the minimum permissible distance should be ~2.7A, indicating a variation of the order 0.5A, a quantity which is not negligible.

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[14] C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, Inc., New York, 1947).

[15] F. Halla and E. Z. Mehl, Z. anorg. u. allgem. Chem. **199**, 379–383 (1931).

[16] W. Hofmann, Z. Krist. **78**, 279–333 (1931).

[17] Strukturbericht, *Band II* (1928–1932), p. 94.

[18] R. Wyckoff, *Structure of Crystals* (Reinhold Publishing Corporation, 1931), second edition, p. 93.

For an adequate quantum-mechanical treatment of the properties of the salt, the wave function of the paramagnetic ions must be known accurately. This calls for a much better picture of the crystal structure than is available at present, and to this end the problem is being investigated by Dr. Max Bredig and Mr. B. S. Borie of the Metallurgy Division of ORNL, who have begun preliminary fourier analysis of the x-ray pictures taken of single crystals grown in this laboratory.

The three crystallographic axes (a, b, c) are very nearly in the ratio (3, 4, 2). The a axis makes an angle of 106° 56′ with the c axis in cobalt ammonium sulfate. The Co^{++} ions lie in the points mentioned previously and are surrounded by an octahedron of water molecules, four of which lie nearly at the corners of a square at a distance of about 1.9A from the Co^{++} and the other two slightly farther away at about 2.15A. The electric crystalline field per ion then should have approximately tetragonal symmetry about the line joining the more distant waters. As already indicated, however, there are two Co^{++} ions per unit cell and in a spatial average over the crystal one has two tetragonal axes equally inclined to the *ac* plane. The angle between the tetragonal axes and the *ac* plane, in cobalt ammonium sulfate, is about 33°.

It is known from microwave measurements that magnetic anisotropy exists, and it is necessary to correlate the readily identifiable crystallographic axes with the magnetic axes. In Fig. 4 are shown views of a crystal drawn from an actual specimen grown in the laboratory. It is not a perfect crystal, in that all faces are not equally developed; but it is a typical crystal. In (a) is seen a view taken along the crystallographic b axis. Note the well-defined *ac* axes. In (b) is shown a side elevation and also in (c) in the directions indicated. In (d) is shown a perspective view of the entire crystal. The circles in Fig. 4 (a) and (b) show from what portion the spherical samples actually used in the experiment were cut. The view given by (b) determines what size crystal must be grown to obtain a sphere of given diameter. The dotted line in (a) shows the direction of the principal magnetic axis K_1 with respect to the crystallographic axis. This was determined by placing the crystal in a strong magnetic field (~5 kilogauss) at room temperature and observing the orientation of the crystal suspended along various axes. Observe also that the K_1 axis is very nearly, within a few degrees, the short diagonal of the parallelogram representing the *ac* plane of the crystal. Furthermore, it was found that the K_1 axis is in the *ac* plane, in good agreement with Bleaney *et al.*[19]

The relationship between the various axes—crystalline electric field, magnetic, and crystallographic—is shown in Fig. 5. Note that the K_1 axis lies in the *ac* plane and that the major projections of the tetragonal axes lie along it.

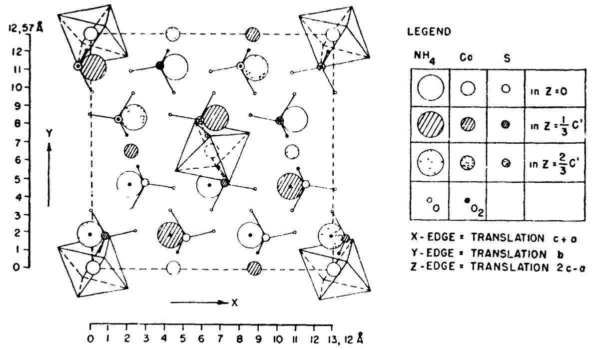

FIG. 3. Crystal structure of cobalt ammonium sulfate.

Paramagnetic absorption measurements[20] indicate that g-values have tetragonal symmetry the values of which are 6.2, 3.0, and 3.0, respectively, and these values have been used in the calculations in this paper.

The crystals used in the present experiments were grown from saturated solutions in a constant temperature bath. Growth rate was controlled by keeping moistened paper covers on the beakers. The diluted crystals were grown by mixing together saturated solutions of the isomorphous salts. The resultant crystals were checked by means of x-rays, and the dilution was found to be random indeed. No evidence of order could be found in the Mg diluted salt, and the tacit assumption is made that Zn behaves in a similar fashion. The magnetic dilution was performed using Zn and Mg as the dilution ions. The manufacturer's specifications for the cobalt ammonium sulfate lists, as impurities: Fe=0.001 percent, Ni=0.06 percent and Zn=0.005 percent (J. T. Baker Chemical Company, lot No. 41548). Analyses of impurities in the isomorphous salts are not available.

VI. APPARATUS AND EXPERIMENTAL PROCEDURES

The measurements were carried out below 1°K, and this necessitated the use of the adiabatic demagnetiza-

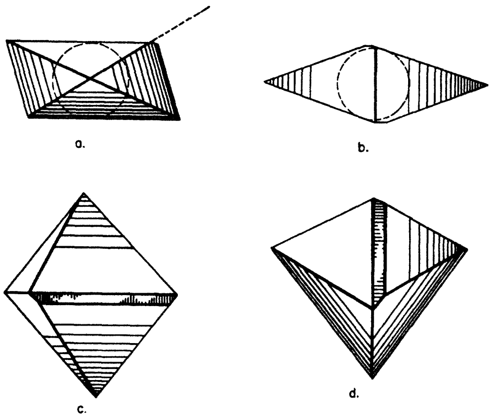

FIG. 4. Actual crystal grown in the laboratory.

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[19] Bleaney, Penrose, and Plumpton, Proc. Roy. Soc. (London) **A198**, 406 (1949).

[20] B. Bleaney and D. J. E. Ingram, Nature **164**, 116 (1949).

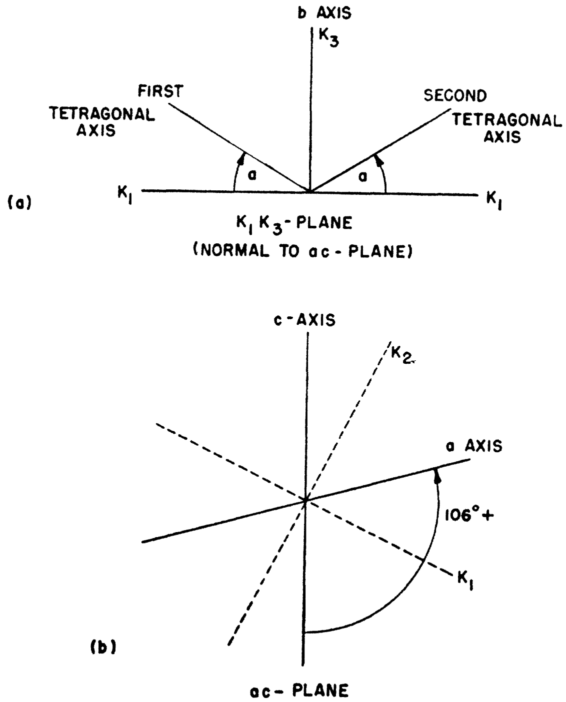

FIG. 5. Relationship of axes in cobalt ammonium sulfate.

tion technique. The magnet used in the adiabatic demagnetizations was a large Weiss-type electromagnet. The field was very uniform over a cylindrical volume, and variation was negligible over the diameter of the spherical single crystal of ~13.5 millimeter diameter.

The current through the coils was controlled to 0.1 percent by means of an amplidyne-controlled saturable reactor. The maximum magnetic field over the 2-inch gap was about 13 kilogauss at slightly less than 6-kw input. The magnet was mounted on a carriage and track and could be rolled away when necessary.

The present cryostat was constructed so that the sample could be changed quite easily, even during a run, if one could afford the loss of the helium boiled off by inserting a relatively warm sample. The details of the cryostat are shown in Fig. 6. The measured heat leak to the salt was 3.6 ergs per minute.

The loss rate of liquid helium as measured over an eight hour period was 22.6 cc per hour. The liquid helium could be pumped down to 0.95°K.

The experimental measurements were made with an ac mutual inductance bridge of the Hartshorn type, which was first applied to low temperature methods in the paramagnetic relaxation experiments of DeHaas and DuPré.[21–23]

The circuit is shown in Fig. 7, where it can be seen that the primaries and secondaries are connected in series with common points as shown. The secondary consists of, in addition to the mutual inductance, secondary coils, an amplifier, tuned circuit, cathode follower, and the detector, a vibration galvanometer tuned to 35 cps. The amplifier contained a specially designed filter having a resonant frequency of 35 cps and a bandwidth ~4 cps. A cathode follower, essentially an impedance transformer, was required to match the output of the amplifier to the galvanometer. The ac bridge method is chosen because it enables one to measure both components of a complex susceptibility

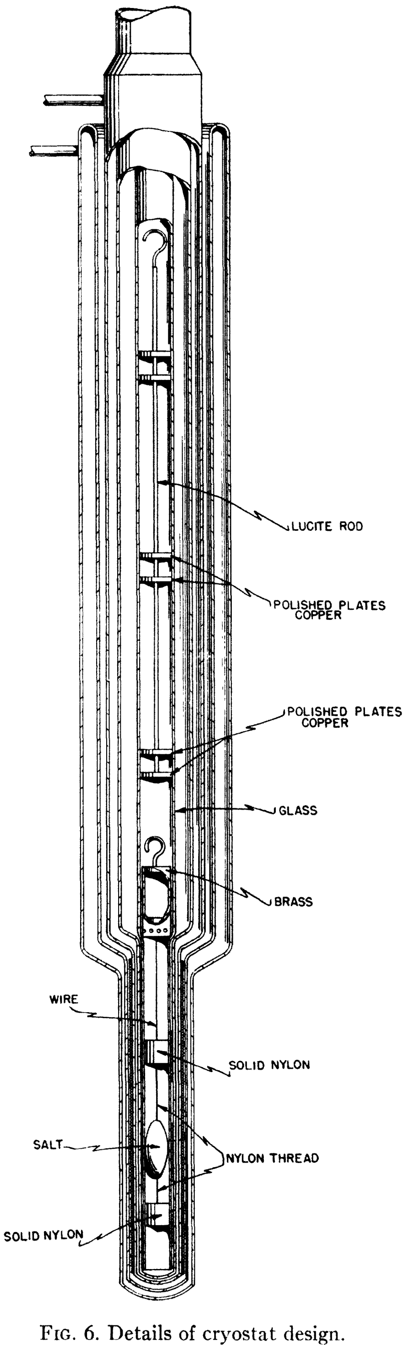

FIG. 6. Details of cryostat design.

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[21] W. J. DeHaas and F. K. DuPré, Physica 6, 705 (1939).
[22] D. DeKlerk, thesis, Leiden (1948), unpublished.
[23] D. Bijl, thesis, Leiden (1950), unpublished.

simultaneously and rapidly. A low frequency was required because one does not desire complications arising from spin-lattice relaxation in the salt.

It can be shown that the real and imaginary parts of the susceptibility denoted by χ' and χ'', respectively, can be measured in arbitrary units without calibrating for absolute susceptibilities. Thus one gets

$$\chi' = (C/K)\Delta\mathfrak{M} \tag{17}$$

and

$$\chi'' = (C/K\omega)(\Delta R_{\text{eff}}), \tag{18}$$

where C is the Curie constant, ω is 2π times the frequency, K is the slope of the temperature calibration curve in the liquid helium temperature region, $\mathfrak{M}$ is the mutual inductance in arbitrary units, and R_{eff} is defined by $R_{\text{eff}} = r_1r_2/(R_0+r_1+r_2)$, where r_1, r_2, and R_0 are shown in Fig. 7.

The results presented here were obtained in 16 helium runs and well over 100 demagnetizations, the results being quite reproducible.

Demagnetizations were made from various H/T values, and during the ensuing warm-up time many Ξ values could be obtained. The measurements were taken over a period of about 45 minutes, after which it was assumed temperature inhomogeneities might exist. Because of the very small heat input (~0.06 erg/sec), the warm-ups were very slow and good values of the Ξ parameter could be obtained.

Since at the very low temperatures, the effects of the earth's magnetic field could be quite large, two measurements were always made, one with the superposed constant magnetic field directed upward and one with the field downward. The Ξ-parameter was calculated from the equation,

$$\Xi = \frac{1}{3H^2}\left[\frac{\mathfrak{M}\uparrow - \mathfrak{M}\uparrow_0}{\mathfrak{M}\uparrow_0} + \frac{\mathfrak{M}\downarrow - \mathfrak{M}\downarrow_0}{\mathfrak{M}\downarrow_0}\right], \tag{19}$$

where $\mathfrak{M}\uparrow$ is the susceptibility in arbitrary units with the applied field up and $\mathfrak{M}\uparrow_0$ is the susceptibility the salt would have if the field were not applied, and similarly for $\mathfrak{M}\downarrow$. The $\mathfrak{M}\uparrow_0$ were obtained by plotting from the normal warm-up curve with no applied field.

In our case the constant magnetic field was supplied by a double-layered solenoid, operating on storage batteries, the magnitude of the fields being 1 to 75 gauss.

VII. EXPERIMENTAL RESULTS

The measured values of Ξ for pure cobalt ammonium sulfate plotted against T^* (see Fig. 8) show that it is indeed a constant in the region of about 0.125 to 0.6°. Its value, as calculated from the average of several dozen points, is 2.43×10^{-6} gauss^{-2}. Above 0.6°K it decreases slightly because of the effect of the lattice. Using the value of 2.43×10^{-6} gauss^{-2} for Ξ and the Curie constant of 0.858, one obtains for CT^2 a value of $42.5\times10^{-4}R$. Assuming exchange and quadrupole effects are negligible, this value of CT^2 is made up of two contributions, namely, dipole-dipole coupling and hyperfine structure coupling specific heats.

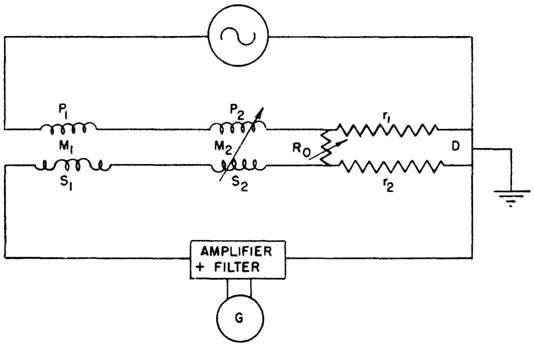

FIG. 7. Bridge circuit for measurement of complex susceptibility.

Because of the extreme anisotropy of the crystal, the calculation of the dipole-dipole specific heat with Eq. (3) is not feasible. By the aforementioned dilution procedure, however, one can reduce the dipole-dipole contribution and obtain two equations with two unknowns, A_N and A_{DD}. The values measured on the Zn diluted salt were not so accurate as those for the pure salt, because of the faster warm-up rate, but averaging several dozen points gives a good result. The warm-up rate of the Mg diluted salt was relatively more rapid and consequently the measured Ξ-values had a larger spread, although the constancy of the parameter was evident. The results of the Ξ-measurements are tabulated in Table I, and the resultant curves are shown in Fig. 8. If one defines the Curie point as that temperature at which hysteresis absorption commences, this temperature is $T^* = 0.120°$. Note the sudden increase in Ξ due to saturation effects as one reaches the Curie point. From this it would appear that the TT^* relationship is linear ($T = T^*$) in cobalt ammonium sulfate down to about 0.125°K.

In Table I and Fig. 8 are also shown the final T^* temperatures reached on demagnetizing from H/T equal to 13.5 kilogauss/degree. The pure crystal went through a maximum in susceptibility and its decrease below the Curie point indicates that cobalt ammonium sulfate becomes antiferromagnetic. No susceptibility

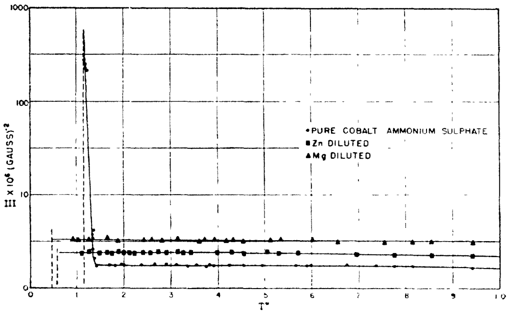

FIG. 8. Ξ as a function of T^*. The vertical dashed lines show T^* final after demagnetizing from same H/T (13.5 kilogauss degree).

TABLE I. Chemical data and specific heat values for single crystals.

Crystal	Weight (grams)	Relative conc. of Co^{++}	$\Xi\times10^6$ (gauss^{-2})	Weight percentage of Co^{++}	A[e]	T_f^*
Pure CAS[a]	2.461	1.000[d]	2.43	14.91	42.55×10^{-4}	0.117
CAS diluted with ZAS[b]	2.729	0.436	3.76	6.5 ± 0.2	27.45	0.059
CAS diluted with MAS[c]	2.351	0.174	5.01	2.6 ± 0.1	20.61	0.048

[a] Cobalt ammonium sulfate.
[b] Zinc ammonium sulfate.
[c] Magnesium ammonium sulfate.
[d] The theoretical percentage of Co^{++} in CAS is 14.91 percent; the gravimetric sample analysis was 14.9 percent.
[e] $A=CT^2/R$.

maximum was found for the diluted salts but much lower T^* final temperatures were reached because of the decreased dipole-dipole interaction. An indication of the behavior of cobalt ammonium sulfate at very low temperatures is given in Fig. 9, which shows χ' and χ'' plotted against time as a parameter. The heating in this region is due entirely to absorption, because the natural heat leak was negligible in magnitude as compared to that supplied by the ac field. While only a few points are shown on the curves, there are actually many hundred points measured all along the curve. This curve (χ'') is of use in the calculation of absolute T below the Curie point. The curve is actually a composite of about a dozen warm-up curves all of which were readily reproducible.

In Fig. 10 are shown the final results in plotting the values of the specific heat constant in terms of concentration of the Co^{++} ion. The intercept gives the nuclear contribution to the specific heat CT^2/R, and the value of 16.1×10^{-4} is in excellent agreement with the value 16×10^{-4} derived from microwave measurements.[13] The value of A from Ξ is in good agreement with that derivable from the slope of S/R against $1/2T^{*2}$ in the region above $T^*=0.5$°K. A representative selection of demagnetization data are shown in Table II, where H_i is the initial field in kilogauss, T_i is the initial temperature, and T_f^* is the temperature reached upon demagnetization. Remembering that the demagnetization is adiabatic and assuming (a) that the entropy ($H=0$) is given by $S=S_0+\frac{1}{2}(A/T^2)$, where A is the specific heat constant, and (b) that $T=T^*$, one can calculate the entropy removal on magnetization at T_i; some experimental values are represented by points in Fig. 2. The points do not fall on the calculated entropy removal curve, but below it. If the assumptions (a) and (b) are true, then one can fit the experimental data with an equation exactly like Eq. (12) but with a g-factor of 6.55. The curve so calculated is given by the dotted line.

VIII. DISCUSSION

The agreement of the thermodynamic measurement of the nuclear specific heat with that calculable from microwave data is good. The concentration coordinates used in Fig. 10 are the most probable values of the concentration. The chemical analyses of the dilute salts were made polarimetrically and colorimetrically with an accuracy of ±3 percent. This uncertainty of absolute concentration would shift the intercept up or down somewhat, so that the best one can say is that the nuclear specific heat is $(16.1\pm0.3)\times10^{-4}R$.

The absence of a Curie-Weiss constant Δ seems to indicate that exchange is very small, and this is substantiated by microwave data.[20] It can be shown that if the susceptibility follows a Curie-Weiss law instead of a Curie law that the Garrett parameter has the form,

$$\Xi=C/A(1+\chi\Delta/C)^3, \qquad (20)$$

where C and A are as previously, χ is the susceptibility, and Δ is the Curie-Weiss constant. From Fig. 8 and Eq. (20) it can be seen that the constancy of Ξ indicates that $\Delta\leq0.005$°K down to about 0.125°T^*.

The change in slope of both χ' and χ'' in Fig. 9 seems to indicate that one is over a specific heat hump, and it would be of interest to investigate this point. Unfortunately, the magnetic fields available for the experiment at present are not sufficient to pursue the point further.

The crystals were spherical in shape, and no correction for shape in the T^* values have been included. The usual shape demagnetization factors are calculated on the assumption of an isotropic substance with the ions placed at the points of a cubic lattice and are certainly not applicable in the present case of an anisotropic monoclinic lattice.

An interesting point, determinable from Fig. 8, is that the slow decrease of the value of the Ξ-parameter with temperature indicates that the factor B in the lattice specific heat $C_L=BT^3$ is very small or that the spin-lattice relaxation time is no longer short compared with the period of the ac measuring field. Susceptibility measurements at various frequencies would distinguish between the effects.

The diluted salts showed no hysteresis absorption, no maximum in susceptibility, and no saturation effects in the temperature region available with the present magnet. Measurements of the Curie points in the diluted salts may shed some light on the mechanism that produces antiferromagnetism in cobalt ammonium sulfate. It is very astonishing that antiferromagnetisms should occur, since the exchange effects seem to be very small. The Curie-Weiss $\Delta\leq0.005$° seems to be much too small to be felt at the Curie point temperature of about 0.12°K. One might infer dipole-dipole coupling as a possible mechanism, a process which has achieved considerable success in the theory of ferroelectricity. An alternative is that the Curie point is due to nuclear interaction; but, since this is an internal interaction, it does not seem probable that it can cause large scale cooperative phenomena. Neutron diffraction experiments by Wollan, Strauser and Shull,[24] of the Oak Ridge

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[24] Shull, Strauser, and Wollan, Phys. Rev. **83**, 333 (1951).

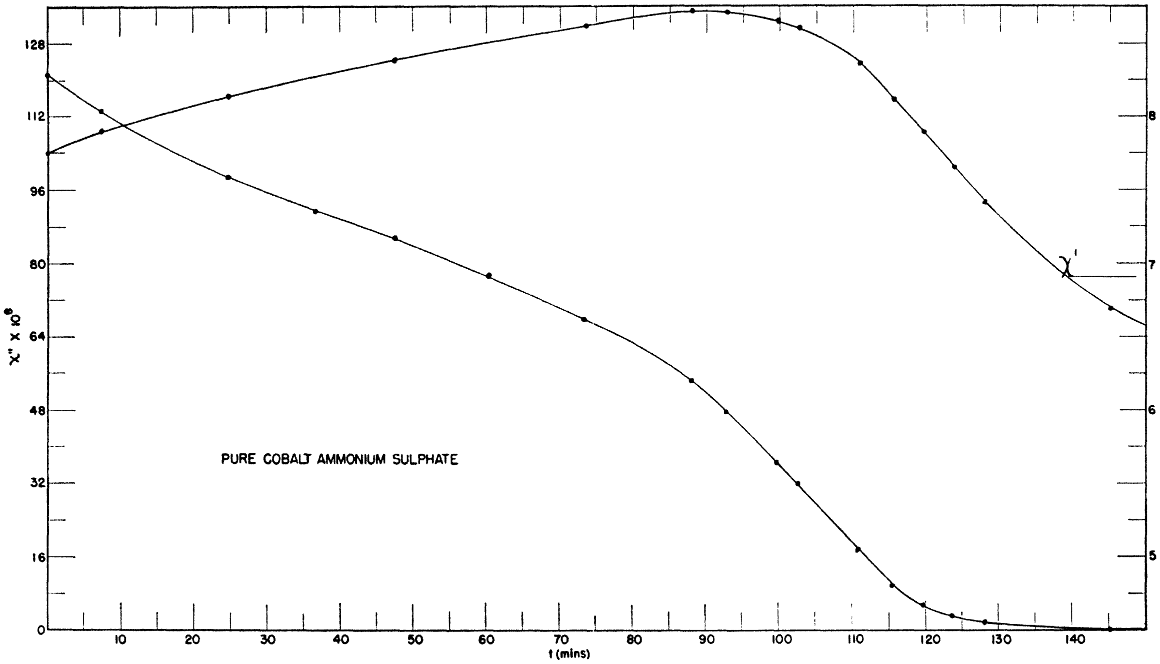

FIG. 9. Real and imaginary components of susceptibility using time as a parameter.

National Laboratory, on even-even isotopes show antiferromagnetism for substances in which there are no nuclear moments, but this does not exclude the possibility of hyperfine structure coupling or quadrupole coupling as a mechanism in cobalt ammonium sulfate.

Assuming the measured nuclear specific heat of $16.1\times 10^{-4}R$ to be the true value, this leaves for the pure cobalt ammonium sulfate a dipole-dipole specific heat of $26.4\times 10^{-4}R$, which is some 40 percent higher than that calculable from Van Vleck's formula given by Eq. (3) using $\bar{g}^2=18.8$. As pointed out previously, the Stark specific heat is zero.

The experimentally determined g-value along the K_1 axis is 6.55, which is some 5 percent higher than the published values from microwave measurements. This would increase the susceptibility along K_1 by about 10 percent.

It would be very desirable to continue the investigation of cobalt ammonium sulfate single crystals, pure and diluted, since the disparity of the g-factors along the various magnetic axes make the crystals almost ferromagnetic and because information may be obtained on antiferromagnetism-producing phenomena.

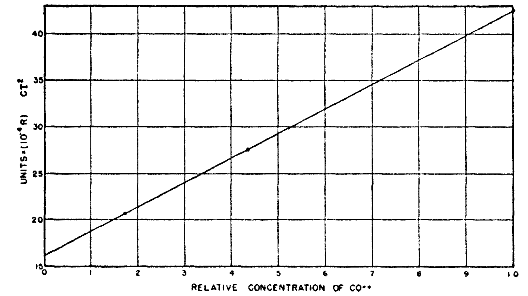

FIG. 10. CT^2 as a function of Co^{++} concentration.

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TABLE II. Entropy calculated from demagnetization data.

H_i (kilogauss)	T_i (°K)	H_i/T_i	T_f*	$\frac{A}{2}\left[\frac{1}{T_f^2}-\frac{1}{T_i^2}\right]$
0.625	1.125	0.55	0.803	0.003
1.25	1.125	1.11	0.345	0.019
1.50	1.125	1.33	0.272	0.027
1.52	0.989	1.53	0.174	0.047
1.68	0.989	1.70	0.148	0.077
12.1	1.005	11.94	0.114	——