

(at  $t=0$ ) was found necessary for the evaluation of the expected average lattice behavior from first- and second-order perturbation terms.

Higher order effects can, in principle, be studied directly with the ALW analysis. However, it turns out to be increasingly difficult to determine the relative importance of various errors in the perturbation solutions, the statistics employed, and the other physical effects omitted from the simple atomic model as one attempts to refine the calculations.

Further work on the extension of the ALW analysis to the quantum treatment to eliminate the high-temperature restriction is now near completion and should be published shortly. The application of the

attenuating wave technique to other many-body quantum wave-transport mechanisms (e.g., electron conduction) is also under investigation.

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## Temperature Dependence of Paramagnetic Resonance Lines\*†

I. SVARE‡ AND G. SEIDEL§

*Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts*

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Changes in the position and shape of paramagnetic absorption lines of  $\text{Nd}^{3+}$  in neodymium ethyl sulfate,  $\text{Ni}^{2+}$  in nickel fluosilicate, and  $\text{Cu}^{2+}$  in copper potassium sulfate have been observed at 30 kMc/sec in the temperature range from 0.4 to 4.2°K. The observed shifts are compared to first and second line moments calculated from spin-spin interactions when the average populations of the spin levels are weighted by the proper Boltzmann factors. In this manner it is possible to determine the magnitude and sign of the exchange interaction  $\mathcal{H}_{ij} = A\mathbf{S}_i \cdot \mathbf{S}_j$  between spins. We find a ferromagnetic interaction  $A = -(3.9 \pm 0.4) \times 10^{-18}$  erg between nearest-neighbor  $\text{Ni}^{2+}$  ions in  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$  with no evidence of anisotropic exchange. Nearest-neighbor spins at similar lattice positions in  $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  appear to be coupled by an exchange interaction of approximately  $A = -9 \times 10^{-18}$  erg, while the exchange between the two neighboring dissimilar  $\text{Cu}^{2+}$  ions in the unit cell is  $A = -1.4 \times 10^{-18}$  erg. Evidence for a weak anisotropic and antiferromagnetic coupling in  $\text{Nd}(\text{C}_2\text{H}_3\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  is presented. We have observed magnetostatic modes in copper salts at low temperature, and this effect is briefly discussed in relation to the present type of experiment.

### I. INTRODUCTION

PARAMAGNETIC resonance lines in solids may be broadened by several effects. (a) The crystal field may vary over the ionic positions in the lattice because of crystal imperfections. (b) The spin-lattice interaction may be sufficiently strong that the lines are lifetime broadened. (c) The spins may interact strongly via dipolar and exchange forces. (d) There may exist unresolved hyperfine interactions.

In a magnetically concentrated salt effect (c) will usually be dominant at low temperature. Van Vleck<sup>1</sup> first calculated the resonance line shape in the presence

of weak spin-spin coupling by the method of line moments, and his theory has been used in a number of cases to explain observed line shapes. The strength of the exchange interaction can be deduced from measured line moments since the dipolar part of the coupling is calculable from the dimensions of the crystal lattice and the  $g$  values.

The theory given by Van Vleck is a high-temperature approximation, valid when  $kT \gg h\nu$ , in that the spin levels are all taken to have the same populations. For  $kT \leq h\nu$  the populations of the levels have to be weighted by the proper Boltzmann factors, and this may influence the line moments. The temperature dependence of the line moments has been considered by Pryce and Stevens,<sup>2</sup> by Kambe and Usui<sup>3</sup> and in more detail by McMillan and Opechowski.<sup>4</sup> Qualitatively it is easy to

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‡ Present address: Physics Department, Norwegian Institute of Technology, Trondheim, Norway.

§ Present address: Physics Department, Brown University, Providence, Rhode Island.

<sup>1</sup> J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

<sup>2</sup> M. H. L. Pryce and K. W. H. Stevens, Proc. Phys. Soc. (London) A63, 36 (1950).

<sup>3</sup> K. Kambe and T. Usui, Progr. Theoret. Phys. (Kyoto) 8, 302 (1952).

<sup>4</sup> M. McMillan and W. Opechowski, Can. J. Phys. 38, 1168h (1960).

see that the magnetization of a paramagnetic crystal at low temperature and in a strong field may shift the position of the resonance line; that is, give a finite first moment. Also, the local order increases as the spin system is aligned so that the linewidth and the second moment are reduced.

Except for Bloembergen's<sup>5</sup> demonstration of proton resonance shifts in magnetized  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , we are not aware of any experimental investigation of line moments under conditions where  $kT \leq h\nu$ . It is the purpose of this paper to report some line-shape measurements performed down to temperatures where  $h\nu/kT \approx 4$  on the salts  $\text{Nd}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$  and  $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . The results can be explained with help of the temperature-dependent line moment theory, and new data on the exchange interaction in these salts are presented. A brief account of this work has already appeared in the literature.<sup>6</sup>

## II. THEORY

The  $n$ th moment of a resonance is defined by

$$\langle \nu^n \rangle = \int_0^\infty \nu^n f(\nu) d\nu, \quad (1)$$

where  $f(\nu)$  is the normalized absorption amplitude at the frequency  $\nu$  so that  $\int_0^\infty f(\nu) d\nu = 1$ . We are usually interested in the first moment about the unperturbed line position  $\nu_0$

$$\langle \Delta\nu \rangle = \langle \nu \rangle - \nu_0 \quad (2)$$

and the second central moment about the position  $\langle \nu \rangle$

$$\langle (\Delta\nu^2) \rangle_{\text{central}} = \langle (\nu - (\nu_0 + \langle \Delta\nu \rangle))^2 \rangle = \langle \Delta\nu^2 \rangle - (\langle \Delta\nu \rangle)^2. \quad (3)$$

Measurements are usually performed at a constant frequency and varying magnetic field. Hence, we will also use  $\langle \Delta H^n \rangle = (-\hbar/g\beta)^n \langle \Delta\nu^n \rangle$ , which is valid for small shifts and narrow lines.

The Hamiltonian for a system of  $N$  interacting spins is

$$\mathcal{H} = \sum_{i=1}^N \mathcal{H}_i^{(0)} + \frac{1}{2} \sum_{i,j}' \mathcal{H}_{ij}^{(1)}, \quad (4)$$

where  $\mathcal{H}_i^{(0)}$  is the energy operator for an individual spin  $i$  in a constant external magnetic field  $H_0$ . The perturbation  $\mathcal{H}_{ij}^{(1)}$  is the sum of dipolar and exchange interactions between spins  $i$  and  $j$ , and the sum  $\sum_{i,j}'$  is to be taken over all values of  $i$  and  $j$  so that  $i \neq j$ .

The well-known approximation in the moment calculation is to treat  $\mathcal{H}_{ij}^{(1)} = \mathcal{H}_{ij}^{(1)}{}_{\text{dip}} + \mathcal{H}_{ij}^{(1)}{}_{\text{ex}}$  as small compared to the Zeeman energy  $\mathcal{H}_i^{(0)}$  and to keep only first-order perturbation terms; that is, the terms in  $\mathcal{H}_{ij}^{(1)}$  that commute with  $\mathcal{H}_i^{(0)}$  and that can be diagonalized in a representation where  $\mathcal{H}_i^{(0)}$  is diagonal. These

terms will slightly shift the energy levels  $a_r$  of a single spin and thus broaden the line. The second-order terms in  $\mathcal{H}_{ij}^{(1)}$  will weakly couple together different levels  $a_r \cdots a_{r'}$  of a single spin and permit transitions in the microwave field where  $\Delta m \neq \pm 1$ . The resulting satellite lines are weak, but their contributions to the moment are not negligible since they have a large separation from the main line. The calculation would therefore not be improved, but made incorrect by including the second-order terms in the approximation, and the non-commuting part of the interaction operator has to be thrown away.

The properly truncated  $\mathcal{H}^{(1)}$  will be designated  $\tilde{\mathcal{H}}^{(1)}$ , and  $\tilde{\mathcal{H}} = \mathcal{H}^{(0)} + \tilde{\mathcal{H}}^{(1)}$ . If the spectrum consists of more than one line, the microwave field operator  $M = \sum_i m_i$  also has to be truncated to  $\tilde{M}$  to include only the matrix elements for the resonance transition of interest. Kambe and Usui<sup>3</sup> have shown that the first two moments then can be written

$$\hbar \langle \nu \rangle = - \frac{1}{2} \frac{\text{Trace}\{b(\tilde{\mathcal{H}})[\tilde{M}, [\tilde{\mathcal{H}}, \tilde{M}]]\}}{\text{Trace}\{b(\tilde{\mathcal{H}})[\tilde{M}_-, \tilde{M}_+]\}}, \quad (5)$$

$$\hbar^2 \langle \nu^2 \rangle = \frac{\text{Trace}\{b(\tilde{\mathcal{H}})[[\tilde{M}_-, \tilde{\mathcal{H}}], [\tilde{\mathcal{H}}, \tilde{M}_+]]\}}{\text{Trace}\{b(\tilde{\mathcal{H}})[\tilde{M}_-, \tilde{M}_+]\}}, \quad (6)$$

where the operators  $\tilde{M}_+$  and  $\tilde{M}_-$  are defined by

$$\begin{aligned} (n|\tilde{M}_+|n') &= (n|\tilde{M}|n') \quad \text{for } E_{n'} < E_n \\ &= 0 \quad \text{otherwise,} \\ (n|\tilde{M}_-|n') &= (n|\tilde{M}|n') \quad \text{for } E_{n'} > E_n \\ &= 0 \quad \text{otherwise.} \end{aligned} \quad (7)$$

$E_n$  are the energy states of the coupled spin system, and the Boltzmann factors are written  $e^{-x/kT} = b(x)$ .

The traces can be evaluated in the most convenient representation; namely, when all spins are individually diagonalized. Hence,  $\tilde{\mathcal{H}}$  and  $\tilde{M}$  are replaced by the corresponding sums over the operators  $S_{z_i}$  and  $S_{\pm i}$  of single spins. As a first approximation the density matrix can be written

$$b(\tilde{\mathcal{H}})b(\sum_i \mathcal{H}_i^{(0)}) = \prod_i b(a_i). \quad (8)$$

For free spins the commutators can be simplified by using the relations  $[S_{z_i}, S_{\pm i}] = \pm \delta_{ij} S_{\pm i}$ ;  $[S_{+i}, S_{-i}] = 2\delta_{ij} S_{z_i}$ . When crystalline field splitting is present, the commutators can be found by straightforward, but cumbersome, matrix multiplication. However, it is then easier to use the general formulas of McMillan and Opechowski<sup>4</sup> derived with the help of projection operators.

The resonance line moments for some cases of interest will be written explicitly. For identical spins with  $S = \frac{1}{2}$  and axial  $g$  tensor the unperturbed Hamiltonian is  $\mathcal{H}_i^{(0)} = g\beta H_0 S_{z_i}$ . If the exchange is isotropic,

<sup>5</sup> N. Bloembergen, *Physica* **16**, 95 (1950).

<sup>6</sup> G. Seidel and I. Svare, *Proceedings of the First International Conference on Paramagnetic Resonance* (Academic Press Inc., New York, 1963).

$\mathcal{H}_{ij}^{(1)\text{ex}} = A_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$  and the truncated interaction is

$$\mathcal{H}_{ij}^{(1)} = a_{ij} S_{z_i} S_{z_j} + \frac{1}{2} b_{ij} (S_{+i} S_{-j} + S_{-i} S_{+j}), \quad (9)$$

where

$$\begin{aligned} a_{ij} &= A_{ij} + g_{11}^2 \beta^2 (1 - 3 \cos^2 \theta_{ij}) r_{ij}^3, \\ b_{ij} &= A_{ij} - g_{11}^2 \beta^2 (1 - 3 \cos^2 \theta_{ij}) 2r_{ij}^3. \end{aligned} \quad (10)$$

Here  $\mathbf{r}_{ij}$  is the vector connecting the spins  $i$  and  $j$  making the angle  $\theta_{ij}$  with  $\mathbf{H}_0$ . The moments are<sup>3,4</sup>

$$\begin{aligned} h\langle \Delta\nu \rangle &= -(2N)^{-1} \tanh(g_{11} \beta H_0 / 2kT) \sum'_{i,j} (a_{ij} - b_{ij}) \\ &= -(4N)^{-1} (2g_{11}^2 + g_{12}^2) \beta^2 \tanh(g_{11} \beta H_0 / 2kT) \\ &\quad \times \sum'_{ij} (1 - 3 \cos^2 \theta_{ij}) / r_{ij}^3, \end{aligned} \quad (11)$$

$$\begin{aligned} (h^2 \langle \Delta\nu^2 \rangle)_{\text{central}} &= (16N)^{-1} (2g_{11}^2 + g_{12}^2)^2 \beta^4 [1 - \tanh^2(g_{11} \beta H_0 / 2kT)] \\ &\quad \times \sum'_{ij} [(1 - 3 \cos^2 \theta_{ij}) / r_{ij}^3]^2. \end{aligned} \quad (12)$$

The Hamiltonian describing the interaction between nonidentical spins ( $S = \frac{1}{2}$  and axial  $g$  tensor) must be truncated further. Terms such as  $S_{+i} S_{-k'}$ , here the prime distinguishes the two sets of spins, do not commute with  $\mathcal{H}^{(0)}$  and must be discarded as not conserving the Zeeman energy. In this case  $\mathcal{H}_{ik'}^{(1)} = a_{ik'} S_{z_i} S_{z_{k'}}$ , where

$$a_{ik'} = A_{ik'} + g_{11} g_{11}' \beta^2 (1 - 3 \cos^2 \theta_{ik'}) / r_{ik'}^3. \quad (13)$$

The contribution to the moment of the absorption line of the unprimed spin system due to the primed spin system is then<sup>7</sup>

$$\begin{aligned} (h\langle \Delta\nu \rangle)' &= -(2N)^{-1} \tanh(g_{11}' \beta H_0 / 2kT) \\ &\quad \times \sum'_{i,k'} [A_{ik'} + g_{11} g_{11}' \beta^2 (1 - 3 \cos^2 \theta_{ik'}) / r_{ik'}^3], \end{aligned} \quad (14)$$

$$\begin{aligned} (h^2 \langle \Delta\nu^2 \rangle)'_{\text{central}} &= (4N)^{-1} [1 - \tanh^2(g_{11}' \beta H_0 / 2kT)] \\ &\quad \times \sum'_{i,k'} [A_{ik'} + g_{11} g_{11}' \beta^2 (1 - 3 \cos^2 \theta_{ik'}) / r_{ik'}^3]^2. \end{aligned} \quad (15)$$

Since  $\tanh(1/x) \rightarrow 1$  for  $x \rightarrow 0$ , the first moment shift may be finite at low temperature whereas the second central moment goes to zero for  $T \rightarrow 0$  as expected. The important point is that an isotropic exchange interaction between spins having  $S = \frac{1}{2}$  contributes to the first two moments only if the spins are not identical.

In this discussion whether spins are identical or not is determined by their resonance conditions. If two spins contribute to different distinct resonance lines resulting from any of a variety of reasons (for example, from different  $g$  values, large local fields arising from close neighbors or hyperfine interactions), they must be treated as dissimilar spins and the simultaneous spin-flip terms discarded from the Hamiltonian. It is

important but not always easy to decide whether spins are identical or not. Some examples will be given in the discussion of the individual salts.

Another interesting case occurs for  $S \geq 1$  when crystalline field splitting is present. McMillan and Opechowski<sup>4</sup> calculated the resonance moments for  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$  as an example. The spin Hamiltonian for  $\text{Ni}^{2+}$  with  $S = 1$  in this salt is

$$\mathcal{H}_i^{(0)} = g\beta \mathbf{H}_0 \cdot \mathbf{S}_i + D(S_{z_i}^2 - 2/3). \quad (16)$$

When  $\mathbf{H}_0$  makes an angle  $\gamma$  with the  $z$  axis, the energy levels for a single ion are approximately

$$\begin{aligned} a_1 &= -g\beta H_0 + \frac{1}{3} D (\frac{2}{3} \cos^2 \gamma - \frac{1}{2}), \\ a_2 &= \frac{1}{3} D (1 - 3 \cos^2 \gamma), \\ a_3 &= g\beta H_0 + \frac{1}{3} D (\frac{2}{3} \cos^2 \gamma - \frac{1}{2}). \end{aligned} \quad (17)$$

With  $\mathbf{H}_0$  parallel to the  $z$  axis ( $\gamma = 0$ ) the first moment of the transition  $h\nu = a_2 - a_1 = g\beta H_0 - D$  is

$$\begin{aligned} (h\langle \Delta\nu \rangle)_{12} &= \left\{ [b(a_3) - b(a_2)] \right. \\ &\quad \times \sum'_{i,j} [A_{ij} - g^2 \beta^2 (1 - 3 \cos^2 \theta_{ij}) / 2r_{ij}^3] + [b(a_3) - b(a_1)] \\ &\quad \left. \times \sum'_{i,j} 3g^2 \beta^2 (1 - 3 \cos^2 \theta_{ij}) / 2r_{ij}^3 \right\} (ZN)^{-1}, \end{aligned} \quad (18)$$

and for the transition  $h\nu = a_3 - a_2 = g\beta H_0 + D$

$$\begin{aligned} (h\langle \Delta\nu \rangle)_{23} &= \left\{ [b(a_2) - b(a_1)] \right. \\ &\quad \times \sum'_{i,j} [A_{ij} - g^2 \beta^2 (1 - 3 \cos^2 \theta_{ij}) / 2r_{ij}^3] + [b(a_3) - b(a_1)] \\ &\quad \left. \times \sum'_{i,j} 3g^2 \beta^2 (1 - 3 \cos^2 \theta_{ij}) / 2r_{ij}^3 \right\} (ZN)^{-1} \end{aligned} \quad (19)$$

where

$$Z = \sum_{i=1}^3 b(a_i).$$

### III. EFFECTS OF SAMPLE MAGNETIZATION

When the spin system is aligned in a strong field at low temperature, the sample becomes magnetized. Paramagnetic resonance under such conditions can then be expected to show behavior qualitatively similar to ferromagnetic resonance. In particular, the resonance frequency must depend on the shape of the sample because of the existence of demagnetizing fields. Higher magnetostatic modes may also appear.

The shape dependence of the first moments are expressed in (11), (14), (18), and (19) by the slowly converging sums  $\sum'_{i,j} (1 - 3 \cos^2 \theta_{ij}) / r_{ij}^3$ . This summation can be performed by dividing it in two parts. Close to the spin  $i$  the sum is performed over the discrete lattice points. But outside a radius  $\rho$  from  $i$  the magnetization

<sup>7</sup>I. Svare and G. Seidel, Tech. Rept. No. 378, Cruft Lab. Harvard University (unpublished).

can be treated as continuous and this part of the sum converted to an integral. The integral will depend on the shape of the crystal, and it will, in general, be different for different lattice points. Only for an ellipsoid will the integral be the same for all points  $i$ , and only for a sphere will it vanish. For a cubic lattice the sum inside  $\rho$  also vanishes.

When the field is along an axis of revolution of an ellipsoidal sample, the shape-dependent part of the sum can be described by a demagnetizing factor  $N_z$ .<sup>8,9</sup>

$$\sum_j' (1 - 3 \cos^2 \theta_{ij}) r^{-3}_{ij} = -N_0 (\frac{4}{3}\pi - N_z), \quad r_{ij} > \rho, \quad (20)$$

where  $N_0$  is the density of spins.

For a cubic lattice the first moment change (11) becomes

$$\langle \Delta\nu \rangle = \frac{(2g_{11}^2 + g_1^2)\beta}{2g_{11}\hbar} (\frac{4}{3}\pi - N_z) M, \quad (21)$$

where the magnetization  $M$  is given by

$$M = \frac{1}{2} N_0 g_{11} \beta \tanh(g_{11} \beta H / 2kT). \quad (22)$$

It is interesting to compare the first moment shift (21) to Kittel's equation for ferromagnetic resonance<sup>10</sup>

$$h\nu = g\beta \{ [H_0 + (N_x - N_z)M] \times [H_0 + (N_y - N_z)M] \}^{1/2}. \quad (23)$$

For a sample of axial symmetry so that  $N_x = N_y = \frac{1}{2}(4\pi - N_z)$ , the resonance condition (23) becomes

$$h\nu = g\beta [H_0 + \frac{3}{2}(\frac{4}{3}\pi - N_z)M], \quad (24)$$

and agrees with (21) for  $g_{11} = g_1 = g$ . For a general ellipsoid with  $N_x \neq N_y \neq N_z$  the first moment shift (21) differs in order  $M^2/H_0$  from the resonance condition (23). This results from the fact that the moment calculation is strictly valid only for samples having cylindrical symmetry about the direction of the magnetic field, as pointed out by Van Vleck.<sup>11</sup> Only in this case is the  $z$  component of the magnetization a constant of the motion.

The factors  $N_x$  and  $N_y$  that appear in the Kittel equation for the first moment represent a dynamic demagnetizing effect and may be thought of as being caused by the spin-flip terms  $S_{+i} S_{-j}$  in the interaction Hamiltonian. If these terms are truncated from the moment calculation as in the case of interacting non-identical spins, we see from (14) that only the static demagnetization is left

$$[(h\langle \Delta\nu \rangle)_{ik'}]_{r_{ik'} > \rho} = g\beta M' (\frac{4}{3}\pi - N_z). \quad (25)$$

The Kittel equation is, therefore, not applicable to this case using the static magnetization  $M$ . For example,

in  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$  the magnetization relevant to the shape-dependent first moment shift of the transition  $a_1 \leftrightarrow a_2$  that must be used in (24) is from (18)

$$M_{a_1 \leftrightarrow a_2} = (N_0 g \beta / 3) [3b(a_1) - b(a_2) - 2b(a_3)] / Z. \quad (26)$$

A different magnetization must be used for transition  $a_2 \leftrightarrow a_3$ .

When a sample deviates from exact ellipsoidal shape, the demagnetizing field will vary from spin to spin. This variation will result in a relatively larger effect on the second moment than on the first moment, and if sufficiently large can mask the narrowing of resonance lines at low temperatures.

The theory of moments assumes that the spins in the sample all precess uniformly. However, they may also precess with different phases in different parts of the sample, and because of dipolar interaction the resulting higher magnetostatic modes will have an energy separation proportional to the magnetization.<sup>12,13</sup> Unless special precautions are taken the microwave field will usually be nonuniform and excite a series of these modes.<sup>14</sup> If the mode separation is sufficiently large, these modes will give rise to separate absorption maxima in the spectrum; otherwise, the resonance may only appear broadened. Magnetostatic modes are well known in ferromagnetic resonance; recently they have also been observed<sup>15</sup> in disks of paramagnetic  $\text{CuK}_2\text{Cl}_4 \cdot 2\text{H}_2\text{O}$  at 24 kMc/sec and 2°K. In this salt a ferromagnetic interaction aids the external field in aligning the Cu spins. We have observed the same phenomena in spheres of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  at 30 kMc/sec, but only below 1°K.

When higher magnetostatic modes are excited, line areas can no longer be used as a measure of resonance intensity. It usually is impossible to measure line moments under such conditions; only if a single mode is well resolved can it be expected to have the same line-width as the uniform precession mode.

If a sample deviates from ellipsoidal shape, the demagnetizing field will vary throughout the sample, the magnetic moments associated with different regions will precess with different frequencies, and there will be no discrete modes for the crystal as a whole. It is possible that a sample may have a shape crude enough to suppress higher magnetostatic modes, but still be close enough to a sphere to be useful for first moment measurements. This view is supported by the fact that we observed these modes only in very good spheres.

The problem of magnetostatic modes is, in general, more complicated for paramagnetic resonance than for ferromagnetic resonance for reasons similar to those discussed above in connection with the application of

<sup>8</sup> J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937).

<sup>9</sup> F. A. Osborn, Phys. Rev. **67**, 351 (1945).

<sup>10</sup> C. Kittel, Phys. Rev. **73**, 155 (1948).

<sup>11</sup> J. H. Van Vleck, Phys. Rev. **78**, 266 (1950).

<sup>12</sup> L. R. Walker, Phys. Rev. **105**, 390 (1957).

<sup>13</sup> L. R. Walker, J. Appl. Phys. **29**, 318 (1958).

<sup>14</sup> J. F. Dillon, Phys. Rev. **112**, 59 (1958).

<sup>15</sup> H. Abe, H. Morigaki, and K. Koga, *Proceedings of the First International Conference on Paramagnetic Resonance* (Academic Press Inc., New York, 1963).

the Kittel equation to the first moment shift. For example, in the case of a paramagnetic salt with several separate, uniform precession modes, associated either with different transitions within the spin system on different spin subsystems, the resonance conditions for higher order modes becomes difficult to calculate.

If the sample size becomes comparable to the microwave wavelength, the finite propagation velocity of the dipolar fields will shift the frequency of the fundamental mode. A correction formula for this has been given by Mercereau,<sup>16</sup> but it was not found necessary to correct for sample size in the present work.

#### IV. EXPERIMENTAL PROCEDURE

The condition for spin alignment  $h\nu > kT$  was satisfied in these experiments by working at 30 kMc/sec and using a He<sup>3</sup> cryostat to cool the samples to 0.3–0.4°K. For  $T=0.35^\circ\text{K}$ ,  $\exp(-h\nu/kT)=0.02$ .

The pumping and gas handling section of the He<sup>3</sup> cryostat are similar to the one described by Seidel and

Keesom.<sup>17</sup> The He<sup>3</sup> gas was first allowed to condense on the walls of a tube passing through the liquid He<sup>4</sup> bath at 1.2°K, and the resulting liquid He<sup>3</sup> collected in a small copper container within an evacuated chamber. The He<sup>3</sup> vapor was then pumped from the bath and the temperature of the He<sup>3</sup> liquid reduced until an equilibrium temperature, determined by heat leak and pumping speed, was reached.

The technique for obtaining heat contact between the sample and He<sup>3</sup> bath is shown in Fig. 1. The sample *S* was glued onto a quartz rod inside a quartz tube that protruded into the resonant cylindrical cavity *C* (TE<sub>012</sub> mode) through a hole beyond cut off for propagation of radiation at 30 kMc/sec. The quartz tube was sealed to a platinum tube which in turn was soldered to a copper tube connected to the wall of the liquid He<sup>3</sup> container. This tube system could be filled with He<sup>4</sup> gas through a stainless steel capillary of inside diameter 0.003 in. The He<sup>4</sup> condensed on the tube walls, forming a superfluid film, which with the gas provided heat contact between the sample and He<sup>3</sup> container. The heat leak between the He<sup>4</sup> bath at 1.2°K and the He<sup>3</sup> bath introduced by the He<sup>4</sup> within the 0.003-in. capillary was minimized by pumping away the gas evaporating from the He<sup>4</sup> film at 1.2°K before it had the opportunity to recirculate and recondense at 0.4°K. It will be noted that in this arrangement only the sample, and not the microwave cavity, was cooled by the He<sup>3</sup> refrigerator. Rough estimates of the flow of He<sup>4</sup> gas in the tube indicate that the power dissipation in the sample had to be maintained below about 10<sup>-9</sup> W at 0.4°K to avoid sample heating.<sup>7</sup> Such low power levels were also required to avoid saturation of the resonance; hence, superheterodyne detection was employed. Two separate resistance thermometers *R*, one placed on the He<sup>3</sup> bath container and the other as close to the sample as possible, were calibrated against the vapor pressure of He<sup>3</sup>. When the microwave power was kept low, no difference in temperature between the two thermometers was observed.

Most samples could be ground fairly easily into spheres by blowing them about the inside wall of a cylinder lined with emery paper. Crystals were x-ray oriented and glued onto the quartz rod with Shell Epon 828 epoxy. The crystal orientation in the horizontal plane could be checked by rotating the magnet. It is believed that the crystal orientation usually was better than  $\pm 2^\circ$ .

The sample size required in the cavity spectrometer was approximately 0.01 mm<sup>3</sup>. As such small samples of soft material are rather hard to handle, another version of the spectrometer where the sample was mounted  $\lambda/2$  above a reflecting short in a waveguide was often employed. Suitable samples were then approximately 1 mm<sup>3</sup> in size and easier to work with but not quite large enough to require size correction for the first

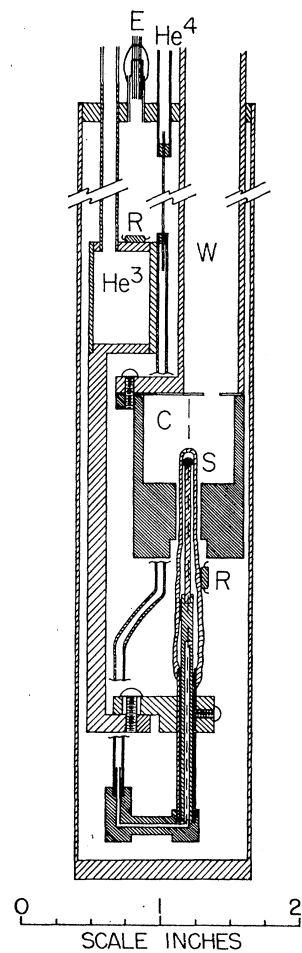


FIG. 1. Diagram of low-temperature apparatus showing the sample *S* inside cavity *C* in contact with the He<sup>3</sup> bath.

<sup>16</sup> J. E. Mercereau, *J. Appl. Phys.* **30**, 184S (1959).

<sup>17</sup> G. Seidel and P. H. Keesom, *Rev. Sci. Instr.* **29**, 606 (1958).

moment.<sup>16</sup> The waveguide spectrometer could also be used with less danger of sample saturation.

#### V. MEASUREMENTS ON NEODYMIUM ETHYL SULFATE

The structure of hexagonal  $\text{Nd}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  has been determined by Ketelaar.<sup>18</sup> The unit cell has dimensions  $a_0 = 13.992 \text{ \AA}$  and  $c_0 = 7.07 \text{ \AA}$ , and it contains two equivalent  $\text{Nd}^{3+}$  ions at positions  $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$  and  $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$ . The ground state of the free  $\text{Nd}^{3+}$  ion is split by the crystalline field of the 9 surrounding water molecules into five Kramers doublets. Only the lowest doublet is populated at liquid helium temperature. This state has effective spin  $S = \frac{1}{2}$  and an axial  $g$  tensor that is the same for both ions in the unit cell. In crystals where the  $\text{Nd}^{3+}$  have been diluted 1:200 with nonmagnetic

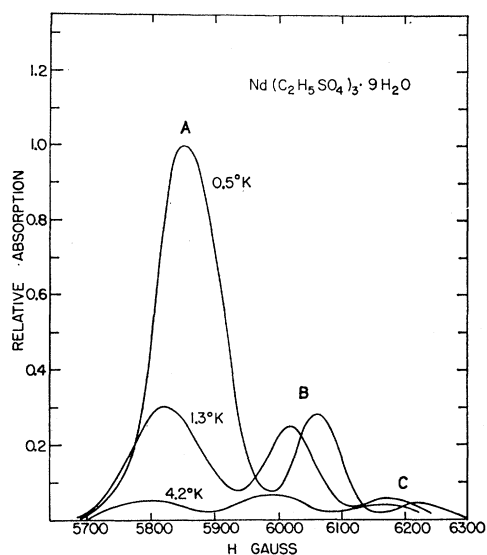


FIG. 2. Resonance absorption of  $\text{Nd}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  at several temperatures with the magnetic field parallel to the hexagonal axis.

$\text{La}^{3+}$  the  $g$  values are<sup>19</sup>  $g_{11} = 3.535 \pm 0.001$ ,  $g_{\perp} = 2.072 \pm 0.001$ . However, in the concentrated salt we have obtained  $g_{11} = 3.60$ , and this value will be used in the following calculations.

Each  $\text{Nd}^{3+}$  ion has two nearest Nd neighbors  $7.07 \text{ \AA}$  along the hexagonal axis. The next-nearest-neighbor spins are  $8.85 \text{ \AA}$  distant in such directions that they contribute little to the dipolar field when  $H_0$  is parallel to the hexagonal axis. For this field orientation a peculiar splitting of the resonance line is observed, which is caused by dipolar interaction and explained by Bleaney, Elliott, and Scovil.<sup>20</sup>

The local field at a  $\text{Nd}^{3+}$  ion is primarily determined

<sup>18</sup> J. A. A. Ketelaar, *Physica* 4, 619 (1937).

<sup>19</sup> B. Bleaney, H. E. D. Scovil, and R. S. Trenam, *Proc. Roy. Soc. (London)* A223, 15 (1953).

<sup>20</sup> B. Bleaney, R. J. Elliott, and H. E. D. Scovil, *Proc. Phys. Soc. (London)* A64, 933 (1951).

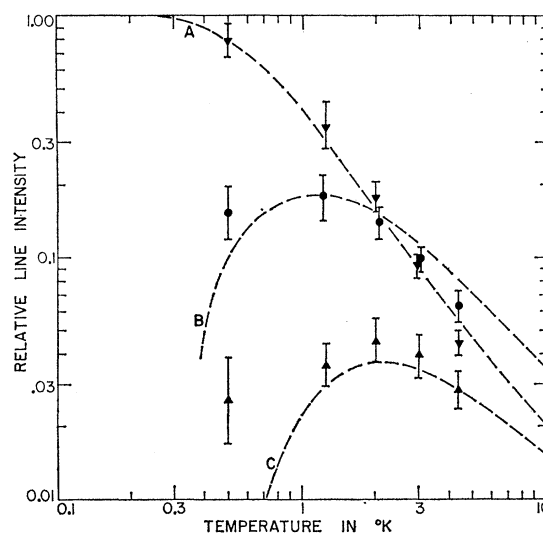


FIG. 3. Measured integrated absorption of the three resonance lines in  $\text{Nd}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  versus temperature. The dashed curves are theoretical absorption ratios.

by its two nearest neighbors the spins of which can have four possible orientations with respect to the external field. Both neighboring spins can be parallel to the external field adding to  $H_0$  a local field of  $2g_{11}\beta/r^3 = 188 \text{ G}$ , both antiparallel thereby subtracting  $188 \text{ G}$ , or one parallel and the other antiparallel producing no local field. This last arrangement can result from two different configurations of the neighbors. The absorption spectrum is therefore split into a triplet, the maxima of which are separated by approximately  $188 \text{ G}$ . At high temperatures where all orientations are equally probable the central component has twice the intensity of the other two. At low temperatures and in high fields that will align the spins in the lowest state, the parallel spin arrangement becomes the most probable. Measured line shapes showing this behavior are illustrated in Fig. 2. The strong line (called line A) appears on the low-field side of the unperturbed resonance, since in this lattice geometry and field direction the dipolar field of the nearest neighbors has the same sign as the external field.

The relative absorption intensities of the three lines are shown in Fig. 3. The results are fitted to the theoretical temperature dependence of the line intensities as indicated by the dashed lines in Fig. 3. These intensities are given by the probability for each arrangement of nearest neighbors

$$p_{\downarrow\downarrow} = 1/[1+b(\Delta)]^2$$

(both neighbors parallel to field),

$$p_{\uparrow\uparrow} = b(2\Delta)/[1+b(\Delta)]^2$$

(both neighbors antiparallel to field),

$$p_{\downarrow\uparrow} = 2b(\Delta)/[1+b(\Delta)]^2$$

(one parallel, the other antiparallel), (27)

multipled by the probability for resonance absorption

$$P \propto [1 - b(\Delta)] / [1 + b(\Delta)]. \quad (28)$$

Here we have written  $\Delta = g_{11}\beta H_0 (= 1 \text{ cm}^{-1})$ . The uncertainties indicated in Fig. 3 result partly from line overlap and partly from nonlinearity of the spectrometer because of the large intensity range covered.

The agreement between measured and calculated intensity changes with temperature is good, except that the weakest line *C* appears to be 10 times too strong at  $T = 0.5^\circ\text{K}$ . However, this absorption can be explained as arising from hyperfine components of the strong line. The neodymium isotopes 143 (natural abundance 12.2%) and 145 (abundance 8.3%) both have nuclear spin  $I = \frac{7}{2}$ . According to the formulas given by Bleaney, Scovil, and Trenam,<sup>19</sup> hyperfine lines of isotope 143 ( $m_I = -\frac{3}{2}$ ) are expected at 325 G and of isotope 145 ( $m_I = -\frac{5}{2}$ ) at 350 G on the high-field side of each resonance line. The combined intensity of these two lines should be 2.5% of the strong line. This is just the intensity of the line observed 350 G from line *A* at  $T = 0.5^\circ\text{K}$ .

The change in the relative intensities of the three absorption maxima is simply a change in the first moment of the spectrum due to the static ( $S_{z_i}S_{z_j}$ ) dipolar interaction between nearest-neighbor ions. There are, however, additional changes in the first moment. In Fig. 2 a small shift in the position of each line can be seen as the temperature is lowered. In fact, the three maxima are not equally spaced at low temperature as shown in Fig. 4 where the field separation between the central peak and the other two lines is plotted versus temperature. This arises from the fact that although all the spins are magnetically identical ( $S = \frac{1}{2}$ , same  $g$  values), the appearance of three, well resolved, absorption maxima requires the interaction terms  $S_{+i}S_{-j}$  be included only between spins contributing to the same absorption line.

The temperature shift of the average peak positions of the three lines shown in Fig. 5 can be explained by first moment theory. The origin of the first moment

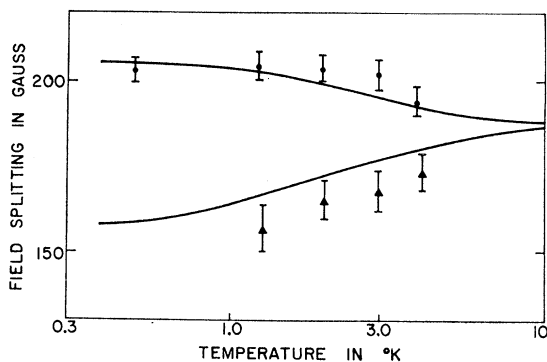


FIG. 4. Field splitting of resonance lines of  $\text{Nd}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  versus temperature.

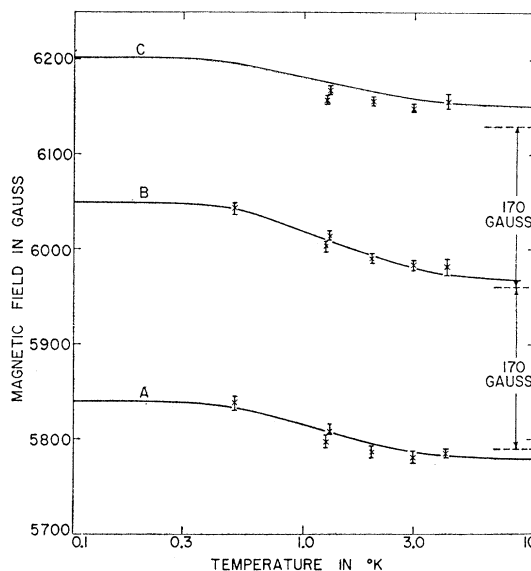


FIG. 5. Position of maxima of lines of  $\text{Nd}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  compared to calculated first moments.

shift can be divided into four parts: (a) the static interaction from  $S_{z_i}S_{z_j}$  terms when the spins  $i$  and  $j$  are nearest neighbors (this gives the splitting of the absorption spectrum into the triplet, has already been considered, and does not affect the shift of the three individual maxima), (b) the spin-flip interactions from terms  $S_{+i}S_{-j}$  between nearest neighbors, (c) the interactions  $S_{z_i}S_{z_j}$  when  $i$  and  $j$  are more distant neighbors, and (d) the interactions  $S_{+i}S_{-j}$  for spins that are not nearest neighbors.

Consider first the  $S_{+i}S_{-j}$  coupling between a pair of nearest neighbors. Such a term is only effective in producing a change in the first moment of the absorption spectrum if the spins upon flipping conserve the Zeeman energy in the magnetic field—sum of the external and local fields. This is only possible for nearest neighbors  $i$  and  $j$  if their other nearest neighbors, spins  $k$  and  $l$ , have the same orientation. If spins  $k$  and  $l$  are in the same state, then the local fields at the sites of spins  $i$  and  $j$  are sufficiently close so that the term  $S_{+i}S_{-j}$  must be included in the Hamiltonian. If  $k$  and  $l$  are in different states the local fields at the sites of spins  $i$  and  $j$  differ by approximately 200 G and there is no way for spins  $i$  and  $j$  to flip and conserve energy. No reorientation of the further neighbors can take up this difference as further neighbor interactions are so much smaller—a statement which is equivalent to the observation of the resolved triplet in the first place. We have, then, an unusual situation where to describe the phenomena of interest no fewer than four spins must be considered together. While the semiclassical description presented here in which the interaction between two spins is modified by other spin interactions is admittedly crude, it does serve to give a physical picture of the problem, and quantitative calculations

can be made. No attempt has yet been made at a more sophisticated approach such as a cluster expansion, etc.

With the above picture in mind it is now a simple problem to calculate the change with temperature in the first moment of each of the three absorption lines of the spectrum due to the  $S_{+i}S_{-j}$  interaction of nearest neighbors. If spin  $i$  is to contribute to line  $A$  of Fig. 2 then spin  $k$  is by necessity aligned with the field. The probability that  $l$  will have the same orientation is  $1/[1+b(\Delta)]$ . When spin  $l$  is aligned then the shift of the resonance of spin  $i$  due to the term  $S_{+i}S_{-j}$  measured in terms of field is  $-g_i^2\beta/2g_{11}r^3$ . Since a spin is coupled with each of two nearest neighbors, the first moment shift of line  $A$  due to this interaction becomes

$$\langle\Delta H\rangle_1 = \frac{h\langle\Delta\nu\rangle_1}{g_{11}\beta} = \frac{g_i^2\beta}{g_{11}r^3[1+b(\Delta)]}. \quad (29)$$

Using similar reasoning the first moment shift of line  $C$  caused by near-neighbor spin flips is

$$\langle\Delta H\rangle_2 = \frac{g_i^2\beta b(\Delta)}{g_{11}r^3[1+b(\Delta)]} \quad (30)$$

and of line  $B$

$$\langle\Delta H\rangle_3 = \frac{g_i^2\beta[1-b(\Delta)]}{2g_{11}r^3[1+b(\Delta)]}. \quad (31)$$

A completely equivalent and perhaps more satisfying description of the above situation is to treat as a unit the dipolar coupled nearest-neighbor spins  $i$  and  $j$  as combining to form a four-level system. It is then possible to associate properly the absorption spectrum arising from this system with the three lines of Fig. 2 when account is taken of the possible states of the other nearest neighbors  $k$  and  $l$ . The results of this procedure are identical with those described above.

The static dipolar field from all neighbors except the two nearest produces identical shifts of the three lines. From (14)

$$\langle\Delta H\rangle_4 = g_{11}\beta \frac{1-b(\Delta)}{2[1+b(\Delta)]} \sum_j^* (1-3\cos^2\theta_{ij})/r^3_{ij}, \quad (32)$$

where the star on the summation means all neighbors except the two nearest ones. From the lattice sum of  $\text{Nd}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  given by Daniels<sup>21</sup> we obtain

$$\sum_j^* (1-3\cos^2\theta_{ij})/r^3_{ij} = 43.3 \times 10^{-20} \text{ cm}^{-3}. \quad (33)$$

The shift due to the spin-flip interaction with all distant neighbors is proportional to the probability that the spins have the same near-neighbor arrangements. This first moment shift for line  $A$  becomes

$$\langle\Delta H\rangle_5 = \frac{g_i^2\beta}{4g_{11}} \frac{1-b(\Delta)}{[1+b(\Delta)]^3} \sum_j^* (1-3\cos^2\theta_{ij})/r^3_{ij}. \quad (34)$$

For line  $B$

$$\langle\Delta H\rangle_6 = \frac{g_i^2\beta [1-b(\Delta)]b(\Delta)}{2g_{11} [1+b(\Delta)]^3} \sum_j^* (1-3\cos^2\theta_{ij})/r^3_{ij}, \quad (35)$$

and for line  $C$

$$\langle\Delta H\rangle_7 = \frac{g_i^2\beta [1-b(\Delta)]b(2\Delta)}{4g_{11} [1+b(\Delta)]^3} \sum_j^* (1-3\cos^2\theta_{ij})/r^3_{ij}. \quad (36)$$

The temperature-dependent local fields  $\langle\Delta H\rangle_1$  to  $\langle\Delta H\rangle_7$  have been computed for  $\Delta=1 \text{ cm}^{-1}$ , and representative values are listed in Table I. They have also been appropriately summed for each separate line, and plotted in Figs. 4 and 5. The measured temperature dependence of the shifts of the individual lines appears to agree very well with the theory. This good agreement is obtained, however, only by making one important modification. The temperature-independent field splitting arising from the  $S_{z_i}S_{z_j}$  interaction term between a spin and its two nearest neighbors has to be taken as 170 G rather than 188 G calculated for the dipolar interaction. This point will be discussed in the next section.

The second moment of each line can also be calculated. Broadening by coupling with all but the two nearest neighbors is given by (12) and (15) when proper account is taken for the interaction between identical and nonidentical spins. The line broadening from spin flips between nearest neighbors must be considered separately. Such a calculation leads to the interesting result that the line  $B$  is the broadest at high temperature since spins contributing to this line have the greatest chance of interacting with identical spins, while at low temperature line  $A$  is the broadest. However, the ratio between the second moments of the lines is only of order  $[(2g_{11}^2+g_i^2)/2g_{11}^2]^2$ ; and since  $g_i^2/2g_{11}^2$  is small for  $\text{Nd}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ , the difference in linewidths is not large. The second moments of the lines are difficult

TABLE I. Local fields (in gauss) in neodymium ethyl sulfate for various temperatures ( $^{\circ}\text{K}$ ).

$T$	0	1	2	$\infty$
$\langle\Delta H\rangle_1$	-32	-26	-21	-16
$\langle\Delta H\rangle_2$	0	6	11	16
$\langle\Delta H\rangle_3$	16	10	5	0
$\langle\Delta H\rangle_4$	73	45	25	0
$\langle\Delta H\rangle_5$	11	4	2	0
$\langle\Delta H\rangle_6$	0	2	2	0
$\langle\Delta H\rangle_7$	0	0	0	0
Contribution to various lines				
$A: \langle\Delta H\rangle_1 + \langle\Delta H\rangle_4 + \langle\Delta H\rangle_5$	52	23	7	-16
$B: \langle\Delta H\rangle_3 + \langle\Delta H\rangle_4 + \langle\Delta H\rangle_6$	89	57	32	0
$C: \langle\Delta H\rangle_2 + \langle\Delta H\rangle_4 + \langle\Delta H\rangle_7$	73	51	36	16
Line separation				
$A$ to $B^a$	207	204	195	186
$B$ to $C^a$	157	164	174	186

<sup>a</sup> Taking temperature-independent contribution arising from nearest-neighbor terms  $S_{z_i}S_{z_j}$  to be 170 G.

<sup>21</sup> M. Daniels, Proc. Phys. Soc. (London) **A66**, 673 (1953).



to measure because of overlap, but approximate agreement between the calculated and observed values of the moments is obtained.

#### VI. DISCUSSION OF POSSIBLE ANTIFERROMAGNETIC COUPLING IN NEODYMIUM ETHYL SULFATE

The first moment changes with temperature of the absorption spectrum of neodymium ethyl sulfate are explained reasonably well on the basis of the dipolar interaction. But to fit the data the line splitting resulting from the static interaction of a spin with its two nearest neighbors has to be taken as about 170 G instead of the calculated 188 G. Some of this difference can, perhaps, be ascribed to systematic error since the position of the maxima were used instead of the first moments of slightly unsymmetric lines. It does not seem likely, however, that the error resulting from this procedure could amount to 18 G. Nor do uncertainties in the lattice parameters of this salt appear capable of explaining the discrepancy. The most obvious reason for the smaller-than-expected separation of the three lines is, then, a weak exchange coupling between the spins.

The exchange coupling being observed is only that between nearest neighbors as an exchange between further neighbors would not contribute significantly to the line separation. Also, the exchange must be antiferromagnetic so as to reduce the line splitting and be anisotropic since appreciable spin-flip terms would destroy the reasonable agreement between the calculated and measured temperature changes of the individual line positions.

An anisotropic exchange of the form

$$3\mathcal{C}_{ij} = A_{ij}S_{z_i}S_{z_j} \quad (37)$$

would require for nearest neighbors  $A = 6 \times 10^{-19}$  erg to produce a shift of lines  $A$  and  $C$  by 18 G. This exchange alone corresponds roughly to a Curie temperature of<sup>22</sup>

$$\theta_{\text{ex}} = -AS(S+1)z/3k = -0.0018^\circ\text{K}, \quad (38)$$

where  $z=2$  is the number of nearest neighbors. This is much smaller than the Curie temperature caused by dipolar interaction in the noncubic lattice of neodymium ethyl sulfate.<sup>21</sup>

Specific-heat measurements have been performed on neodymium ethyl sulfate.<sup>23</sup> The experimental result for the spin contribution to the specific heat is  $CT^2/2R = (8.85 \pm 0.25) \times 10^{-5}$ , which agrees very well with the value  $CT^2/2R = 8.95 \times 10^{-5}$  calculated from the dipolar interaction by Daniels.<sup>21</sup> While this agreement seems to exclude any possible exchange, the specific heat involves  $g$  to the 4th power and  $r_{ij}$  to the 6th power, and small errors in the values of these constants used in the calculation can easily upset the apparent consistency.

The values of  $r_{ij}$  used were taken from room temperature measurements. The coefficient of thermal expansion is unknown for neodymium ethyl sulfate, but it is possible that the dimensions could decrease enough at low temperature to have a significant effect on the calculations. More important, we have measured  $g_{11} = 3.60$  in the concentrated salt, and the use of this instead of Daniels' value of  $g_{11} = 3.535$  increases  $CT^2/2R$  by 6%. The calculated specific heat is then too large; but when the small antiferromagnetic coupling (37) is included, it is reduced again to agree with the experimental data.

The easiest manner in which to include the effect of the exchange in the specific heat is to use an effective  $g$  when interaction between nearest neighbors is considered. The coupling (37) added to the dipolar  $S_{z_i}S_{z_j}$  term in the interaction between nearest-neighbors shifts the line by 18 G out of a total of 188 G and the interaction energy is reduced to

$$\begin{aligned} 3\mathcal{C}_{ij} &= -\left(\frac{2g_{11}^2\beta^2}{r^3} - A\right)S_{z_i}S_{z_j} \\ &= -\frac{2(g_{11}')^2\beta^2}{r^3}S_{z_i}S_{z_j} = -\left(\frac{170}{188}\right)\frac{2g_{11}^2\beta^2}{r^3}S_{z_i}S_{z_j}; \\ g_{11}' &= (170/188)^{1/2}g_{11} = 3.42. \end{aligned} \quad (39)$$

When this apparent  $g'$  is used in Daniels' equation (16) whenever the lattice sums involve one of the nearest neighbors, the specific heat is found to be  $CT^2/2R = 8.35 \times 10^{-5}$ . And although the agreement with the experimental result appears to be much poorer, it is quite possible that the uncertainties in the lattice parameters can account for the discrepancy. Hence, the specific-heat data do not rule out the possibility of the interaction given by (37).

Some weak interaction, in addition to the dipolar forces, should not be too unexpected in neodymium ethyl sulfate. Demagnetization experiments<sup>24</sup> on the isomorphous cerium ethyl sulfate give a specific heat for this salt that is six times larger than that expected from dipolar interactions alone. The Curie temperature in this salt is of the order  $-0.1^\circ\text{K}$ , which corresponds to an antiferromagnetic exchange two orders of magnitude larger than the interaction (37).

Finkelstein and Mencher<sup>25</sup> have suggested that the anomalous behavior of cerium ethyl sulfate may be due to an electric quadrupole-quadrupole coupling between the electronic charge distributions of the cerium ions. Such an interaction would depend upon the magnetic quantum numbers of the ions and give rise to an  $S_{z_i}S_{z_j}$  term in the Hamiltonian. The quadrupole coupling is

<sup>22</sup> C. Kittel, *Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed., p. 404.

<sup>23</sup> L. D. Roberts, C. C. Sartain, and B. Borie, *Rev. Mod. Phys.* **25**, 170 (1953); H. Meyer, *Phil. Mag.* **2**, 521 (1957).

<sup>24</sup> A. H. Cooke, S. Whitley, and W. P. Wolf, *Proc. Phys. Soc. (London)* **B68**, 415 (1955); C. E. Johnson and H. Meyer, *Proc. Roy. Soc. (London)* **A253**, 199 (1959).

<sup>25</sup> R. Finkelstein and A. Mencher, *J. Chem. Phys.* **21**, 472 (1953).

very sensitive to the radius of the 4*f*-electron orbit and to the matrix elements of the interaction connecting the states of the crystal field split *J* multiplet.

Cerium is the first member of the rare-earth series and has a mean 4*f*-electron radius that is considerably larger than that of neodymium. Also, the first excited state of Ce<sup>3+</sup> in the ethyl sulfate is only 4.8 cm<sup>-1</sup> above the ground level<sup>24</sup> while for Nd<sup>3+</sup> the splitting is about 130 cm<sup>-1</sup>.<sup>26</sup> For both these reasons the electronic quadrupole coupling in neodymium ethyl sulfate should be much smaller than in the corresponding cerium salt, but it is reasonable that it may be the physical origin of the weak antiferromagnetic interaction that we have observed in neodymium ethyl sulfate.

### VII. MEASUREMENTS IN NICKEL FLUOSILICATE

Nickel fluosilicate, NiSiF<sub>6</sub>·6H<sub>2</sub>O is isomorphic with NiSnCl<sub>6</sub>·6H<sub>2</sub>O, whose crystal structure has been determined by Pauling.<sup>27</sup> The rhombohedral unit cell contains one molecule, and its trigonal axis coincides with the hexagonal growth axis. The rhombohedral axes of the unit cell in NiSiF<sub>6</sub>·6H<sub>2</sub>O are 6.21 Å long and the angles between them are α=96°5 at room temperature.<sup>28</sup> This is sufficiently close to cubic symmetry (α=90°) so that the sum  $\sum_j (3 \cos^2 \theta_{ij} - 1) / r_{ij}^3$  is found to be essentially the same as for a cubic lattice.<sup>29</sup>

Walsh<sup>30</sup> has measured the thermal expansion of this crystal with strain gauges. He found the expansion to be highly anisotropic and from his results the deviation from cubic symmetry is expected to be slightly larger at low temperatures. However, the lattice sum can probably still be assumed to vanish for spherical samples.

The spin Hamiltonian and the energy levels of Ni<sup>2+</sup> in this salt are given by (16) and (17). We have measured  $g=2.24 \pm 0.01$  at helium temperatures, isotropic to the accuracy of the measurements. Other workers<sup>31-33</sup> have reported somewhat higher and partly anisotropic *g* values ranging from  $g=2.25$  to  $g=2.36$ . Our results for the crystalline field splitting is  $D=-0.113 \pm 0.005$  cm<sup>-1</sup> at helium temperatures, which is in good agreement with the value  $D=-0.12$  cm<sup>-1</sup> measured by Penrose and Stevens.<sup>32</sup> Above 20°K the splitting is a function of temperature and increases to  $D=-0.50$  cm<sup>-1</sup> at 300°K. Hydrostatic pressure at this temperature decreases the splitting, and Walsh<sup>30</sup> has shown that *D* actually goes through zero and changes sign at  $P=6200$  kg/cm<sup>2</sup>. Since the splitting is so sensitive to

lattice distortions, it is not unreasonable to expect that crystalline defects, impurities, and strains introduced on cooling give a slight variation in the value of *D* from one lattice site to another. The present line-shape data were taken mainly with the external field parallel to the trigonal axis (γ=0). For this field orientation two lines are observed separated at high temperatures by  $2|D|/g\beta$ . The two lines are broadened and at low temperatures shifted by an exchange interaction. The resonance spectrum was also measured for the field direction γ=55° where  $(3 \cos^2 \gamma - 1) = 0$  and the two lines coincide. Here the line is exchange narrowed and unshifted. However, the linewidth is not the same for all γ=55° directions as the lattice sum  $\sum_j (3 \cos^2 \theta_{ij} - 1) / r_{ij}^3$  also depends upon the azimuthal angle.

Attempts to grind spheres of NiSiF<sub>6</sub>·6H<sub>2</sub>O in the usual manner were unsuccessful since the crystals are soft and cleave very easily along the hexagonal axis. Instead, reasonably good ellipsoids of revolution resulted with axial ratios ranging from 1.25 to 1.50. The field for resonance then had to be corrected for demagnetizing effects according to (24) and (26). For example, at  $T=0^\circ$  the shape correction is 164 G for a sample of axial ratio 1.50, which is far from negligible.

Several different samples were measured in the cavity version of the spectrometer and several others in the waveguide version. Typical resonance line shapes when *H*<sub>0</sub> is along the hexagonal axis are shown in Fig. 6. The maximum absorption amplitudes are normalized to the same value, and the fields are not corrected for the effect of the nonspherical sample shape. At 4.2°K two resonance peaks of almost equal intensity are observed as expected. Since *D* is relatively small, the lines overlap somewhat. As the temperature is lowered, the absorption due to transitions  $a_3 \leftrightarrow a_2$  becomes weaker relative to the other transition, and below 1°K cannot be separated from the wing of the strong absorption line. The positions of both lines shift with temperature.

The origin of the weak absorption that is observed between the main peaks (see Fig. 6) is not known. Some

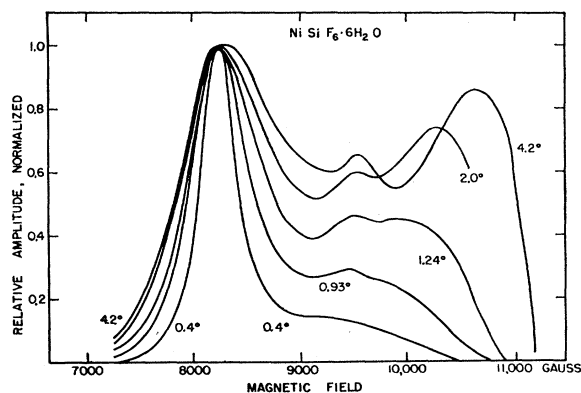


FIG. 6. Resonance absorption of NiSiF<sub>6</sub>·6H<sub>2</sub>O at several temperatures with the magnetic field parallel to the trigonal axis.

<sup>26</sup> R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 387 (1953).

<sup>27</sup> L. Pauling, Z. Krist. **72**, 482 (1930).

<sup>28</sup> O. Hassel and J. R. Salvesen, Z. Phys. Chem. **128**, 345 (1927).

<sup>29</sup> E. Ishiguro, K. Kambe, and T. Usui, Physica **17**, 310 (1951).

<sup>30</sup> W. M. Walsh, Phys. Rev. **114**, 1473 (1959).

<sup>31</sup> J. Bequerel and W. Opechowski, Physica **6**, 1039 (1939).

<sup>32</sup> P. R. Penrose and K. W. H. Stevens, Proc. Roy. Soc. (London) **A63**, 29 (1950).

<sup>33</sup> A. N. Holden, C. Kittel, and W. A. Yager, Phys. Rev. **75**, 1443 (1949).

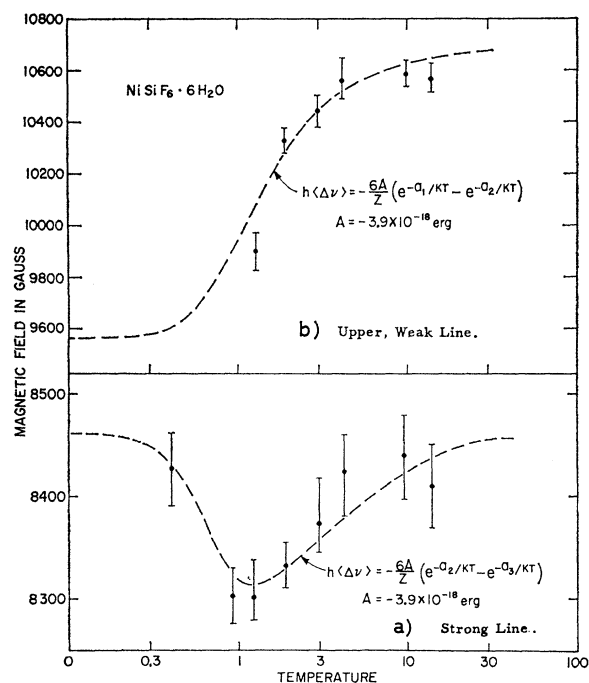


FIG. 7. Position of maxima of absorption lines of  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$  versus temperature.

of the ions are close to crystal imperfections and hence must see a distorted crystalline field. The exchange coupling between neighboring spins may also change at lattice distortions. A possible explanation for this additional absorption is that a significant fraction of the spins have  $|D| < |A|$ , but of this conjecture there is no proof. Several other hypotheses exist, but at the moment they seem even more unlikely.

The peak positions of the lines, corrected for the demagnetizing shift, are shown in Figs. 7(a) and (b). Since this salt is almost cubic, the dipolar part of the lattice sum cancels and does not contribute to the first moment. The first moment shift of the strong line  $a_2 \leftrightarrow a_1$  is from (18)

$$h\langle \Delta\nu \rangle = -6A[b(a_2) - b(a_3)]Z^{-1}, \quad (40)$$

and for the weaker line  $a_3 \leftrightarrow a_2$

$$h\langle \Delta\nu \rangle = -6A[b(a_1) - b(a_2)]Z^{-1}. \quad (41)$$

There can be little doubt that the experimental results confirm the temperature dependence of the line shifts predicted by McMillan and Opechowski.<sup>4</sup>

The best fit of the data is obtained by the choice of an isotropic exchange  $A = (3.9 \pm 0.4) \times 10^{-18}$  erg between a spin and each of its six nearest neighbors. The coupling is ferromagnetic; an antiferromagnetic interaction would shift the lines in the opposite direction. An anisotropic exchange would produce a very different change in the first moment. If an anisotropic exchange

of the form

$$\mathcal{H}_{ij}^{(1)} = A_{ij1}S_{z_i}S_{z_j} + \frac{1}{2}A_{ij1}(S_{+i}S_{-j} + S_{-i}S_{+j}) \quad (42)$$

is assumed, the results of McMillan and Opechowski,<sup>34</sup> who considered the effects of such an exchange, limit the fit of these measurements to

$$\arctan(A_{ij1}/A_{ij1}) = (45 \pm 5)^\circ,$$

or

$$A_{ij1} = A_{ij1} \text{ to within } 20\%.$$

The physical reasons for the nature of the first moment changes illustrated in Fig. 7 have already been briefly outlined.<sup>6</sup>

The square root of the second central moment measured on the nonoverlapping side of the strong absorption line  $a_2 \leftrightarrow a_1$  is shown in Fig. 8. From the results of McMillan and Opechowski the theoretical expression for this moment is

$$\begin{aligned} h^2\langle \Delta\nu^2 \rangle_{\text{central}} &= h^2\langle \Delta\nu^2 \rangle - (h\langle \Delta\nu \rangle)^2 \\ &= 6A^2\{Z^{-1}[b(a_2) + 2b(a_3)] - Z^{-2}[b(a_2) - b(a_3)]^2\} \\ &\quad + 0.626 \frac{\beta^4 g^4}{d^6} \{1 + 4Z^{-1}[2b(a_1) + b(a_3)] \\ &\quad - Z^{-2}[9b(2a_1) - 6b(a_1a_2) + b(2a_2) \\ &\quad - 12b(a_1a_3) + 4b(2a_3) + 4b(a_2a_3)]\}, \quad (43) \end{aligned}$$

where we have used

$$\frac{1}{4} \sum_j' (3 \cos^2 \theta_{ij} - 1)^2 / r_{ij}^6 = 0.626/d^6.$$

The lattice constant is  $d = 6.21 \text{ \AA}$ . Again, the agreement with the experimental results is good for  $A = -3.9 \times 10^{-18}$  erg. Since about 90% of the second moment results from the exchange term this is a good check on the magnitude of  $A$  found from the first moment shifts.

Line shapes were observed with  $H_0$  making an angle  $\gamma = 55^\circ$  with the  $z$  axis. When the crystal field splitting is zero and only a single absorption line is present an isotropic exchange is expected to have no effect on the first and second moments of the line. This was indeed found to be the case. No shift of the absorption outside experimental accuracy was observed, and the measured second moment for this field orientation agreed with that calculated from the dipolar interactions.

The resonance lines showed considerably broadening at room temperature—a result of fast spin-lattice relaxation.

## VIII. DISCUSSION OF THE NICKEL FLUOSILICATE RESULTS

The measurements of resonance line moments are in good agreement with the theory if an isotropic,

<sup>34</sup> M. McMillan and W. Opechowski, Can. J. Phys. **39**, 1369 (1961).

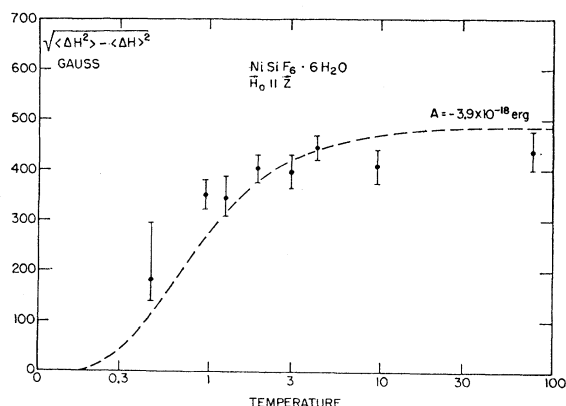


FIG. 8. Measured and calculated square root of second central moment of strong line of  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$  versus temperature.

ferromagnetic interaction of strength  $A = -(3.9 \pm 0.4) \times 10^{-18}$  erg is assumed between nearest neighbors. This result will now be compared to those of other investigations.

The specific heat of  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$  has been measured by Benzie and Cooke<sup>35</sup> and the susceptibility has been found from the optical Faraday effect by Bequerel and Opechowski.<sup>31</sup> These results have been reanalyzed by Ollom and Van Vleck<sup>36,37</sup> using the crystalline field splitting constant  $D$  given by paramagnetic resonance experiments. They found good agreement by assuming an exchange that would give a Curie temperature of  $\theta = 0.1^\circ\text{K}$ . From (38) this corresponds approximately to

$$A = -\frac{3k\theta}{zS(S+1)} = -3.5 \times 10^{-18} \text{ erg}, \quad (44)$$

where  $z=6$  is the number of nearest neighbors. This is in close agreement with our result for the exchange.

Earlier determinations of the magnitude of the exchange from line moments at high temperature served only to confuse the situation because of inadequate measurements. At  $300^\circ\text{K}$  the linewidths are approximately 1800 G for  $H_0$  along the trigonal axis, but at  $77^\circ\text{K}$  are only about 800 G. The resonance is obviously broadened by fast spin-lattice relaxation at room temperature, and one cannot use the previously published line shapes<sup>33</sup> to determine the exchange as has been done by several authors.<sup>29,37</sup> Similarly, the lack of exchange narrowing of the absorption when the crystal field splitting is made zero by the application of pressure<sup>30</sup> is not a result of anisotropic exchange but of lifetime broadening.

## IX. MEASUREMENTS ON COPPER POTASSIUM SULFATE

Hydrated copper potassium sulfate,  $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  is monoclinic. The unit cell contains two  $\text{Cu}^{2+}$  ions, and its dimensions have been deduced from goniometer and density measurements by Tutton<sup>38</sup> to be  $a_0 = 9.040 \text{ \AA}$ ,  $b_0 = 12.069 \text{ \AA}$ ,  $c_0 = 6.141 \text{ \AA}$ ,  $\beta = 104^\circ 28'$ .

Hofmann<sup>39</sup> has x-ray analyzed the isomorphous salt  $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . He found the space group to  $C_{2h}^5$  so that the position of the second molecule in the unit cell can be derived from the first by a translation from  $(0,0,0)$  to  $(\frac{1}{2}, \frac{1}{2}, 0)$  followed by a reflection in the  $ac$  plane. The  $\text{Mg}^{2+}$  ions are surrounded by distorted octahedrons of water molecules and the crystalline electric field should have approximately tetragonal symmetry. However, the detailed structure given by Hofmann has been criticized by Wyckoff.<sup>40</sup> It is important to note for what follows that each  $\text{Cu}^{2+}$  ion has two nearest neighbors on similar sites  $(0,0,\pm 1)$  at a distance of  $6.1 \text{ \AA}$  and four nearest neighbors on dissimilar sites  $(\pm \frac{1}{2}, \pm \frac{1}{2}, 0)$   $7.6 \text{ \AA}$  distant. Further neighbors are at least  $8.9 \text{ \AA}$  distant.

The electron spin resonance behavior of  $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  has been discussed by Bleaney and co-workers.<sup>41,42</sup> Each of the two magnetic complexes in the unit cell can be described by the spin Hamiltonian ( $S = \frac{1}{2}$ )

$$\mathcal{H}_0 = \beta H_0 \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{B} \cdot \mathbf{I} + \mathbf{I} \cdot \mathbf{P} \cdot \mathbf{I}. \quad (45)$$

The directions for maximum  $g = g_z$  are in the crystal-line  $ab$  plane making angles of  $\pm 45^\circ$  with the  $a$  axis.  $g_z$  is reported to be 2.36, but we have measured  $g_z = 2.41$ . In the plane perpendicular to the magnetic  $z$  direction  $g$  varies from 2.05 to 2.12 which indicates a considerable rhombic component of the crystalline field.

The copper isotopes  $\text{Cu}^{63}$  (natural abundance 69%) and  $\text{Cu}^{65}$  (abundance 31%) both have nuclear spin  $I = \frac{3}{2}$ . The tensor  $\mathbf{B}$  gives the electron-nucleus interaction. The tensor  $\mathbf{P}$  gives the electrostatic interaction with the nuclear electric quadrupole moment.

The spin-spin interaction sufficiently broadens the resonance in concentrated crystals so that only in magnetically diluted salts are the hyperfine lines resolved. Normally, the allowed hyperfine lines are those in which the nuclear orientation does not change ( $\Delta m_I = 0$ ), but if the quadrupole interaction is comparable to the magnetic interaction, transitions corresponding to  $\Delta m_I = \pm 2$  are also possible. In addition,  $\Delta m_I = \pm 1$  transitions are allowed if the external field is not along a rhombic axis.

<sup>38</sup> A. E. H. Tutton, Proc. Roy. Soc. (London) **A118**, 367 (1928).

<sup>39</sup> W. Hofmann, Z. Krist. **78**, 279 (1931).

<sup>40</sup> R. W. G. Wyckoff, *Crystal Structure* (Interscience Publishers, Inc., New York, 1948), Vol. III.

<sup>41</sup> B. Bleaney, K. D. Bowers, and D. J. E. Ingram, Proc. Roy. Soc. (London) **A228**, 147 (1953).

<sup>42</sup> B. Bleaney, R. P. Penrose, and B. I. Plumpton, Proc. Roy. Soc. (London) **A198**, 406 (1949).

<sup>35</sup> R. J. Benzie and A. W. Cooke, Proc. Phys. Soc. (London) **A63**, 213 (1950).

<sup>36</sup> J. F. Ollom, thesis, Harvard University, 1952 (unpublished).

<sup>37</sup> J. F. Ollom and J. H. Van Vleck, Physica **17**, 205 (1951).

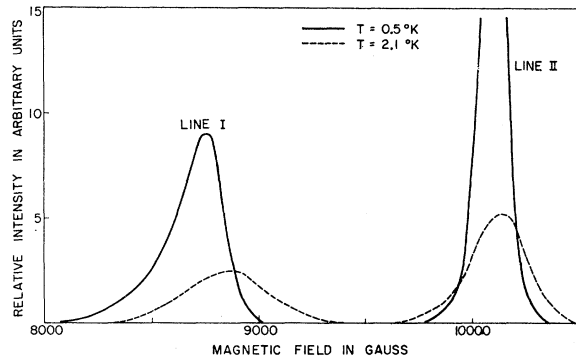


FIG. 9. Resonance absorption of  $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  at two temperatures. The magnetic field is in the  $ab$  plane making an angle of  $45^\circ$  to the  $a$  axis.

The hyperfine and quadrupole interaction constants are only 8% different for the two isotopes, and their weighted means measured on zinc-diluted crystals are<sup>41</sup>:  $B_z = (103 \pm 5) \times 10^{-4} \text{ cm}^{-1}$ ,  $B_x = (34 \pm 5) \times 10^{-4} \text{ cm}^{-1}$ ,  $P = \frac{3}{2}P_z = (11 \pm 1) \times 10^{-4} \text{ cm}^{-1}$ ,  $P_x - P_y$  is small.

When  $H_0$  is along the magnetic  $z$  axis of one type of  $\text{Cu}^{2+}$  ion, the four hyperfine lines for  $\Delta m_I = 0$  of these ions are shifted in field  $\pm 138$  and  $\pm 46$  G. For other orientations the splittings are smaller and more lines may appear.

The resonance absorption has been investigated in an approximately spherical sample of  $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  mounted so that the external field could be rotated in the crystalline  $ab$  plane.  $H_0$  can then be made parallel to the tetragonal axis of one of the magnetic complexes. For this orientation two resonance lines are observed one with  $g = g_z = 2.41$  (called line I) and one with  $g = 2.11$  (line II). When the field is rotated  $45^\circ$  away from this position, the two lines resulting from the dissimilar lattice sites coincide.

Line II is relatively narrow and appears symmetric at all temperatures. Line I is broader because of the larger hyperfine splitting and becomes very unsymmetric at low temperatures as shown in Fig. 9. No separation of the hyperfine components is seen. In Fig. 10(a) the temperature shift of the first moments of the two lines is shown with the field in the direction of maximum line separation. In Fig. 10(b) the change in line position is illustrated for the field along the crystal-line  $b$  axis and the two lines overlapping.

An exact calculation of the line shifts from the first moment theory is hardly possible because of the rhombic character of the two  $g$  tensors. We will use formulas (11) and (14) with the measured  $g$  values and use at first the usual criterion that unseparated lines mean identical spins. Varying  $g$  values in directions perpendicular to  $H_0$  will cause small changes in transition probabilities and possibly in line shapes, but any such effects are small and ignored. For the field along the  $b$  axis, all spins are identical and the lattice sum over the 102 closest neighbors is found to be approxi-

mately

$$\sum_j' (1 - 3 \cos^2 \theta_{ij}) / r_{ij}^3 = -3.7 \times 10^{21} \text{ cm}^{-3}.$$

The resulting moment, using (11),  $g \approx 2.23$ , and  $g\beta H = 1 \text{ cm}^{-1}$  is shown by the dashed line in Fig. 10(b). The agreement with experimental values is reasonably good.

When two resolved lines are observed the lattice sums must be calculated separately for identical and nonidentical neighbors. With  $H_0$  in the  $ab$  plane making an angle of  $45^\circ$  with the  $a$  axis the sums are

$$\left[ \sum_j' (1 - 3 \cos^2 \theta_{ij}) / r_{ij}^3 \right]_{\text{identical}} = -6.6 \times 10^{21} \text{ cm}^{-3},$$

$$\left[ \sum_k' (1 - 3 \cos^2 \theta_{ik}) / r_{ik}^3 \right]_{\text{nonidentical}} = 5.2 \times 10^{21} \text{ cm}^{-3}. \quad (46)$$

In Eqs. (11) and (14),  $g_{11} = 2.41$  and  $g_1 = 2.11$  have been used for line I and  $g_{11} = 2.11$ ,  $g_1 = 2.41$  for line II. The resulting dipolar first moment shifts  $\langle \Delta H \rangle_{\text{dip}}$  are shown by the dashed lines in Fig. 10(a). The difference between  $\langle \Delta H \rangle_{\text{dip}}$  and the experimental values of  $\langle \Delta H \rangle$  must be caused by exchange between nonidentical ions. With  $z = 4$  nearest nonidentical neighbors the total first moment is in best agreement with the experimental values for line II with a ferromagnetic exchange  $A_{ik'} = -1.4 \times 10^{-18} \text{ erg}$ . Here  $A_{ik'}$  refers specifically to

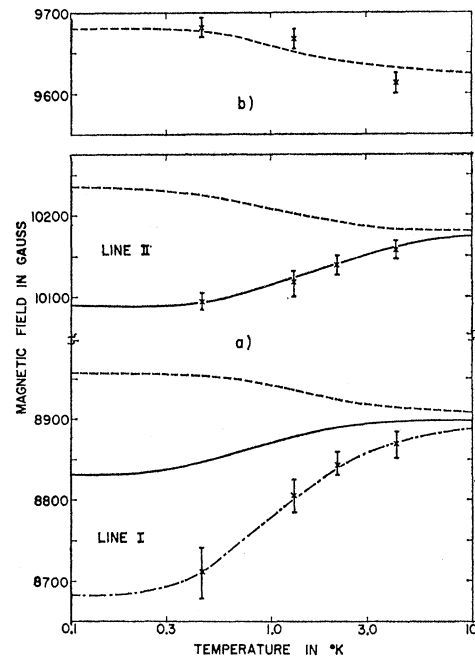


FIG. 10. First moment shift of the resonance lines of  $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  versus temperature. (a) The magnetic field is in the  $ab$  plane making an angle of  $45^\circ$  to the  $a$  axis. (b) The field is parallel to the  $b$  axis.

the exchange interaction between an ion and each of its four nearest-neighbor ions on dissimilar lattice sites. The sum of the first moment shifts resulting from this exchange and the dipolar coupling is shown by the solid curve in Fig. 10(a).

With this value of  $A_{ik'}$  the agreement between the calculated and experimental shifts is very good for line II but very poor for I. The difficulty is that the experimentally measured shifts of the two lines differ by a factor of 3. It is therefore not possible to explain the change in the first moments of both lines with the same isotropic exchange between dissimilar spins. Neither will it help to postulate anisotropic exchange since any such reasonable exchange will shift the two lines in the same direction by approximately the same amount. Also the agreement between the calculated and experimental first moment change of the absorption line with  $H_0$  parallel to the  $b$  axis would be destroyed.

The problem is then to postulate an interaction that will yield an appreciably different first moment shift for the two lines. But it must be remembered that the different  $\text{Cu}^{2+}$  ions giving rise to the two separate absorption lines are dissimilar only by virtue of a reflection. Any interaction at one type of  $\text{Cu}^{2+}$  ion site must also be present at the other type of site, and one must, therefore, look for a process that is orientation-dependent. One such phenomenon is the hyperfine interaction, which produces a markedly anisotropic linewidth. If the hyperfine interaction were sufficiently large so that the lines were resolved into  $2I+1=4$  separate hyperfine components, then spin flip terms  $S_{+i}S_{-j}$  of the spin-spin interactions between ions otherwise identical except for the state which their nuclei are in would have to be truncated from Hamiltonian as not conserving energy. This is equivalent to saying that if the hyperfine interaction is larger than the spin-spin interaction then the former must be treated as part of the unperturbed Hamiltonian  $H_0$  and noncommuting terms truncated from the spin-spin interaction. Resolved hyperfine components are not observed even for line I, which has the maximum hyperfine splitting, so that spin flips are allowed at least for neighboring ions having nuclear quantum numbers  $m_I$  differing by no more than one. Rearrangements within the spin system can take up the energy difference  $B_z$ . But this does not necessarily mean that flips between spins having  $m_I$  values differing by 3 are permitted with the same probability since this involves an energy difference  $3B_z$ .

The idea here is essentially the same as for cross relaxation processes discussed by Bloembergen and co-workers.<sup>43</sup> Spin flips that do not conserve energy are not completely prohibited, but they occur with a probability that decreases exponentially as the energy difference increases. Our interest is in a case where the probability for spin flips between ions having  $m_I$

different by 3 and perhaps by 2 is sufficiently reduced so that such processes do not influence the resonance line shape. However, considered as cross relaxation, these flips may still occur at a very fast rate compared to the spin-lattice relaxation.

The explanation proposed to account for the considerable difference in the change of the first moments of the resolved lines I and II is that a relatively large exchange interaction exists between a  $\text{Cu}^{2+}$  ion and its two nearest-neighbor ions on similar lattice sites. Moreover, in computing the first moment of line I one must exclude  $S_{+i}S_{-j}$  terms between ions on similar lattice sites having  $m_I$  values different by greater than 1. For line II such a restriction should not be placed on the Hamiltonian, as for this absorption line the hyperfine splitting is much smaller.

The partial exclusion of the spin flips between hyperfine components places a limitation on the magnitude of the exchange between nearest neighbors. The exchange field from each ion must be somewhat less than the line width of approximately 280 G. Hence from

$$H_e \approx A_{ij'} S_{z_i} S_{z_j} / S_{z_i} g_{11} \beta, \quad (47)$$

the approximate upper limit of  $|A_{ij'}| < 12 \times 10^{-18}$  erg is obtained, a value considerably larger than the dipolar field from the same neighbors. Here  $A_{ij'}$  means specifically the exchange between an ion and each of its two nearest neighbors on similar lattice sites.

If the  $S_{+i}S_{-j}$  terms are excluded for ions with  $m_I$  different by either 2 or 3, then on the average  $\frac{3}{8}$  of what otherwise are identical spins would appear nonidentical. Then the exchange part of (14) is summed over the 2 nearest neighbors and the result multiplied by  $\frac{3}{8}$ . The experimentally observed first moment shift of line I can then be fit, as shown by the dash-dot curve in Fig. 10(a), by an exchange  $A_{ij'} = -9 \times 10^{-18}$  erg.

The restrictions imposed on the spin-flip terms will, of course, also modify the effects of the dipolar interaction upon the first moment. This effect is relatively small, and in view of the uncertainties in the above arguments is neglected.

A more vigorous approach to this problem by calculating the line moments from the complete Hamiltonian containing hyperfine and exchange interactions of comparable magnitude has not been attempted.

## X. DISCUSSION OF THE EXCHANGE IN COPPER POTASSIUM SULFATE

The observed line shifts in  $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  cannot be explained solely on the basis of an isotropic exchange interaction between the two ions in the unit cell. However, the experimental results can be understood by assuming that the hyperfine interaction for spins contributing to line I is strong enough to reduce the probability for spin flips within this line. It is then possible to obtain order of magnitude estimates for two different exchange interactions within the crystal. The

<sup>43</sup> N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. **114**, 445 (1959).

best fit of the results is found to be given by an exchange between nearest-neighbor ions on dissimilar lattice sites of  $A_{ik'} = -1.4 \times 10^{-18}$  erg and ions on similar sites of  $A_{ij'} = -9 \times 10^{-18}$  erg. The latter value depends upon the spin-flip restriction imposed, but it is in agreement with the condition derived from (47).

The suggestion of partly hyperfine-hindered spin flips will also explain the observed asymmetry of line I. Some of the spins are free to spin flip with their neighbors and their resonance frequencies are not shifted by  $A_{ij'}$ . This portion of the line should be exchange-narrowed and would account for the rather sharp peak seen in Fig. 9 for  $T = 0.45^\circ\text{K}$ . Other spin pairs are restricted in their flips; hence, their resonance frequencies are shifted towards lower fields by the ferromagnetic interaction. The maximum shift would be  $2H_e \approx 400$  G, which is about the magnitude of the line tail seen in Fig. 9.

The Curie temperature of  $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  has been derived from susceptibility and specific-heat measurements on powdered samples. De Klerk<sup>44</sup> found  $\theta = 0.054^\circ\text{K}$ ; data of Kramers, Wasscher, and Gorter<sup>45</sup> seem to be in agreement with this, but Garrett<sup>46</sup> and Benzie and Cooke<sup>35</sup> have found  $\theta = 0.034^\circ\text{K}$  and  $\theta = 0.035^\circ\text{K}$ , respectively. The interaction is ferromagnetic. The contribution from dipolar interaction to the Curie temperature of this salt is only of order  $0.001^\circ\text{K}$ .<sup>21</sup>

The Curie temperature is related to the strength of the exchange by the approximate equation

$$\theta = -(1/3k)(A_{ij'z_{j'}} + A_{ik'z_{k'}})S(S+1), \quad (48)$$

where  $z_{j'} = 2$  and  $z_{k'} = 4$ . Substituting for the exchange interactions as estimated from the present measurements we obtain  $\theta = 0.039^\circ\text{K}$ , a value in as good agreement with the Oxford measurements. While the values of the interactions may be in considerable error, it appears that the exchange between similar neighboring

ions in  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  is appreciably stronger than between dissimilar neighbors. This result is compatible with what is expected from the crystal structure, for the distance of 6.1 Å between similar spins is less than that between dissimilar spins, 7.6 Å.

## XI. CONCLUSIONS

Paramagnetic resonance in concentrated crystals has been observed under the condition  $h\nu > kT$ . The line moments have been analyzed in terms of spin-spin interactions, and it has been demonstrated that information concerning the nature of these interactions can be obtained in many cases. As examples of the varied types of phenomena that occur at low temperatures results have been presented on  $\text{Nd}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$ .

In neodymium ethyl sulfate there appears to be a weak antiferromagnetic coupling between nearest-neighbor  $\text{Nd}^{3+}$  ions. The measurements of the line moments of copper potassium sulfate yield data on two different exchange interactions within the crystal, that between nearest-neighbor ions on similar lattice sites and on dissimilar sites. The results on the line moment changes in nickel fluosilicate are in agreement with the calculations of McMillan and Opechowski and show that the exchange coupling between neighboring  $\text{Ni}^{2+}$  ions is isotropic.

It appears that the measurement of changes at low temperatures in the line moments of spin resonance absorption is a very useful tool in investigating the exchange couplings in paramagnetic crystals.

## ACKNOWLEDGMENTS

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<sup>44</sup> D. de Klerk, *Physica* **12**, 513 (1946).

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