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Spin-Spin Interactions in Cerium Ethyl Sulfate*

J. Dweck† and G. Seidel
Brown University, Providence, Rhode Island

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The spin-spin interactions in cerium ethyl sulfate have been investigated by the method of paramagnetic-resonance line moments under the condition of appreciable spin alignment by the Zeeman interaction, i.e., $h\nu > kT$. The total nondipolar interaction of a cerium ion with all its neighbors was found to be antiferromagnetic, having the magnitude $(0.113\pm0.003)\text{cm}^{-1}$. As previously assumed, this interaction has been ascribed to the electric quadrupole-quadrupole coupling of the $4f$ electrons of neighboring ions. The lack of agreement between the measurements and theory is attributed to the sensitivity of the calculations to parameters not sufficiently well known for the Ce ion in the ethyl-sulfate lattice. Several unusual qualitative features of the resonance spectrum are explainable on the basis of a qq coupling between ions. In addition, the observation of the resonance spectra of various other rare-earth ions in cerium ethyl sulfate has permitted a measurement of the following nearest-neighbor nondipolar interactions in the ethyl sulfates: Ce-Pr: $(0.32\pm0.06)\times10^{-2}\ \text{cm}^{-1}$; Ce-Nd: $(1.2\pm0.2)\times10^{-2}\ \text{cm}^{-1}$; Ce-Gd: $(0.00\pm0.05)\times10^{-2}\ \text{cm}^{-1}$.

I. INTRODUCTION

THE magnetic and thermal properties of cerium ethyl sulfate[1] (CeES) have been considered for many years anomalous in comparison with the behavior of other rare-earth salts of the isomorphic ethyl sulfates. Susceptibility[2] and heat-capacity[3] measurements have shown the existence of an antiferromagnetic transition at 0.08°K requiring a spin-spin coupling between cerium ions six times larger than the dipolar interaction and of opposite sign. It is this large nondipolar coupling that makes the cerium salt unique among the ethyl sulfates.

The mechanism of superexchange usually responsible for magnetic coupling in hydrated crystals has been thought to be an improbable source of the interaction in CeES, since similar effects would seem likely to occur for other rare-earth ions in isomorphoric crystals. Finkelstein and Mencher[4] were the first to explore the possibility that the phenomenon in question is the result of an electric quadrupole-quadrupole interaction of the $4f$ electrons of the cerium ions. We should like to reconsider this problem and compare theoretical calculations with paramagnetic line moment measurements performed under conditions of appreciable spin alignment by the Zeeman interaction, i.e., $h\nu > kT$. With a high degree of spin alignment a nearly uniform internal field exists in a sample having a regular shape, and it is thus possible to observe narrow line spectra in concentrated paramagnetic salts.[5] In addition, the observation of resolved structure in the absorption may permit direct measurement of the interaction between specific pairs of neighboring ions.

II. CRYSTAL STRUCTURE

The isomorphic rare-earth ethyl sulfates, (RE) $(C_2H_5SO_4)_3\cdot 9H_2O$, have a hexagonal crystal structure. The rhombohedral unit cell illustrated in Fig. 1 has dimensions of approximately $a_0 = 14.0$ Å and $c_0 = 7.1$ Å, differing but very slightly with the rare-earth ion. The unit cell contains two equivalent rare-earth sites at positions $(\frac{1}{3},\frac{2}{3},\frac{1}{4})$ and $(\frac{2}{3},\frac{1}{3},\frac{3}{4})$. Thus, each rare-earth ion has two nearest rare-earth neighbors 7.1 Å distant along the hexagonal axis and six next-nearest neighbors 8.8 Å distant, of which the other ion within the same cell is one. All further neighbors are at least 13 Å away.

In the crystal field of C_{3h} symmetry of the rare-earth site the ${}^2F_{5/2}$ state of the free Ce^{3+} ion is split into three Kramers doublets. The spacing of the doublets has been investigated by Cooke, Whitley, and Wolf,[2] and by Meyer and Smith.[6] In addition, Bogle, Cooke, and Whitley[7] have studied the paramagnetic resonance spectra of Ce^{3+} above 1°K. In the dilute paramagnetic salt of lanthanum ethyl sulfate (LaES) containing a small concentration of cerium, they found that the ground doublet could be approximately characterized by $|\pm\frac{1}{2}\rangle$, while the first excited state could be approxi-

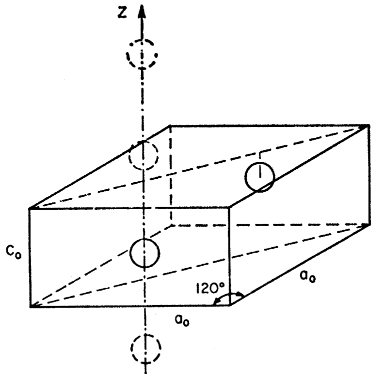

FIG. 1. Unit cell of $RE(C_2H_5SO_4)_3\cdot 9H_2O$ showing position of rare-earth ions and string of nearest neighbors along hexagonal axis.

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† Present address: Magnetism Branch, Naval Research Laboratory, Washington, D.C.

[1] W. J. de Haas and E. C. Wiersma, Physica 2, 335 (1935).

[2] A. H. Cooke, S. Whitley, and W. P. Wolf, Proc. Phys. Soc. (London) **B68**, 415 (1955).

[3] C. E. Johnson and H. Meyer, Proc. Roy. Soc. (London) **A253**, 199 (1959).

[4] R. Finkelstein and A. Mencher, J. Chem. Phys. **21**, 472 (1953).

[5] I. Svare and G. Seidel, Phys. Rev. **134**, A172 (1964).

[6] H. Meyer and P. L. Smith, J. Chem. Phys. Solids **9**, 285 (1959).

[7] A. Bogle, A. H. Cooke, and S. Whitley, Proc. Phys. Soc. (London) **A64**, 932 (1951).

mately characterized by $|\pm\frac{5}{2}\rangle$. In concentrated CeES the positions of the two lowest levels were found to be reversed, the ground state being approximately characterized by $|\pm\frac{5}{2}\rangle$. Elliott and Stevens[8] were able to account for the splittings on the basis of crystal-field theory, and also obtained excellent agreement with the g values observed in the dilute salt. They found that a small admixture of states were required to fit the resonance data.

Since the g values in concentrated CeES are not known as accurately, the calculation by Elliott and Stevens of the amount of admixing of the states is not as precise as for the dilute salt. The energy spacings and states of the three doublets in CeES are given as

$$\begin{aligned}
&\cos\alpha|\pm\tfrac{5}{2}\rangle\mp\sin\alpha|\mp\tfrac{1}{2}\rangle &&\text{at}\quad 0\ \text{cm}^{-1}\\
&\cos\alpha|\pm\tfrac{1}{2}\rangle\mp\sin\alpha|\mp\tfrac{5}{2}\rangle &&\text{at}\quad \delta_1=4.6\ \text{cm}^{-1}\\
&|\pm\tfrac{3}{2}\rangle &&\text{at}\quad \delta_2\approx 130\ \text{cm}^{-1},
\end{aligned}$$

with $\sin^2\alpha=0.024$ giving the best fit to the data.

III. QUADRUPOLE-QUADRUPOLE INTERACTION

Any interaction capable of accounting for the anomalous antiferromagnetic behavior of CeES at low temperatures must give rise to a coupling between the magnetic electrons of the cerium ions that lifts the Kramers degeneracy of the levels. This requires a process in which two electrons make simultaneous transitions, i.e., it must produce matrix elements off-diagonal in both electrons. The electric quadrupole-quadrupole coupling, resulting from the quadrupole moment of the charge distribution of the $4f$ electron of one ion being in the electric field gradient due to the quadrupole moment of the other ion, does not lift the Kramer's degeneracy in first-order perturbation theory but shifts the doublets with respect to one another. In second order the degeneracy is removed, and it is this splitting that Finkelstein and Mencher[4] calculated.

The expression for the Hamiltonian describing the quadrupole-quadrupole interaction can be obtained by performing a multipole expansion of the charge distribution of the $4f$ electron of each of the two interacting ions. The quadrupole-quadrupole term of the Coulomb interaction is proportional to R^{-5} where R is the internuclear distance of the two ions.

To obtain matrix elements of the qq interaction, it is convenient to cast the Hamiltonian into operator-equivalent form. To do this, the Hamiltonian is first expressed in terms of spherical harmonics Y_l^m.

$$\mathcal{H}_{ij}=a\sum_{-2}^{+2} C_m Y_2^{m}(\theta_i,\varphi_i)Y_2^{-m}(\theta_j,\varphi_j)\,, \tag{1}$$

where $c_m=c_{-m}$, $c_0=6$, $c_1=4$, $c_2=1$, and

$$a=4\pi e^2\langle r_i^2\rangle\langle r_j^2\rangle/5\epsilon R^5.$$

$\langle r_i^2\rangle$ and $\langle r_j^2\rangle$ are the mean-square radii of the $4f$ electrons of the ith and jth ions, respectively, and ϵ is an effective dielectric constant introduced to allow for screening of the electric fields by intervening molecules and by the outer electrons of the cerium ions.

Bleaney[9] has given the Hamiltonian in operator-equivalent form for the case where the internuclear line is parallel to the axis of spin quantization, the situation for the nearest-neighbor interaction in the ethyl sulfate lattice. (His result contains a minor numerical error.) When the internuclear line does not coincide with the axis of spin quantization, as is the case for next-nearest neighbors, the Hamiltonian becomes considerably more complicated. In general

$$\begin{aligned}
H_{ij}/\mathcal{A}={}&P_4^0(\cos\beta)[4O_{i2}^0O_{j2}^0-16(O_{i2}^{+1}O_{j2}^{-1}+O_{i2}^{-1}O_{j2}^{+1})+O_{i2}^{+2}O_{j2}^{-2}+O_{i2}^{-2}O_{j2}^{2}]\\
&+(P_4^4/24)(\cos\beta)[O_{i2}^{+2}O_{j2}^{+2}+O_{i2}^{-2}O_{j2}^{-2}]+\tfrac{4}{3}P_4^2(\cos\beta)[O_{i2}^{+1}O_{j2}^{+1}+O_{i2}^{-1}O_{j2}^{-1}]\\
&-(P_4^3/6)(\cos\beta)[O_{ij}^{+2}O_{j2}^{+1}+O_{ij}^{+1}O_{j2}^{+2}+O_{i2}^{-2}O_{j2}^{-1}+O_{i2}^{-1}O_{j2}^{-2}]\\
&+P_4^1(\cos\beta)[O_{i2}^{+2}O_{j2}^{-1}+O_{i2}^{-1}O^1{}_{j2}^{+2}+O_{i2}^{-2}O_{j2}^{+1}+O_{i2}^{+1}O_{j2}^{-2}]\\
&+(P_4^2/6)(\cos\beta)[O_{i2}^{+2}O_{j2}^{0}+O_{i2}^{0}O_{j2}^{+2}+O_{i2}^{-2}O_{j2}^{0}+O_{i2}^{0}O_{j2}^{-2}]\\
&-2P_4^1(\cos\beta)[O_{i2}^{+1}O_{j2}^{0}+O_{i2}^{0}O_{j2}^{+1}+O_{i2}^{-1}O_{j2}^{0}+O_{i2}^{0}O_{j2}^{-1}]\,,
\end{aligned} \tag{2}$$

where the 0_n^m are spin operators defined as

$$0_2^0=3J_z^2-J(J+1)\,,\quad 0_2^{\pm1}=\tfrac{1}{2}(J_zJ_\pm+J_\pm J_z)\,,\quad 0_2^{\pm2}=J_\pm^2. \tag{3}$$

The $P_n^m(\cos\beta)$ of Eq. (2) are associated Legendre functions, and β is the angle between the symmetry axis of the crystal field and the internuclear line connecting the two ions. The coefficient $\mathcal{A}$ is given by

$$\mathcal{A}=(3e^2\langle r_i^2\rangle\langle r_j^2\rangle\langle J_i\|\alpha\|J_i\rangle\langle J_j\|\alpha\|J_j\rangle)/8\epsilon R^5hc, \tag{4}$$

where $\langle J\|\alpha\|J\rangle$ is the reduced matrix element, having the value $-2/35$ for Ce^{3+}. For the interaction between two cerium ions the constant is then given by

$$\mathcal{A}=[3e^2\langle r^2\rangle^2/2450\epsilon R^5hc]\quad(\text{cm}^{-1})\,. \tag{5}$$

The influence of the qq interaction on the ground states of a pair of interacting spins is most easily treated using the representation $|++\rangle$, $|--\rangle$,

$$(1/\sqrt{2})(|+-\rangle+|-+\rangle)\,,$$

and

$$(1/\sqrt{2})(|+-\rangle-|-+\rangle)$$

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[8] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A215**, 437 (1952).

[9] B. Bleaney, Proc. Phys. Soc. (London) **77**, 113 (1961).

to characterize the states of a pair of coupled spins each in its ground doublet. The interaction in second order admixes the single-ion excited states at δ_1 and δ_2 into the ground state and produces a splitting of the energy states of the coupled system. Since the coupling does not remove the degeneracy between the $|++\rangle$ and $|--\rangle$ states, the perturbation of the four levels can be expressed in terms of three parameters, one of which describes the shift of the center of gravity of the levels and is of no interest. The two remaining parameters describe the spacings among the energy levels of the pair of coupled spins. It is therefore possible and convenient to express the splitting of the ground manifold by the qq interaction in terms of a two-parameter spin Hamiltonian, linear in the spin of each ion,

$$\bar{\mathcal{H}}_{ij}=A_{ij}S_zS_{+j}+\tfrac{1}{2}B_{ij}(S_{+i}S_{-j}+S_{-i}S_{+j})\,. \qquad (6)$$

The coefficients A_{ij} and B_{ij} are calculated by considering the perturbation of $\bar{\mathcal{H}}_{ij}$ on the states of the ions in the crystalline field. Since the angle β in Eq. (2) is zero for nearest-neighbor pairs and $P_4^m(1)=0$ unless $m=0$, only the first three terms of Eq. (2) contribute to the interaction between nearest-neighbor cerium ions, and the spin Hamiltonian parameters are found to be

$$\begin{aligned}A_{ij}'&=1600\mathcal{A}'^2/\delta_1+1024(\cos^4\alpha)\mathcal{A}'^2/\delta_2\,,\\ B_{ij}'&=103600(\sin^2\alpha)\mathcal{A}'^2/\delta_1\,.\end{aligned} \qquad (7)$$

The interaction of a cerium ion with one of its next-nearest neighbors is more complicated since $\beta=66.3°$ and all terms in Eq. (2) must be considered. Then

$$\begin{aligned}A_{ij}''&=-15\,000\mathcal{A}''^2/\delta_1-(65\,100)\mathcal{A}''^2/(\delta_1+\delta_2)\,, \qquad (8)\\ B_{ij}''&\approx 0\,.\end{aligned}$$

In A_{ij}'' and B_{ij}'' small terms have been dropped.

The coefficient $\mathcal{A}$ for nearest neighbors is not the same as for next-nearest neighbors because of the dependence upon internuclear spacing. In the above expressions we shall make use of

$$\mathcal{A}''^2=(R'/R'')^{10}\mathcal{A}'^2=(7.11/8.85)^{10}\mathcal{A}'^2=0.111\mathcal{A}'^2\,. \qquad (9)$$

Farther-neighbor qq interactions are not considered because of the very rapid decrease with distance, proportional to R^{-10}, and the fact that all farther neighbors are at least 13 Å distant.

In resonance measurements at low temperature under conditions of appreciable spin alignment the shift in the resonance absorption, i.e., contribution to the first moment, due to the qq interaction is given by

$$h\langle\Delta v\rangle=-(2N)^{-1}\tanh(g\beta H/hT)\sum_{\substack{i,j\\ i>j}}(A_{ij}-B_{ij})\,. \qquad (10)$$

Summing over the two nearest neighbors and six next-nearest neighbors only, the first moment for $\tanh(g\beta H/hT)=1$ is calculated to be

$$\begin{aligned}h\langle\Delta v\rangle&=-\mathcal{A}'^2\left(\frac{1600}{\delta_1}+\frac{102\,400\cos^4\alpha}{\delta_2}-\frac{103\,600\sin^2\alpha}{\delta_1}\right)+\mathcal{A}'^2\left(\frac{5030}{\delta_1}+\frac{21\,700}{\delta_1+\delta_2}\right)\\ &=+\mathcal{A}'^2(-350-750+540)+\mathcal{A}'^2(1095+160)\\ &=-\mathcal{A}'^2(560)+\mathcal{A}'^2(1255)\\ &=+765\mathcal{A}'^2(\mathrm{cm}^{-1})\,.\end{aligned} \qquad (11)$$

Here $\sin^2\alpha=0.024$, $\delta_1=4.6$ cm^{-1}, and $\delta_2\approx130$ cm^{-1} have been used. The contributions of nearest-neighbor (nn) and next-nearest-neighbor (nnn) interactions are shown separately for purposes of later discussion.

The positive sign in (11) implies that the over-all effect of the qq interaction is expected to be *ferromagnetic.* The nearest-neighbor contribution of $-560\ \mathcal{A}'^2$, which alone would predict antiferromagnetic coupling, is seen to be dominated by the larger next-nearest-neighbor contribution of opposite sign.

It is interesting to compare these results with the original calculation of Finkelstein and Mencher (FM). In their calculation the crystal-field levels were assumed to be pure $|\pm\frac{5}{2}\rangle$, $|\pm\frac{1}{2}\rangle$, and $|\pm\frac{3}{2}\rangle$ states. Our calculation employs an admixture of states to give better agreement with the g tensor. Although the term that depends on the admixture ($+540\mathcal{A}'^2$) is not unusually large, its importance is enhanced because the larger terms nearly cancel. Another difference between the two calculations lies in the choice of $\delta_2=100$°K by FM, instead of the more probable value $\delta_2\approx130$ cm^{-1} $=185$°K, which we have used. Insertion of the value $\delta_2=185$°K in the results of FM reverses the sign of their results, giving a total ferromagnetic interaction of the same order of magnitude as the antiferromagnetic interaction they reported.

If the term due to the admixture of states is dropped from our calculation, the first moment is reduced from $+765\mathcal{A}'^2$ to $+220\mathcal{A}'^2$. Use of the value $\delta_2=100$°K in addition, results in the value $-380\mathcal{A}'^2$.

Freeman and Watson[10] have performed a Hartree-Fock calculation for the mean-square radius of the orbit of the Ce^{3+} $4f$ electron, and have obtained the value $\langle r^2\rangle=1.20$ Å^2. Using this value in Eq. (5), together with the values $R=7.11$ Å and $\epsilon=1$, the value $\mathcal{A}'=1.02\times10^{-2}$ cm^{-1} is obtained. From Eq. (11) the

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[10] A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

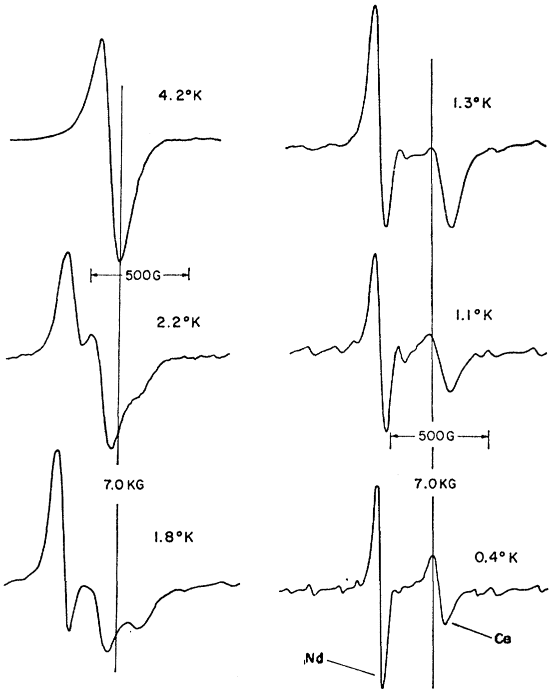

FIG. 2. Resonance spectra of Nd^{3+} and Ce^{3+} in cerium ethyl sulfate at 35 kMc/sec at several different temperatures. The magnetic field is parallel to the hexagonal axis.

first moment is then found to be $h\langle\Delta\nu\rangle=+0.078$ cm^{-1}, which is the correct order of magnitude but opposite in sign to the experimental result.

IV. RESONANCE MEASUREMENTS ON CERIUM ETHYL SULFATE

Paramagnetic resonance of Ce^{3+} in CeES is only observable below 2°K. The spectra of both Ce^{3+} and Nd^{3+} present as an impurity (approximately 0.05% concentration) in a spherical sample of concentrated CeES are shown in Fig. 2 at several different temperatures with the applied field parallel to the hexagonal axis. The data was taken using a 35-kMc/sec spectrometer in conjunction with a He^3 cryostat. Several features of the data are worthy of note.

(1) The absorption due to the Ce^{3+} is less than that of the Nd^{3+} although the latter is present only in small concentration. The assignment of the various parts of the spectra to the different ions is facilitated by a study of the angular variation. Since $g_\perp \approx 2$ for Nd it is concluded that $g_\perp < 0.1$ for Ce.

(2) The Nd resonance is less broad at 4°K than at 2.2°K and shows structure at the lower temperature. There is an observable shift of the absorption to lower fields and a decrease in linewidth below 1.8°K. Hyperfine structure is evident at 0.4°K.

(3) The Ce resonance is only observable below 2°K and consists of a single broad slightly asymmetric, absorption line having a width of approximately 85 G at 0.4°K.

Because of the uncertainty in $g_{\parallel}$ for Ce and the overlap of the Ce resonance with that of Nd above 1°K, it was not possible to determine experimentally the temperature dependence of the first moment of the Ce resonance and extract information relevant to the nature of the nondipolar interaction. However, by performing measurements at two different frequencies, 34.30 and 68.60 kMc/sec, at low temperatures such that the cerium ions are almost completely aligned, both the g value and the internal field can be uniquely determined. Such data is illustrated in Fig. 3 where it can be seen that while at the lower frequency the Ce resonance occurs 300 G higher in field than the Nd resonance, at 68 kMc/sec the Ce occurs at a lower field than the Nd resonance. As before, the assignment is clear from the angular dependence since $g_\perp \approx 2$ for Nd and $g_\perp \approx 0$ for Ce.

Using the relation

$$h\nu = g_{\parallel}\beta(H_0+H_i) \tag{12}$$

at two different measuring frequencies and applied fields H_0, the parameters $g_{\parallel}$ and H_i are calculated.

The internal field H_i is the first moment contribution, expressed in terms of a magnetic field, to the absorption spectrum resulting from spin-spin interactions. That part which is the result of dipolar coupling is strictly calculable and for a spherical sample is 120 G at the rare-earth site in the CeES lattice. (The demagnetizing field for a thin flat plate used to obtain the data illustrated in Fig. 3 is also calculable.) Dipolar spin-flip terms such as $S_{+i}S_{-j}$ are negligible since $g_\perp \approx 0$ for Ce. The g values and net internal field resulting from nondipolar interactions are then for Ce:

$$g_{\parallel} = 3.760 \pm 0.005,$$

$$\underset{\text{nondipolar}}{H_i} = (-650 \pm 15)\ \text{G} \quad \text{or} \quad (0.113 \pm 0.003)\ \text{cm}^{-1},$$

and for Nd:

$$g_{\parallel} = 3.595 \pm 0.005,$$

$$\underset{\text{nondipolar}}{H_i} = (-70 \pm 10)\ \text{G} \quad \text{or} \quad (1.2 \pm 0.2) \times 10^{-2}\ \text{cm}^{-1}.$$

Before discussing the significance of these results it is useful to recall the nature of the resonance of Nd^{3+} in neodymium ethyl sulfate (NdES) for comparison. In that salt the spin-spin interactions are predominantly dipolar, the nearest-neighbor coupling being sufficiently larger than those with farther neighbors that the resonance absorption is split into a triplet.[11,4] This structure results from the different local fields produced at a rare-earth site by the two nearest-neighbor ions. The value of the local field depends upon the orientation of the magnetic moments of the two neighbors: both can be parallel, antiparallel,

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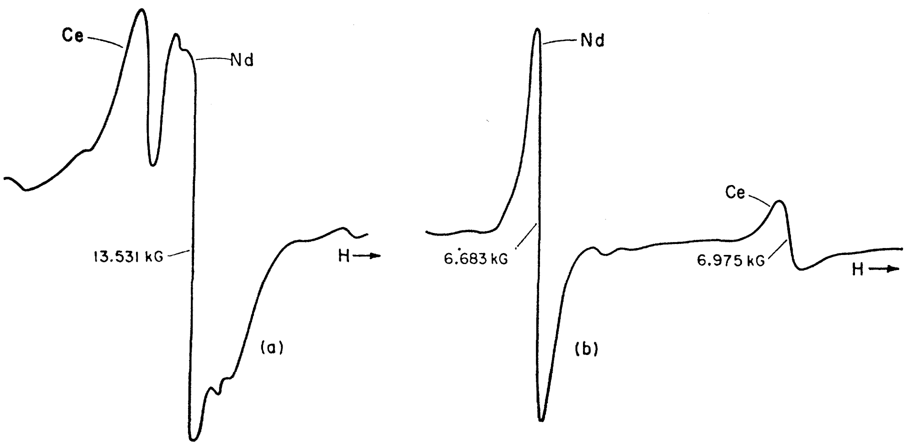
[11] B. Bleaney, R. J. Elliott, and H. E. D. Scovil, Proc. Phys. Soc. (London) A64, 933 (1951).

FIG. 3. Resonance spectra of Nd^{3+} and Ce^{3+} in cerium ethyl sulfate at $T=0.4°K$ at two different frequencies. (a) $\nu=68.60$ kMc/sec. (b) $\nu=34.30$ kMc/sec. The magnetic field is parallel to the hexagonal axis.



or one parallel and the other antiparallel to the external field. It is then possible to measure the nearest-neighbor interaction directly; in the case of Nd in NdES the splitting was found to be 20 G less than predicted from dipolar interactions only, and hence an antiferromagnetic interaction of that magnitude was determined to exist between nearest-neighbor Nd ions.

In contrast to the measurements of Baker[12] on CeES no structure was observed in the Ce resonance at either 68, 34, or 9 kMc/sec. The lack of structure can be understood as being a result of the large nondipolar interaction and will be so explained in the following section.

The observation of structure in the Nd resonance indicates that no such large interactions exist between Nd-Ce pairs. The measured splitting of (120±10) G is, however, considerably different than the calculated dipolar splitting of (195±4) G and indicates an antiferromagnetic nearest-neighbor Ce-Nd interaction of (75±10) G or $(1.26\pm0.16)\times10^{-2}$ cm^{-1}. Since the total nondipolar Ce-Nd interaction is antiferromagnetic and has as the magnitude (70±10) G, the nondipolar interaction of a Nd ion with all further neighbors is zero within experimental error.

In addition to the Nd and Ce resonances the EPR spectra of Gd^{3+} and Pr^{3+} present as impurities in CeES were also observed. In Fig. 4 the Gd resonance arising from the $-\frac{7}{2}\leftrightarrow-\frac{5}{2}$ and $-\frac{5}{2}\leftrightarrow-\frac{3}{2}$ transitions is shown. The main absorption lines result from Gd ions with the magnetic moment of nearest-neighbor Ce ions parallel to the applied field and the weaker lines from Gd ions with one Ce ion antiparallel to the field. The measured splitting of (198±2)G agrees very well with the calculated dipole field. Also, the total internal field from all neighbors as measured by the shift of the $-\frac{1}{2}\leftrightarrow+\frac{1}{2}$ transition (taking $g=1.991$ for Gd as measured in diamagnetic LaES) is in excellent agreement with a calculation of the dipole sum including demagnetizing fields resulting from sample geometry.

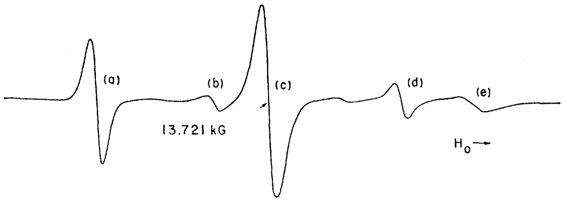


FIG. 4. Resonance spectra of Gd^{3+} and Pr^{3+} in cerium ethyl sulfate at $T=1.2°K$ and $\nu=35.56$ kMc/sec. The magnetic field is parallel to the hexagonal axis. (a) and (b): $-\frac{5}{2}\leftrightarrow-\frac{3}{2}$ transition of Gd with both nearest-neighbor Ce ions parallel to field and with one nearest neighbor antiparallel to field, respectively. (c) and (d): $-\frac{7}{2}\leftrightarrow-\frac{5}{2}$ transition of Gd with both nearest-neighbor Ce ions parallel to the field and with one nearest-neighbor antiparallel to the field, respectively. (e) One of the hyperfine components of Pr with both Ce nearest neighbors parallel to the field. Not shown in the figure is the same Pr resonance with a nearest-neighbor Ce ion antiparallel to the field. The field sweep is nonlinear because of magnet saturation.

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[12] J. M. Baker, Phys. Rev. **136**, A1633 (1964). Baker reported the observation of a triplet structure in the Ce resonance of CeES due to nearest-neighbor interactions. His measurements were performed at 9 kMc/sec and 1.5°K. He also states that measurements at 35 kMc/sec gave similar results.

In the spectra obtained by Baker at 1.5°K, the ratios of the intensities of the three components do not correspond to those calculated using the appropriate Boltzmann factors to compute the population of the spin levels. The energy of interaction between spins is an appreciable fraction of the Zeeman energy at 9 kMc/sec and must be included in the computation. The triplet structure of the absorption of the impurity erbium, which Baker also observed in his sample, does have an intensity distribution close to that calculated in the same manner.

Baker found that the width of the absorption Δ, expressed in frequency units, changed little with the angle θ between the magnetic field and the *c* axis. He suggested that the interacting ions must therefore be regarded as dissimilar, so that Δ is due solely to the component of the interaction tensor in the direction of the magnetic field. With a nearest-neighbor interaction Hamiltonian of the form $H_{ij}=a_{ij}S_{zi}S_{zj}+\frac{1}{2}b_{ij}(S_{+i}S_{-j}+S_{-i}S_{+j})$, and where a_{ij} and b_{ij} contain both dipolar and nondipolar contributions, the width of the absorption was then expressed as $\Delta=2(a_{ij}\cos^2\theta+b_{ij}\sin^2\theta)$. Since Δ varied little with θ he obtained $a_{ij}\approx b_{ij}$.

The constancy of the width of the absorption, however, is due to the fact that $g_\perp\approx0$ for the Ce^{3+} ions. In this case, the spins remain aligned parallel to the *c* axis as the direction of the magnetic field is varied, and the energy of interaction between spins is not altered. There is no justification for assuming that the ions are dissimilar. For similar ions the splitting is given by $(a_{ij}-b_{ij})\times(1-3\cos^2\psi)$, where ψ is the angle between the direction of spin quantization and the *c* axis. When the *g* tensor is isotropic, $\psi=\theta$; but for an axial *g* tensor, $\tan\psi=(g_\perp/g_{\parallel})\tan\theta$. If $g_\perp\approx0$, then $\cos\psi\approx1$, independent of θ. No angular variation of the width of the absorption is then expected, as observed by Baker.

The only interaction between Gd-Ce pairs in the ethyl sulfates is therefore dipolar.

The Pr^{3+} resonance exhibited in Fig. 4 is one of the six hyperfine lines of this non-Kramers ion. Not shown in the figure are the additional spectra resulting from the different orientations of the magnetic moments of the Ce nearest neighbors. The structure splitting was measured to be (150 ± 5) G showing the existence of an antiferromagnetic nearest-neighbor Ce-Pr interaction of (-45 ± 9) G, or $(0.32\pm0.06)\times10^{-2}$ cm^{-1}.

V. DISCUSSION

While the order of magnitude of the calculated quadrupole-quadrupole interaction agrees with the accurately measured nondipolar spin-spin coupling in CeES, the sign of the interaction does not. The total nondipolar interaction of a Ce ion with its neighbors of (0.113 ± 0.003) cm^{-1}, as measured from the first moment of the resonance absorption is in agreement with the less precise determinations by suceptibility and heat capacity.

The source of the error in the calculations is not understood. It may originate from one or several of the following considerations.

(1) The calculation is very sensitive to the amount of admixture to the $|\pm\frac{1}{2}\rangle$ states into the predominately $|\pm\frac{5}{2}\rangle$ ground state by the crystalline field. The value used of $\sin^2\alpha=0.024$, was taken from the work of Elliott and Stevens who fit the resonance data then available. This value of $\sin^2\alpha$ yields $g_{\parallel}=3.80$ and $g_{\perp}=0.26$ for Ce whereas these measurements determined $g_{\parallel}=3.760$ and $g_{\perp}<0.1$. It is of interest to note that the assignment of states as given above cannot yield precisely these g values of the ground state for any value of α. Some admixture of the $|\pm\frac{3}{2}\rangle$ into the $|\pm\frac{5}{2}\rangle$ state would be required, an impossibility for the crystal field of C_{3h} symmetry. It may be that either the perturbation of the $J=\frac{7}{2}$ state must be considered, or the spin-spin coupling is itself modifying the measured g values.

(2) Because of the near cancellation of terms the magnitude and sign of the calculated qq interaction are significantly dependent upon the crystal-field splitting of the $|\pm\frac{3}{2}\rangle$ level, δ_2. The value of $\delta_2\approx130$ cm^{-1} in the calculations was taken from Elliott and Stevens and is possibly in error.

(3) It may be that the dielectric constant ϵ introduced to allow for screening of the interaction should be considered a function of which pair of ions are being treated since the value of ϵ is dependent on the distribution of the intervening water molecules and ethyl sulfate radicals. Although unlikely, a value of ϵ for next-nearest-neighbor interactions a factor of 2 greater than that for nearest neighbors changes the sign of the total interaction. (The use of different dielectric constants for terms in the Hamiltonian giving rise to interactions at different frequencies does not help.)

(4) Bleaney[9] has pointed out that the first-order quadrupole-quadrupole interaction, while not splitting the Kramers doublets, results in energy shifts comparable in magnitude to crystal-field effects, namely several cm^{-1}. Thus a more careful treatment of the full Hamiltonian including both the crystal field and the qq interaction may be required to give meaningful calculations.

In spite of the lack of agreement between theory and experiment several observations suggest that the qq interaction is responsible for the antiferromagnetic coupling.

(a) The fact that the cerium resonance is not observable above 2°K in CeES, whereas its spin lattice relaxation time as measured in LaES is sufficiently long, is explainable as the result of first-order qq interaction between ions in the ground state and those in the first excited state at $\delta_1=4.6$ cm^{-1}. This interaction is expected to severely broaden the ground-state Ce resonance line at all temperatures where the excited state is appreciably populated.

A large first-order interaction would also explain the absence of the resonance from ions in the first excited state having $g_{\parallel}=1.0$ and $g_{\perp}=2.2$, which was looked for but not observed. Ions in the excited state will have near neighbors in the ground state at all temperatures.

(b) From the lack of observation of structure in the Ce resonance it can be concluded that a large interaction must exist of the form $b_{ij}(S_{+1}S_{+j}+S_{-i}S_{+j})$ presumably between nearest neighbors. If the nondipolar interaction were mainly static, $a_{ij}S_zS_{zj}$, then structure would be expected to occur in the Ce resonance, albeit of a different nature than in other rare-earth salts. Because of the crystal structure the nondipolar spin-spin interactions must almost certainly be limited to the two nearest-neighbor ions and six next-nearest-neighbor ions. If the measured nondipolar field of -650 G on complete spin alignment resulted from a static interaction with only eight neighbors the reversal of any one spin would change the internal field sufficiently to produce observable structure. On the other hand, an interaction of the form $b_{ij}(S_{+i}S_{-j}+S_{-i}S_{+j})$ if sufficiently large would wash out the structure otherwise expected. When the exchange frequency b_{ij}/h becomes large, the excitations can no longer be localized and ascribed to the reorientation of a particular spin; and, consequently, the discussion used to explain the structure in the resonance of NdES is no longer applicable.

Roughly speaking the disappearance of resolvable structure should occur when the exchange energy becomes larger than the energy of separation of the resolved lines in the absence of exchange, a condition that appears likely to exist in CeES. In this case perhaps a spin-wave description of the system may be more appropriate.

The presence of structure in the resonance of the impurities Gd, Nd, and Pr can be understood in spite of the fact that one might at first think a large spin-flip interaction between Ce ions would exchange narrow the impurity absorption. A Ce ion that has a Gd, Nd, or Pr nearest neighbor is not identical to a Ce ion that has two Ce nearest neighbors since the Ce-Gd, Ce-Nd, and Ce-Pr interactions differ significantly from the Ce-Ce interaction. Since interchange of spin states between nonidentical Ce ions does not conserve energy, it is not a rapid process. Thus, a Gd, Nd, or Pr ion has nearest-neighbor Ce ions whose properties are describable in terms of localized spin states, in agreement with the experimental observation of structure in the spectra of these three impurity ions in CeES.

Because of the lack of agreement between the calculated *qq* interaction and the measured nondipolar spin-spin coupling for Ce-Ce pairs, no attempt was made to explain the origin of the nondipolar interaction between Ce-Nd and Ce-Pr pairs by a similar calculation. The one comment that can be made is that no *qq* interaction is expected between a Gd ion and any neighbor in accord with experiment. The almost spherically symmetric charge distribution of the $4f^7$ electronic configuration will certainly not possess a significant quadrupole moment.

As mentioned above, the effects of superexchange are thought to be small because of the small size of the $4f$ orbitals, their inclusion within the $5s$ and $5p$ shells, and the large interionic distances in the ethyl sulfate lattice. In addition, an isotropic exchange between real spins transforms to a spin Hamiltonian, Eq. (6), such that $A_{ij}/B_{ij} \approx (g_{\parallel}/g_{\perp})^2$. Unless the exchange between real spins is highly anisotropic in a particular way, the large spin-flip term considered necessary to explain the observed resonance cannot be obtained. On the other hand, the calculation of the second-order *qq* interaction does yield a sizeable B_{ij} for nearest-neighbor pairs.

The possibility of spin coupling through virtual-phonon exchange[13–15] has also been considered. This interaction is magnetic-field-dependent in a Kramers salt as an external field is necessary to lift the Kramers degeneracy. Analysis of the resonance measurements of CeES in terms of such an interaction, predicted to be proportional to H_0^2, leads to a relatively small $g_{\parallel}$ and a ferromagnetic total interaction whereas coupling via the phonon field is antiferromagnetic.

In conclusion, several unusual qualitative features of the resonance spectra of Ce^{3+} in CeES, such as the absence of resolved structure due to the interaction with neighboring ions, the fact that the resonance is only seen below 2°K and that no resonance from ions in the excited state is observed at temperatures where this state is appreciably populated, may be accounted for by a *qq* coupling between cerium ions. These features of the resonance spectra do not appear easily explainable in terms of superexchange. It is possible that the observed interaction is only partly *qq*, and that some other coupling mechanism is also operative. Our measurements have yielded an accurate value for the total interaction, but have not enabled us to determine its origin. The fact that the calculations of the second-order quadrupole-quadrupole interaction are not in agreement with the measurement is thought to be due to the sensitivity of the calculations to parameters not sufficiently well known for Ce.

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