Electric Quadrupole-Quadrupole Interaction in Cerium Ethyl Sulfate*

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Electron paramagnetic resonance (EPR) of cerium ethyl sulfate (CeES) below 2°K gives evidence of a large nondipolar interaction between nearest-neighbor cerium ions. Writing the spin Hamiltonian for the interaction of two spins S_i and S_j as

$$\mathcal{H}_{ij}=(\alpha_{ij}+A_{ij})S_{iz}S_{jz}+\tfrac{1}{2}(\beta_{ij}+B_{ij})(S_{i+}S_{j-}+S_{i-}S_{j+}),$$

where α_{ij} and β_{ij} are the known contributions from dipole-dipole interaction, the experiments suggest that $A_{ij}=0.105\pm0.003$ cm^{-1} and $B_{ij}=0.073\pm0.003$ cm^{-1}. Although there is no proof, there are four pieces of evidence which strongly support the hypothesis that the interaction is due to electric quadrupole-quadrupole (QQ) interaction. Firstly, the order of magnitude of A_{ij} and B_{ij} are reasonable. Secondly, QQ interaction affords an explanation of the differences between the temperature dependence of the EPR spectra of diluted and undiluted CeES. Thirdly, the spectra of rare-earth impurities in CeES, and fourthly, the spectra of pairs of interacting cerium ions in dilute specimens, are consistent with QQ interaction. Finally, it is shown that superexchange and exchange of virtual phonons probably contribute very little to the observed interaction.

FOR some time now there has been discussion in the literature about the cause of an anomaly in the specific heat of cerium ethyl sulfate (CeES) at very low temperatures. On the one hand, it has been attributed to electric quadrupole-quadrupole (QQ) interaction between the $4f$ electron-charge clouds of neighboring ions[1–3]; and on the other hand it has been attributed to a strong spin-phonon coupling which produces an anomaly in the density of states of the phonons[4,5] when the phonon frequency is equal to the separation[2] (4.6 cm^{-1}) of the lowest two Kramers doublets.

We report in this article some EPR measurements on CeES which show that in addition to the classical dipole-dipole interaction, there is between nearest-neighbor ions a large interaction which we believe is due to QQ interaction.

In the ethyl sulfates the two nearest-neighboring paramagnetic ions lie at a distance $R\approx7.1$ Å along the crystal hexad axis. Even in a salt which shows predominantly dipolar interaction, such as neodymium ethyl sulfate (NdES),[6,7] the nearest-neighbor interaction is sufficiently larger than the interactions with more distant neighbors that the EPR line is split into a partially resolved triplet; the outer components correspond to the magnetic moments of both neighbors being aligned parallel or antiparallel to the external field **H**, and the central component of twice the intensity corresponds to the two arrangements when neighbors are antiparallel to one another. When the temperature is lowered the relative intensities of the three lines changes because there is a higher probability for neighbors with moments parallel to **H**; the low field component becomes most intense.[7]

We shall consider only nearest-neighbor interactions, which are axially symmetric, and between two neighbors S_i and S_j have the form

$$\mathcal{H}_{ij}=a_{ij}S_{iz}S_{jz}+\tfrac{1}{2}b_{ij}(S_{i+}S_{j-}+S_{i-}S_{j+}). \quad (1)$$

We shall write $a_{ij}=\alpha_{ij}+A_{ij}$ and $b_{ij}=\beta_{ij}+B_{ij}$, where $\alpha_{ij}(=-2g_{\parallel}^2\beta^2/R^3)$ and $\beta_{ij}(=g_{\perp}^2\beta^2/R^3)$ are the dipolar contributions which can be calculated from the known g values, and A_{ij} and B_{ij} are the nondipolar parts which we wish to discuss.

At 2°K in CeES a wide EPR line is observed (Fig. 1) which shows signs of a partially resolved triplet struc-

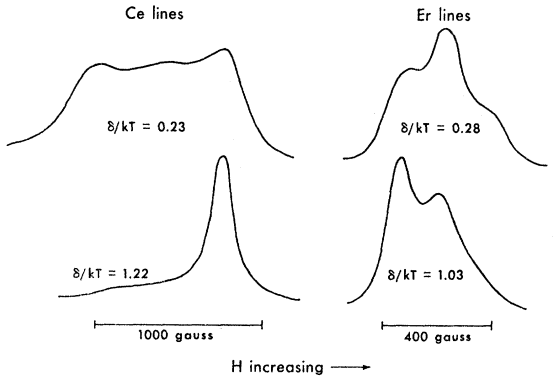

FIG. 1. Integrated derivative curves of the EPR spectra of cerium and erbium for **H** parallel to z at various values of δ/kT, where δ is the separation of the components of the ground doublet of *cerium*.

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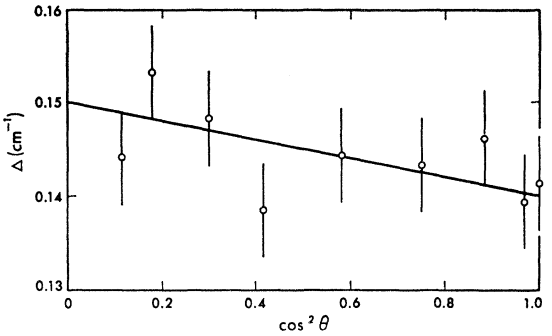

FIG. 2. Variation of the over-all triplet separation Δ for cerium EPR as a function of θ.

ture of over-all separation about 800 G (the calculated dipolar separation would be 390 G). At 0.25°K the *high* field component is most intense (Fig. 1), showing that the effective field exerted by an ion on its neighbor is oppositely directed to the dipolar field. The width of the triplet structure Δ, expressed in *frequency units*, changes little with the angle θ between **H** and the crystal axis. This suggests that the interacting ions have to be regarded as dissimilar,[8] so that Δ is due solely to the component of the interaction tensor in the direction of **H**, i.e.,

$$\Delta = 2(a_{ij}\cos^2\theta + b_{ij}\sin^2\theta).$$

Figure 2 shows the fit to our measured values of Δ of

$$a_{ij} = 0.070 \pm 0.003 \text{ cm}^{-1}$$

and

$$b_{ij} = 0.075 \pm 0.003 \text{ cm}^{-1}.$$

α_{ij} and β_{ij} are calculated to be -0.035 and $+0.002$ cm^{-1}, respectively, so that the additional nondipolar interaction is

$$A_{ij} = 0.105 \text{ cm}^{-1}$$

and

$$B_{ij} = 0.073 \text{ cm}^{-1}.$$

We have no clear proof that this large interaction is due to QQ interaction rather than due to superexchange or some other interaction, but there are several facts which make it appear likely.

First, the size of the interaction is reasonable. Bleaney[3] has written the QQ interaction

$$\mathcal{H}_{QQ} = A[4O_{i2}^0 O_{j2}^0 - 16(O_{i2}^{+1}O_{j2}^{-1} + O_{i2}^{-1}O_{j2}^{+1}) + (O_{i2}^{+2}O_{j2}^{-2} + O_{i2}^{-2}O_{j2}^{+2})], \quad (2)$$

where the O_n^m are spin operators and

$$A = 3e^2\langle r^2\rangle^2/2450\epsilon R^5 hc \text{ cm}^{-1},$$

$\langle r^2\rangle$ is the mean-square radius of the $4f$ electrons, and ϵ is a dielectric constant to allow for the screening by the intervening molecules. The states of the $J=\frac{5}{2}$ manifold of Ce^{3+} in CeES are[9]

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

Using these states and the fact that $\sin^2\alpha$ is known to be small[9] the interaction coefficients are calculated from (2) to be

$$A_{ij} = 1600A^2\delta_1^{-1} + 102\,400\cos^4\alpha A^2\delta_2^{-1},$$
$$B_{ij} = 25\,920A^2(\sin^2 2\alpha)\delta_1^{-1}.$$

The QQ interaction has no matrix elements in first order between the components of a Kramers doublet; the effect we have calculated is a second-order process. Our experimental results correspond to $A = 0.99\times10^{-2}$ cm^{-1}, or $\langle r^2\rangle^2/\epsilon = 0.78$ Å^4 which is not unreasonable; and $\sin^2\alpha = 0.036$. A value of $\sin^2\alpha = 0.039$ was used to interpret the EPR and susceptibility data.[9,10]

Second, a large QQ interaction would explain why it is necessary to go to as low as 2°K to see EPR in the ground doublet, and why one cannot see EPR in the excited doublet at all; although one can see them both at 4°K in LaES (1% Ce) where the spin-lattice relaxation time T_1 is expected to be the same as in CeES, as both are dominated by the Orbach process. Although the interaction between two ions in the ground state is a second-order process, that between one ion in the ground state and another in the excited state is first order in the QQ interaction, and the EPR of both ions is severely shifted and broadened by the interaction. Above 2°K the probability of an ion in the ground state having a nearest or next-nearest neighbor in the excited state becomes high enough to smear out the EPR; and at all temperatures ions in the excited state have ground-state neighbors, so EPR is never observed. The supposition that T_1 is still long is supported by the observation of triplet structures on the EPR of Gd and Er impurities in CeES which do not disappear until 14°K.

Third, the spectra of these impurities provides additional evidence for the QQ interaction. Pure dipolar interaction between the impurity ions and Ce neighbors would give a triplet structure to the EPR of the impurity with separation 390 G for **H** parallel to z and $\lesssim 20$ G for **H** perpendicular to z; this is observed for Gd impurity. As Gd is in an S state, δ_1 is large and one expects no QQ interaction between Gd and Ce, in agreement with the experimental results. Between Er and Ce one does expect a small QQ interaction with $B_{ij}=0$. In accord with this the triplet separation when **H** is parallel to z is observed to be somewhat less than dipolar (325 G) and of the same sign ($A_{ij} = 45\times10^{-4}$

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cm^{-1}); Fig. 1 shows the *low* field component most intense at 0.25°K. No structure is observed for **H** perpendicular to z on a line-50 G wide suggesting that $B_{ij}<0.01$ cm^{-1}. The size of the QQ interaction between Er and Ce may be extrapolated from that between Ce and Ce if one assumes that $\langle r^2\rangle_{Ce}/\langle r^2\rangle_{Er}$ is equal to $[A_2^0\langle r^2\rangle]_{Ce}/[A_2^0\langle r^2\rangle]_{Er}$, where the latter is known from the static crystal-field parameters. The extrapolated value $A_{ij}=51\times10^{-4}$ cm^{-1} is gratifyingly close to the measured value.

Fourth, evidence is provided by EPR spectra in dilute crystals, where the weak spectra of interacting pairs of nearest neighbors can be observed as resolved satellites of the main EPR line due to isolated ions. This evidence is tenuous as the comparison of interactions between Ce ions in yttrium ethyl sulfate (YES) or LaES with CeES is made uncertain by lack of knowledge of the correct wave functions and their energies. In YES (10% Ce, 0.1% Gd) pair spectra are observed at the dipolar separation for Gd-Ce pairs, but no pair spectra are observed for Ce-Ce pairs, presumably because they are too close to be resolved from the main line. For a pair of similar[8] interacting ions one expects a separation of the satellites

$$\Delta=\tfrac{1}{2}(3\cos^2\theta-1)(a_{ij}-b_{ij}),$$

so that the measurements suggest $a_{ij}\approx b_{ij}$, in agreement with the results in the undiluted salt. One does not see EPR in the excited state as it is too little populated.[11] In LaES (10% Ce, 0.1% Gd) the order of the two lowest doublets of Ce^{3+} is reversed. Again pair spectra are observed at the dipolar separation for Gd-Ce pairs, but not for Ce-Ce pairs when at least one of the ions is in the excited state (the same as the ground state in CeES and YES). If both ions are in the excited state the situation is the same as that in YES and the pair spectra are not resolved, and if only one ion is in the ground state the first-order QQ interaction removes the EPR to some distant frequency. Pair spectra are observed when both ions are in the ground state giving a measured value of

$$a_{ij}-b_{ij}=\pm0.014\ cm^{-1}.$$

To make a rough estimate of this quantity theoretically one can assume that nothing is different from the CeES problem except that one is observing ions in the other low-lying doublet state. This has different g values and $\alpha_{ij}-\beta_{ij}$ is calculated to be -0.008 cm^{-1}; also A_{ij} has a smaller value, because of a smaller contribution from the state at δ_2, leading to estimated values of

$$A_{ij}=+0.09\ cm^{-1},$$
$$B_{ij}=+0.08\ cm^{-1},$$
$$A_{ij}-B_{ij}=+0.01\ cm^{-1}.$$

This leads to a calculated value of

$$a_{ij}-b_{ij}=0.002\ cm^{-1}.$$

The disagreement with the measured value is not too disturbing as the value of $A_{ij}-B_{ij}$ is quite sensitive to differences in $\sin^2\alpha$ and δ_2, both of which are unknown. The main deduction from the experiments on dilute crystals is that the interaction is clearly not purely dipolar, or even mainly dipolar; the results are not inconsistent with the possibility of QQ interaction.

The two other nondipolar interactions which should be considered seriously as possible sources of the measured interaction are virtual phonon exchange[12] and superexchange. Virtual phonon exchange can be ruled out as it is expected to be proportional to the square of the applied magnetic field, and measurements at 35 kMc/sec give the same results as those at 9.4 kMc/sec. One would expect the major contribution to superexchange to be an isotropic interaction between *real* spins, which, when it is converted into a spin-Hamiltonian formalism in terms of a fictitious spin $S=\frac{1}{2}$ as in Eq. (1), leads to $A_{ij}/B_{ij}=g_{\parallel}^2/g_{\perp}^2=100$ for CeES. The measured ratio, 1.4, makes it clear that superexchange is not responsible for the whole interaction. Moreover, the fact that there is no observable superexchange interaction between Ce and Gd suggests that it will also be small between Ce and Ce.

In this analysis there are many comparisons which are made uncertain by incomplete knowledge of some parameters. These parameters are susceptible to measurement so that the calculation should become more reliable in the future. In the meantime it appears very probable that the observed interaction in CeES is indeed QQ interaction.

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