ELECTRIC QUADRUPOLE-QUADRUPOLE INTERACTION BETWEEN CERIUM PAIRS IN LANTHANUM CHLORIDE*

R. J. Birgeneau, M. T. Hutchings,† and R. N. Rogers‡

Hammond Laboratory, Yale University, New Haven, Connecticut

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Electric quadrupole-quadrupole interaction (EQQ) has often been suggested as an important coupling mechanism in rare-earth salts.[1] However, from measurements of the interaction coefficients alone, it is difficult to distinguish EQQ from other possible interactions.[2] In this Letter we report a direct quantitative measurement of the EQQ between pairs of Ce^{3+} ions in $LaCl_3$. Because of the simple crystal structure (see Fig. 1) and the Ising-like nature of the spins (for the ground state,[3] $g_\parallel = 4.037$, $g_\perp = 0.23$) this is an ideal system in which to investigate rare-earth interactions. We have observed the EPR spectra of 1% Ce^{3+} in $LaCl_3$ at 4.2°K and 25 Gc/sec, and have identified nearest-neighbor (n.n.) and next-nearest-neighbor (n.n.n.) pair transitions.[4] The n.n.n. spectrum shows an anomalous shift in $g_\parallel$ as a result of cross terms between the EQQ and the Zeeman interaction. This $g_\parallel$ shift is a function of the angle the magnetic field makes both with the c axis and with the bond-axis plane (the plane defined by the pair axis and the c axis). The size of this $g_\parallel$ shift and its angular variation enables one to obtain the quadrupole-quadrupole coupling coefficient for the n.n.n. pairs directly. Because of the axial symmetry of the n.n. pairs, no such $g_\parallel$ shift is allowed. However the n.n. spectrum does indicate, in addition to the ferromagnetic dipolar interaction between the nearest neighbors, a comparable antiferromagnetic interaction which is explained by second-order EQQ.

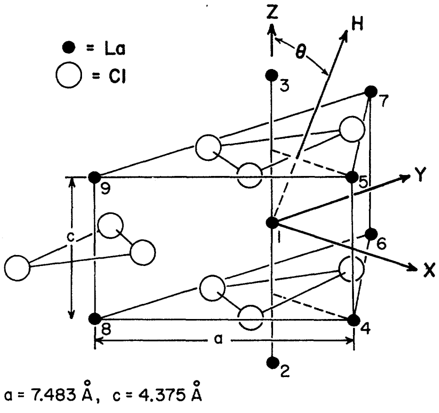

FIG. 1. Structure of $LaCl_3$. The magnetic field is in the x-z plane as defined by the next-nearest-neighbor pairs (1,4), (1,5).

The interaction spin Hamiltonian for a pair is given by

$$\mathcal{H}_{ij} = a_{ij}S_{zi}S_{zj} + \tfrac{1}{2}b_{ij}(S_{+i}S_{-j} + S_{-i}S_{+j}). \tag{1}$$

For the n.n. pairs, for example (1,2) or (1,3) in Fig. 1, this is the most general form. For the n.n.n. pairs, additional terms are allowed by symmetry in the Hamiltonian, but in first order these have the same effect as a small constant shift in $g_\parallel$. If a magnetic field H is applied at an angle θ to the c axis since $g_\parallel \gg g_\perp$, pair transitions should occur at

$$h\nu \approx g_\parallel \mu_B H \cos\theta \pm \tfrac{1}{2}(a_{ij} - b_{ij}) + \tfrac{1}{2}g_\perp^2 \mu_B^2 H^2 \sin^2\theta / h\nu. \tag{2}$$

Thus the pair lines should be symmetrically placed about the main line separated by $(a_{ij} - b_{ij})/(2g_\parallel \mu_B \cos\theta)$ from it. (See n.n. lines in Fig. 2.)

The coefficients a_{ij} and b_{ij} will include contributions from the dipolar interaction, second-order EQQ, superexchange, and possibly spin-phonon interaction.[2] The dipolar contributions are estimated to be $a_{\text{n.n.}}(d\text{-}d) = -2g_\parallel^2/r_{\text{n.n.}}^3 = -0.168\ \text{cm}^{-1}$, $b_{\text{n.n.}}(d\text{-}d) \approx 0$, $a_{\text{n.n.n.}}(d\text{-}d) = g_\parallel^2\mu_B^2(1 - 3\cos^2\theta_{\text{n.n.n.}})/r_{\text{n.n.n.}}^3 = 0.024\ \text{cm}^{-1}$, $b_{\text{n.n.n.}}(d\text{-}d) \approx 0$, where the $LaCl_3$ lattice parameters are used for the pairs.[5] The spin-phonon contribution may be estimated using expressions derived by Huber,[6] and is found to be negligible.

The EQQ spin Hamilonian within a given J manifold in the general case of a pair of spins with coordinate axes parallel, and with the x axes in the plane defined by the z axis and the bond axis, is given by[7,8]

$$\mathcal{H}_{\mathrm{QQ}ij} = A_{ij} \sum_{m_1=-2}^{2} \sum_{m_2=-2}^{2} \mathrm{Q}_{m_1 m_2} \tilde{O}_{2i}^{m_1} \tilde{O}_{2j}^{m_2}, \tag{3}$$

where

$$\tilde{O}_2^0 = \tfrac{1}{2}[3J_z^2 - J(J+1)], \quad \tilde{O}_2^{\pm 1} = \mp(6^{1/2}/4)(J_z J_\pm + J_\pm J_z), \quad \tilde{O}_2^{\pm 2} = (6^{1/2}/4) J_\pm^2,$$

$$\mathrm{Q}_{m_1 m_2} = \frac{(-)^{m_1+m_2}(4\pi)^{1/2}}{3} \left\{ \frac{(4+m_1+m_2)!\,(4-m_1-m_2)!}{(2+m_1)!\,(2-m_1)!\,(2+m_2)!\,(2-m_2)!} \right\}^{1/2} Y_4^{-(m_1+m_2)}(\theta_{ij}, 0),$$

$$A_{ij} = \frac{e^2 \langle r^2 \rangle^2 \langle J \| \alpha \| J \rangle^2}{\epsilon_{ij} R_{ij}^5 hc},$$

where $\langle r^2 \rangle$ is the mean square radius of the $4f$ electrons in Å^2, $\langle J \| \alpha \| J \rangle$ is as defined by Elliott and Stevens,[9] ϵ_{ij} is an effective dielectric constant for the pair, and R_{ij} is the pair separation.

By Kramers's theorem $\mathcal{H}_{\mathrm{QQ}}$ can make no first-order contribution to a_{ij} or b_{ij}.[1] The second-order contribution is given by $a_{\mathrm{n.n.}}(\mathrm{EQQ}) = 137 A_{\mathrm{n.n.}}^2\ \mathrm{cm}^{-1} = 7.68(\langle r^2 \rangle^2/\epsilon_{\mathrm{n.n.}})^2\ \mathrm{cm}^{-1}$, $b_{\mathrm{n.n.}}(\mathrm{EQQ}) = 0$, $a_{\mathrm{n.n.n.}}(\mathrm{EQQ}) = -134 A_{\mathrm{n.n.n.}}^2\ \mathrm{cm}^{-1} = -2.72(\langle r^2 \rangle^2/\epsilon_{\mathrm{n.n.n.}})^2\ \mathrm{cm}^{-1}$, $b_{\mathrm{n.n.n.}}(\mathrm{EQQ}) = 0$, where these are calculated using the $J = \frac{5}{2}$ energy levels at $E_{\pm 5/2} = 0\ \mathrm{cm}^{-1}$, $E_{\pm 1/2} = 38\ \mathrm{cm}^{-1}$, $E_{\pm 3/2} = 110\ \mathrm{cm}^{-1}$.[10]

A second-order effect, not previously considered, is that arising from the cross terms between $\mathcal{H}_{\mathrm{QQ}}$ and $\mathcal{H}_{\mathrm{Zeeman}}$. Because of the axial symmetry of the n.n. pairs there can be no contribution linear in the field and hence these will have no effect, to first order in the Zeeman mixing, on the n.n. angular variation. For the next-nearest-neighbor pairs where $\mathcal{H}_{\mathrm{QQ}}$ has a more general form and, in particular, includes $\tilde{O}_2^{\pm 1}\tilde{O}_2^{0}$ terms, second-order terms between real spins of the form

$$\frac{\langle \tfrac{5}{2}, \tfrac{5}{2} | \mathcal{H}_{\mathrm{Zeeman}\perp} | \tfrac{3}{2}, \tfrac{5}{2} \rangle \langle \tfrac{3}{2}, \tfrac{5}{2} | \tilde{O}_2^{-1} \tilde{O}_2^{0} | \tfrac{5}{2}, \tfrac{5}{2} \rangle}{E_{5/2} - E_{3/2}}$$

occur. The net effect of these cross terms on the pair energy levels is to give an energy shift

$$\Delta E(++) = -\Delta E(--) = (3 \times 5^{1/2}/7E_{3/2}) A_{\mathrm{n.n.n.}} \times (20 \times 30^{1/2} Q_{01}) \eta \mu_{\mathrm{B}} H \sin\theta,$$

$$\Delta E(+-) = \Delta E(-+) = 0,$$

where $Q_{01} = 1.94$ for the $\mathrm{LaCl_3}$ lattice parameters. The coefficient η is a geometrical factor depending on the angle the field makes with the bond-axis plane. For the field configuration in Fig. 1, $\eta(1,5) = 1$, $\eta(1,4) = -1$, $\eta(1,6) = \eta(1,8) = \frac{1}{2}$, $\eta(1,7) = \eta(1,9) = \frac{1}{2}$.

These cross terms act like a Zeeman term with the effective field parallel to the c axis, producing a θ-dependent shift in $g_\|$, the size and sign of the shift depending on the pair under consideration, that is, $g_\| \to g_\| + 1.85 \eta A_{\mathrm{n.n.n.}} \times \tan\theta$. For a given field angle θ, therefore, four sets of n.n.n. pair lines corresponding to the four possible values of η will be seen. These lines should all be explained by the set of parameters $g_\|$, $g_\perp$, $a_{\mathrm{n.n.n.}} - b_{\mathrm{n.n.n.}}$, $A_{\mathrm{n.n.n.}}$.

The solid n.n.n. lines in Fig. 2 are calculated from a least-squares fit to the experimental points on the basis of the above theory; the fit gives $g_\| = 4.054$, $g_\perp = 0.22$, $(a_{\mathrm{n.n.n.}} - b_{\mathrm{n.n.n.}}) = -0.004\ \mathrm{cm}^{-1}$, $A_{\mathrm{n.n.n.}} = +0.035\ \mathrm{cm}^{-1}$.[11] Assuming $\epsilon_{\mathrm{n.n.}} = \epsilon_{\mathrm{n.n.n.}} = \epsilon$, then from the definition of A_{ij} in Eq. (3), this value of $A_{\mathrm{n.n.n.}}$ gives $A_{\mathrm{n.n.}} = 0.058\ \mathrm{cm}^{-1}$, corresponding to $\langle r^2 \rangle^2/\epsilon = 0.25$ Å^4. These values may then be used to calculate the effects of EQQ. In first order $\mathcal{H}_{\mathrm{QQ}}$ acts like an O_2^0 crystal-field term. For the concentrated material $\mathrm{CeCl_3}$ at low temperatures we find that the EQQ contribution to the crystal field is $(A_2^0 \langle r^2 \rangle)_{\mathrm{EQQ}} = -19\ \mathrm{cm}^{-1}$ compared with the total $A_2^0 \langle r^2 \rangle = 65\ \mathrm{cm}^{-1}$ measured in the dilute material.[10] In the second order $\mathcal{H}_{\mathrm{QQ}}$ gives $a_{\mathrm{n.n.}}(\mathrm{EQQ}) = 0.457\ \mathrm{cm}^{-1}$, $a_{\mathrm{n.n.n.}}(\mathrm{EQQ}) = -0.162\ \mathrm{cm}^{-1}$. The interaction constants are summarized in Table I.

Hence the electric quadrupole-quadrupole

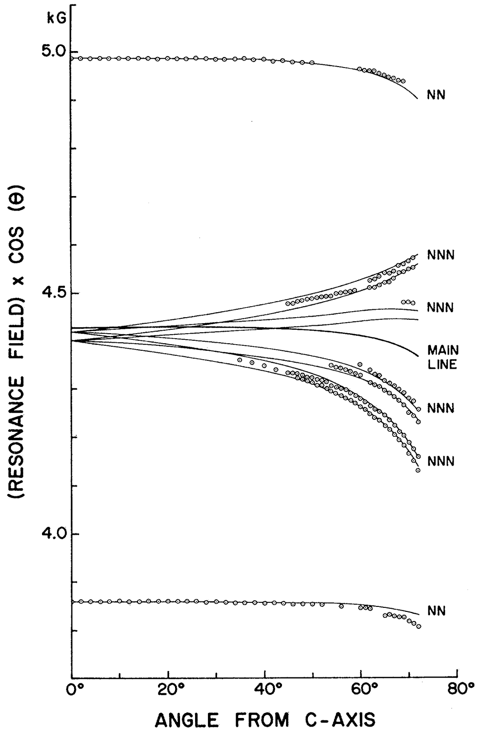

FIG. 2. Angular variation of pair spectra of Ce^{3+} in LaCl$_3$. The solid lines were calculated using (a) for the main line, $g_\parallel = 4.037$, $g_\perp = 0.23$, (b) for the n.n., $g_\parallel = 4.041$, $g_\perp = 0.21$, $a_{\text{n.n.}} - b_{\text{n.n.}} = +0.213$ cm^{-1}, (c) for the n.n.n., $g_\parallel = 4.054$, $g_\perp = 0.23$, $a_{\text{n.n.n.}} - b_{\text{n.n.n.}} = -0.004$ cm^{-1}, $A_{\text{n.n.n.}} = +0.035$ cm^{-1}. Other lines, not indicated, occur symmetrically about the main line at ±42, ±54 G, the expected dipolar splitting of the third-, fourth-, and sixth-nearest neighbor

interaction makes an important contribution to both the nearest- and next-nearest-neighbor pairs. From Table I it is seen that there is also quantitative evidence for other interactions besides EQQ and dipolar interaction.[12]

These results show that the cross terms between the Zeeman interaction and the electric quadrupole-quadrupole interaction lead to the direct measurement of the n.n.n. quadrupole-quadrupole coupling coefficient. For Ce^{3+} in LaCl$_3$, we find that in first order it makes a substantial contribution to the crystal field at low temperatures, and thus there should be a significant difference between the energy levels in the dilute and concentrated materials. In second order the electric quadrupole-quadrupole interaction acts as an important coupling mechanism, of the order of the dipolar interaction.

These results will be related to the thermal and magnetic properties of CeCl$_3$ in a later paper.[8]

Table I. Calculated interaction constants for Ce^{3+} pair interactions (all given in cm^{-1}).

Type	$a(d\text{-}d)$	$a(\text{EQQ})$	$a(d\text{-}d)+a(EQQ)$	Experimental $(a-b)$
n.n.	−0.168	+0.457	+0.289	+0.213
n.n.n.	+0.024	−0.162	−0.138	−0.004

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†Present address: Clarendon Laboratory, Oxford, England.

‡On sabbatical leave from Wesleyan University, Middletown, Connecticut.

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[5] The LaCl$_3$ lattice parameters are $a = 7.483$ Å, $c = 4.375$ Å compared with $a = 7.451$ Å, $c = 4.313$ Å for CeCl$_3$ [W. H. Zachariasen, J. Chem. Phys. 16, 254 (1948)]. Here it is assumed that the Ce^{3+} impurities go exactly into the La^{3+} sites.

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[11] The principal sources of error are the neglect of the effects of mixing from the $J = \frac{7}{2}$ states and the effects of higher order perturbation terms. Order-of-magnitude estimates indicate as much as a 10% contribution to $A_{\text{n.n.n.}}$ from these sources.

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