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Magnetic Interactions between Rare-Earth Ions in Insulators. III. EPR Measurements of Ce^{3+} Pair-Interaction Constants in $LaCl_3$†

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In order to investigate the form of interaction between non-S-state, Kramers rare-earth ions, the electron paramagnetic resonance spectra from pairs of Ce^{3+} ions in $LaCl_3$ have been measured at 4.2°K and at 25 and 36 GHz. The spectra have been fitted to a general effective-spin pair-Hamiltonian in order to obtain values for the $\mathbf{g}$ tensors and certain terms in the interaction tensors $\mathbf{K}$. By using additional data from bulk-property measurements on $CeCl_3$, values for all the terms in $\mathbf{K}$ can be deduced. The contributions to the measured parameters from the various interaction mechanisms thought to be present in rare-earth compounds are discussed in detail. Apart from the usual magnetic dipole interaction, it is generally difficult to identify each contribution unambiguously. In the present case, however, because of the simple nature of the Ce^{3+} wave functions, there is clear evidence for the existence of an electric quadrupole-quadrupole interaction between next-nearest-neighbor ions, and its magnitude has been determined. There is also unambiguous evidence for anisotropic superexchange of the type suggested by Levy and by Elliott and Thorpe, and it is found that this has matrix elements of magnitude compariable with the more usual bilinear exchange interaction, which is also present.

1. INTRODUCTION

IN two previous papers, henceforth referred to as I [1] and II,[2] we have reported the investigation of magnetic and exchange interactions between pairs of Gd^{3+} ions in trichloride lattices. This investigation used the technique of electron paramagnetic resonance (EPR) of a coupled pair of ions. In this paper we shall describe further pair measurements made on the non-S-state, "Kramers" ion cerium, in a lanthanum trichloride host lattice.[3]

A crystal field acting on a rare-earth Kramers ion splits the lowest J multiplet into a number of evenly degenerate states, with typical splittings of the order of 50 to 100 cm^{-1}, and the presence of these low-lying states with large admixtures of anisotropic orbital wave functions may give rise to radically different interaction mechanisms from the usual Heisenberg exchange encountered in the case of S-state ions. It was in order to investigate these that the present measurements were carried out. We shall show that the measurements indicate unambiguously that in addition to the more usual magnetic dipolar and bilinear exchange interactions, there are also present in this case a relatively large electric quadrupole-quadrupole interaction between the ions and a higher-degree anisotropic exchange interaction of more general form. Besides being of intrinsic interest, these results also have an important bearing on energy transfer processes between rare-earth ions.[4]

At low temperatures only the ground doublet will be appreciably populated, and the magnetic properties of a Kramers system may then be treated as an assembly of effective spins, $S'=\frac{1}{2}$. The interaction of one such spin with a relatively small external magnetic field may be described in general by an anisotropic $\mathbf{g}$ tensor, $\mathcal{H}_M=\mu_B\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}'$, and the most general interaction between two such spins may be described by an anisotropic interaction tensor $\mathbf{K}$, $\mathcal{H}_{\text{int}}=\mathbf{S}'(1)\cdot\mathbf{K}\cdot\mathbf{S}'(2)$.

Two ions coupled by this interaction will give rise to four pair states having values of total effective spin T $[\mathbf{T}=\mathbf{S}'(1)+\mathbf{S}'(2)]$ of 0 and 1. If the ions are identical, EPR transitions may be observed only within the $T=1$ triplet states and enable only the anisotropic part of the interaction to be determined. For two different ions, however, all four transitions may be observed. The pair spectrum from a low-symmetry pair of identical Kramers ions will therefore give rise to a spectrum of only two lines for a given magnetic field setting, if there is no hyperfine interaction, and extensive variation of the magnetic field direction, frequency of microwaves, and temperature must be used in order to determine all 15 components of the $\mathbf{g}$ and $\mathbf{K}$ tensors. This is in con-

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trast to the case of the S-state ion Gd^{3+} where for only one magnetic field setting the problem of determining the six significant interaction parameters was grossly overdetermined.[1]

The effective spin-interaction tensor $\mathbf{K}$ may contain contributions from a number of sources which are not always readily separable. The most straightforward is the usual magnetic dipolar interaction, which may be calculated from the measured g values and lattice spacings. The superexchange interaction between two non-S-state rare-earth ions, however, presents somewhat more of a difficulty. Previous authors have frequently written this in the usual Heisenberg form $J_{12}\mathbf{S}(1)\cdot\mathbf{S}(2)$, and used the Wigner-Eckart theorem to project this interaction into $\mathbf{K}$. While this may be useful for order-of-magnitude estimates, it is not necessarily correct to use a Heisenberg form of interaction. Instead, an expression involving orbital operators acting on the orbits of ions 1 and 2 must be used in place of the scalar J_{12}, taking account of the nonspherical symmetry of the magnetic moment distribution on each ion.[5] When this general interaction is projected into $\mathbf{K}$, it may well contribute to each element of the tensor, and, in particular, the anisotropy of $\mathbf{K}$ may no longer be related in any simple way to the $\mathbf{g}$ tensor of the doublet.

In addition to complicating the form of the exchange interaction, the anisotropic nature of the magnetic charge distribution gives rise to the possibility of a coupling between the multipole moments of the distributions that does not involve orbital overlap. This coupling may arise either directly through the usual classical Coulombic interaction[3,6–13] or indirectly through the dynamic interaction of the multipole moments with the lattice.[14–21] In first order the coupling shifts the ground-state pair levels equally, that is, it contributes to the crystal field interaction alone, but in second order it may contribute to $\mathbf{K}$.

Although the principal effect within the ground doublet of all the interactions between the ions will be to contribute to the effective spin-interaction tensor $\mathbf{K}$, there will also be small contributions to the effective $\mathbf{g}$ tensor. These arise from cross terms in the second-order perturbation theory involving the interaction and Zeeman Hamiltonians.[3,22] Furthermore, if observable effects outside the manifold of the ground doublets are considered, then, acting in first order, the interaction between the ions may alter the relative energies of the levels. Thus, although it may be difficult to identify the coupling mechanism mainly responsible for the interaction from its contribution to $\mathbf{K}$, $\mathbf{g}$, or the energy of excited states alone, it may be possible to do so in certain cases by correlating all three effects, that is, by observing how the interaction contributes in different orders of perturbation.

A considerable amount of work has recently been reported on the EPR investigation of interactions between non-S-state rare-earth ions, particularly Nd^{3+} and Ce^{3+}. The pair spectra of Nd^{3+} ions have been investigated in lanthanum ethyl sulphate,[8] lanthanum trichloride,[23–26] lanthanum tribromide,[23,25,26] and calcium fluoride,[27] and pairs of Ce^{3+} ions have been observed in lanthanum ethyl sulphate[9] and lanthanum tribromide,[25,26] where the last represents an extension of the present work. Pair spectra of Dy^{3+}, Tb^{3+}, and Ho^{3+} ions have been observed in the ethyl-sulphate lattice.[10] Further information on the interactions between rare-earth ions, particularly in the ethyl-sulphate lattice, has been obtained from low-temperature measurements of the EPR of the concentrated salts.[11,28] In each of the above experiments, it has been found that there are appreciable nondipolar interactions; however, it has proved extremely difficult to separate out the different possible contributions.

The case of cerium in lanthanum trichloride was chosen for the present investigation for a number of reasons. The Ce^{3+} ion is particularly amenable to theoretical considerations, having the configuration $4f^1$. EPR,[29] optical absorption,[30,31] and susceptibility

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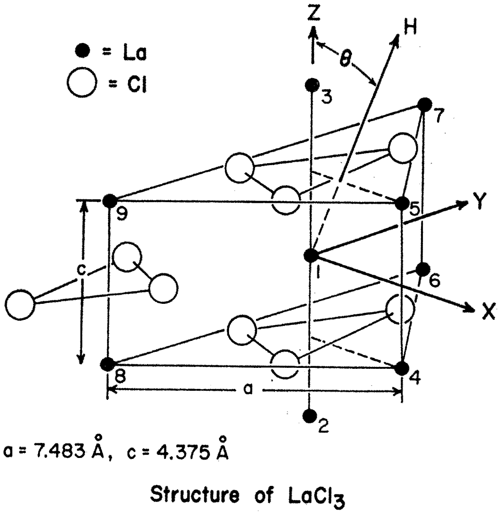

FIG. 1. Structure of $LaCl_3$ and $CeCl_3$. The XZ plane is defined by the nnn pairs (1,4) and (1,5).

measurements[32] show that the ground state in $LaCl_3$ is close to pure $|J=\frac{5}{2}, M_J=\pm\frac{5}{2}\rangle$, so that the spins in the system might be expected to show Ising-like interactions, although, as we shall see, this is not necessarily so. The Ce^{3+} ion also exhibits the largest quadrupole moment of the rare-earth ions Ce^{3+} to Gd^{3+},[33] and it was, therefore, anticipated that the electric quadrupole-quadrupole interaction (EQQ), that is, the first spin-dependent term in the electric multipole interaction, might be particularly important in this case where the ions are separated by only 4 Å. Experimentally, the absence of hyperfine interaction simplifies the EPR spectrum. The bulk magnetic properties of concentrated $CeCl_3$ were determined in an investigation parallel to this work and showed an antiferromagnetic transition at 0.27°K.[34] The parameters describing these bulk magnetic properties may be used as additional information which, combined with the parameters determined from the pair experiments, enables values for most of the terms in the nearest-neighbor and next-nearest-neighbor interaction tensor $\mathbf{K}$ to be found.[35]

The work described in this paper falls into two parts: firstly (Secs. 2–5), the determination of values for the terms in the $\mathbf{g}$ tensors and interaction tensor $\mathbf{K}$, and secondly (Secs. 5–7), the discussion of the contributions to these terms from the different possible interaction mechanisms. In Sec. 2 we shall briefly describe the crystal structure, and in Sec. 3 we shall discuss the work carried out by various authors on the properties of a single Ce^{3+} ion in $LaCl_3$. In Sec. 4 we consider the general spectrum for a pair of identical ions with interaction tensor $\mathbf{K}$ and magnetic moment tensor $\mathbf{g}$ in the case where the $\mathbf{g}$ tensor is highly anisotropic. The experimental results will be described in Sec. 5. In Sec. 6 we review the theories of virtual phonon and electric quadrupole-quadrupole interaction, and we apply these to the experimental results in Sec. 7. The main conclusions will be summarized in Sec. 8.

2. CRYSTAL STRUCTURE AND PREPARATION

The crystal structure of $LaCl_3$ has been described in I, and a diagram of the structure is reproduced in Fig. 1. The lattice parameters and ionic separations are summarized in Table I.[36,37] The space group is $C6_3/m$, and the point symmetry at the rare-earth site is C_{3h}.

The experiments described in Sec. 5 were performed on samples containing 1–10% concentrations of Ce^{3+} ions. The crystals were oriented in the manner described in I so that the magnetic field could be swept from along to perpendicular to the c axis through a next-nearest-neighbor (nnn) pair-bond axis, that is, in the XZ plane in Fig. 1.

The samples were prepared by Garton at Oxford and Mroczkowski at Yale by the Bridgeman-Stockbarger method in the manner described by Garton *et al.*[38]

3. *g* VALUES AND CRYSTAL FIELD PARAMETERS FOR SINGLE Ce^{3+} IONS IN $LaCl_3$

The EPR of Ce^{3+} ions in $LaCl_3$ was first reported by Hutchison and Wong,[29] who measured the $\mathbf{g}$ tensor of the ground state at 4.2°K. They found

$$g_{\parallel}=4.0366(\pm 0.0015)\,,\quad g_{\perp}=0.17(\pm 0.08)\,.$$

Values determined from our 1%-Ce^{3+} sample agree well with these:

$$g_{\parallel}=4.037(\pm 0.002)\,,\quad g_{\perp}=0.23(\pm 0.02)\,.$$

At higher temperatures the Ce^{3+} resonance is broadened by spin-lattice relaxation.

There is now a considerable amount of data available on the crystal field levels in Ce^{3+}-doped $LaCl_3$ and also in concentrated $CeCl_3$. Schneider[32] has deduced crystal field parameters from the susceptibility of $CeCl_3$ as a function of temperature between 4.2 and 300°K, and

TABLE I. Lattice parameters and ionic separations at room temperature in Å.[a]

	$a_0=r_{3n}$	$c_0=r_{nn}$	r_{nnn}
$LaCl_3$	7.483	4.375	4.843
$CeCl_3$	7.450	4.315	4.812

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TABLE II. Crystal field levels for Ce^{3+} in $LaCl_3$, together with wave functions in the form $|JM_J\rangle$.[a,b]

Multiplet	Energy (cm^{-1})	Eigenfunctions
	0	$0.99796\|\frac{5}{2}\pm\frac{5}{2}\rangle\pm0.01072\|\frac{7}{2}\pm\frac{5}{2}\rangle\pm0.06298\|\frac{7}{2}\mp\frac{7}{2}\rangle$
$^2F_{5/2}$	37.5±3.1	$0.99446\|\frac{5}{2}\pm\frac{1}{2}\rangle\mp0.10511\|\frac{7}{2}\pm\frac{1}{2}\rangle$
	110.0±3.9	$0.99924\|\frac{5}{2}\pm\frac{3}{2}\rangle\pm0.03905\|\frac{7}{2}\pm\frac{3}{2}\rangle$
	2166.0±1.8	$\pm0.56659\|\frac{7}{2}\pm\frac{7}{2}\rangle\mp0.82356\|\frac{7}{2}\mp\frac{5}{2}\rangle+0.02709\|\frac{5}{2}\mp\frac{5}{2}\rangle$
	2208.6±1.3	$\pm0.99446\|\frac{7}{2}\pm\frac{1}{2}\rangle+0.10511\|\frac{5}{2}\pm\frac{1}{2}\rangle$
$^2F_{7/2}$	2282.6±5.2	$\pm0.82174\|\frac{7}{2}\pm\frac{7}{2}\rangle\pm0.56692\|\frac{7}{2}\mp\frac{5}{2}\rangle+0.05785\|\frac{5}{2}\mp\frac{5}{2}\rangle$
	2399.5±2.1	$0.99924\|\frac{7}{2}\mp\frac{3}{2}\rangle\pm0.03905\|\frac{5}{2}\mp\frac{3}{2}\rangle$

[a] Calculated using $A_2^0\langle r^2\rangle=64.5$ cm^{-1}, $A_4^0\langle r^4\rangle=-41.0$ cm^{-1}, $A_6^0\langle r^6\rangle=-64.1$ cm^{-1}, $A_6^6\langle r^6\rangle=399.1$ cm^{-1}, and $\zeta=626.5$ cm^{-1}.
[b] Reference 30.

von Klot has determined the position of the first excited state by a relaxation method.[39] More accurate values for Ce^{3+} in $LaCl_3$ have been given by Hellwege *et al.*,[30] who investigated the absorption spectrum of $LaCl_3$ containing 0.5 and 5% Ce^{3+} at low temperatures in the region of the $4f$-$4f$ infrared transitions. These results are summarized in Table II, where the crystal field levels of the $^2F_{5/2}$ and $^2F_{7/2}$ multiplets are given, together with wave functions determined by fitting a C_{3h} crystal field Hamiltonian to the observed splittings. Bagguley and Vella-Coleiro have investigated the Zeeman behavior of the excited states[31] and find that parameters very similar to those of Hellwege give a good description of their results. Note, however, that there is a slight discrepancy between the g values for the ground state calculated on the basis of static crystal field theory and those measured using EPR. In $g_{\parallel}$, however, this discrepancy may be accounted for by a combination of covalency and the virtual phonon process of Inoue.[40,41] In $g_{\perp}$ the theoretical situation is less clear, although the same mechanisms could be involved here as well.

4. GENERAL PAIR SPECTRA

A. nn Pairs

In this subsection we consider the pair spectrum expected for a pair of nearest-neighbor (nn) Ce^{3+} ions in $LaCl_3$ [e.g., (1,2) and (1,3) in Fig. 1]. In this case the symmetry of the pair, a threefold rotation axis and horizontal reflection plane, reduces the general interaction Hamiltonian to

$$\mathcal{H}_{nn}=K^{nn}{}_{\parallel}S_z(1)S_z(2)+\tfrac{1}{2}K^{nn}{}_{\perp}\times[S^+(1)S^-(2)+S^-(1)S^+(2)], \quad (1)$$

where we write $K^{nn}{}_{\parallel}=K^{nn}{}_{zz}$ and $K^{nn}{}_{\perp}=K^{nn}{}_{xx}=K^{nn}{}_{yy}$ and for convenience we have omitted the prime on the effective spin operator $S=\frac{1}{2}$. The **g** tensor for a nn pair has the same form as that for a single ion, and we may write the pair Hamiltonian as

$$\mathcal{H}=\sum_{i=1,2}(g_{\parallel}\mu_BH\cos\theta\, S_z(i)+g_{\perp}\mu_BH\sin\theta\, S_x(i))+K^{nn}{}_{\parallel}S_z(1)S_z(2)+\tfrac{1}{2}K^{nn}{}_{\perp}\times[S^+(1)S^-(2)+S^-(1)S^+(2)]. \quad (2)$$

For convenience we choose as basis states $|++\rangle$,

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

and $|--\rangle$, where $|++\rangle$ is $|M(1)=\frac{1}{2}, M(2)=\frac{1}{2}\rangle$, etc. The states $|++\rangle$, $|S\rangle$, and $|--\rangle$ then correspond to total spin $T=1$, and $|A\rangle$ is the $T=0$ state. As noted in Sec. 1, for a pair of identical ions only the transitions within the $T=1$ state are allowed. In order to calculate the expected pair spectra we assume that $g_{\parallel}\gg g_{\perp}$ for the nn pairs, as in the single-ion case, so that we may then use perturbation theory. This, of course, is a very reasonable assumption, since we would not expect the pair g values to differ very much from those of the single ion.

It is then straightforward to show that the nn pair transitions will be observed at fields H^+, between the perturbed states $|++\rangle$ and $|S\rangle$, and H^-, between $|S\rangle$ and $|--\rangle$, where H^+ and H^- are given to second order by the expressions

$$h\nu=g_{\parallel}\mu_BH^{\pm}\cos\theta\pm\tfrac{1}{2}(K^{nn}{}_{\parallel}-K^{nn}{}_{\perp})+g_{\perp}{}^2\mu_B{}^2H^{\pm 2}\sin^2\theta/2h\nu, \quad (3)$$

where ν is the frequency and we assume that

$$h\nu>\tfrac{1}{2}(K^{nn}{}_{\parallel}-K^{nn}{}_{\perp}).$$

Hence the nn pair lines should be approximately symmetrically placed about the main line separated by $(K^{nn}{}_{\parallel}-K^{nn}{}_{\perp})/2g_{\parallel}\mu_BH\cos\theta$ from it, and $H^{\pm}{}_{nn}\cos\theta$ should show an angular variation similar to that of the single-ion main line. Therefore only the difference $K^{nn}{}_{\parallel}-K^{nn}{}_{\perp}$ can be determined from the line positions. We may note that since $|--\rangle$ corresponds to $|M_J(1)=-\frac{5}{2}, M_J(2)=-\frac{5}{2}\rangle$, then at low temperatures ($kT\sim h\nu$) the transition corresponding to H^- will grow in intensity relative to the transition at H^+. This

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enables the sign of $K^{\mathrm{nn}}{}_{\parallel}-K^{\mathrm{nn}}{}_{\perp}$ to be determined. The isotropic part of **K** can also, in principle, be measured from the relative intensities of the lines as a function of temperature, but for weak interactions this becomes very difficult.[42]

B. nnn Pairs

In the case of the nnn pairs the situation is significantly more complicated. The only symmetry operation for the pair is an inversion through the center of the line joining the ions. Thus the most general symmetric interaction tensor **K** is allowed. Similarly, the most general **g** tensors $\mathbf{g}_1$ and $\mathbf{g}_2$ are allowed, although we might expect the off-diagonal terms and the horizontal plane anisotropy $g_{xx}-g_{yy}$ to be rather small, since they arise only from crystal field distortions and the multipole effects mentioned in the Introduction. It is important to note, however, that because of the inversion through the center, $\mathbf{g}_1$ and $\mathbf{g}_2$ may be shown to be identical if they are defined relative to parallel axes. This need not be true in general, and care must be taken in defining the axes of the **g** tensors for the two members of a pair.

From Fig. 1 it may be seen that there are six nnn pairs (1,5), (1,6), (1,9), (1,4), (1,7), and (1,8), which we shall denote by $n=1,\ 2,\ \cdots,\ 6$. These are related to each other by a reflection in the horizontal plane and rotations about the *c* axis of 120° and 240°. Following Brower, Stapleton, and Brower[23] we choose local axes for each of the six nnn pairs such that z_n is parallel to the threefold rotational axis and in the same direction as the component of the magnetic field along this axis. The x_n and y_n axes are such that the vector $\mathbf{R}_n$ joining the nth pair of ions is in the $(+,+)$ quadrant of the x_nz_n plane. Thus, for example, the axes (x_1,y_1,z_1) of the pair $n=1$ coincide with the axes (X,Y,Z) in Fig. 1, and the axes (x_2,y_2,z_2) for the pair (1,6) are related to (x_1,y_1,z_1) by a rotation through $-60°$ about the Z axis. If (θ,ϕ) are the polar angles that the applied magnetic field H makes with the axis of pair (1,5), we may write, in general,

$$H=\mathbf{H}(\sin\theta\cos\phi_n,\ \sin\theta\sin\phi_n,\ \cos\theta)\,,$$

where

$$\phi_n=\phi_1+(n-1)60°\,,\quad n=1,2,\cdots,6.$$

For the sample orientation used in our experiments, $\phi_1=0$. Relative to the appropriate set of axes defined above, the **g** tensors and interaction tensors **K** for each of the pairs are identical.

In order to determine the nnn resonance fields we may once again use perturbation theory. Since the **g** tensor is expected to be highly anisotropic, it is convenient to retain the *c* axis, rather than the strong field precession axis,[43] as axis of quantization. Our analysis will then be limited to the region where

$$g_{xx}\mu_BH\sin\theta\quad\text{and}\quad g_{yy}\mu_BH\sin\theta\ll g_{zz}\mu_BH\cos\theta\,.$$

In first-order perturbation theory, the resonance fields are given by

$$h\nu=g_{zz}\mu_BH^{\pm}\cos\theta\,(1+\alpha_n\tan\theta)\\ \pm\tfrac{1}{2}[K_{zz}-\tfrac{1}{2}(K_{xx}+K_{yy})]\,,\quad(4)$$

where

$$\alpha_n=(g_{xz}\cos\phi_n+g_{yz}\sin\phi_n)/g_{zz}\,.$$

The $+$ and $-$ signs correspond to the transitions between the perturbed states $|++\rangle'$ and $|S\rangle'$, and $|S\rangle'$ and $|--\rangle'$, respectively. The second-order contributions to Eq. (4) are

$$+2f(H^{\pm},\theta,\phi_n,\pm K_{xy},\pm K_{yz})\\ -f(H^{\pm},\theta,\phi_n,\mp K_{xz},\mp K_{yz})\\ +[\tfrac{1}{16}(K_{xx}-K_{yy})^2+\tfrac{1}{4}K_{xy}{}^2]/\\ \{2h\nu\mp[K_{zz}-\tfrac{1}{2}(K_{xx}+K_{yy})]\}\,,\quad(5)$$

where

$$f(H,\theta,\phi,K_{xz},K_{yz})=(1/2h\nu)[(g_{zx}\mu_BH\cos\theta\\ +g_{xx}\mu_BH\sin\theta\cos\phi+g_{yx}\mu_BH\sin\theta\sin\phi+\tfrac{1}{2}K_{xz})^2\\ +(g_{zy}\mu_BH\cos\theta+g_{yy}\mu_BH\sin\theta\sin\phi+g_{xy}\mu_BH\sin\theta\\ \times\cos\phi+\tfrac{1}{2}K_{yz})^2]\,.$$

The general expressions for the positions of the pair lines, correct to second order, are thus rather complicated. We can see, from Eqs. (4) and (5), however, that only the anisotropic terms in **K** can be determined from the EPR resonance fields. As in the case of the nn pairs, measurement of the small isotropic-interaction term from the variation of intensity of the pair lines with temperature would be difficult.

It is instructive to consider the EPR spectrum predicted by Eqs. (4) and (5) in some detail. It is clear that if g_{xx}, g_{xy}, g_{yx}, and $g_{yy}\ll g_{zz}$ as we anticipate, the second-order terms given by Eq. (5) should have only a small effect on the spectra at low angles θ, contributing mainly to a constant shift in frequency. The expression given in Eq. (4) will then form a good first approximation. A comparison of Eq. (4) with the first-order part of the corresponding *nn* expression, Eq. (3), shows that they have the same form except for the term in $\alpha_n\tan\theta$ arising from g_{xz} and g_{yz}. In our preliminary account of this work,[3] we described this term as a "θ-dependent contribution to g_{zz}," replacing α_n with $1.85\eta_iA_{\mathrm{nnn}}$, where $\eta_i=\cos\phi_i$ in the present notation. The form of Eq. (4) is based on a more general spin Hamiltonian and does not rest on any particular model.

For the sample orientation used in our experiment, $\alpha=\pm g_{xz}/g_{zz}$ and $\pm\frac{1}{2}g_{xz}/g_{zz}\pm\frac{1}{2}\sqrt{3}g_{yz}/g_{zz}$, we might therefore expect 12 distinct pair lines arising from the six different nnn pairs at a general value of θ, coalescing into just two lines when H is along the *c* axis. In the particular case when $g_{yz}=0$, there will be only eight distinct lines, four lines corresponding to $\alpha=\pm g_{xz}/g_{zz}$

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[42] J. Owen, J. Appl. Phys. Suppl. 32, 213S (1961).

[43] B. Bleaney, Phil. Mag. 42, 441 (1951).

and four doubly degenerate lines corresponding to $\alpha = \pm\frac{1}{2} g_{xz}/g_{zz}$. As we shall see, this is in fact the case appropriate to our interpretation of Ce^{3+} pairs in $LaCl_3$. From this discussion it is clear that from the nnn pair spectra one should be able to obtain very accurate values for g_{zz}, g_{xz}, g_{yz}, and $K_{zz} - \frac{1}{2}(K_{xx} + K_{yy})$.

The second-order terms, given in Eq. (5), are somewhat more difficult to categorize. The third term in Eq. (5) has the main effect of producing an apparent shift in frequency, and may therefore only be determined by very precise measurements as a function of frequency. Similarly, it may be seen that the terms in g_{zx}, g_{yx}, g_{xy}, and g_{zy} will have no appreciable effect on the spectra unless they are anomalously large. The terms in g_{xx}^2 and g_{yy}^2 correspond to the terms in $g_\perp^2$ for the nn pairs in Eq. (3). Finally, Eq. (5) includes cross terms between K_{xz} and g_{xx} and also K_{yz} and g_{yy}; these may be written in the form

$$\pm g_{zz}\mu_B H^{\pm} \cos\theta (3/2h\nu)[(g_{xx}/g_{zz})K_{xz} \cos\phi_n + (g_{yy}/g_{zz})K_{yz} \sin\phi_n] \tan\theta . \quad (6)$$

This is similar to the term

$$g_{zz}\mu_B H^{\pm} \cos\theta\, \alpha_n \tan\theta \quad (7)$$

in Eq. (4), except that, because of the change in sign for the two pair transitions, it acts like an interaction term rather than a g value. The same angular variation of the spectra will be given by either Eqs. (6) or (7) acting alone, but they may be distinguished by their different frequency dependences. However, because g_{xx} and g_{yy} are small, we would expect the terms in Eq. (6) to be very small, and therefore they should give rise mainly to a slight additional splitting of the pair lines. This should enable K_{xz} and K_{yz} to be determined accurately.

In summary, of the 15 terms in $\mathbf{g}$ and $\mathbf{K}$, the above analysis suggests that from the angular dependence of the spectra we shall only be able to obtain values for g_{xx}, g_{yy}, g_{xz}, g_{yz}, g_{zz}, $K_{zz} - \frac{1}{2}(K_{xx} + K_{yy})$, K_{xz}, and K_{yz} with any precision. This difficulty arises primarily because g_{xx} and g_{yy} are assumed to be small, and manifests itself experimentally in the very high magnetic fields required to study the spectra with H in the XY plane.

Finally, it should be pointed out that because of the experimental ambiguity in ϕ_n it is only possible to determine $\mathbf{g}$ and $\mathbf{K}$ up to a rotation through some integer multiple of 60°.[44]

C. More Distant Pairs

From Table I it may be seen that the third nearest neighbors are much further apart than the nn and nnn. We expect the interactions between these ions to be mainly dipolar and, from the anisotropy of the g values, to be of the form $K_{zz}S_z(1)S_z(2)$. In addition, we expect the $\mathbf{g}$ tensor to remain axial, since any distortion and multipole effects should be negligible. The nn Eq. (3) should therefore be applicable to all pairs further apart than the nnn.

5. EXPERIMENTAL RESULTS

A. Apparatus and Procedure

The experiments were performed mainly on samples of $LaCl_3$ containing 1% Ce^{3+} at 25.0 (K band) and 36.2 GHz (Q band) and at temperatures between 1.3 and 4.2°K. Straightforward transmission spectrometers were used, incorporating 115 KHz field modulation on a slow field sweep and phase-sensitive detection with chart display. The magnetic field, supplied by a Varian Field Dial system, was measured with a Numar Gaussmeter. The same cavity was used[45] at both frequencies and was turned with a shorting plunger.

The samples were oriented as described in Sec. 2. Because of the low value of $g_\perp$, the spectrum could only be observed for values of $\theta \lesssim 70°$ with the magnetic field available. No resonances that could be attributed with certainty to pairs of ions were observed at X-band frequencies. At the K band, however, the pair lines were observed with signal to noise of $\sim 20:1$ and half-intensity full widths of $\sim 10/\cos\theta$ G. Their positions could be measured to an accuracy of $\sim \pm 4/\cos\theta$ G. At the Q band the linewidth was larger, and although the inherent sensitivity at this frequency is higher, the fact that the cavity used was designed for lower frequencies reduced the net sensitivity, and the lines could be measured to only $\pm 6/\cos\theta$ G.

Samples of 2.5, 5, 10, 20, and 100% concentrations were also investigated, and some of these showed other lines besides those observed in the 1% samples. These will be discussed briefly in Appendix A; most were attributed to impurity effects. Some of the more concentrated samples did show weak resonances at the X band, centered about the known pair-line positions. The resonance observed from concentrated $CeCl_3$ is discussed in Appendix B.

B. Pair Spectra

i. General Spectrum

Typical resonances observed from a 1% sample at 25 GHz are shown in Fig. 2, and the angular variation at this frequency is shown in Fig. 3, the experimental pair lines being marked by circles.

When the magnetic field H is along the c axis, there are a number of small lines nearly symmetrical about the large main single-ion line, in particular, the outer lines in Fig. 2(a). These remain symmetrical about the single-ion line on varying the angle of H, and their splitting from it varies approximately as $(\cos\theta)^{-1}$. In

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[44] We are indebted to Dr. J. D. Riley for drawing our attention to this point.

[45] M. T. Hutchings, thesis, Oxford University, 1963 (unpublished).

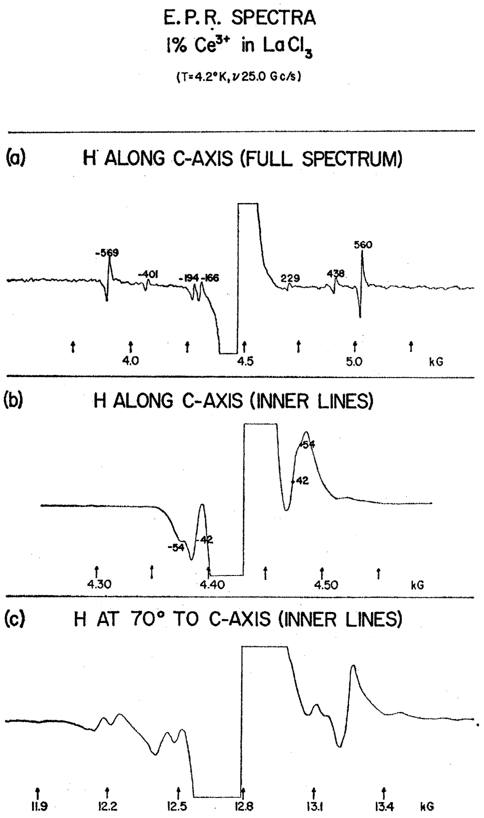

FIG. 2. EPR pair spectra of 1% Ce in $LaCl_3$ at 4.2°K and 25 GHz.

fact, the outermost lines at ~±560 G obey this varia-very well and are indeed attributed to nn pairs. The inner lines, Fig. 2(b), are found to coalesce with the broadening main line at about 50°; these lines are attributed to more distant Ce^{3+} pair transitions. The more asymmetric, or nonsymmetric, inner lines in Fig. 3(a) split up when H is varied away from the c axis and become lost in the noise, and they are probably due to impurities.[46]

When the angle that the magnetic field makes with the c axis is 40° or more, a number of lines with intensities about twice that of the outer pair lines in Fig. 2(a) begin to emerge from the single-ion line, both on the high- and low-field sides, with a splitting that increases rapidly with angle. The central part of the EPR spectrum with $\theta=70°$ is shown in Fig. 2(c); the lines on either side of the single-ion line are those which emerge at $\theta\sim40°$. These lines are attributed to nnn pairs, for reasons given below. We shall now discuss each type of pair in turn.

ii. nn Pairs

The outermost lines in Fig. 2(a), at −569 and +560 G, are attributed to nn pair transitions, since they obey the angular variation expected from Eq. (3), the separation from the main line being $(K^{nn}_{\parallel}-K^{nn}_{\perp})/2g_{\parallel}\mu_B\cos\theta$. The angular variation is plotted in Fig. 3, and the solid line through the experimental points represents the best fit to the points of Eq. (3). The values of $K^{nn}_{\parallel}-K^{nn}_{\perp}$, $g_{\parallel}$ and $g_{\perp}$ giving this fit are listed in Table III. All the points are fitted to within the experimental error out to 60°. Beyond this the slight deviation is very probably due to a small error in θ, although there may also be small terms in $H_{\perp}^2$, not included in Eq. (2), arising from high-order processes. The identification of these lines as nn pairs is confirmed by two other factors. Firstly, the lines do not split out to 70° from the c axis, whereas, if they were due to nnn pairs, we would expect from our discussion of Eqs. (4) and (5) that the lines would split off axis. Indeed, other lines that do split are observed and can be definitely ascribed to nnn pairs, so that, unless there are relatively large long-range interactions present, these lines must be due to the nn. Secondly, the relative intensity of these lines with respect to the single-ion main line in 1, 5, and 10% samples was found to correspond well with that expected theoretically from probability considerations for nn pairs.

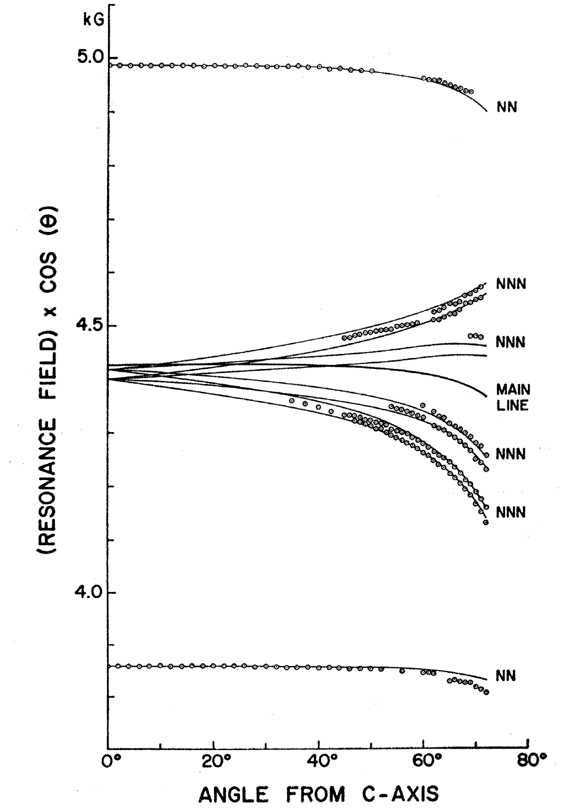

FIG. 3. Angular variation of the pair spectra of Ce^{3+} in $LaCl_3$ at 4.2°K and 25.02 GHz. The circles represent the experimental points, and the solid lines are calculated from the parameters listed in Table III giving the best fit to the spectrum.

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[46] See Appendix A.

TABLE III. Value of spin Hamiltonian parameters found by experiment for the single-ion, nn, and nnn pairs of Ce^{3+} in $LaCl_3$. All energies are expressed in cm^{-1}. The choice of axes and convention used is discussed in Sec. 4 B.

	Freq.	g_{zz}	g_{xx}	g_{yy}	g_{xz}	g_{yz}	g_{xy}	K_{zz} $-\frac{1}{2}(K_{xx}+K_{yy})$	K_{xz}	K_{yz}
Single ion (1%)	K	4.037 (±0.002)	0.23 (±0.02)	0.23 (±0.02)	···	···	···	···	···	···
nn pair (1%)	K Q	4.041 (±0.002)	0.21 (±0.04)	0.21 (±0.04)	···	···	···	0.213 (±0.001)	···	···
nnn pair (1%)	K	4.05 (±0.02)	0.23 (±0.04)	0.23 (±0.04)	0.065 (±0.004)	0.00 (±0.02)	···	0.004 (±0.002)	0.004 (±0.005)	0.000 (±0.002)
	Q	4.04 (±0.02)	0.23 (±0.08)	0.23 (±0.08)	0.063 (±0.008)	0.00 (±0.04)	···	−0.005 (±0.003)	0.000 (±0.010)	0.000 (±0.010)

The sign of the interaction was determined from the relative intensities of the transition at low temperatures. The high-field line was found to correspond to H^-, indicating that $K^{nn}_{\parallel}-K^{nn}_{\perp}>0$. The nn interaction is therefore *antiferromagnetic*. The nn pair field splittings measured at 36.2 GHz were found to agree within experimental error with those measured at 25 GHz, indicating that field-dependent contributions to the interactions are negligible.

We shall postpone discussion of the experimental parameters until Secs. 6 and 7.

iii. nnn Pairs

From Fig. 3 it may be seen that the lines emerging from the main single-ion line when the magnetic field makes an angle greater than 40° from the c axis have the general qualitative features predicted by Eq. (4) for the nnn pairs. The characteristic pattern displayed by the lines indicates a significant term in α_n [see Eq. (4)]. In order to fit the observed spectrum to the expressions given in Eqs. (4) and (5) it is necessary to correlate each pair line with a specific nnn pair, $n=1, \cdots, 6$. As noted previously, this identification is arbitrary up to a rotation of all the pairs by an integer multiple of 60°. In our fitting we assume that g_{xz} dominates over g_{yz}; this necessitates identifying the outer pair lines with $\phi=0°$ and 180°. The significance of this choice will be discussed in Sec. 7.

A general computer program incorporating a least-squares routine written by Powell[47] was used to fit all of the resolved experimental line positions to the expressions given in Eqs. (4) and (5). The parameters giving the best fit to the K-band measurements are listed in Table III. These values were used to calculate the theoretical angular variation shown in Fig. 3, where it can be seen that the general agreement is excellent, the rms deviation in the resonance fields being 9.4 G. Of the large number of possible terms in the general pair Hamiltonian only g_{xz}, $g_{xx}=g_{yy}$, g_{zz}, and $K^{nnn}{}_{zz}-\frac{1}{2}(K^{nnn}{}_{xx}+K^{nnn}{}_{yy})$ are in fact important. The sign of the interaction terms was determined by intensity measurements at 1.3°K as for the nn pairs.

The measurements made at Q-band frequencies gave values of the parameters also listed in Table III; they agree within the experimental error with those determined at the lower frequency. This agreement confirms our assumption that the term α_n in Eq. (7) is responsible for the characteristic nnn spectrum, rather than the expression given in Eq. (6).

Finally, it should be mentioned that the inner low-field nnn lines at the K band were in fact observed to split slightly at magnetic field angles $\theta>65°$. This splitting could arise from a very small term either in K_{yz} or in g_{yz}. Unfortunately, it does not seem possible to distinguish between these. For simplicity we have plotted the mean positions of these lines in Fig. 3.

iv. More Distant Neighbor Pairs

The relatively large pair lines at ±42, and ±54 G in Fig. 2(b) have combined intensities of about $\frac{1}{10}$ to 1/7 of that of the main line. On varying the magnetic field angle θ, the lines were found to remain symmetrically placed about the center with a splitting that varied as $1/\cos\theta$, verifying that they are Ce^{3+} pair lines. Since the nn and nnn have already been accounted for, they must be due to the more distant pairs, and in Sec. 5 C we shall show that they occur at fields close to the predicted dipolar splittings of the third, fourth, and sixth nearest neighbors. The combined theoretical intensities of the third, fourth, and sixth neighbors are consistent with their observed relative intensities.

C. Bulk Magnetic Properties of $CeCl_3$—Final Interaction Parameters

We have seen in Secs. 1 and 2 that the EPR pair spectra from identical ions can only yield values for the *anisotropic* terms of the interaction tensors $\mathbf{K}$, and in our particular case, the pair problem is further underdetermined. Therefore, in order to determine values for all of the interaction terms, use must be made of the bulk magnetic properties of $CeCl_3$ to provide additional experimental parameters. The parameters used are the susceptibility Weiss θ and the high-temperature tail coefficient b for the specific heat,

$$b=C_MT^2/R.$$

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[47] M. J. D. Powell, Computer J. 7, 303 (1965).

TABLE IV. Interaction constants for Ce^{3+} in $LaCl_3$ (in cm^{-1}). $K^{nnn}{}_{\perp}$ is written for $\frac{1}{2}(K^{nnn}{}_{xx}+K^{nnn}{}_{yy})$.[a]

	$K^{nn}{}_{\parallel}$	$K^{nn}{}_{\perp}$	$K^{nnn}{}_{zz}$	$K^{nnn}{}_{\perp}$	$K^{nnn}{}_{xz}$	$K^{nnn}{}_{yz}$
Solution 1	0.262 (+0.028−0.033)	0.049 (+0.032−0.075)	−0.086 (±0.013)	−0.082 (±0.019)	0.004 (±0.002)	0.000 (±0.002)
Solution 2	−0.043 (+0.055−0.021)	−0.256 (+0.021−0.023)	0.015 (+0.011−0.023)	0.019 (+0.029−0.037)	0.004 (±0.002)	0.000 (±0.002)

[a] See Ref. 35.

Both θ and b are related to combinations of the interaction terms. In using these results it is assumed that the interaction tensors for Ce^{3+} ions in $LaCl_3$ are very close to those for Ce^{3+} ions in $CeCl_3$. In view of the good description of the properties of $GdCl_3$ given by the results of pair measurements on Ge^{3+} in $EuCl_3$,[2] an analogous case, this appears to be a valid assumption.

The analysis of both the pair results and the bulk magnetic properties to yield values for the dominant terms in $\mathbf{K}^{nn}$ and $\mathbf{K}^{nnn}$ has been given in a previous publication,[35] and we shall give here only a summary of the results and necessary assumptions.

There are eight unknown terms in $\mathbf{K}^{nn}$ and $\mathbf{K}^{nnn}$. From the pair measurements, Table III, we have values for $K^{nn}{}_{\parallel}-K^{nn}{}_{\perp}$, $K^{nnn}{}_{zz}-\frac{1}{2}(K^{nnn}{}_{xx}+K^{nnn}{}_{yy})$, $|K^{nnn}{}_{xz}|$, and $|K^{nnn}{}_{yz}|$. The Weiss θ, corrected for more distant neighbor dipolar interactions gives a value for $K^{nn}{}_{\parallel}+3K^{nnn}{}_{zz}$, and the specific-heat constant b is given by a quadratic expression involving all eight parameters. In all, there are therefore only six equations to determine eight unknowns. However, by making the reasonable assumptions that $K^{nnn}{}_{xy}<0.035$ cm^{-1} and $|(K^{nnn}{}_{xx}-K^{nnn}{}_{yy})/(K^{nnn}{}_{xx}+K^{nnn}{}_{yy})|<1$, Landau *et al.*[35] were able to determine the values of the interaction constants give in Table IV. For these values $K^{nnn}{}_{xx}-K^{nnn}{}_{yy}$ was taken as zero, but it is found that the other values are relatively insensitive to this anisotropy perpendicular to the c axis, provided that the above assumptions hold.

In Table IV two possible solutions of the expressions are given. Unfortunately, it does not appear to be possible to choose between these on experimental grounds alone. However, we shall see in Sec. 7 that there are theoretical reasons for expecting solution 1 to be the correct alternative.

D. Interaction Contributions to the Pair g Tensor

We have pointed out in the Introduction that there may be contributions to the pair $\mathbf{g}$ tensors arising in second-order perturbation theory from cross terms between the Zeeman term and interaction term in the pair Hamiltonian acting within the full J multiplet.[22] We shall consider as an "interaction" between the ions any effect that depends on the expectation values of total angular-momentum operators acting on *both* ions. Thus we include such effects as EQQ, where the quadrupole is that of the magnetic orbit of a Ce^{3+} ion, but exclude the usual nonmagnetic electrostatic interactions contributing to the crystal field acting on an ion. In this section we shall attempt to isolate the change in g values due to the former effects from those due to the change in nonmagnetic crystal field resulting from distortions.

The distortion in the nonmagnetic crystal field acting on one member of a pair arises because one neighboring La^{3+} ion of the single ion has been replaced with a Ce^{3+} ion. We know from I and II that any shift in position of the two ions is small; from the dipolar interaction between nn Gd^{3+} ions in $LaCl_3$ this shift is found to be $\sim\frac{1}{6}$ the difference in separation of the symmetry positions in $LaCl_3$ and $GdCl_3$. Since this difference is less for $LaCl_3$ and $CeCl_3$, we might expect a smaller shift in our case, and indeed this was found for the analogous case of Gd^{3+} pairs in $EuCl_3$ where within the experimental error the Gd^{3+} ions were found to sit at the Eu^{3+} sites.

In Table V we give the difference in g values found for nn and nnn Ce^{3+} pairs in $LaCl_3$ from those of the single ions. It is seen that, while there is negligible shift in g_{zz} and $g_{\perp}$ for either type of pair, there is an appreciable contribution to $\Delta g_{xz}{}^{nnn}$. Indeed, it is this term that is responsible for the characteristic nnn spectrum. Note that, since the experiments only determine $\mathbf{g}$ up to a rotation of $(n\times 60)°$, the more general result is that $\Delta g_{xz}=0.065\cos\frac{1}{3}n\pi$, and $\Delta g_{yz}=0.065\sin\frac{1}{3}n\pi$. Our assumption that $\Delta g_{xz}>\Delta g_{yz}$ corresponds to the case of $n=0$. However, the following discussion applies for all n.

It is extremely difficult to make a reliable estimate of the contribution to $\Delta\mathbf{g}$ from a distortion of the pair on purely theoretical grounds. Order-of-magnitude estimates based on the maximum likely distortion indicate a contribution that is too small by an order of magnitude. However, the uncertainty in the calculations is such that one may not rule out a distortion-induced g shift of the observed magnitude.

Fortunately, much stronger evidence comes from the experiments of Brower *et al.*[23] and of Riley *et al.*[25] on Nd^{3+} pairs in $LaCl_3$. In this work, an analogous experiment to the present case, it was possible to obtain values for all the components of the pair $\mathbf{g}$ tensor, and these are given together with the single-ion g values as the changes in $\mathbf{g}$ in Table V. In the case of Nd^{3+} pairs, we may confidently estimate the interaction con-

TABLE V. Single-ion $\mathbf{g}$ tensors and pair $\Delta\mathbf{g}$ tensors for Ce^{3+} and Nd^{3+} in $LaCl_3$. $\Delta\mathbf{g}=\mathbf{g}$ (pair) $-\mathbf{g}$(single ion).

Single-ion $\mathbf{g}$	$\Delta\mathbf{g}_{nn}$	$\Delta\mathbf{g}_{nnn}$
Ce^{3+} in $LaCl_3$		
$\begin{bmatrix} 0.23\ (\pm0.02) & 0 & 0 \\ 0 & 0.23\ (\pm0.02) & 0 \\ 0 & 0 & 4.037\ (\pm0.002) \end{bmatrix}$	$\begin{bmatrix} -0.01_4\ (\pm0.05) & 0 & 0 \\ 0 & -0.01_4\ (\pm0.05) & 0 \\ 0 & 0 & 0.004\ (\pm0.003) \end{bmatrix}$	$\begin{bmatrix} 0.00\ (\pm0.05) & \cdots & 0.065\ (\pm0.003) \\ \cdots & 0.00\ (\pm0.05) & 0.000\ (\pm0.003) \\ \cdots & \cdots & 0.00\ (\pm0.02) \end{bmatrix}$
Nd^{3+} in $LaCl_3$[a]		
Single-ion $\mathbf{g}$	$\Delta\mathbf{g}_{nn}$[b]	$\Delta\mathbf{g}_{nnn}$
$\begin{bmatrix} +1.763\ (\pm0.001) & 0 & 0 \\ 0 & 1.763\ (\pm0.001) & 0 \\ 0 & 0 & 3.990\ (\pm0.001) \end{bmatrix}$	$\begin{bmatrix} -0.053\ (\pm0.002) & 0 & 0 \\ 0 & -0.053\ (\pm0.002) & 0 \\ 0 & 0 & 0.022\ (\pm0.003) \end{bmatrix}$	$\begin{bmatrix} 0.005\ (\pm0.003) & -0.009\ (\pm0.002) & -0.002\ (\pm0.001) \\ -0.009\ (\pm0.002) & 0.007\ (\pm0.003) & 0.002\ (\pm0.001) \\ -0.002\ (\pm0.001) & 0.002\ (\pm0.001) & -0.004\ (\pm0.003) \end{bmatrix}$

[a] Reference 25.
[b] Reference 23.

tributions to the $\mathbf{g}$ tensor. We find that the g shift due to EQQ is one to two orders of magnitude smaller than that expected for Ce^{3+} pairs in $LaCl_3$ and that the shift due to superexchange is $\lesssim 0.01$.

The g shifts due to distortions, on the other hand, should be significantly larger than those for Ce^{3+} pairs, for two reasons. Firstly, since the differences between the nn and nnn separations in $LaCl_3$ and $NdCl_3$ are 0.136 and 0.075 Å compared with 0.060 and 0.031 Å for $LaCl_3$ and $CeCl_3$, the distortions for the Nd^{3+} pairs should be at least twice as large as those for the Ce^{3+} pairs. Secondly, for a given distortion, the second- and fourth-degree crystal-field terms arising from the distortion produce g shifts of comparable magnitude in both Ce^{3+} and Nd^{3+} pairs. However, the sixth-degree terms that normally dominate in low-symmetry fields produce large g shifts only in the case of Nd^{3+} pairs, since they do not affect the Ce^{3+} ground multiplet in first order. In general, therefore, we may expect the distortion shifts in the Ce^{3+} pair $\mathbf{g}$ tensor to be at the most a quarter of those found for Nd^{3+}.

An examination of Table V shows that for the Nd^{3+} pairs significant shifts occur in $g^{nn}{}_{\parallel}$ and $g^{nn}{}_{\perp}$; however, the $\Delta\mathbf{g}$ tensor for the nnn has only small contributions in all its components. Since these shifts arise mainly from the distortion, we may put an *upper* limit on the maximum distortion-induced shift likely to be found in Ce^{3+} pairs as ±0.01, and indeed the actual shifts are very probably much smaller.

We may therefore conclude that the observed value of $\Delta g^{nnn}{}_{xz}$ for Ce^{3+} pairs, 0.065, must arise almost wholly from the interaction between the ions. The origin of this term, and the values of the components of the interaction tensor $\mathbf{K}$, will be discussed in Secs. 6 and 7.

6. POSSIBLE INTERACTION MECHANISMS AND THEIR EFFECTS

In this section we shall discuss the possible interactions between the spins that may contribute to the $\mathbf{K}$ and $\Delta\mathbf{g}$ tensors summarized in Tables IV and V. As mentioned in the Introduction, any interaction between the ions will contribute to these tensors in different orders of perturbation theory. In first order the interactions bilinear, or of any odd power, in both total angular-momentum operators may be projected into the ground doublet to give contributions to $\mathbf{K}$. For Kramers ions, the interactions of even degree in the operators will act in first order to affect the relative splittings of higher states of the pair, that is, the crystal field levels, and will only contribute to $\mathbf{K}$ in second and higher orders of perturbation. In a magnetic field there will also be cross terms in second-order perturbation between the Zeeman and interaction terms of both odd and even degree, and these will give rise to contributions to $\mathbf{g}$. In the following subsections we shall discuss each type of interaction in turn.

A. Dipolar Contribution

The first-order effect of the dipolar interaction may be written directly in terms of the effective spins, using the ground-state g values. Because of the large anisotropy in the g values ($g_{\perp}/g_{\parallel}\sim 0.05$), there is only a significant contribution to K_{zz}, and values of this term for pairs out to the sixth nearest neighbors are given in Table VI. The $LaCl_3$ lattice spacings were used to calculate the ionic separations.

If we compare the values of the calculated dipolar interactions for nn and nnn ions with the experimental parameters listed in Table III, we see that there are appreciable nondipolar interactions present for both types of neighbors. Since the dipolar interaction is always present, for convenience we have tabulated the nondipolar parts of solutions 1 and 2 in Table VII. These are the values that must be accounted for by the remaining interactions. In second order the dipolar interaction contributes a negligible amount to $\mathbf{K}$ and $\mathbf{g}$.

If the dipolar interactions of the more distant neighbors are used to calculate the splittings of the third,

TABLE VI. Dipolar contributions to K_{zz} for different types of Ce^{3+} pairs in $LaCl_3$.

Neighbors	1st	2nd	3rd	4th	5th	6th
r (Å)	4.375	4.843	7.483	7.857	8.669	8.750
Angle between $\hat{r}$ and $\hat{z}$	0	63.2	90	33.3	59.7	0
$K_{zz}(d\text{-}d)$: cm^{-1}	− 0.168	0.024	0.017	− 0.016	0.003	− 0.021
G	−897	128	89	−84	14	−112

fourth, and sixth neighbor pair lines, these are found to be 44, 42, and 56 G. A comparison with the lines observed at 42 and 54 G suggests strongly that they arise from these neighbors and that to within the experimental error dipolar interaction alone is sufficient to account for their interactions.

B. Exchange Interactions

In this subsection we first consider the order of magnitude of the exchange interactions and then discuss the most general form of Hamiltonian between rare-earth ions.

With the present lack of detailed understanding of the theory of exchange interaction, we cannot carry out calculations of the superexchange interaction between two Ce^{3+} ions from first principles, but we can make an estimate of its possible magnitude from the measured Gd^{3+} exchange interactions in $LaCl_3$ and $EuCl_3$.[1,2] In doing this we make the assumption that the interaction is of a Heisenberg nature between true spins, $\mathcal{H}_{ex}=J_{12}S^{(1)}\cdot S^{(2)}$, and we project this into the ground doublets. As pointed out in the Introduction, this is not necessarily valid for ions with a large orbital contribution to the wave function[5] but should suffice for an order-of-magnitude estimate.

In I and II it was found that the true Heisenberg exchange between Gd^{3+} ions in $LaCl_3$ was $J_{12}\sim0.05$ cm^{-1}. If the exchange between the real spins of the Ce^{3+} ions were identical to this, the isotropic exchange projected into the ground multiplet would give

$$K^{ex}{}_{zz}\sim[(g_{5/2}-1)^2/g_{5/2}{}^2]g_{\parallel}{}^2J_{12}\sim0.025\ \mathrm{cm}^{-1}.$$

However, we must take into account the increase in overlap with the chlorine ligands in going from Gd^{3+} to Ce^{3+}. The calculations of Ellis *et al.*[48] indicate that typically the $4f$-ligand overlap integrals change by a factor of 2, whereas the $5s$, $5p$-ligand overlap integrals change by ~1.5. We might therefore expect the Ce^{3+}-Ce^{3+} superexchange to be $\sim(1.5)^4$ to $(2)^4$, that is, 5 to 16 times larger than that appropriate to Gd^{3+} pairs. Thus we expect $|K_{zz}|\sim0.2$ cm^{-1} for both types of neighbor, the interaction being antiferromagnetic for the nn and ferromagnetic for the nnn, as between Gd^{3+} ions.[1,2] A comparison with the values given in Table VII indicates that superexchange could in fact produce contributions of the observed order of magnitude to **K**.

In second order, cross terms involving the exchange and Zeeman terms can give rise to shifts in **g** from the single-ion values.[22] However, in order to explain, for example, the observed value of $g^{nnn}{}_{xz}$ by this mechanism we would require a term $J_{xz}S_x(1)S_z(2)$ in the real-spin nnn pair Hamiltonian with $J_{xz}\sim30$ cm^{-1}. A comparison with the 0.2 cm^{-1} estimated above shows that this is clearly out of the question; indeed, such second-order effects will be negligible.

Levy[5] and Elliott and Thorpe[5] have shown that, within a given J multiplet, the most general form of the exchange interaction is given by

$$\mathcal{H}_{12}{}^{ex}=\sum_{nn',mm'}\mathcal{J}_{nn'}{}^{mm'}\tilde{O}_n{}^m(J_1)\tilde{O}_{n'}{}^{m'}(J_2)\,,\qquad(8)$$

where $\tilde{O}_n{}^m$ are Racah operator equivalents,[49–51] and $n+n'$ is even by time-reversal symmetry. For f electrons, n, $n'\leq7$. The forms of the $\mathcal{J}_{nn'}{}^{mm'}$ are restricted by symmetry and may be determined from a microscopic model; they are not necessarily real. Isotropic coupling between the real spins may be written in the form of Eq. (8) as

$$\mathcal{H}_{ex}=(g_J-1)^2J_{12}[\tilde{O}_1{}^0\tilde{O}_1{}^0-(\tilde{O}_1{}^1\tilde{O}_1{}^{-1}+\tilde{O}_1{}^{-1}\tilde{O}_1{}^1)].$$

We shall see in Sec. 7 that our results show evidence for the existence of some sizeable terms $\mathcal{J}_{nn'}{}^{mm'}$ with $n=n'=5$.

C. Virtual Phonon Coupling

The third interaction that we shall consider is the effective multipole coupling that arises from the exchange of a virtual phonon between the Ce^{3+} ions. This coupling, which we call "virtual phonon coupling" (VPC), has been considered most recently by Orbach and Tachiki,[17] by Baker and Mau,[10] and by Allen.[19] The reader is referred to these papers for reference to earlier work. Allen has shown that VPC is of quantitative importance in UO_2, but in our case it appears to have a negligible effect, as we show below.

As in all orbit-lattice interaction problems, VPC is treated correctly in terms of the normal modes of the

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[48] M. M. Ellis and D. J. Newman (private communication).

[49] H. A. Buckmaster, Can. J. Phys. 40, 1670 (1962).

[50] D. Smith and J. H. M. Thornley, Proc. Phys. Soc. (London) 89, 779 (1966).

[51] R. J. Birgeneau, Can. J. Phys. 45, 3761 (1967); J. Phys. Chem. Solids 28, 2429 (1967).

TABLE VII. Nondipolar interactions constants for Ce^{3+} in $LaCl_3$ (in cm^{-1}).

	$K^{nn}{}_{\parallel}$	$K^{nn}{}_{\perp}$	$K^{nnn}{}_{zz}$	$K^{nnn}{}_{\perp}$	$K^{nnn}{}_{xz}$	$K^{nnn}{}_{yz}$
Solution 1	0.430 (+0.028−0.033)	0.046 (+0.032−0.075)	−0.110 (±0.013)	−0.083 (±0.019)	0.004 (±0.006)	0.000 (±0.002)
Solution 2	0.125 (+0.055−0.021)	−0.259 (+0.021−0.012)	−0.009 (+0.011−0.023)	0.018 (+0.029−0.037)	0.004 (±0.006)	0.000 (±0.002)
Calculated EQQ	0.036 (+0.064−0.033)	0.0	−0.162 (±0.020)	0.0	0.0	0.0

rare-earth ion and its surrounding complex. Such an analysis has been carried out in the cubic case by Orbach and Tachiki.[17] However, in low-symmetry cases, such as for the C_{3h} point symmetry in $LaCl_3$, the normal-mode analysis introduces too large a number of completely unknown constants. It is more convenient, therefore, to treat the problem using the phenomenological Orbach[52] and Scott-Jeffries[53] approach for the spin-phonon interaction. This has the major drawback that one loses all of the advantages of knowing the symmetry, but, nevertheless, it is sufficient to obtain an estimate of the order of magnitude of the effect.

In first order (which is actually second order in the orbit-lattice interaction) the virtual-phonon spin Hamiltonian may be written

$$\mathcal{H}_{12}{}^{\mathrm{VPC}}=A_{\mathrm{VPC}}\sum_{nn',m}\alpha_n{}^m\langle r^n\rangle\alpha_{n'}{}^{-m}\langle r^{n'}\rangle \times\chi_n\chi_{n'}\tilde{O}_n{}^m(1)\tilde{O}_{n'}{}^{-m}(2),$$

where

$$|A_{\mathrm{VPC}}|\simeq 3k_DC_R{}^2/2\sqrt{2}\pi^2\rho v^2R_{12}{}^2. \tag{9}$$

Here the $\tilde{O}_n{}^m$ are Racah operator equivalents, χ_n are the reduced matrix elements, and the $\alpha_n{}^m$ are the numerical coefficients in the phenomenological one-phonon relaxation perturbation Hamiltonian

$$\mathcal{H}=\epsilon\sum_{n,m}\alpha_n{}^m\langle r^n\rangle\chi_n\tilde{O}_n{}^m.$$

The pair axis is chosen as axis of quantization. Only even values of n, n' need be included if a single configuration of each ion is considered, since parity causes the odd-n matrix elements to vanish. In the Scott-Jeffries approach, the $\alpha_n{}^m$ are taken as equal to the corresponding static crystal field parameters,[51,53] that is,

$$\begin{aligned}|\alpha_2{}^m\langle r^2\rangle|&\simeq 2|A_2{}^0\langle r^2\rangle|_{\mathrm{exp}},\\ |\alpha_4{}^m\langle r^4\rangle|&\simeq 8|A_4{}^0\langle r^4\rangle|_{\mathrm{exp}},\\ |\alpha_6{}^m\langle r^6\rangle|&\simeq 16|A_6{}^0\langle r^6\rangle|_{\mathrm{exp}},\end{aligned} \tag{10}$$

where the $A_n{}^m$ are the conventional static crystal field parameters.[54] The Hamiltonian, Eq. (9), is derived on the assumption that the crystal field energy ΔE is much less than the phonon energy and is only valid in that approximation. The effect of including the crystal field energy explicitly is to reduce A_{VPC} by approximately $hvk_D/(\Delta E+hvk_D)$. Equation (9) includes only the contribution from the zero-point phonons; however, in the liquid-helium-temperature range this is most certainly a good approximation. In addition, coupling to the optical modes is assumed to be the same as to the accoustic modes; this has, in fact, been verified experimentally for the case of $NdCl_3$.[55]

The parameter C_R occurring in the expression for A_{VPC} is the amount by which the orbit-lattice interaction as estimated above must be scaled in order to bring the theoretical Raman relaxation time into agreement with experiment. Because of the dominance of the Orbach process in the relaxation and its generally anomalous nature, no Raman relaxation time could be measured experimentally for Ce^{3+} in $LaCl_3$,[56,57] so that as a first approximation we take $C_R=1$.

For Ce^{3+} ions in $LaCl_3$, the density $\rho=3.84$ gm/cc and velocity of sound $v\sim 2\times 10^5$ cm/sec. The Debye temperature, on the basis of eight atoms per unit cell, is $150°\times 2^{1/3}=190°$K, so that the cutoff wave vector k_D is 1.2×10^8 cm^{-1}. The dynamic crystal field parameters may be estimated, using Eq. (10), from the static parameters given in Table II.

The VPC in first order will contribute to the electrostatic crystal field and in second- and higher-order perturbation will contribute to the spin-spin interaction tensor **K**. In order to estimate the size of the VPC effects we consider a typical first-order matrix element $\langle\frac{5}{2},\frac{5}{2}|\mathcal{H}_{\mathrm{VPC}}|\frac{5}{2},\frac{5}{2}\rangle$. This is found to be $\sim 3\times 10^{-3}$ cm^{-1}. The contribution to $K^{nn}{}_{zz}$, in second order, will then be typically two orders of magnitude smaller, $\sim 3\times 10^{-5}$ cm^{-1}. Compared with the magnetic dipole-dipole contribution to $K^{nn}{}_{zz}$ of -0.17 cm^{-1}, we see that this is entirely negligible. We can therefore rule out VPC as a possible coupling mechanism for Ce^{3+} ions in $LaCl_3$.

D. Electric Multipole Interaction

We shall discuss the electric multipole interaction in some detail, for, as we shall see, it seems quite likely

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[52] R. Orbach, Proc. Roy. Soc. (London) **A264**, 458 (1961).

[53] P. L. Scott and C. D. Jeffries, Phys. Rev. **127**, 32 (1962).

[54] See, for example, M. T. Hutchings, Solid State Phys. **16**, 227 (1964).

[55] E. Cohen, L. A. Riseberg, and H. W. Moos, Phys. Rev. (to be published).

[56] B. W. Mangum and R. P. Hudson, J. Chem. Phys. **44**, 704 (1966).

[57] R. C. Mikkleson and H. J. Stapleton, Phys. Rev. **140**, A1968 (1965).

that the second-degree term, the EQQ, has a considerable effect in the present case.

The electric multipole interaction (EMI) arises from the Coulombic interaction of the magnetic electrons, which are assumed to have nonoverlapping charge distributions. This Coulombic interaction e^2/r_{12} may be expanded to give terms involving the different moments of each charge distribution. The monopole-monopole interaction is spin-independent, but higher-degree moments on both ions will lead to coupling between the spins on each ion.

In first order the EMI will contribute to the crystal field acting on one ion due to the other, and in second order with the Zeeman term it will contribute to a shift in the pair **g** tensor as discussed above. In this case, it is perhaps just as easy to envisage such a shift as due to a change in crystal field acting on one ion, due to the multipole moment of the other; this admixes the wave functions of each single ion to give a change in g value. Clearly the **g** tensor of the pair will exhibit the lower symmetry of the pair-ion site.

The contribution to **K** of the EMI arises through second- and higher-order processes in which both ions are simultaneously coupled to excited states. The origin of the splitting of the pair states may be seen from a simple example. The EMI admixes the pair ground state $|M_J(1)=\frac{5}{2}, M_J(2)=\frac{5}{2}\rangle$ with the excited crystal field states in a different manner than the complementary ground state $|M_J(1)=\frac{5}{2}, M_J(2)=-\frac{5}{2}\rangle$. Thus the net charge distributions, after the EMI has been switched on, differ for the two pair states, and there is a resultant splitting.

i. General Theory

Several authors have discussed the second-degree electrostatic interaction[6,8–11]; Birgeneau *et al.*,[3] using using the expansions of Carlson and Rushbrooke,[7] have given a general operator form of this interaction for a pair of ions 1, 2, with magnetic charge distributions centered about origins O_1 and O_2. This may readily be extended to give the general EMI Hamiltonian acting within multiplets J and J' of ions 1 and 2. The bond axis is taken at an angle θ_0 with O_1z_1, and the coordinate axes (x_1,y_1,z_1) and (x_2,y_2,z_2) at O_1 and O_2, respectively, are chosen to be parallel and such that x_1 and x_2 lie in the bond-axis plane. This choice of axes is the same as that made for the nnn pairs in Sec. 4 B.

$$\mathcal{H}_{12}{}^{\mathrm{EMI}}=\sum_{ll'=2,4,6} A_{ll'} \sum_{mm'} Q_{ll'}{}^{mm'}\tilde{O}_l{}^m(1)\tilde{O}_{l'}{}^{m'}(2)\,,$$

where

$$A_{ll'}=e^2\chi_l{}^1\chi_{l'}{}^2\langle r_1{}^l\rangle\langle r_2{}^{l'}\rangle/\epsilon_{ll'}R_{12}{}^{l+l'+1} \qquad (11)$$

and

$$Q_{ll'}{}^{mm'}=(-)^{m+m'+l'}\left(\frac{4\pi}{2l+2l'+1}\right)^{1/2}\left(\frac{(l+l'+m+m')!}{(l+m)!(l-m)!}\right.$$
$$\left.\times\frac{(l+l'-m-m')!}{(l'+m')!(l'-m')!}\right)^{1/2} Y_{l+l'}{}^{-m-m'}(\theta_0,0)\,. \qquad (12)$$

In this expression, R_{12} is the distance between O_1 and O_2, and $\tilde{O}_l{}^m$ and χ_l are defined in Sec. 5. The $Y_l{}^m$ are the same as the $\Theta(l,m)e^{im\phi}/(2\pi)^{1/2}$ defined by Condon and Shortley.[58] Within a given configuration of each ion only even values of l and l' will give nonzero matrix elements.

In the expression for $A_{ll'}$ an effective scalar dielectric constant $\epsilon_{ll'}$ has been introduced to represent both the shielding (or antishielding) of the $4f$ electrons by the filled $5s$, $5p$ shells, and the shielding (or antishielding) by the intervening ions. The scalar approximation is clearly very crude, since it neglects completely the microscopic nature of the possible shielding and enhancement effects and, in particular, their spatial anisotropy.[10] However, even in this simplest form it introduces six essentially independent constants ($\epsilon_{ll'}$, l, $l'=2$, 4, 6), and any further refinement is quite unwarranted at the present time. Wolf and Birgeneau[12] have pointed out that the higher-degree terms in Eq. (12) may be as important as the EQQ in certain cases because of these shielding and antishielding effects. The dielectric constants $\epsilon_{ll'}$ must therefore be treated as completely unknown; their values may differ from unity by an order of magnitude in either direction.

We shall now consider the form of the contributions of $\mathcal{H}_{12}$ to the crystal field, the **g** tensor, and the effective interaction tensor **K**. For the latter, we shall limit ourselves to interactions between the lowest doublets.

Let $|\pm G_i\rangle$ represent the ground doublet of atom i and $|\pm E_i\rangle$ represent an excited doublet with energy E_i. Since the contribution of the interaction to the crystal field at site 1 is generally smaller than that due to the usual nonmagnetic effects, we may take it as a perturbation on the latter. The contribution to the crystal field at site 1 due to the ion at site 2 is then given by the operator $\mathcal{H}_{\mathrm{CF1}}=\langle G_2|\mathcal{H}_{12}|G_2\rangle$.

The contribution to the **g** tensor is given by

$$\Delta g_{\alpha z}=2\Big|\sum_{E_1}\big(\langle G_1|L_\alpha+2S_\alpha|E_1\rangle\langle E_1|\mathcal{H}_{\mathrm{CF1}}|G_1\rangle/-E_1$$
$$+\langle G_1|\mathcal{H}_{\mathrm{CF1}}|E_1\rangle\langle E_1|L_\alpha+2S_\alpha|G_1\rangle/-E_1\big)\Big|\,, \qquad (13)$$

with corresponding relations for x and y.

Note that the numerical coefficients in $\mathcal{H}_{\mathrm{CF1}}$ depend on the eigenstate $|G_2\rangle$ and will, in general, be different for each crystal field level of ion 2. Thus in certain favorable cases it may be possible to obtain information about the EMI directly by studying the temperature dependence of the crystal field splitting and **g** tensor in the concentrated material. For pairs, however, the situation is somewhat more complicated.[10]

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[58] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935), p. 52.

In order to calculate the contribution of $\mathcal{H}_{12}$ to the spin-spin interaction tensor **K** we take as the pair basis functions $|+G_1,+G_2\rangle$, $|+G_1,-G_2\rangle$, $|-G_1,+G_2\rangle$, and $|-G_1,-G_2\rangle$. Since the first-order energy levels are still degenerate, it is necessary to use second-order degenerate perturbation theory.[59] Following Baker,[8] the energy pair levels are then given by the eigenvalues of the matrix whose elements are given by

$$(G_1G_2|\mathcal{H}_{\text{eff}}|G_1'G_2')_J = \sum_{E_iE_j} \frac{\langle G_1G_2|\mathcal{H}_{12}|E_{1i}E_{2j}\rangle_J \langle E_{1i}E_{2j}|\mathcal{H}_{12}|G_1'G_2'\rangle_J}{-(E_{1i}+E_{2j})}. \tag{14}$$

In the effective-spin Hamiltonian approach, on the other hand, the pair energy levels are given by the eigenvalues of the matrix arising from the Hamiltonian $\mathcal{H}=\mathbf{S}_1\cdot\mathbf{K}\cdot\mathbf{S}_2$ acting on the basis states $|+_1+_2\rangle$, $|+_1,-_2\rangle$, $|-_1+_2\rangle$, and $|-_1,-_2\rangle$, where $|\pm_1\rangle$ and $|\pm_2\rangle$ are the effective-spin-$\frac{1}{2}$ representations of the lowest Kramers doublets. The contributions of $\mathcal{H}_{12}$ to the effective spin-$\frac{1}{2}$ interaction tensor **K** may then be obtained by first making the matrix $(|\mathcal{H}_{\text{eff}}|)$ traceless and then equating corresponding elements of the two matrices. Thus, for example, the diagonal terms in **K** are given by

$$\begin{aligned} K_{zz} &= 2(+\,+||-\,-)_J - 2(+\,-||+\,-)_J\,, \\ K_{xx}+K_{yy} &= 2(+\,-||-\,+)_J + 2(-\,+||+\,-)_J\,, \\ K_{xx}-K_{yy} &= 2(+\,+||-\,-)_J + 2(-\,-||+\,+)_J\,, \end{aligned} \tag{15}$$

and the off-diagonal elements of **K** may be obtained in a similar manner. In the above formulas, we have written $(||)_J$ to represent $(G_1G_2|\mathcal{H}_{\text{eff}}|G_1'G_2')_J$ as given by Eq. (14). The subscript J implies that the perturbation theory is to be carried out between the J states and not within the effective spin-$\frac{1}{2}$ doublets.

ii. Application to Ce^{3+} Pairs in $LaCl_3$

We now apply the above theory to the particular case of Ce^{3+} pairs in LaCl_3. From Eq. (11) we might expect that the first-order effect of successive terms in the EMI Hamiltonian will each be a factor of

$$\epsilon_{ll'}\langle r^{l+2}\rangle/\epsilon_{l+2,l'}\langle r^l\rangle R_{12}^2$$

smaller than the preceding one. Thus for the nn pairs, using the values for $\langle r^l\rangle$ calculated for Ce^{3+} by Freeman and Watson,[33] we find that the ratio of the 2, 4 to the 2, 2 terms is given by

$$(1/24)(\epsilon_{22}/\epsilon_{24})\,.$$

However, as mentioned above, the effective dielectric constants for the different terms could possibly differ by an order of magnitude, and it is certainly not obvious that it is sufficient to consider only the first term, EQQ, in the multipole expansion. In Sec. 7 we shall see that there is experimental evidence that in the present case the EQQ is in fact dominant, and only this will be considered in detail here.

The Q-coefficient matrices for the EQQ are found from Eq. (12) to be

$$Q_{22}(\text{nn}) = \begin{bmatrix} 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 4 & 0 \\ 0 & 0 & 6 & 0 & 0 \\ 0 & 4 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{bmatrix} \tag{16}$$

and

$$Q_{22}(\text{nnn}, \theta_0=63.2°) = \begin{bmatrix} 2.777 & 2.806 & 0.516 & -0.793 & -0.207 \\ 2.806 & 0.843 & -1.943 & -0.826 & 0.793 \\ 0.516 & -1.943 & -1.239 & 1.943 & 0.516 \\ -0.793 & -0.826 & 1.943 & 0.843 & -2.806 \\ -0.207 & 0.793 & 0.516 & -2.806 & 2.777 \end{bmatrix}, \tag{17}$$

where the matrix indices m, m' go from -2 to $+2$.

As a first approximation, the wave functions for the single-ion Ce^{3+} in LaCl_3, given in Table II, may be taken as pure $|\frac{5}{2},\pm\frac{5}{2}\rangle$, $|\frac{5}{2},\pm\frac{1}{2}\rangle$, and $|\frac{5}{2},\pm\frac{3}{2}\rangle$. In this and the following calculations we omit the small terms arising from the $J=\frac{7}{2}$ admixtures.

The contributions to the static crystal field are then given by

$$\begin{aligned} \mathcal{H}_{\text{CF1}}(\text{nn}) &= \langle\tfrac{5}{2}|\mathcal{H}_{12}(\text{nn})|\tfrac{5}{2}\rangle = 30A_{22}(\text{nn})\tilde{O}_2^0 \\ &= 15A_{22}(\text{nn})O_2^0\,, \end{aligned} \tag{18}$$

$$\begin{aligned} \mathcal{H}_{\text{CF1}}(\text{nnn}) &= 2.58A_{22}(\text{nnn})(\tilde{O}_2^2+\tilde{O}_2^{-2})+9.72A_{22}(\text{nnn}) \\ &\quad\times(\tilde{O}_2^1-\tilde{O}_2^{-1})-6.20A_{22}(\text{nnn})\tilde{O}_2^0 \\ &= 2.58\tfrac{1}{2}(\surd 6)A_{22}(\text{nnn})O_2^2-9.72(\surd 6) \\ &\quad\times A_{22}(\text{nnn})O_2^1-3.10A_{22}(\text{nnn})O_2^0\,, \end{aligned} \tag{19}$$

where the O_n^m are the conventional crystal field operator equivalents as defined by Elliott and Stevens.[54] The contributions to the **g** tensor are found to be

$$\Delta\mathbf{g}_{\text{nn}} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \qquad \Delta\mathbf{g}_{\text{nnn}} = \begin{bmatrix} 0 & 0 & 1.85A_{22}(\text{nnn}) \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \tag{20}$$

and the contributions to the interaction tensors are

$$\mathbf{K}_{\text{nn}}^{\text{EQQ}} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 137[A_{22}(\text{nn})]^2 \end{bmatrix}, \qquad \mathbf{K}_{\text{nnn}}^{\text{EQQ}} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -134[A_{22}(\text{nnn})]^2 \end{bmatrix}. \tag{21}$$

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[59] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Co., New York, 1955), 2nd ed., p. 155.

We see that for a nn pair the EQQ alters the O_2^0 term in the single-ion crystal field, but it does not remove the axial symmetry. For the nnn, however, the EQQ both alters the O_2^0 term and introduces new terms O_2^1 and O_2^2, ruled out for the single ion by the C_{3h} symmetry. For the nn there is no first-order change in the **g** tensor. However, for the nnn a new term $g_{xz}=1.85A_{22}(\text{nnn})$ appears in the **g** tensor. This term arises from the $\tilde{O}_2^0\tilde{O}_2^{\pm1}$ terms in Eq. (11). Finally, for both the nn and nnn the EQQ contributes only to the Ising term K_{zz} in the appropriate interaction tensor. For the nn it gives an antiferromagnetic coupling of $137[A_{22}(\text{nn})]^2$ and for the nnn a ferromagnetic coupling of $-134[A_{22}(\text{nnn})]^2$. Note that the EQQ does not contribute to any of the other elements of K_{nn} and K_{nnn} in second order simply because such terms necessitate a coupling of the $|\frac{5}{2},\frac{5}{2}\rangle$ state to the $|\frac{5}{2},-\frac{5}{2}\rangle$, that is, $\Delta M_J=5$, whereas EQQ in second order only allows terms of $\Delta M_J\leq 4$.

When similar calculations are carried out for the higher-degree terms in the multipole expansion, it is found that 2-4 and 4-4 terms, and also cross terms between the various multipole terms, contribute to g_{xx} and g_{yy} as well as to g_{xz}.[60] Finally, it is of interest to point out that in the approximations that we have made here, the EMI does not contribute at all to g_{xy}, g_{yz}, K_{xy}, or K_{yz} in any order as long as the wave functions are real. This follows simply because the numerical coefficients in the EMI Hamiltonian, Eqs. (11) and (12), are all real. From a physical point of view, this means that by choosing an isotropic scalar dielectric constant we have implicitly assumed reflection symmetry on the plane defined by the bond axis and the Z axis, and this automatically rules out the above terms.

It is therefore clear that EMI, and particularly EQQ, may account for some or all of the observed tensors **g** and **K** if the parameters are suitably chosen. The magnitudes required will be discussed in more detail in the next section.

7. INTERPRETATION OF EXPERIMENTAL RESULTS

In the previous section we have enumerated the different types of interaction that we might expect to give a sizeable contribution to the coupling between Ce^{3+} ions. In this section we shall interpret the measured tensors **K** and **g** in terms of these interactions and shall show that there is, in fact, clear and unambiguous evidence for contributions from each of magnetic dipolar, anisotropic exchange, and electric multipole-multipole interaction.

A. Dipolar Interaction

We have seen that the magnetic dipolar interaction accounts adequately for the measured interaction between the more distant ions. We therefore consider below only the nn and nnn interactions. The dipolar interaction contributes additively to both $\mathbf{K}_{\text{nn}}$ and $\mathbf{K}_{\text{nnn}}$ in a known manner; its effects have been allowed for in Sec. 6 A, leaving the nondipolar contributions to the tensors summarized in Table VII.

B. EMI

A comparison of Eq. (11) with Eq. (8) shows that it is, in principle, difficult to distinguish between the EMI and the general anisotropic exchange interaction. [Indeed, the general VPC, Eq. (9), also has the same form, but we have shown that its contribution will be negligible in our case.] However, the EMI Hamiltonian involves only terms of even degree and consequently can contribute to **K** only in second order. The anisotropic exchange, on the other hand, can involve terms of both odd and even degree, and the odd terms will contribute to **K** in first order. Both contribute to $\Delta\mathbf{g}$ in second order with the Zeeman term. By considering the contributions in different orders, it is possible to distinguish between the two forms of interaction quite unambiguously.

In Sec. 6 we showed that only a very large, and totally unreasonable, value of bilinear anisotropic exchange could give rise to the observed value of $\Delta g^{\text{nnn}}{}_{xz}$. Although this estimate was made on a simple model, we should expect that the order of magnitude would still hold for the more general form of anisotropic exchange, Eq. (8). Indeed, we find that the size of $\mathcal{G}_{22}{}^{01}$ required to give the observed g shift is about 20 times the maximum expected exchange interaction. Furthermore, if such large anisotropic exchange terms did exist, there would almost certainly be correspondingly large contributions in first order to **K**, particularly to $K^{\text{nnn}}{}_{zz}$, which are not observed. We therefore conclude that the g shift $\Delta g^{\text{nnn}}{}_{xz}$ can only arise through the EMI.

If we first consider the EQQ alone, a comparison of the theoretical contributions to $\Delta\mathbf{g}_{\text{nn}}$ and $\Delta\mathbf{g}_{\text{nnn}}$, Eq. (20), with the experimental values in Table V reveals that the forms of the matrices are identical in each case. That is, no g shift is predicted for the nn, and none is observed. For the nnn, only Δg_{xz} is found to be nonzero, as predicted by the simple form of EQQ discussed in Sec. 6. We may note that this agreement is partially a result of our choice of φ_n. A different choice could result in a nonzero value of $\Delta g^{\text{nnn}}{}_{yz}>\Delta g^{\text{nnn}}{}_{xz}$, and this would imply a highly anisotropic ϵ tensor if interpreted on the basis of EMI. However, without any further experimental information to remove the ambiguity in φ_n, it seems most reasonable to assume that our choice is the correct one.

Any higher-degree EMI terms would give comparable contributions to $g^{\text{nnn}}{}_{xx}$ and $g^{\text{nnn}}{}_{yy}$, and to $g^{\text{nnn}}{}_{xz}$. Since no shifts are observed either in $g^{\text{nnn}}{}_{xx}$ or $g^{\text{nnn}}{}_{yy}$ (Table V), it is clear that the higher-degree terms are of smaller magnitude than the predominant EQQ. We may there-

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[60] J. D. Riley (private communication).

fore use the measured $\Delta g^{\mathrm{nnn}}{}_{xz}$ to determine the actual magnitude of the EQQ coupling coefficient for the nnn. We find from Eq. (20) that $A_{22}(\mathrm{nnn})=0.035(\pm0.002)$ cm^{-1}, and, using Eq. (11), this gives a value for $(\langle r^2\rangle)/[\epsilon_{22}(\mathrm{nnn})]^{1/2}=0.50\ (\pm0.02)$ Å^2.[61] We believe this to be the first quantitative measurement of the magnitude of EQQ between rare-earth ions.

It is of interest to compare the measured value of $\langle r^2\rangle/[\epsilon_{22}(\mathrm{nnn})]^{1/2}$ with the value of $\langle r^2\rangle=0.34$ Å^2 calculated for the free Ce^{3+} ion by Freeman and Watson.[33] Although at first sight this agreement appears to be very good, it is perhaps surprising in view of the expected shielding of the field gradient seen by the $4f$ electrons through the quadrupolar polarization of the outer $5s$ and $5p$ shells.[62,63] This shielding should reduce the effective quadrupole moment of the Ce^{3+} ion by about 70%.[62,64] The experimental value implies, therefore, the existence of an antishielding by the intervening ligands of slightly larger magnitude, giving rise to a net value of $\epsilon_{22}(\mathrm{nnn})=0.5$. However, we may note that Sroubek *et al.* have discussed a case where the experimental results could be explained by a point-charge model with no $5s$-$5p$ shielding.[65]

Having established the existence of an EQQ between nnn ions through the value of $\Delta g^{\mathrm{nnn}}{}_{xz}$, we now consider its effect on the crystal field and its contribution to the interaction tensor **K**.

Using Eqs. (18) and (19), the contribution of the first-order EQQ to the crystal field in CeCl$_3$ is found to be

$$[A_2{}^0\langle r^2\rangle]_{\mathrm{EQQ}}=(1/\chi_2)[30A_{22}(\mathrm{nn})-18.6A_{22}(\mathrm{nnn})]. \quad (22)$$

Using standard crystal-field theory, it may easily be shown that the difference in energy of the first excited state of a Ce^{3+} ion in LaCl$_3$ and in CeCl$_3$, due to the quadrupoles at the Ce^{3+} sites in CeCl$_3$, is given at low temperatures by

$$\Delta E_{\pm1/2}=-18[30A_{22}(\mathrm{nn})-18.6A_{22}(\mathrm{nnn})]. \quad (23)$$

Experimentally, the level is found to shift from 38 cm^{-1} in LaCl$_3$ (Table II) to ~41 cm^{-1} in CeCl$_3$.[34] This experimental shift will include nonmagnetic changes as well as those due to EQQ but we expect these to be at most a few cm^{-1}. Using Eq. (23) together with the experimental shift and the value of $A_{22}(\mathrm{nnn})$ obtained from $\Delta g^{\mathrm{nnn}}{}_{xz}$, we find $A_{22}(\mathrm{nn})=0.016(\pm0.011)$ cm^{-1}, where the error includes an uncertainty of 6 cm^{-1} in the nonmagnetic contribution. Using Eq. (11), this value for $A_{22}(\mathrm{nn})$ corresponds to a value of $\epsilon_{22}(\mathrm{nn})=3.5\epsilon_{22}(\mathrm{nnn})$.

The above nonuniformity between nn and nnn dielectric constants would indicate that the ligands do indeed play a central role in the EQQ. If this interpretation is correct, then we might also expect that the antishielding would be anisotropic,[10] thus destroying the simple geometrical relationship between the different terms of the EQQ in Eq. (12). Unfortunately, we have insufficient experimental data to test this. Strictly speaking, we have really only determined through $\Delta g^{\mathrm{nnn}}{}_{xz}$ the coefficient of $\tilde{O}_2{}^0\tilde{O}_2{}^{\pm1}$ in the nnn EQQ Hamiltonian, and we must use the simple approximation of a scalar pair dielectric constant to relate this to other quantities.[66]

The contribution of EQQ to the interaction tensors may now be calculated using Eq. (21) and the above values for $A_{22}(\mathrm{nn})$ and $A_{22}(\mathrm{nnn})$. The results are given in the third row of Table VII; the errors quoted do not include any possible uncertainty in the theoretical relationship used. We see that the EQQ makes a significant contribution to $K^{\mathrm{nnn}}{}_{zz}$ and a somewhat smaller contribution to $K^{\mathrm{nn}}{}_{zz}$. Both these contributions have signs favoring solution 1 as the correct alternative. However, EQQ cannot account at all for the observed values of $K^{\mathrm{nn}}{}_{\perp}$ or $K^{\mathrm{nnn}}{}_{\perp}$ even if the most general form of interaction is used.

C. Superexchange

Although the above estimates of the contributions of the EQQ interaction to the **K** tensors may carry sizeable theoretical uncertainties, it is clear that significant contributions from exchange are also required to explain the experimental results. We have seen in Sec. 6 that the usual bilinear exchange interaction may contribute to $K^{\mathrm{nn}}{}_{zz}$ and $K^{\mathrm{nnn}}{}_{zz}$, and indeed will account for the difference between the EQQ and experimental values. The sign of the estimated exchange interaction, based on the results of I and II, again favors solution 1 in Table VII.

The existence of the comparatively large values of $K_{\perp}$ in Table VII presents an interesting problem. Since the ground Ce^{3+} doublet is very nearly pure $|J=\frac{5}{2},\ M_J=\pm\frac{5}{2}\rangle$, any interaction of low degree will make no contribution to $K_{\perp}$; in fact, since matrix elements between the Kramers conjugate states involve $\Delta M_J=\pm5$, we require an operator of at least fifth degree. Since $J=\frac{5}{2}$, the only such operator acting in first order is $\tilde{O}_5{}^{+5}\tilde{O}_5{}^{-5}$, that is, an operator of the form $J_+{}^5(1)J_-{}^5(2)$. From the discussion of Sec. 6, this can only arise from anisotropic superexchange of the Levy-Elliott-Thorpe form. We thus have the remarkable result that for Ce^{3+} pairs in LaCl$_3$ the effects of the fifth-degree superexchange terms are as large as those of the more usual $\mathbf{J}_1\cdot\mathbf{J}_2$ terms. Using $K^{\mathrm{nnn}}{}_{\perp}$ of solution 1, we find $\mathcal{J}_{55}{}^{5-5}(\mathrm{nnn})=5.9\times10^{-6}(\pm1.5)$ cm^{-1}. Note that this

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[61] The errors quoted arise wholly from the experimental uncertainties and do not include any possible deficiences in the theory.

[62] R. M. Sternheimer, Phys. Rev. **146**, 140 (1966).

[63] A. J. Freeman and R. E. Watson, Phys. Rev. **139**, A1606 (1965).

[64] D. T. Edmonds (private communication).

[65] Z. Sroubek, M. Tachiki, P. H. Zimmermann, and R. Orbach, Phys. Rev. **165**, 435 (1968).

[66] In Refs. 3 and 35, the even simpler model where $\epsilon_{22}(\mathrm{nn})=\epsilon_{22}(\mathrm{nnn})=\epsilon$ was used. However, this is inconsistent with the recent measurements of the crystal field levels in CeCl$_3$.

coefficient multiplies large matrix elements, of $\sim 10^4$, so that its small absolute magnitude is somewhat misleading with regard to its effect.

8. SUMMARY AND CONCLUSION

The pair spectra from both nn and nnn Ce^{3+} ions in $LaCl_3$ have been fitted to a general spin Hamiltonian in order to obtain values for the relevant parameters. These are the $\mathbf{g}$ tensors and certain terms in the interaction tensors $\mathbf{K}$. By using the pair measurements together with measurements of the bulk magnetic properties of $CeCl_3$, values for all the terms in the interaction tensors $\mathbf{K}$ have been deduced.

The various interaction mechanisms between rare-earth ions, and their effects on the pair energy levels and EPR spectrum, have been discussed in some detail. In general, it is difficult to make an unambiguous identification of the mechanisms present. However, by careful consideration of the manner in which each interaction contributes in different orders of perturbation, and the selection rules involved, it is possible to isolate individual coupling terms in certain cases.

From the measured pair $\mathbf{g}$ tensors we have been able to demonstrate the existence of an appreciable electric quadrupole-quadrupole coupling between the nnn ions, and also the absence of any significant higher-degree EMI. The magnitude of the EQQ and its variation between different neighbors indicate that the ligand ions play an important role in the interaction.

The interaction tensors are found to contain contributions from magnetic dipole, electric quadrupole-quadrupole, and anisotropic superexchange interactions. The first of these, the magnetic dipolar interaction, is found to account almost completely for the more distant neighbor pair interactions. For the nn and nnn pairs there are significant contributions from all three mechanisms. However, it is found that certain terms in the interaction tensor can only be accounted for by a generally anisotropic superexchange of the form suggested by Levy and by Elliott and Thorpe. In particular, we find evidence for terms of the form $J_+^5 J_-^5$, having matrix elements of magnitude comparable with those of the more usual bilinear exchange interaction.

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APPENDIX A: ADDITIONAL OBSERVED TRANSITIONS

Several additional transitions besides those discussed in Sec. 5 were observed in the 1%-Ce^{3+} sample. These were also observed along with further lines in some of the more concentrated samples. We shall discuss these only briefly, and merely suggest their possible origin.

The two lines at -401 and $+438$ G relative to the single-ion line [Fig. 2(a)] were observed in all the samples investigated, though their intensities varied somewhat randomly. When the magnetic field was varied in angle away from the c axis, they split up and became unobservable at angles greater than 15°. On reducing the temperature, both lines disappeared at the K band, at about 2.5°K. The splitting between these lines coincides within the experimental error with Nd^{3+} transitions observed by Baker and Riley[67] in their investigation of Nd^{3+}-Ce^{3+} pairs. The lines that they observe have surprisingly large intensities, and consequently the observed transitions in our samples could easily arise from Ce^{3+}-Nd^{3+} pairs due to the small concentration of Nd^{3+} impurity in our samples. The lines at -194 and $+229$ G also have the same separation as transitions observed in the Nd^{3+}-Ce^{3+} pair system of Baker and Riley, and split off axis. The line at -166 G splits off axis, but its source has not been positively identified. Further similar small lines with angular variations not consistent with Ce^{3+} pair transitions were observed in some samples.

Small lines at -489 and $+397$ G, not present in the spectrum shown in Fig. 2(a), were observed in one of the 1%-Ce^{3+} samples and in the 5%-Ce^{3+} samples. In the 10% samples each pair line had "satellites" at -722, -413, $+428$, and $+720$ G. All these lines followed the angular variation of the pair lines quite closely out to 65°; however, their intensities did not seem to have a direct relation with the concentration of Ce^{3+} ions. These lines are certainly not due to Ce^{3+} pairs but could arise from cerium transitions in a Ce^{3+}-impurity ion nn pair. In the 10% sample the satellite lines could arise from triads of Ce^{3+} ions. However, none of these lines has been positively identified.

APPENDIX B: EPR OF CONCENTRATED $CeCl_3$

The EPR spectrum of concentrated $CeCl_3$ was investigated in several oriented spherical samples at 25.0 GHz and at temperatures from 4.2 to 1.3°K. In all cases, when the magnetic field was applied along the c axis, a single exchange-narrowed transition with a maximum derivative peak-to-peak linewidth of about 200 G was observed. No real attempt was made to extract any information about the interactions from the second and fourth moments.

Qualitatively, however, the line shape may be understood on the basis of the Van Vleck theory of resonance-

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[67] J. M. Baker and J. D. Riley (private communication).

line moments. Van Vleck has shown that at high temperatures it is sufficient to consider a truncated Hamiltonian which in our notation is given by

$$\mathcal{H}=g_{\parallel}\mu_B H\sum_j S_{zj}+\sum_{k>j}(K_{\parallel jk}-K_{\perp jk})S_{zj}S_{zk}+\sum_{k>j}K_{\perp jk}\mathbf{S}_j\cdot\mathbf{S}_k.$$

The term in $\mathbf{S}_j\cdot\mathbf{S}_k$ does not contribute to the second moment at all, but it does contribute to the fourth and higher moments. In cases where the $K_{\perp jk}$ are small, that is, when the interactions between the effective spins are mainly Ising, one expects to see a broad line which in simple cases may have structure corresponding to the different relative orientations of the nn. On the other hand, if the $K_{\perp jk}$ terms are comparable with, or larger than, the $K_{\parallel jk}-K_{\perp jk}$ terms, then one observes an effective narrowing of the line due to the increased fourth moment. This is known as "exchange narrowing," although in the effective spin Hamiltonian approach the actual mechanism giving rise to the isotropic term may not be the exchange interactions at all.

From Table IV it may be seen that for both solutions 1 and 2 appreciable $K_{\perp jk}$ terms are found for Ce^{3+} pairs in $LaCl_3$, so that we would expect to see a single exchange-narrowed resonance line in the concentrated material. A prediction of the actual linewidth, however, requires a detailed theory for the line shape. Qualitatively, however, this is in fact what we observe experimentally.

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Data and Speculations on the Electronic Problem for the Relaxed Excited *F* Center*

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The energies of absorption and emission peaks, the lifetime of the relaxed excited state, and the ionization energies of the relaxed excited state of the *F* center in NaF, KF, RbF, RbBr, and RbI have been studied down to the temperature of liquid He. The low-temperature shapes of the absorption and emission *F* bands, which have not been previously reported, are also shown. The data on these crystals represent limiting cases from several points of view and allow us to extend considerably the range of the parameters under study. As a consequence, the phenomenology now at our disposition is much more significant and allows us to propose a simple and realistic solution to the problem of the magnitude of τ_R. For the situation in which the *F* center is excited and relaxed, arguments in favor of the $2p$ level being lower in energy than the $2s$ are discussed.

I. INTRODUCTION

Many efforts have been devoted in the last few decades to the understanding of the *F*-center absorption phenomenology, and in the following this problem will not be dealt with, since the basic facts are by now rather well understood.

The situation for the *F*-center emission has by no means reached a similar level of development. A great amount of fundamental data both on the electronic and on the electron-phonon interaction problem are still lacking. Among the unanswered questions in this subject are the following.

(i) the theoretical prediction of the fraction of the absorbed energy given to the lattice and the fraction emitted;

(ii) the process through which the electron "forgets" the polarization due to the exciting electric field;

(iii) the mean time after which the emitted photon will emerge from the *F* center, restoring the electron to the ground state;

(iv) details concerning the number of channels through which the *F* center can be de-excited—even though the most obvious ones are known;

(v) information regarding the terms system after the lattice relaxes (in other words, the energy levels associated with the *K* band in absorption[1] do not reveal their

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[1] G. Spinolo and D. Y. Smith, Phys. Rev. **140**, A2117 (1965); D. Y. Smith and G. Spinolo, *ibid.* **140**, A2121 (1965).