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Magnetic Interactions between Rare-Earth Ions in Insulators. II. Electron-Paramagnetic-Resonance Measurements of Gd^{3+} Pair and Gd^{3+}-Eu^{3+} Interaction Constants in $EuCl_3$†*

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Paramagnetic resonance has been observed from both single ions and isolated pairs of Gd^{3+} in $EuCl_3$ at 77°K and 25.6 GHz. The pair spectra were analyzed in the same way as those observed previously from Gd^{3+} in $LaCl_3$. The results give accurate values for the interaction parameters between both nearest (nn) and next-nearest neighbors (nnn). The dominant terms are of the form of isotropic exchange ($J\mathbf{S}_1\cdot\mathbf{S}_2$), with $J_{\mathrm{nn}}(\mathrm{pair})=0.0488\pm0.0010\ \mathrm{cm}^{-1}$ and $J_{\mathrm{nnn}}(\mathrm{pair})=-0.0637\pm0.0020\ \mathrm{cm}^{-1}$. The anisotropic parts of the interactions could be accounted for completely by the calculated magnetic dipole-dipole coupling. Combining these results with earlier measurements in $LaCl_3$, good estimates can be made of the exchange interactions in pure $GdCl_3$: $J_{\mathrm{nn}}(GdCl_3)=0.056\pm0.006\ \mathrm{cm}^{-1}$ and $J_{\mathrm{nnn}}(GdCl_3)=-0.064\pm0.003\ \mathrm{cm}^{-1}$. These values are in excellent agreement with those inferred from analyses of susceptibility and specific-heat measurements, and they resolve unambiguously earlier uncertainties in the choice of possible parameters. The magnitudes and even the *signs* of the interactions remain unexplained. From measured g-value shifts relative to Gd^{3+} in $LaCl_3$ it was also possible to estimate the isotropic part of the $Gd^{3+}-Eu^{3+}$ exchange interaction: $J_{\mathrm{nn}}(\mathrm{Gd-Eu})=0.052\pm0.030\ \mathrm{cm}^{-1}$ and $J_{\mathrm{nnn}}(\mathrm{Gd-Eu})=-0.061\pm0.030\ \mathrm{cm}^{-1}$. The similarity of these results to the corresponding $Gd^{3+}-Gd^{3+}$ interactions suggests that the average electron-electron exchange interaction may be relatively insensitive to the particular configuration of the individual ions, as proposed theoretically by Van Vleck. On the other hand, comparisons between the results for different isostructural lattices shows that some of the interactions can be extremely sensitive to even small changes in the neighbor distances, and great care is therefore required in extrapolating from one lattice to another.

1. INTRODUCTION

In a preceding paper,[1] henceforth referred to as I, we have described in some detail a method of determining the magnetic and exchange interactions between pairs of Gd^{3+} ions in $LaCl_3$ from their electron-paramagnetic-resonance (EPR) spectra. The method involves the measurement and identification of the pair line positions for known orientations of the magnetic field and is applicable whenever the isotropic part of the interactions is comparable in magnitude to other interactions present. The high accuracy of the method made it possible to study the variation of the interaction constants with temperature, and hence as a function of the mean ionic separation. Significant changes were observed, which suggested that quite large extrapolations would be required if the pair results were to be applied to concentrated $GdCl_3$. However, the range over which the mean ionic separation can be varied by changing the temperature is very limited, and in order to make a quantitative extrapolation, measurements over a larger range are required.

In this paper we report measurements on Gd^{3+} pairs in $EuCl_3$, a host lattice which is isostructural to both $LaCl_3$ and $GdCl_3$ and has lattice constants intermediate between the two. In principle one might hope to be able to extend measurements of this kind also to the other hexagonal trichlorides ($CeCl_3$, $PrCl_3$, $SmCl_3$), inasmuch as previous experiments on fast relaxing paramagnetic ethylsulphates gave Gd^{3+} resonances without excessive line broadening.[2] Experiments showed, however, that in the trichlorides no such relaxation narrowing occurs and only broad resonances with no structure were observed. The reason for the difference from the ethylsulphates is not clear.

Fortunately, $EuCl_3$ forms an almost ideal host lattice for Gd^{3+} pair measurements because its lattice constants are very close to those of $GdCl_3$, and only a small extrapolation of the pair-exchange constants is therefore necessary in order to relate them to those in $GdCl_3$. There will also be little distortion in the environment of the Gd^{3+} pairs, making it possible to estimate the dipolar interaction with only a small error. This in turn enables us to obtain an upper limit of any possible anisotropic exchange present which will be rather more accurate than previous estimates made from the experiments in $LaCl_3$.

To a first approximation, $EuCl_3$ may be treated as a diamagnet at low temperatures. The electronic ground state is $^7F_0$ and this exhibits only a weak temperature-independent paramagnetism due to second-order admixtures with the excited state $^7F_1$ at about 370 cm^{-1}. To first order the low-temperature Gd^{3+} spectrum will therefore be unaffected by the Eu^{3+} environment and pair spectra may be observed similar to those in diamagnetic $LaCl_3$. In second order the weak paramagnetism shifts the Gd^{3+} spectra in a manner described

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[1] M. T. Hutchings, R. J. Birgeneau, and W. P. Wolf, Phys. Rev. 168, 1026 (1968).

[2] H. E. D. Scovil, thesis, Oxford University, 1951 (unpublished).

by Hutchings and Wolf.[3] The part of the shifts which can be represented as change in the g values is proportional to the interactions with the Eu^{3+} neighbors, and thus by measuring the g values of single ions and Gd^{3+} pairs it is possible to deduce the Gd^{3+}-Eu^{3+} interaction for both nearest and next-nearest neighbors. Although the accuracy of this method is inherently low, it allows some interesting comparisons of the exchange interactions between $(4f)^6$ and $(4f)^7$ configurations.

The crystal structure and lattice parameters of $EuCl_3$ will be described briefly in Sec. 2. In Sec. 3 the spin Hamiltonian for a pair of ions is summarized, and the theory of the shifts in the $\mathbf{g}$ tensor expected for single Gd^{3+} ions and Gd^{3+}-Gd^{3+} pairs in $EuCl_3$ is discussed. The experimental measurements and results are discussed in Sec. 4 and their interpretation in Sec. 5. The values found for the interaction parameters are compared with previous results in $LaCl_3$ and $GdCl_3$ in Sec. 6.

2. CRYSTAL STRUCTURE

The crystal structure of $EuCl_3$ is identical to that of $GdCl_3$ and $LaCl_3$,[4] which has been described previously. (See Fig. 2 of I.) In this structure all the rare-earth ions are magnetically equivalent and each has two nearest neighbors (nn) at a distance c along the hexagonal crystal axis and six next-nearest neighbors (nnn) at a distance $r_{\mathrm{nnn}}=(\frac{1}{4}c^2+\frac{1}{3}a^2)^{1/2}$. The lattice constants are summarized in Table I, and it can be seen that the ionic separations in $EuCl_3$ lie very close to those in $GdCl_3$. No published data are available on the Cl positions in $EuCl_3$ but B. Morosin (private communication) has recently shown that they are very similar to those in $GdCl_3$, as one might expect.

3. THEORY

A. First-Order Spin Hamiltonian

To first order the spin Hamiltonians for both single ions and pairs take the same form as described in I. For the single ions the principal terms are those due an axial crystal field and an applied magnetic field, and for the pairs there are additional terms due to isotropic exchange and magnetic dipole interactions, plus various other very small terms as described in Sec. 5 C of I. The corresponding approximate spin Hamiltonian for a pair is thus

$$\mathcal{H}^{(0)}(1,2)=g\mu_BH_z(S_1{}^z+S_2{}^z)+J\mathbf{S}_1\cdot\mathbf{S}_2+\alpha(\mathbf{S}_1\cdot\mathbf{S}_2-3S_1{}^zS_2{}^z)$$
$$+\sum_{i=1,2}\left(\frac{b_2{}^0}{3}O_2{}^0(i)+\frac{b_4{}^0}{60}O_4{}^0(i)+\frac{b_6{}^0}{1260}O_6{}^0(i)\right),\quad(1)$$

where $\alpha=g^2\mu_B{}^2/r^3$ and the other symbols have their usual meanings, as defined in I. (Here μ_B is again taken to be a positive quantity.) We shall see that we might expect Eq. (1) to be a somewhat poorer approximation for the nnn pairs than in the case of $LaCl_3$, because of the larger crystal-field terms present in $EuCl_3$. Nevertheless, the terms in Eq. (1) still represent the major interactions responsible for the pair spectra.

TABLE I. Lattice constants of $LaCl_3$, $EuCl_3$, and $GdCl_3$ (Å).

	a	$c(=r_{\mathrm{nn}})$	r_{nnn}
$LaCl_3$	7.483[a]	4.375[a]	4.843
$EuCl_3$	7.369[a]	4.133[a]	4.730
$GdCl_3$	7.363[a]	4.105[a]	4.721

[a] Measured at room temperature (see Ref. 4). B. Morosin (private communication) has recently redetermined a number of the lattice parameters of the trichlorides and has found some minor discrepancies with the values given above. However, the uncertainties due to the so far undetermined thermal-contraction effects are much larger than these, and we shall therefore use the published values reduced by an estimated 0.3% to allow for contraction at 77°K and below (see Ref. 1).

To a first approximation we would also expect the parameters in Eq. (1) to be rather similar to those found in $LaCl_3$, with relatively small differences produced by the changes in structure, but there is one interesting and significant shift which is produced by the fact that an Eu^{3+} environment is not completely nonmagnetic, which we consider next.

B. Interaction Induced g Shifts in Hamiltonians

1. General Theory

Because $EuCl_3$ is, in fact, weakly paramagnetic, we may expect small shifts in the spin-Hamiltonian parameters from the values they would have in an otherwise identical diamagnetic lattice. These shifts will arise from magnetic or exchange interactions between the Gd^{3+} ions and neighboring Eu^{3+} host ions. The theory of the interaction shifts in host lattices having a "nonmagnetic" singlet ground state has been given by Hutchings and Wolf[3] and developed fully for the particular case of a host lattice of Eu^{3+} ions by Hutchings, Windsor, and Wolf.[5] We may take over the detailed theory given in the latter paper, and will here give only the main results.

The positions of the $^7F_1$ levels of Eu^{3+} in $LaCl_3$ have been determined by DeShazer and Dieke.[6] They find a doublet at 355 cm^{-1} and a singlet at 405 cm^{-1}. We would expect the corresponding levels in $EuCl_3$ to lie close to this, and for our purposes here it is sufficient to take them as degenerate at their mean energy of $\Delta=370$ cm^{-1}. This simplification may be shown to introduce an error of much less then that associated with the experimental measurements. Other high-lying

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[3] M. T. Hutchings and W. P. Wolf, Phys. Rev. Letters **11**, 187 (1963).

[4] W. H. Zachariasen, J. Chem. Phys. **16**, 254 (1948); D. M. Templeton and C. H. Dauben, J. Am. Chem. Soc. **76**, 5237 (1954); C. Au and R. Au, Acta Cryst. **23**, 1112 (1967).

[5] M. T. Hutchings, C. G. Windsor, and W. P. Wolf, Phys. Rev. **148**, 444 (1966).

[6] L. G. DeShazer and G. H. Dieke, J. Chem. Phys. **38**, 2190 (1963).

levels do not affect the low-temperature g shift to second order.

Following Ref. 5, we shall describe the basic interaction between one particular Gd^{3+} ion and one of the neighboring Eu^{3+} ions by

$$\mathcal{H}=\mathbf{S}(\mathrm{Gd})\cdot\mathbf{K}\cdot\mathbf{S}(\mathrm{Eu}),\tag{2}$$

where $\mathbf{K}$ is a second-rank tensor reflecting the symmetry of the interactions. It should be noted that this is not of the most general form possible, as discussed by Levy,[7] and also more recently by Tachiki and Sroubeck and by Huang and Van Vleck.[8] However, for the present purpose of calculating the g-value shifts, which involve cross terms between the Zeeman and interaction Hamiltonians, Eq. (2) is, in fact, the most general spin Hamiltonian, since it can represent in a completely general way all the requisite matrix elements of *any* interaction between the $J=0$ and $J=1$ states of the Eu^{3+} ion and within the ^8S ground state of Gd^{3+}. For shifts in the other spin-Hamiltonian parameters, higher-order orbital anisotropy will be important.[8] In our particular case the g shifts are very small, and we shall therefore have to approximate Eq. (2) further to pick out the dominant isotropic exchange term.

We choose axes with $g_{zz}(\equiv g_{||})$ along the c axis and g_{xx} in the plane containing two nnn ions and the central Gd^{3+} ion. The shift in the $\mathbf{g}$ tensor describing the additional Zeeman interaction,

$$\mathcal{H}_z'=\mu_B\mathbf{H}\cdot\mathbf{\Delta g}\cdot\mathbf{S}(\mathrm{Gd}),$$

is then given by[5]

$$\mathbf{\Delta g}=\frac{-8}{\Delta}\sum_j \mathbf{Q}(j)\cdot\mathbf{K}^T\cdot\mathbf{Q}(j)^{-1}.\tag{3}$$

Here $\mathbf{K}^T$ denotes the transpose of the interaction tensor $\mathbf{K}$ and j labels the neighboring Eu^{3+} ions. $\mathbf{Q}(j)$ is a rotation matrix taking a vector pointing along the bond axis between the Gd^{3+} and neighbor $j=1$, into vectors pointing along the jth neighbor bond. The matrices $\mathbf{Q}(j)$ thus form a representation of the point group of the particular site. The rotation matrices $\mathbf{R}$ in Ref. 5 have here been set equal to unity since all cation sites in the trichloride structure have the same axes of symmetry.

2. *Single Ion g-value Shift*

Considering first the case of a single Gd^{3+} ion in EuCl$_3$, substituting for the different $\mathbf{Q}(j)$ and summing over (nn) and (nnn), we find that the g shift is given by

$$\mathbf{\Delta g}=-\frac{16}{\Delta}\begin{pmatrix} K_{11}^{\mathrm{nn}}+\frac{3}{2}(K_{11}^{\mathrm{nnn}}+K_{22}^{\mathrm{nnn}}) & & \\ & K_{11}^{\mathrm{nn}}+\frac{3}{2}(K_{11}^{\mathrm{nnn}}+K_{22}^{\mathrm{nnn}}) & \\ & & K_{33}^{\mathrm{nn}}+3K_{33}^{\mathrm{nnn}} \end{pmatrix}.\tag{4}$$

This tensor has axial symmetry appropriate to the C_{3h} point symmetry of the site. We note that any possible antisymmetric exchange between the Gd^{3+} and Eu^{3+} ions does not affect the g shift, as a consequence of the reflection plane of symmetry.

Let us now consider the particular case in which $\mathbf{K}$ arises from isotropic exchange J and magnetic-dipole interactions. We shall see that this approximation will later be justified by the general agreement with the experimental results, though small anisotropic contributions to $\mathbf{K}$ from orbital exchange cannot be ruled out completely. The magnetic-dipole contributions to $\mathbf{K}$ can be written in the form

$$\mathbf{K}_{\mathrm{dipole}}^{\mathrm{nn}}=\alpha_{\mathrm{nn}}'\begin{pmatrix}1&0&0\\0&1&0\\0&0&-2\end{pmatrix}\tag{5a}$$

and

$$\mathbf{K}_{\mathrm{dipole}}^{\mathrm{nnn}}=\alpha_{\mathrm{nnn}}'\begin{pmatrix}1-3r_x^2&-3r_xr_y&-3r_xr_z\\-3r_xr_y&1-3r_y^2&-3r_yr_z\\-3r_zr_x&-3r_yr_z&1-3r_x^2\end{pmatrix},\tag{5b}$$

where $\alpha_i'=g\mu_B^2/r_i^3$ and $\mathbf{r}$ is a unit vector in the direction of the bond. In writing the dipolar interaction in the above form, we have taken advantage of the fact that we only require matrix elements between the $J=0$ and $J=1$ states for which $\mathbf{L}$ and $\mathbf{S}$ have equal and opposite matrix elements.[5] Combining these with the isotropic contributions we find that the single-ion g shift is given by

$$\mathbf{\Delta g}=\begin{pmatrix}\Delta g_\perp&0&0\\0&\Delta g_\perp&0\\0&0&\Delta g_{||}\end{pmatrix},\tag{6}$$

where

$$\Delta g_\perp=(-8/\Delta)[2J_{\mathrm{nn}}+2\alpha_{\mathrm{nn}}'+6J_{\mathrm{nnn}}-3\alpha_{\mathrm{nnn}}'(1-3r_z^2)]+\epsilon_\perp$$

and

$$\Delta g_{||}=(-8/\Delta)[2J_{\mathrm{nn}}-4\alpha_{\mathrm{nn}}'+6J_{\mathrm{nnn}}+6\alpha_{\mathrm{nnn}}'(1-3r_z^2)]+\epsilon_{||}.$$

The terms $\epsilon_{||}$ and $\epsilon_\perp$ here represent the small contributions from the interactions with more distant neighbors; if we make the reasonable assumption that these are primarily due to magnetic-dipole interactions, we find $\epsilon_\perp=-\frac{1}{2}\epsilon_{||}$ for a spherical sample. The contribution to trace $\mathbf{\Delta g}$ thus vanishes identically; for other sample shapes the contributions will still be very small and may be safely neglected.

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[7] P. M. Levy, Phys. Rev. **135**, A155 (1964).

[8] M. Tachiki and Z. Sroubek, Solid State Commun. **5**, 361 (1967); N. L. Huang and J. H. Van Vleck, *ibid.* **6**, 557 (1968).

For a single Gd^{3+} ion in $EuCl_3$, we would therefore expect to find a somewhat anisotropic g value given by

$$\mathbf{g}(EuCl_3)=\mathbf{g}(\text{diamagn.})+\mathbf{\Delta g},$$

where $\mathbf{g}$ (diamagn.) is the g value in an otherwise similar diamagnetic environment. In the present case, we can use for this the isotropic value 1.9915±0.0006 found in $LaCl_3$. (See I.) The isotropic part of the g shift $(\Delta g_{||}+2\Delta g_{\perp})$ is independent of the dipole interactions, and in this approximation gives a direct measure of the sum of the isotropic interactions with the neighbors

$$\Delta g_{||}+2\Delta g_{\perp}=(-48/\Delta)(J_{\text{nn}}+3J_{\text{nnn}}). \qquad (7a)$$

The anisotropic part may be calculated directly from Eq. (6) if we neglect the terms in ϵ and possible contributions from anisotropic exchange, and we find

$$\Delta g_{||}-\Delta g_{\perp}=0.0013. \qquad (7b)$$

We shall find that this is too small to be detected by our experiments.

Besides the shift in the $\mathbf{g}$ tensor there will also be interaction shifts in the other spin-Hamiltonian parameters, such as in the b_n^m, but order-of-magnitude estimates indicate that the effects will almost certainly not be separable from other relatively large changes which may result from differences in the crystal field itself. We shall therefore not give any further details of the theory here.

3. *NN g-Tensor Shift*

For a pair of Gd^{3+} ions in $EuCl_3$ there will also be a g-value shift for each of the Gd^{3+} ions. We shall discuss only the case of *nn* pairs, because only for these can the g value be measured with any accuracy. The shift in the g value of each member of a nn pair will be the same as that for a single Gd^{3+} ion except that one of the nn Eu^{3+} ions has been replaced by a Gd^{3+} ion. The latter will not contribute to the shift mechanism described above and the g shift will therefore differ from that of the single ion by the contribution of just *one* Eu^{3+} nearest neighbor. Using Eqs. (4) and (5a), this gives

$$\Delta g_{||}(\text{single ion})-\Delta g_{||}(\text{nn pair})=(-8/\Delta)K_{33}^{\text{nn}}. \qquad (8a)$$

For the particular case of isotropic exchange and magnetic-dipole coupling, this becomes

$$\Delta g_{||}(\text{single ion})-\Delta g_{||}(\text{nn pair})=(-8/\Delta)(J_{\text{nn}}-2\alpha_{\text{nn}}'), \qquad (8b)$$

where for the $EuCl_3$ parameters $\alpha_{nn}'=0.0123\ \text{cm}^{-1}$. A measurement of $\Delta g_{||}$ for the single ions and pairs thus leads to a direct measure of J_{nn}(Gd-Eu) if we assume predominantly isotropic exchange coupling.

4. EXPERIMENTAL RESULTS

A. Preparation of Samples

The growth of $EuCl_3$ crystals presents a major chemical problem, because europium has a strong affinity for the divalent state, Eu^{2+}. Single crystals of the pure trivalent ion chloride are therefore difficult to grow, especially if they are to be completely free from Eu^{2+} as required for the pair measurements. (Eu^{2+} not only has the same electron configuration as Gd^{3+}, $4f^7$, but it also has a large hyperfine structure which gives rise to lines which might easily be confused with Gd^{3+} pair resonances.) After a considerable number of attempts, S. Mroczkowski of our Materials Laboratory finally developed a method which gave usable single crystals.

High-purity Eu_2O_3 (American Nuclear Corp. 99.9%) was first converted into the chloride by a stream of dry HCl gas using a quartz vessel similar to that described by Fong and Yocom.[9] During this state, the temperature was raised slowly from about 120°C to about 350°C over a period of 48 h. To ensure complete oxidation to $EuCl_3$ a stream of dry Cl_2 gas was next passed through the material and the temperature slowly raised to 520±10°C. Without exposure to the atmosphere, the powder was next transferred to a thick-walled quartz tube with a capillary tail and sealed with a pressure of about 3-atm Cl_2. The tube was then lowered through the temperature gradient of a standard Bridgman furnace, taking care to keep the temperature of the molten material no higher than about 10°C above the melting point (623°C). Under these conditions, only a small fraction of the trichloride decomposed, and it was possible to obtain small single crystals ($\sim$1 mm^3) of $EuCl_3$ from the resulting predominantly polycrystalline mass. These crystals appeared to contain essentially no free Eu^{2+} ($<$0.01%), as judged from their EPR spectra, though it is possible that they might have contained small precipitates of concentrated $EuCl_2$. However, these would give only a very broad resonance which would not interfere with our type of measurement. The Gd^{3+} doping was achieved by introducing about 0.1% $GdCl_3$ to the initial melt and it was found that this resulted in a concentration $\sim\frac{1}{2}$ to 1% Gd^{3+} in the final crystals. Neither the segregation nor the crystal growth itself is understood in detail, but samples which give good Gd^{3+} pair spectra could be produced in this way.

The orientation and mounting of the crystals was accomplished as described in I.

B. General Procedure

At room temperature the excited states of the Eu^{3+} ions are populated and the Gd^{3+} resonance is broadened considerably, as one might expect. However, on cooling to 77°K and below, sharp resonances were observed, with widths comparable to those in diamagnetic $LaCl_3$.

The experiments were performed mainly at 77°K and a frequency of 25.6 GHz, though some measure-

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[9] F. K. Fong and P. N. Yocom, J. Chem. Phys. 41, 1383 (1964).

ments were also made at 4.2 and 2°K. The apparatus and general technique have been described previously in I. The spectra due to single ions, nn and nnn pairs were identified by their intensities, angular dependence, and finally by a detailed fit to the appropriate spin Hamiltonian. In all cases the general similarity of the observed spectra to those found previously in LaCl$_3$ made the identification and analysis relatively straightforward.

The single-ion experiments were performed mainly on samples of EuCl$_3$ containing gadolinium as a trace impurity. These gave very narrow lines, of the order of 6 G in linewidth (half-intensity full width), and thus the single-ion resonance lines could be measured to an accuracy of about +1 G. The pair experiments were performed on samples containing about 0.5% Gd^{3+} and at 77°K these gave pair lines with half-intensity full widths of 20–40 G. In general the pair lines could be measured to an accuracy of about ±7 G. The fact that the pair lines could be seen at helium temperatures in EuCl$_3$, whereas they were saturated in LaCl$_3$, suggests that the Gd^{3+} ions in EuCl$_3$ have shorter relaxation times due to the second-order coupling with the Eu^{3+} ions (although some of the broadening observed in LaCl$_3$ could also have been due to the 1% Ce^{3+} contained in the crystals).

C. Single-Ion Spectrum

The resonance fields relative to the central line at 77°K and 25.6 GHz with the magnetic field H both along and perpendicular to the c axis are given in Table II and the angular variation of the spectrum is shown in Fig. 1. The identification of the lines follows from the relative intensities and from the temperature variation, the negative M transitions increasing in relative intensity at low temperatures. From Table II it can be seen that when **H** is parallel to the c axis, all the lines are symmetric about the center to within ±0.1 G as predicted by the form of Eq. (1). The total spread of the single-ion spectrum is about 1400 G compared with 300 G for Gd^{3+} in LaCl$_3$, showing clearly that the effective crystal field is considerably larger for Gd^{3+} in EuCl$_3$. The angular variation shown in Fig. 1 appears to be mainly due to a large b_2^0 terms, following closely a $(3\cos^2\theta-1)$ variation to a first approximation. The actual values of the parameters occurring in Eq. (1) (with $J=\alpha=0$) were found in the manner described by Bleaney *et al.*[10] from the $\|$ and $\perp$ spectra, and are listed in Table III. It can be seen that the crystal-field terms are indeed dominated by a large value for b_2^0, whereas the other parameters are similar to those found in LaCl$_3$. The value listed for b_6^6 assumes $\phi=0$ when the magnetic field is perpendicular to the c axis in the plane containing a nnn bond axis, the sample being oriented as described in I.

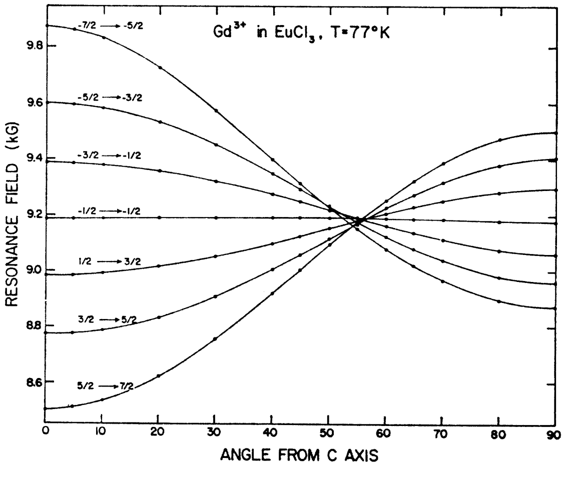

FIG. 1. Measured angular variation of single-ion transitions for Gd^{3+} in EuCl$_3$ at 77°K and 25.680 GHz.

TABLE II. Experimental line positions in gauss of the single-ion resonances of Gd^{3+} in EuCl$_3$ at 77°K and 25.680 GHz.

Transition M M'	Resonance fields H$\|c$ axis	 H$\perp c$ axis	Splittings from central line ΔH$\|c$ axis	 ΔH$\perp c$ axis
$+\frac{7}{2}\leftrightarrow+\frac{5}{2}$	8502.7	9502.3	−683.7	323.4
$+\frac{5}{2}\leftrightarrow+\frac{3}{2}$	8773.5	9406.5	−412.9	227.6
$+\frac{3}{2}\leftrightarrow+\frac{1}{2}$	8983.9	9297.7	−202.5	118.8
$+\frac{1}{2}\leftrightarrow-\frac{1}{2}$	9186.4	9178.9	0	0
$-\frac{1}{2}\leftrightarrow-\frac{3}{2}$	9388.7	9062.6	202.3	−116.3
$-\frac{3}{2}\leftrightarrow-\frac{5}{2}$	9599.5	8961.4	413.1	−217.5
$-\frac{5}{2}\leftrightarrow-\frac{7}{2}$	9870.1	8874.0	683.7	−304.9

The g values which may be obtained with only small corrections from the $|\frac{1}{2}\rangle\rightarrow|-\frac{1}{2}\rangle$ transitions may be compared in Table III with the isotropic g value found in LaCl$_3$ at the same temperature. In all cases the g values were measured both absolutely (from the microwave frequency and the field) and relative to a sample of diphenyl picryl hydrazyl ($g=2.0036$),[11] the agreement being within the experimental error.

The differences between the corresponding values may be taken to a good approximation as the g shifts,

TABLE III. Single-ion spin-Hamiltonian parameters for Gd^{3+} in LaCl$_3$ and EuCl$_3$.

	Gd^{3+} in EuCl$_3$ (77°K)	Gd^{3+} in LaCl$_3$ (77°K)
$b_2^0\times10^4$ cm^{-1}	101.0(±0.2)	16.36(±0.10)[a]
$b_4^0\times10^4$ cm^{-1}	1.47(±0.05)	2.14(±0.02)[a]
$b_6^0\times10^4$ cm^{-1}	0.31(±0.08)	0.21(±0.02)[a]
$b_6^6\times10^4$ cm^{-1}	3.0(±1.5)	1.40(±0.3)[b]
$g_{\|}$	1.9971(±0.0006)	1.9915(±0.0006)[c]
$g_{\perp}$	1.9971(±0.0010)	1.9915(±0.0006)[c]
$\Delta g_{\|}$	0.0056(±0.0012)	...
$\Delta g_{\perp}$	0.0056(±0.0016)	...

[a] Reference 13.
[b] Reference 12 (measured at 90°K).
[c] Mean of several measurements (Refs. 1, 12, and 13).

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[10] B. Bleaney, H. E. D. Scovil, and R. S. Trenam, Proc. Roy. Soc. (London) **A223**, 15 (1954).

[11] R. T. Weidner and C. A. Whitmer, Phys. Rev. **91**, 1279 (1953); L. S. Singer and C. Kikuchi, J. Chem. Phys. **23**, 1738 (1955).

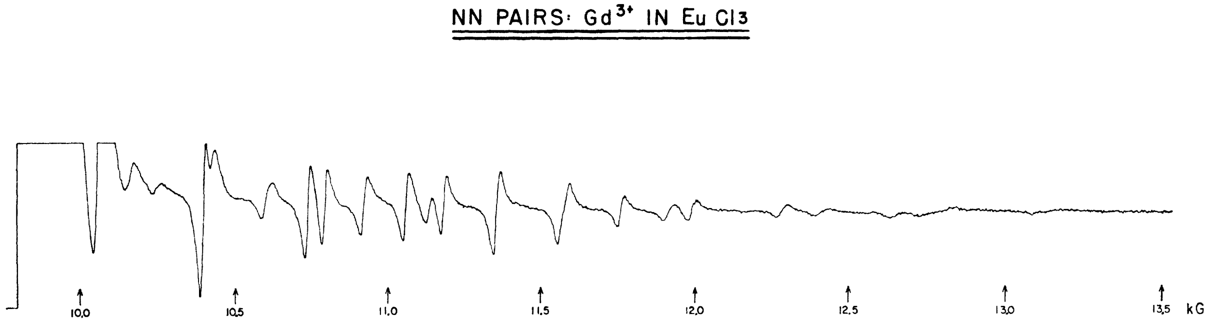

FIG. 2. High-field half of the nn pair spectrum at 77°K and 25.6 GHz with the magnetic field along the c axis.

$\Delta g_{\parallel}$ and $\Delta g_{\perp}$, discussed in Sec. 3 B. It may be seen that although both shifts are small, they are significantly greater than zero, indicating predominantly ferromagnetic Gd^{3+}-Eu^{3+} interactions. An analysis of the shifts in terms of the theory of Sec. 3 will be given in Sec. 5 B.

The spin-Hamiltonian parameters b_4^0, b_6^0, and b_6^6 remain small in EuCl$_3$, and similar in magnitude to those in LaCl$_3$. The larger value of b_2^0 could be due to an interaction shift with the europium ions as mentioned in Sec. 3, but since the value of b_2^0 is quite sensitive to small changes of environment, as shown by the experiments in LaCl$_3$,[12,13] it is possible that the change here is due to an electrostatic or covalency effect independent of magnetic or exchange interactions between the Gd^{3+} and Eu^{3+} ions.

TABLE IV. Relative fields (in gauss) of nn pair lines with respect to the central Gd^{3+} single-ion transition (9168 G at 25.625 GHz), and the mean shift from the center at 77°K. The experimental uncertainty is generally ±7 G.

ΔH_-	ΔH_+	$\frac{1}{2}(\Delta H_+ + \Delta H_-)$
−4042	4027	−7.5
−3536	3542	+3
−3285	3292	+3.5
−3178	3165	−6.5
−2886	2881	−2.5
−2809	2806	−1.5
−2657	2651	−3
−2486	2478	−4
−2462	2455	−3.5
−2254	2246	−4
−2083	2076	−3.5
−2037	2029	−4
−1958	1950	−4
−1819	1813	−3
−1698	1686	−6
−1637	1629	−4
−1500	1496	−2
−1330	1322	−4
−1293	1286	−3.5
−1065	1052	−6.5
−945	939	−3

D. NN Pair Spectrum

The high-field half of the EPR spectrum at 77°K and 25.625 GHz with the magnetic field along the c axis is shown in Fig. 2. As in the case of LaCl$_3$, the spectrum is composed of a group of large single-ion lines (far off full-scale deflection of the chart recorder in Fig. 2) with a number of smaller lines, the nn pair lines, approximately symmetrical about the center and extending out to at least 4000 G from the center. From Fig. 2, it may be seen that the spectrum is very unlike the corresponding one in LaCl$_3$ in that there is no grouping at all and there are a number of smaller outer lines indicating that $|J_{\text{nn}}/\alpha_{\text{nn}}|$ is larger than in LaCl$_3$. Because of the small sample size and lower concentration of Gd^{3+}, small outer lines were difficult to resolve from the noise, but all of the more intense lines with splittings greater than 1200 G from the center were found to turn symmetrically about the c axis as the magnetic field angle is varied, verifying that they do indeed belong to the nn pairs. Measurements of the line positions were made using both chart and scope displays of the absorption derivatives, and the averages of the readings are given in Table IV. The center of

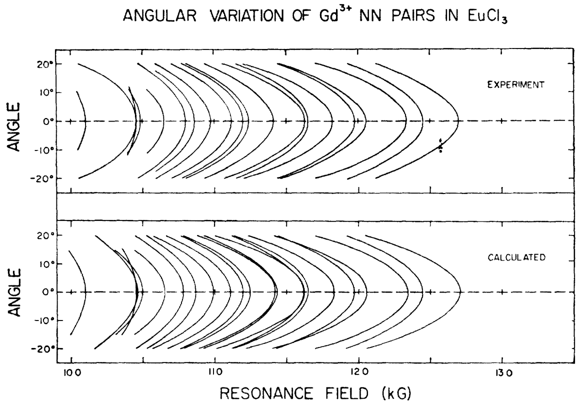

FIG. 3. Angular variation of the nn pair spectrum about the c axis at 77°K and 25.6 GHz. The upper curves are experimental, and the lower curves calculated from the following parameters: $g=1.997$, $J=0.04880\ \text{cm}^{-1}$, $\alpha=0.02462\ \text{cm}^{-1}$, $b_2^0=0.00773\ \text{cm}^{-1}$, $b_4^0=0.00010\ \text{cm}^{-1}$, and $b_6^0=0.00005\ \text{cm}^{-1}$.

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[12] C. A. Hutchinson, B. R. Judd, and D. F. D. Pope, Proc. Phys. Soc. (London) **B70**, 514 (1957).

[13] L. A. Boatner and M. M. Abraham, Phys. Rev. **163**, 213 (1967).

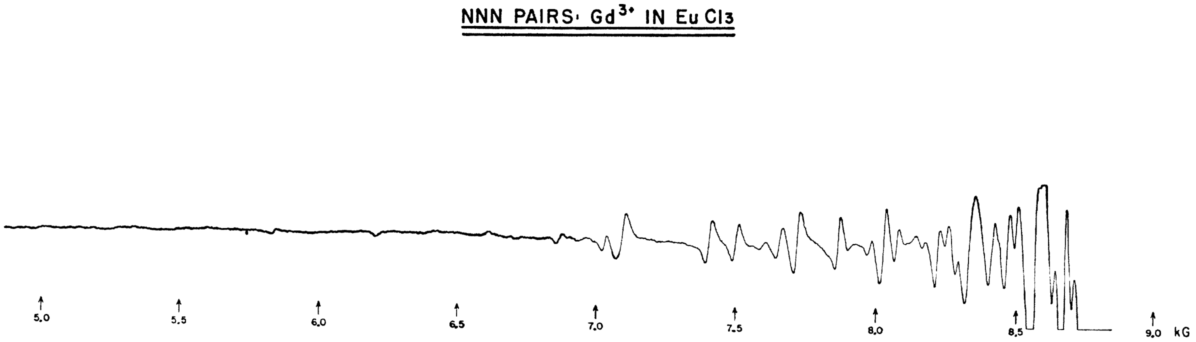

FIG. 4. Low-field half of the nnn pair spectrum at 77°K and 25.6 GHz, with the magnetic field along the calculated nnn bond axis.

the nn pair spectrum is shifted by an average of -3.3 G relative to the single-ion central transition, and corresponds to an nn pair g value of $g_{||}(\text{nn pair}) = 1.9977 \pm 0.0010$. In Sec. 5, we will use this g shift to estimate the nn Gd^{3+}-Eu^{3+} exchange interaction. Nearly all of the main nn lines are symmetrical about this g value to within 1.0 G and even the small outer lines which are more difficult to measure accurately are symmetrical within the experimental error of ±7 G. Again, this is in accord with the predicted spectrum based on the Hamiltonian $\mathcal{H}^{(0)}(1,2)$ of Eq. (1).

The angular variation of the main nn lines over a range of about ±20° from the c axis was studied in detail for the high-field lines. The resonance fields were found to be accurately symmetrical about the c axis as required by the axial symmetry of $\mathcal{H}^{(0)}(1,2)$. The results are shown as the experimental part in Fig. 3. From the figure it can be seen that none of the lines show any unusual behavior which may be used as an unambiguous help to identify the lines or to verify a particular fit. This was also the case for the nn pairs in $LaCl_3$.

As an alternative aid to identifying transitions, the relative intensities of the lines in the nn spectrum were studied at several temperatures. Below 4.2°K, only the negative M states are appreciably populated; by comparing the variation of the intensities of the corresponding low-field transitions, it became apparent that the lines at splittings of 1954, 2079, 2258, 2458, and 2654 G must correspond to transitions between states with the large negative M values. No detailed intensity studies were made, but the qualitative identification proved very useful in the final interpretation, which will be discussed in Sec. 5 A.

E. NNN Pair Spectrum

The low-field half of the EPR spectrum at 77°K and 25.6 GHz with the magnetic field set at 63.4° to the c axis is shown in Fig. 4. This angle corresponds to the nnn bond angle calculated from the lattice constants. Comparison with Fig. 7 of I shows that this spectrum is virtually identical to the nnn spectrum of Gd^{3+} in $LaCl_3$. The line positions were again measured using both chart and scope displays of the absorption derivatives, and the averages of these readings are given in Table V. From the table it may be seen that the more intense inner lines are symmetrical about the center to within the experimental error but some of the outer lines are slightly asymmetric. Because of the wide variation in the mean of corresponding high- and low-resonance fields (see Table V) it is not possible to determine an accurate value for the effective g value for the nnn pairs.

The angular variation of the high-field nnn lines between 43.4° to 83.4° from the c axis is shown in Fig. 5. Some of the lines are quite far from symmetric about the nnn pair axis, and in fact the turning angles vary from about 55° to 70°. This may be compared with the nnn pair lines of Gd^{3+} in $LaCl_3$, which all had turning angles within $\frac{1}{2}$° of the geometrical pair axis.

We shall discuss the asymmetry both in angle and about the center of the spectrum in Sec. 5, and show that it is mainly caused by the larger crystal-field interaction in the $EuCl_3$ lattice.

TABLE V. Relative fields (in gauss) of nnn pair lines with respect to the central Gd^{3+} single-ion transition (9168 G at 25.625 GHz), and mean shifts from the center at 77°K. The experimental uncertainty is generally ±7 G.

ΔH_-	ΔH_+	$\frac{1}{2}(\Delta H_+ + \Delta H_-)$
−4106	4151	22.5
−3245	3245	0
−2490	2515	12.5
−2222	2257	17.5
−2059	2084	12.5
−1993	1998	2.5
−1687	1679	−4
−1588	1589	0.5
−1440	1440	0
−1375	1372	−1.5
−1223	1245	11
−1179	1190	5.5
−1112	1113	0.5
−1064	1062	−1.0
−1017	1025	4.0
−870	872	1.0
−800	811	5.5
−756	759	1.5

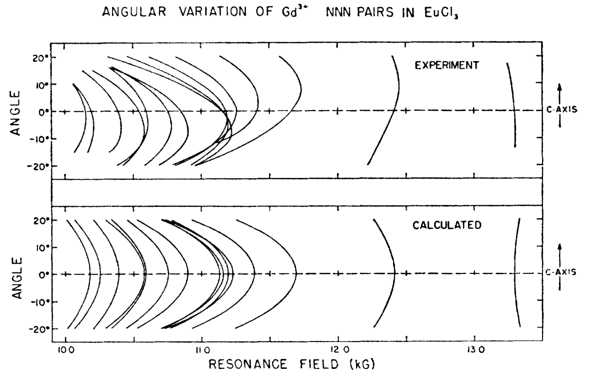

FIG. 5. Angular variation of the nnn pair spectrum about the calculated bond axis at 77°K and 25.62 GHz. The upper curves are experimental, and the lower curves are calculated from the following parameters: $g=1.997$, $J=-0.06368$ cm^{-1}, $\alpha=+0.01660$ cm^{-1}, $b_2^0=-0.00277$ cm^{-1}, $b_4^0=-0.00005$ cm^{-1}, and $b_6^0=+0.00004$ cm^{-1}.

5. INTERPRETATION OF SPECTRA

A. Determination of Gd^{3+}-Gd^{3+} Exchange Interactions from Pair Spectra

1. *General Considerations*

We saw in I that the axial pair Hamiltonian [Eq. (1)] was an excellent approximation for both nn and nnn Gd^{3+} pairs in LaCl$_3$, and would be expected to be so in other cases where the pair lines are both symmetric about the central single-ion transition, and their angular variation symmetric about the bond axis. From Sec. 4, we see that this is the case also for a nn pair of Gd^{3+} in EuCl$_3$ and we would therefore expect Eq. (1) to be an excellent approximation to the Hamiltonian for the nn pairs. The nnn pair lines, on the other hand, are not quite symmetric about the central transition and there are variations in angular dependence of different lines. Thus in the nnn case there will be further off-diagonal terms in the pair Hamiltonian, and it is clear that the major contribution to these will come from the crystal-field terms which have no symmetry about the bond axis. Indeed the situation found for the nnn pairs in EuCl$_3$ might already have been expected in LaCl$_3$, and it is only due to the fact that the parameters b_n^m are so small in LaCl$_3$ that a symmetric spectrum is observed in that case. Referring to Fig. 1, we can see that at 63° the single-ion lines are varying in position quite rapidly with angle, and it is this effect superimposed on a spectrum symmetric in angle about the bond axis which we observe.

Nevertheless, we may still use the Hamiltonian Eq. (1) to interpret the nnn pair spectrum if we first average the splittings of corresponding high- and low-field lines to eliminate the second-order shifts from off-diagonal terms. We then derive *effective* parameters b_n^0(eff) as discussed in I, which will describe the mean splittings correct to second order.

In order to fit the spectra, we require estimates of the expected orders of magnitude of the parameters occurring in $\mathcal{H}^{(0)}(1,2)$; with the knowledge of the parameters for the case of LaCl$_3$, we can make these with some confidence. The dipolar interactions are expected to lie close to those appropriate to the lattice spacings: $\alpha_{\rm nn}({\rm EuCl_3})=0.0245$ cm^{-1} and $\alpha_{\rm nn}({\rm GdCl_3})=0.0250$ cm^{-1}, $\alpha_{\rm nnn}({\rm EuCl_3})=0.0164$ cm^{-1} and $\alpha_{\rm nnn}({\rm GdCl_3})=0.0165$ cm^{-1}. The exchange constants may be extrapolated from the LaCl$_3$ measurements, using the known temperature variation to estimate the separation dependence, and we find $J_{\rm nn}\approx 0.023$ cm^{-1} and $J_{\rm nnn}\approx -0.073$ cm^{-1}. While the actual variation with host lattice may be rather different, the order of magnitudes of these figures should be appropriate.

We have evidence, both from the single-ion spectra and the nnn pair spectra, that the b_n^m terms, particularly b_2^0, are larger than in LaCl$_3$. However, they are still likely to be an order of magnitude smaller than the interaction terms, and a rough estimate of the nn b_2^0 may be made from the fact that in LaCl$_3$, b_2^0 for the pair changed by approximately -0.004 cm^{-1} from the single-ion value. Thus we might expect b_2^0(nn) to be ≈ 0.006 cm^{-1}, although the situation could in fact turn out to be quite different in view of the complex effects which give rise to the crystal-field splittings of S-state ions.

The fitting procedure adopted was similar to that described in I. Spectra were calculated for estimated values of the parameters and a comparison was made with the observed spectrum. Lines were identified from their position, angular variation, intensity, and the variation of intensity with temperature, and $\mathcal{H}^{(0)}(1,2)$ was fitted to these lines using the computer programs described in I. Generally, the experience and confidence gained from the LaCl$_3$ problem enabled the spectra in EuCl$_3$ to be fitted quite quickly.

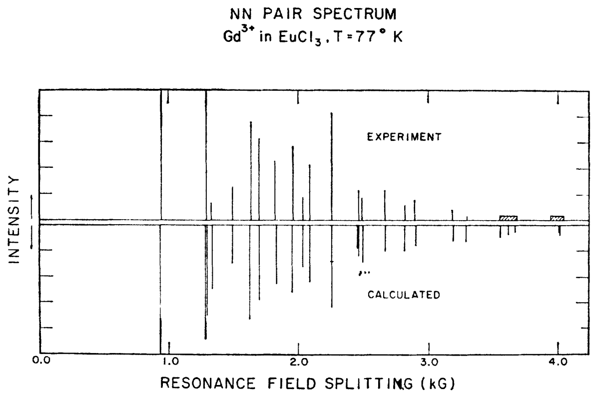

FIG. 6. Best fit to the nn pair line splittings and intensities with the magnetic field along the c axis. The upper portion shows the experimental spectrum at 77°K and 25.62 GHz, and the lower portion shows the theoretical spectrum calculated from the following parameters: $g=1.9977$, $J=0.04880$ cm^{-1}, $\alpha=0.02462$ cm^{-1}, $b_2^0=0.00773$ cm^{-1}, $b_4^0=0.00010$ cm^{-1}, and $b_6^0=0.00005$ cm^{-1}.

2. *NN Pair Spectrum*

The average from the center of the spectrum of corresponding low- and high-field transitions due to nn pairs are shown diagramatically in Fig. 6, which also indicates the mean intensities at 77°K estimated from the peak heights of the absorption derivatives averaged over several recorder charts. As a first step in identifying the transitions, theoretical spectra were calculated for $\alpha_{nn}=0.0247$ cm^{-1}, $J_{\text{nn}}=0.023$ cm^{-1}, $b_2{}^0=0.01$ cm^{-1}, and $b_4{}^0=b_6{}^0=0$, and for the same values with $b_2{}^0=0.005$ cm^{-1}. Both spectra had similar general forms which corresponded closely to the observed spectrum. From the intensities and their temperature variations, and the sensitivities of the calculated lines to small changes in J and $b_2{}^0$, it was found that only two reasonable sets of identifications were possible, of which one gave an appreciably better fit than the other. The final fit obtained, after a few iterations, is shown in Fig. 6; it may be seen that the agreement with the experimental results is very good. The rms deviation for 52 transitions is 7.8 G, compared with typical linewidths of 20–40 G and splittings of up to 3300 G for the lines fitted. The experimental and calculated line positions are given in Table VI, which also includes the final values of the parameters. Most of the well-resolved lines are fitted to within the experimental error of ±7 G, although the fit is generally not quite as good as that for the nn pairs in $LaCl_3$, which had an rms deviation of 5.1 G. The difference is most probably due to the fact that the pair lines are somewhat broader in $EuCl_3$ than in $LaCl_3$. In Fig. 3, the angular variation calculated from the nn best-fit parameters is shown for the high-field lines, along with the experimental angular variation. Again it is seen that the agreement is very good.

TABLE VI. Mean experimental and calculated line splittings (in gauss) for the nn spectrum of Gd^{3+} in $EuCl_3$ at 77°K and 25.6 GHz with $J=0.048804$ cm^{-1}, $\alpha=0.024620$ cm^{-1}, $b_2{}^0=0.007732$ cm^{-1}, $b_4{}^0=0.000098$ cm^{-1}, and $b_6{}^0=0.000045$ cm^{-1}.

Label	Expt.	Calc.	Diff.
3, 1	942.1	932.7	−9.4
4, 1	1289.4	1281.7	−7.7
3, 4	1289.4	1295.8	6.4
2, 8	1326.3	1331.7	5.4
1, 13	1488.1	1487.0	−1.1
5, 1	1632.6	1619.2	−13.4
4, 3	1692.7	1700.3	7.6
3, 7	1815.8	1828.0	12.2
6, 1	1954.0	1944.5	−9.5
2, 11	2033.1	2029.8	−3.3
5, 3	2079.1	2080.3	1.2
7, 1	2249.9	2251.1	1.2
4, 6	2249.9	2258.6	8.7
1, 17	2458.2	2445.9	−12.3
6, 2	2458.2	2458.1	−0.1
3, 10	2482.4	2487.7	5.3
5, 5	2654.1	2659.3	5.2
2, 15	2807.3	2801.7	−5.6
4, 8	2884.0	2892.7	8.7
3, 13	3171.0	3180.5	9.5
1, 21	3287.7	3277.8	−9.9

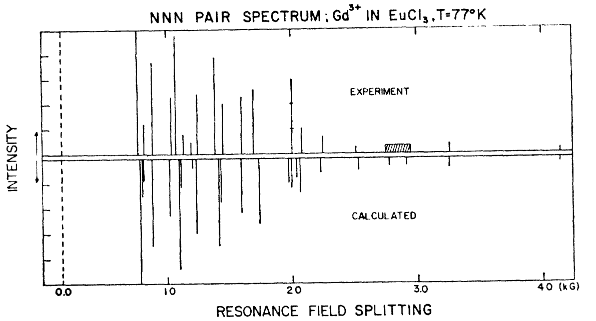

FIG. 7. Best fit to the nnn pair line splittings and intensities with the magnetic field along the calculated bond axis. The upper portion shows the experimental spectrum at 77°K and 25.62 GHz, and the lower portion shows the theoretical spectrum calculated from the following parameters: $g=1.997$, $J=-0.06368$ cm^{-1}, $\alpha=+0.01660$, $b_2{}^0=-0.00277$ cm^{-1}, $b_4{}^0=-0.00005$ cm^{-1}, and $b_6{}^0=+0.00004$ cm^{-1}.

When an isotropic biquadratic exchange term $j(S_1\cdot S_2)^2$ was included in the spin Hamiltonian the fit gave a value for $j=+0.00013$ cm^{-1}, while the bilinear exchange constant J increased by about 0.002 cm^{-1}, the other parameters changing only slightly. Such a relatively large value of j would be quite surprising in the light of current theories of superexchange.[1,14] Since the over-all fit was only slightly improved by the addition of j (the rms deviation decreasing from 7.8 to 6.4 G) and as there are still some remaining discrepancies, we really cannot come to any definite conclusion regarding the presence of biquadratic exchange in this case. In any event, the determination of the principal interaction parameters J and α is affected only slightly.

We see from Table VI that the nn exchange is antiferromagnetic in sign, as in the case of Gd^{3+} in $LaCl_3$, but its magnitude is significantly larger than that predicted from our rough extrapolation. The dipolar interation falls close to that appropriate to the $EuCl_3$ spacing and $b_2{}^0$ is also found to be close to the estimated value. These results will be discussed in Sec. 6.

3. *NNN Pair Spectrum*

The field splittings were averaged in the same manner as for the nn lines, and the resulting spectrum is shown diagramatically in Fig. 7. Apart from a few small lines which are not resolved in the present case, the spectrum is virtually identical to the nnn pair spectrum in $LaCl_3$. The theoretical identifications then are just those for Gd^{3+} in $LaCl_3$ and the best fit resulting from these is given in Table VII. The rms deviation is 20 G, compared with linewidths of 20–40 G and splittings of up to 4100 G. As in the case of the nnn pairs in $LaCl_3$, only a few of the lines are actually fitted to within the experimental error of ±7 G, and there are some individual differences of up to 46 G. However, the over-all quality of the fit

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[14] See, e.g., P. W. Anderson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. 1, p. 41.

TABLE VII. Mean experimental and calculated line splittings (in gauss) for the nnn spectrum of Gd^{3+} in $EuCl_3$ at 77°K and 25.6 GHz, with $J=-0.063677$ cm^{-1}, $\alpha=+0.016597$ cm^{-1}, $b_2^0=-0.002774$ cm^{-1}, $b_4^0=-0.000053$ cm^{-1}, and $b_6^0=+0.000038$ cm^{-1}.

Label	Expt.	Calc.	Diff.
3, 13	757.5	773.2	15.7
1, 9	805.5	798.9	−6.6
2, 11	805.5	805.5	0.0
3, 15	871.0	871.3	0.3
3, 7	1021.0	1012.2	−8.8
4, 10	1063.0	1088.2	25.2
3, 9	1122.5	1095.7	−26.8
1, 12	1184.5	1200.2	15.7
4, 8	1234.0	1222.6	−11.4
5, 5	1373.5	1407.0	33.5
4, 5	1440.0	1422.1	−17.9
5, 6	1588.5	1585.4	−3.1
6, 3	1683.0	1729.3	46.3
5, 1	1995.5	1963.1	−32.4
6, 2	1995.5	1988.1	−7.4
7, 1	2071.5	2056.6	−14.9
3, 1	2239.5	2219.8	−19.7
2, 4	2502.5	2520.9	18.4
2, 1	3245.0	3241.7	−3.3
3, 4	4128.5	4133.5	5.0

seems to rule out the possibility of misidentifications of the fitted lines.

The theoretical angular variation of the high-field nnn pairs, calculated using the best-fit parameters together with the experimental results, is shown in Fig. 5. The experimental and theoretical turning angles are, of course, different since the off-diagonal crystal-field terms are not included in the calculations. Nevertheless, the general shapes of the experimental and calculated variations are seen to correspond quite well, verifying the identification made.

A discussion of the remaining discrepancy between the experimental and calculated line position in Table V gives rise to the same difficulties encountered for the nnn pairs in $LaCl_3$.[1] The general magnitudes of the discrepancies are of the same order (20 G rms in $EuCl_3$, 18 G rms in $LaCl_3$); in fact, individual discrepancies for corresponding lines are similar in the two spectra, suggesting that the same physical mechanism is responsible in both cases. The present case is, of course, further complicated by the presence of larger off-diagonal crystal-field terms, and these give rise to asymmetries in the spectrum parallel to the bond axis of up to 45 G. However, by averaging high- and low-field line positions, as we have done, we eliminate second-order shifts, leaving only the diagonal terms (first order) and third-order effects of the off-diagonal terms. These latter terms will generally be quite negligible. Thus, provided the bond axis direction is chosen correctly, and in $LaCl_3$ the experimental and calculated direction agreed exactly, the axial Hamiltonian of the form of Eq. (1) should suffice to explain the average line positions. The only difference from the $LaCl_3$ case is that we had definite proof that off-diagonal terms were negligible in that case and here we have only an estimate.

We have not attempted to fit these discrepancies by higher-order interactions or exchange striction terms, as we did for $LaCl_3$, because of the lack of success in that case. We may, however, note that whatever effect is causing the discrepancies in the nnn fits, it is not likely to be radically dependent on lattice distortions in the neighborhood of the pair because these are probably small in the case of $EuCl_3$. Moreover, they do not seem to be related to crystal-field effects since they are similar in the two cases while the crystal-field splittings differ by a factor of 5. We believe, therefore, that the discrepancies are most probably due to some higher-order interaction terms not included in $\mathcal{H}^{(0)}(1,2)$ but it seems unlikely that their omission will alter the value found for J_{nnn} by more than a few percent.

From Table VII we see that the nnn exchange interaction is *ferro*magnetic and only slightly larger than that observed with $LaCl_3$ as a host lattice. The dipolar interaction is found to lie very close to that in $GdCl_3$. These results will be discussed more fully in Sec. 6.

B. Determination of the Gd^{3+}-Eu^{3+} Exchange Interaction from g Shifts

The experimental results for the g shifts defined in Sec. 3 are summarized in Table VIII. No accurate estimate could be made for $\Delta g_{\perp}$ for the nn pairs, nor for either of the g values for nnn pairs. We therefore have only three separate pieces of experimental data to determine the five parameters in the general expression for $\mathbf{\Delta g}$ given in Eq. (4). However, if we make the usual approximation that isotropic exchange and magnetic-dipole interactions make the major contributions to the **K**'s we can use Eqs. (7a) and (8b) to determine J_{nn} and J_{nnn}, and we can use Eq. (7b) to check the assumption that anisotropic exchange is indeed small.

From Table VII we find that $\Delta g_{\|}(\text{ion})-\Delta g_{\perp}(\text{ion})=0.0000\pm0.0028$ which is, in fact, consistent with the value 0.0013 given in Eq. (7b). It seems likely, therefore, that anisotropic non-dipolar contributions to the **K**'s are quite small, and that in particular the term K_{33}^{nn} in Eq. (8a) is close to $J_{\text{nn}}-2\alpha_{\text{nn}}'$, as indicated in Eq. (8b).

From the experimental results in Table VIII we also find that

$$\Delta g_{\|}(\text{ion})+2\Delta g_{\perp}(\text{ion})=0.0168\pm0.0044$$

TABLE VIII. g-value shifts for single ions and nn pairs relative to $g(LaCl_3)=1.9915$. $\mathbf{\Delta g}\equiv\mathbf{g}(EuCl_3)-\mathbf{g}(LaCl_3)$.

$\Delta g_{\|}(\text{ion})=0.0056\pm0.0012$
$\Delta g_{\perp}(\text{ion})=0.0056\pm0.0016$
$\Delta g_{\|}(\text{nn pair})=0.0062\pm0.0012$
$\Delta g_{\|}(\text{ion})-\Delta g_{\|}(\text{nn pair})=-0.0006\pm0.0006$

TABLE IX. Summary of nn and nnn exchange and dipolar constants. Most of the results refer to measurement made at 77°K but the variation down to 0°K is expected to be negligible (<1%) (Ref. 1). All energies are expressed in cm^{-1}.

	J_{nn}	α_{nn}	J_{nnn}	α_{nnn}
Gd^{3+} pairs in $LaCl_3$ (expt.[a])	0.0133 (±0.0005)	0.0219 (±0.0003)	−0.0595 (±0.0020)	0.0159 (±0.0005)
Extrapolation to $EuCl_3$ spacing from temperature variation of parameters in $LaCl_3$[a,b]	+0.023		−0.073	
Calculated dipolar constants[c]:				
$EuCl_3$ spacing		0.0245		0.0164
$GdCl_3$ spacing		0.0250		0.0165
Gd^{3+} pairs in $EuCl_3$ (expt.[d])	+0.0488 (±0.0010)	0.0246 (±0.0002)	−0.0637 (±0.0020)	0.0166 (±0.0002)
$Gd^{3+}-Eu^{3+}$ interaction in $(Gd,Eu)Cl_3$ (expt.[d])	+0.052 (±0.030)		−0.061 (±0.030)	
$Gd^{3+}-Gd^{3+}$ interaction in $GdCl_3$:				
(extrapolated from pair results)	+0.056 (±0.006)	0.0250[c]	−0.064 (±0.003)	0.0165[c]
(deduced from bulk properties.[e])	+0.054 (±0.003)		−0.067 (±0.003)	

[a] Reference 1.
[b] Reference 16.
[c] Calculated using $g=1.9915$ and lattice parameters from Table I reduced by 0.3% to allow for thermal contraction.
[d] This work.
[e] After Ref. 23. See also Refs. 20, 21, and 22.

and

$$\Delta g_{\|}(\text{ion})-\Delta g_{\|}(\text{pair})=-0.0006\pm0.0006\,.$$

Using Eqs. (7a) and (8b), these values lead to

$$J_{nn}(Gd^{3+}-Eu^{3+})=0.052\pm0.030\ \text{cm}^{-1}$$

and

$$J_{nnn}(Gd^{3+}-Eu^{3+})=-0.061\pm0.030\ \text{cm}^{-1}\,.$$

The errors here include an additional 10% to allow for the approximations made in the theory, as well as the large experimental errors corresponding to the small g shifts. These values are, in fact, remarkably close to those found for the Gd^{3+}-Gd^{3+} interactions from the pair measurements, and they suggest that the isotropic part of the interaction tensor $\mathbf{K}$ is, in fact, close to the simple Heisenberg interaction parameter. However, the uncertainties in the values are quite large and we cannot reach any strong quantitative conclusions. On the other hand, it is quite striking that the anomalous *signs* found for the Gd^{3+}-Gd-$^{3+}$ interactions are also indicated by the Gd^{3+}-Eu^{3+} results.

6. DISCUSSION

In this section, we shall discuss the results of the experiments on both Gd^{3+}-Gd^{3+} and Gd^{3+}-Eu^{3+} interactions, and compare the results with measurements on concentrated $GdCl_3$.

In Table IX, the values obtained above for the exchange and dipolar constants of nn and nnn Gd^{3+} pairs in $EuCl_3$ are compared with those in $LaCl_3$, and with the values of exchange parameters estimated for the $EuCl_3$ lattice spacings from the extrapolation based on the temperature-variation measurements in $LaCl_3$. The table also includes the dipolar interactions calculated for different lattice spacings, and the exchange constants for pure $GdCl_3$ estimated from both our pair measurements and various bulk properties.

A. Gd^{3+}-Gd^{3+} Pair Interactions

One of the most significant features of all these results which is not shown explicitly by Table IX is the fact that only two constants J and α alone account for the major part of the interactions for each pair. As we have seen, there is no evidence for any significant biquadratic exchange, and the other higher-order effects discussed in I are also small. Comparing the calculated dipolar constants with the measured α, we find that any contribution from anisotropic exchange is less than 3×10^{-4} cm^{-1}, which is quite consistent with the order-of-magnitude estimate[15]

$$J(\text{aniso})\sim(\Delta g/g)^2J(\text{iso})\sim2\times10^{-6}\ \text{cm}^{-1}\,.$$

From the values of J_{nn} in Table IX, we see that the nn exchange interaction increases by more than a factor of 3 between $LaCl_3$ and $EuCl_3$, while the nnn interaction changes only slightly, both increasing in magnitude in the smaller lattice. The dipolar constants may be used to obtain values for the corresponding mean ionic separations in the two cases[1]: For the nn this separation decreases from 4.279 Å in $LaCl_3$ to 4.116 Å in $EuCl_3$, while for the nnn the change is only from 4.766 to 4.695 Å. The relatively large change in J_{nn} compared with that of J_{nnn} is therefore qualitatively reasonable, though the two interaction mechanisms undoubtedly have different and complex dependences on the pair separation. In fact, the earlier measurements of the temperature variation of the J's in $LaCl_3$ [1,16] indicated an appreciably more rapid separation dependence of J_{nnn} compared with J_{nn}. Extrapolating the empirically fitted J versus r_{eff} relation, we find the values shown in Table IX. It may be seen that the

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[15] See, e.g., T. Moriya, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. 1, p. 91.

[16] R. J. Birgeneau, M. T. Hutchings, and W. P. Wolf, Phys. Rev. Letters, **17**, 308 (1966).

extrapolations tend to overestimate the change in J_{nnn} and underestimate J_{nn}; it is evident that the previously determined $J(r)$ relations hold only over very limited ranges of r. As discussed previously, there is also a possibility that the temperature dependence may be affected by harmonic-vibration effects, which could modulate the different superexchange paths in quite complex manners. An additional effect will also arise from changes in the superexchange bond angles with temperature and lattice which we have not allowed for in our extrapolation. It seems quite clear that the variation from lattice to lattice as well as the temperature dependence cannot be explained in any very simple manner and must await more detailed superexchange calculations which, though complicated, do seem to be at least well defined in the present cases.

There is no evidence from our results that the presence of a different and weakly magnetic ion environment affects the exchange to any large extent, although it could possibly contribute to some of the difference between the measured exchange in $EuCl_3$ and $LaCl_3$ and that predicted from the temperature variation. Harris and Owen[17] have found from the EPR of pairs and triads of Ir^{4+} ions NH_4PtCl_6 that the exchange between two ions of a triad is the same as that between the ions in an isolated pair, thus indicating that at least in that particular compound the exchange mechanism is not affected by the presence of nearby magnetic ions. Similar experiments with Gd^{3+} would be quite hard, since each triad would have $8^3=512$ energy levels, and with the exchange comparable with the dipole interactions a very large number of transitions would be allowed. However, it seems most unlikely that the very weak superexchange in the present cases would be affected appreciably by the more distant cation neighbors, and it seems very reasonable, therefore, to use the measured J's in $LaCl_3$ and $EuCl_3$ to estimate the exchange parameters in concentrated $GdCl_3$, allowing only for changes in the lattice dimensions.

Since the lattice spacings of $EuCl_3$ are, in fact, very close to those of $GdCl_3$, the exchange constants measured for Gd^{3+} pairs in $EuCl_3$ may be compared almost directly with those derived from the bulk properties of $GdCl_3$. Estimating the effective pair separation from measured dipolar constants, and extrapolating on a log-log plot of J versus r_{eff}, we find that J_{nn} should increase by about 15%, with an uncertainty of ±10%, while for J_{nnn} the increase should be less than 0.5%, with an uncertainty of 0.5%. Combining the extrapolation uncertainties with the experimental errors in the pair measurements, we finally estimate

$$J_{\mathrm{nn}}{}^{\mathrm{pair}}(\mathrm{GdCl}_3)=+0.056\pm0.006\ \mathrm{cm}^{-1}$$

and

$$J_{\mathrm{nnn}}{}^{\mathrm{pair}}(\mathrm{GdCl}_3)=-0.064\pm0.003\ \mathrm{cm}^{-1}.$$

B. Application to Bulk Properties of $GdCl_3$

The values of J given above have been determined from measurements at 77°K; in order to use them to predict the low-temperature properties of $GdCl_3$, it is first necessary to allow for possible variations with temperature. However, the detailed temperature dependence studies reported in I suggest that the changes below 77°K will, in fact, be very small, amounting to no more than 1% down to 0°K. We shall, therefore, neglect the temperature dependence of the J's over this range.[18] The bulk properties above the Curie point T_c may be characterized by the coefficients in the series expansions in powers of $1/T$ of the inverse susceptibility $1/\chi$ and the magnetic specific heat, C_M

$$\frac{1}{\chi}=\frac{T}{C}\left(1+\sum_{n=1}^{\infty}\frac{B_n}{(kT)^n}\right), \tag{9a}$$

and

$$\frac{C_M}{R}=\sum_{n=2}^{\infty}\frac{C_n}{(kT)^n}. \tag{9b}$$

At temperatures high compared with T_c (2.2°K) the series converge rapidly and only the first terms are needed. Wolf *et al.*,[19] Wyatt,[20] and Marquard[21] have given expressions for these

$$\begin{aligned}B_1&=-\theta=-[21(J_1+3J_2)+0.965-CN_{\|}]\ ^\circ\mathrm{K},\\ C_2&=[331(J_1{}^2+3J_2{}^2)+0.570]\ ^\circ\mathrm{K}^2,\\ C_3&=[-331(J_1{}^3+3J_2{}^3)+6.25\times10^4J_1J_2{}^2+16.7J_1\\ &\qquad+27.8J_2-0.41]\ ^\circ\mathrm{K}^3.\end{aligned} \tag{10}$$

Here $J_1=-\frac{1}{2}J_{\mathrm{nn}}$ and $J_2=-\frac{1}{2}J_{\mathrm{nnn}}$ expressed in °K. These formulas assume that the more distant interactions are purely magnetic dipole in nature, as reflected by the constant terms in B_1 and C_2 and the last three terms in the expression for C_3. Substituting our values for J_{nn} and J_{nnn} and taking $N_{\|}=0$ corresponding to a needle-shaped sample, we obtain

$$\begin{aligned}B_1&=-\theta=-3.0\pm0.2\ ^\circ\mathrm{K},\\ C_2&=3.2\pm0.3\ ^\circ\mathrm{K}^2,\\ C_3&=-4.9\pm1.0\ ^\circ\mathrm{K}^3.\end{aligned}$$

The Weiss θ constant has been measured by Wyatt,[19,20] who finds $\theta=3.2\pm0.2$ °K, in excellent agreement with the calculations based on our pair parameters. Because of the relatively large lattice contribution, the measurement of the magnetic specific heat is very difficult using conventional methods. However, using a high-frequency relaxation method, Boyd and Wolf[22]

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[17] E. A. Harris and J. Owen, Proc. Roy. Soc. (London) **A289**, 122 (1965).

[18] In the light of more recent experimental data on $GdCl_3$, the subsequent discussion supercedes that given by R. J. Birgeneau, M. T. Hutchings, and W. P. Wolf, J. Appl. Phys. **38**, 957 (1967).

[19] W. P. Wolf, M. J. M. Leask, B. Mangum, and A. F. G. Wyatt, J. Phys. Soc. Japan, Suppl. **17**, B-1, 487 (1962).

[20] A. F. G. Wyatt, thesis, Oxford University, 1963 (unpublished).

[21] C. D. Marquard, Proc. Phys. Soc. (London) **92**, 650 (1967).

[22] E. L. Boyd and W. P. Wolf, J. Appl. Phys. **36**, 1027 (1965).

were able to measure the purely magnetic part of the specific heat more directly. They found $C_2 = 2.4 \pm 0.15$ °K^2. This is close to our calculated value, but the discrepancy is in fact outside the quoted errors. Further high-frequency experiments have recently been carried out by Clover and Wolf.[23] These have shown that the earlier measurements were in error, most probably due to uncertainties in sample preparation and systematic dielectric corrections, and they have led to a new value for C_2, namely, 3.24 ± 0.1 °K^2. This is in excellent agreement with our calculated value. By combining their high-temperature measurements with the low-temperature specific-heat measurements of Wyatt[20] and of Landau,[24] Clover and Wolf were also able to estimate a value for C_3. They find $C_3 = -5.3 \pm 0.4$ °K^3, which is again in good agreement with the value calculated from our pair measurements.

An alternative way of comparing the pair and bulk measurements is to combine the specific-heat and susceptibility data and to make the reasonable assumption that only nn and nnn isotropic exchange and magnetic-dipole interactions are important (as our pair measurements have in fact confirmed). One can then solve for J_{nn} and J_{nnn}[23]

$$J_{\mathrm{nn}}^{\mathrm{bulk}}(\mathrm{GdCl_3}) = 0.054 \pm 0.003\ \mathrm{cm^{-1}}$$

and

$$J_{\mathrm{nnn}}^{\mathrm{bulk}}(\mathrm{GdCl_3}) = -0.067 \pm 0.003\ \mathrm{cm^{-1}}.$$

Again, the agreement with our extrapolated pair results is good.

We may conclude from all this that the exchange parameters obtained from a small extrapolation of the pair measurements in EuCl$_3$ do, in fact, provide a good description of the interactions in GdCl$_3$, as we might have hoped. The relative accuracy of our estimates compares very favorably with the best determinations of interactions by other methods. A summary of all the results is given in Table IX.

Perhaps one of the most interesting aspects of the present series of measurements is the result that the effective exchange interaction between the Gd^{3+} and Eu^{3+} spins as estimated from the g shifts is essentially the same as that between two Gd^{3+} spins. The closeness of the agreement may be somewhat fortuitous because of the large error inherent to the g-shift method, but a similar result has also been inferred from experiments on Gd^{3+} in europium gallium garnet.[5] It would thus appear that the isotropic part of the average electron-electron exchange interaction, which is the quantity usually denoted by the parameter J, is not especially sensitive to the particular configurations of the interacting rare-earth ions ($4f^7$ or $4f^6$ in the present case) as predicted theoretically for a simple model of the interaction.[25] From this, one might be led to expect qualitatively similar magnitudes for the isotropic parts of exchange interactions in other situations in which the rare-earth electron configurations and ionic separations are not too different. However, it seems clear that the actual exchange mechanism is, in fact, quite complicated for rare-earth ions, involving not only the ligand ions, but also the two closed $5s^2\ 5p^6$ shells; therefore, no simple relationship can be expected between different cases in general. Indeed, the marked difference between the J_{nn} measured in LaCl$_3$ and EuCl$_3$ shows in a striking manner just how sensitive the interactions can be to even small changes in the overlap geometry and that great care must be used, therefore, in extrapolating from any one case to another.

C. Spin-Hamiltonian Parameters b_n^m

The detailed theory for the parameters b_n^m arising from high-order crystal-field and covalency effects is perhaps even more complex than that for the exchange interactions. We shall only comment on some empirical observations which may be useful for later analyses. The parameters for single ions and Gd^{3+} pairs in both LaCl$_3$ and EuCl$_3$ are summarized in Table X.

It may be seen that the values of the b_4^0, b_6^0, and b_6^6 are quite similar in all cases although the smaller terms in the nnn case carry large errors due to the poorer fit. This similarity is perhaps somewhat surprising inasmuch as one might expect these higher-order terms to be the most sensitive to small changes in the immediate environment of the given ion. For the b_2^0, on the other hand, there are significant changes due to the presence of the neighboring Gd^{3+} ions in a pair. Furthermore, these changes are rather similar in both the LaCl$_3$ and EuCl$_3$ lattices. For the nn pairs $\Delta b_2^0(\mathrm{LaCl_3}) = -0.0037$ cm^{-1} and $\Delta b_2^0(\mathrm{EuCl_3}) = -0.0024$ cm^{-1}; for the nnn

TABLE X. Summary of spin-Hamiltonian parameters b_n^m at 77°K.

	$b_2^0 \times 10^4$ (cm^{-1})	$b_4^0 \times 10^4$ (cm^{-1})	$b_6^0 \times 10^4$ (cm^{-1})	$b_6^6 \times 10^4$ (cm^{-1})
	Quantized along the c axis			
Single ion[a,b] Gd^{3+} in LaCl$_3$	16.36 (±0.10)	2.14 (±0.02)	0.21 (±0.02)	1.4 (±0.3)
Single ion[c] Gd^{3+} in EuCl$_3$	101.0 (±0.2)	1.47 (±0.05)	0.31 (±0.08)	3.0 (±1.5)
nn pairs[d] Gd^{3+} in LaCl$_3$	−20.6 (±2.0)	2.2 (±0.5)	0.3 (±0.1)	
nn pairs[c] Gd^{3+} in EuCl$_3$	77.3 (±3.0)	1.0 (±1.0)	0.5 (±0.2)	
	Quantized along the nnn axis			
Single ion[d] Gd^{3+} in LaCl$_3$	−3.0	−0.5	0	
Single ion[c] Gd^{3+} in EuCl$_3$	−20	−0.3	0	
nnn pairs[d] Gd^{3+} in LaCl$_3$	−29 (±15)	−0.8 (±0.3)	−0.5 (±0.3)	
nnn pairs[c] Gd^{3+} in EuCl$_3$	−28 (±15)	−0.5 (±0.3)	0.4 (±0.3)	

[a] Reference 12. [b] Reference 13. [c] This work. [d] Reference 1.

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[23] R. Clover and W. P. Wolf, Solid State Commun. **6**, 331 (1968).

[24] D. P. Landau, thesis, Yale University, 1967 (unpublished).

[25] J. H. Van Vleck, Rev. Mat. Fis. Teor. (Argentina) **14**, 189 (1962).

pairs $\Delta b_2{}^0(\mathrm{LaCl_3}) = -0.0026$ cm^{-1} and $\Delta b_2{}^0(\mathrm{EuCl_3}) = -0.0008$ cm^{-1}.

We mention these features without any theoretical discussion but we hope that they may ultimately prove useful for the understanding of the interaction of rare-earth S-state ions with their crystalline environment.

7. SUMMARY AND CONCLUSION

By measuring the spectra from single ions and from nn and nnn pairs of $\mathrm{Gd^{3+}}$ in $\mathrm{EuCl_3}$ we have determined the interaction constants between $\mathrm{Gd^{3+}}$-$\mathrm{Gd^{3+}}$ and $\mathrm{Gd^{3+}}$-$\mathrm{Eu^{3+}}$ ions in this lattice. From the pair measurements, we find that the $\mathrm{Gd^{3+}}$-$\mathrm{Gd^{3+}}$ interactions are almost entirely due to isotropic bilinear exchange and dipolar coupling, although the nnn spectrum reveals the possible presence of small additional interactions, as in the earlier experiments on $\mathrm{LaCl_3}$. We have found no conclusive evidence for the presence of any biquadratic anisotropic exchange, and any isotropic bilinear exchange is shown to be less than 3×10^{-4} cm^{-1}.

A small extrapolation permits accurate estimates to be made of the $\mathrm{Gd^{3+}}$-$\mathrm{Gd^{3+}}$ exchange constants in concentrated $\mathrm{GdCl_3}$, and it is found that the values account quantitatively for the observed high-temperature susceptibility and specific heat. The results prove conclusively that the ferromagnetic transition at 2.2°K is caused by a dominant *next*-nearest neighbor exchange coupling, resolving earlier speculations and uncertainties. The combination of nn and nnn interactions with competing signs and comparable magnetic-dipole interactions gives rise to some quite unusual spin-wave modes, as described recently by Marquard and Stinchcombe.[26]

Using the small shifts in the $\mathbf{g}$ tensors of single $\mathrm{Gd^{3+}}$ ions and $\mathrm{Gd^{3+}}$-$\mathrm{Gd^{3+}}$ pairs, we have also been able to determine approximate values for the isotropic components in the $\mathrm{Gd^{3+}}$-$\mathrm{Eu^{3+}}$ exchange interaction between nn and nnn. The values show a marked similarity to the $\mathrm{Gd^{3+}}$-$\mathrm{Gd^{3+}}$ interactions.

There is at present no theoretical explanation for the strengths or even the *signs* of the measured interactions nor for the marked variations with relatively small lattice changes. The absolute magnitudes of the individual interactions are all quite small, but this fact in itself permits their detailed study with unprecedented accuracy; we believe that our results call for serious attempts at quantitative theoretical explanations. Clearly, any such calculations will not be simple, and will involve not only the two interacting $4f$ shells and the $\mathrm{Cl^-}$ ligands but also the closed $5s^25p^6$ shells on each of the $\mathrm{Gd^{3+}}$ ions. However, complications of this kind will occur in all rare-earth superexchange calculations. The present cases may well represent some of the simplest situations which can be found in any ionic rare-earth system. In all rare-earth ions other than $\mathrm{Gd^{3+}}$ (and isoelectronic $\mathrm{Eu^{2+}}$), nonzero orbital angular momentum gives rise to the possibility of a number of complex effects, including high degree electric multipole, spin-phonon and anisotropic exchange interactions; in general these will involve a relatively large number of additional parameters. A discussion of some of these effects is being published as part III of the present series of papers.[27]

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[26] C. D. Marquard and R. B. Stinchcombe, Proc. Phys. Soc. (London) **92**, 665 (1967).

[27] R. J. Birgeneau, M. T. Hutchings, and R. N. Rogers, Phys. Rev. **175**, 1116 (1968); also J. M. Baker, R. J. Birgeneau, M. T. Hutchings and J. D. Riley, Phys. Rev. Letters **21**, 620 (1968).