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ESR Investigations of Nearest-Neighbor Gd^{3+} Pairs in Lanthanum Ethyl Sulfate*†

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The ESR spectrum of nearest-neighbor Gd^{3+} ion pairs in single crystals of hydrated lanthanum ethyl sulfate containing approximately 0.1- and 1-wt.% gadolinium has been identified and measured at 77°K. It has been found that the nature of the pair interaction is primarily dipolar, although a small superexchange interaction is also present. The best theoretical fit of the experimental pair spectrum is obtained with a spin Hamiltonian characterized by the crystalline-field parameters $b_2{}^0=188$, $b_4{}^0=3.2$, $b_6{}^0=0.4$ and the dipolar and exchange interaction constants $d=45$ and $J=2$, all in units of 10^{-4} cm^{-1}.

I. INTRODUCTION

A NUMBER of experimental electron-spin-resonance (ESR) investigations of paramagnetic ion pairs have been performed to obtain information concerning the interaction mechanisms between paramagnetic ions.[1] In most of these experiments, the dominant interaction has been a strong isotropic exchange coupling which only permits an evaluation of the exchange coupling constant from the intensities of the observed ESR transitions. Recently, Hutchings, Birgeneau, Rogers, and Wolf[2–4] have undertaken extensive ESR investigations of ion pairs in systems containing low concentrations ($\sim 1\%$) of paramagnetic ions. In the systems they have considered, the strength of the exchange interaction is comparable in magnitude with those of the ion pair dipolar interaction and the crystalline field splittings; thus, ESR transitions are allowed so that the exchange-coupling constant can be determined from the positions of the resultant ESR lines.

This paper reports the ESR investigation of Gd^{3+} ion pairs in single crystals of lanthanum ethyl sulfate (LaES) containing dilute concentrations of gadolinium ethyl sulfate (GdES). The ESR spectrum, arising from the ion pairs, consisted of many resonance lines whose intensities were considerably smaller than the seven fine structure lines of the isolated Gd^{3+} ions in the crystal. When the external magnetic field **H** was aligned with the c axis of the crystal, the pair spectrum showed a mirror symmetry about the central fine structure line $(\frac{1}{2}\leftrightarrow -\frac{1}{2})$ of the isolated Gd^{3+} ion. From this pair spectrum with $\mathbf{H}\parallel c$ axis, it was possible to obtain the interaction constants of the nearest-neighbor (nn) ion pairs in the crystal. We have found that the Gd^{3+} nn pair interaction in LaES is primarily dipolar, although a small but non-negligible exchange interaction is present.

II. CRYSTAL STRUCTURE AND SINGLE-ION SPECTRUM

The rare-earth ethyl sulfates form a group of isomorphic salts having the chemical composition $R(C_2H_5SO_4)_3\cdot 9H_2O$, where R indicates a trivalent rare-earth ion. Figure 1(a) shows the rhombohedral unit cell of the hexagonal crystal structure of these salts as determined by Ketelaar.[5] There are two rare-earth ions in the rhombohedral unit cell, one at the position $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and the other at $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$. As illustrated in Fig. 1(b), each of these rare-earth ions (taken as the reference ion 4) has two nn rare-earth ions (3 and 5), one on either side at a distance of approximately 7.1 Å along the c axis of the crystal. There are six equivalent next-nearest-neighbor (nnn) rare-earth ions (1, 2, 6, 7, 8, and 9) at 8.8 Å, and the angle between the c axis and a line joining the reference ion with any of these six nnn ions is about 66.3°. Each rare-earth ion in the ethyl sulfate unit cell is surrounded by nine molecules of water and their electric-dipole moments produce a crystalline electric field of C_{3h} symmetry at each rare-

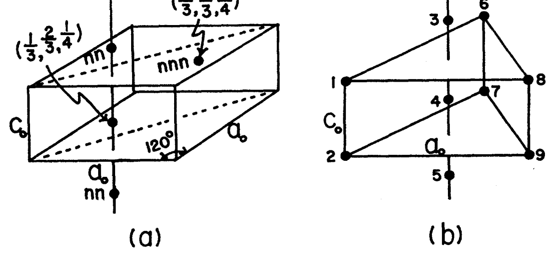

FIG. 1. (a) Unit cell of rare-earth ethyl sulfate. (b) Arrangement of nn (3 and 5) and nnn ions (1, 2, 6, 7, 8, and 9) about a given rare-earth ion (4) in ethyl sulfate.

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earth ion site, so that the two rare-earth ions in the unit cell are magnetically equivalent.

It has been observed that the eightfold spin degeneracy of the ground state ($^8S_{7/2}$) of Gd^{3+} is split into four Kramers doublets in a crystalline electric field of C_{3h} symmetry.[6] In an external magnetic field **H**, these doublets split, resulting in a seven-line fine structure spectrum, which can be observed in diamagnetic ethyl sulfate containing only small concentrations of gadolinium.[7,8]

In a single crystal of LaES containing 1% Gd^{3+} cations, approximately 2% of the gadolinium ions will statistically have one of their two nn diamagnetic lanthanum ions replaced by a gadolinium ion. The crystal should, therefore, display an ESR spectrum associated with the ion pairs in addition to the seven-line fine structure of the isolated ions. Concentrations of much more than 1% increase the probability of producing more complex spin clusters, which would give rise to very complicated ESR spectra. Concentrations of much less than 1% will reduce the nn pairs to a number too small to be detected by ESR methods. Although nnn pairs will occur at a rate three times more probable than nn pairs, it will be difficult to identify their ESR spectra as will be discussed in the following section.

III. THEORETICAL Gd^{3+} PAIR SPECTRUM

The theoretical ESR spectrum expected from the Gd^{3+} ion pair in a crystalline electric field of C_{3h} symmetry can be obtained from a spin Hamiltonian of the form[2]

$$\begin{aligned}\mathcal{H}=g\beta\mathbf{H}\cdot\mathbf{S}_1&+(B_2^0O_2^0+B_4^0O_4^0+B_6^0O_6^0+B_6^6O_6^6)_1\\ &+g\beta\mathbf{H}\cdot\mathbf{S}_2+(B_2^0O_2^0+B_4^0O_4^0+B_6^0O_6^0+B_6^6O_6^6)_2\\ &+J(\mathbf{S}_1\cdot\mathbf{S}_2)+d[\mathbf{S}_1\cdot\mathbf{S}_2-(3/r_{12}^2)\\ &\qquad\times(\mathbf{S}_1\cdot\mathbf{r}_{12})(\mathbf{S}_2\cdot\mathbf{r}_{12})]. \qquad (1)\end{aligned}$$

In this expression, $\mathbf{S}_1$ and $\mathbf{S}_2$ are the spin operators for ions one and two; the O_m^n are the standard crystalline field operators for the single ion[9]; and the B_m^n are constants dependent upon the lattice and whose magnitudes are determined experimentally. The last two terms in Eq. (1) are the isotropic exchange and magnetic dipole interactions, respectively, characterized by the interaction constants J and d. The dipole constant d is theoretically given by $g^2\beta^2/r_{12}^3$, where r_{12} is the radial distance from $\mathbf{S}_1$ to $\mathbf{S}_2$, but J has not yet been derived from first principles. There are many other interaction terms that could be added to the above spin Hamiltonian. Some of these interactions have been considered in detail by Hutchings, Birgeneau, and Wolf[2] for the case of Gd^{3+} pairs in LaCl$_3$, which has the same crystalline field symmetry as LaES, but smaller lattice parameters. However, the additional interactions they considered were found to be negligibly small, and we assume that this is also the case for Gd^{3+} pairs in LaES.

Considering the relatively large separation between the cation sites in LaES, it is reasonable to assume that J will be very small compared to d for Gd^{3+} ion pairs and that the pair interaction will be characterized primarily by the dipolar interaction. Other ESR investigations of rare-earth ion pairs in the ethyl sulfates[10,11] support this assumption. Therefore, to a first approximation, the pair spectrum can be thought of as arising from those Gd^{3+} ions which have their single-ion lines shifted by the dipole moments of their Gd^{3+} neighbors.

The principal angular dependence of the isolated Gd^{3+} ion spectrum in LaES is given by $(3\cos^2\theta'-1)$, where θ' is the angle between the magnetic field **H** and the symmetry axis of the C_{3h} crystalline field which coincides wlth the c axis of the crystal.[7] The principal angular dependence of the dipolar interaction is given by $(3\cos^2\theta-1)$, where θ is the angle between **H** and the bond axis of the particular pair under consideration. For an arbitrary direction of **H**, the six nnn pairs, in general, will be nonequivalent in the sense that the angles between **H** and the bond axes of the nnn pairs will generally be different. Thus, the ESR pair spectrum expected from the sample for an arbitrary direction of **H** would consist of resonance lines arising from the nn pairs and the six nonequivalent nnn pairs all admixed, thereby resulting in a very complex over-all spectrum.

When **H** is parallel to the c axis of the crystal and hence to the bond axis of the nn pairs, all of the six nnn pair bond axes will make an angle of 66.3° with **H**. Thus, the factor $(3\cos^2\theta-1)$ together with the greater distance between the ions of the nnn pairs should result in such a weak dipolar interaction between these ions that their resonance lines will not be resolved from the single-ion fine structure lines. It is, therefore, expected that the pair spectrum for $\mathbf{H}\|c$ axis would consist mainly of the nn resonance lines.

As will be discussed later, the nn pair spectrum will exhibit a mirror symmetry when **H** is parallel to the nn bond axis. In addition, the pair spectrum will have a turning symmetry with respect to the bond axis; that is, the same pair spectrum should appear at equal angles on either side of the bond axis for small angles. This turning symmetry originates from the fact that the nn pair axis coincides with the symmetry axis of the crystalline field (the c axis of the crystal). These symmetry properties are very useful in identifying the nn pair resonance lines from the ESR spectrum obtained

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[6] For a general discussion of the splitting of the $^8S_{7/2}$ Gd^{3+} ground state, see, for example, M. M. Abraham, L. A. Boatner, C. B. Finch, E. J. Lee, and R. A. Weeks, J. Phys. Chem. Solids **28**, 81 (1967).

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

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TABLE I. Dipolar interaction constants of various pairs of the ions shown in Fig. 1(b) when **H** is aligned with the 4-6 nnn pair axis.

Pairs	θ	$3\cos^2\theta-1$	$\dfrac{\lvert d(3\cos^2\theta-1)\rvert}{\lvert d(3\cos^2\theta-1)\rvert_{4-6}}$
4-6	0°	2	1
4-7	48°	0.35	0.17
4-1	106°	−0.74	0.37
4-2	128°	0.20	0.10
4-8	106°	−0.74	0.37
4-9	128°	0.20	0.10
4-3 (nn)	66°	−0.52	0.49
4-5 (nn)	113°	−0.52	0.49

with $\mathbf{H}\parallel c$ axis, should this spectrum contain any resonance lines from nnn pairs and/or impurity ions in the crystal.

There is, unfortunately, no convenient angle for which the nnn ESR spectrum can be isolated, considering the following facts: (1) If, for example, **H** is aligned with the 4-6 nnn bond axis [see Fig. 1(b)], the other pair axes will make angles with **H** as listed in Table I. The relative values of the dipolar interaction $d(3\cos^2\theta-1)$ for the various pairs are also given in Table I. Inspection of this table indicates that the ESR spectrum obtained with **H** parallel to the 4-6 bond axis will probably contain resonance lines of the 4-1, 4-8, 4-3, and 4-5 pairs as well as those of the 4-6 pair. (2) In addition, when **H** is parallel to one of the nnn pair axes, the angle θ' (between **H** and the c axis) is 66.3° so that the single-ion fine structure lines come very close together.[7,8] Therefore, many resonance lines associated with the various pairs mentioned above will not only overlap, but also will be masked by the intense single-ion fine structure lines. (3) In contrast to the nn pair spectrum, the nnn pair spectrum will not show the mirror or turning symmetry, since the large crystalline field terms in LaES have no symmetry about any of the nnn pair axes and will contribute large off-diagonal terms to the energy matrix of the pair when the axis of quantization is taken along **H**.

In view of the preceding considerations, we will primarily be concerned with theoretical and experimental pair spectra only for the nn pairs with $\mathbf{H}\parallel c$ axis. It should be noted that investigation of the theoretical spectrum for this alignment of magnetic field is sufficient to determine all the constants of the pair spin Hamiltonian of Eq. (1) except B_6^6. In addition, the mathematical analysis of the theoretical spectrum is greatly simplified for $\mathbf{H}\parallel c$ axis, as will be seen in the following paragraphs.

When the c axis of the crystal is parallel to **H**, which is taken to be in the z direction, the pair spin Hamiltonian of Eq. (1) simplifies to

$$\begin{aligned}\mathcal{H}={}&g\beta HS_{1z}+(B_2^0O_2^0+B_4^0O_4^0+B_6^0O_6^0)_1\\&+g\beta HS_{2z}+(B_2^0O_2^0+B_4^0O_4^0+B_6^0O_6^0)_2\\&+(J-2d)S_{1z}S_{2z}+\tfrac{1}{2}(J+d)(S_1^+S_2^-+S_2^+S_1^-),\end{aligned}\qquad(2)$$

where $S_1^\pm$ and $S_2^\pm$ are the usual raising and lowering operators.

As already discussed by Hutchings, Birgeneau, and Wolf,[2] the second-order perturbation due to the last term in Eq. (2) proves to be quite large in the representation $\lvert M_1,M_2\rangle$ characterized by the magnetic quantum numbers of the individual spins S_1 and S_2 of the pair. It does not help to use a representation characterized by the total angular-momentum quantum number $T(\mathbf{T}=\mathbf{S}_1+\mathbf{S}_2)$ and its magnetic quantum number T_z, since the crystalline field perturbation is large in this representation, even though the pair interaction is diagonal. It is, therefore, necessary to diagonalize the complete 64×64 matrix that results from the eight possible M values for each spin. Fortunately, the resulting 64×64 energy matrix factors into 15 submatrices, each characterized by states of the same total magnetic quantum number T_z and of dimension $8-\lvert T_z\rvert$. Since the Zeeman terms sum to a constant diagonal term within each submatrix and thus may be factored, all the submatrices occur in pairs, except for the 8×8 submatrix. Because of this pairing of the submatrices, the nn pair spectrum will exhibit a mirror symmetry, and if the g value of the pair spectrum is the same as that of the single-ion spectrum, the center of the mirror symmetry of the pair spectrum will coincide with that of the single-ion spectrum. The theoretical pair spectrum can, thus, be obtained by diagonalizing only eight submatrices (1×1, 2×2, …, 8×8) which contain contributions from just the crystalline field and pair interaction terms of the spin Hamiltonian of Eq. (2).

IV. EXPERIMENTAL

A series of single crystals of LaES doped with various weight concentrations of Gd^{3+} were kindly provided by Professor George Seidel of Brown University where they had been grown from aqueous solutions. The samples specifically investigated in the present experiment had been grown from solutions containing approximately 0.1 and 1% GdES.

All of the ESR measurements were performed at 77°K with a Varian V-4501 ESR spectrometer system operating at a microwave frequency near 9.2 GHz with 100-kHz field modulation. The magnetic field was

TABLE II. Isolated ion and pair spin Hamiltonian parameters for LaES:Gd^{3+} (in units of $10^{-4}\ \mathrm{cm}^{-1}$).

	Isolated ion	Ion pair
g	1.991 ± 0.002	1.991 ± 0.005
$b_2^0\ (3B_2^0)$	$204\ \pm2$	$188\ \pm3$
$b_4^0\ (60B_4^0)$	$-3.7\ \pm0.3$	$-3.2\ \pm0.8$
$b_6^0\ (1260B_6^0)$	$0.4\ \pm0.2$	$0.4\ \pm0.2$
d	···	$47\ \pm2$[a]
J	···	$2.0\ \pm0.5$

[a] The d value calculated using the interionic distance for LaES (see Ref. 7) is $47\pm0.5\times10^{-4}\ \mathrm{cm}^{-1}$.

supplied by a Varian V-3603 12-in. electromagnetic equipped with a Varian Fieldial.

Initial ESR measurements were directed to investigating the seven-line structure arising from the isolated Gd^{3+} ions in the crystal containing 1% GdES. The spin-Hamiltonian constants determined for the fine structure spectrum of the isolated ions in these measurements (see Table II) were consistent with those already reported at the same temperature.[8,10]

In an attempt to observe resonance lines arising from the Gd^{3+} nn pairs in the sample, ESR measurements were then taken with the spectrometer gain considerably higher than that used for the seven-line fine structure spectrum. The ESR spectrum so obtained displayed many additional weak lines in the vicinity of the seven fine structure lines. These additional lines were found to be highly sensitive to the crystal orientation. (If these lines were due to the Gd^{3+} nn ion pairs in the crystal, they should show a mirror symmetry as well as a turning symmetry discussed in the previous section.) By adjusting the magnetic field direction in steps of a few tenths of a degree around the c axis as determined by the seven-line fine structure, we observed a spectrum in which the weak lines were situated symmetrically about the central $(\frac{1}{2}\leftrightarrow-\frac{1}{2})$ fine structure line. Figure 2 shows the first derivative of this spectrum. It was found that the observed mirror symmetry about H_0 [the center of the $(\frac{1}{2}\leftrightarrow-\frac{1}{2})$ fine structure line] for $\mathbf{H}\|c$ axis could be destroyed if the magnetic field direction was changed by a few tenths of a degree. However, the same pair spectrum appeared at equal angles on either side of the c axis for small angles (the turning symmetry). In the spectrum shown in Fig. 2, the intense off-scale lines represent the Gd^{3+} single-ion fine structure and the intensities of these lines were approximately two orders of magnitude larger than those of the nn pair resonance lines; this relative ESR intensity is quite consistent with the relative concentration of the isolated, single ions and the nn pairs in the sample containing 1% GdES. There are at least 58 nn pair lines that are resolved in the spectrum, and, except for the mirror symmetry, they appear to have random positions and intensities. The line spectrum corresponding to the high-field half of the observed nn pair spectrum with $\mathbf{H}\|c$ axis is shown in Fig. 3(a). In this spectrum, the shaded areas represent those parts of the spectrum covered by the intense single-ion fine structure lines.

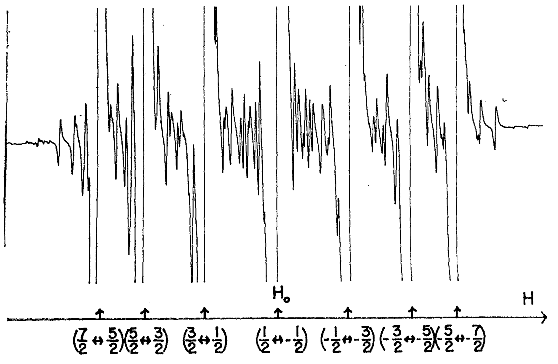

FIG. 2. Gd^{3+} nn pair ESR spectrum obtained from LaES containing 1% gadolinium ions for $\mathbf{H}\|c$ axis.

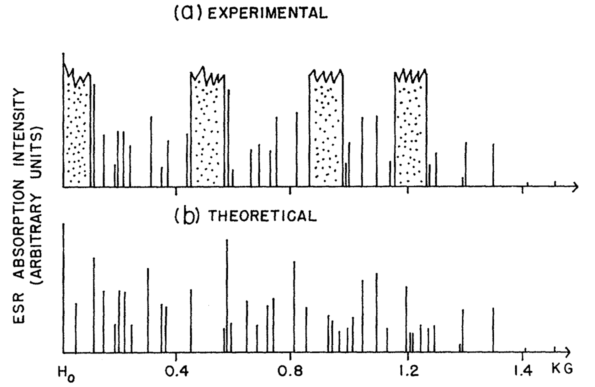

FIG. 3. (a) Line spectrum corresponding to the high-field half of the experimental spectrum shown in Fig. 2. (b) Theoretical nn pairs pectrum calculated from the pair spin Hamiltonian constants of Table II.

The ESR measurements were also performed for many crystal orientations other than the c axis. The observed ESR spectra displayed many resonance lines, whose intensities were comparable to those of the nn pair resonance lines for $\mathbf{H}\|c$ axis. These lines were believed to arise from various ion pairs in the crystal; however, as expected from the discussion in Sec. III, we have not observed any pair spectrum showing mirror symmetry other than for $\mathbf{H}\|c$ axis. No attempt was made to identify the resonance lines associated with the nnn pairs in the crystals for reasons cited in Sec. III.

Investigations of the sample containing 0.1% GdES yielded the nn pair spectrum similar to that shown in Fig. 2, except that the ESR intensity of the pair spectrum was approximately three orders of magnitude smaller than that of the seven-line fine structure.

V. DETERMINATION OF nn PAIR SPIN HAMILTONIAN CONSTANTS

As discussed in detail in Sec. III, the theoretical pair spectrum for the nn pair with $\mathbf{H}\|c$ axis can be calculated from the eigenvalues of the eight submatrices obtained from the general 64×64 energy matrix. To find the theoretical spectrum which best fits the observed nn pair resonance spectrum, the following procedures were adopted. A preliminary theoretical spectrum was calculated from the eight submatrices using the values of the crystalline field parameters for the isolated ion and the dipolar constant d calculated from the x-ray data on the cation nn separation in LaES. (See Table II.) The exchange interaction constant J was set equal to zero for this preliminary spectrum, since J was expected to be small as discussed in Sec. III. The diagonalizations of the resultant matrices were performed numerically with

TABLE III. Positions (measured in G from H_0) of theoretical and experimental Gd^{3+} pair ESR lines shown in Fig. 3. The theoretical lines enclosed in the brackets are plotted as single lines in Fig. 3(b).

Experimental	Theoretical
...	50
121	(116 120)
148	148
187	185
197	201
225	226
250	255
310	(302 306)
355	350
365	363
438	457
...	574
582	(580 585)
603	595
662	643
685	683
732	720
752	741
815	(801 804)
...	851
...	928
...	943
...	974
980	991
993	1012
1035	(1037 1040)
1097	(1087 1094)
1147	1129
...	1199
...	1208
...	1221
...	1251
1285	1286
1301	1293
1386	1391
1399	1398
1504	1500
1626	1611
1729	1725

the aid of an IBM 360/50 computer. The computer also calculated and plotted the positions and intensities of those resonance lines that arise from the transitions ($\Delta M_1=\pm1$, $\Delta M_2=0$) and ($\Delta M_2=\pm1$, $\Delta M_1=0$) between the eigenvalues.

This preliminary calculation showed poor over-all correlation with the experimental data. However, a group of lines in the outermost part of the theoretical spectrum did have the same relative positions and intensities as the observed pair spectrum, although the theoretical values of the line positions were larger by about 5%. The crystalline field parameters for similar ion pairs[2,3] have been found to differ substantially from the values found for the isolated ion in $LaCl_3:Gd^{3+}$ and $EuCl_3:Gd^{3+}$ and B_2^0 is the largest of these parameters in LaES:Gd^{3+}. For this reason the magnitude of B_2^0 was reduced to compensate for the difference between the calculated and observed splittings of the outer lines. When B_2^0 was so adjusted, and when a small exchange interaction of the order of a few G was also introduced, the individual lines in the theoretical spectrum could be identified with the individual experimental spectral lines.

To improve the theoretical fitting, a series of spectra were calculated by varying each of the five parameters (B_2^0, B_4^0, B_6^0, d, and J) in turn, in steps of a few percent about their values from the previous theoretical spectrum. The g value of the pair spectrum was assumed to be the same as that of the single-ion spectrum, since the center of the pair spectrum coincided with the center of the single-ion spectrum. The values of the parameters that yielded the best fit to the experimental spectrum by inspection were then chosen. Based on these improved values a new set of spectra were calculated in the same manner. This iterative procedure was continued until additional variations of the parameters did not yield any further improvement. In practice, the procedure was shortened by concentrating on lines in the spectrum which were particularly sensitive to only one parameter and whose positions were relatively unaffected by variations of a few percent in the other parameters.

A root-mean-square fitting routine would have been a more elegant approach to the problem, as was carried out by Hutchings, Birgeneau, and Wolf.[2] However, the masking of many of the experimental pair lines by the intense single-ion fine structure lines made identification of the individual lines in the pair spectrum quite difficult in the early stage of the fitting procedure, so that the iterative approach was more conveniently employed throughout.

The best theoretical fit with the experimental data was obtained for the values of the spin-Hamiltonian parameters listed in Table II. Figure 3(b) exhibits the resultant theoretical spectrum (high-field half) plotted on the same magnetic field scale as that for the experimental line spectrum of Fig. 3(a). Table III shows the magnetic field values for both experimental and theoretical pair resonance lines.

VI. DISCUSSION

In comparing the two spectra in Fig. 3, it is noted that the theoretical pair spectrum generally agrees with the experimentally observed spectrum, although there are small deviations (as much as 2%) for some of the pair resonance lines. Efforts were made to improve the fitting of these lines by further adjustments of the values of the spin Hamiltonian parameters given in Table II. However, the adjustments of the parameters outside the error limits shown in Table II produced noticeably poorer fittings. For this reason, we do not believe that the indicated discrepancies between the theoretical and experimental pair spectra arise from incorrect values of the pair spin Hamiltonian constants.

One might consider that higher-order pair interaction terms neglected in the spin Hamiltonian of Eq. (2) could be the cause of the indicated discrepancies. Hutchings *et al.*[2] observed discrepancies of similar magnitudes in the line positions of Gd^{3+} nn pairs in $LaCl_3$ and attempted unsuccessfully to explain these discrepancies by considering a number of such higher-order interactions. In addition to an anisotropic exchange interaction, they considered various types of biquadratic exchange interactions having the general form $f(S_1^2,S_2^2)$. The larger separation between the Gd^{3+} ions and the greater shielding effect of the large ethyl sulfate anion compared with the chloride anion in $LaCl_3$ make it unlikely that there is any sizable interaction between the ions of a Gd^{3+} pair in LaES that are not present in $LaCl_3$. Therefore, neglected higher-order interactions of this type are not likely to be the cause of the discrepancies noted for Gd^{3+} nn pairs in LaES.

Another interaction considered by Hutchings *et al.* was that arising from the distortion of the crystal field and the separation dependence of the pair interaction. However, inclusion of this interaction-induced distortion effect did not improve the fit of their theoretical spectrum, even though their estimate of this effect was approximately the same order of magnitude as the observed discrepancies. Since the pair interaction constants (J and d) for the Gd^{3+} ion pairs in LaES are very small compared to their values for $LaCl_3:Gd^{3+}$, this effect should be negligibly small in $LaES:Gd^{3+}$.

The magnitudes of the crystalline field interaction constants for the ion pairs were different from those for the isolated single ions both in $LaCl_3:Gd^{3+}$ and $LaES:Gd^{3+}$, indicating a local distortion of the crystalline field around the ion pairs. Such a local distortion will not only change the strength of the crystalline field, but should also alter its symmetry properties for the ion pairs. If this is the case, the pair spin Hamiltonian should contain additional terms reflecting the distortion of the crystalline field symmetry. It is conceivable that these additional terms may be responsible for the observed discrepancies in $LaES:Gd^{3+}$. Whatever form these terms may take, they must commute with the z component of the total angular momentum (T_z) or else be very small in order to be consistent with the mirror symmetry experimentally observed for the pair spectrum with $\mathbf{H}\|c$ axis.

Since the details of the theoretical pair spectrum depend critically on the signs of the crystalline field interaction constants as well as on their magnitudes, the absolute signs of these constants can be determined unambiguously for the ion pairs. In the case of $LaCl_3:Gd^{3+}$, the sign of B_2^0 for the ion pairs was found to be different from that for the isolated ion. Contrary to this, the sign of the crystalline field interaction constants of the pair spectrum in $LaES:Gd^{3+}$ turned out to be the same as those of the isolated ions in the crystal. Evidently in LaES, the crystalline field for a Gd^{3+} ion which participates in a pair interaction is not greatly affected by the presence of the nn Gd^{3+} ion since this ion is relatively distant and the pair exchange interaction is small. It is indicated that for S-state ion pairs for which the crystalline field interaction is dominant and for which the pair axis coincides with a crystalline field axis as in the case of $LaES:Gd^{3+}$, the signs of the crystalline field parameters for the ion pairs will generally be the same as those for the isolated ions. Therefore, from experimental investigations of the pair spectra, one could infer the signs of the crystalline field parameters for the isolated ion, even in those cases where these signs cannot be determined from the single-ion spectrum by conventional methods.

VII. CONCLUSIONS

From experimental ESR spectra, we have identified and measured the interactions for the nn Gd^{3+} ion pairs in LaES. It was established that the nature of the interaction between the ions is principally dipolar, although a small exchange interaction was also found to be present. The experimental nnn pair spectra were not investigated because of the overlap and great complexity of these spectra.

Small discrepancies were noted between the theoretical and experimental line positions of the pair spectrum. The origin of these discrepancies is not completely clear at this time; however, it is suggested that they arise from a small local distortion in the point symmetry of the crystalline field in the vicinity of the ion pairs.

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