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Spin-Spin and Crystal-Field Interactions in the Rare-Earth Ethyl Sulfates. I. The Spectrum of Gadolinium*

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The interactions between magnetic rare-earth ions in a set of isomorphic salts have been investigated under the experimental condition $g\beta H > kT$ such that the spins are highly aligned by the external magnetic field. Paramagnetic resonance under these conditions is found to show behavior qualitatively similar to ferromagnetic resonance. The high degree of spin alignment results in a nearly uniform internal field for samples having a regular shape, so that it is possible to observe narrow line spectra in concentrated paramagnetic salts. The spin-spin interactions may be directly determined from the line shifts at low temperatures, and from the observation of resolved structure that results from the resonance absorption of ions having a near neighbor ion whose spin is antiparallel to the magnetic field. In dysprosium ethyl sulfate containing gadolinium as an impurity, the interaction of a Gd ion with its first-, second-, and third-nearest-neighbor Dy ions, as well as the total interaction with all Dy neighbors, has been measured. The interaction may be explained in terms of a dipolar coupling between the spins. The influence of the spin-spin interactions on the angular variation of the Gd spectrum is also examined. The spin-lattice relaxation time of a Gd ion is found to depend on its nuclear spin.

INTRODUCTION

THE interactions between magnetic rare-earth ions in the isomorphic ethyl sulfate salts have been investigated under the experimental condition $g\beta H > kT$, such that the spins are almost totally aligned by the external magnetic field. Paramagnetic resonance under these conditions is found to show behavior qualitatively similar to ferromagnetic resonance. The high degree of spin alignment results in a nearly uniform internal field for samples having a regular shape, so that it is possible to observe *narrow line spectra* in a concentrated paramagnet.

Measurements have been performed on low concentrations (0.01%) of gadolinium ions in the paramagnetic cerium and dysprosium ethyl sulfates, as well as in the diamagnetic lanthanum and yttrium salts. Gd^{3+} is an S-state ion having an isotropic g value which does not vary by an experimentally detectable amount with the small changes in the crystalline electric fields between these salts. Thus, differences between the spectra of gadolinium in the diamagnetic and in the paramagnetic salts may often be related directly to the magnetic interactions between spins in the latter. Qualitatively, in the paramagnetic salts at low temperatures, line shifts due to the interaction of an ion with all of its neighbors may be expected. Also, the very small percentage of spins which are antiparallel to the field will lead to shifts in the resonant fields of their neighbors. These shifts can give rise to additional structure in the resonance spectrum, from which the interactions between ions at particular lattice sites may be directly determined.

CRYSTAL STRUCTURE AND EXPERIMENTAL TECHNIQUES

The rare-earth (RE) elements (and yttrium) have very similar chemical properties and form a set of isomorphic ethyl sulfate salts, having the chemical composition $RE(C_2H_5SO_4)_3\cdot 9H_2O$. These ethyl sulfate salts provide a convenient matrix in which to investigate the interactions between the magnetic ions because of the relatively large spacing between the rare-earth ions. This results in weak spin-spin interactions, which may then be treated as a perturbation on the Zeeman energy.

Figure 1 shows the crystal structure as determined by Ketelaar.[1] The over-all symmetry is hexagonal, and the two rare-earth ions at the positions $(\frac{1}{3},\frac{2}{3},\frac{1}{4})$ and $(\frac{2}{3},\frac{1}{3},\frac{3}{4})$ in the rhombohedral unit cell are magnetically

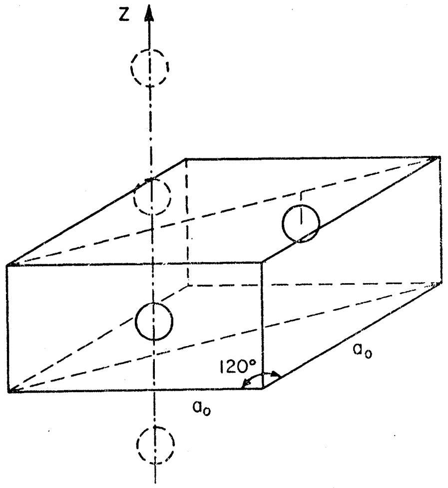

FIG. 1. Unit cell of $RE(C_2H_5SO_4)_3\cdot 9H_2O$ showing position of rare-earth ions.

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* This work was supported by the National Science Foundation and the Advanced Research Projects Agency.

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[1] J. A. Ketelaar, Physica 4, 619 (1937).

TABLE I. Room-temperature lattice constants of the rare-earth ethyl sulfates (in angstrom units).[a]

Ion	c_0	a_0
Lanthanum	7.11 ± 0.02	14.080 ± 0.003
Cerium	7.11 ± 0.01	14.048 ± 0.003
Praseodymium	7.09 ± 0.02	14.007 ± 0.003
Neodymium	7.07 ± 0.02	13.992 ± 0.003
Gadolinium	7.06 ± 0.02	13.931 ± 0.003
Dysprosium	7.04 ± 0.02	13.906 ± 0.003
Yttrium	7.05 ± 0.01	13.903 ± 0.003

[a] See Ref. 1.

equivalent. The room-temperature lattice constants, given in Table I, differ only slightly for the different salts. Each rare-earth ion has two nearest rare-earth neighbors at a distance $c_0=7.1$ Å along the hexagonal or c axis. It also has six equivalent second nearest neighbors, three in each of two planes perpendicular to and intersecting the c axis at $\frac{1}{2}c_0$ from the ion. The angle between the c axis and an internuclear line to a second-nearest neighbor is about 66.3°. The distance to a second-nearest neighbor is approximately 8.8 Å, and within experimental error the value of c_0/a_0 is 0.505 for all of these salts.

Each rare-earth ion is surrounded by 9 waters of hydration. The crystalline electric field at the site of the rare-earth ion is mainly produced by the electric dipole moments of these waters of hydration, and has the symmetry C_{3h}.

In order to achieve experimentally the condition of nearly total spin alignment it was necessary to work at high microwave frequencies and at low temperatures, such that $h\nu=g\beta H>kT$ at resonance. Under this condition only the lowest spin level will be appreciably populated. A superheterodyne cavity spectrometer operating at 35 kMc/sec was therefore constructed, and an all-glass triple-Dewar ^{3}He cryostat was employed to reach temperatures down to 0.3–0.4°K. At the lowest temperatures $h\nu/kT\sim4$ to 5.

The concentrated paramagnetic samples were tumble ground into spheres to ensure uniformity of the field within the samples. All samples were x-ray-oriented and glued to a quartz rod which was then positioned in the microwave cavity.

MAGNETIC PROPERTIES OF GADOLINIUM IN THE ETHYL SULFATES

A gadolinium ion has seven $4f$ electrons, which exactly half fill the shell. The ground state is thus an orbital singlet, $^8S_{7/2}$, and there are no first-order effects of spin-orbit coupling and crystal field on the eightfold spin degeneracy. The observed splitting of the spin levels must result from higher orders in perturbation theory, and is very small. Several mechanisms have been proposed,[2–5] but as yet the splitting of S-state ions is not completely understood.

One result of the very weak interaction of a gadolinium ion with the lattice is a long spin-lattice relaxation time, enabling observation of the resonance at room temperature in several of the ethyl sulfates. Also, the fine-structure splitting is so small (10^{-2} to 10^{-1} cm^{-1}) that it is easily measured by resonance techniques.

A crystal field of C_{3h} symmetry splits the eightfold degeneracy into four Kramers doublets. The spin Hamiltonian for isotropic g is given by[6,7]

$$H_s=g\beta\mathbf{H}_0\cdot\mathbf{S}+B_2^0P_2^0+B_4^0P_6^0+B_6^6P_6^6, \tag{1}$$

where the B_n^m are constants that depend upon the particular lattice, and the P_n^m are spin operators.[7,8] Evaluating the matrix elements, the energy levels with the magnetic field parallel to the symmetry axis (z axis) can be expressed as

$$\begin{aligned}&\pm\tfrac{7}{2}g\beta H_0+7b_2^0+7b_4^0+b_6^0,\\&\pm\tfrac{5}{2}g\beta H_0+b_2^0-13b_4^0-5b_6^0,\\&\pm\tfrac{3}{2}g\beta H_0-3b_2^0-3b_4^0+9b_6^0,\\&\pm\tfrac{1}{2}g\beta H_0-5b_2^0+9b_4^0-5b_6^0,\end{aligned} \tag{2}$$

where $b_2^0=3B_2^0$, $b_4^0=60B_4^0$, $b_6^0=1260B_6^0$. The terms in $b_6^6=1260B_6^6$ have been dropped since they are very small and only have matrix elements between states for which $\Delta M_s=\pm6$.

Between the eight levels there are seven transitions with $\Delta M_s=\pm1$, and the seven line spectrum shown in Fig. 2 is observed. (A nonlinearity in the magnetic field sweep makes the spacings on the high-field side appear larger.) The splitting is symmetric about the central absorption line, which is the result of the $M_s=-\frac{1}{2}$ to

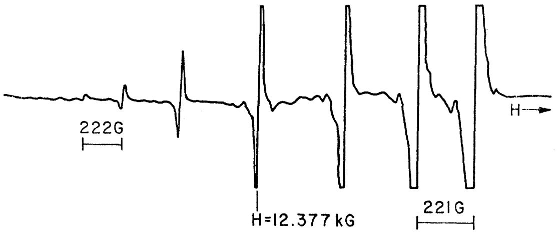

FIG. 2. Spectrum of the seven fine-structure lines of Gd (0.01%) in DyES. The magnetic field is parallel to the c axis. These measurements were made on a 0.86-mm^3 sphere at 35.49 kMc/sec. The observed intensity distribution results from the low temperature of 1.6°K. The magnet sweep is nonlinear.

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[2] J. H. Van Velck and W. G. Penney, Phil. Mag. **17**, 961 (1934).

[3] H. Wantanabe, Progr. Theoret. Phys. (Kyoto) **18**, 405 (1957).

[4] J. Kondo, Progr. Theoret. Phys. (Kyoto) **23**, 106 (1960).

[5] (a) V. J. Folen, Phys. Rev. **139**, A1961 (1965). (b) See Abraham, Boatner, Finch, Lee, and Weeks, J. Phys. Chem. Solids (to be published) for further references.

[6] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 387 (1953).

[7] See W. Low, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Suppl. 2.

[8] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A218**, 553 (1953).

TABLE II. Spin-Hamiltonian parameters for gadolinium in several rare-earth ethyl-sulfate salts. (Units are cm^{-1} times 10^{-4}. Experimental uncertainties are the same throughout and are only given for lanthanum ethyl sulfate at 4°K.)

	Lanthanum Ethyl Sulfate ($g=1.991\pm0.001$)		
	4°K	77°K	290°K[a]
b_2^0	$+(197\pm2)$	$+204$	$+191$
b_4^0	$-(3.85\pm0.3)$	-3.72	-3.68
b_6^0	$+(0.48\pm0.2)$	$+0.43$	$+0.53$
	Yttrium Ethyl Sulfate ($g=1.991\pm0.001$)		
	4°K	77°K	290°K
b_2^0	$+152$	$+157$	155
b_4^0	-3.91	-3.94	-3.78
b_6^0	0.60	$+0.54$	0.48
	Cerium Ethyl Sulfate		
	4°K	77°K	290°K
b_2^0	$+187$	$+194$	Not measured
b_4^0	-3.98	-3.94	(Observable)
b_6^0	$+0.56$	$+0.51$	
	Dysprosium Ethyl Sulfate		
	1.2°K	77°K	290°K
b_2^0	$+156$	Unobservable	Unobservable
b_4^0	-3.93		
b_6^0	$+0.55$		

[a] See Ref. 16.

$M_s=+\frac{1}{2}$ transition. Since the operators P_n^0 depend only on powers of S_z^2, this central transition is not affected by the crystal field to first order, or even to second order when H_0 is parallel to the c axis. The position of this line in the diamagnetic salts thus determines the g value, which is found to be isotropic. The separation of the three high-field lines (or of the three low-field lines) from the central line determines the magnitudes and relative signs of the three b_n^0. The absolute signs of the constants may be determined from the behavior of the spectrum at low temperatures, where the fact that the highest field line is largest in intensity shows that it is due to the $M_s=-\frac{7}{2}$ to $M_s=-\frac{5}{2}$ transition.

Values of the parameters for several salts at a few temperatures are presented in Table II. The values in lanthanum ethyl sulfate agree with those previously reported.[9,10] In the cerium and lanthanum salts, whose lattice constants are closest to each other, the values of b_2^0 are also close to each other. The same is true for the dysprosium and yttrium salts. The constant b_2^0 is temperature-dependent and has a maximum value in the vicinity of 77°K. Since the origins of the splitting of an S-state ion are not well understood, these variations will not be discussed here.

RELAXATION PHENOMENA

In the diamagnetic salts the gadolinium spectrum was observed at room temperature and below. As stated previously, this is due to the weak interaction of this S-state ion with the lattice, resulting in a long relaxation time. The gadolinium spectrum was also observed at room and liquid-nitrogen temperature in cerium ethyl sulfate (CeES). At these temperatures the resonance of the cerium ions is not observable since their very short spin-lattice relaxation time leads to a lifetime broadening. The cerium relaxation is sufficiently rapid that the magnetic interaction of a gadolinium ion with its surrounding Ce ions is averaged to zero. At 4°K the cerium spin-lattice relaxation time[11] is sufficiently long that the Gd resonance is broadened so as to be unobservable for the magnetic field parallel to the c axis. However, for the magnetic field perpendicular to the c axis the Gd resonance is not only observable but very narrow. This extreme anisotropy in the Gd linewidth is the result of the large nondipolar spin-spin interactions[12] (approximately 0.1 cm^{-1} due to electric quadrupole coupling) among the Ce ions in the ethyl sulfate lattice and the anisotropy of the g tensor of the ground-state Kramers doublet of Ce; $g_{\parallel}=3.76$ and $g_{\perp}\approx 0$. When the magnetic field is close to the c axis the Ce ions in the neighborhood of a Gd ion cannot undergo rapid reorientation in the field, in spite of the large spin-flip interactions of the form $S_{+i}S_{-j}$ among them. Each Ce ion in the immediate vicinity of a Gd ion is sufficiently dissimilar (because of differences in spin-spin interactions) that the probability of simultaneous reorientation of two spins is severely reduced by the requirement of conservation of energy. On the other hand, when the magnetic field makes a large angle with respect to the c axis, the Zeeman energy becomes less than the exchange energy. Under these conditions simultaneous transitions involving large numbers of Ce ions can occur, and the frequency of reorientation of any one spin becomes large compared to the static linewidth expressed in frequency units. In short, the Gd resonance is narrowed by cross relaxation within the Ce spin system, a process which is remarkably dependent upon the direction of the static magnetic field for Ce ions in the vicinity of a Gd ion.

Below about 3°K the Gd resonance in CeES with the field parallel to the c axis is observed to narrow as the Ce ions become aligned by the Zeeman interaction. At 0.4°K the linewidth is comparable to that in the diamagnetic salts. The cerium resonance is also seen.

The spin-lattice relaxation times of cerium and dysprosium in the ethyl sulfates are thought to be roughly comparable at high temperatures. However, in contrast to the case of the cerium salt, the gadolinium spectrum was not observable in dysprosium ethyl sulfate at either room or liquid-nitrogen temperatures. This

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

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

[11] P. L. Scott and C. D. Jeffries, Phys. Rev. **217**, 32 (1962).

[12] J. Dweck and G. Seidel, Phys. Rev. **146**, 359 (1966).

phenomenon has not been investigated in detail, but it is thought that the relaxation time of the gadolinium ions is shortened due to a Gd-Dy cross-relaxation process involving an excited state of the dysprosium. At low temperatures the relaxation time of the dysprosium ions is long, and the gadolinium and dysprosium spectra are both observable. At no temperatures was the Gd linewidth in DyES markedly dependent on direction of the field as in CeES. This is due to the fact that while the g tensor of Dy is highly anisotropic with $g_\perp \approx 0$, the Dy spin-spin interactions are strictly dipolar.[13] There exist no large $S_{+i}S_{-j}$ terms to cause rapid reorientation of the Dy spins.

In the diamagnetic salts lanthanum ethyl sulfate (LaES) and yttrium ethyl sulfate (YES) hyperfine structure was observed in the gadolinium spectrum. The isotropic species Gd^{155} and Gd^{157} both have a natural abundance of approximately 15% and nuclear spin $I=\frac{3}{2}$, the ratio of their magnetic moments being approximately $\mu_N{}^{157}/\mu_N{}^{155}=1.4$. Because of the smallness of the hyperfine interaction ion the structure was not well resolved. The best estimate for the hyperfine coupling constant A of $A\mathbf{I}\cdot\mathbf{S}$ is $A^{157}=(11.0\pm1.0\times10^{-4}$ $\mathrm{cm}^{-1})$.

The most remarkable feature of the hyperfine structure was the dependence on microwave power level of the relative intensities of the hyperfine lines compared to the absorption of the 70% abundant isotopes having zero nuclear spin. The $I=0$ transition was observed to saturate much more easily than the hyperfine components of the isotopes having $I=\frac{3}{2}$. At 4.2°K, power levels of 10^{-8} W into a cavity having a Q of 5000 were sufficient to saturate partially the $I=0$ resonance. Larson and Jeffries[14] have observed similar phenomena for a number of rare-earth ions in several host lattices; namely, the spin-lattice relaxation time is markedly dependent upon the nuclear spin. They have explained this observation quantitatively for neodymium and erbium on the basis of the hyperfine interaction admixing excited states into the ground state by rather larger amounts than does the Zeeman interaction in the so-called direct process relaxation, thereby leading to shorter relaxation times for the hyperfine components. It appears that a similar process must occur for Gd although the hyperfine interaction is very small. The direct process is itself extremely weak for Gd because of the S-state character of the ion.

DIPOLAR INTERACTIONS IN CONCENTRATED PARAMAGNETIC SALTS

The dipolar interaction between the paramagnetic ions having magnetic moments $\boldsymbol{\mu}_i$ and $\boldsymbol{\mu}_j$ can be represented by the Hamiltonian

$$\mathcal{H}_{ij\,\mathrm{dip}}=\frac{1}{r_{ij}{}^3}\left\{\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j-\frac{3}{r_{ij}{}^2}(\boldsymbol{\mu}_i\cdot\mathbf{r}_{ij})(\boldsymbol{\mu}_j\cdot\mathbf{r}_{ij})\right\}. \qquad (3)$$

Here r_{ij} is the magnitude of the vector $\mathbf{r}_{ij}$ between the two ions.

Van Vleck[15] has considered the effects of a Hamiltonian of the type $\mathcal{H}=\sum_{ij}\mathcal{H}_{ij\,\mathrm{dip}}$ as a perturbation on a spin system having an unperturbed Hamiltonian consisting of Zeeman and crystal-field terms. His calculation also includes the effects of exchange interactions, $\mathcal{H}_{ij\,\mathrm{ex}}=\mathbf{S}_i\cdot\mathbf{A}\cdot\mathbf{S}_j$. It is found that the static $S_{zi}S_{zj}$ terms contribute to the line moments in first order, but that the spin-flip $S_{+i}S_{-j}$ terms contribute in first order only if the spins i and j are identical. Spins are considered identical when they contribute to the same resonance line, in which case the spin-flip term conserves Zeeman energy. Dissimilarities between spins may, for example, be due to different g values, to large local fields arising from interactions with near neighbors, or to hyperfine interactions.

Terms such as $S_{zi}S_{+j}$ etc., which arise in the dipolar interaction, do not contribute to the line moments in first order, but in second order admix the spin levels and give rise to weak transitions for which $\Delta M_s\neq\pm1$. Since only those transitions for which $\Delta M_s=\pm1$ have been observed experimentally, inclusion of these terms would make the moment calculations incorrect, and they are truncated from the Hamiltonian. However, in a calculation of the line moments to second order, the effects of such terms on the energy of the levels between which the $\Delta M_s=\pm1$ transitions occur must be considered.

In those concentrated rare-earth ethyl sulfates where the interactions are mainly dipolar, the interaction of an ion with its two nearest neighbors splits each resonance absorption into three maxima. Bleaney *et al.*[16] were the first to observe and explain this phenomena, which has been discussed in greater detail by Svare and Seidel.[17] In this case there are three nonequivalent configurations of the two nearest-neighbor spins (considered to have $S=\frac{1}{2}$). As the temperature is lowered the nearest-neighbor configuration corresponding to the lowest field absorption peak becomes most probable, due to the higher degree of spin alignment. This results in a first moment shift of the triplet structure, with the *lowest* field absorption growing at the expense of the other two. At the lowest temperatures, where the spin alignment is essentially complete, only this single peak is observed.

Just as the interaction with the two nearest neighbors splits the resonance into three maxima, the interactions with equivalent further neighbors, if large, may further

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[13] J. Dweck and G. Seidel (to be published).

[14] G. H. Larson and C. D. Jeffries, Phys. Rev. **141**, 461 (1966); **145**, 311 (1966).

[15] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

[16] B. Bleaney, R. J. Elliott, and H. E. D. Scovil, Proc. Phys. Soc. (London) **A64**, 933 (1951).

[17] I. Svare and G. Seidel, Phys. Rev. **134**, A172 (1964).

split the resonance. This additional structure is most likely to be observable at lower temperatures where the resonance lines are somewhat narrower.

RESONANCE OF GADOLINIUM IN DYSPROSIUM ETHYL SULFATE—EFFECT OF THE DIPOLAR FIELDS

From Table II it can be seen that the g value of gadolinium is the same in the diamagnetic lanthanum and yttrium ethyl sulfates. Since the $M_s=-\frac{1}{2}$ to $+\frac{1}{2}$ transition from which it is determined is not affected by small changes in the crystal fields, it is expected to have the same value in dysprosium ethyl sulfate. Thus, at a given temperature and microwave frequency, any difference in the field position of this central absorption line in the dysprosium salt from that in the diamagnetic salts is due to the total magnetic interaction with all of the surrounding dysprosium ions. This interaction is expected to be predominantly dipolar since the radii of the $4f$ orbits of gadolinium and dysprosium are quite small, and the ions are fairly far apart.

The ground state of dysprosium in the ethyl sulfate is a Kramers doublet having $g_{\parallel}=10.8$ and $g_{\perp}\approx 0$. The large value of $g_{\parallel}$ leads to large dipolar interactions, and only the term in $S_{zi}S_{zj}$ need be considered since $g_{\perp}\approx 0$. At high temperatures the two dysprosium levels are equally populated, and each of the seven gadolinium fine-structure lines should exhibit a triplet structure, due to the different nearest-neighbor configurations possible (The small concentration of the gadolinium ensures that almost all of its neighbors will be dysprosium ions.) The lines seen at very low temperatures are actually just the low-field component of each triplet structure. This component dominates because the large $g_{\parallel}$ of dysprosium leads to almost total alignment of the Dy^{3+} spins at the external magnetic field values appropriate to the gadolinium resonance. At very low temperatures the linewidths are not determined by the spin-spin interaction and are essentially the same as those in the diamagnetic salts (~8 G).

Figure 2 shows the spectrum of gadolinium (0.01%) in dysprosium ethyl sulfate at 1.6°K. Using $g=1.991$, the central resonance is found to be shifted to lower fields by 357±5 G. The calculated total shift is given by the lattice sum of the static dipolar interactions with the dypsrosium ions[17]

$$\Delta H_{\text{total}}=\frac{g_{\parallel}\beta}{2}\tanh\frac{g_{\parallel}\beta H}{kT}\sum_j(1-3\cos^2\vartheta_{ij})/r_{ij}^3, \quad (4)$$

where the sum is over all Dy ions. Following the standard approach, the summation is divided into two parts. Within a small sphere about the Gd ion the sum is performed over lattice points whereas outside the sphere the magnetization is treated as being continuous and the sum converted to an integral. For the spherical sample used this integral vanishes. The lattice sum for all ions closer than $a_0\sqrt{10}$ has been computed by Daniels,[18] who finds the value to be $18.7\times a_0^{-3}$. Using this value and $g_{\parallel}=10.8$ for dysprosium, we calculate $\Delta H=348$ G at 1.6°K. The positive sign of ΔH means that it adds to the external field, and that resonance occurs at lower values of the external field.

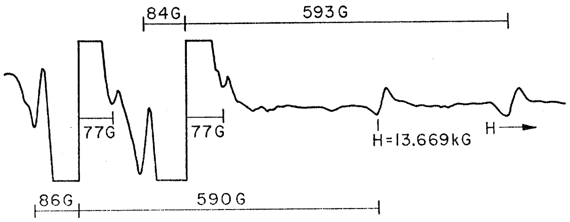

FIG. 3. Resolved structure in the Gd spectrum due to dipolar interactions with specific Dy neighbors. This trace is an expanded section of Fig. 2 showing the two highest field fine-structure lines. The additional structure is explained in the text.

Weak structure in the absorption spectrum, which results from gadolinium ions having a near neighbor dysprosium ion antiparallel to the magnetic field, is shown in Fig. 3. The two main lines are the fine-structure lines ($\Delta M_s=-\frac{7}{2}$ to $=\frac{5}{2}$ and $\Delta M_s=-\frac{5}{2}$ to $-\frac{3}{2}$ transitions) of gadolinium ions having all neighbors parallel to the magnetic field. The weak lines approximately 590 G higher in field than each main gadolinium line are due to a gadolinium resonance absorption with one of the nearest-neighbor ions antiparallel to the external field. Due to the large magnitude of the interaction and to the narrow linewidths these dipole-split lines are completely resolved. Similarly, the lines approximately 77 G above the main lines are due to gadolinium ions with an antiparallel neighbor at a distance $2c_0$ along the c axis. This value is approximately $(\frac{1}{2})^3$, or $\frac{1}{8}$ of the 590-G splitting due to the nearest neighbor at a distance of c_0. The lines at approximately 84 G lower field than the main lines result when one of the six second-nearest-neighbor dysprosium ions at 8.8 Å from the gadolinium ion is antiparallel. The small value and opposite sign of this shift results from the angular dependence factor $(1-3\cos^2\vartheta_{ij})$ of the dipolar field. The experimental and calculated values are given in Table III.

Agreement between the experimental and calculated values is found within the combined errors. The fact that the calculated values are consistently low is at-

TABLE III. Magnetic interaction of gadolinium with dysprosium in the ethyl sulfate. (Units are in gauss.)

	Lattice sum	Nearest neighbor	Neighbor at $2c_0$	Second-nearest neighbor
Experimental	357±5	590± 2	77±4	−84±5
Calculated	348±7	576±12	72±2	−78±2

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[18] M. Daniels, Proc. Phys. Soc. (London) **A66**, 673 (1953).

tributed to the use of room-temperature values of the lattice constants. Any thermal contraction of the lattice on cooling would result in an increase of the dipolar fields, possibly of the order of 1%. This, combined with the possible error in the value of $g_{\parallel}$ of dysprosium, results in a total uncertainty of about 2% in the calculated values, as indicated. The relatively large experimental errors in the 77- and 84-G splittings are due to the fact that the corresponding lines overlapped the main absorption lines.

The fact that the weak structure results from gadolinium ions with antiparallel neighbors is also shown by the temperature dependence and relative intensities of these lines. As the temperature is increased the spin alignment decreases, and the intensity of the weak lines increases. When the temperature is decreased to 0.4°K, where the spin alignment is essentially complete, the weak structure is unobservable. Each gadolinium ion has six second-nearest-neighbor dysprosium ions, two nearest neighbors, and two neighbors at $2c_0$ along the c axis. It is thus expected that the absorption line corresponding to an antiparallel second-nearest neighbor will have approximately three times the intensity of the lines corresponding to antiparallel nearest neighbors and neighbors at $2c_0$, as is observed experimentally. (The lines 590 G higher in field than the main lines appears broader than the other weak lines due to a nonlinearity in the field sweep.)

As expected, the interaction between the gadolinium and dysprosium ions can be explained in terms of a dipolar interaction alone. An upper limit of 14±14 G may be set on the magnitude of any exchange interaction between the two ions when they are at nearest-neighbor sites. Measurements on Gd in CeES have also shown the Ce-Gd interaction to be strictly dipolar as reported previously.[12]

RESONANCE OF GADOLINIUM IN DYSPROSIUM ETHYL SULFATE—ANGULAR VARIATION OF THE SPECTRUM

In the diamagnetic ethyl sulfate salts a gadolinium ion, which has an isotropic g value, is always quantized along the direction of the external magnetic field. The variation of the energy levels as the magnetic field direction is changed can be found from Eq. (1), where the P_n^0 have the same angular properties as the corresponding spherical harmonics $Y_n^0(\theta)$, and θ is the angle between H_0 and the c axis. In the concentrated dysprosium salt this angular variation is complicated by the magnetic interactions.

When calculating the angular variation of the dipolar interaction it must be remembered that the Gd and Dy spins are not quantized in the same direction. For an ion that has an axial g tensor and the external field at an angle θ with respect to the symmetry axis, the axis of spin quantization makes an angle Ψ with the axis, where $\tan\Psi=(g_\perp/g_{\parallel})\tan\theta$.[7] In the case of dysprosium in the ethyl sulfate, where $g_\perp\approx 0$, then $\Psi\approx 0$. This means that the dysprosium spins do not follow the magnetic field as it is rotated but remain aligned along the symmetry axis. Because of this feature the dipolar interaction between a Gd ion and a Dy ion takes a somewhat unusual form.

The interaction of a Gd ion with the external field $\mathbf{H}_0$, which makes an angle θ in the x-z plane with respect to the z axis (symmetry axis), and with its surrounding Dy neighbors can be written as

$$\begin{aligned}\mathcal{H}=&\,g_i\beta H_0(S_{zi}\cos\theta+S_{xi}\sin\theta)+\mathcal{H}_{\mathrm{crystal}}\\&+g_ig_{\parallel j}\beta^2\sum_j\frac{1}{r_{ij}^3}S_{zj}\{S_{zi}(1-3\cos^2\vartheta_{ij})-3S_{xi}\sin\vartheta_{ij}\\&\times\cos\vartheta_{ij}\sin\varphi_{ij}-3S_{yi}\sin\vartheta_{ij}\cos\vartheta_{ij}\cos\varphi_{ij}\}\,.\end{aligned}\qquad(5)$$

Here ϑ_{ij} and φ_{ij} are the polar and azimuthal angles, respectively, of the vector connecting the Gd ion i and the Dy ion j. The Gd ion is taken to have an isotropic g value whereas $g_{\perp j}=0$ for the Dy ions. The $\mathcal{H}_{\mathrm{crystal}}$ represents the crystal-field terms of Eq. (1).

In computing the interaction of a Gd ion with its neighbors at low temperatures when all the Dy ions are aligned, terms containing the azimuthal angle φ_{ij} sum to zero because of the symmetry of the lattice for near neighbors and because of axially symmetric sample geometry for distant ions. (These terms are, however, important at high temperatures in determining the linewidth of the Gd resonance when the magnetic field is not parallel to the symmetry axis.) As a result, the interaction at low temperatures can be expressed as

$$\begin{aligned}\mathcal{H}=g_i\beta\Big\{S_{zi}\Big[H_0\cos\theta+g_{\parallel j}\beta\sum_j\frac{1}{r_{ij}^3}S_{zj}(1-3\cos^2{}_i\vartheta_j)\Big]\\+S_{xi}H_0\sin\theta\Big\}+\mathcal{H}_{\mathrm{crystal}}\,.\end{aligned}\qquad(6)$$

Hence, the interaction of a Gd ion with the Dy lattice can be described by a static-dipole magnetic field $\mathbf{H}_d$ parallel to the c axis. A gadolinium spin experiences a total field $\mathbf{H}_{\mathrm{tot}}=\mathbf{H}_0+\mathbf{H}_d$, which makes an angle α with respect to the c axis.

$$\cot\alpha=\cot\theta+\frac{g_{\parallel j}\beta}{H_0\sin\theta}\sum_j\frac{1}{r_{ij}^3}S_{zj}(1-3\cos^2\vartheta_{ij})\,.\qquad(7)$$

These considerations are of importance in determining the appropriate crystal-field splittings for a given orientation of the external magnetic field.

Consider first the angular variation of the spacing between the central Gd line ($M_s=-\frac{1}{2}$ to $+\frac{1}{2}$ transition) and each of the three higher field fine-structure lines (or equivalently, each of the three lines at lower field). This variation is shown in Fig. 4. The curves are the result of calculations which include the effect of the dipolar fields on the angle of the total field seen by the Gd ions. The angle α is found as a function of θ from Eq. (7) and used in Eq. (1). When $\theta=35°$, for example, α

TABLE IV. Angular variation of the nearest-neighbor dipolar splitting of gadolinium in dysprosium ethyl sulfate. (Units are in gauss.)

θ	590 cosα	Crystal-field corrections	Sum	Experimental splittings
		$M_s=-\frac{7}{2}\rightarrow-\frac{5}{2}$ Transition		
0°	590	0	590	593±2
15°	572	−8	564	566±2
25°	539	−20	519	522±2
35°	492	−35	457	448±3
45°	431	−46	385	383±3

θ	590 cosα	Crystal-field corrections	Sum	Experimental splittings
		$M_s=-\frac{5}{2}\rightarrow-\frac{3}{2}$ Transition		
0°	590		590	590±2
15°	572	−5	567	⋯
25°	539	−13	526	521±2
35°	492	−23	469	459±3
45°	431	−31	400	397±3

is 33.5°. Second-order contributions from both the crystalline and dipolar fields are also included. The agreement with the experimental data is seen to be excellent.

The angular variation of the approximately 590-G splitting due to an antiparallel nearest neighbor has also been examined, a splitting which might at first be expected to vary as 590 cosα. The quantity 590 cosα is the magnitude of the projection of the contribution to $\mathbf{H}_d$ of the nearest neighbors onto the direction of $\mathbf{H}_{\text{tot}}$. However, since $\mathbf{H}_d$ differs by 590 G for Gd ions contributing to the two different resonance lines, the angle α is not the same for these different ions. The crystal-field splittings being very sensitive to angle are thus different for the ions contributing to the two lines. When corrections are made for the differences in crystal-field splittings, the agreement between the observed and calculated angular variation of the dipole field separation are in very good agreement as presented in Table IV. The difference in the angular variation for the $-\frac{7}{2}\leftrightarrow-\frac{5}{2}$ and $-\frac{5}{2}\leftrightarrow-\frac{3}{2}$ transitions appears properly accounted for.

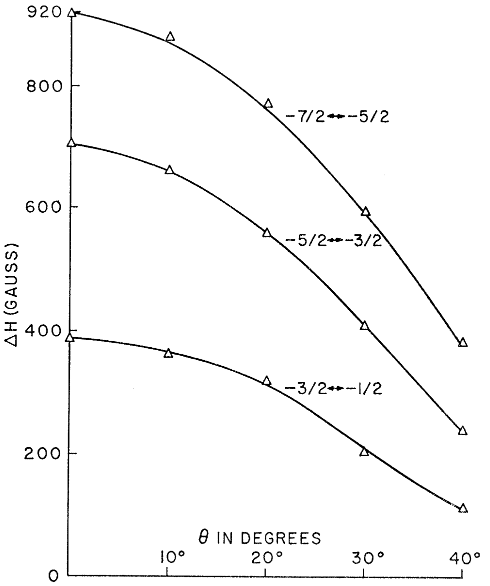

FIG. 4. Angular variation of the fine-structure splitting of the three high-field fine-structure lines with respect to the central line, $-\frac{1}{2}\leftrightarrow+\frac{1}{2}$. θ is the angle between the magnetic field and the c axis. The curve represents the calculated variation while the experimental data is indicated by the points.

TABLE V. Angular variation of the central gadolinium line in dysprosium ethyl sulfate. (Units are in gauss.)

θ	ΔH from Eq. (8)	Experimental value of ΔH	ΔH from Eq. (9)
0°	357	357±4	357
10°	350	346±4	349
20°	330	319±4	323
30°	310	278±4	282
40°	264	224±4	225

A seemingly simple angular variation is that of the central transition itself. Here there are no first-order crystal-field effects, and the second-order corrections that are applied have been experimentally verified for gadolinium in the diamagnetic yttrium ethyl sulfate. The g value is isotropic and the dipolar field is expected to vary as $H_d\cos\alpha$ where $\mathbf{H}_d=357$ G. The theoretical shift of the line to second order in crystal-field and dipolar interactions is given in units of G by

$$\Delta H_{\text{central}}=357\cos\alpha-80\sin^2\alpha\cos^2\alpha+14\sin^2\alpha. \quad (8)$$

Experimental and calculated values are presented in Table V. The agreement is not as good as had been expected. This discrepancy cannot be accounted for by demagnetizing fields that might arise if the sample shape deviated slightly from a sphere, since the same results were obtained for several different spherical samples. This calculation is also not as sensitive to small errors in θ (e.g., from sample orientation) as were the preceding calculations. It may be pointed out, however, that the preceding calculations considered only the spacing between lines, and any effect that shifted all lines equally would drop out there.

A better fit of the data is found by using an empirical relation

$$\Delta H=590\cos\alpha-233, \quad (9)$$

as shown in Table V. This empirical relation would seem to imply that the dipolar fields from the nearest neighbors behave as expected (i.e., vary as cosα), but that the field from all other neighbors do not.

Several phenomena such as incomplete spin alignment of the dysprosium spin system have been considered but do not appear capable of accounting for the experimental results. One consideration, the admixture of excited crystal-field levels into the ground-state Kramers doublet by off-diagonal terms of the Zeeman interaction, is calculated to change $g_{\parallel}$ by 2.5% for $\theta=40°$ and $H=12$ kG, but the corresponding decrease in ΔH is only 7 G, not sufficient to explain the discrepancy. The lack of experimental agreement with Eq. (8) is not as yet understood.