PHYSICAL REVIEW VOLUME 136, NUMBER 5A 30 NOVEMBER 1964

Nondipolar Interaction Between Nearest-Neighbor Neodymium Ions in the Ethyl Sulfate*

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(Received 2 July 1964)

Measurements made on the EPR spectrum of a pair of interacting nearest-neighbor neodymium ions in lanthanum ethyl sulfate show that the interaction is predominantly dipolar, but that there is an additional term $A_{ij}S_{iz}S_{jz}+\frac{1}{2}B_{ij}(S_{i+}S_{j-}+S_{i-}S_{j+})$, with $A_{ij}=(+32\pm6)\times10^{-4}\text{cm}^{-1}$ and $B_{ij}=(-3\pm3)\times10^{-4}\text{cm}^{-1}$. A semiquantitative discussion is given of the possible origins of this nondipolar contribution including superexchange, electric quadrupole-quadrupole, and virtual-phonon exchange interactions.

I. INTRODUCTION

In a recent paper, Svare and Seidel[1] discussed possible deviations from purely magnetic dipole-dipole interactions between nearest-neighbor neodymium ions in neodymium ethyl sulfate (NdES). Their conclusions were drawn from a study of the variation of the EPR line shape of undiluted NdES as a function of temperature. The purpose of this paper is to report some hitherto unpublished work[2] on the EPR spectra of pairs of interacting neodymium ions in NdES diluted with LaES, which is in agreement with the findings of Svare and Seidel. The much narrower lines in the dilute material make possible more accurate measurement of the interactions; but the increase in resolution is somewhat offset by the lack of knowledge of the separation of the interacting ions because of displacements due to local strains in a dilute material. However, evidence will be presented which suggests that impurity ions are incorporated substitutionally into the host lattice without great distortion of the lattice.

The ethyl sulfates are a particularly suitable material for making interaction measurements because of their convenient crystal structure. Figure 1 shows the arrangement of neighboring lanthanon ions. Each lanthanon ion has only two nearest neighbors at about 7Å along the hexad axis of the crystal. The six next-nearest neighbors are about 8.8Å away and in such a direction that for an external field along the crystal axis they contribute a very small dipolar field. Hence, for an external field parallel to the crystal axis, the dipolar field from the two nearest neighbors is much greater than that due to any other neighbors, and this leads to a resolved three-line structure which was first reported by Bleaney, Elliott, and Scovil.[3] If both neighboring magnetic moments are aligned parallel to the field, the EPR line is displaced by about 188 G to lower field; and if both neighbors are aligned antiparallel to the field, the EPR line is displaced in the opposite direction. When the two neighbors are antiparallel to one another, their dipolar fields cancel giving an undisplaced EPR line; and as there are two configurations of antiparallel neighbors, this line is twice as intense as the other two. At low temperatures it is more probable that neighbors are aligned parallel to the external field than antiparallel, so that the relative intensities of the three components varies. So also does their position, and it is from a detailed analysis of the variation of position that Svare and Seidel conclude that, although the interaction with nearest neighbors is predominantly dipolar, there is an additional term of the form $A_{ij}S_{iz}S_{jz}$ (the z direction is along the crystal axis).

The analysis of Svare and Seidel gives careful consideration to the effects of interaction with more distant neighbors. These complications of analysis do not occur in the interpretation of the spectrum of a pair of interacting ions, because they have no other near neighbors. To obtain a reasonable concentration of such pairs, crystals of LaES were used containing between 1 and 10% NdES. Less than 1% gives pair lines which are weaker than the hyperfine lines due to Nd^{143} and Nd^{145}, and more than 10% gives too high a probability of larger clusters of paramagnetic ions. The pair lines appear as satellites to the much more intense line due to isolated ions, but even in the 10% sample

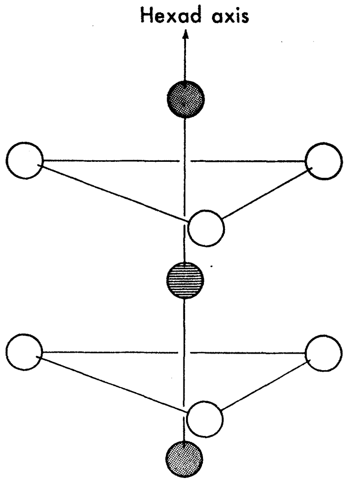

FIG. 1. Position of the rare-earth ions in the ethyl sulfate crystal structure. The lightly shaded circles are the nearest neighbors, and the open circles the next-nearest neighbors.

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* Supported in part by the U. S. Atomic Energy Commission and the U. S. Office of Naval Research.

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

[2] J. M. Baker, thesis, Oxford University, 1954 (unpublished).

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

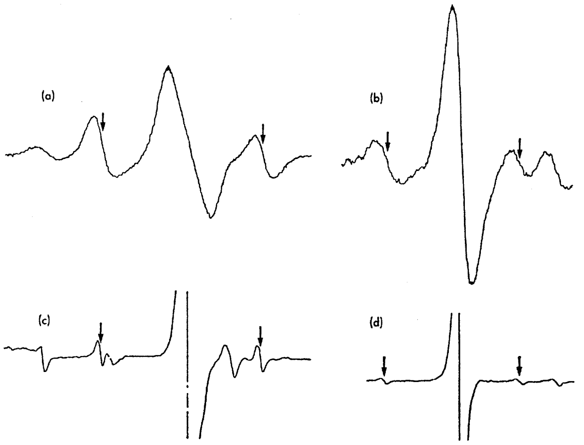

FIG. 2. Chart recording of satellite and main lines for H parallel to the crystal axis (a) central line of LaES containing 10% Nd; (b) hyperfine line of LaES containing 10% Nd; (c) and (d) are the same lines in LaES containing 1% Nd.

where the linewidth is about 50 G, the separation of the satellites is sufficient for them to be quite well resolved in some directions; see Fig. 2. The fact that about 20% of the neodymium ions have a hyperfine structure is quite useful, because one can study the interaction between one of these ions and an even-even isotope. The ions in such a pair are dissimilar, in that their Larmor precession frequencies differ, and terms in $S_{i+}S_{j-}$ do not contribute in first order to the interaction. Such terms do contribute to the interaction between a pair of even-even isotopes, so that a measurement of both types of pairs facilitates a separation of the various terms in the interaction Hamiltonian.

II. THEORY

The spin Hamiltonian for a single isolated neodymium ion is

$$\mathcal{H}=g_{\parallel}\beta H_zS_z+g_{\perp}\beta(H_xS_x+H_yS_y) +AS_zI_z+B(S_xI_x+S_yI_y)\,.$$

The first two terms are the same for all ions; the z axis is parallel to the crystal axis, and $g_{\parallel}=3.535$ and $g_{\perp}=2.073$. The third and fourth terms are hyperfine structure terms which are only present for the isotopes Nd^{143} ($A=0.038$ cm^{-1} and $B=0.020$ cm^{-1}) and Nd^{145} ($A=0.024$ cm^{-1} and $B=0.012$ cm^{-1}). The spin Hamiltonian for a pair of interacting ions comprises the sum of the spin Hamiltonians for two isolated ions plus a term describing the interaction. The states of the whole system will be written $|\langle S_{iz}\rangle\langle S_{jz}\rangle\rangle$.

As the g values of Nd in LaES are anisotropic, the general expression for dipolar interaction between two ions is quite complicated. However, our main concern is with ions which lie on the z axis separated by distance R, when the interaction spin Hamiltonian is

$$\mathcal{H}_{ij}=a_{ij}S_{iz}S_{jz}+\tfrac{1}{2}b_{ij}(S_{i+}S_{j-}+S_{i-}S_{j+})\,,$$

where

$$a_{ij}=A_{ij}-2g_{\parallel}^2\beta^2/R^3\,,$$
$$b_{ij}=B_{ij}+g_{\perp}^2\beta^2/R^3\,.$$

A_{ij} and B_{ij} have been included to allow the possibility of general anisotropic nondipolar interaction, but Svare and Seidel found that $B_{ij}=0$.

When the external field is applied along the crystal axis, the unperturbed $|+\tfrac{1}{2},-\tfrac{1}{2}\rangle$ and $|-\tfrac{1}{2},+\tfrac{1}{2}\rangle$ states of a pair of *similar* ions are degenerate, and the term in b_{ij} is important. Satellites are produced by transitions in which S_z for only one ion changes, and they occur at[4]

$$h\nu=g_{\parallel}\beta H\pm\tfrac{1}{2}(a_{ij}-b_{ij})\,. \qquad (1)$$

If the ions are dissimilar, the effect of b_{ij} is merely to produce a second-order shift $(\tfrac{1}{2}b_{ij})^2/\Delta$ of both satellites, where Δ is the first-order separation of the levels $|+\tfrac{1}{2},-\tfrac{1}{2}\rangle$ and $|-\tfrac{1}{2},+\tfrac{1}{2}\rangle$. If one of the two ions has a hyperfine structure and is in the state $I_z=m$, the separation Δ is equal to Am. The position of the satellites due to the transitions of the ion with hyperfine structure (which therefore appear as satellites of a hyperfine line in the single ion spectrum) are[4]

$$h\nu=g_{\parallel}\beta H+Am+(\tfrac{1}{2}b_{ij})^2/Am\pm\tfrac{1}{2}a_{ij}\,. \qquad (2)$$

When the external field is applied perpendicular to the crystal axis, the expressions for the positions of the satellites can be obtained from (1) and (2) by interchanging the x and z axis, which entails replacing $g_{\parallel}$ by $g_{\perp}$, A by B, a_{ij} by b_{ij}, and b_{ij} by $\tfrac{1}{2}(a_{ij}+b_{ij})$. This gives for two similar ions

$$h\nu=g_{\perp}\beta H\pm\tfrac{1}{4}(a_{ij}-b_{ij})\,, \qquad (3)$$

and for dissimilar ions

$$h\nu=g_{\perp}\beta H+Bm+(a_{ij}+b_{ij})^2/16Bm\pm\tfrac{1}{2}b_{ij}\,. \qquad (4)$$

In both expressions (2) and (4), the second-order effects of the off-diagonal elements of the hyperfine structure have been omitted because they shift both a particular hyperfine line and its satellites equally.

As a function of the angle θ between the direction of the external field and the crystal axis, the separation of the satellites from each other is, for those on the line due to even-even isotopes,

$$\tfrac{1}{2}(1-3\cos^2\theta)(a_{ij}-b_{ij})\,, \qquad (5)$$

and for those on the hyperfine lines,

$$a_{ij}\cos^2\theta+b_{ij}\sin^2\theta\,. \qquad (6)$$

III. EXPERIMENTAL RESULTS

To facilitate the following discussion, we will call the large line in the single-ion spectrum due to even-even isotopes "the central line," and the lines due to Nd^{143} and Nd^{145} "the hyperfine lines." The lines of the single-ion spectrum will be called the "main lines"

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[4] Expressions (1) and (2) are derived in the Appendix.

when it is necessary to distinguish them from the "satellite lines" of the pair spectrum.

Measurements of the satellite positions were made at 20° and 4.2°K at about 25 and 9.4 kMc/sec on several crystals of LaES containing between 1 and 10% NdES [a few measurements were also made using yttrium ethyl sulphate (YES) as a diluent]. The line positions were measured by simultaneous excitation of proton resonance in the same field as that used for EPR. When the external field is parallel to the crystal axis, both of the satellites on the central and the extreme hyperfine lines are well resolved. When the field is perpendicular to the axis, the satellites on the central line are resolved; but in most samples only one satellite was observed on the hyperfine lines, although in two experiments the second satellite was partially resolved. When both satellites were well resolved, a large number of measurements gave a mean square deviation of 1–2 G in the value of the satellite separations which are listed in Table I.

The satellites are never symmetrically placed about the main line, as one would expect from Eqs. (1) to (3) ($b_{ij}^2/4Am$ for $m=\pm\frac{7}{2}$ is only $\frac{1}{2}$ G). When the external field is parallel to the crystal axis, the displacement of the mean position of the satellites from the main line is the same on both the central line and the hyperfine lines, and it is also proportional to the frequency of the microwaves. This indicates that the displacement is due to a change in the g value for the pair of ions, presumably due to local distortions of the crystal structure. The change in $g_{\parallel}$ is $+0.017$ and in $g_{\perp}$ is -0.010. These changes are of the same order as the difference in the g values for CeES and LaES containing 1% Ce.[1,5] The separation of the satellites of a hyperfine line when the field is perpendicular to the axis is expected to be only about 50 G, and the g-value shift, together with the second-order shift $(a_{ij}+b_{ij})^2/16Bm$ of about 5 G for $m=\pm\frac{7}{2}$, displaces one of the satellites so that it lies close to the main line. The value in the table for this measurement is the average of the two cases where both satellites were resolved, and several where only one satellite was resolved, so that the position of the other one had to be estimated from the calculated shift of the satellite structure described above. The larger experimental error reflects the uncertainties in these measurements.

TABLE I. Separation of satellites from each other.

Main line	Direction	Observed G	Separation $\times 10^4$ cm^{-1}	Calculated	Separation[a] $\times 10^4$ cm^{-1}
Central	$\parallel$axis	196 ± 1	324 ± 2	$(a_{ij}-b_{ij})$	-326 ± 5
Central	$\perp$axis	170 ± 2	163 ± 2	$\frac{1}{2}(a_{ij}-b_{ij})$	-163 ± 2
Hyperfine	$\parallel$axis	167 ± 1	277 ± 2	a_{ij}	-277 ± 2
Hyperfine	$\perp$axis	48 ± 4	46 ± 4	b_{ij}	$+49\pm3$

[a] The last column is obtained using values

$$a_{ij}=-277\pm2\times10^{-4}\ \text{cm}^{-1},\ b_{ij}=+49\pm4\times10^{-4}\ \text{cm}^{-1}.$$

TABLE II. g values of Neodymium.

	Parallel	Perpendicular
LaES single ion	3.535 ± 0.001	2.072 ± 0.001
LaES pairs	3.552 ± 0.001	2.062 ± 0.001
YES single ion	3.547 ± 0.001	2.053 ± 0.001
YES pairs	3.521 ± 0.001	2.077 ± 0.001

The measurements of satellite separations at 25 and 9.4 kMc/sec gave the same values within the experimental error. Also, the variation of the satellite separation as a function of angle agreed well with Eqs. (5) and (6), confirming the opposite signs of a_{ij} and b_{ij}; the absolute signs are not determined.

The values of a_{ij} and b_{ij} are so close to the expected contributions from dipolar interactions (-309 and $+52$, respectively) that it is safe to assume that the signs in the last column of Table I correctly describe the data.

The exact contribution to a_{ij} and b_{ij} from dipolar interaction is slightly uncertain, as one cannot assume that the Nd ions are incorporated into LaES without some distortion; indeed, the shift of g value for a pair shows that there definitely is some distortion. To help in assessing how big the distortion is, two other experiments were performed.

Firstly, yttrium ethyl sulfate (YES) was used as a diluent. This has a lattice constant of 7.05 Å, nearly 1% smaller than LaES (7.11 Å).[6] Here the g-value shifts of pairs was in the direction opposite to LaES, suggesting distortion in the opposite sense (the g values for the isolated ion are also slightly different in YES from LaES). The measured values are listed in Table II.

The satellite separation on the central line in YES is 194 ± 2 G, about 1% smaller than in LaES. This difference is accounted for entirely by the difference in g value, suggesting that the pair separation in the two salts is the same. Separations appropriate to the host ions would make the satellite separation 2% *bigger* in YES.

The fact that distortions are in opposite directions in LaES and YES makes it appropriate to take a value of R intermediate between the two lattice constants, say 7.08 Å. This gives

$$-2g_{\parallel}^2\beta^2/R^3=-309\pm4 \quad \text{and} \quad g_{\perp}^2\beta^2/R^3=52.0\pm0.6\,,$$

both in units of 10^{-4} cm^{-1}. The error allows the full range of R from 7.11 to 7.05 Å.

A second experiment to help determine R was the observation of satellites on the gadolinium spectrum in LaES containing 10% Nd and 1% Gd, due to a pair comprising one Nd and one Gd ion. As the ions are dissimilar, the satellites should be separated by a_{ij}. The measured separation of 188 ± 2 G corresponds to

$$a_{ij}=312\pm3(\times10^{-4})\ \text{cm}^{-1}\,,$$

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

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

in excellent agreement with the dipolar value for $R=7.08$ Å. (It was not possible to measure the satellite positions perpendicular to the axis, so that it is not confirmed that the interaction is really dipolar.)

Taking the above values as the appropriate contributions from dipolar interaction leaves as the nondipolar contribution

$$A_{ij}=+32\pm6(\times10^{-4})\ \mathrm{cm}^{-1}(20\pm4\mathrm{G})$$

and

$$B_{ij}=-3\pm3(\times10^{-4})\ \mathrm{cm}^{-1}.$$

These values of the nondipolar contributions are in excellent agreement with Svare and Seidel[1] who obtained $A_{ij}=17$ G and $B_{ij}=0$ for the undiluted salt.

IV. DISCUSSION

Svare and Seidel have given some discussion of the possible origin and validity of the nondipolar interaction. They concentrate mainly on reconciling their measured interaction with the specific-heat measurements[7] which had been shown to be in good agreement with a purely dipolar interaction. They show that use of the correct g values and making allowance for possible thermal contraction could reconcile their own measurements with the specific-heat data. Possible mechanisms of the interactions are mentioned, but no order-of-magnitude estimates are made. A complete discussion of this topic is impossible in the absence of so much necessary information, but is is probably worthwhile considering some of the possible mechanisms semiquantitatively.

Superexchange could be anisotropic, but comparison with the known cases of exchange interaction suggest that the isotropic component between the *spins* of the interacting ions is an order of magnitude larger than anisotropic exchange. Isotropic exchange may be written $J\mathfrak{S}_i\cdot\mathfrak{S}_j$ where the $\mathfrak{S}$ are real spins. This interaction can be transformed into the spin Hamiltonian formalism by noting that

$$\Lambda\mathbf{J}=(\mathbf{L}+2\mathfrak{S})=(\mathbf{J}+\mathfrak{S}),$$

so that $\mathfrak{S}=(\Lambda-1)\mathbf{J}$. The matrix elements of $\Lambda\mathbf{J}$ in the ground doublet are the same as $\mathbf{g}S$ where S is now the fictitious spin. Hence the isotropic exchange between real spins becomes

$$J((\Lambda-1)/\Lambda)^2[g_{\shortparallel}{}^2S_{z_i}S_{z_j}+\tfrac{1}{2}g_{\perp}{}^2(S_{i+}S_{j-}+S_{i-}S_{j+})].$$

Such a term cannot alone fit the experimental data because it requires additions to both a_{ij} and to b_{ij} in the ratio of three to one and both of the same sign, which is likely to be positive.

Another possibility mentioned by Svare and Seidel is electric quadrupole-quadrupole (QQ) interaction discussed by Finkelstein and Mencher,[8] Johnson and Meyer,[9] and Bleaney.[10] Bleaney writes the interaction in a convenient spin Hamiltonian form

$$\mathcal{H}_Q=A\{4O_{i2}{}^0O_{j2}{}^0-16(O_{i2}{}^{+1}O_{j2}{}^{-1}+O_{i2}{}^{-1}O_{j2}{}^{+1})+(O_{i2}{}^{+2}O_{j2}{}^{-2}+O_{i2}{}^{-2}O_{j2}{}^{+2})\},$$

where $O_n{}^m$ are spin operators defined by

$$O_2{}^0=3J_z{}^2-J(J+1),\quad O_2{}^{\pm1}=\tfrac{1}{2}(J_zJ_\pm+J_\pm J_z),\quad O_2{}^{\pm2}=J_\pm{}^2.$$

The coefficient A is

$$A=3e^2\langle r^2\rangle^2\langle J\|\alpha\|J\rangle^2/8\epsilon R^5hc,$$

where $\langle r^2\rangle$ is the mean-square radius of the $4f$ electrons, $\langle J\|\alpha\|J\rangle$ is a coefficient defined by Elliott and Stevens,[11] and ϵ is an effective dielectric constant. From EPR measurements Baker suggests that for Ce^{3+} ions in CeES[12]

$$A=0.99\times10^{-2}\ \mathrm{cm}^{-1}.$$

Using the values of $\langle J\|\alpha\|J\rangle$ from Elliott and Stevens[11] and a value of $\langle r^2\rangle$ for Nd 1.5 times that for Ce (assuming $\langle r^2\rangle_{\mathrm{Nd}}/\langle r^2\rangle_{\mathrm{Ce}}=[A_2{}^0\langle r^2\rangle]_{\mathrm{Nd}}/[A_2{}^0\langle r^2\rangle]_{\mathrm{Ce}}$),[13] one obtains for Nd

$$A=3.3\times10^{-4}\ \mathrm{cm}^{-1}.$$

There are no matrix elements of the operators $O_n{}^m$ between the components of a Kramers doublet, and the diagonal elements of $O_n{}^0$ are equal; otherwise it would be possible for a crystal field to split a Kramers doublet. Hence any interaction due to QQ interaction is through second-order processes involving higher states. Labelling the ground states $|\pm G\rangle$ and the excited states $|\pm E\rangle$, we are interested in matrix elements of the sort

$$\langle a_ia_j|\mathcal{H}_Q|c_ic_j\rangle\langle c_ic_j|\mathcal{H}_Q|b_ib_j\rangle/(E_{c_ic_j}-E_{a_ia_j}).$$

The states a and b are either $|\pm G\rangle$, and c can be either $|\pm G\rangle$ or $|\pm E\rangle$, except that c_i and c_j cannot both be ground states simultaneously. $E_{a_ia_j}$ is approximately equal to $E_{b_ib_j}$. For any pair of states $|a_ia_j\rangle$ and $|b_ib_j\rangle$, the second-order energy must be summed over all intermediate states $|c_ic_j\rangle$. Let

$$\langle a_ia_j|Q|b_ib_j\rangle=\sum_{c_ic_j}\frac{\langle a_ia_j|\mathcal{H}_Q|c_ic_j\rangle\langle c_ic_j|\mathcal{H}_Q|b_ib_j\rangle}{E_{c_ic_j}-E_{a_ia_j}}.$$

One has to be careful in taking this sum, as some states such as $|+G,-G\rangle$ and $|-G,+G\rangle$ are degenerate, and second-order theory cannot be applied correctly

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[7] L. D. Roberts, C. C. Sartain, and B. Borie, Rev. Mod. Phys. **25**, 170 (1953).

[8] R. Finkelstein and A. Mencher, J. Chem. Phys. **21**, 472 (1953).

[9] C. E. Johnson and H. Meyer, Proc. Roy. Soc. (London) **A253**, 199 (1959).

[10] B. Bleaney, Proc. Phys. Soc. (London) **77**, 113 (1961). Note that a numerical error in Eq. (1) of this paper has been corrected in our formula for $\mathcal{H}_Q$.

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

[12] J. M. Baker, Phys. Rev. (to be published).

[13] M. J. D. Powell and R. Orbach, Proc. Phys. Soc. (London) **78**, 753 (1961).

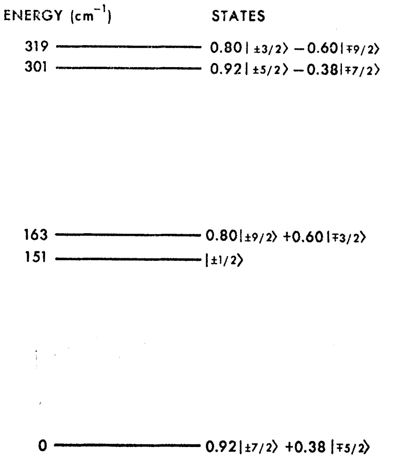

FIG. 3. States and energy levels of Nd^{3+} in LaES.

until states

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

and

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

have been constructed.

The effects of these matrix elements can be described in the same spin Hamiltonian formalism we used in Sec. II.

$$\begin{aligned}A_{ij}=\langle+G,\,+G|Q|+G,\,+G\rangle+\langle-G,\,-G|Q|-G,\,-G\rangle\\ -2_s\langle+G,\,-G|Q|+G,\,-G\rangle_s,\\ B_{ij}={}_s\langle+G,\,-G|Q|+G,\,-G\rangle_s\\ -{}_a\langle+G,\,-G|Q|+G,\,-G\rangle_a\\ =2\langle+G,\,-G|Q|-G,\,+G\rangle.\end{aligned}$$

There are contributions to these coefficients from all four excited Kramers doublets of the $J=\frac{9}{2}$ manifold of neodymium, and no one term dominates all the others. The sum of all the contributions was calculated using the crystal-field splittings and states (Fig. 3) calculated from the crystal-field parameters given by Huffner,[14] who measured the optical absorption spectrum. This calculation gave

$$A_{ij}=+480A^2=+0.5\times10^{-4}\text{ cm}^{-1},$$
$$B_{ij}=-2660A^2=-2.7\times10^{-4}\text{ cm}^{-1}.$$

These are of a reasonable order of magnitude to make some contribution, but even if A is regarded as an adjustable constant, this interaction alone cannot be made to fit the experimental results.

A third possible mechanism for the interaction is via phonon exchange. This mechanism has been discussed by Sugihara,[15] and by Aminov and Kochelaev;[16] and Aminov and Morocha[17] have considered the specific case of the ethyl sulfates and the interaction of nearest-neighbor ions. Aminov and Morcha give as the most important term in the interaction

$$\mathcal{H}_{ij}=-(Q^2/4\pi\rho v^2R^3)[(5/4)(x_i^2x_j^2+y_i^2y_j^2)+\tfrac{1}{2}(x_iy_ix_jy_j)$$
$$+8(x_iz_ix_jz_j+y_iz_iy_jz_j)+\tfrac{3}{4}(x_i^2y_j^2+y_i^2x_j^2)],$$

where $Q\approx500A_2^0$, ρ is the density of the crystal, v is the velocity of sound in the crystal, and x_i, etc., are the coordinates of the magnetic electrons. In terms of the operator equivalents O_n^m, this has the form

$$\mathcal{H}_{ij}=-\frac{250\,000\langle A_2^0r^2\rangle^2\langle J\|\alpha\|J\rangle^2}{4\pi\rho v^2R^3}$$
$$\times[-(2/9)(O_{i2}^0+O_{j2}^0)-\tfrac{1}{9}O_{i2}^0O_{j2}^0$$
$$+(3/32)(O_{i2}^{+2}O_{j2}^{+2}+O_{i2}^{-2}O_{j2}^{-2})$$
$$+(5/32)(O_{i2}^{+2}O_{j2}^{-2}+O_{i2}^{-2}O_{j2}^{+2})$$
$$+16(O_{i2}^{+1}O_{j2}^{-1}+O_{i2}^{-1}O_{j2}^{+1})].$$

This expression is correct only if the energy of the phonon which is emitted and reabsorbed is small compared with the Debye energy; otherwise the interaction is much smaller. Hence, the transitions which cause the emission of the phonon must be within the ground doublet. However, there are no first-order matrix elements of O_n^m between the states of the Kramers doublet, but there are second-order matrix elements involving both $\mathcal{H}_{ij}$ and the Zeeman interactions, such as

$$\langle a_i|\Lambda\beta HJ_{iz}|c_i\rangle\langle a_j|\Lambda\beta HJ_{jz}|c_j\rangle\langle c_ic_j|\mathcal{H}_{ij}|b_ib_j\rangle/(E_c-E_a)^2.$$

For Nd, the only excited state admixed by J_z is

$$0.92|\pm\tfrac{5}{2}\rangle-0.38|\mp\tfrac{7}{2}\rangle$$

at 301 cm⁻¹, from which there are matrix elements of both O_2^0 and $O_2^{\pm1}$ to the ground state. The contributions to the interaction are

$$A_{ij}=-2.5\times10^{-12}H^2\text{ cm}^{-1}$$

and

$$B_{ij}=-1.4\times10^{-10}H^2\text{ cm}^{-1}.$$

At X band, H is about 2 kG and

$$B_{ij}=-5.5\times10^{-4}\text{ cm}^{-1};$$

and at K band, H is about 5 kG and

$$B_{ij}=-14\times10^{-4}\text{ cm}^{-1};$$

at both frequencies A_{ij} is negligible. The experimental results give no indication at all for such a large field-dependent interaction.

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[14] S. Huffner, Z. Physik **169**, 417 (1962).

[15] K. Sugihara, J. Phys. Soc. Japan **14**, 1231 (1959).

[16] L. K. Aminov and B. I. Kochelaev, Zh. Eksperim. i Teor. Fiz. **42**, 1303 (1962) [English transl.: Soviet Phys.—JETP **15**, 903 (1962)].

[17] L. K. Aminov and A. K. Morocha, Fiz. Tverd. Tela **3**, 2480 (1961) [English transl.: Soviet Phys.—Solid State **3**, 1801 (1962)].

V. CONCLUSION

The order-of-magnitude estimates of the possible interaction mechanisms suggest that all three could be contributing to the observed interaction, although the lack of field dependence rules out virtual phonon exchange as a serious contributor. Neither of the other mechanisms on its own gives the correct ratio A_{ij}/B_{ij}, but if both are considered to act simultaneously and to have adjustable magnitudes, one can explain the observed interaction with contributions

from exchange:

$$A_{ij}=30\times10^{-4}\text{ cm}^{-1}$$
$$B_{ij}=10\times10^{-4}\text{ cm}^{-1}$$

and from quadrupole-quadrupole interaction:

$$A_{ij}=2\times10^{-4}\text{ cm}^{-1}$$
$$B_{ij}=-13\times10^{-4}\text{ cm}^{-1}.$$

A contribution of this size from quadrupole-quadrupole interaction requires a constant A about twice as big as that we estimate in Sec. IV, which is certainly possible as the extrapolation from the value of A for cerium is very uncertain.

It is also possible that anisotropic superexchange is the cause of the interaction. This possibility does not seem susceptible to experimental proof by further measurements on Nd in the ethyl sulfate. However, the fact that non-negligible departures from dipolar interaction can be observed in crystals as magnetically dilute at the ethyl sulfates, and the fact that expected interactions are estimated to have observable size, make an extension of such measurements of interest. A systematic measurement of interactions between pairs of other rare-earth ions, and between pairs of dissimilar ions, might be necessary in order to make a complete interpretation. Certainly there are more favorable cases than Nd for observing both the electric quadrupole (e.g., CeES[11]) and the virtual phonon interaction. It would also be an advantage to work in a material where the interionic distance is smaller, so that the relative magnitudes of the various processes would be different, but this raises the problem of finding a host lattice with a suitable crystal structure. Of the host lattices which have so far been used for lanthanon ions, only $LaCl_3$ has the great advantage of one ion in the unit cell (diamagnetic hosts with divalent ion would change the single-ion spin Hamiltonian because of the change in crystal field). It also has a crystal structure which is very similar to that of the ethyl sulfates. Also, there are several similar materials with the same crystal structure with slightly different lattice spacing. A systematic study of such materials would appear to promise some understanding of the roles of the various interaction mechanisms which can operate between lanthanon ions.

ACKNOWLEDGMENTS

It is a great pleasure to acknowledge the hospitality of Professor C. D. Jeffries and the University of California at Berkeley during the period when this paper was prepared. We are indebted to G. H. Larsen for growing some of the crystals, and for making his apparatus available for some of the experiments. We also wish to thank Professor B. Bleaney for originally suggesting the problem, and for his advice and guidance when the original experiments were performed.

APPENDIX

For two similar ions without hyperfine structure, when H is parallel to z, the spin Hamiltonian is

$$\mathcal{H}=g_{i\parallel}\beta HS_{iz}+g_{j\parallel}\beta HS_{jz}+a_{ij}S_{iz}S_{jz}+\tfrac{1}{2}b_{ij}(S_{i+}S_{j-}+S_{i-}S_{j+}).\quad\text{(A1)}$$

The eigenstates of this spin Hamiltonian are

$$\begin{array}{ll}
|+\tfrac{1}{2},+\tfrac{1}{2}\rangle & \text{at}\quad g_{\parallel}\beta H+\tfrac{1}{4}a_{ij},\\
(1/\sqrt{2})\{|+\tfrac{1}{2},-\tfrac{1}{2}\rangle+|-\tfrac{1}{2},+\tfrac{1}{2}\rangle\} & \text{at}\quad -\tfrac{1}{4}a_{ij}+\tfrac{1}{2}b_{ij},\\
(1/\sqrt{2})\{|+\tfrac{1}{2},-\tfrac{1}{2}\rangle-|-\tfrac{1}{2},+\tfrac{1}{2}\rangle\} & \text{at}\quad -\tfrac{1}{4}a_{ij}-\tfrac{1}{2}b_{ij},\\
|-\tfrac{1}{2},-\tfrac{1}{2}\rangle & \text{at}\quad -g_{\parallel}\beta H+\tfrac{1}{4}a_{ij}.
\end{array}$$

The only transitions for $\Delta S_{iz}=\pm1$, $\Delta S_{jz}=0$ or $\Delta S_{iz}=0$, $\Delta S_{jz}=\pm1$ are

$$|+\tfrac{1}{2},+\tfrac{1}{2}\rangle\leftrightarrow(1/\sqrt{2})\{|+\tfrac{1}{2},-\tfrac{1}{2}\rangle+|-\tfrac{1}{2},+\tfrac{1}{2}\rangle\}\quad\text{at}\quad h\nu=g_{\parallel}\beta H+\tfrac{1}{2}(a_{ij}-b_{ij}),$$

$$|-\tfrac{1}{2},-\tfrac{1}{2}\rangle\leftrightarrow(1/\sqrt{2})\{|+\tfrac{1}{2},-\tfrac{1}{2}\rangle+|-\tfrac{1}{2},+\tfrac{1}{2}\rangle\}\quad\text{at}\quad h\nu=g_{\parallel}\beta H-\tfrac{1}{2}(a_{ij}-b_{ij}).$$

When ion i has hyperfine structure, terms

$$AS_{iz}I_z+\tfrac{1}{2}B(S_{i+}I_-+S_{i-}I_+)$$

are added to (A1). The matrix for the set of four states with $\langle I_z\rangle=m$ is

$$\begin{array}{l}
|+\tfrac{1}{2},+\tfrac{1}{2}\rangle\\
|+\tfrac{1}{2},-\tfrac{1}{2}\rangle\\
|-\tfrac{1}{2},+\tfrac{1}{2}\rangle\\
|-\tfrac{1}{2},-\tfrac{1}{2}\rangle
\end{array}
\begin{pmatrix}
g_{\parallel}\beta H+\tfrac{1}{2}Am+\tfrac{1}{4}a_{ij} & 0 & 0 & 0\\
0 & \tfrac{1}{2}Am-\tfrac{1}{4}a_{ij} & \tfrac{1}{2}b_{ij} & 0\\
0 & \tfrac{1}{2}b_{ij} & -\tfrac{1}{2}Am-\tfrac{1}{4}a_{ij} & 0\\
0 & 0 & 0 & -g_{\parallel}\beta H-\tfrac{1}{2}Am+\tfrac{1}{4}A_{ij}
\end{pmatrix}.$$

The effect of $\tfrac{1}{2}B(S_{i+}I_-+S_{i-}I_+)$ is to produce second-order shifts of these levels. The upper two are shifted up in energy by

$$\{I(I+1)-m(m+1)\}B^2/4g_{\parallel}\beta H,$$

and the lower two are shifted down in energy by

$$\{I(I+1)-m(m-1)\}B^2/4g_{\parallel}\beta H.$$

If $\tfrac{1}{2}b_{ij}\ll Am$, the matrix may be diagonalized using perturbation theory, and transitions in which ΔS_{ij}

$=\pm 1$, $\Delta S_{jz}=0$ occur for

$$|+\tfrac{1}{2},+\tfrac{1}{2}\rangle \leftrightarrow |-\tfrac{1}{2},+\tfrac{1}{2}\rangle \quad \text{at} \quad h\nu = g_{\parallel}\beta H + Am + \tfrac{1}{2}a_{ij} + b_{ij}^2/4Am + \{I(I+1)-m^2\}B^2/2g_{\parallel}\beta H\,,$$

$$|+\tfrac{1}{2},-\tfrac{1}{2}\rangle \leftrightarrow |-\tfrac{1}{2},-\tfrac{1}{2}\rangle \quad \text{at} \quad h\nu = g_{\parallel}\beta H + Am - \tfrac{1}{2}a_{ij} + b_{ij}^2/4Am + \{I(I+1)-m^2\}B^2/2g_{\parallel}\beta H\,.$$

These occur as satellites on the hyperfine lines of isolated ions at

$$h\nu = g_{\parallel}\beta H + Am + \{I(I+1)-m^2\}B^2/2g_{\parallel}\beta H\,.$$

Transitions in which

$$\Delta S_{iz}=0, \quad \Delta S_{jz}=\pm 1$$

occur at

$$h\nu = g_{\parallel}\beta H \pm \tfrac{1}{2}a_{ij}\,,$$

but these are not observed in our experiments as they are too weak.

The simplest way to derive the satellite line positions when H is perpendicular to the crystal axis is to interchange S_z and S_x in (A1). The terms in $S_{i+}S_{j+}$ and $S_{i-}S_{j-}$ may be neglected as they produce only very small energy shifts, so that one obtains a new spin Hamiltonian which is identical to (A1) with $g_{\parallel}$ replaced by $g_{\perp}$, a_{ij} by b_{ij}, b_{ij} by $\frac{1}{2}(a_{ij}+b_{ij})$, and when there is hyperfine structure A is replaced by B.

PHYSICAL REVIEW VOLUME 136, NUMBER 5A 30 NOVEMBER 1964

Spin-Lattice Relaxation of *F* Centers in KCl: Interacting *F* Centers

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(Received 9 July 1964)

Spin relaxation of *F* centers in KCl has been observed by a field-sweep inversion recovery technique at liquid-helium temperatures. Intrinsic relaxation behavior was reported previously. Various kinds of extrinsic behavior are reported here. They include distorted resonance line shapes, unusually fast relaxation, and unusual field and temperature dependences of the relaxation. Such effects were always seen at low temperatures and low fields after the following treatments: high *F*-center concentrations, light exposure, the addition of certain impurities, plastic deformation, and low-temperature gamma irradiation. A model is presented which explains all of these effects and is consistent with the extensive lore involving the properties of *F* centers. This model identifies the extrinsic relaxation process as one compounded of spatial diffusion of Zeeman energy in the *F*-center system and cross relaxation from *F* centers to rapidly relaxing centers. These rapidly relaxing centers are composed of loosely bound clusters of *F* centers, which can be formed in a variety of ways.

INTRODUCTION

In an earlier paper (hereafter referred to as I) we presented measurements of the spin-lattice relaxation time of isolated *F* centers in KCl crystals as a function of temperature and magnetic field.[1] The measurements were interpreted in terms of relaxation by phonon modulation of the hyperfine coupling between the *F*-center electron and its surrounding nuclei. This interpretation is consistent with all the observed results except for what we term "extrinsic" behavior which varies from sample to sample, being most evident at low temperatures and low magnetic fields where the intrinsic relaxation times are very long.

The purposes of this paper are several: (1) to present our experimental data showing a wide variety of extrinsic behavior; (2) to show that the extrinsic behavior is in general due to interactions of the *F* centers with other paramagnetic centers; (3) to identify the paramagnetic centers which are involved; (4) to discuss the complex series of steps by which the *F* center relaxes when its behavior is extrinsic; and (5) to identify those steps which must be dominant to explain the various kinds of extrinsic behavior which have been observed.

THEORY

The intrinsic spin-lattice relaxation processes, which were considered in detail in Paper I, are either independent of magnetic field strength H or become more rapid as H is increased. A striking property of the extrinsic behavior, to be discussed below, is the reverse of this, the slowing of relaxation as H is increased. This behavior can be explained in two ways.

One possibility involves cross relaxation of *F* centers to a rapidly relaxing paramagnetic center whose g value differs from that of the *F* center. Under these conditions the two resonance lines overlap more and more as H is decreased, leading to a faster transfer of Zeeman energy from the *F* center to the other center which can then rapidly transfer it to the lattice. Processes of this kind have been discussed by Bloembergen *et al.*[2]

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[1] D. W. Feldman, R. W. Warren, and J. G. Castle, Jr., Phys. Rev. **135**, A470 (1964).

[2] N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. **114**, 445 (1959).