

Determination of the Sign of the Interactions between Pairs of Nd³⁺ Ions in LaCl₃ by Electron Paramagnetic Resonance

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This paper describes measurements of the interactions between nearest-neighbor (nn) and next-nearest-neighbor (nnn) Nd³⁺ ions in LaCl₃ from the electron-paramagnetic-resonance (EPR) pair spectra, which are very similar to those recently reported by Brower *et al.* Our numerical values are in substantial agreement with those of these authors, but by working at much higher frequency we have been able to determine the signs of the interactions. The signs are opposite to those assumed by Brower *et al.*, and this considerably alters the interpretation of the nondipolar part of the interaction. In contrast to the suggestion made by Eisenstein *et al.*, which was apparently confirmed by Brower *et al.*, this part of the interaction cannot be described for nnn by an isotropic exchange between real spins, or for nn by a ferromagnetic isotropic exchange between real spins.

WE have examined the electron spin resonance of pairs of interacting Nd¹⁴⁴ ions in single crystals of LaCl₃ at temperatures between 2 and 20°K and at microwave frequencies between 9 and 70 kMc/sec. This work is an extension of the similar work done on the ethyl sulphates.¹

In the course of our work, we became aware of the independent measurements of Nd pair spectra made by Brower *et al.*² in LaCl₃ and LaBr₃ at 4.2°K and 9 kMc/sec. These authors have made a very large number of measurements of both nearest neighbor (nn) and next-nearest-neighbor (nnn) pairs at one microwave frequency, and have made a very detailed computer analysis in order to find the best values of the parameters in the interaction spin Hamiltonian.

In contrast we have made measurements over a wide frequency range. This was done for two reasons; first, to discover whether there were any contributions to the interaction which depend upon the value of the applied magnetic field; second, by working at high frequencies and low temperatures the sign of the interaction may be measured.

Our results are in substantial agreement with those of Brower *et al.* There are small discrepancies which may be due to field-dependent contributions, but extensive further work is necessary to confirm this. However, our work shows that the signs assumed by Brower *et al.* for the parameters in the interaction spin Hamiltonian are incorrect.

In this short paper it is our main intention to report the sign measurements and to draw attention to their effect upon the interpretation of the interaction mechanism. We have tried to keep the text as short as possible consistent with intelligibility to avoid repetition of Brower *et al.* For a fuller account of the problem the reader is referred to their paper.²

The crystals used in our experiments were grown by the Brigman-Stockbarger method,³ and were oriented

optically and also by using Laue back-reflection x-ray photographs.

LaCl₃ forms hexagonal crystals in which the paramagnetic impurity ions are all equivalent with axial *g* tensors. Isolated Nd³⁺ ions may be described by a spin Hamiltonian with effective spin $S = \frac{1}{2}$:

$$\mathcal{H} = g_{11}\beta H_z S_z + g_{\perp}\beta (H_x S_x + H_y S_y). \quad (1)$$

The nearest neighboring cations, of which there are two, lie at 4.38 Å along the *c* axis. The spin Hamiltonian describing the interaction between a pair of nn spins S_i and S_j is

$$\mathcal{H}_{ij} = a_{ij}S_{iz}S_{jz} + b_{ij}(S_{ix}S_{jx} + S_{iy}S_{jy}). \quad (2)$$

The complete spin Hamiltonian for an interacting pair comprises two terms like (1) plus the interaction term (2). The ions are similar, and the interaction couples the spins to form a triplet state with $\mathbf{S} = \mathbf{S}_i + \mathbf{S}_j = 1$ and a singlet state with $\mathbf{S} = 0$. $\Delta S_z = \pm 1$ transitions are allowed only within the triplet state, and from a measurement of their position a value of $(a_{ij} - b_{ij})$ may be obtained. Figure 1 shows the energy levels of the triplet state taking the sign of the zero-field splitting deduced from our measurements. This sign cannot be determined from the positions of the lines but only from their relative intensities. Because of the different populations of the states the low-field line is weaker than the high-field line roughly in the ratio $\exp(-h\nu/kT)$.

Measurements of relative intensities of the lines at 35 kMc/sec at 4 and 2°K showed a small increase in the relative size of the high field line. However, at 72 kMc/sec the high-field line was twice as intense as the

TABLE I. Measured values of $(a_{ij} - b_{ij})$ in cm⁻¹ for nn pairs.^a

Frequency (kMc/sec)	Direction of <i>H</i>	$(a_{ij} - b_{ij})$
33.81	to <i>c</i>	+0.6321(±6)
33.81	⊥ to <i>c</i>	+0.6269(±6)
27.7	⊥ to <i>c</i>	+0.6318(±6)
72.2	to <i>c</i>	+0.6338(±6)
9	and ⊥ to <i>c</i>	(-0.6246(±2))

^a The last row is taken from Brower *et al.* (Ref. 2).

¹ J. M. Baker, Phys. Rev. **136**, A1341 (1964); **136**, A1633 (1964).

² K. L. Brower, H. J. Stapleton, and E. O. Brower, Phys. Rev. **146**, 233 (1966).

³ G. Garton, M. T. Hutchings, G. R. Shore, and W. P. Wolf, J. Chem. Phys. **41**, 1970 (1964).

TABLE II. Measured values of parameters (in cm^{-1}) for nnn pairs.^a

Frequency (kMc/sec)	a_{zz}	a_{yy}	a_{xx}	a_{xy}
33.14	+0.1043(± 6)	+0.0660(± 6)	-0.1702(± 6)	...
27.70	+0.1041(± 6)	+0.0660(± 6)
72.2	-0.1691(± 6)	...
9	(-).01033	(-).00673	(+).01706	(\pm).00387
	-0.0167	+0.0120	+0.0047	± 0.0329

^a The last row is the calculated dipolar contribution, and the second from last is taken from Brower *et al.* (Ref. 2).

low-field line at 4°K and four times as intense at 2°K, showing beyond doubt that $(a_{ij} - b_{ij})$ is positive. The intensity ratios at 72 kMc/sec are in close agreement with what one would expect for a Boltzmann distribution. The values of $(a_{ij} - b_{ij})$ deduced from our measurements are listed in Table I.

In their discussion of the origin of this interaction, Brower *et al.* subtracted off the magnetic dipole-dipole contribution of -0.0489 cm^{-1} and, following Eisenstein *et al.*,⁴ attributed the remainder of the interaction to an isotropic ferromagnetic superexchange $J\mathbf{S}_i \cdot \mathbf{S}_j$ between the real spins \mathbf{S} of the Nd^{3+} ions. Baker¹ has shown how this interaction may be transformed into an anisotropic interaction between effective spins S through the relation $\mathbf{S} = [(\Lambda - 1)/\Lambda] \mathbf{g} \cdot \mathbf{S}$, where Λ is the Lande g value, giving

$$J\mathbf{S}_i \cdot \mathbf{S}_j = J[(\Lambda - 1)/\Lambda]^2 \times [g_{11}^2 S_{iz} S_{jz} + g_{11}^2 (S_{ix} S_{jx} + S_{iy} S_{jy})]. \quad (3)$$

In order to establish with certainty that the nn interaction is ferromagnetic one would need to find the position of the singlet state, which we cannot determine in our measurements. However, a ferromagnetic exchange between real spins (for which J is negative) predicts that $(a_{ij} - b_{ij})$ is negative, as g_{11} is greater than g_{\perp} , and our results show that this cannot be the case.

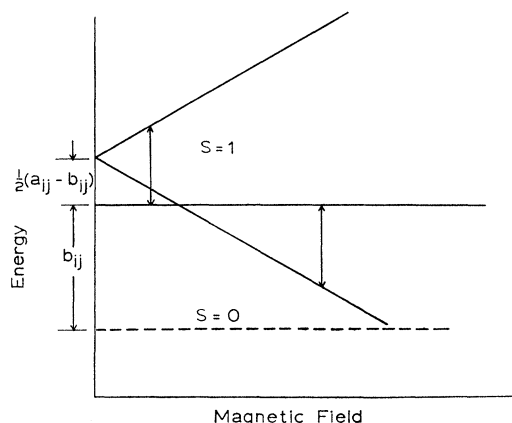


FIG. 1. Variation of the energy levels as a function of applied field H parallel to the crystal c axis for a pair of nearest neighbors. The diagram is drawn for a positive value of $(a_{ij} - b_{ij})$, as we find, and shows the allowed transitions. The position of the singlet level, shown dashed, is not known.

⁴ J. C. Eisenstein, R. P. Hudson, and B. W. Mangum, *Phys. Rev.* **137**, A1886 (1965).

In LaCl_3 there are six next-nearest-neighbor sites lying at 4.83 \AA in a direction making an angle of 63.1° with the c axis. Following Brower *et al.* we express the interaction spin Hamiltonian in terms of a Cartesian coordinate system chosen so that the line joining the ions lies in the xz plane, and so that the z axis coincides with the crystal c axis⁵:

$$\mathcal{H}_{ij} = a_{zz} S_{iz} S_{jz} + a_{xx} S_{ix} S_{jx} + a_{yy} S_{iy} S_{jy} + a_{xz} (S_{ix} S_{jz} + S_{iz} S_{jx}). \quad (4)$$

Our numerical values of the coefficients in (4) are again in substantial agreement with the values of Brower *et al.*, and are listed in Table II. In this case the low-field line was twice as intense as the high-field line at 72 kMc/sec at 4°K, and four times as intense at 2°K, showing that a_{zz} is negative, opposite to the sign assumed by Brower *et al.*

Eisenstein *et al.*⁴ suggested that the nnn interaction is mainly antiferromagnetic isotropic exchange between real spins. Equation (3) shows that such a contribution would have axial symmetry, i.e., $a_{xx} = a_{yy}$. Brower *et al.* noted that the magnitude of the anisotropy in the xy plane ($a_{xx} - a_{yy}$) would be almost accounted for by the magnetic dipole-dipole interaction (see Table II). They therefore concluded that by subtracting off the dipolar interaction they were left with an axial nondipolar contribution as required by the suggestions of Eisenstein *et al.* Our determination of the sign of $(a_{xx} - a_{yy})$ shows that it has the opposite sign to that due to dipolar interaction, so that the nondipolar contribution has an anisotropy of twice the observed value. Such an anisotropy cannot be explained by an isotropic interaction between real spins.

The most likely explanation of the interaction is that it arises from anisotropic superexchange, though there is some evidence from our incomplete measurements of field-dependent effects that there may be a small contribution from electric quadrupole-quadrupole interaction.

⁵ There is some evidence from the angular variation of the spectrum in the xy plane (perpendicular to the crystal c axis), which has been measured at several frequencies, that in addition to the anisotropy of the interaction tensor there is also an anisotropy of the g value. Somewhat unexpectedly the principal values of the g value in the xy plane do not occur in the x and y directions, but in directions making angles of about 45° with the x and y directions. This fact explains some of the small inconsistencies in the interpretation of Brower *et al.*, and might alter their conclusion that there should be very small additional terms in Eq. (4) in a_{xy} and a_{yz} .