SUPEREXCHANGE PATHS INVOLVING TWO OR MORE LIGANDS FROM E. P. R. PAIR MEASUREMENTS OF Nd3+ IONS BEYOND THE FIRST NEIGHBOUR SHELL IN LaCl3 AND LaBr3

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SUPEREXCHANGE PATHS INVOLVING TWO OR MORE LIGANDS FROM E. P. R. PAIR MEASUREMENTS OF Nd³⁺ IONS BEYOND THE FIRST NEIGHBOUR SHELL
IN LaCl₃ AND LaBr₃

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Abstract. — From the E. P. R. pair spectra of Nd³⁺ ions we have been able to measure the interactions of the second shell of neighbours (3 n-7 n) in LaCl₃ and LaBr₃. These measurements yield non-dipolar interactions of up to 50% of the dipolar contribution. The non-dipolar interaction is attributable to superexchange and its magnitude depends more on the detailed nature of the particular ligand superexchange path than on the length of the path.

I. Introduction. — Magnetic interactions between rare earth ions are normally attributed to magnetic dipole-dipole, superexchange, electric multipole-multipole and virtual phonon exchange interactions; see, e. g. Birgenau [1]. By working with the systems Nd/LaCl₃ and Nd/LaBr₃ in which the electric multipole and virtual phonon interactions are inherently small, we have been able to show that the anisotropic superexchange is considerably longer in range than nearest and next-nearest neighbours.

The LaCl₃ and LaBr₃ structures are hexagonal with a La³⁺ site symmetry of C₃ᵥ. Pairs of Nd³⁺ ions replacing pairs of La³⁺ ions in nearest and next-nearest neighbour (1 n and 2 n) positions form the first shell of neighbours around the central ion. The first shell neighbour-neighbour bonds are of the form Nd-Cl-Nd; their interactions have been measured previously and have large non-dipolar contributions attributable to superexchange, Riley [2] and Baker [3]. 3 n to 7 n comprise the «second shell» of neighbours and have bonds mostly of the form Nd-Cl-Nd or Nd-Cl-La-Cl-Nd. Their interactions have previously been assumed to be almost purely dipolar. The second shell neighbour positions and ligand bonds are indicated in the LaCl₃ plan structure of figure 1.

From the angular variation of the EPR pair spectra we have been able to measure the elements of the anisotropic interaction tensors for the second shell neighbours in both LaCl₃ and LaBr₃. The spin Hamiltonian for an interacting pair of Nd³⁺ ions with Kramers doublet ground states. S_i = S_j = ½, is: H = -βH.S_i + βH.S_j + J_ii S_i.S_j + S_i.A_ij.S_j, where J_ii is the isotropic part of the interaction and A_ij the anisotropic, traceless interaction tensor. If (g_i - g_j) is small we are only able to determine the A_ij part of the interaction.

II. Measurements. — The spectra were taken with the magnetic field rotated in a plane perpendicular to the hexagonal c-axis. For these orientations there is considerable spatial degeneracy of the various equivalent neighbour sites which simplifies the identification of the different neighbours. Correlation of the pair spectra with neighbour positions is complicated by the low symmetry of the sites; the misfit of the Nd³⁺ ions gives distortions which cause g-shifts and the principal axes of the g-tensor do not coincide with those of the interaction tensor. Since the systems of different neighbours are not distinct we have identified corresponding high field and low field satellites by plotting their means and differences, thus separating the g-shifts and interactions respectively. The identifications so obtained have been confirmed by making measurements at two different microwave frequencies. The experimentally fitted A_ij tensor elements are listed in Table I along with the non-dipolar interactions deduced from them. Unfortunately, no measure-
SUPEREXCHANGE PATHS INVOLVING TWO OR MORE LIGANDS FROM E. P. R. PAIR MEASUREMENTS C 1 - 949

Interaction parameters. Units are \((\text{cm}^{-1} \times 10^{-4})\) and errors are typically \(\pm 1\) in the last figure.

<table>
<thead>
<tr>
<th>(n)</th>
<th>(A_{xx})</th>
<th>N. D.</th>
<th>(A_{xy})</th>
<th>N. D.</th>
<th>(A_{yy})</th>
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<td>(\text{LaCl}_3)</td>
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<td>-15</td>
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<tr>
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<td></td>
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<td>17</td>
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<td></td>
<td>5</td>
<td>-52</td>
<td>-20</td>
<td>-3</td>
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<td></td>
<td></td>
<td>6</td>
<td>+73</td>
<td>-2</td>
<td>+73</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7</td>
<td>-54</td>
<td>+2</td>
<td>-3</td>
</tr>
<tr>
<td>(\text{LaBr}_3)</td>
<td>b)</td>
<td>3</td>
<td>-111</td>
<td>-17</td>
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</table>

Experiments were possible for 5 \(n\) in \(\text{LaBr}_3\), since the pair lines lay under the single ion line at both frequencies.

III. Discussion. — Bradbury and Newman [4], in their semi-quantitative calculation for 1 \(n\) and 2 \(n\) Gd\(^{3+}\) ions in \(\text{LaCl}_3\), point out the importance of considering all possible paths linking the 4 \(f\) electrons on the two ions, including «circular paths» involving two different routes. Secondly they emphasise the contribution of exchange paths involving the outer 5 \(s^2\) 5 \(p^6\) closed shells on the rare earth ion, which makes it extremely difficult even to predict the sign of the interaction, since the 5 \(s^2\) 5 \(p^6\) spin polarisation at the ligand is opposite to that of the 4 \(f\), Watson [5].

Quantitative predictions are prohibitive for long exchange paths, but we can use our results to make very general comments about the relative importance of different paths. The first interesting feature is that 3 \(n\) in \(\text{LaCl}_3\) have extremely small superexchange interaction whereas 5 \(n\) have a quite large superexchange contribution: this points to the fact that it is the detailed nature of the superexchange path, rather than the ionic separation, which is important. The negligible superexchange between 7 \(n\) corresponds to the extra- \(\text{Cl}\) - or \(\text{Cl}^-\) \(\text{La}\) in the 7 \(n\) linkage. The smallness of the 6 \(n\) exchange may indicate that exchange paths via two intermediate halogens are stronger than those via \(\text{La}^{3+}\) ions, since 6 \(n\) have only exchange paths of the form \(\text{Nd}-\text{Cl}-\text{La}-\text{Cl}-\text{Nd}\) whereas 3 \(n\) in 5 \(n\) also have \(\text{Nd}-\text{Cl}-\text{Cl}-\text{Nd}\) paths.

The relative size of the 3 \(n\) and 5 \(n\) exchange is particularly striking as it seems likely that the dominant exchange paths for both neighbours are via the same two intervening halogens, see figure 1. The 3 \(n\) lie in the plane perpendicular to the c-axis through the central ion, but one of the halogens in the superexchange paths must lie out of this plane. The smallness of the exchange may be accounted for by the fact that all paths have to bend through a sharp angle in moving up an atomic plane and in coming down again. Since 5 \(n\) lie directly above 3 \(n\) the paths are similar except that instead of returning to the initial atomic plane the path continues up to the next atomic plane giving a much gentler bend and consequently greater superexchange. In the absence of any accidental cancellation, one particular superexchange path dominates the others for both 3 \(n\) and 5 \(n\), because \(A_{xy} \approx 0\) in both cases, which implies that the \(x - z\) plane (defined to contain the pair bond) has reflection symmetry with respect to the ligand superexchange path. This restricts the dominant superexchange paths to the single one which lies within the \(x - z\) plane and precludes the possibility of circular paths.

In both \(\text{LaCl}_3\) and \(\text{LaBr}_3\), 4 \(n\) have substantial superexchange contributions which are particularly interesting since they yield quite large values of \(A_{xy}\) : a glance at figure 1 shows that there is no superexchange path which has reflection symmetry in the \(x - z\) plane. In this more general case it seems probable that both \(\text{Nd}-\text{Cl}-\text{Cl}-\text{Nd}\) superexchange paths will contribute, and possibly circular paths too. In each case it seems that the path involves a \(\pi\)-bond, because although the paths include one bend of almost 90\(^\circ\), the superexchange is still appreciable.

Finally our results for 7 \(n\) suggest that the interactions for neighbours beyond the second shell are almost completely dipolar.

References