Investigation of V^{3+} Pairs in Al_2O_3 by Phonon Frequency-Crossing Spectroscopy

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An investigation has been made of V^{3+} pairs in Al_2O_3 by phonon frequency-crossing spectroscopy. The crossing spectrum can be interpreted with an interaction Hamiltonian $J\vec{S}_1\cdot\vec{S}_2$ and pairs have been identified with $|J| = 0.29$ and 1.50 cm^{-1}. Pairs have been detected at concentrations $\sim 2\times10^{-2}$ ppm, and it is probable that concentrations $\sim 2\times10^{-3}$ ppm could be detected in this way.

We have used the technique of phonon frequency-crossing spectroscopy[1] to investigate V^{3+} pairs in Al_2O_3. Little is known about this system although recent optical work[2] suggests that the coupling between second and more distant neighbors is much less than that between nearest neighbors.

If we neglect hyperfine interaction, the lower three levels of V^{3+} can be described by the spin Hamiltonian

$$\mathcal{H} = D[S_Z^2 - \tfrac{1}{3}S(S+1)] + g_{\parallel}\beta B_Z S_Z + g_{\perp}\beta(B_X S_X + B_Y S_Y),$$

with $S_1 = 1$, $D = 8.29$ cm^{-1}, $g_{\parallel} = 1.91$, and $g_{\perp} = 1.72$,[3] and these levels and those of a pair of V^{3+} ions coupled by a Hamiltonian $\mathcal{H} = J\vec{S}_1\cdot\vec{S}_2$ with $|J| \ll D$ are shown in Figs. 1(a) and 1(b), respectively, for fields along the c axis. The systems give rise to resonant phonon scattering at the frequencies shown in Tables I and II and plotted in Fig. 2 for $|J| = 0.29$ cm^{-1}. In Table I we place them in groups a to d. We assume that all transitions are allowed and neglect scattering involving the four higher pair levels which should be weak at the temperatures (~2 K) and fields ($\lesssim$6 T) of the experiments. With the frequency-crossing technique we determine the magnetic fields at which two resonant frequencies become equal and, as shown in Table II, the spectrum consists of a septet of equally spaced lines centered at a field $B = D/3g_{\parallel}\beta = 3.11$ T and a low-field triplet with lines at $B \sim |J|/g_{\parallel}\beta$ (e.g., $B \sim 0.35$ T for $|J| \sim 0.3$ cm^{-1}). The spacing of the septet lines is $\Delta B = |J|3g_{\parallel}\beta$. As $|J|$ increases, the odd-numbered septet lines move to higher fields by $\delta/3g_{\parallel}\beta$ (δ is defined in Table I) and the first line of the triplet splits into three. There will also be small shifts $\sim A^2/3g_{\parallel}\beta D$ due to biquadratic or anisotropic exchange terms $\sim A$. We recall that a frequency crossing normally produces a sharp minimum in the magnetothermal resistivity. However, if it is accompanied by strong level anticrossing, as may occur at $B = |J|/g_{\parallel}\beta$ at the point marked by the circle in Fig. 1(b), the minimum is replaced by a maximum.[4]

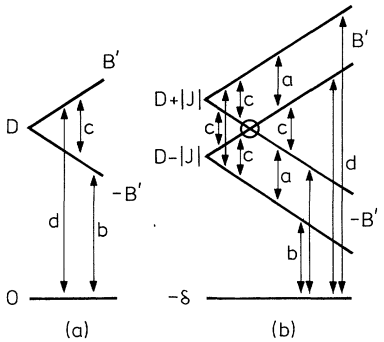

FIG. 1. The energy levels of V^{3+} in Al_2O_3 for fields $B' = g_{\parallel}\beta B$ along the c axis. (a) ions; (b) pairs with $|J| \ll D$; the four pair levels with energies $\sim 2D$ are omitted.

The magnetothermal resistivity has been measured on five samples with concentrations of V^{3+} of 74, 200, 267, 640, and 1170 ppm and of other iron-group impurities ranging from ~0.1 to 5 ppm. Their dimensions are given elsewhere.[5] The temperature gradient was measured with carbon resistors mounted 15 cm above the sample and shielded from the fringe field with Nb foil. Thermal contact was made with 0.7-mm Cu wires held by 40-μm nylon fibers to reduce noise from vibrational heating. The resistors were in opposite arms of an inductive bridge and

TABLE I. The transition frequencies of V^{3+} ions (ν_I) and pairs (ν_p) for $|J| \ll D$. $\delta = D[(1 - J/D + 9J^2/4D^2)^{1/2} - (1 - J/2D)]$; $\delta \to 0$ as $J/D \to 0$.

	a	b	c	d
ν_I	...	$D - B'$	$2B'$	$D + B'$
ν_p	$2\|J\|$	$D \pm J + \delta - B'$	$\|2B' \pm 2J\|$	$D \pm J + \delta + B'$

TABLE II. The fields $B' = g_{\|}\beta B$ at which frequency crossings occur when $B' < D$. There are also crossings at $B = 0$.

bc (7)	*ac* and *cc* (3)	*bd* (3)
$D/3$	$\|J\|/2$	$(\|J\| \pm \delta)/2$
$(D \pm J + \delta)/3$	$\|J\|$	$\|J\|$
$(D \pm 2J)/3$	$2\|J\|$	
$(D \pm 3J + \delta)/3$		

the out-of-balance signal was plotted against magnet current on a recorder. A 0.5-T sweep took 3 min, and, to see pair lines in the 74-ppm sample, ten sweeps were stored in a signal averager. Figure 3 shows measurements on the 1170-ppm sample for $B \| C$ and at 2.2 K (the fields of the minima were independent of temperature, as expected). Now the depth of a crossing signal depends on the strength of the *weaker* of the two processes[5] and this must be due to V^{3+} ions or pairs for most of the lines in Fig. 3 since they are found to increase with V^{3+} concentration (the principal exceptions are the Fe^{2+}/Fe^{2+} and Fe^{2+}/V^{3+} lines[6] which depend mainly on the Fe^{2+} concentration and are much weaker in the 650- than the 74-ppm sample). Few ions when present at the parts-per-million level could provide the stronger process, and the exceptions such as Mn^{3+}, Cr^{2+}, and Ni^{3+} would probably give strain-broadened lines wider than most of those observed. We conclude that most of the lines present are associated with V^{3+} pairs, although the line at $B_0 = 3.11$ T is the V^{3+}/V^{3+} crossing referred to earlier. Of particular note are the equally spaced lines on either side of B_0. In a few plots there are seven lines including B_0 with an average spacing $\Delta B = 0.110 \pm 0.004$ T, although in Fig. 3 the weak first line is only marked by a slope change. We associate these lines with the septet predicted by the analysis and, from the value of ΔB, find that the exchange interaction for these pairs is $|J| = 3g_{\|}\beta\Delta B = 0.29 \pm 0.01$ cm^{-1}. With this value the displacement, $\delta/3g_{\|}\beta$, of the odd lines is only 4 mT and, if $A < |J|$ as is usual,[7] the shifts due to these terms will also be small. The low-field triplet due to these pairs should occur at 0.16, 0.33, and 0.65 T, as shown in Fig. 3; and there are indeed weak minima at 0.16 and 0.65 T and a shallow maximum near 0.33 T which could be due to anticrossing. We conclude that the crossing spectrum is consistent with the presence of pairs with $|J| = 0.29 \pm 0.01$ cm^{-1}.

As $|J|$ increases the septet lines are no longer

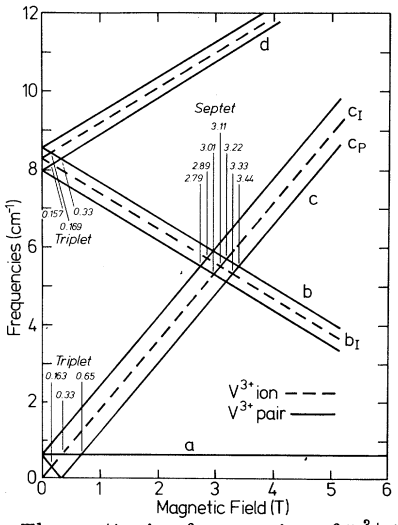

FIG. 2. The scattering frequencies of V^{3+} ions and pairs with $|J| = 0.29$ cm^{-1} showing the fields at which crossing occurs. [The $\nu(c_p)$ which coincides with $\nu(c_I)$ is omitted from Fig. 3 and Table I.]

approximately equally spaced and so are harder to identify. We assume, though, that the first strong line above the $|J| = 0.29$ cm^{-1} septet is line 5 of the next septet. (It approximately coincides with a Fe^{2+}/V^{3+} line[6] but this should be much weaker.) This requires $|J| = 1.50$ cm^{-1} and the septet for this value is shown in Fig. 3. The predicted lines coincide with some of the stronger lines in the spectrum to $\lesssim 2\%$, and this could be evidence for pairs with $|J| = 1.50 \pm 0.05$ cm^{-1} although the fit with the triplet lines is less convincing. (We note too that there is a Fe^{2+}/V^{3+}

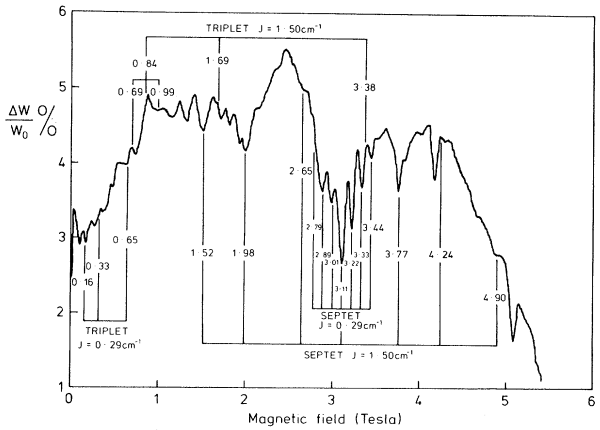

FIG. 3. The magnetothermal resistivity $\Delta W/W_0$ of an *a*-axis sample of Al_2O_3 containing 1170 ppm of V^{3+} ($T = 2.2$ K, $B \| c$). The lines and field values are theoretical values for pairs with $J = 0.29$ and 1.50 cm^{-1}. The minimum of the crossing at $B = 0$ is at $\Delta W = 0$.

line near[6] to 4.90 T and the seventh septet line could be the 5.09-T line.) Little can be said about the remaining lines in Fig. 3, although they could be due to excited levels of the pairs discussed here, to pairs of higher J, or even to triads or other complexes.

We turn next to the height of a pair-crossing line which should be given by $\Delta W \gtrsim (D_\omega L_B)^{1/2}$, where D_ω is the strength of the weaker of the two processes involved and L_B is the phonon mean free path for boundary scattering.[5] From Fig. 2, lines 4 and 6 are due to transition b_1 crossing c_1 and c_p, respectively. Now we know[5] that $D(c_1) < D(b_1)$ so that $\Delta W(4) \propto D(c_1)^{1/2}$. Thus, since $\Delta W(6) < \Delta W(4)$ (for $|J| = 0.29$ cm^{-1}), it cannot be determined by $D(b_1)$ and we can conclude that $\Delta W(6) \propto D(c_p)^{1/2} \propto x_p^{1/2}$, where x_p is the pair concentration. For a random distribution of V^{3+} ions, we have $x_p \simeq 3x^2$, where x is the ion concentration; and we take the average number of equivalent pair sites to be three, so that $\Delta W(6) \propto (x^2 L_B)^{1/2}$. Figure 4 shows the septet lines for the five samples. $\Delta W(6)$ clearly varies more rapidly with x than $\Delta W(4)$, as expected, and the plot of $\Delta W(6)$ against $(x^2 L_B)^{1/2}$ is consistent with a random distribution. [A least-squares fit suggests that $\Delta W(6) \gtrsim (x^2 L_B)^{0.7}$ and $\Delta W \gtrsim (xL_B)^{0.7}$; the higher power is explained by the presence of hyperfine splitting[5].]

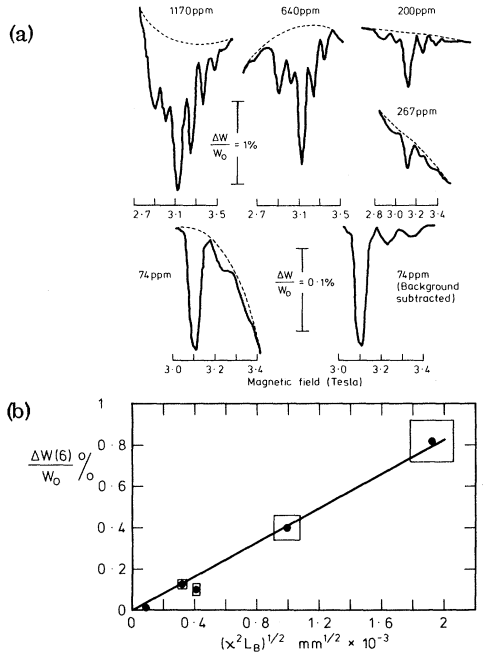

FIG. 4. (a) The frequency-crossing septet ($|J| = 0.29$ cm^{-1}) for the five samples ($T \sim 2$ K). The curve for the 74-ppm sample, which is an average of nine sweeps, is also shown after the curved background has been subtracted. Note the difference in scale. (b) The height of the sixth line, $\Delta W(6)$, corrected to 2 K (see Ref. 8), plotted against $(x^2 L_B)^{1/2}$.

The pair lines also provide information on the magnetoelastic constants $\bar{G}$ for pair transitions averaged over the phonon modes. For a first-order process $D \propto \bar{G}^2 \Gamma$; and for transition c_1, and so probably c_p, the linewidth $\Gamma \propto (\bar{G}\bar{\epsilon})^2$ where $\bar{\epsilon}$ is the average strain in the sample.[5] Hence $D \propto \bar{G}^4$ and from this it follows directly that

$$\bar{G}(c_p) \sim \bar{G}(c_1)[x\Delta W(6)^2 / x_p \Delta W(4)^2]^{1/2},$$

where $\bar{G}(c_1) \sim 150$ cm^{-1}.[5] From Fig. 3 we see that $\Delta W(6)/\Delta W(4) \sim \frac{1}{3}$ and for this sample $x/x_p \sim 285$ so that $\bar{G}(c_p) \sim 360$ cm^{-1}.

In summary, then, we identified V^{3+} pairs with $|J| = 0.29$ cm^{-1} and determined a value $\bar{G}_p \sim 360$ cm^{-1} for the magnetoelastic constant of one of the pair transitions. It also seems likely that there are pairs present with $|J| = 1.50$ cm^{-1}. Preliminary measurements have been made of the angular dependence of the lines which may help to determine the pair axes. Pair lines have been detected in a 74-ppm sample at a concentration of $\sim 2 \times 10^{-2}$ ppm. Since the volume of this sample was 40 mm^3 this corresponds to 3×10^{13} pairs and it should be possible to detect concentrations ~ 10 times smaller. We note, too, that the signal size observed was determined by the 2% of pairs in the excited state so that the technique would be more sensitive for crossings between two ground-state transitions, for narrower signals, and of course for more strongly coupled systems such as localized donors and acceptors.

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[1]For a recent example of this technique see L. J. Challis and D. L. Williams, J. Phys. C 10, 621–624 (1977).

[2]J. W. Allen, Phys. Rev. Lett. 36, 1249 (1976).

[3]J. Pontnau and R. Adde, J. Phys. Chem. Solids 36, 1023 (1975); other experimental values are listed in Ref. 1.

[4]B. R. Anderson and L. J. Challis, J. Phys. C 8, 1495 (1975); J. L. Patel and J. K. Wigmore, J. Phys. C 10, 1829 (1977).

[5]L. J. Challis and D. L. Williams, J. Phys. C (to be published). This paper, which is concerned with the size of the V^{3+}-ion line, contains further sample details including values of L_B.

[6]D. L. Williams, Ph.D. thesis, Nottingham University, 1977 (unpublished).

[7]J. Owen and E. A. Harris, in *Electron Paramagnetic Resonance*, edited by S. Geschwind (Plenum, New York, 1972), p. 427.

[8]The temperature dependence of $\Delta W(6)$ should be similar to that of $\Delta W(4)$, and the data have been corrected to 2 K using experimental data for $\Delta W(4)$ given in Ref. 5.