Paramagnetic Resonance from Pairs of Mn²⁺ Ions in Mn, ZnF₂

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Paramagnetic resonance techniques have been used to measure exchange interactions between nearest neighbour Mn²⁺ ions in mixed crystals of Mn, ZnF₂ with Mn:Zn≈1:50. The two ions are separated by the short edge (c ≈3.2Å) of the body centred tetragonal unit cell. The general procedure has followed that used for previous investigations[1],[2] of exchange coupled pairs of spins, $S^i=S^j=5/2$.

The results can be described by the following spin-Hamiltonians. For one ion of the pair, omitting interactions with the other ion

$$\mathcal{H}^i = g\beta \boldsymbol{H} \cdot \boldsymbol{S}^i + D_c\left[(S^i{}_z)^2 - \tfrac{1}{3}S^i(S^i+1)\right] + E_c\left[(S^i{}_x)^2 - (S^i{}_y)^2\right], \quad (1)$$

where $g=2$, $S^i=5/2$, $D_c=-0.0135\pm0.004$ cm⁻¹, $E_c=0\pm0.006$ cm⁻¹. There is a similar Hamiltonian $\mathcal{H}^j$ for S^j. For the interacting pair the Hamiltonian is

$$\mathcal{H}^{ij} = \mathcal{H}^i + \mathcal{H}^j + J\boldsymbol{S}^i \cdot \boldsymbol{S}^j + D_e[3S^i{}_z S^j{}_z - \boldsymbol{S}^i \cdot \boldsymbol{S}^j], \quad (2)$$

where $J/k=-0.4\pm0.2°$K and $D_e=-0.051\pm 0.009$ cm⁻¹. The z-axis is parallel to c, that is, to the line joining the ions. The isotropic exchange term $JS^i \cdot S^j$ gives rise to states of total spin $(S=S^i+S^j)$ with $S=0, 1, 2, 3, 4$ and 5, and with relative energies, 0, J, $3J$, $6J$, $10J$ and $15J$ respectively. Since J is negative for the present case, $S=5$ is lowest and $S=4$ is $5|J|$ higher in energy and most of the measurements have been made on transitions within these two lowest total spin states, (see Figure 1).

The values of the parameters D_c and D_e, which determine the position and anisotropy of the lines in the spectrum, have been confirmed by fitting more than 20 transitions in the wavelength range 0.85 to 3.3 cm. The crystal field contributions, $D_c=-0.0135$ cm⁻¹, $E_c=0$, are of the same order as those found for isolated Mn²⁺ ions in very dilute crystals

which are[3] $D_c=-0.0186$ cm⁻¹, $E_c=-0.0041$ cm⁻¹. The other contribution D_e appears to be consistent with the expected dipole-dipole interaction $-g^2\beta^2/r^3{}_{ij}$, since the value can be fitted by choosing $r_{ij}=3.21$ Å which lies between the expected[4] separations 3.13 Å for ZnF₂ and 3.31 Å for MnF₂.

The magnitude of the isotropic exchange J has been estimated by using intensity measurements to find the separation between
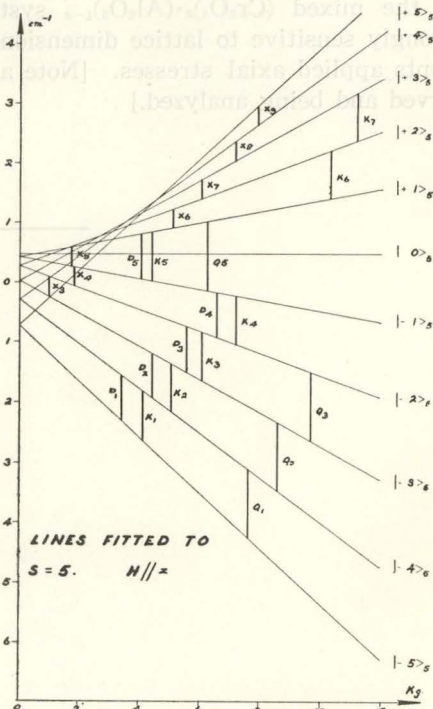

Fig. 1. Comparison between calculated energy levels and observed transitions for the $S=5$ state for a nearest neighbour pair of Mn²⁺ ions with $H||c$, i.e., parallel to the line joining the ions. The wavelengths used are in the region 3 cm (X), 1.2 cm (K and D) and 0.8 cm (Q). The observed transitions for $S=5$, $H\perp c$, and for $S=4$, $H||c$ and $H\perp c$ show similar good agreement with the calculated levels.

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different energy levels given by Eq. (2). This has involved the determination of the intensities of a number of lines in the spectrum both relative to each other (see Fig. 2) and relative to a comparison specimen in the temperature range 1.5 to 20°K. All the measurements agree in giving the exchange ferromagnetic in sign and close to the value $J_{nn}/k = -0.4°K$. Preliminary measurements have also been made on next nearest neighbour Mn-Mn pairs which give the approximate result $J_{nnn}/k = 4°K$ (antiferromagnetic).

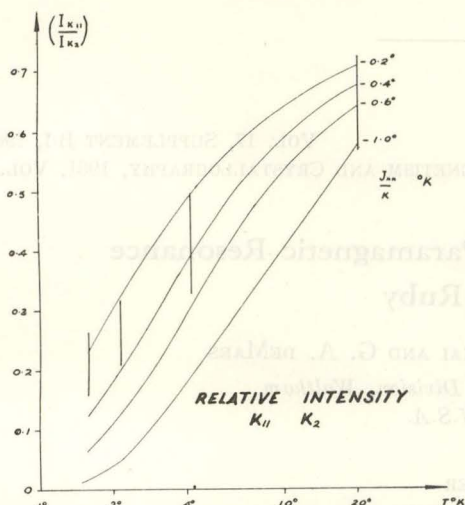Fig. 2. The observed intensity of the transition $|-3>_4 \to |-2>_4$, (K_{11}), is compared with that of $|-4>_5 \to |-3>_5$, (K_2), in the range 20°K to 1.5°K and with $H||c$. The curves represent the calculated intensity ratio for different values of J. The averaged results of these and similar measurements on other transitions give $J = -0.4 \pm 0.2°K$.

This preliminary result for next nearest neighbours is in reasonable agreement with a molecular field interpretation of the bulk properties of the antiferromagnetic MnF_2 as

was expected. The ferromagnetic sign of the nearest neighbour exchange, on the other hand, was not expected. If, as seems reasonable, a similar ferromagnetic interaction is present in MnF_2, then in order to account for the susceptibility properties it may be necessary to assume appreciable antiferromagnetic exchange between further neighbours on the same magnetic sublattice, e. g. 3rd, 4th, 6th or 7th nearest neighbours. However, this is a rather tentative conclusion because the experimental value of the Curie-Weiss θ is not very well defined at the present time.

Finally, it is of interest to note that the nearest and next nearest neighbour pair structure in MnF_2 is in some way similar to that in MnO but the ratio J_{nnn}/J_{nn} is surprisingly different, being about -10 for MnF_2 and $+1$ for MnO[1]. This is not understood, but a possible explanation may be that there is direct ferromagnetic exchange of magnitude a few degrees Kelvin between nearest neighbours in both salts, and that this is the dominant interaction in MnF_2 where the antiferromagnetic superexchange interactions are smaller.

References

1 B. A. Coles, J. W. Orton and J. Owen: Phys. Rev. Letters **4** (1960) 116.
2 J. Owen: Journ. Appl. Phys. Supplement **32** (1961) 213S.
3 M. Tinkham: Proc. Roy. Soc. **A236** (1956) 535.
4 J. W. Stout and S. A. Reed: J. Amer. Chem. Soc. **5** (1954) 5279.

DISCUSSION

C. J. Gorter : Could you indicate why transitions between different values of S could not be observed ?

J. Owen ; With $H||c$, some transitions are weakly allowed between Zeeman levels belonging to total spin states which differ by 2, e.g. between $S=5$ and $S=3$. These could give an accurate direct measurement of J. So far, we have not identified such transitions unambiguously mainly because the lines are expected to be rather weak.

T. Nagamiya : You suggested the possibility of a partial cancellation of the super-exchange interaction between corner ions by the direct exchange interaction. Why

don't you expect a similar cancellation between corner ion and body-center ion?

J. Owen: The Mn-Mn separation is about 3.2Å for nearest neighbours and about 3.8Å for next nearest neighbours so the direct exchange may be expected to be much smaller for the latter case.

L. R. Walker: As far as the relation of these reults to the susceptibility measurements is concerned I would like to mention that recent results of H. J. Williams at Bell Telephone Laboratories on the susceptibility of MnF_2 show that the paramagnetic Curie temperature agrees closely with the Néel temperature. If the ratio of J_1/J_2 required to give this result is calculated it appears to fall between -0.15 and -0.20. The Néel temperature is here calculated by looking for a singularity in the staggered susceptibility.

Exchange Interactions in the Paramagnetic Resonance Spectrum of Ruby

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We have continued the investigation[1,2] of the paramagnetic resonance spectrum of concentrated ruby. Progress has been made in the investigation of more distant exchange coupled chromium ion pairs and also in the study of the spin-lattice relaxation of pairs and their effect on the relaxation of single ions.

The pair spectrum in ruby has previously been analyzed with the aid of the spin Hamiltonian

$$H_{pair} = g\beta H \cdot (S_1 + S_2) + D(S_{z1}^2 + S_{z2}^2) + JS_1 \cdot S_2 + \frac{4\beta^2}{r_{12}^3}\left[S_1 \cdot S_2 - 3\frac{(r_{12} \cdot S_1)(r_{12} \cdot S_2)}{r_{12}^2} \right]. \quad (1)$$

The first two terms in (1) represent the sum of the spin Hamiltonians of the individual ions in the usual notation[2] and the last two terms represent the isotropic exchange coupling and the dipolar interaction, respectively.

For large J, i.e., $J \gg D$, isotropic exchange couples the spins of two ions together to form states of $S = 3, 2, 1,$ and 0 with energies $6J, 3J, J,$ and 0, respectively. Furthermore, if H is parallel to the z-axis the eigenstates can still be described by the z-component of the spin angular momentum m_s. Microwave transitions occur between neighboring m_s values within the same spin multiplet. J does not enter into the line position as long as $J \gg D$. Since the dipolar interaction for most pairs is small as compared to D, the transitions are essentially determined by D and H. In other words, neglecting dipolar interaction and for large J all the different pairs give microwave absorption lines which coincide. If the above assumptions are dropped, lines from the various pairs do not exactly coincide and clusters of lines are found in the spectrum. The large number of lines observed in each cluster indicates many neighbor shells with sizable exchange interactions.

We had investigated the cluster corresponding to $S = 3$, $m_s = 2 \rightarrow m_s = 1$ transitions. By