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 $\mathrm{MnF_2}$ 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.

JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 17, SUPPLEMENT B-I, 1962
PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. I

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

$$H_{\mathrm{pair}}=g\beta\boldsymbol{H}\cdot(\boldsymbol{S}_1+\boldsymbol{S}_2)+D(S_{z1}^2+S_{z2}^2)+J\boldsymbol{S}_1\cdot\boldsymbol{S}_2+\frac{4\beta^2}{r_{12}^3}\left[\boldsymbol{S}_1\cdot\boldsymbol{S}_2-3\frac{(\boldsymbol{r}_{12}\cdot\boldsymbol{S}_1)(\boldsymbol{r}_{12}\cdot\boldsymbol{S}_2)}{r_{12}^2}\right]. \quad (1)$$

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 counting the lines and by making assignments on the basis of computer solutions we were tentatively led to the conclusion[2)] that out to the eleventh neighbor shell $J>D$. Lines corresponding to 2nd and 4th neighbors have not been identified and even first neighbor lines have proved to be very illusive. These difficulties may be due to a combination of high J values with fast relaxation or anisotropic exchange shifting the lines from positions calculated by Eq. (1). We still can identify clearly only one line with a high J value as belonging to first neighbors. The line does not split as non z-oriented pairs do when H is moved off the z direction. From the temperature dependence of the line intensity it was found that $J=390\pm50\,\mathrm{cm}^{-1}$ provided this line belongs to the $S=3$ multiplet. This value agrees well with simple molecular field calculations. However, if one were to make the assumption that it is an $S=2$ line we find $J\approx800\,\mathrm{cm}^{-1}$, while for an $S=1$ line, $J\approx2000\,\mathrm{cm}^{-1}$. Optical measurements may make the assignment more clearcut. It should also be mentioned that for J values of the order of a few thousand wave numbers the spin Hamiltonian may no longer be valid and a molecular orbital treatment may be more adequate. One also finds the relative intensity of the first neighbor line higher than would be expected on a statistical basis. This could be explained by a binding energy. The term $JS_1\cdot S_2$ already depresses the $S=0$ state by $(15/4)J$ and thus constitutes binding. The first neighbor interaction is far from being understood and it is conceivable that there are clusters of more than two Cr^{+++} ions.

In considering the structure of $\mathrm{Al_2O_3}$ or $\mathrm{Cr_2O_3}$ we find that each chromium ion is surrounded by six oxygen ions. For the first four neighbor shells, one or more of these six surrounding oxygens are shared by the two chromium ions, while from the 5th neighbor shell on this is no longer the case and the operative superexchange interaction has to make use of chains of oxygen consisting of two or more ions. One may thus naively expect that the first four neighbor shells have larger exchange interactions. Experimentally, this has not been observed. The measured J values for the $S=3$, $m_s=2\rightarrow m_s=1$ cluster are shown in Fig. 1. The indicated J values are estimated to be accurate to about $0.3\,\mathrm{cm}^{-1}$. The exchange constant of the line at 8.51 kgauss was not measured from the temperature induced variation of the intensity, but from the position of this and other lines belonging to the same pair. It appears that

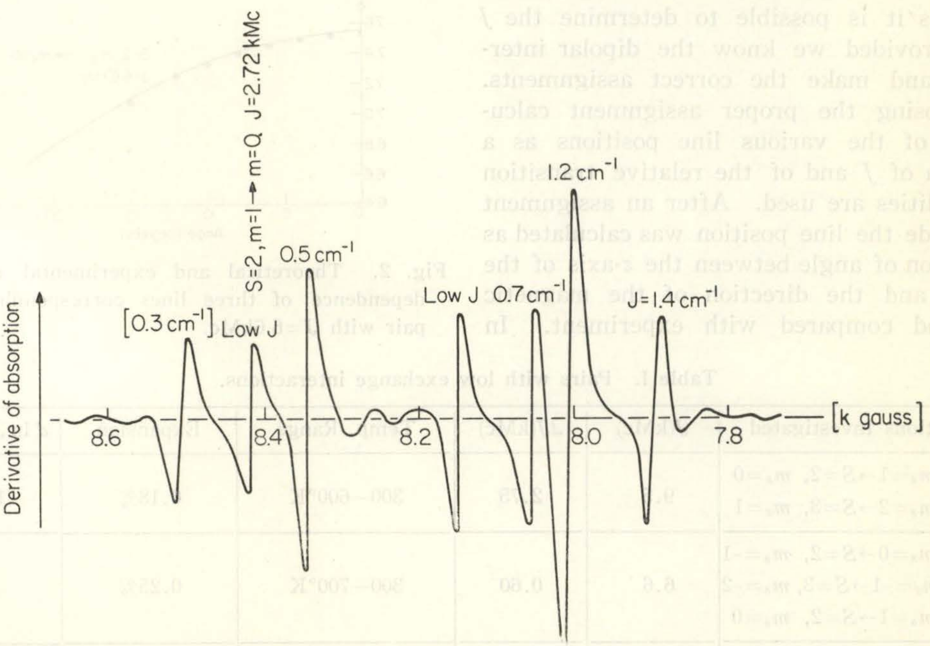

Fig. 1. Line cluster corresponding to $S=3$, $m_s=2\rightarrow m_s=1$ transitions. Thermally measured exchange constants (J) are shown. (Frequency 15.74kMc.)

the line at 8.45 kgauss does not belong to the cluster. Its location is consistent with an $S=2, m_s=1 \rightarrow m_s=0$ transition with $J=2.72$kMc. The fifth neighbor line has a rather large dipolar contribution and thus lies outside the cluster shown in Fig. 1. By checking the angular dependence of $S=3$ and $S=2$ lines, we could positively identify this neighbor and it has been possible to determine for this pair $2D=-11.207$ kMc and $4\beta^2/r_{12}^3=0.999$ kMc, which is to be compared with $2D=-11.495$ kMc for single ions and a value for $4\beta^2/r_{12}^3$ of 0.956 kMc as calculated under the assumption of point dipoles separated by the internuclear distance of the ion pair. The J value of the fifth neighbor is found to be about 2 cm^{-1}.

As previously mentioned[2)] for zero exchange the pair lines lie in the immediate vicinity of the main ruby lines displaced from them by the dipolar interaction. For exchange interactions which are comparable to D the lines lie somewhere between the clusters and the isolated chromium lines. In addition there are some lines which correspond to transitions between different S multiplets. For low J, these transitions are no longer completely forbidden. Some of these lines are found at high magnetic field values well above all the clusters. From the position of the lines it is possible to determine the J value provided we know the dipolar interaction and make the correct assignments. In choosing the proper assignment calculations of the various line positions as a function of J and of the relative transition probabilities are used. After an assignment was made the line position was calculated as a function of angle between the z-axis of the crystal and the direction of the magnetic field and compared with experiment. In addition, certain assignments predict other lines, and these predictions were borne out by experiment. As an example, three lines were identified as belonging to pairs with $J=6.6$ kMc. Neglecting the dipolar interaction which is small for distant neighbors and assuming the single ion D value, Fig. 2 shows these three lines, their angular dependence, and the experimental results. The calculations were carried out on an IBM 704 computer by diagonalizing the full 16×16 Hamiltonian matrix. For low J values, the states contain components with different S and m_s values. In labeling the states the S and m_s value of the corresponding high J eigenfunctions are

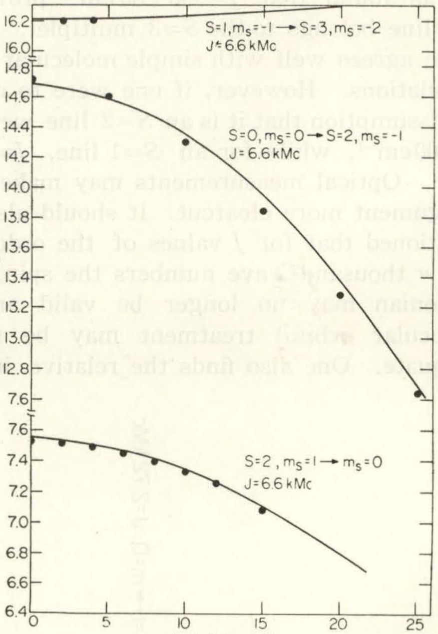

Fig. 2. Theoretical and experimental angular dependence of three lines corresponding to a pair with $J=6.6$kMc.

Table I. Pairs with low exchange interactions.

Transitions Investigated	J(kMc)	ΔJ(kMc)	Temp. Range	Expansion	$d \ln J/d \ln R$
$S=2,\ m_s=1\rightarrow S=2,\ m_s=0$ $S=3,\ m_s=2\rightarrow S=3,\ m_s=1$	9.5	2.75	300—600°K	0.18%	160
$S=0,\ m_s=0\rightarrow S=2,\ m_s=-1$ $S=1,\ m_s=-1\rightarrow S=3,\ m_s=-2$ $S=2,\ m_s=1\rightarrow S=2,\ m_s=0$	6.6	0.60	300—700°K	0.25%	36
$S=0,\ m_s=0\rightarrow S=2,\ m_s=-1$ $S=1,\ m_s=1\rightarrow S=3,\ m_s=0$	2.72	0.33	300—700°K	0.25%	49

used.

Using the techniques above described, the J-values listed in Table I are found. These findings supplement the thermally measured exchange constants of Fig. 1. Other computer calculations of line position as a function of J show that the $S=3$, $m_s=2\rightarrow 1$ transition with $J=6.6$ kMc is still expected to lie in the cluster shown in Fig. 1. The lowest J pair of Table I, however, will no longer give rise to a line in that part of the spectrum. Also listed in Table I are the changes in J due to thermal expansion of the lattice as determined from the shift of the lines as a function of temperature. In general, the J as determined from the line position is expected to be characteristic not only of the lattice spacing, but also of the amplitude of the lattice vibrations. This is because of nonlinearities in J as a function of internuclear distance. The shifts in J listed are thus only indicative of their order of magnitude.

Pairs also relax differently and generally much faster than isolated ions[3,4]. In the direct or one phonon process, exchange enters in two important ways. First, the various spin multiplets are separated by energies of one to a few times J. By a two-step relaxation process involving transitions between the various spin multiplets, high energy phonons are active and since the density of phonon states varies as ω^2, the transition probability is accordingly enhanced. Second, since exchange interactions are very sensitive to the separation of the two ions, the modulation of the exchange interaction by thermal lattice vibrations is more pronounced than the modulation of the crystalline field. If we assume an isotropic solid with equal masses for all ions, the thermally induced transition probability P can be written as

$$P=\frac{\omega^2}{3\pi\hbar^2 v^5}\frac{V}{M}R_1^2 kTC^2\left|\left\langle\begin{matrix}S_1\cdot S_2\\ S_1\times S_2\end{matrix}\right\rangle\right|^2. \qquad (2)$$

In Eq. (2), R_1 is the separation of the two ions, V the volume and M the mass of the crystal, $\hbar\omega$ is the energy difference between the two states in question, v is the velocity of sound where longitudinal and transverse sound waves are assumed to have the same velocity and $kT\gg J$. The interaction energy between the electronic levels and the lattice vibrations is assumed to be

$$H_{\mathrm{int}}=\begin{Bmatrix}S_1\cdot S_2\\ S_1\times S_2\end{Bmatrix}Cr_1. \qquad (3)$$

In Eq. (3), r_1 is the relative displacement of the two ions, C is a constant essentially equal to dJ/dr_1 and $S_1\cdot S_2$ or $S_1\times S_2$ are operators referring to the isotropic or the Moriya[5] type anisotropic exchange forces. Equation (3) is representative for most cases and can be readily extended for more quantitative calculations. Using the modulation of the isotropic exchange and C inferred from line shifts with temperature and inserting values appropriate for pairs with $J=1\ \mathrm{cm}^{-1}$, one obtains $P\approx 300T$. This result is of about the right order of magnitude to explain measurements of relaxation times[3]. Spin-lattice relaxation of pairs via modulation of the crystalline field and a two step process gives nearly comparable values. Relative saturation measurements carried out in this laboratory indeed indicate that pairs in a cluster with large J values relax faster than those with smaller exchange interactions at low temperatures. For very large exchange interactions theory predicts that relaxation may occur predominantly through anisotropic exchange of the form $S_1\times S_2$. It appears conceivable that this mechanism may even broaden large J lines to an extent that they escape experimental detection.

Raman type relaxation processes may also be enhanced through exchange interactions, due to their strong dependence on the separation of the ion pair. It can readily be shown that the relaxation is very fast when $J\approx D$ and d^2J/dr_1^2 is large. Experimentally certain lines are found with $J\approx 0.32\ \mathrm{cm}^{-1}$ which are lifetime broadened above room temperature and which become unobservable above 700°K. Cross relaxation to fast relaxing pairs can enhance the relaxation of single ions and thus produce a concentration dependent relaxation time.

References

1 Rimai, Statz, Weber, deMars and Koster: Phys. Rev. Letters **4** (1960) 125.

2 Statz, Rimai, Weber, deMars and Koster: J. Appl. Phys. **32** (1961) 218S.

3 J. C. Gill: Nature **100** (1961) 619.

4 Weber, Rimai, Statz and deMars: Bull. Am. Phys. Soc. **6** (1961) 141.

5 T. Moriya: Phys. Rev. **120** (1960) 91.

DISCUSSION

W. P. WOLF: I should just like to remark that the two-phonon relaxation mechanism which you mentioned has been successfully used for some time in explaining spin-lattice relaxation times of various rare earth salts. For these, the phonons modulate the crystal field, which is comparable in energy with the exchange energy in this case. This is the mechanism due to Orbach.

H. STATZ: I agree that the two-step relaxation process is also important in other systems.

M. TACHIKI: Did you determine the exchange integrals between ions in the same sublattice?

H. STATZ: In order to answer your question I have to know which J-values belong to the various neighbor shells. While the given Hamiltonian allows in principle to assign the various lines to certain neighbors there are ambiguities because of possible changes in D or due to anisotropic exchange. We are at the present time investigating the symmetries of the lines as a function of the orientation of the magnetic field and hope to specify with certainty which J belongs to which neighbor shell.