fitted with an (isotropic) exchange splitting of 24.4 cm^{-1} of the lowest lying Kramer's doublet of the $J = 7/2$ state. They also analyze Pauthenet's[4] data on saturation magnetization in YbIG to obtain a theoretical splitting of about 26 cm^{-1}. Our present results are in full accord with these observations, which represent in each case an average of the two inequivalent ground-state splittings distinguishable in the optical spectra. (See Fig. 2.) The exchange splitting is, however, two or three times larger than one would expect from extrapolation of the exchange coupling of gadolinium in the iron garnet as deduced from saturation magnetization or antiferromagnetic resonance data.[6] Corroborative information on the anomalously large exchange coupling of the Yb^{+++} ion is accumulating; for instance, differences in the vibrational spectrum of the crystal for the $J = 5/2$ and $J = 7/2$ states of the ytterbium ion indicate that the $4f$ electrons are participating perceptibly in the chemical bonding.

The large anisotropy of the exchange splitting is harder to understand. Paramagnetic resonance on Yb^{+++} in yttrium aluminum garnet and yttrium gallium garnet indicates that the g factor for the two inequivalent sites differs by only about 3% for H_{ext} in a [111] direction as compared with the 100% difference in exchange splitting observed here. A mapping of the exchange splitting in YbIG as a function of the crystallographic orientation of H_{ext} will be carried out as soon as experimentally feasible.

Theoretical calculations aimed at discovering the extent to which combined crystal field and exchange effects can break down the strong $\vec{L}\cdot\vec{S}$ coupling of this ion (destroying J as a "good" quantum number) are in progress. An analysis of the total optical spectrum of Yb^{+++} in the garnets to determine the crystal fields involved is also under way. It is further anticipated that a detailed investigation of the optical spectrum of other rare earth iron garnets will lead to the measurement of additional exchange splittings.

We wish to acknowledge the assistance of Dr. R. A. Lefever, who grew the single crystals used in this study. We also wish to thank Professor R. A. Satten and Mr. S. Pollack for allowing us to use the UCLA spectrograph and for assisting us with its operation.

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PARAMAGNETIC RESONANCE OF EXCHANGE-COUPLED Cr^{3+} PAIRS IN RUBY

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We have investigated the paramagnetic resonance spectrum of ruby (Cr-doped Al_2O_3) crystals with concentrations of Cr^{3+} between 0.05 and 1.0% by weight. In addition to the Cr^{3+} lines, a very large number of weak lines are observed in the more concentrated samples. We believe that many of these weak lines arise from exchange coupling between neighboring chromium ion pairs.[1]

Measurements have been made at both 10 and 16 kMc/sec in various ruby samples. More detailed investigations were carried out using a crystal with 0.6% Cr^{3+} and a frequency of 15.74 kMc/sec. Comparison of the various crystals showed that the additional spectrum was strongly concentration dependent. Furthermore, the intensity of this additional spectrum was about what would be expected from Cr^{3+} ion pairs occupying neighboring lattice sites. The intensity of the lines reported below as measured in the 0.6% sample was ~1% of that of the isolated Cr^{3+}

lines.

In ruby, nearest-neighbor cations occupy lattice sites on lines parallel to the hexagonal *c* axis having a distance of 2.73 A. From the antiferromagnetic properties of Cr_2O_3, one expects these nearest-neighbor pairs to be coupled antiferromagnetically. Thus an $S=0$ state with no paramagnetic resonance will be lowest and will be the only one occupied at sufficiently low temperatures. To select the spectrum of such pairs from the great multitude of observed lines, we focused our attention on those lines which decreased in intensity with decreasing temperature and which showed a symmetric behavior as a function of the angle θ between the magnetic field H and the crystalline *c* axis. In Fig. 1 we show a portion of the paramagnetic resonance spectrum at three temperatures which exhibit a temperature-dependent line near 7 kilogauss for $\theta=9°$. All lines studied which decrease with decreasing temperature are listed in Table I with the value of H for resonance at $\theta=0$. Several different temperature dependences are found; some lines decrease in intensity rapidly with temperature, by about a factor of 2 between 290°K and 260°K. Another set of lines decreases by about a factor of 2 between 290°K and 193°K. There is one line which first increases with temperature, reaches a maximum at about 200°K, and then decreases. We refer to these three temperature dependences in Table I as "fast," "medium," and "slow." In the present study, other lines which decrease only at temperatures below that of liquid nitrogen have been omitted. All the lines listed have been found to show a symmetric behavior with respect to the angle θ.

For the theoretical analysis of these lines we begin with a Hamiltonian for a *z*-oriented Cr-Cr pair of the form:

$$H=D(S_{z1}^2+S_{z2}^2)+g\beta\vec{H}\cdot(\vec{S}_1+\vec{S}_2)+J\vec{S}_1\cdot\vec{S}_2+J_z(\vec{S}_1\cdot\vec{S}_2-3S_{z1}S_{z2}). \qquad (1)$$

The first two terms are the sum of the spin Hamiltonians for the individual Cr^{3+} ions; the third term is the isotropic exchange coupling; the fourth term arises from dipolar and lowest order anisotropic exchange interactions. We assume that $J\vec{S}_1\cdot\vec{S}_2$ is the largest term by orders of magnitude; hence we may diagonalize the Hamiltonian first using this term alone. This yields eigenstates of the total spin of $S=3, 2, 1, 0$ having energies with respect to the ground state

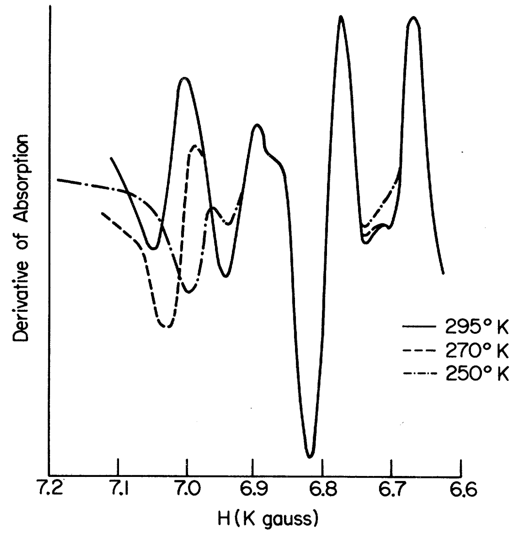

FIG. 1. Superposition of absorption spectra showing a line decreasing with temperature.

Table I. Positions of observed lines and their assignments

Observed lines (kilogauss)	Temperature variation	S	Assignment Initial and final m	Theoretical position (kilogauss)
1.77	medium	2	(2, 1)	3.2
4.15	fast	3	(-2, -3)	3.9 (4.10)
4.29	slow	1(?)	(0, -1)	2.0
4.44	fast	3	(-1, -2)	4.6 (4.48)
4.67		2	(1, 0)	4.9
4.98	fast	3	(0, -1)	5.3 (4.92)
6.31	fast	3	(1, 0)	6.0 (6.31)
6.62	medium	2	(0, -1)	6.4
6.75	fast	3	(2, 1)	6.7 (6.75)
7.14	fast	3	(3, 2)	7.3 (7.14)

$S=0$ of $6J$, $3J$, and J, respectively. The remaining degeneracies are removed by the other terms in the Hamiltonian (1).

From the above model the temperature dependence of the paramagnetic resonance lines between substates of the $S=3$ multiplet should have the following temperature dependence:

$$A(T)=\frac{\exp(-6J/kT)-\exp[-(6J+\hbar\omega)/kT]}{1+3\exp(-J/kT)+5\exp(-3J/kT)+7\exp(-6J/kT)}. \tag{2}$$

If we assign the lines which decrease "fast" to transitions within the $S=3$ multiplet, we obtain $J\sim 250\ \mathrm{cm}^{-1}$. Similarly, for the "medium" lines we obtain the same J value if we assign them to transitions within the $S=2$ multiplet. For the "slow" line the data are not sufficient to determine a J value; however, they do not appear to be inconsistent with an $S=1$ assignment. In view of the average exchange constant determined from the antiferromagnetic transitions in Cr_2O_3, the present J value for the nearest-neighbor pairs is not unreasonable.

A comparison has been made between the experimental data and a spectrum calculated from (1) using a constant D value[2] of -5.79 kMc/sec and adjusting J_z to obtain a best over-all fit. The positions of the calculated lines for $J_z=1.5$ kMc/sec are given in Table I. The rather large discrepancies between theory and experiment cannot be attributed solely to a different value of D for a Cr^{3+}-Cr^{3+} pair as compared to that for a single ion. This is because the level separations within each S multiplet depend only on a single linear combination of D and J_z. Apparently higher order exchange terms have to be included.

To reduce the remaining discrepancies we may introduce phenomenologically higher order diagonal exchange terms. This we do for $S=3$ by writing down the field dependence of the energies of the seven sublevels as determined from three experimentally measured transitions ($\theta=0$):

$$\begin{aligned} E_{\pm 3} &= -9.33\ \mathrm{kMc/sec} \pm 3g\beta H,\\ E_{\pm 2} &= -5.07\ \mathrm{kMc/sec} \pm 2g\beta H,\\ E_{\pm 1} &= -1.91\ \mathrm{kMc/sec} \pm g\beta H,\\ E_0 &= 0. \end{aligned} \tag{3}$$

The remaining three transitions are calculated from (3) and the results are given in parentheses in Table I. The residual differences between the measured and calculated data indicate the presence of off-diagonal matrix elements of the order of 1 kMc/sec resulting from higher order exchange terms. Note that the additional diagonal matrix elements introduced in (3) are of the same order of magnitude; however, they appear in first order perturbation theory while off-diagonal elements enter only in second and higher order.

Using the zero-field splittings of Eq. (3), we have obtained the eigenvalues of the 7×7 matrix describing the $S=3$ multiplet for magnetic fields making an angle θ with the crystalline c axis. The theoretical and the experimental values are plotted in Fig. 2. Unfortunately it is rather difficult to obtain good experimental data. This accounts for the fact that we have not yet measured the angular dependencies of all the transitions. From second order perturbation theory it is apparent that the theoretical curves depend very critically on energy denominators $E_i - E_j$ and also on the matrix elements of $S_{1x}+S_{2x}$ between the various m_S substates. The agreement between the calculated curves and experimental points provides supporting evidence that the

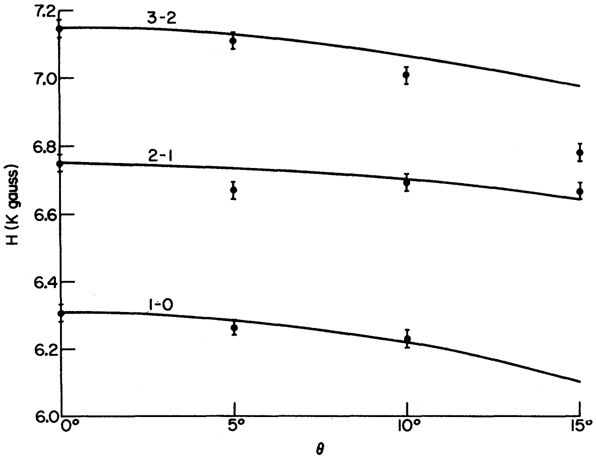

FIG. 2. Calculated and experimental angular dependence of absorption lines in the $S=3$ multiplet.

assignment given is indeed correct.

From an examination of the resonance spectrum in the liquid nitrogen to helium temperature range, other antiferromagnetically coupled pairs with smaller exchange constants appear to be present. In addition there is evidence for the existence of ion pairs coupled by weaker ferromagnetic exchange. Further work is being done to confirm the present assignment by introducing higher order exchange terms into Eq. (1) and to study the interactions between other chromium neighbors. A further study of these interactions should also provide a firmer basis for the theory of spin relaxation phenomena in concentrated crystals.

We thank Dr. S. Aisenberg for independent measurements of the pair spectrum at 10 kMc/sec and Miss W. Doherty for her help in the computations.

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DOUBLE-QUANTUM ELECTRON SPIN RESONANCE TRANSITIONS OF NICKEL IN MAGNESIUM OXIDE*

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We have examined the electron spin resonance spectrum of Ni^{+2} as an impurity in single crystals of MgO at X band and wish to report the observation of a double-quantum absorption between the $S_z = -1$ and $S_z = +1$ levels.

The Ni^{+2} ions are present in approximately cubic crystal surroundings, the ground state having effective spin $S = 1$.[1] At 77°K the spectrum consists of an isotropic broad line (50 gauss between points of maximum slope) with a sharp line (2 gauss peak to peak) superimposed on its center. The width of the broad line may be attributed to the presence of small distortions in the MgO lattice; the sharp line has a width similar to that of lines from other impurity ions in the same crystal.

At low microwave powers the sharp central line is found to be inverted (i.e., the derivative of the absorption curve has a 180° phase shift relative to all other lines; displayed directly on an oscilloscope, the absorption curve shows a "dip" at the center of the broad line). The line inversion at low powers is an effect which is probably not directly connected with the double-quantum transitions discussed here. As the power is increased, this inverse line is reduced in amplitude and then changes to the normal "positive" line which we interpret as arising from the simultaneous absorption of two quanta, the absorbing ions being excited from the $S_z = -1$ to the $S_z = +1$ state. If this interpretation is correct, the intensity of absorption is expected to increase with the square of the microwave power and this we observe over the range of powers at present available to us.[2] The inversion of the line at low powers is probably due to another effect. We are engaged in attempts to elucidate this phenomenon which we have not found described elsewhere.

It may be noted that the phenomenon of multiple-quantum absorption by ions in a cubic field would be expected to occur for any system having effective spin $S = 1$ or $3/2$ (for $S > 3/2$ the situation is modified by the existence of a cubic field splitting) but in our case the inhomogeneous broadening of the $\Delta M = 1$ transitions provides particularly favorable conditions for its observation. The effect of small departures from exact cubic symmetry is to split the $S_z = 0$ from the $S_z = \pm 1$ levels, shifting the $\Delta M = 1$ transitions slightly. The separation of the $S_z = -1$ and $S_z = +1$ levels in a magnetic field is affected only to negligible extent.

As a further test of the "double-quantum" interpretation of the sharp line we arranged our samples to be situated simultaneously in two microwave fields having slightly different frequencies and looked for simultaneous absorption of one quantum of each.[3] This was achieved by using a rectangular resonant cavity, not quite square in cross section, excited in its two TE_{011} modes. The samples were mounted along the