ing terms" with the resonant phonons, for which there is no simple criterion. It is desirable to keep the interaction between the paramagnetic centers and the phonons weak so that the phonon distribution is not distorted; because of this such a detector would normally have a relatively slow response time. The most promising systems we know of for constructing such a phonon detector are the F center in the alkali halides[3] and divalent thulium in the alkaline-earth halides,[7] sinch both have strong paramagnetic circular dichroism and under certain conditions the spins are coupled primarily to the resonant phonons.

Most of the references are concerned with the application of classical optical pumping techniques, such as those used to study the alkali vapors, to paramagnetic centers in solids. In the solid the spins interact with the lattice vibrations instead of with a buffer gas or container walls, but the optical techniques can be used to study the spin-phonon interactions as they can be used to study the corresponding interactions in the vapor. The important new point is that once the spin-phonon interaction is understood in a particular crystal, these techniques can be used to study the phonons in that crystal.

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DAVYDOV SPLITTING OF THE ^2E LINES IN ANTIFERROMAGNETIC Cr_2O_3

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This Letter reports the observation of a Davydov splitting in the optical absorption spectrum of Cr_2O_3. In zero external field, a transition to only one level of the Davydov pair is observed. With H parallel to the c axis, an additional line having a field-dependent absorption appears. The extrapolated zero-field splitting is 3.75(±0.25) cm^{-1}.

The recent observation of two-magnon absorption[1] and magnon side bands[2] in some transition-metal fluorides has stimulated an investigation of the spectra of other transparent antiferromagnets. This paper is the first report of the observation of a Davydov splitting[3] in the optical exciton spectrum of an antiferromagnet, Cr_2O_3.[4]

Wickersheim[5] has investigated the sharp line-absorption spectrum of Cr_2O_3, and Stager[6] has measured the Zeeman effect of these lines. There are four sharp lines with the following energy (cm^{-1}) and polarization: 13 747.0, σ, 13 769.5, π, 13 909.5, π, and 13 931.4, σ. The positions of the absorption lines were found to be slightly crystal dependent. The energies given here are approximately 5 cm^{-1} higher than Wickersheim's data. Their explanation was in terms of the single-ion molecular field approximation and was found to be inadequate to explain the observed results. A more appropriate description of the excited states of insulating concentrated crystals is in terms of Frenkel excitons.[4]

Cr_2O_3 has the corundum structure with four chromium ions per rhombohedral unit cell.[7] Below 308°K the spins are antiferromagnetically aligned in chains along the threefold axis.[8] The site symmetry of the chromium ion is $C_3 = 3$, and using the international notation,[9] the symmetry of the magnetic lattice is described by the magnetic space group $R\bar{3}'c'$. Denoting the time-reversal operator by R, the operations of the space group are $\{E|0\}$, $2\{C_3|0\}$, $3\{C_2'|\vec{\tau}\}$, $\{RI|0\}$, $2\{RIC_3|0\}$, $3\{R\sigma_v|\vec{\tau}\}$, and the products of these with $\{E|\vec{R}_n\}$ and $\{\bar{E}|\vec{R}_n\}$. Here $\vec{\tau}$ is the nonprimitive translation $\frac{1}{2}(\vec{t}_1+\vec{t}_2+\vec{t}_3)$, and $\vec{R}_n$ is a lattice translation.

The selection rule for exciton absorption permits us to limit the discussion to excitons near the center of the Brillouin zone. These exciton states can be classified according to the representations of the factor group of the magnetic space group.[4,10] The representations are obtained by considering the representations of the unitary subgroup $R32$.[11,12] The exciton states resulting from the single-ion transitions are shown in Fig. 1. There are two states transforming as the two-dimensional representation E, and states which transform as the one-dimensional representations A_1 and A_2. The four chromium ions in the unit cell consist, for the present purpose, of two equivalent pairs. Thus two degenerate excitons are obtained for each representation. The electric dipole moment operator z transforms as A_2 and $x \pm iy$ as E. Transitions to these exciton states are allowed from the A_1-symmetry ground state; the dipole transition to the A_1 state is forbidden.

In the molecular field approximation, the single-ion transitions to the high-energy exchange-split levels are not allowed. Thus the upper σ and π exciton transitions do not occur in this case. To explain these transitions, Wickershrim[5] postulates an exchange interaction which mixes the ground-state single-ion states. The direct cation-cation interaction discussed by Goodenough[13] would for example produce such a mixing. The reduction of the sublattice magnetic moment from the spin-only value gives us an estimate of the mixing and allows the calculation of the relative optical absorption strength to the upper and lower exciton levels. Neutron diffraction data indicates reduction of the sublattice moment to $2.76\mu_\beta$ from a spin-only value of $3\mu_\beta$.[14] If we consider mixing of the $S_z = \pm\frac{3}{2}$ levels, the ratio of the upper to lower energy absorption strength is computed to be 0.042. The experimental ratio is about 0.5.[12] We are thus led to the conclusion that ground-state mixing cannot fully explain the observed absorption strength to the upper levels.

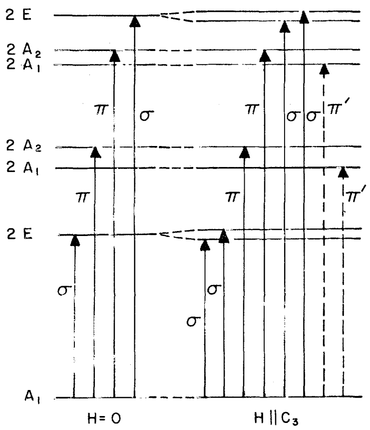

FIG. 1. Exciton levels derived from the ^2E single-ion levels of Cr_2O_3. In the field, the π'-polarized transitions shown as dotted lines become allowed.

We have shown that transitions to the upper levels, with an adequate absorption strength are obtained by an exchange interaction within the ^2E state which couples together the two single-ion states resulting in the σ exciton transitions, and also couples the states resulting in the π-polarized lines.[12] The four transitions thus have a different interpretation from Wickersheim's single-ion molecular field approximation in that (a) they are excitons and (b) the absorption strength of the higher energy lines does not come from ground-state mixing.

As shown in Fig. 1, the Davydov splitting between the levels A_1 and A_2 will not be directly observable. But consider now the effect of a magnetic field parallel to the c axis. In $R\bar{3}'c'$ the magnetic moment transforms as A_2, and since $A_2 \times A_1 = A_2$, the wave function corresponding to the A_1 exciton is to first order

$$|A_1\rangle' = |A_1\rangle + |A_2\rangle\langle A_2|\mu(A_2)|A_1\rangle H/[E(A_1)-E(A_2)],$$

and a field-dependent electric dipole absorption (π polarization) becomes allowed.

The absorption spectrum of the lines at 13 747.0 and 13 769.5 cm^{-1} for several magnetic field strengths are shown in Fig. 2(a). The σ-polarized line is seen to split uniformly with increasing field. The present measurement gives $g = 4.62$ in reasonable agreement with Stager's value. The field dependence of the π-polarized line is strikingly different, however. In a field, the π line present at $H = 0$ shifts to larger wave numbers, and as predicted by the theory, a new π-polarized component appears whose absorption strength increases with increasing field. Figure 2(b) shows the field dependence of the energy levels. The scale of the drawing obscures the finer details of the A_1 and A_2 exciton field dependence. The size of the circles indicates the experimental error. Measurements of greater precision than shown in Fig. 2(a) yield a field dependence consistent with the diagonalization of the Hamiltonian of the magnetic interaction between the A_1 and A_2 excitons and an experimental value of the Davydov splitting of 3.75(±0.25) cm^{-1} in zero external field.[12]

The splitting results from the exchange of excitation between translationally inequivalent ions. An approximate theoretical value of the

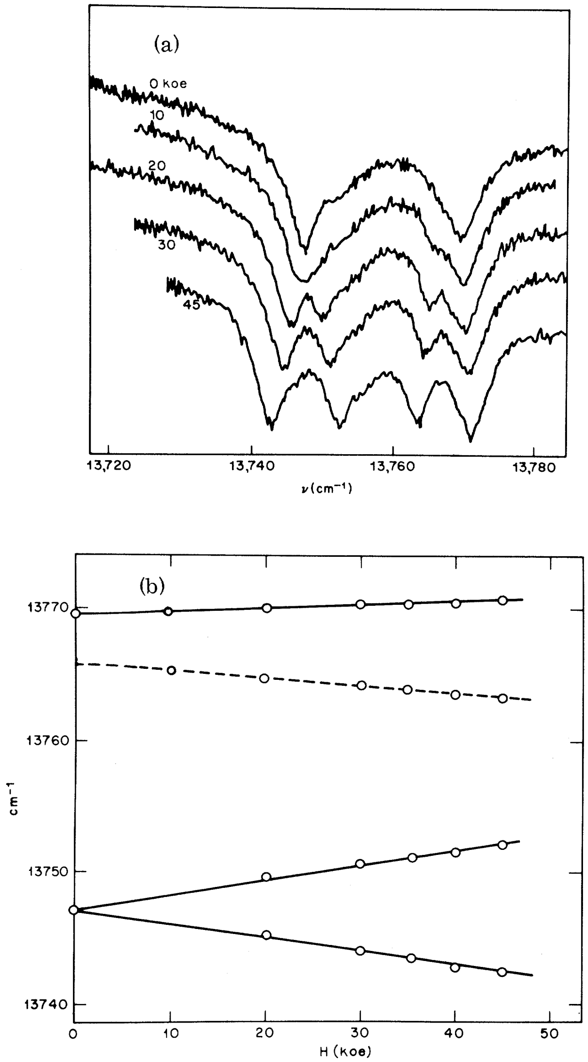

FIG. 2. (a) Absorption traces of the 13 747.0- and 13 769.5-cm^{-1} lines in a magnetic field (unpolarized spectrum). (b) Field dependence of the absorption lines.

splitting is obtained by extending the work of Imbusch[15] on the energy-transfer mechanisms in Al_2O_3:Cr^{3+} to the case of Cr_2O_3. Contributions from exchange and the multipole moments of the electrostatic interaction have been considered. The quadrupole-quadrupole interaction appears to be dominant and gives a splitting of the correct magnitude.[12]

Stager[6] interpreted his data in terms of the removal of the sublattice degeneracy by the field. The π-polarized line was consequently taken to have a g factor of 3.9 and a shift of the center gravity of this line corresponding to a g of 1.3. A more careful analysis of Fig. 1 in Stager's paper indicates, as is observed here, the presence of a Davydov splitting in zero applied field. These results are striking evidence of the exciton nature of the electronic excitation in Cr_2O_3.

The σ-polarized line at 13 931.4 cm^{-1} splits uniformly with $g = 4.66$. The absorption at 13 909.5 cm^{-1} shifts less than 0.5 cm^{-1} in a field of 50 kOe from its zero-field value, and no line with a field-dependent absorption coefficient is observed. It is consistent with the theory if we assume this A_1 exciton does not interact appreciably with the other levels.

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