process itself. These optical studies do indeed provide a useful probe, since both the exciton dispersion and the coupling constants, α and δ, are directly and sensitively related to the detailed nature of the interionic exchange. The exchange interaction, including both "kinetic" and "potential" exchange, between adjacent sites i and j has the form[3]

$$2\sum_{\rho\tau} J_{\rho\tau}^{(ij)} \vec{s}_{\rho}^{(i)} \cdot \vec{s}_{\tau}^{(j)}, \tag{4}$$

where $\vec{s}_{\rho}^{(i)}$ is the spin operator for the electron occupying orbital ρ on site i. More generally, the interaction includes operators which change the orbital occupancy, but these need not be included in dealing with the states considered here. We write the $S_z' = \frac{3}{2}$ component of the excited multiplet: $|^4\Gamma_{\frac{3}{2}}\rangle = \sum_{\rho} G_{\rho} |\rho\rangle$, where $|\rho\rangle$ has the spin or orbital ρ down, the others up; ρ is summed over $\xi, \eta, \zeta, \theta, \epsilon$. The G's may be chosen to be real. The various exchange and transfer constants can be easily identified by substituting

$$\vec{s}_{\rho}^{(i)} \rightarrow [1-N^{(i)}]\tfrac{1}{3}\vec{S}^{(i)} + N^{(i)}(1-2G_{\rho}^{2})\tfrac{1}{3}\vec{S}^{(i)} - (G_{\rho}/\sqrt{2})\vec{T}^{(i)}.$$

The exciton dispersion is determined by n.n. exchange:

$$L_1 = \tfrac{1}{2}\sum_{\rho\tau} J_{\rho\tau}^{(11')} G_{\rho} G_{\tau}, \tag{5}$$

while the exciton-magnon coupling parameters are determined by n.n.n. exchange:

$$\alpha = (25J_2)^{-1}\sum_{\rho\tau} J_{\rho\tau}^{(12)} 2G_{\rho} G_{\tau},$$

$$\delta = -(25J_2)^{-1}\sum_{\rho\tau} J_{\rho\tau}^{(12)} (G_{\rho}^{2} + G_{\tau}^{2}). \tag{6}$$

Note that if all, or even nearly all, $J^{(12)}$'s are positive, we expect $-\delta > |\alpha| > 0$.

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EXCITON-MAGNON BOUND STATE IN MnF_2 AND THE EXCITON DISPERSION IN MnF_2 AND $RbMnF_3$†

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The absorption of MnF_2 and $RbMnF_3$ in the 4000-Å region has been examined. Evidence is presented for the assignment of a sharp line at the edge of a magnon sideband to a magnon-exciton bound state.

There has been considerable interest recently in the optical spectra of antiferromagnetic crystals since the identification of magnon additions to exciton lines.[1] There is now evidence from several sources that magnon-exciton interaction affects the shapes of magnon sidebands.[2-4] Theories of magnon-magnon interactions have predicted the formation of bound pairs of magnons under certain circumstances, but there has been no experimental evidence thus far. Since the two magnon case may be considered as a special case of the interacting exciton-magnon system, the formation of bound states for the more general case is a possibility. We now have direct evidence for such a state in the form of a sharp line at the edge of a magnon sideband (at 25 239.1 cm^{-1} in MnF_2). This interpretation of the sharp line was suggested by Professor J. J. Hopfield, and

has been reinforced by the recent work of Freeman and Hopfield.[5] Here we provide fuller experimental evidence that this is the correct interpretation.

The absorption spectra of MnF_2 and $RbMnF_3$ were taken at a temperature of 4.2°K, using both photographic and photoelectric recording. The behavior of the MnF_2 spectrum under uniaxial strain and magnetic fields below and above the spin-flop transition are described elsewhere.[6-8] The $RbMnF_3$ was grown by one of us in the laboratory of Professor Stout[9] and the first sample of MnF_2 was given to us by Professor Stout. The second and third MnF_2 samples were grown by Guggenheim and were given to us by Dr. Dietz.[10] Samples 1 and 3 showed a distinct sharp line at 25 239.1 cm^{-1}, while in sample 2 a definite shoulder at the same position and of about the same height as the line appeared on the edge of a continuum. Sample 3 was zone refined, and had the lowest impurity level of the three, according to the fluorescence criterion of Dietz.[11] Sample 1 showed faint impurity absorption lines at 25 223.5 and 25 229.8 cm^{-1}, while the others did not. We thus believe that we have eliminated the possibility that the strong spectral features of interest to us have anything to do with impurities.

Figures 1 and 2 show the 4000-Å region of the spectra of MnF_2 and $RbMnF_3$ corresponding to the ${}^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$ transitions. The magnetic dipole exciton lines of MnF_2 are indicated in the figure as $M1, M2$. The broad structure associated

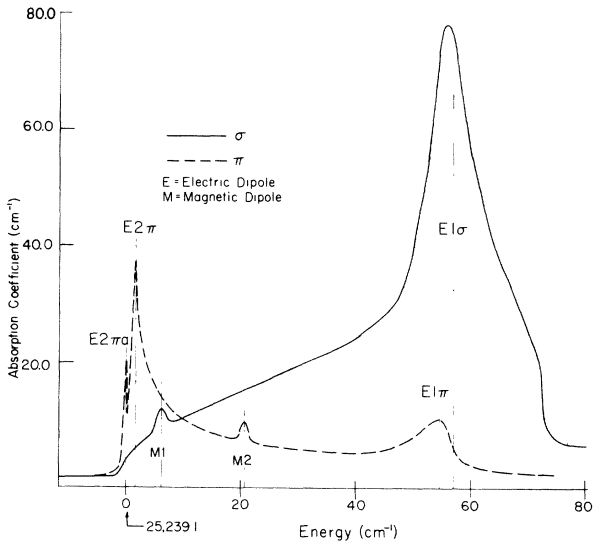

FIG. 1. Absorption of MnF_2 near the magnetic dipole origins of the transition ${}^6A_{1g} \rightarrow {}^4A_{1g} {}^4E_g(I)$ at 4.2°K.

with the excitons corresponds to the magnon sidebands, as shown by their absence of splitting in a magnetic field.[6] The MnF_2 spectrum has considerable absorption at energies lower than the exciton origins, and in the π polarization a sharp peak at 19.4 cm^{-1} below the 25 260.1-cm^{-1} line and a sharp line (0.7-cm^{-1} width at half-height) 21.0 cm^{-1} below. Uniaxial strain experiments show that both of these π-polarized features belong to the upper exciton at 25 260.1 cm^{-1}.[7,8] The peak at 25 240.7 cm^{-1} and in fact most of the unusual features of the magnon sidebands in this region are reproduced with a transition probability expression incorporating exciton dispersion parameters giving strong negative dispersion of 74 cm^{-1} in the z direction of the Brillouin zone and little or no dispersion in the basal plane.[4] The exciton dispersion is larger than the magnon dispersion and, being negative, is responsible for the appearance of the peak on the low-frequency side of the magnetic dipole origin at $k = 0$. The line at 25 239.1 cm^{-1} is not explained in this way, however. The possibility was considered that it arises from the difference of two special points on the zone surface, Z and A, which give rise to sharp features in the sideband in the π polarization. These points correspond to the same energy if J_3, the third-nearest-neighbor exchange, is zero and are separated by 1.6 cm^{-1} for $J_3 = 0.08$ cm^{-1}. Since the peaks due to Z and A are affected differently by exciton dispersion in the basal plane, separation of the peaks by a small amount of such dispersion was also considered. For values of J_3 lying between 0 and 0.08 cm^{-1}, sufficient exciton dispersion was included to separate the points to the observed splitting. However, in all cases the calculated linewidths were such that two separate peaks are not resolvable. Thus the possibility that the sharp line can be explained simply as due to a critical point of the density of states is not a reasonable one.

The $RbMnF_3$ spectrum shows a weak line at 25 143.6 cm^{-1} with a shoulder at 25 147 cm^{-1}. The line strength of $f = 1.05 \times 10^{-8}$ is the correct value for a magnetic dipole transition to the $4E$ state.[7] Under uniaxial strain three components are observed. It is possible that these are transitions to the three $M_S = \frac{3}{2}$ components of the ${}^4E_g$, ${}^4A_{1g}$ states, with the peak 80 cm^{-1} above corresponding to a magnon sideband. This interpretation requires a small amount of positive exciton dispersion and a magnon having the dispersion expected from neutron scattering exper-

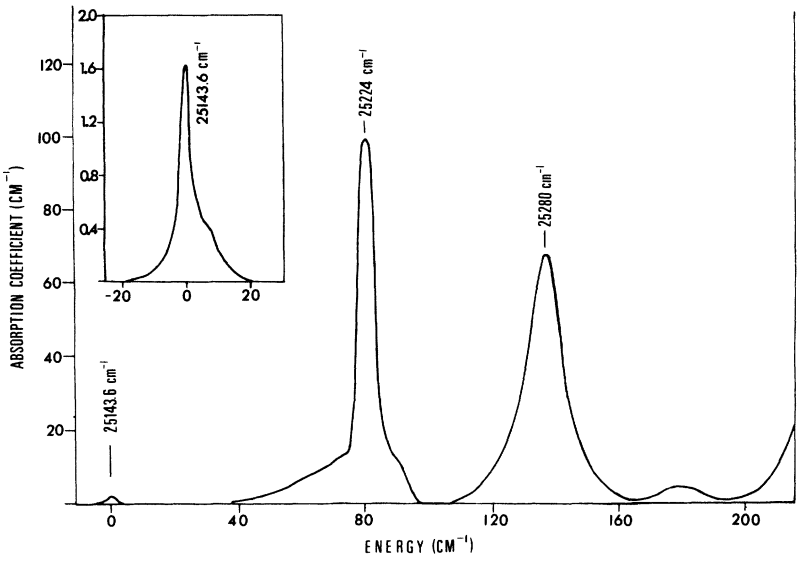

FIG. 2. Fine structure of the $RbMnF_3$ ${}^6A_{1g} \rightarrow {}^4A_{1g}{}^4E_g(I)$ transitions in the 4000-Å region at 4.2°K.

iments.[12] A complete analysis of the observed structure has not been made as yet but there appears to be no evidence for any large negative exciton dispersion.

Considerations of the structures of $RbMnF_3$ and MnF_2 lead one to expect that exciton dispersion should be considerably greater in MnF_2. In MnF_2 the nearest neighbor along the c direction (tetragonal axis) belongs to the same sublattice and excitation exchange may be rapid, leading to strong dispersion in the z direction of the first Brillouin zone of the exciton.[13] Each ion in $RbMnF_3$, on the other hand, is surrounded by ions of the other sublattice, and since excitation exchange is only strong between ions of the same spin projection, exciton dispersion should be slight. With the above preliminary assignment of the $RbMnF_3$ spectrum, the comparison of the spectra of the two compounds is thus additional evidence that the interpretation of the 25 240.7-cm^{-1} peak in terms of negative exciton dispersion is correct.

Since the maximum density of states of both exciton and magnon occurs at the zone edge, the peak at 19.4 cm^{-1} is at the Z or A point of the zone and corresponds to the maximum of the joint density of exciton-magnon states in this region. A bound state of the two entities would lie at lower frequencies in the spectrum than their sum; it should be most prominent when there is a high density of states available; and should be most easily resolved under the present conditions in which it is not overlapped by the continuum states. Thus the line at 25 239.1 cm^{-1} is reasonably ascribed to a bound state.

In the noninteracting model, the states which give magnon sidebands consist of an exciton and magnon on opposite sublattices. These states, however, are degenerate with those in which the spin deviation and the electronic excitation have exchanged sites, i.e., the exciton and magnon have exchanged sublattices. The possibility of this exchange gives rise to an interaction term in the Hamiltonian analogous to a Davydov interaction in a molecular crystal, and we postulate that this may be the origin of the binding energy. The "Davydov splitting" occurs in the sideband but not in the exciton, because in the former, the total spin projection is conserved in an intersublattice exchange act, while in the latter it is not.

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