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EXCITON-MAGNON INTERACTION IN MAGNETIC INSULATORS

S. Freeman
RCA Laboratories, Princeton, New Jersey

and

J. J. Hopfield*
Princeton University, Princeton, New Jersey
(Received 10 July 1968)

The one-exciton, one-magnon system is treated for a suitable antiferromagnetic insulator, MnF_2. Zone-edge excitons and magnons are found to interact quite strongly. Bound states are found to exist under favorable circumstances. The line shapes of magnon sidebands of excitonic transitions are modified. Expressions are given for the exciton-magnon coupling constants in terms of the parameters describing interionic exchange.

We have studied the one-exciton, one-magnon system in an antiferromagnetic insulator. Interionic exchange (including superexchange) provides the major source of interaction between these excitations. Approximations of the type customary in dealing with antiferromagnets reduce the many-body problem to a two-particle scattering problem; the latter has a simple structure permitting explicit solution. The extent to which interaction modifies the dominant features of the magnon sideband of the excitonic transition can then be displayed. The most dramatic effect is the existence of bound states below or above the two-particle continuum when certain conditions are satisfied.[1]

We have concentrated particularly on the magnon sideband of the lower ${}^6A_1 \rightarrow ({}^4A_1, {}^4E_\theta)$ absorption line in MnF_2. In this we were motivated by the description of preliminary experimental results most kindly provided by D. S. McClure and R. S. Meltzer. Their results indicate a large, negative exciton dispersion in the c direction. The sideband peak corresponding to constituent Z-point excitations thus lies some 19 cm^{-1} below the zero-magnon line, while the presence of an additional split-off component 1.6 cm^{-1} lower still suggests the presence of a bound state.[2]

The exciton state considered has the same orbital occupancy as the ground state. This ensures that coupling to lattice distortions is unimportant. Moreover, it is easily shown that the coupling of the exciton to adjacent spins through a direct Coulomb interaction plus spin-orbit coupling is small compared with typical exchange energies. On the other hand, Anderson's expression for the interionic exchange,[3] which is expressed as a sum of contributions from electrons occupying individual orbitals (more strictly, Wannier states) centered on adjoining sites, gives rise directly to exciton dispersion and to exciton-magnon coupling comparable in magnitude with exchange energies in the ground state (~50 cm^{-1}). Each of the interaction terms coupling a pair of sites i and j has the form of a scalar product of operators which transform as spin vectors at the two sites. One such interaction term is the usual exchange $\vec{S}^{(i)} \cdot \vec{S}^{(j)}$. It will suffice to consider only nearest-neighbor (n.n.) pairs (same sublattice) and next nearest (n.n.n.) (opposite), since only they have nonzero exchange constants in the ground state. The exchange constant is modified if a site is occupied by an exciton. We write the modified exchange constants J_1' for nearest and J_2' for next-nearest neighbors. In general, an exciton will experience different exchange interactions with the inequivalent n.n.n. in perpendicular (110) planes. This complication does not affect the qualitative features of the solution, and it will be ignored here for clarity. Another type of interaction term transfers the exciton from site to site. Define a standard form, $\vec{T}^{(i)}$, for the $|\Delta S|=1$ vector operator connecting ground and excited multiplets at site i by requiring that $\vec{T}$ be Hermetian and

$$\langle \text{exciton}, S_z' = \tfrac{3}{2} | (T_x - iT_y) \times | \text{ground}, S_z' = \tfrac{5}{2} \rangle = -\sqrt{2}.$$

In the present case, $\vec{T}$ is invariant under the operations of the site symmetry group acting on the orbital functions. The transfer term coupling n.n. on the same sublattice, $2L_1\vec{T}^{(i)}\cdot\vec{T}^{(j)}$, leads to exciton dispersion $4L_1\cos(k_z)$. In lowest order, transfer of an exciton to the other sublattice via $2L_2\vec{T}^{(i)}\cdot\vec{T}^{(j)}$ can take place only to a n.n.n. occupied by a spin deviation. Thus the effect of this term on the exciton dispersion is negligible, but it provides an important form of interaction between an exciton and magnon on opposite sublattices. Finally, there are terms $\vec{S}^{(i)}\cdot\vec{T}^{(j)}$. These only connect states far apart in energy (~3 eV) compared with the magnitude of the coupling, and thus have no important effect. They will be neglected in the following. Our Hamiltonian thus contains exchange terms, which are allowed to be different for the excited multiplet, and exciton transfer terms both within and between sublattices. Single-site anisotropy terms can also be included. It will prove convenient to measure energy in units of $16J_2S$. The strengths of the exciton-magnon interactions are summarized by dimensionless coupling constants $\delta=[(S-1)J_2'/SJ_2]-1$ and $\alpha=L_2/S^2J_2$. Here S is the ground-state spin, $\frac{5}{2}$ for MnF_2. The potential experienced by a magnon on the sites adjacent to an exciton is described by δ, while α scales the sublattice interchange scattering. We expect $\delta<0$ (attractive interaction); α may have either sign.

The method we have used for calculation corresponds to the Holstein-Primakoff method in spin-wave theory. An exciton creation operator $\Psi^\dagger$ is defined which leads from the n spin-deviation component of the ground multiplet, $S_z'=\pm(\frac{5}{2}-n)$, to the n spin-deviation component of the excited multiplet, $S_z'=\pm(\frac{3}{2}-n)$, with unit matrix element. So defined, $\Psi^\dagger$ commutes with the usual spin-deviation operators a and $a^\dagger$. For a site on the "up-spin" sublattice, the vector operator $\vec{T}$ is replaced by quasiboson operators as follows:

$$T_- = -\Psi^\dagger(2-n/S)^{1/2}[1-n/(2S-1)]^{1/2} + \Psi(a^\dagger)^2/[S(2S-1)]^{1/2},$$

$$T_z = \Psi^\dagger S^{-1/2}[1-n/(2S-1)]^{1/2}a + \text{H.c.} \qquad (1)$$

Here $n=a^\dagger a$. The operator $\vec{S}$ is expressed in terms of a and $a^\dagger$ in the usual fashion. Note, however, that if an exciton occupies a site, then S, the ground-state spin, is replaced by $S-1$. Also, the various exchange terms must be provided with projection operators $N=\Psi^\dagger\Psi$ or $(1-N)$ as appropriate. The Hamiltonian is expanded in successively higher powers of the quasiboson operators in the usual fashion. Interaction appears first as the terms biquadratic in exciton and magnon operators. In the usual spirit of the Holstein-Primakoff method, we ignore higher order interaction terms. We also neglect magnetic "polaron" effects, which would clothe the exciton in virtual magnons; they can be shown to be unimportant in this system. Finally, certain interaction terms are discarded which arise from the lack of perfect alignment in the spin-wave ground state[4] and vanish for zone-edge magnons. This is justifiable since the interesting interaction effects involve excitations at the zone edge, where there is a high density of states. The states of interest have an exciton and magnon present on opposite sublattices and total crystal momentum zero. Labeling such states by the exciton's momentum, the two-particle energy $\mathcal{E}_2(k)$ of the noninteracting excitations has D_{4h} symmetry. The states are degenerate under sublattic interchange, since no magnetic field is assumed present. The interaction terms retained merely cause the exciton and magnon to scatter off one another, possibly switching sublattices in the process. The effective fourfold symmetry is preserved. The symmetry of the Hamiltonian enables one to separate the exciton-magnon wave function into noninterfering components. In the equation of motion for such a component the interaction takes the form of a separable potential. Thus the solution of the wave equation can be written down without further approximation.

The line-shape function will be presented here only for the π-polarized, electric dipole absorption (E_z). This will be applicable to the experimental observations mentioned above. The true crystal symmetry is only $D_{2h}{}^{12}$, lower than that used to classify the exciton-magnon states. Consequently, the absorption moment couples to two different "components," which differ by their partiy under sublattice interchange but transform alike under D_{2h}[12]. We take the absorption amplitudes for these two components proportional to κ and λ, and assume the pair of excitations to be created initially on n.n.n. sites. Then the line-shape function for the exciton-magnon sideband has the form

$$S(\xi) = -4\,\mathrm{Im}\left[\frac{\kappa^2 R_{zxy}(\xi)}{|1-(\delta-\alpha)R_{zxy}(\xi)|^2} + \frac{\lambda^2 R_z(\xi)}{|1-(\delta+\alpha)R_z(\xi)|^2}\right]. \quad (2)$$

Here ξ is the scaled energy (in units of $16J_2S$), and $R_z(\xi)$ is defined by

$$R_z(\xi) = \int \frac{d^3k}{(2\pi)^3} \times \frac{[u(k)\cos\tfrac{1}{2}k_x \cos\tfrac{1}{2}k_y \sin\tfrac{1}{2}k_z]^2}{\xi + i\epsilon - \mathcal{E}_2(k)}; \quad (3)$$

$R_{zxy}(\xi)$ is defined analogously with the cosines replaced by sines. The imaginary parts of these R functions are just the noninteracting approximations to the corresponding absorptions, as one sees by setting $\alpha = \delta = 0$ in Eq. (2). The function $u(k)$ appearing in Eq. (3) has its usual meaning for antiferromagnetic spin waves. The absorption by the two "components" is superposed incoherently. If those scattering terms which break the effective, fourfold, dynamical symmetry had been retained in the Hamiltonian, interference terms would be present by which the relative sign of κ and λ could be observed (in principle). Note that if ImR has a peak at some critical point, the effect of the factor in the denominator is to reduce the absorption at that point to a very small value. The peak appears shifted by an amount and in a direction determined by $\delta \pm \alpha$ and the sign of the real part of R. The bound-state condition for the κ component is $(\delta-\alpha)\times R_{zxy}(\xi) = 1$; for the λ component, it is $(\delta+\alpha)\times R_z(\xi) = 1$. The R's are purely real outside the energy range of the two-particle continuum. The ξ for which one of these conditions holds gives a bound-state energy; it is easy to see that there can be at most one such bound state per component. The integrated absorption by a bound state in the κ component, if one exists, is $4\pi\kappa^2\{(\delta-\alpha)^2 \times[(-d/d\xi)R_{zxy}(\xi)]\}^{-1}$.

For definiteness, we now suppose $-\delta \gtrsim \alpha > 0$. This is consistent with the restrictions imposed by Eq. (6) below when the exciton is pure $^4A_1$. For large enough negative exciton dispersion, the band minimum corresponds to the Z point where a high density of states causes the R functions to be singular. Taking the lower band edge as the zero of energy, for either component, $R \approx -A \times |\xi|^{-1/2} + B$ close below the band edge and $R \approx -iA\xi^{-1/2} + B$ close above it. For the observed exciton dispersion, $A \approx B \approx 0.2$ in each case. Each component has a bound state. The κ bound state has a relatively large binding energy, $-\xi_\kappa = \{(\alpha-\delta)A/[1+(\alpha-\delta)B]\}^2$. Its integrated absorption is $8\pi\kappa^2\xi_\kappa/\{(\alpha-\delta)[1+(\alpha-\delta)B]\}$. Note that this quantity is essentially proportional to $(\alpha-\delta)$ or $\xi_\kappa^{1/2}$. For a splitting comparable with that observed, the total integrated absorption by the bound state is not much less than that of the κ continuum itself. This continuum absorption band now starts out like $\xi^{+1/2}$ rather than $\xi^{-1/2}$. It has a rounded peak at $+\xi_\kappa$ and then falls off like $\xi^{-1/2}$. Of course, the observed band is the incoherent superposition of the κ and λ bands. From the observed ratio of bound-state to continuum absorption, one can determine $\kappa/\lambda \approx 0.4$. The binding energy of the λ bound state is given by an expression analogous to that above, but with $\alpha-\delta = \alpha + |\delta|$ replaced by $|\delta| - \alpha$. Its binding should be at least an order of magnitude smaller than that of the κ bound state, and the shift of the peak of the λ continuum should be correspondingly less. Consequently, the splitting between these λ-absorption peaks might well be unresolved, as appears to be the case.

To compare theory with experiment, values of α and δ are needed. For purposes of illustration, we may adopt the Anasatz used by Stout[5] to discuss the temperature dependence of the exciton energy. The exciton is identified as $^4A_1$, and the n.n.n. exchange is attributed exclusively to interaction of the e orbitals. One then finds that $-\delta = \alpha = \frac{3}{5}$. (The possible anistropy in J_2' is truly absent in this case.) For $\alpha + \delta = 0$, the λ component is unaffected by the interaction. With $\kappa/\lambda = 0.4$, the peak in the continuum is not shifted from the band edge, and the splitting is predicted to be just the binding energy, $\xi_\kappa = 0.043$. The observed splitting is 0.035 in our units. The agreement is amazingly good in view of the crudeness of this model of the exchange.

Interest in the magnon sidebands of excitonic transitions is largely motivated by a desire to understand more fully the nature of the exchange 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: $|{}^4\Gamma\tfrac{3}{2}\rangle = \sum_\rho G_\rho |\rho\rangle$, 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

$$\vec{s}_\rho^{(i)} \to [1 - N^{(i)}]\tfrac{1}{5}\vec{S}^{(i)} + N^{(i)}(1 - 2G_\rho^{\,2})\tfrac{1}{3}\vec{S}^{(i)} - (G_\rho/\sqrt{2})\vec{T}^{(i)}.$$

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 $-\delta > |\alpha| > 0$.

We wish to thank D. S. McClure and R. S. Meltzer for informing us of their experimental results prior to publication. One of us (S.F.) is also indebted to them and to their co-worker M. Lowe-Pariseau for helpful discussions concerning the implications of their findings.

*Work supported by U. S. Air Force Office of Research, Air Research and Development Command under Contract No. AF 49(638) 1545.

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

Richard S. Meltzer*
James Franck Institute, University of Chicago, Chicago, Illinois 60637

and

Ming Y. Chen, Donald S. McClure, and Marian Lowe-Pariseau
Department of Chemistry, Princeton University, Princeton, New Jersey 08540
(Received 9 August 1968)

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