TWO-MAGNON ABSORPTION IN ANTIFERROMAGNETIC MnF_2

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We have observed an electric-dipole active two-magnon absorption near 100 cm^{-1} in antiferromagnetic MnF_2. The strength, temperature dependence, and insensitivity to magnetic fields of this line are similar to those reported for absorptions recently found in FeF_2[1] and CoF_2.[2] Since the Mn^{2+} ion ground state is an S state, the two-magnon absorption mechanism proposed by Halley and Silvera[1] cannot account for a strong absorption in MnF_2. The observed strength is compatible, however, with the mechanism proposed by Tanabe, Moriya, and Sugano.[3] An analysis is presented of the selection rules for the absorption of radiation with $E \perp$ and $\parallel$ to the c axis. This permits the optical determination of two critical points of the magnon dispersion curve for MnF_2. In order to fit the observed line shapes, it is necessary to postulate an interaction that extends over several antiferromagnetic neighbors.

The attenuation coefficients for the two polarizations, $\alpha_\perp$ and $\alpha_\parallel$, measured with a resolution of 0.5 cm^{-1} at 4.2°K, are shown by the solid curve in Fig. 1. The experiments give

$$\int(\alpha_\perp/\nu)d\nu \approx 0.09\ \mathrm{cm}^{-1}, \quad \int(\alpha_\parallel/\nu)d\nu \approx 2.3\ \mathrm{cm}^{-1}, \quad (1)$$

for the integrated absorption intensities. The absorption for $E \parallel c$ decreases in intensity and shifts to lower frequencies as the temperature is raised, becoming unobservable above 55°K where the centroid of the absorption has shifted to about 80 cm^{-1}. Although the weaker absorption for $E \perp c$ cannot be seen above 30°K, it appears to behave in a similar way. No perceptible changes can be induced in either polarization with fields up to 50 kG. The corresponding absorption line discovered in FeF_2 by Halley and Silvera[1] is found to have an integrated intensity of ~6 cm^{-1} for $E \parallel c$. These authors observed a weaker absorption for $E \perp c$ but did not detect any dependence of line shape on polarization. They showed that the results in FeF_2 are consistent with a process in which the electric vector of an absorbed photon induces the simultaneous creation of a pair of oppositely polarized magnons with wave vectors $\vec{k}$ and $-\vec{k}$ (the photon wave vector is negligible). The absorption in MnF_2 is ascribed to the same process.

The frequencies and line shapes of the two-magnon absorption can be calculated by assuming an electric-dipole-induced spin-spin interaction between two antiferromagnetically coupled neighbors. A two-magnon excitation is produced by terms in the interaction proportional to products of transverse components of the spin operators of the two ions. Taking account of the crystal symmetry of MnF_2 in its magnetic phase,[4] and assuming that the in-

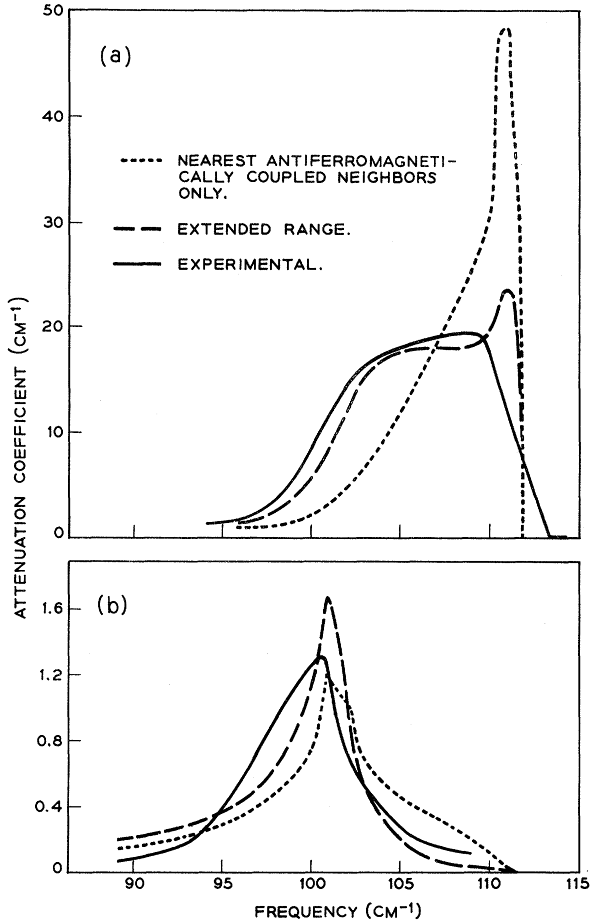

FIG. 1. Theoretical and experimental attenuation coefficients for the two-magnon absorption in MnF_2 at 4.2°K; (a) electric vector parallel to the c axis, (b) electric vector $\perp$ to the c axis.

teraction couples only nearest neighbor antiparallel ions, the electric-dipole–induced two-magnon transition process can be conveniently represented by the spin Hamiltonian

$$H=\sum_{\langle i,j\rangle}\{\pi_1(S_i^xS_j^x+S_i^yS_j^y)(E_x\sigma_y+E_y\sigma_x)+\pi_2(S_i^xS_j^y-S_i^yS_j^x)(E_x\sigma_y-E_y\sigma_x)+\pi_3(S_i^xS_j^x+S_i^yS_j^y)E_z\sigma_x\sigma_y\sigma_z\}. \quad (2)$$

In this expression, i runs over one magnetic sublattice and j runs over the nearest neighbors on the other sublattice; π_1, π_2, and π_3 are unknown constants; and $\sigma_\alpha=\operatorname{sign}(\vec{r}_j-\vec{r}_i)_\alpha$ ($\alpha=x, y, z$) has the value +1 or −1 depending on the sign of the α component of the vector joining ions i and j. The z axis is the crystal c axis, and x and y are coordinates in the directions $\vec{t}_1$ and $\vec{t}_2$ defined by Dimmock and Wheeler.[4] The spin Hamiltonian[2] is invariant under all the operations of the MnF_2 magnetic symmetry group including those which contain time reversal. Other possible terms in H allowed by the crystal symmetry do not give rise to two-magnon absorption.

The electric-dipole matrix elements for the creation of two oppositely directed magnons are

$$M_\perp(k)=-8S[i\pi_1+\pi_2(u_k^2+v_k^2)]\cos(k_xa/2)\times\sin(k_ya/2)\cos(k_zc/2) \quad (3)$$

for $E\parallel x$ (i.e., $E\perp c$), and

$$M_\parallel(k)=8iS\pi_3\sin(k_xa/2)\sin(k_ya/2)\sin(k_zc/2) \quad (4)$$

for $E\parallel z$ (i.e., $E\parallel c$). Here u_k and v_k are the coupling coefficients which diagonalize the magnon Hamiltonian.[5] The absorption coefficient may now be written

$$\alpha_i(\nu)=(\nu/n)\int d^3k\,|M_i(k)|^2\delta(h\nu c-2E_k), \quad (5)$$

where n is the refractive index, ν is the frequency in cm^{-1}, and E_k is the energy of a magnon of wave vector k (assuming $E_k=E_{-k}$). Expression (5) is the magnon density of states weighted by the square of the appropriate matrix element.

The high-frequency portion of the unweighted density of states, and the location of the critical points in the Brillouin zone of MnF_2, are shown in Fig. 2. This density of states is based on the magnon dispersion relation[6] for MnF_2 using exchange couplings $J_1=0.34$°K, $J_2=1.74$°K, $J_3=0.05$°K between first, second, and third neighbors and a uniaxial anisotropy field $H_A=1.05$°K. These values reproduce the magnon frequencies at Γ determined by antiferromagnetic resonance,[7] at Z determined by neutron scattering,[6] and at X and A determined by the present work (the magnon frequency at X determined by us agrees with that measured by neutron scattering). The values of J_2 and H_A quoted above differ slightly from those deduced by Trapp and Stout[8] on the basis of antiferromagnetic resonance and perpendicular susceptibility measurements.

The theoretical absorption curves obtained from (5) normalized to the experimental integrated intensity, are shown by the dotted lines in Fig. 1. For $E\perp c$ the small variation of $u_k^2+v_k^2$ in (3) away from its Brillouin-zone boundary value of unity has been neglected. Irrespective of any particular absorption mechanism, it is possible to show group-theoretically that for $E\parallel c$ the only sharp feature in the density of states reproduced in the absorption spectrum should be the high-frequency cutoff corresponding to two magnons at A. For $E\perp c$ the only sharp feature should occur at the critical point associated with two magnons at X. It is seen from Fig. 1 that the weighting factors (3) and (4) correctly satisfy these requirements, and the comparison with experiment provides in

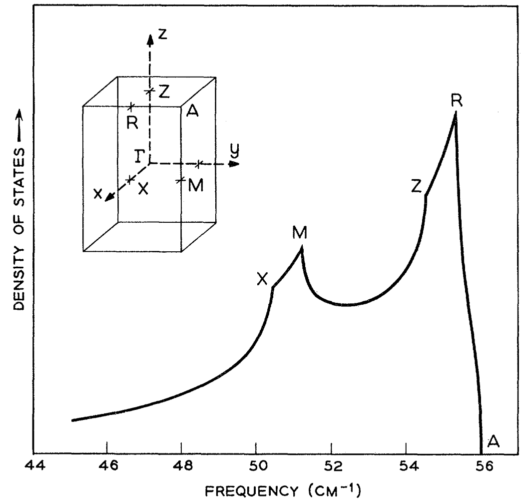

FIG. 2. Brillouin zone and relevant portion of magnon density of states in MnF_2 using exchange and anisotropy constants $J_1=0.34$°K, $J_2=1.74$°K, $J_3=0.05$°K, and $H_A=1.05$°K.

principle a means for determining the magnon frequencies at X and A. The predicted line shape, particularly for $E \parallel c$, is not, however, in good agreement with experiment. The X point can be unambiguously determined from the measurement $\alpha_\perp$ to be 50.4 cm^{-1}, but the sharp high-frequency cutoff in the experimental $\alpha_\parallel$ suggests an A point at 56.5 cm^{-1}, which is 0.5 cm^{-1} above the A point chosen for the best fit of the theoretical line shape.

For both polarizations the theoretical intensity is concentrated at higher frequencies than the experimental absorption. Due to the inclusion of only nearest-neighbor coupling, the Hamiltonian (2) gives greatest weight to the magnons whose wave vector k lies close to the Brillouin-zone boundary. Inclusion of coupling between more distant pairs of ions favors magnons of smaller k and hence of lower frequency. To estimate the range of coupling required to bring theory and experiment into better agreement, we have calculated the line shapes which result when the summation over pairs in (2) extends to more distant neighbors on opposite sublattices. We assume that π_1, π_2, and π_3 now fall off exponentially with the separation between atoms i and j; for example,

$$\pi_1(\vec{r}_i, \vec{r}_j) = \pi_1 \exp(-|\vec{r}_j - \vec{r}_i|/r_0). \qquad (6)$$

A good fit to the experimental results is obtained for a range of interaction $r_0 \approx 0.4a$, where a is the lattice dimension $\perp$ the c axis. The calculated spectra are shown as dashed lines in Fig. 1.

The assumed absorption mechanism involves the simultaneous excitation of pairs of magnetic ions by a single photon. The theory of electric-dipole-induced two-ion transitions was first discussed for the case of a solid by Dexter[9] in order to explain experimental observations by Varsanyi and Dieke.[10] The mechanisms so far proposed for the two-magnon absorption can be regarded as extensions of Dexter's theory.

Halley and Silvera have ascribed the two-ion coupling to the interaction between a spin-orbit-induced electronic quadrupole moment on atom j and the electronic dipole moment of atom i. The even-parity excited-state energies of the magnetic ion appear as energy denominators in the theoretical expressions for π_1, π_2, and π_3. The even-parity excited-state energies of Fe^{2+} are in the region 1000 to 2000 cm^{-1} above the ground state, while the corresponding excitation energy for Mn^{2+} is about 20 000 cm^{-1}. Since the energy denominator appears to the fourth power, this theory predicts the two-magnon absorption in MnF_2 to be about four orders of magnitude smaller than that in FeF_2. Since the absorption intensities are comparable, we conclude that the theory of Halley and Silvera does not account for the observations.[11]

However, in addition to the terms resulting from the multipole expansion of the Coulomb interaction between two ions treated by Halley, there are additional exchange terms resulting from overlap of the wave functions. Such two-ion interactions were also considered by Dexter.[9] Tanabe, Moriya, and Sugano[3] have ascribed the two-magnon absorption to this type of coupling. The energy denominators which arise in the theory involve the odd-parity excited states of the magnetic ion. Since these levels occur at comparable energies for Fe^{2+} and Mn^{2+}, the two-magnon absorption is predicted to have the same order of magnitude in both materials. Our results therefore favor the theory of Tanabe, Moriya, and Sugano, modified so as to include a longer range of interaction.

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[11] Tanabe, Moriya, and Sugano[3] have argued that the interaction used by Halley and Silvera vanishes due to a cancellation of terms on account of time reversal. This cancellation is not complete in the ordered state of MnF_2, which is not invariant under pure time reversal. However, the remaining partial cancellation produces a substantial reduction in the magnitude of the Halley and Silvera interaction.

RESISTANCE "MAXIMUM" IN DILUTE MAGNETIC ALLOYS

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It has been experimentally demonstrated that the temperature dependence of the resistivity in very dilute magnetic alloys often exhibits a minimum.[1] This behavior is attributed to the Kondo mechanism which adds a $\log T$ term to the resistivity due to the effect of the Pauli exclusion principle in the intermediate states of the higher order scattering amplitude for spin-dependent s-d scattering. As the concentration of the magnetic impurities is increased, there often appears a local maximum[1] in addition to the minimum. It is the purpose of this note to present a model which encompasses both anomalies.[2]

Our model is a union of the Yosida[3]-Kondo[4] calculations of the effects of s-d scattering on the resistivity with the Marshall[5]-Klein-Brout[6,7] (M-K-B) concepts of effective molecular fields as seen by magnetic ions in dilute random alloys. In the M-K-B theory, it has been shown that magnetic ions in dilute alloys are subjected to effective molecular fields, the values of which can be described by a symmetric probability distribution function $P(H)$. The physics of the maximum within our model is now clear, viz., as the temperature is decreased the molecular fields cause a redistribution among the Zeeman levels of the magnetic ions and thus a suppression of the spin disorder scattering. This suppression, coupled with the rise of the Kondo $\log T$ term, causes a local maximum to appear.

The calculation is relatively straightforward.[3] The total collision integral is given by the sum of the elastic and inelastic contributions,

$$\left(\frac{\partial f_k{}^{\sigma}}{\partial t}\right)_{\text{coll}} = \vec{c}\, s(s+1) A(\mathcal{E}_k) E \left[1 - \frac{1}{s(s+1)} \left\langle\!\!\left\langle s_z \tanh\left(\frac{\mu_B g H}{2KT}\right)\right\rangle\!\!\right\rangle\right]. \tag{1}$$

In arriving at Eq. (1), we have used the symmetric nature of the molecular field distribution function $P(H)$ and have thus discarded all terms odd in the magnetic fields. The physical effect described above is due to the reduction in scattering caused by the second term in the brackets. The terms in the above expression are defined in the following manner:

$$\left\langle\!\!\left\langle s_z \tanh\left(\frac{\mu_B g H}{2KT}\right)\right\rangle\!\!\right\rangle = \int_{-\infty}^{+\infty} dH \tanh\left(\frac{\mu_B g H}{2KT}\right)\left[\sum_{m=-s}^{+s} m \exp\left(\frac{-\mu_B g H m}{KT}\right) \Big/ \sum_{m=-s}^{+s} \exp\left(\frac{-\mu_B g H m}{KT}\right)\right] P(H)$$

$$= \tfrac{1}{2} - (s+\tfrac{1}{2}) \int_{-\infty}^{+\infty} dH\, P(H) \coth\left[(s+\tfrac{1}{2})\left(\frac{\mu_B g H}{KT}\right)\right] \tanh\left(\frac{\mu_B g H}{2KT}\right); \tag{2}$$

E is the electric field; and $A(\mathcal{E}_k)$ is given through the second Born approximation by

$$A(\mathcal{E}_k) = \frac{1}{2\pi\hbar^4} \frac{V}{N} (2m)^{3/2} k_x \frac{\partial f_k{}^0}{\partial \mathcal{E}_k} \mathcal{E}_k{}^{1/2} \Phi(\mathcal{E}_k) J^2 \left[1 - \frac{2|J|}{N} \sum_{k_1} \frac{(1-2f_{k_1}{}^0)}{\mathcal{E}_{k_1} - \mathcal{E}_k}\right]. \tag{3}$$