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One-magnon Raman scattering in a $S=\frac{5}{2}$ antiferromagnet

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We report the first observation of one-magnon Raman scattering in pure MnF_2. The results for the magnon frequency and the integrated intensity over the temperature range 4 to 50 K are found to be in good agreement with theory. We deduce that quadratic magneto-optic coupling is small.

Despite considerable efforts following the initial discovery of light scattering by magnons in ordered antiferromagnets[1] there have been no reported measurements of one-magnon Raman scattering in pure manganese compounds.[2] The first theory[3] of such scattering proposed a reason for a low scattering cross section in weakly anisotropic antiferromagnets: The scattering frequency and intensity both vary as the square root of the effective anisotropy field, H_A, which is relatively small in spin $S=\frac{5}{2}$ insulators.[2] However, Raman scattering has been observed from the manganese mode in the mixed antiferromagnets $Co_{1-x}Mn_xF_2$, $Fe_{1-x}Mn_xF_2$, and $Cd_{1-x}Mn_xTe$.[4-6] The one-magnon scattering associated largely with the Mn^{2+} ions in these mixed compounds is found to be quite strong at intermediate concentrations but becomes weak and eventually unobservable as x approaches unity.[4,5] From the $Co_{1-x}Mn_xF_2$ study it was concluded that the lack of an orbital contribution to the magnon may also diminish the scattering cross section.[4] In this Rapid Communication we report the first observation of one-magnon light scattering in a *pure* antiferromagnet with $S=\frac{5}{2}$, MnF_2. The magnetic excitations of rutile structured MnF_2 have previously been studied in detail using neutron scattering[7] and the two-magnon Raman spectrum has already been characterized.[1,3] As expected, the one-magnon Raman scattering was found to be extremely weak and could be studied as a function of temperature from 4 to 50 K only. The antiferromagnetic ordering temperature T_N is 68 K. The experimental results are shown here to be in good agreement with theory.

The experiments were performed on a single-crystal sample of MnF_2 grown for us at Oxford University. The sample faces were cut parallel to (100) and (001) crystal planes to form a cuboid of dimensions $5\times5\times5$ mm^3. The Raman spectrum was excited with 760 mW of argon laser light at 476.5 mm. Light scattered at 90° was analyzed with a double monochromator at a spectral resolution of 1.8 ± 0.1 cm^{-1} and recorded with an integration time of 60 s. The sample was mounted in the helium exchange-gas space of a low-temperature cryostat, where the temperature was controlled to within 0.1 K. Despite the high incident power, the local laser heating was found to be small, ~0.7 K, and the measured sample temperatures have been corrected accordingly.

The low-frequency Stokes Raman spectrum of MnF_2 recorded in $Z(XZ)Y$ polarization at various temperatures is shown in Fig. 1. A peak was found at 8.5 cm^{-1} at low temperatures that shifted to lower frequency when the temperature was raised. This peak was also observed in $Z(YZ)Y$ polarization (see Fig. 1) but was absent in $Z(YX)Y$ polarization. From its frequency, temperature dependence, and polarization characteristics this line can be assigned to light scattering from $\vec{k}\simeq0$ magnons. A search for one-magnon anti-Stokes Raman scattering was precluded by the slightly higher instrumental background for negative frequency shifts.

The spectra were computer curve resolved to eliminate the sloping baseline due to stray light. Fits to the $Z(YX)Y$ spectrum showed that this background was well represented by a Gaussian line shape. The magnon scattering was fitted

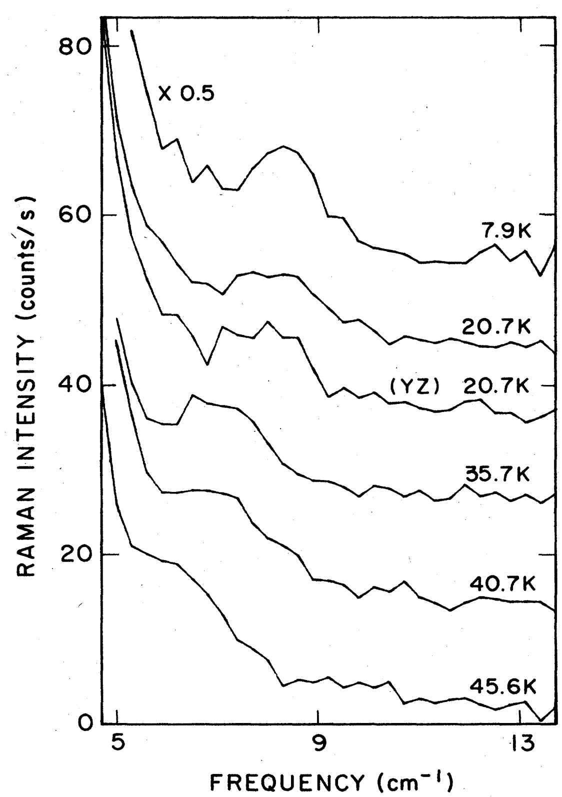

FIG. 1. Temperature dependence of the low-frequency Raman spectrum of MnF_2 recorded in $Z(XZ)Y$ polarization and $Z(YZ)Y$ polarization [marked (YZ) in the figure].

to a harmonic oscillator line shape and the results obtained for the frequency and integrated intensity (including the Bose factor) are plotted in Figs. 2 and 3, respectively. Owing to thermal damping of the magnons, the linewidth [full width at half maximum (FWHM)] increases smoothly from $\sim 2.5\ \mathrm{cm}^{-1}$ at 4 K to $\sim 6.5\ \mathrm{cm}^{-1}$ at 45 K, a considerable increase when allowance is made for the instrumental resolution of $1.8\ \mathrm{cm}^{-1}$. The $Z(YZ)Y$ and $Z(XZ)Y$ spectra give identical results for the magnon line shape and frequency at a given temperature, but the intensity appears to be marginally higher in $Z(YZ)Y$ polarization (see Fig. 3). The one-magnon scattering is very weak compared with the two-magnon scattering. For example, at 8 K the ratio of the one-magnon integrated intensity in $Z(XZ)Y$ polarization compared to the two-magnon scattering in $Z(YX)Y$ polarization is $(3.2 \pm 0.3) \times 10^{-3}$.

A theoretical analysis of the magnon frequency and integrated intensity data has been carried out using the Hamiltonian

$$H = \sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j - g\mu_B H_A(T) \left(\sum_i S_i^z - \sum_j S_j^z \right) , \qquad (1)$$

where $\vec{S}_i$ and $\vec{S}_j$ denote spin operators at sites i and j on opposite sublattices; J_{ij} is the exchange interaction, and for simplicity we neglect the weak intrasublattice exchange. The quantity $H_A(T)$ is an effective field representing the uniaxial anisotropy. The approximate values of the above parameters are known from inelastic neutron scattering,[7] and we assume $g\mu_B H_A(0) = 0.74\ \mathrm{cm}^{-1}$ with $J = 2.45\ \mathrm{cm}^{-1}$ for the dominant exchange which occurs between a Mn^{2+} ion and its eight next-nearest neighbors. For the temperature dependence of the anisotropy it is conventional to take $H_A(T) \propto \langle S^z \rangle^n$, where $\langle S^z \rangle$ is the sublattice spin average and n a positive index. If $H_A(T)$ were due to single-ion anisotropy the appropriate choice would be $n = 2$, but for MnF_2 it has been estimated that the anisotropy arises mainly from magnetic dipole-dipole interactions.[8,9] If the neighboring spins are regarded as being either completely uncorrelated (in the sense that $\langle S_i^z S_j^z \rangle = \langle S_i^z \rangle \langle S_j^z \rangle$ for $i \neq j$, as in mean field theory) or completely correlated, then this would lead to $n = 1$ and $n = 2$, respectively.[10] At low temperatures ($T \lesssim 20$ K) spin-wave calculations by Oguchi[10] for dipolar anisotropy indicate $n = 1.9$, which is broadly confirmed by antiferromagnetic resonance (AFMR) data[11] in this temperature region. At fairly high temperatures ($T \gtrsim 50$ K) a similar value has been deduced experimentally,[12] namely, $n = 1.88 \pm 0.16$. However, it is unclear whether this dependence persists through the intermediate region from about 20 to 50 K, or whether a mean-field-type behavior ($n = 1$) is approximated.[9,11] Because of this uncertainty we have considered two cases, $n = 1$ and $n = 2$, in analyzing our Raman data.

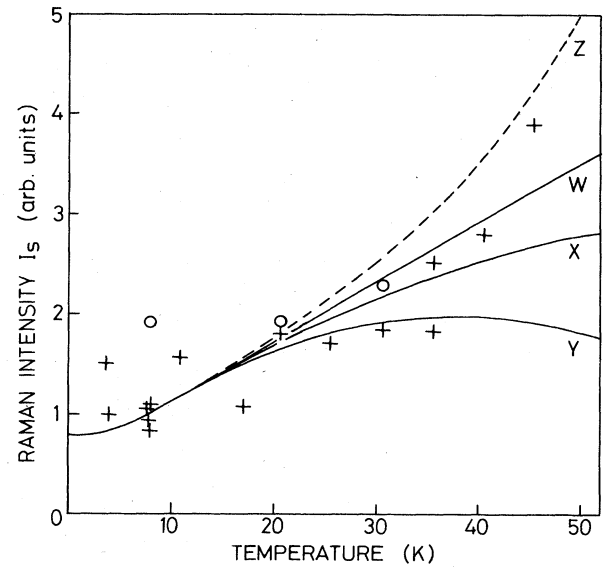

FIG. 3. Integrated Stokes intensity I_S ($\pm 25\%$) as a function of temperature. The crosses and circles indicate measurements in $Z(XZ)Y$ and $Z(YZ)Y$ polarizations, respectively. The theory curves W, X, Y, and Z are discussed in the text.

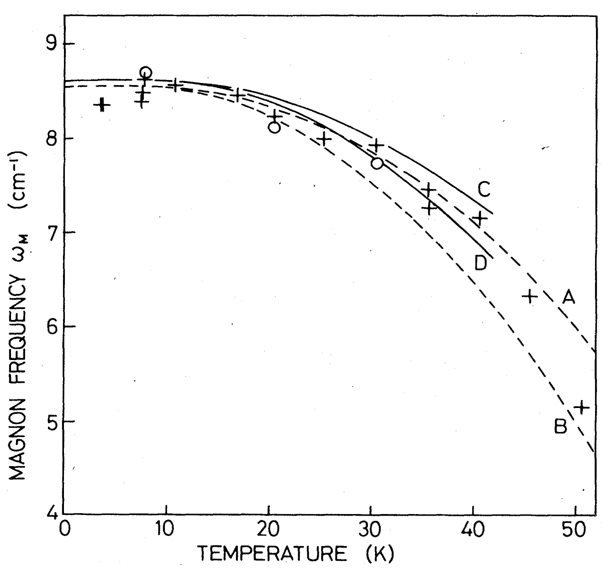

FIG. 2. Magnon frequency ω_M ($\pm 0.3\ \mathrm{cm}^{-1}$) as a function of temperature. The crosses and circles indicate measurements in $Z(XZ)Y$ and $Z(YZ)Y$ polarizations, respectively. The theory curves A, B, C, and D are discussed in the text.

Some of the theoretical results for the magnon frequency are shown in Fig. 2. Curves A and B (corresponding to $n = 1$ and $n = 2$, respectively) were obtained using a linear spin-wave theory with random-phase approximation (RPA) decoupling for the exchange terms. The $\vec{k} = 0$ magnon frequency ω_M can be written simply as[3]

$$\omega_M = [\omega_A (2\omega_E + \omega_A)]^{1/2} , \qquad (2)$$

where $\omega_A = g\mu_B H_A(T)/\hbar$, $\omega_E = 8\langle S^z \rangle J/\hbar$, and $\langle S^z \rangle$ has been calculated self-consistently using a Brillouin function. In separate calculations we have also taken account of magnon-magnon interactions using the high-density perturbation method of Cottam and Stinchcombe.[13] When this is modified for $S = \frac{5}{2}$ systems[14] and applied to MnF_2, we obtain the curves C and D (for $n = 1$ and $n = 2$, respectively) shown in Fig. 2. The latter calculations involve performing numerical integrations over the Brillouin zone, and approximations are made which limit the validity to $T \lesssim 42$ K. On the basis of a linear spin-wave theory it can be seen that the $n = 1$ curve (A) gives better agreement with the Raman data than the $n=2$ curve (B), but when magnon-magnon interactions are taken into account the reverse seems to apply.

To analyze the results for the Raman intensity we have employed a Green's function theory[15] which has successfully accounted for the temperature dependence and polarization dependence in another rutile-structure antiferromagnet FeF_2. This model allows for the inclusion of a magneto-optic coupling which is quadratic in the spin operators, as well as the usual linear coupling. Quadratic magneto-optic coupling is known to be important in many iron compounds,[2] including FeF_2, and it is of interest to determine whether it influences the Raman scattering in MnF_2. The general expression for the integrated Stokes intensity I_S in zero magnetic field can be written as

$$I_S = A\langle S^z\rangle (n_M+1)(F_{\text{in}}+F_{\text{out}})/\omega_M \quad , \tag{3}$$

where A is a temperature-independent factor,[15] and

$$\begin{aligned} F_{\text{in}} &= |e_A^- \omega_A^{1/2} K_+ - 2p\langle S^z\rangle e_S^- (2\omega_E+\omega_A)^{1/2} G_+|^2 \quad , \\ F_{\text{out}} &= |e_A^+ (2\omega_E+\omega_A)^{1/2} K_- - 2p\langle S^z\rangle e_S^+ \omega_A^{1/2} G_-|^2 \quad . \end{aligned} \tag{4}$$

Here, n_M is the Bose population factor evaluated at the magnon frequency ω_M given by Eq. (2), and $e_S^{\pm}$ and $e_A^{\pm}$ are symmetric and antisymmetric combinations of the polarization vectors, as defined in Ref. 15. The quantity p is a thermal factor; for $T \lesssim 0.5T_N$ it can be approximated by $\langle S^z\rangle (2S-1)/2S^2$, whilst its general form is quoted in Ref. 15. The coefficients K_+ and G_+ refer, respectively, to the linear and quadratic magneto-optic coupling terms for in-phase scattering, whilst K_- and G_- are the corresponding coefficients for out-of-phase scattering. This latter contribution is allowed by symmetry because the two sublattices in MnF_2 are not equivalent, due to the coordination of the nonmagnetic F^- ions. Nevertheless, it seems likely that, because of the relatively small deviation from tetragonal symmetry at a Mn^{2+} site, the in-phase scattering dominates.

The results of some of the numerical calculations obtained using Eqs. (3) and (4) are shown in Fig. 3. Curves W, X, and Y all refer to in-phase scattering only ($K_- = G_- = 0$), and with the ratio G_+/K_+ of the magneto-optic coefficients taken equal to 0, 0.01, and 0.1, respectively. It is seen that the closest agreement with the experimental data is provided by curve W, indicating that the influence of quadratic magneto-optic coupling is small. This contrasts with the behavior in FeF_2,[2,15] where recent estimates give $G_+/K_+ \approx 0.44$ at the same excitation wavelength.[16] Curve Z in Fig. 3 illustrates the effect of out-of-phase scattering only ($K_+ = G_+ = 0$) for the case of linear magneto-optic coupling ($G_-/K_- = 0$). In fact, the predicted intensity I_S is sensitive to even a relatively small amount of out-of-phase scattering. This is because the coefficient of K_- in Eq. (4) is much larger than the coefficient of K_+ (since $\omega_E >> \omega_A$), and the optimum admixture of in-phase and out-of-phase scattering for agreement between theory and experiment corresponds to $|K_-/K_+| \sim 0.01$. Hence, we conclude that the dominant magneto-optic coefficient in MnF_2 is K_+. The polarization dependence of the intensity can also be used to obtain information about the magneto-optic coefficients. At three different temperatures (8.0, 20.7, and 30.7 K) we have measured I_S in (YZ) polarization as well as in (XZ) polarization, and in each case the integrated intensity was found to be slightly larger in (YZ) polarization. Using Eqs. (3) and (4) we are able to estimate that $|G_+/K_+| \sim 10^{-3}$, which is consistent with results from the temperature dependence of I_S. The above estimate and the theory curves shown in Fig. 3 have all been obtained assuming that $H_A(T) \propto \langle S^z\rangle^2$; similar results are obtained on taking $H_A(T) \propto \langle S^z\rangle$.

In conclusion, we have observed for the first time one-magnon Raman scattering in pure MnF_2. The integrated intensity is very weak, both in comparison with two-magnon scattering in MnF_2 and in comparison with one-magnon scattering in other rutile-type antiferromagnets (FeF_2, NiF_2, etc.). This is partly a consequence of the small anisotropy in MnF_2, but it is also partly due to the smallness of the K_+ coefficient. For example, using Eqs. (3) and (4) and Raman data on FeF_2 (Ref. 16) and MnF_2 recorded under similar conditions, we estimate

$$K_+(MnF_2)/K_+(FeF_2) \sim 10^{-1} \quad .$$

The temperature dependences of magnon frequency and the integrated Stokes intensity were well reproduced by the theory. In the case of the intensity we were able to conclude that the out-of-phase scattering is small as is the quadratic magneto-optic coupling (corresponding to $|G_+/K_+| \lesssim 10^{-3}$), again contrasting with the situation in FeF_2. In a later publication we intend to present further details of the experimental and theoretical results, including an analysis of the damping.

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