Two-Magnon Raman Scattering and Infrared Absorption in MnF$_2$,*

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Recent work has shown that it is essential to include magnon–magnon interaction effects in order to calculate the two-magnon line shape for optical processes in antiferromagnets. These experiments are very sensitive to any structure in the density of states, and so it is necessary to include both $J_1$ and $J_2$ (obtained from inelastic neutron scattering measurements) even though $J_1$ is much smaller than $J_2$. We have calculated line shapes for Raman scattering and infrared absorption in MnF$_2$ and obtained much improved agreement with the experimental results. We show that the sharp structure in the density of states and magnon–magnon interactions are equally important in determining the line shape. Simple arguments based on the Ising model to get the shift in peak position that are valid for RbMnF$_3$, where there is a single sharp peak in the density of states, are no longer correct in MnF$_2$. We conclude that a small $J_3$ exchange and a possible extended range of interaction between light and the magnetic system can only have a small effect on the optical spectra.

It has been shown that the two-magnon optical experiments can only be understood satisfactorily if the interaction between the two magnons is included in the theory. The interaction of the light with the magnetic system is such that the incident photon creates spin deviations on neighboring sites where they interact strongly. Previous work did not include these interaction effects and so a satisfactory explanation of the optical line shapes in MnF$_2$ was not possible. This inability of noninteracting spin wave theory to explain the observed spectra was recognized, and in an attempt to improve the line shape a coupling of the light to pairs of magnetic ions that fell off exponentially with distance was postulated. This broadened the spectra and so improved the agreement if the range of the coupling was suitably chosen.

The magnon dispersion in MnF$_2$ ($S=\frac{3}{2}$) has been measured by inelastic neutron scattering and can be described with three exchange parameters $J_1$, $J_2$, and $J_3$. The original experiments gave $J_1$ and $J_2$ but only an upper limit for the absolute value of $J_3$; more complete recent work has yielded a value for $J_3$. Because the density of states peaks near the zone boundary, the two-magnon optical experiments probe magnons on or near the zone boundary. It is therefore important to know the structure of the density of states near the zone boundary in some detail.

If we attempt to describe the magnon dispersion with just the largest exchange parameter $J_3$, the density of states has a single peak. This has the effect that...
optical properties may be described by the cubic group and so, for example, the \( x y \) and \( y z \) Raman modes would have similar shapes. This is clearly not so (Fig. 1). If we also include the next largest exchange parameter \( J_5 \), the density of states develops two sharp peaks (Fig. 2).

The real and imaginary parts of the crystal Green functions have been calculated by Tongeaw8,9 for the parameters \( J_1 = 0.22 \text{ cm}^{-1} \), \( J_2 = 1.24 \text{ cm}^{-1} \) and \( H_A = 0.8 \text{ cm}^{-1} \) to give a spin wave band between 8.7 and 54.8 \text{ cm}^{-1} \). The inclusion of a uniaxial field \( H_A \) to give an anisotropy gap is of no importance for our purposes as it has no effect on the optical spectra. The inclusion of the very small \( J_5 \) exchange would split the two main peaks in Fig. 2 and introduce more critical points.6 However, the resolution in the optical experiments (\( \approx 5 \text{ cm}^{-1} \)) is not sufficiently good to see this extra structure (\( \approx 1 \text{ cm}^{-1} \)) and so we ignore \( J_5 \).

The optical spectra may be classified according to the nonmagnetic group \( D_m \) which describes the arrangement of Mn ions in the paramagnetic phase. [For a discussion of this see Elliott and Thorpe.7] Spin deviations on the eight nearest neighbors of a Mn\(^{2+}\) ion contain the representations of the \( \Gamma_4^+ \) and \( \Gamma_4^- \) modes are infrared active. The \( \Gamma_4^+ \) modes do not show any resonant behavior and we shall not consider it further. The case where the magnon–magnon interaction is omitted has been discussed in detail.8 The expression for the cross section is proportional to \( \text{Im}G_0(\omega) \), where

\[
G_0(\omega) = N^{-1} \sum_k \left[ \frac{\sin \left( \frac{1}{2} k_x a \right)}{\cos \left( \frac{1}{2} k_x a \right)} \right] \left[ \frac{\sin \left( \frac{1}{2} k_y a \right)}{\cos \left( \frac{1}{2} k_y a \right)} \right] \left( \omega^2 - 4\omega_c^2 \right),
\]

and

\[
\omega_c^2 = \left( 16SJ_2 + H_A - 8SJ_3 \sin^2 \frac{1}{2} k_m \right)^2 - \left( 16SJ_2 \cos^2 \frac{1}{2} k_m \cos \frac{1}{3} k_m \cos \frac{1}{2} k_m \right)^2.
\]

The various combinations of \( \sin \) and \( \cos \) in (1) are used to give the matrix elements for scattering from the various modes. We include the interaction between the magnons as described elsewhere and the cross section is modified to become

\[
\text{Im}[G_0(\omega) / (1 + \alpha G_0(\omega))],
\]

where \( \alpha = 4J_3^3(32S - 1) \). The interaction parameter \( \alpha \) also contains small terms in \( J_3 \) and \( J_3 \) which we neglect. The calculations are compared to experiments in Figs. 2 and 3. (There are no adjustable parameters except the peak height.) A molecular field calculation shows that the peak in the cross sections should be at \( 2J_3 = 2.5 \text{ cm}^{-1} \) below the peak in the density of states. The two modes associated with the upper peak (\( \Gamma_4^+ \) and \( \Gamma_4^- \)) are shifted by rather more than \( 2.5 \text{ cm}^{-1} \) whereas the two modes associated with the lower peak (\( \Gamma_4^+ \) and \( \Gamma_4^- \)) are shifted by less. Also the modes associated with the upper peak are much broader than the modes associated with the lower peak.

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13 The crystal Green functions calculated by Tongeaw are not exactly of the form required in Eq. (1), but contain small additional factors in the numerators which can be approximated by their value on the zone boundary to give the required Green's functions rather accurately.
15 See Refs. 3 and 4. We take the interaction between the radiation and the magnetic system to act only between nearest neighbors.