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MARCH 1975
Two-Magnon Resonant Raman Scattering in MnF$_2$

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ABSTRACT

We have studied two-magnon resonant Raman scattering in MnF$_2$ around the magnon sidebands. The resonant scattering involves a different physical mechanism than the non-resonant case and leads to a number of new results. A simple theoretical description explains the experimental observations successfully.
Resonant Raman scattering (RRS) has so far been limited to semiconductors. We report here the first investigation on RRS in a magnetically ordered crystal, e.g., MnF$_2$ in the antiferromagnetic phase. Because of space limitation, we shall discuss only RRS by two magnons in MnF$_2$ in some detail.

The magnon spectrum of the antiferromagnetic MnF$_2$ is well known. The optical properties of MnF$_2$ has also been well studied, especially those involving magnons. There is a set of sharp absorption lines around 18450 cm$^{-1}$ (see Fig. 1) arising from transitions within the $^6A_{1g}(^6s) \rightarrow ^4T_{1g}(^4G)$ manifold. Lines $e_1$ and $e_2$ are due to creation of $E_1$ and $E_2$ excitons respectively via direct magnetic-dipole transitions while lines $\sigma_1$, $\tau_1$, and $\sigma_2$ are the corresponding magnon sidebands. In the luminescence spectrum, direct and magnon-assisted recombinations of the $E_1$ excitons give rise to the $e_{1L}$ and $\sigma_{1L}$ ($\tau_{1L}$) luminescence lines respectively.

The Raman spectrum of MnF$_2$ has also been thoroughly studied. It consists of four phonon modes and one two-magnon line. No one-magnon line has yet been observed. We are interested in the changes of the Raman and luminescence spectrum when the excitation scans through the absorption lines in Fig. 1.

Theoretically, the peak position and the cross-section of the two-magnon line for excitation near $\sigma_1$, $\tau_1$, and $\sigma_2$ lines can be obtained following, for example, Loudon's derivation. The spin Hamiltonian is of the form (unless specified, we use the notations of Ref. 6)

$$H_s = \sum_{<i,j>} \sum_{\alpha,\beta} C_{ij}^{\alpha\beta} E_i^{\alpha} E_j^{\beta} S_i^{\alpha} S_j^{\beta}$$
where $c_{ij}^{\alpha \beta} = A_{ij}^{\alpha \beta} + B_{ij}^{\alpha \beta}$

$$A_{ij}^{\alpha \beta} = \sum_{\mu, \nu} \frac{\langle g_1 g_i \uparrow | e_{\beta \downarrow} | g_1 g_i \uparrow \rangle \langle g_1 g_i \uparrow | v_{\nu \downarrow} | v_{\mu \uparrow} e_{\beta \downarrow} | g_1 g_i \uparrow \rangle \langle g_1 g_i \uparrow | e_{\alpha \downarrow} | g_1 g_i \uparrow \rangle}{(E_\nu - \hbar \omega_s)(E_\mu - \hbar \omega_s)} + 11 \text{ similar terms}$$

$$B_{ij}^{\alpha \beta} = \sum_{\mu, \nu} \frac{\langle g_1 g_i \uparrow | e_{\beta \downarrow} | g_1 g_i \uparrow \rangle \langle g_1 g_i \uparrow | v_{\mu \uparrow} e_{\beta \downarrow} | g_1 g_i \uparrow \rangle \langle g_1 g_i \uparrow | e_{\alpha \downarrow} | g_1 g_i \uparrow \rangle}{(E_\nu - \hbar \omega_s)(E_\mu - \hbar \omega_s)} \frac{\hbar \omega_s}{\hbar \omega_k} \frac{1}{e^{\hbar \omega_k} + 1}$$

In the above equations, $<g_1|$ is the ground state of the $i$th Mn ion, $<\mu|$ and $<\nu|$ are the allowed excited states with energies $E_\mu$ and $E_\nu$ respectively, and $<e|$ is either the $E_1$ or the $E_2$ excitonic state with its energy denoted by $\hbar \omega_E$. The magnon frequency is $\omega_m$. The quantities $E_\chi^{\alpha}$ and $E_\chi^{\beta}$ represent the $\alpha$ component of the exciting field and the $\beta$ component of the scattered field respectively, and $V$ and $V_{ex}$ are respectively the direct and exchange terms of the Coulomb interaction. From Eq. (1) we find for the two-magnon Raman cross-section,

$$\frac{d\sigma^{\alpha \beta}}{d\omega_s} = \sum_k \frac{a^{\alpha \beta}}{|x_0^{\alpha \beta}(k)|^2} + \frac{b^{\alpha \beta}}{|x_0^{\alpha \beta}(k)|^2} \frac{2}{f^{\alpha \beta}(k)} \frac{\Gamma'}{\omega_s - \omega(k) + i\Gamma}$$

where $a^{\alpha \beta}$ and $b^{\alpha \beta}$ are constant coefficients if we assume the matrix elements in Eq. (1) are constant and $f^{\alpha \beta}(k)$ is a function of $k$. Since the $b^{\alpha \beta}$ term is obtained from higher-order perturbation than the $a^{\alpha \beta}$ term, the former should be negligible in comparison with the latter unless the excitation frequency is close to one of the magnon sidebands, i.e., $(\omega_k - \omega_m + \omega_E(k))$. Near such a resonance, if we use the approximation $|x + i\Gamma|^{-2} \approx 2\pi \delta(x)/\Gamma$, we can write
The total two-magnon Raman cross-section is then given by

\[ \frac{d\sigma_{\alpha\beta}/d\omega_s}{s} \approx \left( \frac{d\sigma_{\alpha\beta}/d\omega_s}{s} \right)_{NR} + \left( \frac{d\sigma_{\alpha\beta}/d\omega_s}{s} \right)_R \]  

with

\[ \left( \frac{d\sigma_{\alpha\beta}/d\omega_s}{s} \right)_{NR} = (\pi |a_{\alpha\beta}|^2 / \Gamma') \sum_{\vec{k}} f_{\alpha\beta}(\vec{k}) \delta[\omega - \omega_s - 2\omega_m(\vec{k})] \]  

\[ \left( \frac{d\sigma_{\alpha\beta}/d\omega_s}{s} \right)_R = (\pi^2 |b_{\alpha\beta}|^2 / \Gamma'') \sum_{\vec{k}} f_{\alpha\beta}(\vec{k}) \delta[\omega - \omega_E(\vec{k}) - \omega_m(\vec{k})] \delta[\omega - \omega_s - 2\omega_m(\vec{k})]. \]  

The total two-magnon Raman cross-section is then given by

\[ \sigma_{\alpha\beta} = (\sigma_{\alpha\beta})_{NR} + (\sigma_{\alpha\beta})_R \]  

where \( (\sigma_{\alpha\beta})_R \propto \left[ (d\sigma_{\alpha\beta}/d\omega_s = 2\omega - 2\omega_E)/d\omega_s \right]_{NR}. \)

Equation (3b) shows that at resonance, if \( (d\sigma_{\alpha\beta}/d\omega_s)_R > (d\sigma_{\alpha\beta}/d\omega_s)_NR \), the peak position of the two-magnon line is determined by

\[ \omega - \omega_s = 2\omega_m(\vec{k}) = 2\omega - 2\omega_E(\vec{k}). \]  

The above results are easy to understand physically since the resonant part can be considered as due to a magnon-assisted absorption immediately followed by a magnon-assisted emission.

A cw dye laser with a linewidth of 0.2 cm\(^{-1}\) was used as the excitation source and the sample was immersed in superfluid He at 1.6°K. The luminescence spectrum was essentially identical to those reported in the literature but with less impurity lines, none in the range between 18340 and 18440 cm\(^{-1}\), except the one (denoted by I in Fig. 2) overlapping with
Our results on resonance fluorescence (RF) and RRS by phonons in MnF$_2$ will be reported elsewhere. Here, we discuss only RRS by two magnons. We found that the two-magnon line showed a resonance enhancement at the magnon sidebands but not at the e$_1$ and e$_2$ exciton lines, just as we expected. Figure 2 shows a set of two-magnon Raman spectra at several different excitation frequencies around $\sigma_1$ and $\sigma_2$. It is seen that the two-magnon line (denoted by M) varies in frequency with $\omega_1$. Deep in resonance, the line is considerably sharper (limited by instrument resolution in Fig. 2). When $\omega_1$ falls in the region where $\sigma_1$ and $\sigma_2$ overlap, two two-magnon lines show up, due to simultaneous resonances in $\sigma_1$ and $\sigma_2$ with two different sets of magnon modes involved. We have plotted the Raman peak shift of the two-magnon line as a function of $\omega_1$ in Fig. 3(a), and the corresponding Raman cross-section $\sigma_{xy}$ (corrected for absorption) vs $\omega_1$ in Fig. 3(b). The same results for $\sigma_{xz}$ are given in Fig. 4.

The results of Figs. 3 and 4 agree well with our earlier description. When $\left(\frac{d\sigma_{AB}}{d\omega_s}\right)_R > \left(\frac{d\sigma_{AB}}{d\omega_s}\right)_NR$, the Raman shift should obey Eq. (5). We find that we can indeed fit that portion of the data by Eq. (5) assuming $\omega_E(k)$ is independent of $k$. This is shown by the straight lines in Figs. 3(a) and 4(a). The values of constant $\omega_E$ deduced from the fit, for RRS near $\sigma_1$, $\sigma_2$, and $\pi_1$ peaks respectively, are $\omega_E(\sigma_1) = 18420.7$ cm$^{-1}$, $\omega_E(\sigma_2) = 18429.5$ cm$^{-1}$, and $\omega_E(\pi_1) = 18405$ cm$^{-1}$. If $\sigma_1(\pi_1)$ and $\sigma_2$ are indeed magnon sidebands of e$_1$ and e$_2$ and if the assumption of dispersionless $\omega_E(k)$ is correct, then $\omega_E(\sigma_1)$ and $\omega_E(\pi_1)$ should be equal to the frequency of the e$_1$ absorption peak and $\omega_E(\sigma_2)$ to the frequency of the e$_2$ peak. The observed e$_1$ and e$_2$ lines are at $\omega_{e1} = 18419.5$ cm$^{-1}$ and $\omega_{e2} = 18436.5$ cm$^{-1}$.
The agreement between \( \omega_E(\sigma_1) \) and \( \omega_{e1} \) is within the experimental uncertainty, supporting the previous suggestion that the dispersion of the E\(_1\) exciton is less than 0.5 cm\(^{-1}\). There is a discrepancy of 7 cm\(^{-1}\) between \( \omega_E(\sigma_2) \) and \( \omega_{e2} \). This indicates that the E\(_2\) exciton has a negative dispersion of 7 cm\(^{-1}\) from the zone center to the zone edge, in agreement with the 6.2 cm\(^{-1}\) estimate of Sell et al.\(^3\), The fact that the data can still be fitted by a straight line suggests a negligible dispersion of E\(_2\) near the zone edge. There is a big discrepancy of 14.5 cm\(^{-1}\) between \( \omega_E(\pi_1) \) and \( \omega_{e1} \). Since we know E\(_1\) is nearly dispersionless, this makes us suspect that \( \pi_1 \) is not a magnon sideband of E\(_1\) but of a lower-energy excitonic state. However, no such state has been found in absorption. Similar difficulty exists in the interpretation of the \( \pi_1 \) absorption band.\(^3\) Sell et al.\(^3\) have found that the observed \( \pi_1 \) peak is shifted by about -9 cm\(^{-1}\) from the predicted position.

The rest of the data in Figs. 3(a) and 4(a) can be interpreted qualitatively as follows. On the low-energy side of a magnon sideband, when \((d\sigma_{\alpha\beta}/dw)_{NR}\) becomes more and more dominant over \((d\sigma_{\alpha\beta}/dw)_{R}\), the two-magnon line gradually changes into its off-resonance lineshape and the Raman peak shift moves towards the off-resonance value. On the high-energy side close to the peak of a magnon sideband, the resonance enhancement of those two-magnon modes near the zone edge still dominates (consider Eq. (2) with finite damping constants), leaving the peak position of the two-magnon line more or less unchanged.

We have also found that Eq. (4) describes the observed two-magnon resonance Raman enhancement near magnon sidebands quite well. In Figs. 3(b) and 4(b), the theoretical curves are obtained from Eq. (4) using
the experimental lineshape of $\frac{d\sigma_{AB}}{d\omega_s}$ and with $\left(\sigma_{AB}\right)_R$ normalized to its peak value. The discrepancy between theory and experiment is probably a result of the $\delta$-function approximation in the theoretical derivation.

In summary, we have observed two-magnon RRS in MnF$_2$ around the magnon sidebands. The mechanism for the two-magnon RRS is different from that for the non-resonant case. With a given excitation frequency $\omega_\chi$, it selects a particular set of two-magnon modes to be most strongly resonantly enhanced. Consequently, because of the presence of magnon dispersion, the two-magnon line shifts in frequency as $\omega_\chi$ varies, and two two-magnon lines show up when simultaneous resonance with two magnon sidebands occurs. The resonance enhancement agrees quite well with a simple theoretical description.

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REFERENCES


FIGURE CAPTIONS

Fig. 1. Absorption spectrum of MnF₂ at 1.6K between 18400 and 18500 cm⁻¹.
The solid and the dashed curves are for polarizations Ⅰ and Ⅱ to the c-axis respectively. The inset is a sketch of the relevant energy levels.

Fig. 2. Two-magnon Raman spectra (denoted by M) at several different excitation frequencies ω₂. Peaks I and σ₁L correspond to impurity and magnon-assisted luminescence lines respectively.

Fig. 3. (a) Two-magnon Raman shift and (b) Two-magnon Raman cross-section as a function of the excitation frequency ω₂. The exciting and the scattering radiation are polarized along y and x respectively (x,y,l,c).

Fig. 4 (a) Two-magnon Raman shift and (b) Two-magnon Raman cross-section as a function of the excitation frequency ω₂. The exciting and the scattering radiations are polarized along z and x respectively (x,l,c and x,l,c).
Fig. (1)
Slit Width

\[ \sigma_{1L} \omega_l = 18450.1 \text{ cm}^{-1} \]

\[ \omega_l = 18474.6 \text{ cm}^{-1} \]

\[ \omega_l = 18478.5 \text{ cm}^{-1} \]

\[ \omega_l = 18483.9 \text{ cm}^{-1} \]

\[ \omega_l = 18494.5 \text{ cm}^{-1} \]

Frequency (cm\(^{-1}\))

18400 18370 18340

Fig. (2)
Fig. (4)
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