Zeeman Effect of the Magnetic Excitations in a Diluted Magnetic Semiconductor: A Raman Scattering Study of $Cd_{1-x}Mn_xTe$

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(Received 28 December 1981)

The electron paramagnetic transition of a magnetic ion in light scattering is reported. Intense Raman lines are observed corresponding to the $\Delta m_S = \pm 1$ transitions within the Zeeman multiplet of Mn^{++}, as well as their combinations with the zone-center longitudinal-optical phonons which interact with band electrons and, in turn, through exchange interaction, with Mn^{++}. The phase transition to the magnetically ordered low-temperature phase is manifested in the evolution of the paramagnetic transition into a magnon line.

PACS numbers: 78.30.Gt, 75.30.Ds, 75.50.Ee

The presence of the magnetic ion (Mn^{++}) in a diluted magnetic semiconductor like $Cd_{1-x}Mn_xTe$ results in many spectacular properties such as extraordinarily large g factors of electrons and holes and a giant Faraday rotation; they are the consequences of the important exchange interaction between the spins of the band electrons and Mn^{++}.[1] In this Letter we report Raman lines associated with transitions within the Zeeman multiplet of the ground state of Mn^{++} which, studied as a function of composition (x), temperature, and applied magnetic field (H), reveal experimentally the evolution of the paramagnetic into the magnetically ordered phase.

Galazka *et al.*[2] discovered magnetically ordered low-temperature phases in $Cd_{1-x}Mn_xTe$; for $0.17 < x < 0.6$ it undergoes a paramagnetic to a spin-glass transition as the temperature is lowered, whereas for $x > 0.6$ the low-temperature phase is antiferromagnetic. Our previous investigations[3] on the Raman spectra of this alloy system showed an inelastic wing close to the laser line when observed in the paramagnetic phase. On the other hand, a well-defined magnon line was observed in the magnetically ordered phases. In this paper we report studies using the same experimental arrangement[3] involving a double (triple) monochromator with the addition of a variable-temperature optical magnet cryostat allowing measurements up to 60 kG, over a temperature range 1.5–300 K, and in a variety of scattering geometries. A Babinet-Soleil compensator in the incident beam was used to produce circularly polarized light.

Figure 1 shows the room-temperature Raman spectrum of $Cd_{0.6}Mn_{0.4}Te$ with an external magnetic field of 59.7 ± 0.2 kG applied along $z' \| [110]$. The incident light is along z', circularly polarized as $\hat{\sigma}_\pm = (1/\sqrt{2})(\hat{x}' \pm i\hat{y}')$; the scattered radiation is collected along $x' \| [001]$ and analyzed along z'. As can be seen, an extremely strong Stokes/anti-Stokes pair is observed with a shift of $\omega_{PM} = 5.62 \pm 0.02$ cm^{-1}. The Stokes (anti-Stokes) line is observed in the $\hat{\sigma}_+$ ($\hat{\sigma}_-$) polarization. Within experimental errors the frequency shift is linear in the magnetic field.

We interpret the new Raman line as the $\Delta m_S = \pm 1$ transitions within the $S = \frac{5}{2}$ multiplet of Mn^{++} whose degeneracy has been lifted by the external

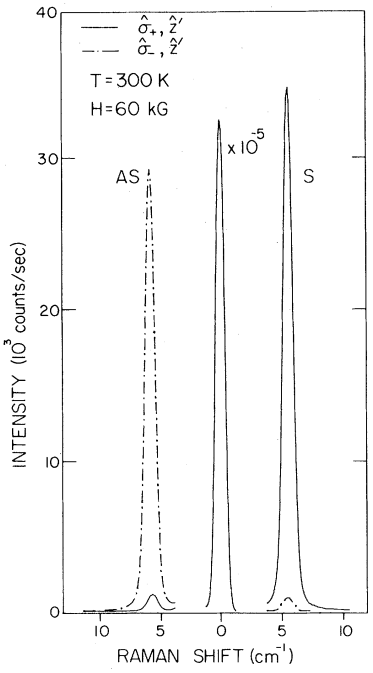

FIG. 1. The Stokes (S) and anti-Stokes (AS) Raman lines at ω_{PM} resulting from $\Delta m_S = \pm 1$ transitions within the Zeeman multiplet of Mn^{++} in $Cd_{0.6}Mn_{0.4}Te$. Wavelength of exciting line $\lambda_L = 6764$ Å. Applied field $H = 60$ kG; x', y', and z' are along [001], [1$\bar{1}$0], and [110], respectively. $\hat{\sigma}_\pm = (1/\sqrt{2})(\hat{x}' \pm i\hat{y}')$ denotes circularly polarized light propagating along $\hat{z}'$.

magnetic field. The crystal-field splitting of the ground state of Mn^{++} in CdTe (Ref. 4) is too small to be observed in our experiment. Thus, for a finite $\vec{H}$, the energy levels of the ground state of Mn^{++} are $E(m_S) = g\mu_B H m_S$ where g is the gyromagnetic ratio, μ_B is the Bohr magneton, and $m_S = -\frac{5}{2}, -\frac{3}{2}, \ldots, +\frac{5}{2}$. With the energy separation between adjacent levels of $\Delta E = g\mu_B H$, we find $g = 2.01 \pm 0.02$. We have observed ω_{PM} for a variety of compositions with x ranging from 0.175 to 0.75. We have also observed it in $Zn_{1-x}Mn_xTe$ and $Cd_{1-x}Mn_xSe$. The width of the ω_{PM} line in our measurements, somewhat in excess of the instrumental resolution, is found to increase with x. It appears reasonable to attribute this to the Mn^{++} exchange interaction expected to be significant even at room temperature for these compositions. The position and width of the ω_{PM} line was found to be the same for right-angle, back, and forward scattering, presumably because of the localized nature of the excitation involved. The above paramagnetic transition associated with the electrons localized in Mn^{++} is analogous to that very recently reported for Ce^{3+} in cerium magnesium nitrate.[5]

Following Fleury and Loudon[6] we consider, as a possible mechanism for the Raman line, electric dipole transitions with intermediate states having $L = 1$, $S = \frac{5}{2}$. Incident light of $\hat{\sigma}_\pm$ polarization couples initial and intermediate states which differ by $\Delta m_J = \pm 1$; the transition from the intermediate to the final state analyzed for $\hat{z}'$ polarization is allowed for $\Delta m_J = 0$. Hence the Stokes component corresponding to $\Delta m_S = +1$ appears in the $(\hat{\sigma}_+, \hat{z}')$ polarization whereas the anti-Stokes component ($\Delta m_S = -1$) is observed in the $(\hat{\sigma}_-, \hat{z}')$ polarization. It is also possible to visualize a mechanism involving interband electronic transitions together with an exchange interaction between a band electron and Mn^{++} ion.[1] In a magnetic field the Γ_8 valence band splits into four subbands with $m_J = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}$, and $\frac{3}{2}$ whereas the Γ_6 conduction band splits into $m_J = \frac{1}{2}$ and $-\frac{1}{2}$ subbands. The $\hat{\sigma}_+$ incident light induces an electric dipole transition from the $m_J = -\frac{1}{2}$ Γ_8 subband to the $m_J = +\frac{1}{2}$ Γ_6 subband; this is followed by the exchange interaction inducing a $\Delta m_S = +1$ transition in Mn^{++} and a simultaneous $\Delta m_J = -1$ transition in the conduction or valence band. Finally, the electron makes an interband transition of $\Delta m_J = 0$ with $\hat{z}'$ polarization. In a similar fashion one can construct a sequence of transitions yielding the anti-Stokes line with the requisite polarization characteristics. The two mechanisms can be experimentally explored by studying resonance effects associated with the internal transitions of Mn^{++} on the one hand and interband transitions on the other. Indeed, we have observed a resonance enhancement of the line at ω_{PM} by several orders of magnitude as the exciting laser energy approaches the band gap.

In Fig. 2 we show the Raman spectra of $Cd_{1-x}Mn_xTe$, with $x = 0.2$, in the region of the CdTe-like and the MnTe-like zone-center longitudinal (LO) and transverse (TO) optical phonons[3] with $H = 60$ kG. As can be seen, each of the two LO phonons is accompanied by two new lines with shifts of $\omega_{LO} \pm \omega_{PM}$. These lines appear only when the line at ω_{PM} is resonantly enhanced. The $\omega_{LO} \pm \omega_{PM}$ transitions involve the creation of LO phonons through the Fröhlich interaction and provide a natural explanation for the polarization features as well as for the absence of $\omega_{TO} \pm \omega_{PM}$ transitions. Under the resonant condition we observed a weak line with a shift of $2\omega_{PM}$; in forward scattering the Stokes component appears in the $(\hat{\sigma}_+, \hat{\sigma}_-)$ polarization and the anti-Stokes component in the $(\hat{\sigma}_-, \hat{\sigma}_+)$ polarization. These also follow from the mechanisms considered for ω_{PM}.

In the context of the magnetically ordered low-temperature phases,[2] we have studied the paramagnetic line as the temperature is lowered through the Néel temperature, T_N. In Fig. 3 we show the line at ω_{PM} for an $x = 0.7$ sample. As can be seen, the line broadens and shifts to higher frequencies as a consequence of the increased dominance of the Mn exchange interaction at low-

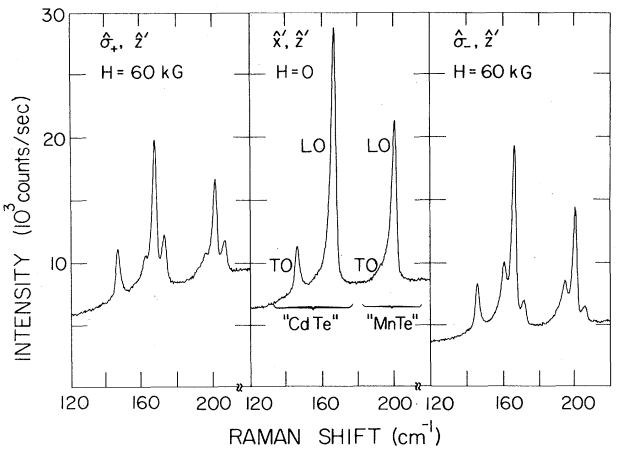

FIG. 2. Raman spectra of $Cd_{0.8}Mn_{0.2}Te$ at $T = 80$ K excited with $\lambda_L = 6764$ Å showing the $\Delta m_S = \pm 1$ transitions in combination with the "CdTe-like" and the "MnTe-like" LO phonons.

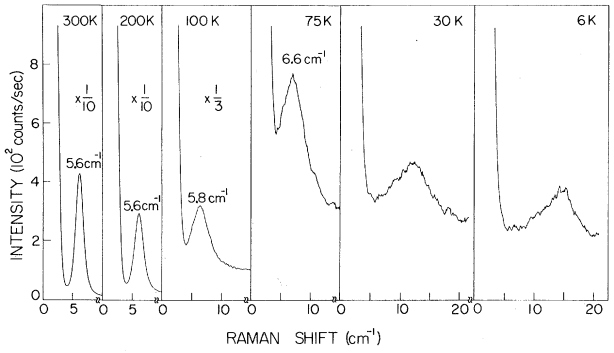

FIG. 3. The evolution of the Raman line at ω_{PM} of $Cd_{0.3}Mn_{0.7}Te$ into the magnon feature as the temperature is lowered from room temperature to below the Néel temperature. Spectra recorded with $H = 60$ kG, $\lambda_L = 6764$ Å in the $(\hat{\sigma}_+, \hat{z}')$ polarization, x', y', and z' being along [110], [1$\bar{1}$0], and [001], respectively.

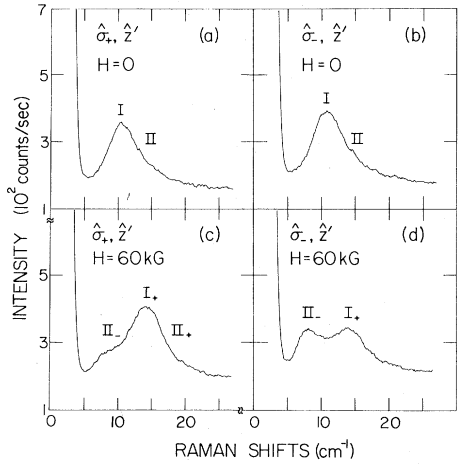

FIG. 4. The Zeeman effect of the magnon line in $Cd_{0.35}Mn_{0.65}Te$ at $T = 5$ K with $\lambda_L = 6764$ Å. The spectra shown are the averages of multiple scans.

er temperatures; already at $T = 75$ K, a shift of about 1 cm^{-1} is evident. At temperatures well below $T_N \sim 40$ K,[3] the line appears considerably broadened with a peak at 15 cm^{-1}. All these lines appear in the $(\hat{\sigma}_+, \hat{z}')$ polarization. These polarization results, unambiguous at room temperature, deteriorate gradually as the temperature is lowered as a result of the increasing birefringence and Faraday rotation under an applied magnetic field.

In contrast to the paramagnetic phase, in the magnetically ordered phase a distinct Raman line appears for $H = 0$ [see Figs. 4(a) and 4(b)]. This line has been attributed to a magnetic excitation[3] which, if the medium exhibits long-range magnetic order, is a long-wavelength magnon at ω_M. Under an applied magnetic field the magnon line is expected to split into two lines at $\omega_M \pm g\mu_B H$ appearing in the $(\hat{\sigma}_\pm, \hat{z}')$ polarization.[6] The results for $H = 60$ kG are shown in Figs. 4(c) and 4(d). Clearly two distinct components are seen, the one with the larger shift in $(\hat{\sigma}_+, \hat{z}')$ polarization and the other in $(\hat{\sigma}_-, \hat{z}')$ polarization. The lack of clean polarization effects has been discussed above. The spacing between the two peaks, however, is well below $2g\mu_B H$. Prompted by this observation and the results of elastic neutron scattering data,[7] we consider the following interpretation. The neutron scattering data suggest the presence of spin clusters of varying sizes. This is consistent with the broad and asymmetric nature of the line at zero field, the asymmetry being on the high-energy side. A given Mn^{++} ion in the lattice may have up to twelve Mn^{++} ions as nearest neighbors, arranged in a type-III antiferromagnetically ordered fcc lattice. The exchange field, H_E, that a Mn^{++} ion experiences depends upon the number of nearest neighbors. In a finite cluster one expects the Mn^{++} ions to have different fractions of their full complement of nearest neighbors; those ions with more neighbors and hence larger H_E contribute to the high-energy asymmetric tail. Indeed, for higher values of x, the zero-field line becomes more symmetric as this tail becomes more pronounced.

In the light of these comments, we proceed to interpret magnetic results [Figs. 4(c) and 4(d)] as follows. The features identified as I_+ and II_+ in Fig. 4(c) are shifted from the features I and II in Fig. 4(a) by approximately $g\mu_B H$; on the basis of the polarization in which these features predominate, we attribute them to the Mn^{++} ions which have their magnetic moments parallel to the applied field. In Fig. 4(d) the feature labeled II_- is due to Mn^{++} ions having their moments antiparallel to the field; the separation between the features II_+ in Fig. 4(c) and II_- in Fig. 4(d) is approximately $2g\mu_B H$. The features II_- in Fig. 4(c) and I_+ in Fig. 4(d) can be attributed to imperfect polarization results due to factors already discussed. The inability to resolve a well-defined peak corresponding to II_+, coupled with the absence of clear-cut polarization results, makes our interpretation somewhat speculative at this stage. Measurements with the applied field along different crystallographic directions yield similar results, implying that the anisotropy field is small compared to the applied field.

Finally we constrast the localized excitations underlying the phenomena discussed in this Letter with the spin-flip Raman scattering associated with free and bound electrons (holes).[8] In $Cd_{1-x}Mn_xSe$ and $Cd_{1-x}Mn_xS$ such transitions are characterized by large g factors arising from the band-electron–Mn^{++} exchange interaction.[9] In $Cd_{1-x}Mn_xTe$ we have observed a spin-flip Raman line with effective g factors in excess of 80.

The work reported in this Letter has been supported in part by the National Science Foundation Grant No. DMR81-06144 and the National Science Foundation–Materials Research Laboratory Program No. DMR80-20249. We wish to thank R. L. Aggarwal and J. K. Furdyna for stimulating discussions and help. A. P. is a David Ross Fellow and D. L. P. is a Kodak Fellow.

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Electron-Electron Umklapp Scattering in Organic Superconductors

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(Received 23 December 1981)

A theory of the tetramethyltetraselenafulvalene (TMTSF) salts and their sulfur analogs is developed. It is shown that the phase diagram is controlled by electron-electron umklapp scattering. The theory accounts for differences between the sulfur and selenium series, and the absence of Peierls transitions. Predictions of the pressure dependence of the spin-density-wave critical temperature and correlations of the dimerization of the organic stacks with critical pressures and temperatures are verified experimentally.

PACS numbers: 61.65.+d, 72.15.Nj, 74.10.+v, 75.25.+z

Much of the recent interest in the study of organic metals has been focused upon the tetramethyltetraselenafulvalene salts $(TMTSF)_2X$ where X is AsF_6, PF_6, TaF_6, ClO_4, BF_4, etc. These materials are structurally anisotropic and, by the standards of organic metals, are very good conductors. At low temperatures they undergo transitions to states which are insulating at low pressure but superconducting at higher pressure.[1] Attempts to observe a Peierls distortion have so far been unsuccessful[2] and, quite early on, there were speculations that the metal-insulator transition might be brought about by the formation of a spin-density-wave (SDW) state.[3] Recent experiments[1] strongly support this idea.

It is interesting to contrast these properties with those of the closely related tetramethyltetrathiafulvalene salts, $(TMTTF)_2X$, in which seleni-