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[13]This may be due to an experimental aspect of the apparatus of Ref. 1, viz., their energy resolution ΔE ~ $0.007E_b$; therefore, as the Born approximation is approached their energy resolution approaches or exceeds the spin-orbit splitting of the $3d$ core levels being discussed.

[14]ELS (Ref. 1) sees large differences between Ge(111) 8×8 and Ge(100) 2×2.

Comment on "Two-Magnon Resonant Raman Scattering in MnF$_2$"

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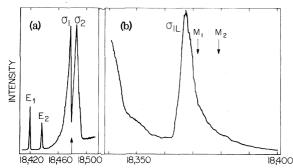(Received 4 August 1975; revised manuscript received 22 December 1975)

We have not been able to reproduce the recently reported resonance enhancement of Raman scattering from magnons in MnF$_2$ by Amer, Chiang, and Shen. Fifteen crystals ranging from extremely pure samples to ones with high concentrations of impurities, in addition to one supplied by Amer, Chiang, and Shen, were investigated. By observing the off-resonance scattering, we conclude that if an enhancement of greater than a factor of 2 were present, it would have been seen in our resonance spectra.

Recently Amer, Chiang, and Shen (ACS)[1] reported very interesting two-magnon resonance-Raman-scattering spectra from MnF$_2$. They excited MnF$_2$ with a dye laser in the region of the magnon sidebands of the E_1 and E_2 excitons and observed the three two-magnon Raman modes, corresponding to the σ_1, π_1, and σ_2 sidebands, to be resonantly enhanced. We found this experiment particularly intriguing because it may lead both to better understanding of the basic resonance-Raman processes in crystals and to better understanding of the very complex exciton-magnon dynamics in MnF$_2$. On the other hand, it is quite surprising that this very intense Raman scattering was not observed by Dietz et al.[2] when they pressure tuned the π_1 sideband through the 5419-Å output of a xenon laser, nor was it reported by Macfarlane and Luntz[3] in their lifetime experiments in which a dye laser was tuned through the σ_1 sideband.

We undertook to study resonant-Raman scattering from MnF$_2$ in the region of the magnon sidebands by illuminating a MnF$_2$ crystal of extremely high purity with the output of a cw dye laser (Rhodamine 110). The laser output power was about 100 mW throughout the region of interest around the magnon sidebands. Several experiments were performed. In some, the beam was focused into crystals which were immersed in superfluid helium at $< 2°$K. In others, crystals were placed on the cold finger of an Air Products Heli-Tran cryostat. In this case we estimate the crystal temperature to have been about 10°K. The scattered light was gathered at 90° and analyzed with a Spex 1401 double monochromator.

In all of our experiments the utmost care was used to assure that no experimental artifacts were present in our data. Specifically we took the following measures: (1) Careful alignment and aperaturing was done to minimize the amount of dye-laser fluorescence reaching the spectrometer. (2) To be sure that no exciton migration occurred, the diameter of the intrinsic luminescence emanating from the waist of the focused laser beam was measured. It was found to be less than 20 μm, roughly what we would expect for the width of the dye-laser waist itself. This guaranteed that misalignment effects in which we could have observed intrinsic luminescence but not Raman scattering would be impossible in our experiments. (3) Excitation spectra were run after any change in optical alignment to determine if any thermal-heating effects were occurring at resonance. When such effects were

EXCITATION FREQUENCY (cm⁻¹)   SCATTERED FREQUENCY (cm⁻¹)

FIG. 1. (a) Excitation spectrum of MnF_2 showing the σ_1 and σ_2 sidebands. The arrow indicates the laser frequency used to obtain the scattering spectrum in (b). (b) Scattering spectrum of MnF_2 excited at ~18 480 cm⁻¹. The strong feature at 18 367 cm⁻¹ is the intrinsic σ_{1L} luminescence. The M_1 and M_2 arrows designate the expected frequencies of the two-magnon resonance Raman scattering associated with the σ_1 and σ_2 sidebands, respectively.

seen the laser power was accordingly reduced.

Many crystal orientations were tried in our experiments although emphasis was placed on looking at tensor components expected to exhibit the strongest nonresonant, two-magnon, Raman scattering[4] (σ_{xz} and σ_{xy}). In addition, emphasis was placed on orienting the crystal so as to observe the scattering along the c axis. In this axial orientation[2] we were able to eliminate nearly completely the Zn^{++} and Mg^{++} impurity exciton lines[5] at 18 383 and 18 372 cm⁻¹, respectively, from our spectra.

In Fig. 1(a) we show the fluorescence excitation

spectrum of one of our most pure crystals (No. 1 in the Table I). As expected, in the orientation shown here (incident polarization perpendicular to the c axis) we were able to see the E_1 and E_2 excitons and the σ_1 and σ_2 sidebands.[2] By rotating the incident polarization we were able to observe the π_1 sideband. In Fig. 1(b) we present the $X(YX)Z$ Raman scattering spectrum at 2°K with the dye-laser frequency set in the valley between the σ_1 and σ_2 sidebands (~18 480 cm⁻¹). This position is designated by the arrow in the excitation spectrum. Note that the Zn^{++} and Mg^{++} impurity lines are absent from our luminescence spectrum and the only feature is σ_{1L} at 18 367 cm⁻¹. The long tail from 18 370 to 18 400 cm⁻¹ does not result from impurities but is the expected intrinsic σ_{1L}-luminescence shape.[2] For this incident frequency from the data presented in Fig. 3 of Ref. 1, two two-magnon Raman bands are located at the M_1 and M_2 positions designated by the arrows. It should be noted that at approximately this same excitation frequency in the report of ACS[1] one of the two-magnon resonance Raman lines had a peak intensity of ~50% of the peak intensity of the σ_{1L} intrinsic luminescence. We investigated many excitation frequencies covering the entire range which they[1] studied. In no case were we able to observe the two-magnon Raman scattering in the resonance region. Furthermore, because of our crystal orientation and high purity, in our spectra we were able to completely eliminate the Mg^{++} impurity luminescence at 18 372 cm⁻¹ which was the strongest feature in the spectra of ACS[1] and partially masked the two-

TABLE I. Source, growth method, and total impurity content of crystals studied from emission spectrographic analysis.

Crystal	Source	Growth method	Total impurities (ppm)
1	BTL	Horizontal zone	<300
2	Stanford	Unknown	<300
3	BTL	Horizontal zone	<300
4	BTL	Unknown	<300
5	BTL	Bridgeman	<300
6	BTL	Horizontal zone	<400
7	BTL	Horizontal zone	<400
8	BTL	Horizontal zone	<400
9	BTL	Bridgeman	<400
10	BTL	Horizontal zone	10^2–10^3 Si, Ag; <300 other metals
11	BTL	Unknown	10^3–10^4 Mg, Fe; <300 other metals
12	BTL	Unknown	10^2–10^3 Ni; <400 other metals
13	BTL	Horizontal zone	10^2–10^3 Ni; 10^3–10^4 Co; <400 other metals
14	BTL	Horizontal zone	10^2–10^3 Ca; <200 other metals

magnon Raman lines. We would therefore expect to have greater sensitivity than theirs for detecting these Raman lines.

To determine whether or not this first crystal was unique in its failure to exhibit the reported resonance spectra, we investigated several other crystals. All of our crystals with their method of growth and impurity content are listed in Table I. The impurity contents listed in Table I are upper limits of the total cation impurities based on emission spectrographic analysis and confirmed by secondary ion mass spectrometry and spark-source mass spectroscopy. For the purest crystals we believe a realistic estimate of the total cation impurity level to be in the range of 100 ppm. In the excitation spectrum of some of the crystals with high impurity concentrations we observed either a splitting or a substantial broadening of the intrinsic exciton and magnon sideband lines. However in none of the crystals were we able to see the two-magnon resonance-Raman scattering. Recently we have exchanged crystals with ACS. We found that their crystal exhibited several strong impurity lines. As in our crystals we were unable to observe any resonance enhancement of the two-magnon Raman scattering.

To determine the expected intensity of the two-magnon Raman scattering in the resonance region we investigated an additional crystal at $\sim 10°K$ cut from the same boule as crystal No. 1. In this series of experiments we repeated the off-resonance Raman measurements of Fleury, Porto, and Loudon[4] with 4880-Å excitation and then using the discrete lines of argon and krypton lasers we followed the Raman scattering to the 5308-Å krypton laser excitation which overlapped the wavelength range of the dye laser. The Raman scattering was then followed as the dye laser was tuned into resonance. In Fig. 2 we show two of these spectra when the excitation is near resonance with σ_2. M is the two-magnon scattering. For 18 524 cm^{-1} excitation the two-magnon scattering lies to the high-energy side of the $E1$ exciton, while at 18 506 cm^{-1} it has moved into the wing of the magnon sideband. As the excitation frequency was moved further into resonance with σ_2 the two-magnon Raman scattering became lost in luminescence from the sharply sloping magnon sideband.

ACS[1] reported a factor of 7 enhancement of the two-magnon Raman scattering at resonance with the σ_2 sideband. In addition they reported that in the resonance region the two-magnon line-
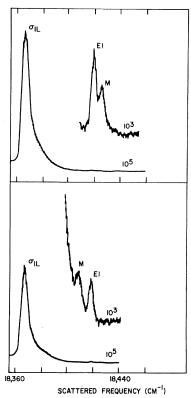

FIG. 2. Re-emission spectrum from MnF$_2$ slightly away from resonance with the σ_2 sideband. The 10^3 and 10^5 refer to counts per second full scale. $E1$, σ_{1L}, and M refer to emission from the $E1$ exciton, its magnon sideband, and the two-magnon Raman scattering, respectively. The top spectrum was obtained with 18 524-cm^{-1} excitation and the bottom with 18 506-cm^{-1} excitation.

width was instrumentally limited. To determine the limits of our sensitivity for detecting the two-magnon resonance Raman scattering we measured the re-emission with excitation of about 18 530 cm^{-1} so that both the $E1$ emission with an instrumentally limited width and the off-resonance Raman emission were resolved and observed in the same spectrum. These data were stored on one quadrant of a multichannel analyzer. The integrated intensity of the exciton was adjusted to equal that of the Raman scattering. The excitation frequency was then tuned to the peak of σ_2 and a spectrum was obtained [it appeared qualitatively similar to that shown in Fig. 1(a)] and stored in a different quadrant of the analyzer. The positions of the two spectra were adjusted such that the $E1$ exciton line in the first spectrum coincided with the expected position of the two-magnon resonance Raman scattering in the sec-

ond spectrum. By adding the two spectra and varying their relative intensities we then were able to determine the level of enhancement observable on the σ_{1L}-luminescence background in our experiments. From these measurements a factor of 7 enhancement, as reported by ACS,[1] would be very readily observable in our data. Indeed if the enhancement were as small as a factor of 2 we would have been able to observe it.

The contrast between our results and those of ACS[1] is striking. They report an enhancement of an order of magnitude and a peak intensity of the resonance Raman scattering comparable to that of σ_{1L}. Any possible enhancement in our crystals is less than a factor of 2 and the total Raman two-magnon intensity is down from σ_{1L} by more than two orders of magnitude. We have examined several crystals ranging from some which we believe to be among the purest available to others which have high concentrations of impurities, hoping to determine if a certain impurity level was responsible for the scattering data reported by ACS,[1] but in no cases were we able to observe any enhancement.

Aside from our inability to reproduce the resonantly enhanced Raman spectra of ACS,[1] we believe there are other strong grounds for rejecting the validity of their claims. Most importantly, they neglect the strong exciton-magnon interaction which was shown by Dietz et al.[2] to be *solely* responsible for the difference in shapes between σ_1 and σ_2. This was demonstrated by showing that the magnon sidebands of $E1$ and $E2$ have different shapes *only* in an absorption process when the exciton and magnon are created simultaneously. In fluorescence, the exciton is annihilated with the subsequent creation of a mag-

non, with the result that there is no strong interaction, and consequently both sidebands have the same shape, indicating that $E1$ and $E2$ have identical dispersions. A calculation of the emission sideband shape[6] using neutron-scattering parameters[7] for the magnon dispersion demonstrated that *both* $E1$ and $E2$ had less than 0.5 cm^{-1} dispersion, contrary to the dispersion of 7 cm^{-1} assumed for $E2$ in the analysis by ACS.[1] The effect of a dispersionless $E2$ exciton would be to shift the position of the σ_2 resonance well outside the range of their experimental uncertainty. Appropriate treatment of the exciton-magnon and magnon-magnon interaction would significantly broaden (5–10 cm^{-1}) the resonance Raman scattering.

In view of the serious irreproducibility of the results of ACS coupled with the theoretical objections raised above, we believe the differences between our results and theirs must lie in some experimental artifact in their data.

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