$^3A_2 \rightarrow {}^1E_a$. The respective shifts are 265 and 120 cm^{-1}, compared with the measured 170 and 50 cm^{-1}.[5] However, such calculations have been shown to be extremely unreliable, as in the case of $KNiF_3$, where the molecular-field shift ~330 cm^{-1}, is much larger than the experimentally determined 170 cm^{-1}.[22]

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RAMAN SCATTERING FROM LOCALIZED MAGNETIC EXCITATIONS IN Ni^{2+}- AND Fe^{2+}-DOPED MnF_2†

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We have studied Raman scattering at low temperatures from MnF_2 doped with Ni^{2+} and Fe^{2+}. Three temperature- and polarization-dependent lines have been observed for each impurity. For each dopant we have identified one line as a two-magon excitation of the impurity and some linear combination of the host spins. When corrections are made for magnon-magnon interactions, the predicted energy is in excellent agreement with the experimental results.

There has been considerable theoretical interest in the problem of impurity spin-wave modes in antiferromagnetic crystals.[1-4] Little experimental information on these modes has been available, until the recent measurements by neutron diffraction,[5] fluorescence,[6] infrared absorption,[7] and ESR[8] of localized magnons due to Co^{2+}, Ni^{2+}, and Fe^{2+} in MnF_2. We report here previously unobserved Raman scattering from more complex impurity modes in both Ni- and Fe-doped MnF_2.

The experiment employed the conventional

technique of focusing polarized light from an argon ion laser through oriented single crystals of MnF_2 containing 0.13% and 0.98% Ni^{2+}, and 0.2% and 0.65% Fe^{2+}. The samples were mounted in a variable-temperature Dewar, and cooled by helium vapor. Light scattered by 90° was analyzed with a Spex double monochromator and recorded with photon-counting techniques. The incident power was varied over a 10-to-1 range to guard against sample heating by the laser beam; no changes were observed in the Raman energies. The experimental geometry was chosen to allow the study of the different components of the Raman scattering tensor, α_{ij}. Care was taken to avoid the depolarization of the scattered radiation by the birefringence of the crystal.

In addition to the previously reported two-magnon peaks in pure MnF_2,[9] we find three extra lines for each of the impurities when $T < 0.8T_N$. Above this temperature the lines were too broad to be easily measured. In each case we have identified one of these lines as a two-magnon excitation of the impurity and the nearest antiferromagnetically coupled host spins. These signals have integrated intensities roughly proportional to impurity concentration, and are about seven to ten times smaller than the host (Mn-Mn) two-magnon line. In the Ni^{2+}-doped samples the impurity-host line appears at 162.5 and 165 cm^{-1} for α_{xy} and α_{xz}, respectively, while for Fe^{2+} the xy component is at 140 cm^{-1}, and the xz at 143 cm^{-1}. In addition, both systems exhibit a weaker line at 185 cm^{-1} with α_{xx} polarization. The Ni^{2+} doped crystals also give a strong α_{xz} polarized line at 26.5 cm^{-1}, while the Fe^{2+} samples give a line at 164 cm^{-1} with α_{xx} and α_{xz} polarizations. The uncertainty in the position of the lines is about ± 1 cm^{-1}. Representative spectra are shown in Fig. 1.

For a body-centered rutile-type lattice, there are nine impurity modes whose symmetries are approximately s-, p-, d-, and f-like.[2,3] Only the two s-like modes involve the precession of the impurity spin itself, while the others consist of magnons excited on the host ions. When the host-impurity exchange J' and the impurity spin S' are sufficiently different from the exchange and spin of the host, Green's function calculations show that one of the s type modes (s_0) has a frequency which appears well outside the host spin manifold.[2,3] Most of the spin-wave amplitude of this s_0 mode is associated with the impurity spin, and in some limiting cases the mode is well approximated by a molecular-field model in which the impurity spin precesses in the effective magnetic field $2J'Sn$ of the n antiferromagnetically coupled neighbors.[6,7] For Fe^{2+},[7] Ni^{2+},[6] and Co^{2+} [5] in MnF_2 the s_0 mode has been found to be well outside the spin-wave band. In the molecular-field approximation, excitation of the s_0 impurity mode corresponds to a $\Delta m_S = \pm 1$ magnetic dipole transition. Experimentally, no Raman lines are observed at the local-mode energies, but this is not unexpected since previous experimental and theoretical work on Raman scattering from magnons leads one to expect a rather small one-magnon cross section.[10,11] We do observe lines which can be interpreted as two-magnon processes corresponding to a simultaneous excitation of the impurity s_0 mode and neighboring Mn spins. In all probability, the photon-magnon coupling mechanism is the same excited-state exchange mechanism which holds in the pure crystal.[11,12]

Considering the predominance of nearest neighbor interactions and the fact that it does not seem necessary to include extended range calculations to explain the pure crystal two-magnon line,[13] a simple model for the position of the observed

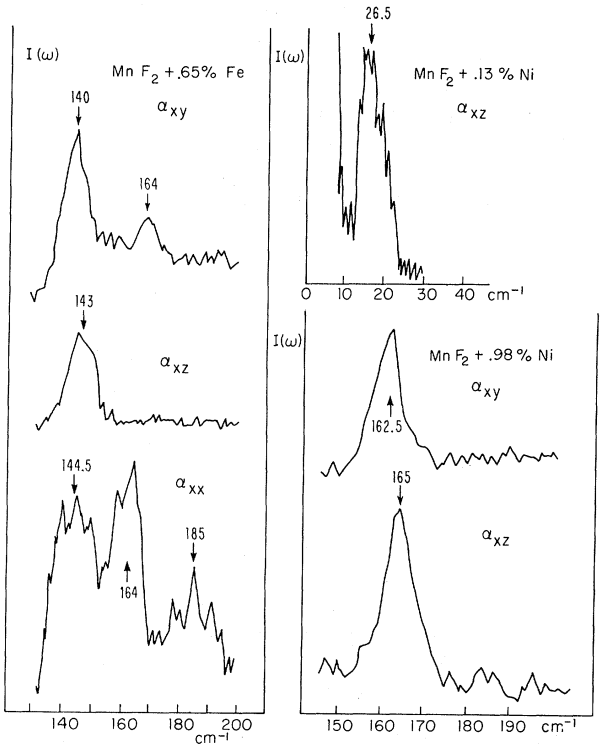

FIG. 1. Typical Raman spectra from Ge- and Ni-doped crystals at 10°K. Resolution is about 6 cm^{-1}. All intensities are arbitrary. The α_{xy} and α_{xz} Fe lines have about twice the intensity of the corresponding Ni lines.

two-magnon line would sum the local (s_0) mode energy and the exchange plus anisotropy energy necessary to excite one near neighbor Mn^{2+} spin ($\Delta m_S = \pm 1$). Since the latter excitation corresponds approximately to the magnon energy at the Brillouin zone boundary and since different points on this noncubic boundary have different energies (e.g., the X and Z points are at 50.4 and 54.8 cm^{-1}, respectively), one also expects small shifts in the two-magnon spectrum for different polarizations of the incident and scattered light. The observed values for the local modes are 120 cm^{-1} for Ni^{2+} [6] and 94.5 cm^{-1} for Fe^{2+},[7] the latter value coming from a measurement of a magnetic dipole absorption in the far infrared. On the basis of this model, we estimate the Ni-Mn and Fe-Mn two-magnon lines to be centered in the vicinity of 170-175 cm^{-1} and 145-150 cm^{-1}, respectively, depending on which zone-boundary magnon is involved.

To obtain a more sophisticated model, one can do a Green's function calculation which considers both the actual impurity modes and the magnon-magnon interaction between them. Such calculations are in progress and will be reported in detail later. Preliminary results indicate that with the exception of s_0, all the impurity modes have similar energies which lie quite close to the Brillouin zone edge. Thus, the simple model would be reasonably accurate if it also included magnon-magnon interactions, which are important because we are describing the simultaneous creation of two magnons that are physically near to one another.[13] We can obtain a rough estimate of these interactions by considering an Ising calculation of the energy difference between adjacent and distant magnons.

The creation of simultaneous spin deviations on an impurity and on a distant host requires an antiferromagnetic exchange energy of $2nS(J+J')$, while deviations on neighboring spins require $2nS(J+J')-2(JS-J'S'+J')$. The difference between these expressions, $2(JS-J'S'+J')$, includes the magnon-magnon interaction energy $2J'$. In MnF_2, $J=-1.24$ and $S=\frac{5}{2}$, while $J_{\text{Ni-Mn}}' = -3.11$ [6] and $S_{\text{Ni}}' = 1$. $J_{\text{Fe-Mn}}'$ has been estimated to be equal to -1.9,[7] while $S_{\text{Fe}}' = 2$. With these values, we compute the magnon-magnon corrections to be 6.2 cm^{-1} for Ni^{2+} and 2.4 cm^{-1} for Fe^{2+}. The corresponding two-magnon modes should then occur at 163.8 and 168.8 cm^{-1} for Mn^{2+} magnons at X and Z points in the Ni^{2+}-doped crystals; and at 142.6 and 147.6 cm^{-1} in the Fe^{2+}-doped crystals. The calculated positions are in good agreement with the experimental data, particularly for the α_{xy} Ni^{2+} line. In all cases the estimated energies are higher than that which is observed. This is to be expected, since we have approximated the actual Mn^{2+} modes (which lie a few cm^{-1} below the top of the spin-wave manifold) by zone-edge magnons.

An additional confirmation of the two-magnon assignment is provided by the temperature shift of the two impurity lines (shown in Fig. 2 for the α_{xy} component) which closely follows that of the Mn-Mn two-magnon line.

The origin of the 185-cm^{-1} α_{xx} line is not understood at this time, nor is it clear why the Fe^{2+}-doped sample has α_{xx} and α_{xy} polarized lines at 164 cm^{-1}. They do not appear to be related to the lines of similar energy that occur in Ni^{2+}-doped MnF_2, since in the latter samples we find an α_{xz} but no significant α_{xx} component. Also, the Fe^{2+}-doped crystals have been analyzed and found to contain less than 0.002% Ni.

The 26.5-cm^{-1} line in the Ni^{2+} doped crystals has the proper polarization components to be a one-magnon line, but it does not seem to shift with temperature. Instead, it simply broadens with increasing T, becoming unmeasurable around 40°K. In addition, its intensity does not appear to increase with increasing impurity concentration, as do the 140/143 cm^{-1} (Fe^{2+}:MnF_2)

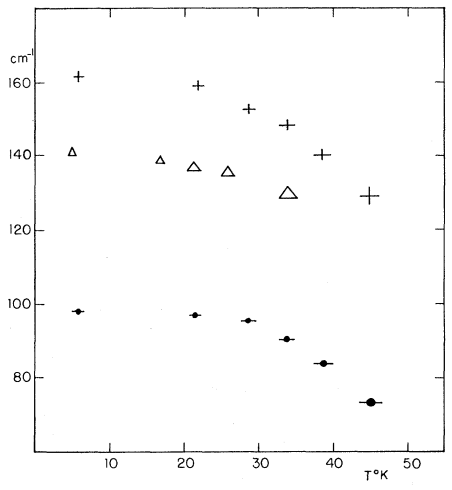

FIG. 2. Temperature dependence of the xy component of the Ni-Mn (plusses), Fe-Mn (triangles), and Mn-Mn (knotted lines). The Fe-Mn line was much narrower at higher temperatures than the Ni-Mn line. It could not be followed above 35° because it merged with the very broad 164-cm^{-1} line. There is a possibility of 10% error in the absolute value of the temperature scale due to poor coupling between the temperature sensor and the sample.

and 162.5/165 cm^{-1} (Ni^{2+}:MnF_2) lines. Measurement of the possible antisymmetry of the scattering tensor for this line has been precluded so far by the small size of the available samples. This measurement should be done since a one-magnon line would have an antisymmetric scattering tensor ($\alpha_{xz} + \alpha_{zx} = 0$).

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OBSERVATION OF LOCALIZED MAGNONS BY RAMAN SCATTERING IN Ni-DOPED MnF_2

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Weak Raman scattering from nickel-doped MnF_2 observed below T_N has been identified with the simultaneous excitation of pairs of single-spin-deviation impurity magnon modes. The polarization and scattering frequency are accurately predicted by a simple model allowing for an interaction between the modes.

In this Letter we describe the first experimental observation of localized magnons using Raman spectroscopy.[1] Localized magnon modes have already been identified by other experimental techniques such as fluorescence studies,[2] ESR,[3] and neutron scattering.[4] The localized magnons associated with nickel impurities in MnF_2 comprise a particularly favorable system for investigation since the spin-wave spectrum of MnF_2 is well known and a magnon impurity mode has been observed in fluorescence at 120.4 cm^{-1}. Futhermore, both the Ni^{2+} and Mn^{2+} low-lying states have essentially no orbital momentum, which greatly simplifies their theoretical description.

Raman scattering was studied in a single crystal of MnF_2 containing 1-2% Ni using a double-grating CODERG monochromator and a linearly polarized argon ion laser providing 30-100 mW in the 4880-A line. The Raman scattered light was detected by photon counting using a cooled photomultiplier with "S" sensitivity. The spectral slit width was energy limited to about 3 cm^{-1}. For low-temperature studies the sample