Talk given at the 18th Annual Conference
on Magnetism and Magnetic Materials
Denver, Colorado, Nov. 28–Dec. 1, 1972

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ABSTRACT

Far-infrared powder spectra show two resonant absorption modes throughout the concentration range from pure FeF_2 or CoF_2 to pure MnF_2. At each end of the concentration range these correspond to the usual antiferromagnetic resonance (AFMR) of the majority ions and a defect mode of the isolated minority ions. In nearly pure CoF_2 the modes are located at 36 cm^{-1}(AFMR) and 28.5 cm^{-1} (defect), and in nearly pure FeF_2 at 53 cm^{-1} (AFMR) and 50 cm^{-1} (defect). Other modes have been discovered in CoF_2 containing a few percent MnF_2. Those at 32 and 35.5 cm^{-1} are attributed to clusters of 2 and 3 defects, and those near 70 cm^{-1} are attributed to neighbors of impurities.

INTRODUCTION

Far-infrared antiferromagnetic resonance in the iron group fluorides was first studied in FeF_2 by Ohlmann and Tinkham.[1] In their work a single AFMR mode was observed at ~ 53 cm^{-1} (1.58 THz). Subsequently, one of us (PLR) reported two far-infrared resonance modes in nominally pure CoF_2 (at 28.5 cm^{-1} and 36 cm^{-1}) and in FeF_2 (at 50 cm^{-1} and 53 cm^{-1}), rather than the single mode expected from theory in each substance.[2,3] More recently experiments with neutron diffraction on $(Co,Mn)F_2$ alloy samples by the Chalk River Group have revealed the presence of two modes.[4-6] This work suggested that one of the two far-infrared modes reported in nominally pure CoF_2 and FeF_2 might be due to the presence of a Mn impurity, even though various analysis techniques had placed an upper limit of one part in 10^4 on the mole fraction of Mn. We have found that doping CoF_2 and FeF_2 with MnF_2 strengthens and finally shifts the extra modes, and so we can attribute them to unintentional trace quantities of Mn.

EXPERIMENTAL TECHNIQUES

Polycrystalline samples were grown from the melt using nominally pure CoF_2, MnF_2, and FeF_2. The samples were then ground to powder with average grain size $< 100\mu$. Samples weighing either 28 or 276 mg were then formed into cylinders, 0.48 cm in diameter and saturated with paraffin.

Far-infrared spectra of these samples were measured at LHe temperatures over the frequency range 5 - 100 cm^{-1} by Fourier transform

spectroscopy using a Michelson interferometer. The spectral resolution varied from 0.3 to 1.3 cm^{-1} and was selected to resolve all features seen. The spectra were ratioed against similarly prepared samples of ZnF_2 so as to remove the effects of phonon absorption and powder scattering.

RESULTS

The frequencies of the observed modes in $(Co,Mn)F_2$ are shown as a function of concentration in Fig. 1. (Points in the figure

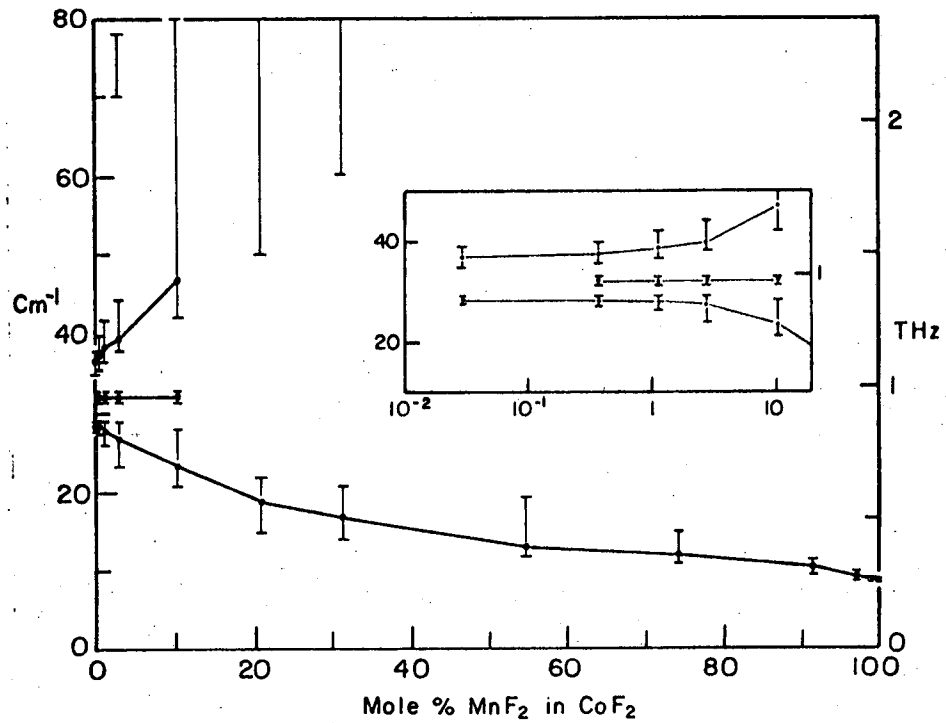

Fig. 1. Center frequencies and widths of far-infrared absorption lines in $[Co,Mn]F_2$.

indicate absorption peaks, while flags indicate the approximate widths of the resonances.) In nearly pure CoF_2 the 36 cm^{-1}(1.08 THz) mode is identified as the CoF_2 AFMR. As the impurity level is increased this mode shifts rapidly upwards in frequency in the direction of the 124 cm^{-1} (3.72 THz) mode of isolated Co ions in MnF_2.[7] It also broadens asymmetrically towards higher frequencies. Scattering at frequencies above 100 cm^{-1} in the powder samples used prevented measurements of the behavior of this mode at high Mn concentrations.

The 28.5 cm^{-1} (0.85 THz) mode is relatively narrow and weak in the nearly pure CoF_2 samples. The mode intensity increases linearly with concentration up to about 1% impurity and after that increases much more slowly. This mode may be identified with the 30 cm^{-1} (0.9 THz) defect mode predicted by Cowley and Buyers[5] from their

Green's function calculations. The defect mode drops in frequency with increasing Mn concentration to become the 8.7 cm^{-1} (AFMR) mode in pure MnF_2.[8] In our nearly pure MnF_2 samples a small and very sharp second mode appeared at 8.3 cm^{-1}.[2] This mode was not visible above 1% concentrations of either Co or Fe and is presumably due to some unintentional and as yet unidentified impurity in our MnF_2 starting material.

The third mode at 32 cm^{-1} (0.96 THz) which appears in CoF_2 doped with 0.3%-10% MnF_2 is most reasonably ascribed to pairs of Mn impurities on opposite sublattices. Its position may be roughly calculated from an Ising approximation. Assuming that the 28.5 cm^{-1} mode is a defect mode, each next nearest neighbor contributes $\approx 1/8$ of the energy. Therefore if we add 7/8 of the lower mode energy (24.9 cm^{-1}) to the 6.2 cm^{-1} Mn-Mn exchange energy, we obtain 31.3 cm^{-1} which is very close to the observed value. Further evidences for this assignment are: (1) there is no change of frequency or linewidth with concentration; (2) the resonance appears at relatively high impurity concentrations compared with the defect mode, and then disappears as the concentration increases further. Such a mode would necessarily be localized.

Another mode at 35.5 cm^{-1} (not shown in Fig. 1) appears in the 0.38% to 10% samples and is probably due to a Mn defect site with two Mn next nearest neighbors. This triplet mode is twice as far from the defect mode as is the pair mode and has about one-fourth the pair mode intensity.

Cowley and Buyers also predict five localized modes between 71 cm^{-1} (2.12) THz and 76 cm^{-1} (2.27) THz. Weak absorptions have been observed at 67.0 ± .5, 70.5 ± .5, 72.5 ± .5, and 75.0 ± .5 cm^{-1} in single crystal specimens of CoF_2 with $\lesssim$ 0.03 percent Mn. These neighbor modes can also be seen in the powder samples, being most intense in CoF_2: 3% Mn. The relative weakness of the neighbor modes may result from their being split off from the upper edge of the band and coupling poorly with q = 0 excitation.

The frequencies of the observed modes in $(Fe,Mn)F_2$ are shown as a function of concentration in Fig. 2. These modes are similar in most respects to those seen in $(Co,Mn)F_2$. If there exists a pair mode in $(Fe,Mn)F_2$ which corresponds to the 32 cm^{-1} mode in $(Co,Mn)F_2$, it should have a frequency of about 56 cm^{-1}. No such mode has been observed; therefore, this mode must be considerably weaker than the corresponding pair mode in $(Co,Mn)F_2$.

The AFMR of pure FeF_2 is at 53 cm^{-1} (1.59 THz) as observed by Ohlmann and Tinkham.[1] Its behavior with added Mn is similar to that of the AFMR in CoF_2. The 50 cm^{-1} (150 THz) mode fits the description of a defect mode predicted by Tonegawa.[9] A simple Ising calculation of the mode frequency gives a result of 48.8 cm^{-1}, very close to the observed value. This lower mode differs from the corresponding 28.5 cm^{-1} mode in $(Co,Mn)F_2$ in that it is considerably narrower and stronger throughout the impurity concentration range. There is a broad absorption between 78 and 80 cm^{-1} in the 0.1% to 3% Mn concentration range which closely corresponds to the 79 cm^{-1} Ising calculation of the neighbor mode frequency of Mn in FeF_2.

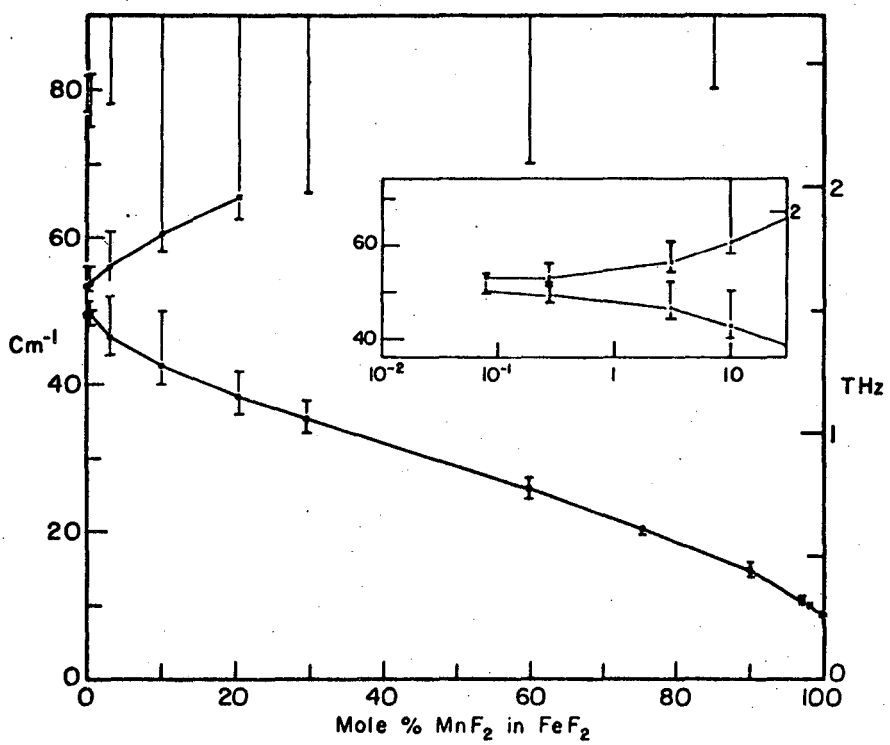

Fig. 2. Center frequencies and widths of far-infrared absorption lines in $[Fe,Mn]F_2$.

We find good qualitative agreement between the measured far-infrared modes in $(Co,Mn)F_2$ and the q = 0 mode positions calculated by Economou,[10] except at small Mn concentrations where he has neglected multiple defect modes and the splitting between the AFMR and the defect mode. At the concentrations for which q = 0 neutron diffraction measurements are available, the shapes and relative intensities of the infrared absorptions agree roughly with the neutron results when the extra factor of ω^2 in the infrared absorption coefficient is included.

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REFERENCES

1. R. C. Ohlmann and M. Tinkham, Phys. Rev. 123, 425 (1961).
2. P. L. Richards, J. Appl. Phys. 34, 1237 (1963).
3. P. L. Richards, Bull. Am. Phys. Soc. [Ser. II] 10, 33 (1965).
4. E. C. Svensson, W. J. L. Buyers, T. M. Holden, and R. A. Cowley, Magnetism and Magnetic Materials 1971, C. D. Graham, Jr. and J. J. Rhyne, eds. (AIP, N.Y., 1971), p. 1315.
5. R. A. Cowley and W. J. L. Buyers, Rev. Mod. Phys. 44, 406 (1972).

6. W. J. L. Buyers, D. E. Pepper, and R. J. Elliott, J. Phys. C5, 2611, (1972).
7. R. Weber, J. Appl. Phys. 40, 995 (1969).
8. F. M. Johnson and A. H. Nethercot, Phys. Rev. 114, 705 (1959).
9. T. Tonegawa, Prog. Theor. Phys. 40, 1195 (1968).
10. E. N. Economou, Phys. Rev. Letters 28, 1206 (1972).

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