PHYSICAL REVIEW B VOLUME 30, NUMBER 6 15 SEPTEMBER 1984

Raman scattering by phonons in $Fe_{1-x}Zn_xF_2$ and $Fe_{1-x}Mn_xF_2$

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(Received 12 December 1983)

First-order Raman spectra are reported for the entire composition range of $Fe_{1-x}Zn_xF_2$ and $Fe_{1-x}Mn_xF_2$ at several temperature values. The B_{1g} and A_{1g} modes behave similarly in both families. Their frequencies shift with x in a nonlinear manner, with a relative minimum at $0 < x < 1$. The behavior of the E_g mode in $Fe_{1-x}Mn_xF_2$ is similar but in $Fe_{1-x}Zn_xF_2$ a two-mode behavior is observed. Both families exhibit large disorder-induced phonon broadening.

In recent years, the behavior of disordered antiferromagnetic insulators has attracted considerable attention. Among the important materials of this class are the rutile fluorides $Fe_{1-x}Zn_xF_2$ and $Fe_{1-x}Mn_xF_2$, which have simple three-dimensional magnetic interactions that make them ideal for theoretical modeling.

The initial interest in these systems was directed toward the understanding of their magnetic excitations.[1,2] More recently they have attracted renewed attention because of the variety of phase transitions and critical phenomena they exhibit.[3-5]

A number of techniques such as neutron scattering,[1-3] NMR,[6] Raman light scattering,[7,8] far-infrared spectroscopy,[9] and optical birefringence,[5,10] have been used to study these systems, but they all have concentrated on the magnetic properties. The study of their elastic properties, for example, has received little attention in the past.[11]

In this paper we report on Raman scattering by optical phonons in the mixed crystals $Fe_{1-x}Mn_xF_2$ and $Fe_{1-x}Zn_xF_2$ $(0 < x < 1)$ and discuss their behavior in light of available theoretical models.

The present measurements were made with crystals grown by N. Nighman of the University of California at Santa Barbara. Single crystals of $Fe_{1-x}Zn_xF_2$ and $Fe_{1-x}Mn_xF_2$ of good optical quality with several different concentrations in the range of $0.01 < x < 1.0$ were used in this study. The samples were mounted on the cold tip of a Helitran refrigerator (Air Products) and the temperature was measured with a thermocouple attached close to the tip.

The spectra were obtained using an argon-ion laser of linear polarized output at 4880 Å. The right-angle-scattered light was analyzed using a Spex 1403 double monochromator and a low-noise FW 130 photomultiplier with dc current detection.

The materials studied have a rutile structure in which the cations are arranged on a body-centered-tetragonal lattice. The point symmetry at the positions of the metal ions is D_{4h}. There are four Raman active vibrational modes of A_{1g}, B_{1g}, B_{2g}, and E_g symmetry which involve only the fluorine ions.

The measured phonon frequencies versus concentration for the B_{1g} and E_g modes in the system $Fe_{1-x}Mn_xF_2$ are shown in Fig. 1(a) for two temperature values. Both phonon modes exhibit one-mode behavior[12] for temperatures in the range 4.2–298 K and their frequencies show a nonliner dependence with the concentration between the corresponding values of FeF_2 and MnF_2.[13] The behavior of the phonon frequencies with temperature in the mixed system is essentially the same as that in pure FeF_2.[14] As the tempera-

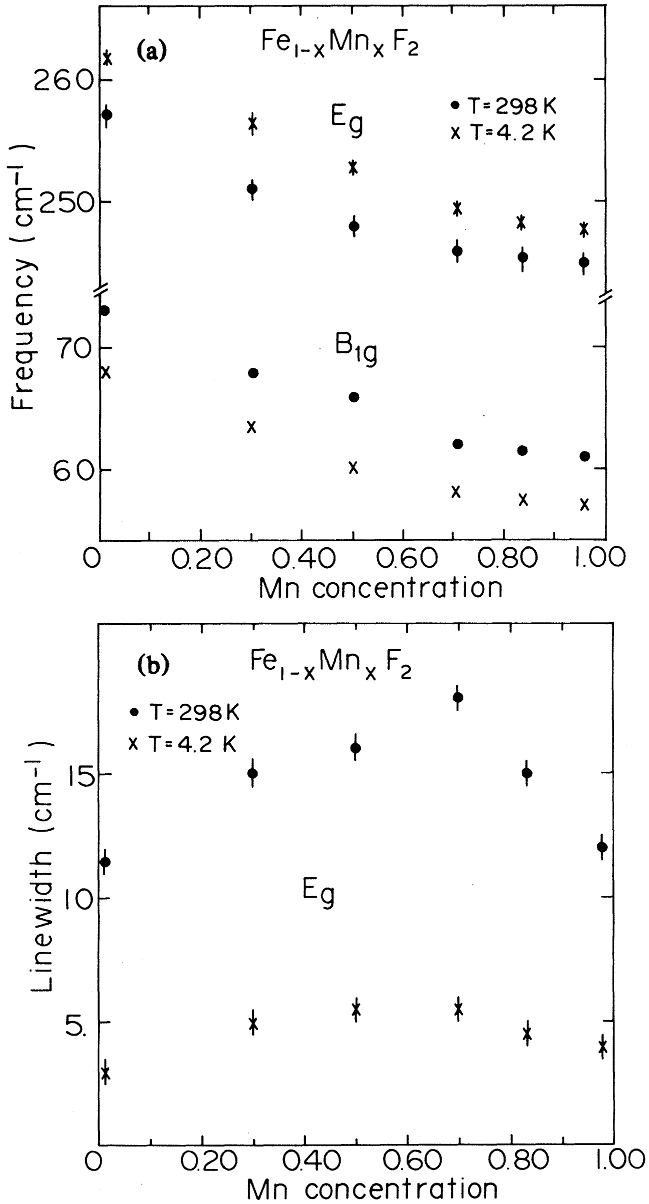

FIG. 1. (a) Variation with Mn concentration of the B_{1g} and E_g phonons frequencies in $Fe_{1-x}Mn_xF_2$ at 4.2 K (×) and 298 K (●). The error bars indicate the incertainty in the measurements. (b) Linewidth of the E_g mode as a function of the Mn concentration.

ture decreases the E_g mode shifts to higher frequencies while the B_{1g} mode exhibits an anomalous frequency softening. This behavior has been recently studied in pure crystals with the rutile structure and indicates a strong lattice thermal contraction.[14] The A_{1g} phonon frequency was not studied in detail because it changes only from 340 cm^{-1} in FeF_2 to 341 cm^{-1} in MnF_2 at 298 K.[13]

As expected, the phonon linewidths in the mixed crystals are greater than those in the pure cyrstals, because of "inhomogeneous strains" and breakdown of the translational symmetry. The linewidth of the E_g mode as a function of the manganese concentration indicates a maximum near $x = 0.50$, as shown in Fig. 1(b). The B_{1g} mode linewidths are smaller than the spectral resolution (~ 3 cm^{-1}) in the whole concentration range and thus could not be measured. These two modes display a symmetric line shape in the whole temperature range studied here.

The behavior of the A_{1g} and E_g phonon frequencies in $Fe_{1-x}Zn_x F_2$ crystals is more complex. Figure 2 shows the frequency concentration dependence of the A_{1g} and E_g modes in this system at $T = 20$ K. As can be seen the A_{1g} frequency shows a relative minimum near $x \simeq 0.2$. Its linewidth is inhomogeneously broadened. On the other hand, the doubly degenerate E_g mode has minimum frequency at about $x = 0.8$. However, for this mode, two peaks are resolved for $x \leqslant 0.3$. Figure 3 shows the Raman spectra of the E_g mode for different concentrations at 20 K. For $x = 0.05$ a low-frequency component is observed, and its intensity increases with increasing x, while the intensity of the higher-frequency component decreases. These two peaks appear in the scattering with (xz) and (yz) polarization, indicating that no symmetry distortion occurs. For $x > 0.3$ only one peak is observed, showing an asymmetric line shape with a pronounced tail on the high-frequency side. The two-mode behavior[12] is similar to that observed in $Mn_{1-x}Zn_xF_2$.[15] The line shape of the E_g mode is also affected by the disorder due to the Zn admixture, exhibiting an inhomogeneous broadening with a maximum of 26 cm^{-1} at $x = 0.5$. As the temperature is increased, the two peaks broaden. At room temperature the double-peak structure becomes masked and it is observed only for $x = 0.12$.

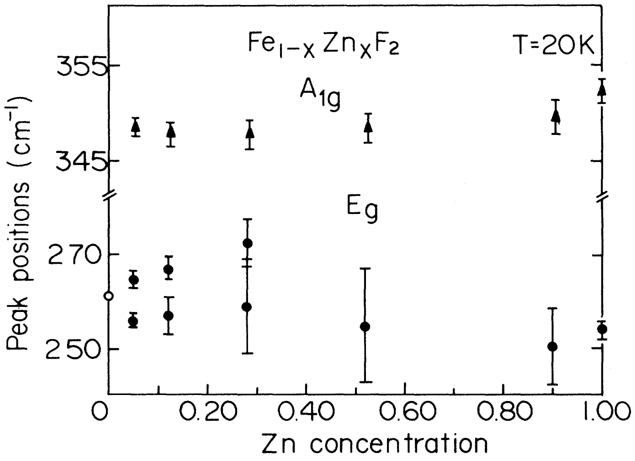

FIG. 2. Peak positions of A_{1g} and E_g modes in $Fe_{1-x}Zn_x F_2$ at 20 K for various values of x. Two-mode behavior is observed for $x < 0.30$ (see Fig. 3) and single-mode behavior at large x. The vertical bars indicate the full width at half height of the lines for the E_g mode, and the uncertainty in the measurements for A_{1g} mode. Open circle (o) corresponds to measurements from Ref. 14.

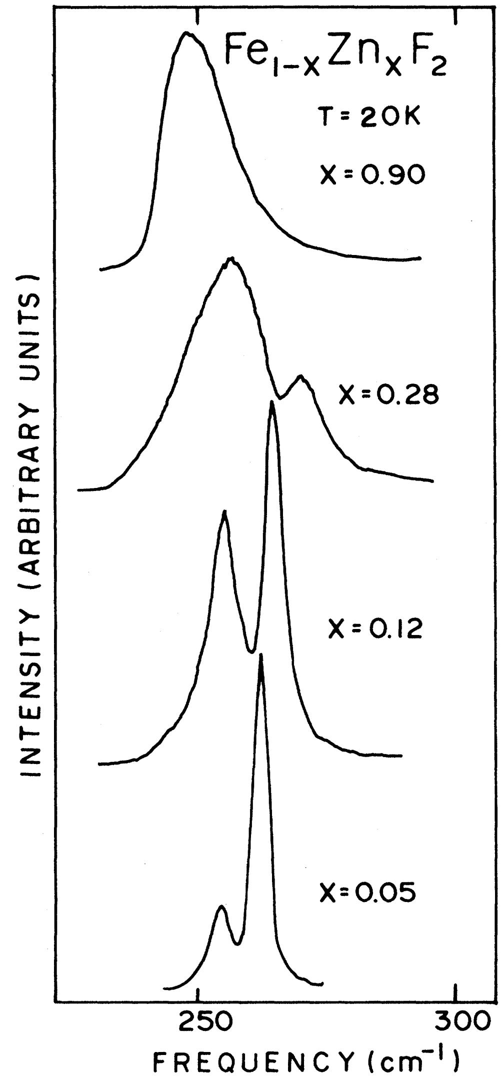

FIG. 3. Double structure with E_g symmetry in $Fe_{1-x}Zn_xF_2$ at 20 K.

The present results may be analyzed based on the theoretical models in the literature. Firstly, we notice that various experimental studies of the vibrational spectra of the $A_{1-x}B_xC$-type crystals have been made by optical techniques.[12,16,17] The results show three types of behavior for the optically active phonons in these systems: namely, "one-mode," "two-mode," and "intermediate"-type behavior. The first type is observed mostly in ionic crystals. The two-mode behavior is observed in covalent mixed crystals such as the IV-IV, III-V, and II-VI compounds, whereas the "intermediate behavior" has been observed in the III-V compounds.

The most successful lattice-dynamical calculations for the pure crystals with rutile structure have been made on the basis of the rigid-ion model[18] and the shell model.[19] Since the pure crystals of FeF_2, MnF_2, and ZnF_2 are reasonably described by the rigid-ion model[20] we apply this model to the compounds studied here in order to calculate the behavior of the phonon energies as a function of concentration. The following additional assumptions are made: (i) changes in the Coulomb part of the crystalline potential are neglected; (ii) variations of the force constants between nearest-neighbor fluorine ions are assumed negligible; (iii) the force constants between nearest-neighbor cation-anion pairs enter in the expressions for the phonon frequencies weighted by x and $(1-x)$, corresponding to the number of bonds associated to each cation; (iv) the force constants between cation-anion pairs vary linearly with concentration.

The considerations lead to an expression for the phonon frequencies of the form

$$\omega_i^2(x) = \omega_{0i}^2 - \gamma_i x + \delta_i x^2, \tag{1}$$

where ω_{0i} is the frequency of the i mode in the pure crystal; γ_i and δ_i are parameters which involve the force constant between cation-anion pairs associated with the i mode for $x=0$ and $x=1$. Using the above assumptions we find for the E_g mode

$$\gamma_{E_g} = \frac{2e^2}{mV}[0.5B_1 + (1-\alpha)B_2 + \alpha A_2], \tag{2}$$

$$\delta_{E_g} = \frac{e^2}{mV}[0.5(B_1 + B_1') + (1-\alpha)(B_2 + B_2') + \alpha(A_2 + A_2')], \tag{3}$$

where e is the electronic charge, V is the unit-cell volume, m the mass of the anion, α a structure related constant, and A_i, B_i, A_i', and B_i' are dimensionless crystalline potential parameters as defined in Ref. 18 for $x=0$ and $x=1$. Analogous expressions can be obtained for the other vibrational modes.

Notice that Eqs. (1)–(3) exhibit a nonlinear dependence of the phonon frequency with concentration which could in principle explain the data of Figs. 1 and 2. However, using the force constants derived by Striefler and Barsch[20] we find poor quantiative agreement between theory and experiment with regard to the absolute values of the frequencies and the positions of the extrema of $\omega(x)$. Moreover, this treatment cannot describe the two-mode behavior of the E_g phonon. According to Chang and Mitra[12] a two-mode behavior occurs if the phonon optical bands do not overlap in the corresponding pure crystals. Of course, verification of the Chang-Mitra criteria would require knowledge of the phonon-dispersion relation in the entire Brillouin zone for mixed crystals, and this has not been measured to date.

We notice that the observed concentration dependence of the frequency and the intensities of the two peaks of E_g symmetry in $Fe_{1-x}Zn_xF_2$ are qualitatively similar to the results obtained using the cluster model[17] for $Ba_xSr_{1-x}F_2$. This model is a generalization of the above treatment with more degrees of freedom for the optical modes. In order to apply this model to $Fe_{1-x}Zn_xF_2$ one has to consider the six possible basic nearest-neighbor ion units corresponding to the six different arrangements of one first neighbor and two second neighbors of the Fe^{2+} or Zn^{2+} ions around a F^- ion. In order to describe properly the Raman-active modes one should distinguish the four fluorine ions in the unit cell by considering 24 basic units.[17]

To describe the probabilities of occurrence of these basic units, two different distances R_a and R_b, between the cations in the basic unit should be considered, and two cluster parameters[16] β_a and β_b related to R_a and R_b are required. If $0<\beta_i<1$ $(i=a,b)$, the probability of finding two Fe^{2+} ions at one particular distance will be enhanced over the random case, which corresponds to $\beta_a=0$ (or $\beta_b=0$). This type of disorder (β_a or $\beta_b>0$) is expected in $Fe_{1-x}Zn_xF_2$ since the magnetic Raman scattering of this compound already exhibited a structure which is attributed to cluster excitations.[8]

The same interactions considered for pure crystals should be taken into account, but they should be represented by different force constants depending on the unit that each ion pair belongs to. For each vibration direction there will be a set of equations of motion involving six sublattice coordinates for each F^- ion and five sublattice coordinates for each cation.[17] We believe that these equations of motion in principle can be solved, for the eigenfrequencies and normal modes of the mixed system. However, this is a major computational task which we have not undertaken.

In conclusion, the concentration dependence of the frequencies of Raman-active phonon modes has been measured in the mixed systems $Fe_{1-x}Mn_xF_2$ and $Fe_{1-x}Zn_xF_2$ at several temperature values. In addition to the nonlinear dependence of the frequency with concentration, the E_g mode shows a two-mode behavior in $Fe_{1-x}Zn_xF_2$ in a narrow range of x. We hope that the present results will stimulate further lattice dynamics calculations in mixed crystals.

We acknowledge useful discussions with F. G. Brady Moreira and J. R. Rios Leite, and the technical assistance of J. C. Albuquerque, A. Nascimento, F. A. M. Leal, and S. R. P. Silva. We also acknowledge the finanical support of the Brazilian agencies Financiadora de Estudos e Projetos (FINEP), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), and Organização dos Estados Americanos (OEA).

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[1] R. A. Cowley and W. J. L. Buyers, Rev. Mod. Phys. 44, 406 (1972).

[2] R. A. Cowley, in *Proceedings of the 21st Conference on Magnetism and Magnetic Materials, Philadelphia—1975*, edited by J. J. Becker, G. H. Lander, and J. J. Rhyne, AIP Conf. Proc. No. 29 (AIP, New York, 1975), p. 243.

[3] R. A. Cowley, in *Excitations in Disordered Systems*, edited by M. F. Thorpe (Plenum, New York, 1982), p. 373.

[4] R. J. Birgeneau, R. A. Cowley, G. Shirane, H. Yoshizawa, D. P. Belanger, A. R. King, and V. Jaccarino, Phys. Rev. B 27, 6747 (1983).

[5] D. P. Belanger, A. R. King, V. Jaccarino, and J. D. Cardy, Phys. Rev. B 28, 2522 (1983).

[6] H. Yasuoka, S. P. Vernon, and V. Jaccarino, J. Appl. Phys. 53, 2707 (1982).

[7] D. J. Lockwood, in *Light Scattering in Solids III*, Topics in Applied Physics, Vol. 51, edited by M. Cardona and G. Güntherodt (Springer, Berlin, 1982), p. 59.

[8] E. Montarroyos, Cid B. de Araújo, and S. M. Rezende, J. Appl. Phys. 50, 2035 (1979); Cid B. de Araújo, Phys. Rev. B 22, 266 (1980); S. M. Rezende, Cid B. de Araújo, and E. Montarroyos, J. Raman Spectrosc. 10, 173 (1981).

[9] B. Enders, P. L. Richards, W. E. Tennant, and E. Catalano, in *Magnetism and Magnetic Materials*, Proceedings of the 18th Annual

Conference on Magnetism and Magnetic Materials, Denver, edited by C. D. Graham and J. J. Rhyne (AIP, New York, 1972), p. 179.

[10] D. P. Belanger, A. R. King, and V. Jaccarino, Phys. Rev. Lett. 48, 1050 (1982).

[11] E. Montarroyos, S. S. Vianna, Cid B. de Araújo, S. M. Rezende, and A. R. King, J. Magn. Magn. Mater. 31–34, 557 (1983).

[12] I. F. Chang and S. S. Mitra, Adv. Phys. 20, 359 (1971).

[13] S. P. S. Porto, P. A. Fleury, and T. C. Damen, Phys. Rev. 154, 522 (1967).

[14] D. J. Lockwood, R. S. Katiyar, and V. C. Y. So, Phys. Rev. B 28, 1983 (1983).

[15] M. Buchnan, W. J. L. Buyers, R. J. Elliott, R. T. Harley, W. Hayes, A. M. Perry, and I. D. Saville, J. Phys. C 5, 2011 (1972).

[16] A. S. Barker, Jr. and A. J. Sievers, Rev. Mod. Phys. 47 Suppl. 2, 141 (1975).

[17] H. W. Verleur and A. S. Barker, Jr., Phys. Rev. 164, 1169 (1967); H. W. Verleur and A. S. Barker, Jr., Phys. Rev. 149, 715 (1966).

[18] R. S. Katiyar, J. Phys. C 3, 1693 (1970).

[19] G. C. Gran and M. J. L. Sangster, J. Phys. C 7, 1937 (1974).

[20] M. E. Striefler and G. R. Barsch, Phys. Status Solidi (b) 59, 25 (1973).