have energy enough to give rise to impact ionization.

The movement of the carriers in the electric field creates a space charge whose field opposes the external one, thus reducing it exponentially with a time constant $\tau = 1.5-3$ msec. When the applied voltage is removed, the space-charge field gives rise to the processes leading to the effect.

ACKNOWLEDGMENTS

The author is grateful to Professor R. Fieschi and to Professor E. Fatuzzo for useful discussions. The Gruppo Nazionale della Materia (GNSM) has supported this work.

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[1] S. Unger and K. Teegarden, Phys. Rev. Letters 19, 1229 (1967).

[2] R. Cooper and C. T. Elliott, J. Phys. D 1, 121 (1968).

[3] J. J. O'Dwyer, J. Appl. Phys. 39, 4356 (1968); 40, 3887 (1969).

[4] See, for example, K. Teegarden, in *Luminescence of Inorganic Solids*, edited by P. Goldberg (Academic, New York, 1966).

[5] C. Paracchini and G. Schianchi, Solid State Commun. 8, 1769 (1970).

[6] A. Rose, Helv. Phys. Acta 29, 199 (1956).

[7] W. Shockley, Bell System Tech. J. 30, 990 (1951).

[8] A. G. Chynoweth, in *Semiconductors and Semimetals*, Vol. 4, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1968), pp. 268–286.

PHYSICAL REVIEW B VOLUME 4, NUMBER 8 15 OCTOBER 1971

Influence of Magnetic Ordering on a Phonon Resonant Mode in Chlorine-Doped MnF$_2$[†]

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(Received 21 May 1971)

The far-infrared absorption spectra of chlorine-doped MnF$_2$ show a strong phonon resonant mode at 35.79 ± 0.03 cm^{-1} (1.2 °K). The electric vector of this mode is polarized perpendicular to the *c* axis of the crystal. In order to study the influence of magnetic ordering on this mode, the center frequency and half-width were measured as a function of temperature from 1.2 °K through the Néel point up to 100 °K. The resonant frequency increases monotonically with temperature. An additional shift was observed at the onset of magnetic ordering, and was accompanied by additional broadening of the line. These anomalies are explained by considering magnetoelastic effects.

I. INTRODUCTION

In MnF$_2$ many studies have been done in connection with optical absorption associated with magnetic impurities. However, in this substance little is known about phonon impurity modes and nothing about their interaction with the magnetic lattice.

The first measurements on the far-infrared vibrational absorption of Eu^{2+} and Tm^{3+} in MnF$_2$ were done by Alexander and Sievers.[1] To our knowledge, in MnF$_2$ no phonon modes due to anion substitutes are known.

In this paper we report on a phonon resonant mode which we found in Cl$^-$-doped MnF$_2$.[2] The influence of magnetic ordering on this mode was studied by measuring the center frequency and half-width of the resonance as a function of temperature from 1.2 °K through the Néel point ($T_N = 67.3$ °K) up to 100 °K.

II. EXPERIMENTAL

Single crystals of pure and Cl$^-$-doped MnF$_2$ were oriented by the Laue back-reflection method within a few tenths of a degree and cut perpendicular and parallel to the *c* axis of the crystal. The far-infrared absorption spectra of pure and doped samples were measured for both polarizations in the region from 3 to 90 cm^{-1}. Between 3 and 50 cm^{-1} a lamellar interferometer was used with a He^3 cooled bolometer detector; for the higher-energy region, a Michelson interferometer was used with a 1.2 °K bolometer. The maximal instrumental resolution was about 0.1 cm^{-1} in both cases.

The most remarkable feature in the absorption spectra of the doped samples is a strong absorption line at 35.79 ± 0.03 cm^{-1} (1.2 °K). The dipole moment in this mode is perpendicular to the *c* axis of the crystal. The impurity-induced absorption coefficient is shown in Fig. 1 for different sample temperatures. The integrated absorption of the line, $\int \alpha(\omega) d\omega$, decreases from 1.2 to 100 °K by $(16 \pm 12)\%$. The error is caused by uncertainty in determining the absolute baseline of the absorption. At 1.2 °K no change in center frequency was observed when the doping with Cl$^-$ in the melt varied between 0.5 and 2%.[3]

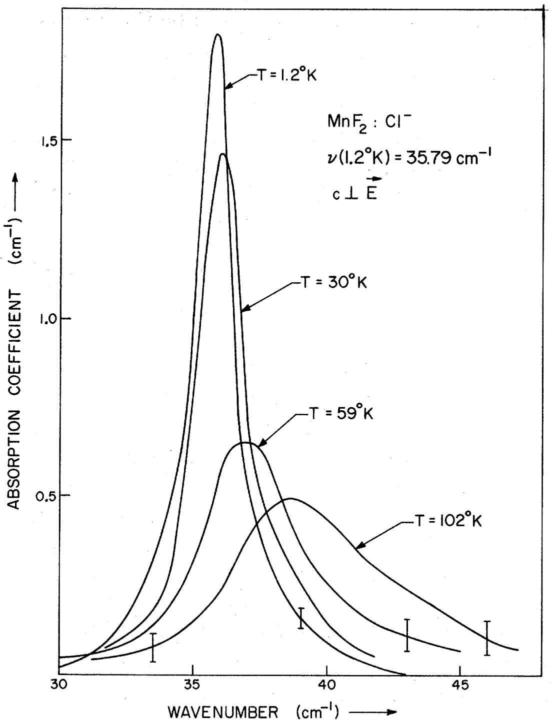

FIG. 1. Difference spectra of the chlorine mode in MnF_2 for different sample temperatures. The electric vector of the mode is polarized ⊥ to the c axis of the crystal.

In a magnetic field up to 50 kOe, the line shift is $< \pm 0.03\ \text{cm}^{-1}$. Furthermore, the line does not disappear when the crystal is warmed above the Néel temperature.

For the polarization $c \parallel \vec{E}$ no sharp absorption could be observed ($\alpha_{max} \leq 0.1\ \text{cm}^{-1}$).

The temperature dependence of the mode frequency is shown in Fig. 2. Single experimental points represent averages of several runs, especially in the high-temperature region. The dominant feature is a monotonic increase in the mode frequency with temperature. However, in the region of the Néel temperature, a clear change in slope occurs.

Figure 3 shows a similar anomaly in the temperature dependence of the half-width. The primary source of uncertainty was again in determining the absolute baseline of the absorption.

III. DISCUSSION

From the polarization and temperature-dependence studies as well as from the behavior of the mode in a magnetic field we suggest that the additional absorption in Cl^--doped MnF_2 is due to a phonon resonant mode. Because the perturbed crystal lacks inversion symmetry, the absorption could originate from even parity modes of the pure crystal. Heuristically we can understand the low-frequency mode as due to a vibration in which the Cl^- ion moves perpendicular to the Mn-F-Mn force constants (defined by Matossi with k_1 and k_2).[4]

The small increase in integrated absorption with decreasing temperature can be understood by the anharmonicity in the resonant mode itself.[1,5] Because of anharmonicity the oscillator levels are no longer equidistant. With decreasing temperature the population of the vibrational ground state will increase and therefore those higher transitions which otherwise produce absorption at frequencies outside the line will disappear. Compared with the situation in MnF_2: Eu^{2+}, the effect is very small in the present case. Indeed, the only supporting evidence is a small asymmetry present in the 102 °K curve (Fig. 1).

For a description of the temperature dependence of the center frequency and linewidth we consider the following terms: firstly, anharmonic effects which were studied in connection with phonon impurity modes in nonmagnetic lattices such as phonon decay, phonon-phonon scattering, and "normal" thermal expansion,[5–7] and secondly, effects arising through the phonon-magnon interaction.

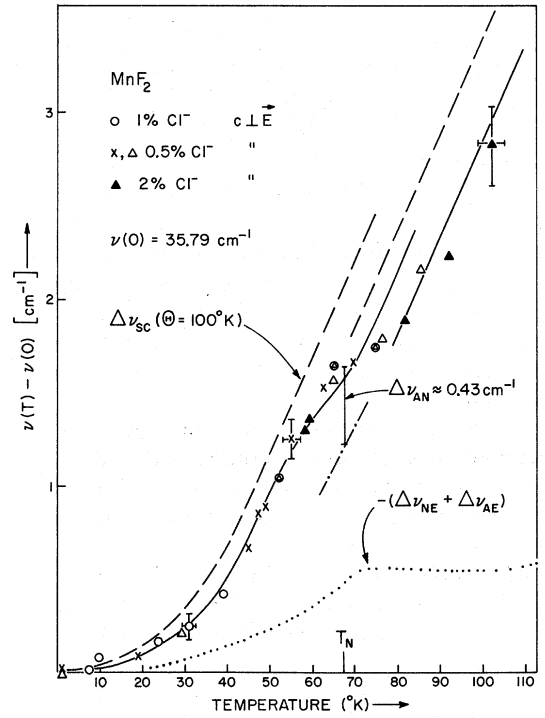

FIG. 2. Observed temperature dependence of the center frequency of the chlorine resonant mode. The full line is a theoretical curve which represents the difference of $\Delta\nu_{SC}$ (phonon-phonon scattering) and $\Delta\nu_{NE} + \Delta\nu_{AE}$ ("normal" and "anomalous" thermal expansion). The auxiliary lines are discussed in the text.

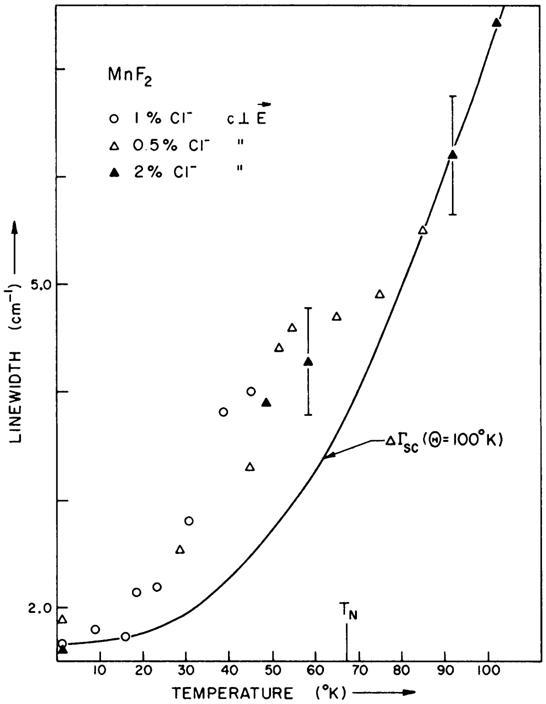

FIG. 3. Temperature dependence of the linewidth of the chlorine mode. The full curve shows the contribution from phonon-phonon scattering to the linewidth.

In the decomposition process the excited vibrational state associated with the impurity decays into band phonons. For resonant modes, sum as well as difference processes are possible. The former are expected to be small in our case, because in the Debye region the phonon density is small. The contribution from difference processes could be large, e.g., if the convolution

$$N(\omega) = \int\int N^{(1)}(\omega')N^{(1)}(\omega'')\delta(\omega' - \omega'' - \omega)\,d\omega'\,d\omega''$$

yielded a large value at $\omega = \omega_0$. [$N^{(1)}(\omega')$ is the one-phonon density at $\omega = \omega'$ and ω_0 is the resonant-mode frequency.] In spite of the fact that this could happen accidentally, the similar behavior of the temperature dependence of the center frequency and linewidth for resonant modes in different systems[7] encourages us to neglect in the following the influence of phonon decay.

The contribution of elastic phonon scattering to the line shift is proportional to the mean vibrational energy of the system.[6] For a Debye spectrum this is

$$\Delta\nu_{SC} = \nu(T) - \nu(0) = \delta\left(\frac{T}{\Theta_D}\right)^4 \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1}\,dx \ . \qquad (1)$$

Using $\Theta_D = 100$ °K (this value best fits the half-width data), we obtain the dashed line in Fig. 2.

There is also a shift from the "normal" thermal expansion, $\Delta\nu_{NE}$, which is caused by the anharmonicity of the band modes. In addition, near the phase transition the ordering spins cause via spin-lattice forces an "anomalous" shift $\Delta\nu_{AE}$ due to the change in the lattice parameters associated with spontaneous magnetostriction. Both contributions to the shift will be lumped together here and approximated by

$$\Delta\nu_E = \Delta\nu_{NE} + \Delta\nu_{AE} \approx -A\left(2\,\frac{\Delta a(T)}{a(0)} + \frac{\Delta c(T)}{c(0)}\right) , \qquad (2)$$

where $a(0)$ and $c(0)$ are the lattice parameters and $\Delta a = a(T) - a(0)$. A represents an average of two strain coupling coefficients. In reality our mode is polarized ⊥ to the c axis and is therefore affected differently by Δa and Δc. Furthermore, in the temperature region considered, $\Delta a (< 0)$ and Δc are of opposite sign. On the other hand, Δa is more than one order of magnitude smaller than Δc. A more correct description requires the experimental determination of the strain coupling coefficients, e.g., by uniaxial stress experiments. For a calculation of $\Delta\nu_E$, data of Gibbons[8] were used for $a(T)$ and $c(T)$. In Fig. 2, $-\Delta\nu_E$ is shown as a dotted line. As we can see, $-\Delta\nu_E$ changes rapidly near the Néel temperature, and shows a plateau before increasing further. This is caused by $\Delta\nu_{AE}$, which reflects the rapid change in the c axis near the critical point.

The parameters of Eqs. (1) and (2), δ and A, are then chosen in such a way that the sum $\Delta\nu_{SC} + \Delta\nu_E$ gives the best fit to the experimental data. In this way we obtain the value of $A \approx 600$ cm^{-1}. This value is of the same order of magnitude as the coupling coefficient for hydrostatic strain for defect centers in alkali halides.[9] The result of the fit is shown in Fig. 2 by the solid line. This curve agrees fairly well with the experimental results. The change in slope near T_N is present but not as marked as in the experimental data. Above 70 °K an agreement between theory and experiment is possible only if the linear region of $\Delta\nu_{SC}$ is shifted to higher temperatures, while the slope is retained. The amount by which we have to shift $\Delta\nu_{SC}$ is equal to $\Delta\nu_{AN}$, the anomalous shift at the Néel temperature, which can be estimated by extrapolating the high-temperature data (see Fig. 2). In a more sophisticated treatment, of course, $\Delta\nu_{SC}$ should rather be shifted continuously. Physically, this means that without magnetostriction we would expect the center frequency of the line for $T = 0$, $\nu(0)$, to be lowered by $\Delta\nu_{AN}$. Furthermore, when we extrapolate the data by Gibbons we can estimate $C_{NE}(0)$ and obtain with the above value for $\Delta\nu_{AN}$ from Eq. (2), $A \approx \Delta\nu_{AN} C_E(0)/[C_{NE}(0) - C_E(0)] = 0.43$ cm^{-1}/$7.7\times 10^{-4} \approx 560$ cm^{-1}, which is in fairly good agreement with the above value.

In the Debye approximation the contribution of elastic phonon scattering to the linewidth is[6]

$$\Delta\Gamma_{\mathrm{sc}} = \Gamma(T) - \Gamma(0) = \beta\left(\frac{T}{\Theta_D}\right)^7 \int_0^{\Theta_D/T} \frac{x^6 e^x}{(e^x - 1)^2}\, dx \quad . \tag{3}$$

This integral has been studied by Ziman.[10] At low temperatures it is proportional to T^7 and at high temperatures to T^2. The best fit of Eq. (3) to the measured curve is obtained for $\Theta = 100$ °K ($\Theta_D = 265$ °K).[11]

Qualitatively, the anomalous broadening of the line near the Néel temperature can be understood by phonon-magnon interaction. Near the critical point the fluctuating spins cause a fluctuation in the lattice parameters and thereby a fluctuation in the phonon frequencies. As a consequence, an additional broadening in the line occurs. Unfortunately, for a quantitative analysis the experimental data are not accurate enough. Of course, this effect also gives a contribution to the anomalous line shift.

In summary we can say that the temperature dependence of the center frequency of the 35.79-cm^{-1} phonon mode in chlorine-doped $\mathrm{MnF_2}$ can be approximated by considering phonon-phonon scattering, normal thermal expansion, and magnetostriction. These measurements together with uniaxial stress experiments would allow one to determine the sign of magnetostriction and an estimation of its magnitude as well. In a more sophisticated treatment the experimental results might provide further information about phonon-magnon coupling, e. g., it should be possible to estimate from the anomalous shift at T_N the derivatives of the exchange integral with respect to the vibrational coordinates of the defect.

ACKNOWLEDGMENTS

We wish to thank Professor A. J. Sievers, Professor J. A. Krumhansl, and Dr. R. L. Melcher for valuable discussions.

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†Work supported by the U. S. Atomic Energy Commission under Contract No. AT(30-1)-2391, Technical Report No. NYO-2391-129. Additional support was received from the Advanced Research Projects Agency through the Materials Science Center at Cornell University, Report No. 1557.

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[1] R. W. Alexander, Jr. and A. J. Sievers in *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite and H. W. Moos (Interscience, New York, 1967).

[2] D. Bäuerle, Bull. Am. Phys. Soc. 16, 312 (1971).

[3] The peak absorption in the 2% sample was only three times that observed in the 0.5% sample.

[4] F. Matossi, J. Chem. Phys. 19, 1543 (1951).

[5] R. J. Elliott, W. Hayes, G. D. James, H. F. MacDonald, and C. T. Sennet, Proc. Roy. Soc. (London) A289, 1 (1965).

[6] H. Bilz, D. Strauch, and B. Fritz, J. Phys. Radium Suppl. 27, C2-3 (1966).

[7] R. W. Alexander, A. E. Hughes, and A. J. Sievers, Phys. Rev. B 1, 1563 (1970).

[8] D. F. Gibbons Phys. Rev. 115, 1194 (1959).

[9] See, e.g., I. G. Nolt and A. J. Sievers, Phys. Rev. 174, 1004 (1968); D. Bäuerle and R. Hübner, Phys. Rev. B 2, 4252 (1970).

[10] J. M. Ziman, Proc. Roy. Soc (London) A226, 436 (1954).

[11] It should be noted that even smaller values of Θ/Θ_D must be used for fitting the temperature dependence of resonant mode linewidths in alkali-halide crystals.