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[16]In the discussion of the general planar Ising models, Hurst and Green [H. S. Green and C. A. Hurst, in *Order-Disorder Phenomena*, edited by I. Preigoine (Interscience, New York, 1964), Sec. 5.3] have considered the same problem from a somewhat different point of view. They considered the simple quartic Ising lattice and introduced at each vertex point a sublattice to generate what is equivalent to our vertex weights. It can be shown that the free-fermion condition (15) is always an identity in their considerations provided that the sublattice introduced at each vertex is planar. The condition (15) therefore also reflects the solubility of planar Ising lattices.
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Elastic Properties of MnF_2 †

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The elastic properties of MnF_2 have been investigated in the temperature range $4.2 < T < 330$ K using a cw transmission technique. The measured values at $T = 300$ K of the six adiabatic elastic constants in units of 10^{11} dyn/cm^2 are $c_{11} = 10.24$, $c_{33} = 16.55$, $c_{44} = 3.185$, $c_{66} = 7.208$, $c_{12} = 7.95$, and $c_{13} = 7.07$. The elastic Debye temperature calculated from the low-temperature elastic-constant data is $\Theta_D(E) = 261.6$ K. Using the force-constant model of Matossi for the rutile structure and the published frequencies of the Raman-active vibrational modes, theoretical values of the elastic constants are calculated and found to be in fair agreement with experiment. Each elastic constant [except $c' = \frac{1}{2}(c_{11} - c_{12})$] shows the expected linear decrease with increasing temperature in the region $T \gtrsim \Theta_D(E)$. On the other hand, c' has not yet reached this limiting high-temperature behavior at $T = 330$ K. The effects on the elastic properties of volume magnetostrictive coupling to the spin fluctuations near the Néel temperature ($T \approx T_N$) and of linear magneto-elastic coupling to the magnetic modes in the antiferromagnetic state ($T < T_N$) are discussed. The elastic constant c_{44} is found to have a component at low temperatures ($T \ll T_N$) decreasing approximately as T^{-1}. This striking phenomenon is discussed on the basis of two possible processes, neither of which provides a completely satisfactory explanation.

I. INTRODUCTION

The study of the propagation of ultrasonic waves in antiferromagnetically ordered media has proven to be a valuable tool for the investigation of a variety of phenomena. Velocity measurements are used to measure the elastic[1,2] and magneto-elastic coupling constants,[3,4] attenuation and velocity measurements are used to study dynamic critical phenomena in the neighborhood of the Néel temperature[5]; anomalies in the elastic properties at the spin-flop transition have been used to study the magnetic phase diagram[6]; and finally, it has been shown that in certain systems resonant nuclear spin-phonon interactions can be studied.[7,8]

In this paper, a systematic study of the elastic properties of MnF_2 is reported. The adiabatic elastic constants associated with longitudinal and transverse ultrasonic propagation along each of the symmetry directions [001], [110], and [100], as well as the nonsymmetry direction perpendicular to the (011) plane have been measured in the temperature region from 4.2 to 330 K. These measurements provide a complete description of the elastic properties of this material.

MnF_2 is an attractive material in which to study

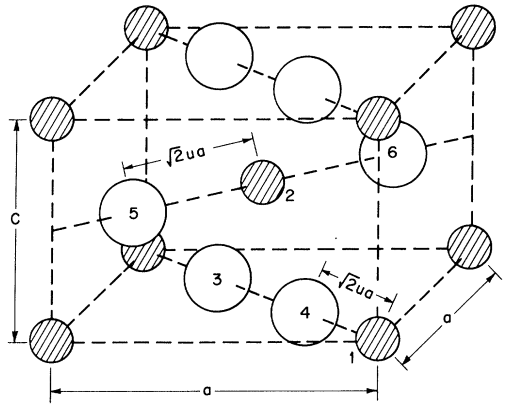

FIG. 1. Rutile structure of MnF_2 showing the six atoms of a unit cell. The solid circles are Mn^{++} ions and the open circles are F^- ions.

the elastic properties for several reasons. It crystallizes with rutile structure (space group D_{4h}^{14}-$P4/mnm$). The tetragonal unit cell (see Fig. 1) containing two MnF_2 molecules has "c" and "a" axis dimensions of 3.3103 ± 0.001 Å and 4.8734 ± 0.0005 Å, respectively, at 298 K. The density (also at $T = 298$ K) is 3.922 ± 0.004 g/cm^3. Each Mn^{++} ion is surrounded by a distorted octahedron of F^- ions. The quantity u which determines the positions of the F^- ions has the value 0.310 ± 0.005. The angle 3-2-4 (see Fig. 1) has the value 76.7°. The distance between atoms 2 and 5 (Fig. 1) is 2.14 Å, while that between 2 and 4 is 2.11 Å.[9]

The magnetic properties of MnF_2 have been extensively studied by a variety of techniques and are believed to be relatively well understood. Below its Néel temperature ($T_N = 67.3$ K) MnF_2 is known to order antiferromagnetically in a simple two sublattice configuration. The c, or [001] axis, is the axis of easy magnetization. The vibrational spectrum and elastic properties of materials with the rutile structure have been of considerable interest in recent years and have been studied extensively using Raman scattering, infrared spectroscopy, and ultrasonic methods.[10-16]

In Sec. II, the samples and the experimental techniques used in the present work are described. Section III is devoted to a presentation of the experimental results which are discussed later in Sec. IV.

II. EXPERIMENTAL

A. Samples and Their Preparation

The two single-crystal samples of MnF_2 (designated 01 and 02) used in the present experiments were approximately in the form of cubes 1 cm on a side.[17] They were of high optical quality. Chemical analysis showed the following impurity content: 0.1–1 ppm of Cr, V, Co, Ni; 1–10 ppm of Ca, Mg, Al, Cu, Na, K; 10–100 ppm of Fe, Si.

The samples were oriented using Bragg angle diffraction x-ray techniques to $\pm 0.15°$ of the desired orientation. Two pairs of surfaces on each sample were then polished flat and parallel to better than $\pm 5 \times 10^{-5}$ cm using Al_2O_3 grit on glass with a 1:1 mixture of H_2O and glycerin serving as carrier.

B. Temperature Measurement and Control

The crystals and temperature sensors were mounted in good thermal contact with a copper holder. The temperature of the holder was maintained constant (typically to ± 0.05 K) with a servo-regulated controller (Artronix Model 5301). Calibrated germanium (Cryocal CR1000) and platinum (Rosemont #118L) resistance thermometers were used for the temperature measurements.

C. Ultrasonic Velocity Measurements

The transmission-type frequency-modulation technique used in the present study for the measurement of ultrasonic phase velocities has been described elsewhere.[18] The measurements reported here were all carried out at a frequency $\nu \simeq 30$ MHz.

Longitudinal and transverse ultrasonic waves were generated and received using resonant X- and AC-cut natural quartz transducers which were bonded to the sample with stopcock grease or silicone transistor grease. The silicone grease provided a more reliable bond at low temperatures.

The thermal expansion data of Gibbons[19] were used to correct for sample length and density changes.

The absolute accuracy of the velocity measurement is about $\pm 1\%$. Each measurement was checked at room temperature using the cw method at both 10 and 30 MHz and with a simple pulse-echo technique at 30 MHz.

D. Calculation of Elastic Constants

The elastic free-energy density of a crystal belonging to the D_{4h}^{14} - $P4/mnm$ space group can be written in terms of six elastic constants c_{ij} and the elastic strains e_{ij} as

$$E = \tfrac{1}{2} c_{11}(e_{xx}^2 + e_{yy}^2) + \tfrac{1}{2} c_{33} e_{zz}^2 + \tfrac{1}{2} c_{44}(e_{xz}^2 + e_{yz}^2) + \tfrac{1}{2} c_{66} e_{xy}^2 + c_{12} e_{xx} e_{yy} + c_{13}(e_{xx} e_{zz} + e_{yy} e_{zz}) . \quad (1)$$

The strains are defined in terms of the elastic displacement field $u_i(\vec{r}, t)$, $i = x, y, z$,

$$e_{ij} = (1 - \tfrac{1}{2}\delta_{ij})\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) . \quad (2)$$

All of the elastic constants except c_{13} can be calculated from the measured phase velocity of pure transverse or pure longitudinal modes propagating

along the symmetry axes of the crystals. In order to calculate c_{13}, measurements must be made of the quasilongitudinal and/or quasitransverse modes obtained from off-axis propagation. The modes studied and the expressions used to calculate the elastic constants are summarized in Table I.

Elastic stability[20] requires that the elastic free-energy density [Eq. (1)] be a positive definite quadratic form in the strains e_{ij}. This imposes the conditions that c_{11}, c_{33}, c_{44}, c_{66}, $c' = \frac{1}{2}(c_{11} - c_{12})$ and $c \equiv c_{33}(c_{11} + c_{12}) - 2c_{13}^2$ are each positive. The latter condition must be used to elimate an extraneous solution when calculating the value of c_{13} from the measured value of either c_{QL} or c_{QT} (see Table I).

III. EXPERIMENTAL RESULTS

The values of the combination of elastic constants at four temperatures, obtained from each of the several elastic modes studied as well as the derived constants c_{12} and c_{13}, are summarized in Table II. The temperature coefficient of each mode at $T = 300$ K defined as $-(\partial/\partial T)[\ln c_{ij}]$ is also given along with the "athermal" values determined by linear extrapolation of the high-temperature data to $T = 0$ K.[21] The temperature coefficient for $c' = \frac{1}{2}(c_{11} - c_{12})$ is not given because the limiting high-temperature behavior has not been reached for this mode at $T = 330$ K (Fig. 2). The elastic Debye temperature $\Theta_D(E)$ is also given at each temperature.

The absolute accuracy of the directly measured elastic constants is $\pm 2\%$ while the derived constants c_{12} and c_{13} have an accuracy of $\sim \pm 4\%$. The significant figures retained in Table II refer to the relative precision of the data, which is considerably higher. Numerous internal consistency checks on the values of the elastic constants are possible from the measured values of the eleven modes given in Table I. Consistency was found in each case to be well within the quoted error.

The calculation of the elastic Debye temperature $\Theta_D(E)$ from the measured values of the adiabatic elastic constants was performed using the tetragonal harmonic method of Betts *et al.*[22] By ignoring all harmonics of degree $l = 8$ or higher, the accuracy of the calculation should be $\approx 2\%$. The number density N/V was taken to be the number density of MnF_2 molecules. The low-temperature value of $\Theta_D(E) = 261.6 \pm 6.0$ K compares to the value $\Theta_D = 253$ K obtained from low-temperature calorimetric measurements.[23]

The temperature dependence of the elastic modes for each propagation direction is presented in Figs. 2–5. In Fig. 6, the low-temperature behavior of c_{33} and c_{44} obtained from propagation along the [001] axis is shown in more detail. Measurements of c_{44} obtained from transverse propagation along the [110] and [100] axes (see

TABLE I. Elastic modes and relationship to elastic constants.

Mode[a]	Sample	Sample length l_S (cm)	ρv^2
$\vec{k}_{long} \parallel [100]$	02	0.939 42	c_{11}
$\vec{k}_{long} \parallel [001]$	01	1.0263	c_{33}
$\vec{k}_{trans} \parallel [001]$	01	1.0263	c_{44}
$\vec{k}_{trans} \parallel [110]$ $\hat{e} \parallel [001]$	01	1.0304	c_{44}
$\vec{k}_{trans} \parallel [100]$ $\hat{e} \parallel [001]$	02	0.939 42	c_{44}
$\vec{k}_{trans} \parallel [100]$ $\hat{e} \parallel [010]$	02	0.939 42	c_{66}
$\vec{k}_{trans} \parallel [110]$ $\hat{e} \parallel [1\bar{1}0]$	01	1.0304	$c' \equiv \frac{1}{2}(c_{11} - c_{12})$
$\vec{k}_{long} \parallel [110]$	01	1.0304	$c_L \equiv \frac{1}{2}(c_{11} + c_{12} + 2c_{66})$
$\vec{k}_{trans} \perp (011)$ $\hat{e} \parallel [100]$	02	1.0716	$c_T \equiv m^2 c_{66} + n^2 c_{44}$ [b]
$\vec{k}_{long} \perp (011)$	02	1.0716	$c_{QL} = \frac{1}{2}\{(c_{11}m^2 + c_{33}n^2 + c_{44}) + [(c_{11}m^2 - c_{33}n^2 + c_{44}(n^2 - m^2))^2 + 4m^2n^2(c_{13} + c_{44})^2]^{1/2}\}$ [b]
$\vec{k}_{trans} \perp (011)$ $\hat{e} \perp [100]$	02	1.0716	$c_{QT} = \frac{1}{2}\{(c_{11}m^2 + c_{33}n^2 + c_{44}) - [(c_{11}m^2 - c_{33}n^2 + c_{44}(n^2 - m^2))^2 + 4m^2n^2(c_{13} + c_{44})^2]^{1/2}\}$ [b]

[a] $\vec{k}_{trans}$ and $\vec{k}_{long}$ are, respectively, the wave vectors associated with transverse and longitudinal propagation. $\hat{e}$ is the polarization vector of the transverse modes.

[b] (l, m, n) are the direction cosines of the wave vector with respect to the [100], [010], and [001] axes, respectively. In MnF_2 at $T = 298$ K and for $\vec{k} \perp (011)$ plane $(l, m, n) = (0, 0.5619, 0.8272)$.

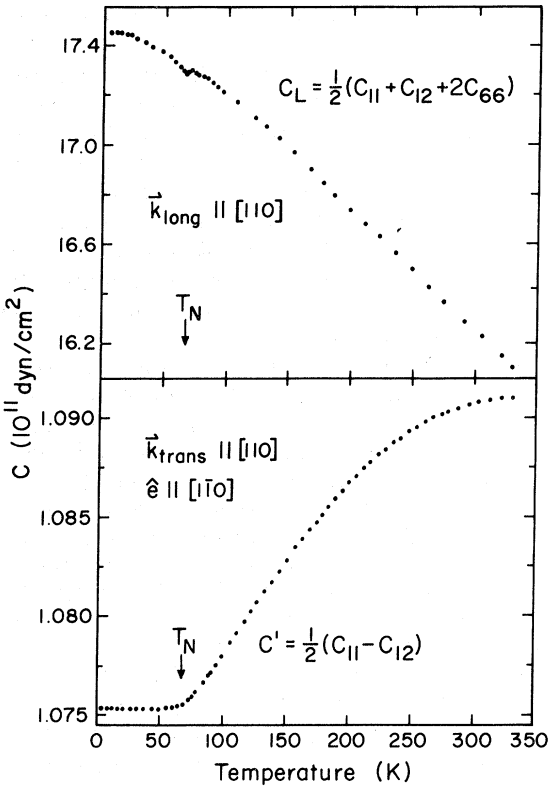

FIG. 2. Elastic constants c_{33} and c_{44} versus temperature, $1.5 < T < 330$ K, $\nu \simeq 30$ MHz, $\vec{k} \parallel [001]$.

Table I) were identical to those obtained from propagation along the [001] axis and are not shown in Figs. 2 and 3.

IV. DISCUSSION

A. Theoretical Elastic Constants

Matossi[10] has proposed a model based on nearest-neighbor interactions to describe the vibrational spectrum of materials with the rutile structure. He defined seven force constants between nearest-neighbor atoms (see Fig. 1) as follows: K_1, Mn-F atoms 2–5, etc.; K_2, Mn – F atoms 2–4, etc., K', F–F atoms 4–3, etc.; K'', F–F atoms 4–5, etc.; d_1, d_2, and d_3 are bond-bending forces at the Mn^{++} and F^- sites. Using the assumptions that $d_3 = 0$ and $K' = K''$, the Raman frequencies measured by Porto *et al.*[15] can be used to determine the constants K_1, K_2, and $K' = K''$. K'' and K_2 are determined by the modes $\omega_3(B_{1g}) = 61$ cm^{-1} and $\omega_5(E_g) = 271$ cm^{-1}. K_1 is then determined by either $\omega_1(A_{1g}) = 341$ cm^{-1} or $\omega_4(B_{2g}) = 476$ cm^{-1}. The value K_1 used in the present calculation is the average of these two values. The force constants obtained in this way in units of 10^5 dyn/cm are $K_1 = 1.03$, $K_2 = 0.369$, $K' = K'' = 0.0964$. The ratio $K_1/K_2 = 2.8 \pm 0.9$ indicates that the Mn – F bond between atoms 2 and 5 (Fig. 1) is significantly stronger than the Mn – F bond between atoms 2 and 4, although the interatomic distance is similar for both types of bonds.

The method outlined by Pandey[11] can be used to express the elastic free-energy density in terms of these force constants and one additional constant ($K = -0.352 \times 10^5$ dyn/cm) describing the nearest-neighbor interaction between Mn^{++} ions along the c axis.[24] Comparing the coefficients of the strains in this expression with those of Eq. (1) results in relations between the force constants and the elastic constants c_{ij}. The theoretical elastic constants thus calculated are compared to the measured values at 300 K in Table III. The agreement between theory and experiment is rather good for the elastic constants c_{11}, c_{33}, c_{66}, and c_{12}. However, the calculated value for c_{44} is 22% high and that for c_{13} is 45% low. The lack of complete agree-

TABLE II. Summary of the elastic properties of MnF_2.

Elastic constant[a]	Temperature (K) 300	200	100	4.2	Athermal[b]	Temperature coefficient at 300 K (10^{-6} K^{-1})
c_{11}	10.24	10.50	10.75	10.92	11.03	258
c_{33}	16.55	16.91	17.20	17.39	17.62	215
c_{44}	3.185	3.201	3.208	3.202	3.237	54.6
c_{66}	7.208	7.442	7.652	7.736	7.918	328
c'	1.091	1.087	1.078	1.075	...	...
c_L	16.25	16.73	17.20	17.45	17.70	297
c_T	4.439	4.519	4.588	4.609	4.679	181
c_{QL}	14.77	15.07	15.32	15.45	15.67	202
c_{QT}	2.985	3.031	3.070	3.130	3.127	158
c_{12}	7.95	8.20	8.47	8.64	...	...
c_{13}	7.07	7.26	7.44	7.46	...	...
$\Theta_D(E)$	259.7	260.6	261.2	261.6	...	...

[a]Values of the elastic constants are in units of 10^{11} dyn/cm^2.
[b]Athermal values are obtained by linear extrapolation of the limiting high-temperature behavior to $T = 0$.

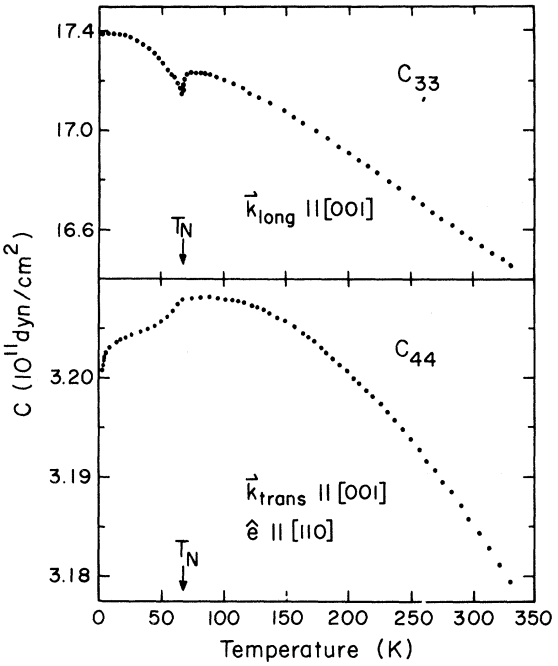

FIG. 3. Elastic constants c_L and c' versus temperature, $4.2 < T < 330$ K, $\nu \simeq 30$ MHz, $\vec{k} \parallel [110]$.

ment is not unexpected, since the calculation can be criticized on several points. As has been pointed out by Porto *et al.*,[15] there exist inconsistencies in the Matossi model of up to 30% when attempts are made to predict the frequency of the optically inactive mode $\omega_2(A_{2g})$ from the observed Raman frequencies. Determination of the force constant K_1 from the individual Raman modes $\omega_1(A_{1g})$ and $\omega_4(B_{2g})$ results in values of 0.70×10^5 dyn/cm and 1.3×10^5 dyn/cm to be compared to the average value of 1.03×10^5 dyn/cm used in the present calculation. Finally, the exclusion of other than nearest-neighbor forces is difficult to justify.

Recent work by Gubanov and Shur[12] and by Shur and Tsarev[13] on the vibrational spectrum of the rutile structure includes the effect of long-range Coulombic and dipolar forces. Unfortunately, data on the infrared active modes of the vibrational spectrum of MnF_2 have not been reported.

B. Temperature Dependence

1. *Paramagnetic Region* ($T > T_N$)

As seen in Figs. 2–5 for $T \gtrsim \Theta_D(E)$, the elastic constants associated with each mode [except $c' = \frac{1}{2}(c_{11} - c_{12})$] decrease linearly with increasing temperature as expected from the very general thermodynamic theory of anharmonic lattices.[21] On the other hand, the mode c' shows quite different behavior (Fig. 3). The decrease in c' as the temperature is lowered ceases at $T \simeq T_N$. However, it is difficult to explain this behavior on the basis of the existence of magnetic order for $T < T_N$. It is known (see Secs. IV B 2 and IV B 3) that this mode couples to the magnetic modes via neither the linear magneto-elastic interaction nor the volume magnetostriction.

In Matossi's model the magnitude of c' is determined solely by the force constant K''. (This is readily seen from the expressions for the elastic constants in terms of the force constants.) On the other hand, the Raman mode $\omega_3(B_{1g})$ is also completely determined by K''.[10] One might hope that the decrease in c' corresponds to a softening of $\omega_3(B_{1g})$. However, $\omega_3(B_{1g})$ is found experimentally to increase from 61 cm^{-1} at $T \simeq 300$ K to $\approx 71\,cm^{-1}$ for $T \lesssim 20$ K.[15]

2. *Critical Region*

Minima in the sound velocity and attenuation maxima in the neighborhood of magnetic phase transition are well documented effects.[5] The results of the present investigation are in qualitative agreement with the results of previous ultrasonic studies in the critical region of MnF_2.[25,26] In particular, the absence of minima in the transverse elastic constants leads to the conclusion that

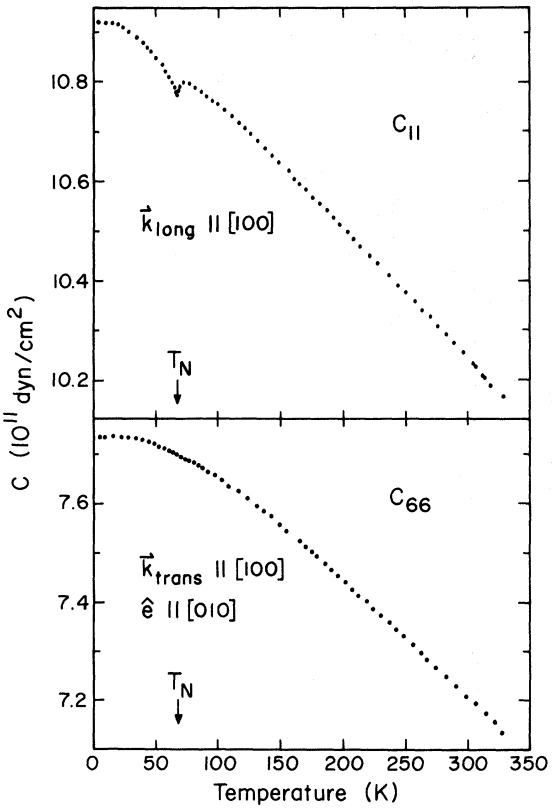

FIG. 4. Elastic constants c_{11} and c_{66} versus temperature, $4.2 < T < 330$ K, $\nu \simeq 30$ MHz, $\vec{k} \parallel [100]$.

TABLE III. Comparison of theoretical and experimental elastic constants.

Elastic constant[a]	c_{11}	c_{33}	c_{44}	c_{13}	c_{66}	c_{12}
Theor	10.9	16.6	3.9	3.9	7.5	7.5
Expt	10.2	16.6	3.2	7.1	7.2	8.0
% diff	+7%	0	+22%	−45%	+4%	−6%

[a]The elastic constants are in units of 10^{11} dyn/cm^2.

the volume magnetostrictive spin-phonon interaction is responsible for the observed minima in the longitudinal modes. Comparison of the magnitude of the effect for the c_{33} mode with that for the c_{11} and c_L modes reveals an anisotropy of about a factor of 3.

3. *Antiferromagnetic State*

In the magnetically ordered state of the system ($T < T_N$) the linear magneto-elastic (LME) interaction couples the elastic waves to the magnetic modes[4] producing an added contribution to the measured elastic constants:

$$c_{ij}^{*} = c_{ij} - \alpha_{ij}\,(2b^2/K). \tag{3}$$

c_{ij}^{*} is the measured elastic constant, c_{ij} is the elastic constant in the absence of LME coupling, b is the LME coupling constant, and K is the magnetic anisotropy constant. The assumption has been made that the LME interaction has uniaxial symmetry rather than the full tetragonal symmetry of the rutile structure (there is, therefore, only one coupling constant). This is a very good approximation for MnF_2. At $T = 4.2$ K in MnF_2, $b = (5.4 \pm 0.5) \times 10^6$ erg/cm^2, and $K = 4.6 \times 10^6$ erg/cm^3.[4] The coefficients α_{ij} are zero for all the elastic modes described in Table I except c_{44}, c_T, c_{QL}, and c_{QT}. In an obvious notation one finds that $\alpha_{44} = 1$, $\alpha_T = n^2 = 0.683$, $\alpha_{QL} = \frac{1}{2}(1+\delta) = 0.766$, and $\alpha_{QT} = \frac{1}{2}(1-\delta) = 0.234$. δ is defined by

$$\delta = \frac{[c_{44} + (c_{11}m^2 - c_{33}n^2)(n^2 - m^2) + 4m^2n^2c_{13}]}{[(c_{11}m^2 - c_{33}n^2 + c_{44}(n^2 - m^2))^2 + 4m^2n^2(c_{13} + c_{44})^2]^{1/2}}. \tag{4}$$

The temperature dependence of both b and K can be assumed to be roughly proportional to the square of the sublattice magnetization. Since $\alpha_{ij} \lesssim 1$ and $(2b^2/K)_{max} \simeq 10^7$ dyn/cm^2, the coupling term is expected to be observable only as it affects the temperature dependence of the elastic constants and then only in favorable circumstances.

Figures 2 and 6 clearly show an abrupt change in slope of elastic constant c_{44}^{*} versus T, for T just below T_N caused by the coupling term $-(2b^2/K)$. The sharp decrease in c_{44}^{*} at lower temperatures will be discussed below. The effect on c_{QL}^{*} is obscured by the minimum at $T \simeq T_N$ discussed in the Sec. IV B 2, while the effect on c_T^{*} is barely

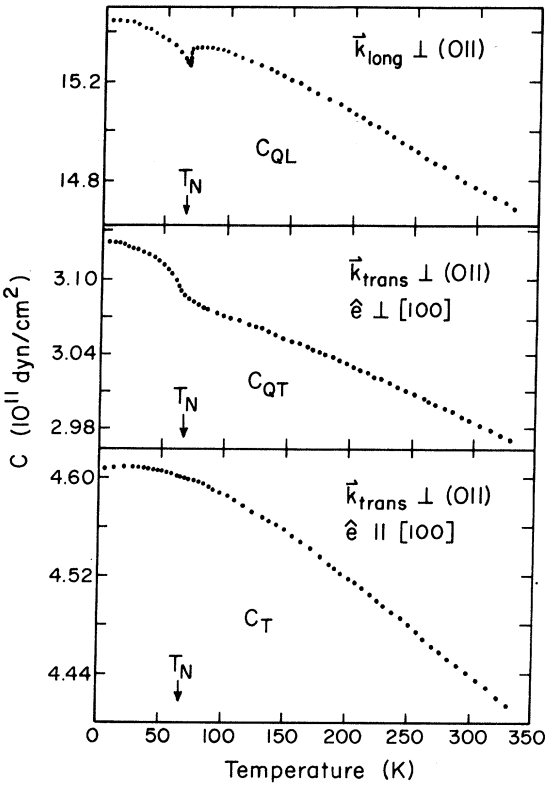

FIG. 5. Elastic constants c_{QL}, c_{QT}, and c_T versus temperature, $4.2 < T < 330$ K, $\nu \simeq 30$ MHz, $\vec{k} \perp (011)$ plane.

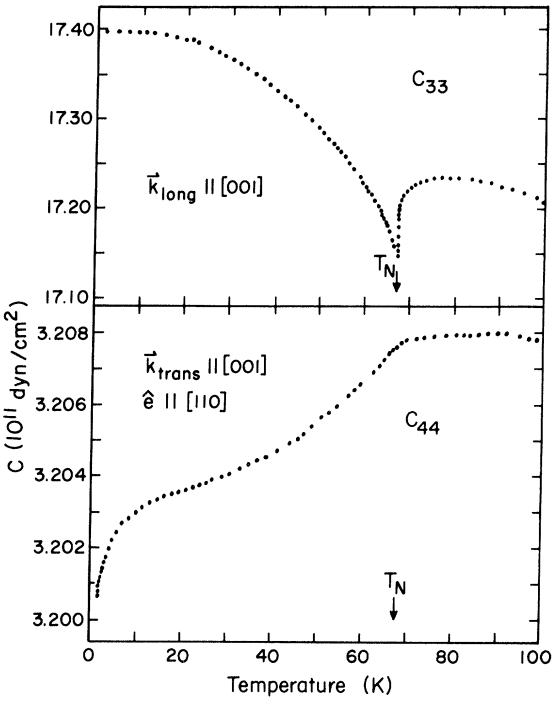

FIG. 6. Elastic constants c_{33} and c_{44} versus temperature, $1.5 < T < 100$ K, $\nu \simeq 30$ MHz, $\vec{k} \parallel [001]$.

perceptible. On the other hand, c^*_{QT} unexpectedly shows a positive increase at $T \simeq T_N$, which cannot be explained by the LME theory. The behavior of c^*_{QT} is quite similar to that observed for the c_{44} mode in cubic $RbMnF_3$,[2] but is not at present understood.

Somewhat more surprising is the decrease in c_{44} (approximately proportional to T^{-1}) as the temperature is lowered further (see Figs. 2 and 6). The LME theory is incapable of explaining this phenomenon; for $T \ll T_N$, both b and K are essentially independent of temperature. Similarly, for $T \ll \Theta_D$ the c_{ij} themselves must be temperature independent.

Since the only physical quantity in the material which has a T^{-1} temperature dependence at low temperatures is the nuclear-spin susceptibility, it is tempting to attribute the effect to a coupling of the elastic mode to either the Mn^{55} or F^{19} spin systems. It can be shown[27] that the magnon-coupled nuclear spin-phonon interaction[28] will make a contribution to c^*_{44} of the form

$$-2(AbM_0/K)^2 \chi_N(T)[\omega^2/(\omega_0^2 - \omega^2)] , \qquad (5)$$

where A is the hyperfine constant, M_0 is the electronic sublattice magnetization, $\chi_N(T) \sim T^{-1}$ is the nuclear-spin susceptibility, ω is the frequency, and ω_0 is the nuclear Larmor frequency as determined by the hyperfine field. Of the modes propagating along symmetry axes of the crystal only c_{44} will be coupled to the nuclei. However, order-of-magnitude estimates indicate that this contribution is 6–8 orders of magnitude too small to account for the experimentally observed behavior of c^*_{44}. Other types of coupling mechanisms can be estimated to be much weaker still.

Another possible explanation is that the phenomenon results from the relaxation of anelastic defects.[29] This possibility is difficult to eliminate but it should be noted that there is no defect whose symmetry is allowed by the rutile structure which would couple to only the c_{44} mode. The coupling to other modes, however, may be very weak for reasons other than those based on symmetry alone.

Experiments are presently being carried out at lower temperatures and at higher frequencies with the hope that these measurements will result in some insight into the origin of this interesting effect.

Note added in proof. Henderson, Meyer, and Guggenheim (private communication) have recently found a low-temperature calorimetric Debye temperature of 255 ± 3 K in MnS_2.

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[24]Reference 11, Eq. (5) is incorrect as written. In the notation of Ref. 11 the correct expression is

$$U = \tfrac{1}{2}K_1[\Delta r^2_{1,2} + \Delta r^2_{1,3} + \Delta r^2_{10,14} + \Delta r^2_{10,16}] K[\Delta r^2_{1,4} + \Delta r^2_{1,5} + \Delta r^2_{10,2} + \Delta r^2_{10,12}] + \tfrac{1}{2}K'[\Delta r^2_{2,12} + \Delta r^2_{4,6}] + K''[\Delta r^2_{2,4} + \Delta r^2_{2,5} + \Delta r^2_{2,6} + \Delta r^2_{2,7} + \Delta r^2_{2,13} + \Delta r^2_{2,14} + \Delta r^2_{2,15} + \Delta r^2_{2,16}] + \tfrac{1}{2}K[\Delta r^2_{1,8} + \Delta r^2_{1,9}].$$

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