Ultrasonic Attenuation and Mechanism for the 250°K Antiferrodistortive Transition in $BaMnF_4$ †

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Critical attenuation measurements are reported for two anomalous acoustic modes near the 250°K transition of $BaMnF_4$. A mechanism for the transition involving rotations of the MnF_6 octahedra about the orthorhombic b axis is proposed, with a pair of phonons at the Brillouin zone S points $\pi(0, 1/b, \pm 1/c)$ being the soft modes. This mechanism, which suggests strong two-dimensional correlations, appears consistent with previous work on $BaMnF_4$ as well as with the ultrasonic data.

I report here measurements of ultrasonic attenuation in the vicinity of the 250°K antiferrodistortive transition of $BaMnF_4$. These yield the first determination of critical attenuation exponents for an antiferrodistortive transition in a material not of the perovskite structure and thus provide a new test of recent general theories of ultrasonic anomalies associated with this important class of structural phase transitions. I also present a proposed mechanism for the transition which appears consistent with the experimental work done so far on $BaMnF_4$. In particular, this mechanism suggests critical fluctuations which are strongly correlated in two dimensions, and this provides an explanation for the observed longitudinal-mode attenuation exponent being significantly larger than in the perovskites.

The 250°K transition was first observed in ultrasonic attenuation studies by Spencer, Guggenheim, and Kominiak.[1] Ryan and Scott[2] investigated the transition by Raman scattering and showed that it is antiferrodistortive and involves a doubling of the unit cell. Recently the author[3] reported ultrasonic velocity measurements for the pure modes propagating along the principal axes and showed that there are sharp velocity dips for the longitudinal mode propagating along the c axis (v_{cc}) and for the shear mode propagating along the c (or b) axis and polarized along the b (or c) axis ($v_{cb}=v_{bc}$). There has not been a direct experimental determination of the structure of the low-temperature phase, so that the actual mechanism of the transition is not established.

In the present work the attenuation of the two modes with sharp velocity anomalies was measured by the pulse-echo technique for temperatures between 190 and 300°K. Within about 0.5°K of the transition the data exhibit rounding effects, presumably due to sample imperfections.[4] Data were obtained at frequencies between 14 and 90 MHz. For the shear mode (α_{cb}) data were obtained and analyzed both above and below the transition temperature T_0. For the longitudinal mode (α_{cc}) the data could only be analyzed above T_0 because of domain effects below T_0.

Typical critical attenuation data are shown in Fig. 1, which is a log-log plot of the longitudinal-mode critical attenuation versus reduced temperature ϵ for $T>T_0$. The critical attenuation exponent η defined by $\alpha=A(\omega)\epsilon^{\eta}$ is $\eta=\eta_{cc}{}^{>}=2.2\pm0.3$. The frequency dependence $A(\omega)$ of the attenuation (at fixed temperature) does not appear to follow

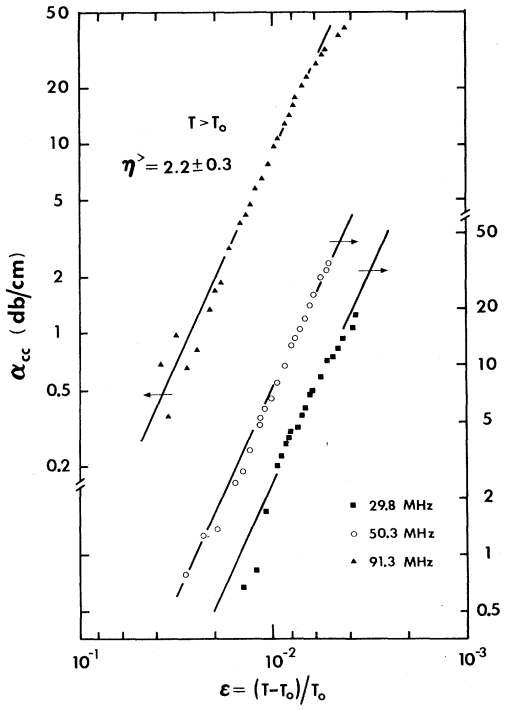

FIG. 1. Critical attenuation data for the longitudinal C_{33} mode.

a simple power-law dependence; however, the data are not conclusive in this regard, because of the limited frequency range.[5] For the shear mode above T_0 the critical attenuation exponent is $\eta_{cb}^{>} = 3.9 \pm 0.1$, and the frequency dependence appears quadratic. The critical attenuation exponent below T_0 has an unusually large value of $\eta_{cb}^{<} = 5.7 \pm 0.3$, with the frequency dependence being unusually weak, i.e., $A(\omega) \sim \omega^{0.8}$.

The results of the various experiments done on $BaMnF_4$ impose strict constraints on the possible mechanism for the 250°K transition. These are most easily understood by referring to the a-axis projection of the room-temperature structure shown in Fig. 2.[6] The structure consists of layered sheets of linked MnF_6 octahedra with the layer planes normal to the b axis, and with the Ba atoms between the layers. The space group is $A2_1am$, so that the lattice is base-centered orthorhombic, with the centered faces being in the b-c plane shown in Fig. 2. The primitive translations of $(0, b/2, \pm c/2)$ join equivalent sites in adjacent layer planes.

Low-temperature antiferromagnetic-resonance and NMR studies[7] have recently shown the presence of a weak ferromagnetic moment in the antiferromagnetic phase that exists below $T_N \approx 25$°K. This moment can be produced only if the 250°K transition causes the reflection symmetry normal to the c axis to be destroyed. X-ray diffraction experiments have been unsuccessful in detecting a structural change at the transition.[8] These two facts suggest that the transition mechanism might involve small, rigid (or nearly rigid) rotations of the MnF_6 octahedra about the a or b axis: The small displacements of the weakly scattering F atoms produced by such a rotation might not be detected by x-ray diffraction.

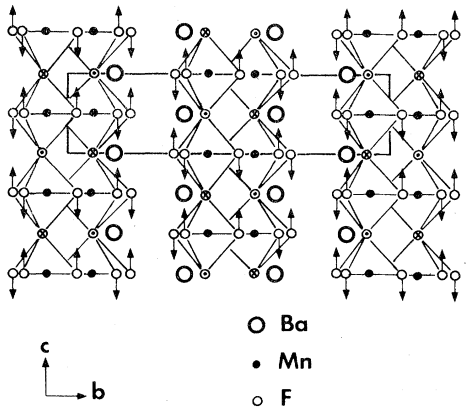

FIG. 2. a-axis projection of the $BaMnF_4$ structure (after Keve, Abrahams, and Bernstein, Ref. 6). Arrows indicate the proposed displacement pattern for $T < T_0$.

The mechanism I propose for the transition is suggested by the atomic displacements indicated by arrows in Fig. 2. This mechanism involves rotations of the MnF_6 groups about the b axis, with the sign of the rotation angle alternating for adjacent groups within a layer plane and also along $(0, b/2, -c/2)$ but not for adjacent groups along $(0, b/2, +c/2)$. An energetically equivalent distortion would have the intraplanar "antiparallel" ordering direction along $(0, b/2, +c/2)$. Because adjacent octahedra within a layer plane are tightly linked, we expect that the critical order-parameter fluctuations should be much more strongly correlated within the planes than between them. The symmetry of the structure produced by this distortion is monoclinic (pseudo-orthorhombic) with space group $P2_1$ (point group C_2). This symmetry allows displacements of the Ba and Mn atoms from their original positions, e.g., by a shearing of the lattice in the b-c plane. We will assume, with partial justification given below, that these displacements are extremely small, and possibly not detected in the x-ray measurements.

For the present model of the transition the soft phonon modes are a pair of degenerate modes at the S points $\pi(0, 1/b, \pm 1/c)$ of the Brillouin zone. We will denote the coordinates of these modes as Q_1 and Q_2. The part of the free energy that depends on only Q_1 and Q_2 has the following form[9]:

$$U(Q_i) = U_0(T) + \tfrac{1}{2}a(T)(Q_1^2 + Q_2^2) + \tfrac{1}{4}b_1(Q_1^4 + Q_2^4) + \tfrac{1}{2}b_2 Q_1^2 Q_2^2. \quad (1)$$

For $a(T) > 0$ the equilibrium of the system is at $Q_1^0 = Q_2^0 = 0$, while for $a(T) < 0$ there are two possible situations depending on the relative magnitudes of b_1 and b_2.

Solution A.—For this case we have

$$Q_1^0 = [-a(T)/b_1]^{1/2}, \quad Q_2^0 = 0 \quad (2)$$

or a symmetrical result obtained by interchanging Q_1^0 and Q_2^0. This solution is stable for $b_2 > b_1 > 0$.

Solution B.—Here we have

$$Q_1^0 = \pm Q_2^0 = \pm[-a(T)/(b_1 + b_2)]^{1/2}, \quad (3)$$

and the solution is stable for $|b_1| > |b_2|$ with $b_1 > 0$.

Solution A corresponds to the present microscopic picture of the transition, and we will assume that this is the stable solution. The dynam-

ics of the soft-mode system may be treated phenomenologically[10] by expressing the kinetic energy as $K=\frac{1}{2}I(\dot{Q}_1^2+\dot{Q}_2^2)$, where I is a generalized mass (moment of inertia), and solving linearized Lagrange equations. For $T>T_0$ we obtain two soft modes with (degenerate) frequencies ω_0 given by

$$\omega_0^2=a(T)/I. \tag{4}$$

For $T<T_0$ we have two soft modes with frequencies ω_1 and ω_2 where

$$\omega_1^2=-2a(T)/I$$

and (5)

$$\omega_2^2=-a(T)(b_2-b_1)/b_1I.$$

To discuss the effect of the soft-mode system on ultrasonic propagation it is necessary to include strain variables, which we treat phenomenologically as has been done for the perovskites by other investigators.[9,11-13] If we denote the (symmetrized) strains as x_i $(i=1,2,\ldots,6)$, the form of the interaction energy allowed by symmetry is

$$U(Q_i,x_i)=\tfrac{1}{2}(\beta_1x_1+\beta_2x_2+\beta_3x_3)(Q_1^2+Q_2^2)+\tfrac{1}{2}\beta_4x_4(Q_1^2-Q_2^2). \tag{6}$$

Thus the compressional strains along the three principal axes a, b, and c as well as the b-c shear strain couple to the soft modes. The purely elastic part of the free energy involving the coupled strains only is

$$U(x_i)=\tfrac{1}{2}(C_{11}x_1^2+C_{22}x_2^2+C_{33}x_3^2+C_{44}x_4^2)+C_{12}x_1x_2+C_{13}x_1x_3+C_{23}x_2x_3. \tag{7}$$

To minimize the total free energy, which is the sum of Eqs. (1), (6), and (7), the usual procedure[11] of first minimizing with respect to the strain variables and then eliminating the strains and minimizing with respect to the Q_i may be followed. Two main results are obtained: First, spontaneous strains x_i^0 $(i=1,2,3,4)$ are induced in the low-temperature phase with magnitudes proportional to the square of the order parameter; secondly, the results of Eqs. (2), (3), and (5) are modified slightly, because the coefficients b_1 and b_2 are effectively renormalized by the strain interaction for $T<T_0$. As an example of the first effect, the spontaneous strain x_4^0 is $x_4^0=-\beta_4(Q_1^0)^2/2C_{44}$. It is to be expected that β_4 is small, as it involves forces between rotating octahedra in different layer planes, and this may explain why x_4^0 has not been observed by x-ray diffraction. The expressions for the other spontaneous strains are somewhat complicated and will not be given. The small renormalization effects mentioned above are not important for the present purposes.

Ultrasonic anomalies are usually discussed in terms of two distinct mechanisms.[12] The first, the resonance interaction, is simply the effect of terms of the form $Q_i^0\delta x_j\delta Q_k$ in the expansion of the free energy about equilibrium for $T<T_0$. This effect causes step discontinuities in the elastic constants at the transition and an attenuation in the ordered phase which peaks just below T_0. The discontinuities in the elastic constants for the present model are given by

$$\Delta C_{ii}=\beta_i^2/2b_1, \quad i=1,2,3,4. \tag{8}$$

Experimentally, only ΔC_{33} is observed to have a large step at T_0. Since all three strains x_1, x_2, and x_3 are of the same symmetry (A_1), it follows that either all or none of C_{11}, C_{22}, and C_{33} are allowed to have discontinuities, independent of the model used for the transition, so that ΔC_{11} and ΔC_{22} must be nonzero but much smaller than ΔC_{33}. Possible evidence for small steps in C_{11} and C_{22} can be seen in Ref. 3. No significant step is observed in C_{44} at T_0, and this may be another indication that β_4 is small.

The second kind of effect expected in the ultrasonic experiments is due to the fluctuation interaction and is caused by terms of the form $\delta x_i\delta Q_j\times\delta Q_k$. This mechanism contributes in both phases and produces sharp velocity dips at T_0 and strong attenuation anomalies both above and below T_0. We expect anomalies of this type for the principal strains x_i with $i=1,2,3,4$. No significant effect is observed for $i=1,2$ but again this does not indicate a fault in the model, as x_1, x_2, and x_3 have the same symmetry. Apparently the fluctuation interaction for the x_3 and x_4 modes is strong in $BaMnF_4$, as the velocity dips are quite large.

Theoretical approaches used to describe ultrasonic attenuation at antiferrodistortive transitions include phenomenological,[12] microscopic,[14] mode-mode coupling,[15] and most recently ϵ-expansion[16] methods. In any approach it is necessary to account correctly for the dimensionality of the fluctuations, the dispersion and damping of the soft zone-boundary phonons, and the effect of any central peak component. Because of theoretical uncertainties, and because the present proposed mechanism has not been tested, it would be premature to make an extensive critical

comparison of the $BaMnF_4$ exponents with the various theoretical results. Therefore, the discussion will be limited to a brief comparison of the present experimental results with the recent theoretical results obtained by Murata[16] using ϵ-expansion techniques. Murata's calculations give critical attenuation exponents for $T > T_0$ for several possible physical situations. For an overdamped or central-peak soft-mode response, the calculations are in good agreement with the experimental $BaMnF_4$ results for the case of a two-component order parameter with two-dimensional fluctuations, as expected from the present proposed model. The calculated exponents are $\eta_{cc}{}^{>} = 2.2$ and $\eta_{cb}{}^{<} = 3.5$. The larger value of $\eta_{cc}{}^{>}$ compared to the value of ≈ 1.3 for the C_{11} mode in $SrTiO_3$[12] and $KMnF_3$[17] (where the fluctuations are three-dimensional) thus appears to support the idea of a transition mechanism involving critical fluctuations that are strongly correlated in two dimensions.

In conclusion, it appears that the present proposed model for the transition is consistent with the work done to date on $BaMnF_4$. Neutron scattering measurements on this crystal would be useful, both to test directly the proposed transition mechanism and to investigate the soft-mode dynamical response characteristics.

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