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Brillouin scattering spectra are reported and analyzed for the layered perovskite compound $(CH_3NH_3)_2FeCl_4$. Particular attention has been given to successive phase transitions in this system: $D_{4h}^{17} \leftrightarrow D_{2h}^{18} \rightleftarrows D_{4h}^{16}$. It is found that the elastic constant c_{66} is the major contributor to instabilities in this system. A two-dimensional order parameter at the Brillouin zone boundary X point is introduced into the Landau free-energy to account for this sequence of transitions. An additional secondary instability (one-dimensional order parameter) at the Z point is used to generate the $D_{2h}^{18} \rightleftarrows D_{4h}^{16}$ phase transition: inclusion of the two order parameters circumvents the need for postulating a D_{2h}^{10} phase between the D_{2h}^{18} and D_{4h}^{16} phases and for higher order temperature dependent terms in the free energy expansion. The $D_{4h}^{17} \leftrightarrow D_{2h}^{18}$ phase transition is characterized by a strong Landau–Khalatnikov contribution to c_{66} and a large dynamical critical behavior.

I. INTRODUCTION

Methyl ammonium iron chloride $(CH_3NH_3)_2FeCl_4$, (MAFeCl) possesses a perovskite layer structure which consists of infinite sheets of corner sharing divalent transition metal–halogen octahedra.[1] The crystal exhibits quasi-two-dimensional antiferromagnetic ordering in the (001) plane[2] but weak ferromagnetic ordering along the [001] direction below 93 K.[3] In addition to the magnetic transition at low temperature, this system also possesses successive structural phase transitions. These have been studied by means of lattice dynamics and far infrared spectroscopy,[4] birefringence, x-ray, and neutron diffraction,[5] specific heat and ultrasonic sound velocity measurements,[6] and ultrasonic attenuation measurements.[7]

The sequence of successive phase transition is quite unusual in general, although common throughout the series[1,8]

$$D_{4h}^{17}(I4/mmm) \underset{z=1}{\overset{333\text{ K}}{\underset{2\text{nd order}}{\leftrightarrow}}} D_{2h}^{18}(Cmca) \underset{z=2}{\overset{234\text{ K}}{\underset{1\text{st order}}{\rightleftarrows}}} D_{4h}^{16}(P4_2/ncm). \quad z=4$$

According to a group theoretical analysis of the successive phase transitions in $(CH_3NH_3)_2MCl_4$ (with M = Mn and Cd),[9–12] this sequence can be explained by successive freezings of a two dimensional order parameter at the Brillouin zone boundary X point (D_{2h} symmetry) of the D_{4h}^{17} high symmetry high temperature "parent" phase. The star of the wave vector at the X point contains two arms—$\mathbf{k}_{x1} = (00\frac{1}{2})$ and $\mathbf{k}_{x2} = (\frac{1}{2}-\frac{1}{2}0)$. The two dimensional order parameter (η_1,η_2) transforms according to the small representations of the group of the wave vector (little group) $X_2^+(B_{2g})$ for η_1 at X_1 and $X_4^+(B_{3g})$ for η_2 at X_2. The Landau free energy expression in terms of η_1 and η_2 is given in Ref. 12.

The D_{4h}^{17} phase is described by the trivial solutions $\eta_1 = \eta_2 = 0$. The solutions with $\eta_1 \neq 0$ $\eta_2 = 0$ and $\eta_1 = 0$ $\eta_2 \neq 0$ lead to the D_{2h}^{18} phase and account for twin domains which are, more precisely, ferroelastic if the strain e_6 is included in the Landau free energy.[9] The coordinate system for the D_{2h}^{18} phase is rotated by 45° about the D_{4h}^{17} fourfold axis. Since only one arm of the star is involved in this second order phase transition, the unit cell size is expanded by only a factor of 2.

Solutions with $\eta_1 = \eta_2 \neq 0$ and $\eta_1 = -\eta_2 \neq 0$ lead to the D_{4h}^{16} phase. These solutions correspond to antiphase domains. The D_{4h}^{16} phase is nonferroelastic. The tetragonal unit cell is primitive, with a coordinate system rotated by 45° with respect to the high temperature D_{4h}^{17} coordinate system. Since, in this case, both arms of the star of $\mathbf{k}$ are involved in the phase transition, the unit cell is fourfold expanded with respect to the D_{4h}^{17} parent phase unit cell.

Goto *et al.*[6] have measured ultrasonic velocities between 4.2 and 400 K in this crystal. They found a large critical softening of the c_{66} elastic constant in the D_{4h}^{17} phase. Assuming a simple power law behavior, they obtain 0.42 as the critical index of this softening. The c_{66} elastic constant is related to a TA mode which propagates along the [100] direction and is polarized along the [010] direction in the D_{4h}^{16} phase.

The same TA mode (c_{66} governed) also exhibits almost complete softening around the $D_{2h}^{18} - D_{4h}^{16}$ phase transition as the temperature approaches the transition temperature in the D_{4h}^{16} (low temperature) phase. This c_{66} elastic constant in the D_{4h}^{17} phase becomes the $(c_{11} - c_{12})/2$ constant in the D_{4h}^{16} phase due to the 45° axis rotation mentioned above. For simplicity of the discussion, every elastic constant in the D_{2h}^{18} and D_{4h}^{16} phase will be labeled by the elastic constants of the D_{4h}^{17} phase.

This softening can be well fit by a mean field type behavior given as

$$c_{66} = c_{66}^0(T_c - T)/(T_\theta - T),$$

in which T_c is the actual transition temperature and T_θ is a bare transition temperature. Such temperature dependence is typically a consequence of bilinear coupling between an

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order parameter and an elastic strain. Unfortunately, it is not possible to detect the ultrasonic pulse echo in the D_{2h}^{18} phase because the pulse is strongly scattered by the ferroelastic domain structure.

The other elastic constants of MAFeCl behave normally except for c_{44} which only slightly decreases as temperature decreases above the magnetic phase transition.

The specific heat anomaly in the vicinity of the $D_{4h}^{17} - D_{2h}^{18}$ phase transition has also been measured.[6] The specific heat behavior can be fit to a logarithmic form in both phases

$$\Delta c \sim \log|T - T_c| \sim |T - T_c|^{-\alpha}, \quad \alpha \simeq 0.$$

These results on the c_{66} elastic constant and the specific heat in the D_{4h}^{17} phase have been analyzed by renormalization group techniques for the three-dimensional $X - Y$ model. Reasonable agreement between theory and experiments obtains.

Yoshizawa *et al.*[7] measured ultrasonic attenuation between 5 and 70 MHz in the D_{4h}^{17} phase for the [100] *TA* mode; critical attenuation as a function of temperature and frequency has been observed. Assuming a simple Debye relaxator frequency dependence, the characteristic relaxation time of the order parameter fluctuations as a function of temperature can be expressed as

$$\tau \sim 0.92\left(\frac{T - T_c}{T_c}\right)^{-1.40} \times 10^{-14}\ \text{s}.$$

Within a few degrees of the transition temperature, the relaxation time becomes long, greater than 10^{-10} s, as a result of the critical slowing down of the fluctuations. However, for these experiments it is still the case that the overall processes are fast compared to the experimental frequency, $\omega\tau \ll 1$.

The Brillouin scattering method provides for measurements in a different regime; i.e., $\omega\tau \sim 1$. Hence, the elastic constant c_{66} obtained by the Brillouin scattering technique should be predictably different from that derived from the ultrasonic results. The situation may be similar to that found for ammonium chloride[13] in which case a frequency dependent critical anomaly has been reported for the order–disorder phase transition.

Brillouin scattering studies of the similar phase transitions in $(CH_3NH_3)_2MnCl_4$ (MAMnCl) and $(C_2H_5NH_3)_2MnCl_4$ (EAMnCl) have been reported by Kärä-jämäki *et al.*[14] Ultrasonic results for MAMnCl are very similar to the MAFeCl results.[15,16] Although the Brillouin results confirm the c_{66} softening $[(c_{11} - c_{12})/2$ in their notation] in the D_{4h}^{16} phase, the c_{66} elastic constant in the D_{2h}^{18} and D_{4h}^{17} phases has not been reported. In addition to the critical softening, the nearly complete c_{66} softening at the $D_{4h}^{16} - D_{2h}^{18}$ phase transition and the mean field type behavior in the D_{4h}^{16} phase are unique because this phase transition is actually not a symmetry related one. A soft mode which can bilinearly couple to the *TA* mode cannot be expected and the phase transition should be strongly first order. Such softening in the D_{4h}^{16} phase is a common feature of the methyl ammonium compounds but is not found in the other crystals. Recent studies of the phase transition in EAFeCl by Suzuki *et al.* do not evidence this softening, although the critical softening in the D_{4h}^{17} phase has been confirmed.[17]

Two possibilities have been proposed to explain this $D_{4h}^{16} - D_{2h}^{18}$ softening behavior for the c_{66} governed mode: temperature dependences of the Landau free energy expansion coefficients other than the usual quadratic one,[15] and an intermediate phase between the D_{2h}^{18} phase and the D_{4h}^{16} phase.[16] Based on group theoretical considerations, the intermediate phase should possess a D_{2h}^{10} (Pccn with $Z = 4$) space group.[10–12] Goto *et al.*[6] tried to detect the D_{2h}^{10} phase under hydrostatic pressure up to 6 kbar using the ultrasonic technique. They only observed a decrease of the transition temperature at both transitions. To the best of our knowledge, the existence of the D_{2h}^{10} phase has not beeen experimentally confirmed and the origin of the c_{66} softening at the $D_{4h}^{16} - D_{2h}^{18}$ phase transition has not as yet been elucidated.

In order to understand the origin of the c_{66} softening and the correct sequence and number of phase transitions for this system, it is essential to establish the c_{66} elastic constant behavior in the D_{2h}^{18} phase. In this report, we will present Brillouin scattering results for MAFeCl and the temperature dependence of the c_{66} elastic constant between 345 and 50 K covering the $D_{4h}^{17} - D_{2h}^{18} - D_{4h}^{16}$ phase transitions.

II. EXPERIMENTAL PROCEDURES

The Brillouin scattering apparatus, including temperature control and measurement, used in this experiment has been reported previously.[18] An oven has been prepared for the high temperature (290–350 K) studies reported. The oven consists of three parts—a plastic cylinder, a copper cylinder wrapped with heating wire, and a copper block for sample mounting. Samples are affixed to the copper block using G. E. varnish 7031 and then placed in the copper cylinder which is sealed. Finally, the plastic cylinder is sealed to minimize thermal perturbation. The temperature of the oven is controlled with a proportional controller with a thermistor sensor to within ± 0.1 K. Sample temperatue is measured with a copper–constantan thermocouple placed just above the sample. Temperature fluctuations and drift are less than $\pm 2\,\mu$V for a data accumulation time of 30 min. to 1h.

Single crystals of MAFeCl have been provided by Dr. T. Goto and Professor T. Fujimura of Tohoku University. These ocher colored crystals are platelets of $\sim 5 \times 5 \times 2\text{mm}^3$ and are usually covered with clay colored powder which can be removed with methanol. Crystals are readily cleaved along the largest crystal surface [the (001) face]. Under a polarizing microscope, the crystals show clear domain structure even at room temperature. Observation of this domain structure allows an easy determination of crystal axes in the D_{4h}^{17} phase. Since the crystals are easily cleaved and quite soft, a sharp razor blade is used to cut the sample under the polarizing microscope. The prepared surfaces for right angle scattering are carefully polished using methanol wet lens tissue or Q-tips.

The laser employed in these studies is a Spectra Physics Model 165 argon ion laser operating at 5145 Å in a single cavity mode. Since a fairly large sample heating effect (~ 1 K/5 mW) has been observed, power at the sample did not

exceed more than 5 mW. Relatively strong Brillouin signals could be observed with such low power with 500 accumulations. A 25 point smoothing program is used to obtain well-defined Brillouin spectra of good signal to noise ratio. Unfortunately, the crystals show a bright path about the laser beam propagation direction; this causes a very strong Rayleigh component in the Brillouin spectra.

Free spectral ranges of 28, 35.5, and 40 GHz are used to analyze the Brillouin spectra with a typical finesse of 45 for a triple pass optical system.

III. RESULTS

Figure 1 presents five phonon frequencies in three directions as a function of temperature from 30 to 345 K. As can be seen from this figure, the [110] *LA* mode and the [101] *TA* mode exhibit similar and remarkable temperature dependence—softening in the D_{4h}^{16} phase, large discontinuity ($\sim$2 GHz) at the $D_{2h}^{18} - D_{4h}^{16}$ phase transition, and softening above 270 K in the D_{2h}^{18} phase. The [110] *LA* mode spectra are very similar to those of the [100] *LA* mode in MAMnCl.[14] (Note that their coordinate system is 45° rotated from that employed in this work.)

Elastic constants which govern the [110] *LA* mode and the [101] *TA* mode are $c_{66} + (c_{11} + c_{12})/2$ for the [110] *LA* mode and $(c_{44} + c_{66})/2$ for the [101] *TA* mode. The [100] *TA*-mode frequency is governed by the elastic constant c_{44} and it exhibits only a monotonic and weak decrease in frequency as temperature is decreased. Therefore, the observed behavior of these two modes, the *LA* [110] mode and the *TA* [101] mode, may be attributed to the c_{66} elastic constant.

The [101] *TA*-mode intensity rapidly decreases and its width exhibits anomalous broadening about 310 K, as shown in Fig. 2. The phonon peak can no longer be observed in the 317.5 K spectrum. Above this temperature, the phonon peak is absent, even in the D_{4h}^{17} phase. Figure 3 shows the temperature development of the [101] *TA*-mode Brillouin spectrum around the $D_{2h}^{18} - D_{4h}^{16}$ phase transition temperature. This mode abruptly changes in both peak position (7→4.5 GHz) and intensity ($\sim$10 times stronger just below the transition temperature) at the $D_{2h}^{18} - D_{4h}^{16}$ phase transition. The phonon intensity rapidly decreases as the temperature decreases in the D_{4h}^{16} phase and is finally zero below 90 K.

Figure 4 shows the temperature development of the [110] *LA*-mode spectrum around the $D_{2h}^{18} - D_{4h}^{16}$ phase transition. A spectrum obtained at 229 K clearly reveals a two phase coexistence associated with a first order transition.

The Brillouin shift in an anisotropic crystal is given by[19]

$$\Delta\nu_B = \pm\frac{v}{\lambda_0}(n_i^2 + n_s^2 - 2n_i n_s \cos\theta_s)^{1/2}$$

in which v is the sound velocity, λ_0 is the wavelength of the incident beam, and θ_s is the scattering angle. Refractive indices n_i and n_s are defined in the direction of the incident and scattered beams and depend not only on the scattering

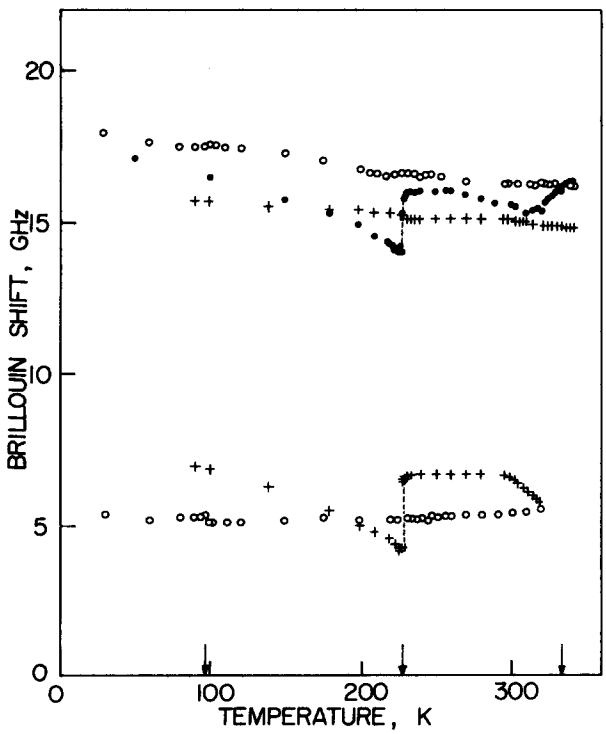

FIG. 1. Temperature dependence of the acoustic phonon frequencies obtained in three phonon propagation directions. The propagation directions and related elastic constants are as follows: (○): $\mathbf{q}\|[100]$, *LA*: c_{11}, *TA*: c_{44}. (●): $\mathbf{q}\|[110]$, *LA*: $(c_{11} + c_{12})/2 + c_{66}$. (+): $\mathbf{q}\|[101]$, *QLA*: $[c_{11} + c_{33} + 2c_{44} + \sqrt{(c_{11} - c_{33})^2 + 4(c_{13} + c_{44})^2}]/4$, *TA*: $(c_{44} + c_{66})/2$. The *LA* modes ($\Delta\nu_B \gtrsim 15$ GHz) and *TA* modes ($\Delta\nu_B \lesssim 8$ GHz) are well separated. Two structural phase transitions at 334 and 229 K and a magnetic phase transition at 98 K are indicated by arrows in the figure.

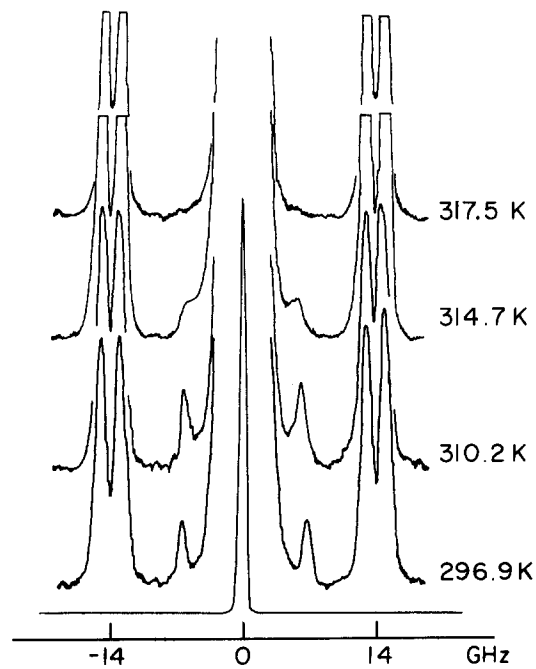

FIG. 2. Temperature development of Brillouin spectrum due to the [101] phonons in the D_{2h}^{18} phase. Since the free spectral range is 28 GHz, the *QLA* peaks at $\sim$15 GHz are overlapped from different orders. Note the temperature development of the *TA* phonon peak.

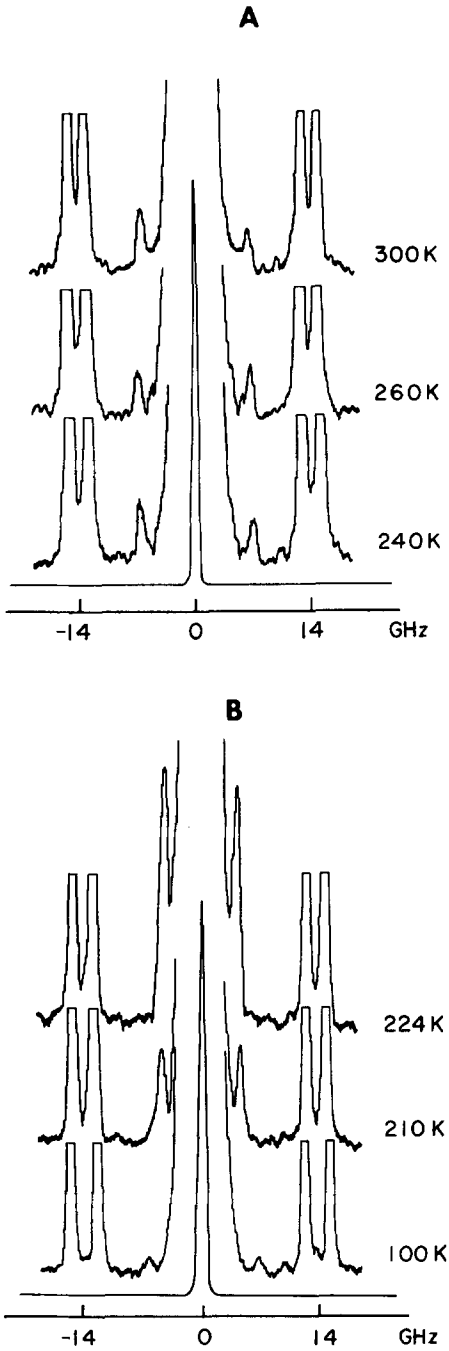

FIG. 3. Temperature development of the [101] phonon spectrum around the $D_{2h}^{18} - D_{4h}^{16}$ phase transition. (a) The D_{2h}^{18} phase and (b) the D_{4h}^{16} phase.

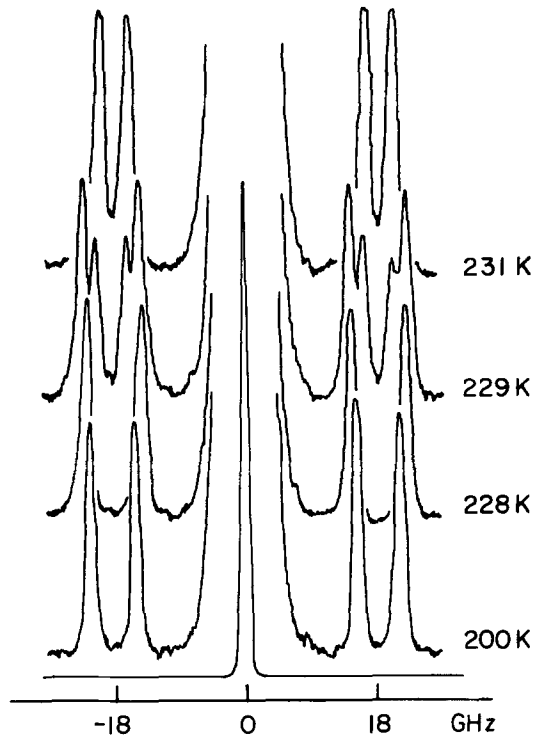

FIG. 4. Temperature development of the [110] phonon spectrum around the $D_{2h}^{18} - D_{4h}^{16}$ phase transition. As the free spectral range is 36 GHz, no overlap of the *LA*-phonon peaks takes place. The 229 K spectrum clearly shows a two phase coexistence.

geometry employed but also on which phonon modes, *LA* mode ($\sim V_V$) or *TA* mode ($\sim V_H$), are observed. Since no refractive index data have been reported for MAFeCl, the above expression is too complicated to analyze our present results. We are thus forced to assume an isotropic behavior ($n_i = n_s = n$) instead of the actual anisotropic one ($n_i \neq n_s$) throughout. Under these conditions

$$\Delta\nu_B = 2nv/\lambda_0 \sin(\theta_s/2)$$

and the elastic constant c is defined by

$$c = \rho v^2 = \rho/2\left(\frac{\lambda_0 \Delta\nu_B}{n}\right)^2$$

in which $\theta_s = 90°$.

The elastic constant c_{11} has been obtained by Goto *et al.*[6] between 4.2 and 400 K. The [100] *LA*-phonon frequency is governed by the c_{11} elastic constant. Assuming no frequency dependence of the c_{11} elastic constant, the refractive index n can be estimated at 300 K; the result is $n = 1.569$. This value will be used to calculate all the elastic constants.

In Fig. 5, the c_{11} and

$$(c_{11} + c_{12})/2 + c_{66}$$

constant are shown above 300 K. The c_{11} elastic constant exhibits a small decrease in value at the $D_{4h}^{17} - D_{2h}^{18}$ transition temperature. The $(c_{11} + c_{12})/2 + c_{66}$ elastic constant appears to evidence a weak softening in the D_{4h}^{17} phase; it is smoothly connected through the phase transition to its D_{2h}^{18} phase value. In the D_{2h}^{18} phase, the constant has a minimum ~ 315 K. Figure 6 shows the elastic constant over a wider temperature range (345–150 K) in which case the minimum can be more readily seen.

Two scattering geometries have been examined: geometry I, incident beam parallel to the laminar structure and perpendicularly scattered; and geometry II, 90° rotation of the geometry I about the fourfold axis such that the incident beam is perpendicular to the laminar structure and the scattered beam is parallel to it. The same sample is employed for both experiments. Phonons observed in these geometries correspond to the [110] and [1$\bar{1}$0] phonons in the D_{4h}^{17} phase,

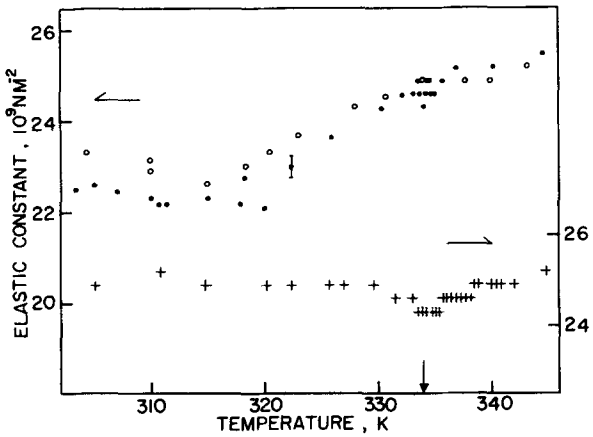

FIG. 5. Temperature dependnence of the elastic constants c_{11} (+) and $(c_{11}+c_{12})/2+c_{66}$ (● and ○). The $(c_{11}+c_{12})/2+c_{66}$ constant has been obtained in two scattering geometries which are equivalent in the D_{4h} phases but not in the D_{2h}^{18} phase. The incident beam is parallel to the fine laminas [(100) plane] and perpendicularly scattered (●) and the sample is rotated 90° from this orientation about the fourfold axis in the D_{4h}^{17} phase (○). The arrow marks the $D_{4h}^{17} \leftrightarrow D_{2h}^{18}$ phase transition.

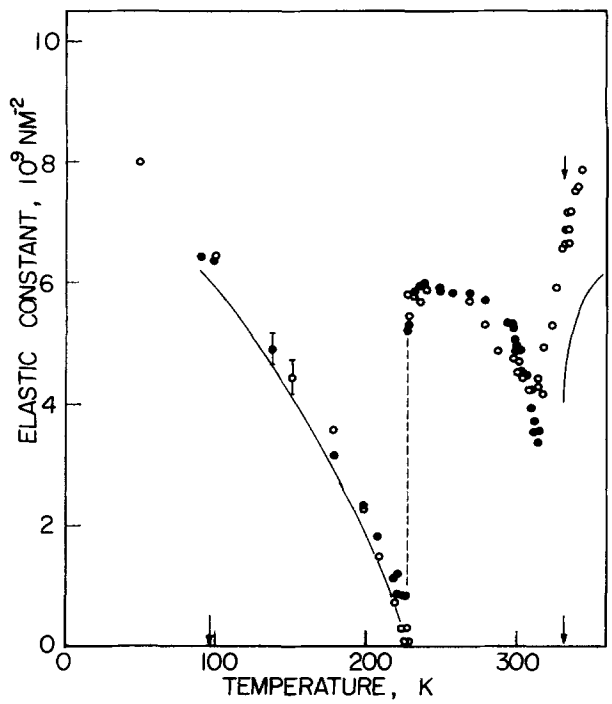

FIG. 7. Temperature dependence of the c_{66} constant. (●): obtained from the [101] *TA* mode and the [100] *TA* mode. (○): obtained from the [110] *LA* mode. For these derivations, see the text. Full lines show the ultrasonic results obtained at 5 MHz. The $D_{4h}^{17} - D_{2h}^{18}$ phase transition and the magnetic phase transition are indicated by arrows.

the [1′00] and [001′] phonons in the D_{2h}^{18} phase, and the [1″00] and [01″0] phonons in the D_{4h}^{16} phase. One can expect the same Brillouin shift for the *LA* mode in the D_{4h} phases but not in the D_{2h}^{18} phase.

Figures 5 and 6 demonstrate this latter result as expected. The frequency differences for the two geometries in the D_{2h}^{18} phase should be proportional to the square of the order parameter. Since the difference is quite small, no attempt to subtract values from different phases has been made.

The full circles in Fig. 7 represent the temperature dependence of c_{66} obtained from the [101] *TA* mode $[(c_{44}+c_{66})/2]$ and the [100] *TA* mode (c_{44}). As already mentioned, the [101] *TA* mode can be observed in Brillouin scattering only between 90 and 317 K. The c_{66} elastic constant

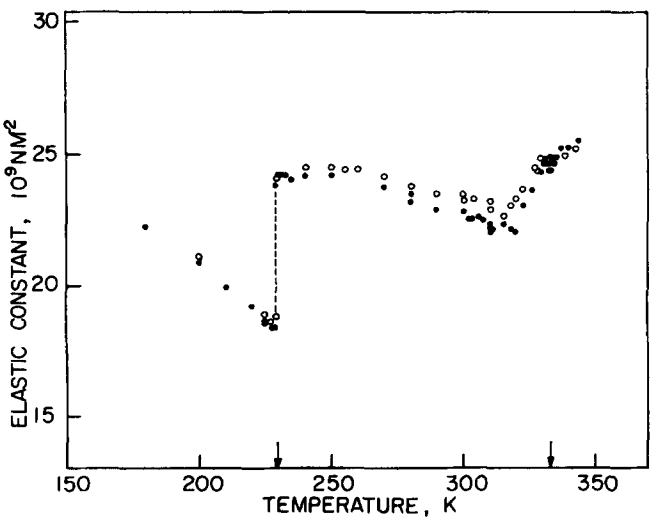

FIG. 6. Temperature dependence of the $(c_{11}+c_{12})/2+c_{66}$ constant over a wide temperature range covering the $D_{4h}^{17} - D_{2h}^{18} - D_{4h}^{16}$ phase transitions.

can, in addition, be obtained from the [110] *LA* mode whose frequency is governed by

$$(c_{11}+c_{12})/2+c_{66}.$$

In order to obtain c_{66} in this manner, $(c_{11}+c_{12})/2$ must be subtracted. According to the ultrasonic results the c_{11} and $(c_{11}-c_{12})/2$ elastic constants behave normally between 100 and 400 K except for a small anomaly at the $D_{4h}^{17} - D_{2h}^{18}$ phase transition in c_{11}. Hence the $(c_{11}+c_{12})/2$ constant also behaves normally in this temperature range. A simple form given by

$$(c_{11}+c_{12})/2 = 19.9 - 6.5\times10^{-3}T(10^9 N/m^2)$$

has been assumed. These parameters were determined at 100 and 300 K using the c_{66} values just obtained. The c_{66} elastic constant values thus derived from the [110] *LA* mode are represented by open circles in Fig. 7. Both results for c_{66} coincide well in spite of the approximate treatment employed.

This is the first determination of the c_{66} elastic constant in these layer perovskite crystals throughout the entire temperature range covering the $D_{4h}^{17} - D_{2h}^{18} - D_{4h}^{16}$ phase transitions.

The ultrasonic results are also included in Fig. 7 for comparison. The ultrasonic and Brillouin data coincide in the D_{4h}^{16} phase, but the Brillouin results give a much higher value for c_{66} than the ultrasonic results do in the D_{4h}^{17} phase. Moreover, there is substantially less softening of c_{66} in the D_{4h}^{17} phase based on the Brillouin data. These observations in the D_{4h}^{17} phase suggest the existence of frequency dependent critical softening for c_{66} within the range 5 MHz and 10

GHz. Similar results have been found for ammonium chloride.[13]

In the D_{2h}^{18} phase, a Landau–Khalatnikov process contributes to the c_{66} anomaly. This process smooths a step to lower elastic constant at the transition temperature and is a consequence of the Landau theory with linear strain-quadratic order parameter coupling at a second order phase transition.[20]

At the $D_{2h}^{18} - D_{4h}^{16}$ phase transition, the c_{66} constant exhibits a huge jump from the D_{2h}^{18} phase value ($\sim 6\times 10^9$N/m^2) to the D_{4h}^{16} phase value ($\leqslant 0.5\times 10^9$N/m^2). In the low temperature tetragonal phase (D_{4h}^{16}), the c_{66} elastic constant rapidly increases as the temperature decreases. The present Brillouin results confirm the ultrasonic values in the D_{4h}^{16} phase.

Direct measurements of the c_{66} elastic constant have been attempted. The *TA* phonon whose frequency is governed by the c_{66} elastic constant can be observed in the $X+Z(Y,X+Z)Z-X$ scattering geometry.[18d] Since, however, the crystals are quite thin (typically 1 to 2 mm) in the Z direction and exhibit strong cleavage in the XY plane, we were not able to prepare samples which allow direct *TA* phonon measurements.

IV. DISCUSSION

The $D_{4h}^{17} - D_{2h}^{18}$ phase transition has been well studied by group theoretical techniques.[9–12] The order parameter belongs to the X point $(00\frac{1}{2})$ of the Brillouin zone of the D_{4h}^{17} space group. The little co-group is D_{2h} and there are two arms to the star of the wave vector, $\mathbf{k}_{x_1} = (00\frac{1}{2})$ and $\mathbf{k}_{x_2} = (\frac{1}{2}\bar{\frac{1}{2}}0)$. Since eight one dimensional small representations exist for each arm, the order parameter is two dimensional—η_1 for the $\mathbf{k}_{x_1}$ arm and η_2 for the $\mathbf{k}_{x_2}$ arm. These components of η transform according to the small representations $X_2^+/B_{2g}(\eta_1)$ and $X_4^+/B_{3g}(\eta_2)$. Blinc *et al.*[21] developed a microscopic theory to describe the successive phase transitions of MAMnCl and MACdCl. The methyl ammonium group possesses a hydrogen bonding scheme involving four equivalent NH...Cl bonds known as the "orthorhombic modification" in the D_{4h}^{17} phase.[22] According to Blinc *et al.*,[21] probabilities of occupation of these four bonding geometries are equal in the D_{4h}^{17} phase: $n_1 = n_2 = n_3 = n_4 = \frac{1}{4}$. The D_{4h}^{17} phase can be regarded as a time and spatial averaged structure of these configurations.

In the D_{2h}^{18} phase the probabilities are no longer equal and are given by $n_1 > n_2 = n_4 > n_3$. Furthermore, the D_{4h}^{16} phase can be characterized by $n_1 = n_2 > n_3 = n_4$.

Group theoretical analysis shows that the D_{2h}^{18} phase is characterized by $\eta_1 \neq 0$, $\eta_2 = 0$, or $\eta_1 = 0$, $\eta_2 \neq 0$ in terms of the two dimensional order parameter. These order parameters correspond to two types of domains; only one arm of the star is involved in this instance. If both arms of the star are involved in the transition, the D_{4h}^{16} phase, which is characterized by $\eta_1 = \eta_2 \neq 0$ or $\eta_1 = -\eta_2 \neq 0$ and $Z = 4$, obtains. One can define the two dimensional order parameter(η_1,η_2) using the occupation probabilities n_1 to n_4 as follows[11]:

$$\eta_1 = 2(n_1 - n_3) \text{ and } \eta_2 = 2(n_2 - n_4).$$

These order parameters can be related to the orientational motion of the methyl ammonium group.

Employing standard group theoretical methods,[23] one can obtain the Landau free energy in terms of the order parameter. It is found that

$$G_\eta = \tfrac{1}{2}\alpha(T)(\eta_1^2 + \eta_2^2) + \tfrac{1}{4}\beta(\eta_1^2 + \eta_2^2)^2 + \tfrac{1}{2}\gamma\eta_1^2\eta_2^2 \quad (1)$$

in which $\alpha(T) = \alpha_0(T - T_0)$, $\beta > 0$, and $\gamma > 0$. The elastic energy can be included as

$$G_{el} = \tfrac{1}{2}c_{11}^0(e_1^2 + e_2^2) + \tfrac{1}{2}c_{33}^0 e_3^2 + c_{12}^0 e_1 e_2 + c_{13}^0(e_1 + e_2)e_3 + c_{44}^0(e_4^2 + e_5^2) + \tfrac{1}{2}c_{66}^0 e_6^2 .$$

Since, however, the c_{66} elastic constant exhibits the most pronounced anomalies, only the last term of the G_{el} expression will be considered,

$$G_{el} = \tfrac{1}{2}c_{66}^0 e_6^2. \quad (2)$$

The strain e_6 couples to an order parameter fluctuation $(\eta_1^2 - \eta_2^2)$ to the lowest order. A bilinear product of the two dimensional order parameter components $\eta_1\eta_2$ is transformed as a basis function which belongs to the Brillouin zone boundary Z point, transforming as the Z_3^+ basis function. This conclusion follows from:

$$\mathbf{k}_{x_1} + \mathbf{k}_{x_2} = (\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}) = (\tfrac{1}{2}\bar{\tfrac{1}{2}}\tfrac{1}{2}) = \mathbf{k}_z.$$

Therefore, one may include the secondary order parameter related to the Z_3^+ representation,[12] $\zeta \propto \eta_1\eta_2$ in the form

$$G_\zeta = \tfrac{1}{2}a\zeta^2. \quad (3)$$

The reason for this particular inclusion is physical and will become apparent in the subsequent discussion. This addition to G has no effect on the $D_{4h}^{17} \leftrightarrow D_{2h}^{18}$ phase transition but will be shown necessary for the $D_{2h}^{18} \leftrightarrow D_{4h}^{16}$ transition.

Finally, the coupling terms can be given by

$$G_{int} = Ae_6(\eta_1^2 - \eta_2^2) + B\zeta\eta_1\eta_2. \quad (4)$$

The total Landau free energy is then represented as

$$G = \tfrac{1}{2}\alpha(T)(\eta_1^2 + \eta_2^2) + \tfrac{1}{4}\beta(\eta_1^2 + \eta_2^2)^2 + \tfrac{1}{2}\gamma\eta_1^2\eta_2^2 + \tfrac{1}{2}c_{66}e_6^2 + \tfrac{1}{2}a\zeta^2 + Ae_6(\eta_1^2 - \eta_2^2) + B\zeta\eta_1\eta_2 \quad (5)$$

in which

$$\alpha(T) = \alpha_0(T - T_0),$$

$\beta > 0$, and $\gamma > 0$.

A. Sequence of successive phase transitions

In order to discuss the phase transitions under free crystal conditions, the strain e_6 and the secondary order parameter ζ must be eliminated in Eq. (5); i.e. $\partial G/\partial e_6 = \partial G/\partial\zeta = 0$. The strain and secondary order parameter can be obtained in terms of the other parameters as

$$e_6 = \frac{-A}{c_{66}^0}(\eta_1^2 - \eta_2^2) \quad (6)$$

and

$$\zeta = \frac{-B}{a}\eta_1\eta_2. \quad (7)$$

Substituting these expressions into Eq. (5), the Landau free energy for the free crystals then becomes

$$G=\frac{1}{2}\alpha(T)(\eta_1^2+\eta_2^2)+\frac{1}{4}(\beta-2A^2/c_{66}^0)(\eta_1^2+\eta_2^2)^2 + \frac{1}{2}\left(\gamma+\frac{4A^2}{c_{66}^0}-\frac{B^2}{a}\right)\eta_1^2\eta_2^2. \quad (8)$$

In order to ensure that the $D_{4h}^{17}-D_{2h}^{18}$ transition is a second order one, the coefficient $[\beta-2A^2/c_{66}^0]$ must be positive. The stable solutions of Eq. (8) are found in the usual manner, setting

$$\partial G/\partial\eta_1=\partial G/\partial\eta_2=0.$$

Three types of stable solutions are obtained:

(i) $\eta_1=\eta_2=\zeta=e_6=0.$

This set of solutions minimizes Eq. (8) for $T>T_0$ and corresponds to the D_{4h}^{17} phase

$$\text{(ii)}\ \eta_1=\left[-\alpha(T)/\left(\beta-\frac{2A^2}{c_{66}^0}\right)\right]^{1/2},$$

$$\eta_2=0,\quad e_6=\frac{-A}{c_{66}^0}\eta_1^2,\quad \zeta=0 \quad (10)$$

or

$$\eta_1=0,\quad \eta_2=\left[-\alpha(T)/\left(\beta-\frac{2A^2}{c_{66}^0}\right)\right]^{1/2},$$

$$e_6=\frac{A}{c_{66}^0}\eta_2^2,\quad \zeta=0,\quad \text{for } T<T_0$$

and

$$\left(\gamma+\frac{4A^2}{c_{66}^0}-\frac{B^2}{a}\right)<0.$$

These sets of solutions correspond to the D_{2h}^{18} phase and represent different domain structures in that phase.

$$\text{(iii)}\ |\eta_1|=|\eta_2|=\left[-\alpha(T)/\left(2\beta+\gamma-\frac{B^2}{a}\right)\right]^{1/2},$$

$$e_6=0,\quad \zeta=-\frac{B}{a}\eta_1\eta_2,\ \text{for } T<T_0 \quad (11)$$

and

$$\left(\gamma+\frac{4A^2}{c_{66}^0}-\frac{B^2}{a}\right)<0.$$

This set of solutions gives the nonferroelastic D_{4h}^{16} phase.

It is also possible that another solution set exists mathematically with the parameters

$$\eta_1\neq\eta_2\neq0,\quad e_6\neq0,\zeta\neq0.$$

This set corresponds to a D_{2h}^{10} (Pccn) structure which has not been observed in the methyl ammonium compounds. This phase will be discussed later.

The $D_{2h}^{18}-D_{4h}^{16}$ phase transition takes place at a temperature which satisfies

$$\gamma+\frac{4A^2}{c_{66}^0}-\frac{B^2}{a}=0. \quad (12)$$

In order to explain the $D_{2h}^{18}-D_{4h}^{16}$ phase transition, an additional instability for the Z_3^+ secondary order parameter is introduced such that

$$a=a_0(T-T_1). \quad (13)$$

Then Eq. (12) can be rewritten

$$\gamma+\frac{4A^2}{c_{66}^0}-\frac{B^2}{a}=\left(\gamma+\frac{4A^2}{c_{66}^0}\right)\left(\frac{T-T_2}{T-T_1}\right) \quad (12')$$

in which

$$T_2=T_1+\left(\frac{B^2}{\gamma a_0}\right)\frac{c_{66}^0}{c_{66}^0+\dfrac{4A^2}{\gamma}}>T_1.$$

In this development, T_2 can be considered to be the $D_{2h}^{18}-D_{4h}^{16}$ phase transition temperature. At T_2, the crystal changes the stable solution given by Eq. (10) to the solution given by Eq. (11) and the phase transition is a first order one because of the sign change for the coefficient. Below T_2, the secondary order parameter ζ possesses the finite value given by Eq. (11) and the Z_3^+ instability will be stabilized.

The assumption of a temperature dependence for the quadratic coefficient of the secondary order parameter given by Eq. (13) effectively introduces a strong temperature dependence into one of the fourth order coefficients in the Landau free energy.

As already mentioned in the Introduction, Goto *et al.*[15] discussed the possibility of a strongly temperature dependent fourth order coefficient in the Landau free energy. The Landau free energy used by Goto *et al.* is given by

$$G_\eta=a(\eta_1^2+\eta_2^2)+\tfrac{1}{2}b(\eta_1^4+\eta_2^4)+c\eta_1^2\eta_2^2$$

in which b and c are renormalized coefficients. This expression can be rewritten as

$$G_\eta=a(\eta_1^2+\eta_2^2)+\tfrac{1}{2}b(\eta_1^2+\eta_2^2)^2+(c-b)\eta_1^2\eta_2^2.$$

According to their calculation for the D_{4h}^{16} phase

$$c_{66}=c_{66}^0-\frac{2g_4^2}{b-c}$$

in which g_4 is the equivalent of the A constant in Eq. (5). From Eqs. (8) and (12')

$$(c-b)\propto\frac{T-T_2}{T-T_1}.$$

B. The c_{66} elastic anomalies

Within the framework of the Landau theory, an effective elastic constant is calculated by a set of equations given by[24]

$$\partial G/\partial\eta_1=\partial G/\partial\eta_2=\partial G/\partial\zeta=0$$

and (14)

$$\partial G/\partial e_6=X_6=c_{66}^{\text{eff}}e_6.$$

As is well known, this treatment cannot account for the possibility of critical fluctuations and a more sophisticated approach is required[25] in that case. Using the prescription of Eq. (14) with Eq. (5) in order to keep the derivatives simple, Eq. (14) can be rewritten as

$$\partial G/\partial\eta_1=[\alpha(T)+\beta(\eta_1^2+\eta_2^2)+\gamma\eta_2^2 + 2Ae_6]\,\eta_1+B\eta_2\zeta=0,$$

$$\partial G/\partial \eta_2 = [\alpha(T) + \beta(\eta_1^2 + \eta_2^2) + \gamma\eta_1^2 - 2Ae_6]\eta_2 + B\eta_1\zeta = 0, \quad (14')$$
$$\partial G/\partial \zeta = a\zeta + B\eta_1\eta_2 = 0,$$

and

$$\partial G/\partial e_6 = c_{66}^0 e_6 + A(\eta_1^2 - \eta_2^2) = X_6.$$

1. D_{4h}^{17} phase

Since the quantities e_6, η_1, η_2, and ζ possess only fluctuations in the high symmetry, high temperature tetragonal phase, one should set

$$\eta_1 = \delta\eta_1, \quad \eta_2 = \delta\eta_2, \quad e_6 = \delta e_6, \quad \text{and } \zeta = \delta\zeta$$

in Eq. (14).

Then the effective value of the c_{66} elastic constant becomes

$$c_{66}^{\text{eff}} = c_{66}^0.$$

The substitution of these fluctuating values is appropriate for the force equations (14') and not the full free energy equation (5) because it is the external force that induces the fluctuations that are related to the susceptibilities. Coupling between those parameters ensures that all equations in Eq. (14') are appropriately treated with the same set of fluctuation substitutions.

The c_{66} elastic constant measured by the ultrasonic method shows large critical softening in the D_{4h}^{17} phase. However, the same constant obtained by Brillouin scattering shows a strong suppression of the softening. This critical softening observed by ultrasonic techniques[6] can be described by a simple power law of the form

$$c_{66}(0) = c_{66}(\infty) - \Delta c_{66}\left(\frac{T - T_0}{T_0}\right)^{-0.42}$$

in which $c_{66}(0)$ and $c_{66}(\infty)$ are the low and high frequency elastic constants, respectively, and $c_{66}^0 = c_{66}(\infty)$.

Ultrasonic attenuation results have also been reported between 5 and 70 MHz in this phase.[7] The results are analyzed assuming a simple Debye-type frequency dependence for the ultrasonic attenuation:

$$\alpha(\omega) \sim \frac{v(\infty)^2 - v(0)^2}{2v(0)^3}\frac{\omega^2\tau}{1 + (\omega\tau)^2} \sim \frac{c_{66}(\infty) - c_{66}(0)}{2\rho v(0)^3}\omega^2\tau, \quad \text{for } \omega\tau \ll 1.$$

In this analysis, the temperature dependence of the characteristic relaxation time of the order parameter fluctuation τ has been determined to be

$$\tau \sim 0.92 \times 10^{-14}\left(\frac{T - T_0}{T_0}\right)^{-1.40} \text{ s}.$$

Around the transition temperature the relaxation time becomes of the order of 10^{-10}–10^{-11} s or longer. Since the phonon frequency observed by Brillouin scattering is about $10^{10}\ \text{s}^{-1}$, $\omega_B\tau \sim 1$ around the transition. Hence, the frequency dependence of the c_{66} elastic constant obtained in Brillouin scattering becomes important and must be considered. Similar frequency dependent behavior of the elastic constant has been reported for ammonium halides.[13]

The most straightforward way to treat the frequency dependence is to assume the Debye form for the elastic constant:

$$c_{66}(\omega) = c_{66}(\infty) - \Delta c_{66}\left(\frac{T - T_0}{T_0}\right)^{-0.42} \Big/ 1 + (\omega\tau)^2 \quad (16)$$

in which

$$\tau \sim 0.92 \times 10^{-14}\left(\frac{T - T_0}{T_0}\right)^{-1.40}.$$

As $\omega\tau$ increases ($T \to T_0$), the critical anomaly decreases.

2. D_{2h}^{18} phase

In the orthorhombic phase, η_1 and e_6 possess spontaneous values. For simplicity only one type of domain is considered in this discussion since the elastic anomaly is the same for both domains. The parameters can then be considered to be combinations of spontaneous and fluctuating values

$$\eta_1 = \tilde{\eta}_1 + \delta\eta_1, \quad \eta_2 = \delta\eta_2, \quad e_6 = \tilde{e}_6 + \delta e_6, \quad \text{and } \zeta = \delta\zeta$$

in which $\tilde{\eta}_1$ and $\tilde{e}_6$ are the spontaneous values given by Eq. (10). Equation (14') can then be rewritten to linear order in the fluctuation as

$$[\alpha + 3\beta\tilde{\eta}_1^2 + 2A\tilde{e}_6]\delta\eta_1 + 2A\tilde{\eta}_1\delta e_6 = 0,$$
$$[\alpha + \beta\tilde{\eta}_1^2 + \gamma\tilde{\eta}_1^2 - 2A\tilde{e}_6]\delta\eta_2 + B\tilde{\eta}_1\delta\zeta = 0,$$
$$a\delta\zeta + B\tilde{\eta}_1\delta\eta_2 = 0,$$

and

$$c_{66}^0\delta e_6 + 2A\tilde{\eta}_1\delta\eta_1 = X_6. \quad (17)$$

From this set of equations the effective elastic constant can be found to be

$$c_{66}^{\text{eff}} = c_{66}^0 - \frac{2A^2}{\beta}.$$

The effective value c_{66} shows a step at the transition temperature; however, Brillouin results exhibit a continuous and smooth behavior through the phase transition. Similar behavior has been observed in several other crystals (chloranil[26], thiourea[27], TGS[28], TGSe[29], etc.) which also exhibit second order phase transition with linear strain-quadratic order parameter couplings in their high temperature phases. This behavior can be understood by a Landau-Khalatnikov process.

With the inclusion of this process, the elastic anomaly given by Eq. (17) should be replaced by

$$c_{66}^{\text{eff}} = c_{66}^0 - \frac{2A^2}{\beta}\chi'(\omega). \quad (18)$$

$\chi(\omega)$ is the dynamic susceptibility of the order parameter and $\chi'(\omega)$ is the real part of this susceptibility. Usually one can assume a Debye form for the susceptibility in order-disorder crystals,

$$\chi(\omega) = \frac{1}{1 + i\omega\tau_{\text{LK}}} \quad (19)$$

in which τ_{LK} is the order parameter fluctuation time relaxa-

tion previously introduced. This relaxation time also strongly depends on temperature; the assumed form is

$$\tau_{LK} \sim \tau_{LK}^0 \left(\frac{T_0 - T}{T_0}\right)^{-\gamma'} \tag{20}$$

in which γ' is the critical index for the order parameter susceptibility.

In order to see how the Landau-Khalatnikov process modifies the step given by Eq. (17), assume that $\omega\tau_{LK} \gg 1$ for $T \sim T_0$ and $\omega\tau_{LK} \ll 1$ for $T \ll T_0$. Then $\chi'(\omega)$ continuously changes from 0 to 1, yielding $c_{66}^{\text{eff}} = c_{66}^0$ to $c_{66}^{\text{eff}} = c_{66}^0 - 2A^2/\beta$ as the temperature decreases from the transition temperature.

In addition to the Landau-Khalatnikov process, a restoring of the c_{66} elastic constant can be expected in the D_{2h}^{18} phase as temperature decreases from T_0. This increase in c_{66} can be expressed in a manner similar to the critical softening of Eq. (16). The full expression for the c_{66} anomaly in the D_{2h}^{18} phase is then given by

$$c_{66}(\omega) = c_{66}(\infty) - \Delta c_{66} \frac{\left(\frac{T_0 - T}{T_0}\right)^{-\rho'}}{1 + (\omega\tau')^2} - \frac{2A^2}{\beta} \frac{1}{1 + (\omega\tau_{LK})^2} \tag{21}$$

in which

$\tau' \sim \tau_0' \left(\frac{T_0 - T}{T_0}\right)^{-\rho_\alpha'}$. The critical indices ρ' and ρ_α' will be close to the high temperature D_{4h}^{17} phase values.

The existence of the deep minimum for the c_{66} elastic constant in the D_{2h}^{18} phase suggests that the second term in Eq. (21), the Landau–Khalatnikov term, provides a large contribution to the overall magnitude of c_{66}. In addition, it may also be that the frequency dependence of c_{66} in the D_{4h}^{17} phase which suppresses critical contributions to the high frequency elastic constant is not as effective in the low temperature D_{2h}^{18} phase. Therefore, a possible simplification of Eq. (21) may be adequate for the D_{2h}^{18} phase in the form

$$c_{66}(\omega) \simeq c_{66}(\infty) - \Delta c_{66} \left(\frac{T_0 - T}{T_0}\right)^{-\rho'} - \frac{2A^2}{\beta} \frac{1}{1 + (\omega\tau_{LK})^2}. \tag{22}$$

Since these data are not precise enough for further quantitative discussion, an actual numerical fit has not been attempted; qualitatively, however, Eq. (21) or Eq. (22) will reproduce the observations for c_{66}.

Finally, the Brillouin spectra shown in Fig. 2 clearly exhibit anomalous line broadening above 300 K. Due to the lack of intensity mentioned in the last section, however, we were not able to determine whether the broadening can be ascribed to the Landau-Khalatnikov process or critical fluctuations.

3. D_{4h}^{16} phase

In the low temperature tetragonal phase η_1, η_2, and ζ possess spontaneous values which have already been given in Eq. (11). The variables of the free energy can be written according to the above prescription

$$\eta_1 = \tilde{\eta} + \delta\eta_1, \quad \eta_2 = \tilde{\eta} + \delta\eta_2, \quad e_6 = \delta e_6,$$

and $\zeta = \tilde{\zeta} + \delta\zeta$

in which $\tilde{\eta}$ and $\tilde{\zeta}$ are given the spontaneous values of the variables. Then Eq. (14′) can be reevaluated, up to linear terms in the fluctuations, as

$$\begin{aligned}
&[\alpha + 4\beta\tilde{\eta}^2 + \gamma\tilde{\eta}^2]\delta\eta_1 + [(2\beta + 2\gamma)\tilde{\eta}^2 + B\tilde{\zeta}]\delta\eta_2 \\
&\quad + 2A\tilde{\eta}\delta e_6 + B\tilde{\eta}\delta\zeta = 0, \\
&[(2\beta + 2\gamma)\tilde{\eta}^2 + B\tilde{\zeta}]\delta\eta_1 + [\alpha + 4\beta\tilde{\eta}^2 + \gamma\tilde{\eta}^2]\delta\eta_2 \\
&\quad - 2A\tilde{\eta}\delta e_6 + B\tilde{\eta}\delta\zeta = 0, \\
&\alpha\delta\zeta + B\tilde{\eta}(\delta\eta_1 + \delta\eta_2) = 0,
\end{aligned} \tag{23}$$

and

$$c_{66}^0 \delta e_6 + 2A\tilde{\eta}(\delta\eta_1 - \delta\eta_2) = X_6.$$

Subtracting the first two equations of Eq. (23) gives

$$\begin{aligned}
\delta\eta_1 - \delta\eta_2 &= \frac{-4A\tilde{\eta}\delta e_6}{\alpha + (2\beta - \gamma)\tilde{\eta}^2 - B\tilde{\zeta}} \\
&= \frac{-2A}{\left(\gamma - \frac{B^2}{a}\right)\tilde{\eta}} \delta e_6.
\end{aligned}$$

The second equality in this last equation arises from the stability condition for the D_{4h}^{16} phase. The effective elastic constant is then given by

$$\begin{aligned}
c_{66}^{\text{eff}} &= c_{66}^0 - \frac{4A^2}{\gamma - \frac{B^2}{a}} \\
&= c_{66}^0 \left(1 + \frac{4A^2}{\gamma c_{66}^0}\right) \frac{T_2 - T}{T_3 - T}
\end{aligned} \tag{24}$$

in which

$$T_3 = \left(T + \frac{B^2}{a_0\gamma}\right) > T_2.$$

As already pointed out, the $D_{2h}^{18} - D_{4h}^{16}$ phase transition takes place at $T = T_2$; hence, Eq. (24) applies only below that temperature. At $T = T_2$, c_{66} becomes exactly zero. The temperature dependence given by Eq. (24) has been confirmed by Goto *et al.*[6] Their numerical expression is given by

$$c_{66} = 27.24\ (233.9 - T)/(708.5 - T) \times 10^{10} \text{dyn/cm}^2.$$

The effective elastic constant in the D_{2h}^{18} phase is temperature independent; i.e.,

$$c_{66}^{\text{eff}} = c_{66}^0 - \frac{2A^2}{\beta}.$$

At the $D_{2h}^{18} - D_{4h}^{16}$ transition point, the effective elastic constant suddenly changes from the above value to zero as shown in Fig. 7.

An intermediate (hypothetical) orthorhombic D_{2h}^{10} (Pccn)($Z = 4$) phase has been introduced between the D_{2h}^{18} phase and the D_{4h}^{16} phase[16] in order to account for the $D_{2h}^{18} - D_{4h}^{16}$ phase transition. The D_{2h}^{10} phase can be induced by the B_{1g}/Γ_3^+ irreducible representation of the D_{4h}^{16} space group. There is an allowed bilinear coupling between the B_{1g} symmetry order parameter and the elastic strain e_6 which becomes strain $e_1 - e_2$ in the D_{4h}^{16} phase. Such coupling could lead to the observed temperature dependence. How-

ever, the D_{2h}^{10} phase has not been detected for MAFeCl, even under hydrostatic pressure to 6 kbar.[6] Since the D_{2h}^{10} phase can be described by $\eta_1 \neq \eta_2 \neq 0$, $e_6 \neq 0$, and $\zeta \neq 0$, the phase is also ferroelastic. Ferroelastic domain structure in the D_{2h}^{10} phase will be similar to the domain structure in the D_{2h}^{18} phase and the ultrasonic technique will not be able to detect the presence of the D_{2h}^{10} phase if it exists. As pointed out above, it is not necessary to introduce this phase if X and Z point order parameters are considered.

Although the above development can reasonably explain the sequence of the successive phase transitions and the c_{66} anomalies in MAFeCl assuming a Z_3^+ instability in addition to the X-point instability, group theoretical analysis of lattice vibrations in the D_{4h}^{17} phase reveals no Z_3^+ lattice mode allowed in this series of compounds. Hence, the Z_3^+ instability should be considered to be of an order–disorder rather than a displacive type.

V. CONCLUSIONS

A new set of elastic constant results for MAFeCl between 345 and 30 K obtained by Brillouin scattering have been reported in this paper. The specific findings can be summarized as follows:

(i) Based on a comparison between low frequency ultrasonic results and the present Brillouin results, the elastic constant c_{66} evidences strong frequency dependent critical softening in the D_{4h}^{17} phase. There appears to be little residual critical fluctuation softening in this phase at ~ 10 GHz.

(ii) c_{66} possesses a minimum about 15 K below the $D_{4h}^{17} - D_{2h}^{18}$ phase transition temperature. The c_{66} elastic constant smoothly changes in the immediate vicinity of the phase transition. The existence of the minimum and the smooth behavior suggests that critical fluctuations and a Landau-Khalatnikov process in the D_{2h}^{18} phase are responsible for the c_{66} anomalous behavior at this transition.

(iii) At the $D_{2h}^{18} - D_{4h}^{16}$ phase transition, c_{66} suddenly jumps from the D_{2h}^{18} phase value ($\sim 6 \times 10^9 \mathrm{N/m^2}$) to the extremely low D_{4h}^{16} phase value ($< 0.5 \times 10^9 \mathrm{N/m^2}$). Below this transition, c_{66} rapidly increases as the temperature decreases. The Brillouin data and ultrasonic results are quite similar in the D_{4h}^{16} phase and no dispersion is suggested for this phase.

(iv) The other elastic constants c_{11}, $(c_{11} + c_{12})/2$, and c_{44}, show no clear anomalies at these phase transitions.

The c_{66} elastic anomalies have been treated within the framework of Landau theory. In addition to the two dimensional X-point order parameter, a secondary order parameter at the Z point has been introduced. The secondary order parameter is important for $D_{2h}^{18} - D_{4h}^{16}$ phase transition because it couples linearly to the X-point order parameter components and becomes finite in the D_{4h}^{16} phase. In a sense, an unrealized phase transition, due to the secondary order parameter, has been introduced in addition to the X-point transition.

Based on this X-Z point model, the sequence of successive phase transitions $D_{4h}^{17} - D_{2h}^{18} - D_{4h}^{16}$ can be obtained. Moreover, a step anomaly at the $D_{4h}^{17} - D_{2h}^{18}$ transition, the large discontinuity at the $D_{2h}^{18} - D_{4h}^{16}$ transition, and the $(T_2 - T)/(T_3 - T)$ dependence of the elastic constant in the D_{4h}^{16} phase as observed in ultrasonic experiments can be successfully derived. Although the present treatment can explain the essential features of the c_{66} anomalies, it does not account, at present, for the critical anomaly observed around the $D_{4h}^{17} - D_{2h}^{18}$ phase transition.

Dynamics of the critical fluctuations (dispersion) have been observed by Brillouin scattering; unfortunately, the c_{66} elastic constant could only be indirectly determined and the results are not precise enough at this time for a detailed discussion of the dynamics of the critical anomaly.

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