

Pressure and temperature dependence of the elastic constants of ammonium fluoroberyllate

K. Weishaupt,* M. Takesada,[†] A. Simon,* M. P. Gelfand, A. Onodera,[‡] and H. D. Hochheimer
Department of Physics, Colorado State University, Fort Collins, Colorado 80523

(Received 19 June 1997)

We have studied the temperature and pressure dependence of the elastic constants of ammonium fluoroberyllate $[(\text{NH}_4)_2\text{BeF}_4$ or AFB] using Brillouin scattering. Combining the results of the Brillouin-scattering study with those of the measurements of the isothermal compressibility and the volume thermal expansion allows the determination of the anharmonicities, which play an important role in producing the observed anomalies in certain elastic constants at the normal to incommensurate and commensurate to incommensurate phase transitions. Furthermore, we have compared the results of our high-pressure Brillouin-scattering study with the results of an ultrasonic study at high pressure, and have discussed our results based on theoretical models developed to explain the elastic anomalies observed in K_2SeO_4 . [S0163-1829(98)05710-5]

I. INTRODUCTION

Compounds in the A_2BX_4 family have garnered much attention because many of them exhibit structurally incommensurate phases. One of the best studied materials of this type is K_2SeO_4 . In particular, the elastic anomalies in the vicinity of the normal (N) to incommensurate (I) transition and the incommensurate to commensurate (C) transition have been studied extensively using ultrasonic resonance and Brillouin-scattering methods.¹⁻⁴ Li *et al.*² achieved a breakthrough in the analysis of its elastic anomalies using a Landau free energy with coefficients determined by independent experimental data rather than being considered as free fitting parameters. In the formulation of this theory, the anharmonic terms were treated in lowest order through cubic coupling of the strain to pairs of soft modes above T_I or to pairs of amplitudons and phasons below T_I . Higher-order anharmonic terms may, however, contribute significantly in the I phase, as noted in Ref. 2. A high pressure study could, in principle, address that issue. K_2SeO_4 , however, is not well suited for such a study, because the anomalies in its sound velocities and damping are only weakly affected by pressure.⁵ Therefore we looked for another material in the A_2BX_4 family which would better suited for such a high pressure study of its elastic anomalies, and which, we hoped, could be analyzed in as much detail as had K_2SeO_4 . We excluded Rb_2ZnCl_4 and Rb_2ZnBr_4 from consideration because Li *et al.*² had pointed out that their elastic anomalies are very weak⁶ compared to the strong C_{33} anomalies in K_2SeO_4 . We decided to study $(\text{NH}_3)_2\text{Be}_4\text{F}$ (ammonium fluoroberyllate, AFB), since a Brillouin-scattering study by Kudo and Hikita⁷ revealed anomalies in C_{22} and C_{55} in that compound comparable in strength to those of C_{33} and C_{44} in K_2SeO_4 . However, AFB has the disadvantage that its I phase, modulated along the a axis, is stable only in the narrow temperature interval from 183 K (T_I) to 177 K (T_C) at ambient pressure,^{8,9} in contrast with the I phase in K_2SeO_4 , which is stable from 93 to 130 K. The pressure dependences of the transition temperatures in AFB are¹⁰ $dT_I/dp = -1.7 \pm 0.1$ K/kbar, and $dT_C/dp = -2.2 \pm 0.1$ K/kbar, and so at a pressure of 10 kbar the temperature range of the I phase is

increased to 11 K. This is still so small that a detailed analysis along the lines of that carried out by Li *et al.* turns out to be infeasible in the I phase of AFB. Nevertheless, we have been able to obtain some information about the anharmonicities in the N and C phases of AFB.

For AFB, the normal paraelectric phase above T_I , as well as the commensurate ferroelectric phase below T_C are orthorhombic with space groups D_{2h}^{16} ($Pnam$) (Refs. 11,12 and C_{2v}^9 ($Pn2_1a$),¹² respectively. The lattice constant a is doubled below T_C and a spontaneous polarization appears along the b axis.¹³ The order parameter describing the phase transitions belongs to a two-dimensional representation of $Pnam$ at the X point on the Brillouin-zone boundary, and a Lifshitz invariant in the free energy is allowed by symmetry.^{14,15}

In an previous paper,¹⁶ we have discussed differences in the values of the elastic constants for AFB as determined by Brillouin scattering^{7,16,17} and ultrasound¹⁸ techniques. We also mentioned that a detailed analysis of the anomalies of the elastic constants would follow when suitable equation of state data for AFB were available. We subsequently performed an energy-dispersive x-ray-diffraction study at high pressure and different temperatures, which is reported in Ref. 19, and obtained the equation of state of AFB. That has allowed the analysis which we present here.

II. EXPERIMENT

The experimental details of the Brillouin-scattering measurements have been described elsewhere.¹⁶ In order to avoid any ambiguity, we present in Fig. 1 the scattering geometries used to determine the elastic constants C_{ii} , $i = 1, 2, 3, 5, 6$, that are reported in the present work. The directions in Fig. 1 refer to the choice of crystal axes for AFB which follows the IRE "Standards on Piezoelectric Crystals" (1949): $c < a < b$. No data are reported concerning C_{44} because the Brillouin scattering from the associated transverse mode was so weak that the frequency of the peak could not be determined with reasonable precision.

Brillouin measurements of other elastic constants (such as C_{12}) would have been desirable and feasible. Unfortunately,

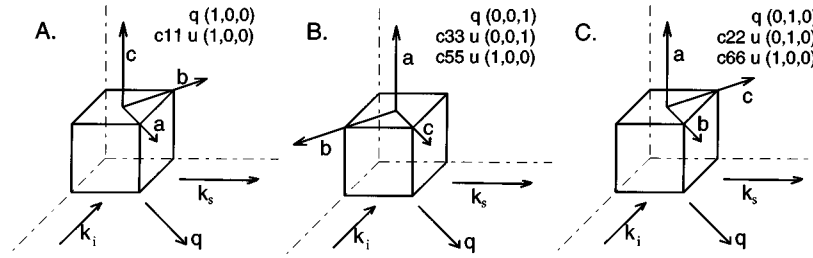


FIG. 1. Scattering geometries used to determine the elastic constant C_{ii} , $i=1,2,3,5,6$. The arrows labeled a , b , and c denote the crystal axes; \mathbf{q} denotes the phonon wave vector; \mathbf{k}_i and \mathbf{k}_s represent the wave vector of incident and scattered light, respectively.

we exhausted our supply of AFB crystals and it has not been possible to grow more, because the starting materials have become practically impossible to obtain.

III. RESULTS

Any particular elastic constant can be expressed as the product of the mass density ρ and the square of an appropriate sound velocity v . In order to calculate v from the Brillouin shift measured in the 90° scattering geometry (as done here), the index of refraction n has to be known at the pressure p and temperature T of the measurement. Given the isothermal equation of state and the volume thermal expansion one can determine the p and T dependence of n using the Lorenz-Lorentz equation or, equivalently, assuming a constant specific refraction r given by²⁰

$$r = (n^2 - 1) / \rho(n^2 + 2). \quad (1)$$

This approximation neglects changes of n due to changes of the polarizability caused by pressure and temperature. In the case of molecular crystals this approximation is justified, as the corrections²¹ are of order 0.01%.

Optical measurements by Kobayashi *et al.*²² showed that n changes by about 0.2% in the temperature range from -88 to -100 °C. Based on x-ray data at ambient pressure by Onodera and Shiozaki,¹² we estimate $\Delta n/n < 0.12\%$ in the temperature range from room temperature to -140 °C. This variation in the index of refraction is smaller than the error in the Brillouin shift measurements (about 1%) and has therefore been neglected. Based on the equation-of-state data, we estimate that pressure-induced changes in n can be in the range 1–2 % in the course of our Brillouin-scattering measurements. Consequently, we have accounted for those changes when extracting the elastic constants from the Brillouin data.

Figure 2 shows the isobaric temperature dependence of the elastic constants C_{11} at 225 MPa (A), C_{22} at ambient pressure and 223 MPa (B), and C_{33} at 250 MPa (C). The transition temperatures, T_I and T_C , indicated in the figure are taken from the linear interpolation by Gesi *et al.*¹⁰ and therefore do not always agree precisely with the transition temperatures one would estimate based on our data. (This caveat applies to all values of transition temperatures and pressures in all succeeding figures, as well.)

In Fig. 3 we display the isothermal pressure dependence of C_{11} at 178.9 K (A), of C_{22} at 177.8 K (B), and of C_{33} at 170 K (C). The bars indicate the transition pressures from the I phase to the N phase at the corresponding temperatures. In Fig. 3(C) we have also plotted, as crosses, the elastic constants calculated assuming constant ρ and n over the pressure range of the measurement. The effect of properly accounting for the pressure variation of those quantities is clearly evident.

In Fig. 4, isothermal pressure dependences of the same modes as in the preceding figure are shown, but at temperatures where the C phase is present at ambient pressure and increasing pressure causes a transition into the I phase. In Fig. 5 we show the isobaric temperature dependence of C_{55} at ambient pressure and 255 MPa (A) and of C_{66} at 223 MPa (B). T_I and T_C are taken again from Ref. 10. In Fig. 6 the isothermal pressure dependence of C_{55} at 178.2 K (A) and 170.3 K (B) is displayed. The transition pressures¹⁰ p_I , in Fig. 6(A) and p_C in Fig. 6(B) are indicated by bars. (Note that on increasing p one follows the sequence C to I to N.)

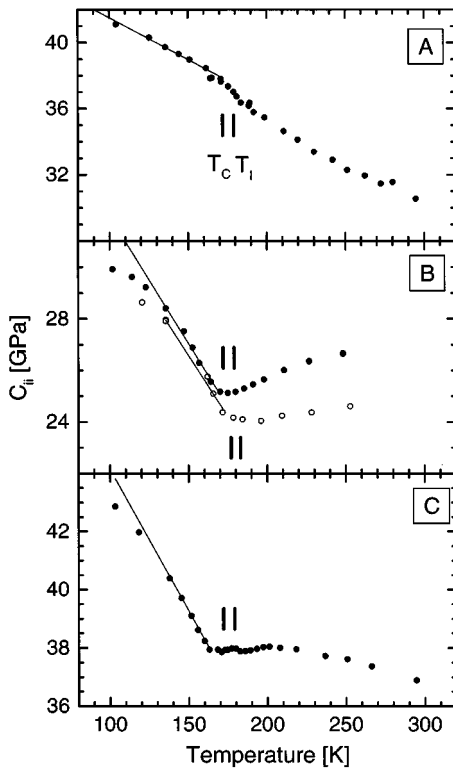


FIG. 2. Elastic constants C_{ii} , $i=1,2,3$, versus temperature. (A) C_{11} at 225 MPa. (B) C_{22} at ambient pressure (open circles) and 223 MPa (solid circles). (C) C_{33} at 250 MPa. The vertical bars indicate the transition temperatures T_I and T_C .

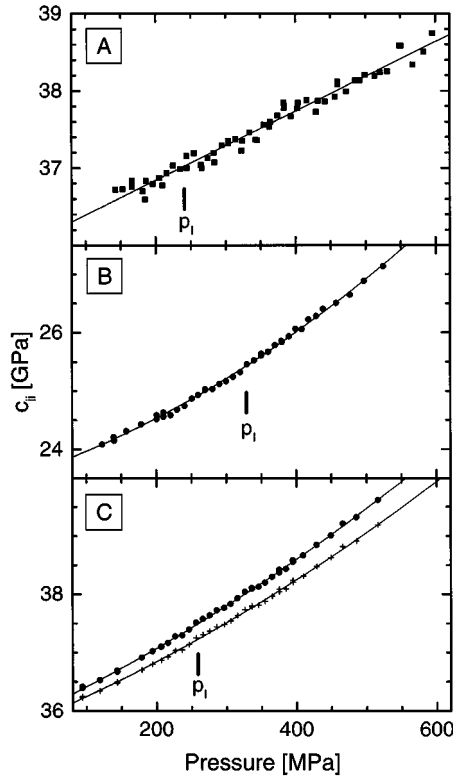


FIG. 3. Elastic constants C_{ii} , $i=1,2,3$ versus pressure at constant temperature at the normal to incommensurate transition. (A) C_{11} at 178.9 K. (B) C_{22} at 177.4 K. (C) C_{33} at 178.6 K (solid circles). The crosses represent values of the elastic constants calculated with constant density and constant index of refraction. The bars indicate the transition pressures from the normal to the incommensurate phase at the above temperatures.

The general features of the temperature dependences of the elastic constants, in particular the existence (or nonexistence) of anomalies in the various elastic constants at T_I and T_C , agree well with the results of the Brillouin-scattering measurements at constant pressures by Kudo and Hikita.⁷ However, our data do not agree quantitatively with theirs: this illustrates again the importance of accounting for variations in the index of refraction when extracting values of the elastic constants from Brillouin shifts.

A comparison of our results with those of an ultrasonic study at ambient and high pressure by Hikita *et al.*¹⁸ shows that in general the results are consistent, when one takes into account the greater precision of ultrasonic measurements of elastic constants. Thus the ultrasonic measurements reveal features in C_{22} at T_I and in C_{33} and C_{55} at T_I and T_C which are not evident in Brillouin measurements. An interesting exception to that trend is that the ultrasonic study reveals no clear anomalies in C_{66} at T_I or T_C , whereas our Brillouin study [see Fig. 5(B)] as well as the one by Kudo and Hikita,⁷ show an anomaly at T_I .

The present measurements of the pressure dependences of elastic constants at constant temperature (Figs. 3, 4, and 6) are the only ones of this type for AFB, and they are quite interesting. The pressure dependence at constant temperature appears to be completely smooth through the N-I transition for C_{ii} ($i=1, 2, 3$), while anomalies are clearly seen at the I-C transition. C_{55} shows anomalies at both the N-I and I-C

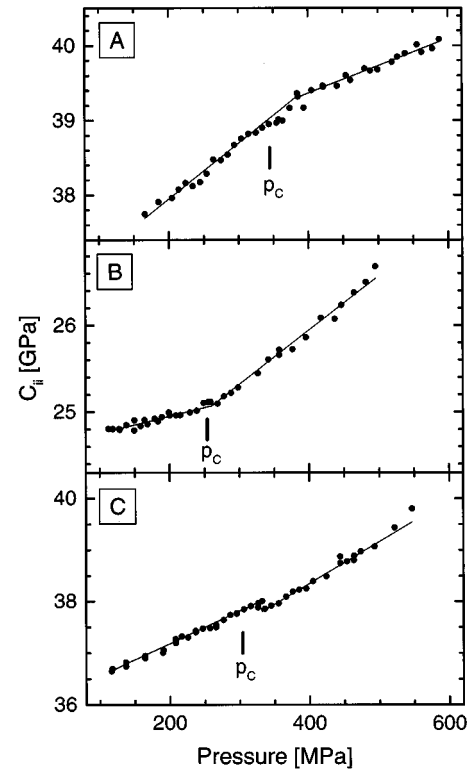


FIG. 4. Elastic constants C_{ii} , $i=1,2,3$ versus pressure at constant temperature at the incommensurate to commensurate transition. (A) C_{11} at 169.4 K. (B) C_{22} at 171.4 K. (C) C_{33} at 170.3 K. The vertical bars indicate the transition pressures from the incommensurate to the commensurate phase at the above temperatures.

transitions. It is not entirely clear what to make of these findings. Compared to the C_{ii} ($i=1, 2, 3$), C_{55} exhibits a somewhat stronger anomaly in its temperature dependence (at constant p) at the N-I transition. The small value of $dT_I/dp \approx -2$ K/100 MPa suggests that the pressure dependence of all quantities that vary singularly at the transition should be weaker in the constant p scans than in the constant T scans. [This follows from the simplest assumption for the p and T dependence of the elastic constants near the N-I transition line: a sum of a smooth p -dependent term and a singular function of $T - T_I^0 + (dT_I/dp)p$, where T_I^0 is the ambient pressure transition temperature.] Nonetheless, the complete absence of any observable anomaly at p_I for C_{11} , C_{22} , and C_{33} seems surprising. Also note that C_{55} exhibits a ‘knee’ around p_I in the constant- T scans, rather than a single change of slope with smooth behavior on either side of the transition, as one would ordinarily expect. A similar knee is evident in the constant- p ultrasound measurements by Hikita *et al.*,¹⁸ particularly at pressures greater than ambient.

IV. DISCUSSION

A. Anharmonic interaction analysis

A rather simple analysis of elastic constant data can sometimes be informative of the nature of the anharmonic interactions among phonons. Anharmonicity leads to a phonon self-energy, the real part of which (Δ) shifts the phonon

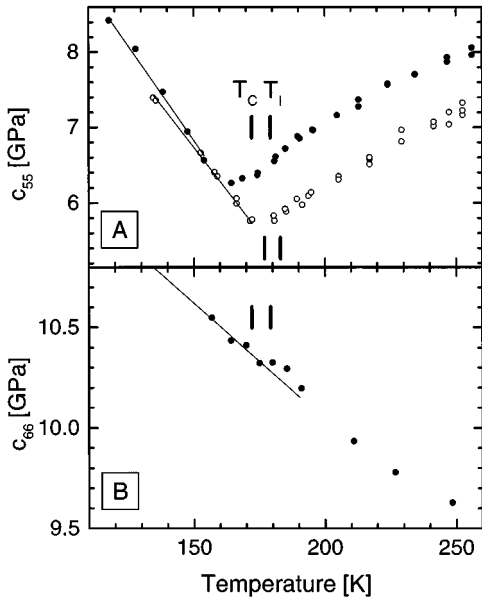


FIG. 5. Elastic constants C_{55} and C_{66} versus temperature (A) C_{55} at ambient pressure (open circles) and at 255 MPa (solid circles). (B) C_{66} at 223 MPa. The vertical bars indicate the transition temperatures T_l and T_c .

frequency from its “harmonic” value. Cowley²³ and Maradudin and Fein²⁴ have calculated Δ for cubic and quartic anharmonicities. To lowest order in perturbation theory it may be expressed as

$$\Delta = \Delta_E + \Delta_A, \quad (2)$$

where Δ_E is the frequency shift associated with thermal expansion (“volume term”) and Δ_A accounts for the remainder of the shift (“multiphonon term”). They showed that the

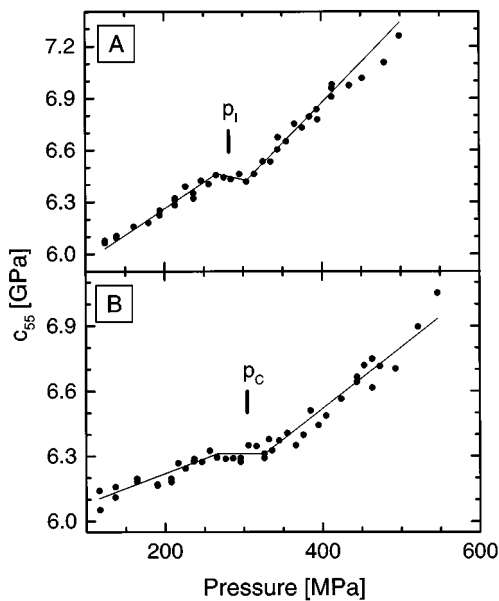


FIG. 6. C_{55} versus pressure at constant temperatures. (A) 178.2 K. (B) 170.3 K. The bars show the transition pressure at the normal to incommensurate transition in (A) and at the incommensurate to commensurate transition in (B).

contribution of cubic anharmonicity to Δ_A is always negative, while the contribution of quartic anharmonicity can be of either sign.

In order to split the measured frequency shift for some experimentally observed phonon mode into volume and multiphonon contributions, one looks at the frequency of the mode as function of volume and temperature. The total differential of the mode frequency ν_B is given by

$$\Delta \nu_B = (\partial \nu_B / \partial V)_T \Delta V + (\partial \nu_B / \partial T)_V \Delta T. \quad (3)$$

If one takes the partial differential at constant pressure and divides by $(\Delta T)_p$ and ν_B , one obtains²¹

$$(\partial \ln \nu_B / \partial T)_p = (\partial V / \partial T)_p (\partial \ln \nu_B / \partial V)_T + (\partial \ln \nu_B / \partial T)_V. \quad (4)$$

Elementary thermodynamics then yields

$$(\partial \ln \nu_B / \partial T)_p = - \frac{\beta}{\kappa_T} (\partial \ln \nu_B / \partial p)_T + (\partial \ln \nu_B / \partial T)_V \quad (5)$$

with β the volume thermal expansion and κ_T the isothermal compressibility. Though this analysis is strictly true only for cubic crystals, thermal-expansion measurements²⁵ for AFB indicate that changes in the aspect ratios of the unit cell with temperature are about an order of magnitude smaller than the relative volume changes, so it is probably a good approximation.²¹

It is possible to correlate the first term on the right side of Eq. (5) with Δ_E and the second one with Δ_A . With presently available experimental data, one can determine both the left side of Eq. (5) and the first term on the right side, and thus deduce the second term on the right side, for a variety of phonon modes and at several temperatures and pressures. We shall be mainly interested in the *sign* of the second term on the right side of Eq. (5): a positive sign will indicate that quartic anharmonicities are not negligible compared to cubic anharmonicities.

As noted by Cowley,²³ this entire analysis is not appropriate if the modes are strongly interacting, which would be indicated by short phonon lifetimes. Li *et al.*^{2,3} found that for K_2SeO_4 the damping of acoustic modes increases in narrow temperature intervals close to the phase transitions, and our linewidth data for AFB have similar character. The quasiharmonic approximation would not apply in those temperature intervals. Nevertheless, outside that region the damping is small and nearly constant, and the analysis described above gives physically meaningful results. We present, in Table I, the terms in Eq. (5) based on Brillouin data in the C and N phases which are close to the phase transitions (so that they might be informative in constructing Landau theories for the transitions) but not so close that the quasiharmonic approximation breaks down. The values for κ_T and β were taken from Refs. 19 and 25, respectively.

One sees that $(\partial \ln \nu_B / \partial T)_V$ changes sign with increasing pressure for the mode associated with C_{22} , indicating that quartic anharmonicities become dominant with increasing pressure for that mode. It is also clear that quartic anharmonicities play a important role in the temperature dependences of C_{33} and C_{55} . In the case of C_{11} such a statement is not possible, because $(\partial \ln \nu_B / \partial T)_V$ is negative.

TABLE I. Values of terms in Eq. (5). In each row, the value of ν_B corresponds to the listed temperature and pressure, associated with either a normal-to-incommensurate or incommensurate-to-commensurate transition. The derivatives are evaluated on the normal side of the former transitions and on the commensurate side of the latter transitions.

Mode	\mathbf{q} vector	T (K)	p (MPa)	ν_B (GHz)	$(1/\kappa_T)(\partial \ln \nu_B / \partial p)_T$	$(\partial \ln \nu_B / \partial T)_p =$ ($10^{-5}/\text{K}$)	$-(\beta/\kappa_T)(\partial \ln \nu_B / \partial p)_T$ ($10^{-5}/\text{K}$)	$+(\partial \ln \nu_B / \partial T)_V$ ($10^{-5}/\text{K}$)
Normal to incommensurate transition								
LA (C_{11})	(1,0,0)	178.9	225	17.9	1.17	-86.5	-4.1	-82.4
LA (C_{22})	(0,1,0)	177.4	0.1	10.3	3.52	-22.3	-12.4	-9.9
LA (C_{22})	(0,1,0)	177.4	223	14.8	3.52	54.5	-12.4	66.9
LA (C_{33})	(0,0,1)	178.6	250	18.0	2.27	13.9	-8.0	21.9
TA (C_{55})	(0,0,1)	178.2	0.1	7.1	5.49	169.0	-19.3	188.3
TA (C_{55})	(0,0,1)	178.2	255	7.5	5.49	159.0	-19.3	178.3
Incommensurate to commensurate transition								
LA (C_{11})	(1,0,0)	169.4	225	18.1	1.93	-58.0	-3.1	-54.9
LA (C_{22})	(0,1,0)	171.4	0.1	10.4	0.79	-282	-1.3	-280.7
LA (C_{22})	(0,1,0)	171.4	223	14.7	0.79	-21.8	-1.3	-20.5
LA (C_{33})	(0,0,1)	170.3	250	18.0	1.71	124.0	-2.7	126.7
TA (C_{55})	(0,0,1)	170.3	0.1	7.1	1.97	-325.0	-3.2	-321.8
TA (C_{55})	(0,0,1)	170.3	255	7.4	1.97	-336.0	-3.2	-332.8

B. Other remarks

The standard Landau theory description of the N-I transition in AFB (see Ref. 18) implies discontinuities in C_{ii} ($i = 1, 2, 3$) and discontinuous derivatives in C_{jj} ($j = 4, 5, 6$) and ϵ_b (the static dielectric constant associated with polarization along the b axis). Though the theory works reasonably well for C_{11} and C_{33} it fails to explain the peculiar temperature dependence of C_{22} in the N and I phases. The large softening of C_{55} in the N phase is also not understandable within that phenomenological theory. Recently, Li *et al.*² have demonstrated, in the context of K_2SeO_4 , that anharmonic fluctuation contributions from the Σ_2 soft branch can account for elastic constant softening in the N phase. Their analysis was facilitated by the existence of much data for K_2SeO_4 which does not exist for AFB; because of this, and also the narrow temperature range of the I phase in AFB, an analogous analysis is not feasible for AFB. We suggest that the softening of C_{22} and C_{33} in the normal phase of AFB may be due to such an anharmonic contribution. But note the further complication that, particularly at high pressures, the sign of $(\partial \ln \nu_B / \partial T)_V$ indicates that quartic anharmonicities need to be considered in modeling the temperature dependence of those elastic constants, in contrast to the cubic interaction considered by Li *et al.*

Li *et al.*³ have also analyzed the anomalies of the transverse-acoustic modes in K_2SeO_4 . They showed that the anomaly in C_{44} can be explained by a bilinear coupling, $a_4 Q_B \epsilon_4$, of the strain ϵ_4 with a soft mode with amplitude Q_B . They pointed out that this optic mode is not on the Σ_2 soft branch, but is instead the lowest temperature-dependent B_{3g} optical mode, which they have observed with Raman scattering. If the softening of C_{55} in the N phase of AFB is to be due to such a coupling, one needs to look for a temperature-dependent mode of B_{2g} symmetry. There are no Raman-scattering data for AFB, but group theory²⁶ predicts Raman-active modes of B_{2g} symmetry in the normal phase. Again, the sign of $(\partial \ln \nu_B / \partial T)_V$ for this mode indicates that

quartic anharmonicities play an important role in the temperature dependence of C_{55} in the normal phase upon approaching T_I .

The anomaly in C_{66} at T_I in K_2SeO_4 could be described³ by the interaction of the strain ϵ_6 with the order parameter through a quartic coupling $g_6 \epsilon_6^2 Q Q^*$. The corresponding anomaly in AFB might be accounted for by the same type of coupling.

The temperature dependence of the elastic constants of AFB in the C phase can be accounted for straightforwardly. They all increase quite linearly with decreasing T , at least close to the transition. This would be consistent with a coupling of the strain to the order parameter which was quadratic in both, assuming mean field [$\sim (T_C - T)^{1/2}$] behavior of the order parameter. If we take the order parameter to be the polarization P_y , which has symmetry B_2 in C_{2v} , then all the elastic constants can couple to the order parameter via coupling terms $g_i \epsilon_i^2 P_y^2$, because P_y^2 and ϵ_i^2 ($i = 1, \dots, 6$) all have A_1 symmetry in C_{2v} . Hoshino *et al.*¹³ have found experimentally that the spontaneous polarization follows the mean-field behavior very well.

Finally, let us comment on the suggestion by Hikita *et al.*,¹⁸ that the temperature dependence of the elastic constants at constant pressures can only be explained by assuming a pressure dependence of the third-order coupling coefficients. For K_2SeO_4 , Benoit *et al.*⁵ derived an expression for the pressure dependence of the velocity and damping for longitudinal-acoustic waves propagating along [001] on the basis of $\epsilon_3 Q^2$ and $\epsilon_3^2 Q^2$ couplings between strain and order parameter, and without any explicit pressure dependence in the coupling coefficients. Their expression could account for many features of the experimental data. Due to the narrow temperature range of the I phase in AFB and the limited precision of Brillouin-scattering data, it is not feasible to carry out fits to such a detailed model; however, it seems plausible that such a model would be appropriate.

V. SUMMARY

We have measured the temperature and pressure dependence of the elastic constants C_{ii} , $i=1, 2, 3, 5, 6$. Our results indicate that quartic anharmonicities play an important role in determining the temperature dependence of the elastic

constants in the normal and commensurate phase upon approaching T_I and T_C , respectively. We have compared our Brillouin-scattering results with results from previous ultrasonic studies, and discussed them in the context of various theoretical models.

*Present address: Abt. Experimentelle Physik, Universitt Ulm, Albert-Einstein-Allee 11, D-89069 Ulm, FRG.

†Present address: Research Institute for Electronic Science, Hokkaido University, Sapporo 060, Japan.

‡Permanent address: Department of Physics, Faculty of Science, Hokkaido University, Sapporo 060, Japan.

¹H. Z. Cummins, *Phys. Rep.* **185**, 211 (1990).

²Gen Li, N. Tao, Le Van Hong, H. Z. Cummins, C. Dreyfus, M. Hebbache, R. M. Pick, and J. Vagner, *Phys. Rev. B* **42**, 4406 (1990), and references therein.

³Gen Li, X. K. Chen, N. J. Tao, H. Z. Cummins, R. M. Pick, and G. Hauret, *Phys. Rev. B* **44**, 6621 (1991).

⁴K. Parlinski, R. Currat, C. Vettier, I. P. Aleksandrova, and G. Eckold, *Phys. Rev. B* **46**, 106 (1992).

⁵J. P. Benoit, G. Hauret, Y. Luspin, A. M. Gillet, and J. Berger, *Solid State Commun.* **54**, 1095 (1985).

⁶J. J. L. Horikx, A. F. M. Arts, J. I. Dijkhuis, and H. W. Wijn, *Phys. Rev. B* **39**, 5726 (1989).

⁷S. Kudo and T. Hikita, *J. Phys. Soc. Jpn.* **45**, 1775 (1978).

⁸M. Iizumi and K. Gesi, *Solid State Commun.* **22**, 37 (1977).

⁹B. A. Strukov, T. L. Skomorokhova, V. A. Koptsik, A. A. Boiko, and A. N. Izrailenko, *Sov. Phys. Crystallogr.* **18**, 86 (1973).

¹⁰K. Gesi and K. Ozawa, *J. Phys. Soc. Jpn.* **36**, 1496 (1974).

¹¹Y. Makita and Y. Yamauchi, *J. Phys. Soc. Jpn.* **37**, 1470 (1974).

¹²A. Onodera and Y. Shiozaki, *J. Phys. Soc. Jpn.* **46**, 157 (1979).

¹³S. Hoshino, K. Vedam, J. Okaya, and R. Pepinsky, *Phys. Rev.* **112**, 405 (1958).

¹⁴A. P. Levanyuk and D. G. Sannikov, *Sov. Phys. Solid State* **18**, 245 (1977).

¹⁵Y. Ishibashi, *Ferroelectrics* **24**, 119 (1980).

¹⁶A. Simon, M. Takesada, K. Weishaupt, M. Gelfand, A. Onodera, and H. D. Hochheimer, *Solid State Commun.* **101**, 139 (1997).

¹⁷K. S. Aleksandrov, A. T. Anistratov, A. I. Krupnyi, V. G. Martynov, Yu. A. Popkov, and V. I. Fomin, *Sov. Phys. Crystallogr.* **21**, 296 (1976).

¹⁸T. Hikita, T. Tsukahara, and T. Ikeda, *J. Phys. Soc. Jpn.* **51**, 2900 (1982).

¹⁹K. Weishaupt, J. Th. Held, S. Kohn, A. Onodera, and H. D. Hochheimer, *J. Phys. Chem. Solids* **58**, 1603 (1997).

²⁰F. Kohlrausch, *Praktische Physik I* (Teubner Verlagsgesellschaft, Stuttgart, 1953), p. 406.

²¹P. S. Peercy and B. Morosin, *Phys. Rev. B* **7**, 2779 (1973).

²²J. Kobayashi, Y. Uesu, and B. A. Strukov, *Ferroelectrics* **64**, 49 (1985).

²³R. A. Cowley, *Philos. Mag.* **11**, 673 (1965); *Adv. Phys.* **12**, 421 (1963).

²⁴A. A. Maradudin and A. E. Fein, *Phys. Rev.* **128**, 2589 (1962).

²⁵Y. Uesu, J. Ogawa, N. Hanami, B. A. Strukov, and J. Kobayashi, *Phys. Status Solidi A* **67**, 693 (1981).

²⁶V. Fawcett, R. J. B. Hall, D. A. Zong, and V. N. Sankaranarayanan, *J. Raman Spectrosc.* **3**, 229 (1975).