PHYSICAL REVIEW B
CONDENSED MATTER

THIRD SERIES, VOLUME 46, NUMBER 14 1 OCTOBER 1992-II

Ferroelastic phase transition in $K_3Na(SeO_4)_2$: Brillouin-scattering studies and theoretical modeling

B. Mróz
The Institute of Physics, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

H. Kiefte and M. J. Clouter
Department of Physics, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7

J. A. Tuszyński
Department of Physics, University of Alberta, Edmonton, Alberta, Canada T6G 2J1
(Received 10 February 1992)

High-resolution Brillouin spectroscopy was used to study the elastic properties of ferroelastic $K_3Na(SeO_4)_2$. The temperature dependence of nine Brillouin modes of the acoustic phonons propagating in the [100], [010], [001], and [011] directions were measured in the temperature range 290–380 K. These results indicate a $\bar{3}m \rightarrow 2/m$ transition at $T_c = 334$ K followed, by approximately 12 K, by a transition involving an unknown mode Q. Mode softening in the c_{66} and c_{44} elastic constants results from the main first-order transition while an additional softening in c_{33} and c_{44} is due to coupling with Q. A Landau-type free-energy expansion has been postulated and discussed in order to explain the qualitative features of the system.

I. INTRODUCTION

Ferroelastic properties are exhibited by several crystals belonging to such different families as A_2BX_4, $ACBX_4$, and $A_3C(BX_4)_2$, where $BX_4 = SO_4, SeO_4, CrO_4$, and $A, C = $ Li,Na,K,Rb,Cs and is usually a consequence of the spatial ordering of BX_4 tetrahedrons.[1–7] The family of interest here includes $K_3Na(CrO_4)_2$, $K_3Na(SO_4)_2$, and $K_3Na(SeO_4)_2$, which for convenience will be referred to respectively as KNCr, KNS, and KNSe. Brillouin scattering studies of KNCr around its ferroelastic phase transition at 239 K have been presented in a recent paper.[1] The present paper is devoted to similar studies of KNSe.

It was recently shown by Krajewski, Piskunowicz, and Mróz[8] that KNSe exhibits ferroelastic properties at room temperature. The ferroic phase exists up to the 334–346 K range, where the structural phase transition to the prototype phase takes place. This transition was detected by a set of independent experiments, namely, dielectric, thermal expansion, differential thermal analysis (DTA), optical, and elastic properties studies.[8] The ferroelastic character of the relevant transition was concluded from observation of domain structure in polarized light, and from the temperature behavior of the elastic properties which showed acoustic phonon softening for $T \rightarrow T_c$.

Another interesting experimental feature of KNSe is evident on comparing the phase-transition temperature obtained from the DTA, expansion, and dielectric studies, which was found to be 346 K, and that from the sound velocities minima of the elastic properties measurements, which was found to be 10–12 degrees lower, i.e., at 334 K. In addition, the heat-capacity measurements point to the continuous character of the transition since no latent heat was detected. Results of the elastic properties studies, however, support Landau theory in that the $\bar{3}m \rightarrow 2/m$ transformation is predicted to be first order from symmetry considerations.[9,10]

From DTA studies (carried out in the temperature range from 100 to 1200 K) two other phase transitions were found (at 730 and 758 K) besides the ferroelastic phase transformation in the 334–346 K range. The melting point of KNSe was found at 1170 K. Assuming a similar temperature behavior of other glaserit structure compounds such as KNS and KNCr,[11,12] along with the directions of ferroelastic domain walls and the lack of pyroelectric and piezoelectric properties, the following phase transition sequence was proposed for KNSe:[8]

$$\begin{array}{ccccccccc} 2/m & \leftarrow & \bar{3}m & \leftarrow & \text{unknown} & \leftarrow & 6/mmm & \leftarrow & \text{melt} \\ 334\text{–}346\ \text{K} & & 730\ \text{K} & & & & 758\ \text{K} & & 1170\ \text{K} \end{array}$$

To date there is no complete information about x-ray studies of KNSe in both low- and high-temperature phases around 334 K. Preliminary structural investigation[12] of the room-temperature phase, however, points to the $2/m$ group. This, together with the results of elastic property measurements, using the torsion vibration technique and composite bar method,[8] strongly supports the suggestion that the ferroelastic phase transition of KNSe is of the type $\bar{3}m \rightarrow 2/m$. Such a transition is known to be driven by the two-component order parameter[9] $\alpha(e_1-e_2)+\beta e_4$, where (e_1-e_2) and e_4 are the strain tensor components corresponding to the elastic constants $c_{66}=\frac{1}{2}(c_{11}-c_{12})$ and c_{44}, respectively of the prototype phase $\bar{3}m$. From the temperature dependence[8] of the torsion moduli $G_1(c_{55},c_{66})$, $G_2(c_{44},c_{66})$,$G_3(c_{44},c_{55})$ (and taking into account that for trigonal symmetry $c_{44}=c_{55}$), it is in fact evident that both c_{44} and c_{66} are affected by the transition, but not to the same degree. This in turn leads to differing values of the coefficients α and β describing the order parameter, as distinct from the results for the Brillouin studies of KNCr.[1]

In the present paper, Brillouin scattering studies of KNSe, in the temperature range from 290 to 380 K, are reported. The temperature dependences of nine Brillouin modes of the four phonons propagating in the [100], [010], [001], and [011] directions were measured. From these data, it was possible to determine the values of all components of the elastic stiffness tensor of the prototype group $\bar{3}m$. The advantage of using the Brillouin scattering technique to study elastic properties of the crystal around its phase transition is that the temperature behavior of at least two acoustic modes (L—longitudinal and T—transverse) related to the same phonon can be observed simultaneously. This seems to be important in the case of KNSe because of a rather complicated picture of the ferroelastic phase transition as given in Ref. 8. A theoretical model based on the mean-field approximation is presented in Sec. IV.

II. EXPERIMENTAL PROCEDURE

Single crystals of KNSe were grown isothermally from a saturated aqueous solution of the product of synthesis of chemically pure sodium, potassium hydroxide, and selenate acid at 315 K. The synthesized compound was purified by recrystallization from distilled water. Colorless and transparent crystals were obtained in the form of hexagonal prisms with pseudohexagonal twins visible in polarized light. The density of KNSe was found to be[8] 3.15 g/cm^3. Samples of four different orientations were prepared from untwinned parts of the crystal to study the sound velocity propagations of the [100], [010], [001], and [011] phonons. Samples were typically of sizes $4\times4\times4$ mm^3.

The Brillouin spectrometer has been described in detail by Ahmad *et al.*[13] The incident light, polarized perpendicularly to the scattering plane, was provided by a stabilized single-mode argon-ion laser (INNOVA 90-5, Coherent) operating at 514.5 nm. The scattered light was analyzed by 90° using a piezoelectrically scanned triple pass Fabry-Pérot interferometer (Burleigh RC-110) with free-spectral ranges (FSR) of 22.04, 24.75, and 18.10 GHz. Spectra were accumulated with a photon-counting data acquisition and stabilization system (DAS-1, Burleigh).

Sound velocities v were deduced from the measured frequency shifts using the Brillouin equation:

$$v=\lambda\Delta\vartheta(n_i^2+n_s^2-2n_in_s\cos\theta)^{-1/2} , \quad (1)$$

where λ is the wavelength of the incident light, n_i and n_s are refractive indices for the incident and scattered light, respectively, and θ is the scattering angle ($\theta=90°$). The refractive indices for KNSe were found at room temperature by comparing the crystal samples with liquids (Cargille Labs) of known refractive indices. It was found that $n_x=n_y=1.550$, $n_z=1.542\pm0.002$. The temperature dependence of the density has been neglected since the volume expansion coefficient changes by only 2×10^{-5} K^{-1} at T_c. The refractive indices of KNSe are therefore taken to be constant in the entire temperature region studied. This is also supported by the dielectric properties studies[8] where only slight changes in the slopes of $\varepsilon'(T)$ curves at T_c are indicated.

The Brillouin scattering experiments on KNSe were performed from 290 to 380 K, using a sealed container. It was equipped with three windows and a double thermal screen and clamping device to minimize the temperature gradient along the sample. The temperature of the sample was regulated with a stability of ±0.02 K using a THOR Cryogenics (model 3010 II) temperature controller.

III. EXPERIMENTAL RESULTS

At room temperature KNSe exhibits ferroelastic properties with monoclinic point symmetry $2/m$; this suggests a trigonal $\bar{3}m$ prototype symmetry.[8] The elastic stiffness tensor of the trigonal group $\bar{3}m$ contains six independent components, namely, c_{11}, c_{33}, c_{44}, c_{12}, c_{13}, and c_{14}; $(2c_{66}=c_{11}-c_{12})$. Table I presents expressions of ρv^2 as a function of elastic constants for the trigonal ($\bar{3}m$ prototype) and $2/m$ (ferroelastic) phase. These were found from the solution of the equation of motion for the three acoustic waves propagating in direction **Q**, as given by

$$|c_{ijkl}q_jq_k-\rho v^2\delta_{il}|=0 , \quad (2)$$

where q_j, q_k are the direction cosines of **Q**, ρ is the density of the crystal[8] (3.15 g/cm^3), and c_{ijkl} are the elastic stiffness tensor components.

In the present work, nine of the twelve Brillouin modes listed in Table I have been observed. It should be noted that in the case of phonons [010], [001], and [011] the temperature dependence of the sets of modes $(\gamma_4,\gamma_5,\gamma_6)$, (γ_7,γ_9), and $(\gamma_{10},\gamma_{11},\gamma_{12})$, respectively, were measured simultaneously. Because of the rather weak scattering power of phonon [100], only the temperature dependence of the longitudinal mode γ_1, related directly to the c_{11} elastic constant (see Table I), was observed. About 260 experimental points from over 150 spectra have been collected in Fig. 1. The relative accuracy of the frequency shifts from one temperature to another is less than 0.5%. The absolute accuracy, because of uncertainty in crystal refractive index, density, and geometry, is estimated to be about 2%.

TABLE I. ρv^2 as a function of the elastic constants in the trigonal ($\bar{3}m$) and monoclinic ($2/m$) phases. The asterisks indicate which modes were observed in the present experiment.

	$\bar{3}m$ paraelastic	$2/m$ ferroelastic
$^*\gamma_1^L$	c_{11}	$\frac{1}{2}\{c_{11}+c_{55}+\sqrt{(c_{11}-c_{55})^2+4c_{15}^2}\}$
[100] γ_2^T	$\frac{1}{2}\{c_{44}+c_{66}+\sqrt{(c_{44}-c_{66})^2+4c_{14}^2}\}$	$\frac{1}{2}\{c_{11}+c_{55}-\sqrt{(c_{11}-c_{55})^2+4c_{15}^2}\}$
γ_3^T	$\frac{1}{2}\{c_{44}+c_{66}-\sqrt{(c_{44}-c_{66})^2+4c_{14}^2}\}$	c_{66}
$^*\gamma_4^L$	$\frac{1}{2}\{c_{11}+c_{44}+\sqrt{(c_{11}-c_{44})^2+4c_{14}^2}\}$	c_{22}
[010] $^*\gamma_5^T$	$\frac{1}{2}\{c_{11}+c_{44}-\sqrt{(c_{11}-c_{44})^2+4c_{14}^2}\}$	$\frac{1}{2}\{c_{66}+c_{44}+\sqrt{(c_{44}-c_{66})^2+4c_{46}^2}\}$
$^*\gamma_6^T$	$c_{66}=\frac{1}{2}(c_{11}-c_{12})$	$\frac{1}{2}\{c_{66}+c_{44}-\sqrt{(c_{44}-c_{66})^2+4c_{46}^2}\}$
$^*\gamma_7^L$	c_{33}	$\frac{1}{2}\{c_{33}+c_{55}+\sqrt{(c_{33}-c_{55})^2+4c_{35}^2}\}$
[010] γ_8^T	c_{44}	$\frac{1}{2}\{c_{33}+c_{55}-\sqrt{(c_{33}-c_{55})^2+4c_{35}^2}\}$
$^*\gamma_9^T$	c_{44}	c_{44}
$^*\gamma_{10}^L$	$\frac{1}{4}(c_{11}+c_{33}+2c_{44}-2c_{14})+\frac{1}{2}\sqrt{\frac{1}{4}(c_{11}-c_{33}-2c_{14})^2+(c_{13}+c_{44}-c_{14})^2}$	
[011] $^*\gamma_{11}^T$	$\frac{1}{2}(c_{44}+c_{66})+c_{14}$	
$^*\gamma_{12}^T$	$\frac{1}{4}(c_{11}+c_{33}+2c_{44}-2c_{14})-\frac{1}{2}\sqrt{\frac{1}{4}(c_{11}-c_{33}-2c_{14})^2+(c_{13}+c_{44}-c_{14})^2}$	

It is evident that all observed modes are affected by the transition. The Brillouin shift for the γ_1 mode [Fig. 1(a)] increases linearly with decreasing temperature, decreases slightly, remains constant in the temperature region from 345 to 335 K, and then slowly increases again with decreasing temperature. These two temperatures (335 and 345 K), taken with an accuracy of ±2°, are characteristic for all the anomalous changes in the observed modes. For example, the γ_5 mode [Fig. 1(b)] exhibits two very slight minima at 336 and 344 K, whereas the γ_6 mode shows a more typical softening and falls from 9.63 GHz at 347 K to 5.71 GHz at 334.5 K. The longitudinal γ_7 mode [Fig. 1(c)] shows softening with a minimum frequency shift at about 346 K. The transverse mode γ_9, of the same [001] phonon, has a temperature behavior similar to the γ_5 mode with indications of two anomalies at about 337 and 346 K. The Brillouin shifts of the modes γ_{10}, γ_{11}, and γ_{12} of phonon [011] are presented in Fig. 1(d). All three modes are temperature dependent and show acoustic softening. The quasilongitudinal mode γ_{10} reaches a minimum at 343 K and then increases with further temperature decrease. A minimum in the sound velocity for quasitransverse mode γ_{11} was detected at about 335 K. The phase transition for the γ_{12} mode is less pronounced and a minimum in sound velocity was found at about 339 K.

The anomalous behavior of the Brillouin frequency shifts of KNSe is also reflected in the temperature dependence of the elastic constants or their combinations (see Fig. 2). For modes γ_1, γ_6, γ_7, and γ_9, the expressions of ρv^2 give the direct values of elastic constants c_{11}, c_{66}, c_{33}, and c_{44}, respectively, of the high-temperature trigonal phase. Values of all the elastic constants of the prototype phase, calculated far from the transition at 373 K, are presented in Table II. It is worth noting the very small value of the c_{14} elastic constant, indicating that the system is elastically close to hexagonal symmetry in the high-temperature phase.

The results presented in this paper did not allow for calculation of the elastic constants for the room-temperature monoclinic $2/m$ phase. The elastic constants for the ferroelastic phase may, however, depend on the actual configuration of domain walls,[14] since the measurements were performed using untwinned but polydomain samples.

As is evident from Fig. 2, the largest temperature dependence was found for the elastic constant c_{66}. The related sound velocity changes from 2270 m/s at 347 K to 1340 m/s at 334.5 K. Another elastic constant which should be sensitive to the onset of criticality with respect to the $\bar{3}m \rightarrow 2/m$ ferroelastic phase transition is c_{44}. The relevant temperature dependence is presented in Fig. 2(c). In contrast to KNCr,[1] c_{44} for KNSe changes only slightly but shows two minima, one at 346 and another at 337 K. According to the theoretical model developed for KNCr,[1] the slopes of $c_{66}(T)$ and $c_{44}(T)$ while approaching minima are a measure of the α and β coefficients describing the order parameter $\alpha(e_1-e_2)+\beta e_4$. The slope of $c_{66}(T)$ was found to be about five times higher than that of $c_{44}(T)$ (7×10^{-2} and 1.5×10^{-2} N/m^2 K, respectively). This was in agreement with the results obtained by Krajewski, Piskunowicz, and Mróz[8] and indi-

TABLE II. Elastic constants of $K_3Na(SeO_4)_2$ at 373 K in units of 10^{10} Nm^{-2}. The noted uncertainties are relative values.

c_{11}	c_{33}	c_{44}	c_{12}	c_{13}	c_{14}
5.67±0.08	6.29±0.10	1.46±0.08	2.31±0.07	0.74±0.09	0.052±0.08

cated the leading role of the (e_1-e_2) strain component in the transition being studied. As was shown by Boccara,[11] the soft elastic constant related to the order parameter $\alpha(e_1-e_2)+\beta e_4$ is $c_{2s}=\frac{1}{2}\{c_{44}+2c_{66}-\sqrt{(2c_{66}-c_{44})^2+8c_{14}^2}\}$. The temperature dependence of c_{2s} at the paraelastic trigonal phase has been calculated and is shown in Fig. 3. The temperature dependence of c_{2s} is less pronounced than that observed for c_{66}. The minimum of the sound velocity relevant to c_{2s} was calculated to be 1897 m/s at 334.5 K.

Finally, the adiabatic-isothermal correction has been evaluated, since the Brillouin scattering technique measures the adiabatic elastic constants, whereas, the mean-field approximation refers to the isothermal elastic constants. The c_{11}, c_{12}, c_{13}, and c_{33} elastic constants are affected by this;[15] however, the largest correction is about 2% (for c_{33}) close to the transition temperature. Consequently, this effect is neglected and in the theoretical model and it is assumed that $c_{ij}^S \simeq c_{ij}^T$. This is entirely consistent with the absolute accuracy of the present measurements.

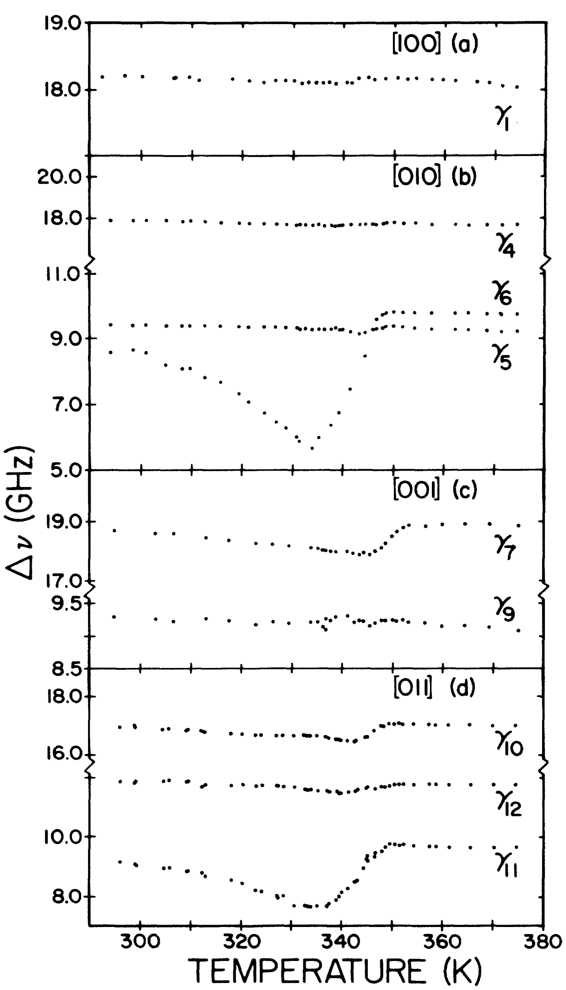

FIG. 1. Temperature dependence of Brillouin frequency shifts for phonons propagating in the directions (a) [100], (b) [010], (c) [001], (d) [011] in $K_3Na(SeO_4)_2$.

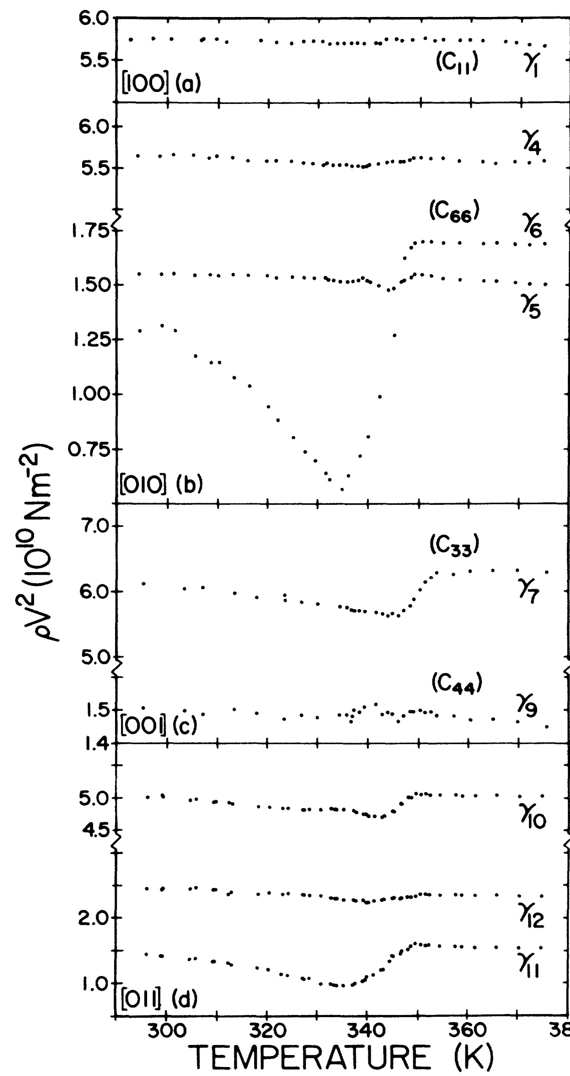

FIG. 2. Temperature dependence of the elastic constants and their combinations [for the paraelastic $\bar{3}m$ phase of $K_3Na(SeO_4)_2$] as determined from the data in Fig. 1 (refer to Table I).

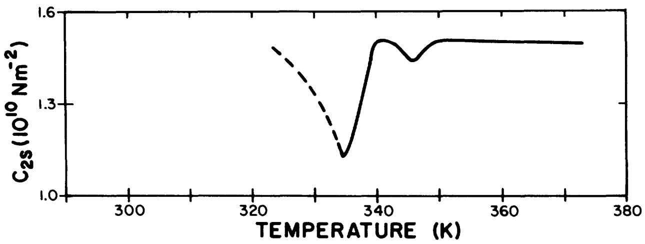

FIG. 3. Temperature dependence of the soft elastic constant c_{2s} for $K_3Na(SeO_4)_2$.

IV. THEORETICAL MODEL

As was argued throughout this paper, the experimental data presented here are consistent with a $\bar{3}m \rightarrow 2/m$ type of transition. There are, however, specific differences between the present case and the general transition type. Relative qualitative experimental features are summarized in Fig. 4. In this section a step-by-step theoretical model will be developed which accounts for the qualitative features revealed by the experiment.

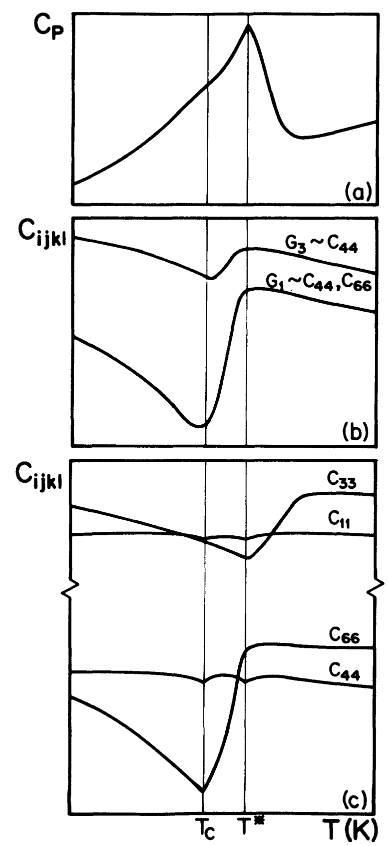

FIG. 4. Anomalous experimental features of $K_3Na(SeO_4)_2$. (a) Temperature dependence of heat capacity (Ref. 8). (b) Elastic constant measured using the torsion vibration technique (Ref. 8). (c) Elastic constant measured using the Brillouin scattering technique.

A. The primary order parameter

The $\bar{3}m \rightarrow 2/m$ type of transition has been discussed by Boccara[9] in the context of classes of phase transitions characterized by a deformation of the unit cell. This transition exhibits the loss of the ternary axis of symmetry $(0x_3)$ and is necessarily of first order due to strict symmetry requirements. Because $G=2/m$ is an invariant subgroup of G_0 with the order of 4 while the order of G_0 is 12, the factor group G_0/G is of order 3, and terms cubic in the order parameter σ are admitted in the free-energy expansion. According to Boccara's[9] theorem four this implies the existence of a cubic invariant. As mentioned before, following Boccara[9] the order parameter σ is assumed to take the form of a linear combination of e_6 and e_4, i.e.,

$$\sigma=\alpha(e_1-e_2)+\beta e_4 \ , \tag{3}$$

where α and β are in general arbitrary but can be determined from experiment. Following Toledano, Fejer, and Auld,[16] the corresponding free-energy expansion takes the form

$$F=c_2(e_6^2+e_4^2)+c_3(e_4^3-3e_4e_6^2)+c_4(e_6^2+e_4^2)^2 \ . \tag{4}$$

Minimizing F with respect to e_6 and e_4 yields the following two simultaneous equations:

$$(2c_2-6c_3e_4+4c_4e_4^2)e_6+4c_4e_6^3=0 \tag{5a}$$

and

$$(2c_2+4c_4e_6^2)e_4+3c_3e_4^2+4c_4e_4^3=3c_3e_6^2 \ . \tag{5b}$$

Equation (4) implies that either $e_6=0$ or e_6 is a nonzero solution of the following algebraic equation:

$$e_6^2=-(c_2-3c_3e_4+2c_4e_4^2)/2c_4 \ . \tag{6}$$

If $e_6 \neq 0$, then Eqs. (5a) and (5b) can be solved to yield

$$e_6=\pm\sqrt{3}e_4 \ , \tag{7}$$

i.e., the two seemingly independent variables are proportional to each other. As a result, the problem reduces to an equation of state for first-order phase transitions with a single-component order parameter, namely,

$$-2c_2+6c_3e_4-16c_4e_4^2=0 \ . \tag{8}$$

Assuming that $c_2=a(T-T_0)$, the transition temperature is found to be

$$T_c=T_0+\frac{c_3^2}{4ac_4} \ . \tag{9}$$

This case was discussed at length in our previous paper[1] devoted to KNCr and the reader is referred to it for more details. The important point is, however, that the elastic constants (both c_{66} and c_{44}) exhibit a single dip at $T=T_c$ with their lowest values of

$$c_{2s}^{\min}(T_c)=c_3^2/2c_4 \ . \tag{10}$$

This is illustrated graphically in Fig. 5(a). Note that, as usual, the elastic constants are calculated according to the formula

$$c_{ij}=\partial^2 F/\partial e_i \partial e_j \ . \tag{11}$$

Comparing the diagrams in Fig. 4 with that of Fig. 5 it has to be concluded that another mode bifurcates at a temperature slightly above T_c and that it is coupled to e_4 but not e_6. Since c_{33} also exhibits softening at this temperature, it is possible that e_3 is the mode in question. Without presupposing this we denote this mode Q and label $e_4=\sigma$. In the next subsection it will be shown that a bilinear coupling between σ and Q results in a double dip in c_{44}, as seen in experiment.

B. Coupling to a secondary order parameter

The effective free energy which describes the interactions involving e_4 and the yet unidentified secondary order parameter Q undergoing a transition at T^* is postulated in the form

$$F_{\text{eff}}=a_2\sigma^2+a_3\sigma^3+a_4\sigma^4+b_2Q^2+b_3Q^3+b_4Q^4+\lambda\sigma Q \ , \tag{12}$$

where $a_2=\alpha(T-T_0)$ and $b_2=\beta(T-T_1)$. The coefficients a_2, a_3, and a_4 are related to the coefficients c_2, c_3, and c_4 of the previous subsection through

$$a_2=4c_2, \quad a_3=-8c_3, \text{ and } a_4=16c_4 \ , \tag{13}$$

in order to account for a relationship between the e_4 and e_6 modes. Thus, for $\lambda=0$, e_4 undergoes a transition at T_c, as argued before. Minimizing F_{eff} with respect to both e_4 and Q yields

$$2a_2\sigma+3a_3\sigma^2+4a_4\sigma^3+\lambda Q=0 \tag{14}$$

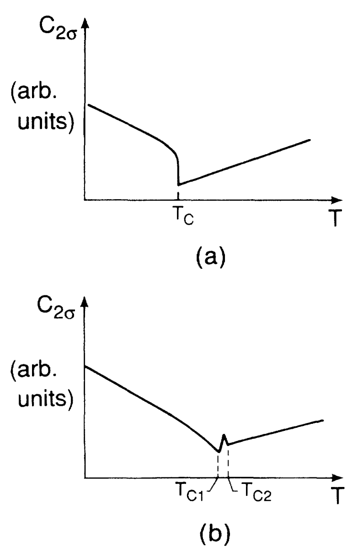

FIG. 5. Graphical illustration of the elastic constant behavior for the free energy of Eq. (4), where the comparison is made between the single-dip profile in the case for decoupled modes (a) and the double-dip profile in the case for two coupled modes.

and

$$2b_2Q+3b_3Q^2+4b_4Q^3+\lambda\sigma=0 \ . \tag{15}$$

Solving Eq. (14) for Q and substituting into Eq. (15) effectively decouples the two modes and provides a "renormalized" equation of state for the mode e_4;

$$d_1\sigma+d_2\sigma^2+d_3\sigma^3+\cdots=0 \ , \tag{16}$$

where

$$d_1=-\frac{4a_2b_2}{\lambda}+\lambda, \quad d_2=\frac{6}{\lambda}\left[\frac{2b_3a_2^2}{\lambda}-b_2a_3\right] ,$$

and

$$d_3=-\frac{8}{\lambda}\left[\frac{4b_4a_2^3}{\lambda^2}-a_4b_2\right] . \tag{17}$$

The above equation of state allows two first-order phase transitions to occur in succession since *both* a_2 and b_2 are temperature dependent. A necessary condition for this is that d_1 change sign and that does take place at the two different values of T which are solutions of the equation $d_1=0$, namely

$$T_{01/02}=\frac{T_1+T_0}{2}\pm\left[\left[\frac{T_1-T_0}{2}\right]^2+\delta\right]^{1/2} , \tag{18}$$

where $\delta\equiv\lambda^2/(4\alpha\beta)$. At both of these temperatures T_{01} and T_{02} the modes σ and Q bifurcate in a discontinuous manner, so that Eq. (16) is satisfied identically. Also, the elastic constants exhibit incomplete softening as in a single transition case, but this now occurs at each of the two transition temperatures T_{c1} and then at T_{c2}, which are determined below. Defining

$$c_{2\sigma}\equiv\partial^2F_{\text{eff}}/\partial\sigma^2=2a_2+6a_3\sigma+12a_4\sigma^2 \ , \tag{19}$$

and similarly

$$c_{2Q}\equiv\partial^2F_{\text{eff}}/\partial Q^2=2b_2+6b_3Q+12b_4Q^2 \ , \tag{20}$$

we see that the initial transition occurs at $T_{c1/c2}$ such that

$$d_1=\frac{2}{9}\frac{d_2^2}{d_3} \ (\text{at } T_{c1/c2}) \ , \tag{21}$$

and at which the minimum values of the elastic constant are

$$c_{2\sigma}(T_{c1/c2})=d_1 \ . \tag{22}$$

A detailed calculation of these two conditions in Eqs. (21) and (22) can be found in Ref. 1, where a single first-order phase transition was studied within the Landau model. A schematic plot of $c_{2\sigma}$ as a function of T for this case [see Fig. 5(b)] very closely resembles that shown in experiment (Fig. 3). Also note that *both* e_4 and Q have the same qualitative behavior. This indeed rules out e_3 as the secondary order parameter since it (c_{33}) only softens at T^* (now identified with T_{c1}) but not at T_c (identified with T_{c2}). Obviously, e_3 must be coupled to Q as well to manifest a softening through c_{33}.

C. The curvature of $c_2(T)$

In this subsection we wish to briefly discuss the profile of the elastic constants c_{33}, c_{44}, and c_{66} on the approach to the critical temperature from above. It can be seen from Fig. 4 that all these coefficients exhibit a crossover from one nearly linear dependence above T^* (almost constant but decreasing slightly with temperature) to another which is increasing with temperature (between T_c and T^*). Our working hypothesis here is that fluctuations are responsible for the crossover at T^*.

To focus attention on a simple model, only one degree of freedom will be retained, i.e., σ. Then, the approximate free energy is

$$F_0 \cong a_2\sigma^2 + a_3\sigma^3 + a_4\sigma^4 . \tag{23}$$

The corresponding elastic coefficient is

$$c_{2\sigma} = \frac{\partial^2 F_0}{\partial \sigma^2} = 2a_2 + 6a_3\sigma + 12a_4\sigma^2 . \tag{24}$$

It is clear that in the disordered phase (above T_c)$\sigma=0$ and with $a_2=\alpha(T-T_0)$; $c_{2\sigma}$ in this temperature regime is a linear function of temperature, i.e.,

$$c_{2\sigma} = 2\alpha(T-T_0) . \tag{25}$$

However, this has been found assuming a mean-field approach with *no* accounting for fluctuations. The simplest way of taking fluctuations into account is to weight various order-parameter values σ with a statistical (Boltzmann) probability. Then, a more accurate estimate of $c_{2\sigma}$ which accounts for fluctuations in the order parameter is

$$c_{2\sigma} = 2\alpha(T-T_0) + 12_{a4}\langle \sigma^2 \rangle . \tag{26}$$

Within the Gaussian approximation, and neglecting the $a_3\sigma^3$ term, $\langle \sigma^2 \rangle$ can be estimated in a standard way as[17]

$$\langle \sigma^2 \rangle \cong \frac{kT}{2a_2} \tag{27}$$

where k is the Boltzmann constant. This is valid sufficiently far away from T_c. Thus, assuming that $T \gg T_0$ or T_c we may expand the denominator in a series of (T_0/T) such that in the lowest order the elastic coefficient becomes

$$c_{2\sigma} \cong 2\alpha(T-T_0) + \frac{6a_4 k}{\alpha}\left[1+\frac{T_0}{T}\right] + \cdots . \tag{28}$$

This explains the crossover region's curvature of $c_{2\sigma}(T)$.

On the other hand, close to the transition temperature fluctuations become significant and a non-Gaussian approach has to be used. Based on recent results we find that in general[18]

$$\langle \sigma^2 \rangle = \sqrt{kT/8a_4}\, D_{-3/2}(x)/D_{-1/2}(x) , \tag{29}$$

where D_{-a} is a parabolic cylinder function and $x \equiv \sqrt{a_2^2/2kTa_4}$. For small values of x, i.e., close to T_0, we obtain a first-order approximation to $c_{2\sigma}$ in the form

$$c_{2\sigma} \cong -2.05\alpha(T-T_0) + 4.05\sqrt{kTa_4} , \tag{30}$$

where we have used the values of $\Gamma(\frac{5}{4})$ and $\Gamma(\frac{3}{4})$. It is important to note that on comparing Eq. (30) with (28) the linear coefficient has changed its sign on going from high to low temperatures (with respect to T_0). This is in qualitative agreement with all the plots for c_{33}, c_{44}, and c_{66}. The near equality of the magnitude (i.e., 2 versus 2.05) of these linear temperature-dependence coefficients is not borne out by experiment [see Fig. 4(c)]. Our cursory derivation provided in this subsection, however, was not meant to give all details and such aspects as mode-mode coupling and the inclusion of cubic terms in the calculations of $\langle \sigma^2 \rangle$ were not taken into consideration. Undoubtedly, taking these into account would affect the values of the coefficients, leading to a more pronounced asymmetry.

V. SUMMARY

This paper was concerned with the vicinity of the ferroelastic phase transition in $K_3Na(SeO_4)_2$. Through Brillouin scattering studies it was demonstrated that a $\bar{3}m \rightarrow 2/m$ transition takes place at 334 K. However, the plots of elastic coefficients c_{11}, c_{33}, c_{44}, and c_{66} revealed that the transition is not of proper type since c_{33} exhibited a softening some 10 K above the actual transition. Moreover, c_{44} showed two pronounced dips: one at T_c and the other coincided with that for c_{33}. It was then concluded that, in addition to the primary order parameter $\sigma=\alpha(e_1-e_2)+\beta e_4$ characterizing the transition at T_c, a secondary order parameter called Q must exist which governs the pretransition at T^*. Since c_{33} shows no anomaly at T_c while c_{44} has two anomalies, one at T_c and another at T^*, it was inferred that most likely Q is different from e_3 and that it couples to both e_4 and e_3. A theoretical analysis was carried out on the premise that σ and Q are responsible for driving two closely located transitions and that σ and Q are coupled linearly. It was then shown that a Landau model based on the above leads to qualitative features consistent with experiment. Finally, the shape of the elastic constant curves as a function of temperature was discussed with particular attention given to a crossover region. The change of slope occuring in the crossover region was explained as resulting from critical fluctuations.

ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada and the Polish Academy of Sciences. The authors wish to thank Professor T. Krajewski for kindly providing them with crystals grown in his laboratory and also for many helpful discussions. One of the authors (B.M.) wishes to thank the faculty and staff of the Department of Physics at Memorial University of Newfoundland, for their hospitality during his stay in St. John's.

[1]B. Mróz, H. Kiefte, M. J. Clouter, and J. A. Tuszyński, Phys. Rev. B **43**, 641 (1991).
[2]W. K. Lee and H. Z. Cummins, Phys. Rev. B **39**, 4456 (1989).
[3]L. Ethier, N. E. Massa, A. Beliveau, and C. Carlone, Can. J. Phys. **67**, 657 (1989).
[4]H. Schulz, U. Zucker, and R. Frech, Acta Crystallogr. B **41**, 21 (1985).
[5]H. Klapper, Th. Hahn, and S. J. Chung, Acta Crystallogr. B **43**, 147 (1987).
[6]Y. Makita, A. Sawada, and Y. Takagi, J. Phys. Soc. Jpn. **41**, 167 (1976).
[7]B. Mróz, J. A. Tuszyński, H. Kiefte, and M. J. Clouter, J. Phys. Condens. Matter **1**, 5965 (1989).
[8]T. Krajewski, P. Piskunowicz, and B. Mróz, Phys. Status Solidi A (to be published).
[9]N. Boccara, Ann. Phys. (N.Y.) **47**, 40 (1964).
[10]J. C. Toledano and P. Toledano, *The Landau Theory of Phase Transition* (World Scientific, Singapore, 1987).
[11]E. M. Hilmy, Am. Mineral **38**, 118 (1953).
[12]W. Eysel, Z. Kristallogr. **132**, 426 (1970); Am. Mineral **58**, 736 (1973); T. Breczewski (private communication).
[13]S. F. Ahmad, H. Kiefte, M. J. Clouter, and M. D. Whitmore, Phys. Rev. B **26**, 4239 (1982).
[14]B. Gu, M. Copic, and H. Z. Cummins, Phys. Rev. B **24**, 4098 (1981).
[15]J. F. Ney, *Physical Properties of Crystals* (Clarendon, Oxford, 1957).
[16]P. Toladano, M. M. Fejer, and B. A. Auld, Phys. Rev. B **27**, 5717 (1983).
[17]J. A. Tuszyński, M. J. Clouter, and H. Kiefte, Phys. Lett. A **108**, 272 (1985).
[18]J. A. Tuszyński, M. J. Clouter, and H. Kiefte, Phys. Rev. B **33**, (1986).