Ferroelastic phase transition in $K_3Na(CrO_4)_2$: Brillouin scattering studies and theoretical modeling

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For $K_3Na(CrO_4)_2$, Brillouin shifts related to elastic constants have been measured in the range of temperatures between 140 and 300 K. All modes have been affected, to various degrees, by the $2/m \rightarrow \bar{3}m$ transition at about 231 K. A Landau model has been proposed in order to provide a qualitative description of the ferroelastic transition. It is argued that it is a weakly first-order transition.

I. INTRODUCTION

Among the crystals containing BX_4 (SO_4, SeO_4, CrO_4) tetrahedrons, described by the formulas A_2BX_4, $ACBX_4$, and $A_3C(BX_4)_2$, where A,C = Li, Na, K, Rb, Cs, NH_4 there is a large group of materials that show an interesting sequence of phase transitions and the appearance of ferroic phases[1-6] as a consequence of spatial ordering of BX_4 groups. $K_3Na(CrO_4)_2$ is such a material and on which very little experimental work has been carried out. Even within the very sparse literature, there is a controversy regarding the nature of the relevant phase transition.

As was recently found from dielectric, thermal, optical, and elastic studies performed by Krajewski *et al.*,[7] $K_3Na(CrO_4)_2$ exhibits a ferroelastic phase transition at about 239 K. No discontinuity in the elastic distortion ($\Delta L/L$) was detected in the course of thermal expansion studies of $K_3Na(CrO_4)_2$ and could point to the second-order character of the transition. A very small, but detectable, entropy change, however, was determined from DTA (differential-thermal-analysis) measurements. The ferroelastic character of the observed transition was confirmed by the observation of domain structure and a strong decrease in the torsional vibration frequencies related to the acoustic phonon softening. From the morphology of the crystal, the lack of pyro- and piezoelectric properties, and the analysis of the domain structure, it was concluded that the phase transition observed at 239 K is of the $\bar{3}m \rightarrow 2/m$ type. As will be elaborated below, this particular symmetry change implies a first-order transition.

In addition, from the DTA studies,[7] it was found that $K_3Na(CrO_4)_2$ undergoes another structural phase transition at 853 K. This information together with the known structural isomorphism of the corresponding sulfates and selenates suggests the following sequence of phase transitions for $K_3Na(CrO_4)_2$:

$$2/m \underset{T_1=239\text{ K},}{\leftarrow} \bar{3}m \underset{T_2=853\text{ K},}{\leftarrow} 6/\text{mmm} \underset{T_m=1160\text{ K}}{\leftarrow} \text{melt}\ .$$

This sequence is also supported by the recent (room temperature) x-ray studies of Madariga and Breczewski.[8] From their work, the space group is $P\bar{3}m1$ with $a=5.8580(6)$ Å, $c=7.523(2)$ Å, $Z=1$, and density $\rho=2.77(2)$ g cm^{-3}. Using ultrasonic techniques, they also found that the c_{44} elastic constant is strongly temperature dependent as $T \rightarrow T_c$. Furthermore, from studies of the elastic properties using the torsion pendulum technique,[7] it is evident that all torsion moduli G_i ($i=1,2,3$) are affected by the phase transition. Since the G_i are functions of the elastic constants, $G_1(c_{55},c_{66})$, $G_2(c_{44},c_{66})$, $G_3(c_{44},c_{55})$, and from the symmetry of the point group $\bar{3}m$, namely, $c_{44}=c_{55}$, $2c_{66}=c_{11}-c_{12}$, and the results of the domain structure analysis, it was concluded that the observed transition is driven by a two-component order parameter related to the c_{44} and c_{66} elastic constants, namely, e_4 and $e_6=\frac{1}{2}(e_1-e_2)$.

In the present work Brillouin scattering studies of $K_3Na(CrO_4)_2$ in the temperature range from 140 to 300 K are reported. The temperature dependences of eight Brillouin modes have been measured. This allowed for the determination of the temperature changes of all six elastic-stiffness tensor components for the prototype phase $\bar{3}m$. The possible forms of the soft elastic constants related to the $\bar{3}m \rightarrow 2/m$ transition are also discussed. A theoretical model based on the mean-field approximation using Landau theory is presented from which satisfactory agreement with the experimental results is noted and the nature of the phase transition is clearly defined.

II. EXPERIMENTAL PROCEDURE

Single crystals of $K_3Na(CrO_4)_2$ were grown, at 315 K, from aqueous solutions using chemically pure sodium

and potassium hydroxides and chromium acid anhydride. Light-yellow crystals were obtained with a maximum edge length of about 20 mm. The standard choice of axes[9] was taken with the $\bar{3}$ axis parallel to Z and the two-fold axis coinciding with the X direction. Samples of three different orientations were prepared in the form of cubes $4\times4\times4$ mm^3. The prepared orientations allowed the measurement of sound velocities propagating along the crystallographic axes and the bisectors of these axes.

A detailed description of the Brillouin spectrometer is given elsewhere.[10] The incident light was provided by a stabilized single-mode argon-ion laser (Spectra Physics 2020) operating at 514.5 nm and polarized perpendicularly to the scattering plane. To avoid sample heating, the laser output power was reduced to about 60 mW. The scattered light was analyzed at $\Theta=90°$ with a triple-pass Fabry-Perot interferrometer (Burleigh RC-110), using free spectral ranges of 16.51 and 26.76 GHz, and detected by a cooled photomultiplier tube (ITT FW 130). Spectra were accumulated with a photon-counting data-acquisition and stabilization system (Burleigh DAS-1).

The sound velocities were found from the measured frequency shifts, $\Delta\nu$, using the Brillouin equation

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

where λ is the wavelength of the incident light, n_i and n_s are the refractive indices for the incident and scattered light, respectively. The refractive indices of $K_3Na(CrO_4)_2$ were found from the data presented in Ref. 11 to be $n_x=n_y=1.7361$, $n_z=1.7278$. The Brillouin scattering experiments were performed in the temperature range from 140 to 300 K using the cryostat described in a previous paper.[12] The temperature of the sample was regulated with a stability of ±0.05 K.

III. EXPERIMENTAL RESULTS AND ANALYSIS

At room temperature $K_3Na(CrO_4)_2$ belongs to the trigonal point group $\bar{3}m$ for which the elastic stiffness tensor contains six independent components: c_{11}, c_{33}, c_{44}, c_{12}, c_{13}, and c_{14}. Table I contains the expressions of ρv^2 as a function of elastic constants for the trigonal $\bar{3}m$ and monoclinic $2/m$ point groups. These expressions were found from solving the equations of motion[13] for the three acoustic waves propagating in the direction Q given by

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

where q_j, q_k are direction cosines of Q, ρ is the density of the crystal (2.772 g cm^{-3}), and c_{ijkl} are the elastic stiffness tensor components. The temperature dependence of the density and refractive index was neglected in the data analysis. Table I does not contain the relations $\rho v^2(c_{ijkl})$ for the phonons propagating in the [101] and [110] directions since the solutions of Eq. (2) for those directions are of third order.

Eight of the 12 Brillouin modes listed in Table I have been observed. As evident from Figs. 1(a)–1(d) each of the observed modes is affected by the transition. The frequency shifts of the longitudinal modes γ_1 and γ_7 increase linearly with decreasing temperature and a change in slope of the function $\Delta\nu(T)$ is clearly visible at about 240 K. The other modes were found to be more strongly temperature dependent. A steplike behavior was ob-

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
$^*\gamma_1L$	c_{11}	$\frac{1}{2}\{c_{11}+c_{55}+\sqrt{(c_{11}-c_{55})^2+4c_{15}^2}\}$
[100]$^*\gamma_2T$	$\frac{1}{2}\{c_{44}+c_{66}+\sqrt{(c_{44}-c_{66})^2+4c_{14}^2}\}$	$\frac{1}{2}(c_{11}+c_{55}-\sqrt{(c_{11}-c_{55})^2+4c_{15}^2}\}$
γ_3T	$\frac{1}{2}\{c_{44}+c_{66}-\sqrt{(c_{44}-c_{66})^2+4c_{14}^2}\}$	c_{66}
$^*\gamma_4L$	$\frac{1}{2}\{c_{11}+c_{44}+\sqrt{(c_{11}-c_{44})^2+4c_{14}^2}\}$	c_{22}
[010] γ_5T	$\frac{1}{2}\{c_{11}+c_{44}-\sqrt{(c_{11}-c_{44})^2+4c_{14}^2}\}$	$\frac{1}{2}\{c_{66}+c_{44}+\sqrt{(c_{44}-c_{66})^2+4c_{46}^2}\}$
$^*\gamma_6T$	$c_{66}=\frac{1}{2}(c_{11}-c_{12})$	$\frac{1}{2}\{c_{66}+c_{44}-\sqrt{(c_{44}-c_{66})^2+4c_{46}^2}\}$
$^*\gamma_7L$	c_{33}	$\frac{1}{2}\{c_{33}+c_{55}+\sqrt{(c_{33}-c_{55})^2+4c_{35}^2}\}$
[001] γ_8T	c_{44}	$\frac{1}{2}\{c_{33}+c_{55}-\sqrt{(c_{33}-c_{55})^2+4c_{35}^2}\}$
$^*\gamma_9T$	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]$^*\gamma_{11}T$	$\frac{1}{2}(c_{44}+c_{66})+c_{14}$	
$\gamma_{12}T$	$\frac{1}{4}(c_{11}+c_{33}+2c_{44}-2c_{14})-\frac{1}{2}\sqrt{\frac{1}{4}(c_{11}-c_{33}-2c_{14})^2+(c_{13}+c_{44}-c_{14})^2}$	

TABLE II. A sampling of measured Brillouin frequency shifts (in GHz) for the eight observed modes in (γ_i) in $K_3Na(CrO_4)^2$. These measurements are considered to have uncertainties of the order of 1%.

$T(K)$	γ_1	γ_2	γ_4	γ_6	γ_7	γ_9	γ_{10}	γ_{11}
295	22.25	16.12	22.30	16.04	24.50	11.25	21.33	14.62
270	22.35	16.20	22.40	16.06	24.65	11.31	21.42	14.70
237	22.50	16.25	22.52	16.08	24.78	11.41	21.56	14.74
231	22.51	14.80	22.27	14.35	24.80	10.52	21.23	14.05
220	22.53		22.42	15.53	24.81		21.33	14.32
210	22.53		22.50		24.83		21.50	14.51
185	22.55	16.50	22.65	16.20	24.85		21.85	14.80
140	22.60	16.67	22.94	16.30	24.93		22.30	14.96

served in the case of transverse modes γ_2, γ_6, γ_9, and γ_{11}. The frequency shifts of those modes increase linearly with decreasing temperature and then abruptly decrease at about 237 K. Minimum values are reached at about 231 K and then nonlinearly increase with further temperature decrease. The frequency shifts of the observed modes for a few characteristic temperatures, from a total of over 160 measurements (as shown by data on Fig. 1), are listed in Table II. Because of the low signal-to-noise ratio below T_c the γ_2, γ_6, and γ_9 modes could not be observed in the entire temperature region studied. The broken lines in the plots $\gamma_2(T)$ and $\gamma_6(T)$ indicate regions of extremely weak scattering. In the case of the γ_9 mode, the region of very weak scattering extends almost over the entire range of the low-temperature ferroelastic phase.

The temperature dependence of the elastic constants and their combinations are given in Fig. 2. The simple relation $\rho v^2(c_{ij})$ is valid for the modes γ_1, γ_6, γ_7, and γ_9

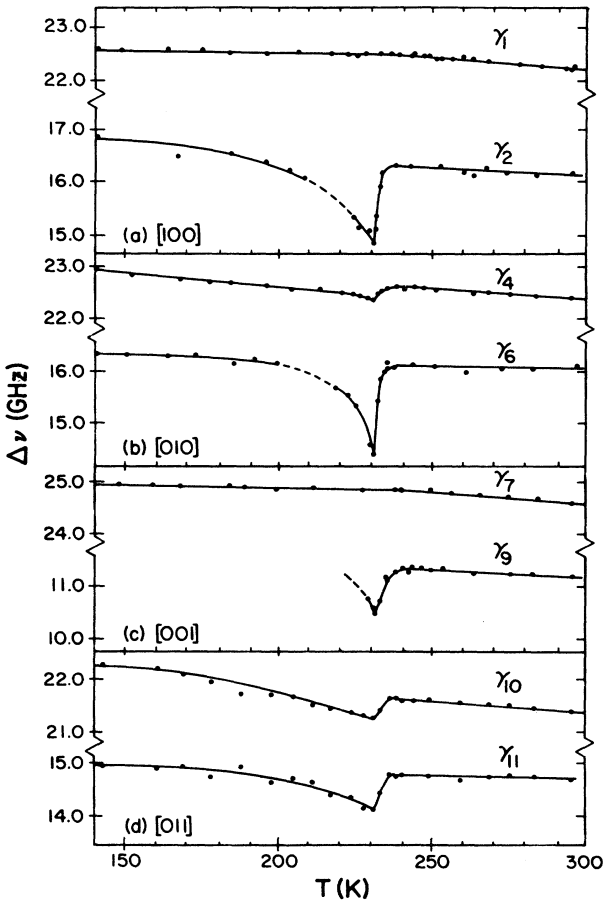

FIG. 1. Temperature dependence of the Brillouin frequency shifts of $K_3Na(CrO_4)_2$ for phonons propagating in the directions: (a) [100], (b) [010], (c) [001], (d) [011]. (Refer to Table I).

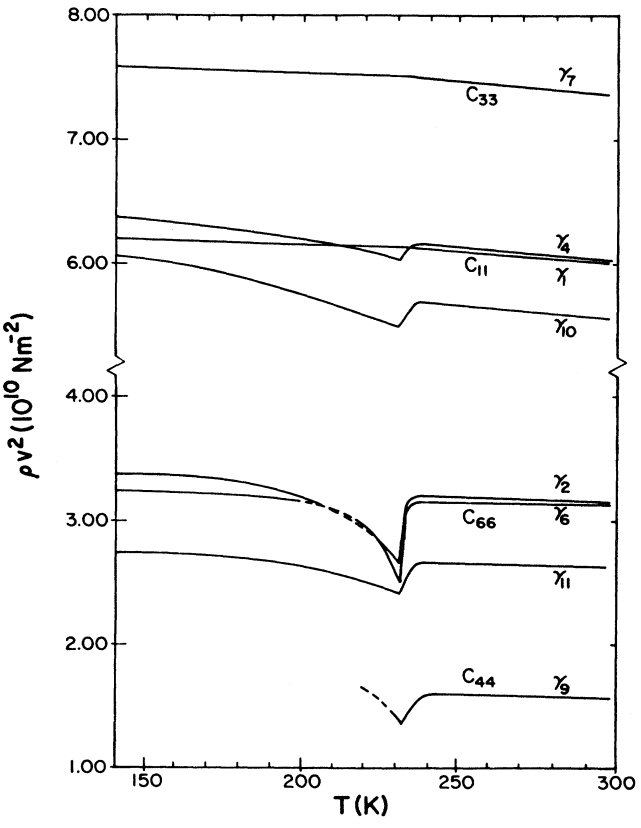

FIG. 2. Temperature dependence of the elastic constants and their combinations (for the paraelastic phase $\bar{3}m$) as determined from the data in Fig. 1. (Refer to Table I.)

TABLE III. Elastic constants of $K_3Na(CrO_4)_2$ at room temperature (295 K) in units of 10^{10} N m^{-2}.

c_{11}	c_{33}	c_{44}[a]	c_{12}	c_{13}	c_{14}
6.02±0.10	7.34±0.12	1.55±0.12	−0.24±0.08	2.80±0.33	0.27±0.06

[a]Using ultrasonic techniques $c_{44}=1.47\times10^{10}$ N m^{-2} at 295 K from Ref. 8.

which in the paraelastic phase $\bar{3}m$ are related to the elastic constants c_{11}, $c_{66}=\frac{1}{2}(c_{11}-c_{12})$, c_{33}, and c_{44}, respectively. The room temperature elastic constants and the associated uncertainties of $K_3Na(CrO_4)_2$ as determined from this work are presented in Table III. Since the solution of $\rho v^2(c_{ijkl})$ for the longitudinal mode γ_{10} gives two sets of values for c_{13}, the proper value of this component were obtained by checking the consistency of the velocity extremums in the pure-mode direction.[14,15]

The greatest anomaly of elastic constants versus temperature were found for the c_{66}, c_{44}, and the transverse elastic constant related to the phonon propagating in the [100] direction

$$\rho v^2=\tfrac{1}{4}[c_{44}+c_{66}-\sqrt{(c_{44}-c_{66})^2+4c_{14}^2}]\ .$$

In those cases the observed steplike changes were about 20%. As is evident from the experimental results presented in this section there is no single distinct soft mode for $K_3Na(CrO_4)_2$. The symmetry change which occurs during the transition studied here involves the onset of the two-component order parameter (mentioned earlier) and makes the form of the soft elastic constant more complicated.

The ferroelastic phase transition of type $\bar{3}m\rightarrow 2/m$ may be described after Boccara[16] and Toledano *et al.*[17] using the order parameter of form $\alpha(e_1-e_2)+\beta e_4$ since this expression is invariant under the symmetry operation of the group of binary axis parallel to X_1 and the group of mirror plane parallel to X_2. The corresponding eigenvalues of the elastic constant matrix are given by

$$\begin{vmatrix} c_{11}-c_{12} & c_{14} \\ 2c_{14} & c_{44} \end{vmatrix}\ .$$

Consequently, the elastic constant which goes to zero at T_c (when the transition is of the second order) can be found as[18]

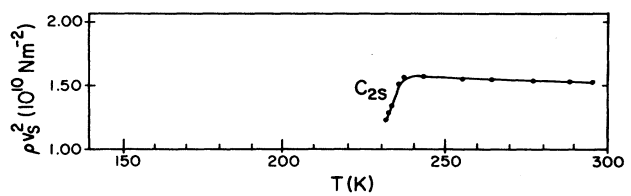

FIG. 3. Temperature dependence of the "soft" elastic constant $c_{2s}=\frac{1}{2}[(c_{44}+2c_{66})-\sqrt{(2c_{66}-c_{44})^2+8c^2{}_{14}}]$.

$$\rho v_s^2=\tfrac{1}{2}(c_{44}+2c_{66}-\sqrt{(2c_{66}-c_{44})^2+8c_{14}^2})$$
$$=c_{2s}\ . \tag{3}$$

In the present work the temperature dependence of the ρv_s^2 elastic constant was found from the measured relations $c_{44}(T)$, $c_{66}(T)$, and from $c_{14}(T)$ as calculated from $\gamma_{11}(T)$. As is shown in Fig. 3 the temperature dependence of ρv_s^2 is similar to those observed for the other transverse elastic constants.

IV. LANDAU MODELING AND DISCUSSION

The $\bar{3}m\rightarrow 2/m$ type of transition has been discussed in the context of classes of phase transitions characterized by a deformation of the unit cell by Boccara.[16] This transition exhibits the loss of the ternary axis of symmetry $(0x_3)$ and is necessarily of first order due to strict symmetry requirements. Thus, terms cubic in the order parameter σ are admitted in the free-energy expansion. The specific reason for the free energy to contain a cubic term in σ is that $2/m$ is an invariant subgroup of G_0 with the order of 4 while the order of G_0 is 12, so the factor group G_0/G is of order 3. According to Boccara's[16] theorem 4 this implies the existence of a cubic invariant. As mentioned before, following Boccara[16] the order parameter σ is assumed to take the form of a linear combination of e_6 and e_4, i.e.,

$$\sigma=\alpha(e_1-e_2)+\beta e_4\ , \tag{4}$$

where α and β are in general arbitrary but can be determined from experiment.

Because the range of temperatures studied far exceeds the critical region, the postulated free energy should include both critical and noncritical contributions (as commonly done in Landau expansions[17,19])

$$F=F(\sigma)+F_0(e_1,e_2,e_3,e_4)\ , \tag{5}$$

where

$$F_0(e_1,e_2,e_3,e_4)=\tfrac{1}{2}\sum_{i=1}^{4}c_{ii}^0e_i^2+\sum_{i\neq j=1}^{4}c_{ij}^0e_ie_j \tag{6}$$

is a noncritical part and, as argued before,

$$F(\sigma)=A_2\sigma^2+A_3\sigma^3+A_4\sigma^4 \tag{7}$$

is the critical part. In the above

$$A_2=a(T-T_0),\quad a>0,\quad A_4>0\ ,$$

and A_3 is of an arbitrary sign but nonzero in order for a discontinuous transition to occur. For the sake of argu-

ment and without loss of generality A_3 will be taken as positive. Minimizing F with respect to σ yields

$$0=\frac{\partial F}{\partial \sigma}=2A_2\sigma+3A_3\sigma^2+4A_4\sigma^3 \tag{8}$$

which means that either $\sigma_0=0$ or

$$\sigma_{\pm}=\frac{-3A_3\pm\sqrt{9A_3^2-32A_2A_4}}{8A_4} . \tag{9}$$

For $\sigma\neq 0$ to be real the square-root expression must be positive in Eq. (9). Thus, the ordered phase may only exist when

$$T\leq T_0+\frac{9A_3^2}{32aA_4}\equiv T_s . \tag{10}$$

The transition temperature is calculated by solving the two simultaneous equations

$$F(\sigma)=A_2\sigma^2+A_3\sigma^3+A_4\sigma^4=0 \tag{11}$$

and

$$\frac{\partial F}{\partial \sigma}=2A_2\sigma+3A_3\sigma^2+4A_4\sigma^3=0 \tag{12}$$

which gives

$$T_c=T_0+\frac{A_3^2}{4aA_4} . \tag{13}$$

Next, the stability condition is examined and

$$0\leq\frac{\partial^2 F}{\partial\sigma^2}=2A_2+6A_3\sigma+12A_4\sigma^2 . \tag{14}$$

For $\sigma=0$, it is immediately obtained that the range of stability of the disordered phase is

$$T\geq T_0 .$$

On the other hand, for the two ordered phases $\sigma_{\pm}$, condition (14) should be taken together with Eq. (9). This yields (for $A_3>0$) σ_- to be metastable between $T_c<T<T_s$ and absolutely stable for $T<T_c$. Also, σ_+ is unstable for $T>T_0$ and metastable for $T<T_0$. In Fig. 4 the effects of metastability are illustrated through the plots of the free energy $F(\sigma)$ at different temperatures. Figure 5(a) shows how σ depends on temperature in the various phases. The order parameter discontinuity at $T=T_c$ can be calculated from Eq. (9) as

$$\Delta\sigma=(\sigma_--\sigma_0)(T=T_c)=-\frac{A_3}{2A_4} . \tag{15}$$

Thus, for weakly first-order transitions, as appears to be the case in discussion and as verified later on, $A_3\ll A_4$. The soft-mode elastic constant is readily found as

$$c_{2s}\equiv\frac{d^2F(\sigma)}{d\sigma^2}=2A_2+6A_3\sigma+12A_4\sigma^2 . \tag{16}$$

Substituting Eq. (9) into the above results in

$$c_{2s}(\sigma_{\pm})=-4a(T-T_0)+\frac{9A_3^2}{8A_4}\mp\frac{3A_3}{8A_4}\sqrt{9A_3^2-32A_2A_4} \tag{17}$$

which is of the (nonlinear) form

$$c_{2s}(\sigma_{\pm})=\alpha_0+\alpha_1T\pm\alpha_2\sqrt{\gamma+\eta T} , \tag{18}$$

where

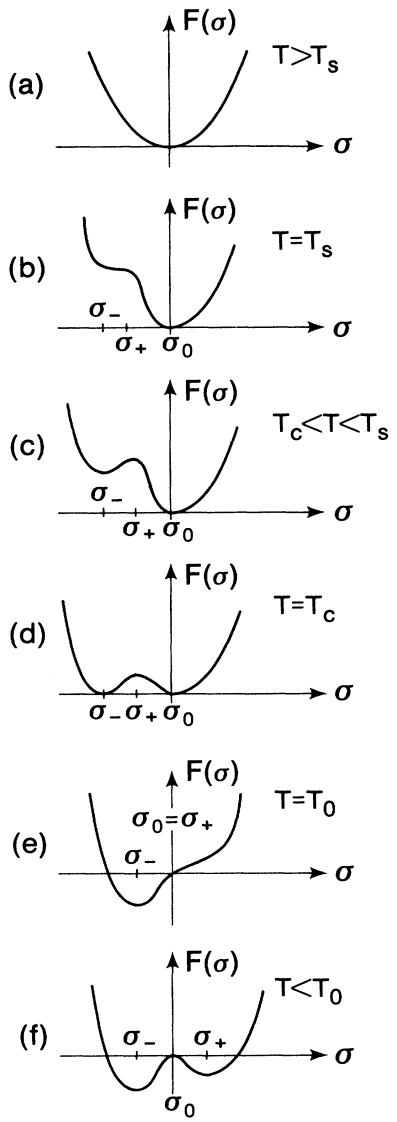

FIG. 4. Schematic illustration of the temperature variation of the Landau free energy. [Refer to Eq. (7) in text.]

$$\alpha_0=9A_3^2/8A_4+4aT_0,\quad \alpha_1=-4a\ ,$$
$$\alpha_2=3A_3/8A_4,\quad \gamma=9A_3^2+32aA_4T_0\ ,$$
$$\eta=-32aA_4\ .$$

On the other hand, for the disordered phase, the elastic constant has the linear temperature dependence

$$c_{2s}(\sigma_0)=2a(T-T_0)\ . \tag{19}$$

By finding the difference $\Delta c_{2s}\equiv c_{2s}(\sigma_-)-c_{2s}(\sigma_0)$ using Eqs. (18) and (19) and evaluating it at T_c given by Eq. (13) yields

$$\Delta c_{2s}(T_c)\equiv 0\ . \tag{20}$$

This zero soft-mode discontinuity is confirmed by the present experimental data.

In addition, $2a$ in Eq. (19) is found from the slope of ρv_s^2 versus T in Fig. 3 as $2a=0.075\times10^{10}$ N/m^2 K and will be used for comparisons below. Likewise, calculating

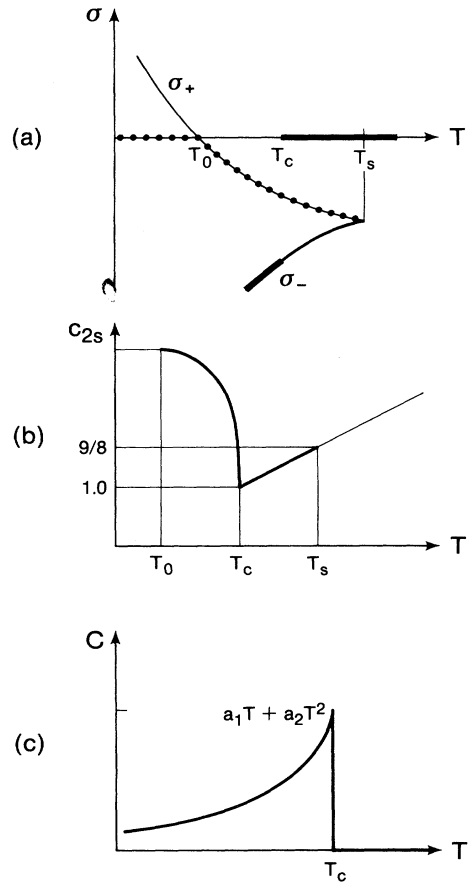

FIG. 5. Temperature variations of (a) order parameter σ. [Refer to Eq. (9).] (b) soft mode elastic constant c_{2s}. [Refer to Eq. (17).] In this figure the solid circles correspond to the unstable region, the light solid lines to the metastable region and the heavy solid lines to the stable region.

c_{2s} at the three characteristic temperatures T_0, T_c, and T_s from Eqs. (18), (19), (13), and (10) gives

$$c_{2s}(T_s)/c_{2s}(T_c)=\tfrac{9}{8}\ ,$$

which is reasonably consistent with the experimental value of 1.2 from Fig. 3, and

$$c_{2s}(T_0)/c_{2s}(T_c)=\tfrac{9}{2}\ ,$$

which could not be verified due to lack of experimental data below T_c. From the raw experimental data and Eq. (3), $c_{2s}(T_c)=1.22\times10^{10}$ N/m^2. In addition, by substituting Eq. (13) into Eq. (19)

$$c_{2s}(T_c)=A_3^2/2A_4 \tag{21}$$

and therefore from Eq. (13)

$$T_c-T_0=\frac{c_{2s}(T_c)}{2a}=16\ \text{K} \tag{22}$$

and from Eq. (10)

$$T_s-T_c=\frac{9c_{2s}(T_c)}{8(2a)}=18\ \text{K}\ . \tag{23}$$

These results are consistent with the total range of criticality as observed experimentally to be about 30 K. It is assumed also that from the present experimental data $T_c=231$ K.

From Eqs. (4)–(7) the elastic constants can be written as

$$c_{11}=c_{11}^0\ , \tag{24a}$$
$$c_{33}=c_{33}^0\ , \tag{24b}$$
$$c_{44}=c_{44}^0+\beta^2c_{2s}\ , \tag{24c}$$
$$c_{66}=\tfrac{1}{2}(c_{11}^0-c_{12}^0)+\alpha^2c_{2s}\ . \tag{24d}$$

It is readily seen from the above that the c_{44} and c_{66} elastic constants are the only ones affected by the onset of criticality. From the comparison of the behavior of c_{66} to that of c_{11}, it is evident that the order parameter σ must include the *difference* between e_1 and e_2 and any separation of the two is meaningless. This is consistent with the fact that, generally, mode softening occurs only for shear modes (and strongly mixed ones). Consequently, the ratio in the slopes of γ_6 and γ_9 in the critical region $T_c<T<T_s$ (from Fig. 1) is a measure of $4(\alpha/\beta)^2\simeq4$, i.e., $\alpha=\beta$.

Finally, the entropy and specific heat will be considered within this model. The entropy in the critical region is calculated as

$$S=-\frac{\partial F(\sigma)}{\partial T}=-a\sigma^2\ . \tag{25}$$

Therefore, the entropy discontinuity at T_c is

$$\Delta S=-a(\Delta\sigma)^2=a\frac{A_3^2}{4A_4^2}\ . \tag{26}$$

Making use of Eq. (21) and from $2a=$ slope of ρv_s^2 vs T

(as used before) allows the calculation of the coefficient A_4 as

$$A_4=\frac{(2a)c_{2s}(T_c)}{4\Delta S} . \tag{27}$$

Thus, from Eq. (15)

$$(\Delta\sigma)^2=2\Delta S/(2a) . \tag{28}$$

Thus extreme smallness of the entropy discontinuity would imply a related lack of significant discontinuity in the elastic distortion.

The specific heat is given by

$$C=T\frac{\partial S}{\partial T}=-T\frac{\partial^2 F(\sigma)}{\partial T^2} \tag{29}$$

and using the Landau expansion for $F(\sigma)$ in Eqs. (5)–(7) becomes

$$C=-2aT\sigma\frac{d\sigma}{\partial T} . \tag{30}$$

As elaborated on earlier, for $A_3>0$, σ_- is absolutely stable below T_c and σ_0 above T_c. For σ_0, $C=0$ while for σ_-, C decreases monotonically with decreasing temperature below T_c [see Fig. 5(c)]. From Eq. (30) it is easy to calculate the associated specific heat discontinuity at T_c as

$$\Delta C=\frac{2a^2}{A_4}T_c . \tag{31}$$

Thus, when a^2/A_4 is small enough (e.g., due to a large value of A_4), the discontinuity ΔC will not be very pronounced as is indeed observed in experiment.[7] In fact, using a convenient representation

$$\Delta C=\frac{2(2a)(\Delta S)T_c}{c_{2s}(T_c)} . \tag{32}$$

With $T_c\cdot\Delta S=Q$ denoting the latent heat of transition, the magnitude of ΔC is approximately on the order of one-tenth of Q. Again, the very small values of both the latent heat Q and (even smaller) specific heat discontinuity ΔC seem to explain the lack of calorimetric support for a first-order transition.

Furthermore, the variation of the specific heat for $T_0<T<T_c$ may be approximated by the quadratic dependence on T

$$C\cong\frac{a^2T}{A_4}\left[1+\frac{8}{9}\frac{aA_4}{A_3^2}(T-T_0)+\cdots\right] \tag{33}$$

which was found by substituting Eq. (9) into (30) and Taylor expanding the small terms therein.

V. SUMMARY

In this work Brillouin shifts related to elastic constants have been determined over a temperature range of 140–300 K for $K_3Na(CrO_4)_2$ with particular emphasis on the phase transition ($\bar{3}m\rightarrow 2/m$) region from 210 to 240 K. The experimental results confirm the choice of the order parameter as a linear combination: $\alpha(e_1-e_2)+\beta e_4$ where $\alpha\simeq\beta$. A Landau model has been presented and satisfactory agreement with experimental results achieved with respect to the range of criticality, continuous behavior of the elastic constants, and the value of the ratio $c_{2s}(T_s)/c_{2s}(T_c)$. Based on calculations of the entropy, specific heat, and elastic distortion using present experimental data it is clearly evident that the transition is weakly first order. This explains previous experimental inconsistencies in defining the order of this transition.

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