Ferroelastic Phase Transition in Crystalline K$_3$Na(CrO$_4$)$_2$: Acoustic Studies


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Abstract—Ultrasonic studies of the temperature behavior of the velocity and damping of sound for the $xx$ and $zz$ longitudinal and $yx$ and $zx$ transverse waves in K$_3$Na(CrO$_4$)$_2$ have been carried out in the temperature interval 185–295 K, which includes the region of the ferroelastic phase transition. The acoustic parameters for both shear and longitudinal waves were found to have anomalies in the region of the phase transition with a Curie temperature of 235.5 K. A theoretical analysis of the softening of the elastic moduli $c_{44}$ and $c_{66}$ was performed on the basis of the Landau expansion in terms of the strain tensor components $e_{44}$ and $(e_{22} - e_{11})/2$ considered as the linearly coupled primary and secondary order parameter, respectively. The absolute values of the elastic moduli $c_{11}$, $c_{33}$, $c_{44}$, $c_{66}$, $c_{12}$, and $c_{14}$ at 295 K were calculated.

1. INTRODUCTION

K$_3$Na(CrO$_4$)$_2$ belongs to crystals with the structural formula $A_3B(CO_4)_2$, where A and B are Li, K, Na, Rb, Cs, or NH$_4$ and CO$_4$ stands for the SO$_4$, CrO$_4$, or SeO$_4$ tetrahedra. Many members of this family undergo ferroelastic phase transitions. K$_3$Na(CrO$_4$)$_2$ passes through two structural phase transitions at 239 and 853 K [1]. On the basis of x-ray diffraction measurements [2, 3], it was suggested in [1] that the low-temperature transition can be represented by the scheme $\bar{3}m \rightarrow 2lm$ and that the observation of ferroelastic domains below 239 K indicates the transition to be of ferroelastic nature. This stimulated a study of the temperature variation of the dynamic elastic moduli of the crystal in the vicinity of $T_c$. However, earlier ultrasonic measurements were performed only for the elastic modulus $c_{44}$ [2], as the strong ultrasound scattering from the domain structure permitted study above the phase transition only. Nevertheless, the noticeable softening of this modulus observed to occur as one approached the Curie point was attributed to the ferroelastic character of the transition. The temperature behavior of the elastic moduli for the K$_3$Na(CrO$_4$)$_2$ crystal was studied in [4] by Mandelshtam–Brillouin scattering of light in the interval 140–300 K. In the vicinity of $T_c$, one observed a noticeable softening (which was similar in magnitude) of the moduli $c_{44}$ and $c_{66}$ and a break in the temperature dependences of $c_{11}$ and $c_{33}$. As in the ultrasonic experiments, light scattering from the domain structure confined the studies of $c_{66}$ and $c_{44}$ to the region below the Curie point. Based on the change in the crystal symmetry, the phase transition was interpreted in [4] as first order, although no temperature hysteresis of the velocity was observed. It was suggested in [4] to describe the phase transition in terms of Landau theory with a mixed order parameter introduced in [5]. This interpretation does not, however, fit well with the group-theoretical description of ferroelastic phase transitions proposed later in [6].

We present here the results of ultrasonic studies of the K$_3$Na(CrO$_4$)$_2$ crystal carried out in the interval 185–295 K, which includes the Curie point. We measured the temperature variations in the velocity and damping coefficients (with respect to their room-temperature values) for longitudinal acoustic waves propagating along the $x$ and $z$ crystallographic axes of the trigonal system and $x$-polarized transverse waves moving along the $y$ and $z$ axes. The interpretation of the experimental data obtained was based on the phenomenological model [6] involving two linearly coupled order parameters. Our acoustic studies identified one of these parameters as primary, (i.e., responsible for the phase transition) and the other as secondary. These studies were complemented by room-temperature measurements of the absolute velocities of a number of acoustic modes, which permitted calculation of six elastic moduli of the K$_3$Na(CrO$_4$)$_2$ crystal.
2. THEORETICAL MODEL

According to the group-theoretical analysis performed in [6], the ferroelastic phase transition from point group $\bar{3}m$ to group $2/m$ is a first-order transition described by two order parameters, one of which is primary, i.e., responsible for the phase transition itself, and the other is secondary, i.e., linearly coupled with the primary parameter. Depending on the actual properties of a crystal, the primary, $\eta_1$, and secondary, $\eta_2$, order parameters can be the strain tensor components $\varepsilon_3$ and $(\varepsilon_2 - \varepsilon_1)/2$, respectively, or vice versa. Because of the symmetry being $\bar{3}m$ and of the transition being first-order [6], the Landau expansion should contain an invariant of third order in $\eta_1$. Thus, the Landau expansion for the $\bar{3}m \longrightarrow 2/m$ ferroelastic phase transition can be written as

$$
\Phi = \Phi_0 + \frac{1}{2} c_{1n} \eta_1^2 + \frac{1}{3} c_{1n}^{(3)} \eta_1^3 + \frac{1}{4} c_{1n}^{(4)} \eta_1^4 + \frac{1}{2} c_{2n} \eta_2^2 + c_{1n2} \eta_1 \eta_2,
$$

(1)

where $c_{1n}$, $c_{2n}$, and $c_{1n2}$ are elastic moduli of the second order and $c_{1n}^{(3)}$ and $c_{1n}^{(4)}$ are elastic moduli of the third and fourth order, respectively. The modulus $c_{1n}$ scales with temperature as $c_{1n} = c_0(T-T_0)$, where $T_0$ is a characteristic temperature. Using Eq. (1), one can readily verify that the effective elastic moduli associated with the primary and secondary order parameters, respectively, and acting here as the inverse susceptibilities behave differently with temperature above $T_c$. To derive an expression for the elastic modulus $\bar{c}_{n1}$ related to the primary order parameter, one has to add the term $-\eta_1 H_1$, accounting for the interaction of $\eta_1$ with the corresponding field $H_1$, to expansion (1). Furthermore, limiting ourselves to the case of $T > T_c$, we drop in Eq. (1) the terms that involve the third and fourth powers of the primary order parameter. Thus, in the presence of a field, the equilibrium equations can be cast as

$$
c_{1n} \eta_1 + c_{1n2} \eta_2 - H_1 = 0,
$$

(2)

$$
c_{2n} \eta_2 + c_{1n2} \eta_1 = 0.
$$

(3)

Deriving the inverse susceptibility from Eq. (2)

$$
\frac{\partial H_1}{\partial \eta_1} = c_{1n} + c_{1n2} \frac{\partial \eta_2}{\partial \eta_1}
$$

(4)

and substituting $\partial \eta_2/\partial \eta_1$ into Eq. (4) with the use of Eq. (3), one readily obtains an expression for $\bar{c}_{n1}$

$$
\bar{c}_{n1} = c_0(T - T_0).
$$

(5)

where

$$
T' = T_0 + \frac{c_{1n2}^2}{c_0 c_{n2}}.
$$

(6)

In a similar way, one can derive an expression for the temperature behavior of the modulus $\bar{c}_{n2}$ related to the secondary order parameter:

$$
\bar{c}_{n2} = c_0(T - T'_0)/(T - T_0).
$$

(7)

Note that the corresponding expressions for a second-order phase transition were derived in a general form, for instance, in [7, 8].

As follows from Eqs. (5) and (7), the effective modulus related to the primary order parameter depends linearly on temperature above the phase transition point, whereas the dependence of $\bar{c}_{n2}$ on $T$ deviates from a straight line. The difference in the theoretical temperature dependences between the effective elastic moduli related to the primary and secondary order parameters makes it possible to experimentally determine which of the two coupled order parameters, $\varepsilon_4$ or $(\varepsilon_2 - \varepsilon_1)/2$, is primary for K$_3$Na(CrO$_4$)$_2$.

3. EXPERIMENT AND RESULTS

Transparent, yellowish crystals of K$_3$Na(CrO$_4$)$_2$ were grown in an aqueous solution at a constant temperature of 315 K. The crystal composition was monitored by chemical and x-ray diffraction analysis. The $6 \times 5 \times 5$-mm sample chosen for measurements was parallelepiped-shaped, with the edges parallel to the trigonal crystallographic axes. The crystal orientation was set to no worse than 1°.

The measurements were performed using two modifications of the pulse echo method at a frequency of 4 MHz. The technique of Williams–Lamb [9] was used to measure the absolute velocities of sound at room temperature and the temperature behavior of the parameters of longitudinal acoustic waves (damping was insignificant in these cases). The temperature behavior of the parameters of transverse waves was investigated by studying the interference of a pulse that has passed through the sample with that reflected from its front face. This technique was developed for acoustic measurements in strongly absorbing media [10]. All measurements were carried out under slow cooling and heating of the sample. Below 245 K, the rate of temperature variation did not exceed 0.05 K min$^{-1}$. The temperature gradient in the sample was not over 0.02 K cm$^{-1}$. The relative error was 0.01% for the velocity and 6% for the damping. The error of room-temperature measurements of absolute velocities was 0.4 and 0.7% for the longitudinal and transverse waves, respectively.

The experimental data obtained for the absolute velocities at room temperature permitted calculation of the six elastic moduli of K$_3$Na(CrO$_4$)$_2$, which are listed...