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ELASTIC PROPERTIES OF TRIS-SARCOSINE CALCIUM CHLORIDE (TSCC) AND AMONIUM FLUOBERYLLATE (AFB) SINGLE CRYSTALS*

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Near the structural phase transition of TSCC the temperature dependence of the elastic stiffness coefficients can be described by the Landau—Devonshire theory, whereas ultrasonic damping can be ascribed to energy fluctuations (Nattermann). The results obtained near the upper transition temperature of AFB-crystals can be interpreted in the same way.

УПРУГИЕ СВОЙСТВА МОНОКРИСТАЛЛОВ ТСЦЦ ГЛОРИДА КАЛЬЦИЯ И ФТОРБЕРИЛЛИЕВОЙ СОЛИ АММОНИЯ

Вблизи структурного фазового перехода ТСЦЦ хлорида кальция температурная зависимость коэффициентов сопротивления деформации в интервале упругости может быть описана с помощью теории Ландау–Дэвоншаира, в то время как ультразвуковое затухание может быть отнесено к флюктуациям энергии (Натterман). Результаты, полученные вблизи верхней точки фазового перехода кристалла фторбериллиевой соли аммония, могут интерпретироваться аналогичным образом.

I. INTRODUCTION

The critical behaviour of ferroelectrics, both theoretically and experimentally, has aroused widespread interest during the past few years. The aim of this paper is to report some results on the critical behaviour of elastic coefficients and ultrasonic attenuation coefficients of Tris-sarcosine calcium chloride, TSCC, $(CH_3NHCH_2COOH)_3CaCl_2$ and of Amonium fluoberyllate, AFB, $(NH_4)_2BeF_4$.

Tris-sarcosine calcium chloride is an uniaxial ferroelectric with an order-disorder phase transition $(D^{16}_{2h} \rightarrow C^{9}_{2v})$ at $T_c = 129.6$ K of the second order [1, 2, 3]. This

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transition may be triggered by the dynamics of the protons in the hydrogen bonds [2].

Amonium fluoberyllate exhibits a ferroelectric phase transition of the first order at $T_1 = 176$ K [4] and a further transition of the second order at $T_2 = 183$ K [5]. Below T_1 the space group symmetry is C_{2v}^{9} and above T_2 it is D_{2h}^{16} [6, 7]. It is an improper ferroelectric with an incommensurable interphase in the temperature range between T_1 and T_2 [8, 9]. The transition at T_1 is triggered by the BeF_4^{2-} ions [10].

In both crystals the ferroelectric axis is the b-axis. Both crystals are ferroelastic in the paraelectric paraphases (TSCC above T_c, AFB above T_2) with a pseudohexagonal symmetry viewed along the a-axis [11, 12].

II. METHODS

The elastic stiffness ceofficients c_{11} and c_{22} of TSCC crystals were determined from ultrasound velocity, which was measured by the pulse-echo technique [13], and the ultrasonic damping measurements were performed by a supplementary unit [14] at 20 MHz and 60 MHz. The specimens were rectangular parallelepipeds with a propagation length ~5 mm. Quartz transducers were attached to the samples with Cenusil [15], a silicon caoutchouc, or Nonaq.

The temperature dependences of the elastic compliances s_{11}, s_{22} and s_{33} of AFB in the ferroelectric phase were measured by the piezoelectric resonator using a special method in the case of a very small piezoelectric coupling [16]. A dc field was superimposed in order to make the samples ferroelectrically monodomain. This was proved by dielectric hysteresis loops. In the nonpiezoelectric paraphase the temperature dependence of s_{ij} was determined by a composite resonator. A very small piezoelectric ceramic transducer was attached in the node of vibration of the bar.

In order to obtain ferroelastic monodomain specimens for compliance and stiffness measurements we proceeded as described by Makita et al. [11, 12]. Ferroelastic domains could be observed by means of a polarizing microscope. For ultrasonic measurements it was difficult to get ferroelastic monodomain specimens because of the large dimensions of the specimens. The temperature control system is described elsewhere [17].

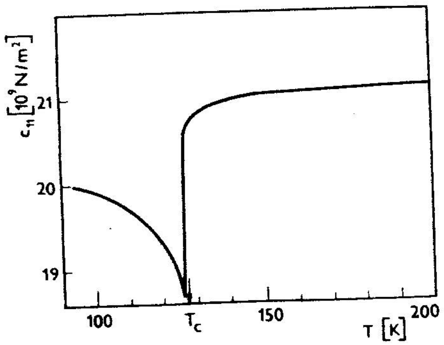
In order to investigate the critical behaviour simultaneous dielectric measurements were performed to determine the Curie-temperature.

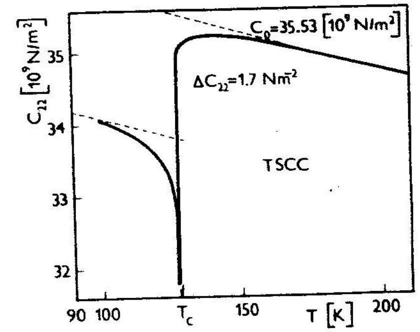
III. RESULTS

As can be seen in Fig. 1 and Fig. 2 the temperature dependence of the elastic stiffness coefficients of TSCC c_{11} and c_{22} shows a step-like change at the transition

temperature. From this result it can be inferred that the free energy function contains an electrostrictive term if we assume that TSCC is a proper ferroelectric with a second order transition [18].

This behaviour resembles that of $SrTiO_3$, where the energy function contains an electrostrictive-like term. In the sound attenuation we observe a peak at the transition temperature (Fig. 3).





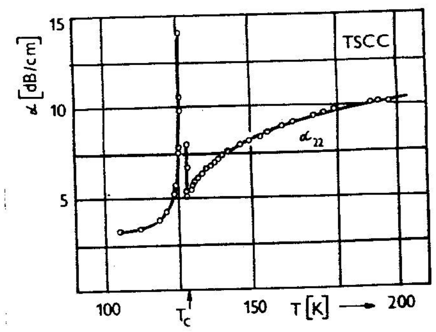


Fig. 1. Temperature dependence of the elastic stiffness coefficient c_{11} of TSCC at 20 MHz

Fig. 2. Temperature dependence of the elastic stiffness coefficient c_{22} of TSCC at 20 MHz

Fig. 3. Sound attenuation coefficient α_{22} of TSCC versus temperature in the vicinity of the transition temperature T_c

Fig. 4 shows the temperature dependence of the elastic compliance coefficients s_{ii} of AFB. These results are in agreement with the results of ultrasonic velocity measurements reported by Aleksandrov et al. [19]. The s_{ii} are of the same order of magnitude as $1/c_{ii}$; $s_{22} > s_{33} > s_{11}$ corresponds to $c_{11} > c_{33} > c_{22}$ and the anomalies of the temperature are of the same type, especially the jump of c_{11} and of s_{11} at T_2. The jump of s_{11} and c_{11}, resp., at T_2 seems also to be a consequence of a phase transition of the second order [20, 19].

From a log-log plot the critical index of c_{22} of TSCC was determined to be 0.23 and the critical exponent of s_{11} of AFB to be 1/2.

The temperature dependence of the ultrasonic attenuation coefficient α_{11} of AFB at 20 MHz and 60 MHz is plotted in Fig. 5. Significant anomalies were observed at T_2 in both cases, but no anomaly at T_1. The appearance of further maxima of α_{11} between T_1 and T_2 is not very clear. It is possible that they may be a consequence of the incommensurable interphase. Further measurements are in progress. The critical behaviour of α_{22} of TSCC and α_{11} of AFB in the paraphases was proved by a log-log plot and a semi-log plot of the square root of the sound attenuation coefficients versus $T - T_c$ and $T - T_2$, resp.

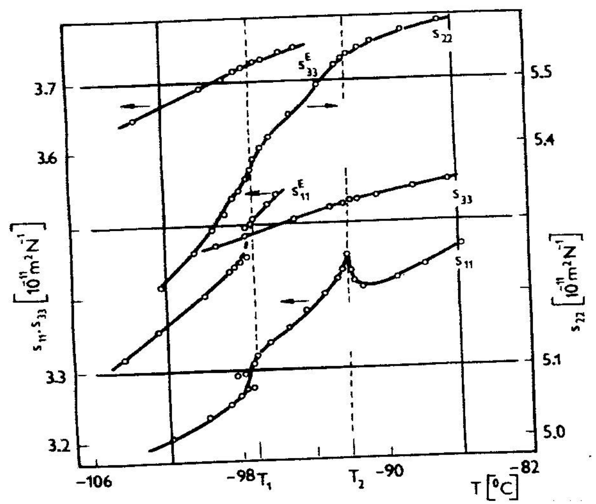


Fig. 4. Elastic compliance coefficients s_{11}, s_{22}, s_{33} measured by a composite resonator and s_{11}^E, s_{33}^E of AFB as a function of the temperature in the vicinity of the transition temperatures T_1 and T_2

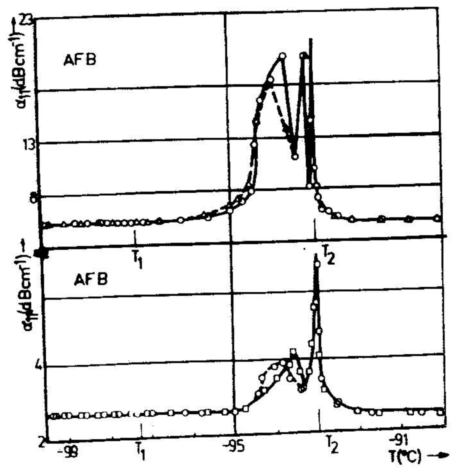


Fig. 5. Temperature of the sound attenuation coefficient α_{11} of AFB in the vicinity of the transition temperature T_1 and T_2 at 20 MHz (O, □ — below) and 60 MHz (△, O — above)

IV. DISCUSSION

From the jump of the elastic stiffness coefficient c_{11} and c_{22} of TSCC (Fig. 1 and Fig. 2) and also from the jump of the elastic compliance s_{11} and the elastic stiffness coefficient c_{11} of AFB we can conclude that for a phase transition of the second order the thermodynamical potential must contain a coupling term quadratic in the order parameter η and linear in the elastic strain S_{ij} (or stress T_{ij}): $\eta^2 S_{ij}$ and $\eta^2 T_{ij}$, resp. For example the electrostrictive term in the case of proper ferroelectrics.

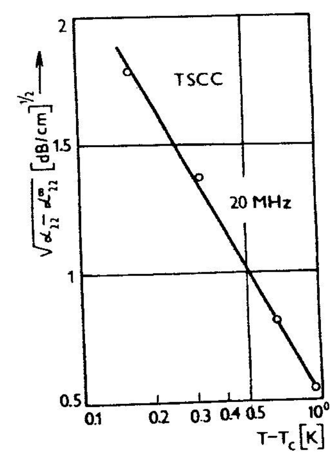


Fig. 6. Semilogarithmic plot of the square root of the sound attenuation coefficient α_{22} versus T_c $(T > T_c)$

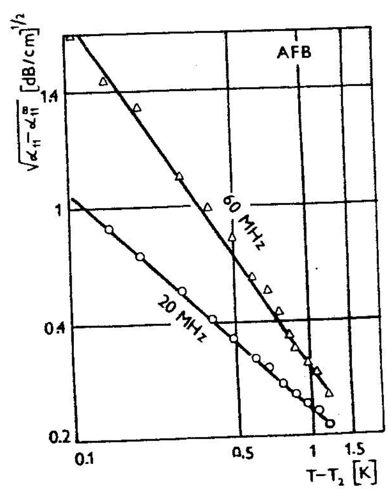


Fig. 7. Semilogarithmic plot of the square root of the sound attenuation α_{11} versus $T - T_2$ $(T > T_2)$. The circles and triangles denote the 20 and 60 MHz data, resp.

Actually Makita [1] has expanded the Helmholtz free energy function for TSCN also in terms of the elastic energy:

$$(q_{12}x_x - q_{22}y_y - q_{32}z_z)P_y^2,$$

where q_{ij} is the electrostrictive coefficient, x_x... the components of elastic strains and P_y the polarization along the ferroelectric b-axis. We can conclude that the potential of Makita describes the elastic behaviour of TSCC. Up to now no thermodynamical potential for AFB, which also contains elastic energy terms, has been known.

On the basis of the Larkin—Khmelnitzkij theory for statical critical behaviour, Nattermann [21] has recently calculated that if the thermodynamical free energy potential contains a coupling term $\eta^2 S_{ij}$ or $\eta^2 T_{ij}$, resp., the sound attenuation coefficient α shows in the first approximation the following frequency and temperature dependence:

$$\alpha(t) \sim A\omega^2 \tau_{eo} \left(\frac{b}{3} \ln \frac{t_0}{t}\right)^2,$$

where ω is the angular frequency of the ultrasound wave, $t = \frac{T - T_c}{T_c}$ the reduced temperature; A, t_0 and b are non-universal parameters. This equation describes in a good agreement the behaviour of the ultrasonic attenuation coefficients of TSCC and AFB, which is demonstrated by the semilogarithmic plots in Figs. 6 and 7. Therefore the ultrasonic attenuation results are in agreement with the upper results on elastic coefficients.

In order to prove the connection $\alpha \sim \omega^2$ the sound attenuation of AFB (Fig. 5) was measured at 20 MHz and 60 MHz. But the results are only in a qualitative agreement with the theoretical prediction, because it seems to be difficult to determine absolute values of the sound attenuation with our method.

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