Acoustic anomaly and nature of the phase transition in the uniaxial weakly polar ferroelectric TSCC

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(Submitted 25 August 1984)
Zh. Eksp. Teor. Fiz. **88**, 1020–1031 (March 1985)

The change from a "dipole" to an "Ising" type of behavior of the uniaxial ferroelectric TSCC crystal near TC is investigated both in the paraphase and in the ferroelectric phase. This specific crossover manifests itself in an appearance of a jumplike anomaly of the velocity of longitudinal sound waves propagating along the polar axis, and in the appearance of a new type of relaxational maximum of damping for these sound waves. In the paraelectric phase, the crossover manifests itself in a transition from a logarithmic to a power-law dependence in the behavior of the fluctuational corrections to the longitudinal sound-wave velocities. The presence of the crossover is attributed to the anomalously small effective charge of the soft mode. A phenomenological theory of a weakly polar ferroelectric of the displacement type is developed and is used to explain the unusual properties of the TSCC.

I. INTRODUCTION

The long-familiar[1] ferroelectric phase transition in TSCC–$(CH_3N{\cdot}HCH_2COOH)_3CaCl_2$ crystals has recently attracted many researchers. The unusual behavior of TSCC crystals became obvious after a pronounced soft mode of the Raman-scattering spectra was observed in the ferroelectric phase.[2] This result points to a displacement phase transition and does not agree with the previously held notion[3] that the transition is of the order-disorder type. Recent investigations of the absorption spectra in the far IR yielded new evidence in favor of a ferroelectric phase transition of the displacement type without change of the unit-cell volume.[4]

The soft mode in TSCC is weakly polar: the *LO* and *TO* components of the soft mode soften in accordance with the same law and the splitting in the entire temperature interval investigated is <0.5–$1\ \mathrm{cm}^{-1}$ (Ref. 5). The TSCC crystal can thus be regarded now as a unique uniaxial displacement ferroelectric with a weakly polar soft mode.

The dynamics of uniaxial ferroelectrics is known to have a number of specific features: macroscopic dipole-dipole interaction leads to an anisotropic polarization-fluctuation spectrum, so that the influence of the fluctuations reduces only to the appearance of logarithmic corrections to the temperature dependences of the thermonuclear quantities.[6,7] The depolarizing macroscopic field should also suppress at T_c the velocity discontinuity of longitudinal sound waves propagating along the polar axis.[8,9] From this viewpoint, the behavior of the TSCC crystals was found to be anomalous.

On one hand, recent observations revealed in these crystals logarithmic corrections to the behavior of the dielectric constant, [10] the sound velocity,[11] and apparently also the specific heat.[12] On the other hand, in the phase-transition region jumplike anomalies were discovered in the velocities of sound waves propagating both parallel and perpendicular to the polar axis.[11] We have already discussed this contradiction in Ref. 11 and concluded that a previously unobserved situation is realized in TSCC, viz., the dipole-dipole interaction turns out to be quite weak and plays a significant role only in the vicinity of T_c. Away from this region, the usual "dipole" behavior of the crystal takes on an "Ising" character, which corresponds to nearly equal hardness in the longitudinal and transverse order-parameter fluctuations.[11]

The dynamics of the order parameter in a weakly polar uniaxial ferroelectric was thus found to be quite unusual. The TSCC are the only example we know of compounds of this type. We have therefore undertaken a detailed investigation of the acoustic anomalies near the phase transition in TSCC. Particular attention was paid to the manifestation of the specific crossover in the behavior of the velocity and the sound damping and in the behavior of the fluctuation corrections.

2. CRYSTAL DATA, MEASUREMENT PROCEDURE

TSCC crystals have D_{2h}^{16} symmetry in the paraelectric phase with four formula units per unit cell.[14] Spontaneous polarization sets in below T_c along the b axis of the paraphase, and the crystal becomes a uniaxial ferroelectric. The structure of the ferroelectric phase was not investigated in detail, but many results indicate preservation of orthorhombic syngony. The most probable space group for the ferroelectric phase is C_{2v}^9, and the transition is not accompanied by a change of the unit cell. In this case B_2 is an active representation that induces the phase transition. The behavior of the longitudinal acoustic phonons in the transition region is then determined by a coupling that is quadratic in the order parameter and linear in the strain.

Different studies have yielded different values of the Curie temperature of TSCC, so an interval 127–132 K is frequently indicated for T_c.[4] The discrepancy may be connected with the sample quality. The relations between the unit-cell parameters in the paraphase are such that the direction a can be regarded as a pseudohexagonal axis. Grown crystals have indeed a pseudohexagonal faceting. The para-

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electric phase is frequently also the ferroelectric phase.[15] No transition to a high-temperature hexagonal paraphase was observed, however, although the investigations were carried out right up to the crystal-decomposition temperature ≈ 500 K. The hypothetical ferroelastic transition manifests itself in the fact that the grown crystals are usually subdivided into ferroelastic domains that can be easily seen in a polarization microscope. Our measurements were performed on single-domain samples ($5\times5\times5$ cm) cut from a large faceted crystal. The samples were oriented under a microscope: the a direction is the acute bisector of the angle between the optical axes that lie in the ab plane.

In the present study, the temperature behavior fo the acoustic phonons in TSCC was investigated by using Brillouin scattering. The scattering spectra were excited with a single-mode Spectra-Physics argon laser, and the wavelengths used were 0.51 and 0.48 μm. To measure more accurately the Brillouin components and their half-widths, the interferometer free spectral range was set in the range 7–15 KHz. As a result, the Brillouin components corresponding to scattering by longitudinal acoustic phonons in 180° geometry appeared in the second to fifth order spectra relative to the undisplaced component. The instrument sharpness was maintained at level 45. The instrumental broadening of the laser line did not exceed 160–200 MHz (depending on the free spectral range). In accordance with the assumed crystal orientation, the scattered-light spectra have the designations customarily used for this group of crystals, e.g., $b\,(cc)\bar{b}$ for the observation of scattering in a 180° geometry (the outer symbols denote the propagation directions of the incident and scattered light while the direction of the electric vector **E** is designated in the parentheses).

The crystals being studied were placed in an optical cryostat in a stream of cold nitrogen vapor. The temperature was stable to within 0.1 K. The laser power incident on the crystal did not exceed 50 mW. Control measurement at reduced power have shown that the crystal heating by the laser beam can be neglected.

3. BEHAVIOR OF BRILLOUIN COMPONENTS

We investigated light scattering by longitudinal acoustic phonons propagating along the a, b, and c directions in the crystal. The shift of the Brillouin components was determined from spectra of three types: $a(cc)\bar{a}$, $b\,(cc)\bar{b}$, and $c(aa)\bar{c}$. When the TSCC crystals are cooled below 300 K the frequency shift of the Brillouin components changes linearly with temperature. Near ~ 200 K, however, a deviation from linearity is observed (Fig. 1). The temperature dependences of the corresponding elastic moduli are shown in Fig. 2. Lowering of the temperature further increases the deviation of the phonon frequency from the extrapolation of the linear region to the phase-transition region. The damping of the phonons in the approach to the transition is quite distinct, albeit small, for all three spectra. For phonons propagating along b and a, the frequencies at $T\approx T_C$ differ from the values expected in linear extrapolation by only 1.3%; the difference is even smaller for the phonons along c.

The temperature dependence of the anomalous part of

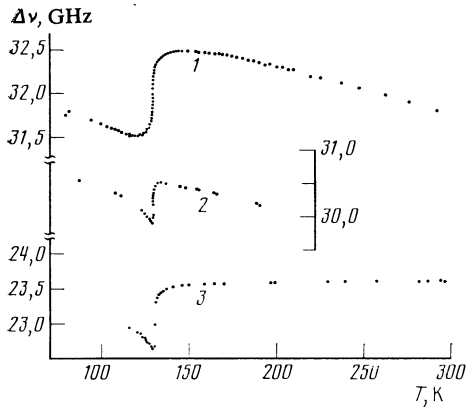

FIG. 1. Temperature dependence of the Brillouin-component shift $\Delta\nu$. The light scattering which was investigated was from longitudinal acoustic phonons propagating along the polar axis b (1), c (2), or a (3).

the sound velocity is close to logarithmic, a fact we attributed to the characteristic form of the fluctuation corrections in a uniaxial ferroelectric (see Fig. 3 of Ref. 11). The true behavior of the anomalous contribution was found to be more complicated, as will be described in the next section.

Measurement of the Brillouin-component shifts has made it possible to calculate the velocities of the longitudinal acoustic phonons and the corresponding elastic constants as functions of the temperature, using well-known formulas.[16] The birefringence in TSCC crystals is weak, and in the calculations for all the spectra we used for the refractive index a single value, 1.558, measured with an Abbé refractometer at room temperature. The crystal density was taken from Ref. 1. The temperature dependences of the refractive index and of the density were neglected.

Let us consider in greater detail the difference in the behavior of sound waves propagating perpendicular to and along the polar axis. In the former case the jumps of the corresponding elastic constants c_{11} and c_{33} are quite abrupt

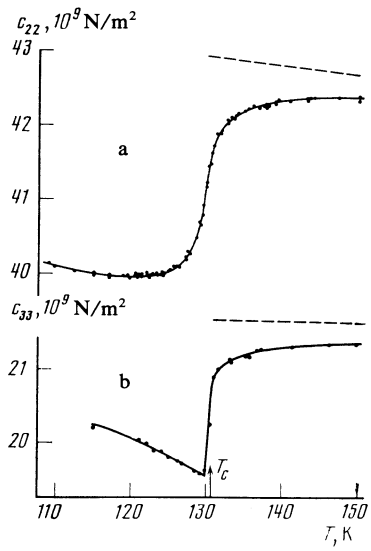

FIG. 2. Temperature dependence of the elastic moduli c_{22} (a) and c_{33} (b) in the phase-transition region. Points—experimental values, through which the lines were drawn to emphasize the difference between the behavior of c_{22} and c_{33}. Dashed line—expected behavior of c_{22} and c_{33} in the paraphase in the absence of fluctuation corrections.

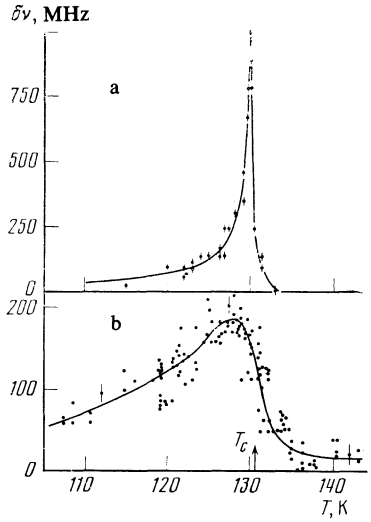

FIG. 3. Temperature dependence of the damping of the longitudinal acoustic phonons propagating perpendicular (a) and parallel (b) to the polar axis. The width $\delta\nu$ of the Brillouin components measured at half-maximum of the phonon line is shown; the instrumental broadening is subtracted.

(see Fig. 2), the damping is markedly asymmetric about T_C, as expected in the Landau-Khalatnikov approximation (Fig. 3). In our experiments at hypersound frequencies ($\sim$30 GHz) the discontinuity is spread out over an interval on the order of 0.7 K and the dispersion of the hypersound waves is less pronounced than, e.g., in TGS.[17] Analysis of the dispersion data yields for the relaxation time of the ordering in TSCC below T_C a value $\tau^- \approx 4.8\cdot 10^{-12}(T_C - T)^{-1}$ s, lower by an order of magnitude than in TGS.[17] On the whole, the behavior of the velocity and of the damping of sound waves propagating perpendicular to the polar axis agrees with that obtained for other ferroelectrics that have no piezoelectric properties in the paraelectric phase.

In the second case, in contrast to uniaxial ferroelectrics, there is no suppression of the acoustic anomalies in longitudinal sound wave propagating along the polar axis. A jumplike change of c_{22} is observed near T_C (Fig. 2), and the maximum of the damping α_2 is shifted far into the ferroelectric phase (Fig. 3). This behavior of c_{22} and α_2 is even more surprising in view of the presence of logarithmic fluctuation corrections in the paraphase.

4. ACOUSTIC ANOMALIES IN A WEAKLY POLAR FERROELECTRIC

The experimentally observed unusual behavior of the velocity and damping of longitudinal sound propagating along the polar axis can be analyzed phenomenologically. In our earlier description[11] of the behavior of longitudinal sound waves with change of temperature we neglected the difference of the background dielectric constant ε^* from unity and assumed that the transition in TSCC is very close to the tricritical point. We do not make these assumptions here. It will be shown below that a more detailed analysis, while not changing in principle the interpretation of the phenomenon, will be quite important in the discussion of the qualitative and quantitative aspects of the problem.

We begin with a Landau expansion of the density of the thermodynamic potential F which is a minimum at a fixed electric field $\mathbf{E}$ defined so that

$$-\partial F/\partial E_\alpha = P_\alpha^{\text{п}} = P_\alpha + (\hat{\varepsilon}_{\alpha\beta}^* - \delta_{\alpha\beta})E_\beta/4\pi, \tag{1}$$

where $\mathbf{P}^p$ is the total dielectric polarization and P_α is the contribution made to it by the nonzero single-component order parameter:

$$F = {}^1/_2\alpha P^2 + {}^1/_4\beta P^4 + {}^1/_6\gamma P^6 + {}^1/_2 c_{ij}U_iU_j + q_iP^2U_i - \mathbf{PE} - ({}^1/_{8\pi})\mathbf{E}(\hat{\varepsilon}^* - 1)\mathbf{E}, \tag{2}$$

where U_i are the components of the strain tensor. Since we kept the induction $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}^p$ constant for the sound propagation, the equation of motion for P is

$$\partial\tilde{F}/\partial P = -\mu\dot{P}, \quad \tilde{F} = F - E^2/8\pi + \mathbf{ED}/4\pi, \tag{3}$$

where μ is the polarization viscosity and F is the thermodynamic potential which is a minimum at fixed D. Starting from (1) and (3) as well from elasticity theory and the Maxwell equations, we obtain in the low-striction limit for the complex increment to the elastic modulus below T_C:

$$\Delta c_{ii} = -\frac{4q_i^2P_0^2}{\chi^{-1}}\frac{1}{1-i\omega\tau}, \tag{4}$$

where

$$\chi^{-1} = \begin{cases} \alpha^- \equiv \alpha + 3\beta P_0^2 + 5\gamma P_0^4 & \text{for } c_{11} \text{ and } c_{33}, \\ \alpha^- + 4\pi/\varepsilon_{22}^* & \text{for } c_{22}, \end{cases}$$

and the spontaneous polarization P_0 is determined from the equation

$$\alpha + \beta P_0^2 + \gamma P_0^4 = 0.$$

For the moduli c_{11} and c_{33}, Eq. (4) takes the form

$$\Delta c_{11,33} = -\frac{2q_{1,3}^2}{(\beta^2 - 4\alpha\gamma)^{0.5}}\frac{1+i\omega\tau}{1+(\omega\tau)^2}. \tag{4a}$$

At $\omega\tau \ll 1$ we obtain for the change of the sound velocity, as in Ref. 13, an inverse-square-root dependence that extends to the temperature

$$T_n = T_C + n, \text{ where } n = \beta^2/4\alpha'\gamma, \quad \alpha' = \partial\alpha/\partial T.$$

The sound damping is described in this case by the Landau-Khalatnikov mechanism, but the strong temperature dependence of the first fraction in (4a) makes the low-temperature falloff of the maximum steeper than $1/\alpha^-$. If the damping peak is narrow enough and hence close enough to T_C, so that $4\alpha'\gamma < \beta^2$ in the region of the maximum damping, the temperature dependence of the first fraction in (4a) can be neglected. From the width ΔT of the damping maximum, measured at half its height, we can obtain the position of T_C relative to the temperature determined by the position of the maximum, as well as the polarization viscosity μ:

$$T_C = T_m + \Delta T/2\sqrt{3}, \quad \mu = \alpha'\Delta T/\sqrt{3}\omega. \tag{5}$$

The limit $\omega\tau \ll 1$ always holds for the modulus c_{22} under the conditions of our experiment. Indeed, the presence of the depolarizing field that accompanies the sound causes χ^{-1} not to vanish at $T = T_C$ but to assume its minimum value $4\pi/\varepsilon_{22}^*$, so $\omega\tau$ cannot exceed

$$(\omega\tau)_{\max} = \varepsilon_{22}^* \Delta T / \sqrt{3} C,$$

where C is the high-temperature Curie–Weiss constant. In our experiments $(\omega\tau)_{\max} \approx 1/30$, so that the condition $\omega\tau \ll 1$ is satisfied easily. Taking this into account, we get

$$\operatorname{Re} \Delta c_{22} \sim \frac{P_0^2}{\alpha^- + 4\pi/\varepsilon_{22}^*}, \tag{6}$$

$$\operatorname{Im} \Delta c_{22} \sim \frac{P_0^2 \omega}{(\alpha^- + 4\pi/\varepsilon_{22}^*)^2}. \tag{7}$$

Analysis of relations (6) and (7) yields the following expressions for the temperatures T_R and T_I at which the minimum velocity and maximum damping are reached for longitudinal waves:

$$T_C - T_R = T_{cr}/4 + (T_{cr} n)^{1/2}, \tag{8}$$

$$T_C - T_I = \frac{T_K}{12}\left[1 + \frac{10}{1 + (3T_{cr}/n + 1)^{1/2}}\right], \tag{9}$$

where $T_{cr} \equiv C/\varepsilon^*$.

Let us analyze our experimental data by using the equations thus obtained. The second equation of (5) permits an estimate of the order-parameter relaxation time. Substituting the experimental width ΔT of the damping maximum and putting $\mu/\alpha' = \tau^-$ we get $\tau^- \approx 4 \cdot 10^{-12} (T_C - T)^{-1}$ s, in good agreement with the estimate given above, obtained by another method. We note that this method of estimating τ offers some advantage, since it obviates the need for exact measurement of the temperature T_C. We used the first equation of (5) to monitor the position of T_C in our crystals in the analysis of the fluctuation contribution in the paraphase.

The parameter n, which is a measure of the proximity of a phase transition to a tricritical point, was obtained directly from our experimental data, which are plotted (Fig. 4) in accordance with Eq. (4a). Our value $n = 8.5$ K agrees with the results of Ref. 13, where similar measurements at lower frequencies ($\sim$20 MHz) yielded $n = 7.5$ K. It must be noted that the values of n determined directly from an acoustic experiment noticeably exceed the values that can be calculated from the coefficients α', β, and γ obtained from dielectric measurements. In Ref. 18 are listed the values of these coefficients as obtained by different workers. Using them we obtain for n the values 2, 0.74, and 1.8 K. It is possible that the disparity in the values of n obtained by different methods is due to an inaccurate determination of γ, which was measured only in Ref. 19.

Expressions (8) and (9) enabled us to determine from the experimental data (Figs. 2 and 3) the parameter $T_{cr} = 7$ K. Several measurements of the background dielectric constant ε^* yielded the values 3 (Ref. 10) and 4.2 (Refs. 4 and 18). Substituting the known values of the Curie–Weiss constants determined in the same work, we obtain values of T_{cr} that are in fair agreement with our result, viz., 7.6, 9.1, and 6.25

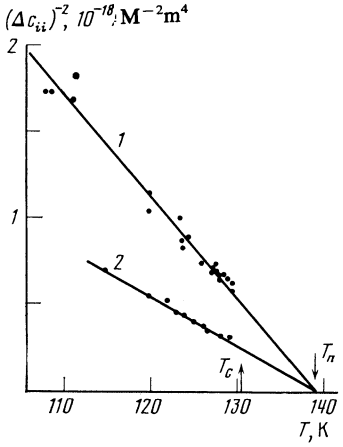

FIG. 4. Temperature dependences of $(\Delta c_{11})^{-2}$ (curve 1) and of $(\Delta c_{33})^{-2}$ (curve 2), which characterize the proximity of the phase transition to the tricritical point. $n = T_n - T_c = 8.5$.

K. The scatter of the values of C, noted in many papers, is apparently due to the fact that the considerable fluctuational corrections to ε, obtained for a wide range of temperatures in Ref. 10, violate the Curie–Weiss law.

The acoustic anomalies in TSCC at $T < T_C$ are thus consistently described by the Landau phenomenological theory. It is easily seen that all the features of the TSCC properties are governed mainly by the smallness of the parameter T_{cr}. This parameter determines both the temperature scale spanned by the velocity discontinuity and the width of the relaxational maximum of the damping of sound propagating along the polar axis. For substances with normal values of the Curie–Weiss constant, not an anomalously small one like TSCC, for example for TGS, we have $T_{cr} \approx 300$ K and the extended velocity discontinuity and damping maximum can be interpreted to mean that these anomalies are absent. TGS and TSCC have different physical behavior because the former is subject to a substantial dipole-dipole interaction at all temperatures, whereas in the latter this interaction is substantial only in the immediate vicinity of TC at $|T_C - T| \lesssim |T_C - T_R|$, while farther from the transition it is negligible compared with the short-range interactions. Thus, in the case of TGS the macroscopic dipole interaction has completely suppressed the sound-velocity discontinuity and the relaxational damping maximum for sound propagating along the polar axis. In the case of TSCC this interaction only stretched out the discontinuity and delayed the appearance of the damping maximum until temperatures were reached at which it no longer played a decisive role. These acoustic properties of TSCC stem from the fact that in the dynamics of the order parameter a crossover occurs from a dipole to an "Ising" type. In this sense T_{cr} can be referred to as the crossover parameter.

It is natural to expect this crossover to appear also in the fluctuation spectrum of the soft mode and to lead to a specific temperature dependence of the fluctuational corrections. Thus, the fluctuational correction to the sound velocity should vary logarithmically far in the "dipole region" and follow a power law far in the "Ising region."

An expression for the fluctuational correction Δc_{fl} to the elastic modulus in the crossover region can be obtained if the anisotropy of the gradient term in the thermodynamic-potential density is neglected. At $T > T_C$ we have

$$\Delta c_{\text{fl}} = \Delta c_L \beta T (4\pi\varkappa)^{-1,5} (\varepsilon^*)^{0,5} \ln (1+\tau^{-0,5}),$$
$$\Delta c_L = -2q^2/\beta, \quad \tau = (T-T_C)/T_{\text{cr}}, \tag{10}$$

where $\varkappa$ is the coefficient of the gradient term in the Landau expansion.

It is easily seen that Eq. (10) ensures correct asymptotic forms in the "dipole" ($\tau \ll 1$) and "Ising" ($\tau \gg 1$) regimes. From our experimental data taken below T_C we have obtained a crossover parameter $T_{\text{cr}} = 7$ K and monitored with good accuracy the location of T_C. We can thus in fact match the theoretical equation (10) to our measurment results without adjusting parameters. It can be seen from Fig. 5 that at $1 < T - T_C < 60$ K the experimental points agree well with calculations in accordance with Eq. (10). At $T - T_C < 1$ K, however, the experimental points lie below the theoretical curves, which in our opinion is not surprising. Indeed, Eq. (10) is valid only at $\Delta c_{\text{fl}}/\Delta c_{\text{L}} \ll 1$. In our case, at $T - T_c \approx 1°$, this ratio is of the order 0.3–0.4, so that in this region we are at the borderline of the applicability of Eq. (10). Since the next fluctuational correction should be of opposite sign, Eq. (10) is certainly an overestimate. Moreover, no account was taken in the derivation of (10) of the frequency dispersion of the fluctuational correction. It is known that allowance for the dispersion also lowers the value of the correction.[20] We call attention to the fact that in this temperature interval the fluctuational correction does not reach any of the asymptotic regimes. This enabled us to observe the specific temperature dependence of the fluctuational corrections precisely in the crossover region.

We note that this behavior of all the acoustic properties of the TSCC is determined in the final analysis by the smallness of the parameter T_{cr}. It will be shown in Sec. 5 that the physical cause of the smallness of T_{cr} is that TSCC is weakly polar (the soft mode has a small effective charge).

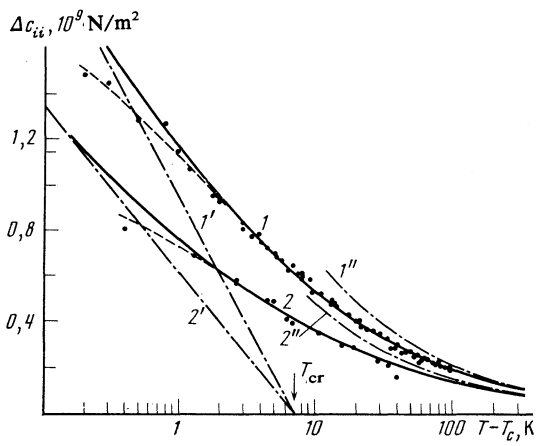

FIG. 5. Semilog plots of the anomalous parts Δc_{22} (1) and Δc_{33} (2) vs temperature in the paraelectric phase. Points—experimental values. The solid curves 1 and 2 were calculated from Eq. (10): 1′ and 2′—asymptotes of the form $\Delta c \propto \ln\tau$; 1″ and 2″—asymptotes of the form $\Delta c \propto \tau^{-5}$. The dashed lines that meet curves 1 and 2 show that reduced values of Δc are observed at $T < t - T_c = 2$ K (see the text).

5. ROLE OF BACKGROUND DIELECTRIC CONSTANT ε^*

In conclusion we discuss the importance of taking $\varepsilon^* - 1$ into account when describing physical processes in which macroscopic dipole-dipole interaction plays a substantial role. In the analysis of physical phenomena in ferroelectrics it is not customary to take into account the difference between the background dielectric constant ε^* and unity, since this difference is small compared with the lattice contribution to ε. In the case of TSCC, $\varepsilon \approx \varepsilon^*$ already in the immediate vicinity of the transition, and the importance of taking $\varepsilon^* - 1$ into account might seem obvious. We point out, however, that in all our equations ε^* entered as a factor and not as a term. This indicates that the energy of the macroscopic "dipole-dipole" interaction is inversely proportional to ε^*.[21] Therefore even in substances for which $\varepsilon^* \ll \varepsilon_0$ in the entire temperature interval it may be important to take the difference between ε^* and 1 into account. For example, in the analysis of the angular dependence of sound damping in uniaxial ferroelectrics use is made of an expression for the total reciprocal susceptibility χ^{-1} as a function of the angle between the wave vector $\mathbf{k}$ and the polar axis. It is easy to show that when account is taken of the difference between ε^* and 1 this expression takes the form

$$\chi^{-1}(\mathbf{n}) = \chi_0^{-1} + 4\pi n_y^2/(\mathbf{n}\hat{\varepsilon}^*\mathbf{n}), \quad \mathbf{n} = \mathbf{k}/|\mathbf{k}|. \tag{11}$$

It can be seen from (11) that neglect of the difference between $\hat{\varepsilon}^*$ and 1 not only changes the strength of the angular dependence of the damping by roughly a factor ε^*, but also yields a qualitatively incorrect form of this dependence even when the anisotropy of ε^* is not small. Failure to take $\varepsilon^* - 1$ into account explains the inconsistency of a recent attempt at a quantitative theoretical account of the angular dependence of sound in TGS,[22] where to explain the experimental results the authors had to assume that the factor 4π contained in (11) depends on the Lorentz factor (!).

6. NATURE OF PHASE TRANSITION IN TSCC

It follows from the preceding section that the unusual behavior of the acoustic properties of TSCC is due to the smallness of the parameter T_{cr} compared with T_C. The physical cause is small macroscopic dipole–dipole interaction of the order-parameter fluctuations compared with the characteristic energies responsible for the phase transition in the crystal. In this case the Lorentz component of the dipole-dipole interaction, which should be of the same order as its macroscopic component, clearly cannot be the cause of the ferroelectric instability in TSCC. The instability in this crystal should therefore be of the same type as in structural nonferroelectric phase transitions. This was deduced in Ref. 4 from the smallness of the dielectric contribution of the soft mode. In view of the arguments above, the transition in TSCC should in our opinion be classified as pseudo-intrinsic ferroelectric.

Whether the phase transition in TSCC is of the displacement type or of the order-disorder type has been debated until recently.[3,4] The main arguments favoring the order-disorder transitions are the low values of the Curie–Weiss

Quantity	Crystal		Units	Ratio
	TSCC	$BaTiO_3$		
P_0	0,26	25	$\mu C/cm^2$	10^{-2}
C	~50	$1{,}7\cdot10^5$	K	$\sim10^{-4}$
β	10^{-5}	10^{-12}	cgs	10^7
γ	10^{-11}	10^{-22}	cgs	10^{11}

constant, $C\approx 50$ K, and of the spontaneous polarization, $P_0 = 0.27\ \mu C/cm^2$ (at 77 K). Favoring the displacement transition is the presence of soft modes of the oscillator type.[4,5] Now, in light of the premise that the phase transition in TSCC is pseudo-intrinsic, the arguments in favor of the order-disorder transition become untenable, since a classification of transitions on the basis of the values of the Curie–Weiss constant and of the spontaneous polarization is valid only for truly intrinsic ferroelectric transitions. This fact can be easily traced within the framework of the simplest single-ion approach.[21] Moreover, analysis of the values of C and P_0 and of the coefficients β and γ of the higher powers of the polarization in the thermodynamic potential expansion also indicates that the phase transition in TSCC is pseudo-intrinsic ferroelectric of the displacement type.

Indeed, let us compare the TSCC parameters with those of the most thoroughly investigated ferroelectric $BaTiO_3$.[18,23] It can be seen from the table that they are very different. The difference, however, lies in the fact that we are dealing with two weakly anharmonic displacement ferroelectrics, but in one of them the effective charge of the soft mode is of the order of the electron charge e ($BaTiO_3$), while in the other (TSCC) this charge is of order $10^{-2}e$. Indeed, as follows from the basic theory of displacement ferroelectrics (see, e.g., Ref. 21), the density of the thermodynamic potential F in a structural transition of the displacement type can be estimated as

$$F=\mathscr{E}_{at}\{[(T-T_c)/T_{at}](\xi/a)^2+(\xi/a)^4+(\xi/a)^6+\ldots\}, \qquad (12)$$

where $\mathscr{E}_{at}\approx e^2/a^4$ and a are the characteristic density of the atomic energy and the interatomic distance, respectively; $T_{at}\approx \mathscr{E}_{at}a^3/k_B\approx 10^5$ K and ξ are the displacements corresponding to the order parameter. Rewriting the expansion in powers of the contribution made to the polarization by the displacements in the soft mode, $P = Q\xi/a^3$ (Q is the effective charge of the soft mode), we obtain

$$C=T_{at}(Q/e)^2, \quad \beta=\mathscr{E}_{at}^{-1}(Q/e)^4, \quad \gamma=\mathscr{E}_{at}^{-2}(Q/e)^6. \qquad (13)$$

For ferroelectrics with normal effective soft-mode charge $Q\approx e$, expressions (13) yield the well-known estimates that hold, e.g., for $BaTiO_3$. If, however, the soft-mode charge is anomalously small, $Q\approx 10^{-2}e$, the estimates obtained from (13) differ from the standard ones by 10^{-4}, 10^8, and 10^{12} for C, β, and γ, respectively. It can be seen from the table that to within the accuracy of our analysis the differences between the $BaTiO_3$ and TSCC parameters agree with the theoretical estmate.

An interesting question, in our opinion, is whether the anomalous smallness of the effective soft-mode charge is due to an accidental conjunction of parameters or to some regular law. It is not excluded that the weak behavior is due to the pseudohexagonal character of the paraelectric phase, i.e., the effective charge of the soft mode is small to the extent that the pseudohexagonal distortions are weak. In this case the soft mode should turn out to be nonpolar in the hexagonal paraphase.

It can thus be concluded from the foregoing experimental data that TSCC is a pseudo-intrinsic uniaxial displacement ferroelectric with an anomalously small effective charge of the soft mode.

We have observed in our experiments rather appreciable logarithmic corrections to the sound velocity at $t > T_C$. In our opinion this is also the result of the pseudo-intrinsic nature of the transition in the TSCC. Thus, it is well known that after subtraction of the long-range macroscopic contribution the dipole-dipole interaction decreases quite slowly with distance. This corresponds to an excessively wide range of validity of the Landau theory in intrinsic ferroelectrics[21] and to exceedingly small fluctuation corrections. In our case of a pseudo-intrinsic ferroelectric, the transition is due to forces with a shorter range than the Lorentz component of the dipole-dipole interaction, so that we are justified in expecting a narrowing of the region of applicability of the Landau theory and large fluctuation corrections.

7. CONCLUSION

We have analyzed the acoustic anomalies near a phase transition in the uniaxial ferroelectric TSCC. Four expressions, (4a), (8), (9), and (10) were obtained to describe four independent experiments. The form of all these expressions is determined by only two parameters, n and T_{cr}. Satisfactory agreement between theory and experiment is reached for $n = 8.5$ and $T_{cr} = 7$ K. Analysis of our experimental results, as well as of the values of the coefficients in the expansion of the free energy in powers of the order parameters, as obtained by others,[18] has allowed us to conclude that we are dealing with the previously unobserved case of a pseudo-intrinsic ferroelectric of the displacement type, with an anomalously small charge of the soft mode. The most pronounced feature in crystals of this type is the presence of a crossover from order dynamics of the dipole type to the Ising type. We have shown the crossover to exist both above and below T_C. The interpretation is based on the concept of a soft mode in a defect-free crystal.

Defects seem to play a minimal role in the critical phenomena we have observed. This is supported by the fact that we have not observed near T_C the increase, typical of the defect contribution, of the rate of change of the critical contribution to a thermodynamic quantity, an increase observed, e.g., in TGS.[24] The probable reason why no "defect" contribution was observed in our experiment near T_C is that this contribution (like the fluctuational one) should undergo dispersion, and it was found that at our frequencies the dispersion sets in before the "defect" contribution becomes dominant. It is possible that a contribution from defects can

become observable in measurements at substantially lower acoustic frequencies than in our experiment.

The authors thank A. P. Levanyuk for a helpful discussion.

[1]R. Pepinsky and Y. Makita, Bull. Am. Phys. Soc., Ser. II **7**, 24 (1962).
[2]G. A. Smolenskiĭ, I. G. Siniĭ, S. D. Prokhorova, E. G. Kuz'minov, and V. D. Mikvabiya, Izv. AN SSSR Ser. Fiz. **43**, 1664 (1979).
[3]W. Windsch, Ferroelectrics **12**, 63 (1976).
[4]G. V. Kozlov, A. N. Volkov, J. F. Scott, G. E. Feldkamp, and J. Petzelt, Phys. Rev. **B28**, 255 (1983).
[5]S. D. Prokhorova, G. A. Smolensky, I. G. Siny, E. G. Kuzminov, V. D. Mikvabia, and K. Arndt, Ferroelectrics **25**, 629 (1980).
[6]A. P. Levanyuk, Izv. AN SSSR Ser. Fiz. **29**, 879 (1965).
[7]A. I. Larkin and D. E. Khmel'nitskiĭ, Zh. Eksp. Teor. Fiz. **56**, 2087 (1969) [Sov. Phys. JETP **29**, 1123 (1969)].
[8]S. Ya. Geguzina and M. A. Krivoglaz, Fiz. Tverd. Tela (Leningrad) **19**, 3055 (1977) [Sov. Phys. Solid State **19**, 1546 (1977)].
[9]K. A. Minaeva, B. A. Strukov, and K. Warstropff, *ibid.* **10**, 2125 (1968) [10, 1665 (1969)]. B. A. Strukov, S. K. Khanna, and K. A. Minaeva, *ibid.* **18**, 3318 (1976) [18, 1934 (1976)].
[10]E. Sandvold and E. Courtens, Phys. Rev. **B27**, 5660 (1983).
[11]G. A. Smolenskiĭ, I. Siniĭ, A. K. Tagantsev, S. D. Prokhorova, V. D. Mikvabiya, and W. Windsch, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 307 (1984) [JETP Let. **39**, 368 (1984)].
[12]M. A. Perez Jubindo, A. Lopez-Echarri, and M. J. Tello, Ferroelectrics **39**, 1171 (1871).
[13]G. Sorge, U. Straube, and N. R. Ivanov, Phys. Stat. Sol. (a) **65**, 189 (1981).
[14]T. Ashida, S. Bando, and M. Kakuda, Acta Crystallogr. **B8**, 1560 (1972).
[15]A. Sawada, Y. Makita, and Y. Takagi, J. Phys. Soc. Jpn. **42**, 1918 (1977).
[16]R. Vacher and L. Boyer, Phys. Rev. **B6**, 639 (1972).
[17]R. W. Gammon and H. Z. Cummins, Phys. Rev. Lett. **17**, 193 (1966).
[18]J. Bornarel and V. H. Schmidt, J. Phys. **C14**, 2014 (1981).
[19]G. Sorge and U. Straube, Phys. Stat. Sol. (a) **51**, 117 (1979).
[20]A. P. Levanyuk, Zh. Eksp. Teor. Fiz. **49**, 1304 (1965) [Sov. Phys. JETP **22**, 901 (1966)].
[21]V. G. Vanks, Vvedenie v mikroskopicheskuyu teoriyu segnetoélektrikov (Introduction to Microscopic Theory of Ferroelectrics), Nauka, 1973, pp. 40, 49.
[22]Y. Tsujimi, X. Yagi, and I. Tatsuzaki, J. Phys. Soc. Jpn. **52**, 1469 (1983).
[23]F. Jona and G. Shirane, Ferroelectric Crystals, Pergamon, 1962.
[24]B. A. Strukov, Izv. AN SSSR Ser. Fiz. **47**, 548 (1983).

Translated by J. G. Adashko