Transition from a dipole behavior to an "Ising" behavior in the uniaxial ferroelectric TSCC

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Logarithmic corrections and a jump in the sound velocity along the polar axis have been observed in the uniaxial ferroelectric TSCC. This unusual behavior is attributed to an anomalously weak macroscopic dipole interaction, which is important only in a small, asymmetric neighborhood of T_c.

Crystals of $(CH_3NHCH_2COOH)_3CaCl_2$ (TSCC) are uniaxial ferroelectrics.[1] It is well known that in such crystals the dipole-dipole interaction, suppressing fluctuations, gives rise to only weak, logarithmic corrections to the behavior of thermodynamic quantities near the phase transition[2] and suppresses the jump at T_c in the velocity of longitudinal sound propagating along the polar axis.[3]

We have studied the Brillouin scattering near the ferroelectric phase transition in TSCC, using the experimental procedure described in Ref. 4. Jumps are observed near T_c in the velocity of longitudinal sound propagating either along (V_2) or perpendicular

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to (V_3) the polar axis (Figs. 1 and 2). Above the transition, on the other hand, we can see anomalous parts ΔV_2 and ΔV_3 near T_c which vary logarithmically (Fig. 3).

Can we find a noncontradictory explanation of these anomalies? The jump in the sound velocity at the transition to a ferroelectric phase can be described by the following expression[5] if damping is ignored[2)]:

$$\Delta V \sim P_0^2 / \chi^{-1}, \tag{1}$$

where P_0 is the spontaneous polarization, and χ^{-1} is the reciprocal of the susceptibility. In a uniaxial ferroelectric we have to consider the contribution of the macroscopic dipole-dipole interaction to χ^{-1}, so that we would write $\chi^{-1} = \chi_0^{-1} + 4\pi k_2^2/k^2$, where **k** is the sound wave vector. The exceedingly small Curie-Weiss constant of TSCC,[6,7] combined with the low frequency of the soft mode and the weak LO-TO splitting,[7,8] indicates that the effective charge due to the soft optical vibration is very small. We would thus expect that at a certain temperature T_0, not greatly different from T_c, the contribution to χ^{-1} from the short-range forces in TSCC would become equal to the contribution of the dipole-dipole interaction (which is anomalously small in our case). At the temperature T_0 we would then observe a transition from a dipole behavior (with a suppression of fluctuations along the polar axis and with logarithmic corrections) to an ordinary "Ising" behavior, corresponding to approximately equal stiffnesses for the longitudinal and transverse fluctuations in the order parameter.

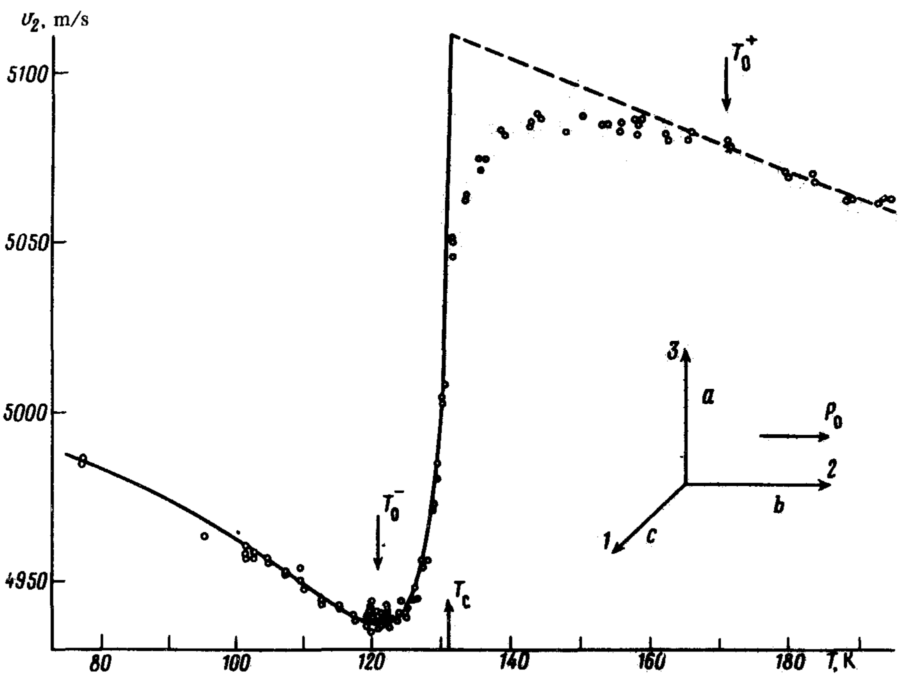

FIG. 1. Temperature dependence of the longitudinal sound velocity V_2 for sound propagating along the polar axis. Dashed line—extrapolation from the region far from the transition; solid curve—calculated from Eq. (3).

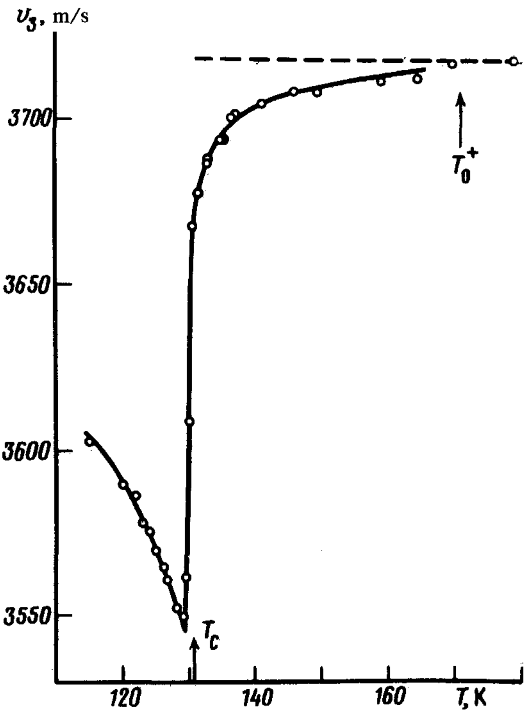

FIG. 2. Temperature dependence of the longitudinal sound velocity (V_3) for sound propagating perpendicular to the polar axis, along the a direction (Fig. 1), which is a pseudohexagonal axis in TSCC. The dashed line has the same meaning as in Fig. 1.

It is easy to show that such a temperature T_0 can in fact be found. Since the transition in TSCC is near the critical point,[3] we can write $P_0^2 \sim (\alpha/\gamma)^{0.5}$ and $\chi_0^{-1} = 4$, where α, β, and γ are coefficients in the expansion of the thermodynamic potential in powers of the polarization P_0. We then find the following expressions for the jumps in the sound velocity from (1):

$$\Delta V_3 \sim (T_c - T)^{-0.5} \text{ and } \quad (2)$$

$$\Delta V_2 \sim (T_c - T)^{0.5} (T_c + C/4 - T)^{-1}, \quad (3)$$

where C is the Curie-Weiss constant. The jump ΔV_2 has a minimum at $T = T_0^- = T_c - C/4$. At $T \ll T_0^-$, the jumps ΔV_2 and ΔV_3 behave similarly, in accordance with expression (2); i.e., at these temperatures the dipole-dipole forces have only a small effect on the dynamics of the order parameter. At $|T - T_c| < |T_0^- - T_c|$, in contrast, the dipole-dipole contribution to χ^{-1} is greater than that of the short-range forces. If T_0^- is quite close to T_c, as in our case, then a change in the velocity of longitudinal sound propagating along the polar axis will be seen as a jump which is stretched out over a temperature interval on the order of $T_c - T_0^-$. The jump will remain sharp for the direction perpendicular to the polar axis. These conclusions agree qualitatively with our results for the ferroelectric phase (Figs. 1 and 2).

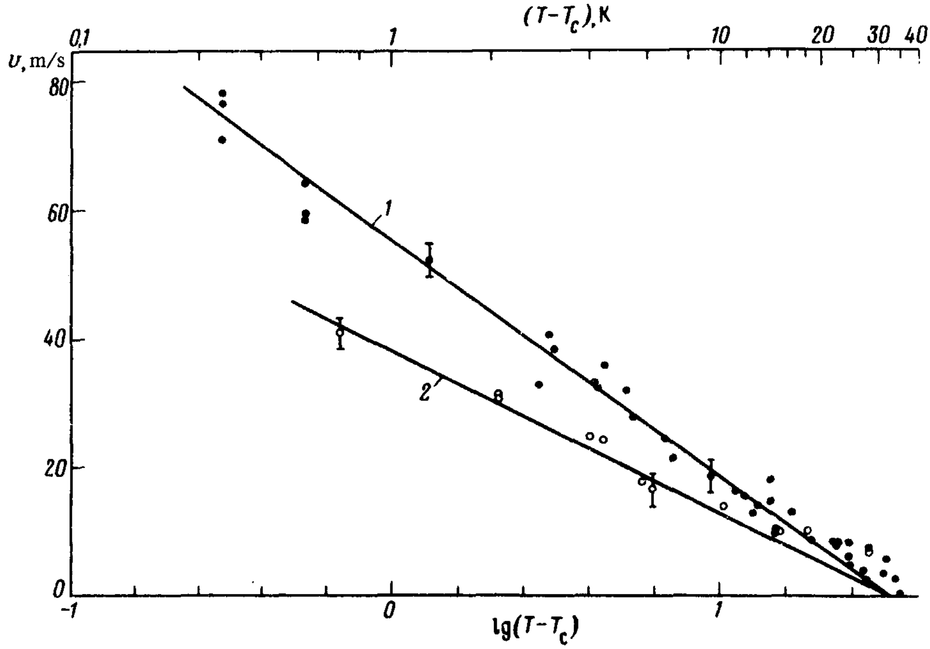

FIG. 3. The anomalous parts of ΔV_2 and ΔV_3 vs the temperature. 1—ΔV_2; 2—ΔV_3.

Above the transition, the short-range and dipole-dipole contributions become comparable at a temperature $T_0^+ = T_c + 4(T_c - T_0^-)$, because the phase transition occurs near a tricritical point. The temperature region in which the dipole-dipole interaction is important is thus asymmetric with respect to T_c. Taking into account the scatter in the values reported[6,7] for C, we find values ranging from 6 to 15 K for $\Delta T_0^- = T_c - T_0^- = C/4$, while for $\Delta T_0^+ = T_0^+ - T_c$ we find the region 24–60 K. We can find T_0^- from our data on the minimum of ΔV_2 (Fig. 1): $\Delta T_0^- \cong 10$ K. Consequently, if logarithmic corrections are observed in the paraelectric region, then they should be observed at temperatures below T_0^+. In our case the logarithmic dependence of ΔV_2 has been observed over a temperature interval on the order of 32 K above T_c, in agreement with the expected value $\Delta T_0^+ = 4\Delta T_0^- = 40$ K.

Measurements of the dielectric function ϵ_2 by Sandvold and Courtens[9] have revealed logarithmic corrections to the Curie-Weiss law which agree with the results of Ref. 2 over an interval no greater than 20 K above the transition. This result does not contradict our estimates of ΔT_0^+.

In summary, according to the experimental data available, TSCC is the only case of a ferroelectric exhibiting a small dipole-dipole interaction. It thus becomes possible to observe an equalization of the contributions of the short-range and dipole-dipole forces to the reciprocal of the susceptibility near T_c.

The weak macroscopic dipole-dipole interaction of TSCC which we have been discussing here should mean that the Lorentzian component of the dipole-dipole interaction is weak and thus could not explain the ferroelectric instability. The transition in TSCC thus appears to be pseudofree.

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[2)]The sharpness of the velocity jump for sound propagating perpendicular to the polar axis (Fig. 2) indicates that at our frequencies damping can be ignored in a region which is not too close to T_c.

[3)]A measure of the proximity of the transition to the critical point is the small temperature difference between T_c and T^*, at which we have $\beta^2 = 4\alpha\gamma$. According to the data of Ref. 6, we have $|T^* - T_c| \approx 1$ K.

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