Effect of large-scale inhomogeneities on the phase transition in ferroelectric triglycin sulfate single crystals

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An influence of large-scale inhomogeneities on the elastic anomalies of triglycin sulfate crystals has been observed near the phase-transition temperature. It is shown that in a defect-free crystal no anomalous "peaks" are observed in the temperature dependence of the elastic modulus at $|T-T_c|\gtrsim 0.02$ K, and that the jump predicted by the Landau-Ginzburg theory is observed at the phase-transition point.

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It is known that the suppression of polarization fluctuations by long-range Coulomb forces in unaxial ferroelectrics leads to an expansion of the region of applicability of the phenomenological Landau-Ginzburg theory (compared with multiaxial ferroelectrics and with phase transitions of non-electric nature).

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Uniaxial triglycin sulfate (TGS) crystals serve as the models for the theory of second-order phase transitions. A detailed experimental investigation of the singularities of the thermodynamic quantities near the phase-transition point (T_c) in these crystals is of interest both as a check on the conclusion of the theory and as a check on the methods used in the theory.[1,3] In these and in crystals of close compositions, various workers have observed in experiments anomalies of the λ type near T_c in the heat capacity,[4] the elastic moduli,[5] and the coefficient of thermal expansion,[6] anomalies attributed to the presence of fluctuation effects at temperatures at which the Levanyuk-Ginzburg criterion is satisfied.[2] At the same time, in some studies no anomalies were observed near T_c.[7]

We have previously observed a layered defect structure in TGS crystals grown in the ferroelectric phase.[8] It was established, furthermore, that the crystals obtained above T_c have no such defective macrostructure and are elastically homogeneous. The growth conditions thus determine the degree of defectiveness and the homogeneity of the impurity distribution in the crystals.

To bring to light the effect of the observed effects on the thermodynamic behavior of the crystal in the phase-transition region, we investigated the critical anomalies of the velocity and of the absorption of ultrasonic waves of frequency ~ 10 MHz in the interval $|T-T_c|<0.3$ K by an acousto-optical method[9] in crystals grown above T_c ("pure crystals") and below T_c ("defective crystals").

Prior to the measurements all the TGS crystal samples were annealed for 4–5 hours at 90–100 °C. The accuracy of measurement and stabilization of the temperature was not worse than 10^{-3} K.

The measurements performed on the defective crystals (dashed lines in Figs. 1 and 2) coincide with those obtained earlier.[5,10] For the pure crystals, on the other

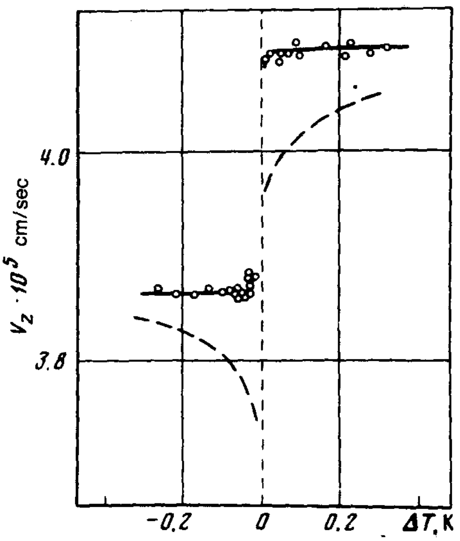

FIG. 1. Temperature dependence of the velocity of a quasi-longitudinal wave propagating along the z axis in the vicinity of T_c of the TGS crystal (the dashed line shows the temperature dependence of the speed of sound in a crystal with defects).

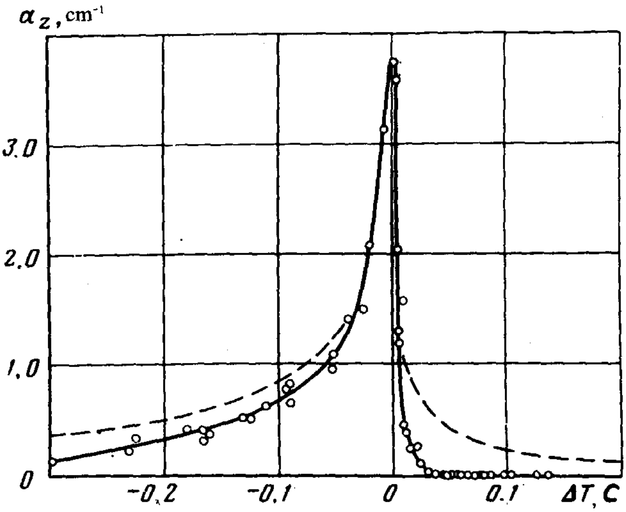

FIG. 2. Temperature dependence of the absorption coefficient of a quasilongitudinal sound wave propagating along the z axis in the vicinity of T_c of a TGS crystal (the dashed line shows the analogous dependence for a crystal with defects).

hand, it turns out that the velocity of the longitudinal sound propagating perpendicular to the ferroelectric axis does not depend on the temperature down to $|T-T_c|\approx 0.02$ K, and at $T-T_c$ it undergoes the jump predicted by the Landau-Ginzburg theory (Fig. 1). Measurements at lower $|T-T_c|$ are made difficult by the large absorption of the sound waves. The speed of sound in the case of wave propagation along the ferroelectric axis does not experience the previously observed anomaly,[5] and this agrees with the theory that takes into account the long-range dipole-dipole interaction in a perfect crystal.[11]

The anomalies previously observed in TGS crystals were attributed to enhancement of the fluctuations of the polarization near T_c. However, the correlation parameter of the theory, estimated from the experimental data ($\delta \sim 10^{-16}$ cm^2)[5] contradicted to some degree the idea of the phenomenological approach: the bulk energy of the crystal should be of the order of the correlation energy when the polarization is varied over distances l which are at any rate not smaller than the distance a between the elementary dipoles. In this case it turned out that $l \sim (\delta/2T_c)^{1/2} \sim 1.3\times 10^{-8}$ cm, whereas for the TGS crystals $a \sim 5\times 10^{-8}$ cm.

It is clear from our experiments that the fluctuations of the polarization do not come into play down to $|T-T_c|\approx 0.02$ K, and the sound-speed anomalies observed in the crystals grown above T_c are due to the presence of a defect structure. It can thus be concluded that if at $|T-T_c|\leqslant 0.02$ K there does exist a temperature region where the fluctuations are significant, then the value of the correlation parameter must be larger and the values of the corresponding corrections smaller. From measurements of the sound-absorption coefficient in a defect-free crystal in the paraelectric phase (Fig. 2) it follows that $\delta \sim (10-15)\times 10^{-16}$ cm^2, which fits better the situation in ideal uniaxial ferroelectrics and correlates better with the fluctuation-theory estimates of the anomalous quantities.[12]

Practically all the investigations of critical phenomena in TGS crystals were made on crystals grown below T_c. It can be assumed that the temperature dependences of the heat capacity and of the coefficient of thermal expansion of defect-free TGS crystals near T_c will be analogous to the temperature dependence we obtained for the adiabatic elasticity, i.e., the corresponding quantities should behave in defect-free crystals like in the ideal system considered by the Landau-Ginzburg theory, at least up to $|T-T_c| \approx 0.02$ K.

The question of the influence of defects on the behavior of a crystal near T_c has recently been under discussion in the literature.[13,14] Our data confirm the conclusion that impurities suitably implanted in the crystal lattice can enhance rather than smear out the anomalies in second-order phase transition.

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