Critical anomalies of the velocity and absorption of sound in a quasi-one-dimensional ferroelectric material CsH_2PO_4

E. D. Yakushkin, A. I. Baranov, and L. A. Shuvalov
Institute of Crystallography, USSR Academy of Sciences

(Submitted 13 November 1980)

Pis'ma Zh. Eksp. Teor. Fiz. **33**, No. 1, 27–31 (5 January 1981)

It was discovered that, in contrast to known uniaxial ferroelectric materials, a cesium dihydrogen phosphate crystal has no long-range, dipole-dipole interaction, and the critical anomalies in this ferroelectric material are similar to those observed in systems with short-range interaction forces.

PACS numbers: 77.80. – e, 43.20.Hq

Interest in small-dimensional systems is attributable to their practical applications and to their importance in the analysis of different model representations. It was established relatively recently that ferroelectric ordering in CsH_2PO_4 (CDP) and CsD_2PO_4 (DCDP) crystals is quasi-one-dimensional.[1,2] The order-parameter correlations in this case are highly anisotropic; the correlation length $l_c^{\parallel}$ in the polar axis direction of the crystal is more than an order of magnitude greater than the correlation length $l_c^{\perp}$ at right angles to it.[2] It was also established that the temperature dependence of the dielectric susceptibility of this crystal differs from the classical temperature dependence (predicted by the Landau theory) within a wide temperature range.[3]

To understand the unique features of the macroscopic behavior of this crystal near the phase-transition temperature (T_c), we have investigated the velocity and absorption of longitudinal ultrasonic waves (with a frequency of ~ 10 MHz).

The use of the conventional echo-pulse method gives the following relative accuracy of measurements of the ultrasonic-wave velocity and the absorption coefficient: $\Delta v/v \sim 10^{-5}$ and $\Delta\alpha/\alpha \sim 10^{-2}$, respectively. The accuracy of the temperature measurement and stabilization was better than 10^{-3} K. The studied $Cs(H_{1-x}D_x)_2PO_4$ single crystal $x \approx 0.1$, $T_c \approx 175$ K, and C_{2h}^2 symmetry of the high-temperature phase) was a rectangular parallelepiped with dimensions of $8 \times 9 \times 13$ mm^3 along the x, y, and z crystallographic axes, which were chosen in such a way that the y axis corresponds to the direction of the "2" polar axis.[4]

It is known that the long-range dipole-dipole forces in polar dielectrics give rise to a strong dependence of the dielectric susceptibility and elastic moduli on the direction of the wave vector $\mathbf{k}$.[5] This dependence is attributable to the macroscopic depolarizing field $\mathbf{E} = -4\pi(\mathbf{P}\cdot\mathbf{n})\mathbf{n}$, where $\mathbf{n} = \mathbf{k}/k$, which is associated with the longitudinal sound wave. As a result, the velocity and absorption anomalies of longitudinal sound waves in uniaxial ferroelectric materials with homogeneous, three-dimensional ordering at $T \leqslant T_c$, which propagate along the singular polar axis of the crystal, are either not observed experimentally or are much weaker than the analogous anomalies produced as a result of propagation of sound waves at right angles to the polar axis. In the latter case, these anomalies are similar to those predicted by Landau theory (a surge of the sound velocity at $T = T_c$ and λ is the absorption peak)

The maximum sound velocity and absorption anomalies in the CDP crystal are

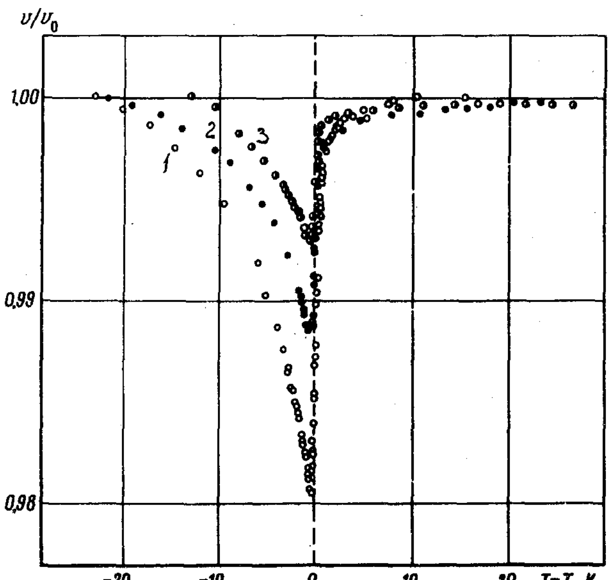

FIG. 1. Temperature dependences of the relative velocities of quasi-longitudinal sound waves along the three crystal-physical directions in the vicinity of T_c of a CDP crystal: 1—○, v_y/v_{0y}; 2—●, v_x/v_{0x}; 3—◑, v_z/v_{0z}.

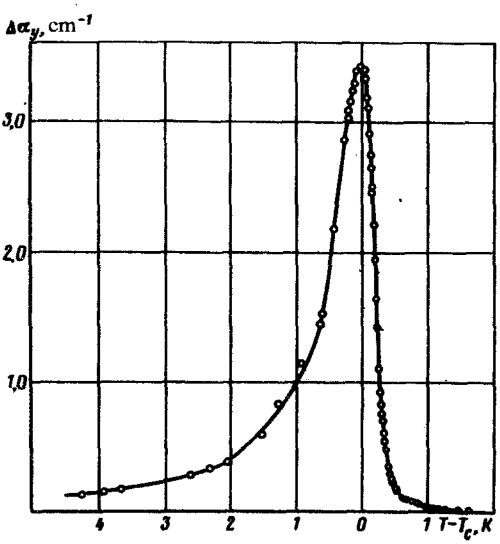

FIG. 2. Temperature dependence of the absorption coefficient of a longitudinal sound wave propagating along the y polar axis in the vicinity of T_c of a CDP crystal.

observed when the wave propagates along the y polar axis (Figs. 1 and 2) i.e., the macroscopic depolarizing field has no effect. Since the screening effect of free charges can be ignored in this crystal, the spontaneous polarization in the low-temperature phase of the crystal much be highly inhomogeneous.

Generally, the fluctuational effects must also contribute to the sound velocity and absorption anomalies; moreover, they are independent of the direction of **k** at $kl_c \ll 1$. However, the critical region, which is very small $[(T - T_c)/T_c \sim 10^{-4}$, according to theoretical estimates[6]] in systems with dipole-dipole interaction, normally cannot be achieved experimentally.[7]

The critical region for the CDP crystal (Fig. 3) is much broader than that predicted for uniaxial ferroelectrics materials. The sufficiently high relative accuracy of the measurements and the high temperature resolution made it possible to perform a quantitative analysis of the $\Delta v(T)$ and $\Delta\alpha(T)$ dependences in order to determine their analytical formula in the $T > T_c$ region. The anomalous part of $\Delta v(T)$ was defined as the difference between the sound velocity extrapolated from the region of sufficiently high temperatures and the measured values; the extrapolation curve $v_0(T)$ was a nonlinear polynomial.

It was found that the $\Delta v(T)$ and $\Delta\alpha(T)$ dependences for $T > T_c$ can be represented in the form $\Delta v \sim (T - T_c)^{-\alpha}$ and $\Delta\alpha \sim (T - T_c)^{-\theta}$, and for a sound wave, which propagates along the polar y axis, $\alpha = 1.00 \pm 0.05$ and $\theta = 2.30 \pm 0.05$ in the interval $2\times 10^{-1} \lesssim T - T_c \lesssim 5$ K (Fig. 3). Similar large values of the critical index θ are observed only in systems with short-range interaction forces—ferromagnetic and antiferromagnetic materials.[8] If the relation $\theta = \alpha + \gamma$, which follows from the so-called "bound-mode theory",[9] is used for the critical indices, then $\gamma = 1.3$ in the same temperature range, i.e., the index for the dielectric susceptibility is also characteristic of systems with short-range forces. This value of γ was obtained in Ref. 4 for the CDP

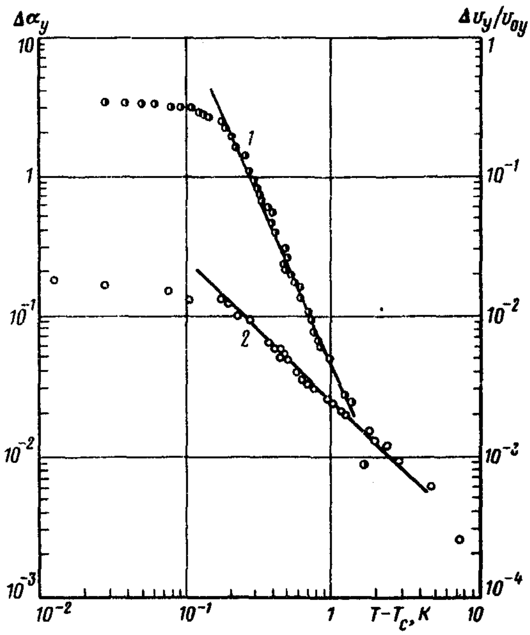

FIG. 3. Temperature dependences of the quantities $\Delta\alpha$ (1—◑) and Δv(2—○) in a logarithmic scale for temperatures $T > T_c$.

crystal in a broad temperature range. It is noteworthy that we obtained $\alpha = 0.50 \pm 0.05$ in the interval $5\times10^{-2} \lesssim T - T_c \lesssim 10$ K for the sound velocity anomalies in the propagation of waves along the x and z axes. It must be noted that the $\Delta v(T)$ and $\Delta\alpha(T)$ anomalies in the ferroelectric phase transition normally cannot be represented in the form of power dependences on $(T - T_c)$ within such a broad temperature range above T_c.

The observed critical anomalies indicate that there is no quenching of fluctuation due to long-range, dipole-dipole interaction, which is characteristic of ordinary ferroelectric materials. This is apparently attributable to a strong anisotropy of the correlations; it is known from the experiments on neutron scattering in this crystal that $l_c^{\parallel}$ reaches a value of 600 Å for $T - T_c \approx 0.3$ K, whereas $l_c^{\perp} \approx 30$ Å.[2]

A quantitative analysis of the dependences for $T < T_c$, which has some difficulties, is the subject of a separate investigation.

In conclusion, the authors thank A. P. Levanyuk for his comments during a discussion of the manuscript of this paper and A. N. Izrailenko for providing the CDP single crystals.

[1]D. Semmingsen, W. D. Ellenson, B. C. Fraser, and G. Shirane, Phys. Rev. Lett. **38**, 1299 (1977).
[2]B. C. Frazer, D. Semmingsen, W. D. Ellenson, and G. Shirane, Phys. Rev. B **20**, 2745 (1979).
[3]R. Blinc, B. Zeks, A. Levstik, C. Filipic, J. Slak, M. Burgar, I. Zupancic, L. A. Shuvalov, and A. I. Baranov, Phys. Rev. Lett. **43**, 231 (1979); A. I. Baranov, V. S. Ryabkin, L. A. Shuvalov, and L. N. Rashkovich, Krisotallografiya **24**, 524 (1979) [Sov. Phys. Crystallogr. **24**, 300 (1979)].
[4]Y. Uesu and J. Kobayashi, Phys. Status Solidi A **34**, 475 (1976).
[5]M. A. Krivoglaz, Fiz. Tverd. Tela **5**, 3439 (1963) [Sov. Phys. Solid State **5**, 2526 (1963–64)].
[6]V. L. Ginzburg, Fiz. Tverd. Tela **2**, 2031 (1960) [Sov. Phys. Solid State **2**, 1824 (1960)]; A. P. Levanyuk,

Izv. Akad. Nauk SSSR Ser. Fiz. **29**, 879 (1965).
[7]B. A. Strukov and E. D. Yakushkin, Pis'ma Zh. Eksp. Teor. Fiz. **28**, 16 (1978) [JETP Lett. **28**, 14 (1978)].
[8]Fizicheskaya akustika (Physical Acoustics), Ed. W. Mason, Vol. 7, Chap. 2, Mir, Moscow, 1974.
[9]F. Schwabl, Phys. Rev. B **7**, 2038 (1973).

Translated by Eugene R. Heath
Edited by S. J. Amoretty