

Critical phenomena in potassium dihydrophosphate (KDP)

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The behavior of the linear coefficient of expansion and linear compressibility of KDP single crystals in the region of the ferroelectric phase transition at pressures to 4.5 kbar has been investigated for the first time by means of a capacitive dilatometer. Existence of the tricritical point with coordinates $T_t = 109.8 \pm 0.2$ K and $P_t = 2640 \pm 40$ bar has been reliably established. It is shown that the behavior of the thermal expansion and compressibility in the case of KDP is adequately described by means of the Landau theory (index $\alpha = 0.5$) under the condition that the coefficients in the Landau expansion are considered to be functions of pressure and temperature.

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As is well known, the unique feature of ferroelectric phase transitions in KDP-type crystals is the narrowness of a region (several degrees only) in which the behavior of the thermodynamic quantities is anomalous, as is typical for phase transitions of the second kind and similar transitions of the first kind (see, for example, Ref. 1). This behavior of the thermodynamic quantities is in poor agreement with the conclusions of the Landau theory for phase transitions of the first kind, close to the second;^{2,3} this has led to doubts concerning the applicability of the Landau theory for describing in general KDP-type ferroelectrics. Recently, however, Schmidt *et al.*⁴ have offered evidence in support of the existence of a tricritical point at the phase transition boundary in KDP near 2 kbar. This means that when analyzing the behavior of thermodynamic quantities near the transition point even at the atmospheric pressure, proximity of the tricritical point must be taken into account. Earlier, we showed⁵ that a consistent description of tricritical phenomena in antimony sulfoiodide within the framework of the Landau theory requires us to take into account the fact that, near the tricritical point the coefficient B in the fourth order term in the following expansion

$$\phi = \phi_0 + \frac{1}{2} A \eta^2 + \frac{1}{4} B \eta^4 + \frac{1}{6} C \eta^6 + \dots \quad (1)$$

is a function of both pressure and temperature. We note that Dolino *et al.*⁶ have arrived at a similar conclusion when analyzing the behavior of the order parameter near the tricritical point in NH_4Cl .

Thus, difficulties associated with applying the Landau theory to KDP-type ferroelectrics conceivably occur as a result of the aforementioned fact.

In this work we report on an investigation of the special features in the behavior of the thermal expansion and compressibility of a KDP single crystal in the region of the ferroelectric phase transition at pressures to 4.5 kbar. The experiments were carried out using an advanced version of the dilatometric equipment described in Ref. 5.

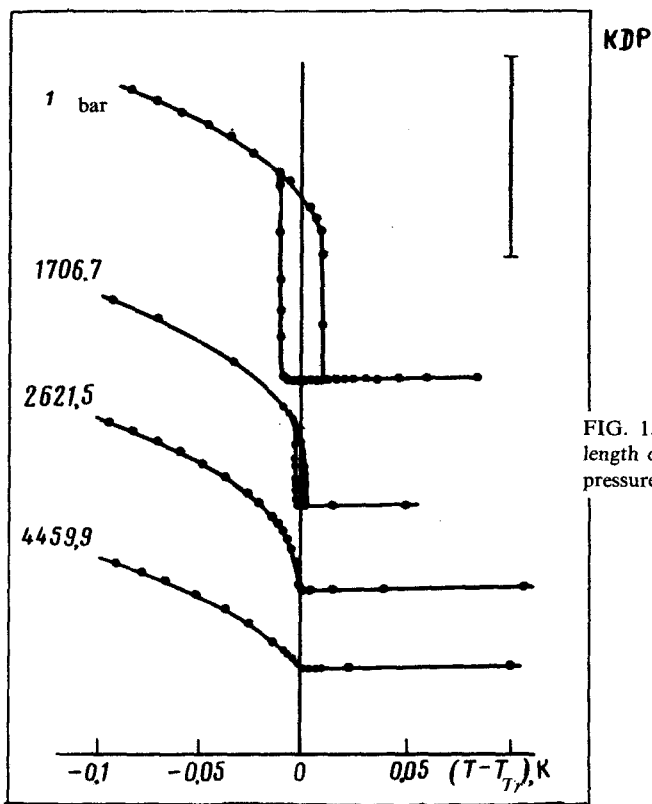


FIG. 1. Temperature dependence of the length of a single KDP crystal at various pressures.

The elongation was measured with an accuracy not less than 10 \AA , and the temperature and pressure were stabilized within 0.2 mK and 0.2 bar , respectively. The test specimen was cut from a high-quality single crystal in the form of a $3 \times 3 \times 8 \text{ mm}^3$ parallelepiped; its long side, where the measurements were made, is directed along the tetragonal axis. Specimen quality may be characterized by the steepness of the step of the measured quantity for a phase transition of the first kind. In our case, this step was not greater than $5 \times 10^{-4} \text{ K}$ in widths at the atmospheric pressure.

Figure 1 shows a family of length—temperature isobars at pressures in the range 1–4500 bar. It is clearly seen that the size of the length step Δl and temperature hysteresis ΔT decrease with increasing pressure; processing of the dependence of these parameters on temperature and pressure by the least square method resulted in the following coordinates for the tricritical point: $T_t = 109.8 \pm 0.2 \text{ K}$ and $P_t = 2640 \pm 40 \text{ bar}$. The coefficient of thermal expansion and compressibility were determined by numerical differentiation of the curves $l(T)$ and $l(P)$, respectively. The temperature dependence of the coefficient of thermal expansion is shown in Fig. 2 for two values of pressure, 2621 and 4460 bar.

As was pointed above, when analyzing the experimental data within the framework of the Landau theory, coefficients A and B in the expansion (Eq. (1)) must be

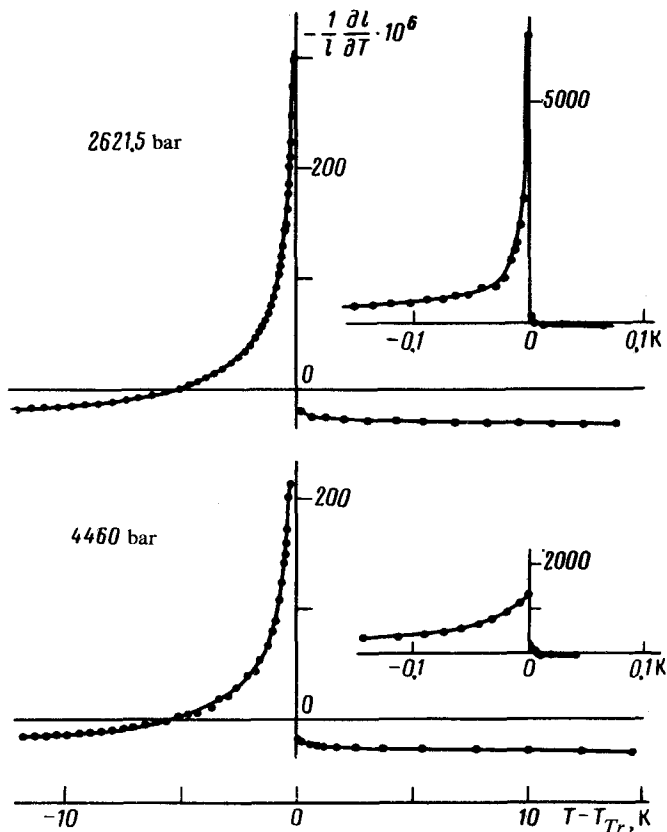


FIG. 2. Temperature dependence of the coefficient of linear expansion $\frac{1}{l} \frac{\partial l}{\partial T}$ near the tricritical point (a) and near phase transition of the second kind (b).

taken to be functions of temperature and pressure. If we limit our consideration in the neighborhood of the tricritical point to the first terms of the expansion of the corresponding functions, we get: $A(T, P) \approx a_1(T - T_t) + a_2(P - P_t)$ and $B(T, P) \approx b_1(T - T_t) + b_2(P - P_t)$. In this case, as shown in Ref. 5, changes in the derivative $(\partial l / \partial T)_P \equiv \kappa$ near the transition may be expressed as follows:

$$\kappa - \kappa_{\text{reg}} = \kappa_0 + \kappa_1 |\tau|^{-\alpha} + \kappa_2 |\tau|^{0.5}, \quad (2)$$

where $\tau = (T - T_{Tr}) / T_{Tr}$, κ_0 , κ_1 , κ_2 are constants, κ_{reg} is the regular part, T_{Tr} is the transition temperature corresponding to the tricritical temperature T_t , $\alpha = 0.5$.¹⁾ A similar expression may also be written for the derivative $(\partial l / \partial P)_T$.

To statistically process the copious experimental data for the derivatives $(\partial l / \partial T)_P$ and $(\partial l / \partial P)_T$ we used the maximum probability method;^(7,8) the dispersion resulting from a single measurement was estimated in accordance with the rules of error propagation⁽⁷⁾ on the basis of the aforementioned values for the accuracy in measuring elongation and the stability of temperature and pressure. The residual value of the probability function served as an adequacy criterion.

The search for the "most probable" values of κ_0 , κ_1 , κ_2 , α and T_{Tr} to fit an

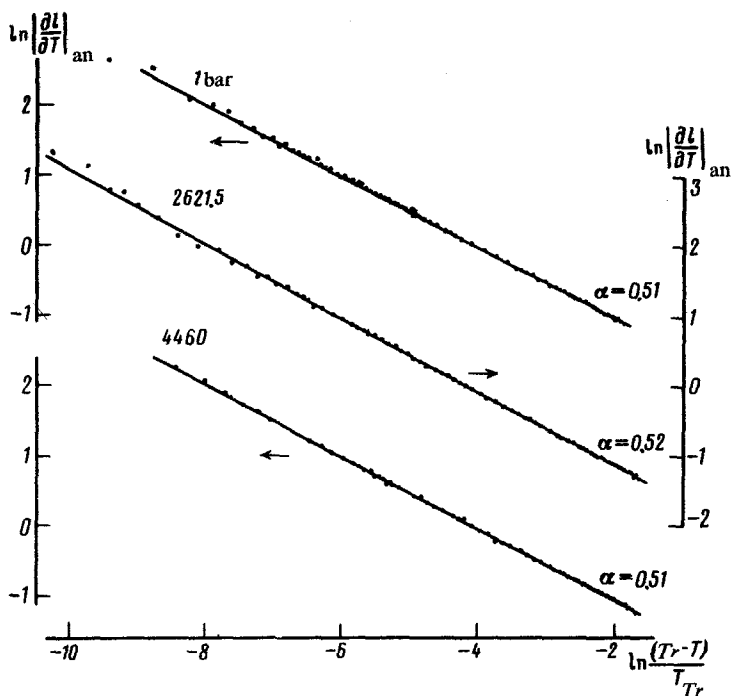


FIG. 3. Temperature dependence of the anomalous portion of the derivative $\left(\frac{\partial l}{\partial T}\right)_{an} \equiv \kappa \tau^{-\alpha}$ at three values of pressure (the solid lines are constructed from parameters evaluated in Eq. (2) by means of the maximum probability method).

expression of the form of Eq. (2), which corresponds to the 2621.5-bar isobar, showed that this expression describes the experimental data sufficiently, and yielded the values $\alpha = 0.52 \pm 0.02$ and $T_{Tr} = 109.845 \pm 0.006$ K at the 95% probability level (τ varied in the range $5 \times 10^{-5} - 0.15$). The experimentally determined value of the transition temperature is 109.8452 ± 0.0002 K. Processing the compressibility data yielded $\alpha = 0.504 \pm 0.03$.

We note that Eq. (2) should be useful for describing the behavior of the corresponding derivatives also at transition coordinates T_{Tr} and P_{Tr} that substantially differ from coordinates of the tricritical point, providing that for the transition temperature value in Eq. (2) is substituted some dispersion temperature T_{Tr}^+ which is slightly higher than the transition temperature. The analysis of data obtained at both atmospheric pressure and 4460 bar showed that Eq. (2) indeed may sufficiently describe the experimental functions $(\partial l / \partial T)_p$ at the 95% probability level, both in the region of phase transition of the first kind and in the region of transition of the second kind. Moreover, $\alpha = 0.51 \pm 0.02$, and a difference between T_{Tr}^+ and T_{Tr} was ~ 0.015 K. The temperature dependence of the singular part of the derivative $(\partial l / \partial T)_p$ is shown in Fig. 3 in a double logarithmic scale.

Thus, in this work we have reliably established the existence of a tricritical point with coordinates $T_c = 109.8 \pm 0.2$ K and $P_c = 2640 \pm 40$ bar on the phase transition

curve in KDP. The special features that characterize the behavior of thermodynamic quantities in the ferrophase near the phase transition in KDP are well described by the Landau theory, providing the coefficient B in the expansion (Eq. (1)) is assumed to be a function of pressure and temperature, a fact that necessarily follows from the very existence of the tricritical point in the KDP phase diagram.

¹We note that provision for the fluctuation corrections⁽⁹⁾ on account of the uniaxiality of KDP and the presence of the piezoeffect in the paraphase therein fails to alter the form of Eq. (2).

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Potassium dihydrogen phosphate and its isomorphs are representative of hydrogen-bonded materials that possess important piezoelectric, ferroelectric, electrooptic, and nonlinear optical properties. Since the first report of the ferroelectric properties of KDP by Bush and Scherrer in 1935, numerous studies on their electrical and optical properties have been reported. They have attracted the interests of many theoretical and experimental researchers, probably because of their comparatively simple structure and very fascinating properties associated with a hydrogen bond system involving a large ...^Â The very first materials to be used and exploited for their nonlinear optical and electro-optical properties were KDP and ADP. At increasing quantities of an entered carbonate of the sodium, the formed salt sodium dihydrophosphate, transmuted in sodium hydrophosphate on reaction: $\text{NaH}_2\text{PO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{HPO}_4 + \text{NaH}_2\text{PO}_4 + \text{CO}_2 + \text{H}_2\text{O}$ Regulating the ratio $\text{Na}_2\text{O} : \text{P}_2\text{O}_5$ it is possible to achieve the necessary maintenance mono- and disodiumphosphate in a solution. However, the obtained mixture of sodium orthophosphate contains 0,50-0,64% of magnesium oxide, which in final total reduces quality of sodium polyphosphate. KDP) KTiOPO_4 (Potassium titanyl phosphate, KTP) $\text{NH}_4\text{H}_2\text{PO}_4$ (Ammonium dihydrogen phosphate, ADP) RbTiOPO_4 (Rubidium titanyl phosphate, RTP) Pb (Lead) Pd (Palladium) Pr (Praseodymium) Pt (Platinum) Rb (Rubidium) Re (Rhenium) Rh (Rhodium) Ru (Ruthenium) Ag_3AsS_3 (Silver arsenic sulfide) AgGaS_2 (Silver gallium sulfide, AGS) As_2S_3 (Arsenic trisulfide) CS_2 (Carbon disulfide) CdS .^Â Optical constants of KH_2PO_4 (Potassium dihydrogen phosphate, KDP) Zernike et al. 1964: $n(o)$ 0.214-1.53 $\text{Å}\mu\text{m}$. Wavelength: $\text{Å}\mu\text{m}$.