

CRITICAL PHENOMENA IN $\text{Sn}_2\text{P}_2\text{S}_6$ FERROELECTRIC CRYSTALS UNDER HIGH PRESSURE

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It has been investigated volume compressibility in $\text{Sn}_2\text{P}_2\text{S}_6$ ferroelectric crystals in the vicinity of Lifshitz point, induced by an external pressure. It has been analysed for pressure behaviour of compressibility's critical index as well as the coefficients values were defined in the expansion of thermodynamical potential density in term of the order parameter and their change along the p,T-diagram.

An investigation of structure phase transitions (PT) in solids as one of the most general phenomena is still in progress as one of the most active fields for solid state physics. The external pressures are of importance in these studies. This is due to that pressure is the best and often the only external parameter whereby we can change balance of competitive interactions in solid and consequently a thermodynamical potential of system.

By means of external pressure we can induce both new phases of substance and high-order polycritical points on their phase diagrams. In this connection particular attention is given to $\text{Sn}_2\text{P}_2\text{S}_6$ type crystals and solid solutions on their basis, where under uniform compression appears an incommensurate modulated structure and on phase p,T-diagram realizes a new polycritical point, splitting commensurate and incommensurate phase transitions. From the above papers [1] it was established that in $\text{Sn}_2\text{P}_2\text{S}_6$ proper ferroelectric at $p=p_{\text{atm}}$ and temperature $T_0=337\text{K}$ a continuous PT in nonpolar phase with change of symmetry from P_c to $P_{21/c}$ takes place. With increase in pressure simultaneously with decreasing of PT temperature at $p \cong 0.18\text{GPa}$ occurs PT line splitting $T_0(p)$ on second-order PT line $T_i(p)$ and first-order PT line $T_c(p)$ bounding incommensurate phase region in p,T- space.

For the purpose of further investigation these phenomena character in the above ferroelectrics we have made pressure behaviour studies for compressibility of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals in PT region along to p,T - diagram.

A relative change for crystal volume under uniform compression can be obtained by summation of linear deformations in three

mutually arrangement of perpendicular directions. By means of optical interference technique [2] we have investigated the $\Delta l_i/l_i$ a linear deformations of $\text{Sn}_2\text{P}_2\text{S}_6$ crystal as the external pressure increases. In this case the lines of measurements inquiry where mutually perpendicular. Two of them coincided with crystallographic directions [100] and [010], and the third was perpendicular to them. A relative change of volume one can represented

$$\frac{\Delta V}{V} = \frac{\Delta l_1}{l_1} + \frac{\Delta l_2}{l_2} + \frac{\Delta l_3}{l_3} + \frac{\Delta l_1 \Delta l_2 \Delta l_3}{l_1 l_2 l_3} \quad (1)$$

Since a relative linear deformation value for solids is sufficiently small (in proportion to 10^{-3}), we can neglect a last term in (1) (its value is proportional to 10^{-9}). Thus a relative volume change was defined by sum of three linear deformations.

In Fig.1 is shown (curve 1) the pressure dependence for a relative volume change of $\text{Sn}_2\text{P}_2\text{S}_6$ crystal obtained at temperature 296K. Under pressure $p_0=0.18\text{GPa}$ on this plot a sharply defined anomaly occurs, which is due to PT in paraelectric phase.

Through differentiation plot $\Delta V/V(p)$ over pressure was obtained the pressure dependence for volume compressibility

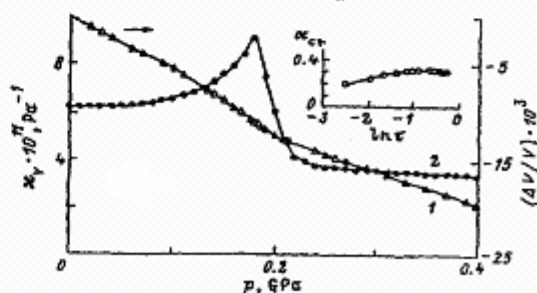


Fig.1 The pressure dependences of $\Delta V/V$ value(1) and volume compressibility $\chi_V(p)$ $\text{Sn}_2\text{P}_2\text{S}_6$ crystal at $T=256\text{K}$. (In insert - the pressure dependences of critical index of compressibility α_{cr}).

$\chi_V = - \frac{1}{\Delta p} \frac{\Delta V}{V}$ (curve 2 on Fig.1). The differentiation was performed in the following way: through every five points conducted a curve approximated by method of least squares, and in a middle point was derivative.

Taking into account that the PT observed under pressure $p_0=0.18\text{GPa}$ and temperature $T=296\text{K}$ is close to polycritical point [1,3], whose character is variously interpreted in the literature [1,3,4], we consider in some detail of pressure behaviour analysis χ_V with the aim to define critical index and coefficients in thermodynamic potential expansion.

The $\chi_V^{an}(p) = \chi_V(p) - \chi_V^{reg}(p)$ anomalous part of compressibility is proportional to $(p-p_0)^{-\alpha_{cr}}$ value, where α_{cr} - a critical index of compressibility (heat capacity and temperature expansion coefficient). Experimentally the $p > p_0$ regular part of compressibility $\chi_V^{reg}(p)$ is linearly decreased with increasing an external pressure in paraelectric phase. In order to define the α_{cr} critical index was plotted $\ln \chi_V^{an}(p)$ from $\ln(p-p_0)$ dependence for pressure range $p < p_0$, determining a ferroelectric phase.

The dependence α_{cr} vs $\ln \tau$ is shown in the insert of Fig.1 (where $\tau = (p_0 - p)/p_0$), characterizing an anomalous trend of volume compressibility for $\text{Sn}_2\text{P}_2\text{S}_6$ crystal in the vicinity of PT. For $-2 < \ln \tau < 0$ the α_{cr} value agrees closely with 0.3 ± 0.03 value, which is characteristic of Lifshitz point [5]. With further the τ ($\ln \tau < -2$) decrease the α_{cr} value is monotone reduced to 0.2 value. Such behaviour α_{cr} seems due to the change-over from polycritical to critical behaviour.

PT in proper $\text{Sn}_2\text{P}_2\text{S}_6$ ferroelectric in liquid-typed crystal model approximation an one-dimensional modulation for incommensurate phase may be describe through expansion density of thermodynamical potential Φ by power series order parameter $\eta = P_s$ (P_s - spontaneous polarization) with regard to space derivatives [6]

$$\Phi = \Phi_0 + \frac{\alpha}{2} \eta^2 + \frac{\beta}{4} \eta^4 + \frac{\gamma}{6} \eta^6 +$$

$$+ \frac{\delta}{2} \left(\frac{d\eta}{dz} \right)^2 + \frac{q}{2} \left(\frac{d^2\eta}{dz^2} \right)^2, \quad (2)$$

where $\alpha = \alpha_0 (T - T_0)$, β, γ, δ and q being expansion coefficients, which in general case are an external pressure dependent. At PT ($T = T_0$) $\alpha = 0$, and $\alpha_0 = 1/\varepsilon_0 C_W$, where C_W - Curie-Weiss constant.

For second-order PT through the $\Delta \chi_V$ jump compressibility and the known α_0 and dT_0/dp values, making use of a common relation

$$\Delta \chi_V = \frac{\alpha_0}{2\beta} \left(\frac{dT_0}{dp} \right)^2, \quad (3)$$

we may define the β -coefficient in thermodynamical potential expansion. The $\Delta \chi_V$ jump value was obtained by the χ_V^{-2} vs $p_0 - p$ extrapolation dependence to $p = p_0$. It was found in such way the $\Delta \chi_V$ value at PT amounted to $5.67 \cdot 10^{-11} \text{Pa}^{-1}$. For $\text{Sn}_2\text{P}_2\text{S}_6$ crystal at $p = 0.18 \text{GPa}$ Curie-Weiss constant $C_W = 0.642 \cdot 10^5 \text{K}$, and coefficient $dT_0/dp = -220 \text{K/GPa}$. Substituting these data in [3], we have $\beta = 13.2 \cdot 10^8 \text{J} \cdot \text{m}^5 / \text{Cl}^2$.

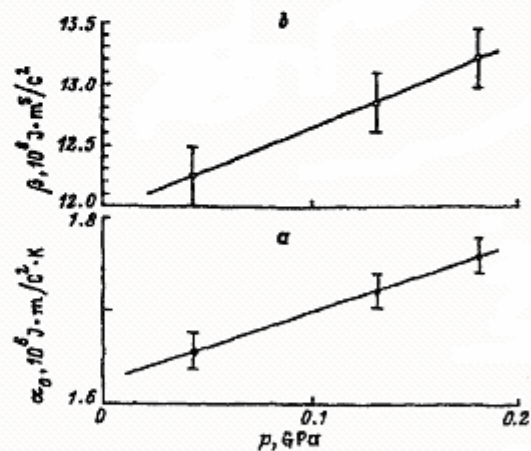


Fig.2 The pressure dependences the α_0 (a) and β coefficient (b) in expansion of thermodynamical potential density along the phase p, T -diagram for $\text{Sn}_2\text{P}_2\text{S}_6$ crystal.

The similar investigations and pressure behaviour of isothermal volume compressibility $\chi_V(p)$ were conducted as well as for other temperatures in range $T > 296\text{K}$.

The obtained results in conjunction with the above findings of investigations into dielectric properties of $Sr_2P_2S_6$ crystals under high pressures [1,3] allowed to study a pressure behaviour of α_0 and β coefficients in expansion for thermodynamical potential density along the phase p,T-diagram in the line of $T_0(p)$. The findings of investigation are given in Fig.2, where is seen that as we approach to polycritical point ($p_0 \approx 0,18$ GPa)

along the phase diagram the α_0 and β coefficients increase occurs, i.e. a splitting $T_0(p)$ line takes place with positive value β . As this takes place the δ coefficient vanishing. Hence it follows from isothermal volume compressibility along the phase p,T-diagram that with increase in pressure PT for $Sr_2P_2S_6$ crystal drifts apart from a tricritical point ($\beta=0$), which evidently exists in negative pressures range, approaching to Lifshitz point ($\beta>0, \delta=0$).

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КРИТИЧНА ПОВЕДІНКА ОБ'ЄМНОЇ СТИСЛИВОСТІ СЕГНЕТОЕЛЕКТРИЧНИХ КРИСТАЛЛІВ $Sr_2P_2S_6$

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Досліджено поведінку об'ємної стисливості кристалів $Sr_2P_2S_6$ в околі точки Ліфшиця індукованої високим тиском. Проаналізовано баричну поведінку критичних індексів об'ємної стисливості і коефіцієнтів розкладу термодинамічного потенціалу по параметру порядку вздовж фазової p,T-діаграми.