

# THE MEAN-FIELD ANALYSIS OF $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$ THERMODYNAMICAL PROPERTIES IN THE PARAELECTRIC, INCOMMENSURATE AND FERROELECTRIC PHASES

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In the mean-field approximation, assuming the linear concentration dependence of the thermodynamic potential coefficients and taking into account the higher harmonics of spatial order parameter modulation in the incommensurate phase and interaction between order parameter and elastic deformation, the temperature and concentrational dependencies of the principal thermodynamical characteristics of  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$  uniaxial ferroelectrics are calculated and compared with the experimental data. Some discrepancy exists at the quantitative comparison of calculated and experimental data for the temperature dependencies of heat capacity, amplitude and wave vector of modulation, essentially in the vicinity of the lock-in phase transition in incommensurate phase.

**Key words:** phase transitions, incommensurate phase, uniaxial ferroelectrics, thermodynamic properties.

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## I. INTRODUCTION

When describing the anomalies in the physical properties of the crystal in the vicinity of the structural phase transitions (PT) one has to take into account the interaction of the order parameter fluctuations with different spatial nonuniformity scale as well as their relation to the other degrees of freedom of the crystalline lattice, in particular, with elastic deformations. These aspects are also essential when analyzing the anomalies of the thermodynamical functions at the phase transitions which restrict the incommensurate (IC) phases. Up to date one has only to understand the peculiarities of the critical behaviour of improper  $\text{K}_2\text{SeO}_4$  like ferroelectrics with the IC phase (of the I type according to classification [1]). Here the anomalies of the properties in the vicinity of the PT from the paraelectric to the IC phase ( $T_i$ ) obey, in general, three-dimensional Heisenberg model with the double component order parameter (the  $3d\ xy$  model) [2]. In this case the transition from the IC phase to the ferroelectric phase ( $T_c$ ) called the “lock-in” transition as well as the evolution of the properties at the temperature decrease in the IC phase are satisfactorily described with the allowance made for the higher harmonics of the order parameter modulation in terms of the suggestion about the sine polarization wave transformation into the domain-like structure (the solution lattice) [3]. For the proper  $\text{NaNO}_2$  like ferroelectrics with the II type IC phase [1], one may also expect to describe the critical behaviour of the properties in the vicinity of  $T_i$  within the framework of the  $3d\ xy$  universality class [2]. However, the origin of the lock-in transition remains here unclassified [4]. The elucidation of the role of the higher harmonics of the order parameter modulation at the low-temperature boundary of the IC phase and the

description of quite distinct first order PT at  $T_c$  remain problematic. Here one has to consider not only the interaction of the order parameter with elastic deformations [4] but also the contribution to the energy of the system of interactions resulting from the presence of thermal fluctuations of domain walls (the van der Waals type interaction) [5].

The  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{Se}_{1-x})_6$  crystals are the uniaxial ferroelectrics. Their temperature-concentration diagram passes at  $x_{LP} \approx 0.28$  the Lifshitz point (LP) and the type II IC phase occurs at  $x > x_{LP}$  (Fig. 1) [6]. The critical behaviour of such a type of crystals has been analyzed theoretically [7], [8]. The experimental data on the properties of the  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{Se}_{1-x})_6$  crystals are compared with the predictions of theory in [9]–[11]. However, both the origin of the lock-in transition in  $\text{Sn}_2\text{P}_2\text{Se}_6$  and the concentrational variation of the properties in the IC phase and along the  $T_c(x)$  line under the variation of the concentration of the mixed  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{Se}_{1-x})_6$  crystals to the Lifshitz point call for further clarification.

In the present paper, phenomenological analysis of the properties of  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{Se}_{1-x})_6$  crystals has been performed with allowance made for the higher harmonics of the order parameter spatial modulation and the influence of long-range elastic forces.

## II. TRANSITION FROM PARAELECTRIC TO FERROELECTRIC PHASE. $\text{Sn}_2\text{P}_2\text{S}_6$ CRYSTAL

It is known that the tin thiohypodiphosphate ( $\text{Sn}_2\text{P}_2\text{S}_6$ ) undergoes at  $T_0 \approx 337$  K the structural second order PT [6]. The paraelectric phase symmetry  $\text{P2}_1/\text{c}$  decreases in this case to the  $\text{Pc}$  subgroup in the low-temperature ferroelectric phase. The spontaneous polar-

ization vector  $P_s$  lies in the symmetry plane close to the [100] direction and is mainly due to the displacement of the Sn atoms from the centrally symmetric positions by  $0.26\text{\AA}$ . One may conclude the following on the basis of the mentioned above: the  $\text{Sn}_2\text{P}_2\text{S}_6$  crystal is a proper uniaxial ferroelectric with the single-component order parameter ( $P_s \equiv P_x$ ).

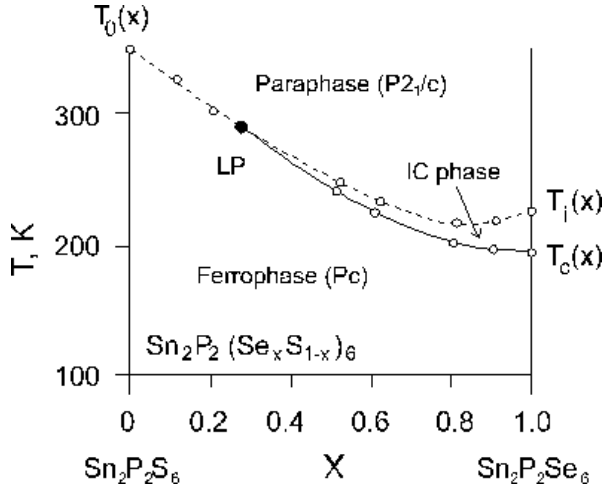


Fig. 1. Temperature-concentrational phase diagram for the  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$  system. LP—Lifshitz point; broken line—second order phase transitions; solid line—first order phase transitions.

Recall that the symmetry aspect is the central one when analyzing the PT in terms of Landau theory. This allows one to construct the thermodynamical potential in the form of the expansion into a power series in the order parameter. The further procedure is known as the thermodynamical potential method [12] where the differentiation of the state function  $F(P, T, x)$  over the independent variables gives the expressions for the observed physical parameters.

For the  $\text{Sn}_2\text{P}_2\text{S}_6$  crystal we shall write the thermodynamical potential density as:

$$\varphi = \varphi_0 + \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \frac{\gamma}{6}P^6, \quad (1)$$

where, as usual, the coefficient  $\alpha = a(T - T_0) \equiv at$  ( $t = (T - T_0)$ ,  $a = (\partial\alpha/\partial T)$  is related to the Curie-Weiss constant). To achieve the second-order PT, the coefficient  $\beta$  has to be positive. The last term in (1) with the coefficient  $\gamma > 0$  is satisfied if the system, similarly to  $\text{Sn}_2\text{P}_2\text{S}_6$  is close to the triple point (in that case the coefficient  $\beta$  is much less than its atomic value,  $\beta \ll \beta at$ ).

From the minimum condition

$$\frac{\partial\varphi}{\partial P} = 0, \quad \frac{\partial^2\varphi}{\partial P^2} > 0 \quad (2)$$

we find out the equilibrium value of the order parameter in the ferroelectric phase:

$$P_0^2 = \frac{\beta}{2\gamma} \left( \sqrt{1 - 4At} - 1 \right), \quad \text{where } A = \frac{\gamma a}{\beta^2}. \quad (3)$$

Substituting (3) into (1) we obtain the expression for the energy of the ferroelectric phase:

$$\varphi_f = \varphi_0 - \frac{\beta^3}{24\gamma^2} \left[ (1 - 4At)^{3/2} - 6At - 1 \right]. \quad (4)$$

Here  $\varphi_0$  is the value of the energy for the paraelectric phase. The isobaric heat capacity in the ferroelectric phase is

$$C_P^{E=0} = -T \left( \frac{\partial^2\varphi}{\partial T^2} \right)_P^E = C_{P,0}^E + \frac{a^2}{2\beta} \cdot \frac{T}{\sqrt{1 - 4At}}. \quad (5)$$

Here  $C_{p,0}$  is the value of the heat capacity in the paraelectric phase.

The equation of state in the presence of constant electric field  $E$  has the following form:  $E = (\partial\varphi/\partial P)$ .

Hence, we find routinely the expression for the dielectric susceptibility:

$$\left( \frac{\partial^2\varphi}{\partial P^2} \right)_{p,T}^{E=0} = \chi^{-1} = at + 3\beta P^2 + 5\gamma P^4. \quad (6)$$

Taking into account that in the paraelectric phase the order parameter is  $P = 0$ , while in the ferroelectric phase it is equal to the equilibrium value (3), we have:

$$\chi^{-1} = \begin{cases} at & , T > T_0 \\ \frac{\beta^2}{\gamma} (1 - \sqrt{1 - 4At} - 4At) & , T < T_0 \end{cases}. \quad (7)$$

The temperature dependence of the pyroelectric coefficient in the ferroelectric phase is found as:

$$\begin{aligned} \gamma_i^p &= - \left( \frac{\partial^2\varphi}{\partial E_i \partial T} \right)_p = - \left( \frac{\partial P_0}{\partial T} \right)_p \\ &= \frac{\sqrt{2}}{2} \cdot \frac{\alpha T \gamma^{1/2}}{\beta^{3/2}} \cdot \left[ (1 - 4At)^{3/2} + 4At - 1 \right]^{-1}. \end{aligned} \quad (8)$$

The occurrence of the polarization vector  $P$  in the ferroelectric phase is accompanied by the deformation  $u_{ij}$  of the crystalline lattice. This, in turn, results in the rise of a leap in the temperature dependence of the elastic module  $c_{ijkl}$  at the PT point. To make this sure, let us consider again the expansion (1) with adding that part of free energy which is responsible for the elastic degrees of freedom, namely:

$$\varphi_{el} = \frac{1}{2}cu^2 + ruP^2. \quad (9)$$

Here  $c = c_{ijkl}$  is the elastic module matrix,  $u \equiv u_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$  is the deformation tensor,  $r = r_{ijkl}$  is the electrostriction coefficient. The equilibrium condition (2) is supplemented by the expression for the elastic modulus:

$$c = \left( \frac{\partial^2 \varphi}{\partial u^2} \right) = c^0 - \frac{2r^2}{\beta} (1 - 4At)^{-1}. \quad (10)$$

where  $c$  is the elastic modulus value for the paraelectric phase.

### III. PHASE TRANSITIONS SEQUENCES : PARAELECTRIC-INCOMMENSURATE- FERROELECTRIC PHASE. $\text{Sn}_2\text{P}_2\text{Se}_6$ CRYSTAL

In the  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystal, the transition to the paraelectric phase is preceded by the second-order PT to the IC phase at  $T_i \approx 221$  K [6]. The temperature interval of the existence of the IC phase is near 28 K. The modulation wave-vector  $\mathbf{k}$  lies in the symmetry plane of the crystal normally to the [010] axis. The modulation period is 12–14 cells of the initial structure [17]. With temperature decrease the vector  $\mathbf{k}$  decreases smoothly (Fig. 2) and at the point  $T_c \approx 193$  K assumes abruptly the zero value: here the first order lock-in transition to the commensurate ferroelectric state occurs. The symmetry of the paraelectric phase  $P2_1/c$  is reduced to the  $Pc$  subgroup in the ferroelectric phase [6].

To describe the PT restricting the IC phase, the expansion of the thermodynamical potential (1) should be complemented by the gradient terms  $\sim \frac{\partial P_i}{\partial x_j}$ . Here one may distinguish two cases: 1) the symmetry of the system allows one to construct the Lifshitz invariant of the  $\sim \left( \frac{\partial P_i}{\partial x_j} - \frac{\partial P_j}{\partial x_i} \right)$  type using the spatial derivatives, and such IC transition are assigned to the type I (according to classification [1]). The PT restricting the IC phase in those crystals whose initial paraelectric phase symmetry forbids the existence of the Lifshitz invariant are classified among the type II transitions.

Since the  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystal is a proper uniaxial ferroelectric, the PT to the IC phase should be considered as the type II PT, similarly to the situation in the  $\text{NaNO}_2$  crystal. In that case the thermodynamical potential for  $\text{Sn}_2\text{P}_2\text{Se}_6$  is expressed in the following form [4]

$$\begin{aligned} F &= \int \varphi dV, \\ \varphi &= \varphi_0 + \frac{\alpha}{2} P^2 + \frac{\beta}{4} P^4 + \frac{\gamma}{6} P^6 + \frac{\delta}{2} (P')^2 \\ &\quad + \frac{\lambda}{2} (P'')^2 + \frac{\eta}{2} (P')^2 P^2. \end{aligned} \quad (11)$$

Again  $\alpha \equiv at$ . Here  $P'$  are the spatial derivatives. The coefficients  $\lambda$  and  $\eta$  are positive,  $\delta < 0$  and this describes

the presence of the IC phase [4], [6]. Now one has to consider  $\beta < 0$  in the uniform part of the expansion (1), since in the absence of the IC phase the PT to the ferroelectric phase would be the first order PT [9]. The last term in (11) is of the same order of smallness as the other gradient terms. The inclusion of this term is important when describing the temperature dependence of the wave-vector in the IC phase and the behaviour of the physical properties at the lock-in transition [4].

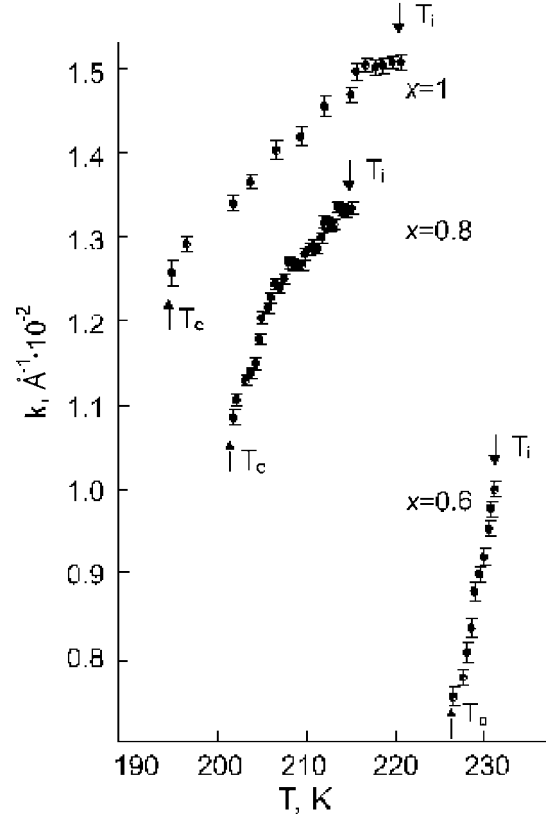


Fig. 2. The temperature dependencies of wave vector modulation in the incommensurate phase for the  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$  crystals [19].

The Euler-Lagrange equation of motion for the order parameter in the IC phase has the following form:

$$\begin{aligned} \lambda P^{IV} - \delta P^{II} - \eta \left[ P^2 P^{II} + P (P^I)^2 \right] \\ + \alpha P + \beta P^3 + \gamma P^5 = 0. \end{aligned} \quad (12)$$

The general solution of such equation is quite problematic, however, the partial solutions are known [13] which indicates that among the variety of solutions the soliton ones (the domain-wall type) exist too.

Indeed, one can show that the single-periodic solution of the first modified Corteweg-de Vries equation [13]:

$$P^{III} - 6AP^2P^I + BP^I = 0, \quad (13)$$

which has the form of a soliton lattice  $P \approx \text{sh}(z)$ , equation (12) at the proper choice of constants  $A, B$  and the second integral  $C$ . The constants  $A, B, C$  in this case are expressed via the coefficients of the thermodynamical potential as follows [13]:

$$\begin{aligned} A &= \frac{\eta}{\lambda} \pm \sqrt{\left(\frac{\eta}{\lambda}\right)^2 - 32\frac{\gamma}{3\lambda}}, \\ B &= \frac{\left(\frac{\beta}{\lambda} - \frac{2A\delta}{\lambda}\right)}{\left(20A - \frac{2\eta}{\lambda}\right)}, \\ C &= \frac{\left(\frac{\alpha}{\lambda} + \left(B + \frac{\beta}{\lambda}\right)B\right)}{\left(\frac{\eta}{\lambda} - 12A\right)}. \end{aligned} \quad (14)$$

The exact solutions of equation (12) have been found in [14] for certain cases, however, the transition from the IC phase to the ferroelectric phase appears to be the continuous one which contradicts the available experimental data (in particular, those for  $\text{Sn}_2\text{P}_2\text{Se}_6$ ) stating that a distinct first-order transition must occur in this case [6].

The above mentioned cases, when the solution for the order parameter in the form of a soliton lattice can be

obtained imply the compressed crystal and do not allow for the elastic degrees of freedom. When performing the experiment, as a rule, the free crystal is under operation, i.e. one has to take into account the elastic degrees of freedom. When describing the properties of the IC phase the allowance made for these degrees of freedom is even more necessary since the spatially non-uniform polarization distribution results in the occurrence of the spatially non-uniform deformation. As is known [4], an energy “gap” due to the long-range elastic forces arises between the states with the uniform and non-uniform deformations.

When solving (12) with the allowance made for the elastic degrees of freedom we might expect to obtain the first-order lock-in transition, since the long-range elastic forces, as will be shown below, affect “dominantly” the evolution of the sine distribution of the order parameter in the mode of soliton or domain-like distribution.

Further we shall follow the way of the authors of. Ref. [4] to describe the PT in  $\text{NaNO}_2$ . Let us take the one-harmonical (sinusoidal) approximation as the basis for this consideration. Then we shall take into account the first by order “higher” harmonics and define the importance of their inclusion in describing the temperature behaviour of physical properties of the IC phase. And, finally, we shall try to define the influence of long-range elastic forces on the lock-in transition.

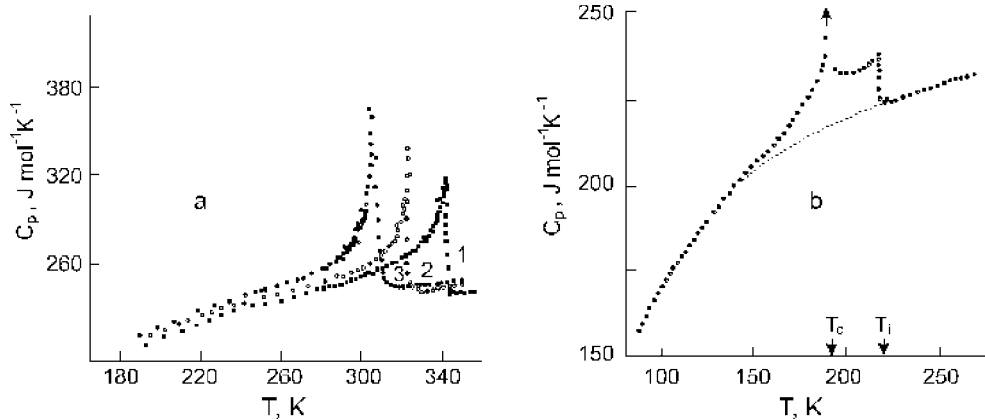


Fig. 3. The heat capacity temperature dependencies for the  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$  crystals. a —  $x=0$  (1);  $x=0.1$  (2);  $x=0.2$  (3). b —  $x=1$  [9].

When considering the ferroelectric phase in (11) the gradient terms may be omitted and we shall analyze only the uniform part of the expansion in the following form:

$$\varphi = \varphi_0 + \frac{1}{2}atP^2 + \frac{1}{4}B_0P^4 + \frac{1}{6}\gamma P^6. \quad (15)$$

Here  $\varphi_0$  is the paraelectric phase energy,  $B_0 = \beta - 4K$  is the coefficient  $\beta$  renormalized by the uniform deformation (note that for  $\text{Sn}_2\text{P}_2\text{Se}_6$   $B_0 < 0$ , i.e. in the absence of the IC phase the immediate transition from the paraelec-

tric phase to the ferroelectric one becomes the first-order transition. [9]).

Minimizing (15) over  $P$ , we find the expression for the order parameter:

$$P^2 = -\frac{B_0}{2\gamma} \left(1 + \sqrt{1 - 4At}\right), \quad \text{where } A \equiv \frac{a\gamma}{B_0^2}. \quad (16)$$

Inserting (16) into (15) gives the energy of the ferroelectric phase:

$$\varphi_f = \varphi_0 + \frac{B_0^3}{24\gamma^2} \left[ (1 - 4At)^{3/2} - 6At + 1 \right]. \quad (17) \quad \text{as :}$$

The reciprocal of the dielectric susceptibility is:

$$\chi^{-1} = \frac{B_0^2}{\gamma} \left[ (1 - 4At)^{1/2} - 4At + 1 \right]. \quad (18)$$

The isobaric heat capacity is described by the relation:

$$\Delta C_p^E = \frac{a^2}{2B_0} \cdot \frac{T}{\sqrt{1 - 4At}}. \quad (19)$$

In the paraelectric phase, the order parameter is zero,  $P = 0$ , and the energy is  $\varphi_0$ , while the heat capacity is  $C_{p,0}^E = -T \left( \frac{\partial^2 \varphi}{\partial T^2} \right)_E$  in the presence of the electric field. The equation of state has the following form for the paraelectric phase:

$$atP_0 = E, \quad (20)$$

where  $P_0$  is the polarization induced by the field  $E$ . Then the reciprocal of the dielectric susceptibility, of the paraelectric phase is:

$$\chi^{-1} = \left( \frac{\partial E}{\partial P_0} \right)_{E \rightarrow 0} = at. \quad (21)$$

### A. Incommensurate phase. An one-harmonical approximation

The occurrence of the spatially non-uniform distribution of polarization in the modulated IC phase results in the appearance of the non-uniform deformation. Taking into account the elastic degrees of freedom in the form of addend (9) to the expansion (11) of the thermodynamical potential in the deformation tensor  $u_{ij}$ , we shall distinguish the uniform part  $u_{ij}^0$ :

$$u_{ij} = u_{ij}^0 + \sum_{k=0} ik_j u_i(k) e^{i\mathbf{k}_j \mathbf{r}}. \quad (22)$$

Here  $u_i(k)$  is the Fourier-component of the displacement component  $u_i$ . Minimizing expression (9) separately over the uniform and non-uniform deformation, we obtain [15].

$$F_{ee} = \int \varphi_{ee} dV = -K \sum_k P_k^2 P_{-k}^2 - \sum_{k \neq 0} \tilde{K} P_{k^i} P_{-k^i - k} P_{-k^i i} P_{k^i i + k}. \quad (23)$$

Coefficients  $K$  and  $\tilde{K}$  in the isotropic case are written

$$K = \frac{r^2}{2\alpha}, \quad \tilde{K} = \frac{r^2}{2(\chi + \frac{4}{3}\mu)}, \quad (24)$$

where  $r = r_{ijjj}$  are, the electrostriction coefficients,  $\chi$  and  $\mu$  are the bulk and shear elastic module, respectively.

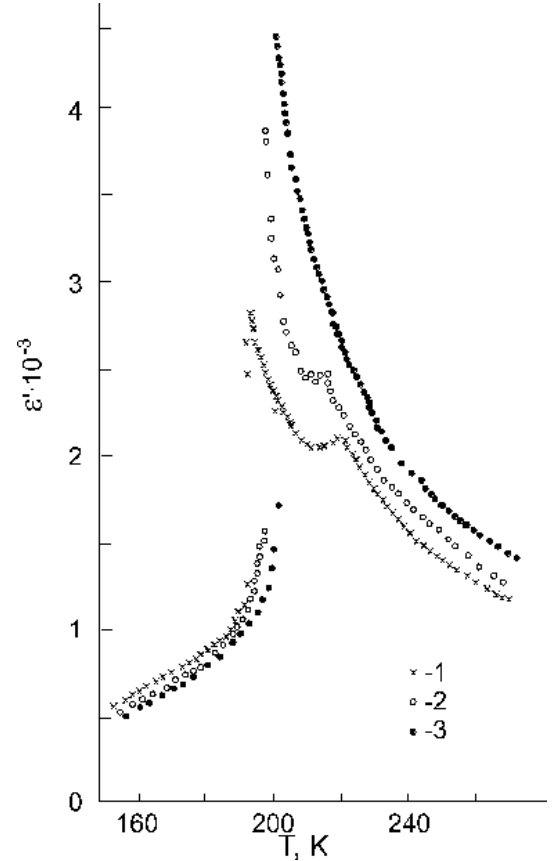


Fig. 4. The dielectric constant temperature dependencies for  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$  crystals.  $x=1$  — (1);  $x=0.9$  — (2);  $x=0.8$  — (3) [9].

For the IC phase the thermodynamical potential (11) with the allowance made for the elastic degrees of freedom (23) in the one-harmonical approximation has the following form:

$$\varphi_{IC} = \alpha(k) P_k P_{-k} + \frac{3}{2} B_1 P_k^2 P_{-k}^2 + \frac{10}{3} \gamma P_{-k}^3 P_k^3. \quad (25)$$

Here:

$$\alpha(k) = \alpha + \delta k^2 + \lambda k^4, \quad (26)$$

$$B_1 = B_0 + \Delta + \frac{2}{3} \eta k^2, \quad (27)$$

$$B_0 = \beta - 4K, \quad \Delta = \frac{4}{3} (K - \tilde{K}). \quad (28)$$

$\Delta$  is an energy “gap” defined by the long range elastic forces [4, 15].

From the condition  $\frac{\partial \alpha(k)}{\partial k} = 0$  the temperature  $T_i$  at the transition to the IC phase is found as:

$$T_i = T_0 + \frac{\delta}{4\lambda a}, \quad (29)$$

and the modulation wave-vector at the point  $T_i$  is:

$$k_i = -\frac{\delta}{2\lambda}. \quad (30)$$

Below  $T_i$  the vector  $\mathbf{k}$  has the temperature dependence derived from the condition of minimum:

$$\frac{\partial \varphi_{IC}}{\partial k} = 0, k^2 = k_i^2 - \frac{\eta}{2\lambda} P_k P_{-k}. \quad (31)$$

Substituting (31) and (30) into (25) gives the following form of the thermodynamical potential of the IC phase:

$$\varphi_{IC} = (\alpha - \alpha_i) P_k P_{-k} + \frac{3}{2} B_1^* P_k^2 P_{-k}^2 + \frac{10}{3} \gamma^* P_k^3 P_{-k}^3, \quad (32)$$

where

$$\alpha_i = \frac{\delta^2}{4\lambda} \equiv a(T_i - T_0), \quad (33)$$

$$B_1^* = B_0 + \Delta + \frac{2}{3} \eta k_i^2, \quad (34)$$

$$\gamma^* = \gamma - \frac{3}{40} \frac{\eta^2}{\lambda}. \quad (35)$$

From the condition of minimum  $\frac{\partial \varphi_{IC}}{\partial P_{\pm k}} = 0$  we find the expression for the temperature dependence of the squared polarization wave amplitude in the IC phase:

$$P_k P_{-k} = \frac{3B_1^*}{20\gamma^*} \left( \sqrt{1 - \frac{40}{9} A^* t_i} - 1 \right), \quad (36)$$

where  $A^* \equiv \frac{a\gamma^*}{B_1^*}$ ,  $t_i \equiv (T - T_i)$ .

The energy of the IC phase is:

$$F_{IC} = -\frac{27B_1^*}{1200\gamma^{*2}} \cdot \left[ \left( 1 - \frac{40}{9} A^* t_i \right)^{3/2} + \frac{180}{27} A^* t_i - 1 \right]. \quad (37)$$

The temperature behaviour of heat capacity in the IC phase is described by the relation:

$$\Delta C_p = \frac{a^2}{3B_1^*} \cdot \frac{T}{\sqrt{1 - \frac{40}{9} A^* t_i}}. \quad (38)$$

The constant electric field  $E$  induces the polarization  $P_0$  which adds to the expansion (25) for the IC phase the additional term  $P_0 P_k P_{-k}$ . Leaving for simplicity only the terms essential when considering the dielectric susceptibility in (25) we shall write this part of the potential in a form:

$$\varphi_{IC} = [\alpha(k) + 3B_2 P_0^2] P_k P_{-k} + 15\gamma P_0^2 (P_k P_{-k})^2 + \alpha P_0^2 - P_0 E. \quad (39)$$

Here:

$$B_2 = B_0 + 2\Delta + \frac{1}{3} \eta k^2. \quad (40)$$

From expansion (39) we shall find in the usual way the expression for the reciprocal of the dielectric susceptibility in the one-harmonical approximation

$$\chi_{0h}^{-1} = \alpha + 6B_2 P_k P_{-k} + 30\gamma P_k P_{-k}, \quad (41)$$

or, after substituting the expression for the  $P_k P_{-k}$  from (36), we have:

$$\chi_{0h}^{-1} = at - \frac{3\gamma B_1^{*2}}{\gamma^{*2}} A^* t_i + \frac{9B_1^*}{10\gamma^*} \left( B_2 - \frac{3\gamma B_1^*}{2\gamma^*} \right) \cdot \left( \sqrt{1 - \frac{40}{9} A^* t_i} - 1 \right). \quad (42)$$

## B. Incommensurate phase. The inclusion of higher harmonics

Lets us find the expression for the dielectric susceptibility which takes into account the contribution of the higher polarization modulation harmonics. Since the electric field  $E$  generates all harmonics (odd and even), then the first further harmonics after the fundamental one,  $P_{\pm k}$  will be the second harmonics  $P_{\pm 2k}$ . In that case the following terms should be added to expansion (25) or (39) (these terms being of the same order of smallness and essential in considering the dielectric susceptibility):

$$\begin{aligned} \Delta\varphi_{IC}(2k) &= [\alpha(2k) + 6B_2^1 P_k P_{-k} + 30\gamma P_k^2 P_{-k}^2] P_{2k} P_{-2k} \\ &+ 3B_3 P_0 (P_k^2 P_{-2k} + P_{-k}^2 P_{2k}) + 20\gamma P_0 P_k P_{-k} (P_{-k}^2 P_{2k} + P_k^2 P_{-k}) \end{aligned} \quad (43)$$

Here  $\alpha(2k)$  is similar to expression (26) with  $k$  being substituted by  $2k$ :

$$B_2^1 = B_0 + 2\Delta + \frac{5}{3}\eta k^2, \quad (44)$$

$$B_3 = B_0 + 3\Delta + \eta k^2. \quad (45)$$

As a result of minimizing the potential  $\Delta\varphi_{IC}(2k)$  over the second harmonics  $P_{\pm 2k}$  we shall find the additional contribution given by the latter to the “one-harmonical” dielectric susceptibility (41,42) [4]:

$$\Delta\chi_{2h}^{-1} = -\frac{2(3B_3 + 20\gamma P_k P_{-k}) P_k^2 P_{-k}^2}{\alpha + 8\alpha_i + 6B_2^1 P_k P_{-k} + 35\gamma P_k^2 P_{-k}^2}. \quad (46)$$

Here one has to use expression (36) for  $(P_k P_{-k})$ . If one decides to simplify the situation and not to consider the non-linear terms of the  $P_k^3 P_{-k}^3$  order in the IC phase, i.e. to set  $\gamma = 0$ , then expressions (41), (46) for the dielec-

tric susceptibility are simplified and after the insertion of amplitudes

$$P_k P_{-k} = -\frac{\alpha - \alpha_i}{3B_i^*}, \quad (47)$$

will take the following form:

$$\begin{aligned} \chi_{IC}^{-1} &= \chi_{0h}^{-1} + \chi_{2h}^{-1} = \alpha - 2(\alpha - \alpha_i) \frac{B_2}{B_1^*} \\ &- \frac{2(\alpha - \alpha_i)^2 \left(\frac{B_2^1}{B_1^*}\right)}{\alpha + 8\alpha_i - 2(\alpha - \alpha_i) \frac{B_2}{B_1^*}}. \end{aligned} \quad (48)$$

Consider now the contribution of higher harmonics to the heat capacity of the IC phase. For a more vivid representation we shall use the “weak” non-linearity approximation, i.e. set  $\gamma = 0$ , and  $\eta = 0$  in expansion (11). Moreover, we shall neglect the elastic degrees of freedom.

In the absence of electric field  $E$  the non-linear term  $\beta \cdot P^3$  generates the odd higher order harmonics, i.e. the third harmonics  $P_{\pm 3k}$  becomes the next one after the fundamental harmonic  $P_k$ . Then the expansion of the thermodynamical potential of the IC phase in the accepted approximation takes the following form:

$$\begin{aligned} \varphi_{IC}^{E=0} &= \alpha(k) P_k P_{-k} + \frac{3}{2}\beta P_k^2 P_{-k}^2 + \alpha(3k) P_{3k} P_{-3k} + \frac{3}{2}\beta P_{3k}^2 P_{-3k}^2 \\ &+ 6\beta P_k P_{-k} P_{3k} P_{-3k} + \beta (P_k^3 P_{-3k} + P_{-k}^3 P_{3k}). \end{aligned} \quad (49)$$

From the condition of minimum  $\frac{\partial\varphi}{\partial P_{\pm 3k}} = 0$  we obtain:

$$P_{\pm 3k} = -\frac{\beta P_{\mp k}^3}{\alpha(3k) + 6\beta P_k P_{-k}}, \quad (50)$$

where  $\alpha(3k)$  is similar to (26) with the substitution  $k \rightarrow 3k$ . Inserting (50) into (49) gives:

$$\varphi_{IC}^{E=0} = (\alpha - \alpha_i) P_k P_{-k} + \frac{3}{2} P_k^2 P_{-k}^2 - \frac{\beta^2}{\alpha + 36\alpha_i} P_k^3 P_{-k}^3. \quad (51)$$

Minimizing (51) we obtain the temperature dependence of the polarization wave amplitude in the IC phase with the allowance made for the “higher” harmonics:

$$P_k P_{-k} = \frac{\alpha + 63\alpha_i}{2\beta} \left[ 1 - \sqrt{1 - \frac{4}{3} \frac{\alpha - \alpha_i}{\alpha + 63\alpha_i}} \right]. \quad (52)$$

Inserting (52) into (51) we find the energy and then obtain the expression for the heat capacity of the IC phase with the induction of higher harmonics:

$$\Delta C_p^{E=0} = \frac{T_i a^2}{3\beta} \left[ 1 - \frac{2}{3} \cdot \frac{\alpha - \alpha_i}{\alpha + 63\alpha_i} \right]. \quad (53)$$

#### IV. INCOMMENSURATE PHASE EVOLUTION WITH APPROACHING THE LIFSHITZ POINT. THE CONCENTRATIONAL DEPENDENCE OF PHYSICAL PROPERTIES OF $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$ CRYSTALS

When the Se atoms in  $\text{Sn}_2\text{P}_2\text{Se}_6$  are substituted by the S atoms, the continuous series of solid solution  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$  is obtained. The temperature  $T_0$  of the second order transition in  $\text{Sn}_2\text{P}_2\text{S}_6$  decreases with Se concentration. The second order PT line  $T_0(x)$  is formed on the  $T-x$  diagram and this line is split at the Lifshitz point ( $x_{LIP} \approx 0.28$ ) into the  $T_i(x)$  line of the second order transitions and the  $T_c(x)$  of the first order transitions (these lines fringe the IC phase). In  $\text{Sn}_2\text{P}_2\text{Se}_6$  the temperature interval of the existence of the IC phase is 28 K (Fig. 1) [6].

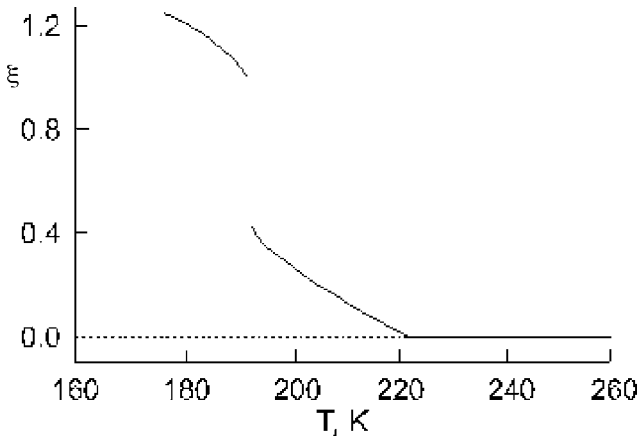


Fig. 5. The heat expansion of the  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystal [18].  $\xi$ —the normalized on the value at  $T_c = 193\text{K}$  anomalous part of linear dimension temperature changes.

In the subsections 1.2 we have performed the phenomenological analysis of the temperature behaviour of the principal physical characteristics at the phase transformations “*paraelectric-ferroelectric phase*” and “*paraelectric phase- IC phase-ferroelectric phase*” which correspond the situation in the  $\text{Sn}_2\text{P}_2\text{S}_6$  and  $\text{Sn}_2\text{P}_2\text{Se}_6$ . When analyzing the situation in  $\text{Sn}_2\text{P}_2\text{Se}_6$  with the IC phase we have applied the almost thermodynamical potential of  $\text{Sn}_2\text{P}_2\text{S}_6$  with the addition of the gradient terms. Since the physical properties of solid solu-

tions  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$  depend continuously on the impurity concentration, the thermodynamical potential coefficients  $\alpha, \beta, \gamma, \delta, \lambda$  and  $\eta$  which characterize uniquely the state of the crystal are so assumed to depend on the impurity concentration. Thus, unlike the pure crystals, the solid solutions, besides the usual parameters, possess the specific characteristics, i.e. the impurity component concentration describing new additional degrees of freedom which should be taken into account when constructing the thermodynamical potential.

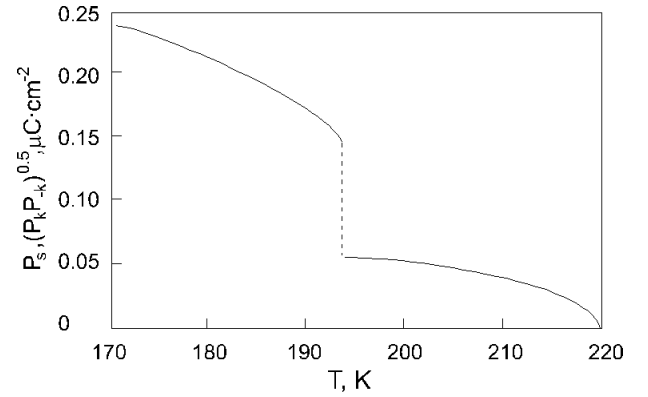


Fig. 6. The calculated by relation (52) temperature dependencies of spontaneous polarization  $P_s$  in ferroelectric phase ( $T < T_c = 193\text{K}$ ), and of amplitude modulation  $(P_k P_{-k})^{0.5}$  in incommensurate phase ( $T_c < T < T_i = 221\text{K}$ ) for the  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystal.

According to the Landau theory of solutions [12], the thermodynamical potential density of the system per single solvent molecule can be expressed for the simplest binary solution as

$$\Phi = \varphi(P, T) + xkT \ln \frac{x}{1-x} + x\varphi_1(p, T) + x^2\varphi_2(P, T), \quad (54)$$

where  $x$  defines the impurity concentration; the first item governs the behaviour of the thermodynamical potential at  $x = 0$  (i.e. the potential of the main subsystem in the form of expansion (11)), while the second item dictates the contribution of the concentrational subsystem and two last ones characterize their interaction with  $\varphi$ ,  $\varphi_1$  and  $\varphi_2$  being the functions of the same variables. The thermodynamical potential of the whole system in this case is presented in a form of a superposition of three components ( $\Phi = \Phi_f + \Phi_x + \Phi_{fx}$ ), where the first item describes the ferroelectric subsystem (an expansion into a power series in polarization  $P$  and  $P'$ ), the second one defines the concentrational subsystem (an expansion into a power series in impurity concentration:  $x^i, (1-x)^i, x^j(1-x)^j$ , where  $i, j = 1, 2$ ) and the third item governs the interaction between the subsystems (an expansion with the transition terms of  $x^i P^{2j}$  type, where



$i, j = 1, 2 \dots$ ). Grouping the terms with the same polarization powers and performing elementary transformations we may reduce the thermodynamical potential of the system to the customary form, where the expansion coefficients depend on concentration:

$$\begin{aligned} \Phi &= \Phi_0 + \frac{1}{2}\alpha(T, x)P^2 + \frac{1}{4}\beta(T, x)P^4 \\ &+ \frac{1}{6}\gamma(T, x)P^6 + \frac{1}{2}\delta(T, x) \left( \frac{\partial P}{\partial z} \right)^2 \\ &+ \frac{1}{2}\lambda(T, x) \left( \frac{\partial^2 P}{\partial z^2} \right) + \frac{1}{2}\eta(T, x)P^2 \left( \frac{\partial P}{\partial z} \right)^2, \end{aligned} \quad (55)$$

where  $\alpha(T, x) = a(x)[T - T_0(x)]$ . If one introduces the notation for the extreme compounds  $\text{Sn}_2\text{P}_2\text{Se}_6$  and  $\text{Sn}_2\text{P}_2\text{S}_6$   $a(x=0) \equiv a_1, a(x=1) \equiv a_2$  and, similarly  $T_0(x=0) \equiv T_{01}, T_0(x=1) \equiv T_{02}$ , then in the linear approximation over concentration we can write:

$$\begin{aligned} \alpha'_T(x) &= (1-x) \cdot a_1 + x a_2, \\ T_0(x) &= (1-x) \cdot T_{01} + x T_{02}. \end{aligned} \quad (56)$$

Similarly, for  $\beta$  and  $\gamma$  coefficients we have:

$$\begin{aligned} \beta(x) &= (1-x)\beta_{01} + x\beta_{02}, \\ \gamma(x) &= (1-x)\gamma_{01} + x\gamma_{02}. \end{aligned} \quad (57)$$

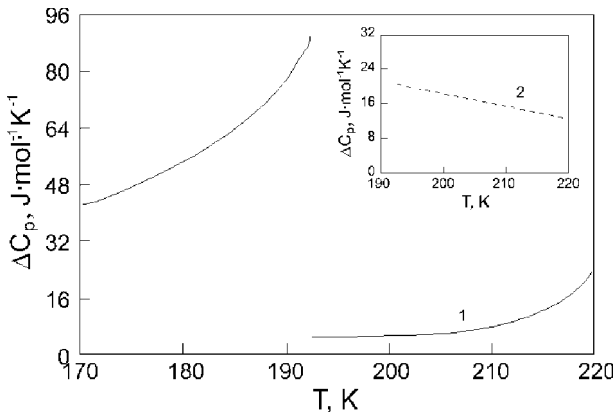


Fig. 7. The calculated by relations (19),(53) temperature dependence of heat capacity for the  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystal. 1- the nonlinearity are taking into account ( $\gamma \neq 0$ ), but high harmonics of modulation are neglected ( $P_{3k}P_{-3k} = 0$ ); 2-  $P_{3k}P_{-3k} \neq 0, \gamma = 0$ .

At the Lifshitz point  $\delta(T_{LP}, x_{LP}) = 0$  and in the vicinity this coefficient can be expanded into a power series in  $(x - x_{LP})$  and  $(T - T_{LP})$ . Leaving the first order terms, we have [16,17]:

$$\delta(T, x) = \left( \frac{\partial \delta}{\partial x} \right)_T (x - x_{LP}) + \left( \frac{\partial \delta}{\partial T} \right)_x (T - T_{LP}), \quad (58)$$

or  $\delta(T, x) = \delta_x(x - x_{LP})$  where

$$\delta_x \equiv \left\{ \left( \frac{\partial \delta}{\partial x} \right) + \left( \frac{\partial \delta}{\partial T} \right) \left( \frac{\partial T_0}{\partial x} \right)_{LP} \right\}. \quad (59)$$

Other expansion coefficients ( $\lambda, \eta$ ) should be considered constant. Then the modulation wave vector  $k_i$  at the line  $T_i(x)$  in the vicinity of the Lifshitz point has the following concentrational dependence:

$$k_i^2(x) = -\frac{\delta(x)}{2\lambda} = \frac{\delta_x}{2\lambda}(x_{LP} - x). \quad (60)$$

Using the analytical expressions for the physical characteristics of extreme compounds  $\text{Sn}_2\text{P}_2\text{S}_6$  and  $\text{Sn}_2\text{P}_2\text{Se}_6$  obtained in subsections 1 and 2, and employing conditions (56–59) for the concentrational dependence of the thermodynamical potential coefficients, we obtain the transformation of the temperature anomalies of thermodynamical functions when approaching the Lifshitz point.

## V. DISCUSSION OF THE RESULTS AND THE ANALYSIS OF THE EXPERIMENTAL DATA

Let us compare the results of phenomenological analysis with the available experimental data. To do this we shall calculate the thermodynamical potential coefficients  $\alpha_T, B_0, \gamma$  for the  $\text{Sn}_2\text{P}_2\text{S}_6$  crystal. With the temperature behaviour of dielectric permittivity in the paraelectric phase we find the value of the Curie-Weiss constant  $C = 0.7 \cdot 10^5 \text{ K}^{-1}$  [9]. Coefficient  $a = (C\varepsilon_0)^{-1}$ , where  $\varepsilon_0$  is a dielectric constant. As a result we have  $a \approx 1.6 \cdot 10^6 \text{ J} \cdot \text{m} \cdot \text{K}^{-1} \cdot \text{C}^{-2}$ . The coefficient  $B_0 = \beta - K$  is found from the heat capacity leap in  $\text{Sn}_2\text{P}_2\text{S}_6$  at  $T_0$  using the relation  $\Delta C_p = \frac{T_0 a^2}{2B_0}$ . Taking the heat capacity leap of  $\Delta C_p = 170 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  (3) and employing the above values for  $\alpha_T$  we have  $B_0 = 7.4 \cdot 10^8 \text{ J} \cdot \text{m}^5 \cdot \text{C}^{-4}$ . The atomic value  $\beta_{at}$  at far from the PT point is found from the condition  $aT_0 \sim \beta_{at} P_{sat}$  where  $P_{sat} = 0.15 \text{ C} \cdot \text{m}^{-2}$ . Hence, we obtained quite low a value of  $B_0$  indicating that the second-order PT in the  $\text{Sn}_2\text{P}_2\text{S}_6$  crystal is sought to be close to the TCP, where  $B_0 \rightarrow 0$ . The low value of the coefficient  $B_0$  substantiates the inclusion of the next invariant  $P^6$  in to the thermodynamical potential expansion. The coefficient  $\gamma$  is derived from the temperature dependence of the heat capacity in the ferroelectric phase:  $\gamma = 3.5 \cdot 10^{10} \text{ J} \cdot \text{m}^9 \cdot \text{C}^{-6}$  [9]. The relations for the temperature dependence's of polarization (3), heat capacity (5) and dielectric permittivity (7) allow one to calculate their anomalies at PT. We obtain a good agreement with the experimental data with the exception of a small temperature domain of the paraelectric phase ( $T_0, T_0 + 5K$ ) where

the “tails” of the dependence’s  $C_p(T)$  and  $P_s(T)$  occur [11] and the deviation from Curie–Weiss law is observed for  $\varepsilon(T)$  [10].

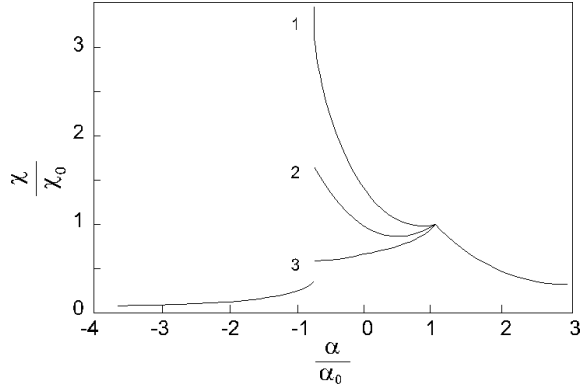


Fig. 8. The calculated temperature dependence of dielectric susceptibility relative value by relation (42, 46, 48) for the  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystal at different conditions: 1 — high harmonics  $P_{2k}P_{-2k}$  are take into account but energy “gap”  $\Delta = 0$ ; 2 —  $P_{2k}P_{-2k} \neq 0$ ,  $\Delta \neq 0$ ; 3 —  $P_{2k}P_{-2k} = 0$ ,  $\Delta = 0$ . For all cases  $\gamma = 0$ .

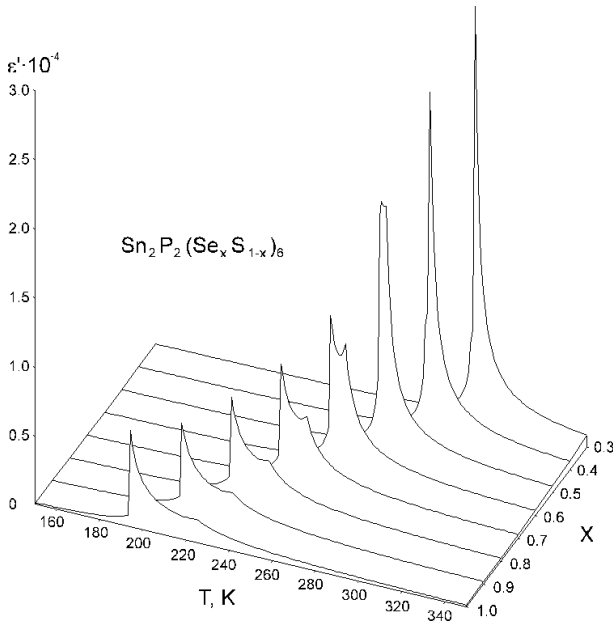


Fig. 9. The calculated by relation (48) concentrational evolution of dielectric constant temperature dependence for the  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$  crystals  $P_{2k}P_{-2k} \neq 0$ ;  $\Delta \neq 0$ .

For the  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystal, the coefficients  $a, \beta_0$  and  $\gamma$  are obtained similarly to the case of  $\text{Sn}_2\text{P}_2\text{S}_6$ . Here  $a = 1.6 \cdot 10^6 \text{ J} \cdot \text{m} \cdot \text{C}^{-2} \cdot \text{K}^{-1}$ , since Curie–Weiss constant is nearly constant [9],  $B_1 = 1.2 \cdot 10^9 \text{ J} \cdot \text{m}^5 \cdot \text{C}^{-4}$ . One may conclude in terms of the approximation about the linear concentrational variation of  $B_0$  coefficient that at  $\text{S} \rightarrow \text{Se}$  substitution  $B_0$  changes its sign at  $x = 0.6$  and for  $\text{Sn}_2\text{P}_2\text{Se}_6$

$B_0 = -4.8 \cdot 10^8 \text{ J} \cdot \text{m}^5 \cdot \text{C}^{-4}$ . Hence, in the absence of the IC phase in  $\text{Sn}_2\text{P}_2\text{Se}_6$  the first order PT must arise. However, since the second order PT to the IC phase occurs at  $T_i$ , the following condition should hold:  $\frac{\delta^2}{4\lambda} > \frac{3B_0^2}{16\gamma}$ .

From the expressions (29) and (30) for the IC phase width and the value of the wave vector  $\mathbf{k}_l$  we find the coefficients  $\delta$  and  $\lambda$ :  $\delta \approx 4 \cdot 10^{-10} \text{ J} \cdot \text{m}^3 \cdot \text{C}^{-2}$ ,  $\lambda \approx 2.2 \cdot 10^{-27} \text{ J} \cdot \text{m}^5 \cdot \text{C}^{-2}$ . The value of  $\eta$  is found from the temperature dependence of the wave vector  $k$  in the IC phase:  $\eta \approx 1.2 \cdot 10^{-8} \text{ J} \cdot \text{m}^7 \cdot \text{C}^{-4}$ . The electrostriction coefficients  $r_{ijkl}$  can be estimated in different ways: using the data on the linear thermal expansion and those on the longitudinal ultrasound velocity leap at the PT point. The estimations of  $K$  and  $\tilde{K}$  give the value of the energy “gap”:  $\Delta = 1.7 \cdot 10^8 \text{ N} \cdot \text{m}^{-2}$  [9].

Figure 6 shows the temperature dependence of the order parameter calculated for  $\text{Sn}_2\text{P}_2\text{Se}_6$ . Formulae (52) describe well the experimental data [18]. However, in the IC phase in the vicinity of the  $T_c$  the order parameter has somewhat different experimental temperature dependence. The isobaric heat capacity calculated by formula (53) for  $\gamma \neq 0$  is plotted in Fig. 7. This figure also presents the temperature dependence of the heat capacity at  $\gamma = 0$  with the allowance made for the next (third) harmonic. A distinct increase of  $C_p$  is seen against the “plateau” typical for the sinusoidal approximation on cooling down to  $T_c$ . This leap illustrates the “contribution” of higher harmonic.

The results of the temperature dependence of dielectric permittivity calculations by relations (42), (46) and (48) is plotted in Fig. 8. Here the contribution of the “first” and “second” harmonics is indicated. It is seen that the “second” harmonic plays an essential role in the behaviour of  $\varepsilon'$  in the IC phase close to  $T_c$ . The influence of the long-range elastic forces is also seen in Fig. 8 where the dielectric permittivity is shown as calculated with the allowance made for the “gap”  $\Delta$  and its absence. It is seen that the presence of  $\Delta$  in the expression for  $\varepsilon'$  enhances the indications of the first-order lock-in transition.

Let us compare the calculated data with the experimental results. In general, if one takes into account the higher harmonics of the order parameter spatial modulations, the relationship of the order parameter with the elastic deformations and the non-linearity’s ( $\frac{\gamma}{6}P^6, \frac{\eta}{2}P^2(P')^2$  invariants), the temperature dependence of the real part of the dielectric susceptibility over the entire temperature region of the existence of the IC phase is described satisfactorily (see Fig. 4, 9). The principal features of the concentrational variation of the anomalies in  $\varepsilon(T)$  in the mixed  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$  crystal under the composition variation with approaching the LP (Fig. 9) are also explained. However, for the composition in the vicinity of the LP the calculated dependence’s  $\varepsilon'(T)$  reveal a minimum. The lack of this minimum in the measured dependence (Fig. 4) may result from a slight nonlinearity of concentrational dependence of the thermodynamical potential coefficients. This discrepancy can also be attributed to the defectiveness of the mixed crystal structure.

For the  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystal at those thermodynamical potential coefficients which allow one to describe the dependence  $\varepsilon'(T)$  a distinct divergence between the experimental data and calculations is observed in the temperature dependence's of the heat capacity (Fig. 3, 7) and squared order parameter (Fig. 5, 6) at the low-temperature boundary of the IC phase. It is obvious that the higher harmonic of the order parameter modulation taken into account are not sufficient in describing the increase of  $C_p$  and  $P^2$  observed in the IC phase on cooling down to  $T_c$ .

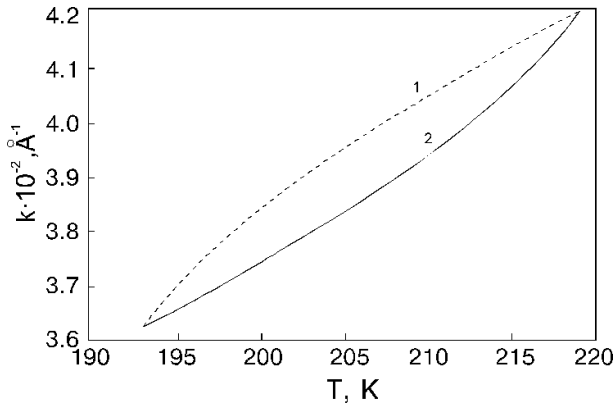


Fig. 10. The calculated by relation (31) temperature dependence of wave vector modulation value in incommensurate phase of the  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystal. The higher harmonic of modulation is taking into account ( $P_{2k}P_{-2k} \neq 0$ ). 1- $\gamma = 0$ ; 2- $\gamma \neq 0$ .

The most distinct disagreement between the calculated and experimental data is revealed when analyzing the temperature dependence of the modulation wave vector  $k(T)$  in the IC phase (Fig. 2, 10). Thus, for  $\text{Sn}_2\text{P}_2\text{Se}_6$  the rise of the rate of  $k$  decrease on cooling down to  $T_c$  is observed. The inclusion of the higher modulation harmonics, indeed, allows one to describe that tendency. However, that made for the nonlinearity (the  $\frac{7}{6}P^6$  invariant) results in the occurrence of a clear deviation of the calculated dependence  $k(T)$  from the experimental one: the calculations in this case give the dependence  $k(T)$  with the opposite curvature sign. It should be noted that just the non-equality of the  $\gamma$  value to zero allows a considerable increase of heat capacity in the IC phase on crystal being heated to  $T_i$  to be explained (Fig. 7).

## VI. CONCLUSIONS

In the mean-field approximation, assuming the linear concentrational dependence of the thermodynamical po-

tential coefficients and taking into account the higher harmonics of the spatial order parameter modulation in the IC phase, as well as the relationship between the order parameter and the elastic deformations in the proper uniaxial  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$  ferroelectrics, the following items are satisfactorily described: I) the form of the temperature-composition diagram with the Lifshitz point at  $x_{LP} \approx 0.28$  and the "virtual" triple point near  $x = 0.6$ ; II) the anomalies of the temperature dependencies of the principal thermodynamical characteristics (i.e. the order parameter, the dielectric susceptibility, the heat capacity) at the stability boundary of the paraelectric phase ( $T_0(x)$  at  $x < x_{LP}$ ,  $T_i(x)$  at  $x > x_{LP}$ ) and in the IC phase in the vicinity of the lock-in transition (the  $T_c(x)$  line at  $x > x_{LP}$ ). However, difficulties emerge when we compare the data of the quantitative calculations of the anomalies of various properties with the experimental data, essentially for the temperature vicinity of the lock-in phase transition ( $T_c$ ). That discrepancy is revealed most distinctly when analyzing the temperature dependence of the structure modulation wave-vector in the IC phase. By the way, to date no indications are available as to the revelation of the higher harmonics of the structural modulation in the IC phase of the  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystal [19] which complicates their adequate inclusion when analyzing the thermodynamical properties.

To achieve the best understanding of the origin of the lock-in transition in the proper ferroelectrics with the IC phase one has, evidently, to take into account the attraction energy of domain walls which arise from their thermal fluctuations. Such an interaction in the vicinity of  $T_c$  appears to be essential [5]. The possibility of solitonic and sinusoidal structural modulations coexistence [20], [21] also must be defined for the IC phase of the  $\text{Sn}_2\text{P}_2\text{Se}_6$  crystals.

The amplitudes of the fluctuational effects in  $\text{Sn}_2\text{P}_2\text{S}_6$  and  $\text{Sn}_2\text{P}_2\text{Se}_6$  ferroelectrics are not so much to  $T_0(T_i)$  [10], [11]. But, as follows from theoretical analysis [22], for solids the fluctuations in any case may shift the coordinates of the triple point. So, the shape of  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$  ferroelectrics phase diagram which we have defined in mean field approximation probably is to be reanalyzed taking into account the fluctuations influence. It is natural to believe that defects may also have a strong effect on the properties of the IC phase.

## VII. ACKNOWLEDGEMENTS

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**АНАЛІЗ У НАБЛИЖЕННІ СЕРЕДНЬОГО ПОЛЯ ТЕРМОДИНАМІЧНИХ  
ВЛАСТИВОСТЕЙ КРИСТАЛІВ  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$  У ПАРАЕЛЕКТРИЧНІЙ, НЕСУМІРНІЙ  
ТА СЕГНЕТОЕЛЕКТРИЧНІЙ ФАЗАХ**

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У наближенні середнього поля, припускаючи лінійну концентраційну залежність коефіцієнтів термодинамічного потенціалу та враховуючи вищі гармоніки просторової модуляції параметра порядку в несумірній фазі, а також взаємодію параметра порядку з пружними деформаціями, розраховано температурні та концентраційні залежності одноосісних сегнетоелектриків  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$ . Результати розрахунків зіставлено з експериментальними даними. При кількісному зіставленні спостерігаємо деяку відмінність розрахованих та спостережуваних температурних залежностей для питомої теплоємності й амплітуди хвильового вектора модуляції в несумірній фазі в околі lock-in фазового переходу.