The lock-in transition in proper $Sn_2P_2(Se_xS_{1-x})_6$ ferroelectrics

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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 dependencies of dielectric constant of $Sn_2P_2(Se_xS_{1-x})_6$ uniaxial ferroelectrics are calculated and compared with experimental data. The vicinity of the lock-in phase transition in incommensurate phase analysed.

Keywords: phase transition, incommensurate phase, dielectric constant.

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 for improper ferroelectrics with the IC phase of the I type according to classification [1]. 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 [2]. For the proper ferroelectrics with the II type IC phase [1] the origin of the lock-in transition remains unclassified [3]. 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.

The crystals $Sn_2P_2(Se_xSe_{1-x})_6$ 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 $x > x_{LP}$ [4]. The experimental data on the critical behaviour of the

properties of the $Sn_2P_2(Se_xSe_{1-x})_6$ crystals in the vicinity of the $T_0(x)$, $T_i(x)$ lines are presented in [4]. The analysis performed within the framework of the mean-field approximation describes in general the concentrational evolution of the properties of these crystals at the paraelectric phase stability boundary [5]. However, both the origin of the lock-in transition in $Sn_2P_2Se_6$ 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 $Sn_2P_2(Se_xSe_{1-x})_6$ crystals to the Lifshitz point call for further clarification. In this paper the phenomenological analysis of the dielectric properties of $Sn_2P_2(Se_xSe_{1-x})_6$ 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.

The mean field analysis

$Sn_2P_2S_6$ undergoes at $T_0 \approx 337$ K the structural second order PT [4]. The paraelectric phase symmetry $P2_1/c$ decreases to the Pc subgroup in the low-temperature ferroelectric phase. So, the $Sn_2P_2S_6$ crystal is a proper uniaxial ferroelectric with the single-component order parameter ($P_s \equiv P_x$). In the $Sn_2P_2Se_6$ crystal the transition from paraelectric phase to IC phase is proceeded by the second-order PT at $T_i \approx 221$ K. The first order lock-in transition to the commensurate ferroelectric state occurs at $T_c \approx 193$ K [4].

In that case the thermodynamical potential is expressed in the following form [3]

$$F = \int \varphi dV, \qquad \varphi = \varphi_0 + \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \frac{\gamma}{6}P^6 + \frac{\delta}{2}(P')^2 + \frac{\lambda}{2}(P'')^2 + \frac{\eta}{2}(P')^2 P^2. \quad (1)$$

Here $\alpha \equiv at$, $a \equiv \left(\frac{\partial \alpha}{\partial T}\right)$; $t \equiv (T - T_0)$; P' are the spatial derivatives. The coefficients λ and η are positive. For solid solutions δ and β are linear function of concentration [4,5]. The last term in (1) is of the same order of smallness as the other gradient terms. The inclusion of this term is important when describing the behaviour of the physical properties at the lock-in transition [3].

The occurrence of the spatially non-uniform distribution of polarization in the modulated IC phase results in the appearance of the non-uniform deformation . We will take into account the elastic degrees of freedom in a form of next addend to the expansion (1) of the thermodynamical potential:

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

Here $c=c_{ijkl}$ is the elastic module matrix , $u = u_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)$ is the

deformation tensor, $r=r_{ijkl}$ is an electrostriction coefficient. In the deformation tensor u_{ij}, we shall distinguish the uniform part u^0_{ij}:

$$u_{ij} = u^0_{ij} + \sum_{k\neq0}{}' ik_j u_i(k)e^{i\vec{k}\vec{r}}.$$ (3)

Here $u_i(k)$ is the Fourier-component of the displacement component u_i. Minimizing expression (2) separately over the uniform and non-uniform deformation , we obtain [6].

$$F_{el} = \int \varphi_{el}dV = -K\sum_k P_k{}^2 P_{-k}{}^2 - \sum_{k\neq0}{}'\sum_{k',k''} \tilde{K}P_{k'}P_{-k'-k}P_{-k''}P_{k''+k}$$ (4)

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

$$K = \frac{r^2}{2\chi}, \quad \tilde{K} = \frac{r^2}{2\left(\chi + \frac{4}{3}\mu\right)},$$ (5)

where $r=r_{iijj}$ are, the electrostriction coefficients, χ and μ are the bulk and shear elastic module, respectively.

For the IC phase the thermodynamical potential (1) with the allowance made for the elastic degrees of freedom (4) in the oneharmonical approximation has the following form:

$$\varphi_{IC} = \alpha(k)P_k P_{-k} + \frac{3}{2}B_1 P_k{}^2 P_{-k}{}^2 + \frac{10}{3}\gamma P_{-k}{}^3 P_k{}^3.$$ (6)

Here: $\alpha(k) = \alpha + \delta k^2 + \lambda k^4$,

$$B_1 = B_0 + \Delta + \frac{2}{3}\eta k^2, \quad B_0 = \beta - 4k, \quad \Delta = \frac{4}{3}(K - \tilde{K}).$$ (6a)

Here also Δ is an energy "gap" defined by the long range elastic forces [2,6].

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:

$$P_k P_{-k} = \frac{3B_1^*}{20\gamma*}\left(\sqrt{1 - \frac{40}{9}A^*t_i} - 1\right), \tag{7}$$

where $A^* \equiv \dfrac{a\gamma*}{B_1^*}$, $\quad t_i \equiv (T - T_i)$, $\quad B_1^* = B_0 + \Delta + \dfrac{2}{3}\eta k_i^2$, $\quad \gamma* = \gamma - \dfrac{3}{40}\dfrac{\eta^2}{\lambda}$.

The constant electric field E induces the polarization P_0 which adds to the expansion (6) for the IC phase the additional term $P_0 P_k P_{-k}$. Leaving in (6) for simplicity only the terms essential when considering the dielectric susceptibility we shall write this part of the potential in a form:

$$\varphi_{IC} = \left[\alpha(k) + 3B_2 P_0^2\right]P_k P_{-k} + 15\gamma P_0^2 (P_k P_{-k})^2 + \alpha P_0^2 - P_0 E. \tag{8}$$

Here $B_2 = B_0 + 2\Delta + \dfrac{1}{3}\eta k^2$.

From expansion (8) we shall find in common way the expression for the reciprocal of the dielectric susceptibility in the oneharmonical approximation

$$\chi_{0h}^{-1} = \alpha + 6B_2 P_k P_{-k} + 30\gamma P_k P_{-k}, \tag{9}$$

or, after substitution of expression for the $P_k P_{-k}$ from (7), we have:

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

Lets 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 (6) or (8) (these terms being of the same order of smallness and essential in considering the dielectric susceptibility):

$$\Delta\varphi_{IC}(2k) = \left[\alpha(2k) + 6B_2' P_k P_{-k} + 30\gamma P_k^2 P_{-k}^2\right]P_{2k}P_{-2k} + $$
$$+ 3B_3 P_0 (P_k^2 P_{-2k} + P_{-k}^2 P_{2k}) + 20\gamma P_0 P_k P_{-k}(P_{-k}^2 P_{2k} + P_k^2 P_{-k}) \tag{11}$$

Here $\alpha(2k)$ is similar to expression (6a) with k being substituted by 2k, and

$$B_2^1 = B_0 + 2\Delta + \frac{5}{3}\eta k^2, \qquad B_3 = B_0 + 3\Delta + \eta k^2.$$

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 "oneharmonical" dielectric susceptibility (9,10) [3]:

$$\Delta\chi_{2h}^{-1} = -\frac{2(3B_3 + 20\gamma P_k P_{-k})P^2{}_k P^2{}_{-k}}{\alpha + 8\alpha_i + 6B_2' P_k P_{-k} + 35\gamma P^2{}_k P^2{}_{-k}} \tag{12}$$

where $\alpha_i = \dfrac{\delta^2}{4\lambda} = a(T_i - T_0)$. Here one has to use expression (7) for $(P_k P_{-k})$. If one decides to simplify the situation and not to consider the non-linear terms of $P_k^3 P_{-k}^3$ order in the IC phase, i.e. to set $\gamma=0$, then expressions (9), (12) for the dielectric susceptibility are simplified and after the insertion of amplitudes

$$P_k P_{-k} = -\frac{\alpha - \alpha_i}{3B_1^*} \quad , \tag{13}$$

will take the following form:

$$\chi_{IC}^{-1} = \chi_{0h}^{-1} + \chi_{2h}^{-1} = \alpha - 2(\alpha - \alpha_i)\frac{B_2}{B_1^*} - \frac{2(\alpha - \alpha_i)^2 \left(\dfrac{B_2^1}{B_1^*}\right)}{\alpha + 8\alpha_i - 2(\alpha - \alpha_i)\dfrac{B_2}{B_1^*}} \tag{14}$$

Discussion of the results

At first we shall calculate the thermodynamical potential coefficients a, B_0, γ for $Sn_2P_2S_6$ crystal. With the temperature behavior of dielectric permittivity in the paraelectric phase we find the value of the Curie-Weiss constant $C \approx 0.7 \ 10^5$ K [5]. Coefficient $a = (C\varepsilon_\infty)^{-1}$, where ε_∞ is a dielectric constant. As a result we have $a \approx 1.6 \cdot 10^6$ J·m·K^{-1}·C^{-2}. The coefficient $B_0 = \beta - K$ is found from the heat capacity leap in $Sn_2P_2S_6$ at T_0 using the relation $\Delta C_p = \dfrac{T_0 a^2}{2B_0}$. Taking the heat capacity leap of $\Delta Cp=170$ J·mol^{-1}K^{-1} [5] and employing the above values for a we have $B_0=7.4 \cdot 10^8$ J·m^5·C^{-4}. The atomic value β_{at} at far from the PT point is found from the condition $aT_0 \sim \beta_{at}P_{sat}$ where $P_{sat} \approx 0.15$ Cm^{-2}. Hence, we obtained quite low value of B_0 indicates that the second-order PT in the $Sn_2P_2S_6$ crystal is sought close to the tricritical point (TCP), where $B_0 \to 0$. The low value of the coefficient B_0 substantiates the inclusion of

the next invariant P^6 in the thermodynamical potential expansion. The coefficient γ is derived from the temperature dependence of the heat capacity in the ferroelectric phase: $\gamma = 3.5 \cdot 10^{10}$ J·m^9·C^{-6} [5].

For the $Sn_2P_2Se_6$ crystal, the coefficients a, B_0 and γ are obtained similarly to the case of $Sn_2P_2S_6$. Here $a \approx 1.6 \cdot 10^6$ J·m·C^{-2}·K^{-1}, since Curie-Weiss constant value is nearly constant [5], $B_1 = 1.2 \cdot 10^9$ J·m^5·C^{-4}. One may conclude in terms of the approximation about the linear concentrational variation of B_0 coefficient that at S by Se substitution B_0 changes its sign at $x \approx 0.6$ and for $Sn_2P_2Se_6$ $B_0 = -4.8 \cdot 10^8$ J·m^{5}C^{-4}. Hence, in the absence of the IC phase in $Sn_2P_2Se_6$ 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:

$$\delta^2 / 4\lambda > 3B_0^2 / 16\gamma .$$

From the data for the IC phase width and the value of the wave vector $\vec{k}_i$ we find the coefficients δ and λ: $\delta \approx -4 \cdot 10^{-10}$ J·m^3·C^{-2}, $\lambda \approx 2.2 \cdot 10^{-27}$ J·m^5·C^{-2}. The value of η is found from the temperature dependence of the wave vector k in the IC phase: $\eta \approx 1.2 \cdot 10^{-8}$ J·m^7·C^{-4} [5]. The electrostriction coefficients r_{ijkl} can be estimated: 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": $\Delta = 1.7 \cdot 10^8$ N·m^{-2} [5].

The results of temperature dependence of dielectric permittivity calculations by relations (10), (12) and (14) is plotted in fig.1. Here the contribution of the "first" and "second" harmonics are indicated. It is seen that the "second" harmonic plays an essential role in the behavior of ε' in the IC phase close to T_c. The influence of the long-range elastic forces also is seen in Fig.1, where the dielectric permittivity is shown being calculated with the allowance made for the "gap" Δ and its absence. It is seen that the presence of Δ in the expression for ε' 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 dielectric susceptibility over the entire temperature region of the existence of IC phase is described satisfactorily (see fig.2,3). The principal features of the concentrational variation of the anomalies in $\varepsilon(T)$ for the mixed $Sn_2P_2(Se_xS_{1-x})_6$ crystal under the composition variation with approaching to LP (fig.3,a) are also explained with taking into account the dependencies $\delta \sim (0.28-x)$ and $B_0 \sim (0.6-x)$ [5]. However, for the composition in the vicinity of the LP the calculated dependence's $\varepsilon'(T)$
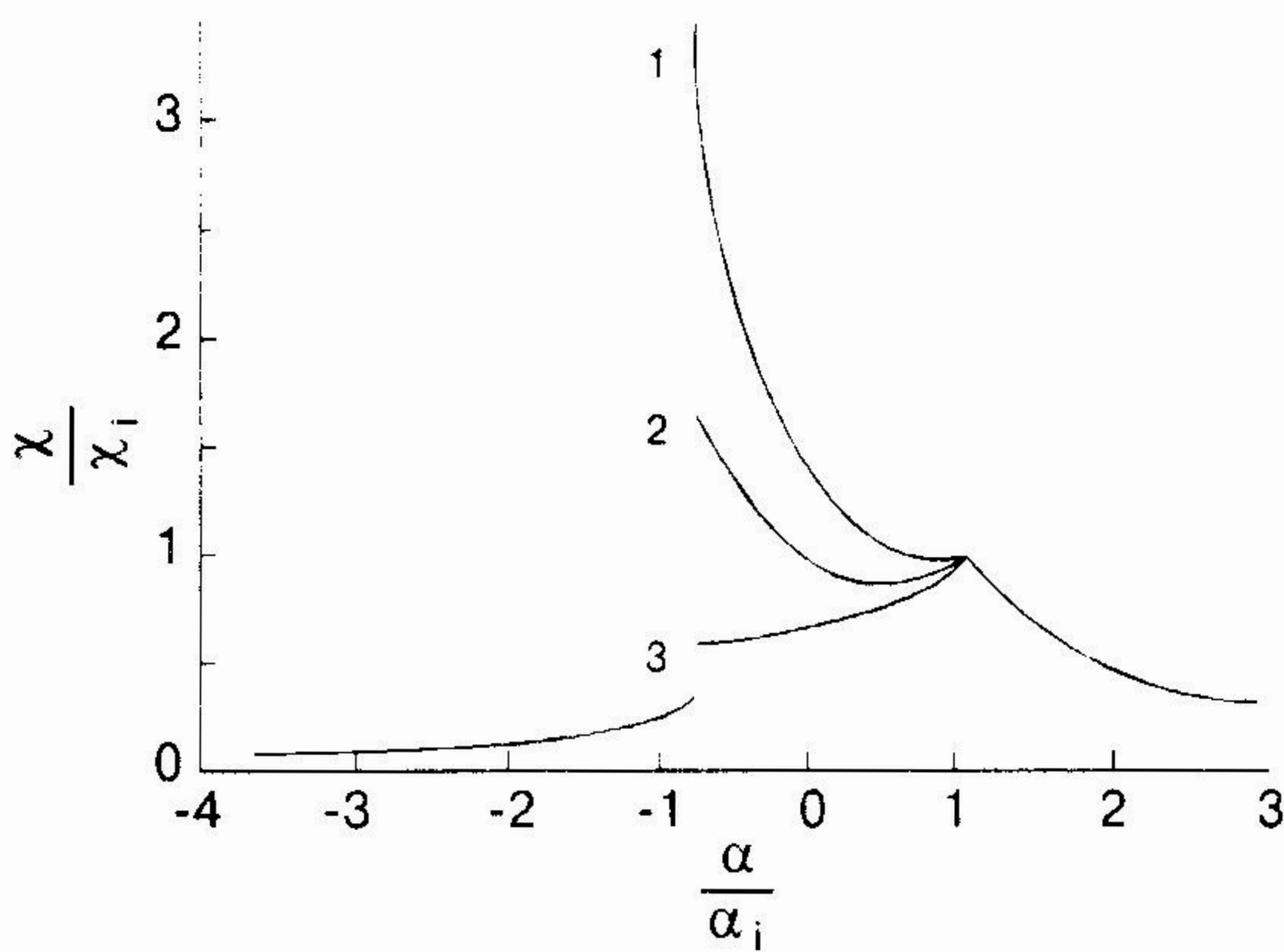
Fig. 1. The calculated temperature dependence of dielectric susceptibility relative value by relation (10,12,14) for $Sn_2P_2Se_6$ crystal at different conditions: 1- high harmonics $P_{2k}P_{-2k}$ are take into account but energy "gap" Δ =0; 2- $P_{2k}P_{-2k} \neq 0$, $\Delta \neq 0$; 3-P_{2k} $P_{-2k}=0$, $\Delta=0$. For all cases $\gamma=0$.
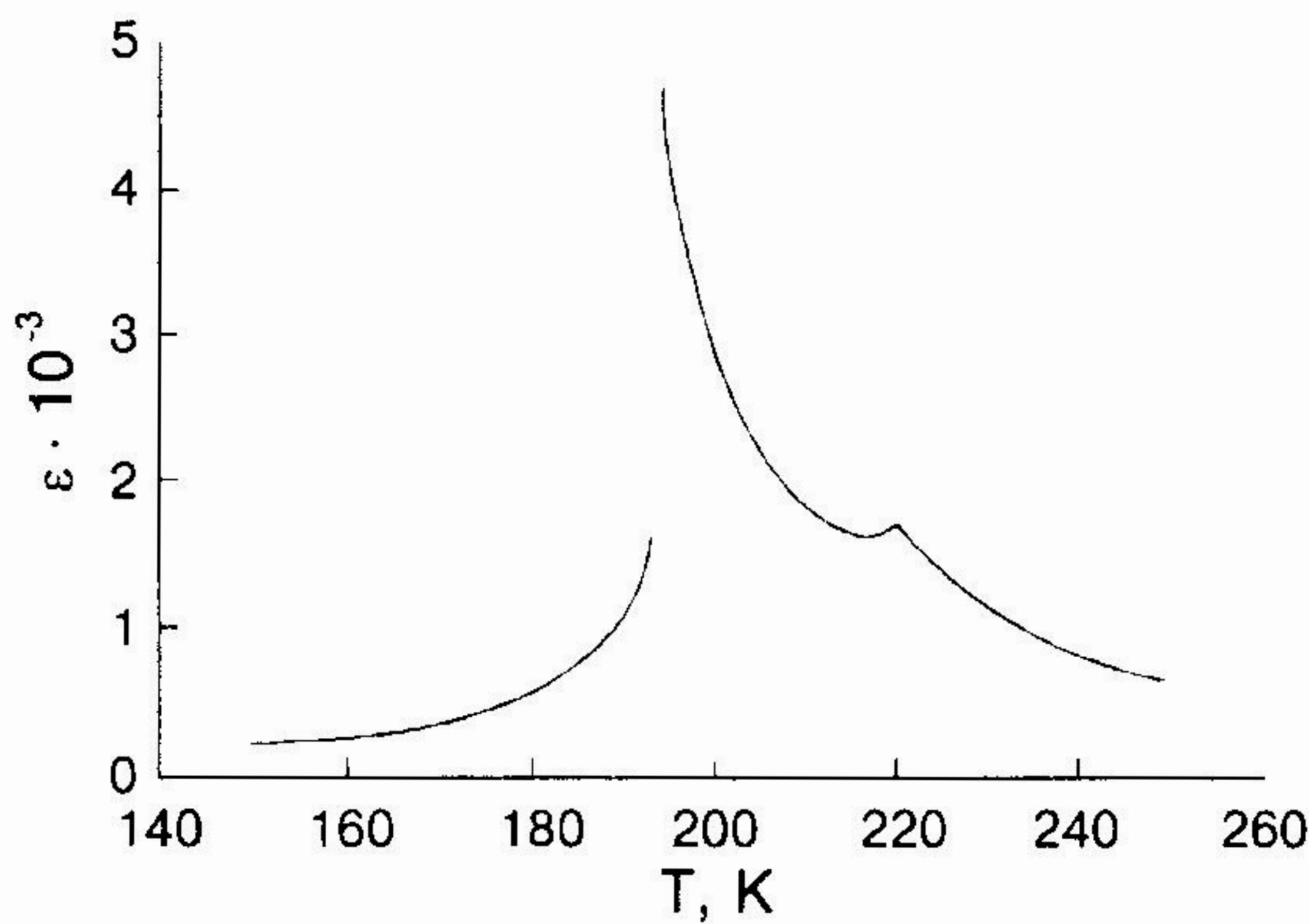
Fig. 2. The calculated-by relation (14)- temperature dependence of dielectric constant for $Sn_2P_2Se_6$ crystal at $P_{2k}P_{-2k} \neq 0$; $\Delta \neq 0$.

reveal a minimum. The lack of this minimum in the measured dependence's (fig.3,b) may result from a slight nonlinearity of concentrational dependence's of the thermodynamical potential coefficients. This discrepancy can also be attributed to the defectness of the mixed crystal structure.
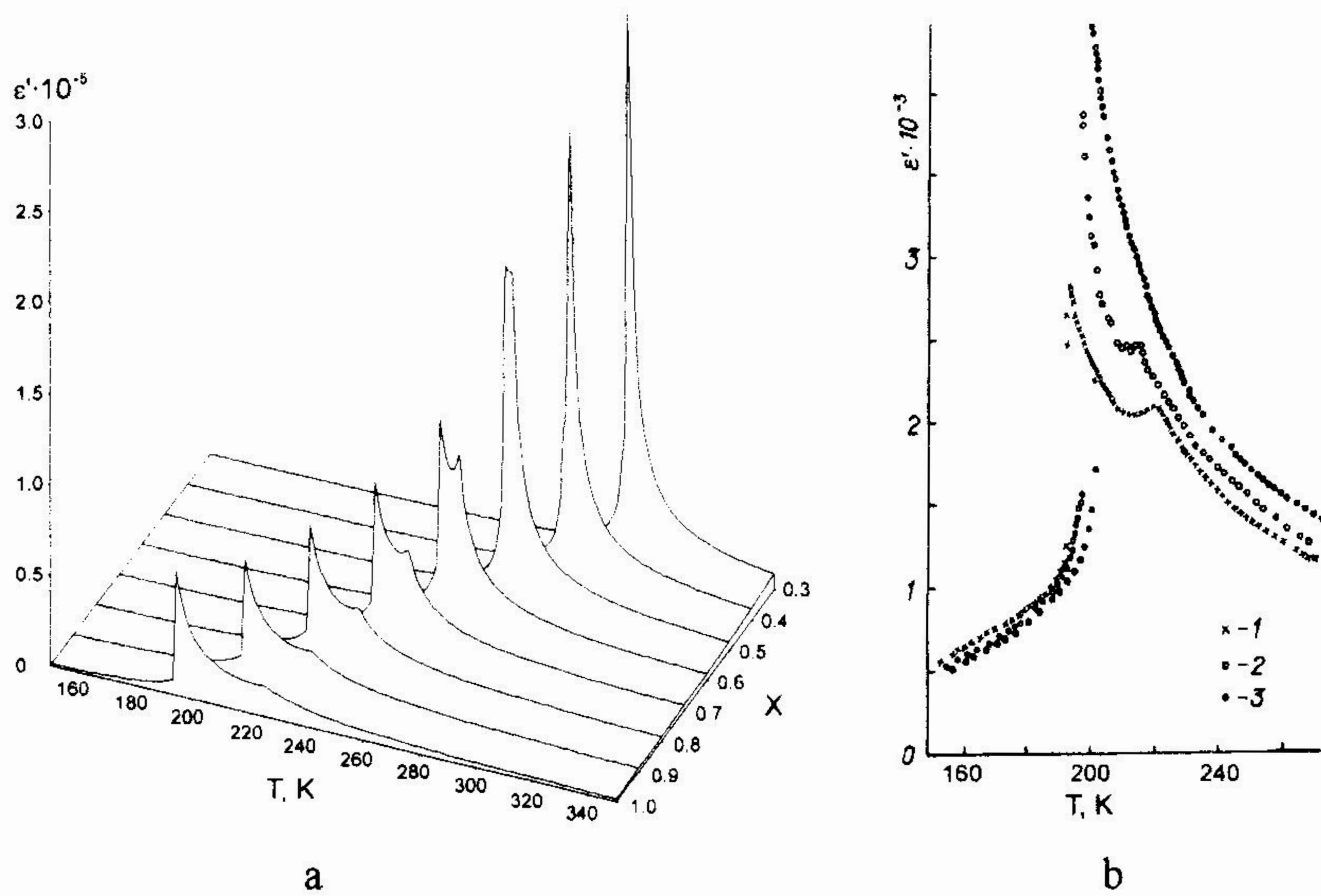
Fig.3. a - the calculated by relation (14) concentrational evolution of dielectric constant temperature dependence for $Sn_2P_2(Se_xS_{1-x})_6$ crystals. The conditions are the same as on Fig.2; b - The dielectric constant temperature dependencies for $Sn_2P_2(Se_xS_{1-x})_6$ crystals. x=1-1; 0.9-2; 0.8-3 [5].

Conclusion

In the mean-field approximation , assuming the linear concentrational dependence of the thermodynamical potential 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 $Sn_2P_2(Se_xS_{1-x})_6$ ferroelectrics the anomalies of the temperature dependencies of the dielectric susceptibility 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 $x>x_{LP}$) are satisfactorily described. But, at the same time some descriptions exist at quantitative comparance of calculated and experimental data for the temperature dependencies of heat capacity, amplitude and wave vector of modulation [7]. 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 interaction in the vicinity of T_c appears to be essential [8].

Acknowledgments

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