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The second order phase transition in $Sn_2P_2S_6$ crystals: anharmonic oscillator model

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Statistical theory for ferroelectrics based on triple well anharmonic potential was used for the case of structural second order phase transition in $Sn_2P_2S_6$ crystals. Parameters of effective Hamiltonian of the model were estimated using available experimental data. These findings confirm the assumption that the phase transition in these crystals is located in crossover region between order-disorder and displacive type, and very closely to tricritical point.

Key words: *statistical theory, anharmonic oscillator, triple well potential, ferroelctric phase transition*

PACS: *63.70.+h, 77.80.Bh, 78.20.Bh*

1. Introduction

$Sn_2P_2S_6$ crystals are well known ferroelectrics with a variety of different interesting physical properties [1]. One of the open questions concerning this material is the nature of continuous structural phase transition (PT) at Curie point $T_C \approx 337$ K. Analysis of a set of experimental data lets us make an assumption that this PT is located in a crossover region between PT of order-disorder and displacive type [2]. Moreover, the temperature anomalies of thermodynamic functions and their concentration behavior along the phase diagram of $Sn_2P_2(Se_xS_{1-x})_6$ mixed crystals indicate that PT in pure $Sn_2P_2S_6$ crystals is very close to tricritical point [3,4]. There are a lot of experimental and theoretical works concerning the study of the origin of the PT in crystals under consideration. A part of them refers to lattice dynamics calculations. Rigid ion model was used firstly [5,6]. However, it was impossible to obtain correct symmetry assignment of soft optic mode in this model at lattice instability modelling. Then the polarizable ion models in different variations were applied [7,8]. The results of the latter calculations were found to be in good agreement with experimental and theoretical description of PT in $Sn_2P_2S_6$ crystals. Lattice dynamical instability of the paraelectric phase was modeled by charge transfer between tin and sulfur ions, and by changing the polarizabilities of the latter. The ferroelectric phase was stabilized by tin atom displacement from centrosymmetric positions and a partial reversal recharging. Analyzing the vector of displacement of a soft optic transverse mode (B_u-symmetry mode) and low-energy full symmetric modes (A_g-symmetry modes) the following results were noted. The best description of experimentally observed ions displacement at PT from paraelectric to ferroelectric phase was found using not only soft mode eigenvector but also eigenvectors of a few A_g-modes. It follows that there is a more complex soft vibration responsible for PT. The recent *ab initio* calculations [9] confirm this. The potential energy has a minimum at nonzero displacement (with coexistence of zero-displacement minimum) by taking into account not only polar but also full symmetric vibrations. These facts let us assume that Hamiltonian as a function of order parameter can be described by a triple well potential function.

On the other hand, there are experimental data that confirm this assumption. NMR spectroscopy [10] showed the existence of resonances of paraelectric phase in the ferroelectric phase which are related to centrosymmetrical elementary cells. They are placed in the middle of domain walls in the ferroelectric phase of $Sn_2P_2S_6$. According to dielectric investigations [11] a relaxational

"freezing" process occurs at low temperatures (near 60 K), which is related to the rearrangement of the domain walls at cooling and is described by molecular-dynamic simulations based on the triple well potential.

One of the most well-known statistical theories for ferroelectrics which deals with a triple well potential was developed and applied for $LiTaO_3$ and $LiNbO_3$ crystals by Lines in a series of papers [12–15]. The effective Hamiltonian in this model depends on six temperature independent parameters. The relation between these parameters determines the order and type of PT, and, consequently, the temperature behavior of different physical properties. Following this theory lets us try to analyze the PT in $Sn_2P_2S_6$ crystals.

2. Short description of the model

A "single-mode" approximation is applied in the model. In this approximation we consider a system which has only one strongly temperature-dependent mode. In such a case the effective Hamiltonian can be written as follows:

$$vH_{\text{eff}} = \frac{1}{2}\left(\pi^2 + \omega_0^2\xi^2\right) + A\xi^4 + B\xi^6 - \eta S\xi\left(E + \gamma\langle P_{\text{ion}}\rangle\right), \tag{1}$$

where v is the volume of unit cell; π and ξ are the conjugate coordinates; ω_0, A, B, η, γ, S are the model parameters; E is the external electric field; $\langle P_{\text{ion}}\rangle$ is the ionic polarization. The statistical estimates of different values can be calculated using (1). For example, Curie temperature and ionic polarization as a function of temperature have the following form [12–15]:

$$kT_{\text{C}} = \frac{\eta\gamma S^2}{v}\int\limits_{-\infty}^{\infty}\xi^2 \mathrm{e}^{-U/kT_{\text{C}}}\mathrm{d}\xi \Big/ \int\limits_{-\infty}^{\infty}\mathrm{e}^{-U/kT_{\text{C}}}\mathrm{d}\xi, \qquad E = 0, \tag{2}$$

$$\langle P_{\text{ion}}\rangle = \frac{S}{v}\int\limits_{-\infty}^{\infty}\xi \mathrm{e}^{-V/kT}\mathrm{d}\xi \Big/ \int\limits_{-\infty}^{\infty}\mathrm{e}^{-V/kT}\mathrm{d}\xi, \tag{3}$$

where k is the Boltzmann constant, T is the temperature and

$$U = \frac{1}{2}\omega_0^2\xi^2 + A\xi^4 + B\xi^6, \tag{4}$$

$$V = U - \eta S\xi(E + \gamma\langle P_{\text{ion}}\rangle). \tag{5}$$

The A–parameter in potential (1) can be positive as well as negative. It should be noted that a negative value for the coefficient A does not necessarily lead to a first order PT as it was shown in [12]. Below, we will deal only with the negative-A case. In such a case the system is most conveniently described in terms of temperature independent ratios $\beta'/\alpha' = \omega_0^2/(\eta\gamma S^2/v)$, and $(\beta')^{1/2}/\delta = -A/(B\eta\gamma S^2/v)^{1/2}$, where dimensionless parameters α', β' and δ are defined by

$$\alpha' = \frac{(Bk^2T^2)^{1/3}}{\omega_0^2}, \qquad \beta' = \frac{(Bk^2T^2)^{1/3}}{(\eta\gamma S^2/v)}, \qquad \delta = \frac{(B^2kT)^{1/3}}{-A}. \tag{6}$$

The boundary lines that indicate the changes in the ferroelectric properties of the systems in terms of the mentioned parameters are as follows:

$$\begin{aligned}
\frac{\beta'}{\alpha'} &= 1 + \frac{2}{3}\frac{\beta'}{\delta^2} \quad \text{— ferroelectric vs non-ferroelectric boundary,}\\
\frac{\beta'}{\alpha'} &= 1 + \frac{2}{5}\frac{\beta'}{\delta^2} \quad \text{— first order vs second order boundary,}\\
\frac{\beta'}{\alpha'} &= \frac{1}{2}\frac{\beta'}{\delta^2} \quad \text{— order-disorder vs displacive type boundary,}\\
\frac{\beta'}{\alpha'} &= \frac{2}{3}\frac{\beta'}{\delta^2} \quad \text{— } \omega(T_{\text{C}}) = 0 \text{ vs } \omega(T_{\text{C}}) \neq 0 \text{ for displacive type region boundary,}
\end{aligned} \tag{7}$$

where $\omega(T_{\text{C}})$ is the soft mode frequency at Curie temperature.

3. Determination of the model parameters for $Sn_2P_2S_6$ crystals

3.1. Spontaneous polarization as a function of temperature

The direct measurements of spontaneous polarization as a function of temperature using pyroelectric and hysteresis loop technique have been reported [1]. However, the observed temperature dependence of spontaneous polarization does not represent the order parameter behavior correctly. The reason is that part of the domain cannot be switched by external field. The temperature dependence of the order parameter can be more accurately determined from optical experiments, particularly, from birefringence studies [16]. So, we use these data in our calculations (see figure 1).

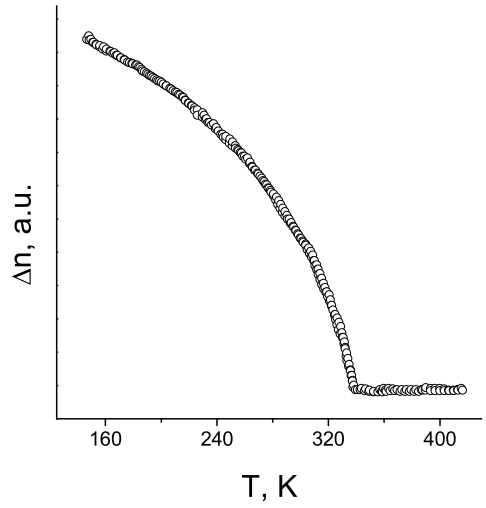

Figure 1. The temperature dependence of anomalous part of birefringence in $Sn_2P_2S_6$ crystals [16].

In terms of dimensionless variable (6), equations (2) and (3) transform to

$$\beta'_{\mathrm{C}} = \int_{-\infty}^{\infty} y^2 \exp\left(-\frac{y^2}{2\alpha'_{\mathrm{C}}} + \frac{y^4}{\delta_{\mathrm{C}}} - y^6\right) \mathrm{d}y \Bigg/ \int_{-\infty}^{\infty} \exp\left(-\frac{y^2}{2\alpha'_{\mathrm{C}}} + \frac{y^4}{\delta_{\mathrm{C}}} - y^6\right) \mathrm{d}y, \tag{8}$$

$$\Gamma' = \int_{-\infty}^{\infty} y \exp\left(-\frac{y^2}{2\alpha'} + \frac{y^4}{\delta} - y^6 + \frac{\Gamma' y}{\beta'}\right) \mathrm{d}y \Bigg/ \int_{-\infty}^{\infty} \exp\left(-\frac{y^2}{2\alpha'} + \frac{y^4}{\delta} - y^6 + \frac{\Gamma' y}{\beta'}\right) \mathrm{d}y, \tag{9}$$

where $\Gamma' = (v/S)(B/kT)^{1/6}\langle P_{\mathrm{ion}}\rangle$, and index C refers to the case $T = T_{\mathrm{C}}$.

In figure 2 we present the results of calculations of reduced polarization P/P_0 (P_0 is the polarization at $T = 0$) as a function of reduced temperature T/T_{C}. This curve was calculated for the particular case $\beta'/\alpha' = 1$ and $(\beta')^{1/2}/\delta \approx 0.87$ as a best fit for experimental data. The same good agreement has been obtained at different values of β'/α' ratio. So we can draw a set of curves P/P_0 versus T/T_{C} which corresponds to the set of β'/α' and $(\beta')^{1/2}/\delta$ ratios and which satisfies the experiments at the same time. A corresponding curve for β'/α' and $(\beta')^{1/2}/\delta$ ratios are shown in figure 3.

In the same manner, the line which corresponds to the Curie temperature was obtained using (8), as well as it was drawn in figure 3.

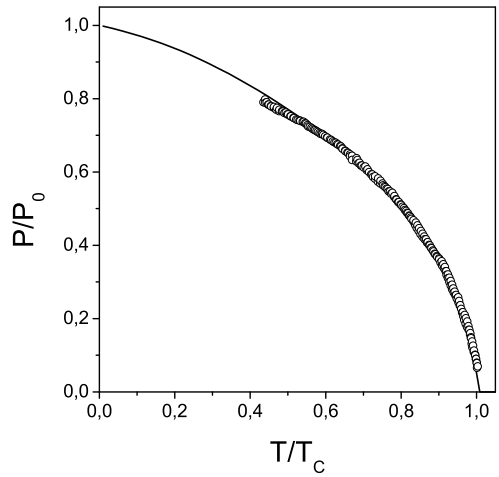

Figure 2. The calculated temperature dependence of reduced polarization as a function of reduced temperature in $Sn_2P_2S_6$ crystals (lines) compared with experimental data (circles).

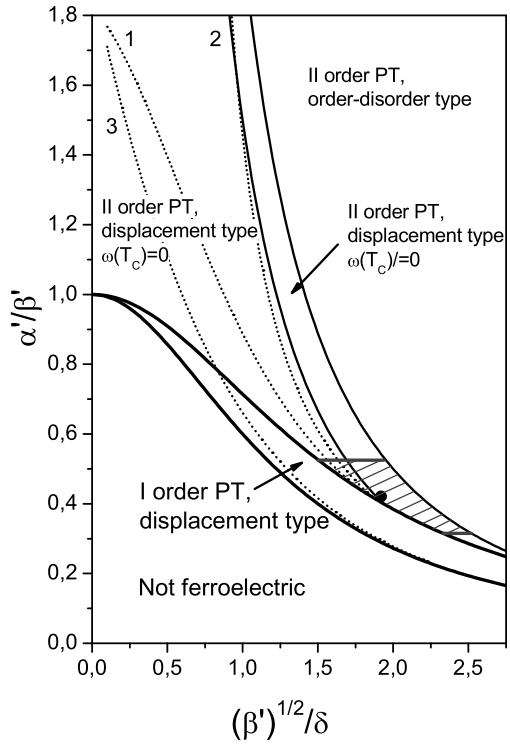

Figure 3. A number of curves (dotted lines) that correspond to the behavior of different physical quantities are compared on β'/α'–$(\beta')^{1/2}/\delta$ phase diagram: (1) — temperature dependence of spontaneous polarization; (2) — Curie temperature; (3) - soft mode frequency at $T \to 0$; the filled circle — soft mode frequency at $T \to T_C$. Shaded area contains the region of β'/α' and $(\beta')^{1/2}/\delta$ ratios where their values can be placed. The solid lines separate the regions which are determined by conditions (7).

3.2. Dielectric constant

The dielectric properties of $Sn_2P_2S_6$ crystals were investigated in a series of works [17,18]. Using a representation of dielectric constant by means of damping oscillators, one can find its frequency dependence as follows:

$$\epsilon = \epsilon_\infty + \sum_j \frac{f_j \Omega_j^2}{\Omega_j^2 - \omega^2 + \mathrm{i}\omega\gamma_j}\,, \tag{10}$$

where f_j, Ω_j, γ_j are the strength, frequency and linewidth of the jth infrared-active mode, respectively. In [1] we have find that the oscillator strength of soft mode is about 100 at room temperature. Approaching the Curie point, the Curie-Weiss law is satisfied. Since Curie-Weiss constant varies significantly in the ferroelectric phase, we use its value only in paraelectric phase. So, we can write

$$\epsilon_{\mathrm{para}} = \frac{0.67 \cdot 10^5\ K}{T - T_{\mathrm{C}}}\,. \tag{11}$$

From the theory we have

$$\epsilon_{\mathrm{para}} = \frac{4\pi\eta'}{\gamma}\frac{T_{\mathrm{C}}}{T - T_{\mathrm{C}}}\frac{1}{\Phi_p}\,, \tag{12}$$

where $\eta' = \langle P\rangle/\langle P_{\mathrm{ion}}\rangle$ is the ratio that controls the part of ionic polarization in the total polarization, $\Phi_p = (2/3 - \mu')$, and μ' is defined as a function of β'_{C} at $T \to T_{\mathrm{C}}$ as follows:

$$\begin{aligned} \langle y^2\rangle_0 &= \beta'_{\mathrm{C}}\left[1 + \mu'(T - T_{\mathrm{C}})/T_{\mathrm{C}}\right], \\ \langle y^2\rangle_0 &= \int_{-\infty}^{\infty} y^2 \exp(-\frac{y^2}{2\alpha'} + \frac{y^4}{\delta} - y^6)\mathrm{d}y \Big/ \int_{-\infty}^{\infty} \exp(-\frac{y^2}{2\alpha'} + \frac{y^4}{\delta} - y^6)\mathrm{d}y. \end{aligned} \tag{13}$$

Using (11) and (12) one can deduce:

$$\frac{\eta'}{\gamma} = 15.8\left(\frac{2}{3} - \mu'\right). \tag{14}$$

3.3. Soft mode frequency

The theory [13] gives a rather complex relation for determination of $\omega = \omega(T)$ dependency of soft mode. However, we have two special cases, where an immense simplification can be reached. It is a low-temperature limit ($T \to 0$) and the vicinity of the Curie point ($T \to T_{\mathrm{C}}$).

3.3.1. Low-temperature limit

The temperature dependence of soft mode frequency in ferroelectric phase of $Sn_2P_2S_6$ crystals was investigated using Raman spectroscopy method in [19,20]. According to these data, the soft mode has a frequency of about 42 cm^{-1} at $T \to 0$, and decreases to 27 cm^{-1} at $T = 300$ K. Using these data one can obtain the following relation [14]

$$\frac{\omega^2(0)}{\omega_0^2} = \frac{\omega^2(0)}{\omega^2(300)}\frac{4\pi}{f}\frac{\eta'}{\gamma}\frac{\alpha'}{\beta'}\,, \tag{15}$$

where f is the oscillator strength of the soft mode at $T = 300$ K, and the ratio η'/γ was defined in (14). On the other hand, it can be shown that there is another relation concerning $\omega(0)$ frequency

$$\omega^2(0) = \omega_0^2 + 12A\xi_0^2 + 30B\xi_0^4 - (\eta\gamma S^2/v), \tag{16}$$

where $\xi_0^2 = 1/(6B)(-2A + \sqrt{4A^2 + 6B[(\eta\gamma S^2/v) - \omega_0^2]})$. The equations (15) and (16) make it possible to obtain another relation between β'/α' and $(\beta')^{1/2}/\delta$ ratios. This curve is also present in figure 3. The left side of equation (15) can be expressed in the terms of these ratios using (16). The ratio $\omega^2(0)/\omega^2(300)$ in the right side of equation (15) can be calculated directly using the experimental values of corresponding frequencies.

3.3.2. Near the Curie point

For temperatures $T \to T_{\mathrm{C}}$ the theory [13] gives the following relation between soft mode frequency ω and temperature T

$$\frac{k(T-T_{\mathrm{C}})\Phi}{(\eta\gamma S^2/v)} \approx \Delta + \int \sum_{n=1}^{\infty} \frac{2\omega^2}{n^2\omega_H^2 - \omega^2} f_{\mathrm{eq}} |\xi_n|^2 \mathrm{d}H, \tag{17}$$

where

$$f_{\mathrm{eq}} = \exp\left(\frac{-H_{\mathrm{eq}}}{kT}\right) \Big/ \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp\left(\frac{-H_{\mathrm{eq}}}{kT}\right) \mathrm{d}\pi \mathrm{d}\xi, \tag{18}$$

and H_{eq} is the equilibrium value of Hamiltonian (1); Φ takes on values $(2/3-\mu')$ and $-2(2/3-\mu')$ in the paraelectric and ferroelectric phases, respectively; Δ is the paraelectric value of $\int f_{\mathrm{eq}}|\xi_0|^2\mathrm{d}H$; ξ_0 and ξ_1 are the coefficient of ξ expansion as a periodic function of the angle variable θ (θ and H are the new canonical variables against ξ and π);

$$\xi = \sum_n \exp(-\mathrm{i}n\omega_H\theta). \tag{19}$$

So, the soft mode frequency behavior at $T \to T_{\mathrm{C}}$, reduces to determination of $\xi_0(H)$, $\xi_1(H)$ and ω_H. These values can be calculated by solving a classical mechanical problem of motion in a potential $U(\xi)$ (4). The exact solutions of such an equation of motion turn out to be Weierstrass's functions [21].

It should be noted that there are two types of $\omega = \omega(T)$ dependency at $T \to T_{\mathrm{C}}$. If $\Delta = 0$ in (17) we find $\omega(T_{\mathrm{C}}) = 0$ (small anharmonicity range) against the case of $\Delta \neq 0$, where $\omega(T_{\mathrm{C}}) \neq 0$ (strong anharmonicity). The latter occurred in $Sn_2P_2S_6$ crystals ($\omega(T_{\mathrm{C}}) \approx 10$ cm^{-1}) [19]. Using all these facts we numerically calculate the equation (17) and find that it is satisfied at $\beta'/\alpha' \approx 2.38$ and $(\beta')^{1/2}/\delta \approx 1.92$ (point in figure 3).

Let us return to figure 3. In this figure, we select some region where we believe the parameters for $Sn_2P_2S_6$ crystals can be really found. This region was formed due to an inaccuracy of the experimental data, errors in numerical calculations and in some model approximations. On the other hand, the region is restricted by lines which determine the type and order of PT (experimentally we know that PT in $Sn_2P_2S_6$ crystals is second order). Our findings together with some other experimental data allow us to determine all the parameters of the effective Hamiltonian (1) and to analyze more qualitatively the origin of PT which will be the aim of a next paper.

4. Conclusion

Following the model developed in [12–14] it was shown that the PT of second order in $Sn_2P_2S_6$ ferroelectric crystals can be described using the triple well anharmonic potential function for an order parameter. The absolute values of the model parameters indicate that this PT is located in crossover region on the phase diagramme between order-disorder and displacive type of PT, and very close to the line of tricritical points.

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References

1. Vysochanskii Yu.M., Janssen T., Currat R., Folk R., Banys J., Grigas J., Samulionis V. Phase transitions in phosphorous chalcogenide ferroelectrics. Vilnius University Publishing House, Vilnius, 2006.
2. Hlinka J., Janssen T., Dvorak V., J. Phys.: Condens. Matter, 1999, **11**, 3209.
3. Khoma M.M., Molnar A.A., Vysochanskii Yu.M., J. Phys. Studies, 1998, **2**, 524.
4. Vysochanskii Yu.M., et al., Sov. Phys. JETP, 1989, **45**, 1355.
5. Grabar A.A., Vysochanskii Yu.M., Slivka V.Yu., Fiz. Tverd. Tela (Leningrad) [Sov. Phys. Solid State], 1984, **26**, 3086 (in Russian).
6. Rizak V.M., Grabar A.A., Vysochanskii Yu.M., Slivka V.Yu., Fiz. Tverd. Tela (Leningrad) [Sov. Phys. Solid State], 1989, **31**, 154 (in Russian).
7. Smirnov M.B., Hlinka J., Solov'ev A.V., Phys. Rev. B, 2000, **61**, 15051.
8. Yevych R.M., Vysochanskii Yu.M., Khoma M.M., Perechinskii S.I., J. Phys.: Condens. Matter, 2006, **6**, 315.
9. Rushchanskii K.Z., Vysochanskii Yu.M., Strauch D., Phys. Rev. Lett., 2007, **99**, 207601–1.
10. Apperley D.C., Harris R.K., Cleary D.A., Chem. Mater., 1993, **5**, 1772.
11. Iwata M., et al., J. Phys. Soc. Jpn., 1998, **67**, 499.
12. Lines M.E., Phys. Rev., 1969, **177**, 797.
13. Lines M.E., Phys. Rev., 1969, **177**, 812.
14. Lines M.E., Phys. Rev., 1969, **177**, 819.
15. Lines M.E., Phys. Rev. B, 1970, **2**, 698.
16. Vysochanskii Yu.M., et al., Ferroelectrics, 2000, **(**237), 193.
17. Grigas J., Kalesinskas V., Lapinskas S., Gurzan M.I., Phase Transitions, 1988, **12**, 263.
18. Volkov A.A., et al., Fiz. Tverd. Tela (Leningrad) [Sov. Phys. Solid State], 1983, **25**, 2575 (in Russian).
19. Bokotei A.A., et al., Ukr. Fiz. Zh., 1997, **42**, 55 (in Ukrainian).
20. Hlinka J., Gregora I., Vorlicek V., Phys. Rev. B, 2002, **65**, 1.
21. Khare A., Behera S.N., Pramana, 1980, **14**, 327.

Фазовий перехід другого роду в кристалах $Sn_2P_2S_6$: модель ангармонічного осцилятора

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Статистична теорія для сеґнетоелектриків, що базується на трьохямному ангармонічному потенціалі, використана для випадку структурного фазового переходу другого роду в кристалах $Sn_2P_2S_6$. Параметри ефективного гамільтоніану моделі оцінені використовуючи наявні експериментальні дані. Встановлено, що фазовий перехід в цих кристалах розташований в кроссоверній області між фазовими переходами типу "лад-безлад" та типу зміщення, а також близько до трикритичної точки.

Ключові слова: *статистична теорія, ангармонічний осцилятор, трьохямний потенціал, сеґнетоелектричний фазовий перехід*

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