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Dipole models of proper ferroelectrics $NaNO_2$ and $Sn(Pb)_2P_2S(Se)_6$

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We consider a $NaNO_2$ crystal as to the peculiarities of Ising dipole models of ferroelectic crystals. The models with the local field of a macroscopic sample and without this field were considered. A dipole Ising model of $Sn_2P_2S(Se)_6$ ferroelectics has been developed. As a result of the calculations done by the Monte-Carlo method it has been found that when a certain short-range interaction coefficient in $Sn_2P_2S_6$ is selected, the intermediate modulated phase disappears in a model with the local field. In this case the temperatures of phase transitions (PT) are as follows: for the $Sn_2P_2S_6$ model $T_o^* \sim 10.5$; for the $Sn_2P_2Se_6$ model $T_c^* \sim 8.5$, $T_i^* \sim 9.5$ (in effective temperatures). These data are in satisfactory agreement with the results of the real experiment. The concentration dependences of temperatures of PT in $Sn_2P_2(S_xSe_{1-x})_6$ crystals are simulated and the Lifshitz point is observed. In mixed $(Pb_ySn_{1-y})_2P_2S_6$ and $(Pb_ySn_{1-y})_2P_2Se_6$ crystals the increase of Pb concentration causes reduction of temperatures of PT to 0 K. In this case the character of PT remains unchanged. By the method of the diluted Ising lattice the concentration dependences of temperatures of PT in these crystals are simulated.

Key words: *ferroelectrics, phase transition, Monte-Carlo procedure, Ising lattice*

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1. Introduction

There are two reasons for our interest in the crystals of the $Sn(Pb)_2P_2S(Se)_6$ system: first, on the temperature-concentration diagram for $Sn_2P_2(Se_xS_{1-x})_6$ solid solutions the Lifshitz point is reached – a proper ferroelectric PT of the second order (for $Sn_2P_2S_6$ To$\sim$337K) at x>0.28 splits into the second and the first order transitions that limit the incommensurate (IC) phase (for $Sn_2P_2Se_6$ $T_i \sim 221$K, $T_c \sim 193$K) (figure 1) [1]. The modulation period of a spontaneous polarization in the IC phase equals 12-15 primitive cells [2]. The second point of interest is that with the substitution of Sn for Pb the PT temperature in sulphide and selenide series of the solid solutions decreases, the character of transitions remaining unchanged. For $(Pb_ySn_{1-y})_2P_2S_6$ the T_0(y) line reaches 0 K at y$\sim$0.61 and for $(Pb_ySn_{1-y})_2P_2Se_6$ the T_i(y) and T_c(y) lines reach 0K at y$\sim$0.4 and 0.64, respectively [3].

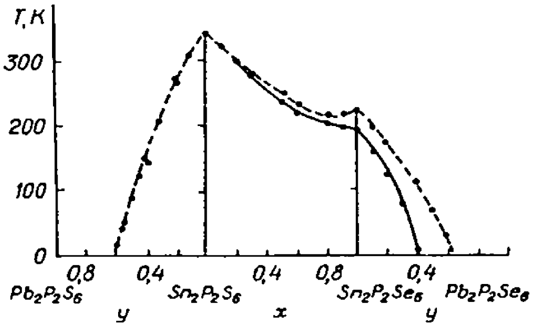

Figure 1. Concentrational dependences of the temperatures of the second (dotted line) and first (solid line) - order phase transitions in mixed $Sn_2P_2(Se_xS_{1-x})_6$, $(Pb_ySn_{1-y})_2P_2S_6$ and $(Pb_ySn_{1-y})_2P_2Se_6$ crystals.

According to inelastic neutron scattering data [4] in $Sn_2P_2S_6$ and $Sn_2P_2Se_6$ compounds an interaction between soft optic and acoustic modes plays an important role for the IC phase stabilization in the solid solutions $Sn_2P_2(Se_xS_{1-x})_6$ with x>0.28. Structure investigations also support the based on the results of dynamic calculations [5] conclusion about the increase of short-range interactions of ions and the variation of these interactions effective values at the substitution of sulfur by selenium in the above mentioned compounds. A remarkable improvement of the lone pair Sn-Se stereoactivity in the case of $Sn_2P_2Se_6$ is also discussed in [6]. In $Sn_2P_2S(Se)_6$ ferroelectrics mainly displacive transitions occur, but order- disorder effects are also observed. For example, the temperature behaviour of high frequency optic modes in the Raman spectra of $Sn_2P_2S_6$ indicates that the $(P_2S_6)^{4-}$ anions do not become centrosymmetric just above T_0 in the paraelectric phase [7]. The Raman and Brillouin scatterings [7,8], infrared spectroscopy [9] and inelastic neutron scattering [4] show for $Sn_2P_2S_6$ the evidences of soft optic mode coupling to a low frequency excitation or an order - disorder component in the neighbourhood of T_0. Also, specific heat measurements for $Sn_2P_2(Se_xS_{1-x})_6$ crystals [10] reveal a large transition entropy at the second order PT temperatures T_0 (x$\leqslant$0.28) and T_i (x$\geqslant$0.28) typical of the order-disorder transition. The most important evidence is that the refinement of the x-ray diffraction data for the paraelectric phase of a $Sn_2P_2Se_6$ crystal reveals a disorder of Sn^{2+} cations [11]. At cooling the tin ions shift from the individual disorder sites in the paraelectric phase to the corresponding tin positions in the ferroelectric phase. So, $Sn_2P_2S(Se)_6$ crystals permit us to study order- disorder effects in mainly displacive transitions.

It is interesting to compare the properties of $Sn_2P_2S(Se)_6$ ferroelectrics with a model system – ferroelectric crystals $NaNO_2$. Both the systems demonstrate the type II incommensurable (IC) phase, which appears in the case of the Lifshitz invariant absence in the thermodynamic potential [12]. At the same time in $NaNO_2$ a typical order-disorder critical dynamics is observed which is related to the rotational disorder of NO_2 molecules [13].

In this article we examine, by using the Monte-Carlo method, a dipole Ising model for uniaxial ferroelectrics on the example of a $NaNO_2$ crystal and then develop this model for ferroelectrics in the $Sn(Pb)_2P_2S(Se)_6$ system.

2. Model calculations and their analysis

The classical method of building an Ising model with the dipole long-range interaction is as follows:

The parallelepiped-shape area is noted for the reflection of the dipole long-range interaction. It is called a Lorenz cavity. The interaction between the neighbouring dipoles inside this cavity is calculated exactly according to the dipole interaction formula. Interaction with other dipoles is approximately calculated, similarly to the Lorenz cavity in dielectric – by introduction of a local field [14]. Additional factor I, a correction for a short-range interaction, was introduced for better accordance with the real experiment. This correction takes into account other (except for the dipole) short-range forces: quadrupole, octupole, etc. [15].

The difference between the energy of the given dipole 0 in the initial state and the energy in the offered inverted state for the standard Monte-Carlo (MC) [14] procedure was calculated according to the formula:

$$\Delta U_{12} = 2m_o[(\mathbf{abc})\sum_j \mathbf{J}_{0j}m_j + \mathbf{I}\sum_n m_n + 2LP_0]/T^*, \tag{1}$$

$$\mathbf{J}_{0j} = (3\cos^2\theta_{0j} - 1)/r_{0j}^3 \tag{2}$$

where m_o, m_j, m_n $= +1/-1$ are Ising variables; r_{0j} – a distance between 0 and j dipoles; θ_{0j} – an angle between dipole axis a and radius-vector r_{0j}; P_0 – an average dipole polarization (calculated by averaging at a MC cell); L – a shape factor of the Lorenz cavity, for our case L-factors of crystals were calculated like in [16]. Here and further temperature is expressed in terms of effective temperature $T^* = \mathbf{abc}K_bT/M_0^2$, M_0 – the value of the effective dipole momentum.

We simulate a macroscopic sample as a limited Ising lattice with imposed periodical boundary conditions (a Monte-Carlo cell).

We consider a $NaNO_2$ crystal [13] as an example of such a method. The parameters of the $NaNO_2$ crystal body centered lattice are as follows: a=3.560A, b=5.563A, c=5.384A. Lorentz factor L = 3.04. The calculations were done on the MC cell with the dimensions 8*8*8 of the lattice periods and with the Lorentz void of 7*7*7 periods. The calculations were started from the initial ordered state and, as a result, the following sequence was obtained: a ferroelectric phase – a phase modulated along "a" – a paraelectric phase. The phase transition temperatures: $T_c^*\sim3.1$, $T_i^*\sim4.9$ (calculations were done with I=0). The period of a modulated structure is 4a.

The local field stabilizes an ordered structure in this model. Without this field a modulated structure even at temperatures close to 0K was obtained.. We can introduce order parameter W - the absolute polarization average in the plane of modulation. It was found that there appear two phase transitions depending on W(T*) (figure 2.): the first order transition at $T_c^* \sim 2.0$ from rectangular domain walls (ferroelectric phase) to the sinusoidal IC phase and the second order phase transition at $T_i^* \sim 4.8$ to the paraelectric phase. This dependance was obtained for the $NaNO_2$ model at I=0.

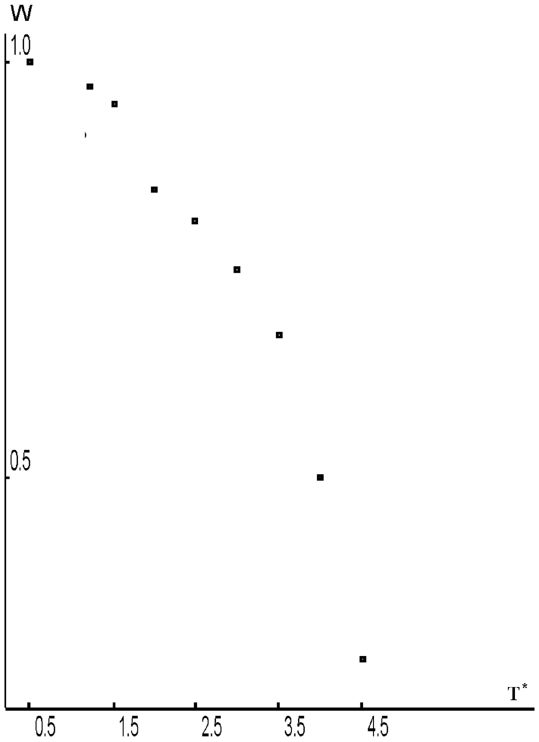

Figure 2. Temperature dependence of order parameter W for the $NaNO_2$ model without a local field.

Now we will consider a dipole model for ferroelectrics in the $Sn(Pb)_2P_2S(Se)_6$ system.

The last structure investigations testify in favour of the validity of the Ising model for the given crystals. They show that in $Sn_2P_2Se_6$ in a paraelectric phase each atom Sn has a pair of the most probable positions [11]. Besides, we suppose that the statistical approach to the calculation of the system state functions will allow us to eliminate peculiarities of the dynamic motion of single atoms. A ferroactive sublattice contains Sn cations. In the first approximation we can suggest that at PT they are shifting parallelly to the crystallographic axis “a” on equal distances. So it is natural to place four identical dipoles parallelly to axis “a” in the locations of four Sn atoms forming the Ising dipole model of those crystals. We use the classical method described earler. For $Sn_2P_2S_6$ L = 2.94, for $Sn_2P_2Se_6$ L = 2.80.

The main calculations were started from the initial ordered state (ferroelectric phase). The MC cell had the dimensions 16a*16b*16c and the Lorenz cavity had the dimensions 5a*5b*5c. The short-range interaction coefficient I was chosen for the best accordance with the real phase diagrams of both pure crystals $Sn_2P_2S_6$ and $Sn_2P_2Se_6$ and reached 1.1.

Phase transitions were calculated for the models of pure crystals $Sn_2P_2S_6$ and $Sn_2P_2Se_6$. Their characteristics were close to the real ones. There is a bend near to the point $T_0^* \sim 10.3$ on the dependence of the reduced internal energy per spin for $Sn_2P_2S_6$ and a maximum on the dependence of the specific heat (figure 3). So the model demonstrates a PT of the second order. There is a jump on the dependence of the reduced internal energy per spin near $T_c^* \sim 8.7$ for a $Sn_2P_2Se_6$ crystal and a break on the dependence of the specific heat. At temperature $T_i^* \sim 9.7$ the dependence of the reduced internal energy per spin has a bend and the dependence of the specific heat has a maximum (figure 4). Therefore, the model demonstrates consequent PT of the first and the second order. Besides that we received a relative width of the temperature range of the IC phase for crystal $Sn_2P_2Se_6$ in close accordance with the experimental data [1]. The period of the modulated structure was from 3c to 4c in calculations with the Lorenz cavity 5a*5b*5c. However, the following calculations show that at rather large dimensions of the Lorenz cavity the period of the phase modulation close to the experimentally observed one can be obtained. For example, for the Lorenz cavity 13*13*13 and MC cell 24*24*24 the calculated period of modulation was 8c-9c.

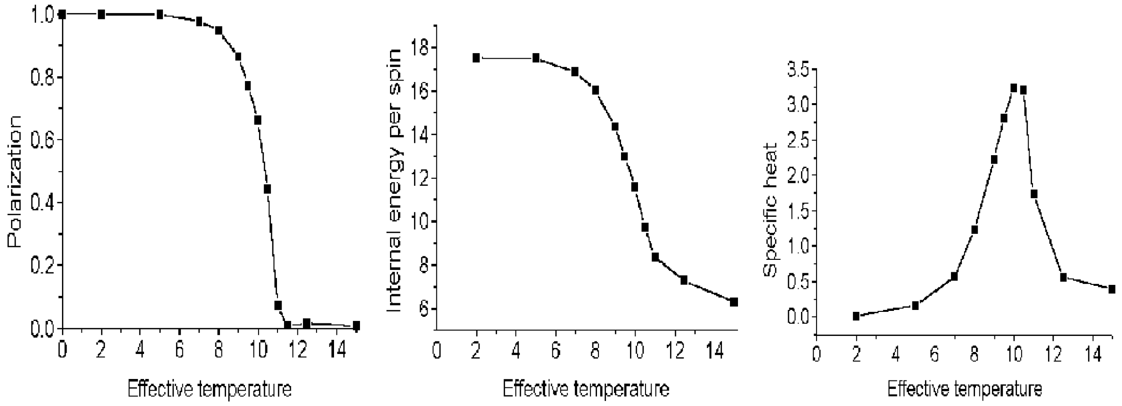

Figure 3. Temperature dependences of the functions of state for a $Sn_2P_2S_6$ crystal: 1 – polarization; 2 – internal energy per spin (dipole); 3 – specific heat.

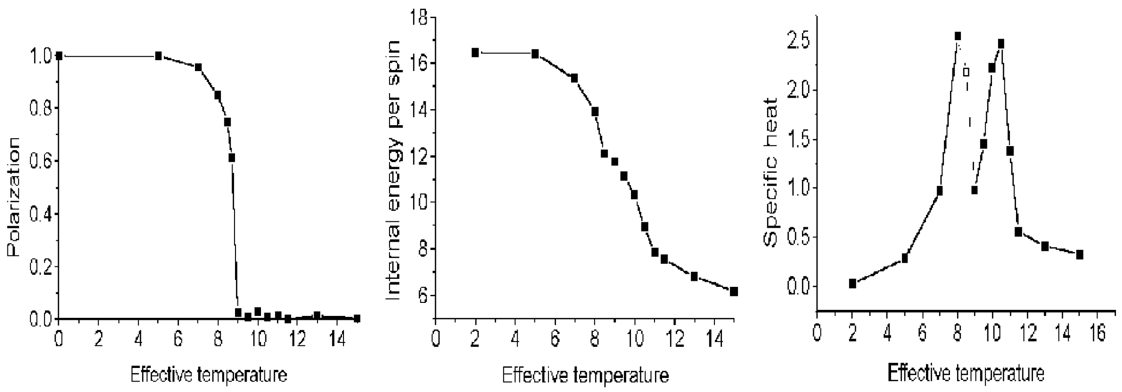

Figure 4. Temperature dependences of the functions of state for a $Sn_2P_2Se_6$ crystal. 1 – polarization; 2 – internal energy per spin (dipole); 3 – specific heat.

Supposing that the substitution of S atoms by Se atoms induces a linear variation of geometrical characteristics of the crystal lattice, we can easily obtain a model of mixed crystal $Sn_2P_2(S_xSe_{1-x})_6$. The phase diagram of such a model is shown in figure 5. The Lifshitz point can be observed at x∼0.27. This value is close to the experimental data.

Due to the fact that Pb atoms play the role of admixture with a null dipole momentum in mixed crystals $(Pb_ySn_{1-y})_2P_2S_6$ and $(Pb_ySn_{1-y})_2P_2Se_6$ we can build a diluted Ising model for them. We suggest the following method of dilution registration. All the neighbours of the given dipole, over which summation of the dipole and the short-range interacting part ΔU_{12} is done, are checked for the possibility of admixture with the probability WPb, and the local field is multiplied by (1-y). Phase diagrams for the both series of mixed crystals are represented in figure 5. Although we can note qualitative accordance with the real experiment, – T_0^* for $(Pb_ySn_{1-y})_2P_2S_6$, T_c^* and T_i^* for $(Pb_ySn_{1-y})_2P_2Se_6$ are decreasing proportionally to dilution – but we have been unable to reach quantitative accordance with the experiment: according to the data of the calculations $T_0^*(y) \to 0$ at y∼0.37, $T_c^*(y) \to 0$ at y∼0.29, $T_i^*(y) \to 0$ at y∼0.34.

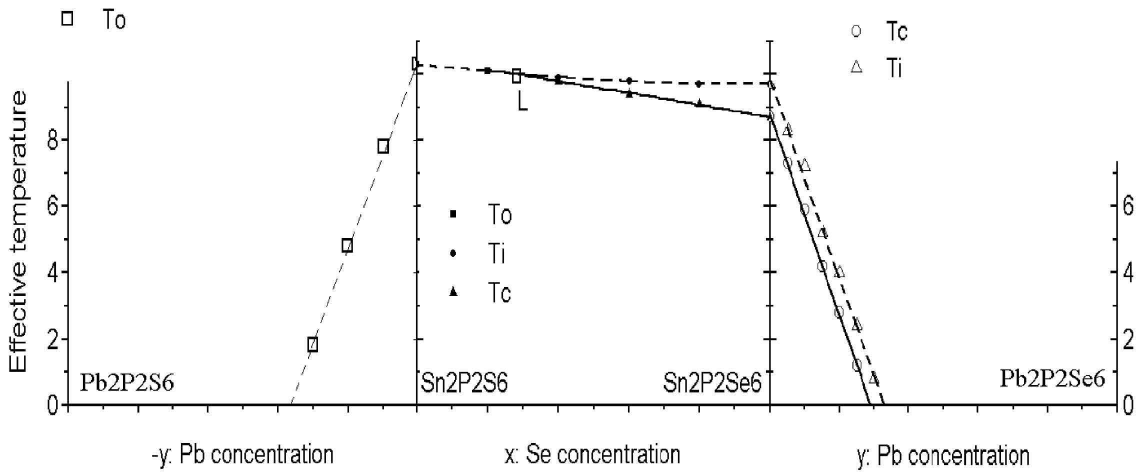

Figure 5. Phase diagram for $Sn_2P_2(Se_xS_{1-x})_6$, $(Pb_ySn_{1-y})_2P_2S_6$ and $(Pb_ySn_{1-y})_2P_2Se_6$ crystal models.

3. Conclusion

It can be noted that Ising dipole models are useful for the simulation of thermodynamical behaviour of proper ferroelectrics with the II order IC phase. For a simple $NaNO_2$ model we show an alternative method of simulation of phase transition from the ferroelectric phase to the modulated one – by introducing order parameter W, the absolute polarization average in the plane of modulation. A dipole Ising model of the $Sn_2P_2S_6$ family of ferroelectics has been developed. The resulting data of Monte-Carlo calculations are in satisfactory agreement with the results of the real experiment. The principal "moving force" of the changes of phase transitions in the considered models is the change of geometrical parameters of the model at constant short-range interactions. For a more realistic consideration we must take into account the dependence of a short-range parameter on the geometrical parameters of the model.

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Дипольні моделі власних сегнетоелектриків $NaNO_2$ та $Sn(Pb)_2P_2S(Se)_6$

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На прикладі кристалу $NaNO_2$ аналізуються ізінгівські дипольні моделі сегнетоелектричних кристалів з введенням локального поля макровзірця і без нього. Нами розроблена ізінгівська дипольна модель сегнетоелектриків сім'ї $Sn(Pb)_2P_2S(Se)_6$. Розрахунки методом Монте-Карло показали, що при виборі певного коефіцієнта короткодії можна отримати такі температурні границі фаз для "опорних" кристалів цієї сім'ї: $Sn_2P_2S_6$ – $T_0^* \sim 10.5$; $Sn_2P_2Se_6$ – $T_c^* \sim 8.5$, $T_i^* \sim 9.5$ (в приведених температурах), що кількісно узгоджується з даними експерименту. Точка Ліфшиця з координатою $x \sim 0.27$ спостерігається на концентраційних діаграмах в моделі змішаного кристалу $Sn_2P_2(S_xSe_{1-x})_6$, що узгоджується з реальними даними. Для змішаних кристалів типу $(Pb_ySn_{1-y})_2P_2S_6$ і $(Pb_ySn_{1-y})_2P_2Se_6$ атоми Pb відіграють роль домішок з нульовим дипольним моментом. Для цих кристалів застосовується розбавлена ізінгівська модель.

Ключові слова: *сегнетоелектрики, фазовий перехід, процедура Монте-Карло, решітка Ізинга*

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