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**MAGNETISM  
AND FERROELECTRICITY**

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## Statistical Mechanics of Cation Ordering in $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ and $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ Solid Solutions

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**Abstract**—A model Hamiltonian for  $B$  cation ordering (Sc–Nb(Ta)) in  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  and  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$  solid solutions is constructed. The parameters of the model Hamiltonian are determined from the *ab initio* calculation within the ionic crystal model with allowance made for the deformability and the dipole and quadrupole polarizabilities of the ions. The temperatures of the phase transition due to the ordering of the  $B$  cations are calculated by the Monte Carlo method in the mean-field and cluster approximations. The phase transition temperatures calculated by the Monte Carlo method (1920 K for  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$  and 1810 K for  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ ) are consistent with the experimental data (1770 and 1450 K, respectively). The thermodynamic properties of the cation ordering are investigated using the Monte Carlo method. © 2005 Pleiades Publishing, Inc.

1. Solid solutions of  $AB'_xB''_{1-x}\text{O}_3$  oxides with a perovskite structure have been continuing to attract the attention of researchers for several decades. The physical properties of these compounds have been investigated experimentally and theoretically. The  $AB'_xB''_{1-x}\text{O}_3$  solid solutions are of great interest from both the applied and scientific standpoints owing to their unusual electrical and mechanical properties [1–3], as well as to the interesting phenomena revealed in these compounds that have not been observed earlier in oxides with a perovskite structure [4, 5]. Among the large number of  $AB'_xB''_{1-x}\text{O}_3$  solid solutions, it is possible to distinguish an important class of so-called heterovalent alloys, i.e., solid solutions with  $B'$  and  $B''$  elements belonging to different groups of the periodic table.

The solid solutions  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$  (PST) and  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  (PSN), which belong to this class of compounds, have been intensively studied both experimentally and theoretically [6–10]. In particular, these compounds undergo phase transitions due to the ordering of  $B'$  and  $B''$  cations; in this case, the degree of ordering depends on the cooling rate [6]. In turn, the physical properties of these solid solutions (for example, the ferroelectric phase transition and its attendant anomalies observed in the electrical and mechanical properties) substantially depend on the degree of ordering of the  $B$  cations [1, 5].

The phase transitions associated with the  $\text{Sc}^{3+}\text{--Nb}^{5+}(\text{Ta}^{5+})$  ordering have been investigated theoretically by a number of researchers [7–10]. Bellaiche and Vanderbilt [7] studied an electrostatic model of atomic ordering with allowance made only for the Coulomb

interactions of excess (as compared to the average charge  $q = +4$ ) charges  $\Delta q = \pm 1$  localized at sites of a simple cubic lattice. The authors of [7] established that, within the model under consideration, the structure with  $\text{Sc}^{3+}\text{--Nb}^{5+}(\text{Ta}^{5+})$  ordering along the [111] spatial diagonal of the perovskite cell is energetically most favorable, which corresponds to the experimentally observed type of ordering. A somewhat changed electrostatic model that accounts for the probability of  $B$  cations jumping over the sites of the crystal lattice was investigated by Gao *et al.* [8] using the Monte Carlo method with the interaction constant serving as an adjustable parameter.

Burton and Cohen [9] considered  $B$  cation ordering in the  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$  compound within the cluster approximation. In this case, the interaction constants involved in the model Hamiltonian describing the cation ordering were obtained from the *ab initio* calculation of the energy of the crystal within the so-called potential-induced breathing (PIB) model, i.e., within the model of an ionic crystal with a spherical deformability of the ions. However, it is known that, in oxide compounds, the dipole and quadrupole distortions of the electron density have a substantial effect on the static and dynamic properties.

In this work, we investigated the phase transitions occurring in the  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  and  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$  solid solutions due to the ordering of scandium and niobium (tantalum) ions. For this purpose, we performed *ab initio* calculations within the ionic crystal model taking into account the dipole and quadrupole polarizabilities and the deformability of the ions. Then, we introduced a model Hamiltonian describing a phase transition of the order–disorder type in the system of a binary

alloy ( $B'/B''$ ). The parameters of the model Hamiltonian accounting for the interactions within three coordination shells were determined by calculating the total energy of the crystal in different ordered phases. The temperatures of the phase transitions were calculated using the Monte Carlo method in the mean-field and cluster approximations with the obtained parameters of the model Hamiltonian.

2. The phase transitions occurring in  $AB'B''O_3$  solid solutions due to the ordering of  $B$  cations will be described using a model Hamiltonian accounting for only those degrees of freedom that are associated with the positional disorder of scandium and niobium (tantalum) atoms located at sites of the crystal lattice (the position  $b$  in the space group  $O_h^1$ ). In this case, the problem of  $B$  cation ordering in the  $AB'B''O_3$  solid solution is equivalent to the problem of ordering in a binary alloy. Hence, we can use a model based on the assumption that the atoms involved in the solid solution are located at sites of a rigid crystal lattice [11]. Therefore, the configuration energy of the solid solution can be represented as the sum of all pair atomic interaction potentials. Within this model, the Hamiltonian of the system can be written in the form

$$H = \frac{1}{2} \sum_{k,j} [v_{B'B'}(\mathbf{r}_k, \mathbf{r}_j) n_k^{B'} n_j^{B'} + v_{B''B''}(\mathbf{r}_k, \mathbf{r}_j) n_k^{B''} n_j^{B''} + 2v_{B'B''}(\mathbf{r}_k, \mathbf{r}_j) n_k^{B'} n_j^{B''}] - \sum_j [n_j^{B'} \mu_{B'}(\mathbf{r}_j) + n_j^{B''} \mu_{B''}(\mathbf{r}_j)], \quad (1)$$

where  $v_{B'B'}$ ,  $v_{B''B''}$ , and  $v_{B'B''}$  are the pair interaction potentials of the  $B'$  atoms, the  $B''$  atoms, and the  $B'$  and  $B''$  atoms, respectively, which are located at lattice sites described by the vectors  $\mathbf{r}_k$  and  $\mathbf{r}_j$ ; and  $\mu_{B'}$  and  $\mu_{B''}$  are the chemical potentials of the  $B'$  and  $B''$  cations, respectively. The quantities  $n_j^{B'}$  and  $n_j^{B''}$  are random functions determined as follows: if the  $j$ th site is occupied by the  $B'$  atom, we have  $n_j^{B'} = 1$  and  $n_j^{B''} = 0$ ; and, if the  $j$ th site is occupied by the  $B''$  atom, we have  $n_j^{B'} = 0$  and  $n_j^{B''} = 1$ . The quantities  $n_j^{B'}$  and  $n_j^{B''}$  are related by the expression  $n_j^{B'} + n_j^{B''} = 1$ .

Taking into account this relationship, expression (1) can be rewritten in the following form [11]:

$$H = \frac{1}{2} \sum_{k,j} v(\mathbf{r}_k, \mathbf{r}_j) n_k^{B'} n_j^{B''} - \mu \sum_j n_j^{B'} + H_0, \quad (2)$$

where

$$v(\mathbf{r}_k, \mathbf{r}_j) = v_{B'B'}(\mathbf{r}_k, \mathbf{r}_j) + v_{B''B''}(\mathbf{r}_k, \mathbf{r}_j) - 2v_{B'B''}(\mathbf{r}_k, \mathbf{r}_j)$$

is the effective interaction constant,

$$\mu = \mu_{B'}(\mathbf{r}_j) - \mu_{B''}(\mathbf{r}_j) + \sum_{i,k} (v_{B'B'}(\mathbf{r}_k, \mathbf{r}_j) - v_{B''B''}(\mathbf{r}_k, \mathbf{r}_j))$$

is the chemical potential of the system, and  $H_0$  is the energy independent of the arrangement of the  $B'$  and  $B''$  ions (this energy can be taken as the origin).

For the binary alloy considered in our case, in which the concentration of both components is equal to 1/2, relationship (2) can be written in the equivalent form through the Pauli matrices  $\sigma_i^z = \pm 1$ :

$$H = \sum_{i \neq j} J_{ij} \sigma_i^z \sigma_j^z. \quad (3)$$

The effective interaction constants can be obtained from the *ab initio* calculation of the total energy of the crystal within the Gordon–Kim model taking into account the dipole and quadrupole polarizabilities of the ions [12, 13]. The expression for the total energy has the form

$$E_{\text{total}} = E_s + E_p + E_q + E_{pq} + E_{\text{self}}, \quad (4)$$

where

$$E_s = -\frac{1}{2} \sum_{i,j=1}^{N_a} Z_i C_{ij}^{(0)} Z_j + \sum_{i,j=1}^{N_a} \Phi_{ij}^{(00)}(V_i, V_j, |\mathbf{R}_i - \mathbf{R}_j|), \quad (5)$$

$$E_p = \frac{1}{2} \sum_{i,j=1}^{N_a} \sum_{\alpha,\beta=1}^3 P_i^\alpha \left( \frac{\delta_{ij}}{\alpha_i^\beta(V_i)} + \Phi_{ij,\alpha\beta}^{(11)}(V_i, V_j, |\mathbf{R}_i - \mathbf{R}_j|) - C_{ij,\alpha\beta}^{(2)} \right) P_j^\beta \quad (6)$$

$$+ \sum_{i,j=1}^{N_a} \sum_{\alpha=1}^3 P_i^\alpha (\Phi_{ij,\alpha}^{(10)}(V_i, V_j, |\mathbf{R}_i - \mathbf{R}_j|) - C_{ij,\alpha}^{(1)} Z_j),$$

$$E_{pq} = \frac{1}{2} \sum_{i,j=1}^{N_a} \sum_{\alpha,\beta,\gamma,\delta=1}^3 q_i^{\alpha\beta} \left[ \frac{\delta_{ij}}{\alpha_i^\gamma(V_i)} - \frac{1}{36} (\Phi_{ij,\alpha\beta\gamma\delta}^{(22)}(V_i, V_j, |\mathbf{R}_i - \mathbf{R}_j|) - C_{ij,\alpha\beta\gamma\delta}^{(4)}) \right] q_j^{\gamma\delta} \quad (7)$$

$$- \frac{1}{6} \sum_{i,j=1}^{N_a} \sum_{\alpha,\beta=1}^3 q_i^{\alpha\beta} (\Phi_{ij,\alpha\beta}^{(20)}(V_i, V_j, |\mathbf{R}_i - \mathbf{R}_j|) - C_{ij,\alpha\beta}^{(2)} Z_j),$$

$$E_q = -\frac{1}{6} \sum_{i,j=1}^{N_a} \sum_{\alpha,\beta,\gamma=1}^3 q_i^{\alpha\beta} (\Phi_{ij,\alpha\beta\gamma}^{(21)}(V_i, V_j, |\mathbf{R}_i - \mathbf{R}_j|) - C_{ij,\alpha\beta\gamma}^{(3)} P_j^\gamma) \quad (8)$$

Here,  $E_s$  is the energy of interaction of the spherically symmetric ions;  $E_p$ ,  $E_q$ , and  $E_{pq}$  are the energies of interaction of the dipole and quadrupole moments;  $E_{\text{self}} = \sum_{i=1}^{N_a} E_i^{\text{ion}}$  is the self-energy energy of the ions;  $C_{ij}^{(n)} = \nabla^n \frac{1}{|\mathbf{R}_i - \mathbf{R}_j|}$  is the long-range part of the interactions,

which is calculated by the Ewald method;  $\Phi_{ij,\alpha\beta\gamma}^{(mn)}(V_i, V_j, |\mathbf{R}_i - \mathbf{R}_j|)$  is the short-range part of the interactions; and  $P_i^\alpha (q_i^{\alpha\beta})$  are the dipole (quadrupole) moments of the ions, which are calculated from the minimum condition of the total energy of the crystal [13].

In order to determine the energy of the crystal in the disordered phase, we use the virtual crystal approximation. In this approximation, the short-range part of the pair interactions of the virtual ion  $\langle B \rangle$  with other ions ( $i$ ) has the form

$$\Phi_{iB}^{ll'} = \frac{1}{2} \Phi_{iB'}^{ll'} + \frac{1}{2} \Phi_{iB''}^{ll'}. \quad (9)$$

The contribution of the virtual ion to the self-energy energy is given by the formula

$$E_B^{\text{ion}} = \frac{1}{2} E_{B'}^{\text{ion}} + \frac{1}{2} E_{B''}^{\text{ion}}. \quad (10)$$

The dipole and quadrupole polarizabilities of the virtual ion  $B$  are defined as

$$\alpha_B^{d,q} = \frac{1}{2} \alpha_{B'}^{d,q} + \frac{1}{2} \alpha_{B''}^{d,q}. \quad (11)$$

In the calculation of the long-range Coulomb contributions, the charge of the virtual ion  $B$  is determined as follows:

$$Z_B = \frac{1}{2} Z_{B'} + \frac{1}{2} Z_{B''}. \quad (12)$$

3. Using the model Hamiltonian, we restrict our consideration to the special case of interactions within three coordination shells. In order to obtain the effective interaction constants, we calculate the energies of several structures with different degrees of ordering of the  $B'$  and  $B''$  ions. We consider only ordered structures with a perovskite cell volume enlarged by a factor of 8 (Fig. 1). The first column in Table 1 presents the configuration motif of the ordered structures with the notation taken from the paper by Burton and Cohen [9], who carried out a similar calculation for the  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$  solid solution. The second column in this table lists the lattice parameters of the ordered structures. The calculated energies  $E_i$  per formula unit  $\text{ABO}_3$  are given in

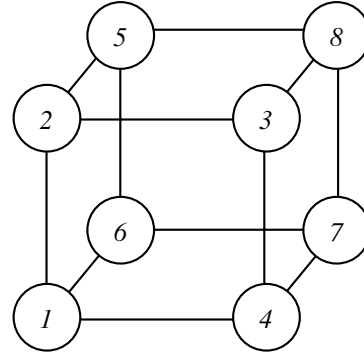


Fig. 1. Perovskite cell enlarged by a factor of 8 (only the  $B$  cations are shown).

columns 3 and 4 for the  $PSN$  and  $PST$  solid solutions, respectively:

$$E_i = E_{\text{total}} - E_{\text{self}} - E_0. \quad (13)$$

Here,  $E_{\text{total}}$  is the total energy of the crystal,  $E_{\text{self}}$  is the self-energy energy of the ions [see relationship (4)], and  $E_0$  is the energy independent of the arrangement of the  $B'$  and  $B''$  ions, which is equal to  $-161.455721$  eV for the  $PSN$  solid solution and  $-157.692153$  eV for the  $PST$  solid solution.

In column 5 in Table 1, the energies of the ordered structures are expressed through the effective interaction constants involved in expression (3). It should be noted that, since the model Hamiltonian accounts only for the degrees of freedom associated with the positional disorder of the  $B'$  and  $B''$  ions, the effective interaction constants are calculated in terms of the energies of the unrelaxed structures.

The calculated effective interaction constants are presented in Table 2. It can be seen from this table that the effective interaction constants  $J_1$ ,  $J_2$ , and  $J_3$  have the same sign and correspond to the attraction of the scandium and niobium (tantalum) ions in the first, second, and third coordination shells. Therefore, we are dealing here with competition between antiferromagnetic interactions. It is known that, in this case, the mean-field approximation leads to substantially incorrect numerical values of the phase transition temperature. Actually, in the mean-field approximation, the phase transition temperature is given by the expression

$$T_c^{\text{mf}} = \frac{6J_1 - 12J_2 + 8J_3}{k_B}. \quad (14)$$

The calculated values of the phase transition temperature  $T_c^{\text{mf}}$  are listed in Table 3. As can be seen from this table, the calculated temperatures  $T_c^{\text{mf}}$  exceed the experimental values by a factor of more than 3. Such a large difference between the calculated and experimentally obtained temperatures of the phase transition is associated with the fact that, in the system with compet-

**Table 1.** Energies of ordered structures of the  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$  and  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  solid solutions

Configuration {IJKL} {MNOP} ( $B' = +1, B'' = -1$ )	Lattice parameters	Calculated energies, $E_i$ , eV		Energies expressed through the effective interaction constants $J_i$
		$PSN$ ( $a_0 = 3.95 \text{ \AA}$ )	$PST$ ( $a_0 = 4.01 \text{ \AA}$ )	
1	2	3	4	5
{-1 1 -1 1} {1 -1 1 -1} ( $B'B''$ along the [111] direction)	$a = b = c = 2a_0$	-0.399357	-0.448150	$-6J_1 + 12J_2 - 8J_3$
{-1 1 -1 -1} {1 1 1 -1}	$a = b = c = 2a_0$	-0.193832	-0.292024	$-8J_3$
{1 1 1 1} {-1 -1 -1 -1} ( $B'B''$ along the [100] direction)	$a = b = a_0,$ $c = 2a_0$	-0.125324	-0.239982	$2J_1 - 4J_2 - 8J_3$
{1 -1 1 -1} {1 -1 1 -1} ( $B'B''$ along the [110] direction)	$a = b = \sqrt{2}a_0,$ $c = a_0$	-0.349156	-0.378210	$-2J_1 4J_2 + 8J_3$
{-1 -1 -1 1} {1 1 1 -1}	$a = b = c = 2a_0$	-0.305748	-0.361138	$-2J_1$
{1 -1 -1 -1} {1 1 1 -1}	$a = b = c = 2a_0$	-0.237239	-0.309096	$-4J_2$
{1 1 1 1} {1 1 1 1}+ {-1 -1 -1 -1} {-1 -1 -1 -1}	$a = b = a_0,$ $c = 4a_0$	0.848736	1.031372	$4J_1 + 4J_2$

ing interactions, an important role is played by the short-range correlations, which are ignored in the mean-field approximation. It is known that these correlations can be taken into account in another version of the self-consistent field approximation, the so-called cluster approximation [14, 15].

4. The algorithm employed in the cluster field method was described in detail by Vaks *et al.* [14, 15]. We will use this method for calculating the temperatures of the phase transition in the  $PSN$  and  $PST$  solid solutions. In the cluster field method, the crystal lattice whose sites are occupied by ordering atoms is separated into clusters containing some number of “spins” and the relationships between the cluster fields are established.

In our case, we deal with antiferromagnetic interactions. Therefore, we can separate the crystal lattice into two sublattices, namely, the  $A$  and  $B$  sublattices, in such a way that, in the ordered state with the lowest energy, the scandium ions will occupy sites of the  $A$  sublattice

( $\sigma_A^z = +1$ , spins 1, 3, 5, 7 in Fig. 1), whereas the niobium ions will be located at sites of the  $B$  sublattice ( $\sigma_B^z = -1$ , spins 2, 4, 6, 8 in Fig. 1). For the interactions occurring within three coordination shells, there exist six cluster fields, namely,  $\phi_1, \phi_2, \phi_3, \psi_1, \psi_2$ , and  $\psi_3$  (where  $\phi$  and  $\psi$  are the cluster fields acting on the spins of the  $A$  and  $B$  sublattices, respectively).

In order to obtain relationships between the cluster fields, we separate the crystal lattice into six clusters (see Fig. 1): an eight-particle cluster containing spins 1–8; two seven-particle clusters, namely, the  $7_a$  cluster containing spins 1–7 and the  $7_b$  cluster containing spins 1–6, 8; a six-particle cluster containing spins 1–6; and two five-particle clusters, namely, the  $5_a$  cluster containing spins 1–5 and the  $5_b$  cluster containing spins 1–4, 6. As a result, the free energy can be written in the form

$$\beta D = \frac{11}{4} \ln Z_8 - \frac{5}{2} \ln Z_{7a} - \frac{5}{2} \ln Z_{7b} - 3 \ln Z_6 + 3 \ln Z_{5a} + 3 \ln Z_{5b}, \quad (15)$$

where  $\beta = \frac{1}{kT}$ ,  $Z_i = \text{Sp}\{\exp(-\beta H_i)\}$  are the corresponding cluster partition functions, and  $H_i$  is the cluster

**Table 2.** Calculated effective interaction constants

Crystal	Effective interaction constants, eV		
	$J_1$	$J_2$	$J_3$
$PSN$	0.152874	0.0593099	0.024229
$PST$	0.180569	0.077274	0.036503

Hamiltonian. For brevity, we present explicit expressions only for the cluster Hamiltonian  $H_i$ ; that is,

$$\begin{aligned}
 H_8 = & J_1(\sigma_1(\sigma_2 + \sigma_4 + \sigma_6) + \sigma_3(\sigma_2 + \sigma_4 + \sigma_8)) \\
 & + \sigma_5(\sigma_2 + \sigma_6 + \sigma_8) + \sigma_7(\sigma_4 + \sigma_6 + \sigma_8)) \\
 & + J_2(\sigma_1\sigma_3 + \sigma_1\sigma_5 + \sigma_1\sigma_7 + \sigma_2\sigma_8 + \sigma_2\sigma_4 + \sigma_2\sigma_6 \\
 & + \sigma_3\sigma_5 + \sigma_3\sigma_7 + \sigma_4\sigma_6 + \sigma_4\sigma_8 + \sigma_5\sigma_7 + \sigma_6\sigma_8) \quad (16) \\
 & + J_3(\sigma_1\sigma_8 + \sigma_2\sigma_7 + \sigma_4\sigma_5 + \sigma_3\sigma_6)
 \end{aligned}$$

$$\begin{aligned}
 & + (3\phi_1 + 9\phi_2 + 7\phi_3)(\sigma_1 + \sigma_3 + \sigma_5 + \sigma_7) \\
 & + (3\psi_1 + 9\psi_2 + 7\psi_3)(\sigma_2 + \sigma_4 + \sigma_6 + \sigma_8),
 \end{aligned}$$

$$\begin{aligned}
 H_{7a} = & J_1(\sigma_1(\sigma_2 + \sigma_4 + \sigma_6) + \sigma_3(\sigma_2 + \sigma_4) \\
 & + \sigma_5(\sigma_2 + \sigma_6) + \sigma_7(\sigma_4 + \sigma_6)) \\
 & + J_2(\sigma_1\sigma_3 + \sigma_1\sigma_5 + \sigma_1\sigma_7 + \sigma_2\sigma_4 + \sigma_2\sigma_6 \\
 & + \sigma_3\sigma_5 + \sigma_3\sigma_7 + \sigma_4\sigma_6 + \sigma_5\sigma_7) \quad (17)
 \end{aligned}$$

$$\begin{aligned}
 & + J_3(\sigma_2\sigma_7 + \sigma_4\sigma_5 + \sigma_3\sigma_6) + \sigma_1(3\phi_1 + 9\phi_2 + 8\phi_3) \\
 & + (\sigma_3 + \sigma_5 + \sigma_7)(4\phi_1 + 9\phi_2 + 7\phi_3) \\
 & + (\sigma_2 + \sigma_4 + \sigma_6)(3\psi_1 + 10\psi_2 + 7\psi_3),
 \end{aligned}$$

$$\begin{aligned}
 H_6 = & J_1(\sigma_1(\sigma_2 + \sigma_4 + \sigma_6) + \sigma_3(\sigma_2 + \sigma_4) \\
 & + \sigma_5(\sigma_2 + \sigma_6))
 \end{aligned}$$

$$\begin{aligned}
 & + J_2(\sigma_1(\sigma_3 + \sigma_5) + \sigma_2\sigma_4 + \sigma_2\sigma_6 + \sigma_3\sigma_5 + \sigma_4\sigma_6) \\
 & + J_3(\sigma_4\sigma_5 + \sigma_3\sigma_6) + \sigma_1(3\phi_1 + 10\phi_2 + 8\phi_3) \quad (18)
 \end{aligned}$$

$$\begin{aligned}
 & + (\sigma_3 + \sigma_5)(4\phi_1 + 10\phi_2 + 7\phi_3)
 \end{aligned}$$

$$\begin{aligned}
 & + \sigma_2(3\psi_1 + 10\psi_2 + 8\psi_3)
 \end{aligned}$$

$$\begin{aligned}
 & + (\sigma_4 + \sigma_6)(4\psi_1 + 10\psi_2 + 7\psi_3),
 \end{aligned}$$

$$\begin{aligned}
 H_{5a} = & J_1(\sigma_1(\sigma_2 + \sigma_4) + \sigma_3(\sigma_2 + \sigma_4) + \sigma_5\sigma_2) \\
 & + J_2(\sigma_1(\sigma_3 + \sigma_5) + \sigma_2\sigma_4 + \sigma_3\sigma_5) \\
 & + J_3\sigma_4\sigma_5 + (\sigma_1 + \sigma_3)(4\phi_1 + 10\phi_2 + 8\phi_3) \quad (19)
 \end{aligned}$$

$$\begin{aligned}
 & + \sigma_5(5\phi_1 + 10\phi_2 + 7\phi_3) + \sigma_2(3\psi_1 + 11\psi_2 + 8\psi_3) \\
 & + \sigma_4(4\psi_1 + 11\psi_2 + 7\psi_3).
 \end{aligned}$$

The expressions for  $H_{7b}$  and  $H_{5b}$  can be obtained from relationships (17) and (19) with the changes  $\phi_i \longleftrightarrow \psi_i$ ,  $\sigma_1 \longleftrightarrow \sigma_2$ ,  $\sigma_3 \longleftrightarrow \sigma_4$ ,  $\sigma_5 \longleftrightarrow \sigma_6$ , and  $\sigma_7 \longleftrightarrow \sigma_8$ .

The cluster fields  $\phi_i$  and  $\psi_i$  can be found from the variational condition

$$\partial F / \partial \phi_i = \partial F / \partial \psi_i = 0, \quad (20)$$

which, in this case, leads to a system of six equations.

The temperature of the phase transition due to the  $B$  cation ordering can be calculated from expression (20).

**Table 3.** Calculated and experimental temperatures of the phase transition due to the  $B$  cation ordering (in degrees Kelvin)

Crystal	$T_c^{\text{mf}}$	$T_c^{\text{cl}}$	$T_c^{\text{mc}}$	$T_c^{\text{exp}}$
<i>PSN</i>	4630	2250	1810	1480
<i>PST</i>	5200	2400	1920	1770

Note: mf is the mean-field approximation, cl is the cluster approximation, mc is the Monte Carlo method, and exp is the experimental data [6].

For this purpose, expression (20) is expanded in powers of  $\phi_i$  and  $\psi_i$  up to linear terms and the determinant composed of the coefficients of the cluster fields  $\phi_i$  and  $\psi_i$  is taken equal to zero.

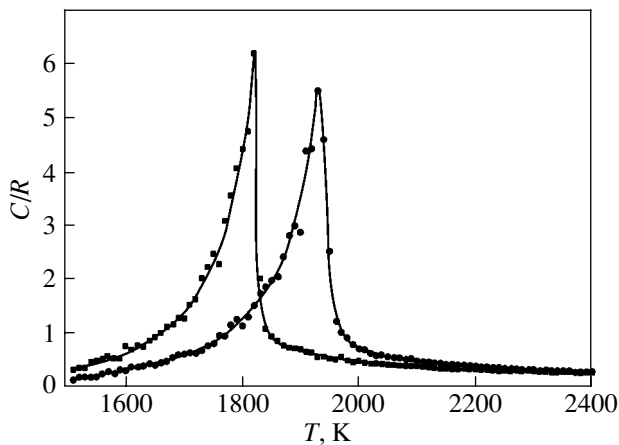
Using the effective interaction constants  $J_1$ ,  $J_2$ , and  $J_3$  presented in Table 2, we can determine the temperature of the phase transition (Table 3). As can be seen from Table 3, the obtained temperatures of the phase transition are substantially less than the phase transition temperature  $T_c^{\text{mf}}$  calculated in the mean-field approximation. It should be noted that, within a simple Ising model, in which competing interactions are disregarded, the phase transition temperatures calculated using the cluster field method do not differ greatly from those obtained in the mean-field approximation [15].

Thus, the partial inclusion of the short-range correlations associated with the competition of the interactions leads to a considerable decrease in the critical temperatures (as compared to those obtained in the mean-field approximation) of the phase transitions due to the cation ordering in the *PSN* and *PST* solid solutions. However, the phase transition temperatures  $T_c^{\text{cl}}$  obtained in the framework of the cluster field method are appreciably higher than the experimental values.

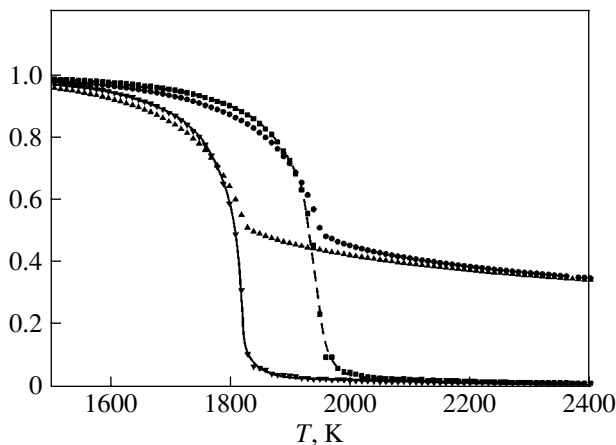
**5.** For a more complete inclusion of the correlation effects in the description of the phase transition caused by the  $B$  cation ordering, we used the numerical Monte Carlo method, which has been successfully applied in the investigation of the phase transitions in different systems, including those observed in ordering alloys [16, 17].

We examined crystal lattices  $12 \times 12 \times 12$ ,  $18 \times 18 \times 18$ , and  $30 \times 30 \times 30$  in size with periodic boundary conditions. The first 10 000 steps for each temperature were rejected and disregarded in the averaging. The average values of the energies, order parameters, and heat capacities were calculated in two stages. After 50 steps, we determined the group averages and, then, carried out the averaging over 500 groups.

The temperature dependences of the heat capacity and those of the short-range order parameter and long-range order parameter for the  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  and  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$  solid solutions with a  $30 \times 30 \times 30$  lat-



**Fig. 2.** Temperature dependences of the excess heat capacity due to the ordering of the *B* cations in the *PSN* (squares) and *PST* (circles) solid solutions.



**Fig. 3.** Temperature dependences of the long-range order parameter for the *PSN* (solid line) and *PST* (dashed line) solid solutions and the short-range order parameter for the *PSN* (triangles) and *PST* (circles) solid solutions.

tice are shown in Figs. 2 and 3, respectively. It should be noted that the size of the lattice does not affect the temperature of the phase transition or the temperature dependences of the order parameters. As the size of the lattice increases, the peak of the heat capacity becomes sharper. The calculated temperatures of the phase transitions are listed in Table 3. These temperatures are in agreement with the experimental data.

**6.** Thus, the temperatures of the phase transitions associated with the cation ordering in the  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$  and  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$  solid solutions were calculated using the model Hamiltonian within the

ionic crystal model accounting for the dipole and quadrupole distortions of the electron density and the deformability of the ions. It was established that the effective interactions between ordering cations exhibit a competitive nature. The temperatures of the phase transition due to the cation ordering, which were calculated in the framework of the cluster approximation and the Monte Carlo method, are in reasonable agreement with the experimental values.

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