

Heat Capacity Study of Relaxor $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ in a Wide Temperature Range

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Abstract—Heat capacity of the $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ compound is measured using the methods of adiabatic and differential scanning calorimetry in the temperature range 80–750 K. Two blurred anomalies on the $C_p(T)$ dependence are observed in wide temperature intervals of 200–400 K and 500–700 K. The results of studies are discussed together with data on the structure and phonon spectrum in the framework of spherical random bond–random field model. © 2003 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

Perovskite-like compounds attract considerable interest owing to rich diversity of their physical properties and possible applications in various technological schemes. Magnetic, dielectric, optical, and electric properties of perovskite-like materials have been studied extensively. New phenomena observed in doped (mixed) perovskites are of special importance.

The perovskite structure is characterized by relative simplicity of the crystal lattice structure, on the one hand, and by striking flexibility, on the other hand, which makes it possible to vary the set of ions forming the lattice over a wide range, thus obtaining the required combination of properties of the material. The substitution of a combination of two cations B and B' of different valence for cation B in the ABX_3 perovskite, which gives $\text{AB}_x\text{B}'_{1-x}\text{X}_3$, is one of the methods modifying the perovskite properties. Among mixed oxygen-based perovskites, compounds with $x = 1/2$ and $x = 1/3$ have been studied most extensively. Depending on the size and valence of the cations, both these types of the compound can be obtained either in an ordered or a disordered state.

The main type of ordering in the cation sublattice in compounds with the $\text{AB}_{1/2}\text{B}'_{1/2}\text{X}_3$ composition is alteration of layers of B and B' ions perpendicular to the triad axis [111] of the simple cubic cell. This gives rise to a structure of the so-called ordered perovskite, or elpasolite, with the $Fm\bar{3}m$ symmetry; the formula of this compound can be written as $\text{A}_2\text{BB}'\text{X}_6$. Such an ordering emerges when the sizes and charges of the B and B' ions differ significantly.

In the case of $\text{AB}_x\text{B}'_{1-x}\text{X}_3$ perovskites with $x = 1/3$, ordered structures with alternating B, B', and B' layers are formed for A = Ba and B = Zn, Mg; B' = Nb, Ta [1]. On the other hand, compounds with A = Pb demonstrate ordering of B' and B'' = (1/3)B' + (2/3)B layers alternating along the [111] direction. This type of ordering with a long-range order is observed in $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$. In other Pb-containing compounds, no long-range order is observed. According to the results of structural analysis, ordered regions have a size on the order of 20–800 Å [1, 2].

Compounds with such a small correlation length of ordering are characterized by relaxor-type behavior. Relaxors possess three main features of dielectric response. The phase transition has a clearly manifested diffusion nature, and the permittivity and the temperature corresponding to its maximal value depend significantly of the measuring field frequency. The response in weak fields does not obey the Curie–Weiss law. The room-mean-square polarization exists in a temperature range 200–300 K higher than T_{max} (the temperature corresponding to the permittivity peak), but the average polarization P differs from zero at a temperature much lower than T_{max} .

The $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) compound belongs to the family of an oxygen-containing mixed perovskite-like compound and is a classical representative of materials with relaxor behavior [3]. This compound has a broad peak of ϵ in the vicinity of $T_{\text{max}} \approx (250\text{--}270)$ K and displays a strong low-frequency permittivity dispersion. On the other hand, spontaneous polarization is observed at low temperatures (below 250 K) only in polarized samples in electric fields of strength higher than a certain critical value [4] or in those with PbTiO_3 admixtures [5]. Such dielectric behavior was initially

explained by the diffusion nature of the ferroelectric phase transition associated with fluctuations of the concentration of Mg^{2+} and Nb^{5+} ions of different valence in the B sites of the $Pm3m$ -cubic structure of the ABO_3 perovskite.

Over several decades, PMN has been studied using various methods, but a large number of questions concerning the nature of phase transitions and anomalous behavior of physical properties of this crystal in a wide temperature range remain unanswered. Moreover, the crystal structure and its variation in a wide temperature range are still objects of discussion.

The main attention in the study of relaxors is paid to dielectric properties of these materials, their structure, and spectral parameters. Thermodynamic properties, especially heat capacity and its behavior in a wide temperature range, were studied casually. Nevertheless, thermal parameters of the system may be important in the developing and refining models of the phenomena in question. Calorimetric studies have indisputable advantages since this method makes it possible to detect any type of heat capacity anomalies, which are associated with the electric as well as with the elastic subsystem.

The temperature dependence of heat capacity of PMN was studied by many authors [6–8]. In [6], heat capacity was measured by the differential scanning calorimeter method in the temperature range 140–790 K. The spread in experimental points exceeded 15%, and analysis of heat capacity was carried out only after averaging, which did not allowed the authors of this work to draw unambiguous conclusions on the type of the $C_p(T)$ behavior. In [7, 8], measurements were confined to a temperature of 300 K, which is insufficient for tracing the variation of heat capacity in the region of the permittivity maximum (about 250–350 K). The authors of these publications were mainly interested in the behavior of heat capacity at low temperatures and in the form of the vibrational spectrum of the compound.

Here, we report on the results of heat capacity studies in PMN in a wide temperature range of 80–750 K and analyze its behavior in temperature regions in which anomalies in the electrical and structural properties were observed by many authors.

2. SAMPLE AND MEASURING TECHNIQUE

The experimental sample was in the form of a finely dispersed powder and was prepared at the Center of Material Development and Structural Studies (CEMES) in Toulouse (France). The compound was manufactured using solid phase synthesis from a mixture of corresponding oxides [9].

Heat capacity was measured using two methods. In the temperature range 80–350 K, measurements were made using the adiabatic calorimetry method enabling us to obtain absolute values of the total heat capacity to a high degree of accuracy. A powder sample was placed

into an indium container, which was sealed in a helium atmosphere. Helium was used as a heat-exchange gas for leveling out the temperature over the sample. The sample mass was 3.17 g and the container mass was 8.5 g. Measurements were made using the traditional method of discrete heating and in an automated regime of continuous heating [10] at a temperature variation rate of $dT/dt \approx 10^{-1} \text{ K min}^{-1}$. In our experiments, we measured the total heat capacity of the sample and the container. The heat capacity of the container was measured separately. The error of heat capacity measurements depends on the method of heating and amounts to (0.1–1.0)%.

In a high-temperature range of 360–750 K, measurements were made on an updated and automated DSM-2M differential scanning calorimeter. In this case, the sample mass was 0.51 g. The error of heat capacity measurements with such a calorimeter is slightly larger than that with an adiabatic calorimeter and amounts to 2–3%.

3. RESULTS AND DISCUSSION

The results of heat capacity measurements in PMN are presented in Fig. 1. The spread in experimental points relative to the smoothing curve does not exceed 1.5%. The error of measurements slightly exceeding the conventional value is due to the fact that the heat capacity of the sample amounts to only a small part of the total heat capacity of the container–sample system. The obtained results are in good agreement with the data obtained in [7, 8] in the temperature range 80–270 K and differ from the results obtained in [6]. The curve describing the temperature dependence of specific heat does not exhibit clearly manifested anomalies typical of traditional phase transitions. However, in temperature regions near 300 and 650 K, two broad, blurred anomalies in heat capacity are observed.

3.1. Separation of the Lattice Component of Heat Capacity

Since we are dealing here with experimental results obtained in a wide temperature range, we must take into account in our analysis the anharmonic contributions to the lattice heat capacity at high temperatures, which may lead to a considerable difference between the isobaric and isochoric heat capacities. Thermal expansion of PMN has been studied repeatedly [9, 11]. The volume expansion coefficient in the temperature range from 300 to 700 K varied from 4×10^{-6} to $30 \times 10^{-6} \text{ K}^{-1}$. To our knowledge, data on compressibility of PMN are not available. We estimated the value of this quantity using the result of publication [12], devoted to the study of the effect of pressure on the unit cell parameters of the $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ compound allied with PMN. The bulk compressibility modulus was estimated as $2.3 \times 10^{-11} \text{ Pa}^{-1}$.

Using the above estimates, we calculated the anharmonic contribution to the heat capacity of PMN, which amounts to approximately 1 J/mole K at 700 K. In view of the smallness of this value, which is within the experimental error, the difference between C_p and C_v was disregarded in the subsequent analysis. The small value of the anharmonic contribution is due to a small value of the thermal expansion coefficient.

The expression for the lattice heat capacity C_L can be derived from the general relation

$$C_L = \frac{\partial E}{\partial T} = \frac{\partial}{\partial T} \left(\int d\omega G(\omega) n(\omega) \hbar \omega \right), \quad (1)$$

where E is the internal energy of the system, $n(\omega)$ is the Bose–Einstein distribution function, and $G(\omega)$ is the density of vibrational states.

The density of state function $G(\omega)$ for crystals with a complex composition is unknown as a rule in the entire frequency range. For this reason, we must resort to a simplified approach to obtain a quantitative description of the temperature dependence of heat capacity. In most cases, the analysis of the temperature dependence of heat capacity and the separation of the lattice and anomalous contributions are carried out using a simple model describing the lattice heat capacity of the compound by a combination of the Debye and Einstein functions.

In the case of PMN, such an approach was used in [6], but the treatment of the temperature dependence of heat capacity in a wide temperature range (140–790 K) in the framework of the Debye model with $\Theta_D = 422.1$ K obviously does not fit the real situation. The results of analysis of the data obtained in this approximation are represented by the dashed curve in Fig. 1 and lead to a different value of $\Theta_D = 520$ K. It can clearly be seen that the temperature dependence of heat capacity in the low-temperature range has a non-Debye form [7, 8]: the heat capacity of PMN decreases with temperature almost linearly down to the minimal values attained in experiment. Such deviations from the $C \propto T^3$ dependence are attributed in [8] to the excitation of Einstein oscillators, are typical of a large number of crystals, and are associated with anomalies of real frequency distribution functions in the low-frequency spectral region (below 100 cm^{-1}). The results of lattice heat capacity treatment by a combination of the Debye and Einstein functions are shown by the dashed curve in Fig. 1. In the temperature range 30–200 K, the latter model describes experimental results much better.

Another version of the lattice capacity approximation was implemented in the framework of the fracton model proposed on the basis of analysis of the lattice vibration spectrum of PMN by the inelastic neutron scattering method [13]. Gvasaliya *et al.* [7, 13] believe that the phonon regime is realized at frequencies of

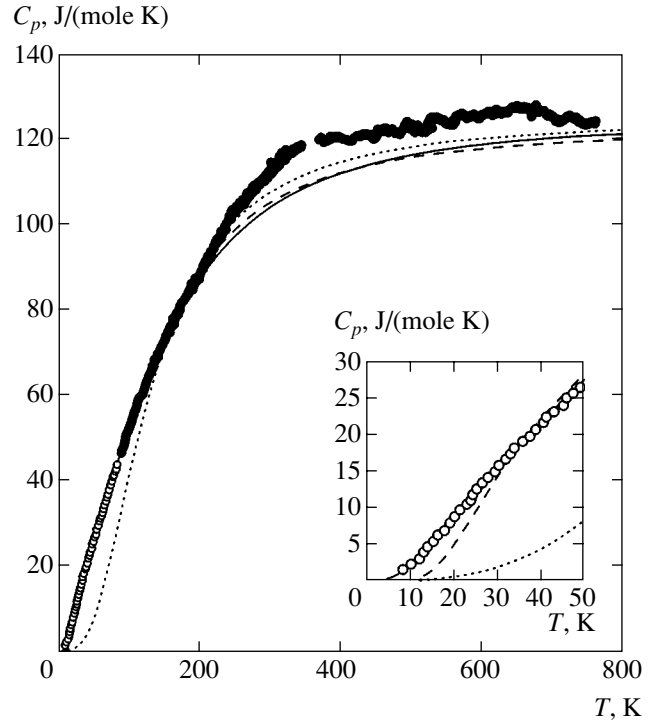


Fig. 1. Temperature dependence of the heat capacity of $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$. Data for the temperature range 7–80 K are borrowed from [8]. Lattice heat capacity is approximated in the framework of the Debye model (dotted curve), a combination of the Debye and Einstein functions (dashed curve), and in the framework of the model developed in [7, 13] (solid curve). The inset shows heat capacity in the temperature range 0–50 K.

$\omega \leq \omega_1$, while the fracton regime with spectral dimension d is observed for $\omega_1 \leq \omega \leq \omega_2$:

$$G(\omega) \propto \begin{cases} \omega^2, & \omega \leq \omega_1, \\ \omega^{d-1}, & \omega_1 \leq \omega \leq \omega_2. \end{cases} \quad (2)$$

Three parameters (d , ω_1 , and ω_2) were determined by us from analysis of experimental data: $\hbar\omega_1/k_B = 43.7$ K, $\hbar\omega_2/k_B = 800$ K, and $d \approx 0.8$. A rather nonrealistic value of fracton dimension d is obtained, in all probability, since the dependence $G(\omega) \propto \omega^{d-1}$ was assumed to be valid for $\omega \geq \omega_1$, although it follows from the results obtained in [13] that such a dependence holds only in a narrow frequency range.

Thus, the $G(\omega)$ function used here is rather a certain approximate description of the real frequency spectrum and cannot serve as an argument supporting or rejecting the existence of fractons in the lattice vibration spectrum [7, 13]. Nevertheless, such an approximation makes it possible to describe the lattice heat capacity correctly in the entire temperature range under investigation (see Fig. 1).

The anomalous component $\Delta C_p = C_p - C_L$ of heat capacity, separated by all of the above three methods, is

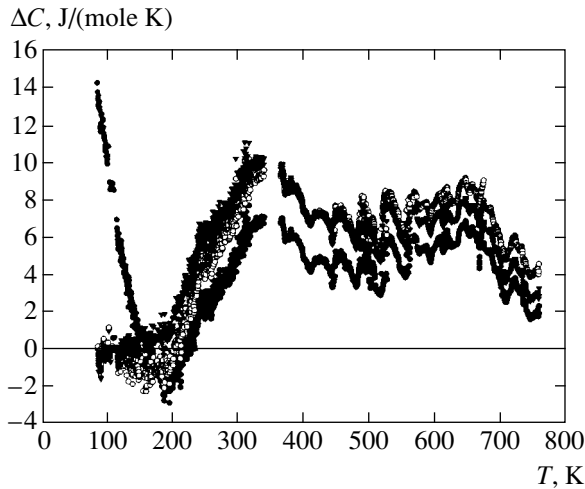


Fig. 2. Anomalous component of the heat capacity of the $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ compound determined by interpolating the lattice heat capacity in the framework of the Debye model (●), Debye–Einstein model (○), and the model proposed in [7, 13] (▼).

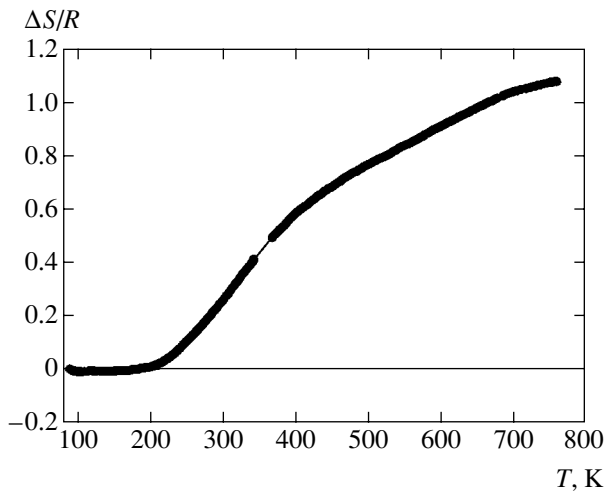


Fig. 3. Temperature dependence of the anomalous entropy of the $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ compound.

depicted in Fig. 2. In the temperature range $T > 100$ K, the heat capacity has a low sensitivity to fine details of the vibrational spectrum, and the difference in the values of ΔC_p obtained by approximating the lattice heat capacity by a combination of the Debye and Einstein functions and on the basis of a simple description of the lattice vibration spectrum is small and lies within the error of measurements. It should also be noted that the value of $C_p - C_v$ estimated above does not exceed 10–15% of the anomalous heat capacity.

The $\Delta C_p(T)$ dependence clearly displays two regions of anomalous behavior of heat capacity. The temperature range 200–450 K coincides with the region of anomalous behavior of permittivity [3],

while deviations from the regular behavior of the refractive index [14], lattice parameters, and thermal expansion coefficient [9] were observed earlier in the temperature range 550–700 K.

The change in entropy associated with the anomalous behavior of heat capacity and calculated by the formula

$$\Delta S(T) = \int_{100 \text{ K}}^T \frac{\Delta C_p}{T} dT$$

is depicted in Fig. 3.

In order to find reasons for the emergence of anomalous behavior of heat capacity of PMN, we consider the structural features of this material and the available models of phenomena occurring in it.

3.2. Anomalous Behavior at High Temperatures

The concept of polar nanoregions is one of the most important concepts associated with microscopic properties of relaxors. The first experimental proof of the existence of such regions was obtained by Burns, who studied the refractive index $n(T)$ of single crystals of some disordered ferroelectrics and relaxors including PMN [14]. The refractive index behavior deviates from the linear dependence at temperature T_d (600–650 K for PMN), which is much higher than T_{max} . It was supposed that such an unexpected behavior is due to randomly oriented local polarized regions, which are formed in a nonpolar crystal structure below T_d . This temperature is often referred to as the Burns temperature.

Later, high-resolution electron microscopy studies of PMN [15] at $T < T_d$ revealed the presence of chemically ordered (1 : 1) clusters in which Mg^{2+} and Nb^{5+} ions, which are in the position B, alternate along the axes of the perovskite cubic lattice. The size of these clusters is on the order of 10 Å. In [16, 17], a two-phase model of the PMN structure was proposed on the basis of structure analysis by the neutron elastic scattering method at low temperatures, viz., a cubic structure with a long-range order and nanoregions with a rhombohedral $R3m$ structure and with a correlation length on the order to 100 Å. In these polar nanoregions, Pb and Mg/Nb ions are displaced relative to oxygen ions in the $[111]_c$ directions.

Neutron inelastic scattering experiments [18, 19] with relaxors above the Burns temperature revealed a TO vibration branch for all wave vectors and a TO mode at the center of the Brillouin zone. The value of $(\hbar\omega_0)^2$, where ω_0 is the frequency of this mode, decreases linearly upon cooling down to T_d . Such a behavior matches the behavior of the soft mode in PbTiO_3 and other displacement-type ferroelectrics. At the Burns temperature, a phase transition occurs, leading to a rhombohedral ($R3m$) distortion of Nb-rich clus-

ters and to the emergence of polarization in these clusters. However, the correlation length of such clusters is quite small and macroscopic polarization does not appear in the sample.

In the region of soft mode condensation at the Burns temperature, anomalous behavior of heat capacity of PMN can be expected, which was indeed observed in our experiments in the temperature range 600–700 K. The anomaly blurring is probably due to the fact that individual clusters have different phase transition temperatures.

The approximate change in entropy during the high-temperature transition is on the order of $(0.4\text{--}0.5)R$ (R is the universal gas constant); this means that processes of the order–disorder type, which are associated with ordering of lead ions in interoctahedral cavities below the Burns temperature, play a significant role in the formation of polar nanoregions.

Taking into account the results of structural studies and the fact that polarization may have eight equivalent directions of the $[111]_c$ type, we could expect that the entropy variation as a result of ordering in the entire crystal is $\Delta S = R \ln 8$. The obtained value of entropy variation amounts to only 20–25% of this value and is in accordance with the volume fraction of polar nanoregions obtained from an analysis of structural data [17].

3.3. Analysis of the Behavior of Heat Capacity in the Framework of the Random Bond–Random Field Theory

Since the discovery of relaxors more than 30 years ago, several models have been proposed for explaining the existence of the ϵ peak and other peculiar dielectric properties. These are the models of diffusion phase transitions, dipole glasses, reorienting polar clusters, etc. In recent years, the spherical random bond–random field (SRBRF) model has become most popular [20, 21].

The PMN compound below the Burns temperature is treated in the model [20] as a heterogeneous material consisting of Nb-rich regions (or polar clusters) implanted in a quasi-regular array of chemically ordered (1 : 1) regions (chemical clusters). Polar clusters have a typical size of several nanometers and can be reoriented. It is these clusters that are responsible for the observed dielectric behavior. On the contrary, chemical clusters are static and are regarded as sources of random electric fields.

The model Hamiltonian of the system of interacting polar clusters can be formally written in the form

$$H = -\frac{1}{2} \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - \sum_i \mathbf{h}_i \cdot \mathbf{S}_i - g \sum_i \mathbf{E}_i \cdot \mathbf{S}_i, \quad (3)$$

where \mathbf{S}_i is the dimensionless order parameter, proportional to the dipole moment of a cluster; J_{ij} are random interactions or bonds; \mathbf{h}_i are random local electric

fields; and \mathbf{E}_i is the external electric field [20]. As in the theory of spins and dipole glasses, it is assumed that random bonds have a Gaussian distribution and

$$[J_{ij}]_{av}^c = J_0/N, \quad [(J_{ij})^2]_{av}^c = J^2/N. \quad (4)$$

Random fields also obey the Gaussian distribution, and

$$[h_{i\mu}]_{av}^c = 0, \quad [h_{i\mu} h_{j\nu}]_{av}^c = \Delta \delta_{ij} \delta_{\mu\nu}, \quad \mu = x, y, z. \quad (5)$$

Equilibrium values of polarization,

$$P_\mu = \frac{1}{N} \sum_i \langle S_{i\mu} \rangle,$$

and of the order parameter of dipole glass (or the Edwards–Anderson parameter),

$$q_\mu = \frac{1}{N} \sum_i \langle S_{i\mu}^2 \rangle,$$

can be determined from the conditions of the free energy minimum:

$$-\frac{2}{3} \beta f = \beta J_0 P^2 - \frac{1}{2} \beta^2 J^2 q^2 - 2z + \ln(2z + \beta^2 J^2 q) - \frac{\beta^2 J^2 q + \Delta + (J_0 P + gE)^2}{2z + \beta^2 J^2 q}, \quad (6)$$

$$\partial f / \partial P = \partial f / \partial q = \partial f / \partial z = 0, \quad (7)$$

where z is a Lagrangian multiplier introduced to enhance the spherical conditions, simplifying the solution [20]. Equilibrium values of P , q , and z are defined by the following expressions:

$$\begin{aligned} P &= \beta(1-q)(J_0 P + gE), \\ q &= \beta^2(1-q)^2(J^2 q + \Delta) + P^2, \\ 2z + \beta^2 J^2 q &= 1/(1-q). \end{aligned} \quad (8)$$

In zero external field ($E=0$), the system has two sets of solutions. One of them ($P=0, q \neq 0$) corresponds to the phase without a long-range order, or dipole glass (SG), while the other ($P \neq 0, q \neq 0$) describes the phase with a long-range order, or ferroelectric (FE) phase. The ferroelectric phase ($P \neq 0$) can exist only if the parameter J_0 of interaction between clusters exceeds a certain critical value, $J_0 > J_{0c} = \sqrt{J^2 + \Delta}$.

The temperature of transition to the ferroelectric state is defined as

$$T_c = J_0 \left(1 - \frac{\Delta}{J_0^2 - J^2} \right) \theta \left(\frac{J_0}{J} - 1 \right). \quad (9)$$

The phase diagram of the model is shown in Fig. 4. In the case of PMN, the interaction parameter J_0 is

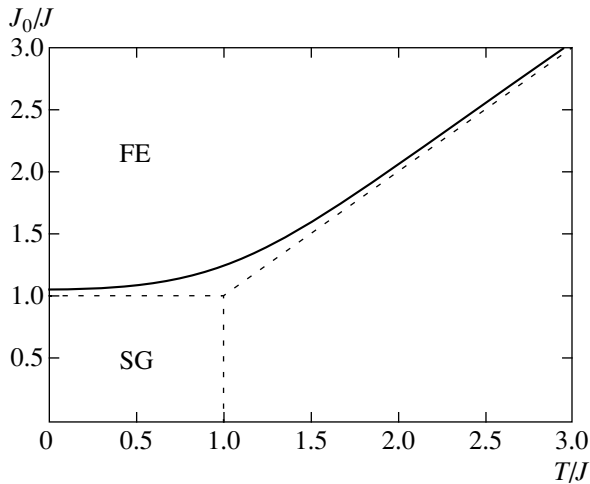


Fig. 4. Phase diagram of the random bond-random field model. Dotted lines correspond to $\Delta = 0$.

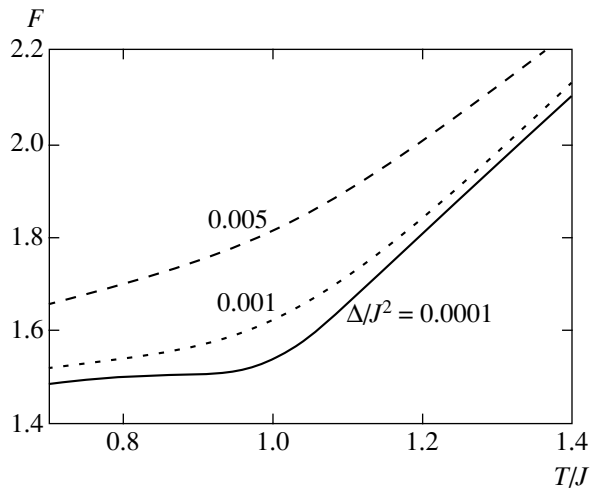


Fig. 6. Temperature dependence of the free energy in the SRBRF model for $E = 0$, $J_0 = 0$, and $\Delta/J^2 = 0.0001$, 0.001, and 0.005.

apparently smaller than the critical value, and a transition to the ferroelectric phase with the emergence of a macroscopic order parameter (polarization) is not observed. Accordingly, classical heat capacity anomalies are also absent. However, the existence of parameter q and its temperature variation leads to the emergence of an additional contribution to free energy and heat capacity.

The form of temperature dependences of these contributions was determined as a result of our numerical calculations for various values of the model parameters. The results of calculation of the temperature dependences of order parameter, free energy, entropy, and heat capacity for $\Delta/J^2 = 0.0001$, 0.001, and 0.005 and for $E = 0$, $J_0 = 0$ are presented in Figs. 5–8. It can be seen that, even in the absence of a phase transition to the ferroelectric phase, the heat capacity has a broad anomaly with a peak at $T = J$. For PMN, the value of J

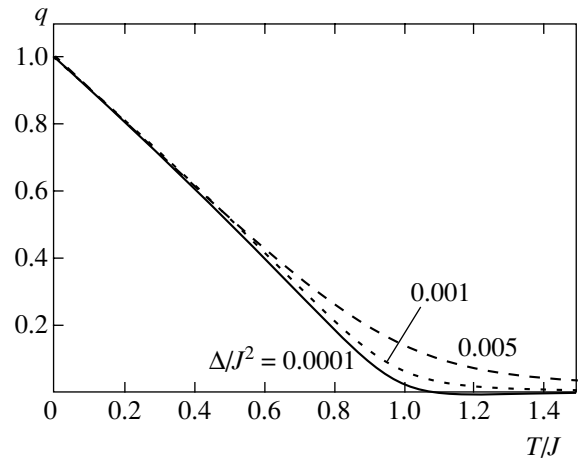


Fig. 5. Temperature dependence of the order parameter q for $E = 0$, $J_0 = 0$, and $\Delta/J^2 = 0.0001$, 0.001, and 0.005.

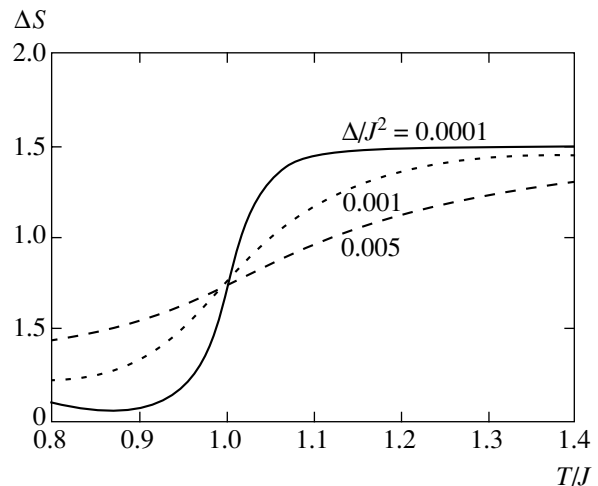


Fig. 7. Temperature dependence of entropy in the SRBRF model for $E = 0$, $J_0 = 0$, and $\Delta/J^2 = 0.0001$, 0.001, and 0.005.

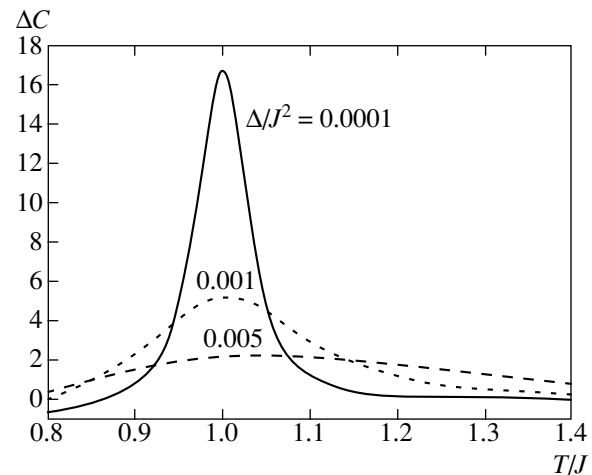


Fig. 8. Temperature dependence of heat capacity in the SRBRF model for $E = 0$, $J_0 = 0$, and $\Delta/J^2 = 0.0001$, 0.001, and 0.005.

is on the order of 300 K, and the observed heat capacity anomaly in the temperature range from 150 to 450 K is in qualitative agreement with the SRBRF model [18, 19].

4. CONCLUSIONS

Our results and the data from the literature lead to the following pattern of the processes occurring in PMN. Above the Burns temperature (≈ 700 K), PMN is a heterogeneous material containing ordered (1 : 1) regions as well as regions rich in niobium. The sizes of these regions are on the order of tens of nanometers. As the temperature decreases, a transition to the polar $R3m$ phase takes place at the Burns temperature in regions with an excess of niobium; this transition is accompanied by soft mode condensation and appearance of the blurred heat capacity anomaly. The polarization directions in polar nanoclusters are distributed at random, and macroscopic polarization does not emerge in the system. Further cooling does not lead to any structural changes. Anomalous behavior of dielectric properties and heat capacity in the temperature range 200–400 K is associated with changes occurring in the system of reorientable polar clusters and a transition to the glass-like state.

The results obtained are in good agreement with the results of structural studies and with conclusions of the spherical random bond–random field (SRBRF) model.

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