FERROELECTRICITY

Local Structure of Disordered PbSc$_{1/2}$Nb$_{1/2}$O$_3$ in the Region of the Diffuse Tetragonal Phase–Rhombohedral Phase Transition

I. P. Aleksandrova[a], A. A. Sukhovsky[a], Yu. N. Ivanov[a], and I. P. Raevsky[b]

[a] *Kirensky Institute of Physics, Siberian Branch of the Russian Academy of Sciences,*
Akademgorodok 50–38, Krasnoyarsk, 660036 Russia
[b] *Research Institute of Physics, Southern Federal University, pr. Stachki 194, Rostov-on-Don, 344090 Russia*
e-mail: lvv@iph.krasn.ru
Received July 19, 2011

Abstract—The local structure of the ferroelectric–relaxor PbSc$_{1/2}$Nb$_{1/2}$O$_3$ in the temperature range from 550 to 220 K has been investigated using ^{45}Sc nuclear magnetic resonance. It has been found that, in the paraelectric phase at temperatures below 550 K, the crystal consists of regions of an ordered elpasolite structure and inclusions of the disordered tetragonal perovskite phase with displacements along directions of the [001] type. The relative weight of the tetragonal structure in the region of the paraelectric phase is approximately equal to 0.28. Below the temperature of the phase transition from the disordered modification to the polar phase, the relative weight of the tetragonal phase decreases with decreasing temperature. The tetragonal structure is replaced by the trigonal polar structure. In a wide temperature range (~50 K), there exists a heterophase structure that is characteristic of relaxors. Note that the correlation length of displacements in the tetragonal phase should be very small to explain the absence of indications of the existence of this phase in the diffraction data.

1. INTRODUCTION

Up to now, the origin of specific dielectric properties of relaxor ferroelectrics is not clearly understood. In this respect, investigation of the relationship between the local and average structures of complex perovskites is an important problem. That is why it is important to compare the data obtained by local methods of nuclear magnetic resonance (NMR) and electron paramagnetic resonance with the data obtained using diffraction techniques and diffuse scattering.

In this work, we have performed the NMR study of a PbSc$_{1/2}$Nb$_{1/2}$O$_3$ (PSN) ferroelectric crystal that belongs to the group of substitutionally disordered complex perovskites.

There is a large number of works in which the Pb(Sc$_{1/2}$Nb$_{1/2}$)O$_3$ structure has been determined by diffraction methods. In the discussion of the results obtained from ^{45}Sc NMR measurements, we will predominantly use the results of the most recent studies by Malibert et al. [1] and Perrin et al. [2].

In the paraelectric phase, there are two modifications of PSN crystals. The elpasolite structure with the double parameter along three cubic directions is ordered over positions of alternating Sc and Nb ions in one-dimensional chains along the edges of the cube and its diagonals. The space group is *Fm*3*m*. It should

be noted that, even in the elpasolite structure, the ordering of Sc–Nb cations has a coherence length of approximately 200 Å. The cubic structure, which is randomly disordered over the Sc/Nb positions and has space group *Pm*3*m*, belongs to perovskites. Both modifications undergo phase transitions from the cubic phase to the trigonal ferroelectric phase *R*3*m*. The phase transition occurring in the PSN compound is observed at approximately 350 K in the ordered modification and at approximately 375 K in the disordered modification [3–5]. Frequently, in rather large single-crystal samples, two modifications coexist in weight ratios depending on the growth conditions of the crystal [4].

The trigonal polar phase is formed as the result of a weak first-order phase transition accompanied by a very small jump in the lattice constants. A reduction of the symmetry leads to displacements of the Pb ions and Sc/Nb positions toward the same direction along the threefold symmetry axis [111]$_p$ of the high-temperature phase [1, 3, 5]. This direction becomes the polar axis.

For the PSN modification with the elpasolite structure, the permittivity ε' is rather low and no relaxation in the peak of ε' is observed. The PSN modification with the perovskite structure is characterized by a high value of the permittivity ε' and a significant relaxation in the peak of ε', which is typical of relaxors [4, 5].

The displacements of the Sc and Nb ions during the phase transition are very small (~0.16 Å), and the *R* factor in the Rietveld analysis of PSN almost does not depend on the direction of the displacement of these ions, which results in the loss of some information regarding the structure.

As is known, the average structure of the crystal is determined from an analysis of the Bragg peaks. Investigations of the displacement ellipsoids and diffuse scattering have revealed deviations of the symmetry of local regions from the average structure [1, 2]. Resonance spectroscopy provides a somewhat different information. The electric-field gradient tensor in place of the localization of a resonant nucleus is determined by its nearest environment in a range of approximately 20 Å [6]. The quadrupole constant is sensitive to variations in the interatomic distances by a value of ~0.05 Å. For ^{45}Sc nuclei (with spin $I = 5/2$), the electric-field gradient tensor is determined from the orientation dependences of a relatively small shift in the central component of the spectrum on the Larmor frequency. A specific difficulty encountered in investigating the spectra of relaxors is that the observed NMR line is a superposition of the central components in the spectrum of the crystal with a fine multidomain structure. Moreover, relaxors are characterized by extended regions of the coexistence of crystallographic phases with different symmetries, which also increases the number of components in poorly resolved spectra of ^{45}Sc nuclei. In this case, it is impossible to perform a reliable decomposition of the superposition into spectral components. However, by using the hypothetical symmetry of displacements of the scandium ions, it is possible to calculate the orientation dependence of the shape of the spectral distribution. The calculation is carried out using not only to the shape of the spectra but also the difference in types of orientation dependences of the line shape for different symmetries of the displacements. This significantly improves the reliability of the determination of the variational parameters. In our recent works, this technique has been applied to investigate the local structure of the Na$_{1/2}$Bi$_{1/2}$TiO$_3$ (NBT) crystal [7, 8].

It should be noted that the PSN crystals have already been studied by the NMR method; however, the spectra have been interpreted using a rather arbitrary decomposition of the most allowed ^{45}Sc spectra into components [9].

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

We studied isometric PSN single crystals (4−6 mm in size along the edge) prepared through the bulk crystallization from a solution in the melt with the PbO−B$_2$O$_3$ system used as a solvent [4].

The orientation dependences of the shape of the superposition of the central components in the ^{45}Sc

NMR spectra were measured on a Bruker AVANCE-300 pulsed spectrometer at a Larmor frequency of 72.9 MHz. The rotation of the PSN single crystal in the coordinate system of the cubic unit cell of the high-temperature phase was performed around the pseudocubic axis $[110]_p$. It should be noted that, during this rotation, the vector of the external magnetic field turns to be consequently directed along the symmetry axes of the cubic unit cell C_4 ($[001]_p$), C_3 ($[111]_p$), and C_2 ($[011]_p$). The spectra were obtained by the Fourier transformation of the accumulated induction signal observed after a 90-degree pulse, or by the solid echo method. The duration of a 90° pulse was approximately equal to 2.5 μs. The orientation dependences were measured at twenty fixed temperatures in the range from 140 to 549 K. At temperatures of 200, 295, and 420 K, the orientation dependences were measured in steps of 5°−10°. At other temperatures, the spectra were measured in the orientations where the magnetic field vector was directed along the symmetry axes $[001]_p$, $[111]_p$, and $[011]_p$.

3. DESCRIPTION OF THE MODELS

The method used in our work for analyzing the NMR spectra is based on relationship (1) for the second-order quadrupole shift of the central component in the NMR spectrum of the nucleus with spin I and quadrupole moment Q [6]:

$$\nu = \alpha \nu_Q^2,$$

$$\alpha = -\frac{1}{16} \frac{(I(I+1) - 3/4)}{\nu_L} (1 - \cos^2\theta)(9\cos^2\theta - 1); \quad (1)$$

$$\nu_Q = \frac{3(eV_{zz}Q/h)}{2I(2I-1)},$$

where ν_L is the Larmor frequency, θ is the angle between the principal axis z of the axially symmetric electric-field gradient tensor and the direction of the external magnetic field H_0, V_{zz} is the principal value of the electric-field gradient tensor, e is the elementary charge, and h is the Planck constant.

The use of relationship (1) for the axially symmetric electric-field gradient tensor imposes some restrictions on the displacements analyzed in our models. These can be displacements of the scandium ion along the symmetry elements of the cubic unit cell. It should be noted that the displacements of the *B*-type ions, which are observed during the phase transitions in complex perovskites, correspond to this restriction.

In the simulation of the orientation dependence of the spectral shape, we specify the direction of the displacement of the scandium ions from the position in the cubic structure and, thus, determine the direction of the principal axis of the electric-field gradient tensor, which corresponds to the principal value of the tensor V_{zz}. The quadrupole coupling constant $q =$

eQV_{zz}/h is the variational parameter. In the simulation of the spectrum, all equally probable directions of the chosen displacement from the position of the studied nucleus in the cubic phase are taken into account. Certainly, the electric-field gradient tensor is identical for structurally equivalent nuclei in the crystal; however, the angle θ involved in relationship (1) has different values for the nuclei belonging to different domains. Such "magnetically inequivalent" scandium positions lead to the fact that, in the NMR spectrum, there appears a group of lines corresponding to the structurally equivalent nuclei. This complicates the observed spectrum; however, to any chosen symmetry of the displacement, there corresponds an inherent orientation dependence of the shift of the central component. The superposition of the orientation dependences of the frequencies of the lines in the spectrum of the multidomain crystal is also determined by the symmetry of the displacement.

It is these factors that make it possible to develop a computer program for determining quadrupole coupling constants and their temperature dependences from the superposition of the broadened central components of the spectra. For comparison with the actual experimental spectra, in this program it is necessary to introduce the corresponding values of the broadening of individual spectral components. The broadening of the lines is caused both by the existence of a chemical disorder and by magnetic dipole−dipole interactions.

In an ordered structure with long-range order, the homogeneous Gaussian broadening of the lines is a good enough approximation. The replacement of the Sc/Nb positions leads to a random spread in the electric-field gradients in places of the localization of the Sc nuclei. Since the dependence of the second-order quadrupole shift on the principal value of the electric-field gradient tensor V_{zz} is nonlinear, the broadening of the line due to the spread in the electric-field gradients is inhomogeneous.

We have used the function describing the inhomogeneous broadening of the spectrum due to a random spread in the electric-field gradients, which was proposed in the work by Laguta et al. [10]:

$$P(\nu) = \frac{1}{\sqrt{2\pi\alpha\nu}\Delta} \exp\left(-\frac{\nu + \alpha(\nu_Q^0)^2}{2\alpha\Delta^2}\right) \cosh\frac{\nu_Q^0}{\Delta^2}\sqrt{\frac{\nu}{\alpha}}, \quad (2)$$

where Δ is the width of the Gaussian distribution with respect to the average value of the electric-field gradient tensor V_{zz}^0, α is the parameter determined in relationship (1), and ν_Q^0 is the frequency corresponding to the average value V_{zz}^0.

The shape of the individual component of the spectrum is a result of the convolution of the homogeneously broadened line and the function $P(\nu)$; that is,

$$I(\nu) = \frac{1}{\delta\sqrt{2\pi}} \int_{-\infty}^{\infty} P(\nu')\exp\left[\frac{(-\ln 2(\nu - \nu')^2)}{\delta^2}\right]d\nu', \quad (3)$$

where δ is the inhomogeneous broadening parameter.

The deviation of the experimental profile of the spectrum from the calculated curve was minimized using the least-squares method. The degree of coincidence of the line profiles was estimated by the R factor with variations over a set of ten spectra constituting the orientation dependence. The program includes a version of the coexistence of different displacements and makes it possible to evaluate the relative fractions of the corresponding structures.

4. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the ^{45}Sc NMR spectra measured in the paraelectric phase at a temperature of 505 K for three orientations of the PSN crystal in a magnetic field. The spectrum represents a superposition of a narrow intense line and a broad component. The same shape of the ^{45}Sc NMR spectrum was observed in the paraelectric phase of the PSN single crystals of another origin [9]. As can be seen from this figure, the position of the narrow intense line in the spectrum does not depend on the orientation of the crystal in a magnetic field. The maximum in the intensity of this narrow line is located at the Larmor frequency ν_L accurate to within a small magnitude of the chemical shift. The zero (to within the accuracy of the measurement) value of the shift in the quadrupole frequency for the narrow component of the spectrum indicates that it is attributed to regions of the structure with the cubic symmetry. The small width of this line is associated with the fact that it corresponds to a long-range order structure, i.e., the elpasolite structure. The inhomogeneous broadening parameter δ was determined from the orientation dependence of the second moment of the ^{45}Sc NMR line, which was calculated from the known coordinates of the atoms in the PSN structure [1]. The magnetic dipole−dipole interactions with neighboring nuclei were taken into account in the sphere with a radius of 50 Å within the rigid lattice approximation. Since the spectra were calculated in a very wide temperature range, the inhomogeneous broadening parameter δ in the calculation had a small variable correction.

The broad component of the spectrum, whose shape and position depend on the orientation of the crystal in a magnetic field, indicates the presence of regions with a structure lower that cubic even in a deep paraelectric phase. Since the Burns temperature in PSN is approximately equal to 630 K, the presence of such regions in the crystal can be expected, for example, from data on diffuse scattering [1, 11]. Our purpose was to determine the structure (or structures)
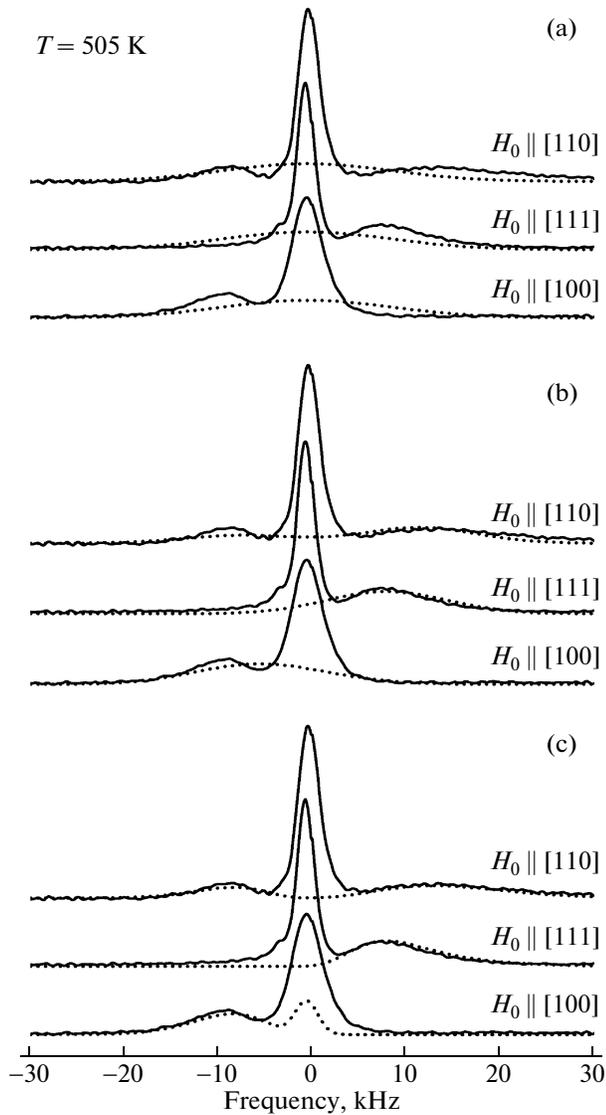
Fig. 1. ^{45}Sc NMR spectra measured in the paraelectric phase at a temperature of 505 K for three orientations of the PSN crystal in a magnetic field. The solid and dotted lines represent the experimental and calculated spectra, respectively. In the model, the displacement of scandium ions is specified as follows: (a) along the directions of the $[111]_p$ type and (b, c) along the directions of the $[001]_p$ type. (a, b) Homogeneous Gaussian broadening of the components and (c) inhomogeneous broadening added at the expense of the spread in the parameters of the electric-field gradient tensor.

Fig. 2. ^{45}Sc NMR spectra measured in the ferroelectric phase (325 K). The dot-dashed line shows the ^{45}Sc NMR spectrum of trigonal domains in the elpasolite structure, and the dotted line represents the contribution to the line shape from the tetragonal perovskite structure disordered over the Sc/Nb positions. The dashed line indicates the calculated total spectrum.

All lines of the spectra shown in Figs. 1a and 1b were approximated by the Gaussian broadening. The experimental spectrum is in rather close agreement with the calculated spectrum presented in Fig. 1b. In the second approximation, for the ^{45}Sc displacements along directions of the $[100]_p$ type, we introduced a random distribution of the quadrupole coupling constants with the use of relationship (2). This led to a very good coincidence between the experimental and calculated spectra (Fig. 1c). Thus, according to the performed analysis, the broad ^{45}Sc NMR line in the spectrum of the paraelectric phase corresponds to position-disordered regions with a tetragonal distortion of the cubic structure. The shape of the ^{45}Sc NMR spectrum, which is shown in Fig. 1c, is retained over the entire region of the existence of the paraelectric phase under investigation. An increase in the temperature leads only to a gradual narrowing of the components of the NMR spectrum.

Below the temperature of the phase transition to the polar phase, the line of the cubic elpasolite structure has already ceased to be a singlet. The minimum of the R factor is achieved for the displacement of the scandium ion along four equivalent directions of the $[111]_p$ type (Fig. 2). For the magnetic field directed along $[110]_p$, there are two lines of elpasolite with the double intensity.

Figures 3 shows the temperature dependences of the quadrupole coupling constants q_{tetr} and q_{trig}, which were obtained from analyzing the profile of the superposition of the central components in the ^{45}Sc spectra. It should be noted that the very small quantity $q_{trig} \neq 0$, which is shown in Fig. 3 in the region of the paraelectric phase, is a necessary "seed" value for the operation

responsible for the broad spectral component in the paraelectric phase. We used different structural models and a program for computer simulation of the spectra.

In the simplest model (hereinafter, it will be referred to as model 1), for the ^{45}Sc displacements corresponding to the broad line of the spectrum, we tested directions of the types $[111]_p$ (Fig. 1a) and $[100]_p$ (Fig. 1b).

Fig. 3. Temperature dependences of the quadrupole coupling constants q_{tetr} (squares) and q_{trig} (triangles) in model 1.

Fig. 4. Temperature dependence of the relative contents of the tetragonal and trigonal phases in the PSN crystal.

of the variational program. The corresponding frequency shift of the lines in the spectrum is less than the experimental accuracy of its determination. The non-linear temperature dependence of the quadrupole coupling constant q_{trig} at temperatures below 350 K in model 1 reflects the phase transition to the ferroelectric phase in the ordered PSN modification with the elpasolite structure. The quadrupole coupling constants q_{tetr} presented in Fig. 3 corresponds to a sufficiently strong tetragonal distortion of the cubic PSN structure in disordered regions. However, the value of this constant in the phase transition region changes only insignificantly.

The model considered above completely describes the spectrum of the paraelectric phase, but the phase transition in it is clearly pronounced only in regions of the crystal with the ordered structure. The obtained result can be explained by the fact that model 1, which is adequate for the paraelectric phase, is too simple to describe the polar state.

In the polar phase, we analyzed the set of displacements and, accordingly, the group of lines in the spectrum of the PSN structure ordered over the Sc/Nb positions, as well as the group of displacements and spectral lines that makes it possible to simulate the situation observed in disordered regions of the crystal (hereinafter, it will be referred to as model 2). In the disordered PSN modification, this model allows for the coexistence of displacements scandium ions along the directions $[111]_p$ and $[100]_p$. Above the temperature of the phase transition to the polar phase, the presence of the trigonal phase in the compound is determined by a fraction of ~0.25 (Fig. 4). At temperatures below 375 K, the content of this phase begins to increase at the expense of the disordered tetragonal phase and reaches a value of ~0.4 at a temperature of 275 K. The fraction of the tetragonal structure at 275 K decreases to the level of accuracy in the determination of the weight contributions in model 2. At lower temperatures, the spectrum of disordered regions in PSN loses a well-defined structure and the
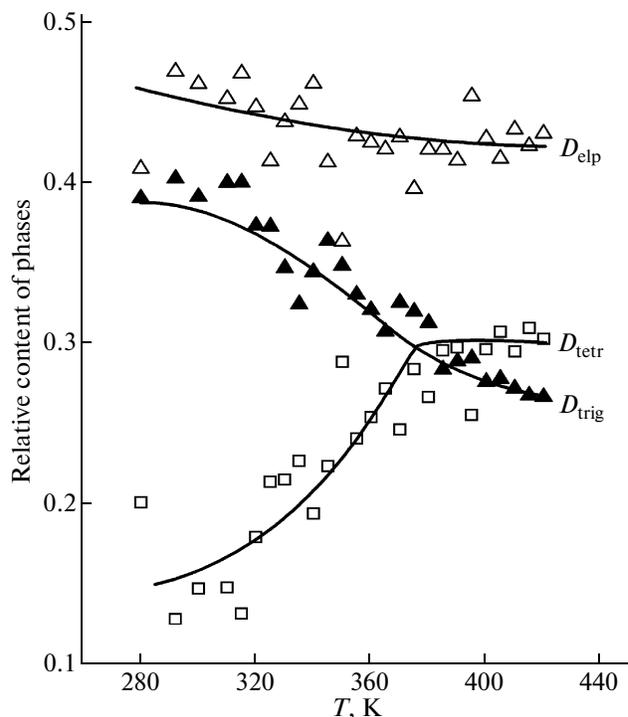
relative contributions of the tetragonal and trigonal phases are determined with a low accuracy. The fraction of the ordered elpasolite structure in the paraelectric phase is equal to ~0.43.

Figure 5 shows the temperature dependences of the quadrupole coupling constants. In this figure, white triangles indicate values of the quadrupole coupling constant q_{elp}, which corresponds to the elpasolite structure. At a temperature of ~350 K, this constant nonlinearly increases from the "seed" value in the paraelectric phase. The temperature dependence of the quadrupole coupling constant q_{elp} is close to that obtained in model 1. Black triangles indicate values of the quadrupole coupling constant q_{trig} for disordered regions of the crystal with displacements of scandium ions along directions of the [111] type. The value of this constant at high temperatures is significantly greater than the "seed" value for the elpasolite structure. Because of the large spread in the values of q_{trig}, it is difficult to exactly determine the temperature at which the quadrupole coupling constant begins to slowly increase. Nonetheless, in Fig. 4, we can see a well-defined range of temperatures at which the content of the disordered trigonal phase in this model begins to increase. This temperature, which is equal to 375 K, corresponds to the phase transition to the polar phase in the disordered PSN modification. The temperature dependence of the quadrupole coupling con-

stant q_{tetr} for disordered regions with the tetragonal structure also exhibits a phase transition at 375 K.

Thus, according to model 2, in the paraelectric phase, apart from the regions ordered over the Sc/Nb positions of the cubic elpasolite structure, there also exist regions of the disordered structure with trigonal and tetragonal distortions. The relative content of these structures at different temperatures is presented in Fig. 4. The trigonal disordered phase at temperatures below 375 K gradually replaces the disordered tetragonal phase. By this means, model 2 describes the diffuse phase transition occurring in the PSN crystal disordered over the Sc/Nb positions. The disadvantage of model 2 is a rather large spread in the model parameters with variations in the temperature. Upon minimization of the R factor, there appear local minima with somewhat different combinations of the parameters. Nonetheless, in this model, it is clearly seen that, in the disordered PSN modification, there occurs a diffuse phase transition from the tetragonal phase to the trigonal phase.

Model 2 most completely describes the changes occurring in the PSN structure in the temperature range under investigation. The changes observed in the elpasolite structure are in agreement with the diffraction data [1, 2] over a wide range of temperatures. However, the broad line in the ^{45}Sc NMR spectrum of the PSN structure disordered over the entire region of the existence of the paraelectric phase is adequately described by the displacements of the scandium ions along directions of the $[100]_p$ type, rather than along those of the $[111]_p$, as follows from data on the structure determination using the Rietveld method [1, 2].

In the disordered PSN modification, according to the neutron diffraction data, the average cubic structure exists before the phase transition to the polar phase at a temperature of 375 K [1, 2]. However, at temperatures below 630 K, the local structure differs significantly from the average structure, which has been revealed from the increase in diffuse scattering around some of the Bragg peaks with decreasing temperature [1, 2]. The results presented by Malibert et al. [1] and Perrin et al. [2] are in agreement with the data obtained by Takesue et al. [11], who reported on the enhancement of ferroelectric fluctuations, according to the observations of diffuse scattering around three hundreds reflections with decreasing temperature in the paraelectric phase down to the phase transition temperature. Unfortunately, because of the weak intensity of diffuse scattering in PSN, one could not determine the magnitude and direction of the displacement of the Pb atoms from the positions in the cubic structure. In the previously studied crystal PbMg$_{1/3}$Nb$_{2/3}$O$_3$ (PMN), the observed increase in diffuse scattering at temperatures above the phase transition to the polar phase was interpreted as a result of the nucleation and growth of clusters that are precursors of the rhombohedral polar phase in the cubic phase.
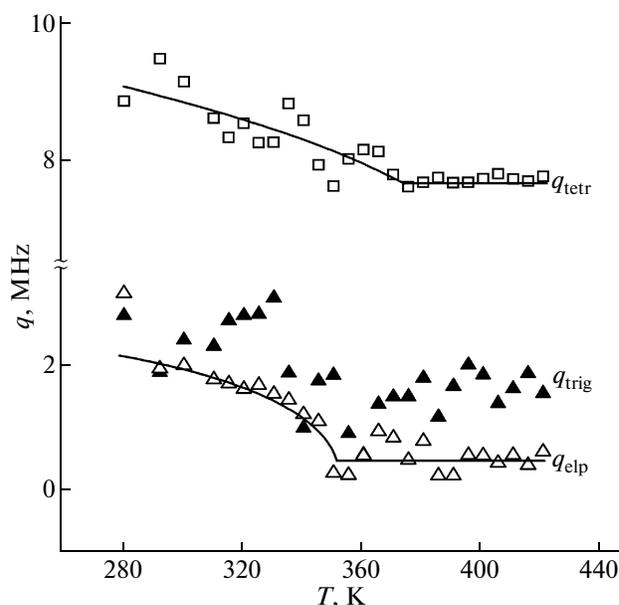
Fig. 5. Temperature dependences of the quadrupole coupling constants in model 2.

This interpretation of the behavior of diffuse scattering with approaching the temperature of the ferroelectric phase transition was used in [1, 2] for explaining a similar phenomenon observed in the PSN structure.

The growth of clusters, which are precursors of the phase transition to the ferroelectric phase, should be accompanied by a noticeable increase in the intensity of the ^{45}Sc NMR lines, which correspond to displacements of the scandium ions along directions of the $[111]_p$ type. As a consequence, the PSN structure should exhibit a pronounced temperature dependence of the shape of the broad component of the spectrum over a very wide temperature range, from approximately 635 K to the phase transition temperature of ~350 K. Experimentally, we have observed only a broadening of the lines forming a superposition. From this point of view, it is of interest to compare our data with the results of the investigation of the Pb(Sc$_{1/2}$Ta$_{1/2}$)O$_3$ (PST) compound with similar structure and properties [12]. The diffraction data in that work were obtained using synchrotron and pulsed neutron radiation. The average crystallographic structure was determined by the Rietveld method. At temperatures below the ferroelectric phase transition, the PST crystal undergoes a trigonal distortion, which corresponds to the displacements of Pb atoms along the [111] direction, i.e., the easy polarization axis for the perovskite structure. The local structure was investigated using the pair-density function (PDF) method, which has made it possible to determine the distribution of atomic density as a function of the interatomic distances in periodic structures, glasses, and liquids. This method has also been employed for determining

local deviations of the structure from the average structure by comparing the pair-density function calculated for the long-range order structure with the pair-density function obtained from diffraction data [13]. Experimentally, the pair-density function can be obtained by the Fourier transformation of diffraction data, including Bragg diffraction peaks and diffuse scattering.

The analysis performed by Dmowski et al. [12] has demonstrated that, locally, in the region of the structure expanding during the simulation from the radius of ~8 Å to eight unit cells, the displacements of lead atoms occur along directions of the $[100]_p$ type. Such a large difference between the local and average structures should lead to the formation of a complex frustrated structure. Dmowski et al. [12] considered a hypothetical structure where the direction of a local displacement of the lead atoms changes at large distances from point to point between three equivalent directions of the $[111]_p$ type, thus resulting in the formation of an average cubic structure. It should be noted that a similar situation is encountered not only in complex perovskites containing lead but also in simple perovskites, for example, $PbTiO_3$ [14] and $PbZrO_3$ [15], which do not exhibit properties of relaxors.

The X-ray diffraction patterns of PSN and PST do not contain any indications of the existence of tetragonal distortions. However, it is known that, if the correlation length of the displacements is small (a few unit cells), the Rietveld method includes these displacement in the thermal factor. For the cubic phase of the PSN crystal, the determination of the structure in the temperature range 375–653 K gave anomalously large thermal B factors for lead ($B_{iso} = 4.5$ Å^2), sufficiently large B factors for oxygen, and normal B factors for Sc/Nb.

From the analysis of the diffuse scattering lines in the paraelectric phase, Malibert et al. [1] and Perrin et al. [2] drew the conclusion that, in the cubic structure of PSN, there exist small regions with displacements of Pb atoms in the ($1\bar{1}0$) planes that are orthogonal to the $[111]_p$ direction. For the disordered PSN modification, the displacement approximately equal to 0.25 Å along the directions [100], [110], and [111] leads to the normal value of the B factor approximately equal to 2.1 Å^2 [1].

At low temperatures, the position of the Pb atom along the polar axis is fairly well determined, but there remains a positional disorder in the plane orthogonal to this axis. At a temperature of 100 K, in addition to the Bragg peaks 010, 110, and 200, photographs show the diffuse scattering lines parallel to the directions [$1\bar{1}0$] and [110]. This diffuse scattering suggests the existence of static or dynamic correlated displacements in the ($1\bar{1}0$) planes. A clear minimum of the R factor is obtained for the displacement along the [110]

direction. When the displacements of the Pb atom in the plane orthogonal to the threefold axis are taken into account, the thermal B factor decreases from 1.76 Å^2 to the normal value of 0.66 Å^2. The existence of a positional disorder of lead ions is also indicated by a disk-shaped displacement ellipsoid elongated along the directions orthogonal to the C_3 axis [1, 2]. The width of the reflections corresponds to the correlation length of the order of several lattice parameters. The intensity of the superstructure reflections is very low, so that they have detected neither by neutron diffraction nor by X-ray diffraction. The results obtained from the electron diffraction investigations for the polar phase $PbZr_xTi_{1-x}O_3$ (PZT) were used to propose a multidomain model with the correlated displacements along the $[100]_p$ direction, which are overlapped with the displacements along the $[111]_p$ direction [16]. It is interesting to note that the aforementioned disk-shaped ellipsoid of the displacements of Pb atoms observed in PSN can be obtained by the spatial averaging over the three displacements of lead atoms in the $[100]_p$ directions. The weak superstructure reflections (1/2 3/2 0) and (5/2 3/2 0) observed in PSN are also consistent with this model.

5. CONCLUSIONS

Corker et al. [16] noted that, because of the low penetrability of the radiation, the surface layer of the sample has been investigated using the electron diffraction method. In the NMR method, information comes from local regions of the crystal, irrespective of their location in the sample. In the diffraction data cited in this paper, the R factor in the Rietveld analysis is almost completely independent of the direction and magnitude of the displacements of scandium ions in the PSN structure. Our data have revealed local displacements of the scandium atoms from positions in the cubic structure of the paraelectric phase along the same directions of the $[100]_p$ type as those observed for the Pb atoms according to the data reported by Dmowski et al. [12].

It should be noted that the fraction of crystal regions with such displacements, according to our data, is large enough (see Fig. 4) to speak about the existence of the tetragonal phase of disordered PSN at temperatures above 375 K. Possibly, the temperature of 630 K, which is considered in the literature as the Burns temperature, is actually the temperature of the phase transition from the cubic phase to the tetragonal disordered modification. Unfortunately, this temperature is not achievable in our spectrometer. As we noted earlier, in disordered PSN at temperatures above 375 K, there also exist regions of the trigonal phase. In the temperature range where a strong dielectric relaxation is observed, the disordered modification of PSN has a heterophase structure, like other relaxors, for example, NBT [8].

In the studied crystals, regions of the tetragonal phase with a small correlation length of displacements of the Pb and Sc atoms are randomly distributed in the cubic matrix of elpasolite. As the temperature T_c is approached, the fraction of the trigonal structure in disordered regions of the crystal increases. At temperatures below ~320 K, the tetragonal structure is completely replaced by the trigonal polar phase (Fig. 4).

Note that the observation of the tetragonal phase eliminates the problem of the large difference between the local and average structures of PSN.

ACKNOWLEDGMENTS

REFERENCES

1. C. Malibert, B. Dkhil, J. M. Kiat, D. Durand, J. F. Bérar, and A. Spasojevic-de Biré, J. Phys.: Condens. Matter **9**, 7485 (1997).
2. C. Perrin, N. Menguy, E. Suard, Ch. Muller, C. Caranoni, and A. Stepanov, J. Phys.: Condens. Matter **12**, 7523 (2000).
3. G. A. Smolenskii, V. A. Isupov, and A. I. Agranovskaya, Sov. Phys. Solid State **1**, 150 (1959).
4. I. P. Raevski, S. A. Prosandeev, S. M. Emelyanov, V. G. Smotrakov, V. V. Eremkin, I. N. Zakharchenko, S. I. Raevskaya, E. S. Gagarina, F. I. Savenko, and E. V. Sahkar, Ferroelectrics **298**, 267 (2004).
5. C. G. F. Stenger and A. J. Burggraaf, Phys. Status Solidi A **61**, 275 (1980).
6. A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961; Inostrannaya Literatura, Moscow, 1963).
7. I. P. Aleksandrova, A. A. Sukhovskii, Yu. N. Ivanov, Yu. E. Yablonskaya, and S. B. Vakhrushev, Phys. Solid State **50** (3), 496 (2008).
8. I. P. Aleksandrova, A. A. Sukhovsky, Yu. N. Ivanov, Yu. E. Yablonskaya, and S. B. Vakhrushev, Ferroelectrics **378**, 16 (2009).
9. V. V. Laguta, M. D. Glinchuk, I. P. Bykov, R. Blinc, and B. Zalar, Phys. Rev. B: Condens. Matter **69**, 054103 (2004).
10. V. V. Laguta, M. D. Glinchuk, S. N. Nokhrin, I. P. Bykov, R. Blinc, A. Gregorovic, and B. Zalar, Phys. Rev. B: Condens. Matter **67**, 104106 (2003).
11. N. Takesue, M. Maglione, and H. Chen, Phys. Rev. B: Condens. Matter **51** (10), 6696 (1995).
12. W. Dmowski, M. K. Akbas, P. K. Davies, and T. Egami, J. Phys. Chem. Solids **61**, 229 (2000).
13. T. Egami, Mater. Trans., JIM **31**, 163 (1990).
14. R. J. Nelmes, R. O. Piltz, W. F. Kuhs, Z. Tun, and R. Restori, Ferroelectrics **108**, 165 (1990).
15. S. Teslic and T. Egami, Acta Crystallogr., Sect. B: Struct. Sci. **54**, 750 (1996).
16. D. L. Corker, A. M. Glazer, R. W. Whatmore, A. Stallard, and F. Fauth, J. Phys.: Condens. Matter **10**, 6251 (1998).

Translated by O. Borovik-Romanova