

RELAXOR FERROELECTRICS

^{23}Na NMR in the Relaxor Ferroelectric $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$

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Abstract—The ^{23}Na NMR spectra of a $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ crystal are studied at frequencies of 79.4 and 15.7 MHz in the temperature range 150–720 K. It is revealed that, at all temperatures, the crystal contains regions with a nearly cubic matrix and polar clusters. The temperature dependence of the local distortion of the Na environment in the clusters is determined. The dynamics of the reorientation of the local cluster polarization in the tetragonal and trigonal NBT phases is analyzed.

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1. INTRODUCTION

The compound $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ (NBT) belongs to the class of relaxor ferroelectrics of the ABX_3 perovskite type with substitution in the A position. As the temperature decreases, this compound undergoes a sequence of phase transitions from the cubic phase ($Pm\bar{3}m$) to the tetragonal phase ($P4bm$, $Z = 2$) at a temperature of 813 K (T_1) and to the trigonal phase ($R3c$, $Z = 6$) at approximately 600 K (T_2) [1–5]. According to some authors (see, for example, [2–5]), the tetragonal and trigonal phases coexist over a wide temperature range (533–693 K). However, it has been repeatedly suggested that an intermediate phase also exists in this range.

There is presently also a lack of certainty concerning the relation between the local structure of polar clusters and the volume-averaged structure of the tetragonal and trigonal phases. The NMR technique is employed to advantage to investigate the local structure of partially disordered crystals and inhomogeneous media. The purpose of this study was to examine the symmetry of the distortion of the ^{23}Na environment in different regions of the heterophase structure of the NBT relaxor ferroelectric over a wide temperature range encompassing phase transitions. The phenomenon of positional exchange of Na ions is considered in connection with the fluctuation reorientation of the local cluster polarization. It should be noted that earlier NMR studies were carried out only for true relaxors of the general formula $AB_{1-x}B'_xX_3$, whose volume-averaged structure remains cubic down to the lowest temperatures [6, 7]. These studies included simulations of the observed NMR line within several models of a pseudospin glass (see, for example, [7]).

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The ^{23}Na NMR spectra of an NBT single crystal were measured at Larmor frequencies of 79.4 and 15.7 MHz in the temperature range 150–720 K. The measurements in a strong magnetic field were carried out on an Avance-300 spectrometer in the solid-echo pulse sequence mode. The duration of a 90° pulse was 2.5 μs , and the spacing between the pulses was 12 μs . The measurements in a weak magnetic field were performed continuously with accumulation of the first derivative of the line shape.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The characteristic line shape in true relaxors is essentially a superposition of the broadened central line of the $-1/2 \longleftrightarrow 1/2$ transition with overlapping first-order satellites forming a broad pedestal [7]. The quadrupole coupling constant e^2qQ/h for the cubic phase is equal to zero, and the observed quadrupole effects in the spectrum are associated with the low symmetry of the polar clusters. The shape of the narrow component considered in the limit of fast motion is actually a convolution of the inhomogeneous broadening $f(\nu')$ associated with both the distribution of the local cluster polarization and the homogeneous width, which is primarily determined by the internuclear dipole–dipole interaction:

$$F(\nu) = \int f(\nu')L(\nu - \nu')d\nu. \quad (1)$$

The volume-averaged NBT structure in the temperature range covered has a symmetry lower than cubic, thus greatly complicating interpretation of the quadrupole effects revealed in the spectrum. We recall, however, that the Na nucleus in both the tetragonal and trig-

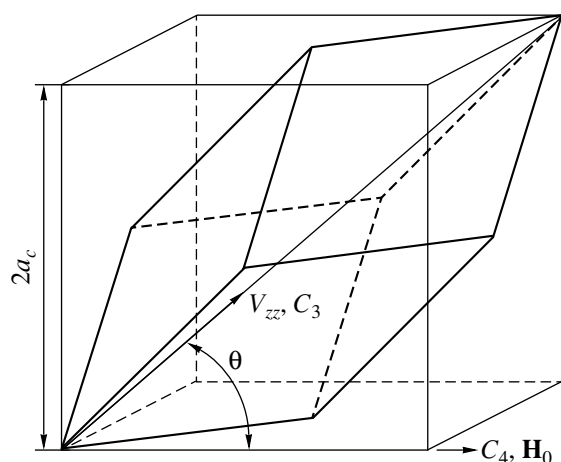


Fig. 1. Orientation of the cell of the NBT trigonal phase with respect to the pseudocubic cell with the parameter $a_p = 2a_c$ and the directions specifying the orientation of the crystal in the magnetic field \mathbf{H}_0 .

onal phases lies on the symmetry axes C_4 and C_3 , respectively. In this particular case, the orientation of the principal electric-field gradient (EFG) tensor axes is known and the asymmetry parameter is zero. In the trigonal phase, the principal axis V_{zz} of the EFG tensor is aligned with the threefold symmetry axis C_3 of the pseudocubic cell (Fig. 1). The ²³Na line ($I = 3/2$) was measured in a special orientation of the magnetic field along the fourfold axis C_4 (Fig. 2). In this case, the angle θ between the principal axis V_{zz} and the direction of the magnetic field \mathbf{H}_0 , which enters into standard relation (2) (see, for example, [8]), corresponds to the magic value $54^\circ 44'$ when the quadrupole splitting of the satellites Δv in the first-order perturbation theory,

$$\Delta v = \frac{3}{4I(2I-1)} \frac{e^2 q Q}{h} \frac{1}{2} (3 \cos^2 \vartheta - 1) \quad (2)$$

is zero for all equally probable orientations of the C_3 axis. The spectrum has a broadened central component and a clearly pronounced pedestal formed by first-order satellites. This line shape can be observed in a trigonal structure only as a result of a loss of long-range order. There should be a set of orientations of the principal axes of the EFG tensor in local regions with respect to the C_3 axis of the volume-averaged structure. The shift of the central component in the second-order perturbation theory,

$$\delta v = -\frac{9}{64} \frac{I(I+1) - 3/4}{(I(2I-1))^2} \left(\frac{e^2 q Q}{h} \right)^2 \times \frac{1}{v_L} (1 - \cos^2 \vartheta) (9 \cos^2 \vartheta - 1) \quad (3)$$

is inversely proportional to the Larmor frequency v_L . Thus, in weak magnetic fields, the linewidth is gov-

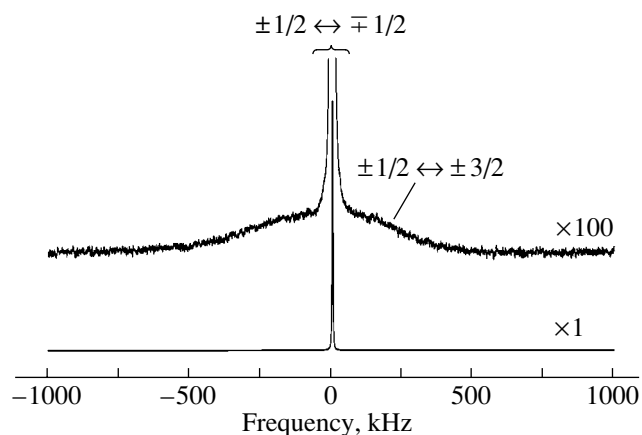


Fig. 2. ²³Na NMR line shape at a frequency of 79.4 MHz with the magnetic field oriented along the C_4 axis of the cubic cell.

erned primarily by the distribution function of second-order shifts $f(v)$. A comparison of the second moments M_2 of the line (corresponding to the $-1/2 \leftrightarrow 1/2$ transition) in weak and strong magnetic fields suggests that, in our case, the contribution of the dipole-dipole broadening in the weak field does not exceed 1% of the total value of M_2 .

The temperature dependences of the line shape of the central component were measured at a frequency of

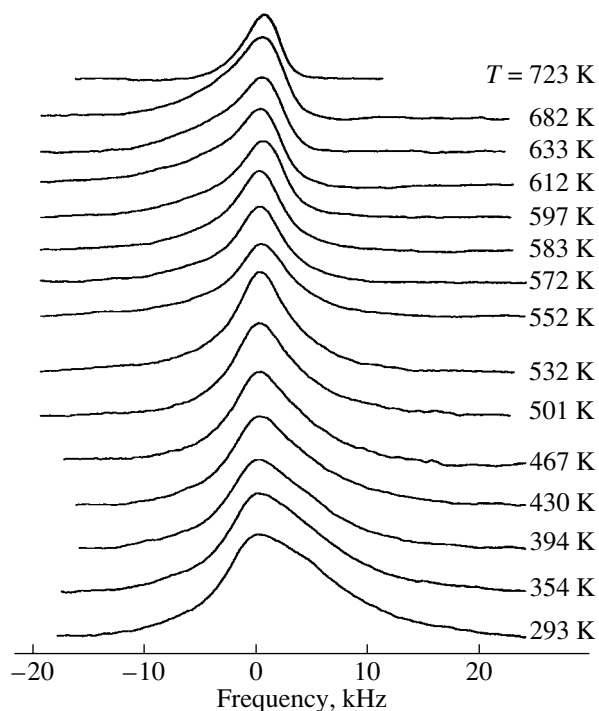


Fig. 3. Evolution of the central line with variations in temperature.

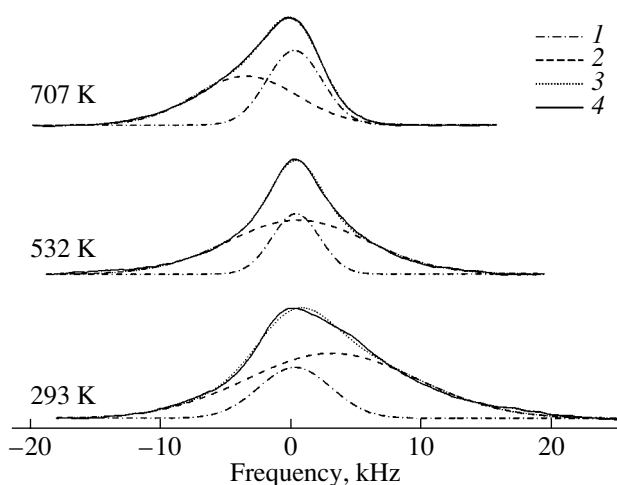


Fig. 4. Decomposition of the central line into components 1 and 2 at different temperatures. Profile 3 is the sum of curves 1 and 2, and 4 is the experimental curve.

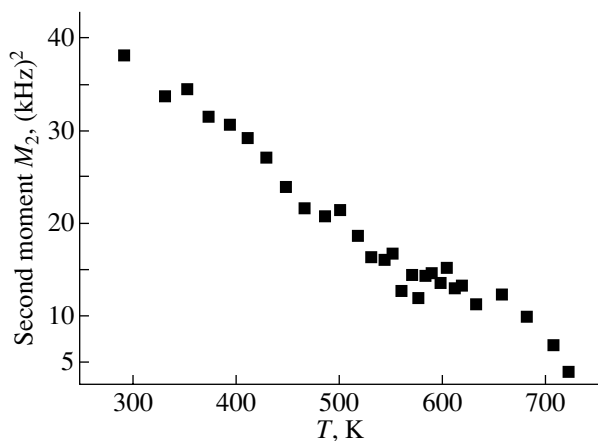


Fig. 5. Temperature dependence of the second moment of the central line in the spectrum.

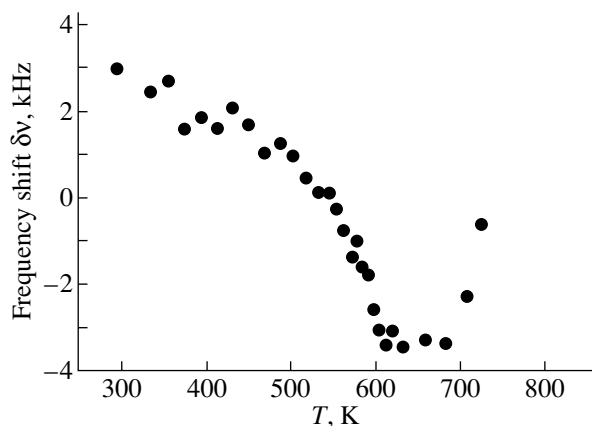


Fig. 6. Temperature dependence of the second-order quadrupole shift for line 2.

15.7 MHz. Figure 3 displays some of the spectra obtained. The line is asymmetric throughout the temperature range covered, and its shape varies continuously. This suggests the presence of at least two overlapping lines with a temperature-dependent mutual arrangement. In Fig. 4, the line at several temperatures has the form of a superposition of two Gaussian components, 1 and 2. The comparatively narrow component 1 is centered on ν_L , and its position and width do not vary within the limits of experimental error throughout the temperature range covered. The broader component 2 has a temperature-dependent second-order shift (Fig. 5) and a temperature-dependent linewidth (Fig. 6). The relative intensity of lines 1 and 2 is about 1 : 3 below 680 K. As the temperature increases even further, the intensity of the narrow component increases and the intensity ratio tends to 1 : 2.

The Na ions contained in the unit cell of the $R3c$ trigonal structure are of the same structural type and lie on the threefold symmetry axis. The presence of two overlapping central components implies the existence of regions with different distortions of the nuclear environment. Line 1 characterizes regions with slight distortions from the cubic structure. Since it is highly sensitive to changes in the nearest environment of a nucleus in the chosen crystal orientation, the NMR method does not detect a noticeable variation in the frequency and width of this line throughout the temperature range covered. The pronounced quadrupole shift of line 2, which varies with temperature, derives from distorted regions of the structure.

The characteristic narrowing of this line with increasing temperature (Fig. 6) suggests positional exchange of the Na ion among several minima of its potential relief. This type of motion is possible if the Na ion is displaced away from the symmetry axis and occupies a special position only on a time-averaged basis. Positional exchange occurs both in the tetragonal phase and in the trigonal phase, because the limit of the fast motion is reached above 550 K. The displacement of the Na ion away from the fourfold axis in the tetragonal phase lowers the local symmetry of the cluster to monoclinic. It is quite probable that, when the Na ion is in the tetragonal phase, it is displaced to an intermediate position between the [001] and [111] directions. Fast exchange among the four possible Na positions leads to a nonzero time-averaged displacement along the [001] direction and to a corresponding contribution to the electric dipole moment. In the trigonal phase, the displacement fluctuates among the three equally possible positions with respect to the [111] direction. Below 300 K, the second moment of the spectrum varies little with a variation in temperature and the positional exchange is frozen out on the NMR scale. The volume-average trigonal structure exists at low temperatures as a statically averaged phase. This accounts for the line shape in a strong field at room temperature (Fig. 2). The above considerations provide a schematic explanation for the character of the cluster dipole moment fluctua-

tions in the tetragonal and trigonal NBT structures and for the ratio between the local and volume-averaged symmetries of these phases. Note also that the observed motions should be consistent with the frequency of exchange correlated within a polar region. These are substantially lower frequencies than could be expected for independent hops among the minima of the potential relief of the Na ion.

It is of interest that, for the tetragonal phase, an increase in the temperature leads to subsequent strong narrowing of the line practically down to the instrumental modulation-induced broadening. This narrowing implies the onset of diffusion exchange among all lattice positions of the Na ion. The nature of this process is easy to understand from an analysis of Fig. 5, in which the second-order quadrupole shift above 680 K tends rapidly to zero. The fast positional exchange of Na ions between the clusters and the matrix is an essential feature of the high-temperature region of the tetragonal phase. The above data shed light on the abrupt decrease of the Na/Bi shift near 680 K, which was revealed by neutron diffraction in [2].

The main contribution to the second-order shift comes from the displacement of the Na ion from its equilibrium position in the cubic phase. The temperature dependence of $\delta\nu$ obtained under heating clearly reveals a phase transition point at 610 K. Below this temperature, the local distortion of the Na environment in polar regions increases gradually. By measuring the temperature dependence of $\delta\nu$, one can usually examine the changes in the distortion of the nuclear environment more accurately. However, the temperature dependence contains a specific point (Fig. 5) where $\delta\nu$ reverses its sign. The orientational dependence described by relationship (3) and its specific points are determined by the symmetry and should persist within one phase. Reversal of the sign of the frequency shift implies an unusual situation. The results of our preliminary studies have demonstrated that the orientational dependences for the trigonal phase of NBT change significantly with a variation in temperature. This unusual phenomenon can result from the coexistence of the tetragonal and trigonal phases over a wide temperature range. In this stage of the study, we also cannot rule out

the possible existence of an intermediate phase between the tetragonal and trigonal phases. We are presently carrying out measurements of the orientational dependences of the second-order quadrupole shift at different temperatures and a computer simulation of possible variants of their interpretation.

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REFERENCES

1. G. A. Smolenskii, V. A. Isupov, A. I. Agranovskaya, and N. N. Kraiĭnik, *Fiz. Tverd. Tela (Leningrad)* **2** (11), 2982 (1960) [*Sov. Phys. Solid State* **2** (11), 2651 (1960)].
2. G. O. Jones and P. A. Thomas, *Acta Crystallogr., Sect. B: Struct. Sci.* **58**, 168 (2002).
3. S. B. Vakhrushev, B. E. Kvyatkovskii, N. M. Okuneva, É. L. Plachenova, and P. P. Syrnikov, *Pis'ma Zh. Éksp. Teor. Fiz.* **35** (3), 111 (1982) [*JETP Lett.* **35** (3), 134 (1982)].
4. S. B. Vakhrushev, B. E. Kvyatkovskii, R. S. Malysheva, N. M. Okuneva, and P. P. Syrnikov, *Fiz. Tverd. Tela (Leningrad)* **27** (3), 737 (1985) [*Sov. Phys. Solid State* **27** (3), 455 (1985)].
5. S. B. Vakhrushev, B. E. Kvyatkovskii, R. S. Malysheva, N. M. Okuneva, É. L. Plachenova, and P. P. Syrnikov, *Kristallografiya* **34** (1), 154 (1989) [*Sov. Phys. Crystallogr.* **34** (1), 89 (1989)].
6. M. D. Glinchuk, I. P. Bykov, and V. V. Laguta, *Ferroelectrics* **124**, 225 (1991).
7. R. Blinc, B. Zalar, A. Gregorovič, R. Pirc, and M. D. Glinchuk, *Ferroelectrics* **240**, 207 (2000).
8. A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, Oxford, 1961; *Inostrannaya Literatura*, Moscow, 1963).

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