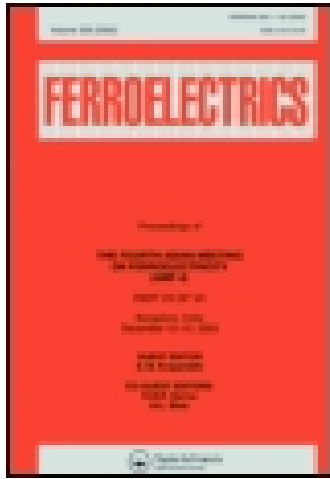


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## Ferroelectrics

Publication details, including instructions for authors and subscription information:

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I. P. Aleksandrova<sup>a</sup>, A. A. Sukhovskiy<sup>a</sup>, Yu. N. Ivanov<sup>a</sup>, Yu. E. Yablonskaya<sup>a</sup> & S. B. Vakhrushev<sup>b</sup>

<sup>a</sup> L.V. Kirensky Institute of Physics, Siberian Branch RAN, Krasnoyarsk, 660036, Russia

<sup>b</sup> A.F. Ioffe Physico-Technical Institute RAN, St-Petersburg, 194021, Russia

Published online: 20 Sep 2010.

To cite this article: I. P. Aleksandrova, A. A. Sukhovskiy, Yu. N. Ivanov, Yu. E. Yablonskaya & S. B. Vakhrushev (2009) Local and Average Structure of Relaxor  $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$  from the Point of View of NMR, *Ferroelectrics*, 378:1, 16-22, DOI: [10.1080/00150190902844809](https://doi.org/10.1080/00150190902844809)

To link to this article: <http://dx.doi.org/10.1080/00150190902844809>

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# Local and Average Structure of Relaxor $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ from the Point of View of NMR

I.P. ALEKSANDROVA,<sup>1,\*</sup> A.A. SUKHOVSKY,<sup>1</sup>  
YU. N. IVANOV,<sup>1</sup> YU. E. YABLONSKAYA,<sup>1</sup> AND  
S. B. VAKHRUSHEV<sup>2</sup>

<sup>1</sup>L.V. Kirensky Institute of Physics, Siberian Branch RAN, Krasnoyarsk, 660036, Russia

<sup>2</sup>A.F. Ioffe Physico-Technical Institute RAN, St-Petersburg, 194021, Russia

*<sup>23</sup>Na NMR spectra have been measured in a very low magnetic field at temperatures between 203 K and 780 K. The orientation dependences of the second-order quadrupole shifts of the central component were studied. The achieved spectral resolution is sufficient to test various models of short-range order in the  $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$  (NBT) structure using computer simulations of the spectral line shape. The polar monoclinic areas were found to coexist with the tetragonal phase insertions till the lowest investigated temperature 203 K. In the temperature range 203 K – 640 K the NMR spectra also display the presence of areas with very small deviation from the cubic structure (matrix).*

## Introduction

To date the averages structures of majority of ferroelectrics-relaxors are determined. The investigations of the local structures are complicated by a few reasons, particularly by anomalously large thermal factors that can be ambiguously interpreted when determining the structure. The NMR is a local method of structure analysis, as it is known. It is very sensitive probe to detect in measurement process any small changes of a “working” nucleus nearest surroundings. Earlier, the studies of quadrupole shift of central spectral components have been performed on Pb-containing crystals under high magnetic field [1, 2]. Advantage of high magnetic field techniques is well known however the quadrupole shift is inversely proportional to magnetic field value. In sufficiently low field the quadrupole shifts completely determine the shape of a spectral distribution of the overlapped central components [3]. The achieved spectral resolution was sufficient to test various structural models of NBT by modeling the shape of the observed spectral distribution.

## Results and Discussion

The <sup>23</sup>Na NMR spectra of NBT single crystal were measured at Larmor frequency 15.7 MHz. The angular dependences of the line shape were obtained at the rotation around the  $[110]_p$  direction of the pseudo-cubic cell at 203 K, 243 K, 293 K, 350 K, 400 K, 450 K,

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Received June 15, 2008.

\*Corresponding author. E-mail: alexin@iph.krasn.ru

475 K, 500 K, 540 K, 580 K, 640 K, 729 K and 780K. The continuous wave technique with a signal accumulation was used.

The compound under investigation,  $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$  (NBT), belongs to the ferroelectrics-relaxor of the  $\text{ABX}_3$  perovskite type with substitution in the A-position. In contrast to “true” relaxors, remaining to be cubic till the lowest investigated temperature, NBT exhibits a sequence of spontaneous phase transitions from the cubic phase ( $Pm\bar{3}m$ ) to the tetragonal phase ( $P4bm$ ,  $Z = 2$ ) at 813 K ( $T_{C1}$ ) and then to the trigonal phase ( $R3c$ ,  $Z = 6$ ) at approximately 600 K ( $T_{C2}$ ) [4–6]. The cubic and tetragonal phases are long-range ordered structures. In the trigonal phase, the long-range order is lost, the space group  $R3c$  describes an average structure.

In complex perovskites  $A'A''BX_3$  and  $AB'B''X_3$  the main contribution to the dipole moment of the polar cluster comes from the displacement of cation  $A$  from its equilibrium position in the cubic phase. The same displacement determines a value of quadrupole coupling constant ( $q$ ) on the  $^{23}\text{Na}$  nucleus. Since there is a fairly direct relation between the  $^{23}\text{Na}$  quadrupole coupling constant and the displacement making the main contribution to the electric dipole moment of polar areas one can use quite simple models. The type of Na ions displacements in our models have been chosen taking into account the neutron and x-ray data for NBT [4, 6].

In Model 1, a Na displacement in a polar areas is assumed to occur equally probably along  $[111]_p$ -type directions of the pseudocubic unit cell coinciding with a  $C_3$  axis of the rhombohedral  $R3c$  unit cell. The Na atom is located in a multi-welled (8-positions) potential around its averaged special position. The other type of assumed Na displacements corresponds to six  $[100]_p$  equally probable directions coinciding with the  $C_4$  symmetry axes of the  $P4bm$  space group. The model allows the coexistence of independent Na displacements along  $[111]_p$  and  $[100]_p$  directions at any of investigated temperature.

Model 2. This model, in addition to the displacements used in Model 1, also assumes regions of structure with a very small deviation from the cubic symmetry, a “matrix”. The position of the corresponding NMR line is varied within narrow interval around the Larmor frequency.

Model 3. The displacements of A ions (Na) in the polar areas occurs along  $[100]_p$ -type directions as was proposed for the Pb-containing relaxors. The Ti, Mg and Nb in this case are shifted along the  $[111]_p$  directions [7].

The second-order quadrupole shift,  $\delta\nu$ , of the central component ( $+1/2 \rightarrow -1/2$ ) for any Na positions in the crystal was calculated using known relation [8]:

$$\begin{aligned}\delta\nu &= -\frac{9}{64} \frac{(I(I+1) - 3/4) q^2}{(I(2I-1))^2} \frac{1}{\nu_L} (1 - \cos^2\theta)(9\cos^2\theta - 1) \\ &= Kq^2(1 - \cos^2\theta)(9\cos^2\theta - 1).\end{aligned}\quad (1)$$

Here,  $q = e \cdot Q \cdot V_{zz} / h$  is quadrupole coupling constant (where  $V_{zz}$  is the main value of the electric field gradient tensor (EFG) on the nucleus;  $Q$ , the nuclear quadrupole moment;  $e$ , the elementary charge;  $h$ , the Planck constant),  $\theta$  is the angle between the magnetic field direction and the principal  $z$  axis of EFG tensor,  $\nu_L$  is the Larmor frequency,  $I$ , the nuclear spin ( $I = 3/2$  for  $^{23}\text{Na}$ ).

The central component of the spectrum is a superposition of lines belonging to numerous magnetically and structurally nonequivalent positions of a  $^{23}\text{Na}$  nucleus (in detail see [9]). In the low magnetic field the shape of this non-resolved line noticeably depends on the crystal orientation.

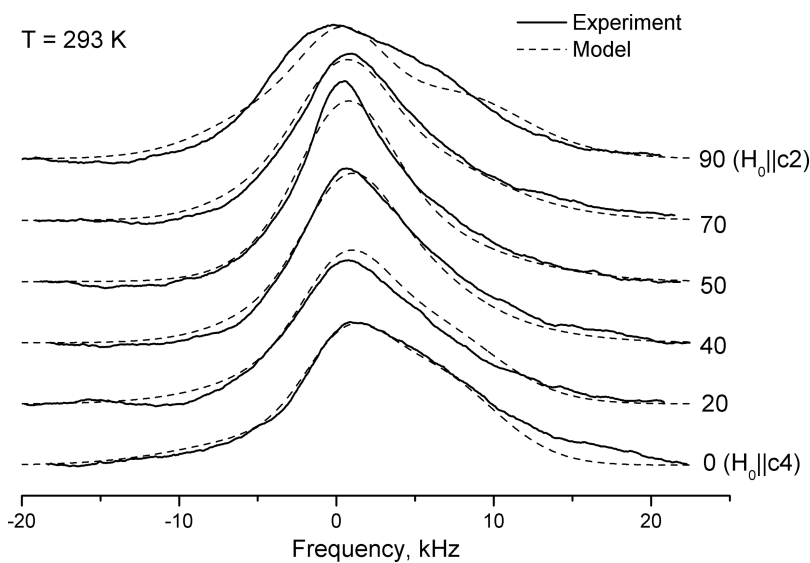
**Table 1**

The most important variables, corresponding to the minimal deviation  $\Delta$  between the experimental and simulated line shapes at different temperatures

Temperature, K	$q_{\text{trig}}$ , MHz	$q_{\text{tetr}}$ , MHz	$W_{\text{trig}}$ , kHz	$W_{\text{tetr}}$ , kHz	$W_{\text{matr}}$ , kHz	$X_{\text{trig}}$	$X_{\text{tetr}}$	$X_{\text{matr}}$	$\Delta$
Model 2									
203	1,24	1,22	3,99	6,45	2,78	0,44	0,25	0,29	0,010
243	1,21	1,29	4,16	5,96	2,68	0,46	0,23	0,30	0,005
293	1.18	1.13	3.94	6.13	2.60	0.43	0.29	0.28	0.018
350	1.19	1.11	3.68	5.94	2.66	0.45	0.28	0.27	0.013
400	1.17	1.05	3.54	5.49	2.54	0.29	0.35	0.37	0.011
450	1.14	1.03	3.12	5.00	2.42	0.29	0.33	0.38	0.011
475	1.18	1.04	3.08	4.97	2.43	0.20	0.31	0.49	0.012
500	0.93	0.98	3.42	4.71	1.96	0.25	0.50	0.25	0.015
540	1.05	0.91	1.63	4.38	1.91	0.06	0.59	0.35	0.019
580	0.03	1.05	1.37	4.00	1.89	0.01	0.70	0.29	0.019
Model 1									
Temperature, K	$q_{\text{trig}}$ , MHz	$q_{\text{tetr}}$ , MHz	$W_{\text{trig}}$ , kHz	$W_{\text{tetr}}$ , kHz	$W_{\text{trig}}(1)$ , kHz	$W_{\text{tetr}}(1)$ , kHz	$X_{\text{trig}}$	$\Delta$	
640	0.01	1.03	1.34	2.74	2.42	0.01	0.08	0.038	
729	0.03	0.87	2.39	0.419	1.94	0.05	0.00	0.031	

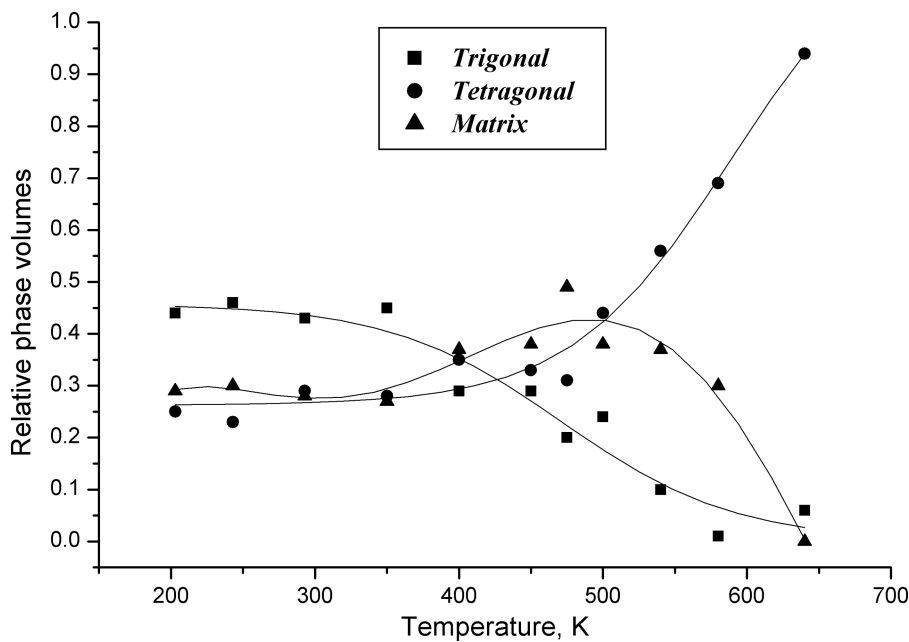
To obtain information on the temperature evolution of NBT structure from the NMR spectra we developed a computer program. The program allows one to calculate the spectral line shape for any crystal orientation in a magnetic field using a proposed structural model. When simulating the spectral shapes, the variable parameters are taken to be the values of  $q$  for the polar areas and the tetragonal phase; the peak intensity  $A$  and half-width  $W$  of the Gaussian broadening functions. The peak intensity and width of the matrix line are also variable parameters. The relative phase volumes  $X$  of the structurally different regions are determined from the integral intensities of the related spectral lines. The data array for each temperature includes ten spectra corresponding to the rotation angles,  $(\theta)$ , changing from  $0^\circ$  to  $90^\circ$  in steps of  $10^\circ$ . A comparison of the calculated and experimental spectra was performed using the least square technique.

The Table 1 lists the main variables corresponding to the minimal deviation  $\Delta$  between the profiles of the experimental and calculated spectra. From the data presented in the Table 1, it follows that, in the temperature range 203 K–580 K, the best agreement between the calculated and measured spectra is achieved for the structure in which the matrix and regions with displacements along directions of types  $[111]_P$  and  $[100]_P$  coexist. As an example, the experimental and calculated spectra at 293K are shown on the Fig. 1. From the Table 1 also one can see how the phase volumes  $X$  of the regions with different type of distortions of nearest surroundings of  $^{23}\text{Na}$  nuclei are changed with temperature. The relative phase volumes as a function of temperature are shown on the Fig. 2. Attempts to fit the orientation dependences using Model 2 for temperatures above  $T_{c2}$  ( $\sim 610$  K) lead to noticeable increase of  $\Delta$ . For the orientation dependences at 640 K and 729 K the best fit shows the Model 1, in which the matrix is absent. The results are presented in the Table 1. In Model 1 in addition to Gaussian broadening  $W$ , a broadening proportional to the second-order shift,  $W_{\text{trig}}(1)$  and  $W_{\text{tetr}}(1)$  was introduced.

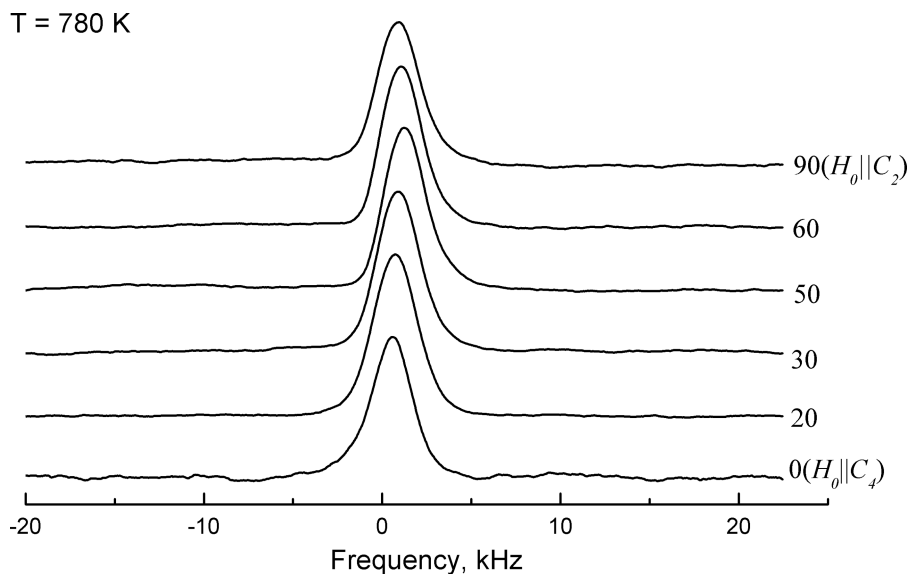


**Figure 1.** Angular dependences of  $^{23}\text{Na}$  NMR spectra at 293 K. Solid line shows the experimental shape, dashed line – the simulated one.

At temperatures above 700 K the quadrupole shift is gradually averaged due to diffusion of  $^{23}\text{Na}$  nuclei over all positions in the tetragonal structure [3]. The Fig. 3 shows the nearly symmetric central line in all orientations of the crystal at 780 K. The shifts  $\delta\nu$  at all orientations are very small, less than 500 Hz. These data indicate the approach to the fast-motion



**Figure 2.** The phase volumes  $X$ , as a function of temperature.



**Figure 3.** Angular dependences of  $^{23}\text{Na}$  NMR spectra at 780 K.

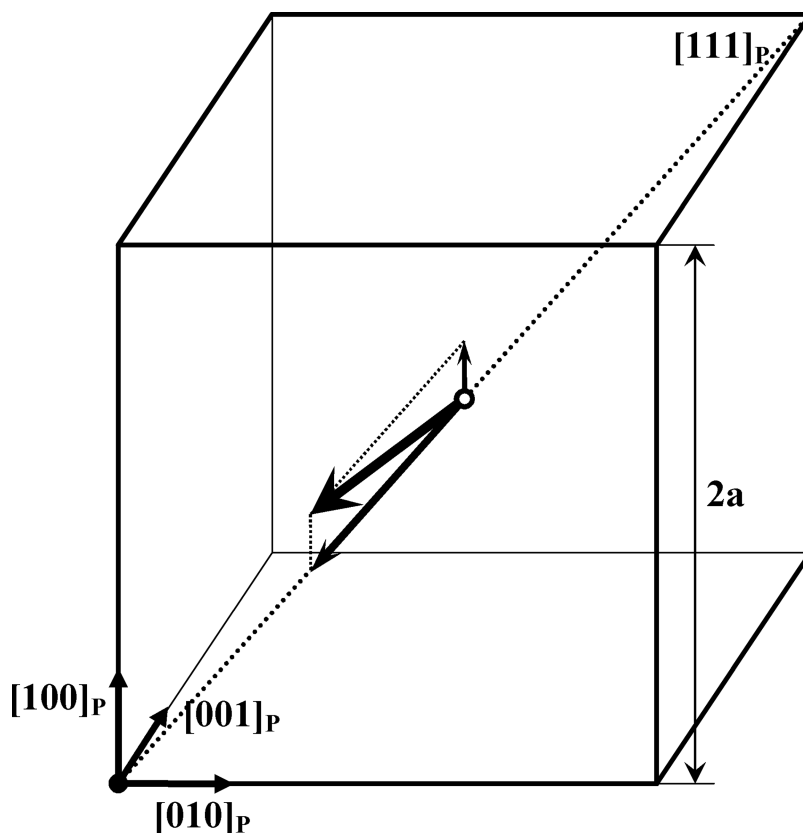
limit recovering the cubic symmetry. The pronounced influence of  $^{23}\text{Na}$  diffusion on the spectral shape restricts application of our models by nearly 730 K.

Our attempt to use Model 3 showed dramatic disagreements between the measured and calculated spectra.

Model 2 describes fairly well the shape of the measured  $^{23}\text{Na}$  NMR spectrum over a wide temperature range where the average trigonal structure exists. However, the exchange of the Na ion between the eight minima of the potential relief should cause its average position to become cubic. This result is not correct for the average R3c structure. The dynamical averaging that recovers the cubic structure is observed near 780 K. We assume that the Na displacements in the polar area in addition to the cooperative (longitudinal) shift along the polar  $[111]_p$  axis have small components disordered over six  $[100]_p$  directions (Fig. 4). If the displacements of Na ions from the three-fold symmetry axis are small, the axially symmetric approximation (1) is applicable.

At low temperatures, reorientation of the electric dipole moments is frozen [3, 9, 10]. In the ordered structure of the polar region the small component of the Na displacement is oriented along one of  $[100]_p$  directions. On the average, the crystal remains trigonal structure. At high temperature the motional averaging over six  $[100]_p$ —directions results in again the trigonal structure. Above 500 K the widths of the lines related to the polar areas exhibit noticeable narrowing (see the Table 1) indicating the exchange between the Na sites. As we suppose, reorientations of the disordered components are correlated within the polar regions. This cause significantly lower frequencies of Na exchange than those we can expect for independent Na hops between the potential-relief minima.

The temperature behavior of the quadrupole constant  $q_{\text{trig}}$ , related to polar areas is of particular interest. As it is shown in the Table 1,  $q_{\text{trig}}$  changes over relatively narrow temperature range 540 K–580 K on more than an order of magnitude. Below nearly 500 K the macroscopic spontaneous polarization appears in NBT, as it is known [4]. Also, one can refer to a sharp increase of the level of second optical harmonic generation revealed in a close temperature range [6]. We think, that above presented NMR data revealed the direct



**Figure 4.** The  $[111]_P$  displacements of Na in the polar areas supplemented by small shift along one of six equivalent  $[100]_P$  directions.

connection between the increase of spontaneous polarization below 500 K and Na-ions displacements in the polar areas along  $[111]_P$  directions.

Above 580K the displacements along  $[111]_P$  becomes very small at approaching  $T_{c2}$ . The Na ions in the polar areas exhibit the shifts nearly along  $[100]_P$  directions. This makes possible the appearance of heterophase fluctuations. Thus, the polar clusters in this temperature region may act as the tetragonal phase nucleation centers. With further temperature increase, fast growth of the tetragonal nuclei results in the transition into the long-ranged  $P4bm$  structure. Such the transition does not require complete reorganization of the structure of polar regions as it would take place at the change of symmetry  $R3c \rightarrow P4bm$  (for example [11]).

An anomalous dielectric relaxation and broad  $\varepsilon'$  maximum are observed just in the region about 30 K below  $T_{c2}$  [12] where according to above presented data fast reorientation of the local polarization and heterophase fluctuations occur. Low potential barriers which prevent the local polarization hopping are certainly caused by a small values of Na displacements along  $[111]_P$  in this temperature region.

The phase volume, of the tetragonal phase remains on the level of about 30% in broad temperature region 293–500 K and then start to increase with temperature, as it is shown in Fig. 2 and in Table 1. Note that the value of  $X_{\text{tetr}}$  found by NMR at low temperature

is significantly higher than that obtained earlier from the temperature dependences of the superlattice reflections [6, 10]. Subsequent increase of tetragonal phase volume occurs due to nucleation processes of the cost of  $X_{\text{trig}}$  (see Table 1). In the tetragonal phase the values of the quadrupole constant  $q_{\text{tet}}$  is the same as in the region where tetragonal phase and trigonal structure coexist. It is possible that NMR has revealed regions of tetragonal phase with a long-range order that persist in the average trigonal structure till low temperature. This fraction does not participate in the processes of nucleation of the tetragonal phase when approaching  $T_{c2}$ .

### Concluding remarks

In the above studied models the number of the local polarization directions is not large. The shape of the  $^{23}\text{Na}$  line in NBT at the low field evidently is not typical for the RBRF model earlier suggested for description of NMR spectra in “true” relaxors [2]. It is difficult to say now is it a problem of a relatively small contribution of second-order quadrupole effects to NMR line shape at high magnetic field, or probably, “true” relaxors and such crystals as NBT are of different nature. However the ability of our model to explain in the level of structure the appearance of the macroscopic spontaneous polarization near 500 K as well as revelation of the peculiar local structure in the region of anomalous dielectric relaxation give the evidence that used approach is fully acceptable.

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