

NMR Evidence for the Coexistence of Order-Disorder and Displacive Components in Barium Titanate

Boštjan Zalar, Valentin V. Laguta,* and Robert Blinc

J. Stefan Institute, University of Ljubljana, Jamova 39, 1000 Ljubljana, Slovenia

(Received 10 September 2002; published 21 January 2003)

A quadrupole coupling induced ^{47}Ti and ^{49}Ti satellite background which transforms into well-defined satellite lines below T_c in the ferroelectric phase has been observed in the cubic phase of an ultrapure BaTiO_3 single crystal. The results demonstrate the coexistence of a displacive and order-disorder component in the phase transition mechanism and tetragonal breaking of the cubic symmetry due to biased Ti motion between off-center sites in the paraelectric phase above T_c .

DOI: 10.1103/PhysRevLett.90.037601

PACS numbers: 77.84.Dy, 76.60.-k

The ferroelectric phase transition in BaTiO_3 is generally considered to be the classical example of a displacive soft-mode-type phase transition [1,2] describable by anharmonic lattice dynamics [3]. The question of the possible existence of a displacive to order-disorder crossover close to the paraelectric-ferroelectric phase transition is however still open [4–7]. The problem to be solved is whether the potential for the Ti motion in the cubic paraelectric phase exhibits a minimum at the center of the oxygen cage or whether the Ti ion is disordered between several off-center sites. Since the electric field gradient (EFG) tensor is zero by symmetry at the central position and nonzero at the off-center sites, the above problem could be definitely solved by quadrupole perturbed Ti NMR. Here we report on the results of such a study.

Inelastic neutron scattering [2] and Raman measurements [8] in BaTiO_3 have clearly revealed the softening of a transverse optic phonon near the Brillouin zone center and helped to establish the soft-mode picture of displacive ferroelectric phase transitions. Near the cubic-tetragonal phase transition the soft mode becomes strongly overdamped at small wave vectors somewhat similar to the recent results in the relaxor lead zinc niobate-lead titanate (PZN-PT) [9]. In this temperature region the diffuse x-ray scattering in BaTiO_3 is anomalous and has been claimed [4] to show the presence of pretransitional correlated clusters of quasistatic off-center Ti ions as expected for an order-disorder transition. Later it has been suggested [2,5,6] that this scattering can also result from the strong anisotropy of the soft phonon dispersion relation. The controversy over whether the “quasistatic” anomalous x-ray diffuse scattering [4] can be indeed explained within the displacive model [2,5,6] or whether a “vibronic” approach [10] predicting off-center potential minima for the Ti ion along the $\langle 111 \rangle$ directions is more appropriate is still not settled [7,11–14].

At present, the opinion prevails that the Ti ion is sitting at its cubic perovskite site in the center of the oxygen octahedron [12,15] and that the transition in BaTiO_3 is of

pure displacive character. Recent molecular dynamics simulations [6,11] have however shown that the collective particle dynamics is governed by different time and length scales giving rise to a central peak in addition to the soft mode and a coexistence between order-disorder and displacive regimes. The definitive experimental evidence for that has been however still missing. EPR measurements [13,14] of Fe^{3+} and Mn^{4+} ions in BaTiO_3 , which substitute Ti^{4+} ions, have shown a strong local anharmonicity of the potential at the Ti sites indicating the possibility of a reorientational motion of these ions and a ferroelectric order-disorder behavior. The possible existence of such a reorientational motion has been also inferred from Ti spin-lattice relaxation time measurements [16]. Recent extended x-ray-absorption fine structure spectroscopy (EXAFS) studies [17] of the local structure changes in PbTiO_3 as well suggest some order-disorder element in this typical displacive-type ferroelectric, but the detailed nature of the transition in this system is still open.

In this Letter we present the first NMR observation of quadrupole coupling induced ^{47}Ti and ^{49}Ti satellites in the cubic phase of an ultrapure BaTiO_3 single crystal above the ferroelectric transition. Previous [16,18] Ti NMR studies revealed no cubic symmetry breaking above T_c and no first order satellites either above or below T_c . The presence of this satellite background which exists in addition to the central $-1/2 \leftrightarrow 1/2$ Ti NMR transitions and its angular dependence demonstrate a dynamic local tetragonal breaking of the cubic symmetry. Such a behavior is indeed expected if an order-disorder component is present in the phase transition mechanism. Below T_c the satellite background transforms into well-defined satellite lines. Our results show that in the paraelectric phase near T_c all Ti ions are disordered between several off-center sites and order into well-defined positions below T_c . This agrees with the early view of Slater of a “rattling” Ti ion in BaTiO_3 as well as with the original interpretation of the diffuse x-ray scattering [4], the conclusions of Müller *et al.* [13,14] derived from Mn^{4+}

and Fe^{3+} EPR, and the theoretical predictions of Bussmann-Holder [6]. It also explains the heavy damping of the optic soft mode close to T_c as suggested by Chaves *et al.* [7]. The biased dynamic Ti disorder above T_c is accompanied by a displacive-type tetragonal distortion of the unit cell. The results have also important implications for the nature of the relaxor state in substitutionally disordered $A(B_x^I B_{1-x}^{II})O_3$ perovskites.

The NMR measurements were performed on an optically clear pure BaTiO_3 single crystal grown by the “top-seeded solution” method. The T_c was 415 K on heating and 407 K on cooling. The sample dimensions were $4 \times 4 \times 4$ mm with the surfaces parallel to the crystallographic (001) planes. The ^{47}Ti ($I = 5/2$) and ^{49}Ti ($I = 7/2$) NMR spectra and relaxation times were measured in a magnetic field of 9.2 T corresponding to a Larmor frequency of 21.42 MHz for the two Ti isotopes. The ratio of the quadrupole moments of the two isotopes is $^{49}Q/^{47}Q = 0.819$ [18] and the difference in their Larmor frequencies in the cubic phase is about 5.7 kHz. As their natural abundances are relatively low ($^{47}\text{Ti}:c = 7.3\%$, $^{49}\text{Ti}:c = 5.5\%$), between 6000 and 20 000 scans were collected for the spectra in the paraelectric ($Pm\bar{3}m$) and the tetragonal ferroelectric ($P4mm$) phases, respectively. A two 90° -pulse, four-phase ($XX, XY, X-X, X-Y$) “exorcycle” [19] pulse sequence was used to form a principal echo at time τ after the second pulse with minimal distortions due to antiechoes, transients, ill-refocused signals, and piezoresonances [20]. With the standard $\pi/2 - \pi$ and $(\pi/2)_x - (\pi/2)_y$ sequences only the narrow central components [16,18] can be seen.

The $^{47,49}\text{Ti}$ NMR spectra of BaTiO_3 at 420 K (i.e., for $T > T_c$) are shown in Fig. 1 for the external magnetic field \mathbf{B} directed along [001]. All spectra were obtained on heating. As expected for the paraelectric cubic phase, the

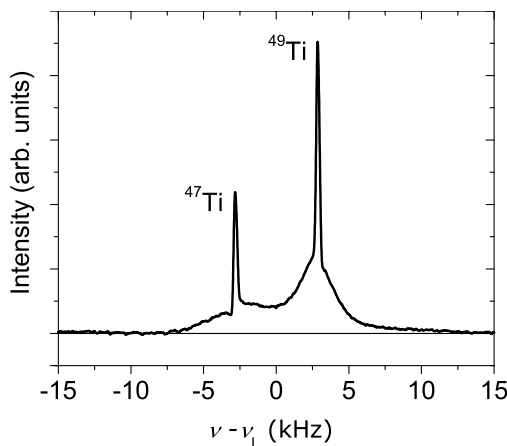


FIG. 1. ^{47}Ti and ^{49}Ti NMR spectra of BaTiO_3 at $T = 420 \text{ K} > T_c$ for $\mathbf{B} \parallel [001]$. The two sharp $^{47,49}\text{Ti} - 1/2 \leftrightarrow 1/2$ central lines are “sitting” on broad background components originating from unresolved $\pm 1/2 \leftrightarrow \pm 3/2$, $\pm 3/2 \leftrightarrow \pm 5/2$, and $\pm 5/2 \leftrightarrow \pm 7/2$ satellite transitions.

spectra show two sharp lines belonging to the $-1/2 \leftrightarrow 1/2$ magnetic transitions of the ^{47}Ti and ^{49}Ti isotopes. The two sharp lines are separated by about 5.7 kHz due to the different values of the magnetic moments of the two isotopes. The new and unexpected feature is that each of these two sharp lines “sits” on a broad background component. Below $T_c = 415 \text{ K}$ the broad components disappear and are replaced by well-resolved satellites (Fig. 2) revealing the existence of three physically nonequivalent 90° ferroelectric domains [18]. Instead of two we now have four narrow $-1/2 \leftrightarrow 1/2$ $^{47,49}\text{Ti}$ lines due to 90° domains.

We believe that the broad components observed above T_c are due to unresolved Ti NMR satellites:

$$\nu_{m-1 \leftrightarrow m} = \nu_L - \nu_Q(m - 1/2)(3 \cos^2 \theta - 1)/2, \quad (1)$$

i.e., due to the $m - 1 \leftrightarrow m$ transitions $-7/2 \leftrightarrow -5/2$, $-5/2 \leftrightarrow -3/2$, $-3/2 \leftrightarrow -1/2$, $1/2 \leftrightarrow 3/2$, $3/2 \leftrightarrow 5/2$, and $5/2 \leftrightarrow 7/2$ of $^{47,49}\text{Ti}$ which appear in addition to the central $-1/2 \leftrightarrow 1/2$ line if the quadrupole coupling is nonzero. Here ν_L is the nuclear Larmor frequency, $\nu_Q = 3e^2qQ/[h \cdot 2I(2I - 1)]$ is the quadrupole frequency, e^2qQ/h is the quadrupole coupling constant, and θ is the angle between the direction of the external magnetic field and the largest principal axis of the EFG tensor. We also assumed that the EFG tensor is axially symmetric. The above interpretation of the broad components as

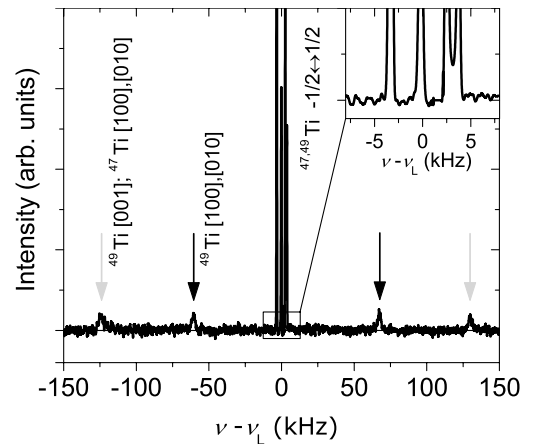


FIG. 2. ^{47}Ti and ^{49}Ti NMR spectra of BaTiO_3 at $T = 415 \text{ K} < T_c$ for $\mathbf{B} \parallel [001]$ demonstrating the appearance of 90° ferroelectric domains. The ^{47}Ti and ^{49}Ti central transition spectrum consists of four lines (inset). The broad satellite background is replaced by well-resolved peaks corresponding to $^{49}\text{Ti} \pm 1/2 \leftrightarrow \pm 3/2$ satellite transitions in [100] and [010] domains (black arrows) and to overlapping contributions from the $^{49}\text{Ti} \pm 1/2 \leftrightarrow \pm 3/2$ transitions in [001] domains and $^{49}\text{Ti} \pm 3/2 \leftrightarrow \pm 5/2$ transitions in [100] and [010] domains (gray arrows). The $^{49}\text{Ti} \pm 3/2 \leftrightarrow \pm 5/2$ [001]-domain satellites, $^{49}\text{Ti} \pm 5/2 \leftrightarrow \pm 7/2$, and all ^{47}Ti satellites lie outside the spectral window.

unresolved first order satellites is supported by the following observations.

(i) The integral intensities of the two central sharp lines and the broad components are in the ratio $9/26 = 0.35$ and $8/34 = 0.24$, respectively, as indeed predicted for the ratio of the intensities $|\langle m|I_x|m+1\rangle|^2$ of the central component and the satellites in the ^{47}Ti ($I = 5/2$) and ^{49}Ti ($I = 7/2$) spectra. This also demonstrates that all Ti ions are off center so that the system is spatially homogeneous and there are no undistorted cubic regions.

(ii) The width of the broad component for ^{47}Ti is approximately twice as large as that for the ^{49}Ti one in agreement with Eq. (1) and the values of the quadrupole frequencies of the two isotopes [$\nu_Q(^{47}\text{Ti})/\nu_Q(^{49}\text{Ti}) \approx 2.5$].

Another fact in favor of this interpretation is the angular dependence of the widths of the two components. In Fig. 3 we compare the observed angular dependence of the second moment of the unresolved ^{47}Ti satellite background with theoretical values derived for the cases that the largest principal axis of the EFG tensor points along the three cubic unit cell edges ($N = 3$), the four body diagonals ($N = 4$), and the six face diagonals ($N = 6$). By far the best agreement is obtained for $N = 3$, i.e., for Ti displacements leading to a tetragonal breaking of the cubic symmetry. A similar tetragonal distortion has been observed by XAFS measurements in PbTiO_3 [21]. Orthorhombic ($N = 4$) or rhombohedral ($N = 6$) distributions of EFG tensors as well as a random distribution of defects or stresses are definitely ruled out. From the fit of the experimental data at $T = 420$ K to the theoretical angular dependence of the second moment for $N = 3$,

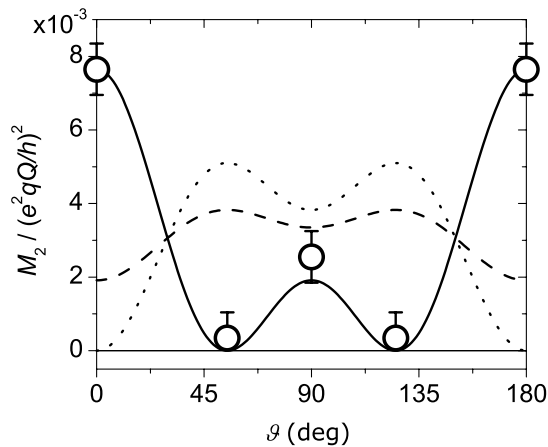


FIG. 3. Comparison between the experimental (open circles) and theoretical angular dependencies of the second moment of the unresolved ^{49}Ti satellite background at $T = 420$ K. The calculated curves refer to tetragonal ($N = 3$, solid line), orthorhombic ($N = 4$, dotted line), and rhombohedral ($N = 6$, dashed line) deviations from cubic symmetry.

$$M_2(N = 3) = \left(\frac{e^2qQ}{h}\right)^2 \frac{9(2I + 3)(1 + 3\cos^2\vartheta)^2}{2560I^2(2I - 1)}, \quad (2)$$

we obtained for the ^{49}Ti quadrupole coupling constant in the paraelectric phase $e^2qQ/h \approx 18.4$ kHz and a corresponding quadrupole frequency $\nu_Q(^{49}\text{Ti}) \approx 1.3$ kHz. In expression (2) ϑ is the angle between the [001] direction and \mathbf{B} . The crystal was rotated in such a way that \mathbf{B} was always perpendicular to the [1-10] direction.

From the angular dependence of the ^{49}Ti $1/2 \leftrightarrow 3/2$ satellite line just below T_c we find, on the other hand, $\nu_Q(^{49}\text{Ti}, T = T_c^-) \approx 125$ kHz. This agrees with the data of Bastow and Whitfield [18] if an extrapolation from $T = 296$ K to $T_c = 415$ K is made according to the ν_Q vs T plot of Kanert and Schulz [16].

Let us now try to relate the above data to the phase transition mechanism in BaTiO_3 . According to the hypothesis of Comes *et al.* [4]—later investigated in detail by Chaves *et al.* [7]—the Ti ion is at all temperatures above T_c located at one of the eight positions shifted from the center along the body diagonals of the unit cell. In view of the 180° symmetry of the EFG tensor, only four of these EFG tensor orientations are distinguishable by Ti NMR. In the cubic phase all eight sites are equally populated, $n_1 = n_2 = n_3 = n_4 = n_5 = n_6 = n_7 = n_8$. In the tetragonal phase we have in a given 90° domain $n_1 = n_2 = n_3 = n_4 \neq n_5 = n_6 = n_7 = n_8$ so that the Ti ion moves preferentially between the four sites in the x - y plane leading to an effective displacement in the z direction. This is true for one 90° domain. All three 90° domains together then result in effective Ti displacements along the three cubic unit cell edges ($N = 3$) as indeed observed. In each of these 90° domains the Ti EFG tensor is a dynamic average over the four off-center sites located at the body diagonals.

For a pure order-disorder transition where the Ti potential surface does not change at T_c the EFG tensor in the paraelectric phase would be an average of the EFG tensors in the different ferroelectric domains. In the displacive limit, on the other hand, the Ti potential surface significantly changes on going through T_c so that the EFG tensor above T_c is far from being an average of the ferroelectric phase EFG tensors.

To discriminate between these two limits let us first assume that we deal with a pure order-disorder transition according to the Comes-Chaves model. The Ti ions are displaced along the body diagonals and the EFG tensors are axially symmetric with the largest principal axes pointing along the body diagonals. The motion of the Ti ion between four such off-center sites in an ideal cubic cell in a given 90° domain would average the Ti EFG tensor to zero. This is so as the body diagonals are tilted with respect to the cubic axes for the magic angle $\vartheta = 54.7^\circ$ so that $3\cos^2\vartheta - 1 = 0$. This is obviously not quite correct as $\nu_Q(T > T_c) \approx 1.3$ kHz is not exactly zero. The predictions of the above model are however not far from

being true as the quadrupole frequency in the paraelectric phase is reduced by a factor of 100 with respect to the ferroelectric phase. If, however, in the cubic phase the order-disorder phase transition mechanism coexists with a displacive one, the unit cell is tetragonally distorted at any given instant of time with, e.g., $c/a \neq 1$, the magic angle orientation is lost and the biased motion of the Ti ion between the off-center sites does not average the EFG tensor completely to zero, in agreement with the experimental results. Below T_c where the displacive soft-mode component freezes out, the tetragonal distortion of the unit cell increases and becomes static, resulting in an increase of the quadrupole frequency, as indeed observed.

The spin-spin relaxation time T_2 of the satellite background is $T_2 \approx 200 \mu\text{s}$ and does not vary with temperature in the paraelectric phase up to 450 K, i.e., in the whole interval above T_c we investigated. This means that the off-center sites of the Ti potential field are present in a broad temperature range above T_c and are not a critical phenomenon. This agrees with the original model of Chavez *et al.* used to explain the anomalous diffuse x-ray scattering. The angular dependence of T_2 qualitatively follows that of the second moment M_2 , as expected for the Chavez model.

It should be stressed that if the T_2 would be due to soft-mode fluctuations, the order-disorder induced quadrupole coupling would be motionally averaged out, the broad background would disappear, and only the central lines would be observed. Our results imply a relaxation frequency for the motion of the Ti ion of the order of 10^8 Hz which is by 4 orders of magnitude smaller than the value 10^{12} Hz characteristic of an overdamped optic soft mode.

The above results demonstrate tetragonal breaking of the local cubic symmetry at the Ti sites in the paraelectric phase of BaTiO₃. They also show the coexistence of order-disorder and displacive components in the ferroelectric transition mechanism in the cubic phase as predicted by molecular dynamics simulations [11]. It should be stressed that our results cannot be explained by anisotropic soft phonons as the frequencies involved are much too high. The clusters of off-center Ti ions seen by x-ray diffuse scattering [4] thus indeed exist above T_c . The early view of Slater and Mason and Matthias [22] of a rattling Ti ion as being at the heart of the ferroelectric phase transition mechanism in perovskites is thus confirmed. The order-disorder dynamics is introduced by the relaxational motion of the Ti ion between several off-center sites while the much faster displacive dynamics is due to soft quasiharmonic oscillations around the equilibrium positions. The obtained results have also important implications for the physics of relaxors [23] and other substitutionally disordered perovskites.

It should be also pointed out that whereas our present results show the coexistence of order-disorder and displacive components in the paraelectric-ferroelectric phase transition in barium titanate, recent studies of potassium

dihydrogen phosphate (KDP) and squaric-acid-type hydrogen-bonded ferroelectrics show some displacive character in these prototypes of order-disorder ferroelectrics [24,25].

*On leave from the Institute for Problems of Material Sciences, Ukrainian Academy of Sciences, Krjijanovskogo 3, 03142 Kiev, Ukraine.

- [1] W. Cochran, *Adv. Phys.* **9**, 387 (1960).
- [2] J. Harada, J. D. Axe, and G. Shirane, *Phys. Rev. B* **4**, 155 (1971).
- [3] R. Migoni, D. Bäuerle, and H. Bilz, *Phys. Rev. Lett.* **37**, 1155 (1976).
- [4] R. Comes, M. Lambert, and A. Guinier, *Solid State Commun.* **6**, 715 (1968).
- [5] W. Cochran, *Phys. Status Solidi* **30**, K157 (1968).
- [6] M. Stachiotti, A. Dobry, M. Migoni, and A. Bussmann-Holder, *Phys. Rev. B* **47**, 2473 (1993); A. Bussmann-Holder and A. R. Bishop, *Phys. Rev. B* **56**, 5297 (1997).
- [7] A. S. Chaves, F. C. S. Barreto, R. A. Nogueira, and B. Zeks, *Phys. Rev. B* **13**, 207 (1976).
- [8] P. A. Fleury and J. M. Worlock, *Phys. Rev.* **174**, 613 (1968).
- [9] P. M. Gehring, S.-E. Park, and G. Shirane, *Phys. Rev. Lett.* **84**, 5216 (2000).
- [10] I. B. Bersuker, *Phys. Lett.* **20**, 589 (1966).
- [11] A. Bussmann-Holder, *Physica (Amsterdam)* **263B-264B**, 408 (1999).
- [12] O. E. Kvjatkovskij, *Fiz. Tverd. Tela* **43**, 1345 (2001).
- [13] K. A. Müller and W. Berlinger, *Phys. Rev. B* **34**, 6130 (1986).
- [14] K. A. Müller, W. Berlinger, K. W. Blazey, and J. Albers, *Solid State Commun.* **61**, 21 (1987).
- [15] R. E. Alonso, A. P. Ayala, P. De La Presa, C. Horowitz, and A. Lopez-Garcia, *Ferroelectrics* **274**, 17 (2002).
- [16] O. Kanert, H. Schulz, and J. Albers, *Solid State Commun.* **91**, 465 (1994).
- [17] T. Miyanaga, D. Diop, S. I. Ikeda, and H. Kon, *Ferroelectrics* **274**, 41 (2002).
- [18] T. J. Bastow, *J. Phys. Condens. Matter* **1**, 4985 (1989); T. J. Bastow and H. J. Whitfield, *Solid State Commun.* **117**, 483 (2001).
- [19] R. Ernst, G. Bodenhausen, and A. Wokaun, in *Principles of NMR in One and Two Dimensions* (Oxford University Press, New York, 1987).
- [20] Y. Dumazy, J.-P. Amoureux, and C. Fernandez, *Mol. Phys.* **90**, 959 (1997).
- [21] N. Sicron, B. Ravel, Y. Yacoby, E. A. Stern, F. Dogan, and J. J. Rehr, *Phys. Rev. B* **50**, 13168 (1994).
- [22] W. P. Mason and B. T. Matthias, *Phys. Rev.* **74**, 1622 (1948).
- [23] R. Blinc, A. Gregorovič, B. Zalar, R. Pirc, J. Seliger, W. Kleemann, S. G. Lushnikov, and R. Pankrath, *Phys. Rev. B* **64**, 134109 (2001).
- [24] N. S. Dalal, A. Klymachyov, and A. Bussmann-Holder, *Phys. Rev. Lett.* **81**, 5924 (1998).
- [25] A. Bussmann-Holder, N. S. Dalal, R. Fu, and R. Migoni, *J. Phys. Condens. Matter* **13**, L231 (2001).