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Dynamic Disorder in Perovskites: Local Symmetry Breaking at the Sr Site in SrTiO₃

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A-site symmetry breaking in the macroscopically cubic paraelectric phase of SrTiO₃ was observed by quadrupole perturbed ⁸⁷Sr NMR. The local symmetry breaking at the A (Sr) site is connected with slow and biased disorder dynamics similarly as at the B (Ti) site.

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1. Introduction

Perovskites such as SrTiO₃ and BaTiO₃ have been considered to be classical displacive systems where the phase transitions are connected with a soft mode instability. Only recently a disorder component has been detected in addition to the soft mode. It has been shown [1–3] by quadrupole perturbed ⁴⁷Ti ($I = 5/2$) and ⁴⁹Ti ($I = 7/2$) NMR that in the high temperature cubic phases of BaTiO₃ and SrTiO₃ the Ti ions are dynamically disordered between 8 off-center sites so that the ideal O_h symmetry is locally broken. The electric field gradient (EFG) tensor is non-zero at the Ti sites whereas it should be zero by symmetry in the ideal perovskite lattice with the Ti ion in the center of the oxygen octahedron.

The Ti off-center sites are located at the cubic body diagonals in agreement with the extended X-ray absorption fine structure (EXAFS) data [4, 5], the early X-ray work of Comes et al. [6], and the theoretical model of Chaves et al. [7] (Fig. 1). The off-centering of the Ti ions is accompanied by a local tetragonal distribution of the unit cell, so that fluctuating tetragonal nanodomains ($+a, -a, +b, -b, +c, -c$) are formed in the cubic phase (Fig. 2). The macroscopic cubic symmetry is the result of space and time averaging. Below the cubic-tetragonal transition long range correlations appear and the nanodomains transform into macroscopic 90° domains.

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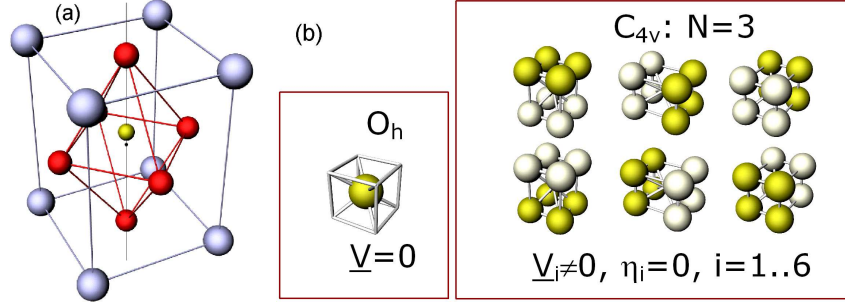


Fig. 1. Displacive (a) and dynamic order–disorder (b) scenarios of the cubic to tetragonal phase transition in BaTiO_3 . The different shades of the off-center Ti sites indicate different occupation probabilities.

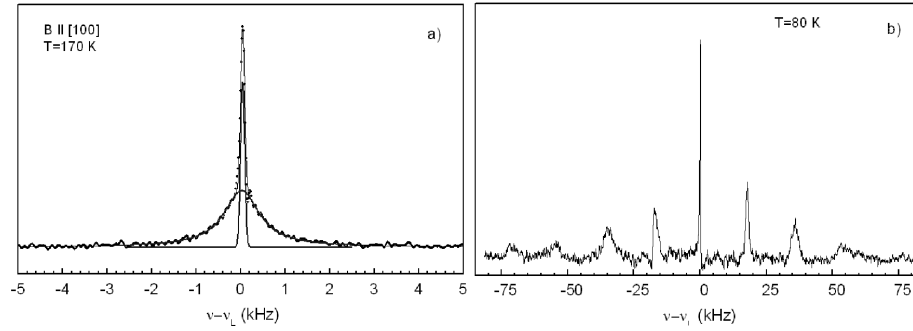


Fig. 2. (a) ^{87}Sr NMR spectrum in the cubic phase of SrTiO_3 showing the narrow $1/2 \rightarrow 1/2$ central line sitting on the motionally narrowed unresolved satellite background. (b) Spectrum of SrTiO_3 below $T_a = 105$ K showing well resolved quadrupolar satellites in addition to the $1/2 \rightarrow 1/2$ transition.

Whereas the above work showed the presence of symmetry breaking at the B-sites in the ABO_3 perovskite lattice, we report here on the observation of local symmetry breaking at the A-sites.

The system investigated was an SrTiO_3 (abbreviated as STO) single crystal and the technique used was ^{87}Sr ($I = 9/2$) NMR in a magnetic field of $B = 9.2$ T corresponding to a Larmor frequency of 16.471 MHz. The length of the 90° pulse was 3–4 μs .

SrTiO_3 has been until recently considered to be a classical displacive system where the low temperature ferroelectric phase is suppressed by zero point quantum fluctuations of the soft mode. An antiferroelectric transition from the cubic to the tetragonal phase connected with antiparallel rotations of adjacent oxygen octahedra takes place at $T = 105$ K due to the condensation of a non-polar soft mode at the Brillouin zone boundary.

2. Results and discussion

The EFG tensor at the Sr site (i.e., A-site) is zero by symmetry for the perovskite structure in the ideal cubic phase. In this case we would expect a single sharp ^{87}Sr NMR line in SrTiO_3 . In fact, the real situation is quite different.

As we can see from Fig. 2a, the ^{87}Sr NMR spectrum of SrTiO_3 at $\mathbf{B} \parallel [100]$ and $T = 170$ K consists of a sharp central line sitting on a broad background. The spectrum is thus quite similar to the ^{47}Ti and ^{49}Ti NMR spectra observed in the cubic phases of BaTiO_3 and SrTiO_3 [1–3]. The sharp central line can be assigned to the $1/2 \rightarrow -1/2$ transition which is not affected by quadrupole coupling in the first order. The broad background line, on the other hand, originates from motionally averaged first order quadrupole satellites: $3/2 \rightarrow 1/2$, $5/2 \rightarrow 3/2$, $7/2 \rightarrow 5/2$, and $9/2 \rightarrow 7/2$. The ratio of the intensities of the central line and the background line supports this assignment. The ^{87}Sr quadrupole frequency ν_Q is here of the order of 0.2–0.5 kHz.

Below $T_a = 105$ K the broad background line disappears and is replaced by well resolved first order satellites (Fig. 2b). This demonstrates that the fluctuating tetragonal nanodomains produced by Ti disorder in the high temperature cubic phase (Fig. 3) have transformed below T_a into regular macroscopic 90° domains. The ^{87}Sr quadrupole frequency increases to about 40 kHz.

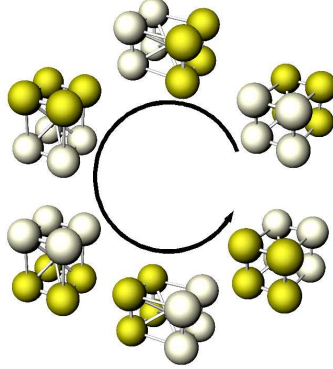


Fig. 3. Exchange between the six differently oriented tetragonal nanodomains in the cubic phase.

To get some information on the timescale of these processes we measured the ^{87}Sr spin–lattice and spin–spin relaxation rates.

It should be mentioned that T_1^{-1} measures the spectral density of fluctuations at the Larmor frequency ω_L and twice the Larmor frequency $2\omega_L$ whereas the satellite T_2^{-1} is sensitive also to very low frequency fluctuations, i.e. to $J(0)$ [8]:

$$1/T_1 = K[J(\omega_L) + J(2\omega_L)] \quad (1a)$$

and

$$1/T_2 = [C_0 J(0) + C_1 J(\omega_L) + C_2 J(2\omega_L)]. \quad (1b)$$

Here $C_0 = 0$ for the $1/2 \rightarrow -1/2$ transition whereas $C_0 \neq 0$ for satellite transitions. The obtained results show that the decay of the transverse magnetization indeed contains two very different components: the T_{2C} of the central transition, which is long and nearly temperature independent, and the satellite T_{2S} , which is short and strongly varies with temperature on approaching T_a (Fig. 4). The disorder dynamics is thus much slower than $\omega_L/2\pi = 16.471$ MHz.

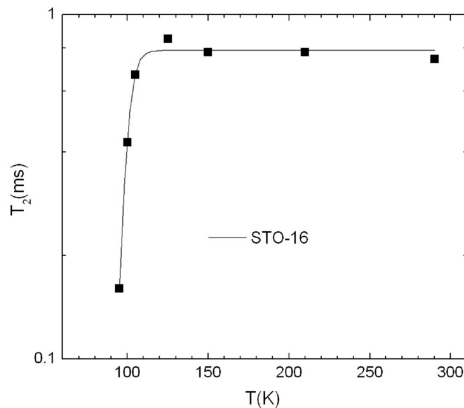


Fig. 4. Temperature dependence of the satellite T_2 in SrTiO_3 on approaching the cubic-tetragonal antiferrodistortive transition. The T_2 of the $1/2 \rightarrow 1/2$ central line, on the other hand, is much longer and nearly temperature independent.

The interesting thing is that T_2 stays short down to 30 K indicating the persistence of low frequency fluctuations and dynamic disorder in the tetragonal phase. T_1 , on the other hand, is long and temperature independent and mirrors the behavior of the T_2 of the central line.

The above interpretation is supported by the fact that low symmetry non-centrosymmetric clusters have been also seen below T_a in SrTiO_3 by “second harmonic generation” microscopy [9]. In addition, rhombohedral clusters which lead to an inhomogeneous ferroelectric phase below $T_c = 24$ K in ^{18}O isotopically enriched SrTiO_3 (STO-18) have been observed below 70 K in STO-16 as well [3]. It should be noted that a similar spectrum consisting of a sharp central line sitting on a broad satellite background has been also observed by Ba quadrupole perturbed NMR in the cubic phase of BaTiO_3 . A-site symmetry breaking in the cubic phase thus takes place in BaTiO_3 as well as in SrTiO_3 and seems to be a general property of ferroelectric perovskites.

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