Polar-Soft-Mode-Driven Structural Phase Transition in $SrTiO_3$

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(Received 27 June 2007; published 19 October 2007)

The structural phase transition of $SrTiO_3$ at 105 K, which has been believed to be independent of the ferroelectric soft mode [Phys. Rev. **177**, 858 (1969)], is shown, on the contrary, to be driven by the *same* long-wavelength polar instability. Isotope replacement of ^{16}O by ^{18}O is predicted to cause an increase in the structural phase transition temperature by 3.8 K. In both isotopic cases, dynamical polarizability-induced ferroelastic-type cluster formation takes place above the structural phase transition, which is intrinsic and a consequence of electron-lattice driven mode-mode coupling. Distinct length and time scales are identified. The precursor domains are evidence that order-disorder effects *coexist* with displacive dynamics.

DOI: 10.1103/PhysRevLett.99.167603 PACS numbers: 77.80.−e, 63.10.+a, 64.60.−i

$SrTiO_3$ has been known for almost 50 years and is one of the best investigated oxide perovskites, exhibiting a variety of unusual properties. At $T_S = 105$ K a structural phase transition takes place where adjacent oxygen octahedra rotate relative to each other and the crystal symmetry is lowered from cubic to tetragonal [1]. The tilting angle here plays the role of an order parameter [1,2]. This latter phase transition is accompanied by the freezing of a transverse zone boundary acoustic mode, which coexists with a long-wavelength polar soft mode [1]. The latter continuously decreases in energy with decreasing temperature suggesting the onset of a ferroelectric instability [3]. Around 20 K, however, quantum fluctuations set in, which inhibit the complete softening, and consequently classify this system as a "quantum paraelectric" [4]. Upon Ca doping a ferroelectric state is obtained, which changes its character with increasing Ca doping from an XY, $n = 2$ quantum ferroelectric to a random-field field-induced domain state [5]. Ferroelectricity can also be induced through oxygen isotope exchange and exhibits, upon full exchange, a transition temperature $T_C = 24$ K [6]. Analogous to the ^{16}O system, $SrTi^{18}O_3$ also shows a soft-mode behavior which is a typical signature of a displacive transition [7,8]. This conclusion is, however, incorrect since the long-wavelength soft mode coexists with locally distorted regions which are indicative of order-disorder behavior [9,10]. A coexistence of both types of transition dynamics has indeed been postulated early on for $SrTi^{16}O_3$ [11].

The structural phase transition of $SrTiO_3$ has been the focus of experimental and theoretical research for a long time since, in the vicinity of T_S, a central peak emerges which increases in intensity upon approaching T_S [12,13]. In addition, various experiments have provided evidence that this transition involves different length and time scales where at least two components must be involved [14,15]. While the central peak has been explained as being either due to intrinsic or quenched defects [16,17], the two components have been attributed to the host lattice and local strain fields, or to intrinsic effects and inhomogeneous quasistatic domains [18,19]. Here, we show that *self-induced* local strain fields give rise to the two-component behavior where dynamically broken symmetry finite length scale domains appear as a consequence of mode-mode coupling. These domains do not arise from ionic displacements but are a consequence of intrinsic local polarization (dipole) fluctuations [20].

It has been believed until now that both instabilities, the long-wavelength polar one and the zone boundary related one, are completely independent of each other. Contrary to this belief we show in the following that the structural instability is totally driven by the polar soft mode. In addition, we predict that this instability is also isotope dependent which should not be the case if the modes were unrelated. The observation of two components is shown to be an *intrinsic* effect, since the polar soft mode strongly interacts through nonlinear local electron-lattice coupling with the related acoustic mode, thereby leading to finite momentum dynamical anomalies in the frequency dispersion [20] well above T_S [9]. These anomalies shift to smaller momentum values with decreasing temperature and simultaneously become more pronounced. Such a behavior is typical for strain fields and ferroelastic-type instabilities. In spite of the strong interaction between the polar and the structural soft mode, the polar mode shows no anomaly at the structural phase transition temperature.

In order to demonstrate the interdependence of the structural and the polar soft mode we use a polarizability model which is based on a double-well potential in the electron-ion interaction [21,22]. This type of "Φ-four" potential differs significantly from those used in rigid ion models since strong polarizability-induced temperature-dependent renormalizations of dynamical properties result. In addition, new nonlinear excitations are supported [23]. The simplest version of this model is its pseudo-one-dimensional analogue with Hamiltonian [22]:

$$H = \frac{1}{2}\sum_n \Big[M_1 \dot{u}_{1n}^2 + m_2 \dot{u}_{2n}^2 + f'(u_{1n+1} - u_{1n})^2 + f(v_{1n} - u_{2n})^2 + f(v_{1n+1} - u_{2n})^2 + g_2 w_{1n}^2 + \frac{1}{2} g_4 w_{1n}^4 \Big]. \quad (1)$$

Here, the first terms refer to the kinetic energy of the ionic cores with site n-dependent displacement coordinates u_{in}, while the following ones are the potential energies stemming from the interactions between next nearest neighbors (f') and interactions between the shells and the first nearest neighbors (f). The on-site potential in the relative core-shell displacement w is anharmonic and consists of an attractive part proportional to g_2 and a repulsive fourth order term g_4, which together with f' guarantees the stability of the lattice. These on-site terms are a consequence of the oxygen ion $2p^6$ instability [24]. The mass M_1 refers to a cluster representing the BO_3 unit in ABO_3, whereas m_2 represents the A-ion sublattice. The relative core-shell displacement w corresponds to an *effective polarizability coordinate* which measures the long-wavelength dipole moment. It is important to note that this dipole moment exclusively determines the temperature-dependent properties of the system within the self-consistent phonon approximation (SPA) through

$$\begin{aligned} g_2 w + g_4 w^3 &= w(g_2 + 3g_4 \langle w^2 \rangle_T) \\ &= w\Big(g_2 + 3g_4 \sum_{q,j} \frac{\hbar}{2N\omega_{q,j}} w_{q,j}^2 \coth\frac{\hbar\omega_{q,j}}{2k_B T}\Big) \\ &= w g_T. \end{aligned} \quad (2)$$

Here the dynamical information enters through the SPA eigenvalues $\omega_{q,j}$ and related eigenvectors $w_{q,j}^2$ for all momentum q-dependent phonon branches j. The soft polar mode frequency $\omega_{\mathrm{TO}}(q = 0)$ is shown in Fig. 1(a) for SrTi^{16}O$_3$ and SrTi^{18}O$_3$. As can be seen, nearly perfect mode softening sets in for both isotopic forms which is reminiscent of a displacive transition. However, close to T_C for SrTi^{18}O$_3$, a discontinuity is present which is typical of a first order transition [7]. This prediction is in disagreement with data from Ref. [8], but agrees with recent measurements of Ref. [24]. Note, that the soft mode in the ferroelectric phase of SrTi^{18}O$_3$ does not exhibit a Ginzburg-Landau temperature dependence but saturates at rather small values in the quantum regime [7].

We now calculate the structural instability within the same framework as the polar-soft-mode-driven instability using precisely the same parameters, except that the second nearest neighbor force constant is changed to be attractive in order to model the rotational instability of the oxygen octahedra. The change in sign in the nearest neighbor force constant has no effect on the long-wavelength polar mode. The temperature dependence of the zone boundary mode is obtained by using the *same* self-consistently derived values of the *polarizability coordinate* [Eq. (2)] as above. The calculated results are shown in Fig. 1(b) and compared to experimental data for SrTi^{16}O$_3$ together with predictions for SrTi^{18}O$_3$ for which experimental data are not presently available. The good agreement between experiment [1,18] and theory clearly suggests that the structural instability is a consequence of the temperature-dependent long-wavelength dipole moment.

Most strikingly, however, our calculations predict an isotopic effect on the structural transition temperature T_S of +3.8 K as can be seen in the inset to Fig. 1(b). This isotopic effect is not present in conventional rigid ion Φ-four models and should also not be present for a ferroelectric transition at these elevated temperatures. Here it is a consequence of the isotope effect on the dipole moment which, for the polar soft mode, is effective only at low temperatures [25].

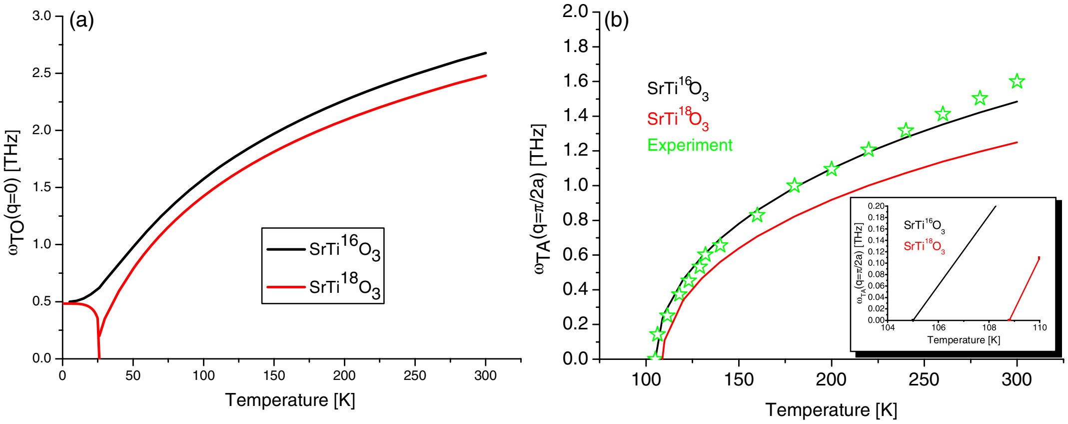

FIG. 1 (color online). (a) Calculated temperature dependence of the polar soft mode in SrTi^{18}O$_3$ (light grey line) and SrTi^{16}O$_3$ (black line). (b) Calculated temperature dependence of the zone boundary soft mode in SrTi^{18}O$_3$ (light grey line) and SrTi^{16}O$_3$ (black line). Experimental data (open stars) have been taken from Refs. [1,18]. The inset to (b) shows the same results as displayed in the main figure, however, within a smaller temperature range in order to highlight the change in the transition temperature caused by the ^{16}O-^{18}O isotopic exchange.

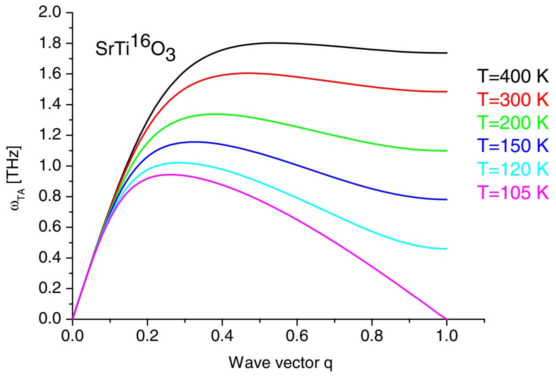

FIG. 2 (color online). Calculated wave vector q dependence of the acoustic soft mode for the various temperatures given.

The calculated dispersion of the acoustic mode which drives the structural instability is shown in Fig. 2. In agreement with experiment [1] the calculated results also reveal the pronounced softening at the zone boundary mode which is already present at high temperatures.

Even though it might be speculated from Fig. 1(b) that the structural instability has displacive character, various experiments which test *local* properties, such as NMR [10] and EPR, [26], have provided convincing evidence that for temperatures $T \gg T_S$ local cluster formation takes place pointing to order-disorder dynamics. These local dynamics are investigated here by searching for finite momentum anomalous softening in the acoustic mode dispersion which in turn defines the corresponding cluster size. While the normalized acoustic mode which softens at the structural transition shows an inflection point at small q values, a more interesting behavior is displayed by the acoustic mode related to the soft polar mode. With decreasing temperature both optic and acoustic modes start to couple strongly through polarizability fluctuations, whereby an anomaly at finite q-values in the acoustic mode dispersion is induced. In order to highlight this anomaly, the acoustic mode dispersion is normalized to its high temperature ($T = 400$ K) dispersion where the optic-acoustic mode coupling is vanishingly small. Again the calculations have been performed for both, SrTi^{16}O$_3$ and SrTi^{18}O$_3$, and the predictions are shown in Figs. 3(a) and 3(b).

Around 250 K an anomalous softening in the acoustic mode dispersion at a finite incommensurate momentum has clearly developed and becomes very pronounced with decreasing temperature. These features are reminiscent of superstructure formation [20], and such a behavior is also typical for a ferroelastic instability but appears here on a finite length scale characterized by the momentum at which the softening is strongest. These regions correspond to dynamically broken symmetry domains which are *self-induced* through polarizability fluctuations causing strong mode-mode coupling. Contrary to previous models where defects have been postulated to be the origin of local symmetry breaking [17,18], the symmetry breaking is here a consequence of strong nonlinearity in the local dipole moment (proportional to w). While for high temperatures the instability, which always remains dynamical, appears around $q = 0.5$, it shifts to smaller q-values with decreasing temperature corresponding to a growth in the dynamical clusters size. However, the $q = 0$ limit, which is the homogeneous case, is never reached; i.e., there is a coexistence of homogeneous solutions corresponding to the structural phase transition, and dynamical dipole induced strained domain states which persist in the tetragonal phase and remain present even in the ferroelectric low temperature phase of SrTi^{18}O$_3$. Most interestingly, the local dynamical domain formation is much more pronounced in STO18, where the softening is increased by more than 10% as compared to STO16. The size of the distorted regions (domains) is obtained from the critical q-value at which the softening is most pronounced and is shown in Fig. 4. For high temperatures they approach a size of 2.5 lattice constants in SrTi^{18}O$_3$, and their size is de-

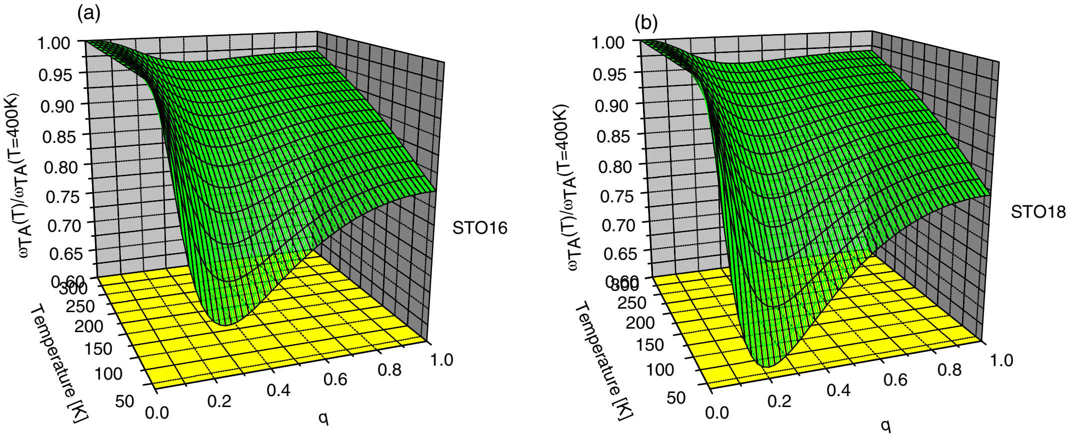

FIG. 3 (color online). (a) Calculated temperature and momentum dependence of the normalized acoustic mode for SrTi^{16}O$_3$ (STO16). (b) Calculated temperature and momentum dependence of the normalized acoustic mode for SrTi^{18}O$_3$ (STO18).

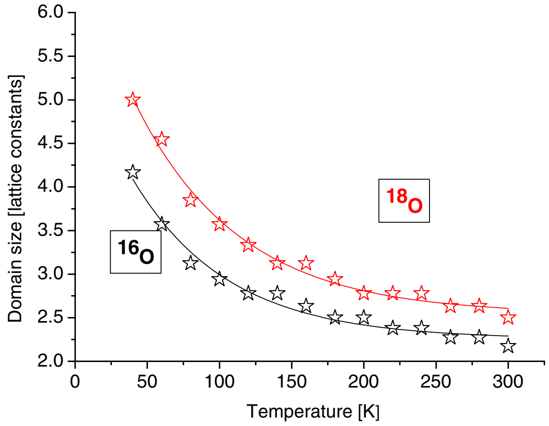

FIG. 4 (color online). Calculated temperature dependence of the domain size as derived from the acoustic mode anomaly. (Black symbols refer to calculated results for STO16; light grey symbols refer to calculated results for STO18; black and light grey full lines are an exponential fit to the symbols; the step-like features in the calculated values are a consequence of using finite size steps in the momentum dependence).

creased in $SrTi^{16}O_3$ by 10%. With decreasing temperature the domain size increases approximately exponentially to reach a size of 6.7 lattice constants in STO18 at $T = 0$ K, and of 5.6 lattice constants in STO16.

Note that the structural instability has no influence on this exponential growth. On the other hand, the polar instability of $SrTi^{18}O_3$ at $T = 24$ K causes a sudden decrease of this growth, but the domain size remains finite in the ferroelectric state [9]. This finding, which is consistent with dielectric measurements [27] and recent Raman scattering data [28], shows that the ferroelectric state is incomplete.

The coexistence of two soft modes and local ferroelastic-type dynamical domains demonstrates that the phase transitions in $SrTi^{16,18}O_3$ are not of purely displacive origin but also carry a substantial order/disorder component. The strong anharmonicity in the electron-ion interaction (proportional to g_T) causes dynamically broken symmetry domains which, opposite to local effects in the displacements, are here obtained already at the SPA level due to polarizability-induced strong mode-mode coupling [20]. Two length and time scales are involved as has been suggested previously [9] and recently by coherent x-ray diffraction [18]. The two-component behavior is an *intrinsic* property resulting from the increasing optic-acoustic mode coupling strength with decreasing temperature. In particular, the short-wavelength structural instability is intimately related to the long-wavelength polar soft mode and driven by the temperature-dependent fluctuating dipole moment. An isotopic effect on this instability is predicted which would be absent if both phase transitions were independent of each other.

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