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Incomplete ferroelectricity in $SrTi^{18}O_3$

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Abstract. Motivated by recent experiments demonstrating suppression of ferroelectricity with pressure in $SrTi^{18}O_3$, the dynamics of the phase transition mechanism are reinvestigated within a nonlinear polarizability model. For temperatures far above the phase transition polar micro domains are formed which increase in size with decreasing temperature to freeze out at T_c without forming long range order. Experimentally, soft mode dynamics are simultaneously observed, evidencing that displacive and order/disorder features coexist. In the ferroelectric phase both components persist whereby an incomplete and inhomogeneous ferroelectric state is formed.

PACS. 77.80.Bh Phase transitions and Curie point – 77.80.-e Ferroelectricity and antiferroelectricity – 05.45.-a Nonlinear dynamics and chaos

$SrTiO_3$ exhibits in its paraelectric phase classical soft mode behaviour which is typically observed for displacive ferroelectric phase transitions. However, and analogous to $KTaO_3$ [1,2] the structural instability is suppressed by quantum fluctuations which dominate the low temperature dynamics. Doping both of these systems with, e.g., Ca [3] or Nb [4], induces ferroelectricity already at very low doping levels. While oxide perovskite ferroelectrics with finite transition temperature T_c are known to show no isotope effect on T_c, the situation in the quantum paraelectric $SrTiO_3$ is different. There it was shown that the replacement of ^{16}O by ^{18}O induces ferroelectricity at a transition temperature T_c of 24 K for maximum isotope exchange [5]. The picture of isotope-induced ferroelectricity in $SrTi^{18}O_3$ (STO18) which emerges experimentally is novel, since soft mode dynamics are clearly present [6,7] but in addition results from NMR [8,9] and ESR [10] experiments provide substantial evidence that an order-disorder component is present simultaneously. Also the ferroelectric phase is rather unconventional since Raman [11], dielectric [12–14] and NMR [8–10] data support the view that this phase has no long range order and remains inhomogeneous at all temperatures. Additionally, the pressure dependence of T_c in STO18 is much larger than expected [6] when compared to other perovskite oxide ferroelectrics [15] since quantum fluctuations compete with the soft mode energy scale.

Theoretically, different approaches have been taken to explain isotope induced ferroelectricity in STO18. While in reference [16] this phase has been interpreted in terms of a transition into a three state quantum order-disorder phase, results from susceptibility measurements have been analyzed in terms of nonlinear and scaling properties [17]. Both of these approaches remain incomplete since the displacive soft mode dynamics are not incorporated. We have concentrated on these latter aspects in an earlier work and achieved consistent agreement with experimental data as well as the isotope effect on T_c [18]. However, the local dynamics observed in STO18 have not been addressed by us so far and these are known to be crucial for the dynamical properties of relaxor [19,20] and order/disorder ferroelectrics [21].

Here we extend out previous calculations [18] by investigating the pressure dependence of the ferroelectric phase transition and the local dynamics within the nonlinear polarizability model [20–24]. The model differs considerably from conventional Φ_4 models, since not only are electron lattice interactions explicitly included, but various exact solutions in terms of breathers, solitary excitations, domain wall dynamics, kinks and travelling kinks exist [19, 25,26]. The global lattice potential has been shown to be extremely sensitive to changes in the ionic masses and new dynamical solutions in terms of travelling waves appear [27]. The vanishing isotope effect on T_c in the classical limit has been predicted together with a finite one in the quantum limit [28]. Besides describing correctly the soft mode temperature dependence, the coexistence of displacive and order/disorder components has been predicted to be not only present in perovskite ferroelectrics [21] but also in hydrogen bonded ones [29,30]. While in perovskite ferroelectrics the time scales of both components are very different, with the consequence that different experimental techniques have to be used to detect them separately, the

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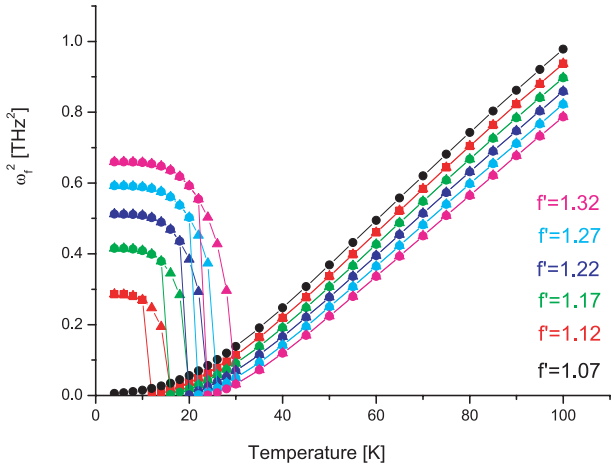

Fig. 1. Temperature dependence of the squared soft mode frequency for various values of the coupling constant f'.

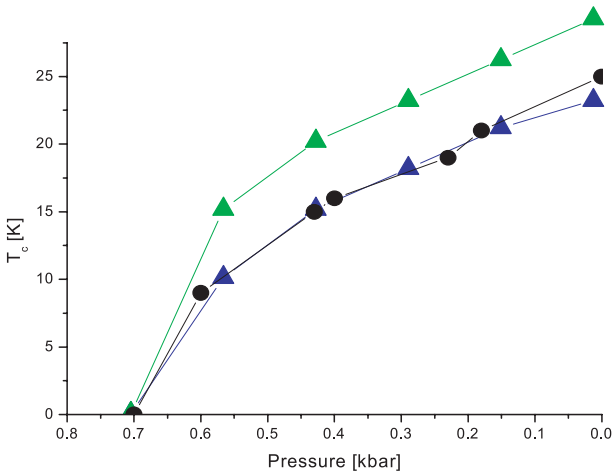

Fig. 2. T_c as a function of pressure. Green triangles and lines give the onset temperature for the simultaneous stability of paraelectric and ferroelectric solutions. Blue triangles and lines are the calculated transition temperatures. Black circles refer to the experimental data taken from reference [6].

time scales of these components are similar in hydrogen bonded ferroelectrics [30].

In order to model the novel dynamics of STO18, we first analyze the origin of the unusual pressure dependence on T_c. As has been shown previously [31], pronounced variations of T_c are obtained if either the local double-well potential height is varied, or the elastic constants are modified. In the quantum limit, variations in the ionic masses are crucial for T_c whereas optic properties play only a minor role at all temperatures. In reference [6] it has been suggested that changes in the local double-well potential cause the pressure dependence of T_c. This can, however, be ruled out since a linear dependence of T_c with potential barrier height results which differs from experimental data. For this reason we concentrate here on the pressure dependence of the elastic constants and vary these linearly with pressure. Within the polarizability model the elastic constants are determined by the second nearest neighbour rigid ion coupling constant f', which dominates the acoustic mode frequency in the long wave length limit.

Throughout the following we use the nonlinear polarizability model and apply the self consistent phonon approximation to it, keeping all parameters constant and the same as in reference [18], allowing only f' to vary. The calculations are based on the model Hamiltonian as defined in references [18,23], the mass of the TiO_6 polarizable cluster is, however, increased by 10% as compared to reference [18] in order to fit the experimental value of T_c of 24 K [5], which within our previous approach was underestimated by 25%. First the soft mode of STO18 is calculated as a function of temperature and f', and is shown in Figure 1.

With decreasing f' T_c is rapidly depressed and the ferroelectric instability vanishes at a critical value of $f' = 1.07$. For values of $f' > 1.07$ T_c is always finite and a transition to a ferroelectric phase takes place. In the ferroelectric phase the soft mode rapidly recovers and approaches a temperature independent plateau in the quantum limit, where the soft mode energy depends on the corresponding T_c, i.e., the larger T_c the higher is its energy at $T = 0$ K. Obviously, it never obeys a Curie-Weiss law and a first order transition takes place. Most interestingly, we observe that in a limited temperature interval above T_c, both, the paraelectric and the ferroelectric solutions are simultaneously stable. This provides evidence that an order-disorder component is present together with the displacive one due to the soft mode. The coexistence regime depends on the transition temperature and grows with increasing T_c. The pressure dependence of T_c is calculated by assuming that f' scales linearly with pressure as $df'/dP = -0.036$ erg cm^{-2}/kbar. Experimental data [6] and theoretical results are compared in Figure 2 where the coexistence regime of paraelectric and ferroelectric solutions is also shown. The very satisfactory agreement between the experimental data and our results supports the assumption that the increasing softness of the elastic constants causes the pressure dependence of T_c. Note again, that no other parameter than f' has been changed.

So far, local lattice anomalies, as observed by ESR [10] or NMR [8,9], have not been addressed. These can be investigated by searching for finite momentum q anomalies in the acoustic mode dispersion. While in stable solids such anomalies are mostly not observed, they are common to displacive ferroelectrics, where the softening of the transverse optic mode frequency with decreasing temperature leads to optic- acoustic mode coupling [23,32]. As a consequence anomalies appear at temperature dependent finite momenta which give rise to the formation of finite size dynamical micro domains. The size of these domains can be estimated from the q value at which the anomalies appear. At T_c, optic and acoustic modes are degenerate and the micro domains coalesce to form a homogeneously polarized state. Thus, the character of the ferroelectric state of STO18 can be studied in more detail by calculating the acoustic mode dispersion as a function of wave vector and temperature. In order to highlight possible anomalies we have normalized the acoustic mode frequency to its value at $T = 100$ K where its dispersion

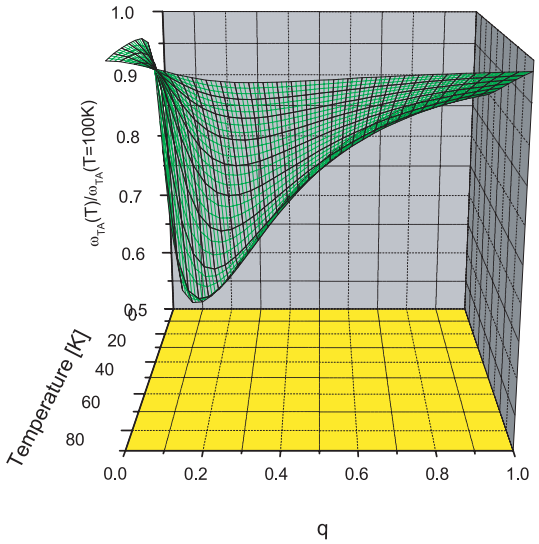

Fig. 3. Normalized acoustic mode frequency as a function of momentum q and temperature for $f' = 1.07$.

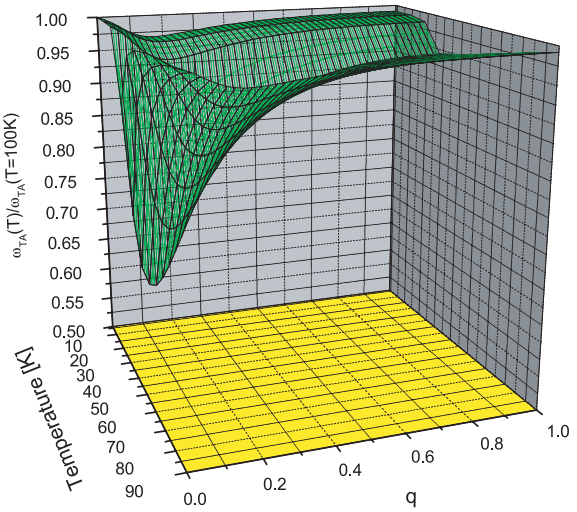

Fig. 4. Normalized acoustic mode frequency as a function of momentum q and temperature for $f' = 1.32$.

follows a q^2 dependence in the long wave length limit as expected from harmonic theories. We first investigate the limiting case where the phase transition is suppressed at all temperatures corresponding to $f' = 1.07$. As can be seen in Figure 3, with decreasing temperature a dip in the dispersion appears and becomes gradually more pronounced with decreasing temperature where simultaneously the q value, at which it develops, shifts from large q values to the long wave length limit. As outlined above, this finding implies that at high T finite size dynamical polar clusters form which grow with decreasing temperature and become more pinned to the underlying lattice. They freeze, however not totally, since a complete softening does not take place. Correspondingly, they can be identified as fluctuating polar domains with slowing dynamics. In the case of the system with the highest T_c of 24 K a similar behaviour is observed (Fig. 4). However, opposite to the

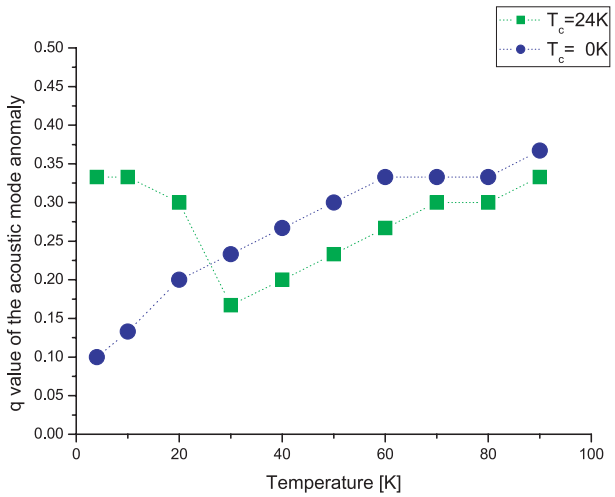

Fig. 5. The anomalous q value at which the anomaly is observed as a function of temperature.

previous case, the anomalies develop at smaller q values at all temperatures, which implies that the domain size is always larger than in the incipient ferroelectric system. At T_c the q value reaches its minimum and is pinned at $q = 0.17$ corresponding to a domain size of approximately 12 lattice constants. Below T_c it would be expected that a homogeneous state is formed with q being zero. This is not the case for STO18 as can be seen from Figure 5, where the anomalous q value is shown as a function of temperature, but the domains shrink and converge to a size of only 6 lattice constants in the quantum regime. Since a ferroelectric state has been confirmed experimentally in STO18 through the observation of a hysteresis in the polarization and by Raman and birefringence measurements [5,33,34], it must be concluded that this state is incomplete and governed by cluster dynamics. Similar conclusions have recently been reached from NMR [8,9] and susceptibility [14,16] measurements.

The dynamical behaviour of all other investigated systems with $0 < T_c < 25$ K is similar to the one with maximum T_c. Here a systematic trend appears since the dynamical micro domains decrease in size with decreasing T_c.

The evolution of finite size polar clusters at temperatures much higher than the actual transition temperature has also been observed experimentally and it was concluded that the phase transition carries a substantial order/disorder component [8,9,14,16]. From our results these conclusions are confirmed. It is, however, important to emphasize that the length scales of the displacive and the order-disorder components differ substantially, so that experiments testing the long wavelength limit, as e.g. Raman and infrared measurements, will only detect the displacive part, whereas local probes like NMR, EXAFS will detect the order-disorder one. The coexistence of both components should be accessible to inelastic neutron scattering experiments, where small momentum q anomalies as well as soft mode dynamics can be tested.

In conclusion, we have shown that the dynamics of STO18 and the pressure dependence of T_c can be explained consistently within the nonlinear polarizability model. We predict that, close to T_c, paraelectric and ferroelectric solutions coexist within a temperature regime which decreases with increasing pressure. Far above T_c, finite size soft clusters develop which grow in size with decreasing temperature, but never form a homogeneous state and always remain dynamic even though they slow down with decreasing temperature. The existence of these clusters at high temperatures provides clear evidence that in spite of perfect soft mode behaviour, order-disorder dynamics are present simultaneously. Important in this respect is the fact that the associated length scales differ considerably so that the detection by a single experiment is difficult. A further important outcome of our results is the observation that the ferroelectric phase remains incomplete, governed by the soft polar cluster dynamics. This conclusion has also been reached in references [9,10] where the transition at T_c was postulated to stem from a percolation process.

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