

## Central peak in SrTiO<sub>3</sub> studied by dielectric spectroscopy

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(Received 26 June 1997)

Dielectric relaxation phenomena are studied in detail at the 107 K structural phase transition in SrTiO<sub>3</sub>. These loss phenomena are explained in terms of the dynamics of domain walls that occur at the cubic-to-tetragonal phase transition and exist as precursor phenomena (locally ordered regions) in the high-temperature phase. We speculate that the same dynamics is responsible for the occurrence of a central peak in neutron-scattering experiments and we predict a relaxation rate of  $1 \times 10^6 \text{ sec}^{-1}$  at the structural phase transition. Finally we compare our results with predictions of  $\Phi^4$  lattice models. [S0163-1829(97)05742-1]

Three decades ago SrTiO<sub>3</sub> was studied intensively experimentally, as well as theoretically. It was characterized as an incipient ferroelectric, with a Curie temperature close to 40 K and it has been shown conclusively that quantum fluctuations suppress long-range ferroelectric order.<sup>1</sup> Utilizing inelastic neutron-scattering techniques, Cowley<sup>2</sup> has demonstrated that the Lyddane-Sachs-Teller relation holds in this material. At  $T_S = 107 \text{ K}$ , SrTiO<sub>3</sub> undergoes a structural phase transition from a cubic high-temperature phase into a tetragonal ground state. This phase transition is close to second order and is driven by the softening of a transverse optical phonon at the zone-boundary *R* point of the Brillouin zone. The soft modes are well defined and underdamped and can be followed as far as close to  $T_S$ .<sup>3</sup> Recently, SrTiO<sub>3</sub> attracted renewed interest: Müller and co-workers<sup>4</sup> detected indications of a low-temperature phase transition in electron-paramagnetic resonance (EPR) experiments. This observation was interpreted as a transition into a coherent quantum state.

Above the 107 K structural phase transition, in addition to the soft mode a central peak (cp) has been detected at the  $\frac{1}{2}$  (113) reciprocal lattice point.<sup>5,6</sup> Later on cp phenomena have been found to be ubiquitous at structural phase transitions but still they are theoretically not well understood. In neutron-scattering studies the cp in SrTiO<sub>3</sub> has been observed some 50 K above the structural phase transition temperature with a weight that grows relative to that of the phonon sidebands and diverges for  $T \rightarrow T_S$ . The most puzzling phenomenon is the extreme narrowness of the central peak: Even in high-resolution neutron-scattering studies it has been shown that the width of the cp close to  $T_S$  was limited by the experimental resolution and the width was estimated to be smaller than 0.08 meV ( $\sim 2 \times 10^7 \text{ sec}^{-1}$ ).<sup>7</sup> From EPR experiments<sup>8</sup> a relaxation rate of  $6 \times 10^7 \text{ sec}^{-1}$  has been deduced at  $T = T_S + 2 \text{ K}$ . And finally, from Mössbauer experiments using 14.4 keV  $\gamma$  rays,<sup>9</sup> it has been concluded that the energy width at  $T_S$  must be smaller than  $8 \times 10^8 \text{ eV}$ , corresponding to an upper limit of the relaxation rate of  $2 \times 10^7 \text{ sec}^{-1}$ .

Presently, no unique and fully accepted theoretical description exists. The cp in SrTiO<sub>3</sub> has been described by

Schwabl<sup>10</sup> using a phenomenological ansatz, where the phonons are coupled to an external mode or by Siberglitt<sup>11</sup> and by Cowley and Coombs<sup>12</sup> in terms of anharmonicity. It has been proposed to be due to defect states by Halperin and Varma<sup>13</sup> and to be due to clusters of locally ordered regions by Schneider and Stoll.<sup>14</sup> Finally, it was described in terms of slow dynamics of domain walls by Krumhansl and Schrieffer,<sup>15</sup> Aubry,<sup>16</sup> and Varma.<sup>17</sup> The elastic nature of the central peak provided some evidence that the defect (domain) origin might be the adequate description and contradicted theories suggesting an intrinsic origin in terms of anharmonic lattice excitations. Theoretically the cp came into the focus of interest again with the development of  $\Phi^4$  lattice models<sup>18-20</sup> and their connection to the mode-coupling theory describing the dynamics at the glass transition.<sup>21</sup>

In this Brief Report we present investigations of the dielectric loss at temperatures close to the structural phase transition. These results are by-products from earlier detailed investigations of the quantum regime at low temperatures.<sup>22</sup> Nevertheless we can draw some important conclusions: dielectric loss appears around the structural phase transition at 105 K and obviously originates from the same dynamics as the central peak in neutron-scattering experiments. We try to demonstrate that the loss phenomena are due to dynamic heterogeneities above  $T_S$  and are due to the domain dynamics below. We make a prediction concerning the width of the central peak at  $T_S$ . And finally, we try to relate our results to recent mode-coupling models of structural phase transitions.<sup>18-20</sup>

In this Brief Report we report measurements of the dielectric loss in a frequency range from 100 Hz  $< \nu < 100 \text{ MHz}$  and temperatures from 60 K  $< T < 150 \text{ K}$ . The measurements were performed using the impedance analyzers 4284A and 4191A from Hewlett-Packard in home-built He-flow cryostats. The nominally pure samples of SrTiO<sub>3</sub> were obtained from Crystal Co. and Goodfellow Co. All crystals investigated in the course of this work revealed phase transitions at  $T_S = 107 \text{ K} \pm 1 \text{ K}$ . Their stoichiometry was checked by electron microprobe measurements using wavelength-dispersive techniques. We found the fraction of alkaline ions to be well below 400 ppm. In order to study surface effects several

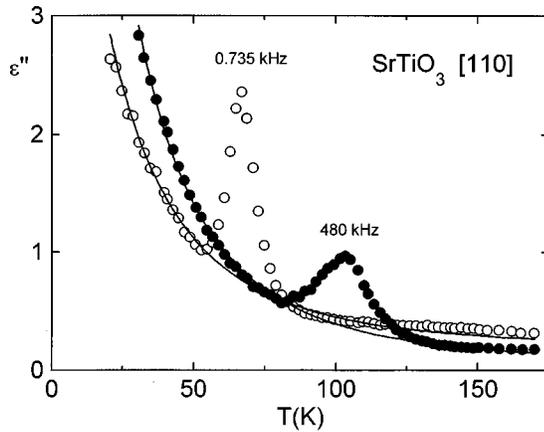


FIG. 1. Temperature dependence of the dielectric loss in SrTiO<sub>3</sub> at measuring frequencies of 735 Hz and 480 kHz. In the experimental setup the electric field was parallel to the [110] direction. The solid lines are spline fits to get an estimate of the frequency-independent loss, on which the relaxation peaks are superimposed

samples were examined before as well as after etching in orthophosphoric acid. No qualitative changes of the dielectric properties could be established. It is interesting to note that in high-resolution x-ray-diffraction measurements<sup>23</sup> two length scales have been detected for the central component of SrTiO<sub>3</sub>. In subsequent neutron-scattering studies it has been concluded that the sharp component, corresponding to the long length scale, is absent in the neutron results and hence originates from surface regions.<sup>24</sup>

Because of the high dielectric constant, measurements in the radio-frequency range are hampered by the occurrence of resonances due to the sample geometry. For frequencies  $\nu > 1$  MHz we used small samples, platelets of approximately 1 mm<sup>2</sup> of various thicknesses between 0.1 and 1 mm, which were put directly onto the inner conductor of the home-built air line.<sup>25</sup> However, despite enormous efforts, we were unable to observe reliable results for frequencies above 100 MHz. At these frequencies resonance phenomena dominate the dielectric response and prevent a careful analysis.

Figure 1 shows the temperature dependence of the dielectric loss in SrTiO<sub>3</sub> as measured at 735 Hz and 480 kHz, respectively. With decreasing temperatures the loss increases continuously and reveals a weak frequency dependence only. This increase is due to the fact that SrTiO<sub>3</sub> is close to a ferroelectric instability at low temperatures. The occurrence of constant loss has been discussed in detail elsewhere.<sup>18</sup> Superimposed on this constant loss, weak but pronounced relaxation peaks can be detected, which shift to lower temperatures with decreasing measuring frequencies. These loss peaks appear at 150 K in the frequency window of our experiment and can be detected down to the lowest temperatures. It is intriguing to assume that these relaxation phenomena are directly related to the 105 K structural phase transition.

For a proper analysis we subtracted the frequency-independent loss using a spline fit as indicated by the solid lines in Fig. 1. Finally, the background corrected experimental data were transformed into dielectric loss peaks vs measuring frequencies for a set of given temperatures (Fig. 2). The loss peaks are symmetric and close to a Debye shape at

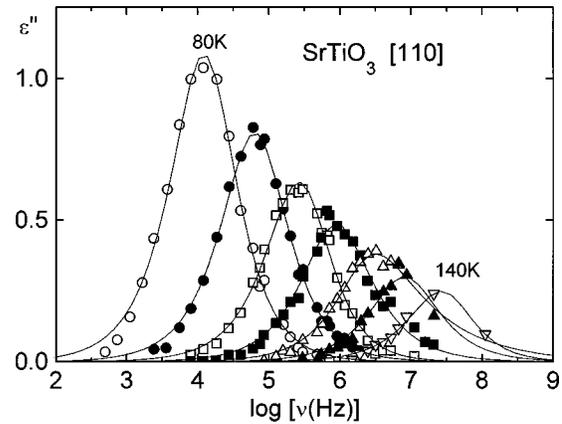


FIG. 2. Background corrected dielectric loss vs the logarithm of measuring frequency with the electric field parallel to [110] between 80 and 140 K. The different loss peaks were taken in equidistant temperature steps of 10 K. The solid lines are fits using the Cole-Cole distribution function as described in the text.

all temperatures. We fitted the data using the Cole-Cole formalism that allows for a symmetrical broadening of the line-width. However, the additional parameter  $\alpha$ , describing the broadening of the loss peaks, was always close to 1, indicating almost pure Debye behavior. Note that Debye-like relaxation in the frequency domain corresponds to an exponential decay of the dielectric polarization in the time domain.

From this analysis we derived the mean relaxation rate  $\Gamma^*$ , which for symmetric loss peaks coincides with the peak maximum ( $\Gamma^* = 2\pi\nu_p$ ). The result is shown in Fig. 3 in an Arrhenius type of presentation. For comparison with the results from neutron scattering and EPR techniques we plotted

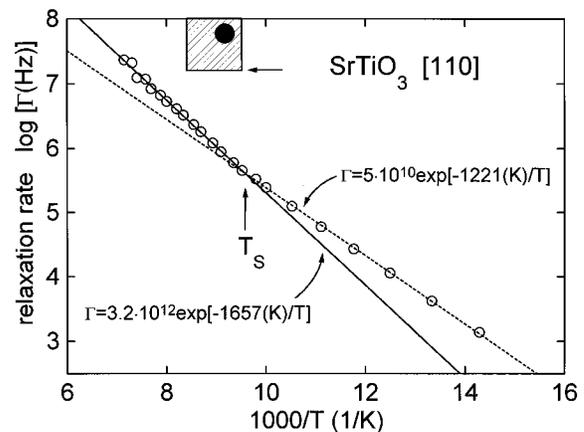


FIG. 3. Temperature dependence of the mean relaxation rates vs the inverse temperature. Note that the relaxation rates are plotted in units of  $\text{sec}^{-1}$  ( $\Gamma^*/2\pi$ ). The solid ( $T > T_S$ ) and dashed ( $T < T_S$ ) lines have been calculated using Arrhenius laws for the high- and low-temperature phases. The dashed area corresponds to the temperature and frequency regime of the high resolution neutron-scattering experiment of Ref. 7. Within this temperature/frequency window no finite width of the central peak could be detected. The horizontal arrow indicates the upper limit of  $\Gamma$  that has been set by the Mössbauer experiment (Ref. 9) and the full dot represents the relaxation rate that has been estimated from EPR experiments (Ref. 8).

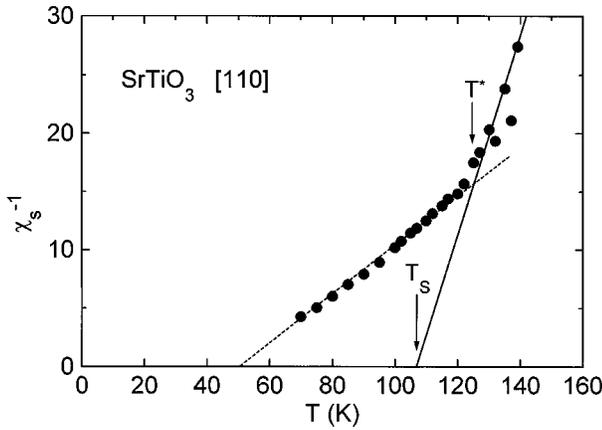


FIG. 4. Temperature dependence of the static inverse dielectric susceptibility. The solid ( $T > T_S$ ) and dashed ( $T < T_S$ ) lines have been calculated assuming the functional form of Curie-Weiss laws.  $T_S$  is the phase-transition temperature.  $T^*$  indicates the crossover between two different regimes. In molecular-dynamics simulations (Ref. 19) this crossover corresponds to a suppressed phase transition.

the relaxation rates in units of  $\text{sec}^{-1}$  ( $\Gamma = \Gamma^*/2\pi$ ). The temperature dependence of the relaxation rates can be described by a pure exponential behavior,  $\Gamma = \Gamma_0 \exp(-E/k_B T)$ , however, with slightly different energy barriers  $E$  and slightly different attempt frequencies  $\Gamma_0$  above (solid line) and below (dashed line) the structural phase transition. In the cubic high-temperature phase the energy barrier amounts 1657 K and the attempt frequency is of the order of  $3.2 \times 10^{12} \text{ sec}^{-1}$ . In the low-temperature phase  $E/k_B = 1221 \text{ K}$  and  $\Gamma_0 = 5 \times 10^{11} \text{ sec}^{-1}$ . Theoretically it has been proposed<sup>13</sup> that relaxing defect cells have to surmount an energy barrier of  $10 k_B T_S$  corresponding to 1100 K in the case of  $\text{SrTiO}_3$ .

Finally, we analyzed the temperature dependence of the static susceptibility that is determined by the area of the dielectric loss peaks. Figure 4 shows the inverse susceptibility vs temperature. The high- and low-temperature regions can be approximately described assuming Curie-Weiss type of behaviors,  $\chi = C/(T - \Theta)$ . The results are indicated as dashed ( $T < T_S$ ) and solid ( $T > T_S$ ) lines in Fig. 4. The characteristic temperatures  $\Theta$  were found to be 107 and 50 K, for the high- and low-temperature regime, respectively. It is interesting to note that the former value corresponds to the structural phase transition temperature  $\Theta \sim T_S$ , while the change of slope between the two regions definitely appears at higher temperatures ( $\sim 120 \text{ K}$ ). In neutron-scattering experiments a dependence of the central-peak intensity of the form  $(T - T_S)^{-1}$  has been found by Hastings and co-workers.<sup>26</sup> In the high-resolution experiments Töpler and co-workers<sup>7</sup> reported a power law proportional to  $(T - T_S)^{-1.2}$ . Our data, especially those observed at high temperatures, are in rough agreement with these results but are not precise enough to make a more detailed analysis.

The most relevant result of this investigation is the detection of a dipolar relaxation mode above and below the structural phase transition. It is clear that dielectric measurements are not sensitive to the softening of optical phonons at the zone boundary<sup>3,27</sup> and it is also clear that at the temperatures of the present investigation the optic modes at the zone

boundary are at or above THz frequencies and also do not contribute to the dielectric response in the radio-frequency regime. Loss anomalies have been reported in a number of perovskites and were interpreted to arise from almost localized polarons.<sup>28</sup> These anomalies appear at much lower temperatures and hence are characterized by significantly lower-energy barriers. The only slow dynamics that seems to be relevant is the creation and decay of clusters of ordered regions above  $T_S$  (dynamic heterogeneities) and the motion of domain walls below the structural phase-transition temperature. It seems plausible and straightforward to assume that the same dynamics governs the low-frequency response in neutron-scattering experiments. For any realistic three-dimensional system, the domain dynamics cannot be calculated and the wave-vector dependence is unclear. However, it seems plausible the  $q=0$  contributions also can be detected. Further evidence for this assumption can be taken from the observation of a strong attenuation peak in vibrating reed experiments<sup>29</sup> that have been performed at a frequency of 3.5 kHz. From Fig. 3 we predict the relaxation peak for this measuring frequency at 75 K, in close agreement with the results reported by Nes *et al.*<sup>29</sup>

Hence Fig. 3 predicts the temperature dependence of the relaxation rates in  $\text{SrTiO}_3$  due to the domain wall dynamics. At  $T_S$  we estimate a width of approximately  $1 \times 10^6 \text{ sec}^{-1}$  (0.004 meV) that will be hard to resolve even with modern high-resolution spectrometers. However, at 140 K the relaxation rate amounts to 25 MHz, yielding an energy width of 0.1 meV that could be detected, e.g., in spin-echo neutron-scattering experiments. Of course at 140 K the intensity of the central component is already rather weak and the proposed experiment has to be carefully optimized.

Here we would like to make some comments on how our results fit into predictions of recent lattice models and mode-coupling approaches of structural phase transitions. A decade ago Aksenov *et al.*<sup>18</sup> explained the appearance of a narrow central peak using the scalar  $\Phi^4$  lattice model. The central component appears as a consequence of precursor clusters of the low-symmetry phase at temperatures above the structural phase transition. The narrowness was explained via the freezing of the cluster system analogous to what is observed in supercooled liquids. In this theory self-consistent equations were derived, similar to the mode-coupling equations that have been studied in detail by Götze, Sjögren, and co-workers<sup>21</sup> to describe the liquid-to-glass transition. The most characteristic feature of the mode-coupling theory is the occurrence of a dynamic phase transition where the separation of the dynamics into a slow and a fast component starts. At the liquid-to-glass transition scaling laws were predicted that can be checked experimentally at high frequencies in measurements of the imaginary part of the dynamical susceptibility.<sup>21</sup> In their model of  $\text{SrTiO}_3$ , Aksenov *et al.*<sup>18</sup> found that the dynamic phase transition appears at  $T_g > T_S$ , which means that a dynamic phase transition is a precursor of the second-order structural phase transition. However, later on it had been shown that in different scenarios both transition temperatures coincide.<sup>20</sup>

The relaxation dynamics for a one-dimensional  $\Phi^4$  lattice model has also been studied by Flach and Siewert<sup>19</sup> using molecular-dynamics techniques. The static susceptibility of the propagating domain walls follows Curie-Weiss laws for

high and low temperatures with a change of slope in the temperature dependence of the inverse susceptibility at  $T^*$  that was considered as the suppressed phase-transition temperature. It is possible that size effects are responsible for this anomaly. Note that in Fig. 4 the susceptibility also follows Curie-Weiss laws and reveals a similar significant change of slope at 120 K, which is clearly above the structural phase-transition temperature  $T_S$ . In the work of Flach and Siewert<sup>19</sup> the slow dynamics was explained in terms of propagating kinks, yielding relaxation peaks which shift to lower frequencies with decreasing temperature (compare to Fig. 2). The shape of the loss peaks was found to be symmetric and only slightly broadened compared to the Debye width, again in good agreement with our findings. It would be highly interesting to extend the present dielectric results to higher frequencies to prove the scaling predictions of the  $\Phi^4$  models<sup>19</sup> and of the mode-coupling theory.<sup>21</sup> However, as has been pointed out earlier, measurements on SrTiO<sub>3</sub> in the microwave region are extremely hard to perform. It is interesting to note that the activation energy becomes smaller in passing the structural phase transition from above. This contradicts naive expectations but is a common observation

in the relaxation dynamics at glass transitions.<sup>30</sup> In glass-forming liquids it is assumed that cooperativity (“interactions between domain walls”) is responsible for high-energy barriers, but that the relaxation can be described as a single defect relaxation (noninteracting domain walls) in the glassy (ordered) state.

In conclusion, we predict the width of the central component in SrTiO<sub>3</sub> which could be resolved on high-flux, high-resolution neutron-scattering instruments, at least 10 to 20 K above the structural phase-transition temperature. We assume that the cp occurs as a consequence of the dynamics of domain walls ( $T < T_S$ ) and precursor clusters ( $T > T_S$ ). We provide some experimental evidence for an anomaly in the static susceptibility well above the structural phase-transition temperature and speculate about its origin in the light of  $\Phi^4$  models that predict a dynamic phase transition for  $T > T_S$ . However, we are aware that recent developments of these lattice models do not provide any indications for  $T^* > T_S$ .<sup>20</sup>

Stimulating discussions with R. Schilling and S. Flach are acknowledged. This research has been partly supported by the Sonderforschungsbereich 262.

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