

## Dielectric spectroscopy in SrTiO<sub>3</sub>

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(Received 20 April 1994)

Measurements of the complex dielectric permittivity in nominally pure SrTiO<sub>3</sub> are reported for frequencies  $10^{-3} \text{ Hz} \leq \nu \leq 10^8 \text{ Hz}$  and temperatures  $0.1 \text{ K} \leq T \leq 300 \text{ K}$ . The experiments reveal relaxation phenomena similar to those reported from elastic measurements. The onset of constant loss below 50 K and a low-temperature relaxation reveals characteristic features of a tunneling motion. These phenomena can be interpreted to be characteristic of a quantum phase transition into a coherent quantum state.

In the 1960s and 1970s SrTiO<sub>3</sub> was the subject of extensive research activities. It was the first material for which it has been demonstrated that the strong increase of the static dielectric constant at low temperatures is associated with the softening of a long-wavelength transverse optic phonon mode.<sup>1</sup> SrTiO<sub>3</sub> is 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 at low temperatures.<sup>2</sup> In addition, at  $T_s = 105 \text{ K}$ , SrTiO<sub>3</sub> undergoes a structural phase transition from a cubic high-temperature to a tetragonal low-temperature phase. This phase transition is almost of second order and is accompanied by a well-defined underdamped soft mode.<sup>3</sup> It is also interesting to note that SrTiO<sub>3</sub> was the first crystal in which a "central peak" has been identified by neutron-<sup>4</sup> and light-scattering techniques.<sup>5</sup>

Recently, SrTiO<sub>3</sub> attracted renewed interest due to the fact that indications for a phase transition in the quantum paraelectric regime were detected in electron-paramagnetic-resonance (EPR) measurements by Müller, Berlinger, and Tosatti.<sup>6</sup> These observations were interpreted in terms of a coherent quantum state in analogy to liquid He-II. Subsequent light-scattering and neutron-scattering studies<sup>7</sup> and vibrating-reed investigations<sup>8</sup> provided indications for a phase transition at low temperatures. However, a clear and unique interpretation of the results could not be given. The main objective of the present investigation was to study the low-temperature regime of SrTiO<sub>3</sub> in full detail by dielectric techniques in order to gain insight into the quantum paraelectric behavior and to find further experimental evidence for or against the proposed phase transition close to 40 K.

Despite the fact that SrTiO<sub>3</sub> single crystals of high quality are available and that SrTiO<sub>3</sub> was the subject of an extremely active research area, dielectric loss data on SrTiO<sub>3</sub> are relatively scarce. A detailed dielectric study was performed on monodomain SrTiO<sub>3</sub> samples by Müller and Burkard,<sup>2</sup> however, focusing only on the real part of the dielectric constant  $\epsilon'$  down to 35 mK. The complex permittivity at a single frequency of 10 kHz was reported by Fischer and Hegenbarth<sup>9</sup> down to 100 mK. Radio-frequency results were presented by Maglione, Rod, and Höchli<sup>10</sup> and microwave losses have been studied by Rupprecht and Bell.<sup>11</sup> In view of some exciting results<sup>6-8</sup> a comprehensive dielectric study covering simultaneously a broad frequency and temperature range is highly warranted.

In this article we present the results of measurements of the real and the imaginary parts of the dielectric constant in a frequency range  $10^{-3} \text{ Hz} \leq \nu \leq 10^8 \text{ Hz}$  and for temperatures  $0.1 \text{ K} \leq T \leq 300 \text{ K}$ . Single-crystalline samples from three different commercial crystal growers were studied and measured systematically along the cubic [110] and [100] directions. No special measures were taken to obtain monodomain crystals at low  $T$ . All results obtained were very similar and here we present only data on single crystals with a small ac electric field ( $< 5 \text{ V/mm}$ ) applied along the [110] direction.

Figure 1 shows the temperature dependence of the real part  $\epsilon'$  (upper frame) and the imaginary part  $\epsilon''$  (lower frame) of the dielectric constant.  $\epsilon'(T)$  is almost frequency independent at all temperatures. The static dielectric constant reaches approximately  $10^4$ , a value that is by a factor of 2 smaller than reported previously for monodomain samples.<sup>2</sup> This confirms that the sample under investigation is in a multidomain state. With decreasing temperature  $\epsilon'(T)$  increases steadily and resembles the well-known quantum paraelectric behavior of SrTiO<sub>3</sub> with a saturation at a very high level at low temperatures. It is a characteristic feature of a quantum paraelectric that the dielectric constant remains large and roughly constant for  $T \rightarrow 0 \text{ K}$ ,<sup>2</sup> due to the fact that quantum fluctuations stabilize the paraelectric behavior. However, in the left inset we show that  $\epsilon'$  reveals a slight anomaly close to 1 K. Its existence has been reported already by Fischer and Hegenbarth.<sup>9</sup>

The lower frame of Fig. 1 shows the dielectric loss  $\epsilon''$  vs the logarithm of temperature as observed at two measuring frequencies. The dielectric loss is much smaller, typically by a factor of  $10^3$ , as compared to  $\epsilon'$ . With decreasing temperature  $\epsilon''$  increases steadily, however, with two characteristic loss peaks in the vicinity of 80 and 10 K superimposed. At these temperatures  $\epsilon''$  reveals dispersion effects characteristic for dielectric relaxation phenomena. The overall temperature dependence of the imaginary part of the dielectric constant closely resembles that of the internal friction as measured by Nes *et al.*<sup>8</sup> at a frequency of approximately 3.5 kHz.

$\epsilon'(T)$  vs temperature can be parametrized in certain temperature ranges using the Curie-Weiss law  $\epsilon' \sim (T - \Theta)^{-1}$ . From the high- $T$  data ( $T > 100 \text{ K}$ ), a Curie-Weiss temperature of  $\Theta = 40 \text{ K}$  can be deduced (cf. the curved line in Fig. 1). This result is in rough agreement with results from Müller and Burkard<sup>2</sup> and from Rupprecht and Bell,<sup>11</sup> who estimated  $\Theta = 35.5 \text{ K}$  and  $37 \text{ K}$ , respectively. However, a closer in-

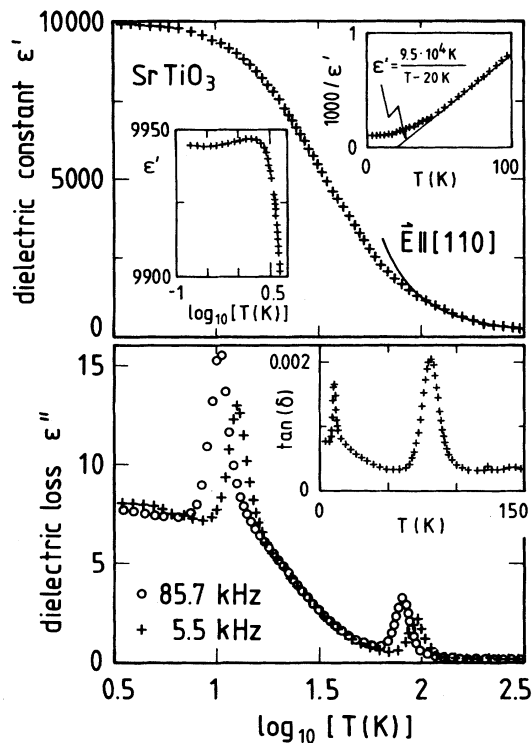


FIG. 1. Dielectric permittivity (upper panel) and loss (lower panel) versus  $\log_{10}[T \text{ (K)}]$  as measured for several frequencies along the  $[110]$  direction of  $\text{SrTiO}_3$ . The curved line in the upper panel is a fit with the Curie-Weiss law  $\epsilon' = 7.5 \times 10^4 \text{ K}/(T - 40 \text{ K})$ . In the uppermost inset we have plotted the inverse of  $\epsilon'(T)$  for temperatures below  $T_s$ . The left inset in the upper panel shows a detailed view of  $\epsilon'(T)$  at low temperatures. The lowest inset depicts the temperature dependence of the loss angle  $\tan \delta = \epsilon''/\epsilon'$  at a frequency of 5.5 kHz.

spection of  $1/\epsilon'(T)$  reveals a change of slope at  $T_s = 105 \text{ K}$ . Using the data below  $T_s$  ( $50 \text{ K} < T < 100 \text{ K}$ ) only, a Curie-Weiss temperature of 20 K follows. This behavior is documented in the upper inset of Fig. 1. Our data, when plotted as the loss factor  $\tan \delta = \epsilon''/\epsilon'$  (lower inset of Fig. 1), look similar to the internal friction data by Nes *et al.*,<sup>8</sup> which have been interpreted to confirm a  $T_c$  in the vicinity of 40 K. However, a clear mark of a thermodynamic transition was not obtained. The “background”-loss factor steadily increases below 50 K and saturates at the lowest temperatures. The lower part of Fig. 1 reveals that dispersion effects appear in the regions of the loss peaks, but that the loss is frequency independent in between. Such a constant loss behavior usually occurs at temperatures close to and below polar phase transitions and is usually ascribed to dissipation effects due to domain-wall motions.

In Fig. 2 we present details of the relaxation dynamics in the temperature and frequency regime of the two loss peaks. It has to be stated clearly that  $\epsilon''$  is by orders of magnitude smaller than  $\epsilon'$ . Therefore both relaxation phenomena are obscured by the strong increase of  $\epsilon'$  and are barely detectable in the real part of the dielectric constant. Both loss peaks increase in intensity and decrease in width with decreasing temperature. It is suggestive to connect the origin of these two loss phenomena with phase transitions. The high- $T$

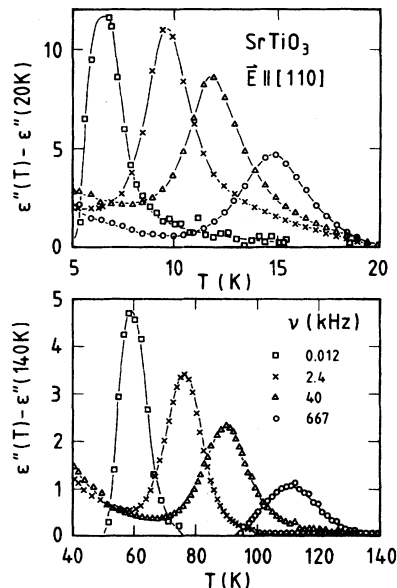


FIG. 2. Temperature dependence of the dielectric loss of the high-temperature and the low-temperature relaxations shown in the upper and lower panel, respectively. The dissipative processes are associated with dynamic heterogeneities that accompany the cubic-to-tetragonal transition and with a (probably) solitonic domain-wall motion in the coherent quantum state, respectively. Solid lines are drawn to guide the eyes.

relaxation which was observed for temperatures  $60 \text{ K} < T < 130 \text{ K}$  can clearly be associated with the structural phase transition at  $T_s = 105 \text{ K}$ . It is due to dynamic heterogeneities above  $T_s$  and is connected with the dynamics of domain walls (or relaxing entities within domain walls) below  $T_s$ . Similar loss phenomena have been detected in elastic measurements below the structural phase transition temperature and have been ascribed to domain scattering.<sup>8,12</sup> In a similar manner the low-temperature loss peaks could be interpreted as arising from the domain dynamics of the low-temperature phase as predicted by Müller, Berlinger, and Tosatti.<sup>6</sup>

For a closer inspection of the relaxation dynamics we plotted the temperature dependence of the most probable relaxation rates vs the inverse temperature, see Fig. 3. The high-temperature relaxation exhibits thermally activated behavior and can be described by an Arrhenius law  $\nu_p = \nu_0 \exp(-E/kT)$  with an attempt frequency  $\nu_0 = 2 \times 10^{11} \text{ Hz}$  and a hindering barrier  $E = 120 \text{ meV}$ . It is instructive to compare the dielectric relaxation dynamics with the results of central peak measurements obtained by inelastic-neutron-scattering experiments for temperatures  $T > T_s$ . In  $\text{SrTiO}_3$  the width of the central peak in all neutron experiments reported so far was limited by the experimental resolution, indicative for relatively slow relaxation phenomena. Using high-resolution backscattering experiments, an upper limit of the relaxation rate was set to be of order 20 MHz close to  $T_s$ .<sup>13</sup> In the present dielectric experiments the relaxation rate at the structural phase transition is approximately 1 MHz and reaches 50 MHz at 140 K, a temperature at which no high-resolution neutron data were reported to date.

We now focus on the low-temperature relaxation for which  $\epsilon''(\log_{10} \nu)$  data are presented in the inset of Fig. 3.

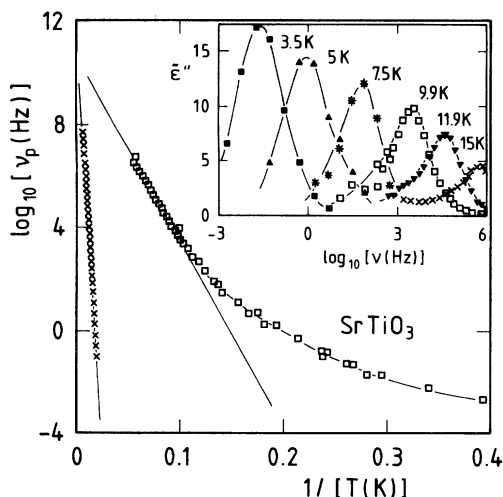


FIG. 3. Arrhenius plot for the high-temperature ( $\times$ ) and low-temperature relaxations ( $\square$ ) in SrTiO<sub>3</sub>. The straight lines represent Arrhenius behavior with the parameters given in the text. The inset shows the background corrected dielectric loss  $\tilde{\epsilon}''(\log_{10}\nu)$  in the quantum paraelectric state. The most probable relaxation rate has been determined from the center of the dielectric loss peaks. Upon heating the almost symmetrically broadened peaks develop a low-frequency tail and the area under the loss peaks, which is proportional to the dispersion strength, strongly decreases. The solid lines in the inset are drawn to guide the eyes.

Our results differ from dielectric results as obtained in quantum paraelectrics doped with impurities insofar as in the latter compounds, in which the order-parameter fluctuations (characteristic for SrTiO<sub>3</sub>) are stabilized by percent amounts of substitutional defects,  $\epsilon'(T)$  always reveals a well-defined maximum and  $\epsilon''(T)$  exhibits loss peaks which are by orders of magnitude larger than those observed in the present work.<sup>14-16</sup> The temperature dependence of the loss process (Fig. 2, upper panel) can be described by an Arrhenius-type behavior for temperatures  $T \geq 10$  K, with parameters  $\nu_0 = 6.3 \times 10^{10}$  Hz and  $E = 13.8$  meV. However, Fig. 3 provides clear evidence for significant deviations from thermally activated behavior at lower temperatures. Already at 5 K the relaxation rate is four orders of magnitude faster as compared to what would be expected if thermally activated processes persisted to lower temperatures.

Before drawing speculative conclusions concerning a quantum phase transition, we now summarize the experimental facts that were borne out by the present dielectric study:

(i) We have analyzed the Curie-Weiss behavior of  $\epsilon'(T)$ . A (hypothetical) ferroelectric ordering temperature of  $T_c \approx 20$  K follows from an extrapolation of the inverse susceptibility taking into account data of the tetragonal phase only. Including anharmonic effects would reduce this value even further.<sup>2</sup> In previous work  $T_c$  has been determined to be close to 40 K.

(ii) We detected an unusual high-temperature relaxation, which seems to be connected with the structural phase transition at 105 K. This antiferrodistortive transition is caused by a condensation of a zone-boundary mode<sup>3</sup> and should not be accompanied by any anomalies in the dielectric constant. This relaxation process is due to the slowing down of polar

modes at defect states within domain walls and may be related to the central peak phenomenon as observed in neutron-scattering studies.<sup>13</sup>

(iii) A continuous increase of a frequency-independent loss occurs at 50 K, with a saturation below 10 K. This behavior is characteristic for a ferroelectric state and, in ordinary ferroelectrics, is explained by dissipation effects due to domain-wall motion.

(iv) A low-temperature relaxation process is superimposed on the constant loss. Its significant non-Arrhenius behavior bears the characteristics of quantum-mechanical tunneling which seems to be dominant below 10 K and

(v) a slight decrease of the dielectric constant below 1 K for decreasing temperatures.

The phenomena (iii)–(v) may well be related to the occurrence of a phase transition into a coherent state as proposed by Müller, Berlinger, and Tosatti.<sup>6</sup>

Phenomenologically the latter two points, (iv) and (v), reveal similarities with experimental findings in the elastic susceptibility of the superfluid phase of <sup>4</sup>He.<sup>17</sup> Frequency-dependent peaks in the absorption of sound were reported well below the  $\lambda$  transition and were explained by relaxation processes due to the second viscosity by Khalatnikov.<sup>18</sup> In addition, a decrease in the velocity of sound was found below 0.7 K which closely resembles that in the dipolar susceptibility as shown in the upper frame of Fig. 1 (left inset). In the case of He-II this anomaly, which is a signature of the coherent state, was ascribed to the coupling between first and second sound.<sup>19</sup>

So far, on a pure phenomenological basis only similarities between the dielectric properties in SrTiO<sub>3</sub> and the elastic properties in He-II have been pointed out. Similar suggestions were drawn from elastic measurements in SrTiO<sub>3</sub>.<sup>8</sup> In addition, the increase of constant loss (iii) may signal the domain-wall dynamics of a so-far unobserved ferroelectric quantum state: macroscopic ferroelectric domains reorient with a rate significantly larger than our highest measuring frequency. A possible scenario for this quantum phase transition (QPT) can easily be drawn in the following way. At low temperature a second-order phase transition takes place with a free energy barrier separating the new equilibrium positions which is so small that it can easily be passed by tunneling. Below the QPT quantum fluctuations restore the symmetric ground state which would be broken classically.<sup>20</sup> A similar scenario has been worked out for the ground-state properties of the hydrogen halides.<sup>21</sup> In the case of SrTiO<sub>3</sub> the coherent ferroelectric mode in the quantum phase would still have the character of a transverse optic phonon. As a consequence of the QPT, anomalies in the temperature dependence of the energy, linewidth, and intensity of the excitation are to be expected. Neutron-scattering data collected so far, indeed reveal anomalies.<sup>3</sup> However, these anomalies are within the error bars or remain unexplained.<sup>3</sup>

Within this hypothetical scenario the constant loss is a consequence of the domain-wall motion of 90° domains while the relaxation processes originate from solitonic excitations between antiphase domains (or between domains reorienting along the same crystallographic direction but with a given phase shift).<sup>21</sup> The formation of solitons connecting

antiphase domains should easily be possible and the soliton dynamics experimentally shows up via relaxation phenomena in the dielectric loss.

In conclusion, we have found low-temperature anomalies in the dielectric loss and we have presented an interpretation in terms of a QPT as proposed by Müller, Berlinger, and Tosatti.<sup>6</sup> Similar conclusions have been drawn from elastic measurements<sup>8</sup> and experimental evidence for the formation of regions with coherently reorienting defect states in quantum paraelectrics has been provided earlier and was attributed to the particularity of the host lattice.<sup>22</sup> However, we

have to admit that an alternative explanation of our experimental results could partly be also given in terms of ferroelectric microclusters (iv) and in terms of the relaxation of well-defined defect states (v). Further experimental and theoretical work is needed to corroborate the quantum state in SrTiO<sub>3</sub> and we hope that our work stimulates further investigations.

We acknowledge stimulating discussions with K. Binder. One of us (R.V.) acknowledges support from CNPq—Conselho Nacional de Desenvolvimento Científico e Tecnológico do Brasil.

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