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Electric-field-dependent dielectric constant and nonlinear susceptibility in $SrTiO_3$

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$SrTiO_3$ belongs to the class of incipient ferroelectrics in which an electrically ordered state is suppressed by quantum fluctuations. To investigate the nature of these excitations, we have measured the linear and nonlinear susceptibilities of $SrTiO_3$ as a function of temperature T and field E. The application of large fields E counteracts the fluctuations and forces the system into an ordered state. The (E,T) diagram is presented. The field dependence of the dielectric constant can be well described within an Ising model including quantum tunneling. Minima in the third harmonic susceptibility, which is a measure of ferroelectric correlations, are taken as evidence for the onset of coherent tunneling phenomena near $T=33$ K.

I. INTRODUCTION

$SrTiO_3$ is one of the most thoroughly studied materials in solid state physics. During the past decades the topics of main interest were the lattice dynamics, the soft-mode behavior and the central-peak phenomenon at the 105 K structural transition, the experimental proof of the Lyddane-Sachs-Teller (LST) relation, the quantum paraelectric behavior and, very recently, the speculations concerning a coherent quantum state at low temperatures. Since this latter proposal by Müller *et al.*,[1] based on Fe^{3+} electron paramagnetic resonance (EPR) results, neutron scattering,[2,3] Brillouin,[2] ultrasonic,[4] and extended x-ray-absorption fine-structure (EXAFS)[5] experiments were performed to provide further experimental evidence for a possible phase transition close to 37 K. In these experiments a number of anomalies were detected but, so far, no clear and coherent interpretation of all results seemed to emerge. Very recently Martonák and Tosatti[6] have proposed to describe this low-temperature phase transition in terms of a rotational quantum melting.

Using broadband dielectric spectroscopy a low-temperature relaxation was detected, which we interpreted to be due to solitonic domain wall dynamics in the low-temperature phase.[7] This observation suggested a somewhat different origin of the coherent state: We speculated that an almost second order phase transition takes place at low temperatures, but that a coherent tunneling motion restores the symmetric ground state which would be broken classically. Similar scenarios have been obtained from quantum Monte Carlo simulations[8] and have been applied to calculate the ground state properties of hydrogen halides.[9] $SrTiO_3$ may well be considered as another example in solid state physics where quantum effects yield coherence on mesoscopic length scales.[10] Quantum tunneling of polarization appears to be a simple analogue to the quantum tunneling of magnetization.[11] That the low-temperature properties are, indeed, more complicated than generally believed is evidenced by the fact that below 50 K the LST relation is strongly violated and that in neutron scattering experiments by Courtens *et al.* phonon branches of so far unknown origin were detected.[3]

In this article we report measurements on the electric-field dependence of the dielectric permittivity and results of an investigation of the nonlinear dielectric susceptibility $\chi_3(T,E)$. These results allow the construction of an (E,T)-phase diagram of $SrTiO_3$ and provide experimental evidence for a transition into a coherent low-temperature state.

II. EXPERIMENTAL DETAILS

The $SrTiO_3$ samples investigated were commercially available high-purity samples. Electron microprobe measurements using wavelength dispersive techniques were used to determine the impurities of Na^+ and Ca^{2+} ions to be lower than 200 ppm, a value about ten times smaller than the critical concentration of Ca^{2+} above which anomalies in $\varepsilon'(T)$ have been detected.[12] Ba^{2+} and Al^{3+} impurities were not detectable. A typical size of the crystals was $10\times5\times1$ mm^3. The measurements were performed with the field $\vec{E}$ parallel to the cubic [110] direction. Below the structural phase transition the crystals were in a multidomain state. No attempts were made to produce monodomain samples. Electrodes formed by a layer of Au (100 nm) deposited on top of Cr (7 nm) were used throughout the experiments.

The measurements were performed using a modified Sawyer-Tower circuit, in which the sample was connected in series with a reference capacitor whose capacitance was at least by a factor of 1000 larger than that of the sample.[13] The voltage across the reference capacitor is a measure of the polarization P in the sample, while the voltage across the sample determines the macroscopic field E. An electrometer amplifier, with an input impedance $>$ 200 TΩ, was used as impedance transformer enabling the detection of $P(E)$ cycles in the mHz regime. The $P(E)$ data were recorded using digital lock-in techniques and were analyzed with standard Fourier-analysis algorithms.[13] Two different experimental procedures were used in the course of this work: (i) A symmetric, harmonically alternating electric field with a

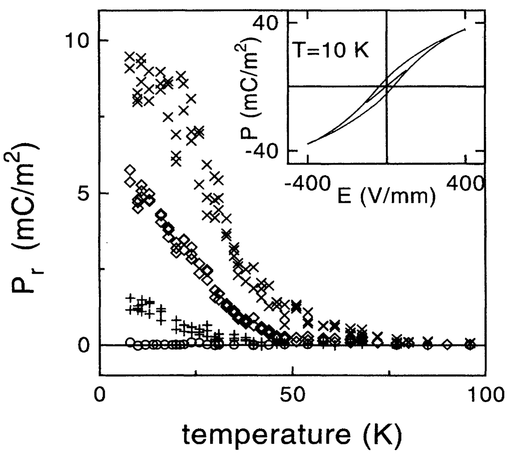

FIG. 1. Temperature dependence of the remnant polarization in $SrTiO_3$ measured for various field amplitudes E_0 (○: 100 V/mm, +: 200 V/mm, ◇ : 400 V/mm, ×: 700 V/mm). The inset shows the field dependence of the polarization at two different measuring cycles with $E_0=100$ V/mm and with $E_0=400$ V/mm.

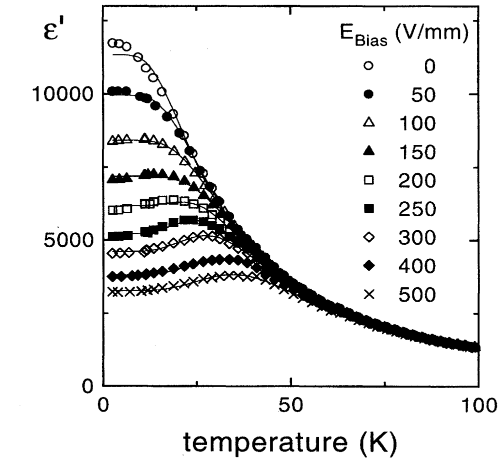

FIG. 2. Temperature dependence of the dielectric constant in $SrTiO_3$ for various bias fields between 0 V/mm and 500 V/mm as described in the figure. The solid lines are fits to a mean field theory, Eqs. (2)–(4).

large amplitude E_0 was used for the determination of the harmonic higher-order terms of the dielectric susceptibility. (ii) A small ac component superimposed on a dc bias field was utilized to determine $\varepsilon(T,E_{\text{bias}})$ via an analysis of the local derivative of $P(E_{\text{bias}})$.

III. RESULTS AND DISCUSSION

Figure 1 shows the results of measurements of the remnant polarization for different fields (100 V/mm $\leqslant E_0 \leqslant$ 700 V/mm). For fields smaller than 200 V/mm no remnant polarization was detectable, even at the lowest temperatures investigated. This behavior indicates strictly paraelectric behavior and is documented in the inset by the absence of any hysteretic effects for a field sweep from -100 V/mm to 100 V/mm. Remnant polarization develops for fields $E_0 \geqslant 200$ V/mm (see the hysteresis loop in the inset of Fig. 1). For the highest fields the remnant polarization P_r reaches values close to 10 mC/m^2 at low temperatures. Early measurements by Weaver[14] revealed 15 mC/m^2 at an excitation voltage of 200 V/mm in rough agreement with our results. A closer inspection of $P_r(T,E_0=700$ V/mm) reveals a significant change of slope close to 40 K. This anomaly probably is due to a transition from a paraelectric state for $T>40$ K to induced ferroelectric (FE) order for temperatures below.

Figure 2 shows the results of measurements of the temperature dependence of the real part of the dielectric constant ε', as measured at various bias fields ranging from $E_{\text{bias}}=0$ to 500 V/mm. For fields $E_{\text{bias}} \geqslant 200$ V/mm maxima occur in $\varepsilon'(T)$ indicating the onset of induced FE order. Well defined loss peaks also emerge from the broad and structureless dielectric loss $\varepsilon''(T)$ at the same fields (not shown here). From these anomalies we have constructed the (E,T) phase diagram for $SrTiO_3$ which is shown in Fig. 3. In this figure we plotted the temperatures of $\varepsilon'_{\max}(T)$ for the different fields and the maxima occurring in ε'' as a function of temperature and field. A similar phase diagram has been proposed already earlier by Hegenbarth and has been explained in terms of a phenomenological model.[15] The peak maxima separate the paraelectric (PE) regime (low-polarization state) at high temperatures and low fields from the FE regime (high-polarization state) at low temperatures and high electric fields. The temperature dependence of $\varepsilon'(T,E)$ (Fig. 2) reveals that, due to quantum fluctuations, the FE regime is still characterized by a large amount of disorder and hence it seems to be more appropriate to interpret the ordered state as an induced FE domain state.[12]

To describe the measured $\varepsilon'(T,E)$ data we have utilized a simple order-disorder-type model based on a two-level

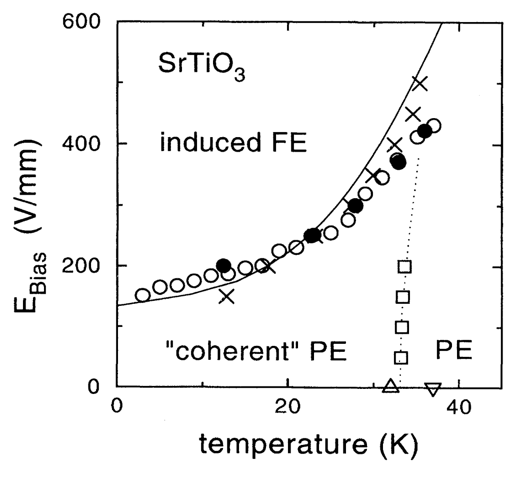

FIG. 3. (E,T) phase diagram of $SrTiO_3$. Crosses (×) represent the maxima occurring in $\varepsilon'(T)$. Full (●) and open (○) circles represent maxima in $\varepsilon''(T)$ and $\varepsilon''(E)$, respectively. The solid line has been calculated using the mean field model and the averaged parameters as described in the text. The minima in $\chi_3(T)$ are indicated by open squares (□). The EPR anomaly [▽: Müller *et al.* (Ref. 1)] and the EXAFS anomaly [△: Fischer *et al.* (Ref. 5)] in zero field are also shown. The dashed line is drawn to guide the eye.

system.[16] If the external bias field is included, the pseudospin formalism yields an Ising-type Hamiltonian of the form

$$\mathscr{H} = -\Omega \sum_i S_i^x - \frac{1}{2} \sum_{i,j} J_{i,j} S_i^z S_j^z - 2\mu E \sum_i S_i^z. \quad (1)$$

Here S_i^α denotes fictitious spin-$\frac{1}{2}$ operators and the three terms, in the order of their appearance, describe quantum mechanical tunneling, dipole-dipole interactions J_{ij}, and coupling of the pseudospins to an external field E. Ω is the tunneling integral, corresponding to the characteristic tunneling frequency between the two spin positions, and μ the dipole moment, caused by the off-centered titanium ions. Evaluation of Eq. (1) in mean-field approximation leads to a self-consistent equation for the expectation value of the occupation difference between the two levels,

$$\langle S^z \rangle = \frac{1}{2} \frac{J_0 \langle S^z \rangle + 2\mu E}{H} \tanh\left(\frac{H}{2k_B T} \right) \quad (2)$$

with an effective field $H = \sqrt{\Omega^2 + (J_0\langle S^z \rangle + 2\mu E)^2}$ and a coupling constant $J_0 = \Sigma_j J_{ij} = J_{0,i}$, which represents the effective exchange interaction between the pseudospins. The static polarization P and the susceptibility χ are connected to $\langle S^z \rangle$ via

$$P = 2n\mu \langle S^z \rangle \quad (3)$$

and

$$\chi = \frac{P(E) - P(E + \Delta E)}{\varepsilon_0 \Delta E}. \quad (4)$$

Here n denotes the number of dipoles per volume.

For zero external field Eq. (2) reduces to the well-known Barret formula.[17,18] To our knowledge, Eq. (2) was only solved analytically in the limit of small fields. In this work self-consistent solutions for $\langle S^z \rangle$ were obtained numerically.[13] The results for different fields E are shown as solid lines in Fig. 2. Although initially we allowed for a variation of all parameters for a given field, a rather good fit for *all* $\varepsilon'(T,E)$ curves yields $J_0 = 145$ K (which corresponds to $T_c = J_0/4 = 36$ K in the notation of Barret[17]) and $\Omega = 87$ K, corresponding to a tunneling frequency of 1.8 THz, and a dipole moment $\mu = 12\ e$ Å. It is important to note that the agreement between theory and experiment is excellent for fields $E_{\text{bias}} \gtrsim 100$ V/mm. Strong and significant deviations appear for low fields and below 30 K. It is the regime where the LST relation is violated and in which the appearance of a coherent quantum state has been predicted to occur.[1]

At high fields the dipole density amounts to $n \approx 3.6 \times 10^{26}$ m^{-3} which is lower by a factor of 45 than the density assuming one dipole per unit cell,[19] $n_0 = 1.6 \times 10^{28}$ m^{-3}. This result may be taken as some evidence that clusters of dipole moments relax rather than that relaxation proceeds via single dipolar jumps.[20] At low fields the parameters n and μ are highly correlated which precludes analysis of them separately.

It is interesting to note that via a free energy expansion for $SrTiO_3$ (Ref. 21) the squared polarization $\langle P^2 \rangle = (n\mu)^2 \approx 4.8 \times 10^{-3}$ (C/m^2)^2 of the clusters can be used to estimate the deviation $\delta\Phi$ of the staggered rotation angle Φ of the oxygen octahedra from their theoretically expected value.[22] Using the known free energy expansion parameters Hehlen *et al.*[23] estimated that $\delta\Phi/\langle\Phi\rangle = \alpha\langle P^2 \rangle$ with $\alpha = 8.3$ (C/m^2)$^{-2}$. Using the $\langle P^2 \rangle$ as obtained in the present study one finds $\delta\Phi/\langle\Phi\rangle = 0.04$, in perfect agreement with the value inferred from the EPR study performed by Müller *et al.*[1]

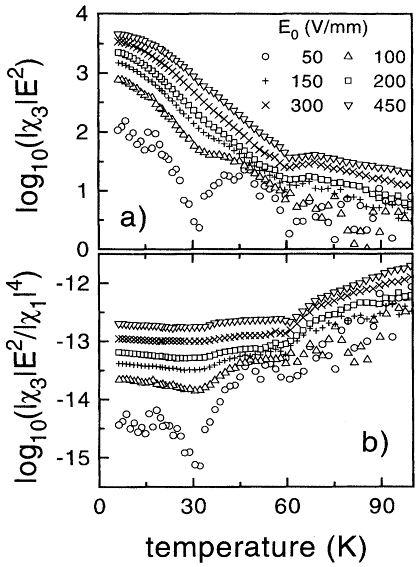

FIG. 4. Upper frame, (a) semilogarithmic representation of the nonlinear dielectric susceptibility $|\chi_3|E^2$ of $SrTiO_3$ as a function of temperature, for electric fields 50 V/mm $\leq E_0 \leq$ 450 V/mm. Lower frame, (b) the same data plotted as $\log_{10}(|\chi_3|E^2/|\chi_1|^4)$ versus T.

None of the previously reported dielectric results (e.g., the cited articles[7,18]) have revealed indications for frequency-independent anomalies in the temperature range 30–40 K, in which the quantum phase transition is expected to take place. In a previous communication[7] we reported on the linear dielectric properties of $SrTiO_3$. Loss features at low temperatures were interpreted as solitonic excitations of domain walls of this quantum state. Now we present results on the nonlinear dielectric susceptibility in $SrTiO_3$. The third order nonlinear susceptibility χ_3 probes ferroelectric pair correlations between the dipole moments.[24]

Figure 4 shows χ_3 for various electric fields plotted as $\log_{10}(|\chi_3|E^2)$ versus T (upper frame) and as $\log_{10}(|\chi_3|E^2)/|\chi_1|^4$ versus T (lower frame). Here χ_3 is the magnitude of the complex third order nonlinear susceptibility. Below 100 K and with decreasing temperatures χ_3 slowly increases. A change of slope appears close to 60 K, indicating the onset of FE correlations. This is due to the fact that in a noninteracting gas of dipoles $\chi_3 \propto T^{-3}$, while close to a FE phase transition a simple Landau theory[25] implies $\chi_3 \propto T^{-4}$. Indeed, for further decreasing temperatures χ_3 increases with the fourth power of χ_1, which is nicely documented in the lower frame of Fig. 4. In addition to the change of slope $\chi_3(T)$ reveals a dip close to 60 K. So far this anomaly remains unexplained, but possibly could be due to the coupling of the polar mode to the structural relaxation (domain wall dynamics) of the tetragonal phase. At approximately 60 K this relaxation crosses the frequency range at which the nonlinear measurements were performed.[7]

At low fields ($E \leqslant 150$ V/mm) a distinct minimum can be detected close to 33 K. Focusing on the 50 V/mm curve, a very simple explanation can be given: For $T_c \approx$ 60 K χ_3 increases due to the growth of FE correlations. At $T \approx 45$ K the drastic decrease indicates that (incoherent) quantum fluctuations tend to suppress these correlations. The strong increase below 33 K provides experimental evidence that FE correlations grow again due to the onset of a coherent tunneling ground state. The temperature of this anomaly in $\chi_3(T)$ exactly corresponds to the anomaly in the temperature dependence of the Debye-Waller factor (DWF) of the oxygen ions as observed by EXAFS spectroscopy.[5] A maximum in the DWF indicates maximum disorder in accordance with our interpretation.

IV. SUMMARY

Anomalies in the temperature and field dependences of the complex dielectric permittivity were used to deduce an (E,T) phase diagram of $SrTiO_3$. We were able to describe the dielectric constant $\varepsilon'(E,T)$ within a simple order-disorder-type two-level system including tunneling. The model reduces to the well known Barret formula[17] at low fields. The deduced squared cluster polarization is compatible in magnitude with the order parameter deviations noted from EPR investigations.[1] This suggests that the cluster polarization measured in our experiments is closely connected to the order parameter of the state evolving below T_q.

Finally we determined the nonlinear third order susceptibility χ_3, which is a measure of ferroelectric correlations, as a function of temperature and field. A significant anomaly in low fields at 33 K signals the onset of coherent tunneling phenomena.

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