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LETTER TO THE EDITOR

Scaling behaviour of strontium titanate

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Abstract. The dielectric susceptibility, $\chi = \chi' - i\chi''$, of nominally pure strontium titanate is measured between 4 and 70 K as a function of an external bias field. Static scaling analysis of the susceptibility reveals a very good scaling behaviour with a quasi-critical exponent $a = \delta/(\delta - 1) = 2.00 \pm 0.02$ extracted consistently from two different experiments.

1. Introduction

Strontium titanate, $SrTiO_3$ (ST), has been a subject of interest both for experimentalists and theorists since 1950 [1] owing to its wealth of unusual and interesting properties, which include superconductivity [2], a structural phase transition [3, 4], and quantum paraelectric behaviour [5]. Despite the relatively long history of investigation many questions concerning this compound are still open and still attract much attention from researchers.

Pure ST is an incipient ferroelectric (quantum paraelectric [5]), whose ferroelectric long-range order is destroyed by sufficiently large quantum mechanical zero-point vibrations [6, 7]. The saturation behaviour of the soft polar ${}^3T_{1u}$ mode at 4.2 K and the large dielectric susceptibility at low temperatures indicate that the ferroelectric phase transition, albeit being close, is not realized at finite temperatures [5, 8]. In addition, according to recent path integral Monte Carlo simulations using an *ab initio* Hamiltonian, it was shown that the quantum fluctuations may even reduce the anti-ferrodistortive structural phase transition temperature by about 20 K to T_a = 105 K [7].

Thus quantum fluctuations are expected to control the system in a relatively large temperature range. This is, for example, seen in the temperature dependence of the dielectric susceptibility. It almost perfectly follows the classic Curie–Weiss law from 300 down to 105 K (see inset of figure 1) just as an ordinary paraelectric, with a critical temperature $T_0 \approx 40$ K and a classic exponent $\gamma = 0.97 \pm 0.01 \approx 1$. However, below $T = 105$ K appreciable departures from the Curie–Weiss law are encountered in accordance with previous reports [5, 9].

Very recently [10], scaling behaviour of the dielectric susceptibility, χ', with respect to temperature and electric field, was observed on ST doped with a small amount of calcium, $SrTiO_3$:Ca^{2+} (SCT). This system is known to exhibit ferroelectric long-range order when the Ca^{2+} concentration exceeds some threshold level, $x_c \approx 0.002$ [11]. Surprisingly, the scaling properties are not restricted to the nearly classic case $x > x_c$, where a phase transition does occur, but also apply to the extreme quantum paraelectric limit, $x < x_c$.

In a preceding paper we have shown [12] that the remarkable non-critical scaling behaviour of ST-like quantum paraelectrics emerges within the framework quantum mechanical mean-field theories. Both the transverse Ising model [13] and the anharmonic quantum mechanic coupled oscillator model [14] have successfully been checked for their scaling properties. They readily emerge when casting the free energy of the system into the shape of a Landau–Devonshire function of the polar order parameter, P, where the ordinary temperature T is replaced by its quantum analogue, $T_Q = T_s \coth(T_s/T)$ [14].

It has to be stressed that the above considerations [12] do not account for the heterogeneity of the polar structure in SCT induced by its doping with Ca^{2+}. Appropriate theories like the inhomogeneous transverse Ising model [15] have to be checked for the validity of scaling in such cases. First of all, however, it seems necessary to check the validity of scaling on the pure host material, ST. To this end, we present in this letter the static scaling analysis of the susceptibility, χ', of nominally pure ST as a function of temperature, T, and of an external electric bias field, E [16].

2. Experimental details

The nominally pure samples of ST were obtained commercially from Crystal GmbH, Berlin, which also provided an impurity analysis with the following result (all concentrations in ppm units): $c(\mathrm{Na}) < 2$, $c(\mathrm{K}) = 2$, $c(\mathrm{Al}) = 44$, $c(\mathrm{Si}) < 2$, $c(\mathrm{Ca}) = 14$, $c(\mathrm{Fe}) < 2$ and $c(\mathrm{Ba}) = 19$. It should be noticed that the Ca content is weak compared to the lowest concentration used in our previous experiments on weakly doped SCT, where $x = 0.002$ corresponds to $c(\mathrm{Ca}) = 400$ ppm. The measurements were performed on a (110)-oriented plate sample with the long edges parallel to $[001]_c$. Following Bednorz and Müller [11] the sample was etched in boiling orthophosphoric acid for about 5 h in order to remove surface layers of about 0.1 mm thickness. After such a procedure the sample reached its final size, $0.35 \times 2.05 \times 9.55$ mm^3, and in contrast with the cut-and-polished state it was completely dark between crossed polarizers. Its geometry favours an oriented state with the tetragonal c axis parallel to the long edges, i.e., parallel to $[001]_c$ [17]. Finally, copper electrodes were vacuum evaporated to cover the major ac faces. In order to prevent oxidation the copper electrode was covered with a silver paste layer. This procedure proves sufficient for low temperature measurements.

The complex susceptibility, $\chi = \chi' - i\chi''$, was measured with a Hewlett–Packard 4192 A impedance analyser at temperatures $4 < T < 300$ K and frequency $f = 1$ kHz, with low ac probing fields, $E_0 = 30$ V/m, in a helium-gas-flow cryostat. Bias fields up to $E_m = 500$ kV/m were applied for measuring the field dependence of the susceptibility, χ' versus E. The data were collected in two different ways: under field cooling conditions at a constant bias field (figure 1), and under isothermal conditions, where the bias field E was scanned. In the latter case, each measurement temperature was reached after zero-field cooling from 150 K, where the sample was refreshed for half an hour. The bias field was applied step-by-step, cycling between $\pm E_m$ in order to record 1.5 periods, i.e. six quarters of the loop at fixed temperature. As a result, characteristic bell-shaped loops of the susceptibility, χ', versus bias field, E, were recorded. For the scaling analysis only the fully reversible last, viz. the sixth quarter of each loop, was used while decreasing the bias field from $+E_m$ to zero (figure 2). In the first mode of experiments (figure 1), the sample was first cooled in zero field from 150 to 70 K. During subsequent measurements, the cooling rate was in the order of 1 K/min and different bias fields were maintained throughout.

3. Results and discussion

Figure 1 shows the temperature dependencies of the real part, χ', of the susceptibility at selected constant bias fields $E \leqslant 500$ kV/m and the imaginary part, χ'', of the susceptibility at zero field. The χ' data in zero field reach a level of the order 2×10^4 and do not possess any maximum in the temperature range $T \geqslant 4$ K. Such high values of the susceptibility, being close to the levels observed previously [5, 8, 11] point to a very good quality of the sample investigated. When increasing the bias field, the value of χ' is lowered, and at $E = 50$ kV/m the first rounded peak at $T_m \approx 4$ K is encountered. In accordance with previous investigations on ST [18–20] the peak considerably shifts towards higher temperatures upon increasing E while simultaneously reducing its height. The losses χ'' are hardly detectable (figure 1): only a small peak in the order of 60 was observed in the vicinity of 10 K. The temperature position of this peak did not depend on the frequency, f. Very probably it is due to the very low background of the unavoidable dopants as listed above. In contrast, in the $SrTiO_3$:Ca system this peak is very

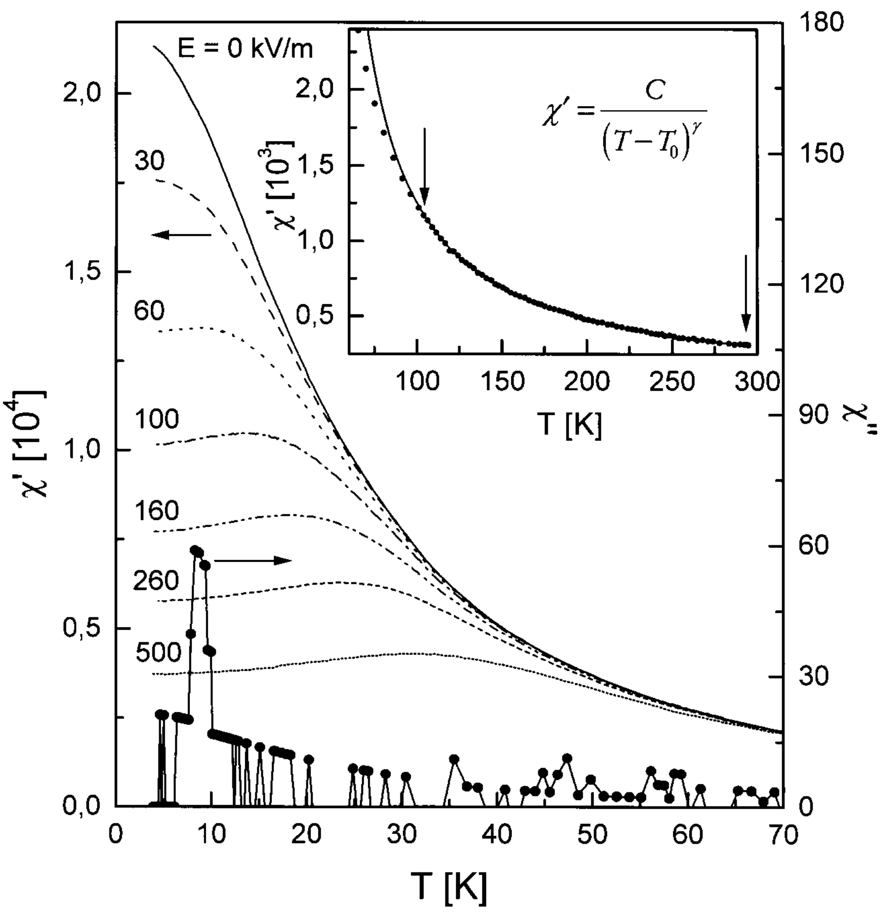

Figure 1. Real part of the ac susceptibility χ' versus temperature at various dc bias field values and imaginary part of the susceptibility χ'' at zero external field. The inset shows the best fit to the classic Curie–Weiss law in the temperature range $110 \leqslant T \leqslant 300$ K with $C = (6.6 \pm 0.2) \times 10^4$ K, $T_0 = 40.5 \pm 0.6$ K and $\gamma = 0.97 \pm 0.01$.

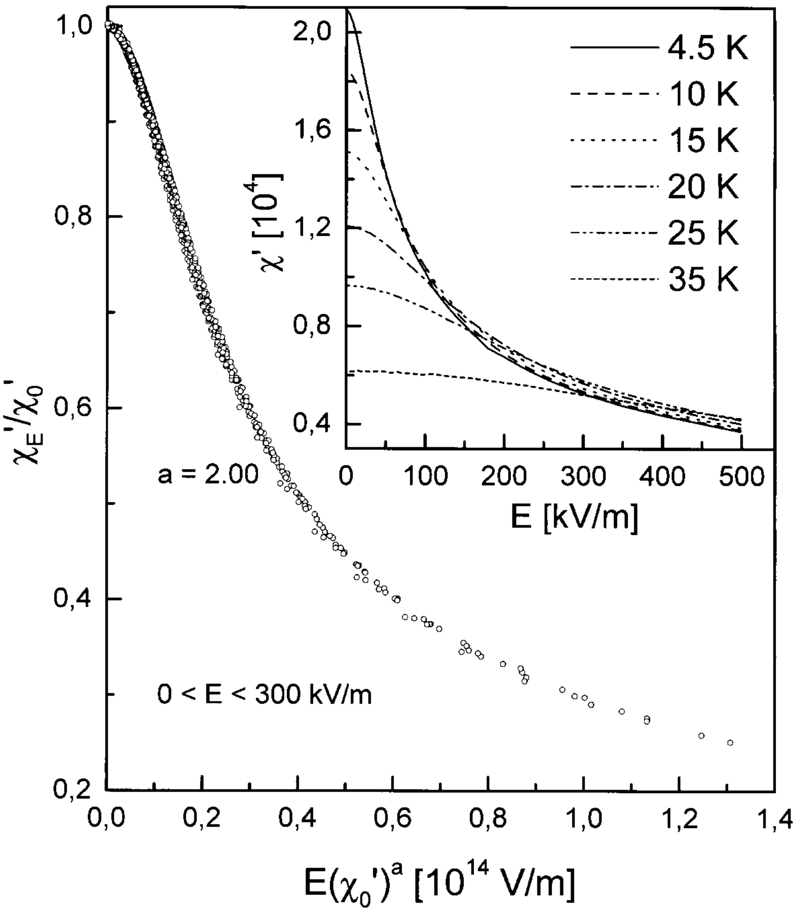

Figure 2. Dependencies of χ_E'/χ_0' on $E(\chi_0')^a$ within $0 \leqslant E \leqslant 300$ kV/m for 14 curves obtained within the temperature range $4.5 \leqslant T \leqslant 35$ K. Best data collapsing is achieved with $a = 2.00$. The inset displays the individual field dependencies of χ_E' at a few representative temperatures.

noticeable [10]. It should further be noticed that unlike Viana *et al* [21] we did not observe any losses in the neighbourhood of the structural phase transition, $T_a \approx 105$ K. Since these are very probably due to structural domain walls, our result is considered to confirm the desired single domain quality of our sample.

The individual isotherms, which show an unusually strong dependence of χ' below 35 K (see inset of figure 2), may be presented in a universal form (figure 2) using the following scaling relation [10, 22]:

$$\chi'(T, E)/\chi'(T, 0) = f\left\{E\left[\chi'(T, 0)\right]^a\right\} \tag{1}$$

where $a = \delta/(\delta - 1)$. In the classic scaling theory [22], δ describes the critical isotherm, $E \propto P^\delta$, i.e. the power-law relation between the external electric field E and the polarization P at $T = T_c$. $\chi'(T, E) \equiv \chi_E'(T)$ is the dielectric susceptibility at temperature T and external bias field E, whereas $\chi'(T, 0) \equiv \chi_0'(T)$ is the zero-field susceptibility at the same temperature.

Equation (1) is very convenient for the scaling analysis of criticality [22] and quasi-criticality [12], since it contains only one fitting parameter a and does not require *a priori* knowledge of the critical temperature T_c. Moreover, the temperature does not appear explicitly. Thus, it may be used for systems being critical either on the normal or on the quantum temperature scale (see section 1) and even for those which do not exhibit any critical behaviour at all [12]. A best-fitting procedure involving equation (1) reveals an exponent $a = 2.00$, where the individual isotherms of ST collapse onto one single common curve as shown in figure 2.

The scaling exponent a may also be extracted from another experiment, since according to the theory of Westwanski and Fugiel [22], the peak values of the susceptibility $\chi'_E(T_m)$ (figure 1) are expected to scale as:

$$\chi'_E(T_m) \propto E^{-1/a}. \qquad (2)$$

To this end, the maximum values of the susceptibility appearing in the temperature characteristics taken at different bias field (figure 1) were determined. These data are plotted as a function of the external bias field, E, in figure 3. When fitting the data within the range of $50 \leqslant E \leqslant 300$ kV/m to equation (2) one obtains an exponent $a = 2.00 \pm 0.02$, which is in excellent agreement with the previous one. It is worthy to note that this value of the exponent a is very close to those obtained earlier on SCT crystals with $x = 0.002$ and 0.007 [10].

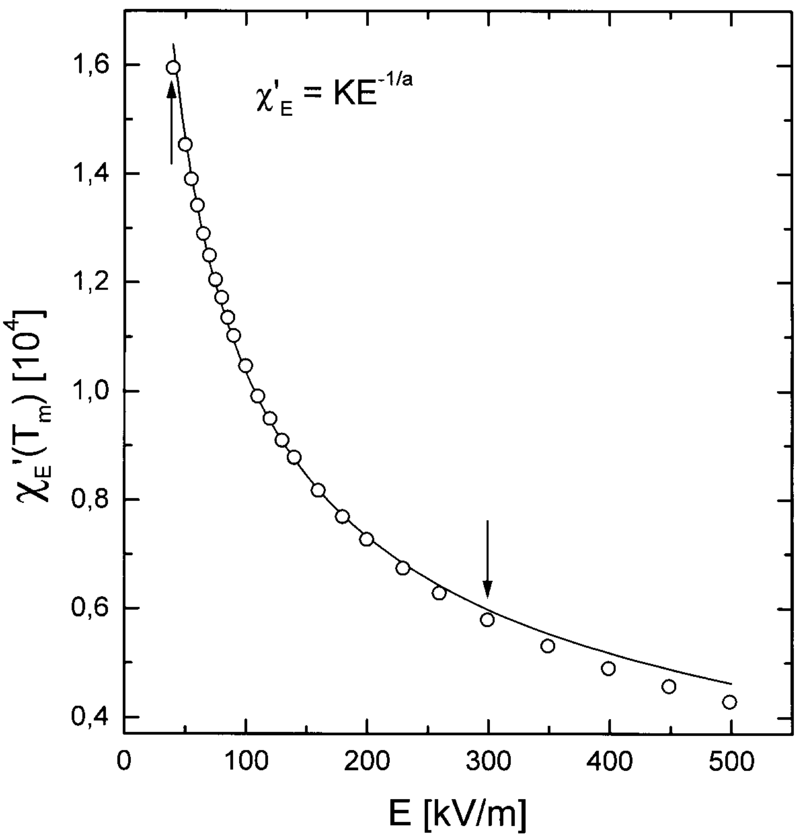

Figure 3. Dependency of $\chi'_E(T_m)$ on the external electric bias field E. The solid line represents the best fit of the data within $50 \leqslant E \leqslant 300$ kV/m to equation (2), $\chi'_E(T_{m)} = KE^{-1/a}$, with $K = (1.03 \pm 0.02) \times 10^5$, $a = 2.00 \pm 0.02$, and E measured in kV/m.

4. Conclusions

The scaling analysis of the experimental susceptibility data of ST discloses good scaling behaviour in the extreme quantum regime. Similarly, as was found for weakly doped SCT [10], also the undoped crystal, ST, reveals a non-classic value of the exponent $a = 2.00 \pm 0.02$. Here we notice that the mean-field Landau model involving either the conventional [22] or the quantum temperature scale, which actually applies to the present case [12], yields $a = 1.5$. Similarly, when describing the quasi-criticality of the susceptibility data versus the quantum temperature, a non-classic exponent of the susceptibility, $\gamma > 1$, emerges [23]. Very probably quantum fluctuations are at the origin of such behaviour of both ST and SCT. Work is presently underway in order to check this conjecture [24].

Acknowledgments

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