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Nonlinear susceptibility and phase transition in $SrTi^{18}O_3$

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The nonlinear dielectric response of $SrTi^{18}O_3$ is measured as a function of temperature and dc bias field strength. In the low-field region the nonlinearity coefficient χ_3/χ_1^4 is found to strongly decrease when approaching $T_c \approx 25$ K. This corroborates the existence of a fluctuation-controlled quantum ferroelectric phase transition despite its smearing due to quenched random fields and excludes a random-bond random-field cluster glass mechanism. Classic field scaling applies to temperatures $T > 1.1T_c$.

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$SrTiO_3$ is probably the best-known example of a quantum paraelectric, whose polar instability is suppressed by quantum fluctuations even in the very-low-temperature limit $T \to 0$.[1] This peculiarity is removed when replacing the ordinary oxygen ions $^{16}O^{2-}$ by the heavier isotope $^{18}O^{2-}$. Itoh *et al.*[2,3] observed ferroelectric Curie temperatures as high as $T_c \approx 25$ K in completely isotope-exchanged $SrTi^{18}O_3$ ("STO18"). The nature of the ferroelectric state is, however, still under discussion. Apart from some broadening of the high peak of the dielectric susceptibility, $\chi'(T_c) \approx 6\times 10^4$, enhanced susceptibility occurs also in the low-T regime in the presence of external fields.[4] It has been argued that this extra response might be due to domain walls, which seem to hint at a random-field (RF) induced domain state as a consequence of excess Sr^{2+} vacancies.[5]

Recent investigations of optical second-harmonic generation have shown that the low-T state of STO18 consists of eight triclinic domains with randomness on a microscale.[6] They transform into an orthorhombic single domain by application of an external electric field along one of the cubic $\langle 110 \rangle_c$ directions. Hence, the spontaneous polarization seems to be slightly tilted out of the $(001)_c$ plane towards the tetragonal axis $[001]_c$, which characterizes the paraelectric structure at temperatures below $T_0 \approx 105$ K.[2,3] The high orientational degeneracy of the order parameter explains the destruction of the ferroelectric phase transition in the presence of quenched RF's (Ref. 7) as indicated by the smeared divergence of χ' at T_c.

The relationship of the smearing to the strong dispersion of the ac susceptibility observed in STO18 (Refs. 4 and 8) is obvious. Since such a behavior is typical of ferroelectric relaxor crystals,[9] one might be inclined to assume similarities in their phase transition mechanisms. The key issue of relaxors is the appearance of polar clusters in the paraelectric phase, which are correlated by the fluctuations of weak RF's.[10,11] In cubic relaxors like lead magnoniobate[9] ("PMN") the dipolar interaction between the polar clusters is proposed to be at the origin of a random-bond random-field dominated glassy transition.[12] Hence, a cluster glass defines the ground state of PMN at $T < T_c$ instead of a domain state. In view of its highly degenerate order parameter a similar structure might also be expected in STO18.

It is the aim of this paper to shed some light onto this fundamental question. In order to decide between a ferroelectric and a glassy phase transition we take advantage of the nonlinear coefficient $a_3 = \chi_3/\chi_1^4$, whose importance was recognized previously.[13] The scaling theory of nonclassic continuous phase transitions[14] predicts vanishing of a_3 at a ferroelectric transition, while a_3 is constant at all temperatures $T > T_c$ for a classic mean-field transition as described in the Landau-Devonshire approximation. However, divergence of a_3 is expected at a freezing transition as observed in dipolar glasses.[13,15] These criteria are helpful when identifying disorder-dominated transitions as being glassy [e.g., in betaine phosphite-phosphate glasses $BP_{1-x}BPI_x$ (Ref. 15)] or ferroelectric [e.g., in strontium barium niobate SBN (Ref. 16)], respectively.

There are different ways for determining the nonlinearity coefficient.[13] In this paper we decided to measure the dielectric susceptibility at constant temperatures while sweeping the dc bias field. In the paraelectric phase $T > T_c$, such kind of data are customarily fitted to a series expansion

$$\chi(E) = \chi_1 - 3\chi_3 E^2 + 5\chi_5 E^4 \tag{1}$$

in order to extract the linear susceptibility χ_1 and the nonlinear susceptibilities χ_3 and χ_5 as fitting parameters; see, e.g., Ref. 12 The above expression is derived from a series expansion of the polarization in a system with a centrosymmetrical paraelectric state at $T > T_c$,

$$P = \varepsilon_0(\chi_1 E - \chi_3 E^3 \pm \cdots), \tag{2}$$

which is assumed to be the inverse of the equation of state[17]

$$E = AP + BP^3 \mp \cdots, \tag{3}$$

where $A = (\varepsilon_0\chi_1)^{-1}$ and $B = \chi_3/(\varepsilon_0^3\chi_1^4) \equiv a_3/\varepsilon_0^3$. It should be noticed that we restrict ourselves to analyze the temperature dependence of B within the paraelectric state $T > T_c$, where Eq. (1) and (2) are expected to hold. Below T_c domain

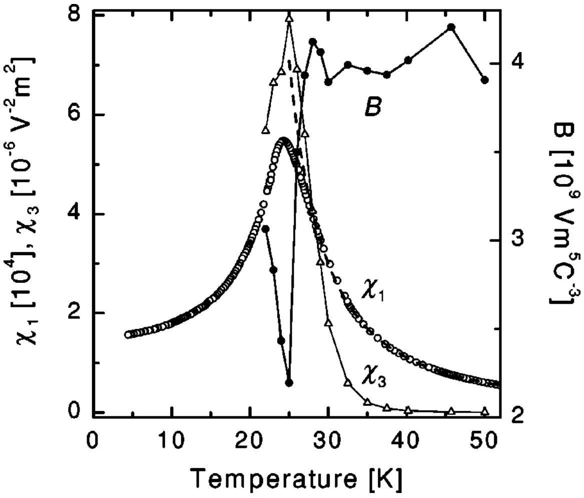

FIG. 1. Temperature dependences of the linear susceptibility χ_1 (open circles) together with its best fit within $30<T<50$ K according to Eq. (4) (dashed line), the nonlinear susceptibility χ_3 (open triangles and eye-guiding line), and of the nonlinearity parameter $B=\chi_3/(\varepsilon_0^3\chi_1^4)$ (solid circles and eye-guiding line).

wall contributions to both χ_1 and χ_3 as well as hysteresis effects will blur the scaling properties in an unpredictable way.

Further, when measuring χ vs E memory effects due to previous poling in high fields have to be excluded. To this end only "virgin" curves as obtained in the very first run after zero-field cooling from high temperatures (see below) were evaluated. It has been ascertained that they clearly maximize at $E=0$ for all temperatures $T>T_c$, a necessary prerequisite of paralectric behavior. Furthermore, full cycles of χ vs E within the interval -30 kV/m$\leqslant E\leqslant 30$ kV/m were observed to be virtually reversible at $T>T_c$, while large-span cycles up to $|E|=110$ kV/m reveal slim butterfly-type wings, which persist even up to $T=40$ K. Obviously reversible paraelectric behavior is encountered in the low-field region, from which our information on dielectric nonlinearity is primarily deduced (see below and Fig. 2). The irreversibility observed in higher fields presumably reflects slight field-induced changes of the internal RF distribution, a phenomenon which is widely spread in quantum paraelectrics containing small amounts of polar impurities.[18] Since all of our data are collected on samples with identical thermal history under zero external field conditions, they can be taken as representative for the virgin unbiased RF distribution.

The experiments were performed on a single-crystal sample of SrTi(^{16}O$_{0.08}$ ^{18}O$_{0.92}$)$_3$ prepared in the same way as described previously,[2,8] with dimensions $0.3\times 3\times 7$ mm^3 parallel to the cubic directions $[110]_c$, $[1\bar{1}0]_c$, and $[001]_c$, respectively. This geometry warrants the formation of a crystallographic single domain with the tetragonal **c** axis along the long sample edges when cooling to below T_0. Vacuum deposition of a thin copper interface and subsequent rf sputtering of gold were used to cover the major faces with electrodes. The dielectric susceptibility was measured with the help of a Hewlett-Packard 4192-A impedance analyzer at temperatures $4<T<50$ K, a frequency $f=10$ kHz, and an ac probing field $E_0=300$ V/m in a helium-gas-flow cryostat. Starting from $E=0$, the bias field was swept up to 110 kV/m at constant temperature. In order to warrant identical conditions for all measurements, prior to each measurement carried out, the sample was refreshed at $T=110$ K for half an hour and then cooled down in zero field to the required temperature.

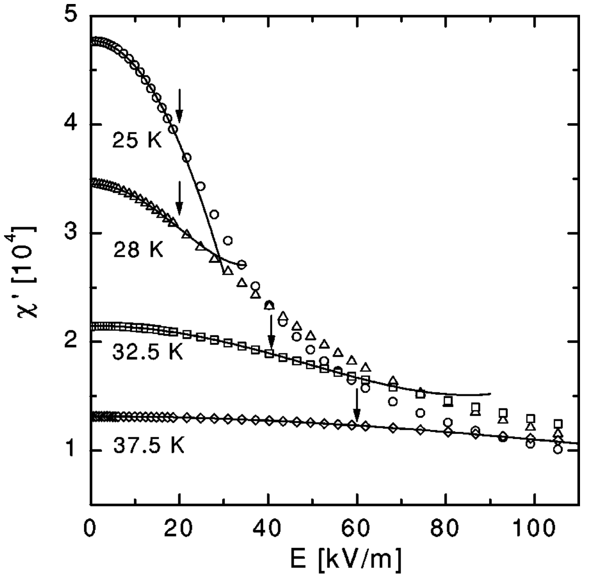

FIG. 2. Isothermal field dependences of χ' measured at $f=10$ kHz and $T=25$, 28, 32.5, and 37.5 K in electric fields up to 110 kV/m applied parallel to the $[110]_c$ direction. The solid lines refer to best fits to Eq. (1) within the field ranges indicated by vertical arrows.

The curve designated as χ_1 in Fig. 1 shows the linear ac susceptibility of STO18 in zero external field as a function of T. As described previously[2,3,5] it clearly shows the rounding of the peak at $T_c\approx 25$ K and finite values as $T\rightarrow 0$. Owing to the very-low-temperature regime encountered, a quantum treatment of the susceptibility is in order. Following previous work on the impurity system Sr$_{1-x}$Ca$_x$TiO$_3$, $x=0.007$ ("SCT"),[19] we use the generalized Barrett formula[20]

$$\chi_0=\frac{C}{[T_S\coth(T_S/T)-T_0]^\gamma}, \tag{4}$$

where C, T_S, T_0, and γ are the Curie constant, the saturation and quantum critical temperatures, and the critical exponent, respectively. A best fit (dashed line) within the temperature range $30<T<50$ K yields $C=(1.13\pm 0.04)\times 10^5$, $T_S=(45.0\pm 2.8)$ K, and $T_0=(46.2\pm 2.0)$ K. The exponent $\gamma=1.04\pm 0.02$ comes close to the mean-field result $\gamma=1$.[21] When extending the fitting interval to $26<T<50$ K its value is shifted towards $\gamma=1.40\pm 0.02$. Hence—as expected—nonclassical behavior is encountered close to T_c.

These conjectures are corroborated by inspection of the isothermal field scaling function $\chi_E/\chi_0=f(E\chi_0^a)$, where $\chi_E\equiv\chi'(E,T=\text{const})$, $\chi_0\equiv\chi'(E=0\ T=\text{const})$, and $a=\delta/(\delta-1)$, δ being the exponent of the critical isotherm, $E\propto P^\delta$ for $T=T_c$.[19] All susceptibility functions refer to con-

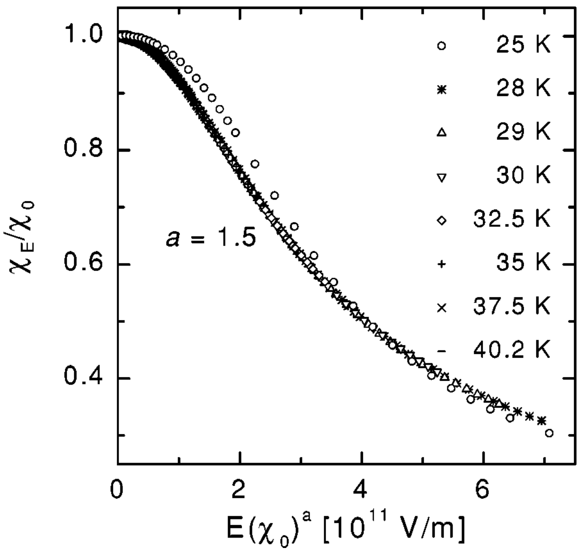

FIG. 3. Scaled plot $\chi_E/\chi_0 = f(E\chi_0^a)$ of the susceptibility isotherms $\chi_E \equiv \chi'(E,T)$ for $T = 25$, 28, 29, 30, 32.5, 35, 37.5, and 40.2 K (see Fig. 2) best fitted with an exponent $a = 1.5$.

stant temperatures as presented exemplarily in Fig. 2 for $T = 25$, 28, 32.7, and 37.5 K and field values up to $E = 110$ kV/m. The scaling plot as shown in Fig. 3 reveals a very good collapse of all data collected at temperatures $28 \leqslant T \leqslant 40.2$ K when using the mean-field exponent $a = 3/2$.[19] Deviations are found only in the vicinity of T_c as shown very drastically for the isotherm referring to $T = 25$ K (open circles). Obviously fluctuations are relevant only in the critical regime. This is at odds with the behavior of SCT, $x_{\mathrm{Ca}} = 0.007$, which shows severe deviations from mean-field quantum behavior in the entire range of temperatures, $T_c \approx 18$ K $< T < 35$ K.[19] It should be noticed that the field scaling function χ_E/χ_0 vs E holds equally well for both quantum and classic systems, since no temperature scale is involved.[21]

The field dependences of the real part of the dielectric susceptibility, $\chi'(E)$ (Fig. 2), corroborate Eq. (1) in the low-field regime. We find perfectly matching polynomials (solid lines) from best fits for field strengths up to $E_0 = 20-58$ kV/m depending on T (indicated by arrows). As shown in Fig. 1 together with χ_1 vs T, the nonlinear susceptibility χ_3 vs T thus determined is steeply rising below $T \approx 35$ K and maximizes at T_{c}. It should be noticed that we are convinced that only the low-field range complies with the scaling form of the equation of state, Eq. (3), when being truncated after the cubic term.[14] Higher fields clearly involve more complicated correlations and interactions. The steep decrease of $\chi'(E)$ at $E > E_0$ probably reflects the rapid growth and finally the saturation of the polar precursor clusters when superimposing the bias field to the local field fluctuations.[10,11]

Unlike our previous practice, when discussing $\chi'(E)$ of the impurity system SCT,[22] we do not attempt to describe the STO18 system by polar clusters embedded in a paraelectric background within a Langevin-type approach.[23] Based on a model of rigid clusters with field-independent sizes and dipole moments, this seems to be a reasonable assumption in the case of an impurity system like SCT, where the nucleation of clusters is well defined by chemical impurities with fixed dipole moment. However, in the case of a homogeneous compound like STO18 such nuclei are lacking. Only statistical correlations of the quenched RF's define the clustering forces. An additional external bias field does not rotate the cluster polarizations, but favors the growth of those polar regions, whose initial orientation matches best with the field direction. A full description of this scenario, where cluster nucleation and growth (“domain wall” motion) will play a dominant role, is left for future research. Very probably an Avrami-Fatuzzo-type[24] saturation behavior has to be invoked within a treatment similar to that proposed by Andelman and Joanny[25] for metastable domains in the *RF* Ising model under the constraint of a superimposed external field.

The nonlinearity coefficient $B = \chi_3/(\varepsilon_0^3\chi_1^4)$ vs T (Fig. 1, solid circles) is roughly constant within $28 < T < 50$ K and steeply decreases in the critical regime $25 \leqslant T \leqslant 28$ K. This behavior corroborates our above results. Obviously (quantum) mean-field behavior, i.e., $B = \mathrm{const}$, dominates outside the critical regime, while the sudden drop of B by about 50% when approaching T_{c} clearly confirms a fluctuation-controlled ferroelectric transition. Since both χ_1 and χ_3 stay finite when approaching T_c, probably as a consequence of RF smearing,[16] $B(T_c)$ does not vanish as it should in thermodynamic equilibrium. Based on these signatures we can clearly state that STO18 does not belong to the family of relaxor systems with a quasicontinuous order parameter like PMN, which undergo a crossover into random-bond random-field glassy behavior.[12]

As might have been anticipated, STO18 rather resembles the related quantum ferroelectric SCT,[22] although quite different fluctuational properties are observed in both systems. Tentatively we propose this to be due to the different transition mechanisms involved. While SCT is an impurity system undergoing a percolation-type transition,[26] STO18 is a homogeneous quantum ferroelectric with mixed displacive and order-disorder signatures.[5] An appropriate interacting anharmonic quantum oscillator model similar to that applied to SCT (Ref. 27) has still to be developed.

In conclusion, by analysis of the nonlinear dielectric susceptibility we have shown that STO18 proves to be a nonclassic quantum ferroelectric in weak electric fields and within a restricted critical temperature regime $T_c < T < 1.1T_c$. Its random-field-induced domain state evolving at $T < T_c$ does not represent a new glassy phase. Mean-field quantum scaling applies to strong fields and higher temperatures $T > 1.1T_c$.

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[1] K. A. Müller and H. Burkard, Phys. Rev. B **19**, 3593 (1979).

[2] M. Itoh, R. Wang, Y. Inaguma, T. Yamaguchi, Y.-J. Shan, and T. Nakamura, Phys. Rev. Lett. **82**, 3540 (1999).

[3] M. Itoh and R. Wang, Appl. Phys. Lett. **76**, 221 (2000).

[4] R. Wang and M. Itoh, Phys. Rev. B **62**, 731 (2000).

[5] L. Zhang, W. Kleemann, J. Dec, R. Wang, and M. Itoh, Eur. Phys. J. B **28**, 163 (2002).

[6] L. Zhang, W. Kleemann, R. Wang, and M. Itoh, Appl. Phys. Lett. **81**, 3022 (2002).

[7] Y. Imry and S. K. Ma, Phys. Rev. Lett. **35**, 1399 (1975).

[8] R. Wang and M. Itoh, Phys. Rev. B **64**, 174104 (2001).

[9] L. E. Cross, Ferroelectrics **151**, 305 (1994) and references therein.

[10] V. Westphal, W. Kleemann, and M. D. Glinchuk, Phys. Rev. Lett. **68**, 847 (1992).

[11] W. Kleemann, J. Dec, P. Lehnen, R. Blinc, B. Zalar, and R. Pankrath, Europhys. Lett. **57**, 14 (2002).

[12] R. Pirc and R. Blinc, Phys. Rev. B **60**, 13 470 (1999).

[13] C. Pappa, J. Hammann, and C. Jacoboni, J. Phys. (Paris) **46**, 637 (1985); M. Maglione, U. T. Höchli, and J. Joffrin, Phys. Rev. Lett. **57**, 436 (1986); A. K. Tagantsev and A. E. Glazounov, J. Korean Phys. Soc. **32**, S951 (1998).

[14] H. E. Stanley, *Phase Transitions and Critical Phenomena* (Clarendon Press, Oxford, 1971), Chap. 11.

[15] J. Hemberger, H. Ries, A. Loidl, and R. Böhmer, Phys. Rev. Lett. **76**, 2330 (1996).

[16] J. Dec, W. Kleemann, V. Bobnar, Z. Kutnjak, A. Levstik, R. Pirc, and R. Pankrath, Europhys. Lett. **55**, 781 (2001).

[17] V. Bobnar, Z. Kutnjak, R. Pirc, R. Blinc, and A. Levstik, Phys. Rev. Lett. **84**, 5892 (2000).

[18] W. Kleemann, Int. J. Mod. Phys. B **7**, 2469 (1993).

[19] W. Kleemann, J. Dec, and B. Westwański, Phys. Rev. B **58**, 8985 (1998).

[20] J. Dec and W. Kleemann, Solid State Commun. **106**, 665 (1998).

[21] S. A. Prosandeev, W. Kleemann, B. Westwański, and J. Dec, Phys. Rev. B **60**, 14 489 (1999).

[22] U. Bianchi, J. Dec, W. Kleemann, and J. G. Bednorz, Phys. Rev. B **51**, 8737 (1995).

[23] A. J. Bell, J. Phys.: Condens. Matter **5**, 8733 (1993).

[24] M. Avrami, J. Chem. Phys. **7**, 1103 (1939); E. Fatuzzo, Phys. Rev. **127**, 1999 (1962).

[25] D. Andelman and J. F. Joanny, Phys. Rev. B **32**, 4818 (1985).

[26] S. A. Prosandeev, W. Kleemann, and J. Dec, J. Phys.: Condens. Matter **13**, 5957 (2001).

[27] S. A. Prosandeev, A. E. Maslennikov, W. Kleemann, and J. Dec, Ferroelectrics **238**, 171 (2000).