Shear elasticity and ferroelastic hysteresis of the low-temperature phase of $SrTiO_3$

A. Binder and K. Knorr
FR10.3 Technische Physik, Universität des Saarlandes, D-66041 Saarbrücken, Germany
(Received 6 June 2000; published 29 January 2001)

$SrTiO_3$ single crystals have been studied by quasistatic twist-torque (shear strain-shear stress) and by low-amplitude torsional resonance experiments around 10 kHz. The hysteresis loops of the tetragonal low-temperature phase are interpreted in terms of ferroelasticity. The low-amplitude elastic data shows anomalies between 30 and 50 K with strong nonlinear contributions.

DOI: 10.1103/PhysRevB.63.094106 PACS number(s): 62.20.Dc, 64.70.Kb, 77.80.Dj, 81.30.Hd

I. INTRODUCTION

A great deal of our understanding of structural phase transitions stems from experimental and theoretical studies of the cubic perovskites, $BaTiO_3$ and $SrTiO_3$ in particular.[1] This crystal structure has two inherent lattice instabilities which lead to soft mode behavior and related structural phase transitions.[1] One of the modes is the zone center TO mode which drives the ferroelectric transition of $BaTiO_3$, the other one is the zone boundary R-point Γ_{25} mode which triggers the antiferrodistortive, improper ferroelastic phase transition ($Pm\bar{3}m$ to $I4/mcm$) of $SrTiO_3$ at $T_c=105$ K. The primary order parameter η of this transition is the staggered rotation angle of the oxygen octahedra about one of the cubic axes. The spontaneous tetragonal distortion of the lattice, represented by $c/a-1$, is the secondary order parameter. $c/a-1$ is rather small, 4×10^{-4} at 80 K. The transition is of second order. $SrTiO_3$ also shows an incipient ferroelectric behavior. Down to about 50 K the polar TO mode and the static dielectric constant ε follow a Curie-Weiss type T dependence $\omega_{TO}^2\propto\varepsilon^{-1}\propto(T-\Theta)$ with $\Theta=37$ K. At low T these quantities saturate, with ε values of the order of 10^4. This behavior has been attributed to quantum effects.[2] Müller *et al.*[3] promoted the idea of $SrTiO_3$ entering a coherent (i.e., macroscopic) paraelectric low-T quantum state at $T_q\approx\Theta$ which lead to a revival of interest in quantum paraelectrics.

This article deals with the shear elasticity as well as with the ''ferroelastic'' properties of the tetragonal phase of $SrTiO_3$ in the original meaning of this word, that is with the switching of domains by external stress. The understanding of ferroelastic hysteresis loops is in a relatively poor state, mainly because of a lack of pertinent experimental results.[4] We have recently reported on torque-twist measurements on another improper ferroelastic, calomel Hg_2Cl_2.[5] For calomel some preliminary understanding of the loops has been achieved in terms of a lamellae model for a twin band of ferroelastic domains. We want to investigate whether the results on the low-T phase of $SrTiO_3$ are similar and can be explained on the same basis. Complications may arise from the fact that in $SrTiO_3$ there are not only two but three domain states. Our study will not only give results on the ferroelastic, but also on the elastic behavior which will cast some light on the low-T anomalous behavior of $SrTiO_3$.

II. EXPERIMENT

The torque-twist setup has been described in more detail elsewhere.[5] The samples are single crystalline bars of nominally pure $SrTiO_3$ which have been cut with a diamond wire saw from (100) plates to the size of $l=6$ mm, $d_1=d_2=1$ mm. The samples are clamped on one end. Torque τ along the long axis of the samples is applied via a magnetic field which acts on a permanent magnet on the free end of the sample. The twist angle φ is recorded via the deviation of a light beam reflected from a small mirror on the free end. We recall that the shear stress and strain resulting from this geometry are inhomogeneous in the sense that they vanish along the axis of the sample and increase with the distance from the axis. The stress and the strain tensor change orientation with the azimuth about the axis.

The crystals have been cut and oriented in two different ways. Our main interest is in an orientation (A) where τ is along $[1\bar{1}0]$, one pair of opposite side facets is (001) and the other one (110). In the second orientation (B) all surfaces are {100} facets and τ is parallel to [100]. In the single crystalline state of the cubic phase, $\varphi=s\tau$, where s is—apart from a geometrical factor—the linear elastic compliance. For orientation A, s is a linear combination of s_{44} and s', $s'=(s_{11}-s_{12})/2=[(c_{11}-c_{12})/2]^{-1}$. For orientation B, $s=s_{44}=c_{44}^{-1}$.[6] Ignoring the slight disortion of the lattice below T_c, this notation also applies to the tetragonal phase. However, in the tetragonal phase the sample exists in a multidomain state with three types of domains x,y,z which have the tetragonal axis oriented (almost exactly) along [100], [010], and [001], respectively. The domains are known to form twin bands with {110} twin walls.[7] For a given pair of domain states there are actually two twin bands possible, the twin planes being mutually perpendicular,[8] e.g., (110) and $(1\bar{1}0)$ for the combination x,y. For orientation B the geometry is such that the torque cannot change the domain pattern, hence the response should be elastic rather than superelastic. For orientation A the torque about $[1\bar{1}0]$ favors domain x on the (100) front facet and domain y on the (100) rear facet whereas there is no effect on the (110) side facets. Hence there is an additional superelastic contribution due to torque induced changes of the domain pattern and finally—for sufficiently large values of τ—one expects φ to be driven into quasisaturation φ_s where the front and rear facets are monodomain. In this situation, the relation $\varphi_s=2l\epsilon_s/d_1$, $\epsilon_s=(c/a-1)$ should hold. The center of the sample remains in the multidomain state however large the torque.

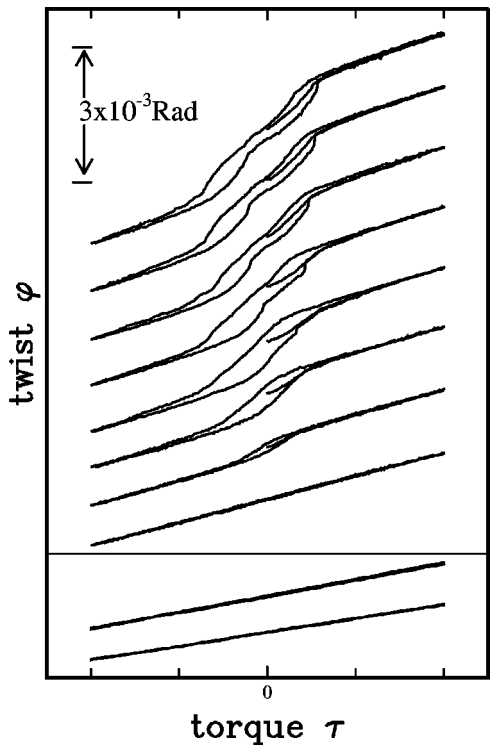

FIG. 1. φ-τ curves for orientation A (top) and B (bottom). The temperatures are 120 (lower) and 50 K (upper curve) for orientation B and 106, 100, 90, 80, 70, 60, 50, and 40 K (from bottom to top) for orientation A.

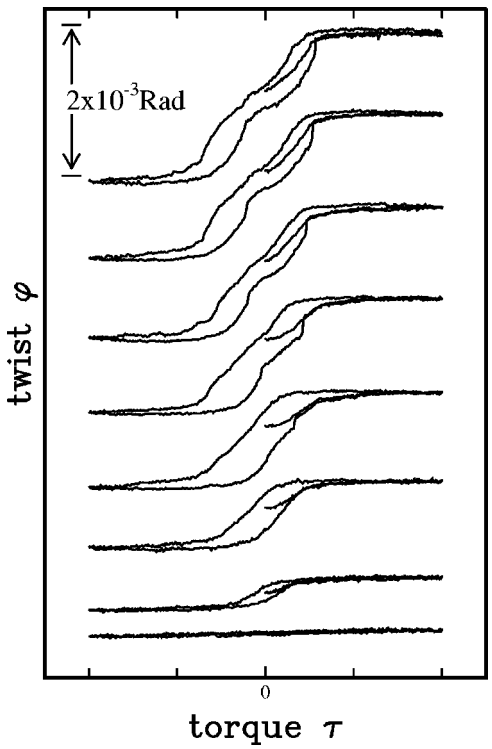

FIG. 2. φ_r-τ curves for orientation A. The temperatures are the same as in Fig. 1.

III. RESULTS

In a first set of experiments, φ-τ curves have been recorded by sweeping τ slowly from positive to negative values and back (Fig. 1). For orientation B, the curves are linear both above and below T_c. The shear compliance s_{44}, as given by the slope, shows a steplike increase at T_c by about 15%. This is consistent with ultrasonic data on c_{44}.[9,10] Obviously there is no contribution from torque-induced domain wall motion let alone saturation, in agreement with the geometrical considerations. Hence we concentrate in the following on samples with orientation A.

For this orientation the φ-τ curves of the cubic phase are again linear, but below T_c they open up to hysteresis loops (Fig. 1). In first experiments on samples used as cut, these loops had highly irregular shapes due to large, irreversible jumps of φ. After removing 5 μm of surface layer and more by etching until all traces of birefringence had disappeared in the cubic phase, the loops finally closed back into themselves and were reproducible in the sense that the data on repeated φ-τ cycles practically superimpose.

Nevertheless the loops are quite different from the more regular ones we have observed on calomel. In contrast to calomel, the present loops show (i) a relatively well defined onset of saturation, the point above which φ is almost indepent of the mechanical history of the sample and (ii) a wasp-tail shape for T less than about 70 K, and (iii) at lower T the hysteretic part of the curves appears to consist of a series of steplike discontinuities, the larger ones could be still resolved in the measurements. On the whole, the φ-τ curves possess inversion symmetry, but the center of symmetry does not coincide with the starting point of the ''virgin'' curves, which are also shown in Fig. 1. This is presumably related to the fact that we have not ''demagnetized'' the samples by a sequence of minor loops with decreasing amplitude before going to the next temperature (as we had done for calomel). We rather stopped each cycles at $\tau=0$ with some small twist $\varphi_{\rm rem}$ remaining.

The loops can be approximately decomposed into an elastic, loss free, linear component $\varphi_e=s_e\tau$ which is thought to represent the elastic deformation of the tetragonal lattice within the domains and a remainder φ_r which represents the τ-induced changes of the domain configuration up to saturation $\varphi(\tau)=\varphi_e+\varphi_r$. s_e is the slope of $\varphi(\tau)$ at maximum τ beyond saturation [this treatment is analogous to the decomposition of $B(H)$ loops into $H+4\pi M(H)$ in ferromagnets[11] with $\varphi_r(\tau)$ playing the role of $M(H)$]. $\varphi_r(\tau)$ loops are shown in Fig. 2. φ_r is practically constant for larger values of τ, $\tau_s<\tau<\tau_{\rm max}$, that is outside the hysteretic center part of the loops. This means that the plateau value φ_s of φ_r represents both, the spontaneous and the saturated part of the twist angle. The T dependence of $\varphi(\tau_{\rm max})$, $s_e\tau_{\rm max}$, φ_s, and the normalized loop area A is shown in Fig. 3.

A very sensitive measurement of the shear response at small τ amplitudes is accomplished by the study of the fundamental torsional resonance. For this purpose resonance curves have been recorded by sweeping the frequency ν of an ac drive field $\tau=\tau_0\cos(2\pi\nu t)$ through the reasonance at $\nu=\nu_0$ (around 10 kHz). The amplitude τ_0 has been held at values three orders of magnitude lower than the value τ_s of the φ-τ loops. In the cubic phase the resonance curves are of

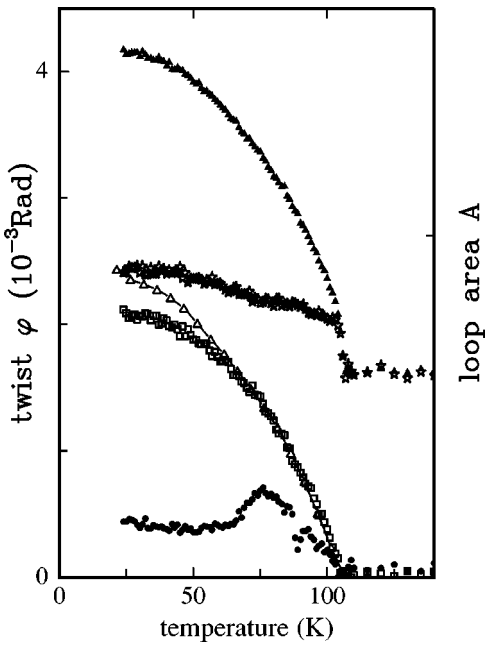

FIG. 3. Temperature dependence of $\varphi(\tau_{\max})$ (full triangles), of its components $s_e\tau_{\max}$ (stars) and φ_s (open squares) $[\varphi(\tau_{\max}) = s_e\tau_{\max}+\varphi_s]$ and of the normalized loop area A (full squares). Also included are data $\epsilon_s(T)\propto\eta^2$ from Ref. 13 (open triangles).

Lorentzian shape, as is appropriate for a damped linear oscillator. The shear compliance s is then proportional to ν_0^{-2} and the internal friction Q^{-1} to the half width. In the tetragonal phase, the first resonance curves measured had a saw-tooth shape with hysteresis with respect to sweeping ν upward and downward. This is characteristic of a nonlinear (Duffing) oscillator vibrating at higher amplitudes. Such curves are difficult to analyze. We therefore reduced the drive amplitudes by another order of magnitude and finally obtained moderately asymmetric curves (Fig. 4) with φ amplitudes φ_0 close to the detection limit of our setup. These curves have then been analyzed on the basis of the nonlinear

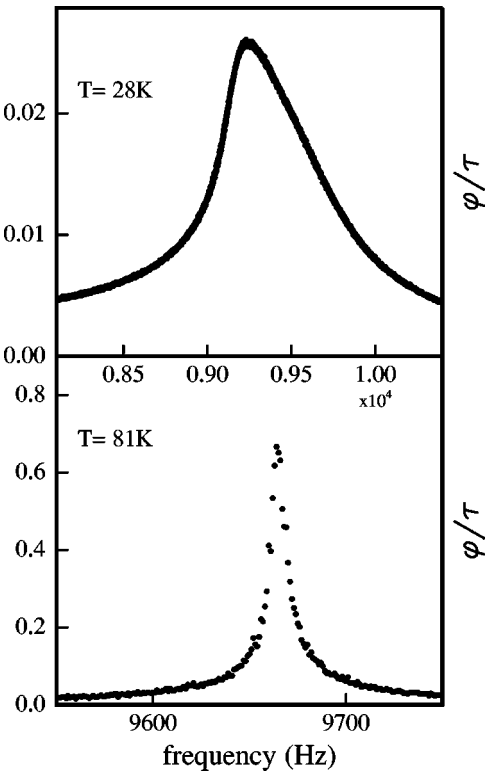

FIG. 4. Two examples of resonance curves (at 81 and 28 K).

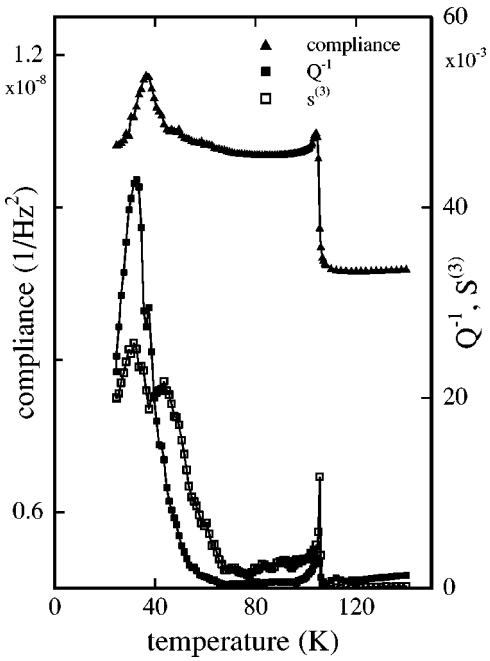

FIG. 5. Temperature dependence of linear elastic compliance (full triangles), internal friction (full squares), and nonlinear compliance ($\times 0.2$) (open squares) of $SrTiO_3$.

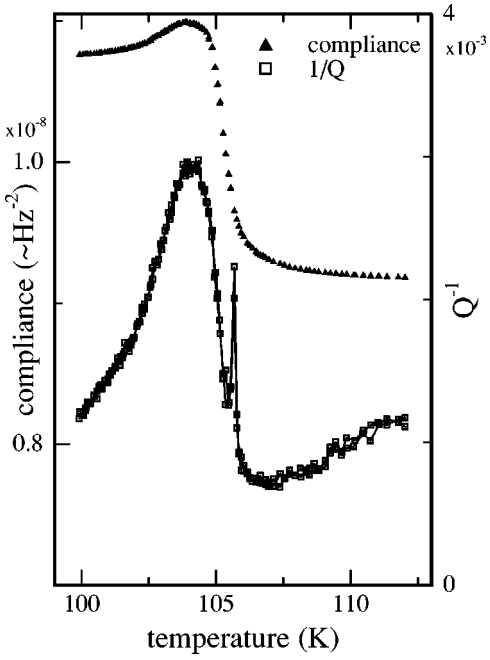

FIG. 6. Behavior of linear elastic compliance (triangles) and internal friction (squares) in the T regime close to T_c.

oscillator with three free parameters s, Q^{-1}, and the nonlinear compliance $s^{(3)}$, $\varphi = s\tau + s^{(3)}\tau^3$. The T dependence of these parameters is shown in Figs. 5 and 6.

We also tried ac measurements with subresonant drive frequencies in the 10 to 500 Hz range, a mode of operation which was very helpful for the detection of elastic dispersion in calomel. It turned out, however, that at least for orientation A the φ_0 signal was very noisy, presumably because of the jumps of the φ-τ curves mentioned above. For orientation B the quality of the signals was much better. For this orientation there is no loss detectable, neither above nor below T_c. The results on orientation B obtained with this ac technique agree with those obtained from the integral slope of the φ-τ curves.

IV. DISCUSSION

The mechanical response of a ferroelastic multidomain state to an external stress is a complex problem. The response depends not only on the geometry of the experiment, but also on the magnitude and frequency of the external stress and on the dc bias stress, which some authors apply in order to drive the sample monodomain. The compilation of Höchli and Bruce[12] on s_{11} data near T_c shows that the results of different authors vary enormously depending on the experimental method (and perhaps on the quality of the crystals) used. All experiments agree that s_{11} is somewhat larger below T_c than above, the increase ranging from 2% to almost 50%. Acoustic resonance measurements in the kHz range show an additional ''singularity'' slightly below T_c, which is absent in ultrasonic data. It appears that high frequency (ultrasonic and Brillouin) techniques basically probe the elastic part of the response of the tetragonal lattice, the domain walls obviously cannot follow such fast oscillations, whereas low-frequency techniques are also susceptible to superelasticity.

The φ-τ curves of the present study allow to separate the elastic and the superelastic part of the response. First we point out that the basic properties of the φ-τ curves are consistent with the geometrical considerations from above: the response for orientation B is strictly elastic and lossfree and compares well with ultrasonic data on c_{44} whereas for orientation A there is superelasticity, loss and saturation what is obviously related to the fact that in this geometry the domain structure can be changed by the external field which in turn is related with the active s' component of the total compliance.

For the φ-τ and φ_r-τ curves of orientation A (Figs. 1 and 2) the inner hysteretic section, $|\tau| < \tau_s$, can be easily distinguished from the outer reversible section $|\tau| > \tau_s$. This is quite different from calomel, where the hysteresis extended up to the maximum τ value reached in the measurement of a loop. The outer section of the φ-τ curves on $SrTiO_3$ represents the state of maximum saturation where any further increase of τ leads to a basically elastic, loss free distortion of the domains without changes of the domain pattern. Thus the slope s_e of this section is the best approximation to the elastic compliance s_e available from the φ-τ experiment. As can be seen from Fig. 3, s_e is somewhat enhanced with respect to the cubic phase with a step at T_c. The relative size of the step around T_c compares well with what can be calculated from ultrasonic data on c_{11}, c_{12}, and c_{44}.[9,10] The T dependence of s_e within the tetragonal phase, a roughly linear increase by about 15% between 90 and 30 K is not consistent with the ultrasonic results. Presumably s_e still contains some superelastic contribution due to residual changes of the domain pattern beyond the apparent saturation torque τ_s. The value of $\varphi_s = \varphi_r(|\tau| > \tau_s)$, which according to our reasoning from above represents the saturated as well as the spontaneous twist angle, shows a T dependence which is close to that of the crystallographic spontaneous strain $\epsilon_s \propto \eta^2$. For comparison Fig. 3 includes a plot of η^2 as given in Ref. 13. An exact proportionality of φ_s and ϵ_s would indicate that each hysteresis cycle performed in the tetragonal multidomain state leads to a saturated state with the same unbalanced weights of the three domains. This situation applies approximately, but not exactly.

Actually the apparent value of saturation, φ_s, amounts to 30% of the ideal geometrical value of $2l\epsilon_s/d_l$, only. Obviously the (100) surface layers cannot be driven completely monodomain, quite in contrast to calomel. This is presumably due to the fact that in calomel there are just two ferroelastic domain states, only. Saturation can be then achieved by tilts of the twin walls as described by the lamellae model. In the tetragonal phase of $SrTiO_3$, however, there are three domain states and a sample is expected to consist usually of six different types of twin bands (three different domain combinations with two possible orientations of the twin plane for each combination). A twin band can only respond to the external torque with a shear deformation if the boundaries to other twin bands can adjust to this deformation. Hence the yield to an external torque involves two processes, the motion of domain walls and of twin band boundaries. The situation is further complicated by the fact that there are twin band boundaries with two different intersection angles of the domain walls in these boundaries, namely 90° and 120°. The incomplete alignment of the domains in $SrTiO_3$ is therefore not very surprising. The rather abrupt change from superelastic behavior to saturation suggests that there is some self-blocking of the domains well before the case of ideal quasisaturation is reached.

The inner section of the φ-τ curves is not only hysteretic, but also has a (integral) slope s larger than s_e, due to the superelastic component s_{se} of the compliance, $s = s_e + s_{se}$, $s_{se} = Rs_e$. At lower T, the enhancement factor R is about 2.5, a relatively modest value compared to values of 10 and more for calomel. Obviously the constraints opposing the stress induced domain wall motion are highly effective in the tetragonal three-domain state of $SrTiO_3$. A smooth shape of the φ-τ loops suggests that the torque induced domain wall motion is of the viscous type.[11,14] This appears to be the case for calomel and also for $SrTiO_3$ at higher temperatures, T larger than about 70 K. At lower temperatures the domain walls of $SrTiO_3$ appear to jump from one obstacle to the next,[11,14] as indicated not only by the minor discontinuities of the loops, but also by the change to the wasp-tail-type shape and the decrease of the normalized loop area of Fig. 3. Thinking in terms of a thermally activated process, the jump

probability is proportional to $\exp(-U/kT)$. The binding energy U of the wall to a pinning center is expected to scale with the domain wall energy which increases with decreasing temperature. On this basis the change of the loops with temperature is plausible.

Recently the mechanical response of tetragonal $SrTiO_3$ has been studied by Kityk *et al.*[15] with forced, flexural and compressional oscillations in the *Hz* regime. Our results on $\varphi(\tau_{\max})$ as function of T agree quite well with T dependence of the Young's modulus Y of this study (Figs. 7, 9, 11 of Ref. 15) and so does $s_e(T)$ of our Fig. 3 and their $Y(T)$ for a bias load of 4200 nm (Fig. 7 of Ref. 15). This obviously means that this bias load drives the sample of this study into saturation (with the consequence that this data essentially represents the elastic response). Quite correctly, Kityk *et al.* interpret their results at lower bias loads in terms of a superposition of elasticity and of domain effects, the latter being proportional to the spontaneous strain order parameter ϵ_s. However, we find the argumentation and the terminology of these authors questionable. Rather than introducing the concept of saturation directly, they refer to superelasticity due to T-independent spring constant between domain walls.

The dominant feature of compliance as obtained with the low-amplitude resonance measurements is the step at T_c. The size of this step and the weak extra hump about 2 K below T_c are consistent with ultrasonic results. The Landau treatment of the phase transition calls for a sawtoothlike T dependence of the static elastic compliance across T_c.[15] Relaxations will lead to a rounding of this feature and to the appearance of concomitant loss in measurements performed at finite frequencies, in agreement with the present experimental data. Critical effects are confined to small T interval right at T_c and we think that the sharp loss peak at 105.6 K (Fig. 6) is due to critical fluctuations.[16,17] These are indications that the low-amplitude resonance experiment essentially probes the elastic response of the lattice within the domains.

Accordingly the low-T anomalies of Fig. 5 should also be related to elastic effects within the domains, rather than to the superelasticity. There might be residual contributions from τ-induced domain effects to these anomalies, but they should be small as suggested by the rather low values of the loss and of $s^{(3)}$ at higher temperatures in the tetragonal multidomain state. The linear compliance peaks at 37 K, which is just the characteristic temperature of the Curie-Weiss-type Θ temperature of the permittivity and of the ferroelectric soft mode and which has been discussed as the onset temperature T_q of the coherent quantum state. The loss is maximum at a slightly lower temperature, 33 K, suggesting that the peaks of the compliance and of the loss are both due to a unique relaxation process. $s^{(3)}$ actually shows two maxima, at 44 and 33 K, the lower one coincides with the loss peak. There are weak features of the linear compliance and of the loss which line up with the upper maximum of $s^{(3)}$.

Anomalies of the linear compliance and of the loss and indications for nonlinear mechanical behavior in the tetragonal phase of $SrTiO_3$ have been reported before. Apart from the work of Kityk *et al.*, mentioned already above, there have been studies of mechanical resonances.[18,19] The assessment of these results is difficult since elasticity has not been separated from domain effects. Furthermore, neutron and light scattering studies[20–23] demonstrate that the behavior of the low-lying phonon branches is anomalous at and below T_q, including anharmonic effects and the appearance of a forbidden branch. It is intuitively clear that all these effects should be related to the presence of polarization clusters characteristic of a paraelectric state with a high dielectric permittivity. In such a situation one expects a coupling of the square of the electric polarization $\langle P^2 \rangle$ to the lattice strain, which then leads to an anticrossing of the ferroelectric TO branch and the TA phonon branch. However, it has been shown that the conventional $\epsilon_i \nabla_j P_k$ term describing such a coupling cannot explain the experimental results on the phonon modes, but that unusual combinations of strain and polarization have to be invoked.[20,22] Courtens[22] proposes that the coefficient of the $\epsilon_i \nabla_j P_k$ term depends on the actual value of the polarization within a cluster rather than being a constant. Kityk *et al.* argue that the strain gradient of their bar bending experiment is equivalent to an electric field which in turn induces electric polarization. The present results emphasize the importance of nonlinear effects and show that not only one but two of such processes have to be considered.

V. SUMMARY

The combination of large- and low-amplitude twist-torque experiments on the tetragonal multidomain state of $SrTiO_3$ allowed a separation of elastic and domain (superelasticity, saturation) effects. The large-amplitude twist-torque curves show a relatively well defined onset of apparent saturation. The saturation achieved is, however, by no means complete in the sense that even the surface layer cannot be driven into the monodomain state. This behavior is quite different from the previously studied calomel. We suggest that the incomplete saturation is due to a self-blocking of the domain walls and twin band boundaries which in turn is related to the fact that there are three domain states (and not only two as in calomel) and hence six twin bands involving two different mesoscopic length scales. The inner hysteretic part of the loops changes from a smooth shape at higher T to a wasp-tail shape at lower T which we interpret as a crossover from a viscous motion of the walls to a jumping over barriers. The low-amplitude results on the elastic response exhibit anomalies at temperatures between 30 and 50 K which is just the T range in which previous authors have observed anomalous behavior and which has been interpreted with the onset of quantum saturation or of a coherent quantum state. The present work shows that it is not so much the linear but the the nonlinear part of the elastic response which is anomalous at $T \approx T_q$. In fact, there is some similarity to the onset of the spin glass state of dilute magnetic systems where theory calls for a divergence of the nonlinear susceptibility at the glass transition temperature.[24] Hence we propose to pursue the idea of a glassy freezing of polarization and strain clusters in $SrTiO_3$.

[1] M. E. Lines, and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon Press, Oxford, 1977).
[2] K.A. Müller, H. Burkard, Phys. Rev. B **19**, 3593 (1979).
[3] K.A. Müller, W. Berlinger, and E. Tosatti, Z. Phys. B: Condens. Matter **84**, 277 (1991).
[4] E. K. H. Salje, *Phase Transitions in Ferroelastic and Co-elastic Crystals* (Cambridge University Press, Cambridge, 1990).
[5] A. Binder, K. Knorr, and Yu.F. Markov, Phys. Rev. B **61**, 190 (2000).
[6] W. Voigt, *Lehrbuch der Kristallphysik* (Johnson Reprint Corporation, New York, 1966).
[7] F.W. Lytle, J. Appl. Phys. **35**, 2212 (1964).
[8] J. Sapriel, Phys. Rev. B **12**, 5128 (1975).
[9] W. Rehwald, Solid State Commun. **8**, 1483 (1970).
[10] W. Rehwald, Solid State Commun. **8**, 607 (1970).
[11] B. D. Cullity, *Introduction to Magnetic Materials* (Addison-Wesley, Reading, MA, 1972).
[12] U.T. Höchli and A.D. Bruce, J. Phys. C **13**, 1963 (1980).
[13] J.C. Slonczewsky and H. Thomas, Phys. Rev. B **1**, 3599 (1970).
[14] B. A. Strukov and A. P. Levanyuk, *Ferroelectric Phenomena in Crystals, Physical Foundations* (Springer-Verlag, Berlin, 1998).
[15] A.V. Kityk *et al.*, Phys. Rev. B **61**, 946 (2000).
[16] K. Fossheim and B. Berre, Phys. Rev. B **5**, 3292 (1972).
[17] B. Berre, K. Fossheim, and K.A. Müller, Phys. Rev. Lett. **23**, 589 (1969).
[18] G. Sorge, E. Hegenbarth, and G. Schmitt, Phys. Status Solidi **37**, 599 (1970).
[19] O.M. Nes, K.A. Müller, T. Suzuki, and F. Fossheim, Europhys. Lett. **19**, 397 (1992).
[20] B. Hehlen, A.L. Perou, E. Courtens, and R. Vacher, Phys. Rev. Lett. **75**, 2416 (1995).
[21] R. Vacher, J. Pelous, B. Hennion, G. Coddens, E. Courtens, and K.A. Müller, Europhys. Lett. **17**, 45 (1992).
[22] E. Courtens, Ferroelectrics **183**, 25 (1996).
[23] B. Hehlen, Z. Kallassy, and E. Courtens, Ferroelectrics **183**, 265 (1996).
[24] K. Binder, and A.P. Young, Rev. Mod. Phys. **58**, 801 (1986).