Mechanical shear measurements on a ferroelastic multidomain state

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The mechanical properties of the improper ferroelastic crystal calomel Hg_2Cl_2 have been investigated with a torque-twist setup. Three methods have been applied: low-amplitude ac measurements on the real and imaginary part of the shear compliance in the Hz–10^2 Hz range, measurements of isothermal torque-twist hysteresis loops, and studies of the twist angle for different torque-temperature histories. The work gives insight into the response of the ferroelastic multidomain state to an external torque.

I. INTRODUCTION

Crystals undergoing a ferroelastic phase transition exhibit at least two orientation states (domains) which differ with respect to the components of the spontaneous strain tensor. Switching of one ferroelastic domain to the other can be induced by applying an appropriate external shear stress and one of the domains can grow at the expense of others via a motion of the domain walls. It is this analogy to ferromagnets and ferroelectrics which led to the name ''ferroelastic.'' Nevertheless direct experimental evidence for switching in mechanical measurements is rare for nonmetallic crystals. Only some few successful measurements of ferroelastic hysteresis loops have been reported in the literature.[1–4] It is, therefore, not surprising that the understanding of the domain pattern and of its response to an external stress is still incomplete. Investigations of ferroelastic phases[5] rather concentrate on diffraction studies of the spontaneous strain, on optical inspections of the domain pattern, on measurements of the elastic constants by ultrasound propagation and Brillouin spectroscopy, and on the measurements of soft modes, e.g., by inelastic neutron scattering.

We report mechanical torque-twist measurements on calomel single crystals. We have chosen this improper ferroelastic rather than a proper ferroelastic, since we are interested in the ''superelastic'' mechanical response due to changes of the domain arrangement. For a proper ferroelastic it is more difficult to distinguish the superelasticity from the intrinsic elastic softness in the vicinity of the ferroelastic phase transition. Calomel is a van der Waals crystal consisting of the linear Cl-Hg-Hg-Cl molecules. It crystallizes in a tetragonal structure D_{4h}^{17} where the molecular axes are aligned along the tetragonal c axis.[6] At $T_c \approx 184$ K the transition into the low-temperature orthorhombic phase (D_{2h}^{17}) is triggered by the soft TA mode at the X point at the boundary of the Brillouin zone.[7–9] The condensed displacement of this mode is the primary order parameter η of the orthorhombic phase. The appearance of η is accompanied by a spontaneous strain, the largest and symmetry breaking component is ε_6 which refers to a pure shear of the basal plane of the tetragonal lattice (ferroelastic species $4/mmmFmm$).[10] At say 100 K the shear angle $\Delta\gamma$ is 0.4 deg. In lowest order the coupling of the order parameter and the strain is of the quadratic-linear type, $\eta^2\varepsilon_6$. The treatment of the transition in terms of the Landau model can be found in Ref. 11. There are two ferroelastic domains which differ in the sign of the spontaneous shear strain ε_s. Either ferroelastic domain forms two translational domains which are separated by antiphase boundaries. The translational domains have no effect on the mechanical properties and will be ignored in the following. The transition appears to be at the borderline between first and second order. Soft-mode spectroscopy, diffraction measurements of the spontaneous strain ε_s and heat-capacity measurements[12] suggest tricritical behavior with $\varepsilon_s \propto \eta^2 \propto (T_c\text{-}T)^{2\beta}$, $\beta = 0.25$. The ferroelastic domains form twin bands of alternating + and − domains. The twin walls are crystallographic (100) or (010) planes.[13] This orientation of the walls is consistent with the concept of zero net strain in the domain boundary.[14] The elastic constants c_{ij} have been determined by Brillouin spectroscopy,[15] above and below T_c.

II. EXPERIMENTAL

We have studied the twist of single crystals subject to an external torque. The samples are prismatic columns with a typical size $L_1L_2L_3 = (7\times2\times1.5)\ \text{mm}^3$. The samples have been cut in two different ways. Most of the data have been obtained for samples with the edges parallel to the crystallographic directions [100], [010], [001], (orientation *A*, see Fig. 1). Some complementary measurement have been made on a sample with the edges L_1, L_2, L_3 along $[1\bar{1}0]$,$[\bar{1}10]$, [001] (orientation *B*). The samples are glued with the bottom facet onto the cold plate of a closed-cycle refrigerator. On the free end they carry a permanent magnet and a mirror. Torque τ about an axis parallel L_1 is applied via a magnetic field. The resulting twist angle φ of the free end is obtained from the deviation of a light pencil reflected from the mirror. A schematic picture of the setup has been shown elsewhere.[16]

The torque-twist method is very versatile and allows several modes of operation. For large torques, i.e., for the measurement of hysteresis loops a 1 T electromagnet with an iron core was used. Here the field and hence the torque was ramped up and down between $+\tau_{\max}$ and $-\tau_{\max}$ with a cy-

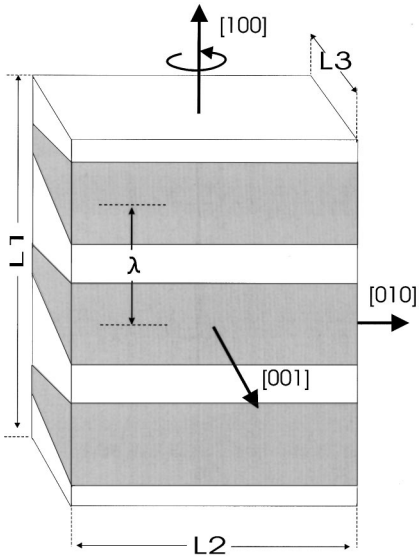

FIG. 1. Schematic picture of a sample of orientation *A*. The sample is assumed to form a periodic twin band with (100) walls separating the + and the − domains. Under the action of the external torque the domain walls tilt out of the original (100) plane thereby increasing the + domains on the front (001) facet and the − domains on the rear (001) facet. Saturation in the sense of this experiment is achieved when the front facet consists of a single + domain and the rear facet of a single − domain.

cling frequency f of typically 0.01 Hz. The torque-twist data are recorded quasicontinuously point by point. The same setup is used for measurements of the twist in a constant torque on cooling and heating. For measurements with smaller amplitudes and higher frequencies, a separate pair of smaller field coils without an iron core was used. Here the torque varies sinusoidally with time, $\tau=\tau_0\cos(2\pi\nu t)$ and the amplitude and the phase delay of the twist, $\varphi=\varphi_0\cos(2\pi\nu t\text{-}\delta)$, are recorded by means of a vector lock-in amplifier. The measuring frequencies ν are in the 1 Hz–100 Hz regime well below the fundamental torsional eigenfrequency of the sample at some kHz. The frequency and the width of the torsional resonance have also been studied occasionally.

III. TWIST DEFORMATION

The application of a homogeneous shear stress to an elastic body is difficult to realize experimentally. It is more convenient to apply a torque to an elongated prismatic sample and to determine the twist angle resulting from the torque. In this configuration, however, shear stress and strain are by no means constant over the volume of the sample. For the homogeneous, single-crystalline state of the paraelastic phase, they rather vanish along the axis (neutral fibre) and increase in magnitude proportional to the distance from the axis. The orientation of the stress and the strain tensor rotates with respect to the crystallographic coordinate system when going around the axis. In the linear elastic regime, the twist angle φ is proportional to the torque τ, $\varphi=CS\tau$. C is a geometrical factor. The effective compliance S is given by a linear combination of the (pure and impure) shear compliances s_{ij} of the crystal system.[17] The coefficients depend on the orientation of the torque axis relative to the crystal axes. The concept holds for samples with an elliptic cross section. The coefficients of the s_{ij} also depend on the aspect ratio of the major and minor axis of the cross section. The twist deformation of a sample with a rectangular cross section is more complicated, but can be approximately described by referring to the elliptic case with the dimensions L_2 and L_3 playing the role of the major and minor axis.[17] For the two orientations and typical values of L_2/L_3 used in the present study, one obtains for the tetragonal paraelastic phase: $S_A=0.2s_{66}+0.8s_{44}$ for τ along [100] (orientation *A*) and $S_B=1.2(s_{11}-s_{12})/2+0.4s_{44}$ for τ along $[1\bar{1}0]$ (orientation *B*). Hence, it is only for orientation *A* that the compliance s_{66} which is related to the symmetry breaking part ϵ_6 of the spontaneous strain tensor is probed.

Below T_C, in the multidomain state of the orthorhombic phase, there are two contributions to the twist angle, $\varphi=\varphi_e+\varphi_{se}$. φ_e represents the linear elastic response of the orthorhombic lattice and is again given by a linear combination of the s_{ij} which can be calculated from the elastic constants c_{ij} of the orthorhombic phase. As the spontaneous deformation is small, one can approximately refer to the linear combination of the paraelastic phase. The second part φ_{se} represents the superelastic response due to stress induced changes of the domain pattern, in particular via the lateral motion of the domain walls. Hence, $\varphi=\varphi_{se}+CS\tau$. This relation has a formal analogy to the $B(H)$, $B=4\pi M+H$, rather than to the $M(H)$ relation of ferromagnets.[18] Of course, one expects mechanical loss to be connected with φ_{se} and not with φ_e.

A calculation of φ_{se} requires assumptions on the domain pattern and is possible for highly idealized situations, only. For orientation *B* the situation is simple, since here the external torque cannot lead to the preference of one domain with respect to the other. Hence φ_{se} should vanish and the mechanical response should remain strictly elastic. See below for the pertinent experimental result.

For orientation *A* we assume that the sample consists of a single periodic (100) twin band with a repeat distance λ, $\lambda=\lambda_++\lambda_-$ (Fig. 1). Thus every domain has the dimensions $L_2L_3\lambda_\pm$. For the twisted state of the sample, we further assume[19] that the domain walls remain planar but tilt out of their original (100) orientation in such a way that the + domains of the front (001) facet will grow at the expense of the − domains, whereas the reverse case holds on the rear (001) facet (Fig. 1). The tilt angle α of the domain walls is related to φ_{se} via $\varphi_{se}=4\varepsilon_sL_1\alpha/\lambda$; $\varphi,\alpha\ll1$. Saturation in the sense of the present experiment is achieved when the surface layers of the front and the rear (001) facet are in the single-domain state. Here $\varphi^{sat}=2\varepsilon_sL_1/L_3$. φ^{sat} can be estimated from the crystallographic data on ε_s and the sample dimensions. It is now important to realize that tilting of the domain walls out of the zero-net-strain (100) orientation involves work W against a restoring torque which is supplied by an elastic deformation of the domain lamellae,[19,20] $W=1/2s_{44}^{-1}\alpha^2(2\varepsilon_s)^2$. Eliminating α, one finally arrives at the following expression for the response in the linear regime: $\varphi=\varphi_e+\varphi_{se}=C[S_e+(2L_3/\lambda)^2s_{44}]\tau=C(S_e+S_{se})\tau$, $S_e=S_A$. Thus one expects a total compliance which is enhanced with respect to the purely elastic response of a single-

domain sample by the factor R, $R=1+A^2 s_{44}/S_A$, where s_{44}/S_A is of the order of unity and $A=2L_3/\lambda$ is the aspect ratio of the domains, that is the ratio of the lateral dimension to the thickness. Neither S_A nor A should show any dramatic T dependence outside the critical regime. At least approximately, the linear φ-τ relation with the slope given by $S_e + S_{se}$ should hold up to the twist angle φ_{se}^{sat} of saturation which is proportional to the spontaneous strain $\varepsilon_s(T)$.

Beyond saturation, the domain tips recede from the surface and the thickness of the single-domain (001) surface layers increases with φ, hence the elastic contribution from the surface layers will increase and eventually dominate the response. In contrast to measurements in a homogeneous external field, as is standard in investigations of ferromagnets and ferroelectrics, there will be no abrupt change of slope of the φ-τ curve at saturation. Even above saturation, an increase of τ will induce small further, presumably hysteretic, changes of the domain pattern, namely in the interior of the sample. Indeed, the results will show that hysteretic behavior extends all the way up to the maximum torque irregardless of whether this torque is above or below saturation. The model assumes that the displacement of the walls is free of loss and ignores any irregularity of the domain pattern such as intersections of (100) and (010) twin bands. The experiments will show, however, that relaxational effects are important and that the enhancement factor R is much smaller than what one would expect from the geometrical dimension of the domains. Obviously there are defects which effectively pin the domain walls, thereby limiting the lateral dimension over which the domain walls can move freely.

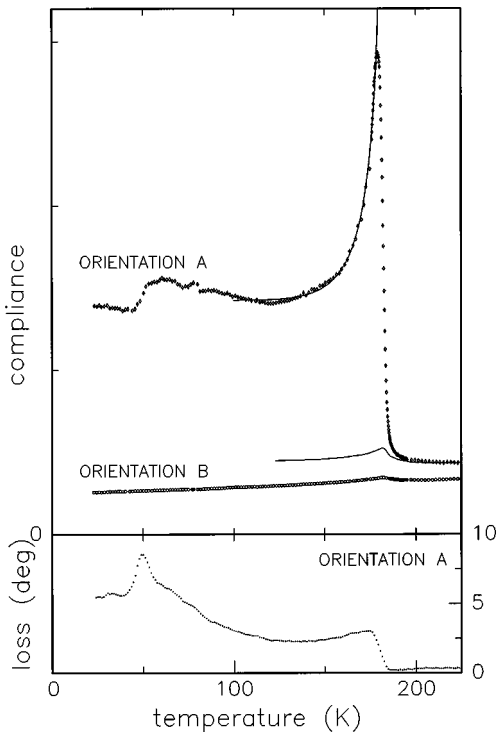

FIG. 2. The low-amplitude ac compliance for both orientations and the loss angle for orientation A as function of temperature. The thin solid line is the compliance for orientation A as derived from Brillouin data. The solid line is a fit based on an expression for the critical contribution to the domain number.

IV. RESULTS AND DISCUSSION

A. Low-amplitude ac measurements

Figure 2 shows the amplitude $S \propto \varphi_0/\tau_0$ and the loss angle δ of the complex elastic shear compliance for orientation A, as measured with a low amplitude τ_0 at a frequency of 128 Hz. The experiment has been conducted in a way that actually φ_0 has been kept constant by adjusting τ_0 accordingly. In the low-T phase S increases with φ_0, thereby indicating nonlinear effects. The figure shows the results obtained with the minimum amplitude which was feasible with our setup. φ_0 is of the order of 0.1% of the low-T limit of φ^{sat}. In terms of the hysteresis loops (see Fig. 4 below), S has to be identified with the initial slope of the virgin curve. The general behavior of $S(T)$ and $\delta(T)$, such as existence of a maximum of S somewhat below T_c, are reproducible from sample to sample, but the absolute readings vary from sample to sample and even by several percent in different temperature scans on the same sample, presumably because the domain pattern is different from run to run. Figure 2 also includes results on the compliance for orientation B. The corresponding loss is negligible, not only above but also below T_c. The compliance for orientation B shows a weak cusp at (182.7 ± 0.2) K which we consider as the most reliable marker of the ferroelastic phase-transition temperature.

We have calculated the T dependence of intrinsic elastic compliance S_e from the Brillouin data[15] on the elastic constants c_{ij} for both orientations of the sample. For orientation B there is a good agreement between the Brillouin and the present mechanical set of data. For this orientation not only the Brillouin, but also the mechanical experiment probes just the elastic response. This is in agreement with the considerations of the last section.

The situation is different for orientation A. Again the elastic compliance S_e as calculated from the Brillouin data changes little across T_c (see the thin curve in Fig. 2), but the compliance of the mechanical experiment is drastically enhanced in the ferroelastic phase with respect to the Brillouin data. The excess part represents the superelastic contribution S_{se}. Obviously the domain pattern can follow the low-frequency field of the present study but is unable to do so for the GHz frequencies of the Brillouin experiment. (In order to separate the elastic from the superelastic response in the ferroelastic phase, we will occasionally refer to the approximation that the elastic part is equal above and below T_c).

The enhancement factor of the compliance, $R=1+S_{se}/S_e$, below T_c varies somewhat from sample to sample and from run to run, typical values range from 2 to 5 at $T=100$ K. This is in qualitative, but by no means in quantitative agreement with the lamellae model. According to the aspect ratio A of the domains of the microscope study,[13] R should be of the order of 10^3. On the other hand it is well known from ferromagnets that the initial slope of the virgin curve is much smaller than the overall inclination of major hysteresis loops. The domain walls are originally pinned to lattice defects. For low external fields the binding of the walls to such pinning centers supplies the dominating contribution to the total restoring force. Accordingly the superelastic part of the low-τ compliance is small. The appearance of

loss shows that the τ-induced motion of the walls is not free, as assumed in the model, but rather of the viscous type.

S_{se} and the loss angle δ have a peculiar T dependence. There a two prominent features, one slightly below T_c and one at about 50 K. We concentrate on the former one first. $S(T)$ is maximum at T_{max}, about 3 K below T_c. This points to critical effects. The experiment is actually not designed for the study of such effects: the temperature is stabilized to 0.1 K, only, and is measured at the metal base plate of the sample. The temperature of the sample may be in fact somewhat higher due to the mechanical loss of the sample in the ferroelastic phase. We nevertheless discuss some aspects. First, the peak at T_{max} and the decrease of $S(T)$ between T_{max} and T_c appears to be a property of the static compliance rather than a dispersion step due to critical relaxations. Otherwise there should be a corresponding, sharp peak of the loss and some shift as function of the measuring frequency. Second, the compliance has been measured with a small, but not with an infinitesimal amplitude. At low T, the ratio $\varphi_0/\varphi^{sat}(T) \ll 1$, but when approaching T_c from below, this ratio increases with the consequence that nonlinear contributions become more and more important, and finally at a temperature T^* saturation is reached. Therefore, we ignore temperatures close to T_c and concentrate on the low-T wing of the feature at T_{max}, $150\,K < T < T_{max}$. This is the T regime in which the domain pattern evolves out of the critical fluctuations. Hence, it is not at all clear whether one should refer to the elastic or the superelastic part of the compliance. In terms of the lamellae model for the superelastic response, a temperature dependence of S_{se} can enter via the repeat distance λ of the twin band. $\lambda = 2L_1/n$ where n is the number of domains in the sample. According to the Ginzburg-Landau treatment of a ferroelastic phase transition, there is a critical contribution n_c in addition to the noncritical background number n_0, $n = n_0 + n_c$, which for the tricritical case varies with temperature according to[5] $n_c \propto \exp(-a(T_c - T)/T)$. Combining this expression with the lamellae model yields the maximum value of S just at T_c and a decrease of $S(T)$ toward low T as shown by the solid line in Fig. 2 which is in acceptable agreement with the experiment for $T < T_{max}$. Alternatively, one can refer to Landau-Khalatnikov-type fluctuations of the elastic part S_e of the compliance. For the tricritical case and a linear-quadratic coupling between the strain and the order parameter, such fluctuations lead to a square root-type singularity[21] at T_c, $\Delta S_e \propto (T_c - T)^{-1/2}$. Fits of this expression to the data are of lower quality than those from above.

The second characteristic feature of Fig. 2 is the small step of $S(T)$ and the concomitant loss peak around 50 K. The compilation of results of different runs and different samples gives the consistent picture of the temperature shift of this feature as function of the measuring frequency. See the Arrhenius plot of Fig. 3. Here the additional data points in the 10^{-2} Hz range come from the hysteresis loops (see below), whereas data points around 10^4 Hz are from the study of the torsional resonance. The results of Fig. 3 propose a thermally activated relaxation process, $\tau = \tau_0 \exp(E/T)$, with an energy barrier E of 850 K and the attempt frequency $1/\tau_0$ of 25 GHz. The value of $1/\tau_0$ is of the order of magnitude of the frequency of a sound wave with a wavelength given by the domain thickness λ. Obviously the torque-induced domain-wall motion outside the critical regime is a thermally activated process and therefore freezes-in at low temperatures. A closer inspection of Fig. 2 suggests that there are further, but weaker loss anomalies below 100 K and that the loss remains finite down to the lowest temperature of our study. Hence, it is likely that there is more than one type of barrier or pinning center for the domain walls. On cooling these relaxational channels freeze out sequentially. Domain-wall freezing has also been observed in studies on ferroelectrics via analogous effects on the dielectric response function.[22]

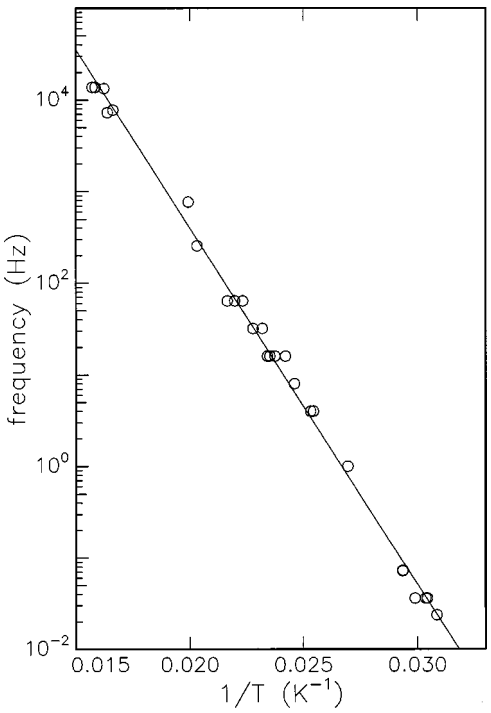

FIG. 3. An Arrhenius plot of the temperature of the low-T loss maximum versus measuring frequency.

In summary, the superelastic response of the multidomain state is lossy with a critical contribution just below T_C and thermally activated processes at lower T. The lamellae model gives a first understanding for the appearance of superelasticity for the particular geometry of our experiment but has to be extended to include pinning and relaxations.

B. Hysteresis loops

We have measured several hundred isothermal φ-τ hysteresis curves and have been surprised by the fact that most samples tolerated this maltreatment without breaking. A selection is shown in Fig. 4. Characteristic quantities derived from such curves are shown in Figs. 5 and 6. φ and τ are given in arbitrary units. The maximum torques τ_{max} applied to the samples are about three orders of magnitude larger than the amplitudes τ_0 of the last section. A torque of 2000 units is about necessary to drive the sample with orientation A into saturation in the low-T limit. In the paraelastic phase, the φ-τ relation is linear and there is almost no loss. A linear relation with about the same slope as above T_c is also obtained in the ferroelastic phase for orientation B. This result is in agreement with the considerations of Sec. III which

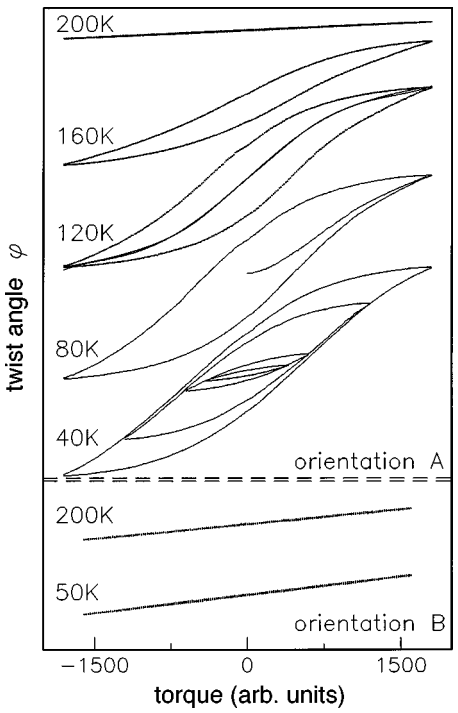

FIG. 4. A series of torque-twist curves for the two sample orientations studied ($\tau_{max}=1800$ for orientation *A*). The curves at 200 K are representative for the single crystalline state of the high-*T* phase. Also shown is a virgin curve (see 80 K), an anhysteretic curve (see 120 K) together with a fit of a tanh function to the data, and a sequence of minor loops ($\tau_{max}=1200,600,400$) which has been used to ''demagnetize'' the sample (see 40 K).

propose that the response for this orientation of the sample cannot involve torque-induced changes of the domain pattern.

For orientation *A*, the linear φ-τ curves above T_c change over into hysteresis loops below T_c. The loops have been actually measured starting at low temperatures after having cooled the sample in zero field. At every temperature a major loop with $\tau_{max}=1800$ has been recorded and then the sample has been ''demagnetized'' by cycling with the τ amplitude being reduced in steps,[18] with τ_{max} values of 1200, 600, and 400, as shown for the 40 K loop of Fig. 4, before changing to the next temperature. In the following we discuss the *T* dependence of the major and the minor loops.

The first point of interest is the amplitude of the twist angle of the loops φ_{max} or more specifically the superelastic part $\Delta\varphi$ of φ_{max} as function of temperature and of τ_{max} $(=1800,1200,600,400)$, see Fig. 5. $\Delta\varphi(T)$ is approximately given by the difference of $\varphi_{max}(T)$ and the value of φ_{max} in the paraelastic phase. φ_{max}/τ_{max} and $\Delta\varphi/\tau_{max}$ are measures of the total and of the superelastic integral compliance, respectively. The $\Delta\varphi(T)$ curves for the minor loops, $\tau_{max}=400,600$, are similar to the low-amplitude ac compliance of Fig. 2, whereas the results obtained with $\tau_{max}=1200$ and in particular with $\tau_{max}=1800$ are reminiscent of the temperature dependence of the spontaneous strain $\varepsilon_s \propto (T_c-T)^{1/2}$. A global understanding of this behavior can be obtained in terms of the following highly simplified picture: Ignoring the elastic part of the response altogether, we assume that the φ-τ relation is linear for torques up to $\tau^{sat}=\varphi^{sat}/S_{se}$ and $\varphi=\varphi^{sat}=$const thereafter. φ^{sat} is proportional to ε_s. For any given value of τ_{max} there is a temperature T^* above which τ_{max} exceeds τ^{sat} with the consequence that $\Delta\varphi(T)$ follows the *T* dependence of φ^{sat} and ε_s. For $T<T^*$, τ_{max} is less than τ^{sat}, hence φ_{max} is proportional to the compliance S_{se}. The higher τ_{max}, the lower T^*. For $\tau_{max}=1800$, T^* is about 100 K.

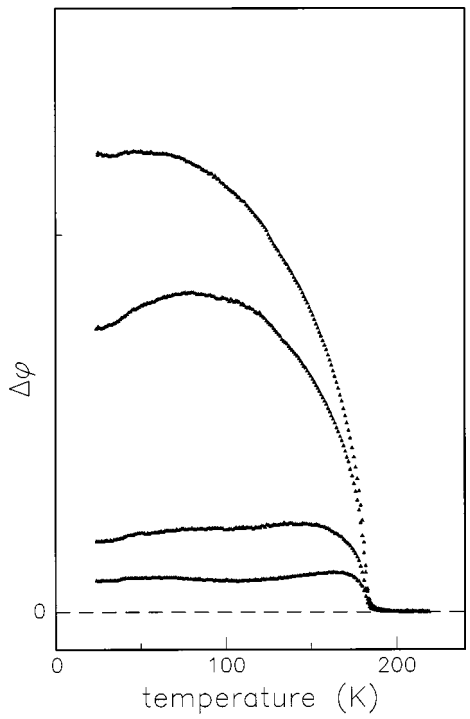

FIG. 5. The superelastic part of the overall amplitude of the twist angle of hysteresis loops for orientation *A* as function of temperature. $\tau_{max}=1800,1200,600,400$ from top to bottom.

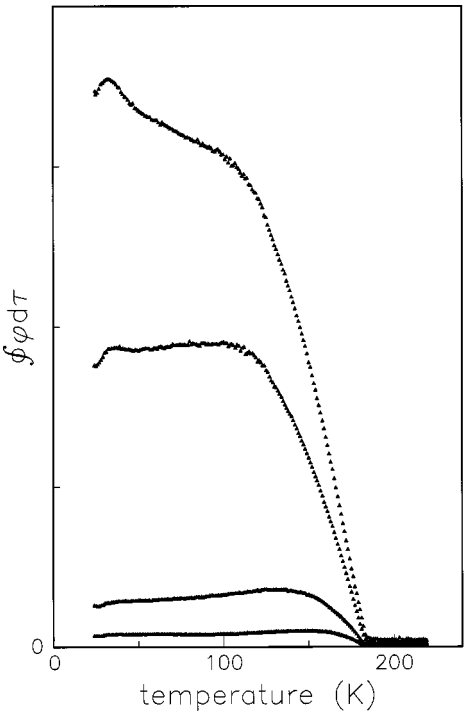

FIG. 6. The area of hysteresis loops for orientation *A* as function of temperature. $\tau_{max}=1800,1200,600,400$ from top to bottom.

The small step of the $\Delta\varphi(T)$ curves around 30 K is related to the thermally activated relaxation process discussed in Sec. IV A. It is not clear why the curve for $\tau_{max}=1200$ shows such a pronounced maximum at intermediate temperatures.

The integral compliance, i.e., the inclination of the loops as function of τ_{max}, starts from low values for $\tau_{max}=400$ which correspond to the rather modest values of the enhancement factor R as already observed in the low-amplitude ac measurements. The maximum inclination with an R value of about 15 is observed for $\tau_{max}=1200$ and T at about 80 K. A further increase to $\tau_{max}=1800$ leads to a slight decrease of the inclination. This general trend is by no means unexpected, since it reflects the changes from a loop based on the first part of the virgin curve, to one which fully exploits the superelastic effects and further to one which is already subject to saturation. Nevertheless a quantitative understanding of this behavior is missing.

The second point of interest is the loss L, as represented by the loop area $\oint\varphi d\tau$. Data on $L(T)$ for the different values of τ_{max} are shown in Fig. 6. Just below T_c, L increases in an approximately linear fashion, whereas at low T the loss depends only weakly on T. For the interpretation of this result we refer to the distinction of the temperature regimes $T<T^*$ and $T^*<T<T_C$ from above. In the low-T regime the hysteresis curves stay short of saturation. Assume that L is a constant fraction f of the superelastic deformation work, $L=\frac{1}{2}fS_{se}(\tau_{max})^2$. Hence for $T<T^*$, $L(T)$ should have the same weak temperature dependence as $S_{se}(T)$. A comparison of Figs. 6 and 2 suggests that this is approximately so. On the other hand, the loss data at a given temperature T, $T<T^*$, say $T=70$ K do not scale with $(\tau_{max})^2$. This suggests that f depends on τ_{max}, and the largest values of f occur for $\tau_{max}=600$. For $T^*<T<T_c$, the loops extend beyond saturation. The assumption that the loss is a constant fraction of the superelastic part of the deformation work now reads as $L=\frac{1}{2}f(\varphi^{sat})^2/S_{se}$ with $(\varphi^{sat})^2\propto T_c-T$. The approximately linear increase of L just below T_c is consistent with this idea, the fact that the experimental results on L depend on τ_{max} is not. Thus the T dependence of L can be explained in terms of a rather simple model, but the τ_{max} dependence remains unexplained.

The anomaly of L around 30 K is due to the thermally activated relaxations already discussed in Sec. IV A. The foregoing discussion referred to a rather simple form of the hypothetical hysteresis-free φ-τ curve. For the experimental determination of the anhysteretic curve we followed a procedure which is common for ferromagnets: An alternating torque and a constant unidirectional torque τ are superimposed. The amplitude of the alternating torque is then reduced and the twist angle converges to a value φ_{ah}. It turns out that the anhysteretic φ_{ah}, τ points are close to the midpoints of horizontal chords of the major hysteresis loop. Complete anhysteretic curves have been constructed from the midpoints of the major loops. An example is shown in Fig. 4 together with a fit of the expression $\varphi_{ah}\propto\tanh(a\tau)$ to the data.

C. History effects

The nonergodicity of the ferroelastic multidomain state is demonstrated by various history-dependent effects, the appearance of isothermal φ-τ hysteresis being the most prominent one. Hysteresis is also manifest in runs with different T, τ histories. Figure 7 shows the twist angle φ for the following history: (1) cooling with no torque applied from above T_C to a minimum temperature in the ferroelastic phase (zfc branch), (2) heating back up to the start temperature in a constant field of moderate strength (fh branch), (3) cooling down in the same field (fc branch), (4) heating in zero field (zfh branch) giving the thermoremanent twist. As can be seen in Fig. 7, the sample comes eventually, for $T>T_C$, back to the original state, i.e., it remembers its original shape at the end of the cycle in spite of the remanence effects in the ferroelastic multidomain state. States of identical temperature and torque, namely zfc and zfh as well as fh and fc, differ because of the history dependence of the domain pattern.

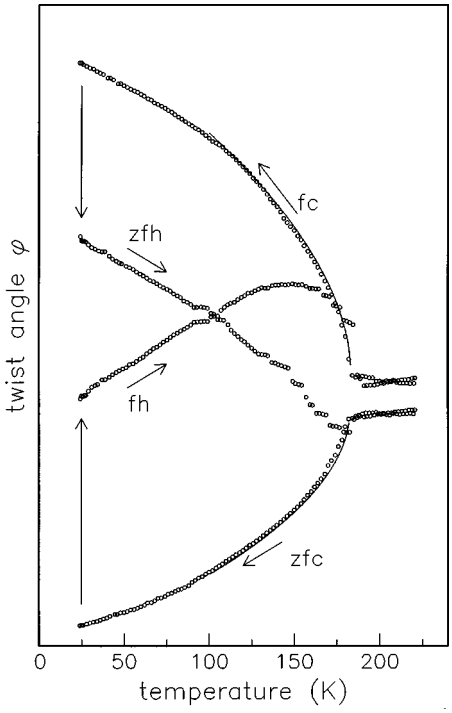

FIG. 7. The twist angle as function of temperature for the four branches of the twofold cooling and heating cycle described in the text. The solid lines represent the square root temperature dependence of the spontaneous strain ε_s.

The appearance of a spontaneous macroscopic twist in the zfc branch is somewhat unexpected, but occurred in all samples investigated, even though the values of φ_{zfc} vary from sample to sample and even from run to run. $\varphi_{zfc}(T)$ shows a square-root-type T dependence which means that $\varphi_{zfc}(T)$ is proportional to $\varepsilon_s(T)$. Obviously the samples leave the critical regime with a grossly unbalanced ratio of + and − domains, presumably because of built-in stresses due to defects. In terms of the lamellae geometry, this calls for nonzero background value α_0 of the tilt angle of the domain walls, an unbalanced thickness ratio $\lambda_+/\lambda_-\neq 1$ is not sufficient. According to the relation $\varphi_{se}=4\varepsilon_s L_1\alpha/\lambda$ from above, one then expects $\varphi_{zfc}(T)$ to be proportional to the spontaneous ferroelastic strain $\varepsilon_s(T)$, provided that the ratio of α $(=\alpha_0)$ and λ is independent of T. The proportionality to $\varepsilon_s(T)$ also holds for the superelastic part of the field-cooled

twist angle: $\varphi_{se}^{fc}=\varphi^{fc}-\varphi_e^{fc}\approx\varphi^{fc}-\varphi(T>T_c)$, see Fig. 7. One concludes that cooling in a constant field, of external or internal origin, leaves the domain pattern essentially unchanged and, therefore, the macroscopic twist angle mimics the temperature dependence of the strain order parameter ε_s. This is not so when the external field is applied or removed at low temperatures, as is the case for the fh and zfh branches of Fig. 7. φ^{fh} has no obvious relation to $\varepsilon_s(T)$. As function of T, the field-induced twist $\varphi^{fh}-\varphi^{zfc}$ is approximately constant between 25 and 150 K and considerably smaller than $\varphi^{fc}-\varphi^{zfc}$. It is only close to T_C that φ^{fh} approaches φ^{fc}. Obviously the adjustment of the domain pattern to a field change at low T is incomplete as compared to the case when the field change is made at high T and the sample is cooled down subsequently. These results emphasize that the field-induced domain-wall motion is at least to some part a thermally activated process. From the fact that $\varphi^{zfc}(T)$ and $\varphi^{fc}(T)$ follow the T dependence of the strain order parameter, one concludes that domain states reached by cooling from the paraelastic phase into the ferroelastic phase in a constant field are closer to thermal equilibrium than states reached by a change of the field within the ferroelastic phase. Analogous observations have been made in other examples of nonergodic systems, namely the spin glasses[23] and the orientational glasses.[24]

V. CONCLUDING REMARKS

We understand our work as an exploratory study of the mechanical response of a multidomain ferroelastic crystal to an external stress. We have pointed out some peculiarities of the employed torque-twist technique, the most important one being the fact that the external field cannot drive the sample into a monodomain state, but only into quasisaturation where true saturation is achieved in surface regions, only, whereas the multidomain arrangement persists in the center of the sample. Consequently the torque-twist hysteresis loops cannot be square like as one might expect from the presence of significant loss, but are rather slim, similar to the $B(H)$ curves of a moderately ''soft'' ferromagnet. The superelastic response, that is the mechanical response due to domain-wall motion, can exceed the elastic response by a factor of 10 and more. The mechanical loss which is apparent from the finite loss angle in the low-amplitude ac measurements and from the finite area of the hysteresis loops is connected with the superelastic part of the mechanical response. The superelastic response and the loss show a peculiar dependence on the external field and the temperature. The general characteristics can be explained by discriminating loops which stay short of saturation from those which extend beyond saturation and by postulating that a constant fraction of the superelastic deformation work is dissipated. There is no superelastic contribution and hence no loss for samples oriented in fashion B where the symmetry is such that the external field does not act on the domain walls.

There are two temperature regimes of anomalous behavior, one just below T_c where the multidomain state develops out of the critical fluctuations and a second one where the thermally activated hopping of the domain walls over special, but unknown types of barriers comes to a halt.

The history dependence of the ferroelastic multidomain state is not only apparent from isothermal torque-twist hysteresis loops but also from the macroscopic twist angle in reaction to various field-temperature histories, including the shape memory effect.

This work has given an overview on the mechanical properties of the multidomain state of a ferroelastic crystal. One wonders of course which aspects are specific to calomel and which are common to ferroelastic crystals in general.

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[1] E. Salje and G. Hoppmann, Mater. Res. Bull. **11**, 1545 (1976).
[2] G. Pakulski, B. Mroz, and T. Krajewski, Ferroelectrics **48**, 259 (1983).
[3] S. A. Gridnev, V. I. Kudrjash, and B. N. Prasolov, Ferroelectrics **26**, 669 (1980).
[4] S. A. Gridnev and L. A. Shuvalov, Ferroelectrics **48**, 113 (1983).
[5] E. K. H. Salje, in *Phase Transitions in Ferroelastic and Coelastic Crystals* (Cambridge University Press, Cambridge, 1990).
[6] H. Mark, J. Steinbach, Z. Kristallogr. **64**, 79 (1926).
[7] C. Barta, A. A. Kaplyanskii, V. V. Kulakov, B. Z. Malkin, and Yu. F. Markov, Zh. Eksp. Teor. Fiz. **70**, 1429 (1976) [Sov. Phys. JETP **43**, 744 (1977)].
[8] E. Rehaber, H. Fischer, and W. Dultz, Phys. Rev. B **25**, 5889 (1982).
[9] J. P. Benoit, G. Hauret, and J. Lefebvre, J. Phys. (France) **43**, 641 (1982).
[10] M. E. Boiko, B. S. Zadokhin, K. Lukaszewicz, Yu. F. Markov, A. Pietraszko, and J. Stepien-Damm, Fiz. Tverd. Tela (Leningrad) **34**, 902 (1992) [Sov. Phys. Solid State **34**, 483 (1992)].
[11] M. E. Boiko, Yu. F. Markov, V. S. Vikhnin, A. S. Yurkov, and B. S. Zadokhin, Ferroelectrics **130**, 263 (1992).
[12] C. Barta, V. P. Zhigalov, B. S. Zadokhnin, and Yu. F. Markov, Fiz. Tverd. Tela (Leningrad) **33**, 2739 (1991) [Sov. Phys. Solid State **33**, 1548 (1992)].
[13] C. Barta, A. A. Kaplyanskii, Yu. F. Markov, and V. Yu. Mirovitskii, Fiz. Tverd. Tela (Leningrad) **24**, 875 (1982) [Sov. Phys. Solid State **24**, 493 (1982)].
[14] J. Sapriel, Phys. Rev. B **12**, 5128 (1975).
[15] C. X. An, G. Hauret, and J. P. Chapelle, Solid State Commun. **24**, 443 (1977).
[16] A. Binder, K. Knorr, and F. Luty, Phys. Rev. B **56**, 2991 (1997).
[17] W. Voigt, in *Lehrbuch der Kristallphysik* (Johnson Reprint, New York, 1966).
[18] B. D. Cullity, in *Introduction to Magnetic Materials* (Addison-Wesley, Reading MA, 1972).
[19] G. G. Krainyuk and A. Otko, Ferroelectrics **111**, 189 (1990).
[20] A. L. Roitburd, in *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich, D. Turnbull, and F. Seitz (Academic, New York, 1978), Vol. 33, p. 317.
[21] J. O. Fossum, J. Phys. C **18**, 5531 (1985).
[22] K. Kuramoto, J. Phys. Soc. Jpn. **56**, 1859 (1987).
[23] K. Binder, A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).
[24] J. Hessinger, K. Knorr, Phys. Rev. B **47**, 14 813 (1993).