Application of real-time, stroboscopic x-ray diffraction with dynamical mechanical analysis to characterize the motion of ferroelastic domain walls

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The dynamic response of ferroelastic twins to an alternating stress has been studied in situ at high temperature using a stroboscopic x-ray diffractometer and combined dynamical mechanical analyzer (XRD-DMA). The XRD-DMA is designed to allow x-ray rocking curves to be collected while the sample is undergoing simultaneous dynamical mechanical analysis in three-point-bend geometry. The detection of diffracted x-rays is synchronized with the applied load, so that rocking curves corresponding to different parts of the dynamic load cycle can be obtained separately. The technique is applied to single-crystal LaAlO₃, which undergoes a cubic to rhombohedral phase transition at 550 °C, leading to the generation of characteristic "chevron" twins. The rocking-curve topology is calculated as a function of crystal orientation for each chevron type. Systematic changes in the rocking curves during heating and cooling under dynamic load demonstrate a clear preference for chevrons containing $\{100\}_{pc}$ walls perpendicular to the sample surface and $\{110\}_{pc}$ walls oriented at 45° to the sample surface. These domain walls are oriented favorably with respect to the applied stress (i.e., they separate domains with contrasting components of spontaneous strain parallel to the sample length). Below 200 °C, the superelastic strain is accommodated by rapid advancement/ retraction of vertical $\{100\}_{pc}$ needle domains, with little effect on the dynamic rocking curves. Above 200 °C, a dynamic shift in peak position between rocking curves measured at the maximum and minimum applied loads is detected. The onset of a dynamic response correlates with the loss of the $\{100\}_{pc}$ needle domains and the transformation of the microstructure to $45^{\circ} \{110\}_{pc}$ walls. Superelastic strain is then accommodated by domain wall displacement/rotation, causing the wall to sweep back and forth across the x-ray beam and diffraction to occur from alternate domains at the maximum and minimum points of the stress cycle. A second sample, oriented so that domain walls in all possible chevrons are unfavorably oriented with respect to the applied stress, shows very different behavior. The rocking curves consist of several well-separated peaks at the minimum load and a single broad diffraction signal at the maximum load. This is caused by the creation of a very high density of twin walls across the sample above a critical applied stress, leading to corrugation of the sample surface. © 2004 American Institute of Physics. [DOI: 10.1063/1.1639949]

I. INTRODUCTION

The dynamic response of transformation-induced twin structures to an external force (either a mechanically applied stress in the case of ferroelastic materials, or an electric field in the case of ferroelectric materials) is of fundamental importance in a wide range of fields spanning solid state physics, materials science, and geology. The interaction of mobile ferroelectric domain walls with lattice defects is a key factor in determining the lifetime of ferroelectric memory devices.¹ The creation and displacement of domain walls in martensitic alloys leads to the shape memory effect.² More pertinently, movements of domain walls are the origin of ferroelastic hysteresis and thus define ferroelasticity.³ Recently, ferroelastic twinning in LaAlO₃ and (Ca,Sr)TiO₃ perovskites, analogs of the (Mg,Fe)SiO₃ perovskite thought to be a major component of the Earth's lower mantle, has been proposed as a possible source of anelasticity in the Earth-a phenomenon responsible for the attenuation of seismic waves.^{4,5} In this context there is great interest in determining the dynamic response of ferroelastic domain walls to an alternating stimulus mimicking the typical characteristics of a seismic wave (i.e., frequencies of the order 1 Hz and strain amplitudes of the order 10^{-6}). This regime is amenable to study via the technique of dynamical mechanical analysis (DMA).⁶ Various geometries may be employed, with a torsional pendulum apparatus commonly used to measure the shear modulus under dynamic conditions of forced oscillation (e.g., the work on KCN, RbBr, KBr solid solutions by Ref. 7). Alternatively, parallel-plate or three-point bend geometry may be used to calculate the dynamic Young's modulus (see Fig. 1 for details).

The mechanical properties of single-crystal LaAlO₃ have recently been studied in some detail using DMA in threepoint bend geometry.⁴ LaAlO₃ has the cubic perovskite structure at high temperatures and undergoes a displacive phase transition to a rhombohedral phase below 550 °C.^{8–13} Measurements of the storage modulus (i.e., the real part of the dynamic Young's modulus) and tan δ (i.e., the energy dissipated per cycle) as a function of temperature are shown

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FIG. 1. (a) Schematic illustration of DMA operation in three-point bend geometry. (b) Applied force consists of a static component (F_S) and dynamic component (F_D) with angular frequency ω . The mechanical response is characterized by static and dynamic components u_S and u_D , and the phase lag δ .

in Fig. 2. The large decrease in storage modulus on cooling below 550 °C and the corresponding increase on cooling below 170 °C occur at the boundaries between different regimes of mechanical behavior. The paraelastic regime (T $>T_c$) corresponds to the stability field of the high-symmetry paraelastic phase. In this regime the material is untwinned, tan δ is small, and the storage modulus corresponds to the intrinsic Young's modulus of the cubic phase. The start of the superelastic regime $(T < T_c)$ coincides with the cubic to rhombohedral phase transition and the formation of transformation twins. In this regime, thermal energy is sufficient to allow domain walls to move in response to an applied stress and the modulus rapidly decreases to its "relaxed" value, more than an order of magnitude lower than that of the cubic phase. Energy is dissipated by the internal friction due to wall-wall, wall-defect, and wall-surface interactions, caus-



FIG. 2. Normalized storage modulus (closed symbols, left axis) and tan δ (open symbols, right axis) as a function of temperature for sample 1. Measurements were obtained using a static:dynamic force of 100:90 mN and a frequency of 1 Hz.

ing tan δ to rise. The domain-freezing regime sets in at some temperature below T_c , and is seen by the point at which the modulus increases on cooling. Domain-wall motion becomes increasingly sluggish at low temperature, as walls are unable to unpin themselves on the time scale of the dynamic force. The storage modulus increases to its low-temperature intrinsic value, corresponding to a change from relaxed to unrelaxed behavior, in the language of anelasticity. The increase in modulus is accompanied by a maximum in the mechanical loss, seen as a Debye-like resonance peak in tan δ .

The first stage in understanding these three regimes of mechanical behavior is to determine how the domain state of the sample changes as a function of temperature and time during prolonged annealing under dynamic stress. Such information can be easily obtained from x-ray diffraction (XRD) rocking curves, which characterize the angular relationships and volumetric proportions of differently oriented twin domains intersecting the surface of a ferroelastic singlecrystal (see Fig. 3 for details). The rocking-curve technique has been applied for many years to the study of ferroelastic domain structures. These studies have been all been conducted as static experiments: the applied load on the sample is usually zero, or is a fixed static stress.^{14,15} In the case of a dynamic stress, we need to observe the response of the microstructure on a time scale much smaller than the period of the alternating load. The time scales are also much shorter than those for standard x-ray rocking curve data collection. However, the dynamic response may be studied at time scales less than the period of the alternating stress using stroboscopic methods. The advent of fast detectors and rapid switching electronics now make it technically feasible to collect diffraction signals from samples on time scales of tenths of milliseconds, and hence makes it possible to use stroboscopic methods to study the varying response of materials to applied stresses as a function of phase angle during the alternating cycle of a dynamically applied load. This has been achieved by combining a DMA with a multichannel detector and a fast-switching data-grabbing system. Here we present diffraction measurements of the effects of dynamic stress on domain state in a ferroelastic perovskite single crystal, using a novel stroboscopic XRD-DMA diffractometer.



FIG. 3. (a) and (b) The general principle of an XRD rocking curve. In a twinned crystal the reciprocal lattice vectors representing a set of equivalent lattice planes in different twin domains will not be parallel (in this case we are dealing with diffraction from the 001_{pc} planes in domains II and III, as defined in Table I). A suitably oriented crystal is placed close to the diffraction condition, with both reciprocal lattice vectors lying within the scattering plane. The sample is rotated by an angle ω about an axis perpendicular to the scattering plane in order to bring it into the diffracting condition for one set of twins at a time. A rocking curve, which is a plot of integrated intensity as a function of ω , will show individual peaks corresponding to each of the twin domains. The angular difference between the peak positions in the rocking curves ($\delta\omega$) corresponds to the angular difference between the reciprocal lattice vectors (projected into the scattering plane). (c) Starting material for the XRD-DMA experiments is a single crystal of LaAlO₃, with surface parallel to (001)_{pc} and length parallel to [110]_{pc}. The microstructure consists of lamellar (110) twins. (d) Stroboscopic XRD rocking curves at room temperature with static:dynamic forces of 200:180 mN and frequency 1 Hz. The four components of the rocking curve, collected at different parts of the dynamic stress cycle, are coincident, indicating that the domain walls of this orientation are not responding to the stress at this temperature.

II. STROBOSCOPIC XRD-DMA

The general principal of DMA in three-point bend geometry is illustrated in Fig. 1. The sample is a single crystal beam with length l, width w, and thickness t, suspended on two knife-edges. A force is applied using a electromechanical force motor with a force resolution of 1 mN. This impinges upon the sample from above via a third knife-edge located halfway along the sample length. The applied force has a static component (F_s) , which ensures that the sample remains in contact with the knife-edges at all times, and a dynamic component (F_D) with frequency (f) the range 0.01–50 Hz. The amplitude (u) and phase lag (δ) of the mechanical response are measured via electromagnetic inductive coupling with a resolution of $\Delta u \sim 10$ nm and $\Delta \delta$ $\sim 0.1^{\circ}$, respectively. The amplitude of displacement is a function of both the Young's (Y) and shear (G) moduli, but in three-point bend geometry the contribution from the shear modulus vanishes for $l \ge t$.¹⁹ Under these conditions, the dynamic Young's modulus parallel to the sample length is simply related to the dynamic force and the amplitude of deflection (u_D) via

$$Y = \frac{l^3}{4t^3w} \frac{F_D}{u_D} \exp(i\,\delta).$$

This expression is derived for an isotropic solid. In an anisotropic material the measured modulus is an effective Young's modulus transformed parallel to l, and hence is a combination of individual tensor components. The real $(Y' = |Y| \cos \delta)$ and imaginary $(Y'' = |Y| \sin \delta)$ components of the dynamic modulus are referred to as the storage and loss moduli, respectively. The ratio $Y''/Y' = \tan \delta$ is the attenuation (energy dissipated per cycle).

The elements of the stroboscopic XRD-DMA diffractometer are shown in Fig. 4. The DMA component is based on a standard Perkin-Elmer DMA-7e, modified in-house to allow access of x rays to the bottom surface of the sample. The DMA is configured in a vertical orientation at the top of the instrument. The sample and flexure head components are all enclosed in a thermally stable furnace with x-ray-transparent windows. The diffractometer comprises an INEL curved position-sensitive detector, covering $120^{\circ}2\theta$, and a sealedtube x-ray source with monochromator optics and collimation system (Cu $K\alpha_1$ radiation). A 100 μ m diameter beam impinges on the lower surface of the sample and is diffracted in reflection geometry to the detector. Since the sample must remain static within the DMA apparatus (neglecting the small strains imposed by the mechanical analyzer), rocking curves are obtained by changing the angle of incidence of the incoming x rays, rather than by rotating the sample itself. The x-ray source is mounted on a rigid vertically oriented optic table, centered on the sample. The source can be rotated about an axis perpendicular to the scattering plane, allowing rocking curves to be measured from the sample while it is under dynamic stress.



FIG. 4. (a) Design of the XRD-DMA. Central vertical column consists of a standard Perkin-Elmer DMA-7e. Cu x-ray tube, monochromator, and INEL 120° position-sensitive detector are mounted on a rotatable vertically oriented optic table. A 700 °C, 1 atm furnace surrounds the three-point-bend sample assembly, shown in detail in (b).

Central to this new instrument is the manner in which data from the x-ray detector and data from the mechanical analyzer are collected in a combined manner. A timing chain takes information from the DMA and passes it through a logic translator to trigger collection of the diffraction pattern at four points in the applied stress cycle (corresponding to the maximum force, the minimum force, the maximum rate of increasing force, and the maximum rate of decreasing force). The diffraction information, extracted from the multichannel analyzer of the curved PSD at four times the frequency of the sample oscillation, is then stored into one of four cumulating data files, corresponding to the diffraction pattern of the sample under each of the four conditions of applied stress at that frequency. By altering the phase shift between the applied stress reference signal and the data collection trigger, the sample can be probed at any condition of applied stress by diffraction. By employing a rocking experiment, the diffraction (from specific domain wall orientations) can be observed at each state of applied stress. If desired, the collection of diffraction data can be synchronized to the sinusoidal response curve of the sample, rather than the applied force. This is useful for materials where there is a large phase lag between the force and response curves. All data presented here were obtained using stress, rather than strain, synchronization. A telescopic lens attached to a charge coupled device camera is mounted directly below the sample, allowing the dynamic response of the twin walls to be viewed in reflected light and recorded digitally.

III. PHASE TRANSITIONS AND TWINNING IN LaAIO3

A. Symmetry and spontaneous strain

The high-temperature phase of LaAlO₃ has the cubic perovskite structure with space group $Pm\overline{3}m$ and lattice parameter $a_{\text{cubic}} \sim 3.79$ Å. Below about 550 °C it undergoes an improper ferroelastic phase transition to the rhombohedral subgroup $R\overline{3}c$, driven by rotation of the AlO₆ octahedra about one of the cubic threefold symmetry axes. Adjacent octahedra rotate in opposite senses, leading to a doubling of the unit cell along the octahedral rotation axis. For the purpose of defining the spontaneous strain associated with the phase transition, however, we can ignore the change in translational symmetry and define a pseudocubic unit cell with rhombohedral shape $(a_{\rm pc}=b_{\rm pc}=c_{\rm pc}\sim3.79\,\text{\AA}$ and $\alpha_{\rm pc}=\beta_{\rm pc}$ $=\gamma_{\rm pc}\neq 90^\circ$) that is directly comparable in size and orientation to the high-temperature cubic unit cell. The lattice parameters have been determined as a function of temperature.^{9,11,12} The symmetry-breaking strain e_4 is negative $(\alpha_{pc} > 90^{\circ})$, which corresponds to compression of the unit cell parallel to the octahedral rotation axis and expansion perpendicular to this axis. The temperature evolution of the twin angle and its structural significance has been measured.^{10,13} The thermodynamic character of the transition is, within experimental resolution, second order, and therefore e_4 varies linearly with temperature (the symmetrybreaking strain couples to the square of the driving order parameter for an improper ferroelastic transition).

B. Twin domains and chevron tiling

Transformation twins form on cooling below T_c due to the degeneracy of four equivalent triad axes about which octahedral rotation can occur (Table I). Given the four pure domain states, there are six possible pairs of domains that can meet to form a domain wall. For each of the six pairs there are two possible orientations of domain wall, one of the form $\{100\}_{pc}$ and one of the form $\{110\}_{pc}$. An optical micrograph of the twin microstructure of a typical LaAlO₃ crystal is shown in Fig. 5. The surface of the sample is parallel to $(001)_{nc}$. The characteristic microstructure, referred to as "chevron tiling," contains each of the four pure domain states, separated by three mutually compatible domain walls (two walls parallel to $\{110\}_{pc}$ and one parallel to $\{100\}_{pc}$) intersecting along a common $\langle 100 \rangle_{pc}$ direction. There are six distinguishable chevron orientations.¹⁶ The chevron in Fig. 5 is of type 1 (Table II). The three domain walls within a given chevron are mutually compatible, allowing a stress-free intergrowth of the four pure domain states.⁸ However, the six chevrons are not mutually compatible with each other, and there are high lattice strains at the boundary between regions containing different chevron orientations. An example is shown in Fig. 6(a), which contains regions of chevron orien-

TABLE I. Twin domain and twin wall orientations in LaAlO₃ [after Bueble et al. (Ref. 8)].

Domain	Ι		II		III		IV		
Axis of rotation Spontaneous strain tensor	$\begin{bmatrix} 1111 \\ 0 & \overline{e} \\ \overline{e} & 0 \\ \overline{e} & \overline{e} \end{bmatrix}$	$\left. \begin{array}{c} \overline{e} \\ \overline{e} \\ 0 \end{array} \right)$	$\begin{bmatrix} 1\\ 0\\ e\\ \overline{e} \end{bmatrix}$	$ \begin{bmatrix} 1 & \overline{1} \\ e & \overline{e} \\ 0 & e \\ e & 0 \end{bmatrix} $	$\begin{pmatrix} 0\\ e\\ e \end{pmatrix}$	$ \begin{bmatrix} \overline{1} \\ 11 \end{bmatrix} \\ e \\ e \\ \overline{e} \\ \overline{e} \\ 0 \end{pmatrix} $		$\begin{pmatrix} 0 \\ \overline{e} \\ e \end{pmatrix}$	$ \begin{bmatrix} 11\overline{1} \\ \overline{e} & e \\ 0 & e \\ e & 0 \\ \end{bmatrix} $
Domain Pair	I, II	I, III		I, IV	II, III		II, IV		III, IV
Orientation of twin wall	(010) (101)	(100) (011)		(001) (110)	(001) (110))	(100) (011)		(010) (101)

tations 1 (right) and 2 (left). On annealing, the high strain at the boundary is partially relieved by the formation of needle twins at the points where $\{100\}_{pc}$ domain walls intersect [Fig. 6(b)]. In addition, lateral migration of the high-energy chevron nodes can lead to the destruction of chevron bands and the gradual transition from chevron tiling to simple lamellar twinning.⁴

IV. SAMPLE CHARACTERISTICS

A. Sample

Two differently oriented samples of single-crystal LaAlO₃ (Crystal GmbH, Berlin) were used in these experiments. The samples were cut from high-quality single-crystal slabs, normally used as substrates for high- T_c superconductors. Sample 1 was 6 mm long, 1.96 mm wide, and 0.52 mm thick. Its surface was parallel to $(001)_{pc}$ and its length parallel to $[110]_{pc}$ (corresponding to $\phi = 45^{\circ}$ in Fig. 7). Sample 2 was 6 mm long, 1.85 mm wide, and 0.25 mm thick. Its surface was parallel to $(001)_{pc}$ and its length parallel to $[100]_{pc}$ (corresponding to $\phi = 0^{\circ}$ in Fig. 7). The orientation of sample 1 was chosen so that the effective force on at least one domain wall in each chevron would be maximum in



FIG. 5. Optical micrograph of the "as-received" starting material showing the chevron microstructure of mutually intersecting $\{100\}_{pc}$ and $\{110\}_{pc}$ domain walls. Labels I, II, III, and IV refer to the pure twin domain states listed in Table I. Ellipses show the orientations of the axes of compression (minor axis) and extension (major axis) in each domain (projected into the plane of the diagram).

three-point bend geometry. The orientation of sample 2 was chosen so that (to a first approximation) the effective force on all domain walls would be zero in all chevron orientations.⁵

B. Rocking curves as a function of chevron orientation

Our use of x-ray rocking curves in detecting strains in single crystal LaAlO₃ follows the earlier pioneering studies described in Refs. 10 and 13. The six chevron types, each containing four domain states, yield 24 physically distinguishable domain orientations, each of which can potentially produce a peak in the rocking curve. This can lead to rocking curves with complex topologies, requiring careful consideration of the inter- and intra-chevron angular relationships between diffracting planes when assigning peaks. The intrachevron angular relationships between (001)_{pc} diffracting planes are well defined (neglecting any effect of surface relaxation) (Fig. 7). Figures 7(a) and 7(b) show the arrangement of domains and domain walls for chevron types 1 and 2. In both these cases, the domain walls intersect along $[001]_{pc}$ and are approximately perpendicular to the $(001)_{pc}$ surface of the sample. The dashed lines in Fig. 7 show the outline of the pseudocubic unit cell (the magnitude of the spontaneous strain has been greatly exaggerated for clarity). Domains are labeled according to the definitions in Table I. Figure 7(c) is a schematic stereogram indicating the orientations of the $(001)_{pc}^{*}$ reciprocal lattice vectors in each domain. The angle between $(001)_{pc}^*$ for domains separated by a domain wall of type $\{100\}_{pc}$ is $0.18^{\circ.8}$ The corresponding angle for domains separated by a domain wall of type $\{110\}_{pc}$ is 0.25°. To calculate the corresponding distance between peaks in a rocking curve, these angles have to be projected into the

TABLE II. Six possible triplets of domain walls forming strain-free chevrons, and their common direction of intersection [after Bueble and Schmal (Ref. 16)].

Chevron label	1	2	3	4	5	6
{100}-type domain wall orientation	(010)	(100)	(100)	(001)	(010)	(001)
{110}-type domain	(110)	(110)	(101)	(101)	(011)	(011)
wall orientations	(110)	(110)	(101)	(101)	(011)	$(01\overline{1})$
Intersection	[001]	[001]	[010]	[010]	[100]	[100]



FIG. 6. (a) Optical micrograph showing the boundary between incompatible chevron orientations 1 and 2 (see Table II for definitions). The chevron orientations are distinguishable by the orientation of their $\{100\}_{pc}$ domain walls. The upper central part of the figure illustrates the high lattice strain associated with the boundary. In the lower part of the figure this strain is relieved by formation of needle twins at the points where the $(010)_{pc}$ walls from chevron 1 intersect the $(100)_{pc}$ walls from chevron 2. The arrangement of domains and domain walls is illustrated schematically in (b).

scattering plane [Fig. 7(d)]. The angular separation between pairs of peaks in the rocking curve varies, therefore, with the cosine of the angle, ϕ , made by the incident x-ray beam (projected into the plane of the sample surface) to the Y axis [see Fig. 7(a) for definitions]. The maximum angular separa-



tion occurs when the projected x-ray beam is perpendicular to the domain wall. The angular separation is zero when the projected x-ray beam is parallel to the domain wall.

Simulated rocking curves for chevron types 1 and 2 are shown in Fig. 8(a) as a function of ϕ . These are calculated by arbitrarily fixing the position of one of the peaks (domain IV in this case), and determining the relative positions of the other peaks self-consistently from the angular separations given in Fig. 7(d). The sample is oriented in the DMA with its length perpendicular to the direction of incoming x rays.





FIG. 8. (a) Simulated room-temperature rocking curves for chevron types 1 and 2 as a function of angle of x-ray incidence (ϕ). For a general angle of incidence, all four peaks of the chevron are resolved. For sample 1 ($\phi = 45^{\circ}$) the rocking curve contains two peaks separated by $\delta \omega = 0.25^{\circ}$ and a central doublet. For sample 2 ($\phi = 0^{\circ}$) the rocking curve contains two doublets separated by $\delta \omega = 0.18^{\circ}$. In a real experiment, the intensity of the peaks is proportional to the volumetric proportion of the corresponding domain state. (b) Simulated room-temperature rocking curves for chevron type 3. The rocking curves for chevron type 5 are identical to those in (b) with the angles of incidence rotated by 90°. The rocking curves for chevron types 4 and 6 consist of a single peak for all values of ϕ .

Hence a value of $\phi = 0$ corresponds to sample 2, with length cut parallel to $\langle 100 \rangle_{pc}$, and a value of $\phi = 45^{\circ}$ corresponds to sample 1, with length cut parallel to $\langle 110 \rangle_{pc}$. In the $\phi = 0$ case, peaks II and IV and peaks I and III are coincident, and the rocking curve consists of two doublets separated by 0.18°. In the $\phi = 45^{\circ}$ case, peaks I and IV are coincident, and the rocking curve consists of two singlets separated by 0.25° surrounding a central doublet. Small misalignment of the sample on the knife-edges leads to splitting of the doublets, so that all four peaks in the chevron can be resolved. The peak separations in Figs. 7(d) and 8 are based on the room-temperature value of the spontaneous strain. The strain decreases linearly with increasing temperature ($e_4 \propto T - T_c$), and the peak separations decrease correspondingly.^{10,13}

A similar analysis can be performed for the other four chevron orientations. For chevrons 3 and 5 the $\{100\}_{pc}$ -type domain wall is perpendicular to the sample surface, whereas the $\{110\}_{pc}$ -type domain walls are at 45° to the sample surface. The rocking curves consist of two doublets for all values of ϕ [Fig. 8(b)] because the $(001)_{pc}$ diffracting planes in domains I and II and in domains III and IV are exactly parallel to each other (this is true for any two domains separated by $\{110\}_{pc}$ walls oriented at 45° to the surface). For chevron types 4 and 6, the $\{100\}_{pc}$ domain wall is parallel to the surface and the $\{110\}_{pc}$ domain walls are at 45° to the surface. In this case, the $(001)_{pc}$ diffracting planes are exactly parallel in all four domains and the rocking curves will consist of a single peak for all values of ϕ .

When assigning peaks it should be borne in mind that, in addition to the geometrical considerations described above, the number of peaks in the rocking curves will depend on the volumetric proportions of each of the four components of a given chevron. Some peaks expected to be present may be small, poorly resolved, or simply absent. Ambiguities in peak assignment must be resolved by direct microscopic observation. The effect of surface relaxations on the trajectories of domain walls and resulting surface topography is also likely to play a significant role in determining the characteristic x-ray rocking curves.

The interchevron angular relationships are not welldefined, due to the variable amounts of lattice strain encountered at the boundaries between differently oriented chevron regions (Fig. 6). Peaks assigned to the same domain state within different chevron regions will be close to each other but not necessarily coincident, leading to splitting or broadening of peaks.

V. EXPERIMENTAL PROCEDURES

All measurements were performed using a dynamic force with frequency f = 1 Hz. Measurements on sample 1 were performed using a static force component F_s = 200 mN and a dynamic force component F_D =180 mN (abbreviated 200:180 mN). Measurements on sample 2 were performed with a range of dynamic loads varying from 50:45 to 200:180 mN. Measurements were also made with zero dynamic load (probe tip of the DMA just resting on the sample surface). Rocking curves were collected during isothermal annealing under dynamic stress. The angle of the x-ray source to the horizontal (ω) was set to a value just lower than the Bragg angle (θ) for the $(001)_{pc}$ reflection. The source position was then rotated in steps of 0.005° and diffracted intensity was collected stroboscopically for 30 s per step (effectively 30/4 s for each of the four component rocking curves). At each step, the diffracted intensity as a function of 2θ recorded by the position-sensitive detector was integrated using an automated peak-finding and integration routine. Rocking curves are presented as integrated intensity as a function of ω . There are four individual rocking curves for each measurement, corresponding to the four parts of the dynamic stress cycle: solid line=minimum force (F_S $-F_D$), dotted line=maximum force (F_S+F_D), medium dashed line=maximum rate of increasing force, and long dashed line=maximum rate of decreasing force.

High-temperature rocking curves were collected during heating from room-temperature to above T_c and back again. Diffraction measurements were made during a series of isothermal annealing steps under dynamic load. Heating and cooling of the sample between measurements was performed at a rate of approximately 10 °C per min under dynamic load. The sample remained in the DMA under dynamic load throughout the measurement of each series. It was then removed for microscopic analysis and replaced in the DMA for measurement of the next series. At some temperatures, rocking curves were measured at infrequent intervals over a period of days to weeks. No changes in the curves were observed as a function of time during isothermal annealing under dynamic load at a given temperature. However, major changes in the rocking curves were observed on heating or cooling. It appears, therefore, that the bulk microstructure is highly sensitive to changing temperature under dynamic load, but is highly stable with respect to time at any fixed temperature. This is presumably due to the generation of thermal stresses during heating and cooling.

Separate experiments were performed under identical conditions to observe optically the domain processes occurring during dynamical mechanical analysis. Careful placement of the illumination allowed one set of twins at a time to be imaged. Movement of the illumination during acquisition was required to image all twins' orientations. Modification of the instrument to permit *in situ* observations in transmitted light under crossed polars is planned.

VI. RESULTS

A. Sample 1 (length parallel to $[110]_{pc}$, $\phi = 45^{\circ}$)

An optical micrograph and room-temperature rocking curve of the starting material are shown in Figs. 3(c) and 3(d). The central portion of the sample contains domains II and III separated by $(1\overline{10})_{pc}$ walls. The rocking curve contains two sharp peaks separated by 0.25° , in good agreement with the expected rocking angle between domains II and III for $\phi = 45^{\circ}$ [Figs. 7(d) and 8(a)]. It is assumed that the microstructure corresponds to chevron type 1 with the (010)_{pc} domain walls (and hence domains I and IV) absent.

The rocking curve was collected under dynamic load of 200:180 mN. All four components of the rocking curve are identical and coincident, indicating that no change in micro-



FIG. 9. Stroboscopic XRD rocking curves as a function of temperature for sample 1, recorded at 1 Hz and 200:180 mN. The four components of the rocking curve correspond to different parts of the dynamic stress cycle: solid line=minimum force (20 mN), dotted line=maximum force (380 mN), medium dashed line=maximum rate of increasing force, and long dashed line=maximum rate of decreasing force. Loss of intensity on heating to 553 °C is due to thermal expansion of the sample assembly, which causes the x-ray beam to miss the sample at high temperatures.

structure occurs in response to the dynamic load. A series of rocking curves collected in isothermal steps during heating is shown in Fig. 9. Little change in the rocking curves occurs on heating from room temperature to 151 °C. Two new peaks appear at 192 °C, which can be attributed to a region of the crystal containing a second chevron orientation (type 2). At temperatures up to 234 °C, all four components of the rocking curve are identical and coincident. Above 234 °C, however, two significant changes occur. First, the diffraction peaks attributed to domain II in both chevron regions disappear, leaving only those due to domain III. Second, the four components of the rocking curve become shifted with respect to each other, with the curve corresponding to the maximum applied force (dotted line) shifting to the right with increasing temperature. This indicates that the microstructure is now responding to the applied dynamic load. The physical origin of the peak shift is discussed below.

After heating above T_c , the sample was cooled to room temperature under dynamic load. An optical micrograph and rocking curve of the cooled sample are shown in Fig. 10. The peaks in the rocking curve can be assigned to two regions of



FIG. 10. (a) Stroboscopic room-temperature rocking curves of sample 1 after heating above T_c and cooling under dynamic load (Fig. 9). Splitting of peaks indicates the presence of chevron orientations 1 and 2 (see Table II for definitions). (b) Optical micrograph of sample 1 after heating above T_c and cooling under dynamic load. The domain walls most clearly visible correspond to the $\{100\}_{pc}$ walls, which are at ~90° to each other in the two chevron orientations. A high strain boundary between the two chevrons is indicated. In other regions the interpenetration of the two chevron orientations is mediated by the formation of needle twins, as shown in Fig. 6(b).

the crystal containing chevron-types 1 and 2 [Fig. 10(a)]. The peak positions indicate a slight misalignment of the sample, corresponding to a value of $\phi = 40^{\circ}$ [Fig. 8(a)]. Diffraction peaks from domain I in chevron 1 and domain IV in chevron 2 are poorly resolved or absent. The presence of chevron orientations 1 and 2 was confirmed by optical examination [Fig. 10(b)].

After optical examination, the sample was reinserted into the diffractometer and another series of high-temperature rocking curves was acquired under identical conditions (Fig. 11). The initial rocking curves are similar to those seen before removal of the sample [Fig. 10(a)], although the peaks from chevron orientations 1 and 2 are less clearly resolved. At 194 °C, the contribution from domain II in chevron 1 increases relative to that of domain II in chevron 2. Simultaneously, the position of the peak from domain II in chevron 1 begins to respond to the dynamic load, causing a shift to higher angles when maximum force is applied (dotted line). No changes are observed in the contributions from domain III in chevrons 1 and 2, however, and neither of these peaks responds to the dynamic load at this temperature. At 237 °C, the contribution from domain III in chevron 2 increases relative to that of domain III in chevron 1. By 280 °C the rocking curves consist of a single peak from domain II in chevron 1, which responds strongly to the dynamic load, and a single peak from domain III in chevron 2, which shows little re-



FIG. 11. Stroboscopic XRD rocking curves as a function of temperature for sample 1, recorded at 1 Hz and 200:180 mN.

sponse to the dynamic load. This situation continues up to 370 °C, at which point both peaks respond in a similar manner to the dynamic load. At 462 °C, only domain II from chevron 1 is observable.

After the sample had been heated above T_c in the second heating run, it was once again cooled to room temperature under dynamic load. The corresponding rocking curve is shown at the top of Fig. 11 and an optical micrograph of the cooled sample is shown in Fig. 12. The nature of the microstructure has changed significantly, with the generation of chevron orientations of types 3–6, characterized by the presence of $\{110\}_{pc}$ domain walls at 45° to the $(001)_{pc}$ sample surface. These domain walls are visible by the birefringent fringes created when viewed under crossed polars.

B. Sample 2 (length parallel to $[100]_{pc}$, $\phi = 0^{\circ}$)

An optical micrograph of the starting material for sample 2 is shown in Fig. 13. The sample contains lamellar $(010)_{pc}$ domain walls parallel to its length, with a single set of vertical $\{110\}_{pc}$ domain walls in the center, corresponding to chevron type 1. A series of rocking curves acquired at 84 °C under varying dynamic loads is shown in Fig. 14(a). The lower curve was acquired with no applied force (probe tip resting on the sample surface). The rocking curve contains just two peaks, as expected for chevrons of this type with $\phi = 0^{\circ}$ [Fig. 8(a)]. When a dynamic load is applied, the rocking curve corresponding to the maximum in the dynamic



FIG. 12. Optical micrograph of sample 1 after a second heating and cooling cycle under dynamic load. The central fringes correspond to $\{110\}_{pc}$ domain walls oriented at 45° to the surface, corresponding to a chevron orientation of types 3–6. Regions containing chevron orientations 1 and 2 are visible in the upper right and lower left corners.

load cycle (dotted line) shifts to lower angles with increasing force. In addition to the shift, there is a noticeable increase in the width of the peaks compared to the widths observed at the minimum of the dynamic load cycle (solid line), especially at high loads [top of Fig. 14(a)]. The nature of the shift in peak position with applied force appears to be different to that observed in sample 1 [Figs. 9 and 11]. First, the direction of shift is opposite to that observed in Figs. 9 and 11. More importantly, however, the peak shifts do not appear to be thermally activated. The peak shifts observed for sample 1 appear only in the superelastic regime. In contrast, the peak



FIG. 13. Optical micrograph of sample 2, with length parallel to $[100]_{pc}$. The microstructure consists predominantly of $(010)_{pc}$ domain walls parallel to the length of the sample, with a single set of $\{110\}_{pc}$ domain walls in the center, corresponding to chevron type 1 (inset). In this orientation, there is no force on the domain walls due to application of the external load.



FIG. 14. Stroboscopic rocking curves for sample 2 recorded at 1 Hz and a range of dynamic forces at a temperature of (a) 84 °C and (b) 298 °C.

shifts in sample 2 occur even at room temperature and for forces as low as 50 mN. This indicates that changes in the diffraction pattern do not represent a dynamic response of the microstructure to the applied load. The magnitude of the peak shifts may be explained by the curvature induced by elastic bending of the sample in response to the applied force.

The behavior observed up to a temperature of 169 °C is identical to that depicted in Fig. 14(a). Significant forcedependent changes occur in the rocking curves at temperatures of 212 °C and above [representative behavior at 298 °C is shown in Fig. 14(b)]. First, a third peak appears, attributable to the presence of a second chevron orientation. For forces up to 100:90 (static:dynamic) mN, the behavior is similar to that seen at lower temperatures, with all three peaks shifting to lower angles by an amount determined by the applied dynamic force. At forces of 150:135 mN and above, however, the nature of the rocking curves at the maximum in the dynamic force cycle (dotted line) changes completely. Rather than three well-defined peaks, the rocking curve becomes smeared out into a broad signal encompassing an equivalent angular range. At the minimum of the dynamic stress cycle (solid line), the three well-defined peaks are reformed. The force required to see this effect is temperature dependent, with larger forces required at lower temperature. Both the temperatures and forces required indicate that the effect is related to domain-wall motion within the superelastic regime.

The mechanical properties of sample 2 as a function of temperature are shown in Fig. 15, recorded using a dynamic load of 100:90 mN. Measurements of storage modulus (circles) and tan δ (squares) made during heating (closed symbols) and cooling (open symbols) at a constant rate of 10 °C/min are shown. Measurements of storage modulus and tan δ made during the acquisition of the rocking curves are shown as closed and open triangles, respectively. The storage modulus decreases by around a factor of 2 on cooling from the paraelastic to the superelastic regime, a much smaller decrease than the factor of 10 drop observed in sample 1 (Fig. 1). Most of this drop in modulus can be attributed to the

elastic softening due to order-parameter strain coupling.^{17,18} The dashed line shows schematically the effect of linearquadratic order parameter-strain coupling for a close-tosecond-order transition.¹⁹ The softening observed in excess of this is due to domain wall processes, as is revealed by the progressive immobilization of domain walls on cooling below 170 °C.

C. In situ optical observations

In situ optical observation of the microstructural response to a dynamic load provides a basis for interpreting the results of the XRD-DMA experiments. Two distinct modes of anelastic response were observed in sample 1. The dominant mechanism at low temperatures is the rapid advance-



FIG. 15. Storage modulus (circles) and tan δ (squares) as a function of temperature for sample 2, made during heating (closed symbols) and cooling (open symbols) at a constant rate of 10 °C/min. Triangles show measurements made during acquisition of rocking curves (Fig. 14). The dashed line shows schematically the form of the elastic constant variation expected for a close-to-second-order improper ferroelastic phase transition (see Ref. 19). This variation is the intrinsic elastic softening due to order parameter-strain coupling (see Ref. 18).

ment and retraction of combs of narrow, vertical {100}_{pc} needle domains. These combs originate at the sides of the sample and advance horizontally across its width. At low temperatures and small loads, continuous advancement and retraction of individual needle tips over small distances is observed in response to the dynamic stress. At high temperatures and large loads, discontinuous advancement and retraction of the needle tips across the entire width of the sample is observed, with rapid movement of the needle tips occurring between discrete pinning points. The ratio of mobile to static needle tips within a comb is a function of temperature, with the ratio decreasing steadily on cooling through the domain freezing regime ($T \le 200 \,^{\circ}$ C). At higher temperatures the alternative mode of anelastic response involves the lateral displacement and rotation of a single $45^{\circ} \{110\}_{pc}$ wall (such as that shown in Fig. 12). Large-amplitude lateral displacements of these walls (of the order of 0.5-1 mm) are facilitated at high temperatures either by the disappearance of $\{100\}_{pc}$ needles, or by their cooperative advancement and retraction.

Sample 2 shows a similar behavior to sample 1 at $T < 200 \,^{\circ}\text{C}$ and forces < 150:135 mN, with the anelastic response accommodated by the formation/advancement/ retraction of small numbers of $\{100\}_{pc}$ needle domains parallel or perpendicular to the sample length. At $T > 200 \,^{\circ}\text{C}$ and forces > 150:135 mN there is rapid advancement of a high density of needle twins across the entire sample when the force is at its maximum, and almost complete retraction when the force is at its minimum.

VII. DISCUSSION

A. Preferred chevron orientation

Our experiments on sample 1 show that there is a strong preference for certain chevron orientations when heating and cooling under dynamic load. Whereas the microstructure of the starting material is dominated by chevron orientations 1 and 2, with all domain walls perpendicular to the $(001)_{pc}$ surface (Figs. 5 and 6), the microstructure after repeated heating and cooling is dominated by chevron orientations 3 and 5, characterized by vertical $\{100\}_{pc}$ walls and 45° $\{110\}_{pc}$ walls (Fig. 12). The gradual change in chevron orientation with increasing temperature is seen in the rocking curves as the disappearance of peaks associated with vertical $\{100\}_{pc}$ and $\{110\}_{pc}$ walls, leaving a single doublet peak for each chevron (Figs. 9 and 11). This observation can easily be explained in terms of the effective force on the domain walls within the different chevrons due to the applied stress. In chevrons 1, 2, 4, and 6, the effective force on at least one domain wall in the chevron is zero (these walls separate domains with an equal component of spontaneous strain parallel to the length of the sample). Such walls are likely to hinder the dynamic response of the microstructure. In chevrons 3 and 5, all walls experience the maximum effective force, and will be able to respond directly to the applied stress.

Another contributing factor to the preferred chevron orientation is illustrated in Fig. 16, which shows schematically the effect of a bending stress on a chevron of type 3 or 5.



FIG. 16. Schematic response of chevron types 3 and 5 to a bending stress. Domains shaded white have a negative component of spontaneous strain parallel to the length of the sample. Domains shaded gray have a positive component. (a) Closely spaced vertical $\{100\}_{pc}$ walls form needle twins (for simplicity the needle tips are shown forming at the top and bottom surfaces, and advancing/retracting vertically. In reality, the needle tips form at the sides of the sample and advance/retract horizontally). The presence of a band of 45° {110}_{pc} walls causes the sign of the needle twins to reverse in the top and bottom halves of the crystal. (b) Retraction of the needles can simultaneously accommodate contraction of the top surface and expansion of the bottom surface. Full retraction leaves a single $\{110\}_{nc}$ wall. (c) Further deformation can be accommodated by rotation of the $\{110\}_{pc}$ wall. (d) Removal of stress allows the wall to relax to its stress-free trajectory. Readvancement of the $\{100\}_{pc}$ needles may also occur. Note the deviation from the 45° {110}_{pc} wall trajectory at the top and bottom surfaces. This surface relaxation is responsible for the dynamic peak-shift observed using XRD-DMA, as the domain wall sweeps past the x-ray beam.

Twin domains shaded white and gray have components of spontaneous contraction and expansion, respectively, parallel to the length of the sample. Vertical $\{100\}_{pc}$ walls form combs of needle twins [Fig. 16(a)]. The presence of a band of 45° {110}_{pc} walls causes the "sign" of the needles to be reversed in the top and bottom halves of the crystal. In threepoint-bend geometry, the top surface is placed under compression whereas the bottom surface is under tension. Retraction of the needles creates exactly the required anelastic response (contraction of the upper surface and expansion of the lower surface), leaving a single 45° {110}_{pc} wall [Fig. 16(b)]. Further deformation can then be accommodated by rotation of this wall [Fig. 16(c)]. On releasing the stress, the wall returns to its stress-free trajectory [Fig. 16(d)]. This may or may not be accompanied by readvancement of the $\{100\}_{pc}$ needles.

B. Microstructural response to dynamic force

A significant observation is that no dynamic response of the rocking curves is observed below 200 °C, despite the fact that domains are mobile at this temperature (Fig. 1). This discrepancy is easily explained by the change in mode of anelastic response on heating. Below 200 °C, and for applied forces≤200:180 mN, the anelastic response is accommodated by continuous advancement and retraction of $\{100\}_{pc}$ needle tips [Fig. 16(a)]. The positions of individual peaks in the rocking curve are unaffected by the movement of the needle tips. If diffraction is occurring from a region well away from the tips, then the intensities of the peaks will be similarly unaffected. Above 200 °C the anelastic response is increasingly accommodated by lateral translation and rotation of $\{110\}_{pc}$ domain walls [Fig. 16(c)]. The trace of a single $\{110\}_{pc}$ domain wall on the surface of the crystal was observed to move by a distance of around 0.5-1 mm, causing it to track back and forth across the x-ray beam during the dynamic force cycle. Hence diffraction occurs from alternate domains at the maximum and minimum points of the force cycle. The shift in peak position is a measure of the angle between (001)pc diffracting planes in adjacent domains. In the bulk, this angle is expected to be zero (Fig. 7). At the surface, however, the trajectory of the domain wall relaxes, producing a small splitting of the peaks.²⁰ An estimate of 0.06° was obtained for the splitting angle using a 3D elastic model based on empirical pair potentials (W. Lee, personal communication). Although the pair potentials were not specifically optimized for LaAlO₃, the splitting angle is the same order-of-magnitude as the peak shift observed using XRD-DMA (values up to 0.045° were observed).

The orientation of sample 2 is such that the component of spontaneous strain parallel to the length of the sample is equal in all domains. Ideally, therefore, there should be no net force on any domain wall and no superelastic softening (neglecting any ferrobielastic contribution). Although the softening is reduced, there is clearly a significant superelastic contribution to the mechanical behavior of sample 2 (Fig. 15). Major changes in the rocking curves occur above 200 °C and 150:135 mN, indicating a first-order transformation of the surface topography between the maximum and minimum points of the dynamic force cycle [Fig. 14(b)]. These changes correlate with the massive increase in twin-wall density observed optically. The broad rocking curve at maximum force indicates that the distance between domain walls approaches the wall width ($\sim 50 \text{ Å}^{10}$), leading to a smoothly corrugated surface. The generation of such a high density of domain walls may be explained if [100]_{pc} is not exactly parallel to the length of the sample. A small angular deviation leads to a small contrast between the component of spontaneous strain parallel to the sample length in adjacent domains. For a given superelastic strain, the density of domain walls is inversely proportional to the contrast in spontaneous strain.⁴ Hence as the contrast tends to zero, the density of domain walls becomes infinite. Balancing this effect is the extra energy required to create the domain walls. This delicate balance leads to a critical force, above which a high density of domain walls is energetically favored.

VIII. OUTLOOK

These experiments have demonstrated that the response of ferroelastic domain walls to a dynamically applied load can be resolved successfully using stroboscopic x-ray diffraction techniques. The nature of the interaction between ferroelastic domain walls and surfaces is an area of active research.^{21,22} Much work has been done using Lennard-Jones type potentials to simulate the structure of ferroelastic domain walls at the surface of a crystal.²⁰ The precise nature of the changes in domain wall structure, orientation, and surface topography that occur in response to the inhomogeneous stress resulting from three-point bending are unknown. We have now established an experimental technique whereby such changes can be probed *in situ* as a function of varying temperature, force, and frequency.

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