

Physics of the Earth and Planetary Interiors 134 (2002) 253-272



www.elsevier.com/locate/pepi

The influence of transformation twins on the seismic-frequency elastic and anelastic properties of perovskite: dynamical mechanical analysis of single crystal LaAlO₃

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Received 16 May 2002; accepted 25 September 2002

Abstract

The low-frequency mechanical properties of single crystal LaAlO₃ have been investigated as a function of temperature, frequency and applied force using the technique of dynamical mechanical analysis (DMA) in three-point bend geometry. LaAlO₃ undergoes a cubic to rhombohedral phase transition below 550 °C. The mechanical response in the low-temperature rhombohedral phase is shown to be dominated by the viscous motion of transformation twin domain walls, resulting in a factor of 10 decrease in the storage modulus relative to the high-temperature cubic phase (super-elastic softening) and a significant increase in attenuation. Super-elastic softening is observed down to 200 °C, below which the mobility of the domain walls decreases markedly, causing a rapid increase in storage modulus and a pronounced peak in attenuation (domain wall freezing). The frequency dependence of the storage modulus close to the freezing temperature is accurately described by a modified Burgers model with a Gaussian distribution of activation energies with mean value 84.1(1) kJ/mol and S.D. 10.3(1) kJ/mol. This activation energy suggests that domain walls are pinned predominantly by oxygen vacancies.

Detailed analysis of the dynamic force-deflection curves reveals three distinct regimes of mechanical response. In the elastic regime, the domain walls are pinned and unable to move. The elastic response is linear with a slope determined by the intrinsic stiffness of the lattice, the initial susceptibility of the pinning potential and the bending of twin walls between the pinning sites. In the super-elastic regime, the domain walls unpin and displace by an amount determined by the balance between the applied and restoring forces. The value of the apparent super-elastic modulus is shown to be independent of the spontaneous strain and hence independent of temperature. At high values of the applied force, adjacent domain walls come into contact with each other and prevent further super-elastic deformation (saturation). The strain in the saturation regime scales with the spontaneous strain and the resulting modulus is strongly temperature dependent.

The possible effects of domain wall motion on the seismic properties of minerals are discussed. It is concluded that, if these results are directly transferred to mantle-forming (Mg, Fe)(Si, Al)O₃ perovskite, the strain amplitude of a typical seismic wave would be sufficient to cause super-elastic softening. However, pinning of domain walls by oxygen vacancies leads to very short relaxation times at mantle temperatures. If translated to (Mg, Fe)(Si, Al)O₃, these would be too short to amount to significant seismic attenuation. Increased pinning of ferroelastic domain walls by defects, impurities and grain boundaries

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in real mantle perovskite, or a significant positive activation volume for oxygen vacancy diffusion, would be sufficient to increase the relaxation time to values resulting in seismic wave attenuation, however. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Phase transition; Anelasticity; Lower mantle; Seismic attenuation; Perovskite; MgSiO₃

1. Introduction

The attenuation of seismic waves is caused by the dissipation of strain energy as they propagate through an anelastic medium. By combining the observations of seismic attenuation with a knowledge of the anelastic properties of minerals, the rheology of the mantle and core may be ascertained. As tomographic techniques have improved, seismologists have begun to develop a detailed picture of how the attenuation of seismic waves varies both laterally and with depth in Earth (Romanowicz and Durek, 2000). Most work to date has focused on attenuation in the Earth's upper mantle, particularly at depths just beneath the lithosphere, where the effect is most marked and the attenuation can reach values greater than $Q^{-1} = 0.01$ (where O is the quality factor). However, the microscopic mechanisms responsible for anelasticity remain controversial. The two currently favoured theories attribute anelasticity in the Earth's upper mantle to either the movement of dislocations (e.g. anelastic unpinning) or grain boundary processes (e.g. grain boundary sliding) (Karato and Spetzler, 1990; Webb et al., 1999; Jackson et al., 2002). Anelastic processes in minerals at high temperature and pressure have been studied using a variety of mechanical spectroscopy techniques (Jackson et al., 1992; Getting et al., 1997; Gribb and Cooper, 1998a,b; Aizawa et al., 2001; Tan et al., 2001). Information regarding attenuation in the Earth's lower mantle is less easily obtained. Most models indicate that Q is at least 400 through the lower mantle (Romanowicz and Durek, 2000), but there are indications of lateral variations (high attenuation centred beneath the Pacific and Africa). Grain boundary viscoelastic processes and dislocation movement are usually assumed as the origins of any such attenuation. Here we consider an alternative mechanism related to the anelastic motion of transformation domain walls as a possible cause of seismic attenuation from perovskite. Here we follow Nowick and Berry (1972), in referring to time-dependent (not instantaneous) but recoverable elastic relaxation as "anelastic", while viscoelastic behaviour is that which is not instantaneous and not recoverable.

Phase transitions involving a loss of point group symmetry lead to the formation of ferroelastic or co-elastic transformation twins below T_c (e.g. Salje et al., 2000). Given the common occurrence of transformation twinning, surprisingly little attention has been paid to the influence of such ferroelastic microstructures on the mechanical properties of minerals. This must principally be because domain walls are unable to move appreciably on the short time scales of conventional ultrasonic and Brillouin-scattering measurements (MHz-GHz). The frequency of a seismic wave is typically in the range mHz-Hz, which we shall see is the region encompassing the natural resonance of domain wall motion. On these much longer time scales the mechanical response of a ferroelastic mineral is dominated by changes in its twin microstructure, leading to pronounced anelasticity and a dramatic apparent elastic softening (Kityk et al., 2000).

Low-frequency mechanical properties are typically measured using the technique of dynamical mechanical analysis (DMA). Various geometries may be employed, with torsion pendulum apparatus commonly used to measure the shear modulus under dynamic conditions of forced oscillation. Alternatively, parallel plate geometry may be employed, or three-point bend geometry may be adopted, whereby the deflection of a thin strip of material in response to an alternating applied force is used to calculate the dynamic Young's modulus (Schranz, 1997). These methods examine the mechanical properties at very large wavelengths (wave vectors at, or just away from, the Brillouin zone centre). In this paper, we present a study of the force, frequency and temperature dependence of the low-frequency mechanical properties of single crystal LaAlO₃ held in three-point bend geometry. This material is commonly used as a substrate for high-temperature superconducting thin films and is therefore commercially available as high-quality single crystals of the required size. Furthermore, LaAlO₃ has the cubic perovskite structure at high temperatures and undergoes a displacive phase transition to a rhombohedral phase below $550 \,^{\circ}$ C. It provides, therefore, a useful analogy to the non-cubic MgSiO₃ perovskite phase thought to make up more than 70% of the Earth's lower mantle and a possible insight into the role of twinning as a source of anelasticity in the Earth.

2. Crystallographic details

The crystallographic details of the phase transition and twin microstructure in $LaAlO_3$ are described by Bueble et al. (1998). Only the basic details required to interpret the DMA experiments are reproduced here.

2.1. Phase transition and spontaneous strain in LaAlO₃

The high-temperature phase of LaAlO₃ has the cubic perovskite structure with space group $Pm\bar{3}m$ and lattice parameter $a_{cubic} \sim 3.79$ Å. Below about 550 °C it undergoes an improper ferroelastic phase transition to the rhombohedral subgroup $R\bar{3}c$, driven by rotation of the AlO₆ octahedra about one of the cubic three-fold symmetry axes. Adjacent octahedra rotate in opposite senses, leading to a doubling of the unit cell along the octahedral phase can be described by a non-primitive unit cell with hexagonal lattice vectors:

$$\begin{pmatrix} a_{\text{hex}} \\ b_{\text{hex}} \\ c_{\text{hex}} \end{pmatrix} = \begin{pmatrix} -1 & 1 & 0 \\ 0 & -1 & 1 \\ 2 & 2 & 2 \end{pmatrix} \begin{pmatrix} a_{\text{cubic}} \\ b_{\text{cubic}} \\ c_{\text{cubic}} \end{pmatrix}$$
(1)

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 pseudo-cubic unit cell with rhombohedral shape $(a_{pc} = b_{pc} = c_{pc} \sim 3.79 \text{ Å} \text{ and } \alpha_{pc} = \beta_{pc} = \gamma_{pc} \neq 90^{\circ})$ that is directly comparable in size and orientation to the high-temperature cubic unit cell. The macroscopic symmetry-breaking strain associated with the phase transition is then of the form (Carpenter et al., 1998):

$$e_4 = e_5 = e_6 = \frac{a_{\rm pc}}{a_0} \cos \alpha_{\rm pc} \tag{2}$$

where a_0 is the hypothetical lattice parameter of the high-temperature cubic phase extrapolated from above T_c to the temperature of interest.

The lattice parameters of the hexagonal unit cell have been determined as a function of temperature by Chakoumakos et al. (1998), Lehnert et al. (2000) and Howard et al. (2000). These data can be transformed to the pseudo-cubic unit cell and used to calculate the symmetry-breaking strain e_4 via Eq. (2) (Fig. 1). The strain is negative ($\alpha_{\rm pc} > 90^\circ$), which corresponds to compression of the unit cell parallel to the octahedral rotation axis and expansion perpendicular to this axis. Since the symmetry-breaking strain couples to the square of the driving order parameter for an improper ferroelastic transition ($e_4 \propto Q^2$), the linear variation of e_4 with temperature implies that $Q^2 \propto (T_c - T)$ and that the thermodynamic character of the transition is second order. A similar conclusion was made on the basis of XRD measurements of the ferroelastic twin angle as a function of temperature (Chrosch and Salje, 1999).

2.2. Transformation twinning in LaAlO₃

Transformation twins form on cooling below T_c due to the choice of four equivalent triad axes about which octahedral rotation can occur (Table 1). Given the four pure twin domain states, there are six possible pairs of domain states 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 $\{100\}$ and one of the form $\{110\}$. This produces a total of 12 physically distinguishable twin domain orientations.

The sample used in these experiments was a single crystal of LaAlO₃ 5 mm long, 1.96 mm wide and 0.52 mm thick (Crystal GmbH, Berlin). The surface of the sample is parallel to $(001)_{cubic}$ and the length of the sample is parallel to $[110]_{cubic}$. An optical micrograph of the twin microstructure of the 'as received' starting material is shown in Fig. 2a. This characteristic microstructure, often referred to as 'chevron tiling', consists of several mutually intersecting domain walls perpendicular to the (001) surface. All domain wall orientations are mutually permissible, allowing a stress-free intergrowth of the four pure twin domain states (Bueble et al., 1998).



Fig. 1. Spontaneous strain (e_4) vs. temperature for LaAlO₃, derived from the lattice parameter data of Howard et al. (2000). The straight line is a fit to the data with an equation of the form $e_4 \propto Q^2 \propto 1/T_c(T_c - T)$, with $T_c = 851$ K. The linear variation confirms the second-order character of the phase transition.

Table	1										
Twin	domain	and	twin	wall	orientations	in	LaAIO ₃	(Bueble	et	al.,	1998)

Domain	Axis of rotation	Spontaneous strain tensor	Domain pair	Orientation of twin wall
I	[111]	$\begin{pmatrix} 0 & \bar{e} & \bar{e} \\ \bar{e} & 0 & \bar{e} \\ \bar{e} & \bar{e} & 0 \end{pmatrix}$	I, II	(010) (101)
П	[111]	$\begin{pmatrix} 0 & e & \bar{e} \\ e & 0 & e \\ \bar{e} & e & 0 \end{pmatrix}$	I, III	(100) (011)
III	[Ī11]	$\begin{pmatrix} 0 & e & e \\ e & 0 & \bar{e} \\ e & \bar{e} & 0 \end{pmatrix}$	I, IV	(001) (110)
IV	[111]	$\begin{pmatrix} 0 & \bar{e} & e \\ \bar{e} & 0 & e \\ e & e & 0 \end{pmatrix}$	п, ш	(001) (110)
		× /	II, IV	(100) (011)
			III, IV	(010) (101)

3. Experimental methods

Mechanical properties have been measured using a Perkin-Elmer dynamical mechanical analyser (DMA-7) operating in three-point bend geometry (Menard, 1999). The principle of DMA is illustrated in Fig. 3. The sample is a single crystal beam with length l, width w and thickness t, supported on two



Fig. 2. (a) Optical micrograph of the "as-received" starting material showing the chevron microstructure of mutually intersecting $\{100\}$ and $\{110\}$ domain walls. Labels I–IV refer to the pure twin domain states listed in Table 1. 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). (b) Optical micrograph of the same sample after repeated heating and cooling under dynamic load at temperatures below T_c . The $\{110\}$ domain walls have disappeared, leaving a microstructure of lamellar $\{100\}$ twins and needle domains.



Fig. 3. (a) Three-point bend geometry of the DMA-7. (b) Dynamic force and response signals during dynamical mechanical analysis.

knife edges (Fig. 3a). 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 $(F_{\rm D})$ with frequency (f) in 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 $\Delta u \sim 10 \,\mathrm{nm}$ and $\Delta d \sim 0.1^{\circ}$, respectively (Fig. 3b). 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 $l \gg w$ (Kityk et al., 2000). 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 $(u_{\rm D})$ via:

$$Y = \frac{l^3}{4t^3w} \frac{F_{\rm D}}{u_{\rm D}} \exp(\mathrm{i}\delta) \tag{3}$$

This expression is derived for an isotropic solid. In an anisotropic material, such as our single crystal low-symmetry perovskite, 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). This quantity is often referred to as Q^{-1} (inverse quality factor) in the geophysics literature. A perfectly elastic material has $\tan \delta = 0$, whereas an anelastic material has $\tan \delta > 0$. The sample assembly is encased in a resistance furnace, permitting measurement up to a temperature of ~700 °C. The absolute accuracy of the values of moduli obtained is affected by measurement errors, zero errors and systematic offsets within the apparatus and is therefore relatively low (10-20%). This means that the technique is not suitable for determining absolute values of the elastic constants. However, the relative precision is better than 1%, allowing changes in mechanical properties as a function of force, frequency and temperature to be determined with a high degree of sensitivity. For this reason, comparisons between different DMA experiments are usually made in terms of the relative modulus.

Three different types of experiment have been performed; temperature scans, frequency scans and dynamic force scans. In a temperature scan, F_S , F_D and f are held constant, while the temperature (*T*) is swept up or down at a rate of 5 °C/min. Values of the storage modulus and tan δ are recorded continuously and then averaged into temperature bins of chosen width (typically 1–5 °C). F_D is set to a value of approximately 0.9 F_S , so that the minimum and maximum forces on the sample are 0.1 F_S and 1.9 F_S , respectively. Values for F_S are typically in the range 100–500 mN. All temperature scans were performed at a frequency of 1 Hz. In a frequency scan, F_S , F_D and *T* are held constant while *f* is swept between 0.1 and 50 Hz. The rate of the frequency sweep is automatically controlled by the data collection software and varies between 0.04 Hz/min at low frequencies and 4 Hz/min at high frequencies. In a dynamic force scan, T and f are held constant while $F_{\rm D}$ is swept between 50 and 500 mN at a rate of 10 mN/min. In these experiments, $F_{\rm S}$ was programmed to maintain a value of $1.2 F_{\rm D}$ at all times.

4. Results and analysis

All experiments have been performed on the same single crystal of LaAlO₃. The results are described in the same sequence that the experiments were performed, so that they can be properly correlated with the changes in twin microstructure that occurred over time.

4.1. Mechanical properties as a function of temperature $(T_{max} < T_c)$

Previous experiments with similar starting materials have demonstrated that LaAlO₃ displays very little twin memory (i.e. the arrangement of domain walls found after heating to temperatures above T_c and then cooling bears no relation to the initial arrangement; Hayward, personal communication). For this reason, initial temperature scans were limited to a maximum temperature $T_{max} < T_c$, in order to preserve as much as possible the chevron microstructure of Fig. 2a.

A temperature scan of the 'as-received' sample from room temperature to 500 °C is shown in Fig. 4a. The corresponding cooling scan is shown in Fig. 4b. The scans were recorded using $F_{\rm S} = 100 \,\mathrm{mN}, F_{\rm D} =$ 90 mN and f = 1 Hz and are normalised relative to the maximum observed modulus. The relative modulus at room temperature is ~ 1 and tan δ is ~ 0.02 . Small changes in modulus and $\tan \delta$ occur between room temperature and 100 °C. Between 100 and 200 °C, however, the relative modulus drops rapidly to a value of ~ 0.15 . This is accompanied by a pronounced peak in $\tan \delta$, which reaches a maximum value of 0.89 at 150 °C. Between 200 and 500 °C, the relative modulus remains at a low value, but shows several small-amplitude discontinuous increases and decreases. A minimum value of 0.092 is reached at 367 °C, which represents more than a factor of 10 decrease in the storage modulus compared to the initial room temperature value. Each abrupt change in modulus between 200 and 500 °C is accompanied by a small discontinuity in $\tan \delta$, which otherwise decreases gradually from 0.32 to 0.16 over this temperature interval. No small-amplitude discontinuities are observed on cooling from 500 °C to room temperature (Fig. 4b), but the behaviour is otherwise reversible. All subsequent heating and cooling scans were identical to Fig. 4b.

The huge apparent elastic softening in Fig. 4 is actually a reflection of the onset of domain wall mobility



Fig. 4. Temperature dependence of the storage modulus (solid circles) and $\tan \delta$ (open circles) of the "as-received" starting material during (a) heating and (b) cooling. Measurement conditions were $F_S = 100 \text{ mN}$, $F_D = 90 \text{ mN}$ and f = 1 Hz. Small-amplitude discontinuities in (a) are caused by the disappearance of the {110} domain walls on annealing under dynamic load (see Fig. 2).

above 100 °C, which results in large sample strains for small applied forces (Kityk et al., 2000). The macroscopic spontaneous strain in the low-temperature rhombohedral phase corresponds to compression of the structure along the octahedral rotation axis and extension in the plane perpendicular to this. The orientation of the axes of compression and extension in each of the four pure twin domain states is illustrated by the ellipses in Fig. 2a (minor axis: compression, major axis: extension). Domains I and IV have their axes of compression oriented parallel to the length of the sample, whereas domains II and III have their axes of compression perpendicular to the length. When a stress is applied, the sample is able to change its length by simply changing the volumetric proportions of the differently oriented domains. For example, a compressive stress applied along the length of the crystal lowers the free energy of domains I and IV with respect to the free energy of domains II and III, producing an effective force on the (010) domain walls. Provided that this driving force exceeds the unpinning force, the domain walls will move. The resulting macroscopic strain is then determined by the magnitude of the rhombohedral distortion, the number of domain walls per unit length and the distance moved by each wall. The resulting storage modulus is very much less than the intrinsic modulus of the lattice (super-elastic softening).

Domain wall motion is anelastic, with a time dependence that results from wall–wall, wall–surface and wall–defect interactions. Furthermore, domain wall unpinning is a thermally activated process. If temperatures are high enough to overcome the energy barriers due to pinning then domain walls will move on the time scale of the DMA measurement and produce the apparent super-elastic softening. If the temperature is too low then domain walls are effectively frozen and only the intrinsic modulus is measured (Zimmermann and Schranz, 1996). The characteristic relaxation time for domain wall motion, τ , varies according to the Arrhenius relationship:

$$\tau = \tau_0 \exp\left(\frac{E}{RT}\right) \tag{4}$$

where *E* is an activation energy. At low temperatures, the relaxation time for domain wall motion is large. Thus, at temperatures below those at which resonance is seen ($\omega \tau \gg 1$, where $\omega = 2\pi f$ is the angular frequency of the DMA experiment), no domain wall motion is possible on the time scale of the measurements. In this case Y' is equal to the intrinsic modulus of the lattice and tan δ is zero ('domain wall freezing'). Super-elastic softening is observed at the other side of the resonance peak ($\omega \tau \ll 1$). In this regime, the energy dissipated per cycle is equal to the work done in overcoming the resistance to the movement of domain walls, leading to the roughly temperature-independent value of tan δ at $T > 200 \,^{\circ}$ C (Fig. 4). The maximum in tan δ occurs at the resonance frequency, when $\omega \tau =$ 1, which defines the freezing temperature T_f .

After several heating and cooling cycles, the sample was removed from the DMA and the twin microstructure was re-examined under an optical microscope. The chevron microstructure of intersecting $\{100\}$ and $\{110\}$ domain walls was found to have changed to a lamellar microstructure consisting predominantly of parallel {100} walls and needle domains (Fig. 2b). The rapid disappearance of the $\{110\}$ domain walls on heating is most likely the cause of the small-amplitude discontinuities in modulus and $\tan \delta$ between 200 and 500 °C. The {110} domain walls have no net force on them due to the externally applied force, since the component of spontaneous strain parallel to the length of the sample is equal in the adjacent twin domains (Fig. 2a). However, twin domains are metastable with respect to a single crystal and will anneal out under thermal activation. It seems that domains with walls that experience a force under dynamic stress, such as the $\{100\}$ walls in the geometry of this experiment, are less susceptible to thermal annealing. This is most likely related to the fact that each domain experiences opposite forces at the top and bottom of the crystal, which hinders the mechanism of domain coarsening. Before annealing, the intersection of the $\{110\}$ and $\{100\}$ walls hinders the movement of the $\{100\}$ walls, contributing to the high stiffness of the starting material below 100 °C. Once the $\{110\}$ walls have been destroyed by thermal annealing, the parallel sets of $\{100\}$ twins are free to move and contribute to the super-elastic softening.

4.2. Mechanical properties as a function of temperature $(T_{max} > T_c)$

After the temperature scans with $T_{\text{max}} < T_c$, the same sample was reinserted into the DMA and



Fig. 5. Temperature dependence of (a) the storage modulus and (b) tan δ during heating and cooling through the cubic-rhombohedral phase transition with small applied forces $F_{\rm S} = 200 \,\text{mN}$, $F_{\rm D} = 180 \,\text{mN}$ and $f = 1 \,\text{Hz}$. The parts (c) and (d) show the temperature dependence with large applied forces $F_{\rm S} = 500 \,\text{mN}$, $F_{\rm D} = 450 \,\text{mN}$ and $f = 1 \,\text{Hz}$. The modulus in (a) is virtually independent of temperature in the super-elastic regime between 200 and 500 °C. The modulus in (c), however, scales with $e_4^{-1} \propto Q^{-2} \propto (T_c - T)^{-1}$.

several temperature scans were performed with $T_{\text{max}} > T_{\text{c}}$ (Fig. 5). The behaviour with $F_{\text{S}} = 200$ mN, $F_{\text{D}} = 180$ mN and f = 1 Hz (Fig. 5a and b) is qualitatively similar to that observed in Fig. 4. There is a rapid decrease in modulus between room temperature and 200 °C associated with the gradual unfreezing of the domain walls and a corresponding peak in tan δ . The heating experiment (closed circles in Fig. 5a) shows a relatively large discontinuity in the modulus at 180 °C, indicating a sudden irreversible change in the twin microstructure at this temperature. The cooling curve (open circles in Fig. 5a) is more typical of the behaviour observed in subsequent temperature scans. The value of the modulus remains roughly constant

in the super-elastic regime between 200 and 500 °C, whereas tan δ decreases gradually over this temperature interval. Between 500 °C and T_c there is a rapid increase in modulus and a rapid decrease in tan δ . This increase is due to a combination of the structural changes associated with the rhombohedral–cubic phase transition and the disappearance of the transformation twins in the high-temperature phase. Typically, the value of the storage modulus measured a few degrees above T_c is a factor of 10 higher than the minimum value observed below T_c .

The observation of a temperature-independent modulus in the super-elastic regime contrasts strongly with the behaviour observed in SrTiO₃, where the modulus



Fig. 6. The compliance (J = 1/Y') vs. temperature measured with $F_S = 500$ mN, $F_D = 450$ mN and f = 1 Hz. The step in compliance at $T = T_c$ is due to the coupling between the order parameter and the spontaneous strain, as expected for a second-order improper ferroelastic phase transition (Carpenter and Salje, 1998). The linear section below T_c is the super-elastic contribution, which scales with $e_4 \propto Q \propto (T_c - T)^{-1}$ in the saturation regime. The decrease in the compliance below 200 °C is due to domain wall freezing.

was observed to scale with $e_4^{-1} \propto Q^{-2} \propto (T_c - T)^{-1}$ (Kityk et al., 2000). This behaviour can be reproduced in LaAlO₃, however, by simply increasing the values of the static and dynamic forces (Fig. 5c and d). A plot of compliance (J = 1/Y') versus temperature measured with $F_S = 500$ mN and $F_D = 450$ mN is shown in Fig. 6. The temperature dependence can be fitted with an equation of the form:

$$J(T) = J_0 \quad \text{for } T > T_c \tag{5}$$

$$J(T) = J_0 + J_{\text{step}} + \delta J \frac{T_c - T}{T_c} \quad \text{for } T < T_c$$
 (6)

where J_0 is the intrinsic compliance of the high-temperature cubic phase, J_{step} the change in the unrelaxed compliance at $T = T_c$ due to coupling between the driving order parameter and the spontaneous strain (Carpenter and Salje, 1998) and δJ is the maximum anelastic contribution to the compliance. Values of $J_{\text{step}} = 0.0055 \text{ GPa}^{-1}$ and $\delta J = 0.214 \text{ GPa}^{-1}$ were derived, which translates to a step decrease in the storage modulus due to order parameter–strain coupling of 26 GPa at $T = T_c$ and a maximum decrease of 53 GPa

due to super-elastic softening. Hence, the magnitude of the super-elastic contribution from mobile domain walls is a factor of two greater than the intrinsic elastic softening (i.e. that which would normally be observed in high-frequency ultrasonic experiments).

After several heating and cooling cycles, the sample was removed from the DMA and the twin microstructure was re-examined under an optical microscope (Fig. 7). Whereas previously, the microstructure was dominated by $\{100\}$ twins oriented at 45° to the length of the sample and perpendicular to the surface (Fig. 2b), it was now found to be dominated by $\{110\}$ twins oriented at 45° to the length of the sample and 45° to the surface. Inclined domain walls can be easily recognised by the complex interference fringes which appear under crossed polars. Domain walls in this orientation do experience a force due to the applied stress, therefore contributing to the super-elastic softening. For example, domains I and II (Fig. 2a and Table 1) have their axes of compression and extension perpendicular to each other and can meet at a domain wall parallel to (101).



Fig. 7. Optical micrograph of the LaAlO₃ sample after repeated heating and cooling through the cubic–rhombohedral phase transition under dynamic load. Central fringes indicate the presence of $\{110\}$ domain walls at 45° to the surface. Away from the central region $\{100\}$ twins are visible.

4.3. Mechanical properties as a function of frequency

To further investigate the changes in the modulus which occur close to the domain wall freezing temperature and determine a value for the activation energy for domain wall motion, the frequency dependence of the storage modulus was measured at a range of temperatures between room temperature and 300 °C (Fig. 8a). At room temperature, the modulus is high and shows no variation with frequency (dispersion) above 5 Hz. With increasing temperature, the overall value of the modulus decreases, whereas the range of values due to dispersion increases to a maximum at 150 °C and then decreases. By a temperature of 300 °C, the modulus has reached its minimum value and the dispersion is again zero.

The frequency dependence of the modulus can be modelled quantitatively using a modified Burgers model of a linear viscoelastic solid (Jackson, 2000; Karato and Spetzler, 1990). The Burgers model consists of a number of elastic springs and viscous dashpots in series and parallel combinations. The response function under constant stress, σ , is given by:

$$J(t) = \frac{e(t)}{\sigma} = J_{\rm U} + \delta J \left[1 - \exp\left(\frac{-t}{\tau}\right) \right] + \frac{t}{\eta}$$
(7)

where J(t) is the compliance, e(t) the strain, J_U and δJ are the instantaneous (elastic) and the time-dependent (anelastic) contributions to the compliance, τ is the anelastic relaxation time (Eq. (4)) and η the steady-state Newtonian viscosity (not required for a purely anelastic relaxation). For an alternating stress with angular frequency ω , the corresponding dynamic compliance $J(\omega)$, is given by (Jackson, 2000):

$$J(\omega) = J_{\rm U} + \frac{\delta J}{1 + i\omega\tau} - \frac{i}{\eta\omega}$$
(8)

with real and imaginary components $J_1(\omega)$ and $J_2(\omega)$, respectively:

$$J_1(\omega) = J_{\rm U} + \frac{\delta J}{1 + \omega^2 \tau^2} \tag{9}$$

$$J_2(\omega) = \frac{\omega\tau\delta J}{1+\omega^2\tau^2} + \frac{1}{\eta\omega}$$
(10)

In a real material, it is usually found that a distribution of characteristic relaxation times is required to fit the experimental data, implying a range in activation energies for the viscous components of the model. Attempts to model our frequency- and temperature-dependent data using a single activation energy resulted in domain wall freezing over much too narrow a temperature range. We have therefore modified the Burgers model to account for a Gaussian distribution of activation energies, D(E):

$$D(E) = \frac{1}{\delta E \sqrt{2\pi}} \exp\left(\frac{-(E - E_{\rm av})^2}{2\delta E^2}\right)$$
(11)

where E_{av} is the average activation energy and δE the standard deviation from the mean. The response



Fig. 8. (a) Frequency dependence of the storage modulus at temperatures close to the domain wall freezing temperature (open symbols). Solid lines represent the results of a fit of the data at all temperatures simultaneously, using the modified Burgers model (Eq. (13)). Fit parameters are $E_{av} = 84.1(1)$ kJ/mol, $\delta E = 10.3(1)$ kJ/mol, $\tau_0 = 2.10(4) \times 10^{-11}$ s, $J_U = 0.011$ GPa⁻¹ and $\Delta = 10$. (b) Comparison of the calculated temperature dependence of the storage modulus for f = 1 Hz using Eq. (13) and the fit parameters derived from (a) (line) with the experimental observations (open circles).

function then becomes (Jackson, 2000):

$$J(t) = \frac{e(t)}{\sigma} = J_{\rm U} \left\{ 1 + \Delta \int_0^\infty D(E) \times \left[1 - \exp\left(\frac{-t}{\tau_0 \exp(E/RT)}\right) \right] dE \right\} + \frac{t}{\eta}$$
(12)

where Δ is the relaxation strength (ratio of anelastic to elastic strain). The real and imaginary components are:

$$J_{1}(\omega) = J_{U} \left\{ 1 + \Delta \int_{0}^{\infty} D(E) \times \left[\frac{1}{1 + \omega^{2} [\tau_{0} \exp(E/RT)]^{2}} \right] dE \right\}$$
(13)

$$J_{2}(\omega) = \omega J_{U} \Delta \left\{ \int_{0}^{\infty} \tau_{0} \exp(E/RT) D(E) \right.$$
$$\times \left[\frac{1}{1 + \omega^{2} [\tau_{0} \exp(E/RT)]^{2}} \right] dE \right\} + \frac{1}{\eta \omega}$$
(14)

Eq. (13) has been used to fit the frequency-dependent measurements at all temperatures simultaneously, yielding values of $E_{av} = 84.1(1) \text{ kJ/mol}$, $\delta E = 10.3(1) \text{ kJ/mol}$, $\tau_0 = 2.10(4) \times 10^{-11} \text{ s}$, $J_U = 0.011 \text{ GPa}^{-1}$ and $\Delta = 10$. The results of the fit are shown as the solid lines in Fig. 8a. The internal consistency of the fit parameters was tested by using them to calculate the temperature dependence of the storage modulus with a frequency of 1 Hz and comparing it to the experimental observations (Fig. 8b). Excellent agreement between the two sets of data is observed, without any change in the fit parameters necessary.

The activation energy of 84.1 kJ/mol is very close to the activation energy of 87–106 kJ/mol commonly associated with oxygen vacancy diffusion in oxide ceramics (Wang et al., 2001; Yan et al., 1999; Wang and Fang, 2002). We are confident, therefore, in attributing the pinning of domain walls to the presence of oxygen vacancies in LaAlO₃. Understanding the mobility and concentration of oxygen vacancies as a function of temperature and pressure will, therefore, be crucial in determining how the seismic properties of mantle minerals are influenced by the presence of twins (see Section 5).

4.4. Mechanical properties as a function of force

The non-linearity of the mechanical response noted earlier (Fig. 5) was investigated further by performing dynamic force scans at a range of temperatures between room temperature and 500 °C (Fig. 9). For a perfectly linear response, the storage modulus should be independent of F_D . At room temperature, the modulus is constant for $F_D > 100$ mN but increases significantly at lower forces. This is believed to reflect an instrumental artefact caused by the decreasing sensitivity of the measurements when the amplitude of deflection is smaller than 1 mm. At 100 °C, the modulus is constant between 100 and 350 mN and then decreases abruptly. This is accompanied by an abrupt increase in tan δ (Fig. 9b). These sudden changes correspond to the unpinning of domain walls above a critical value of F_D (F_D^{crit}). With $F_D < F_D^{crit}$, domain walls remain pinned and the compliance is determined by the intrinsic compliance of the lattice plus larger components due to the susceptibility of the pinning potential (i.e. reversible displacements of the domain walls occur by an amount inversely proportional to the curvature of the pinning potential) and the bending of domain walls between pinning sites. With $F_{\rm D} > F_{\rm D}^{\rm crit}$, domain walls are able to escape their pinning sites and super-elastic softening is observed. The value of $F_{\rm D}^{\rm crit}$ decreases with increasing temperature, as thermal fluctuations enable domain walls to unpin. The maximum instantaneous value of the applied force required to unpin the domain walls (= $2.2 F_D^{crit}$) is shown as a function of temperature in Fig. 10. No unpinning was observed at room temperature up to a maximum applied force of 1760 mN. By 500 °C, no clear value of $F_{\rm D}^{\rm crit}$ could be identified (i.e. unpinning is dominated by thermal fluctuations).

Values of the modulus and $\tan \delta$ vary significantly as a function of F_D in the super-elastic regime



Fig. 9. Dynamic force dependence of (a) the storage modulus and (b) $\tan \delta$ between room temperature and 500 °C. For clarity, modulus and $\tan \delta$ curves have been offset vertically as a function of temperature. Non-linearity of the modulus below dynamic forces of 100 mN is thought to be an instrumental artefact. The sudden decrease in modulus and increase in $\tan \delta$ above a critical value of the dynamic force is associated with the unpinning of domain walls.



Fig. 10. Variation in the maximum applied force required to unpin domain walls as a function of temperature. Line is a guide to the eye.

(Fig. 9). To understand the origin of this non-linear behaviour it is more useful to plot the raw data as $F_{\rm D}$ versus $u_{\rm D}$ (Fig. 11). These plots can either be interpreted as stress-strain curves or (rotated through

 90°) the positive quadrant of the ferroelastic hysterisis loop. At room temperature, the stress-strain curve is a straight line, corresponding to an ideal (Hookian) elastic material with constant modulus. At higher temperatures, the stress-strain curves are linear for $F_{\rm D} \ll F_{\rm D}^{\rm crit}$, but deviate increasing from linearity as the 'yield-point' associated with the unpinning of domain walls is reached. This deviation from linearity may be related to the anharmonicity of the pinning potential as the domain walls begin to pull away from their pinning sites. At temperatures between 200 and 400 °C (i.e. well above the domain wall freezing temperature but significantly less than $T_{\rm c}$) the stress-strain curves show a well-defined linear section at $F_D > F_D^{crit}$. In this super-elastic regime, the stress-strain curves are essentially coincident and have a slope which is a factor of 10 smaller than the slope at $F_{\rm D} < F_{\rm D}^{\rm crit}$. At some higher value of $F_{\rm D}$, we enter a third regime where the slope of the stress-strain curve is effectively infinite. In this regime, any increase in $F_{\rm D}$ produces no further increase in $u_{\rm D}$.



Fig. 11. Dynamic force amplitude, F_D , vs. dynamic deflection amplitude, u_D at f = 1 Hz and temperatures from (a) room temperature to 200 °C and (b) 200–500 °C. The elastic regime occurs for $F_D < F_D^{crit}$. Domain walls are pinned and the slope of the force–deflection curve is determined by the intrinsic stiffness of the lattice. The super-elastic regime occurs for $F_D < F_D^{crit}$. Domain walls unpin and displace by an amount determined by the balance between applied force and the anelastic restoring force. The force–deflection curve is linear with slope 1/10 of that in the elastic regime. Note the coincidence of the force–deflection curves in the super-elastic regime between 200 and 500 °C. The saturation regime occurs when adjacent domain walls come into contact with each other and no further displacements are possible. The constant value of u_D in the saturation regime (u_D^{sat}) is given by Eq. (17) and scales with the spontaneous strain.



Fig. 12. Schematic illustration of how the orientation of domain walls change under load in three-point bend geometry. (a) In the unstressed case, the beam is straight and the domain walls are in their preferred orientation (in this case at 45° to the sample surface, as in Fig. 7). Positive domains have their axes of extension parallel to the length of the sample. Negative domains have their axes of compression parallel to the length. (b) In the stressed case, negative domains grow at the top surface and positive domains grow at the bottom surface, leading to the rotation of adjacent walls in opposite senses. Saturation occurs when the domain walls at the centre of the sample come into contact.

This hardening effect is caused by the transition from a multi-domain state to a mono-domain state at the top and bottom surfaces of the sample (saturation). Fig. 12a shows an unstressed beam containing parallel domain walls at 45° to the surface. The twin domains marked "+" have their axis of extension parallel to the length of the sample, whereas those marked "-" have their axis of compression parallel to the length. As the sample deflects in response to an applied force, contraction of the top surface is accommodated by growth of the negative domains, while expansion at the bottom surface is accommodated by growth of the positive domains. The net effect is that adjacent domain walls rotate in opposite senses (Fig. 12b). If the force is large enough, then the domain walls come in contact with each other at the top and bottom surfaces and no further displacements can take place (in practice there will be a small increase in $u_{\rm D}$ at high forces due to the intrinsic compliance of the lattice).

The amplitude of the deflection in the saturation regime (u_D^{sat}) varies greatly with temperature, increasing to a maximum at 200 °C and then decreasing with temperature as T_c is approached (Fig. 11b). The deflection is proportional to the longitudinal strain at the top surface of the crystal (*e*):

$$u_{\rm D} = \frac{l^2}{6t}e\tag{15}$$

The longitudinal super-elastic strain due to domain wall motion at the top surface of the crystal (e_{se}) is given by:

$$e_{\rm se} = N(e_{\rm A}'' - e_{\rm B}'')\Delta x''$$
 (16)

where N is the number of domain walls per unit length, e''_{A} and e''_{B} are the components of spontaneous strain parallel to the length of the sample in adjacent domains A and B and $\Delta x''$ is the distance moved by each domain wall. The average distance between the domain walls is 1/N and the domain wall displacement at saturation is, therefore, $\Delta x'' = 1/2N$. The deflection at saturation (neglecting the intrinsic elasticity of the lattice) is then:

$$u_{\rm D}^{\rm sat} = \frac{l^2}{12t} (e_{\rm A}'' - e_{\rm B}'') \tag{17}$$

Hence, u_D^{sat} scales linearly with the spontaneous strain, which explains the decrease in u_D^{sat} between 300 °C and T_c (Fig. 11b). The increase in u_D^{sat} between 150 and 200 °C may reflect a difference in the spacing of the domain walls in these two measurements. Although Eq. (17) predicts that u_D^{sat} is independent of N, this only holds if the domain walls are uniformly spaced over the whole length of the sample. Microscopic examination of the samples revealed, however, that twins were generally concentrated at the centre of the sample (where the radius of curvature is greatest), leaving much of the sample twin free. In this case u_D^{sat} is sensitive to both the spontaneous strain and the spacing of domain walls.

5. Discussion

5.1. Change in the temperature dependence of mechanical properties as a function of force

It is clear from Eq. (17) and Fig. 11 that, in the saturation regime, the storage modulus will scale with $e_4^{-1} \propto Q^{-2} \propto (T_c - T)^{-1}$ (Figs. 5c and 6).



Fig. 13. Simple two-domain model of domain wall rotation in three-point bend geometry. The e''_A and e''_B are the components of spontaneous strain parallel to the length of the sample in the two domains A and B. The variable y is the vertical distance from the neutral axis (dashed line). The $\Delta x''$ is the component of domain wall shift parallel to the length of the sample at a given value of y.

In the super-elastic regime, however, the modulus is observed to be independent of temperature. This can be explained in terms of a local model of the domain wall energy. To avoid the complexities of wall interactions, we will consider a simple model containing two twin domains separated by a single domain wall (Fig. 13). To avoid further complexities due to the three-point bend geometry we assume that the displacement of the domain wall, $\Delta x''$, is much smaller than the length of the sample, *l*.

A force, F_D , is applied to the sample in three-point bend geometry, resulting in a deflection, u_D . The longitudinal strain at a distance y from the neutral axis is given by:

$$e = \frac{12u_{\rm D}}{l^2}y\tag{18}$$

If this strain is assumed to be taken up entirely by the displacement of the domain wall, then substituting N = 1/l into Eq. (16) and combining with Eq. (18) leads to:

$$\Delta x'' = \frac{12u_{\rm D}}{l(e''_{\rm A} - e''_{\rm B})}y$$
(19)

Hence, the domain wall displacement is proportional to *y*, resulting in a simple rotation of the wall away from its preferred orientation (Fig. 13).

In the absence of any restoring force, the domain wall will continue to rotate under the influence of the applied force, leading to viscoelastic behaviour (i.e. $u_{\rm D} \rightarrow \infty$ as $t \rightarrow \infty$). In the presence of a restoring force, however, $u_{\rm D}$ relaxes towards an equilibrium value as $t \to \infty$ (anelastic behaviour). Restoring forces are caused predominantly by the pinning of domain walls by defects and the interaction between the neighbouring domain walls (Wang et al., 1996). The latter is neglected in this simple two-domain model, while the effect of pinning is negligible within the super-elastic regime. A third source of restoring force is the elastic anisotropy energy associated with rotating the domain wall away from its preferred orientation (Salje and Ishibashi, 1996). As the domain wall rotates, a lattice mismatch between the adjacent domains develops and an additional 'compatibility' strain is required in each domain to preserve the continuity of the lattice (Tsatskis et al., 1994). The anisotropy energy per unit volume is equal to the elastic energy associated with this compatibility strain. For small displacements, the compatibility strain is proportional to the spontaneous strain multiplied by the twin rotation angle (Salje and Ishibashi, 1996) and the anisotropy energy can be written in its simplest form as:

$$\Delta E_{\text{anisotropy}} = V U_{\text{anisotropy}} e_4^2 \left(\frac{\mathrm{d}\Delta x''}{\mathrm{d}y}\right)^2 \tag{20}$$

where V is the volume, $U_{\text{anisotropy}}$ is a combination of the intrinsic elastic constants and $d\Delta x''/dy$ is the slope of the domain wall relative to its preferred orientation (i.e. the domain wall rotation angle).

Differentiating Eq. (19) and substituting into Eq. (20), the force required to bend the sample can be calculated:

$$F_{\rm D} = \frac{d\Delta E_{\rm anisotropy}}{du_{\rm D}} = \frac{288VU_{\rm anisotropy}e_4^2}{l^2(e_{\rm A}'' - e_{\rm B}'')^2}u_{\rm D}$$
(21)

The storage modulus is then calculated from Eq. (3):

$$Y = \frac{l^3}{4t^3w} \frac{F_{\rm D}}{u_{\rm D}} = \frac{72l^2 U_{\rm anisotropy} e_4^2}{t^2 (e_{\rm A}'' - e_{\rm B}'')^2}$$
(22)

If the orientation of the applied stress is defined by the set of direction cosines, a_i , with respect to the crystallographic axes of the high-temperature cubic phase, then the quantity $(e''_A - e''_B)$ reduces to:

$$(e''_{\rm A} - e''_{\rm B}) = 4e_4(a_1a_2 + a_2a_3)$$
(23)

and the dependence of the storage modulus on the spontaneous strain disappears:

$$Y = \frac{9l^2 U_{\text{anisotropy}}}{2t^2 (a_1 a_2 + a_2 a_3)^2}$$
(24)

5.2. Implications for anelasticity in the earth

Domain microstructures have the potential to modify the velocities and attenuation of both P and S waves. The overall quality factor of a rock, Q_Y^{-1} , is given by:

$$Q_Y^{-1} = \left(\frac{G}{3K+G}\right) Q_K^{-1} + \left(\frac{3K}{3K+G}\right) Q_G^{-1} \quad (25)$$

where *K* is the bulk modulus, *G* the shear modulus and Q_G^{-1} and Q_Y^{-1} are the losses in shear and hydrostratic compressional deformation respectively. This reveals a strong weighting for loss in shear. Dewaele and Guyot (1998) have shown that the attenuation of the compressional modulus is near zero in the lower mantle, while that of the shear modulus dominates. This is also the case for attenuation mechanism proposed here, since the loss due to domain wall motion contributes exclusively to Q_G^{-1} . In rocks where domain wall motion is the dominant cause of attenuation we therefore expect to see $Q_K^{-1} \ll Q_G^{-1}$.

How likely is it that twin microstructures exist in the perovskites of the lower mantle? Transmission electron microscopy observations by Wang et al. (1990, 1992) and Martinez et al. (1997) demonstrated the existence of multiple twins in synthetic run products annealed under lower mantle conditions, probably developing on quenching through a phase transition. However, the presence of domain walls need not imply the existence of a phase transition along the mantle geotherm. Such twin microstructures may develop on annealing at temperatures well before any potential transition occurs. This is especially true for material annealed in the presence of non-hydrostatic stress or subjected to short time scale seismic stress. On the other hand, perovskite material embedded in a mantle deforming under the ambient tectonic stress might reach saturation if the accumulated tectonic strain is sufficient, in which case each crystal would become a poled mono-domain grain. While it is therefore unlikely that twins pervade the entire lower mantle, there may be regions in the lower mantle where conditions favour their presence. In this case, one would expect to observe heterogeneous patterns of seismic attenuation, coupled with low seismic velocities.

To assess the importance of domain wall motion on the mechanical properties of minerals in the Earth. we must consider how the stress, strain and frequency conditions of our laboratory experiments compare to those involved in the propagation of the seismic waves. The amplitude of the strain involved in seismic wave propagation is crucial, since it determines whether the material is in the elastic, super-elastic, or saturation regimes. The boundary between the elastic and the super-elastic regimes is defined by the value of $u_{\rm D}$ at the yield point of the force-deflection curves (Fig. 11), which decreases from 0.6 μ m at 100 °C to 0.1 μ m at $500 \,^{\circ}\text{C}$ ($f = 1 \,\text{Hz}$). The corresponding maximum longitudinal strain at the point of unpinning (i.e. that measured at the top and bottom surfaces of the crystal) is between 7.49×10^{-5} and 1.24×10^{-5} (Eq. 15). This is larger than the strain amplitude of a typical seismic wave $(10^{-8}$ to 10^{-6} : Karato and Spetzler, 1990). implying that the material would remain in the elastic regime. However, the strain at unpinning is sensitive to both frequency and temperature, so at lower seismic frequencies and higher temperatures, the strain required to unpin domain walls will be significantly less-easily within the range of seismic waves. On the



Fig. 14. (a) Anelastic relaxation time vs. depth in Earth calculated assuming an activation energy at atmospheric pressure of 84 kJ/moland a pre-exponential constant of 2.1×10^{-11} s. The pressure and temperature dependence of the activation energy was calculated using Eqs. (26) and (27) and values of K_0 , K' and \dot{K} appropriate for (Mg, Fe)(Si, Al)O₃ perovskite (Duffy and Anderson, 1989). (b) Anelastic relaxation time vs. E_0 , calculated at a depth of 1000 km and a constant pre-exponential factor of 2.1×10^{-11} s. A value of $E_0 = 150 \text{ kJ/mol}$ is sufficient to yield a relaxation time equivalent to that observed in LaAlO₃ at 500 °C and atmospheric pressure, corresponding to a value of tan $\delta = 0.1$.

other hand, it can be assumed that the strains involved are very much less than those required to produce saturation.

For a given mechanism to contribute significantly to seismic attenuation, the relaxation time must be close to the period of seismic waves $(10^{-2} < \tau < 10^4 \text{ s})$. The relaxation time for domain wall motion as a function of depth in the Earth is plotted in Fig. 14a, assuming that the mechanism of domain wall pinning in (Mg, Fe)(Si, Al)O₃ perovskite is the same under mantle conditions as that observed in single crystal LaAlO₃ at atmospheric pressure. The pressure dependence of the activation energy, *E*, was estimated using the equations (Keys, 1958):

$$E = E_0 + PV_a \tag{26}$$

$$V_{a} = \frac{4E_{0}}{K_{0} + K'P + \dot{K}T}$$
(27)

where E_0 is the activation energy at atmospheric pressure, V_a the activation volume for oxygen vacancy diffusion, K_0 the bulk modulus at atmospheric pressure and temperature and K' and K are the first derivatives of the bulk modulus with respect to pressure and temperature, respectively. Values of $K_0 =$ 266 GPa, K' = 3.9 and K = -0.031 GPa/K for (Mg, Fe)(Si, Al)O₃ perovskite were taken from Duffy and Anderson (1989).

Relaxation times decrease rapidly with increasing depth in the upper mantle, but are to a first approximation constant within the lower mantle. For a value of $E_0 = 84 \text{ kJ/mol}$, relaxation times of $\sim 3 \times 10^{-8} \text{ s}$ are predicted within the lower mantle, indicating that twins, if present, would be extremely mobile and able to contribute readily to super-elastic softening. We would not normally consider such rapid processes as important sources of attenuation, however. Having said that, the value of $\tan \delta = 0.1$ observed at 500 °C and 1 Hz (Figs. 4 and 5) is still large, despite the low relaxation time of 10^{-5} s at this temperature. This observation suggests that attenuation due to domain wall motion is still significant for relaxation times well below the period of the applied force. An activation volume of $10^{-6} \text{ m}^3/\text{mol}$ increases the activation energy by 1 kJ/mol for every 1 GPa of pressure. Experimental determinations of the activation volumes for point defect and cation diffusion in mantle minerals are scarce. Eq. (27) provides an estimate of the activation volume at atmospheric pressure of $\sim 1.3 \times 10^{-6} \text{ m}^3/\text{mol}$. Activation volumes of $2-3 \times 10^{-6} \text{ m}^3/\text{mol}$ for cation diffusion in MgSiO₃ and MgO were estimated by Yamazaki and Karato (2001). Fig. 14b shows the relaxation time at 1000 km depth as a function of E_0 . A modest increase in E_0 to 150 kJ/mol is sufficient to produce relaxation times equivalent to those observed in the current experiments and hence equivalent values of tan δ . In any case, our results highlight the fundamental importance of microstructure in determining the low-frequency mechanical properties of minerals and point towards a new range of measurements which need to be investigated in the Earth sciences.

Acknowledgements

This study was funded by the EPSRC under grant GR/M49816. The authors are grateful to Jim Scott and Ekhard Salje for useful discussions and to Ian Jackson and François Guyot for their helpful reviews of the manuscript.

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