Dislocation dissociation and stacking-fault energy calculation in strontium titanate

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The dislocation microstructure of strontium titanate plastically deformed below room temperature shows dipolar configurations of $a\langle 1\,1\,0\rangle$ screw dislocations. The dipole height is so small that dipole annihilation is expected. Here we show why this is inhibited. By high-resolution transmission electron microscopy observations we find that in such dipoles each dislocation is dissociated into two collinear $a/2\langle 1\,1\,0\rangle$ partials on a $\{1\,1\,0\}$ plane. Elasticity theory calculations provide a stacking-fault energy value of 340 ± 90 mJ m^{-2}. Finally, we discuss the effects of this dissociation process on the mechanical behaviour.

Strontium titanate is one of the most important oxides due to its wide use in technology. It is mainly used as a dielectric material in capacitors but is also used for substrates for superconductors [1,2]. Whereas the influence of point defects and grain boundaries on the ionic and electronic conductivity has been studied extensively [3], a detailed study of dislocations was performed only recently [4–10]. Apart from their role in plastic deformation, dislocations in perovskites can also act as easy trans- port paths for point defects and possibly even play a role in the seismic behaviour of the earth's mantle [11]. The mechanical behaviour of strontium titanate has been investigated in a wide temperature range (46–1811 K), and it exhibits a pronounced ductile-to-brittle-to-ductile transition (DBDT) between 1000 and 1500 K [4], low con- stant flow stress between 300 and 1000 K, and increasing flow stress towards low temperatures [5,6]. The high-tem- perature behaviour has been studied in great detail [7,8] and it was demonstrated that the DBDT can be explained by the climb dissociation of $a\langle 1\,1\,0\rangle$ edge dislocation on a $\{1\,1\,0\}$ plane, according to

$$a\langle 110\rangle \rightarrow a/2\langle 110\rangle + a/2\langle 110\rangle + \text{stacking fault} \qquad (1)$$

From the dissociation width (2.5 ± 0.3 nm) an upper limit of the stacking-fault energy (SFE) of 720 ± 280 mJ m^{-2} was reported. Here we will concen- trate on the low-temperature behaviour. In a first step to understanding the low-temperature behaviour we analyzed the dislocation microstructure. We find that it comprises mainly straight $a\langle 1\,1\,0\rangle$ screw dislocations arranged in dipoles [6,7] and that the screw dislocations are dissociated on the $\{1\,1\,0\}$ plane. This dissociation al- lows us to derive more accurate values of the SFE than reported before. It is worth emphasizing that the disso- ciation process has sensitive effects on the mechanical properties, especially on the flow stress [9,10]. Accurate values of SFEs are therefore important for understand- ing the mechanical behaviour of materials.

Quadrangular prisms (2.5 × 2.5 × 6) mm^3 of single- crystalline $SrTiO_3$ were deformed in compression [6]. The specimens, containing as major impurities Ca, Ba, and Mg in a concentration of 30–200 at. ppm, were prepared by sawing and grinding. All side faces were polished to avoid crack initiation. The tests were per- formed with a constant displacement rate ($e\_ \sim 10^{-4}$ s^{-1}). Here we only discuss specimens compressed parallel to the $\langle 0\,0\,1\rangle$ direction. After plastic straining, light-optical micrographs using polarized light attested the activation of the ⟨1 1 0⟩{1 1 0} slip systems. Specimens for transmission electron microscopy (TEM) were prepared parallel to the most activated slip plane for weak-beam dark-field (WB-DF) imaging and perpendicular to the slip plane to perform high-resolution TEM (HRTEM) observations. TEM specimens were prepared by standard procedures involving grinding, dimpling, polishing, and ion milling in a Gatan precision ion-polishing system. Dislocation microstructure was investigated by WB-DF in a Philips CM200 microscope, operating at 200 kV, which allows large tilts. For HRTEM observations, a JEOL JEM-4000EX microscope with a point resolution of 0.17 nm was used, operating at 400 kV.

WB-DF observations reveal that the dislocation microstructure of samples plastically deformed below room temperature comprises essentially a⟨1 1 0⟩ screw dislocations. Most often closely spaced parallel disloca- tions are observed. By taking WB-DF images with opposite diffraction vectors, these parallel dislocations were identified as dipoles (Fig. 1). Trace analyses using large-angle tilt show that the dipole plane, i.e. the plane containing the two dislocation lines, is close to {1 0 0}, and the dipole height is 5–15 nm, which is surprisingly small. At such small heights the attractive interaction stress is very high (several GPa). The fact that this does not lead to mutual annihilation of the dislocation pair indicates that some mechanism involving the dislocation core structure might play a role for the dipole stability. Because the core structure cannot be resolved by the weak-beam technique, we conducted extensive HRTEM studies of the dislocation cores by imaging the dipoles parallel to the dislocation lines at high magnification. Figure 2 shows the most frequently observed configuration. It consists of two horizontal lines of dark contrast of about 3–5 nm in length parallel to the {1 1 0} plane. These two lines are separated almost parallel to the {1 0 0} plane by sometimes only a few nanometers (Fig. 2a). A Burgers circuit around the dark lines reveals that no extra atom planes are inserted. Therefore, the dark lines must be screw dislocations dissociated on the {1 1 0} plane according to reaction (1). This HRTEM result is fully consistent with the dipole config- urations observed by WB-DF (Fig. 1).

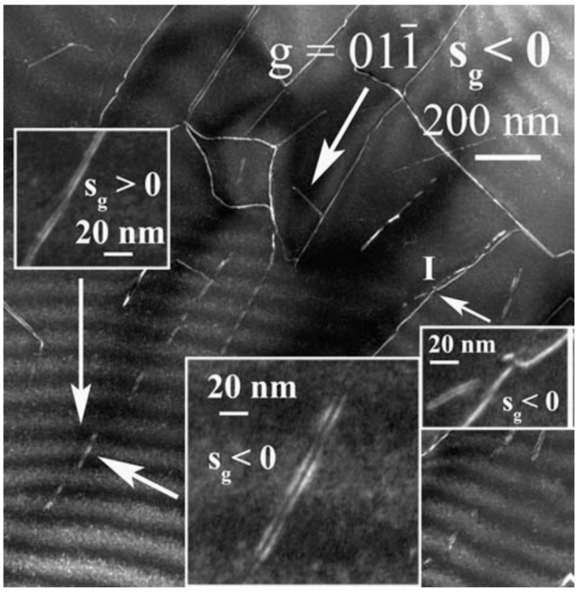

Figure 1. Weak-beam micrograph of $SrTiO_3$ strained by about 3% at 113 K along the ⟨1 0 0⟩ compression axis. The TEM foil is parallel to the {0 1 1} plane, but here it is tilted by about 50° around the [01 ¯1] direction. Two inserts show a very narrow dipole observed by different sign of s_g, and the insert to the right shows the interaction, marked by I, between a dislocation and these narrow dipoles.

It is worth examining the forces acting in such a dipolar configuration (Fig. 2c). First, there is a repulsive interaction force, F^R, between the partials, which is bal- anced by the stacking fault generated between them. Second, in the case of dipoles the partials bordering one stacking fault interact with the partials bordering the other fault. Because the two dissociated dislocations of a dipole have anti-parallel Burgers vectors they attract each other by the interaction force, F^I.

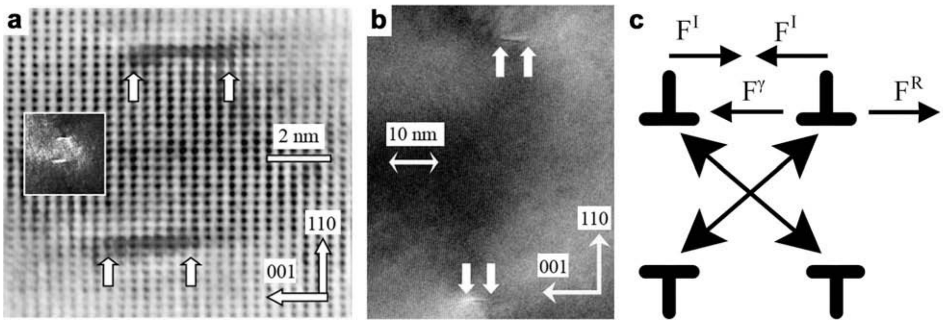

Figure 2. High-resolution micrographs of $SrTiO_3$ deformed below room temperature, showing two dipolar configurations in which each $a\langle 1\ 1\ 0\rangle$ screw dislocation is dissociated into two $a/2\langle 1\ 1\ 0\rangle$ screw partials. The equilibrium distance between the partials depends on the dipole height, being smaller in the narrow dipole (a) than in the wide one (b). A scheme with the repulsive (F^R) and attractive (F^I) forces between partials, and the one due to the stacking fault is given in (c).

Table 1. Dipole heights, dissociation widths and apparent SFE calculated considering only the repulsive interaction force between partials involved in the dissociation process.

Dipole height (nm)	Dissociation width (nm)	Apparent SFE (mJ/m^2)
14–48	4.2 ± 0.4	340 ± 40
8–14	3.4 ± 0.4	430 ± 50
6–8	3.0 ± 0.2	480 ± 30

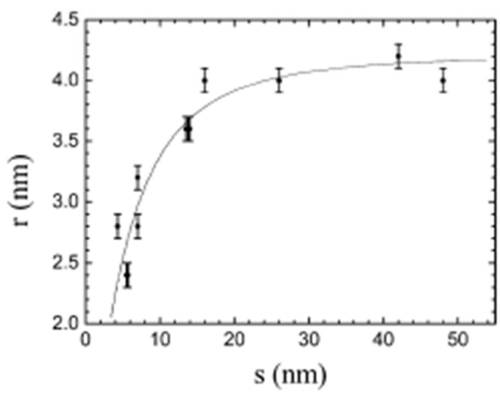

Figure 3. Plot of the dipole height (s) against the equilibrium distance between partials (r) after the dissociation process. The best fit of expression (2) to the experimental data is also shown. Note that a plateau for the dissociation width is reached for dipole heights above about 20 nm.

From the HRTEM images (two of them are shown in Fig. 2a and b) we found that the dissociation width be- tween partials is moderately but perceivably modified by the presence of the other couple of partials (Table 1), i.e. the dissociation width depends on the dipole height. This is clearly due to the attractive interaction force, F^I, which tends to reduce the dissociation width. If this force was neglected, the SFE extracted from the dissoci- ation width would depend on the dipole height, as shown in Table 1, and only for large heights would the extracted SFE correspond to the true value. To determine the true value of the SFE, we use Eqs. (5)–(17) and (5)–(18) of Ref. [12] for the interaction force per unit length between two parallel dislocations. Then, the equilibrium separa- tion, r, for two screw partials bordering a stacking fault, taking into account the attractive interaction coming from the other couple of screw partials, both with anti- parallel Burgers vector with regard to the former pair, is given by the following expression:

$$\frac{\mu b^2}{2\pi r}\left(1-2\left(\frac{r^2}{r^2+s^2}\right)\right)-\gamma=0 \tag{2}$$

where s is the dipole height, b is the modulus of the Burgers vector (= 2.76 nm), and l is the shear modulus (112.5 GPa) [13]. From a least-squares fit of expression (2) to the various (r_i, s_i) pairs measured experimentally (Fig. 3), we obtain the SFE on the {1 1 0} plane as $c_{\{110\}}$ = 340 ± 90 mJ m^{-2}. As expected, this value is close to the apparent value for the widest dipoles (Ta- ble 1), where the effect of F^I on the dissociation width is weakest. The plot shows that for dipole widths above about 20 nm the dissociation width reaches a plateau of around 4 nm.

As mentioned above, Zhang et al. [8] obtained an upper limit of the {1 1 0} SFE of 720 ± 280 mJ m^{-2}. Their data were extracted from climb-dissociated edge dislocations forming a low-angle grain boundary. Only an upper limit was given because the separation of the dislocations (6.6 ± 0.3 nm) forming the grain boundary (all having parallel Burgers vectors) was of similar magnitude as the width of the climb dissociation (2.5 ± 0.3 nm). Taking the repulsive interaction among the dislocations forming the grain boundary into account, we performed calculations based on linear elasticity and find an SFE of 500 ± 100 mJ m^{-2} for the dissociation process (1). Although this value is higher than the value obtained for the screw dislocations of the strained material studied here, it is within the error bar.

Nevertheless, we note that there were other SFE measurements performed in $SrTiO_3$ by means of weak-beam transmission electron microscopy [14,15]. Mao and Knowles [14] found a {1 0 0} stacking fault habit plane and its corresponding energy was deduced as 145 ± 15 mJ m^{-2} if dissociation takes place by glide and 245 ± 30 mJ m^{-2} if dissociation is by climb. Matsunaga and Saka [15] report a value of 136 ± 15 mJ m^{-2} for the {1 1 0} plane. All these SFEs are well below the SFE values reported here, and also far below theoretical data [16,17]. In particular, the very low SFE value for the {1 0 0} plane is contrary to theoretical data which show a ratio $SFE_{\{100\}}/SFE_{\{110\}}$ of about 3. A possible explanation for this discrepancy could be that the dislocation pairs observed in Refs. [14] and [15] were in fact dipoles, i.e. no dissociated dislocations. Unfortunately this was not checked, e.g. by imaging with opposite diffraction vectors. Because the dipole height is larger than the dissociation width, the apparent SFEs are then lower than the real values.

The fact that we found very narrow dipoles to be sta- ble indicates that the SFE on planes inclined to the {1 1 0} plane is considerably higher than $SFE_{\{110\}}$. This is in agreement with ab initio calculations [16], which show that the ⟨1 1 0⟩{1 1 0} stacking fault is the lowest in strontium titanate. However, the quantitative value is found to be a factor of at least two higher than our experimental values. This is also confirmed by DFT calculations of other authors [17]. The possible reason for this discrepancy is presently under study.

The arrangement of dissociated dislocations as shown in Figure 2 has implications on the stability of the dipole. It is known from first-principles calculations [16,17] that the SFE for non-{1 1 0} planes is much higher than for the {1 1 0} plane. Then, dipole annihilation is restricted because the dissociated dislocation cannot move perpendicular to the stacking-fault plane. This means that for annihilation the two partials need to constrict, e.g. by thermal activation or external stresses. After constriction the screw dislocation would have to slip on a non-{1 1 0} plane in order to annihilate with the second screw dislocation. These constrictions have been indeed observed, leading to local dipole annihilation due to the high inter- action forces and the formation of dislocation loops, as has been reported by Sigle et al. [7].

Dipoles and loops do not contribute to plastic defor- mation; rather they form an obstacle to other disloca- tions, thus contributing to work hardening [18]. So the fact that in $SrTiO_3$ dipoles are found to be stable even at surprisingly small height leads to a high dipole density, thus increasing the obstacle density for the glide of other dislocations and as a consequence to an in- crease in work hardening. An example can be observed in Figure 1 marked by character I and magnified in the insert to the right, where a dislocation is interacting with some of these narrow dipoles.

These obstacles can be overcome mainly by two dif- ferent processes, i.e. by glide or by cross-slip. Sketches in Figure 4a–c illustrate the case in which the obstacle density is not very high. Then, when the dissociated dislocation meets an obstacle, a dislocation segment interacts and stops if the resolved shear stress is not strong enough. But the rest of the dislocation continues its glide, surrounds the obstacle and finally leaves a loop behind. Note that in this case dissociation has no influence on the obstacle overcoming.

However, this process cannot take place for all those dislocations that meet an obstacle density that is so high that there are no long enough dislocation segments to glide. This value can be estimated considering that the resolved shear stress *s* must be higher than the maxi- mum value for the line tension σ_0, given by Eq. (4.30) from [19]:

$$\tau \geqslant \tau_0 \approx \frac{\alpha\mu b}{d} \tag{3}$$

where $\alpha \approx 0.5–1.0$ and *d* is the distance between obsta- cles. Then taking the average distance between dipoles *d* 6 400 nm, as we can see in Figure 1, the line tension is σ_0 P 100 MPa, which is almost the flow stress. Since this distance is going to be reduced with deformation, soon dislocations can no longer overcome them by glide. It is worth emphasizing that this value of *d* is not so far from what is observed in Figure 1. Under these condi- tions cross-slip is the only mechanism for overcoming obstacles, especially at low temperature where diffusion is slow. Otherwise, this dislocation contributes to the work hardening since it is sessile and becomes an obsta- cle for the glide of other dislocations.

As we have discussed before, partial dislocations can- not move out of the slip plane because of the high stacking-fault energy on non-{1 1 0} planes. This means that partial dislocations have to recombine to be able to cross-slip and then overcome these obstacles. After that, they could cross-slip again to another {1 1 0} plane and then dissociate, as we show in the sketches in Figure 4d–f.

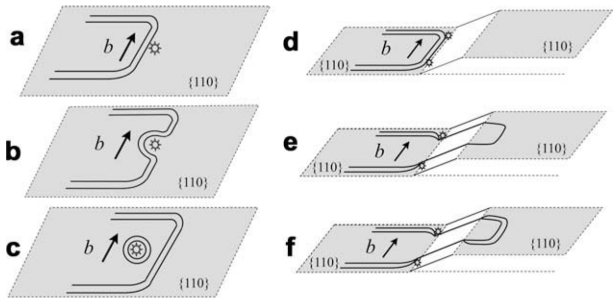

Figure 4. Dissociated dislocation overcoming an obstacle, like an impurity or another dislocation, represented by a star. In sketches (a– c) the obstacle is overcome by glide. However, in (d–f) the obstacle density is high enough that the only way for dislocations to continue its glide is by cross-slip, but before a recombination process is required.

On the other hand, it is reasonable to assume that the recombination process is thermally activated, because the dissociation width fluctuation and consequently the probability of the dissociation to be temporally can- celled increases with temperature. Then, major work hardening below room temperature should be expected. One can find some evidences for this tendency in Fig- ure 3 in Ref. [5], despite the fact that the samples were not strained enough to observe clearly this behaviour.

On the other hand, we would like to remark that Taeri- Baghbadrani et al. [6] found that the work hardening in- creases with temperature at high temperatures in regime A (see Fig. 1 in their work). However, this is not in contradiction with our results since the dislocation microstructure below room temperature is completely different at high temperatures in regime A, as it is shown in Ref. [5]. Finally, with regard to the critical resolved shear stress the only obstacles that could impede the activation of the ⟨1 1 0⟩ dislocation sources is the presence of impurities or the pre-existent dislocation density q_0 in the material before the tests. The former cannot play a role because of the low impurity concentration (30– 200 at. ppm) in this material. A typical value for the latter is $q \sim 10^8$ m^{-2} [20]. Since the average distance between dislocations d is given by q_0[20], we obtain $\bar{d}$ ~ 100 lm, which is much larger than d 6 400 nm calculated above. So we can conclude that the dissociation process by glide reported here should have no influence on the critical resolved shear stress.

In summary, strontium titanate specimens strained below room temperature were investigated by the weak-beam technique, showing a microstructure comprising mainly screw dislocations arranged in dipoles whose height is often surprisingly small. HRTEM observations revealed that each screw dislocation is dissociated into two collinear partials, thus impeding their expected annihilation. A correlation between the dissociation width and the dipole height was observed and ta- ken into account to calculate the SFE. The value obtained was found to be comparable to literature val- ues extracted from climb-dissociated edge dislocations. On the other hand, effects of the dissociation process on the mechanical behaviour have been discussed. We find that dissociation leads to an increase of the work hardening due to the inhibition of partials to cross-slip. However, dissociation by glide has no influence on the critical resolved stress below room temperature.

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