Screw dislocation in zirconium: An ab initio study

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Plasticity in zirconium is controlled by 1/3(1210) screw dislocations gliding in the prism planes of the hexagonal close-packed structure. This prismatic and not basal glide is observed to be linked to the ratio of the corresponding stacking fault energies, which in turn is controlled by the electronic structure. In particular, Legrand5 used a tight binding model to show that prismatic slip in transition metals of the IV B column (Zr, Ti, Hf) originates from the electronic filling of the valence d band. As a consequence, it appears necessary to take into account the anisotropy of the d orbital, and hence the angular dependence of the atomic bonding, to model dislocations in these transition metals. One cannot therefore rely on central forces empirical potential and needs to take account of the electronic structure. Tight binding models7,8 or ab initio calculations3–13 show indeed that a 1/3(1210) screw dislocation, either in Zr or in Ti, spreads in prism planes, in agreement with the prismatic glide observed experimentally. But none of these atomistic simulations calculate the Peierls stress of a screw dislocation. According to some authors,7,14 its core structure is not completely planar, which may be the cause of a high Peierls stress.

It is true, experimentally, that screw dislocations glide with difficulty compared to other dislocation characters in zirconium or titanium alloys: Characteristic microstructures, with long and straight dislocations aligned along their screw orientation, are observed at low temperatures,3,9,15–18 and the flow stress is strongly temperature dependent,3,9,16,19–23 in agreement with the assumption of a high Peierls barrier which must be overcome by the nucleation of double kinks. But experiments also show that the yield stress in zirconium or in titanium strongly decreases with a decreasing amount of interstitial impurities like oxygen.3,16,19,22,23 It is therefore probable that the high Peierls stress of screw dislocations has an extrinsic cause. In pure zirconium or pure titanium, this Peierls stress may not be as high and screw dislocations are probably gliding as easily as other orientations.

Recently, Mendeleev and Ackland24 developed an empirical potential for Zr in the embedded atom method (EAM) formalism. Using this potential, Khater and Bacon25 showed that it leads to a screw dislocation that spontaneously spreads in the prism plane, the configuration dissociated in the basal plane being metastable. They also showed that the Peierls stress of a screw dislocation gliding in the prism plane is not so different from the Peierls stress of an edge dislocation and that this stress is small (22 MPa for the screw and 16 MPa for the edge). These results therefore support experimental findings stating that screw dislocations are gliding in prism planes with a low Peierls stress in pure zirconium. But these simulations rely on a central forces potential, which is not well suited to describe dislocations in a hcp transition metal like Zr, as described above. More reliable atomistic simulations, incorporating a description of the electronic structure, are therefore needed to confirm this easy glide of screw dislocations in pure zirconium.

This article aims to use ab initio calculations so as to fully characterize the core structure of a 1/3(1210) screw dislocation in zirconium and estimate its Peierls stress. We also examine generalized stacking faults as dislocation core structures are closely related to them. Two different ab initio methods, SIESTA26 and PWSCF,27 have been used. SIESTA offers the advantage of efficiency, allowing simulating more atoms than with a standard ab initio code, whereas PWSCF offers the advantage of robustness. All calculations are also performed with Mendeleev and Ackland EAM potential,24 so as to identify its ability to model dislocations in zirconium. In addition, this empirical potential is used to study the convergence of our results with the size of the simulation cell.

II. ATOMIC INTERACTION MODELING

Atomistic simulations have been performed both with an empirical interatomic potential and with ab initio calculations. The empirical potential that we used is the EAM potential developed by Mendeleev and Ackland.24 This potential is labeled #3 in Ref. 24. It is supposed to be well suited to model dislocations, as ab initio values28 of the stacking fault energies in the basal and prism planes have been included in the fitting procedure. Using this potential, Khater and Bacon25 showed that a 1/3(1210) screw dislocation spontaneously dissociates...
in the prism plane and that a metastable configuration dissociated in the basal plane also exists.

The *ab initio* calculations are relying on the density functional theory (DFT) in the generalized gradient approximation (GGA) with the functional proposed by Perdew, Burke, and Ernzerhof (PBE) and the pseudopotential approximation. Two different *ab initio* codes are used, SIESTA\textsuperscript{26} and PWSCF.\textsuperscript{27}

In the SIESTA code,\textsuperscript{26} valence electrons are described by a localized basis set corresponding to a linear combination of pseudatomic orbitals with 13 functions per atom. We used a norm conserving pseudopotential of Troulliers-Martins type with 4p electrons included as semicore. Electronic density of state is broadened with the Methfessel-Paxton function with a broadening of 0.3 eV, and the integration is performed on a regular grid of $14 \times 14 \times 8$ k-points for the primitive hcp unit cell and an equivalent density of k-points for the supercells used for the defect calculations. The charge density is represented on a real space grid with a spacing of 0.08 Å (mesh cutoff: 450 Ry) that is reduced to 0.06 Å (800 Ry) for dislocation calculations. This approach, i.e., the basis and the pseudopotential, has already been used to study vacancy diffusion in zirconium,\textsuperscript{29} and comparison with plane waves DFT calculations has led to a reasonable agreement.

In the PWSCF code,\textsuperscript{27} valence electrons are described with plane waves using a cutoff energy of 28 Ry. The pseudopotential is ultrasoft of Vanderbilt type with 4s and 4p electrons included as semicore.\textsuperscript{30} The same k-point grid and the same electronic broadening are used as with SIESTA code.

To validate these different atomic interaction models, it is worth comparing their results to available experimental data for some bulk properties of Zr. All models lead to an equilibrium lattice parameter and a $c/a$ ratio in good agreement with experimental data (Table I). In particular, a ratio lower than the ideal $\sqrt{8/3} \approx 1.633$ value is obtained in all cases.

**Table I.** Bulk properties of hcp Zr calculated with different atomic interaction models and compared to experimental data: lattice parameter $a$, $c/a$ ratio of the hexagonal lattice, relaxed elastic constants $C_{ij}$, inner elastic constants (Ref. 31) $e_{ij}$ and $d_{ij}$, phonon frequencies $\omega_1$ and $\omega_5$ of the optical branches at the $\Gamma$ point [Eq. (1)], inner elasticity contribution to elastic constant $\delta C_{12}$ [Eq. (2)].

<table>
<thead>
<tr>
<th></th>
<th>Expt</th>
<th>EAM</th>
<th>SIESTA</th>
<th>PWSCF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>3.232</td>
<td>3.234</td>
<td>3.237</td>
<td>3.230</td>
</tr>
<tr>
<td>$c/a$</td>
<td>1.603</td>
<td>1.598</td>
<td>1.613</td>
<td>1.601</td>
</tr>
<tr>
<td>$C_{11}$ (GPa)</td>
<td>155.4\textsuperscript{a}</td>
<td>142.0</td>
<td>140.0</td>
<td>140.0</td>
</tr>
<tr>
<td>$C_{33}$ (GPa)</td>
<td>172.5\textsuperscript{a}</td>
<td>168.0</td>
<td>168.0</td>
<td>168.0</td>
</tr>
<tr>
<td>$C_{12}$ (GPa)</td>
<td>67.2\textsuperscript{a}</td>
<td>75.0</td>
<td>86.0</td>
<td>70.0</td>
</tr>
<tr>
<td>$C_{13}$ (GPa)</td>
<td>64.6\textsuperscript{a}</td>
<td>76.0</td>
<td>68.0</td>
<td>65.0</td>
</tr>
<tr>
<td>$C_{44}$ (GPa)</td>
<td>36.3\textsuperscript{a}</td>
<td>44.0</td>
<td>24.0</td>
<td>26.0</td>
</tr>
<tr>
<td>$C_{56}$ (GPa)</td>
<td>44.1\textsuperscript{a}</td>
<td>33.5</td>
<td>27.0</td>
<td>35.0</td>
</tr>
<tr>
<td>$e_{11}$ (meV Å$^{-1}$)</td>
<td>27.0</td>
<td>17.0</td>
<td>18.6</td>
<td></td>
</tr>
<tr>
<td>$e_{33}$ (meV Å$^{-1}$)</td>
<td>118.0</td>
<td>122.0</td>
<td>101.0</td>
<td></td>
</tr>
<tr>
<td>$d_{12}$ (meV Å$^{-1}$)</td>
<td>30.0</td>
<td>38.9</td>
<td>36.6</td>
<td></td>
</tr>
<tr>
<td>$\omega_1$ (THz)</td>
<td>2.66 ± 0.02 (Ref. 33)</td>
<td>2.60</td>
<td>2.08</td>
<td>2.16</td>
</tr>
<tr>
<td>$\omega_5$ (THz)</td>
<td>4.23 ± 0.15 (Ref. 33)</td>
<td>5.43</td>
<td>5.57</td>
<td>5.03</td>
</tr>
<tr>
<td>$\delta C_{12}$ (GPa)</td>
<td>5.33</td>
<td>14.3</td>
<td>11.5</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Experimental elastic constants (Ref. 34) have been measured at 4 K.

We also compared the theoretical elastic constants with experimental data (Table I): A good agreement is also obtained. The computed elastic constants are the relaxed ones.\textsuperscript{35} As the hcp lattice contains two atoms in its primitive unit cell, some internal degrees of freedom may exist when applying a homogeneous strain. One needs to allow for atomic relaxations when computing $C_{11}$, $C_{12}$, or $C_{44}$ constants.\textsuperscript{31} It is also possible to calculate inner elastic constants to characterize these internal degrees of freedom. These are also given in Table I using the notations introduced by Cousins.\textsuperscript{31} Two of these inner elastic constants, $e_{11}$ and $e_{33}$, are related to the phonon frequencies of the optical branches at the $\Gamma$ point\textsuperscript{31}

$$\omega_i = 2\sqrt{\Omega e_{ii}}/m,$$

where $\Omega = a^2 \sqrt{3}/4$ is the atomic volume and $m$ the atomic mass. The last inner elastic constants $d_{12}$ couples the internal degrees of freedom to the homogeneous strain. It leads to a contribution to the elastic constants\textsuperscript{31}

$$\delta C_{12} = d_{12}^2\omega_{11}^2/\epsilon_{11}^2.$$

If $C_{ij}$ are the unrelaxed elastic constants, i.e., the elastic constants calculated by imposing a homogeneous strain to the hcp lattice without letting atoms relax from their initial positions, the true elastic constants are given by\textsuperscript{31} $C_{11} = C_{11}^0 - \delta C_{12}$, $C_{12} = C_{12}^0 + \delta C_{12}$, and $C_{66} = C_{66}^0 - \delta C_{12}$, all other elastic constants being unchanged.

### III. STACKING FAULT ENERGIES

Dislocation dissociation is controlled by the existence of a metastable stacking fault for the corresponding plane. According to the results obtained by Khater and Bacon\textsuperscript{25} with Mendeleev and Ackland EAM potential,\textsuperscript{24} a 1/3(1210) screw dislocation can dissociate either in a basal or in a prism plane. To characterize these eventual dissociations, we compute generalized stacking fault energies\textsuperscript{14,36}—or $\gamma$-surfaces—for both the basal and the prism planes.

#### A. Methodology

$\gamma$-surfaces describe the energy variation when two parts of a crystal are rigidly shifted for different fault vectors lying in a given crystallographic plane. Atoms are allowed to relax in the direction perpendicular to the fault plane. We calculate these $\gamma$-surfaces for both the basal and prism planes using full periodic boundary conditions. To introduce only one fault in the simulation cell, the same shift as the one corresponding to the fault vector is applied to the periodicity vector perpendicular to the fault plane. No free surfaces are therefore introduced in the simulation cell, which allows a fast convergence of the fault energies with the number of stacked planes. A periodic stacking of at least 16 0001 planes is used for the basal fault and 12 1010 planes for the prismatic fault. This corresponds to a distance between fault planes $h_{0001} = 8c \sim 41$ Å and $h_{1010} = 6\sqrt{3}a \sim 34$ Å. Increasing the number of planes in the stacking modifies the energies by less than 1 mJ m$^{-2}$. Generalized stacking fault energies are
calculated on a regular grid of $10 \times 10$ fault vectors and are then interpolated with Fourier series.

### B. $\gamma$-surfaces

#### 1. Basal plane

$\gamma$-surfaces corresponding to the basal plane are shown in Fig. 1 for the three interaction models we used. In all cases, a local minimum can be found at $1/3[1\bar{1}00]$ which corresponds to the intrinsic $I_2$ fault.\(^{38}\) This minimum does not vary when full atomic relaxations are allowed instead of being constrained to the direction perpendicular to the fault plane. All methods give a close value for the fault energy $\gamma_b$ in this minimum (Table II). A good agreement is also obtained with the values calculated by Domain et al.\(^{28}\) and by Udagawa et al.\(^{37}\) using ab initio code. The depth of this local minimum is more pronounced with the empirical EAM potential [Fig. 1(c)] than in ab initio calculations [Figs. 1(a) and 1(b)]. This appears clearly in Fig. 2 where the fault energy predicted by the different interaction models are compared along the [1100] direction. We will see later that this has consequences on the stability of a screw dislocation dissociated in the basal plane.

The $\gamma$-surface calculated with the EAM empirical potential has another minimum located in $2/3[1\bar{1}00]$. This is an artifact of the potential: One expects instead a maximum as this fault vector transforms the original BABABA stacking of the basal planes in a BABBCB stacking. Ab initio calculations confirm that this fault vector gives a maximum. Finally, it is worth pointing that both ab initio techniques give a very similar $\gamma$-surface: The shapes are identical and the amplitudes do not differ by more than 10%.

#### 2. Prism plane

$\gamma$-surfaces for the prism plane are shown in Fig. 3. Both ab initio methods lead to a similar $\gamma$-surface [Figs. 3(a) and 3(b)]. In particular, both PWSCF and SIESTA predicts the existence of a minimum at halfway of the Burgers vector, i.e., in $1/6[1\bar{2}10]$. Like for the basal fault, this minimum does not vary when full atomic relaxations are allowed. As can be seen on the projection of these $\gamma$-surface along the [1210] direction (Fig. 4), this minimum is a little more pronounced with PWSCF than with SIESTA. The same minimum was also present in the VASP calculations of Domain et al.,\(^{28}\) but they obtained a lower value $\gamma_p$ of the fault energy in this point (Table II). On the other hand, Udagawa et al.\(^{37}\) obtained a value close to our result using also VASP ab initio code with the PAW method and the PBE-GGA functional. They pointed out that the discrepancy arises from an insufficient number of stacked planes in the $\gamma$-surface calculation of Domain et al. The energy of the metastable stacking fault energy in the prism plane appears therefore higher than the value 145 mJ m$^{-2}$ initially suggested by Domain et al.:\(^{28}\) both our PWSCF\(^{39}\) and SIESTA calculations, as well as the Udagawa et al. result,\(^{37}\) leads to a value of about 200 mJ m$^{-2}$.

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**FIG. 1.** (Color online) Generalized stacking fault energy in the basal plane calculated with (a) PWSCF, (b) SIESTA, and (c) EAM potential. The arrows indicate Burgers vectors of the partial dislocations corresponding to a dissociation in the basal plane. The dashed line is the [1100] direction used in Fig. 2. Contour lines are drawn at the base every 50 mJ m$^{-2}$.

**FIG. 2.** (Color online) Generalized stacking fault energy in the basal plane along the [1100] direction (cf. Fig. 1) calculated with PWSCF, SIESTA, and EAM potential.

**FIG. 3.** Both ab initio techniques give a very similar $\gamma$-surface for the prism plane: (a) PWSCF and (b) SIESTA. Contour lines are drawn at the base every 50 mJ m$^{-2}$.
TABLE II. Stacking fault energies in the basal plane, $\gamma_b$, and in the prism plane, $\gamma_p$, calculated with different atomic interaction models, including VASP calculations of Domain et al. (Ref. 28) and of Udagawa et al. (Ref. 37). $R$ is the ratio defined by Legrand (Ref. 5), and $d_{eq}^b$ and $d_{eq}^p$ are the dissociation lengths of a screw dislocation respectively in the basal [Eq. (5)] and in the prism plane [Eq. (6)].

<table>
<thead>
<tr>
<th>Model</th>
<th>$\gamma_b$ (mJ m$^{-2}$)</th>
<th>$\gamma_p$ (mJ m$^{-2}$)</th>
<th>$R = C_{66} \gamma_b / C_{44} \gamma_p$</th>
<th>$d_{eq}^b$ (Å)</th>
<th>$d_{eq}^p$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EAM</td>
<td>198.0</td>
<td>135.0 (274.0)$^*$</td>
<td>1.12</td>
<td>4.0</td>
<td>7.8</td>
</tr>
<tr>
<td>SIESTA</td>
<td>199.0</td>
<td>233.0</td>
<td>0.96</td>
<td>2.0</td>
<td>4.6</td>
</tr>
<tr>
<td>PWSCF</td>
<td>213.0</td>
<td>211.0</td>
<td>1.36</td>
<td>2.7</td>
<td>5.9</td>
</tr>
<tr>
<td>VASP (Ref. 28)</td>
<td>200.0</td>
<td>145.0</td>
<td>1.85</td>
<td>3.4</td>
<td>5.9</td>
</tr>
<tr>
<td>VASP (Ref. 37)</td>
<td>227.0</td>
<td>197.0</td>
<td>2.1</td>
<td>3.2</td>
<td>7.4</td>
</tr>
</tbody>
</table>

$^*$For the EAM calculation of the prismatic stacking fault energy, the value in parenthesis corresponds to the maximum in $a/6[1\overline{2}10]$, whereas the lower value corresponds to the true minimum in $a/6[1\overline{2}10] + 0.14c[0001]$.

The $\gamma$-surface calculated with the EAM potential is quite different [Fig. 3(c)] as the point located in $1/6[\overline{1}210]$ is indeed a maximum and not a minimum like with ab initio calculations. A minimum is found for a point located in $a/6[1\overline{2}10] + 0.14c[0001]$. One therefore expects that a $1/3[1\overline{2}10] \{10\overline{1}0\}$ dislocation dissociates into two partial dislocations with a Burgers vector component orthogonal to the one of the perfect dislocation. In particular, a screw dislocation should dissociate in two partial dislocations with a small edge character. Khater and Bacon showed that the empirical potential of Ackland et al. suffers from the same artefact. As noted by Bacon and Vitek, all central force potentials stabilize indeed such a stacking fault $a/6[1\overline{2}10] + \alpha c[0001]$ with $\alpha \neq 0$, a minimum also predicted by a simple hard sphere model. This minimum either disappears or is located exactly in $a/6[1\overline{2}10]$ ($\alpha = 0$) only when the angular dependence of the atomic interactions is taken into account. The value $\gamma_p$ of the stacking fault energy obtained with Mendelev and Ackland EAM potential for this minimum is much lower than our ab initio value (Table II). This is quite normal as Mendelev and Ackland used the ab initio value of Domain et al. to fit their potential.

C. Dislocation dissociation

Before using atomistic simulations to obtain dislocation core structures and their associated Peierls stress, it is worth looking at what can be learned from these $\gamma$-surface
calculations. Legrand\textsuperscript{5} proposed a criterion based on the elastic constants and the metastable stacking fault energies to determine if glide occurs in the base or prism plane in a hcp crystal. According to this criterion, prismatic glide is favored if the ratio $R = C_{60}γ_b/C_{44}γ_p$ is larger than 1. Table II shows that this is the case for the EAM potential and the PWSCF calculation, as well as for the VASP calculation of Domain et al.\textsuperscript{28} and of Udagawa et al.\textsuperscript{37} On the other hand, SIESTA leads to a value too close to 1 to be able to decide between basal and prismatic glide.

One can also use dislocation elasticity theory\textsuperscript{43} to compute the dissociation distance of a dislocation both in the basal and prism planes. According to elasticity theory, the energy variation caused by a dissociation of length $d$ is

$$\Delta E_{\text{dis}}(d) = -b_i^{(1)}K_{ij}b_j^{(2)} \ln \left( \frac{d}{r_c} \right) + γd,$$

(3)

where $b_i^{(1)}$ and $b_j^{(2)}$ are the Burgers vectors of each partial dislocation, $γ$ the corresponding stacking fault energy, $K$ the Stroh matrix\textsuperscript{44,45} controlling dislocation elastic energy, and $r_c$ the core radius. Minimization of this energy leads to the equilibrium dissociation length

$$d_{\text{eq}} = \frac{b_i^{(1)}K_{ij}b_j^{(2)}}{γ}.$$

(4)

When the hcp crystal is oriented with the $x$, $y$, and $z$ axis respectively along the [10¯10], [0001], and [1210] directions, for a dislocation lying along the $z$ direction, the $K$ matrix is diagonal with its components given by\textsuperscript{46–48}

$$K_{11} = \frac{1}{2\pi}(\tilde{C}_{11} + C_{11}) \sqrt{\frac{C_{44}(C_{11} - C_{13})}{C_{33}(C_{11} + C_{13} + 2C_{44})}},$$

$$K_{22} = \sqrt{\frac{C_{33}}{C_{11}}}K_{11},$$

$$K_{33} = \frac{1}{2\pi}\sqrt{\frac{1}{2}C_{44}(C_{11} - C_{12})},$$

where $\tilde{C}_{11} = \sqrt{C_{11}C_{33}}$.

The $γ$-surface of the basal plane (Fig. 1) indicates a possible dissociation $1/3[12\overline{1}0] \rightarrow 1/3[1\overline{1}00] + 1/3[\overline{1}0\overline{1}0]$. The dissociation length in the basal plane is then for a $1/3[12\overline{1}0]$ screw dislocation,

$$d_{b}^{\text{eq}} = \frac{(3K_{33} - K_{11})a^2}{12γ_b}.$$

(5)

According to the minimum of the $γ$-surface in the prism plane (Fig. 3), a $1/3[12\overline{1}0]$ dislocation can dissociate in this plane in two partial dislocations with Burgers vectors $1/6[1210] \pm αc/a[0001]$. The parameter $α$ controls the position of the stacking fault minimum along the [0001] direction, i.e., $α = 0$ for PWSCF and SIESTA, and $α = 0.14$ for the EAM potential. The dissociation length of a screw dislocation in the prism plane is then

$$d_{p}^{\text{eq}} = \frac{(K_{33}a^2 - 4α^2K_{22}c^2)}{4γ_p}.$$

(6)

The dissociation lengths $d_{b}^{\text{eq}}$ and $d_{p}^{\text{eq}}$ calculated from the elastic constants and the stacking fault energies are given in Table II. Elastic constants predicted by the atomic interaction models are used in each case. For all energy models, one expects a larger dissociation in the prism than in the basal plane. We will compare in the following section these dissociation lengths predicted by elasticity theory with the ones observed in our atomistic simulations of the dislocation core structure.

### IV. SCREW DISLOCATION CORE

#### A. Methodology

Our atomistic simulations of the core structure of a screw dislocation are based on full periodic boundary conditions.\textsuperscript{39} This requires introducing a dislocation dipole in the simulation cell. Two periodic arrangements of the dislocations have been used (Fig. 5). In the $O$ arrangement, dislocations with opposite Burgers vectors are located on the same prism and basal planes, i.e., the two foreseen glide planes. On the other hand, only dislocation with the same Burgers vectors can be found on a given prism or basal plane in the $S$ arrangement.

Periodicity vectors of the $O$ arrangement are, before introducing the dislocations, $\vec{U}_1 = nαa[1\overline{1}0\overline{1}] - mc[0001]$, $\vec{U}_2 = na[1\overline{1}0\overline{1}] + mc[0001]$, and $\vec{U}_3 = a[12\overline{1}0]$. The integers $n$ and $m$ are taken equal to keep an aspect ratio close to a square. This simulation cell has been used for $ab initio$ calculations with $n = 4$ (128 atoms), $n = 5$ (160 atoms), and $n = 6$ (288 atoms).

For the $S$ arrangement, $\vec{U}_1 = na[1\overline{1}0\overline{1}]$, $\vec{U}_2 = mc[0001]$, and $\vec{U}_3 = a[12\overline{1}0]$. $Ab initio$ calculations have been performed with $n = m$ and varying between $n = 5$ (100 atoms) and $n = 8$ (256 atoms).

Both dislocation arrays are quadrupolar: The vector joining the two dislocations composing the primitive dipole is $\vec{D} = 1/2(\vec{U}_1 + \vec{U}_2)$. Because of the centrosymmetry of this arrangement and the symmetry properties of the Volterra elastic field, this ensures that the stress created by other dislocations is minimal at each dislocation position. The cut vector $\vec{A}$ defining the dislocation dipole is obtained by a $π/2$ rotation of $\vec{D}$.

The dislocation dipole is introduced in the simulation cells by applying to all atoms the elastic displacement predicted by anisotropic elasticity theory,\textsuperscript{44,45} taking full account of the

![FIG. 5. Screw dislocation periodic arrangements used for atomistic simulations.](image)
periodic boundary conditions.\(^5\) A homogeneous strain is also applied to the simulation cell so as to cancel the plastic strain introduced by the dislocation dipole and minimize the elastic energy. This strain is given by

\[ \varepsilon_{ij}^0 = -\frac{b_i A_j + b_j A_i}{2S}, \]

where \( S = |(\vec{U}_1 \wedge \vec{U}_2) \cdot \vec{e}_z| \) is the surface of the simulation cell perpendicular to the dislocation lines. This homogeneous strain adds some tilt components to the periodicity vectors. Atoms are then relaxed until all components of the atomic forces are smaller than 5 meV Å\(^{-1}\) for SIESTA, 2 meV Å\(^{-1}\) for PWSCF, and 0.1 meV Å\(^{-1}\) for the EAM potential.

### B. Core structure

Starting from perfect dislocations, atom relaxation leads to dislocations spread in the prism plane, whatever the interaction model (EAM, SIESTA, or PWSCF) and whatever the simulation cell used. This can be clearly seen by plotting differential displacement maps as introduced by Vitek.\(^3\) These maps (Fig. 6) show that the strain created by the screw dislocation spreads out in the (10\(\bar{1}0\)) prism plane and that displacements outside this plane are much smaller.

To characterize this spreading in the (10\(\bar{1}0\)) prism plane, we extract from our atomistic simulations the disregistry \( D(x) \) created by the dislocation. This is defined as the displacement difference between the atoms in the plane just above and those just below the dislocation glide plane. The derivative of this function \( \rho(x) = \frac{\partial D}{\partial x} \) corresponds to the dislocation density. Figure 7 shows the disregistry obtained for the three interaction models. In all cases, the \( b \) discontinuity created by the screw dislocation does not show a sharp interface, but spreads on a distance \( \sim 10 \) Å.

Peierls\(^2\) and Nabarro\(^3\) built a model that leads to a simple expression of the disregistry. The analytical expression they obtained\(^4\) can be extended to a dissociated dislocation. As suggested by the prismatic \( \gamma \)-surface (Fig. 3), we assume that the screw dislocation dissociates in two equivalent partial dislocations.

\[ D_{\text{dislo}}(x) = \frac{b}{2\pi} \left\{ \arctan \left[ \frac{x - x_0 - d/2}{\zeta} \right] + \frac{\pi}{2} \right\}, \]

where \( x_0 \) is the dislocation position, \( d \) its dissociation length, and \( \zeta \) the spreading of each partial dislocation. We need then to take into account that we do not have only one dislocation on a given prism plane but a periodic array (Fig. 5). The disregistry created by an array of period \( L \) is

\[ D_L(x) = \sum_{n=-\infty}^{\infty} D_{\text{dislo}}(x - nL) \]

\[ = \frac{b}{2\pi} \left\{ \arctan \left[ \frac{\tan \left( \frac{\pi}{\zeta} \left( x - x_0 - d/2 \right) \right)}{\tan \left( \frac{\pi}{\zeta} \right)} \right] + \frac{\pi}{2} \right\} + \arctan \left[ \frac{\tan \left( \frac{\pi}{\zeta} \left( x - x_0 + d/2 \right) \right)}{\tan \left( \frac{\pi}{\zeta} \right)} \right] + \frac{\pi}{2} \left[ \frac{x - x_0 + d/2}{L} + \frac{1}{2} \right], \]  

where \( \lfloor \cdot \rfloor \) is the floor function. For the O arrangement [Fig. 5(a)], the disregistry in the prism plane should be given by \( D(x) = D_L(x) - D_L(x - L/2) \) with \( L = 2mc \), whereas it should be \( D(x) = D_L(x) \) with \( L = mc \) for the S arrangement [Fig. 5(b)].
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FIG. 8. (Color online) Dissociation length of the screw dislocation. Symbols correspond to data extracted from atomistic simulations through the fit of the disregistry [Eq. (8)] for both the O and S periodic arrangements and for different sizes of the simulation cell. The solid lines are the predictions of elasticity theory based on the stacking faults (Table II). On the right vertical axis, the experimental c lattice parameter has been used to normalize the dissociation length by the distance \( \lambda_p = c/2 \) between Peierls valleys.

We fit this analytical expression of the dislocation disregistry to the data coming from the atomistic simulations. Figure 7 shows a good agreement between atomistic simulations and the model, using only three fitting parameters: the dislocation position \( x_0 \), the dissociation length \( d \), and the spreading \( \zeta \). This procedure therefore allows us to determine the location of the dislocation center. For all interaction models, we find that this center lies in between two (0001) atomic planes. One can see in Fig. 6 that this position corresponds to a local symmetry axis of the differential displacement map. This is different from the result obtained by Ghazisaei et al. in Ti where the center of the screw dislocation was found to lie exactly in one (0001) atomic plane, a position that corresponds in Zr to the saddle point between two Peierls valleys, as will be shown below.

The dissociation length of the screw dislocation obtained through this fitting procedures are shown in Fig. 8 for both periodic arrangements. We observe variations with the dissociation periodic arrangement used in the simulation, as well as with the size of the simulation cell. The results are nevertheless close to the predictions of elasticity theory (Sec. III C) for all three interaction models. We could even see with the EAM potential that the dissociation lengths extracted from atomistic simulations converge to the value given by elasticity theory for large enough unit cells. It is thus relevant to describe the screw dislocation as dissociated in two partial dislocations linked by a stacking fault, although the dissociation length remains small.

C. Core energy

We obtain the dislocation core energy by subtracting the elastic energy from the excess energy given by the atomistic simulations. This excess energy is the energy difference between the simulation cell containing the dislocation dipole and the same cell without any defect. The elastic energy calculation takes into account the elastic anisotropy and the effect of periodic boundary conditions. The obtained core energy are shown in Fig. 9. Like for the dissociation length, some variations with the size of the simulation cell and the periodic arrangement can be observed. We did not manage to link both quantities, i.e., the core energy and the dissociation length. They are not simply related by the expression of the energy variation with the dissociation length [Eq. (3)], and the change of the elastic interaction between dislocations caused by their dissociation could not fully explain the variation of the core energy either. As the spreading of partial dislocations also depends on the size of the simulation cells, the variation of the core energy probably have a more complex origin than simply a variation of the dissociation length.

We could use, with the EAM potential, a simulation cell large enough to obtain a converged value of the core energy, 163 meV Å\(^{-1}\) for a core radius \( r_c = b \). It is worth pointing that this value does not depend on the periodic arrangement used in the simulation (Fig. 9). This can be achieved thanks to a proper account of the core traction contribution to the elastic energy. A difference of \( \sim 10 \) meV Å\(^{-1}\) would have been observed between the S and O periodic arrangement without this contribution. Ab initio calculations lead to a dislocation core energy of 145 ± 5 meV Å\(^{-1}\) for SIESTA and 125 ± 5 meV Å\(^{-1}\) for PWSCF (\( r_c = b \) in both cases).

FIG. 9. (Color online) Core energy of the screw dislocation obtained for different sizes of the atomistic simulation cell and for both the O and S periodic arrangements (\( r_c = b \)).

D. Dissociation in the basal plane

Basal slip is observed experimentally only at high temperature (above 850 K) and for a higher resolved shear stress than the one needed to activate prismatic slip. At lower temperatures, no basal slip could be observed, even when the monocystal was oriented so as to favor basal slip. Our atomistic simulations lead to a screw dislocation configuration dissociated in the prism plane, which clearly cannot glide easily in the basal plane. It is worth looking if another configuration, which could glide in this basal plane, also exists.

Using the same EAM potential, Khater and Bacon showed that a screw dislocation can also dissociate in the basal plane. The basal configuration is obtained by introducing in the simulation (Fig. 9). This can be achieved thanks to a proper account of the core traction contribution to the elastic energy. A difference of \( \sim 10 \) meV Å\(^{-1}\) would have been observed between the S and O periodic arrangement without this contribution. Ab initio calculations lead to a dislocation core energy of 145 ± 5 meV Å\(^{-1}\) for SIESTA and 125 ± 5 meV Å\(^{-1}\) for PWSCF (\( r_c = b \) in both cases).

D. Dissociation in the basal plane
the atomic positions, the dislocation remains dissociated in the basal plane, as can be seen from the corresponding differential displacement map (Fig. 10). A fit of the screw component of the disregistry created by the dislocation in the basal plane leads to a dissociation length $d = 6.0 \, \text{Å}$, a higher value than predicted by elasticity theory (Table II). This configuration is metastable. It has indeed an energy higher by 62 meV $\text{Å}^{-1}$ than the configuration dissociated in the prism plane.

We check if ab initio calculations also lead to such a metastable configuration. Starting from a screw dislocation dissociated in two partial dislocations in the basal plane, both SIESTA and PWSCF lead after relaxation of the atomic positions to the stable configuration dissociated in the prism plane. This is true both with the S ($n = 5$) and the O ($n = 4$) periodic arrangements. These ab initio calculations show then that such a dissociation of the screw dislocation in the basal plane is unstable. The metastable configuration observed with the EAM potential appears to be an artifact of the empirical potential. This is not specific to the Mendelev and Ackland potential\textsuperscript{24} as a configuration dissociated in the basal plane is stabilized by any central forces potential.\textsuperscript{25,41,57}

V. PEIERLS BARRIER

Before calculating ab initio the Peierls barrier of the screw dislocation, we use the EAM potential to assess the validity of the method and to check the convergence of the Peierls barrier with the size of the simulation cell.

A. Methodology

We determine the Peierls barrier for the screw dislocation gliding in the prism plane. This is done using a constrained minimization between two adjacent equilibrium configurations of the dislocations. We move both dislocations in the same direction by one Peierls distance $\lambda_P = c/2$ between the initial and final states, so as to keep constant the distance between dislocations.

Two different algorithms are used to perform the constrained minimization, the simple drag method and the more robust nudged elastic band (NEB) method.\textsuperscript{58} Intermediate configurations are built by linearly interpolating the atomic coordinates between the initial and final states. We define the corresponding reaction coordinate $\zeta = (\vec{X} - \vec{X}^1) \cdot (\vec{X}^F - \vec{X}^1)/\|\vec{X}^F - \vec{X}^1\|^2$, where $\vec{X}$, $\vec{X}^1$, and $\vec{X}^F$ are the $3N$ vectors defining atomic positions for respectively the intermediate, initial, and final configurations. In the drag method, the minimization is performed on all atomic coordinates with the constraint that $\zeta$ remains fixed for each of the nine intermediate images. Nine intermediate images are also used in NEB method with a spring constant $k = 0.1 \, \text{eV} \, \text{Å}^{-2}$.

So as to obtain the variation along the path of the dislocation energy with its position, we need to determine the dislocation position $x_{\text{Dislo}}(\zeta)$ for each intermediate image, once it has been relaxed. This is done thanks to a fit of the disregistry in the prism plane, as described in Sec. IV B. This allows us to check that both dislocations in the simulation cell are moving in a coordinated way: The distance between them remains fixed.

As a consequence, there is no variation of the elastic energy along the path and the energy variation $\Delta E_P(\zeta)$ obtained by the constrained minimization corresponds to a variation of the core energy, i.e., the Peierls energy. We deduce the Peierls energy $\Delta E_P(x_{\text{Dislo}})$ by eliminating the reaction coordinate $\zeta$ between $\Delta E_P(\zeta)$ and $x_{\text{Dislo}}(\zeta)$.

Figure 11 illustrates the whole procedure for a given dislocation periodic arrangement using both constrained minimization techniques. The variation $\Delta E_P(\zeta)$ slightly differs between both techniques: For a given reaction coordinate $\zeta$, the drag method leads to a state of lower energy than the NEB method. This corresponds to a small difference in the dislocation...
position: This position deviates more with drag than with the NEB method from a linear variation. Nevertheless, one obtains at the end the same Peierls barrier $\Delta E_P(x_{\text{Dislo}})$, whatever the method used. These differences observed for the functions $\Delta E_P(\zeta)$ and $x_{\text{Dislo}}(\zeta)$ between drag and NEB methods increase with the size of the simulation cell, i.e., with the number of degrees of freedom. For large simulation cells (containing more than 3600 atoms in the S periodic arrangement for instance), the drag method sometimes fails to find a continuous path between the initial and final states: One has to use the NEB method in these cases. Only much smaller simulation cells can be studied $ab\text{ initio}$. For these sizes, the drag and the NEB methods always lead to the same result. We will therefore only use the drag method in the $ab\text{ initio}$ calculations, as it costs much less CPU time.

Finally, we interpolate with Fourier series the periodic functions $\Delta E_P(\zeta)$ and $x_{\text{Dislo}}(\zeta) = \lambda P \zeta$. This leads to a smooth function $\Delta E_P(x_{\text{Dislo}})$ that can be derived. The Peierls stress $\sigma_P$ is deduced from the maximal slope of this function,

$$\sigma_P = \frac{1}{b} \text{Max} \left( \frac{\partial \Delta E_P}{\partial x_{\text{Dislo}}} \right). \quad (9)$$

We obtain a Peierls stress $\sigma_P = 24 \pm 1$ MPa for the EAM potential. Khater and Bacon determined, for the same empirical potential, a Peierls stress $\sigma_P = 22$ MPa using molecular statics simulations under applied stress. As the agreement between both methods is good, we see that the Peierls stress can be defined either from the slope of the Peierls barrier or from the minimal applied stress under which the dislocation glides indefinitely.

We now examine, still with the EAM potential, how this Peierls barrier varies when the size of the simulation cell decreases up to reaching a number of atoms that can be handled in $ab\text{ initio}$ calculations (Fig. 12). Both the S and O periodic arrangements give the same Peierls barrier, and hence the same Peierls stress, for a large enough simulation cell ($\gtrsim 1000$ atoms). The Peierls barrier increases when the size of the simulation cell decreases with the S periodic arrangement, whereas it decreases with the O periodic arrangement. As a consequence, the S and O periodic arrangement should respectively lead to an upper and lower limit of the Peierls stress for small simulation cells. We will therefore use the S periodic arrangement to calculate $ab\text{ initio}$ this Peierls barrier. This will allow us to confirm that the Peierls stress is as low as indicated by experiments and this EAM potential. Moreover, it is worth pointing that the dissociation length varies during the dislocation migration, and this variation is

![FIG. 12. (Color online) Variation of the Peierls barrier with the size of the simulation cell calculated with the EAM potential for both periodic arrangements.](image)

![FIG. 13. (Color online) Peierls barrier for a screw dislocation gliding in its prism plane calculated $ab\text{ initio}$ with (a) PWSCF and (b) SIESTA for the S periodic arrangement. Symbols correspond to $ab\text{ initio}$ results and lines to their interpolation by Fourier series.](image)
more pronounced (~10%) for the smallest simulation cells. But, like for the core energy, we did not manage to relate the size dependence of the Peierls barrier to this variation of the dissociation length.

B. Ab initio barriers

The Peierls barriers obtained by ab initio calculations are shown in Fig. 13(a) for PWSCF and Fig. 13(b) for SIESTA. In both cases, the height of the barrier decreases when the number of atoms increases, in agreement with what has been observed with the EAM potential for the same S periodic arrangement. For a given number of atoms, the ab initio barriers are a little bit lower than the ones obtained with the EAM potential. Results obtained with SIESTA are noisy: The energy barrier calculated with our ab initio approach (PWSCF and SIESTA), both in the DFT-GGA approximation, we have shown that a 1/3(1210) screw dislocation in hcp zirconium dissociates in two partial dislocations with a pure screw character. This is in agreement with experiments that the minimum in 1/6(1210) found for the generalized stacking fault energy in the prism plane. We could extract the dissociation length from our atomistic simulations. Although this dissociation length is small (d ~ 6 Å for PWSCF and d ~ 4 Å for SIESTA), it is in reasonable agreement with the one predicted by elasticity theory.

The EAM potential of Mendelev and Ackland leads to the same structure of the dislocation dissociated in the prism plane. The metastable configuration dissociated in the basal plane predicted by this potential is not stable in ab initio calculations, both with PWSCF and SIESTA. This configuration is therefore an artifact of this potential, probably induced by the deep minimum in 1/3(1100) found with this empirical potential for the generalized stacking fault in the basal plane. This minimum is much more shallow in ab initio calculations.

We could also obtain an ab initio estimate of the Peierls stress of the screw dislocation gliding in the prism plane. Calculations with PWSCF lead to an upper limit of 21 MPa for this Peierls stress. This small value shows that screw dislocations can glide quite easily in pure zirconium, thus confirming what had been obtained with Mendelev and Ackland EAM potential. Such a small Peierls stress is in agreement with experimental data, once the hardening of oxygen impurities has been considered.

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VI. CONCLUSIONS

Using two ab initio approaches (PWSCF and SIESTA), both in the DFT-GGA approximation, we have shown that a 1/3(1210) screw dislocation in hcp zirconium dissociates in two partial dislocations with a pure screw character. This is in agreement with experiments that the minimum in 1/6(1210) found for the generalized stacking fault energy in the prism plane. We could extract the dissociation length from our atomistic simulations. Although this dissociation length is small (d ~ 6 Å for PWSCF and d ~ 4 Å for SIESTA), it is in reasonable agreement with the one predicted by elasticity theory.

The EAM potential of Mendelev and Ackland leads to the same structure of the dislocation dissociated in the prism plane. The metastable configuration dissociated in the basal plane predicted by this potential is not stable in ab initio calculations, both with PWSCF and SIESTA. This configuration is therefore an artifact of this potential, probably induced by the deep minimum in 1/3(1100) found with this empirical potential for the generalized stacking fault in the basal plane. This minimum is much more shallow in ab initio calculations.

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35. Elastic constants calculated by Mendelev and Ackland in the original article describing the EAM potential (Ref. 24) did not take into account atomic relaxations. This explains the difference with the ones given in Table I.


48. Foreman (Ref. 59) gave a different expression for $K_{22}$, but the comparison with a numerical evaluation of the $K$ matrix using Stroh formalism (Refs. 44 and 45) shows that the correct expression is the one given by Savin et al. (Ref. 47).


