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## REVISION 1 :

# Complexions and stoichiometry of the $60.8^\circ//[100](011)$ symmetrical tilt grain boundary in $\text{Mg}_2\text{SiO}_4$ forsterite: a combined empirical potential and first-principles study

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### Abstract

In this work we explore the low energy complexions of the symmetrical tilt grain boundary (GB)  $60.8^\circ//[100](011)$  in forsterite through molecular dynamics and first principles calculations. Using conservative sampling, we find six stoichiometric complexions with energies ranging from 0.66 to  $1.25 \text{ J.m}^{-2}$ . We investigate the segregation of MgO vacancy pairs, and find that in most cases it is more favorable for vacancies to lie within the GBs than in the surrounding crystals, leading to new atomic structures. From these results we infer that at finite temperature when vacancies are present in the system, GBs are likely to absorb them and to be non-stoichiometric. We find many GB complexions containing a free oxygen ion, which may have profound implications for geological processes.

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### 1. Introduction

Grain boundaries (GBs) play a key role in numerous physical processes associated with mechanical, chemical diffusion or electrical conductivity behavior of polycrystalline materials (Balluffi and Sutton, 1996). Understanding their properties is therefore particularly important for a mineral like olivine which is the principal constituent of the rocks of the Earth's upper mantle. GBs are involved in several first order processes such as creep (Hirth and Kohlstedt, 1995; Maruyama and Hiraga, 2017a,b), grain boundary migration (Bollinger et al., 2019; Furstoss et al., 2021) or diffusion (Demouchy, 2010; Fei et al., 2016). At the mesoscopic scale, GBs are often viewed as interfaces with particular effective properties, like their mobility or their diffusion coefficient. Unfortunately, their structure at the atomic level is challenging to characterize. At the moment, atomically resolved observations of GB in olivine are scarce as noticed in a recent review by

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11 Marquardt and Faul (Marquardt and Faul, 2018), and the few HRTEM micrographs available in literature  
12 Fei et al. (2016); Heinemann et al. (2005); Marquardt and Faul (2018) do not allow determining the chemical  
13 composition of GB, i.e. whether the stoichiometry is preserved or not at the GB.

14 In complementarity to experimental efforts, simulations at the atomic scale can provide insight towards  
15 the structure of GBs. Yet even that is challenging, due to the complex crystallography of olivine and the  
16 many possible GB configurations to explore. Nonetheless, people have used density functional theory (DFT)  
17 (Ghosh and Karki, 2014) or classical molecular dynamics (MD) (Adjaoud et al., 2012; Mantsi et al., 2017)  
18 to determine physical properties (energy, excess volume) of some select GBs in olivine. Ultimately, the  
19 comparison of numerical models with high-resolution observations will be necessary to assess the relevant  
20 GB structures, and infer their physical properties.

21 Description of a GB can be done at multiple scales involving different degrees of complexity and precision.  
22 At the mesoscopic scale, a GB is generally described by the disorientation between the two adjacent grains,  
23 and its energy is almost always described through this variable using extended Read-Shockley type models  
24 (initially designed only for low angle GBs) (Gui-Jin and Vitek, 1986; Read and Shockley, 1950). However,  
25 a more complete "macroscopic" description should also specify the rotation axis and the crystallographic  
26 planes in contact at the GB. At smaller scales, this description can be enriched by indicating the translation  
27 vector between the neighboring crystals and finally by describing the atomic arrangement of the GB (e.g.  
28 bonds, stoichiometry, charge). Using these lower scale descriptions introduces supplementary degrees of  
29 freedom which also impact the physical properties of GB (Han et al., 2016), and question the common  
30 assumption that a given disorientation is related to a single GB structure. The multiplicity of GB structures  
31 even for a given GB disorientation and contact plane has been considered by several studies essentially for  
32 metals (Oh and Vitek, 1986; Rittner and Seidman, 1996) but more rarely for geological relevant materials  
33 (Hirel et al., 2019). Recently the concept of GB complexion was introduced (Cantwell et al., 2014) to account  
34 for the multiplicity of GB atomic structures. In spite of growing evidence that GBs in a polycrystal may  
35 exist in a wide variety of complexions, numerical studies often account only for the complexion of lowest  
36 energy, discarding a great number of other possible complexions.

37 In the present work we study the low-energy complexions of a particular GB in the Mg-rich end member of  
38 olivine, i.e. forsterite  $\text{Mg}_2\text{SiO}_4$ , using a combination of molecular statics and ab initio calculations. Forsterite  
39 is an orthorhombic crystal in which magnesium ions hold two distinct sites while oxygen ions (three distinct  
40 sites) are arranged in tetrahedra with a silicon ion at the center of it. In the following we use the *Pbnm*  
41 space group (where the cell parameters are ordered such as  $b > c > a$ ) to describe the forsterite crystal. The

42 studied GB corresponds to a symmetrical tilt grain boundary (STGB) with a disorientation of  $60.8^\circ$  about  
43 the [100] direction and (011) planes in contact at GB. This orientation has the particularity to correspond to  
44 a high symmetry of the quasi hexagonal close-packed (hcp) oxygen sub-lattice. In fact in such a GB, the hcp  
45 stacking of oxygen ions is almost identical to the bulk crystal, which might explain its over-representation  
46 in natural olivine aggregates. Indeed, [Marquardt et al. \(2015\)](#) have shown from EBSD measurements on  
47 annealed forsterite polycrystals that among GB with  $60^\circ$  disorientation, already highly represented in the  
48 misorientation distribution function, the rotation about the [100] axis with a (011) GB plane is the more  
49 ubiquitous. Although first principles ([Ghosh and Karki, 2014](#)) and MD ([Adjaoud et al., 2012](#)) works have  
50 examined this special STGB, both have focused on a single complexion, which raises the question of its  
51 relevance and occurrence in natural systems. Most recent studies of GB in metallic systems have revealed  
52 that many metastable configurations are possible and should be accounted for, arguing that materials are  
53 rarely in their lowest energy state [Han et al. \(2016, 2017\)](#). In this work, we follow this guideline to come  
54 apart from the ground-state GB structure, and explore multiple possible complexions of the GB in forsterite.

55 Here, we first review the low-energy complexions of this STGB by determining their energies, excess  
56 volumes and by describing their atomic-scale features. Classical MD simulations allow us to probe the  
57 energy landscape and identify low-energy configurations. Then, we perform ab initio calculations in order  
58 to characterize more accurately the properties of these configurations.

59 Deviation from stoichiometry at GB has been noticed by several experimental and numerical studies ([Baker](#)  
60 [et al., 1990](#); [Farkas, 2000](#)). In fact, GBs are known to be sources and wells of vacancies and therefore it  
61 seems interesting to explore the stoichiometry as an other degree of freedom for complexion prospecting  
62 by deviating locally from the bulk composition at GB. In ionic compounds such as forsterite, an easy way  
63 to deviate from stoichiometry keeping electrically neutral system is to incorporate neutral vacancy pairs.  
64 In forsterite, the energetically most favorable Schottky defect is the MgO one ([Brodholt, 1997](#)). Thus we  
65 investigate, in a second step, the effect of stoichiometry deviation at GB by inserting MgO vacancy pairs.

## 66 2. Methodology

### 67 2.1. Computation techniques

68 Atomistic calculations are performed with LAMMPS ([Plimpton, 1995](#)). Interactions between ions are  
69 modelled with a rigid-ion potential accounting for the long-range Coulomb interaction, and short-range  
70 interactions are described by a Morse function and a repulsive  $r^{-12}$  term. Potential parameters were op-  
71 timized by Pedone et al. ([Pedone et al., 2006](#)), where ions have partial charges of  $1.2e$ ,  $2.4e$  and  $-1.2e$  for

72 Mg, Si and O ions respectively. This allows considering neutral vacancy pairs such as MgO. Moreover this  
73 potential was shown to offer a very good description of a number of properties of forsterite including bulk,  
74 surfaces and defects properties (Hirel et al., 2021). Coulomb interactions are computed using the particle-  
75 particle-particle-mesh (pppm) method (Eastwood et al., 1980). Ion positions are optimized by means of  
76 the conjugate-gradients algorithm until the maximum force is smaller than  $10^{-10}$  eV.Å<sup>-1</sup>. The pressure is  
77 maintained at 0 GPa by rescaling the simulation cell.

78 In order to consolidate our results and to investigate possible changes in ionic charge state, we also  
79 perform first-principles calculations on some systems containing grain boundaries. We use the Vienna  
80 Ab initio Simulation Program (VASP) (Hafner, 2008) with the projector augmented wave (PAW) method  
81 (Kresse and Joubert, 1999) in the generalized gradient approximation (GGA) (Perdew et al., 1996). In  
82 order to treat explicitly only valence electrons, the interactions between valence, core electrons and nuclei  
83 are described by the pseudopotential developed by Perdew and Wang (1992). A cut-off of 500 eV is applied  
84 to the plane wave basis and the first Brillouin zone is sampled with Monkhorst-pack grid (Monkhorst and  
85 Pack, 1976) using a  $2 \times 1 \times 1$  mesh.

86 First-principles calculations give access to the electron density. We perform a Bader analysis, which de-  
87 composes the charge density into atomic basins based on a change of sign in the electron density gradient  
88 (Bader, 1990). The calculations are performed using the software "Bader Charge Analysis" developed by  
89 the Henkelman group (Henkelman et al., 2006; Tang et al., 2009). We use it to quantify the changes in ion  
90 charges in GBs with respect to perfect crystal environment.

## 91 2.2. GB construction

92 We focus on the  $60.8^\circ // [100](011)$  symmetric tilt grain boundary (STGB) in forsterite, i.e. where two  
93 crystals share a common [100] axis and meet along (011) planes with a disorientation of  $60.8^\circ$ . In forsterite,  
94 two different types of (011) planes are possible, with different stoichiometries, as illustrated in Fig. 1. One  
95 type of plane is terminated by a silicon ion and the oxygen ions forming the edge of tetrahedra, which we  
96 will refer to as edge-planes, and the second type is terminated by Mg ions and an oxygen ion belonging to  
97 the tip of a tetrahedron, referred to as tip-planes. We begin by constructing cells of forsterite terminated by  
98 the same type of plane (Fig. 1). Such cells preserve the stoichiometry, but must be truncated by  $1/2[001]$   
99 (which removes one formula unit) to obtain the same type of surface.

100 The GB is constructed by stacking two crystals meeting across (011) planes. In order to avoid any  
101 spurious effect due to charged surfaces, we use 3-D periodic boundary conditions (PBC) and ensure that  
102 the system remains charge-neutral. Moreover, we also make sure that SiO<sub>4</sub> tetrahedra remain unaffected,

103 because breaking Si-O bonds is energetically unfavorable in this system. Since the GB studied is a STGB,  
104 the two crystals are mirror images of each other. Two types of reference GBs are constructed, one by stacking  
105 the "edge-plane" system with its mirror image ("edge-to-edge"), and one by stacking the "tip-plane" system  
106 with its mirror image ("tip-to-tip").

107 Due to PBC, the same GB is formed at the center of the cell and at the edges (Fig.2). This allows  
108 computing the reference GB energy density ( $\gamma_{\text{ref}}$  in  $\text{J}\cdot\text{m}^{-2}$ ) and excess volume ( $V_{\text{ref}}^e$ ):

$$\begin{aligned}\gamma_{\text{ref}} &= \frac{E_{\text{tot}} - E_{\text{bulk}}}{2A}, \\ \Omega_{\text{ref}} &= \frac{V_{\text{tot}} - V_{\text{bulk}}}{2A},\end{aligned}\tag{1}$$

109 where  $E_{\text{tot}}$  and  $V_{\text{tot}}$  are the total energy and volume of the relaxed system containing the GBs,  $E_{\text{bulk}}$  and  
110  $V_{\text{bulk}}$  are the total energy and volume of the equivalent defect free crystal, and  $A$  is the area of the GB.

111 We computed the reference GB energy for different system sizes and found that a height of 180 Å is  
112 necessary for GB energy and excess volume to be converged, which corresponds to a system containing  
113 980 atoms. When performing DFT calculations, we use smaller systems of 420 atoms due to computational  
114 costs. Although GB energies are not converged for this system size, our convergence tests show that the  
115 atomic structure is the same as in larger systems.

### 116 2.3. Conservative sampling

117 The method described above does not guarantee an optimal atomic GB structure. An important degree  
118 of freedom is the relative translation of the two grains, quantified by a vector  $\vec{\tau} = (\tau_x, \tau_y, \tau_z)$ . In order to  
119 explore this degree of freedom, we impose the translation vector  $(\tau_x, \tau_y)$  in the GB plane, and relax ions  
120 in the direction normal to the GB to determine the optimal translation  $\tau_z$ . Computing the GB energy for  
121 each translation vector, one obtains a map of the energy density  $\gamma$  along the GB plane. Similar to the  
122 classical generalized stacking faults approaches (Mishin and Farkas, 1998; Vitek, 1968), this method allows  
123 identifying low-energy configurations of the GB.

124 The use of 3D PBC requires a special attention to the simulation cell construction and the relaxation scheme  
125 involved during the relaxation process (Fig.2). Indeed if a crystal is displaced with respect to the other by  
126 keeping the same cell, then the GBs at the center and at the edges of the cell will not be equivalent anymore,  
127 thus preventing a direct calculation of the interface energy.

128 For this reason, when the top crystal is translated we tilt the box so that the interface at the edges of

129 the cell remains identical, with the energy  $E_{\text{ref}}$ . For the given relative translation  $\vec{\tau}$ , the energy and excess  
130 volume of the central GB are then:

$$\begin{aligned}\gamma(\vec{\tau}) &= \frac{E_{\text{tot}}(\vec{\tau}) - E_{\text{bulk}}}{A} - \gamma_{\text{ref}}, \\ \Omega(\vec{\tau}) &= \frac{V_{\text{tot}}(\vec{\tau}) - V_{\text{bulk}}}{A} - \Omega_{\text{ref}}.\end{aligned}\quad (2)$$

131 For a given imposed translation vector  $(\tau_x, \tau_y)$ , we relax atom positions along the direction  $z$  normal to the  
132 GB. To allow for rotational relaxation of tetrahedra, O ions are relaxed in all directions. Within 25 Å in  
133 the vicinity of the central GB, all ions are left free to relax (see Fig.2).

134 After the identification of the lowest energy configurations, the selected systems are fully relaxed (no ionic  
135 positions fixed) which provides the final GB complexions and allows computing their energies and excess  
136 volumes.

#### 137 2.4. Density and excess volume

138 From the atomistic simulation outputs, we can compute the density profile along a direction normal to  
139 the GB plane. In practice, the mass of each atom is expanded through Gaussian distributions (with standard  
140 deviation of 2 Å) and the density profile  $\rho(z)$  is computed from the contribution of all masses contained in  
141 a elementary volume (grid size of 0.2 Å). These calculations are performed with Atomsk (Hirel, 2015).

142 The GB excess volumes can be expressed as a function of the density profile along the direction normal  
143 to the GB plane. Indeed the density can be related to a infinitesimal change in volume  $dV(z)$ :

$$dV(z) = \left( \frac{\rho_{\text{uc}}}{\rho(z)} - 1 \right) Adz, \quad (3)$$

144 where  $\rho_{\text{uc}}$  is the density of a unit cell. The GB excess volume is then computed by integrating  $dV$  around  
145 the GB in a length  $F$ , and dividing by the GB area:

$$\Omega = \int^F \left( \frac{\rho_{\text{uc}}}{\rho(z)} - 1 \right) dz \quad (4)$$

146 We verified that this methodology yields the same values than the ones given by Eqs. 1 and 2 in the case  
147 of stoichiometric GB structures. For non-stoichiometric GBs, Eqs. 1 and 2 are no longer valid and  $\Omega$  is  
148 computed using Eq. 4.

### 149 3. Stoichiometric grain boundary

#### 150 3.1. Reference grain boundaries

151 As explained in the previous section, the first step toward the calculation of the GB energy landscape  
152 is the construction of a reference configuration containing two equivalent GBs. After full relaxation, the  
153 edge-to-edge GB (labeled E1) has an energy  $\gamma_{E1} = 0.9 \text{ J.m}^{-2}$  and an excess volume  $\Omega_{E1} = 0.39 \text{ \AA}$ . Its  
154 atomic configuration is shown in Fig.4a. Atomic displacements after relaxation are small (about  $1.15 \text{ \AA}$ )  
155 and tetrahedra do not rotate with respect to the [100] direction. Computation of the mass density profile  
156 shows that the GB is less dense than the surrounding crystals, which is consistent with the positive excess  
157 volume.

158 The tip-to-tip GB (labeled T1) has an energy  $\gamma_{T1} = 1.22 \text{ J.m}^{-2}$  and an excess volume  $\Omega_{T1} = 0.76 \text{ \AA}$ .  
159 Displacements are also moderate (about  $1.5 \text{ \AA}$ ), but are associated with significant tetrahedra rotation as  
160 shown in Fig.4d. This is probably due to strong repulsion of O ions at the tip of tetrahedra.

#### 161 3.2. GB energy landscapes

162 Following the methodology presented in section 2.3 we computed the GB energy landscape for the  
163 two types of GB, which are reported in Fig.3. These landscapes are irregular and present abrupt energy  
164 variations, as it was already noticed by Adjaoud et al. (2012). Nonetheless, both surfaces exhibit a central  
165 symmetry, which is consistent with the symmetries of the (011) plane in forsterite. In addition to the  
166 reference GBs E1 and T1, each energy landscape reveals two more low energy basins, labeled E2, E3, T2  
167 and T3. By symmetry, equivalent configurations are found, respectively  $E2'=E2$ ,  $E3'=E3$ ,  $T2'=T2$  and  
168  $T3'=T3$  (see Fig.3).

#### 169 3.3. Stable configurations

170 Each low energy configuration found from the energy landscape sampling is fully relaxed (i.e. without  
171 constraint). We obtain six distinct GB complexions with energies ranging between  $0.66$  and  $1.25 \text{ J.m}^{-2}$ .  
172 Reference GB complexions E1 and T1 were already presented above.

173 The complexion E2 is shown in Fig.4b. Contrary to the reference E1, it shows significant relaxation with  
174 tetrahedra sharing an O ion (orange arrow in Fig.4b), which causes an O ion to become free of any bond with  
175 a Si ion (blue arrow in Fig.4b). Although the presence of this free O ion seems unfavorable, the interface  
176 energy is  $\gamma_{E2} = 0.66 \text{ J.m}^{-2}$ , significantly lower than the reference E1. This complexion is also more compact  
177 as evidenced by the smaller excess volume (i.e.  $0.13 \text{ \AA}$ ) and the density profile.



178 The complexion E3 is shown in Fig.4c. Like E2 it contains joined tetrahedra and free O ions, however  
 179 its energy is the highest with a value  $\gamma_{E3} = 1.25 \text{ J.m}^{-2}$ . This complexion is the least favorable for the  
 180 stoichiometric GBs. It is also associated with a large expansion ( $\Omega_{E3} = 0.60 \text{ \AA}$ ).  
 181 Concerning the tip-to-tip configurations, the complexion T2 (Fig.4e) also presents joined tetrahedra and  
 182 unbound O ions. Its energy  $\gamma_{T2} = 1.08 \text{ J.m}^{-2}$  is lower than the reference T1. Finally, the configuration  
 183 T3 also contains joined tetrahedra and free O ions. Its energy is the lowest for the tip to tip GB type,  
 184  $\gamma_{E3} = 0.95 \text{ J.m}^{-2}$ . It is also the most compact of all complexions, with an excess volume  $\Omega_{T3} = 0.13 \text{ \AA}$ .

GB label	GB energy ( $\text{J.m}^{-2}$ )		Excess volume ( $\text{\AA}$ )		$\Delta E$ (eV)
	MD	DFT	MD	DFT	
E1	0.90	0.94	0.37	0.49	-2.11
E2	0.66	1.02	0.13	0.39	-1.31
E3	1.25	1.39	0.58	0.63	-2.81
T1	1.22	1.54	0.78	0.76	-1.90
T2	1.08	1.39	0.28	0.42	-2.18
T3	0.95	1.38	0.13	0.34	-2.35
(Ghosh and Karki, 2014)		1.15		0.37	unknown
(Adjaoud et al., 2012)	1.30		0.35		unknown

Table 1: Summary of the stoichiometric GB energies and excess volumes for the different GB complexions obtained by MD and DFT. Labels refer to those in Fig.3,  $\Delta E$  corresponds to the segregation energy of a MgO vacancy pair.

185 In summary, the most favorable complexions are E2 for the edge-to-edge type, and T3 for the tip-to-tip  
 186 type. Both are characterized by tetrahedra connected by an O ion and free O ions remaining in the GB. We  
 187 also note a positive correlation between GB energy and excess volume: the lower the GB energy, the lower  
 188 its volume. This is consistent with previous studies on similar GBs (Adjaoud et al., 2012; Ghosh and Karki,  
 189 2014). From the density profiles we estimate the structural width of GBs to be approximately  $10 \text{ \AA}$ .

### 190 3.4. *Ab initio calculations*

191 In order to consolidate results obtained with the interatomic potential, we performed first-principles  
 192 calculations as presented in section 2.1. Starting from our previous configurations relaxed with the potential,  
 193 we perform a full ionic relaxation by means of DFT calculations.

194 Ionic displacements are negligible, so that the GB atomic structures remain the same for all complexions.  
 195 The GB energies and excess volumes obtained by DFT are reported alongside those presented previously  
 196 in Tab. 1. We obtain very good agreement between the two methods, thus confirming the suitability of  
 197 the potential for modeling GBs. The ordering of GB energies is identical in both methods, except for the  
 198 complexions E1 and E2. This small discrepancy may be attributed to the small size of simulation volumes

199 involved in the DFT calculations.

200 Using the electron density from our DFT calculations, we performed Bader analysis to evaluate the charges  
201 of ions. Fig. 5b shows the distribution of charge of O ions in a perfect bulk environment (blue curve), with a  
202 median value about  $-1.61e$ , which we consider as the reference charge here. Charge analysis of oxygen ions  
203 belonging in GBs show that the latter have little effect on this charge distribution. As an example, we show  
204 the charges of O ions in the complexion E2 in Fig. 5b (orange curve). Their distribution is slightly wider  
205 than in the bulk, but remains within 1% of the reference charge. Two noticeable exceptions are indicated  
206 with arrows. The first one (orange S arrow) corresponds to the O ion bonding two tetrahedra, which has a  
207 reduced electron charge. Visualization of its isosurface of charge density (Fig. 5a) shows that it is elongated  
208 in the direction of the two Si ions, which indicates mixed ionic and covalent bonding. The second exception  
209 is the unbound O ion (blue F arrow in Fig. 5), which has a greater charge of about  $-1.65e$ . Its isosurface  
210 is almost spherical, indicating that this ion is free of covalent bonding. Overall, we find that using an  
211 interatomic potential with fixed charges is a reasonable approximation for modelling GBs in forsterite.

#### 212 4. Non-stoichiometric GB: MgO vacancy pairs

213 We investigate the effect of stoichiometry by introducing MgO vacancy pairs in the six GBs presented  
214 above. We construct atomic systems corresponding to all possible combinations of Mg and O vacancies,  
215 which represents about 800 different systems. After relaxation, we obtain several GB complexions that can  
216 be compared with the parent GB complexion. Contrary to the stoichiometric case, the interface energy  
217 cannot be computed unambiguously, which will be discussed in section 5. For that reason, in this section we  
218 focus on the segregation energies of the vacancies, defined as the difference between the energy of a system  
219 where a vacancy pair is inside a grain  $\Delta E_{\text{ref}}^{N-2}$ , and one where it lies inside the GB  $E_{\text{tot}}^{N-2}$ :

$$\Delta E = E_{\text{tot}}^{N-2} - E_{\text{ref}}^{N-2} \quad (5)$$

220 This quantity indicates if it is more energetically favorable for the vacancy to be in the bulk phase (i.e.  
221  $\Delta E > 0$ ) or within the GB (i.e.  $\Delta E < 0$ ). Since in forsterite, two Mg sites and three O sites are possible in  
222 the perfect crystal,  $E_{\text{ref}}^{N-2}$  can take multiple values. We choose to take the one that minimizes  $\Delta E$ , so that  
223 it vanishes in the bulk.

224 Fig. 6 presents the segregation energy  $\Delta E$  as function of the location of the MgO vacancy pair for the  
225 complexion E1. We can see that it takes negative values everywhere within the GB, which corresponds to

226 the preferential segregation of vacancies at the GB. We conclude that when such vacancies are present in  
227 the system, it is energetically favorable for them to be incorporated in the GB rather than inside a grain.  
228 Similar results are obtained for all six complexions, and are available in the supplementary material.

#### 229 *4.1. Configurations of lowest energy*

230 For each initial GB complexion, among all the defective configurations investigated, we select the one  
231 with the lowest energy. This leads to six final non-stoichiometric GB complexions. These complexions are  
232 associated with segregation energies in the order of  $-2$  eV as reported in Tab. 1.

233 Their atomic configurations are presented in Fig. 7. In the reference complexions E1 and T1, the removal  
234 of a MgO pair causes one tetrahedron to miss an O ion and to share one with a neighboring tetrahedron.

235 The stoichiometric complexions E2, E3, T2 and T3 already contained connected tetrahedra and free O ions,  
236 as presented in section 3.3. One would expect the most favorable configuration to be the one where the free  
237 O ion would be removed. We find that this is true only in the complexion T3n, as shown in Fig. 4f. On the  
238 contrary, for complexions E2n, E3n and T2n, we find that the most favorable systems are the ones where  
239 the free O ions are untouched, and three tetrahedra are connected, as shown in Figs. 4b, 4c and 4e.

240 Although vacancies were introduced in the GBs, we find that it has a negligible impact on the formation  
241 volume, as evidenced by the density profiles shown in Fig. 7. As a result, we expect that a simple measure-  
242 ment of the density would not allow to discriminate between the different GB complexions. Here again, we  
243 estimate the GB structural widths to be approximately  $10 \text{ \AA}$ .

#### 244 *4.2. Ab initio calculations*

245 As for the stoichiometric complexions presented in the previous section, we perform DFT calculations  
246 on the six non-stoichiometric GBs. Starting from the configurations relaxed with the interatomic potential,  
247 we perform a full ionic relaxation with DFT. Again, we find that this relaxation does not change the atomic  
248 structure of GBs, indicating that the interatomic potential is efficient for determining GB configurations.  
249 In particular, DFT confirms the stability of tetrahedra sharing O ions, as well as the excess volumes (see  
250 supplementary materials).

251 We apply Bader analysis to the non-stoichiometric GBs. The results are presented for the non-stoichiometric  
252 complexion E2 in Fig. 8. As previously, the shape of isosurfaces allows to recognize mixed ionic and covalent  
253 Si-O bonds in tetrahedra, as well as free O ions. Where tetrahedra are connected, shared O ions (arrows  
254 labeled S) have a decreased charge, while others O ions belonging to those tetrahedra (arrow labeled T)  
255 have a greater charge. As before, free O ions (arrows labeled F) have a higher charge.

## 256 5. Discussion

### 257 5.1. Comparison with literature

258 To the best of our knowledge, we have identified for the first time six stoichiometric complexions of the  
259  $60^\circ//[001](011)$  GB in forsterite, with formation energies ranging from 0.66 to  $1.25 \text{ J.m}^{-2}$ . For the same GB,  
260 [Adjaoud et al. \(2012\)](#) reported an energy of  $1.30 \text{ J.m}^{-2}$  and an excess volume of  $0.35 \text{ \AA}$  using an interatomic  
261 potential. First-principles calculations ([Ghosh and Karki, 2014](#)) reported an energy of  $1.15 \text{ J.m}^{-2}$  and an  
262 excess volume of  $0.37 \text{ \AA}$ . We find that our own values are in good agreement with both numerical studies.  
263 Both stoichiometric and non-stoichiometric GBs that we modeled exhibit structural widths of approximately  
264  $10 \text{ \AA}$ , a value commonly observed by transmission electron microscopy for GBs in olivine as reviewed by  
265 [Marquardt and Faul \(2018\)](#).

266 Experimental determination of GB energies are more scarce. [Duyster and Stöckhert \(2001\)](#) measured GB  
267 energies from dihedral angles in an equilibrated coarse-grained natural peridotite. Their values span between  
268  $1.12$  and  $1.47 \text{ J.m}^{-2}$  which is in good agreement with our results. The values reported by [Cooper and](#)  
269 [Kohlstedt \(1982\)](#) are significantly lower,  $0.9 \pm 0.35 \text{ J.m}^{-2}$ , probably due to the presence of melt at the  
270 interfaces in the olivine-basalt system considered.

271 The linking of tetrahedral units and the free O ions at forsterite GBs, as observed in this work, has never been  
272 noticed by prior studies. The finding of [Mantisi et al. \(2017\)](#) that the GBs are almost structureless above  
273  $3 \text{ \AA}$  cannot be confirmed here. Even differing in their structures, the complexions presented here exhibit  
274 a short range order which can be apprehended looking at figures 4 and 7. Some structural characteristics  
275 highlighted by [Ghosh and Karki \(2014\)](#) are retrieved here such as the conservation of Si ions in a tetrahedral  
276 environment and modification of Si-O bond lengths. A continuous treatment of this particular GB by [Sun](#)  
277 [et al. \(2016\)](#), shows that the O and Si sub-lattices accommodate the main part of the crystal disorientation,  
278 which is in good agreement with the structure of the complexions presented here.

279 The combination of first principles and MD calculations has permitted to improve the confidence on the  
280 interatomic potential of [Pedone et al. \(2006\)](#) to the study of GBs in forsterite. All stable complexions found  
281 with the potential have been confirmed by *ab initio* calculations with good agreement concerning the GB  
282 atomic structures, energies and excess volumes. Charge analysis have shown that the use of fixed partial  
283 charges (so-called rigid ion potential) is justified. The small deviations from the reference charge also justify  
284 the use of the interatomic potential.

285 *5.2. Effect of stoichiometry*

286 The low energy basins in the energy landscapes are separated by high energy barriers. It implies that GBs  
287 cannot change complexion conservatively (e.g. E1 → E2) as it would require too much energy. Adsorption  
288 of vacancies at the GB may provide a more favourable path towards a change in GB complexion. We have  
289 shown that it is more favorable for the vacancy to be within the GB than in the bulk phase. This finding is  
290 in good agreement with the expected vacancy sinks behavior of GBs (Uberuaga et al., 2015).

291 As explained above, the intrinsic GB energy cannot be defined unambiguously when it is non-stoichiometric.

292 One must account for the chemical potential  $\mu_{\text{MgO}}$  of the removed ions:

$$\gamma = \frac{E_{\text{tot}}^{N-2} - E_{\text{bulk}}^N + \mu_{\text{MgO}}}{A} - \gamma_{\text{ref}}, \quad (6)$$

293 The chemical potential depends on environmental conditions. One possible choice is to define it as the  
294 lattice energy of MgO periclase, which is  $\mu_{\text{MgO}} = -16.57$  eV using the same interatomic potential by  
295 Pedone. Nevertheless, other approximations can be done considering for instance  $\mu_{\text{MgO}} = \mu_{\text{Mg}_2\text{SiO}_4} - \mu_{\text{MgSiO}_3}$   
296 (where  $\mu_{\text{Mg}_2\text{SiO}_4}$  and  $\mu_{\text{MgSiO}_3}$  are the lattice energies of forsterite and enstatite respectively), which gives  
297  $\mu_{\text{MgO}} = -17.00$  eV; or  $2\mu_{\text{MgO}} = \mu_{\text{Mg}_2\text{SiO}_4} - \mu_{\text{SiO}_2}$  (where  $\mu_{\text{SiO}_2}$  is the lattice energy of quartz) which  
298 gives  $\mu_{\text{MgO}} = -16.44$  eV. Using these values, the GB energy of the E3n complexions (which has the lower  
299 segregation energy) should range between 1.60 and 1.76 J.m<sup>-2</sup> which is higher than the one of the parent  
300 GB (i.e. 1.25 J.m<sup>-2</sup>). More generally, the energies of the non-stoichiometric complexions are higher than  
301 the one of the parent GB.

302 A comparable numerical study (Chua et al., 2010) has also noticed that for different GBs in SrTiO<sub>3</sub> the  
303 most stable GBs (i.e. with lowest energies) were the stoichiometric ones, which is in contradiction with the  
304 non-stoichiometric GBs experimentally observed SrTiO<sub>3</sub> (Kim et al., 2001; McGibbon et al., 1994; Yang  
305 et al., 2013).

306 The GB can be viewed as a phase at equilibrium with other phase (e.g. neighboring grains) (Cantwell et al.,  
307 2014) and the minimization of the whole system energy does not necessarily lead to minimization of the GB  
308 energy itself. Our calculations show that if vacancies are present in the system, they will segregate at GBs  
309 even it increases the GB energy. The GB structure and its energy therefore depend on external factors,  
310 which emphasizes the lower importance to give on the GB energy to determine stable GB structures.

## 311 6. Implications

312 The atomic structure of GBs is a key input parameter, as all effective physical properties derive from it.  
313 For the one disorientation that we studied here (i.e.  $60.8^\circ$ ), we expect each GB complexion to have different  
314 properties in terms of mobility, diffusion, segregation, and so forth. We want to stress the importance of  
315 considering all possible complexions of GBs when performing atomic-scale simulations, instead of focusing  
316 on a single particular complexion.

317 Our work also evidences the attractiveness of GBs for vacancies (Tschopp et al., 2012; Uberuaga et al., 2015),  
318 highlighting the exchange capacities between crystal and GBs. At finite temperature, these exchanges should  
319 be of first importance for the structure of GBs.

320 A remarkable observation from our study is the presence of an anomalous non-silicate oxygen site in  
321 some GBs, which may have several implications. First, these free O ions may diffuse easier than the others  
322 (which are bound in tetrahedral environment), which could contribute to the high diffusivity of oxygen in  
323 GBs compared to bulk (Yurimoto et al., 1992). It may therefore increase the O vacancy concentration in  
324 forsterite GBs.

325 Second, the occurrence of such an unbound O ion is likely to have implications on water storage. The  
326 same feature is found in the structure of wadsleyite where it has been shown to strongly favor protonation  
327 (Jacobsen et al., 2005; Smyth, 1994). Our calculations suggest the possibility of a strong segregation of  
328 hydrogen at GBs with a maximum concentration of  $1.74 \cdot 10^{-2} \text{ \AA}^{-2}$  on the basis that each unbound O ion  
329 is protonated. Assuming spherical grains the contribution of such a mechanism to hydrogen storage should  
330 be of the order of 390, 40 and 4 H/ $10^6$ Si for grain sizes of 1, 10 and 100  $\mu\text{m}$ , respectively.

331 Finally, some stable GBs can have relatively high free volumes and we can expect these sparsely dense  
332 boundaries to be preferential zones for incompatible elements. Further simulations are required to properly  
333 assess these hypotheses.

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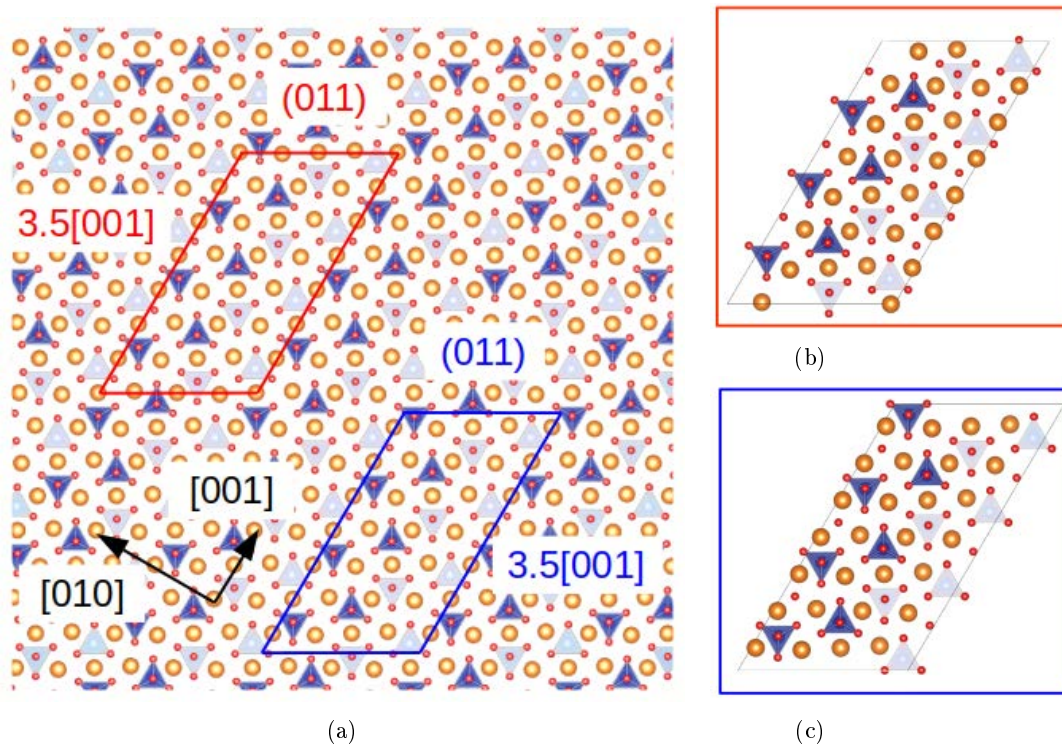


Figure 1: Typical oriented unit cells of forsterite used to construct the STGBs. Basic crystallographic directions  $[010]$  and  $[001]$  are indicated. Crystals are rotated around the  $[100]$  axis normal to the figure. Insets show cells of forsterite terminated by (1c) Si planes, and (1b) Mg planes (see text).

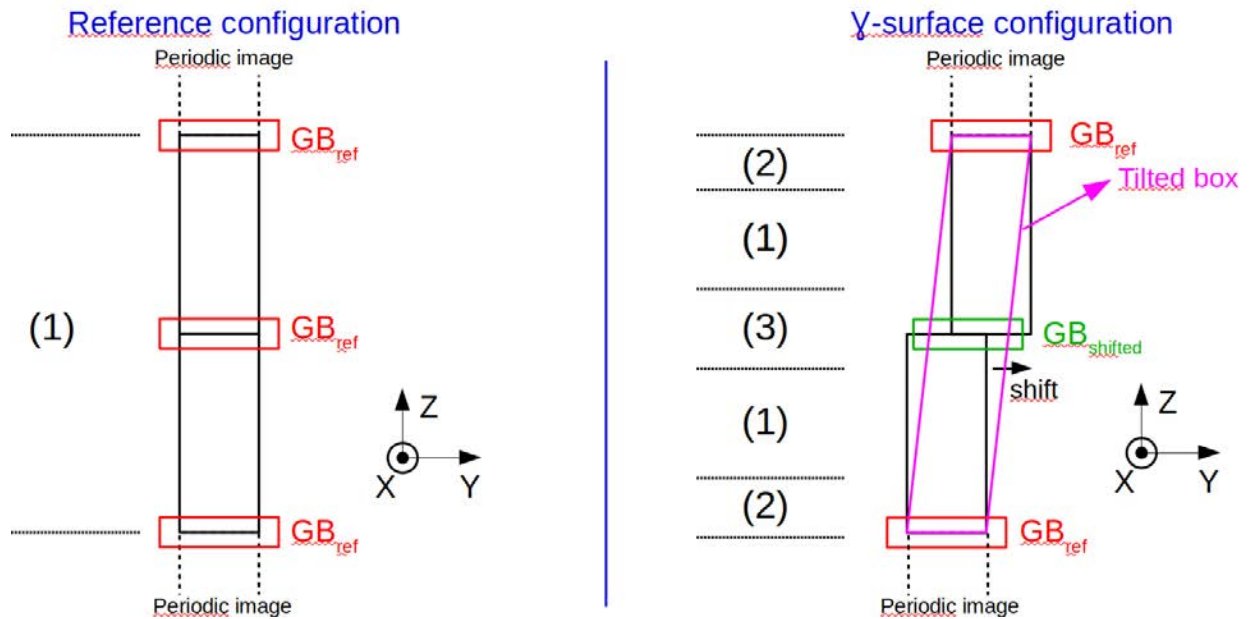


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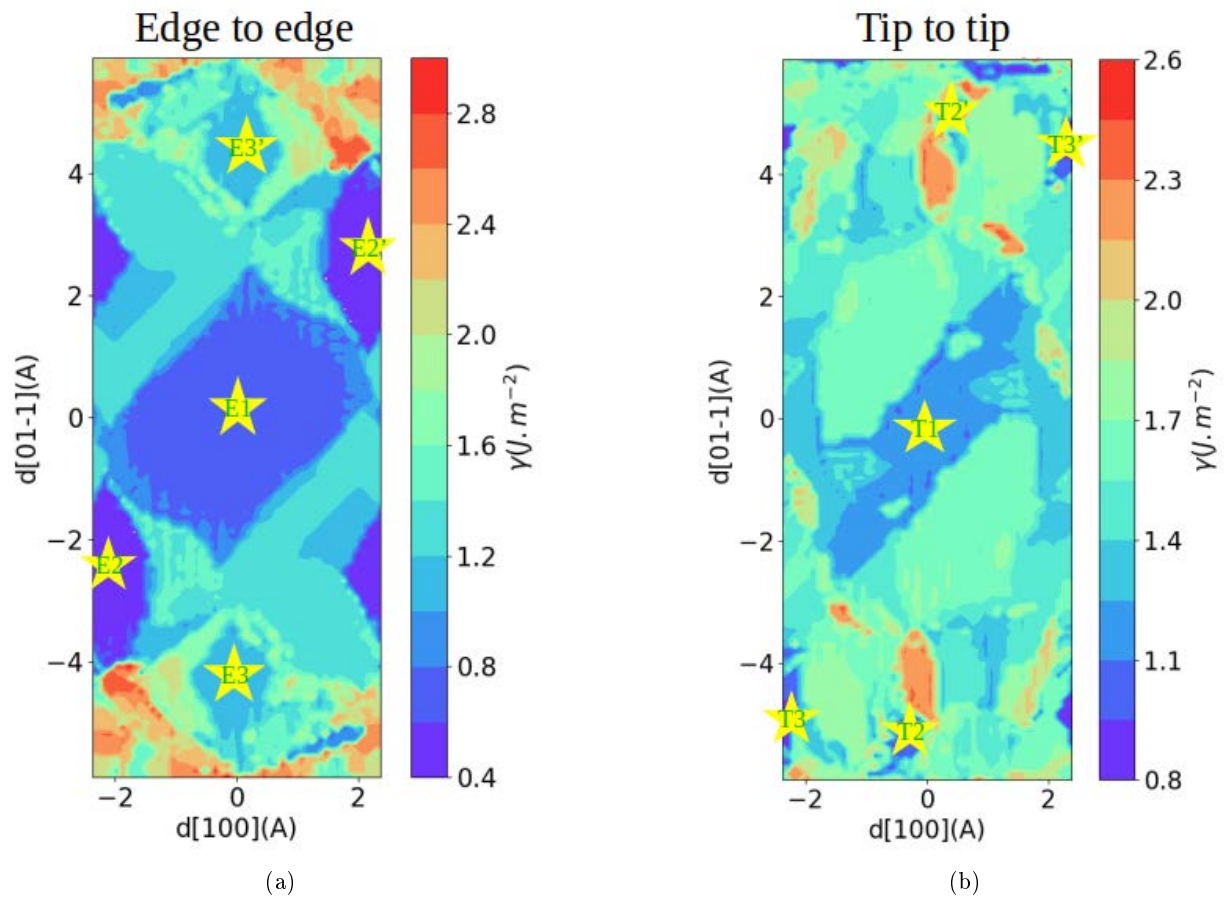


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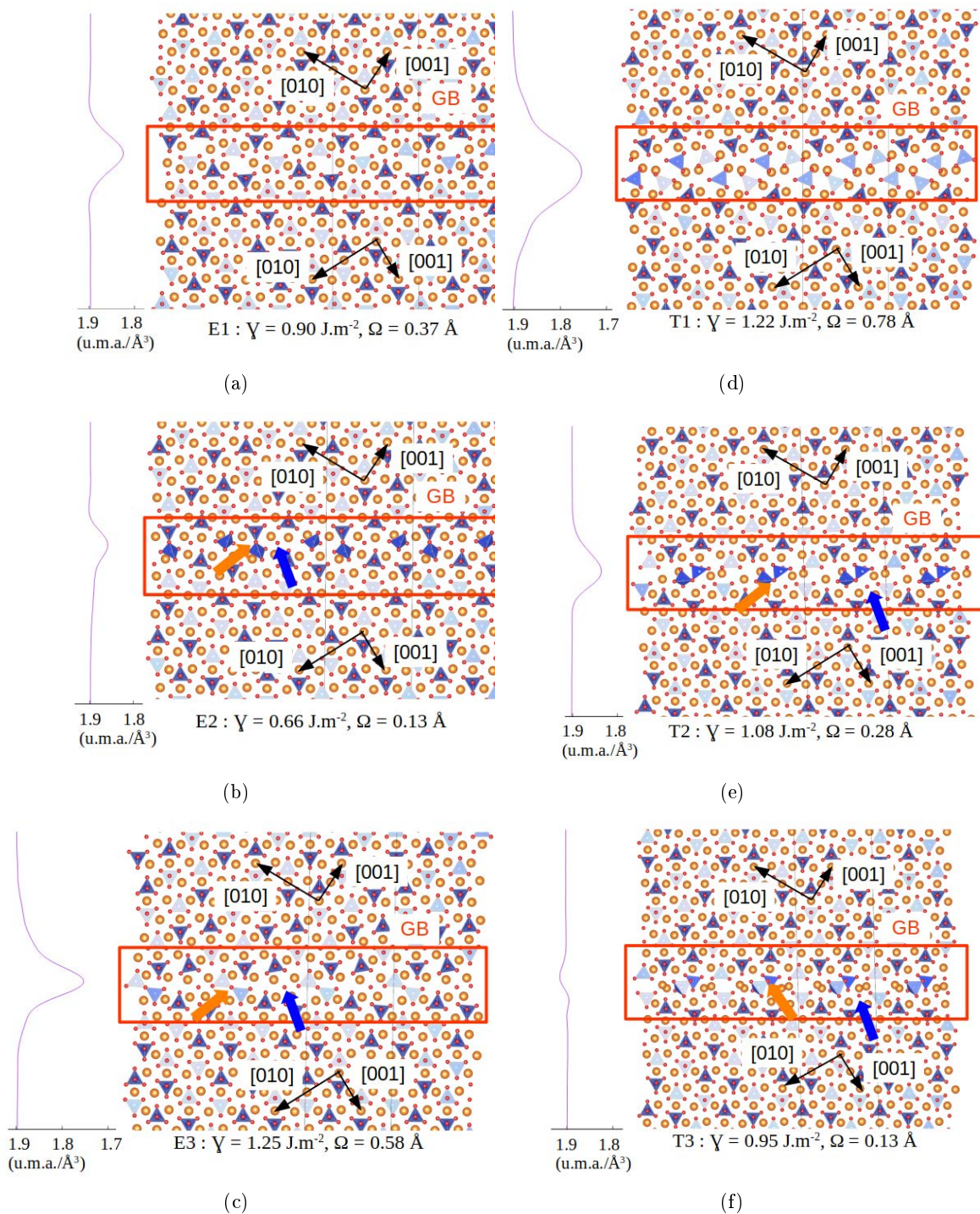


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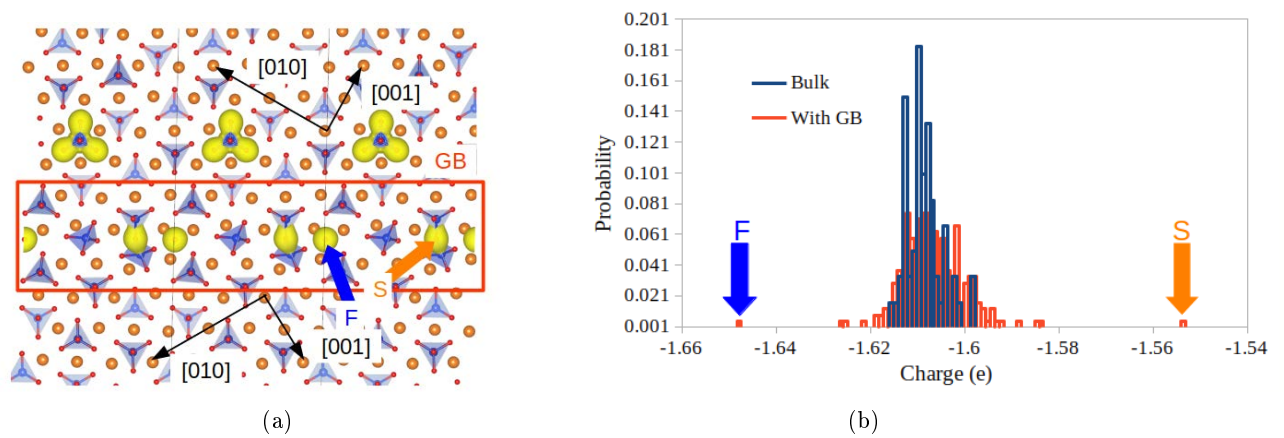


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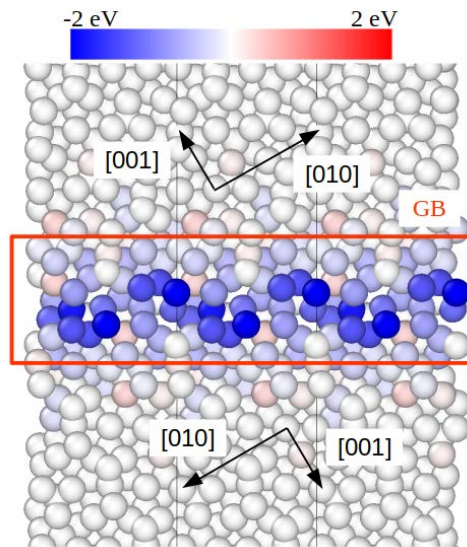


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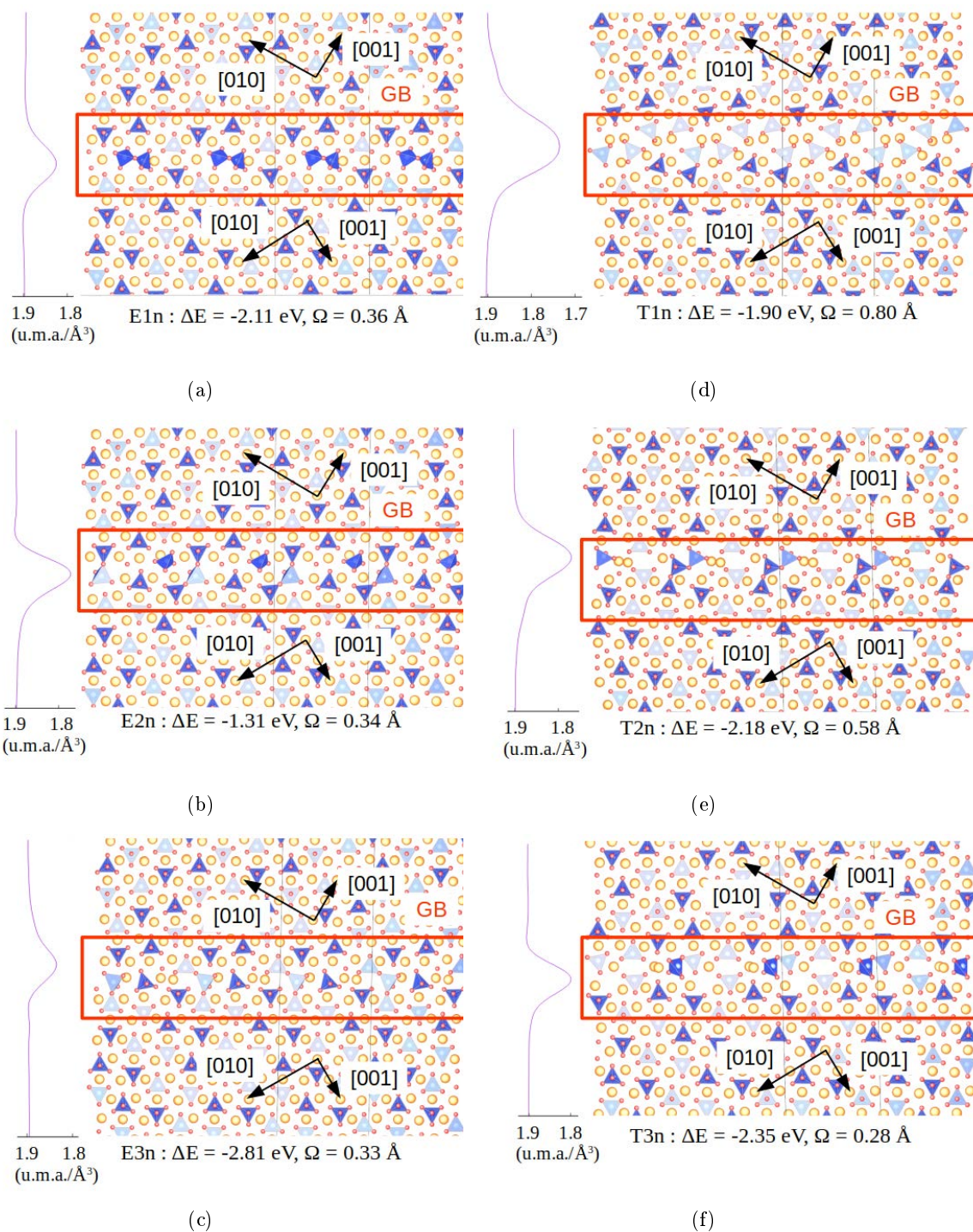


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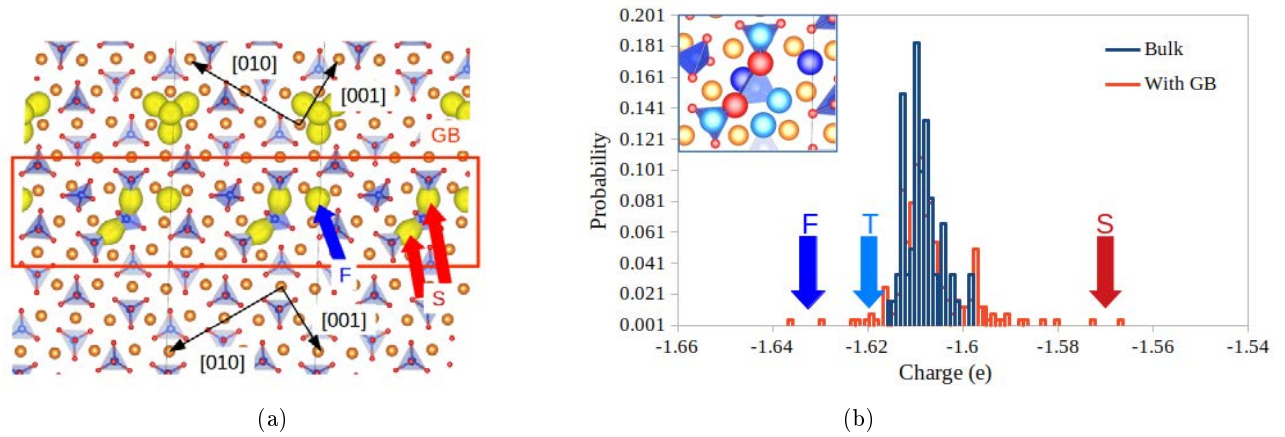


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