

## Structure and coherency of bcc Nb precipitates in hcp Zr matrix from atomistic simulations

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We use atomistic simulations to study the structure and shape of niobium precipitates with a body-centered cubic crystallographic structure in a zirconium matrix with a hexagonal close-packed structure. We consider a Pitsch-Schrader orientation relationship, which is observed experimentally for Nb precipitates appearing under irradiation in zirconium alloys. In this regard, we have developed a Zr-Nb empirical potential using the embedded atom method. This parametrization offers a good description of the interfaces between Nb precipitates and the Zr matrix. The potential includes all the necessary physical ingredients to account for the coherency strain between both phases. The atomistic simulations reveal a significant decrease in the precipitate formation energy when they become semicoherent, with enough misfit dislocations at the interface to eliminate the lattice misfit between the Nb precipitates and the Zr matrix. The “idealized” equilibrium shape that minimizes the formation energy of these semicoherent precipitates matches the experimental shape: platelets lying in the Zr basal planes with a reduced dimension along the  $[0001]$  axis. Our simulations suggest that the platelet shape observed in zirconium for irradiation-induced Nb-enriched precipitates simply results from a minimization of their energy cost.

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## I. INTRODUCTION

The Zr-Nb binary system is a prototypical example of a demixing alloy in which phase separation leads to the formation of two phases with different crystallographic structures, a Zr-enriched hcp  $\alpha$  phase and a Nb-enriched bcc  $\beta$  phase. Used in the nuclear industry as a structural material, particularly for fuel cladding in nuclear power plants [1,2], typical Zr-Nb alloys contain between 1% and 2.5% Nb, i.e., a nominal concentration above the maximal solubility limit [3–5]. Consequently, these alloys form spherical  $\beta$ -Nb precipitates, with a typical size between 20 and 200 nm [6–9], embedded in an  $\alpha$ -Zr matrix. These native  $\beta$ -Nb precipitates do not appear to have an orientation relationship with the matrix [8,10] and are thus considered incoherent, although some specific orientation relationships (OR) have occasionally been reported [7,11,12]. Due to the low diffusivity of Nb in the  $\alpha$ -Zr phase, equilibrium is not reached at the operating temperature, i.e., 300 °C – 350 °C for the fuel cladding, resulting in a higher Nb concentration in the  $\alpha$ -Zr phase than the solubility limit. Under neutron irradiation, this supersaturated solid solution evolves, leading to the nucleation of a second population of  $\beta$ -Nb precipitates, which are smaller than the native ones [6,8,13–19]. These smaller precipitates form due to the accelerated precipitation kinetics induced by irradiation and remain stable when the alloy is annealed postirradiation [20,21].

In neutron-irradiated samples, the high density of  $\langle a \rangle$  dislocation loops created by irradiation in the  $\alpha$ -Zr matrix makes the irradiation-enhanced precipitates visible by transmission electron microscopy (TEM), only with a projected view in a

prismatic plane using a  $g = 0002$  diffracting vector, as this diffraction vector renders  $\langle a \rangle$  loops invisible, thus allowing one to see the  $\beta$ -Nb precipitates. Under these imaging conditions, the nanoprecipitates appear as needlelike particles, with their long dimension lying in the basal plane. Once the irradiation microstructure has been annealed and the  $\langle a \rangle$  loops removed, precipitates can be imaged with different tilts, and it becomes clear that they are actually platelets lying in the basal planes. Initially, they are almost circular with a  $\sim 3$  nm diameter at low irradiation doses, but they become more acicular, elongated in the basal plane, at high irradiation doses [15]. The acicular precipitates exhibit a characteristic size of  $6.5 \pm 3$  nm and  $3.2 \pm 0.9$  nm in the basal plane, with a nearly random orientation of the long direction, and  $1.4 \pm 0.4$  nm along the  $[0001]_\alpha$  direction, resulting in a flattened needle shape [8]. TEM observations with energy-dispersive x-ray spectroscopy (EDS) on neutron-irradiated Zr-Nb M5<sub>Framatome</sub><sup>1</sup> and ZIRLO® alloys, which have not been annealed postirradiation, show the same shape and dimensions of the  $\beta$ -Nb particles [18,22] as conventional TEM. These  $\beta$ -Nb precipitates, which appear during irradiation, have a significant influence on the properties of the Zr-Nb alloys. They contribute to hardening, even after postirradiation annealing, as they remain stable [20,21]. Through their equilibrium with the Nb in solid solution in the  $\alpha$ -Zr phase, they affect the corrosion and hydriding resistance of Zr-Nb alloys [9,23].

Similar  $\beta$ -Nb precipitates appear under proton irradiation [9,23–26], although the length of the needles is usually larger ( $\geq 20$  nm and up to 150 nm) than with neutron irradiation, or

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under electron irradiation [27]. Ion irradiation similarly leads to the formation of Nb-enriched nanoclusters, as observed with atom probe tomography (APT) by Matsukawa *et al.* and Adisa *et al.* [12,17] in Zr-Nb alloys containing 1% or 2.5% Nb. In this case, the Nb clusters have a smaller mean diameter ( $\sim 4$  nm). Although no TEM has been performed to confirm their crystallographic structure, it is reasonable to assume that they have the same bcc structure as the  $\beta$ -Nb particles that appear under neutron or proton irradiation. The flattened shape of these irradiation-induced  $\beta$ -Nb particles along the  $[0001]_\alpha$  direction thus appears to be independent of the irradiation conditions.

As noted by Ribis *et al.* [8], the reason for the thinness of the  $\beta$ -Nb precipitates along the  $[0001]_\alpha$  direction is unknown. Sarce [28–30] has proposed that this shape results from the anisotropy of vacancies and interstitial diffusion. However, the proposed model, which neglects the impact of elastic stress fields on point defects diffusion, may be more relevant for fully incoherent precipitates than for the coherent or semicoherent precipitates corresponding to the  $\beta$ -Nb particles appearing under irradiation [8,23]. Irradiation-enhanced  $\beta$ -Nb precipitates have indeed an orientation relationship with the  $\alpha$ -Zr matrix between the Pitsch-Schrader OR,  $(0\bar{1}1)_\beta \parallel (0001)_\alpha$  and  $[100]_\beta \parallel [2\bar{1}\bar{1}0]_\alpha$ , and the Burgers OR,  $(0\bar{1}1)_\beta \parallel (0001)_\alpha$  and  $[111]_\beta \parallel [2\bar{1}\bar{1}0]_\alpha$  [8,23]. These two ORs only deviate by a small rotation,  $\sim 5.26^\circ$  around the  $[0001]_\alpha$  axis [31], and as explained in [23], the OR of the  $\beta$ -Nb precipitates with the  $\alpha$ -Zr matrix can generally be interpreted as a Pitsch-Schrader or a Burgers OR. This OR between the  $\beta$ -Nb precipitates and the  $\alpha$ -Zr matrix necessarily impacts the shape of the precipitates, either through the energy cost of the corresponding interfaces or the elastic energy arising from the lattice misfit between both phases. In this article we use atomistic simulations to determine if the observed shape of the  $\beta$ -Nb particles appearing under irradiation can be related to their formation energy. Our hypothesis is that the flattened needle shape, with a reduced size along the  $[0001]_\alpha$  direction, minimizes the precipitate formation energy.

We first describe the energy models used to describe the Zr-Nb binary alloy at an atomic scale, considering *ab initio* calculations and an empirical potential we developed to enable larger simulations. We then study infinite coherent interfaces between the  $\beta$ -Nb precipitates and the  $\alpha$  matrix, comparing results from *ab initio* calculations and our empirical potential. Finally, molecular statics simulations are performed to find the precipitate shape that minimizes its formation energy, considering both coherent and semicoherent precipitates.

## II. ENERGY MODELS

### A. *Ab initio* calculations

*Ab initio* calculations are performed to complete the database used for fitting the empirical potential in the next section (Sec. II B) and to determine interface energies (Sec. III C). These calculations rely on the density functional theory, DFT, using the VASP code [32]. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof parametrization [33] is used for the exchange and correlation functional. The interaction between core and valence electrons is modeled

TABLE I. Properties of the hcp phase of pure Zr predicted by the EAM potential (EAM #3 of Ref. [34]) and compared to DFT results and experimental data: cohesive energy  $E^{\text{coh}}$ , lattice parameters  $a$  and  $c$ , and elastic constants  $C_{ij}$  of the hcp phase.

	EAM	DFT	Experiments
$E^{\text{coh}}$ (eV/atom)	6.635	/	6.32 [35]
$a$ (Å)	3.234	3.235	3.232 [36]
$c$ (Å)	5.168	5.179	5.182 [36]
$C_{11}$ (GPa)	142	144	155.4 [37]
$C_{33}$ (GPa)	168	164	172.5 [37]
$C_{12}$ (GPa)	75	64	67.2 [37]
$C_{13}$ (GPa)	76	66	64.6 [37]
$C_{44}$ (GPa)	44	26	36.3 [37]
$C_{66}$ (GPa)	33.5	40.	44.1 [37]

with the projector wave method, including  $4s$ ,  $4p$ ,  $5s$ , and  $4d$  electrons in valence states, both for Zr and Nb, and using a 370-eV cutoff energy for the plane-wave basis. The Brillouin zone is sampled with a Monkhorst-Pack grid with 24  $k$  points per inverse lattice parameter. The electronic density of states is integrated using Methfessel-Paxton broadening with a 0.2-eV smearing parameter. Atomic positions are relaxed until reaching a  $10\text{-meV Å}^{-1}$  threshold on each Cartesian component of atomic forces while keeping the periodicity vectors of the simulation cell fixed. As shown in Tables I and II, these *ab initio* parameters lead to equilibrium lattice parameters and

TABLE II. Properties of pure Nb predicted by the EAM potential and compared to DFT results and experimental data. For the bcc phase: cohesive energy  $E^{\text{coh}}$ , lattice parameter  $a$ , elastic constants  $C_{ij}$ , vacancy and self-interstitial formation energy  $E_{\text{V}}^{\text{form}}$  and  $E_{\text{SIA}}^{\text{form}}$  (for the SIA, the  $\langle 111 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 100 \rangle$  crowdions are considered, as well as the octahedral and tetrahedral positions). For the fcc and hcp phases: energy differences  $\Delta E$  with respect to the bcc ground state and corresponding lattice parameters  $a$  and  $c$ .

	EAM	DFT	Experiments
$E^{\text{coh}}$ (eV/atom)	7.57	/	7.57 [35]
$a$ (Å)	3.304	3.308	3.303 [38]
$C_{11}$ (GPa)	246	242	253 [39]
$C_{12}$ (GPa)	133	128	133 [39]
$C_{44}$ (GPa)	29	31	31 [39]
$E_{\text{V}}^{\text{form}}$ (eV)	2.71	2.7 [5]	$2.6 \pm 0.3$ [40]
$E_{\text{SIA}\langle 111 \rangle}^{\text{form}}$ (eV)	3.86	3.95 [41]	
$E_{\text{SIA}\langle 110 \rangle}^{\text{form}}$ (eV)	4.09	4.31 [41]	
$E_{\text{SIA}\langle 100 \rangle}^{\text{form}}$ (eV)	4.01	4.76 [41]	
$E_{\text{SIAocta}}^{\text{form}}$ (eV)	4.41	4.89 [41]	
$E_{\text{SIAtetra}}^{\text{form}}$ (eV)	4.27	4.56 [41]	
$\Delta E_{\text{fcc}}$ (meV/atom)	184	324 [41]	
$a_{\text{fcc}}$ (Å)	4.02	4.217 [41]	
$\Delta E_{\text{hcp}}$ (meV/atom)	215	297 [41]	
$a_{\text{hcp}}$ (Å)	2.83	2.867 [41]	
$c_{\text{hcp}}$ (Å)	4.76	5.238 [41]	

elastic constants, in good agreement with experimental values for both hcp Zr and bcc Nb.<sup>2</sup>

Supercells used to calculate solution energies have been described in Ref. [5] and contain up to 250 atoms. For the simulation of infinite planar interfaces, we use supercells built from a stacking of  $\beta$ -Nb and  $\alpha$ -Zr elementary cells each containing four atoms (see definition of these elementary cells in Figs. 2–4). These supercells contain up to 96 atoms for a stacking of 12  $\alpha$ -Zr and 12  $\beta$ -Nb elementary cells.

### B. Interatomic potential

We develop an empirical potential to describe the binary Zr-Nb alloy using the embedded atom method (EAM). The aim of this potential is to conduct large-scale atomistic simulations of  $\beta$ -Nb precipitates embedded in an  $\alpha$ -Zr matrix. To predict the elastic energy arising from the coherency constraint between the precipitate and the matrix, this potential must accurately describe both the  $\alpha$ -Zr and  $\beta$ -Nb phases, particularly their equilibrium lattice parameters and their elastic behavior. Additionally, a good description of the interfaces, including their structures and excess energies, between  $\beta$ -Nb precipitate and the  $\alpha$ -Zr matrix is required. As we intend to use this Zr-Nb potential in the near future to study the interaction of a dislocation gliding in the  $\alpha$ -Zr matrix with  $\beta$ -Nb precipitates, the computational cost associated with this potential must be reasonable to enable molecular dynamics simulations on relevant timescales of several nanoseconds and for simulation cells containing typically one million atoms. Despite the rapid advancements in modern machine learning force fields that offer interatomic interactions with  $\mathcal{O}(N)$  scalability and near *ab initio* accuracy, significantly better than traditional force fields, they remain numerically intensive [42–45]. We choose instead to focus on the EAM formalism, which is well suited to meet all our criteria, balancing accuracy and computational efficiency.

While no satisfactory EAM potential exists for the Zr-Nb binary system, Mendeleev and Ackland [34] have developed three different EAM potentials for Zr. Among these potentials, EAM #3 is particularly well-suited to describe the  $\alpha$  hcp phase, including dislocation properties controlling Zr plasticity [46–49]. Therefore, we employ this EAM #3 potential to describe pure Zr and only fit the pure Nb and the Zr-Nb alloying parts (see Appendix A).

The fitting of the potential is performed using the same procedure as that described in Ref. [50]. The pure Nb part is fitted on configurations corresponding to the perfect bcc, fcc, and hcp crystal structures (equilibrium lattice parameters and relative energies), the elastic constants of the bcc crystal, and its  $E(V)$  equation of state in a  $\pm 4\%$  variation range of the lattice parameter. The formation energies of the vacancy and different configurations of the self-interstitial atom (SIA) in the bcc phase are also considered. Table II shows that the obtained EAM potential gives a good description of pure

TABLE III. Properties of Zr-Nb binary alloy. Solution energies of Nb in  $\alpha$ -Zr phase  $\Omega_{\text{mix}}^{\alpha}$  and Zr in  $\beta$ -Nb phase  $\Omega_{\text{mix}}^{\beta}$ . Interface energies  $\Gamma_n^{\alpha/\beta}$  for different orientations  $\vec{n}$  of the interface plane:  $\vec{n} = \vec{x} \parallel [2\bar{1}\bar{1}0]_{\alpha} \parallel [100]_{\beta}$ ;  $\vec{n} = \vec{y} \parallel [01\bar{1}0]_{\alpha} \parallel [011]_{\beta}$ , with interfaces I, II, III corresponding to stable faults identified on the different possible cut planes (see Fig. 4);  $\vec{n} = \vec{z} \parallel [0001]_{\alpha} \parallel [0\bar{1}1]_{\beta}$  with interfaces ABC and ABA corresponding to the different possible stacking of the fault (see Fig. 3). For  $\Gamma_x^{\alpha/\beta}$ , values in italic are obtained by relaxing atoms only in the  $\vec{x}$  direction, i.e., perpendicular to the interface plane (see Sec. III C).

	EAM	DFT
$\Omega_{\text{mix}}^{\alpha}$ (eV)	0.480	0.632 [5]
$\Omega_{\text{mix}}^{\beta}$ (eV)	0.477	0.312 [5]
$\Gamma_x^{\alpha/\beta}$ (meV $\text{\AA}^{-2}$ )	29.2	8.5 (27.4)
$\Gamma_{yI}^{\alpha/\beta}$ (meV $\text{\AA}^{-2}$ )	30.5	20.8
$\Gamma_{yII}^{\alpha/\beta}$ (meV $\text{\AA}^{-2}$ )	78.0	91.2
$\Gamma_{yIII}^{\alpha/\beta}$ (meV $\text{\AA}^{-2}$ )	20.5	11.7
$\Gamma_{zABC}^{\alpha/\beta}$ (meV $\text{\AA}^{-2}$ )	17.2	Unstable
$\Gamma_{zABA}^{\alpha/\beta}$ (meV $\text{\AA}^{-2}$ )	20.1	8.7

Nb. This potential correctly predicts the bcc phase as the most stable one and agrees well with *ab initio* calculations and experiments for the fundamental properties of this bcc phase, particularly its equilibrium lattice parameter and elastic constants. Table II shows that this EAM potential nevertheless underestimates the energy difference of other crystallographic structures with respect to the bcc ground state. In particular, the potential leads to an energy of the hcp phase,  $\Delta E_{\text{hcp}} = 215$  meV/atom, lower than that obtained by *ab initio* calculations (297 meV/atom). One thus expects that this potential will overestimate the energy barrier opposing the nucleation of a bcc Nb embryo in an hcp matrix while still giving a reasonable description of the physical mechanisms. As we only consider Nb precipitates, which already have a bcc crystallographic structure, such a deficiency of the potential should be harmless for the present study. To improve the potential and give a better description of the relative energies of the different crystallographic structures, it would be necessary to go beyond the EAM formalism and to include an angular dependence of atomic bonding, an important ingredient in a transition metal like Nb. But this will be at the detriment of the numerical cost.

The Zr-Nb part is fitted on impurity calculations, i.e., a Nb solute atom in a hcp Zr matrix and an Zr solute atom in a bcc Nb matrix, considering four different simulation cells and thus four different solute concentrations in each case. Melted alloys using six different configurations with compositions ranging between 1/3 and 2/3 are also employed. Atomic forces and structure energies of these different configurations are used in the cost function of the fitting algorithms. Configurations used to model stable  $\beta$ -Nb/ $\alpha$ -Zr interfaces (see Sec. III) are also included in the database to ensure that the potential correctly describes interfaces between the precipitates and the matrix. As shown in Table III, the potential correctly predicts positive solution energies  $\Omega_{\text{mix}}^{\alpha}$  and  $\Omega_{\text{mix}}^{\beta}$ , both for a Nb solute atom in hcp Zr and for a Zr solute atom in bcc Nb, thus

<sup>2</sup>*Ab initio* values are not given for the cohesive energies, as these cohesive energies are notoriously hard to precisely define with DFT, and as they are not necessary for the present study, the EAM potential being fitted on experimental cohesive energies.

correctly describing the binary Zr-Nb system as an unmixing alloy. The energetic description of the alloy is nevertheless not fully quantitative, as values obtained with this EAM potential for solution energies significantly differ from *ab initio* values and the potential fails to reproduce the asymmetry of these solution energies. From a thermodynamic point of view, this potential should be rather considered as prototypical of a phase-separating alloy like Zr-Nb, i.e., a binary system with an unmixing tendency, leading to the formation of an  $\alpha$  and a  $\beta$  phase having properties of  $\alpha$ -Zr and  $\beta$ -Nb, rather than a real quantitative description of this binary alloy. The potential also leads to interface energies in reasonable agreement with *ab initio* values for the different orientations studied, as described in the next section, correctly predicting the energy hierarchy for the different configurations of the  $\vec{y} \parallel [0\ 1\ \bar{1}\ 0]_\alpha$  orientation, for instance. These interface energies are nevertheless slightly too high compared to *ab initio* values. Atomic simulations performed with this potential will therefore give more weight than they should to these coherent interfaces. Despite this overestimation, we will see in the last section that it is the elastic energy, and not the energy cost of the interfaces, which controls the equilibrium shape of the  $\beta$ -Nb precipitates when they remain coherent with the  $\alpha$ -Zr matrix.

The analytical functions and parameters corresponding to this Zr-Nb EAM potential are given in Appendix A.

### III. INFINITE INTERFACES

We first study the structure and the energy of infinite interfaces between  $\alpha$ -Zr and  $\beta$ -Nb corresponding to Pitsch-Schrader orientations between both phases. Specifically, the orientation of the reference axis and the corresponding periodicity lengths of the  $\alpha$  and  $\beta$  crystal structure are

(1)  $\vec{x} \parallel 1/3 [2\ \bar{1}\ \bar{1}\ 0]_\alpha \parallel [1\ 0\ 0]_\beta$  with  $\lambda_\alpha^x = a_{Zr} = 3.234\ \text{\AA}$  and  $\lambda_\beta^x = a_{Nb} = 3.304\ \text{\AA}$ ;

(2)  $\vec{y} \parallel [0\ 1\ \bar{1}\ 0]_\alpha \parallel [0\ 1\ 1]_\beta$  with  $\lambda_\alpha^y = a_{Zr}\sqrt{3} = 5.601\ \text{\AA}$  and  $\lambda_\beta^y = a_{Nb}\sqrt{2} = 4.673\ \text{\AA}$ ;

(3)  $\vec{z} \parallel [0\ 0\ 0\ 1]_\alpha \parallel [0\ \bar{1}\ 1]_\beta$  with  $\lambda_\alpha^z = c_{Zr} = 5.167\ \text{\AA}$  and  $\lambda_\beta^z = a_{Nb}\sqrt{2} = 4.673\ \text{\AA}$ .

The lattice mismatch between the two phases results in significant coherency strains. For illustration, if we assume that the  $\alpha$  phase remains unstrained and all the deformation occurs in the  $\beta$  phase, the  $\beta$  phase coherency strain in direction  $\vec{u}$  is given by  $\varepsilon_{uu}^\beta = (\lambda_\alpha^u - \lambda_\beta^u)/\lambda_\beta^u$ , leading to  $\varepsilon_{xx}^\beta = -2.1\%$ ,  $\varepsilon_{yy}^\beta = 19.9\%$ , and  $\varepsilon_{zz}^\beta = 10.6\%$ . Although these coherency strains are reduced by partitioning between both phases, they remain substantial. Consequently, calculation of the interface energy requires special care, as described below, to withdraw any contribution from the elastic energy.

#### A. Methods

Infinite interfaces are modeled using simulation cells with periodic boundary conditions in all directions. A block of perfect  $\alpha$ -Zr crystal and a block of perfect  $\beta$ -Nb are first prepared, orientated correctly to create an interface with a normal vector  $\vec{n}$  (step 1 in Fig. 1). Each block is then strained to eliminate the lattice mismatch between both phases at the interface plane, resulting in the same interface area  $S_{\vec{n}}$  in both

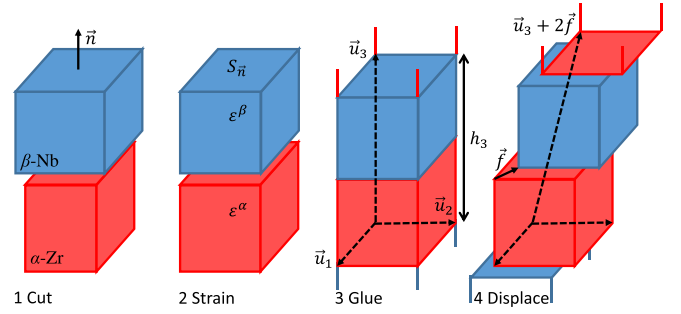


FIG. 1. Sketch describing the different steps used to create an infinite interface of normal  $\vec{n}$  between  $\alpha$ -Zr and  $\beta$ -Nb phases in a periodic simulation cell.

phases (step 2 in Fig. 1). The homogeneous strains  $\varepsilon^\alpha$  and  $\varepsilon^\beta$  are chosen to minimize the elastic energy of the sandwich structure according to linear elasticity (see Appendix B). The two blocks are then joined to create a periodic cell defined by vectors  $\vec{u}_1$ ,  $\vec{u}_2$ , and  $\vec{u}_3$  (steps 3 in Fig. 1). In addition, the blocks are displaced by a relative vector  $\vec{f}$  within the interface plane, and the periodicity vector  $\vec{u}_3$ , initially normal to the interface plane, is modified to  $\vec{u}_3 + 2\vec{f}$  to ensure the same atomic configuration for the two interfaces present in the simulation cell (step 4 in Fig. 1). Finally, the sandwich structure is relaxed with atomic simulations, allowing atomic relaxations only in the direction  $\vec{n}$  perpendicular to the interface plane to prevent the disappearance of the fault introduced in the interface plane during relaxation. The interface energy is thus obtained as a function of the fault vector  $\vec{f}$ . The simulation approach is similar to that used in single-phase crystals to define generalized stacking fault energies [51,52].

The interface energy is defined by

$$\Gamma_{\vec{n}}^{\alpha/\beta} = \frac{E[\text{Zr}_n\text{Nb}_m] - E[\text{Zr}_n] - E[\text{Nb}_m]}{2S_{\vec{n}}}, \quad (1)$$

where  $E[\text{Zr}_n\text{Nb}_m]$  is the energy of the periodic supercell containing the interface with  $n$  Zr and  $m$  Nb atoms, while  $E[\text{Zr}_n]$  and  $E[\text{Nb}_m]$  are the reference energies of the pure  $\alpha$ -Zr and  $\beta$ -Nb phases for the same number of atoms and the same applied strain as in the initial sandwich structure. The factor 2 in Eq. (1) arises from the presence of two interfaces in the periodic supercell, each covering an area  $S_{\vec{n}}$ . Generalized interface energies are obtained by plotting the interface energy as a function of the fault vector. Minima appearing on the two-dimensional (2D) surface defined by this function  $\Gamma_{\vec{n}}^{\alpha/\beta}(\vec{f})$  indicate possible stable configurations of the interface.

These stable configurations are then simulated in simulation boxes with different periodicity lengths  $h_3$  in the direction  $\vec{n}$  normal to the interface, keeping the phase ratio  $n_{Zr}/n_{Nb} = n/m$  constant, where  $n_{Zr}$  and  $n_{Nb}$  are the number of  $\alpha$ -Zr and  $\beta$ -Nb elementary cells stacked in the  $\alpha$  and  $\beta$  blocks composing the periodic sandwich structure. Although most of the elastic contribution to the excess energy has been already excluded in the definition of the interface energy [Eq. (1)], there may be a remaining elastic contribution leading to a linear variation of the interface energy with the periodicity length  $h_3$ . This elastic contribution can be eliminated by considering



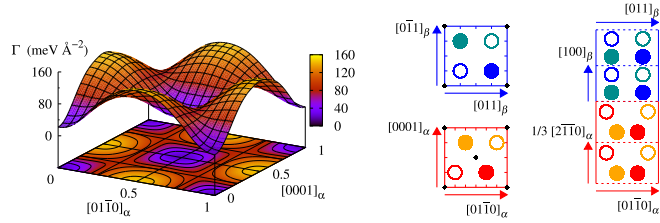


FIG. 2. Generalized interface energy for an interface of normal  $\bar{x} \parallel 1/3 [2 \bar{1} \bar{1} 0]_{\alpha} \parallel [1 0 0]_{\beta}$ . The interface energy  $\Gamma_{\bar{x}}^{\alpha/\beta}$  is presented as a function of the fault vector  $\bar{f}$  on the left, while the crystallographic structures of the  $\alpha$ -Zr (red and orange drawing) and  $\beta$ -Nb phases (blue and cyan drawing) are sketched on the right for two different projection directions. Zr and Nb atoms are drawn as circles, and the elementary cells are depicted with continuous and dashed lines. The positions of the minima appearing on the 2D surface defined by  $\Gamma_{\bar{x}}^{\alpha/\beta}$  are shown by black symbols on the projections in the interface plane: this corresponds to the origin of the elementary cell in the  $\beta$ -Nb phase and to the same position shifted by the fault vector  $\bar{f}$  in the  $\alpha$ -Zr phase.

the value of  $\Gamma_{\bar{n}}^{\alpha/\beta}$  in the vanishing limit  $h_3 \rightarrow 0$  while keeping the phase ratio  $n_{Zr}/n_{Nb}$  constant [53,54].

### B. Generalized interface energies

Generalized interface energies were calculated with the EAM potential for the three interfaces of normal  $\bar{u}_3$  parallel to  $\bar{x}$ ,  $\bar{y}$ , and  $\bar{z}$ . Results are presented in Figs. 2–4, with the crystallographic definition of the elementary  $\alpha$ -Zr and  $\beta$ -Nb phases appearing on the right. All calculations were performed with a phase ratio  $n_{Zr}/n_{Nb} = 1$  using a stacking of six  $\alpha$ -Zr and six  $\beta$ -Nb elementary cells.

Only one minimum exists for the interface of normal  $\bar{x}$  (Fig. 2). It corresponds to a configuration which maximizes the distance between neighboring Zr and Nb atoms at the interface. On the other hand, two minima can be found for the interface of normal  $\bar{z}$  (Fig. 3). In this orientation, the interface is parallel to the basal planes of the  $\alpha$ -Zr phase. The hcp structure can be defined by an *ABAB* stacking of basal planes along the  $[0001]_{\alpha}$  direction. One minimum corresponds to a

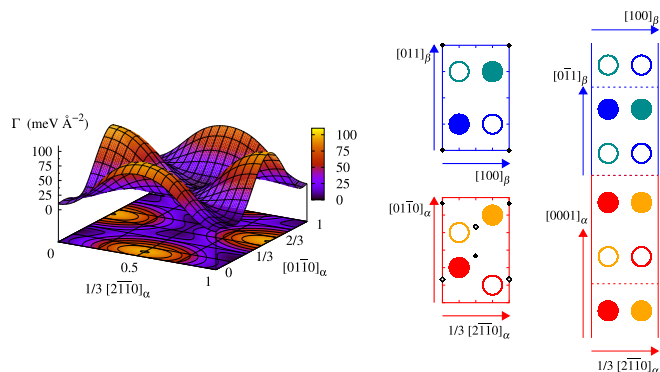


FIG. 3. Generalized interface energy for an interface of normal  $\bar{z} \parallel [0 0 0 1]_{\alpha} \parallel [0 \bar{1} \bar{1}]_{\beta}$ . The positions of the minima corresponding to an *ABA* and an *ABC* stacking are indicated by respectively filled and empty black diamonds on the Nb and Zr unit cell projections.

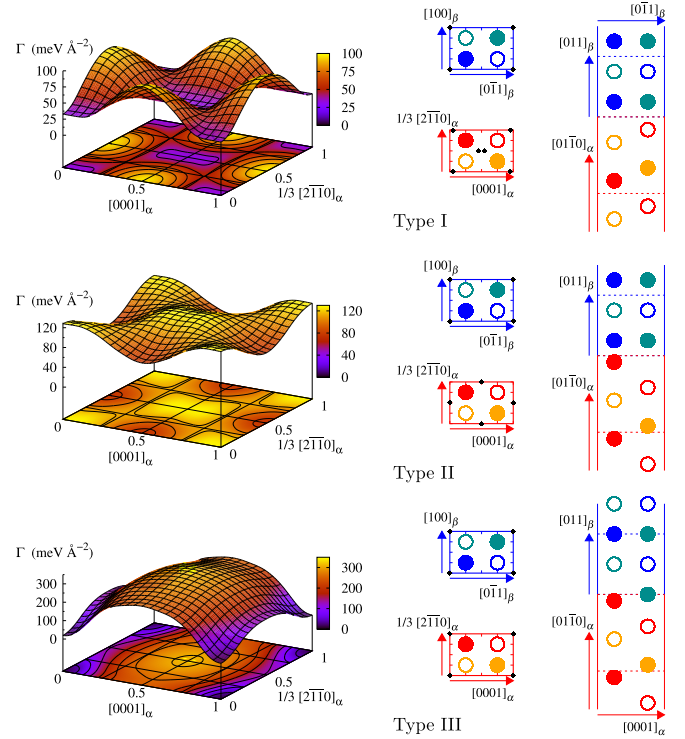


FIG. 4. Generalized interface energy for an interfaces of normal  $\bar{y} \parallel [0 \bar{1} \bar{1} 0]_{\alpha} \parallel [0 1 1]_{\beta}$ .

configuration where the Nb layer lies at the interface in an *A* position, thus following the hcp network, while in the other minimum configuration the Nb atoms lie at the interface in the hollow C sites of the hcp basal planes, leading to an *ABC* stacking, i.e., a stacking corresponding locally to fcc structure. We differentiate these two possible configurations of the  $\bar{z}$  interface by naming them *ABA* and *ABC*.

The situation is more complex for the interface with normal  $\bar{y}$ , as the  $\{0 \bar{1} \bar{1} 0\}$  prismatic planes of the  $\alpha$ -Zr phase parallel to the interface are corrugated. Therefore there are two different positions where the interface plane can be located in the  $\alpha$ -Zr phase, leading to type-I and -II interfaces shown in Fig. 4. In addition to these two different configurations, we consider a third one (type III) where the interface plane is a mixture of Zr and Nb atoms. Each of these three possible  $\bar{y}$  interfaces leads to only one minimum.

### C. Interface energies

We now compute the interface energies for different periodicity lengths  $h_3$ , keeping the phase ratio  $n_{Zr}/n_{Nb} = 1$ , for the different minima previously identified on the generalized interface energies. Calculations are performed with the EAM potential, first allowing atomic relaxations only in the direction  $\bar{n}$  normal to the interface plane and then with full atomic relaxations. For the interface of normal  $\bar{x}$ , full relaxations were not possible due to the large lattice misfits. As a result, the homogeneous strains  $\varepsilon^{\alpha}$  and  $\varepsilon^{\beta}$  applied to both phases are high, and when the structure is fully relaxed, depending on the phase ratio and periodicity length  $h_3$ , at least one of the two phases does not maintain its initial  $\alpha$

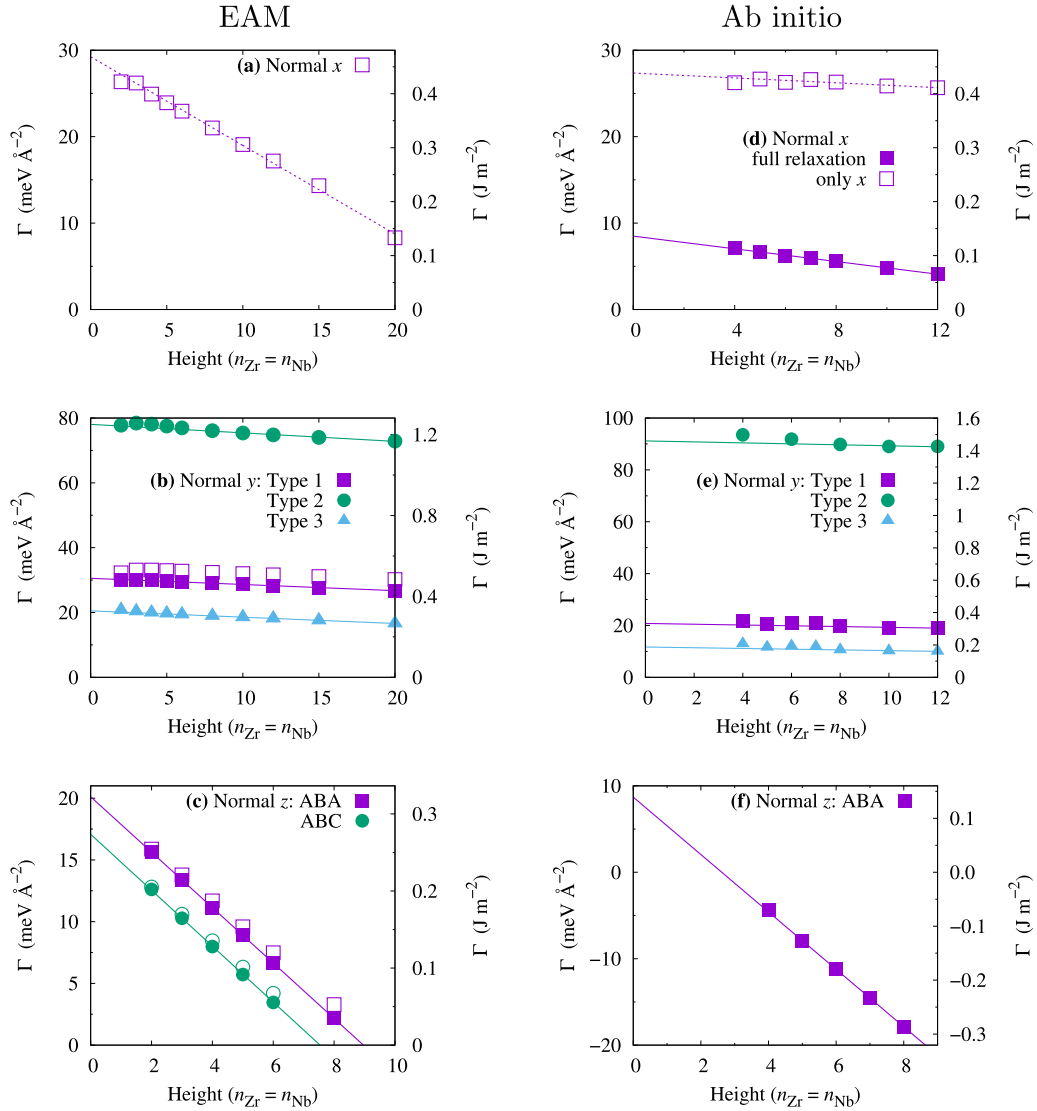


FIG. 5. Variation of the interface energy with the number of stacked planes, i.e., the periodicity length  $h_3$ , for the three different orientations of the interface plane and the different minima identified on the generalized interface energies. Filled and empty symbols are for simulations where atomic positions have been relaxed, respectively, in all directions (EAM, only for  $\bar{y}$  and  $\bar{z}$  interfaces) or only in the direction perpendicular to the interface plane. Subfigures on the left (a–c) and right (d–f) columns are for EAM and *ab initio* calculations, respectively.

or  $\beta$  crystallographic structure. Therefore, only results with relaxations constrained to the direction perpendicular to the interface are considered for this  $\bar{x}$  orientation. For the other two orientations,  $\bar{y}$  and  $\bar{z}$ , full relaxations have only a marginal impact on the obtained interface energies compared to constrained relaxations (see the difference between empty and filled symbols in Figs. 5(a)–5(c)).

As expected, we observe a linear variation of the interface energies with the periodicity length  $h_3$  for all interfaces (Figs. 5(a)–5(c)). The slope of this linear variation is negative, indicating that our definition of the interface energy [Eq. (1)] slightly overestimates the elastic energy. This is expected, as the position of the interface plane can shift during atomic relaxation, allowing a further reduction of the elastic energy compared to the initial guess based on linear elasticity theory. In all cases a clear extrapolation of the interface energy in the limiting case  $h_3 \rightarrow 0$  can be defined, leading to the interface energies shown in Table III.

The same interfaces have been modeled with *ab initio* calculations, maintaining the phase ratio  $n_{Zr}/n_{Nb} = 1$ , leading to the interface energies shown in Figs. 5(d)–5(f). As with the EAM potential, a linear variation of the interface energy as a function of the periodicity length  $h_3$  is observed, allowing a clear definition of the interface energy  $\Gamma_{\bar{n}}^{\alpha/\beta}$  free of any elastic contribution in the limit  $h_3 \rightarrow 0$ .

For the interface of normal  $\bar{x}$  [Fig. 5(d)], calculations have been performed with relaxation of the atomic positions only in the direction perpendicular to the interface plane and also with full relaxation, as the instability of strained phases, which we have encountered for this orientation with the EAM potential, did not appear with *ab initio*. Partial relaxation leads to very close values of the interface energy:  $\Gamma_{\bar{x}}^{\alpha/\beta} = 27.4 \text{ meV } \text{\AA}^{-2}$  for *ab initio* and  $29.2 \text{ meV } \text{\AA}^{-2}$  for EAM. Full relaxation in *ab initio* calculations leads to a lower value ( $8.5 \text{ meV } \text{\AA}^{-2}$ ). Although the fully relaxed structure can still be identified as an interface

between an  $\alpha$  and a  $\beta$  phase, the crystals, in particular the hcp lattice, are severely distorted by the large lattice misfit imposed by the coherent interface for this  $\bar{x}$  orientation. Strong anharmonicity of the lattice elastic response is therefore expected.

For the interface of normal  $\bar{y}$ , the same hierarchy between the different interface types is observed with *ab initio* and EAM [Figs. 5(b) and 5(e)]. Both energy models predict that the type-III interface has the lowest energy, while the type-II interface has a much higher energy than the other two configurations. Interface energies obtained with *ab initio* calculations are lower than with the EAM potential (11.7 vs 20.5 meV  $\text{\AA}^{-2}$  for type III), but the energy difference remains reasonable.

For the interface of normal  $\bar{z}$ , only the ABA configuration has been found stable in *ab initio* calculations, leading to  $\Gamma_{z\text{ABA}}^{\alpha/\beta} = 8.7 \text{ meV } \text{\AA}^{-2}$ . Starting from an ABC configuration for the interface, full atomic relaxation leads to an interface having locally the same ABA configuration, with an additional homogeneous strain spreading across the whole simulation cell to comply with the constraint imposed by periodicity. This contrasts with the results of EAM, where both configurations have been found stable, with the ABC configuration having a lower energy than ABA, 17.2 vs 20.1 meV  $\text{\AA}^{-2}$ . Higher interface energies are also obtained for this  $\bar{z}$  interface orientation with the EAM potential than with *ab initio* calculations, although the difference remains acceptable.

With values varying between 20.1 and 29.2 meV  $\text{\AA}^{-2}$  for the lowest interface energies found for the different interface orientations (Table III), the Zr-Nb EAM potential provides a reasonable description of the Zr-Nb interfaces. It slightly overestimates the energy cost of these interfaces, as *ab initio* calculations predict lower interface energies (between 8.7 and 11.7 meV  $\text{\AA}^{-2}$  for the most stable configurations), with the error remaining acceptable. Moreover, both energy models agree on the weak anisotropy of the interface energy. Hence, this EAM potential appears appropriate for providing a qualitative description of interfaces within this binary system.

#### IV. NIOBIUM PRECIPITATES

We now study the formation energy of a niobium precipitate with a fixed volume but varying shape, embedded in a zirconium matrix, using the Zr-Nb EAM potential with a Pitsch-Schrader orientation. Our goal is to determine the precipitate shape that minimizes the formation energy and compare it to the shape observed experimentally by TEM. We consider both fully coherent precipitates (without misfit dislocations) and semicoherent precipitates (with misfit dislocations) with simplified parallelepiped shapes.

##### A. Methods

The precipitate contains 4800 Nb atoms, corresponding to a volume equal to  $86.5 \text{ nm}^3$  in its unstrained state, closely matching the volume of precipitates observed in experiments. The simulation box dimensions are  $108 \lambda_x^\alpha = 349 \text{ \AA}$ ,  $62 \lambda_y^\alpha = 347 \text{ \AA}$ , and  $68 \lambda_z^\alpha = 351 \text{ \AA}$  in the directions  $\bar{x} \parallel 1/3 [2 \bar{1} \bar{1} 0]_\alpha$ ,  $\bar{y} \parallel [0 1 \bar{1} 0]_\alpha$ , and  $\bar{z} \parallel [0 0 0 1]_\alpha$ , respectively, containing over 1.8 million atoms.

We generate different precipitate shapes, all parallelepipeds with sides of normal  $\bar{x}$ ,  $\bar{y}$ , and  $\bar{z}$  but with varying aspect ratios, and thus varying sizes  $l_x$ ,  $l_y$ , and  $l_z$  in each direction, keeping the precipitate volume  $V = l_x l_y l_z$  constant. Only precipitate shapes with a size larger than  $10 \text{ \AA}$  in all directions are considered. Coherent precipitates are created by removing the same number of Zr atoms in the matrix and inserting the precipitate in the cavity after an homogeneous strain has been applied to cancel the lattice misfit between the precipitate and the matrix. The precipitate is slightly compressed in the  $\bar{x}$  direction and significantly dilated in  $\bar{y}$  and  $\bar{z}$  directions. Atomic positions are then relaxed while keeping the periodicity vectors of the simulation box constant. Finally, the precipitate formation energy is defined as

$$\Delta E = E[\text{Zr}_n\text{Nb}_m] - nE_{\text{Zr}}^{\text{coh}} - mE_{\text{Nb}}^{\text{coh}},$$

where  $n$  and  $m$  are the number of Zr and Nb atoms ( $m = 4800$  and  $n + m = 4 \times 108 \times 62 \times 68$  for a coherent precipitate), and  $E_{\text{Zr}}^{\text{coh}}$  and  $E_{\text{Nb}}^{\text{coh}}$  are the cohesive energies of Zr and Nb, respectively.

We also study semicoherent precipitates by introducing  $n_D^u$  misfit dislocations at the precipitate/matrix interfaces to accommodate the lattice misfit in the  $\bar{e}_u$  direction, initially considering  $u = y$ , which leads to the largest misfit. This is done by keeping fixed the number of Nb atoms in the precipitate ( $m = 4800$ ) and removing in the  $\alpha$  matrix the Zr atoms belonging to  $n_D^u$  planes of normal  $\bar{e}_u$ , which intersect the precipitate. This Volterra procedure creates  $n_D^u$  pure prismatic dislocation loops of Burgers vector  $\bar{b}_u = \lambda_\alpha^u/2 \bar{e}_u$  around the precipitate at the interface with the matrix, as there are two planes per periodicity length  $\lambda_\alpha^u$ . These prismatic loops are interstitial in nature, as the density of the atomic planes is denser in the precipitate than in the matrix, and atoms have been removed in the matrix to compensate for the smallest atomic volume of the  $\beta$ -Nb phase than that of the  $\alpha$ -Zr phase. This Volterra procedure is therefore equivalent to the absorption of interstitial atoms by the precipitate to compensate for the different atomic volumes of the  $\alpha$  and  $\beta$  phases. The eigenstrain necessary to embed the precipitate in the matrix before relaxation becomes

$$\varepsilon_{uu}^\beta = \frac{(n_\beta^u - n_D^u/2)\lambda_\alpha^u - n_\beta^u\lambda_\beta^u}{n_\beta^u\lambda_\beta^u}, \quad (2)$$

where  $n_\beta^u$  is the number of  $\beta$ -phase planes in the precipitate in the  $\bar{e}_u$  direction, and  $l_u = n_\beta^u\lambda_\beta^u$  is the corresponding initial length of the precipitate. In the absence of misfit dislocations ( $n_D^u = 0$ ), the eigenstrain equals those given at the beginning of Sec. III for fully coherent precipitates.

##### B. Formation energy and aspect ratio

For coherent precipitates, Fig. 6(a) shows that the minimum formation energy is achieved when the precipitates have a very small size in the  $\bar{y}$   $\parallel [0 1 \bar{1} 0]_\alpha$  direction: it occurs for the reduced sizes  $\bar{l}_x = l_x/\sqrt[3]{V} = 2.2$ ,  $\bar{l}_y = 0.42$ , and  $\bar{l}_z = 1.1$ , which corresponds to  $l_x = 9.9$ ,  $l_y = 1.9$ , and  $l_z = 4.7 \text{ nm}$  for the precipitate volume considered here. Thus, coherent precipitates with minimum formation energy are elongated in the  $\bar{x}$   $\parallel [2 \bar{1} \bar{1} 0]_\alpha$  direction and small in the  $\bar{y}$   $\parallel [0 1 \bar{1} 0]_\alpha$  direc-

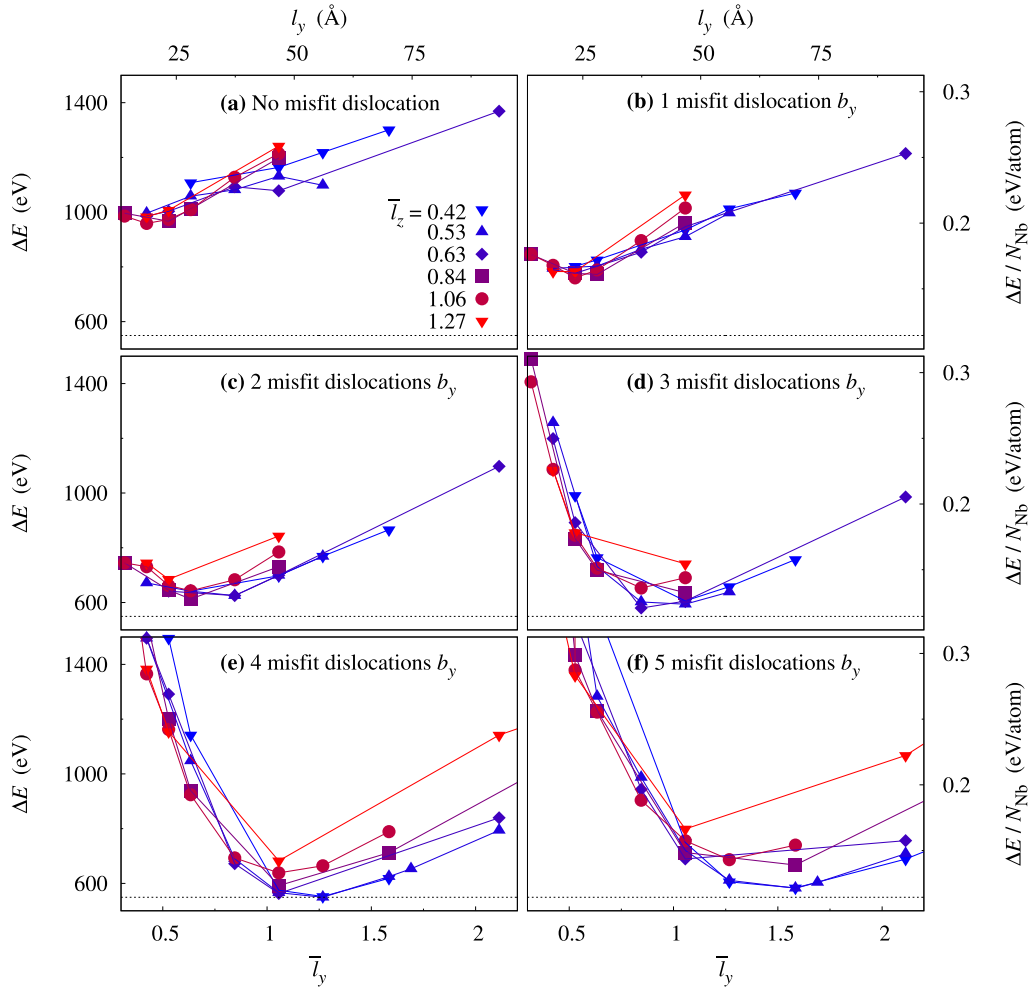


FIG. 6. Formation energy of a niobium precipitate of fixed volume  $V$  as a function of its elongation  $\bar{l}_y = l_y / \sqrt[3]{V}$  (or length  $l_y$ ) in the  $y$  direction and for different elongations  $\bar{l}_z = l_z / \sqrt[3]{V}$  in the  $z$  direction. The precipitate is fully coherent in (a) or contains different numbers of misfit dislocations in (b)–(f) to accommodate the lattice misfit in the  $y$  direction. The horizontal dotted line corresponds to the minimum formation energy.

tion. This equilibrium shape is expected because the lattice misfit is small in the  $\bar{x}$  direction ( $-2.1\%$ ) but much larger in the  $\bar{y}$  direction ( $19.9\%$ ). This elongated shape helps reduce the energy cost of the coherency strain. On the other hand, the slight anisotropy of the interface energy predicted by our EAM potential (see Table III) should favor a different equilibrium shape, where the largest facets would be the ones for an interface normal  $\bar{y} \parallel [0\ 1\ \bar{1}\ 0]_\alpha$ . This shows that the elastic energy is more important than the energy cost of the interfaces in the control of the shape, which minimizes the formation energy of coherent precipitates. However, the reduced dimension in the  $[0\ 1\ \bar{1}\ 0]_\alpha$  and not in the  $[000\ 1]_\alpha$  direction differs from the shape observed in experiments, suggesting that precipitates in experiments are either noncoherent or their shape is not controlled solely by minimizing their formation energy as described in our simulations.

The formation energy of the precipitates is significantly reduced when they become semicoherent (Fig. 6), in particular, with  $b_y$  misfit dislocations accommodating the lattice misfit between the  $\beta$ -Nb and  $\alpha$ -Zr phases along the  $\bar{y}$  direction.

With only these  $b_y$  misfit dislocations, the maximal reduction in formation energy is observed with four dislocations, decreasing the precipitate energy by 85 meV/Nb atom. Besides reducing the formation energy, these misfit dislocations modify the predicted equilibrium shape of the precipitate, making the precipitates with minimal energy more elongated in the  $\bar{y}$  direction as the number of misfit dislocations  $b_y$  increases. The corresponding reduced size  $\bar{l}_y$  increases from 0.42 to 1.27 as the number of  $b_y$  misfit dislocations increases from 0 to 4. Such a variation of the precipitate elongation in the  $\bar{y}$  direction with their coherency appears reasonable. When the precipitate are fully coherent, an important eigenstrain  $\varepsilon_{yy}^\beta$  is associated with this direction  $\bar{y}$ . By reducing the precipitate length in this direction, one reduces the elastic energy necessary to embed the precipitate in the matrix. Introduction of misfit dislocation allows a reduction of this eigenstrain  $\varepsilon_{yy}^\beta$  and thus of the associated elastic energy, which becomes less dominating in the precipitate formation energy compared to the energy cost associated with the lattice misfit in the other directions and also the cost of the interfaces.



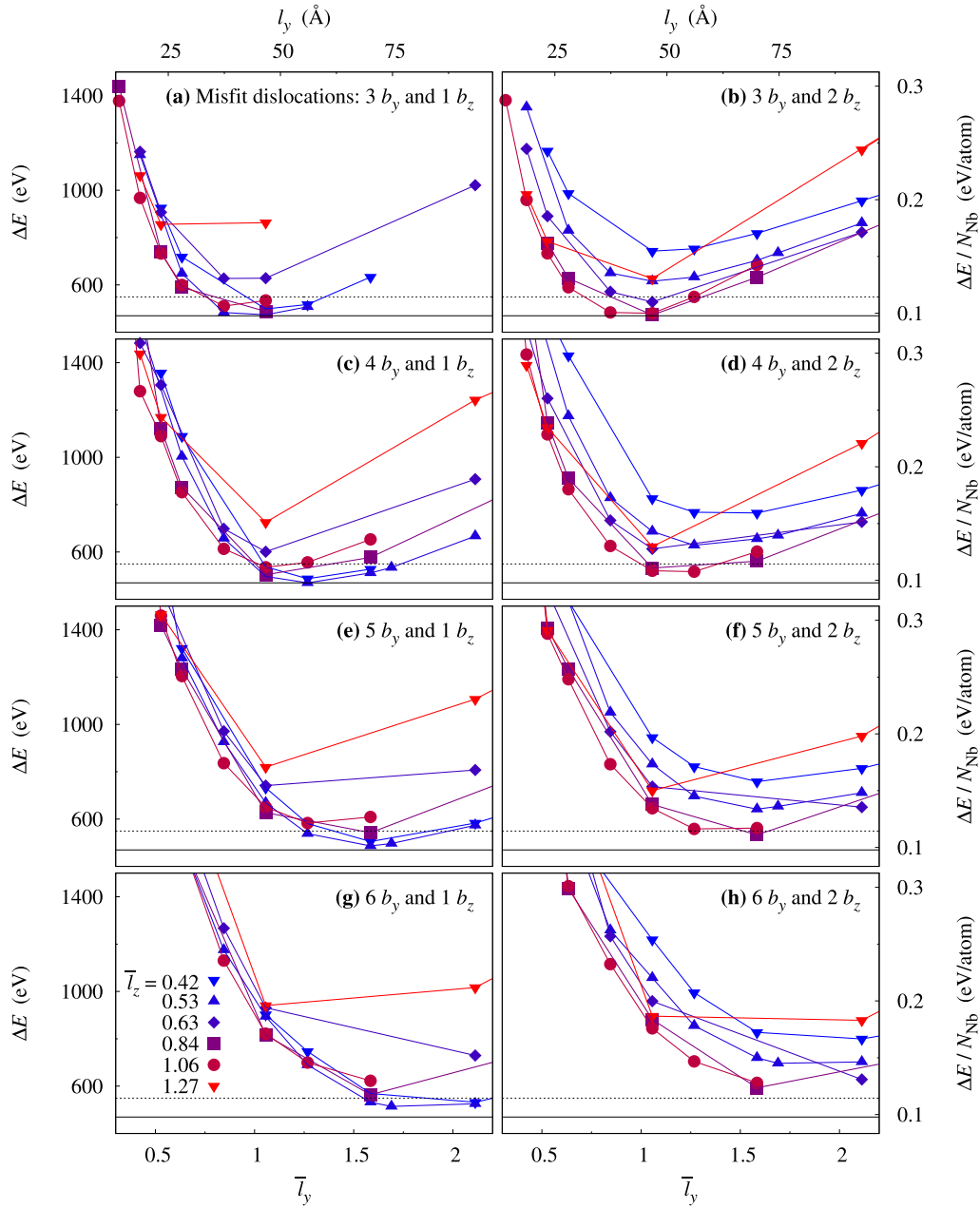


FIG. 7. Formation energy of a niobium precipitate of fixed volume  $V$  as a function of its elongation  $\bar{l}_y = l_y / \sqrt[3]{V}$  (or length  $l_y$ ) in the  $y$  direction and for different elongations  $\bar{l}_z = l_z / \sqrt[3]{V}$  in the  $z$  direction. The precipitate contains different numbers of misfit dislocations to accommodate the lattice misfit in the  $y$  and the  $z$  directions. The horizontal dotted and solid lines correspond to the minimum formation energies, respectively, without and with  $b_z$  misfit dislocations.

The precipitate formation energy can be further reduced by  $b_z$  misfit dislocations accommodating the lattice misfit in the  $\bar{z}$  direction (Fig. 7). With 1 or 2  $b_z$  misfit dislocations, an additional reduction of 80 meV/Nb atom is observed. Precipitates with minimal formation energy have at least 1  $b_z$  misfit dislocation and between 3 and 5  $b_y$  misfit dislocations, leading to precipitate shapes defined by the reduced sizes  $1.1 \leq \bar{l}_x \leq 1.8$ ,  $1 \leq \bar{l}_y \leq 1.5$ , and  $0.5 \leq \bar{l}_z \leq 1$ . These precipitates have similar sizes in the  $\bar{x}$  and  $\bar{y}$  directions and a reduced size in the  $\bar{z} \parallel [0001]_\alpha$  direction. This shape agrees with the experimental observations where precipitates appear as platelets

lying in the basal planes of the  $\alpha$ -Zr matrix. High-resolution TEM observations (HRTEM) [8,23] have shown that misfit dislocations are present at the interfaces between the  $\beta$ -Nb precipitates and the  $\alpha$  matrix.

The reduction of lattice misfit between the precipitate and the matrix due to misfit dislocations significantly impacts the precipitate formation energy and equilibrium shape. This is illustrated by plotting the precipitate formation energy as a function of the misfit strain defined by Eq. (2) (Fig. 8). It is evident that the formation energy is minimal when enough misfit dislocations are present at the interfaces to cancel the

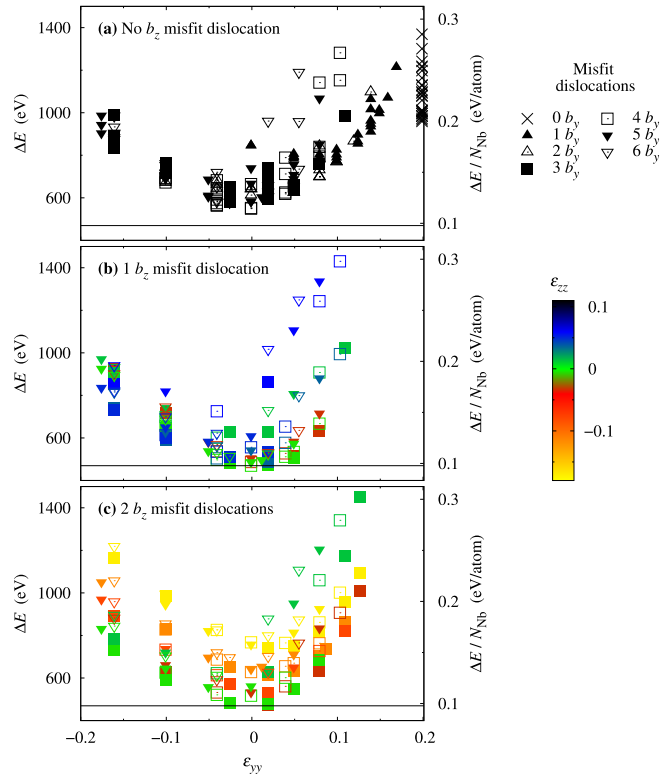


FIG. 8. Formation energy of a niobium precipitate of fixed volume  $V$  as a function of its eigenstrain  $\varepsilon_{yy}$  (abscissa coordinate) and  $\varepsilon_{zz}$  (color map) for different numbers of misfit dislocations [Eq. (2)].

lattice misfit between the precipitate and the matrix, i.e., when the misfit strain  $\varepsilon_{mis}$  is close to zero. This is true for both  $\bar{y}$  and  $\bar{z}$  directions. Although these misfit dislocations increase the cost of the interfaces, which become incoherent, the reduction in lattice misfit, and hence the associated elastic energy, is more significant, ultimately leading to lower formation energies. To go further in the analysis and understand how interface energies vary with the coherency state, it would be possible to use the same approach as in Sec. III to calculate the energy of semicoherent interfaces, either *ab initio* or with the EAM potential, by varying the number of  $\alpha$ -Zr and  $\beta$ -Nb planes at the interface.

4D-STEM [23] has shown that the spacing between  $(0001)_\alpha$  planes in the matrix around the precipitates does not exhibit significant tensile strain, i.e.,  $\varepsilon_{zz} \simeq 0$  with our choice of orientation. This is consistent with our analysis, indicating that precipitates are semicoherent with enough misfit dislocations to cancel the lattice mismatch between both phases and minimize their energy. Although the same [23] and other [8] TEM observations have clearly identified the presence of such misfit dislocations at the precipitate/matrix interfaces, it cannot be excluded that other physical mechanisms, particularly variations in chemical composition of the precipitates and the matrix near the interface, also contribute to the reduction of the lattice misfit. However, the reduction in misfit and the associated elastic energy appears to be a strong driving force for the precipitate shape.

## V. CONCLUSIONS

Atomistic simulations performed with a Zr-Nb potential reveal that the formation energy of  $\beta$ -Nb precipitates, which appear under irradiation in  $\alpha$ -Zr, significantly decreases when the precipitates become semicoherent. The energy is minimal when enough misfit dislocations are present at the interface to cancel the lattice misfit between the  $\alpha$ -Zr and  $\beta$ -Nb phases. The shape of fully coherent precipitate that minimizes the formation energy does not match the experimental observations. However, the most stable semicoherent precipitates are platelets lying in the basal planes of the hcp lattice, with a reduced size along the  $[0001]_\alpha$  direction, in perfect agreement with the shapes observed in experiments. Therefore, atomistic simulations suggest that  $\beta$ -Nb particles formed under irradiation are not fully coherent to minimize their energy, explaining the presence of misfit dislocations seen by TEM at their interface [8,23].

The Zr-Nb EAM potential used in these simulations appears well suited for studying Nb precipitates in zirconium. It incorporates all the necessary physical ingredients to model coherency strain and the associated energy cost between the  $\beta$ -Nb precipitates and  $\alpha$ -Zr matrix. Comparison with *ab initio* calculations shows that it also gives a reasonable description of the interfaces between both phases. This potential offers a promising route to study, at the atomic scale, the impact of  $\beta$ -Nb precipitates, particularly their interactions with gliding dislocations, and gain insights into their hardening contribution.

In our simulations we have assumed that the  $\beta$  precipitates and the  $\alpha$  matrix are pure Nb and Zr phases. However, experiments have shown that native  $\beta$ -Nb precipitates have a Nb composition that decreases with the irradiation dose. Secondary nanoprecipitates appearing under irradiation have a lower Nb concentration than predicted by thermodynamic equilibrium between bulk phases, typically only between 60% and 75% Nb for particles created by neutron irradiation [15,22,55], or even less, around 40% Nb for proton irradiation [9]. Such deviations from equilibrium compositions offer an alternative way to reduce the lattice misfit between  $\alpha$ -Zr and  $\beta$ -Nb phases, thereby decreasing the elastic energy arising from coherency constraints.  $\beta$ -Nb needles are also enriched in Fe [9] compared to the surrounding solid solution, which should also impact the lattice misfit with the  $\alpha$  matrix. Using the same EAM potential, future works can extend this study to investigate how deviations from perfect stoichiometry affect the precipitate structure and energy, considering both misfit dislocations and composition variations. It will also be possible to go beyond the static simulations at 0 K performed in the present work. One expects a dependence to temperature of the precipitate formation energy through a variation with temperature of both the elastic constants and the interface energies. But the most important impact would probably be the varying lattice misfits because of the different thermal expansions of the  $\beta$ -Nb and  $\alpha$ -Zr phases, as well as the anisotropic expansion of  $\alpha$ -Zr.

The coherency between the matrix and precipitates affects the precipitate sink strength [56]. It appears reasonable to assume that  $\beta$ -Nb precipitates are coherent when they start to appear. Because of the smallest atomic volume of the  $\beta$

phase compared to the  $\alpha$  phase, they create a tensile stress field around them in the  $\alpha$  matrix, thus leading to an attractive elastic interaction with interstitial atoms and a repulsion with vacancies. Coherent  $\beta$ -Nb precipitates should therefore be biased, absorbing more interstitials than vacancies. These unbalanced fluxes of point defects should rapidly result in the coherency loss of the  $\beta$ -Nb precipitates, with semicoherent precipitates being more stable than coherent ones, as seen in our atomistic simulations. Once the net flux of absorbed interstitials allows for compensation of the lattice misfit between the  $\alpha$ -Zr and  $\beta$ -Nb phases, the stress field around these semicoherent precipitates becomes small and precipitates are expected to act as unbiased sinks, eliminating both vacancies and interstitials created by irradiation equally. By promoting point-defects recombination without creating unbalanced fluxes between vacancies and interstitials, their effect should be beneficial, slowing down the evolution of the irradiation-induced microstructure.

### ACKNOWLEDGMENTS

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### APPENDIX A: EAM POTENTIAL

We use the EAM formalism to describe atomic interactions. The energy of a system containing  $N$  atoms at positions  $\vec{r}_i$  is given by

$$E(\vec{r}_1, \dots, \vec{r}_N) = \sum_{i=1}^N \left[ F_{X_i}(\bar{\rho}_i) + \frac{1}{2} \sum_{j \neq i} \phi_{X_i X_j}(r_{ij}) \right],$$

with  $r_{ij} = \|\vec{r}_j - \vec{r}_i\|$  the distance between atoms  $i$  and  $j$ .  $X_i$  is the type of atom, either Zr or Nb, located at site  $i$ .  $\phi_{X_i X_j}(r)$  is the pair interaction between atoms of types  $X_i$  and  $X_j$ .  $F_{X_i}(\bar{\rho}_i)$  is the embedding function of atom type  $X_i$  calculated for the density  $\bar{\rho}_i$  existing at site  $i$ . This density is obtained by summing the contributions of neighboring atoms,

$$\bar{\rho}_i = \sum_{j \neq i} \rho_{X_j}(r_{ij}),$$

where  $\rho_{X_j}(r)$  is the elemental density of atom type  $X_j$ .

For Zr we use the EAM potential developed by Mendelev and Ackland, specifically, the potential noted #3 in Ref. [34]. We only fit the functions describing pure Nb interactions, i.e.,  $F_{\text{Nb}}(\rho)$ ,  $\rho_{\text{Nb}}(r)$ , and  $\phi_{\text{NbNb}}(r)$ , as well as the cross-pair interaction  $\phi_{\text{ZrNb}}(r)$  between Zr and Nb atoms. The functions  $F_{\text{Zr}}(\rho)$ ,  $\rho_{\text{Zr}}(r)$ , and  $\phi_{\text{ZrZr}}(r)$  are directly taken from Ref. [34]. Before combining them with the Nb part, we rescale this Zr EAM potential. The description given by an EAM potential for a pure element  $X$  is indeed not altered by the following changes [57]:

$$\begin{aligned} \rho_X(r) &= \rho_X^0(r)/A_X, \\ F_X(\rho) &= F_X^0(A_X \rho) - B_X \rho, \\ \phi_{XX}(r) &= \phi_{XX}^0(r) + 2B_X \rho_X^0(r)/A_X, \end{aligned}$$

where  $\rho_X^0(r)$ ,  $\phi_{XX}^0(r)$ , and  $F_X^0(\rho)$  are the original functions. The original Zr EAM #3 potential is rescaled with the parameters  $A_{\text{Zr}} = 83.3046$  and  $B_{\text{Zr}} = -4.08009$ .

The Nb embedding function takes different forms for low and high density:

$$\begin{aligned} F_{\text{Nb}}(\rho) &= -a_0 \sqrt{\rho} + a_1 \rho + a_2 \rho^2 + a_4 \rho^4, \quad \rho \leq \rho_{\text{max}} \\ &= b_0 + b_1(\rho - \rho_{\text{max}}) + (\rho - \rho_{\text{max}})^2 \\ &\quad \times (b_2 + b_3 \rho + b_4 \rho^2), \quad \rho \geq \rho_{\text{max}} \end{aligned} \quad (\text{A1})$$

with  $b_0 = F_{\text{Nb}}(\rho_{\text{max}})$  and  $b_1 = F'_{\text{Nb}}(\rho_{\text{max}})$  to ensure continuity of the embedding function  $F_{\text{Nb}}(\rho)$  and its first derivative  $F'_{\text{Nb}}(\rho)$  at the density  $\rho_{\text{max}}$ .

The Nb density function is written as a cubic spline:

$$\rho_{\text{Nb}} = \sum_{k=1}^5 \rho_k (r_k - r)^3 H(r_k - r), \quad (\text{A2})$$

where  $H(x)$  is the Heaviside function, equal to 0 if  $x < 0$  and 1 if  $x > 0$ .

The Nb-Nb and Zr-Nb pair functions are also written as cubic splines:

$$\phi_{XY}(r) = \sum_{k=1}^K \phi_k (r_k - r)^3 H(r'_k - r), \quad (\text{A3})$$

with  $K = 15$  and  $13$  for Nb-Nb and Zr-Nb interactions, respectively.

All parameters describing the fitted functions are given in Table IV. Cutoff radius of the pair and density functions correspond to the position of the last knot of the cubic spline, i.e.,  $5.8 \text{ \AA}$  for  $\rho_{\text{Nb}}(r)$  and  $6.0 \text{ \AA}$  for  $\phi_{\text{ZrNb}}(r)$  and  $\phi_{\text{NbNb}}(r)$ .

### APPENDIX B: INFINITE INTERFACE AND ELASTIC ENERGY

We consider a system composed of two phases,  $\alpha$  and  $\beta$ , joined at a plane interface with a normal corresponding to the vector  $\vec{e}_3$  of the Cartesian axis. A homogeneous prestrain,  $\varepsilon^\alpha$  and  $\varepsilon^\beta$ , is imposed on each phase to obtain a coherent interface (step 2 in Fig. 1). This prestrain generates a polarization stress homogeneous in each phase,  $\tau_{ij}^\alpha = \lambda_{ijkl}^\alpha \varepsilon_{kl}^\alpha$  and  $\tau_{ij}^\beta = \lambda_{ijkl}^\beta \varepsilon_{kl}^\beta$ , where  $\lambda^\alpha$  and  $\lambda^\beta$  are the elastic tensors of each phase in the reference frame of the interface.

An additional homogeneous strain increment  $\delta \varepsilon^\alpha$  and  $\delta \varepsilon^\beta$ , imposed on each phase of the slab system, leads to the variation of the elastic energy with respect to the prestrained initial state,

$$\begin{aligned} \Delta E(\delta \varepsilon^\alpha, \delta \varepsilon^\beta) &= N^\alpha \Omega_0^\alpha \left[ \tau_{ij}^\alpha \delta \varepsilon_{ij}^\alpha + \frac{1}{2} \lambda_{ijkl}^\alpha \delta \varepsilon_{ij}^\alpha \delta \varepsilon_{kl}^\alpha \right] \\ &\quad + N^\beta \Omega_0^\beta \left[ \tau_{ij}^\beta \delta \varepsilon_{ij}^\beta + \frac{1}{2} \lambda_{ijkl}^\beta \delta \varepsilon_{ij}^\beta \delta \varepsilon_{kl}^\beta \right], \end{aligned}$$

where  $N^\alpha$  and  $N^\beta$  are the number of atoms in each phase and  $\Omega_0^\alpha$  and  $\Omega_0^\beta$  their equilibrium atomic volumes. To maintain interface coherency, the components  $\delta \varepsilon_{11}$ ,  $\delta \varepsilon_{22}$ , and  $\delta \varepsilon_{12}$  must

TABLE IV. Parameters defining the pure Nb part and the alloying part of the Zr-Nb EAM potential. Distances  $r_k$  are given in Å, and the resulting functions  $F_{\text{Nb}}$ ,  $\phi_{\text{NbNb}}$  and  $\phi_{\text{ZrNb}}$  are expressed in eV.

$F_{\text{Nb}}(\rho)$	$\rho_{\text{Nb}}(r)$	$\phi_{\text{NbNb}}(r)$		$\phi_{\text{ZrNb}}(r)$	
$a_0 = 0.216161$	$r_1 = 2.1$	$r_1 = 2.7$	$\phi_1 = -5.32781$	$r_1 = 2.7$	$\phi_1 = 2.95338$
$a_1 = -18.8405$	$r_2 = 2.9$	$r_2 = 2.9$	$\phi_2 = 31.1461$	$r_2 = 2.9$	$\phi_2 = -3.14252$
$a_2 = 1.68589$	$r_3 = 3.8$	$r_3 = 3.0$	$\phi_3 = -0.639147$	$r_3 = 3.0$	$\phi_3 = 2.01447$
$a_4 = -0.0390124$	$r_4 = 4.7$	$r_4 = 3.3$	$\phi_4 = -1.09298$	$r_4 = 3.3$	$\phi_4 = -0.113563$
$b_0 = -41.0077$	$r_5 = 5.8$	$r_5 = 3.6$	$\phi_5 = 0.692798$	$r_5 = 3.6$	$\phi_5 = 0.527162$
$b_1 = -12.8739$	$\rho_1 = -1.91229$	$r_6 = 3.8$	$\phi_6 = 0.973560$	$r_6 = 3.8$	$\phi_6 = 0.0348147$
$b_2 = 73.7419$	$\rho_2 = 0.931266$	$r_7 = 4.2$	$\phi_7 = 4.07840$	$r_7 = 4.2$	$\phi_7 = 0.555228$
$b_3 = -54.2121$	$\rho_3 = 0.0804986$	$r_8 = 4.4$	$\phi_8 = -4.01382$	$r_8 = 4.4$	$\phi_8 = -0.923716$
$b_4 = 9.96109$	$\rho_4 = -0.0364943$	$r_9 = 4.6$	$\phi_9 = 1.98924$	$r_9 = 4.6$	$\phi_9 = 0.770526$
$\rho_{\text{max}} = 2.7$	$\rho_5 = 0.0120155$	$r_{10} = 4.7$	$\phi_{10} = -1.16498$	$r_{10} = 4.8$	$\phi_{10} = -0.279592$
		$r_{11} = 4.8$	$\phi_{11} = -1.09682$	$r_{11} = 5.2$	$\phi_{11} = -0.249193$
		$r_{12} = 5.2$	$\phi_{12} = 0.539737$	$r_{12} = 5.6$	$\phi_{12} = 0.403934$
		$r_{13} = 5.6$	$\phi_{13} = -0.332176$	$r_{13} = 6.0$	$\phi_{13} = -0.127217$
		$r_{14} = 5.8$	$\phi_{14} = 0.651207$		
		$r_{15} = 6.0$	$\phi_{15} = -0.141713$		

be the same in both phases, while the components  $\delta\epsilon_{33}$ ,  $\delta\epsilon_{13}$ , and  $\delta\epsilon_{23}$  can vary independently in each phase.

Minimizing the elastic energy leads to the equilibrium conditions:

$$\begin{aligned}
 & N^\alpha \Omega_0^\alpha [\tau_{ij}^\alpha + \lambda_{ijkl}^\alpha \delta\epsilon_{kl}^\alpha] + N^\beta \Omega_0^\beta [\tau_{ij}^\beta + \lambda_{ijkl}^\beta \delta\epsilon_{kl}^\beta] \\
 & = 0, \text{ for } ij \in \{11, 22, 12\} \\
 & N^\alpha \Omega_0^\alpha [\tau_{ij}^\alpha + \lambda_{ijkl}^\alpha \delta\epsilon_{kl}^\alpha] = 0, \text{ for } ij \in \{33, 13, 23\} \\
 & N^\beta \Omega_0^\beta [\tau_{ij}^\beta + \lambda_{ijkl}^\beta \delta\epsilon_{kl}^\beta] = 0, \text{ for } ij \in \{33, 13, 23\}.
 \end{aligned}$$

We can choose the prestrains  $\epsilon^\alpha$  and  $\epsilon^\beta$  such that the strain increments  $\delta\epsilon^\alpha$  and  $\delta\epsilon^\beta$  fulfilling these equilibrium conditions are null. This corresponds to an initially prestrained state where the average stress is zero. Replacing polarization

stresses with their expressions, we obtain

$$\begin{aligned}
 & N^\alpha \Omega_0^\alpha \lambda_{ijkl}^\alpha \epsilon_{kl}^\alpha + N^\beta \Omega_0^\beta \lambda_{ijkl}^\beta \epsilon_{kl}^\beta = 0, \text{ for } ij \in \{11, 22, 12\} \\
 & N^\alpha \Omega_0^\alpha \lambda_{ijkl}^\alpha \epsilon_{kl}^\alpha = 0, \text{ for } ij \in \{33, 13, 23\} \\
 & N^\beta \Omega_0^\beta \lambda_{ijkl}^\beta \epsilon_{kl}^\beta = 0, \text{ for } ij \in \{33, 13, 23\}.
 \end{aligned}$$

This set of nine equations is completed by the coherency conditions at the interface. Considering that the phase  $\alpha$  have orthogonal periodicity vectors  $l_1^\alpha \vec{e}_1$  and  $l_2^\alpha \vec{e}_2$ , which match the periodicity vectors  $l_1^\beta \vec{e}_1$  and  $l_2^\beta \vec{e}_2$  of the  $\beta$  phase in the interface plane, the three following equations are obtained:

$$\begin{aligned}
 & (1 + \epsilon_{11}^\alpha) l_1^\alpha = (1 + \epsilon_{11}^\beta) l_1^\beta \\
 & (1 + \epsilon_{22}^\alpha) l_2^\alpha = (1 + \epsilon_{22}^\beta) l_2^\beta \\
 & \epsilon_{12}^\alpha = \epsilon_{12}^\beta.
 \end{aligned}$$

The strains in each phase,  $\epsilon^\alpha$  and  $\epsilon^\beta$ , are finally obtained by inverting this system of 12 equations.

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