Universality of grain boundary phases in fcc metals: Case study on high-angle [111] symmetric tilt grain boundaries

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(Dated: February 14, 2023)

Grain boundaries often exhibit ordered atomic structures. Increasing amounts of evidence have been provided by transmission electron microscopy and atomistic computer simulations that different stable and metastable grain boundary structures can occur. Meanwhile, theories to treat them thermodynamically as grain boundary phases have been developed. Whereas atomic structures were identified at particular grain boundaries for particular materials, it remains an open question if these structures and their thermodynamic excess properties are material specific or generalizable to, e.g., all fcc metals. In order to elucidate that question, we use atomistic simulations with classical interatomic potentials to investigate a range of high-angle [11T] symmetric tilt grain boundaries in Ni, Cu, Ag, Au, Al, and Pb. We could indeed find two families of grain boundary phases in all of the investigated grain boundaries, which cover most of the standard fcc materials. Where possible, we compared the atomic structures to atomic-resolution electron microscopy images and found that the structures match. This poses the question if the grain boundary phases are simply the result of sphere-packing geometry or if material-specific bonding physics play a role. We tested this using simple model pair potentials and found that medium-ranged interactions are required to reproduce the atomic structures, while the more realistic material models mostly affect the grain boundary (free) energy. In addition to the structural investigation, we also report the thermodynamic excess properties of the grain boundaries, explore how they influence the thermodynamic stability of the grain boundary phases, and detail the commonalities and differences between the materials.

I. INTRODUCTION

Grain boundaries (GBs) are defined by five macroscopic degrees of freedom, describing the misorientation of the abutting crystallites and the GB plane [1]. At the atomic scale, GBs have additional microscopic degrees of freedom [1], meaning that a GB with a specific misorientation and GB plane can exhibit different atomic structures. These distinct structures are called GB phases [2] or complexions [3–6] in analogy to bulk phases, because they can be understood using a thermodynamic framework [5–10]. It should be noted, however, that GB phases are not the same as bulk phases insofar they can only exist at interfaces and not on their own, in contrast to, e.g., bulk wetting phases or precipitates, which can also appear at GBs [6, 10]. GB phase transitions have been proposed theoretically already from the 1960s onwards [11–13]. While such transitions can be driven by segregation, as for example in Refs. [4, 14–19], they also occur in pure materials as demonstrated with atomistic simulations [20–29], and experimentally by atomic-resolution (scanning) transmission electron microscopy (TEM, STEM) [28–31]. Experimental observation, however, remains difficult because at least two GB phases have to exist in stable or metastable states under experimental conditions, which appears to be rare. Available data suggest that GB phase transitions may influence diffusivity [32–35], GB motion [36, 37], intergranular fracture [38–40], and electrical conductivity [41], among other material properties.

In the case of pure metals, computer simulations have been performed predominantly to demonstrate the existence of different GB phases for example cases, such as for specific macroscopic degrees of freedom or for a single material. Comprehensive studies have been attempted in the 1970s and 1980s, e.g., for tilt GBs of Al and Cu [42], but were limited by the use of simple pair potentials and by mostly disregarding metastable GB structures. More recently, GB phase transitions have been simulated in a Σ5 GB for Cu, Ag, Au, and Ni [21]; in Cu for different misorientations of [001] tilt GBs [22–24, 27]; in W for a variety of tilt GBs [25–27]; and in Mg tilt GBs [27]. Apart from the early simulations on Σ5 GBs [21], where the same motifs were found for all metals, it was not investigated if specific GB phases and their transitions are generalizable to all fcc, bcc, or hcp materials, respectively. Thus it is not clear to what extent GB phases are influenced by, e.g., bonding, structure, or packing density and if they can be correlated with bulk material properties.

It has, however, long been known for tilt GBs that certain structural motifs exist over a range of misorientations, leading to the development of the structural unit model [42–45]. This model describes GB structures as combinations of motifs resulting from certain delimiting boundaries, which are the GBs containing only a single motif and which serve as reference structures for general GBs. A weakness of the model is the assumption of a single, canonical structure for the delimiting boundaries, which is in opposition to the existence of metastable GB phases. Indeed, different ground states were for example found in copper for the closely-related Σ19b and Σ37c tilt GBs [28, 29], which make the original structural unit model inapplicable. These shortcomings were addressed by the
development of a revised model that includes multiple—possibly metastable—motifs for the delimiting boundaries [46]. In atomistic simulations on tungsten [46], this model demonstrates on one hand that the varying motifs and their combinations lead to different stable GB phases with varying misorientations. On the other hand, it reaffirms that the motifs remain existent across variations of the macroscopic degrees of freedom of the GBs, even if only in a metastable state.

Nevertheless, systematic and quantitative studies among comparable materials are uncommon and the question remains if specific GB phases are universal features (for example of a given lattice structure of the bulk crystal) or very specific to a material. To that end, the present work is dedicated to atomistic computer simulations of symmetric [111] tilt GBs in a range of fcc metals and expands on recent results for Σ19b and Σ37c tilt GBs in copper [28, 29]. While some experimental data regarding the atomic structure of the GB phases is available for Cu and Al [28, 29, 47], we will expand the computer investigation to most of the fcc metals for which reasonable interatomic potentials are available and to a range of misorientations. In addition, we use pair potentials to switch off environment-dependent bond energies (bond order) and/or medium-ranged interatomic interactions beyond the first neighbor shell. This tunability allows us to study if the atomic structures of the GB phases are defined more by packing geometry or the material-specific physics of bonding. We present some common trends and differences between the materials.

II. METHODS

We modeled GBs in bicrystals using embedded atom method (EAM) potentials for Ni [48], Cu [49], Pd [50], Ag [51], Au [52], and Al [53], as well as a modified EAM (MEAM) potential for Pb [54]. The potential files were downloaded from the NIST Interatomic Potentials Repository [55], except for the Pd potential, which we reproduced from the data in the original publication, and the Al potential, which was smoothed as described in Appendix A to overcome numerical problems with free energy calculations. Molecular statics and molecular dynamics (MD) simulations were performed using the software LAMMPS [56, 57].

In addition to the more realistic potentials, we also used generic model pair potentials to evaluate how much material-specific physics is required to reproduce the results of the (M)EAM potentials. For these, we use reduced units in terms of the equilibrium bond length $r_0$ in fcc and the corresponding fcc cohesive energy $E_{coh}$ per atom (which is by the convention used for interatomic potentials related to the total energy in the ground state via $E_{coh} = -E_{0}^{fcc}$). Here, we considered a Lennard-Jones potential with a cutoff of $2.5r_0$ (corresponding to 6 fcc next-neighbor shells), shifted so that the bond energy at the cutoff is zero. The parameters $\sigma_{LLJ} = 0.91303r_0$ and $\varepsilon_{LLJ} = 0.12927915E_{coh}$ were chosen to obtain a lattice constant of $a_{0}^{fcc} = \sqrt{2}r_0$ and $E_{0}^{fcc} = -1E_{coh}$. This parametrization has a stable fcc and metastable hcp phase (energy difference of roughly 0.001$E_{coh}$).

Furthermore, in order to investigate the difference between medium-ranged and next-neighbor-only interactions, we constructed pair potentials of the form

$$E_i = \sum_{j \neq i} \left\{ \begin{array}{ll} C \left( \frac{n_{pp}}{r_{0,j}} \right)^n_{pp} - \left( \frac{\sigma_{pp}}{r_{0,j}} \right)^{m_{pp}} & r \leq R_{inner} \\ \sum_{k=0}^{4} c_k r_k & R_{inner} < r \leq R_{cut} \\ 0 & r > R_{cut}, \end{array} \right.$$

with $R_{cut} = 1.35r_0$, so that only the first fcc neighbor shell is included. It is

$$C = \varepsilon_{pp}n_{pp}(n_{pp} - m_{pp})^{-1} \left( \frac{n_{pp}}{m_{pp}} \right)^{m_{pp}}_{pp},$$

and we used $n_{pp} = 24$, $m_{pp} = 14, 16, 18, 20, 22$. This leads to bond stiffnesses that are higher than the standard Lennard-Jones potential ($n_{pp} = 12, m_{pp} = 6$), but this is required to obtain a reasonably-shaped potential well inside the very short cutoff range. The polynomial with $c_0^{pp}, c_1^{pp}, c_2^{pp}, c_3^{pp}, c_4^{pp}$ is defined so that the potentials are continuous up to the second derivative at $R_{inner}$ and both energy and force are zero at the cutoff $R_{cut}$. We used $R_{inner} = 1.1r_0$. We defined five different potentials (different $m_{pp}$) to see if the bond stiffness influences the GB structures, but found that this is not the case here. We consequently report only the results of the potential with $m_{pp} = 18$ in the rest of this paper. All potential files are available in the companion dataset [58].

A. Bulk properties of fcc crystals and evaluation of the potentials

In order to evaluate the performance of the (M)EAM potentials, we first computed the properties of the bulk fcc and hcp phases (listed in Tables I and II). Ground state energies $E_0$ (which by convention are related to the cohesive energy via $E_{coh} = -E_0^{fcc}$) and lattice constants $a_0$, $c_0$ at temperature $T = 0$ K were calculated using molecular statics calculations on defect-free fcc systems, while vacancy formation energies $E_{f,vac}$, (111) surface energies $\gamma_{(111)}$, and stacking-fault energies $\gamma_{SF}$ were calculated using systems containing the relevant defects. Generalized stacking-fault curves were computed using the procedure described in Ref. [64]. Unstable stacking-fault energies $\gamma_{SF}$ as well as the maximum shear stresses $\tau_{SF}$ along the stacking-fault curves are reported in Tables I and II. We computed the elastic constants $c_{ij}$ and the bulk modulus $K$ for the fcc phase using the scripts distributed with LAMMPS, which derive the stiffness tensor from the stress tensor by systematically applying strains to a periodic fcc cell.
Table I. Material properties of fcc transition metals computed with the EAM potentials (pot.) compared to literature values (ref.). We list experimental ground-state energies $E_0$ from Ref. [59]; experimental lattice constants $a_0^{\text{fcc}}$, elastic constants $c_{ij}$, bulk modulus $K$, and melting points $T_{\text{melt}}$ from Ref. [60]; experimental vacancy formation energies $E_{f,\text{vac}}$ from Ref. [61] (note that the Pd data is only from a single measurement and less reliable than the other data points); surface energies $\gamma_{(111)}$ from DFT calculations for the (111) surface that match the average experimental values reasonably well [62]; experimental stacking-fault energies $\gamma_{\text{SF}}$ and DFT values for the unstable stacking-fault energies $\gamma_{\text{USF}}$ as collected in the literature review in Ref. [63]; and DFT calculations of the maximum shear stress $\tau_{\text{SF}}$ along the generalized stacking-fault curve from Ref. [64].

|        | Ni     | Cu     | Pd     | Ag     | Au     |
|--------|--------|--------|--------|--------|--------|
| $E_0^{\text{fcc}}$ (eV/atom) | -4.450 | -4.44  | -3.540 | -3.49  | -3.910 |
|        | $a_0^{\text{fcc}}$ (Å) | 3.520 | 3.524 | 3.615 | 3.615 | 3.890 |
| $E_0^{\text{hcp}}$ (eV/atom) | -4.428 | -3.532 | -3.878 | -2.846 | -3.929 |
|        | $a_0^{\text{hcp}}$ (Å) | 2.482 | 2.566 | 2.719 | 2.896 | 2.886 |
| $\gamma_0$ (eV/atom) | -0.675 | -0.759 | -0.679 | -0.786 | -0.766 |
| $c_{11}$ (GPa) | 241    | 151   | 127   | 181   | 104   |
| $c_{12}$ (GPa) | 155    | 123   | 76    | 138   | 72    |
| $c_{44}$ (GPa) | 127    | 124   | 76    | 123   | 46    |
| $K$ (GPa) | 181    | 186   | 66    | 195   | 46    |
| $T_{\text{melt}}$ (K) | 1698   | 1728  | 1154  | 1854  | 1266  |
| $E_{f,\text{vac}}$ (eV) | 1.571  | 1.79  | 1.375 | 1.7   | 1.103 |
| $\gamma_{(111)}$ (J/m$^2$) | 1.759  | 2.011 | 1.239 | 1.952 | 1.922 |
| $\gamma_{\text{SF}}$ (mJ/m$^2$) | 134.7  | 125-300 | 181.1 | 175-180 | 17.8 |
| $\gamma_{\text{USF}}$ (mJ/m$^2$) | 297.6  | 269-350 | 211.7 | 265  | 114.9 |
| $\tau_{\text{SF}}$ (GPa) | 5.8    | 3.2   | 2.2   | 3.4   | 2.0   |

Table II. Material properties of other fcc metals computed with the (M)EAM potentials (pot.) compared to literature values (ref.). Reference data sources are the same as in Table I.

|        | Al     | Pb     |
|--------|--------|--------|
| $E_0^{\text{fcc}}$ (eV/atom) | -3.360 | -3.39  |
|        | $a_0^{\text{fcc}}$ (Å) | 4.050 | 4.050 |
| $E_0^{\text{hcp}}$ (eV/atom) | -3.332 | -2.037 |
|        | $a_0^{\text{hcp}}$ (Å) | 2.819 | 3.497 |
| $\gamma_0$ (eV/atom) | -0.675 | -0.759 |
| $c_{11}$ (GPa) | 114    | 107   |
| $c_{12}$ (GPa) | 62     | 60    |
| $c_{44}$ (GPa) | 32     | 28    |
| $K$ (GPa) | 79     | 76    |
| $T_{\text{melt}}$ (K) | 1042   | 933   |
| $E_{f,\text{vac}}$ (eV) | 0.675  | 0.67  |
| $\gamma_{(111)}$ (J/m$^2$) | 0.871  | 1.199 |
| $\gamma_{\text{SF}}$ (mJ/m$^2$) | 145.5  | 135-200 |
| $\gamma_{\text{USF}}$ (mJ/m$^2$) | 167.3  | 175-224 |
| $\tau_{\text{SF}}$ (GPa) | 2.3    | 2.8   |

Melting points were computed with the method and software from Ref. [65], which uses the interface method, i.e., a crystal/liquid interface is constructed and simulated at different temperatures with MD. The movement of the interface is monitored to estimate the melting point.

Finally, we simulated the thermal expansion of the metals by measuring the lattice constant at different temperatures using MD simulations. We used the careful procedure from Ref. [66] to achieve high accuracy: Using a small timestep of $\delta t = 0.5$ fs, a barostat at 0 Pa with damping parameter 0.5 ps, and a Langevin thermostat with a damping parameter of 0.05 ps set to maintain a total force of zero, we equilibrated a simulation cell consisting of $20 \times 20 \times 20$ unit cells in 50 K increments up to the melting point at each temperature for 250 ps. Averaging of the lattice constant was performed over the last 60 ps. The corresponding raw data of the bulk property calculations is available in the companion dataset [58].

The data provided in Tables I and II suggest that the Ni [48], Cu [49], Ag [51], Al [53], and Pb [54] potentials reproduce the bulk properties well. The Pd potential [50] strongly underestimates the melting point, while the Au potential [52] both underestimates the melting point and the stacking-fault energy. The latter should therefore be treated as a model potential for the case of a very low stacking-fault energy. Surface energies are not predicted well in general, but should not affect the simulation of GBs. The Ni, Cu, and Ag potentials are based on closed-form expressions that vary smoothly and continuously as a function of, e.g., bond length. Apart from bulk and defect properties, these potentials were also tested to reproduce thermal expansion and phonon frequencies, which are important for the GB excess free energy calculations. The Al potential was produced with similar care, but it was defined in terms of cubic splines. This can lead to different behavior in different ranges of bond lengths, which manifests for example in the GB free energy as shown later. The Au and Pd potentials were defined to exactly follow an equation of state, which often leads to inferior results [49]. The more well-known, older Pd potential by Foiles et al. [52] has been found to perform worse, with the newer potential used here [50] reproducing the bulk
material properties and stacking-fault energies quite well [67, 68]. There exists to the best of our knowledge no reasonable alternative for the Pb potential. We also tried a Ca MEAM potential [69], but found that we obtain negative excess volumes and excess entropies for some GBs, which seems unreasonable for fcc materials, indicating that the potential is not suitable for the simulation of GBs.

B. Finding GB phases with the $\gamma$-surface method and calculation of GB excess properties

Next, we constructed the bicrystals. There are two sets of symmetric grain boundaries for the $\langle111\rangle$ tilt axis (Fig. 1). Here, we only consider variant I, since two different GB phases have been identified before for $\Sigma$19b (111) $\{178\}$ [28] and $\Sigma$37c (111) $\{11011\}$ [29]. For the symmetric variant II, only one GB phase seems to exist [47, 70, 71]. We thus chose the symmetric $\Sigma$ boundaries listed in Table III. We follow the convention from Ref. [9], where $x$ corresponds to the tilt axis, $y$ to its orthogonal direction inside the GB plane, and $z$ to the GB normal [Fig. 2(a)].

When searching for GB phases, bicrystals are joined together at the desired GB plane and the microscopic degrees of freedom [translations [B], Fig. 2(b)] are sampled ($\gamma$-surface method). We only sample [B1] and [B2] since this can always be made equivalent to a full [B] vector by addition of DSC vectors in our case [Fig. 2(c)]. Typically it is also necessary to consider inserting/removing partial fcc planes at the GB in order to discover all relevant GB structures [21, 22, 24]. This can be expressed via the parameter

$$[n] = \frac{N}{N_{\text{plane}}} \mod 1,$$

where $N$ corresponds to the number of atoms in the bicrystal and $N_{\text{plane}}$ to the number of atoms in a plane of the fcc structure that is parallel to the GB. For the relevant $\Sigma$19b and $\Sigma$37c GB phases, however, such search has found that all defect-free GB phases have $[n] = 0$, i.e., no partial fcc planes [28, 29]. We therefore assume that this is true for the other $\langle111\rangle$ tilt GBs and used the simple $\gamma$-surface method. We verified the assumption of $[n] = 0$ by MD simulations with open surfaces at high temperature [21] for some example cases.

The GB excess properties were defined and calculated as described by Frolov and Mishin [8, 9], except for the microscopic, translational degrees of freedom [B], whose calculation is described in Ref. [29] and in Supplemental Fig. 1 [72]. Detailed definitions are also provided later in the paper together with the results. Structures were visualized with OVITO [73]. Raw data is available in the companion dataset [58].

![Figure 1. In $\langle11\overline{1}\rangle$ tilt GBs in fcc, two symmetric variants exist. Here, part of the dichromatic pattern of a $\Sigma7$ GB is shown. The solid and dashed lines represent all possible symmetric GB planes (not considering translations). Due to the threefold symmetry of the $\langle11\overline{1}\rangle$ plane, all solid and dashed lines, respectively, are equivalent. In this work, we only investigate variant I.](image)

Table III. List of the bicrystalline samples used to construct symmetric $\Sigma$ tilt GBs and to search for GB phases.

| CSL type | tilt axis | misorientation | GB planes |
|----------|----------|----------------|------------|
| $\Sigma$13b | $\langle11\overline{1}\rangle$ | 27.80° | $\{725\}$ | $\{752\}$ |
| $\Sigma$7 | $\langle11\overline{1}\rangle$ | 38.21° | $\langle145\rangle$ | $\{415\}$ |
| $\Sigma$49 | $\langle11\overline{1}\rangle$ | 43.57° | $\{211\overline{1}3\}$ | $\{11\overline{2}1\overline{13}\}$ |
| $\Sigma$19b | $\langle11\overline{1}\rangle$ | 46.83° | $\{178\}$ | $\{718\}$ |
| $\Sigma$37c | $\langle11\overline{1}\rangle$ | 50.57° | $\{110\overline{1}1\}$ | $\{10\overline{1}1\}$ |

C. Excess free energy

In the present work, we are interested in the stability of GB phases and GB phase transitions. In pure materials, such phase transitions can occur under externally applied stress or strain, or with changing temperature. The GB phase transitions can be predicted by computing the GB excess free energies of the different GB phases, which we define here as [8, 9]

$$\gamma = [U] - T[S] - \sigma_{33}[V] - \sum_{i=1,2} [B_i]\sigma_{3i},$$

where $[U]$ is the excess internal energy, $[S]$ the excess entropy, $\sigma_{ij}$ the externally applied stress tensor, and $[V]$ the excess volume. Here, $[B_1]$ and $[B_2]$ are excess shear stresses, which are equal to the microscopic, translational degrees of freedom when no macroscopic stresses or strains are applied [Fig. 2(b)]. The excess volume $[V]$ is not necessarily equal to $[B_3]$ as defined here [see Fig. 2(c)], but only $[V]$ enters the free energy. In contrast to Refs. [8, 9], we relax the normality of the bracket notation for notational simplicity, intending them only as indicators of GB excess values. We define all of them as intrinsic values by normalizing $[U]$, $[S]$, and $[V]$ by the GB area. More details and definitions of the excess properties are provided later in Sec. III B. The free energy at $T = 0$ K under applied stresses and strains can be obtained directly in molecular statics by applying the given stress to the system and computing $[U]$, $[V]$, and $[B_i]$. 
Figure 2. Geometry and excess properties of the bicrystals. (a) The convention used for the coordinate system. (b) The two crystallites are translated with regard to each other by a vector \([\mathbf{B}_3]\), which is specific to a GB phase. Due to the boundary conditions (lengths in \(x\) and \(y\) direction are fixed by the bulk phase and the system is free to expand in \(z\) direction [9]), excess stresses \([\gamma_{11}], [\gamma_{22}],\) and \([\gamma_{12}]\) occur, while the microscopic translations of the top crystallite lead to the excess volume \([V]\) and the excess shears \([B_1]\) and \([B_2]\). These excess properties couple to externally applied stresses \([\sigma_{31}], [\sigma_{23}], [\sigma_{33}]\) and strains \([\varepsilon_{11}], [\varepsilon_{22}], [\varepsilon_{12}]\) (blue text). (c) While the components \([B_1]\) and \([B_2]\) are simple displacements, \([B_3]\) consists of both the excess volume \([V]\) and accounts for the shift by full crystallographic planes normal to the GB. Here, this is illustrated for a hypothetical L3 \([11\bar{1}]\) GB. Different markers indicate the three different \((11\bar{1})\) planes and gray areas the interplanar distance \(d_{(224)}\). The left side only has the \([V]\) component. (i) Removing a \((112)\) plane (black atoms in the middle), then leads to a shift downwards by \(d_{(224)}\) (right side). (ii) This shift can alternatively be expressed by another shift that only changes the \([B_1]\) and \([B_2]\) components. The latter is always true in our GBs.

The influence of temperature, however, cannot be calculated directly, because the entropy is not accessible via simple molecular statics or MD simulations. Since we are dealing with pure systems, the entropy is a vibrational entropy and can be computed either via thermodynamic integration \([60, 74, 75]\) or with the quasi-harmonic approximation (QHA) \([75, 76]\). Here, we chose the latter method for reasons of computational efficiency. Force constant matrices were computed with the \texttt{dynamical\_matrix} command in \textsc{lammps}, from which we then obtained the phononic eigenfrequencies in real space. The free energy \(F\) was approximated by neglecting quantum-mechanical effects as

\[
F = k_B T \sum_{i=1}^{3N-3} \ln \frac{h \nu_i}{k_B T},
\]

where \(\nu_i\) are the phononic eigenfrequencies excluding the three zero-valued eigenvalues. This describes the systems modeled by MD, which are Newtonian systems, but we found that including quantum-mechanical effects (mostly zero-point vibrations and Debye-like thermal expansion at low temperatures) barely influences the GB free energies, especially at room temperature and above [29]. The GB excess free energy was calculated by subtracting the free energy of a defect-free fcc slab containing the same surfaces and number of atoms as the sample with the GB.\(^1\)

Raw data is available in the companion dataset [58].

D. Corroborative MD simulations

In addition to calculating \(\gamma(\sigma_{ij}, T)\), we also verified some example cases using MD simulations at elevated temperature, with and without applied stress and strain. We used systems roughly of size \(6 \times 16 \times 20 \text{nm}^3\) (10 unit cells in tilt axis direction) and a time integration step of 1 fs. Temperature was controlled with a Nosé–Hoover thermostat. We typically ran the simulations for up to 40 ns, or until the expected GB phase transition could be observed. Raw data is available in the companion dataset [58].

For calculations probing the influence of the temperature or the stress \(\sigma_{33}\) normal to the GB, we used open boundaries in \(y\) and \(z\) direction, while using periodic boundaries in the tilt axis direction \((x)\). A barostat at 0 Pa was applied in the periodic direction.

For the influence of a tension or compression in \(y\) direction \((\varepsilon_{22})\), we kept the \(y\) direction periodic and instead introduced open boundaries in the \(x\) and \(z\) directions. Strain was applied in the periodic direction after scaling the system to the appropriate lattice constant for the target temperature and simulation cell length was subsequently kept constant in the periodic direction.

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\(^1\) Note that the subsystem method described in Ref. [75], which would not require a reference system containing the exact same surfaces and number of atoms, only works for thermodynamic integration, but not for the QHA. This is because the calculation of force constant matrices for a subsystem introduces an artificial boundary with its own excess free energy.
Figure 3. (a) GB phases of Σ7 tilt GBs in a selection of fcc metals. The top row shows the domino phase (red colors), the bottom row the pearl phase (blue colors). The scale bar is valid for all images and the axes indicate the crystal directions of the top and bottom crystallites, respectively. The axes on the left are for the top views, the axes on the right for the side views. The coloring serves only to highlight the structural motifs. (b) Different misorientations for copper GBs. The axes are equivalent to (a)—for the exact crystal directions see Table III. Snapshots of the GB structures for all metals and misorientations can be found in Supplemental Figs. 2–6.

E. Experimental sample preparation and STEM imaging

In order to verify the simulations, we also experimentally investigated the atomic structure of a near-Σ49 GB in copper in addition to the already published experimental structures [28, 29, 47].

For this, a Cu thin film was deposited from a high purity (99.999%) Cu target on (0001)-oriented sapphire substrate by magnetron sputtering. The deposition was performed at room temperature with a radio frequency power supply at 250 W, a background pressure of 0.66 Pa, and 20 sccm Ar flow. We obtained a nominal film thickness of 600 nm with a deposition time of 45 min. The film was then annealed at 400 °C for 2 h within the sputtering vacuum chamber.

We identified pure tilt high-angle grain boundaries using electron backscattered diffraction imaging in a Zeiss Auriga scanning electron microscope. In the next step, we lifted out a Σ49 ⟨111⟩ GB using a Thermo Fisher Scientific Scios2HiVac dual-beam secondary electron microscope equipped with a Ga⁺ focused ion beam (FIB). A plane-view sample was extracted and attached to a Cu grid. For the lamella thinning, an initial current of 0.1 nA and voltage of 30 kV was used, reduced sequentially to 7.7 pA and 5 kV. The FIB sample was then transferred to a probe-corrected Thermo Fisher Scientific FEI Titan Themis 80-300 (scanning) transmission electron microscope. A high-brightness field emission gun at an accelerating voltage of 300 kV, semi-convergence angle of 17 mrad, and probe current of 85 pA was used for imaging. The image was recorded with a high-angle annular dark field (HAADF) detector (Fishione Instruments, Model 3000) with a collection angle of 78 to 200 mrad. An image of 50 frames with 1024 x 1024 px² with a dwell time of 2 ps and a step size of 12.45 pm was registered and overlaid using the drift compensated frame integration (DCFII) method. The final image was optimized using second order polynomial background correction, Butterworth, and Gaussian filters. The misorientation between both grains was measured from the angles between {220} lattice planes of both grains, using an average of at least ten different measurements.

III. STRUCTURES IN DIFFERENT FCC METALS

We performed a computational structure search with Ni, Cu, Pd, Ag, Au, Al, and Pb (M)EAM potentials for the GBs in Table III. We found that the possible structural motifs are similar not only across different metals [Fig. 3(a) and Supplemental Fig. 3], but as well across different misorientations from 27.80° to 50.57° [Fig. 3(b) and Supplemental Figs. 2–6]. Indeed, almost all of these
motifs resemble the “pearl” and “domino” structures found previously in copper [28, 29]. In some cases, additional structures were found, which will be discussed later.

Viewed from the [11T] tilt axis direction, the domino phases consist of pairs of squares (light red motifs in Fig. 3), which are distorted and arranged differently depending on the misorientation. From the side, the (11T) planes are approximately aligned, with offsets much smaller than the interplanar spacing.

The pearl phases consist of a single square (light blue motifs in Fig. 3) separated by varying amounts of pearl chains (dark blue or purple) when viewed from the [11T] tilt axis direction. The (11T) planes are shifted by approximately half the interplanar spacing, in contrast to the domino phases. Whereas the atomic structure of the domino phase seems to be independent of the material [Fig. 3(a), upper row], slight changes can be observed in the pearl phase [Fig. 3(a), lower row]. In the Σ7 GBs, two different pearl variants exist, which can be seen by comparing, e.g., Cu and Ag. The variant which occurs in Ag [Fig. 3(a)] and Pb (Supplemental Fig. 3) appears mirror symmetric in the projection (called aligned pearl from here on), while the variant in the other metals appears asymmetric (called sheared pearl from here on). This minor difference can best be seen by inspecting the light blue square motifs. Furthermore, additional motifs occur in the pearl phase of the Σ37c GB (Fig. 4 and Ref. [29]), leading to three distinct pearl variants (pearl #1, #2, and #3). Which of these variants has the lowest energy depends on the material, as discussed later.

For the Σ13b and Σ7 boundaries, some additional low-energy structures occur, which we simply name A, B, and C (shown in Fig. 5). These look different from the pearl and domino phases on visual inspection and are therefore listed separately. We only consider structures that are thermodynamically stable under some condition for at least one element and will later provide a more quantitative analysis of the GB phases, but will otherwise only discuss them where relevant. The A phase of the Σ13b GB occurs in all metals except Au and Pb, but only has a low energy compared to other GB phases in Al. In the Σ7 tilt GBs, Pb has the B phase and the C phase is a higher-energy phase in all metals.

Due to the varying quality of empirical potentials—especially in the case of GB structures which have not been included in the fitting database for the respective potential—an independent validation based on experiment or ab initio methods is desirable. Unfortunately, the unit cells of the high Σ GBs are too big to allow the required high-accuracy density-functional theory (DFT) simulations, especially when one needs to avoid GB/surface elastic interactions by including a sufficient amount of bulk material. In tests we found that, e.g., the excess volume is very sensitive to such effects. We thus limit ourselves here to a comparison to STEM images obtained for Cu and Al. For Cu Σ19b and Σ37c, see Refs. [28, 29]. For these GBs in Al, only the domino phase has been found to date [47]. Additionally, Fig. 6 shows an experimental STEM image of a Σ49 pearl phase in copper. All of the structures in the experiments listed above agree well with the simulated structures. Because of the similarity of motifs across misorientations and materials, we are confident that these structure predictions are therefore quite reliable.

We note that the structures of the [11T] tilt GBs are relatively complex compared to, for example, the more typical kite structures in other (tilt) GBs [21, 30, 38]. Nevertheless, visual inspection already indicates that—except for the special case of the B phase in Pb—material-specific GB structures do not exist and that the presented GB phases are universal in fcc metals. This raises the question of how big the role of the physics and chemistry of a specific material is and how much of that material-specific information needs to be included in a model to reproduce them. We will investigate this in the next section and then proceed to a more quantitative comparison of the GB phases in terms of excess properties.
A (Σ13b)

B (Σ7)

C (Σ7)

Figure 5. Snapshots of the A, B, and C phases. The material is copper for the A and C phases. The B phase only exists in lead. Snapshots for all materials are provided in Supplemental Figs. 2 and 3.

Figure 6. Comparison between a STEM image of a pearl structure in the Σ49 tilt GB in copper with simulations. (a) HAADF-STEM image of a Σ49 tilt GB (misorientation 43.3° ± 0.3°). Note that there is a defect (disconnection) on the right side of the image, where only one blue square is located in between the yellow motifs and where the rightmost yellow motif is mirrored. An image of a longer stretch of the GB can be found in Supplemental Fig. 7. (b) It can be seen that the structure from the MD simulation is the same. The colors in these images highlight that the Σ49 GB consists of alternating motifs from the Σ7 GB (yellow) and the Σ19b GB (blue).

Figure 7. Visual comparison of the Σ7 pearl structure modeled using the copper EAM potential (Cu), a Lennard-Jones pair potential (L-J), and a next-neighbor pair potential (PP1). For comparison, the data from Frost et al. (1982) [77] (rigid displacement of hard spheres) was also reproduced here, but does not exhibit any of the pearl or domino structures. The scale bar for the model potentials is given in reduced units of the equilibrium fcc bond length $r_0$. The axes are the same as in Fig. 3(a).

A. Geometry or material physics?

As a first test, we used a Lennard-Jones pair potential as a simplified, generalized model of a densely-packed metal. Physically, pair potentials cannot reproduce the concept of bond order, i.e., the strength of any interatomic bond simply depends on the bond length and not on the atomic environment (such as for example coordination number). By repeating the structure search with this pair potential, we can nevertheless find the same structural motifs in the GBs (see Fig. 7 for the Σ7 pearl phase).

In the past, hypothetical GB structures have also been constructed using the assumption of hard spheres due to the lack of realistic interatomic potentials [77]. We used our next-neighbor pair potential to explore how realistic the results are under the assumption of very short-ranged interactions. For this, we took the set of all distinct GB structures obtained using all the other potentials and reminimized them with the next-neighbor potential. While both energy minimization using the next-neighbor pair potential and rigid displacement of hard spheres (as performed by Frost et al. [77]) lead to quite open GB structures, the former are at least able to reproduce some of the motifs produced by longer-ranged potentials (Fig. 7). The two bonds drawn in Fig. 7 are
The more realistic, medium-ranged potentials predict an excess properties. If the excess properties are very close in value, we would rather define the structures as defective or as microstates of a GB phase [24, 28, 29, 78]. Furthermore, the excess properties influence the GB thermodynamics (Eq. 4) and are therefore important quantities. We will thus now discuss the individual excess properties introduced in Sec. II C in detail for our GB phases.

Figure 8(a) shows the normalized excess volumes \([V]/a_0\) of all \(\Sigma^7\) GB structures [data for other GBs are shown in Supplemental Figs. 8(a)–12(a)] with
\[
[V] = \frac{V_{GB} - N\Omega}{A_{GB}},
\]
where \(V_{GB}\) is the volume of a region of the simulation cell containing a GB (but no surfaces), \(N\) is the number of atoms in that region, \(\Omega\) is the atomic volume in a defect-free fcc phase, and \(A_{GB}\) is the area of the GB. The normalization by the fcc lattice constant \(a_0\) at \(T = 0\) K makes these volumes unitless and comparable between materials.

In general, domino phases have higher excess volume than pearl phases as indicated by the lines in Fig. 8(a). This trend is reproduced by the Lennard-Jones potential, but not by the next-neighbor pair potential. As already visible in the snapshots and as generally expected, this indicates that the relaxation inside the GB is influenced by several neighbor shells.

Figure 8(b) shows the microscopic, translational degrees of freedom \([\mathbf{B}]\) of the \(\Sigma^7\) GB, which are the relative rigid-body displacements between the two crystallites (data...
for other GBs are shown in Supplemental Figs. 8–12 and
an illustration of the concept can be found in Fig. 2).
[B] = 0 represents the case where coincidence sites in the
dichromatic pattern actually overlap (which is how the
dichromatic pattern is typically plotted), while |B| \neq 0
means that no coincidence sites exist in the dichromatic
pattern, i.e., −|B| represents the shift required to obtain
coincidence sites (see also Supplemental Fig. 1). Due to
this, |B| vectors are equivalent if they can be obtained
by adding or subtracting DSC vectors. The components
[B1] and [B2] are also called excess shears and enter the
GB excess free energy by coupling to externally applied
shear stresses (Eq. 4). Due to the symmetry of the present
bicroystals with symmetric tilt GBs, [B2] and −[B2] are
degenerate states of the same GB phases. This is not the
case for [B1], where −[B1] corresponds to switching the
top and bottom crystallite.

A typical feature of the pearl phases is that the (11T)
planes of the abutting crystallites are not aligned, but
shifted by approximately a half-plane in tilt-axis direction.
This is described by [B1]. All pearl variants are united by
this half-plane shift. The domino phases, in contrast, are
characterized by |B1| \approx 0. The shift [B2] parallel to the
GB plane has two different behaviors in the case of the
Σ7 GB. Both domino (diamond symbols) and the aligned
pearl variant (pentagon symbol) have a fixed value, while
the sheared pearl (circles) has material-dependent values,
i.e., exhibits some excess shear. The difference in this
shift describes the amount of shear that the pearl motifs
undergo. An aligned pearl variant was thus found in Ag
and Pb in the Σ7 GBs, and universally in the Σ19b GBs.
The Σ13b pearl phases are mostly aligned, except for
a small asymmetry in Ag, Pb, and the Lennard-Jones
model, which we do not indentify as a separate pearl
variant. For Σ49 and Σ37c, only sheared pearl variants
exist.

Figure 8(c) and Supplemental Figs. 8(f)–12(f) show the
normalized excess GB stresses [τij]/(σijkK) with

$$[τ_{ij}] = \sigma^{GB}_{ij}/A_{GB},$$

where \(σ^{GB}_{ij}\) corresponds to the average of the relevant
stress tensor component in the region containing the GB.
This definition allows the easy calculation of strain energy
via \(\int (σ^{GB}_{ij})dε\) (cf. Eq. 10), meaning that the excess
stresses are expressed in J/m². Here, the \([τ_{11}]\) excess
stress acts along the tilt axis and \([τ_{22}]\) along its orthogonal
direction within the GB plane [see also Fig. 2(b)]. The
normalization by the ground-state fcc lattice constant \(a_0\)
and the bulk modulus \(K\) makes these stresses unitless and
comparable between materials.

There is a tendency for \([τ_{11}] < 0\) and \([τ_{22}] < 0\) for pearl
and \([τ_{11}] > 0\) and \([τ_{22}] > 0\) for domino. Similar trends
are observed in all GBs. That means that the pearl phase
with lower excess volume is under compression in the in-
plane directions of the GB, while the domino phase with
higher excess volume is under tension. However, there are
several exceptions, such as Al, where the GBs generally
tend more towards tensile stresses. The next-neighbor
pair potential is once again unable to capture this trend.
We will therefore not discuss it any further. The excess
stresses of the pearl variants for Σ37c GBs are very similar
within the same material, with the exception of Al [see
Supplemental Fig. 12(f)], indicating again that they are
closely related.

Supplemental Figs. 8–12 show that the A, B, and C
phases are characterized by a \([B1]\) offset of half an interpla-
near spacing (similar to pearl), but positive \([τ_{22}]\) (similar
to domino), which is why we label them as individual
GB phases. We make the distinction between A and B/C
because they appear at different CSL boundaries, and
differentiate B and C in Pb by their different values of
excess shear \([B2]\) and excess stress \([τ_{22}]\).

IV. THERMODYNAMIC STABILITY

A. Ground state stability

For each of the investigated tilt GBs we showed that at
least two GB phases (domino and pearl) exist. In order
to evaluate which of these GB phases will actually occur,
we have to investigate their thermodynamics. We first
consider the case of \(T = 0\) K and no externally applied
stress or strain. Here, the ground state GB free energy is

$$γ_0 = [U] = E_{GB} - NE_{0}^{f,b},$$

where \(E_{GB}\) is the potential energy of a region of the
simulation cell containing a GB (but no surfaces), \(N\) is the
number of atoms in that region, \(E_{0}^{f,b}\) is the ground-state
energy per atom of the defect-free fcc phase, and \(A_{GB}\) is
the area of the GB. Note that the internal energy is equal
to the potential energy in this section, because we simulate
a classical, Newtonian system at zero temperature, i.e.,
with zero kinetic energy. All GB energies are plotted in
Supplemental Fig. 13.

Figure 9(a) and Supplemental Fig. 14 show the energy
difference \(Δγ = γ_0^{d} - γ_0^{p}\) at \(T = 0\) K between the
domino and pearl phases. In many cases, the pearl
phase is stable, with the highest energy difference being
observed for the Σ19b GB, except for Ni (highest energy
difference for Σ49). The Σ19b GB often also has the lowest
overall GB energy, although for Pd, Al, and Pb the Σ7 GB
has a lower energy (Supplemental Fig. 13). The domino
phase is stable in the Σ37c GB in many materials, and
seems to also become more favorable again towards lower
misorientation angles. Apart from domino and pearl, the
A, B, and C phases are usually high-energy GB phases.
Exceptions are the A phase in Al, which is quite close in
GB energy to the pearl phase, and the B phase in Pb,
which is the lowest-energy GB phase in Σ7. The C phase
only plays a role at higher temperatures, as discussed
later in Sec. IV.C.

The Lennard-Jones potential, in contradiction to the
more realistic (M)EAM potentials, always predicts that
This indicates that the Lennard-Jones potential is not a good “generalized” model for most metals: While it is able to capture structural motifs and their excess properties qualitatively, the material-specific physics play a bigger role in the relative thermodynamic stability of the GB phases. This is also important for the evaluation of early simulation work on GB structures [42]: The present results suggest that it is likely that such simulations predicted the wrong ground state because they used pair potentials instead of more realistic material models.

For the (M)EAM potentials, we tried to find a simple predictor of the relative GB phase stability as a function of the material properties, and focus here on the stacking-fault energy $\gamma_{SF}$. This is a tempting quantity, because both GBs and stacking faults are planar defects and because $\gamma_{SF}$ is indirectly related to the energy of coherent twin GBs. If we normalize both the stacking-fault energy of the metal and the GB energy difference $\Delta \gamma$ between domino and pearl by the respective fcc lattice constant and cohesive energy, we find that low stacking-fault energies tend to be associated with a preference for the domino and pearl by the respective fcc lattice constant of the metal and the GB energy difference $\Delta \gamma$.

Ultimately, the relative energies of GB phases have to be computed with sophisticated models (such as EAM potentials or DFT) and simple rules based on bulk properties will be incomplete. This is especially true since the GB energy differences are often small and on the order of 10 mJ/m², although they can be as high as approximately 120 mJ/m² [Fig. 9(a)].

### B. Stress-dependence of the free energy

The excess free energy at $T = 0$ K under applied stresses $\sigma_{33}$, $\sigma_{23}$, and $\sigma_{31}$ can be described as

$$\gamma = [U] - \sigma_{33}[V] - \sum_{i=1,2} [B_i] \sigma_{3i}$$

in the case of tilt GBs [see Fig. 2(b) for a sketch of the stresses and strains]. The excess free energy under applied strain $\varepsilon_{22}$ can be calculated by integrating the work done by the excess stress $[9]$

$$\gamma = \gamma_0 \frac{A_0}{A_{GB}} + \frac{1}{A_{GB}} \int_{\varepsilon_1}^{\varepsilon_2} A_{GB}(\varepsilon) [\gamma_{22}] \varepsilon \, d\varepsilon,$$

where $A_0$ is the GB area before deformation. The calculation for $\varepsilon_{11}$ and $\varepsilon_{12}$ is equivalent. Because the additional
Figure 10. GB free energies as a function of an applied stress $\sigma_{33}$ normal to the GB for some selected GBs. (a) In copper $\Sigma 7$ GBs, the domino phase becomes stable under tension. (b) The Al potential also predicts that pearl becomes stable under very high compressive stresses. Furthermore, it exhibits some changes of the curvature of $\gamma$ for the pearl phase, which are associated with small rearrangements of the atomic motifs, leading to the prediction that pearl can additionally become stable at very high tensile stresses. This is likely due to the Al potential being described by cubic splines (the change of curvature representing a transition to another polynomial in the spline). Other potentials do not show such behavior, suggesting that this is most likely an unwanted and unphysical feature of the potential at high stresses/strains. (c) The Pd $\Sigma 49$ GB represents an interesting case due to the low stresses required to transition between pearl and domino. Data for all GBs is available in Supplemental Figs. 15–19.

Because the domino phase universally has a higher excess volume than the pearl phase [Fig. 8(a)], it stands to reason that it can be stabilized by a tensile stress $\sigma_{33}$ normal to the GB, while the pearl phase can be stabilized by a compressive stress. Figure 10 and Supplemental Figs. 15–19 show that this is the case, but that the required stresses are usually very high (on the order of gigapascals) and sometimes exceed the range of values that were investigated. One interesting exception is for example the Pd $\Sigma 49$ GB [Fig. 10(c)], where the ground state energy difference between the domino and pearl phases is close to zero. We thus validated this case by MD simulations at $T = 900$ K and $\sigma_{33} = \pm 1$ GPa, starting once from a pearl phase and once from a domino phase. In less than 8 ns, the systems under compression transitioned to the pearl phase and the systems under tension to the

Therefore, $\gamma = [U]$, (11) without need for the integration.

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domino phase, as expected (see Supplemental Fig. 20).

Another interesting excess property is the excess stress \( [\tau_{22}] \) in the GB plane, since it indicates if the GB phase is under compression or tension. Since typically \( [\tau_{22}] < 0 \) for pearl and \( [\tau_{22}] > 0 \) for domino, it seems reasonable that a compressive \( \varepsilon_{22} \) would favor domino, while tension would favor pearl (see Eq. 10). Figure 11 and Supplemental Figs. 21–25 show that this is indeed a general trend. Exceptions are some GBs in Ni, Al, and Pb. For those GBs, however, the value of \( [\tau_{22}] \) is positive for the pearl phase, suppressing a clear trend for a GB phase transition under applied strain. For \( \Sigma13b \) GBs in Cu, Ag, or Pb; \( \Sigma7 \) GBs in Cu or Ag; \( \Sigma49 \) GBs in Pd or Al; \( \Sigma19b \) GBs in Al; and \( \Sigma37c \) GBs in Cu or Ag, the required strains for the GB phase transitions are relatively low and could reasonably be observed experimentally (Supplemental Figs. 21–25). We tested this by performing MD simulations for the \( \Sigma7 \) GB in Cu with \( \varepsilon_{22} = -2\%, +1\% \). We ran the simulations at \( T = 900 \text{K} \) in order to accelerate the transition kinetics. A GB phase transition can be observed after less than 4 ns, obtaining the domino phase under compression and the pearl phase under tension (Supplemental Fig. 26).

In addition to externally applied stresses, the rigid-body displacements between the two crystallites could also be determined by restrictions on GB sliding in polycrystals or by the bonding to a substrate in the thin film case [78]. Then, however, \([B]\) in Eq. 9 no longer corresponds to the displacement, but the excess displacement over the defect-free crystal subject to the same stress \( \sigma_{3i} \) [8, 9]. Thus, knowledge of the resulting, system-size-dependent stress state would be required to be able to calculate the free energy, necessitating mesoscale modeling.

Finally, we found that the A, B, and C phases are not stable, except for the A phase in Al, which becomes stable under compression normal to the GB plane or under tensile \( \varepsilon_{22} \), and the B phase in Pb, which is the lowest-energy GB phase in \( \Sigma7 \) even without applied stress or strain.

In summary, our simulations show that the GB phase transitions both under stress and under strain can be well predicted by the excess properties in the ground state. The GBs thus obey Le Chatelier’s principle and counteract the applied stresses and strains via GB phase transitions.

### C. Temperature-dependence of the free energy

The excess free energy without applied stresses or strains is

\[
\gamma = [U] - T[S]
\]

for finite temperatures. Note that for \( T > 0 \text{K} \), the potential energies \( E \) in Eq. 8 have to be replaced by \( \langle E \rangle \), which are the average total energies at the given temperature. The excess entropy \( S \) is not easily accessible to MD simulations. The change of excess free energy

\[
\gamma(T) = \gamma_0 + \Delta\gamma(T)
\]

\( \gamma(T) \) can instead be calculated using either thermodynamic integration [66, 74, 75] or from the phonon eigenfrequencies using the QHA [75, 76]. We chose the latter due to the lower computational demands. In previous works, both methods were found to give equal results [29, 75].

In most cases, the pearl phase remains stable over the whole temperature range (Fig. 12 and Supplemental Figs. 27–31). If the domino phase is stable at low temperatures (\( \Sigma13b \): Pd, Al; \( \Sigma7 \): Pd, Al; \( \Sigma49 \): Al; \( \Sigma37c \): Cu,
Pd, Ag, Al, Pb) it usually transforms to pearl at higher temperatures, except for Σ7 Pd (domino is always stable). In Σ13b Pb, as well as Σ19b Ag and Pb, pearl transforms to domino at higher temperatures. In Σ49 Pd, both phases have approximately equal free energy. Some limited experimental data is available for copper (Refs. [28, 29] and Fig. 6) and supports the modeling. In Al, only the domino phase has been found to date [47]. That contradicts the data obtained with the Al potential for the Σ19b GB (but not the others). The predicted energy differences between domino and pearl are small, however, which complicates the comparison to experiment: Either the relative stability of the GB phases is predicted incorrectly by the potential or small residual strains in the experiments, which were performed on thin films, could potentially destabilize the pearl phase.

The only non-domino/non-pearl phases that become stable with increasing temperature are the A phase in Al Σ13b GBs and the C phase in Cu and Ag Σ7 GBs (Fig. 12 and Supplemental Figs. 27 and 28). In general, the investigated GBs mostly exhibit domino and pearl phases, with A, B, and C being the exceptions.

In order to furthermore exclude the existence of additional GB phases and to validate the QHA calculations, we ran MD simulations for up to 40 ns with the GBs in contact with open boundaries at elevated temperatures [21] for some example cases. We chose high temperatures to enable GB phase transitions on MD timescales. No additional GB phases were discovered. For the Σ7 GBs, we found that Ni (T = 1300 K) and Al (T = 900 K) transition to the pearl phase at high temperatures independent on the starting structure, as expected (Supplemental Figs. 32 and 36). The Al sample contained many defects after the heat treatment. Both Cu (T = 1100 K) and Ag (T = 1100 K) quickly transitioned to the pearl phase if starting from domino and slowly nucleated the C phase, also as expected (Supplemental Figs. 33 and 35). In the latter case, however, C and pearl phases often appear to coexist, hinting that the C phase is some variant of the pearl phase. The only case that could not confirm the QHA calculations was the Pd Σ7 GB; neither systems containing pearl, nor containing domino would undergo phase transitions when heated to 900 K (Supplemental Fig. 34). This is likely due to the small free energy differences between the GB phases and possibly a result of the low mobility of the phase junction between the two GB phases [28]. Apart from the Σ7 GBs, we also annealed a Ni Σ37c GB at 1000 K (Supplemental Fig. 37). The QHA calculations predict that the pearl #3 variant is stable at low temperatures and pearl #1 and #2 at high temperatures, the latter GB phases having almost equal free energies [Supplemental Fig. 31(a)]. We could indeed observe this transition between pearl variants, although the result at high temperature still contained several pearl #3 motifs. This is not surprising, since these structures should most likely be treated as microstates of a pearl GB phase [29].

Due to the rough tendency of pearl being stable at higher temperatures, it is tempting to treat the pearl structure as a high-entropy GB phase. But while it is universal that domino has higher excess volumes and thus couples to σ_{33}, a higher entropy of the pearl phase cannot be observed in the majority of cases. When pearl is stable over the whole temperature range, the slope of γ(T) is often similar for pearl and domino, indicating approximately equal excess entropies. In pure materials, the excess entropy is vibrational and results from the GB phonon modes. This means that the GB vibrations are therefore quite material dependent.

### D. Latent heat and order of the GB phase transition

Finally, we will shortly discuss the order of the GB phase transition. According to the Ehrenfest classification, first order phase transitions are those that have a discontinuity in the first derivative of the relevant thermodynamic potential. Alternatively, first order phase transitions have a latent heat. In bulk materials, these definitions are virtually equivalent and the latent heat is the difference in enthalpy \( \Delta H = \Delta G + T \Delta S \) of the phases, with \( G \) being the Gibbs free energy and \( S \) the entropy. By definition, it is \( \Delta G = 0 \) at the transition point \( T_r \), allowing us to write \( \Delta H = T_r \Delta S \). The entropy of the system in equilibrium is discontinuous at \( T_r \) for \( \Delta S \neq 0 \) due to the change from one phase to another with different entropy. This means that the phase transition is also of the first order.
according to Ehrenfest because the entropy of a phase is the first derivative of the free energy \( S = -\partial G/\partial T \) at constant pressure. Equation 12 with \( \Delta \gamma = 0 \) leads to a similar result for GBs, namely \( \Delta[H] = \Delta[U] = T \Delta[S] \) for \( \sigma_{li} = 0 \) (no work is done by the system on its surroundings without externally applied stresses, only heat is exchanged). The excess entropy can be calculated as

\[
[S] = -\frac{d\gamma}{dT} + \sum_{i,j=1,2} \left( [\tau_{ij}] - \delta_{ij}\gamma \right) \frac{d\varepsilon_{ij}}{dT},
\]

(see Eq. 14 of Ref. [9], noting that we already normalize \( [S] \) by the GB area) where the strains \( \varepsilon_{ij} \) correspond to the thermal expansion of the grains, which result in work being done by the grain boundary against the expansion, even without externally applied stress. (Note that this work term does not come into play when defining the latent heat as \( \Delta[H] = \Delta[U] \), because the phase transformation takes place at constant \( T = T_i \) and thus constant \( \varepsilon_{ij} \). It is only required to calculate \([S]\).) For cubic systems, we can replace \( d\varepsilon_{ij}/dT \) with the isotropic thermal expansion coefficient \( \alpha_T \) and simplify to

\[
[S] = -\frac{d\gamma}{dT} + \alpha_T \left( [\tau_{11}] + [\tau_{22}] - 2\gamma \right).
\]

We ignore the weak temperature dependence of the excess stresses in further calculations. Figure 13 shows an example for the \( \Sigma 7 \) GB in Al. At the transition temperature of around 405 K, the excess free energy of the system in equilibrium changes slope and the entropy is discontinuous, resulting in a finite latent heat. Equivalent results would be obtained for the other GB phase transitions. The GB phase transitions in this work are thus first order phase transitions.

V. SUMMARY AND CONCLUSION

Simulations using (M)EAM potentials reveal that a range of high-angle, symmetric \( [11\bar{1}] \) tilt GBs in fcc metals exhibit mainly two GB phases, here called domino and pearl. We found that the domino and pearl phases, respectively, have comparable structures and thermodynamic excess properties across different \( \Sigma \) boundaries with misorientations from 27.8° to 50.6° and for all of the seven investigated fcc metals. Indeed, the structures seem universal enough to be modeled using simple pair potentials, although medium-range interatomic interactions are required to recover the trends of the excess properties. The thermodynamic stability as a function of stress, strain, or temperature, however, is more specific to the material:

- In many cases the pearl phases are stable at \( T = 0 \) K and if they are not, they often become stable at higher temperatures due to their higher excess entropy. This is not universal however, suggesting that the GB vibrations are material dependent.

- There does not seem to be a clear predictor of which GB phase is the ground state, although there is some weak correlation with the stacking-fault energy, with low stacking-fault energy favoring pearl.

- The domino phases have higher excess volumes in almost all cases, meaning that they are stabilized by tension applied normal to the GB, while the pearl phases are stabilized under compression.

- The pearl phases tend to exhibit negative excess stresses in the GB plane (\( [\tau_{11}] \) and \( [\tau_{22}] \)), while the domino phases exhibit positive excess stresses. This predicts their thermodynamic stability quite well: compression in the GB plane stabilizes domino, while tension stabilizes pearl, opposite to the previous case of stress applied normal to the GB.

- The required stresses for GB phase transformation can exceed 5 GPa and would be unlikely to occur in real materials. In some cases, however, stresses below 1 GPa or even close to zero, as well as strains below 1%, are sufficient. We confirmed some of the latter cases with MD simulations.

While there are always some exceptions to the above rules, the present results suggest that GB structures and phases discovered for one material are likely generalizable to a whole class of materials (in this case fcc metals). It remains to be seen if that is a feature of densely-packed metals or if it is also true in, e.g., covalently or ionically bonded materials. The addition of alloying elements is also likely to lead to more material-specific GB thermodynamics.

ACKNOWLEDGMENTS

This project has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (Grant agreement No. 787446; GB-CORRELATE).

Author contributions: T.B. and G.D. designed the study. T.B. performed and analyzed the simulations and wrote the initial manuscript draft. L.L. performed the STEM investigation and H.B. synthesized the corresponding thin film. G.D. supervised the project, contributed to discussions, and secured funding for T.B., L.L., and H.B. via the ERC advanced grant GB-CORRELATE. All authors participated in the preparation of the final manuscript.

Appendix A: Numerical issues of the interatomic potentials

The calculation of free energies in the QHA depends on the force constant matrix, which is closely related to the Hessian of the potential energy. This requires that
the interatomic potential is smooth up to the second derivative, otherwise the resulting free energy is noisy. In MD simulations, only first derivatives of the potential energy are used and any noise is averaged out due to the natural thermal fluctuations of the dynamic simulation, making numerical issues with the potential unnoticeable. In the present work, we found that the Pd, Au, and Al potentials result in noisy free energy data in our QHA calculations.

For Al, this is not due to the formalism of the potential, but a consequence of limited precision of the tabulated potential data in the file distributed via the NIST Interatomic Potentials Repository [55]. In LAMMPS, EAM potentials are tabulated—typically with dense sampling of data points—in text files and interpolated during simulation. In current numerical simulations, floating point numbers are usually represented using the IEEE 754 double-precision format, which corresponds to a precision of at least 15 significant digits in decimal representation. The text files used to produce the Al potential file contain fewer significant digits. We tested the potential by using the $\Sigma_{19b}$ domino GB phase and isotropically straining the simulation cell, while recording the potential energy (Supplemental Fig. 38). Taking numerical derivatives of the potential energy, we obtain smooth curves up to the first derivative, but see noise from the second derivative on. This is not surprising, since numerical derivatives are particularly sensitive, even to small noise. We then recovered the original nodal points, reproduced the potential, and constructed a tabulated EAM potential file with full machine precision (see companion dataset [58] for details and the potential file). This leads to smooth results up to the third derivative of the potential energy (Supplemental Fig. 38) while preserving the properties of the potential (we verified this for the bulk properties listed in Table II, as well as the excess properties of the GB phases).

Additionally, the construction of the Al potential from cubic splines leads to changes of curvature of the GB free energy [visible for example in Fig. 10(b) at high stresses or in Fig. 12(b) at around 550 K]. This indicates a shortcoming of the fitting with cubic splines to a limited reference database. It seems that the flexibility of representing the EAM functions with splines would require more strained reference data points in order to correctly model highly strained systems.

For Pd and Au, the first and second derivatives of the potential energy are sufficiently smooth (Supplemental Fig. 39). The problem comes from the cutoff function in these cases. It appears that the cutoff functions are relatively abrupt. This works well for the defect-free crystalline structures, where interatomic distances are usually smaller or larger than the cutoff distance. In the case of our GBs, however, bond lengths around the cutoff distance can appear and certain bond lengths can cross this distance during thermal or mechanical straining. As depicted in Supplemental Fig. 39, this can lead to discontinuities in the forces and thus jumps and/or noise in the second derivatives. It is nontrivial to improve the existing potentials without changing their properties and we therefore use the unchanged potentials here.

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