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Extra variable in grain boundary description

J. Hickman and Y. Mishin

Department of Physics and Astronomy, MSN 3F3, George Mason University, Fairfax, Virginia 22030, USA

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Grain boundaries (GBs) in crystalline materials are traditionally described by five crystallographic angles, which are assumed to fully define the GB structure and energy. It has recently been realized that variations in the atomic density λ in the GB region can drastically alter the GB structure and cause transformations between different GB phases. Here we extend the previous studies of Cu $\Sigma5$ GBs by computing the structures and energies of a set of [001] symmetrical tilt GBs over the entire angular range by allowing arbitrary variations in λ. The results confirm the existence of stable and metastable phases in all GBs studied here. There are three types of structural units that can describe all GB structures obtained in this work. The work demonstrates that λ should be added to the description of GBs as an extra thermodynamic parameter that helps predict the GB phases and transformations among them.

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A grain boundary (GB) is an internal interface separating homogeneous crystalline regions (grains) with different crystallographic orientations [1]. GBs are found in metallic materials, ceramics, and less conventional systems such as colloidal crystals [2], ice [3], solid helium [4,5], graphene [6,7], and organic crystals such as molecular semiconductors [8] and benzene [9]. GBs have a strong impact on materials' properties and behavior and have been extensively studied by experiments [1] and simulations [10] over the past decades. Crystallographically, a GB is fully characterized by five angles describing the lattice misorientation between the grains and the GB plane. Recently, it has been found that the addition or removal of atoms to/from the GB can often lower its excess energy γ, creating new stable structures [11–17]. Some of the newly discovered GB structures behave like two-dimensional phases [18,19], existing in certain temperature intervals and reversibly transforming to each other by first-order phase transformations. Such phases and transformations among them have been studied by atomistic simulations for two $\Sigma5$ [001] symmetrical tilt GBs in Cu (Σ being the reciprocal density of coincident sites and [001] the tilt axis) [14,15].

In this paper we demonstrate that the multiplicity of GB phases is not specific to the particular $\Sigma5$ GBs and that the emergence of new GB structures is a generic phenomenon that must take place in almost every GB. Thus, the atomic density in the GB must be considered as an additional thermodynamic parameter whose variation may cause structural transformations.

As a model system we chose [001] symmetrical tilt GBs in Cu with misorientation angles $0^\circ \leqslant \theta \leqslant 90^\circ$. The atomic interactions were modeled with an embedded-atom method (EAM) potential [20]. The GBs were created by the standard procedures [21]. Each GB can be described by either the indices $(hk0)$ of its plane or the respective θ. Periodic boundary conditions were imposed parallel to the GB plane with open surfaces in the normal direction. The following procedure was applied to minimize the GB energy for different atomic densities. A set of random parallel translations was applied to the upper grain relative to the lower. After each translation, N random atoms were removed from a 0.8-nm-thick layer covering the GB and a molecular dynamics (MD) simulation was implemented on this layer at a temperature of 0.85 of the melting point. During the simulation, the grain atoms remained fixed relative to each other, but the upper grain was free to translate relative to the lower. This simulation served to randomly intermix the atoms in the premelted GB layer. Multiple snapshots of the MD run were "quenched" by minimizing the total energy, each time producing a different GB structure. The structure with the lowest γ was identified and the process was looped over all grain translations and different values of N. This process was repeated for several different cross-sectional areas of the boundary to determine the most favorable 0 K GB structure for each N. See the Supplemental Material [22] for a more detailed description of the methodology.

The GB density was characterized by the relative number λ of atoms removed from the GB: $\lambda = N/N_0$, where N_0 is the number of atoms in a perfect $(hk0)$ layer inside the grains. Because the removal of a whole crystal plane recovers the initial GB, we are only interested in the interval $0 \leqslant \lambda \leqslant 1$. The function $\gamma(\lambda)$ for each GB was constructed by sorting the raw points (γ_i,λ_i) using a binning procedure described in the Supplemental Material [22]. Figure 1 shows representative $\gamma(\lambda)$ plots (see [22] the complete set of plots). We emphasize that each point represents the lowest GB energy obtained for the given value of λ. The numerous metastable states of the boundary with higher energies [23] do not present much interest in this work and are not shown on the plots with only a few exceptions discussed below.

We first focus of the $\Sigma5\,(210)$ and $\Sigma5\,(310)$ GBs studied previously [14,15] [Figs. 1(c) and 1(d)]. Our results exactly recover the GB energies and structures corresponding to the energy minima. The three distinct structural units of these GBs are shown in Fig. 2 and include the well-known kite-shaped structural unit and two additional units referred to in Refs. [14,15] as split kites and filled kites. For brevity, we will call these structural units K, L, and M, respectively, and will symbolize them by a diamond, a square, and a circle. Note that we have redefined the L unit by excluding its tip for a more consistent description of other GBs. In the $\Sigma5\,(210)$ GB, the L units connect to each other head to tail to produce a more favorable structure than the standard K units [14,15].

Low-angle GBs form when θ is small and when it is close to 90°. In the first case, the GB represents an array of dislocations

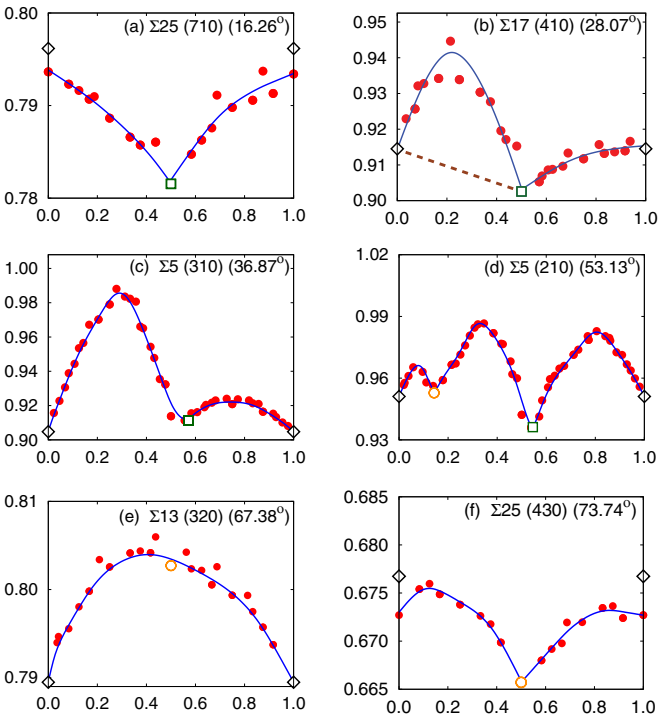

FIG. 1. GB energy (in J m^{-2}) versus GB density λ (fraction of atoms removed) for representative symmetrical tilt GBs in Cu. For GBs composed on identical structural units, the data points are shown by symbols representing the respective structural units (◇ K, □ L, ○ M, see Fig. 2). The diamond symbols in (a) and (f) represent metastable structures composed of structural units K. All other points represent stable structures that minimize the GB energy for each density λ. The dashed line in (b) is an example of a tie line between two GB phases producing cups of the energy. The trend lines are shown as a guide to the eye.

running parallel to the tilt axis. Standard energy minimization without adjusting the GB density predicts that the dislocation cores are composed of K units. This is a typical structure that can be found in the literature [21]. However, Fig. 1(a) presents an example where this structure is, in fact, *not* the ground state. If λ is allowed to vary, γ is reduced by removing an equivalent of a half-plane ($\lambda = 0.5$) and forming a new structure composed of L units. In fact, even if the GB density

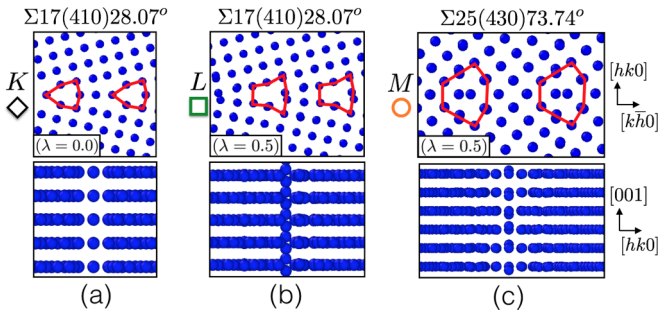

FIG. 2. Structural units (a) K, (b) L, and (c) M found in [001] symmetrical tilt GBs in Cu. The structures are projected parallel to the [001] tilt axis (upper row) and normal to the tilt axis (lower row). The GB density λ is indicated.

remains fixed at the initial value ($\lambda = 0$), our calculations show that the structure composed of K units is still not the ground state. This structure is metastable and is shown in Fig. 1(a) by a diamond symbol. A more favorable structure is composed of alternating L-type and K-type units arranged in the pattern $\cdots$-L-L-K-L-L-K $\cdots$, where the dash indicates that the units are separated several elastically distorted perfect-lattice units. Of course, due to the conservation of atoms, these K and L units contains some defects such as extra atoms or structural vacancies.

This example clearly demonstrates the importance of displacing GB atoms over large distances when searching for the energy minimum. The widely accepted procedure when the energy is minimized with respect to local atomic displacements can easily miss low-energy structures (even if grain translations are applied). The example in Fig. 1(a) is for $\theta = 16.26°$. The same behavior pertains to smaller angles. But as θ increases, the structure composed of K units becomes increasingly more favorable and eventually becomes the ground state at $\lambda = 0$ [Fig. 1(b)]. Nevertheless, the L unit structure appearing at $\lambda = 0.5$ remains even more stable. This trend continues until the angle reaches $\theta = 36.87°$ [22]. At this point, the L unit structure becomes slightly less favorable than the standard K units [Fig. 1(c)].

For the low-angle boundaries near $\theta = 90°$, the lowest-energy structure is again found at $\lambda = 0.5$ [Fig. 1(f)]. This time it consists of the structural units M [Fig. 2(c)]. The structure obtained by the conventional method ($\lambda = 0$) is composed of K units [21] and is less favorable than an array of distorted M units. This confirms again the importance of large atomic displacements during the energy minimization. As the angle decreases, the K units become more stable while the M units less stable. At angles below about 70°, the K unit structure becomes the ground state, whereas the structure composed of M units becomes the least favorable one (the energy peaks at $\lambda = 0.5$) [Fig. 2(e)]. As θ decreases further, the behavior becomes more complex. As the M units come closer together, their interaction apparently becomes attractive. When the angle reaches 53.13° corresponding to the Σ5 (210) GB, the M units form a compact array found in the previous work [14,15], where the units are connected head to tail. This energetically favorable structure creates a local minimum [Fig. 1(d)]. As a result, the Σ5 (210) GB features three energy minima corresponding to three structures composed of the units K, L, and M, respectively.

This analysis demonstrates that λ is a critical parameter controlling the structure and energy of GBs. Variations in λ cause a structural evolution in GBs that can be described in terms of the structural unit model [24] if the misorientation angle is replaced by λ [25]. There is a small number of special structural units that constitute the building blocks of a series of boundaries. There are intervals of angles (respectively, λ values) in which the GB represents an array of two types of structural unit. For the set of GBs studied here, such basic structural units have been identified as K, L, and M.

The function $\gamma(\lambda)$ (Fig. 1) has a thermodynamic meaning similar to the composition dependence of molar Gibbs energy in bulk thermodynamics. The same common tangent construction can be applied to predict the coexistence of different GB phases and their "compositions" λ [26]. When the energy

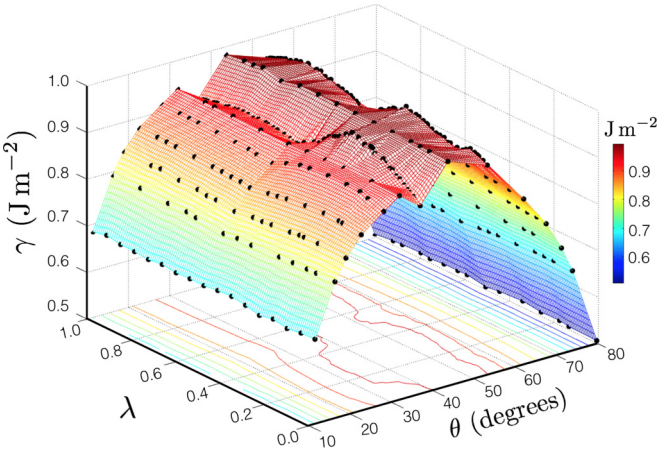

FIG. 3. GB energy as a function of GB density λ and misorientation angle θ for [001] symmetrical tilt boundaries in Cu. The actual simulation points are indicated.

minima are cusps, the common tangent is replaced by a tie line passing through the minimum points [Fig. 1(b)]. Coexistence of GB phases has indeed been observed in the recent atomistic simulations of Σ5 GBs [18]. In both the present work and [14,15], the GB cross sections were kept relatively small. The imposed periodic boundary conditions stabilized the metastable and unstable states of the boundaries, enabling the construction of continuous $\gamma(\lambda)$ plots such as Fig. 1 (see also [22]). As the cross section increases, the boundary will eventually break into single-phase regions separated by a one-dimensional phase boundary [17,18,27]. The common tangent construction does not apply to the frequently used $\gamma(\theta)$ plots since the angle does not constitute an additive variable. Such plots are suitable for predicting GB dissociation transitions [28], but the geometric construction is then different from the common tangent. Nevertheless, it is instructive to plot $\gamma(\lambda,\theta)$, as in Fig. 3. While the energy of low-angle GBs depends primarily on the angle, for high-angle GBs both variables are equally important.

Finally, the foregoing results were obtained for EAM Cu. A few simulations were repeated for Ag modeled with an EAM potential [29]. The results were found to be very similar to those for Cu [22]. This finding is consistent with the previous simulations of the Σ5 GBs for different metals [14] and suggests our results are general for noble FCC metals. For EAM Al [30], however, the general trends were found to be similar but some differences emerged. For example, for the Σ17 (410) GB, the energy minimum at $\lambda = 0.5$ corresponding to the L unit structure [cf. Fig. 1(b)] becomes a maximum [Fig. 4(a)]. The most favorable structure that was found at $\lambda = 0.5$ is an array of highly defected K units, whereas the L unit structure has a slightly higher energy. For the Σ5 (210) GB in Al [Fig. 4(b)], the two minima existing in Cu are replaced by one at $\lambda = 0.5$. The respective GB structure is composed of M units connected head to tail [Fig. 4(c)]. This combination of M units was not seen in Cu. Further tests for other metals are warranted, but it is already evident that the specific GB structures and their relative energies can be material dependent.

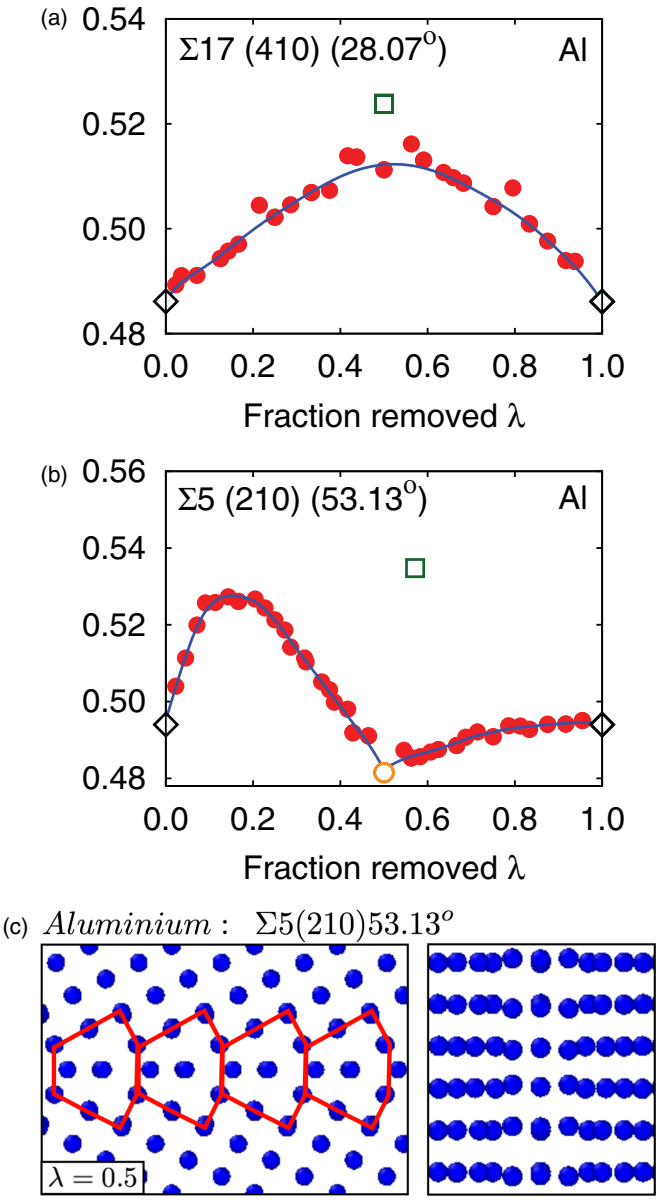

FIG. 4. GB energy (in J m^{-2}) versus GB density λ (fraction of atoms removed) for (a) Σ17 (410) and (b) Σ5 (210) GBs in Al. The square symbols represent metastable structures composed of structural units L. All other points represent stable structures that minimize the GB energy for each density λ. The trend lines are shown as a guide to the eye. The most stable structure of the Σ5 (210) GB is composed of M units as shown in (c).

In summary, we have extended the previous studies of the Σ5 GBs [14–17] to a larger set of [001] symmetrical tilt GBs in order to evaluate the generality of the previous findings. The GB structures and energies have been calculated by allowing variations in the GB density λ and large displacements of atoms during the energy minimization. The results confirm the existence of multiple stable and metastable GB phases over the entire range of misorientation angles. The GBs contain arrays of structural units that follow a systematic behavior that can be rationalized in terms of the structural unit model [24]. Each of the GBs studied here is composed of one or two

types of structural unit, usually separated by a few perfect-lattice units. λ should be included in the descriptions of GBs as an additional parameter capable of predicting GB phases and phase transformations.

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[26] In this work, such predictions can only be made at low temperatures since γ is the GB energy and not free energy.

[27] In fact, we cannot exclude that the mixtures of structural units found in some of the low-angle GBs at $\lambda = 0$ represent early stages of separation in two phases composed of units K and/or L (respectively, M near $\theta = 90^\circ$).

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