Sliding Mechanisms in Aluminum Grain Boundaries

C. Molteni,* Nicola Marzari,† M. C. Payne, and V. Heine
Theory of Condensed Matter, Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 OHE, United Kingdom

(Received 13 March 1997)

We present a detailed investigation, based on ensemble density functional theory simulations, of the microscopic mechanisms that accompany the sliding of grain boundaries in aluminum, a typical ductile metal. We find a variety of sliding behaviors, including coupling to migration, that depend not only on the delocalized character of the metallic bonding, but also on the boundary geometry, the local order, and the presence of defects. While our previous results showed that sliding in germanium is controlled by local stick-slip events involving rebonding of a few atoms, we find that in aluminum larger numbers of atoms act in concert over extended areas, ultimately limited by boundary defects. [S0031-9007(97)03658-2]

PACS numbers: 61.72.Mm, 62.20.Fe

The sliding of a grain boundary is defined to be the relative displacement of the two constituent grains in the direction *parallel* to the boundary interface. It is one of the dominant modes of plastic deformation of polycrystalline materials at high temperatures (above $0.4T_m$, where T_m is the melting point) [1], and it contributes to creep deformation and intergranular fracture. Grain boundary sliding is a complex phenomenon that strongly depends on the nature and structure of the boundaries involved [2]. A different process that can be identified in the dynamics of polycrystals is grain boundary migration, defined as the motion of the interface in the direction *perpendicular* to the boundary plane.

In a recent Letter [3], we addressed the mechanisms characterizing the sliding process at the $\Sigma = 5$ (001) twist grain boundary in germanium, which was chosen as a paradigm for brittle covalent semiconductors. We also evaluated the effects of finite temperature and strain rate [4]. We now contrast these results with the study of the microscopic processes that occur during the sliding of aluminum grains, as a function of their different crystallographic orientations and initial local order. Aluminum is chosen here as a typical example of a ductile metal, with the goal of investigating the role of delocalized metallic bonding in the sliding process.

Ab initio techniques give a reliable and accurate description of the structural properties and of the redistribution of the electrons that accompanies atomic rebonding, and thus provide valuable microscopic insights that complement experimental results and theoretical methods based on more approximate schemes. On the other hand, large scale investigations [5] are precluded, given the current computing capabilities. Therefore, we have studied two simple and qualitatively different grain boundaries: the $\Sigma = 5$ (001) twist grain boundary and the $\Sigma = 11$ $(113)/[1\bar{1}0]$ 50.48° tilt grain boundary. In a twist boundary the rotation axis is orthogonal to the boundary interface, while in a tilt boundary the rotation axis is parallel to the boundary plane.

The $\Sigma = 5$ (001) twist grain boundary is formed by bringing together the (001) faces of two crystals, one of which has been rotated with respect to the other by 36.9°. After such a rotation, the lattices of the two grains share 1 out of 5 lattice sites, defining a new superperiodic lattice, the coincidence site lattice (CSL), whose lattice vectors leave both grains invariant. Once the rotation has been fixed, an additional degree of freedom for the boundary exists, which is a rigid translation of one grain with respect to the other in the boundary plane within the displacement shift complete lattice (DSCL) unit cell. The DSCL unit cell is a subset of the CSL unit cell and contains all nonequivalent translations [6]. We have then studied the $\Sigma = 11$ $(113)/[1\bar{1}0]$ 50.48° tilt grain boundary, whose interface lies in a (113) plane containing the $[1\bar{1}0]$ rotation axis. This boundary is also the subject of a current study about the effects of substitutional gallium impurities in aluminum grain boundaries [7] and of previous experimental and theoretical work [8–10]. The twist and the tilt grain boundaries have been modeled in orthorhombic supercells, containing, respectively, 60 and 44 atoms, divided into 12 and 22 layers in the direction perpendicular to the interface. Because of the periodic boundary conditions, each supercell has to contain two equivalent grain boundaries.

First principles simulations of metals are technically challenging. The discontinuity of the electronic density of states at the Fermi energy dramatically decreases the accuracy of standard Brillouin zone sampling, and it requires a more accurate integration than in the case of semiconductors and insulators. The introduction of a finite temperature for the electronic degrees of freedom greatly improves the convergence with respect to the number of **k** points needed in the Brillouin zone [11], thanks to the "smearing" effect on these discontinuities. The variational functional that is minimized is the finite-temperature electronic free energy and an analytic correction restores the zero-temperature limit for the ground

0031-9007/97/79(5)/869(4)$10.00

state total energy [12]. Even then, the self-consistent Hamiltonian depends critically on the occupation numbers of the Kohn-Sham orbitals, making the minimization toward self-consistency a potentially unstable and ill-conditioned problem. During quasistatic sliding, every step requires a full ionic relaxation, and thus fast and stable convergence of the Hellmann-Feynman forces is of paramount importance. Here we adopt a recently developed scheme (ensemble density functional theory [13,14]) that provides the efficiency necessary for large metallic systems. All the calculations presented are based on the local density approximation for the exchange and correlation potential. An optimized, projector–reduced pseudopotential [15] has been used, where the *s* component only is nonlocal; the plane-wave cutoff required is 80 eV. A sampling of eight **k** points in the full Brillouin zone has been used in all supercells (these are reduced to four **k** points by time-reversal symmetry) together with a Gaussian smearing of 0.5 eV [12]. For these bulk systems the effect of the smearing on the Hellmann-Feynman forces is negligible, and so we did not resort to more elaborate smearing functionals (as in Refs. [13,16]) to recover the zero-temperature limit for the forces. The zero-temperature limit for the energy is derived with the prescriptions of Refs. [11,12].

Sliding has been simulated quasistatically by shifting one grain with respect to the other by a small amount and then relaxing the structure. The atoms in two layers in the middle of each grain have been kept fixed to their relative bulk positions during the whole simulation, while all the other atoms were allowed to relax (all configurations were relaxed to better than 1–2 meV/cell). The simulation cells were initially relaxed in the direction orthogonal to the interfaces in order to reproduce the volume expansion that usually accompanies the presence of a boundary. However, the cells were not relaxed further during the sliding simulation.

Two different translational states have been studied for the $\Sigma = 5$ (001) twist boundary, corresponding to the translation vectors (0,0) and $(-1/20, 1/20)$ (in CSL units) in the (001) plane. The first one corresponds, once relaxed, to the lowest energy structure, and the second one is the same translational state that was studied in the case of germanium [3]. The chosen sliding direction coincides with the CSL cell face diagonal.

Figure 1 shows the evolution of the energy during the sliding of the $\Sigma = 5(001)$ Al twist boundary with the initial translational state set to (0,0). The energy profile is smooth and periodic. This contrasts with our previous results for germanium, where we found that sliding takes place through a series of recurrent stick–slip events, mediated by a rebonding mechanism which affects, in turn, local groups of a few atoms at the boundary interface. The signature of those rebonding events were sudden jumps in the energy profile at the onset of the slipping [3] that are missing here. Also, the maximum energy variation during the sliding is much smaller in the aluminum case than in the germanium one. The periodicity of the energy profile reproduces the periodicity of the DSCL unit cell. The energy minima occur when the atomic "bumps" of the grain on one side of the boundary fit nicely into the "hollows" between the atoms on the other side, while the maxima occur when they are on top of one another. The smooth and periodic energy profile is a clear indication that no remarkable and sudden rearrangements of atoms occur during sliding; all the atoms at the interface "flow" in a continuous and concerted way, and the original structure of the boundary is periodically recovered. In contrast, in germanium, migration of disorder from the boundary interface due to plastic deformation prevents the system from recovering even the CSL superperiodicity [3]. If, starting from a state of minimum energy, we now slide the grain in the reverse direction, we get another smooth energy path that overlaps exactly with that obtained for the forward sliding. This did not happen in Ge, where after backward sliding simulations we found a number of different grain boundary structures for given relative grain displacements, and where thermal fluctuations make the system jump from one structure to another [3,4]. We also show in Fig. 1 the results for the sliding of the twist boundary with translational state set to $(-1/20, 1/20)$ (dashed line in Fig. 1; the simulation has been performed up to 20% of the CSL cell diagonal and then extrapolated). Even if the initial energy is now higher, the energy profile remains smooth and periodic, and the relative variation in the energy is smaller; the atoms at the boundary that belong to the different grains "slalom" around each other in the (001) plane, thus avoiding any high energy configuration.

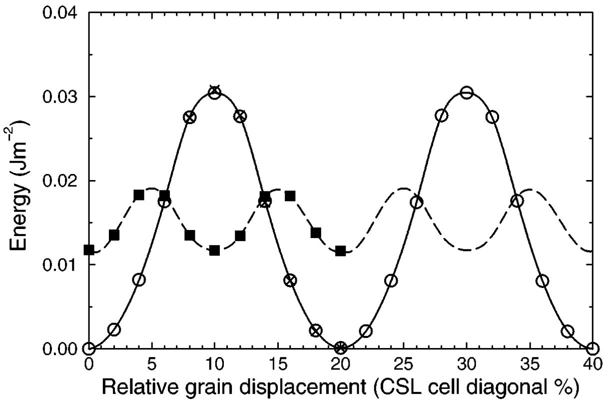

FIG. 1. The variation of the grain boundary energy during the sliding of the $\Sigma = 5$ (001) twist boundary in aluminum. Circles and solid line: translational state (0,0), forward sliding; crosses: translational state (0,0), backward sliding; squares and dashed line: translational state $(-1/20, 1/20)$, forward sliding.

The sudden rebonding in germanium and the cooperative movement of atoms in aluminum are clear examples, in realistic systems, respectively, of the *dynamical locking* and *atomistic locking* mechanisms, which have been proposed to clarify the microscopic origin of friction [17].

To probe the metallic behavior further, we have performed another sliding simulation for the twist boundary with translational state (0,0), after a vacancy has been created by removing one atom in one of the planes adjacent to the boundary. The energy profile during sliding is shown in Fig. 2. There are significant differences from the simulation without a vacancy (Fig. 1, solid line). The initial state no longer corresponds to a minimum, which is reached only after a displacement of 10% along the CSL cell face diagonal, in correspondence to the maximum that we found in the simulation without the vacancy. What happens in the presence of a vacancy on one side is that one atom from the other side pops (halfway) into it, leaving two half-vacancies arranged symmetrically across the boundary. Simultaneously, the atoms in the plane where the vacancy was originally situated rearrange themselves in an almost perfect fcc lattice, taking advantage of the position of the atom now shared by the two planes at the interface. Through this process of sharing atoms and defects, the boundary softens the effects of the vacancy and approaches a more ordered structure.

The important role played by geometry becomes clear in the case of the tilt boundary. The structure of the $\Sigma = 11$ tilt boundary [Fig. 3(a)] is characterized by close-packed $[110]$ rows of atoms arranged in a "herring bone" structure. The sliding direction chosen in this case is $[33\bar{2}]$ [i.e., parallel to the dashed line of Fig. 3(a)]. In Fig. 4 we show the energy variation of the tilt boundary while sliding along a whole CSL cell vector. The energy profile is quite different from the twist boundary: there is no longer any periodicity and three large energy jumps can be observed. By analyzing in detail the atomic configurations, we find that after each jump the boundary recovers its original form, but the interface has migrated in the direction perpendicular to the boundary. At the different jumps the boundary migrates first downward, as shown in Fig. 3, then upward by twice the initial amount, and finally downward again to return to its original position. Substantial atomic rearrangements are involved in the migration process. In the different panels of Fig. 3 we show, counterclockwise, the atomic configurations in the initial state [3(a), 0%] and before [3(b), 32%)], during [3(c), 34%)] and after [3(d), 36%] the first migration event. Just before the energy jump the deformation is localized in the triangular units of atoms at the edge of the boundary, such as the one highlighted in Fig. 3(b). Each unit undergoes a sudden rotation as shown in Fig. 3(c). After that, unstable $[110]$ rows of atoms are left, which have some segment missing. Order and stability are recovered by the movement of activated clusters composed by [110] segments [as the one highlighted in Fig. 3(c) by a thick line], from the "white" $(1\bar{1}0)$ atomic plane to the "black" one, and vice versa, which complete the unstable rows. This is the mechanism that induces the boundary migration, as it becomes apparent by comparing the position of the boundary plane at the beginning [Fig. 3(a)] and after the energy jump [Fig. 3(d)]. These results are consistent with recent experimental evidence showing that boundary migration in Al bicrystals with $\langle 110\rangle$ tilt axis occurs by jumps of close–packed groups of atoms [18], and agree with classical molecular dynamics simulations at finite temperature [19] that showed coupling of sliding with migration. We have also performed a sliding simulation in the backward direction, starting from a point immediately following the first migration event. The results (in Fig. 4) show a different energy path from that obtained in the forward direction. The jump at 4% corresponds to a disordered metastable configuration, and the system requires further sliding to finally recover its ordered structure.

Several points stand out from these results. First, there is a considerable variety of sliding behavior in aluminum grain boundaries, from the smooth "flowing" of one grain over the other in the twist boundary, to the sudden energy

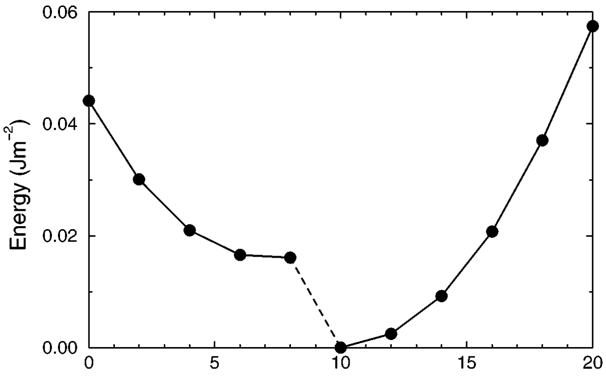

FIG. 2. The variation of the grain boundary energy during the sliding at the $\Sigma = 5$ (001) twist boundary in aluminum, with a vacancy in the boundary.

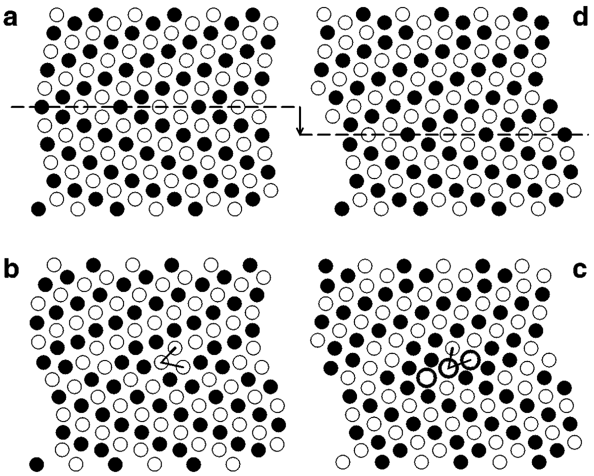

FIG. 3. The mechanism of sliding-induced migration relative to the first energy jump for the $\Sigma = 11$ (113) tilt grain boundary. White and black atoms belong to different $(1\bar{1}0)$ planes. The atomic configuration at the beginning [(a) 0%] and before [(b) 32%], during [(c) 34%] and after [(d) 36%] the first migration event are shown.

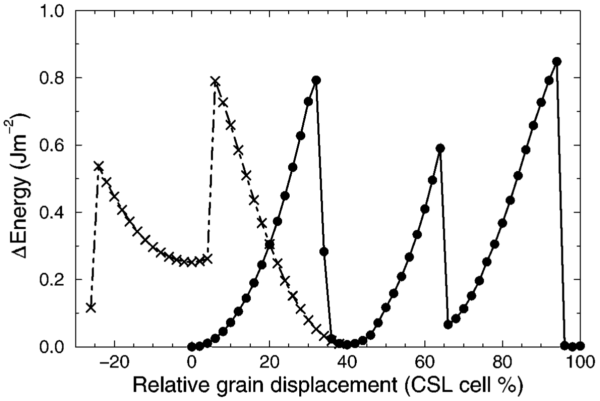

FIG. 4. The variation of the grain boundary energy during the sliding at the $\Sigma = 11$ (113) tilt boundary in aluminum. Circles and solid line: forward sliding; crosses and dot-dashed line: backward sliding.

jumps associated with the migration in the tilt boundary. Second, and more significant, is that in each case the boundary structure recovers its original ideal form, for the relative displacement of the grains that geometrically allows it. We can thus observe a high degree of self–healing in the concerted movement of whole atomic layers, which we suggest is characteristic of the metallic bonding in aluminum. It clearly contrasts with the local rebonding and progressive accumulation of disorder that was seen in the sliding calculations of germanium. Third, the variety of detailed behaviors in our simulations may yet result in a rather similar response under realistic sliding conditions. Our simulations have been performed in the quasistatic limit of slowly increasing strain, but under increasing stress the system would "jump" when the applied stress reaches the maximum slope of the energy curve; it would jump to the next segment with positive gradient. This applies just as much to the smooth behavior in Fig. 1 as to the more discontinuous behaviors in Figs. 2 and 4. For example, the regions of downward curvature in Fig. 1 are inherently unstable. Fourth, in our calculations it is the whole boundary in the unit cell that always recovers. In any real sliding rearrangement, the interface area involved would be larger than the area in our unit cells; the area involved in any such event would be determined by more distant defects in or near the boundary. This again is very different from germanium, where sliding is controlled by the local stick-slip events involving sudden rebonding around just a few atoms at the boundary interface.

Our calculations have been performed on the Hitachi S3600 at Hitachi Europe's Maidenhead (UK) headquarters and on the Hitachi S3600 at the University of Cambridge High Performance Computing Facility. The work was assisted by the HCM (European Communities) Network *"Ab initio (from electronic structure) calculation of complex processes in materials,"* Contract ERBCHRXCT930369 and by HCM Contracts ERBCHBICT920192 (N. M.) and ERBCHBICT941123 (C. M.).

---

*Present address: Max-Plank-Institut für Festkörperforschung, Heisenbergstrasse 1, Stuttgart, Germany.

†Present address: Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey.

[1] A. P. Sutton and R. W. Balluffi, *Interfaces in Crystalline Materials* (Oxford University Press, 1995), p. 745.

[2] H. Kokawa, T. Watanabe, and S. Karashima, Philos. Mag. A **44**, 1239 (1981).

[3] C. Molteni, G. P. Francis, M. C. Payne, and V. Heine, Phys. Rev. Lett. **76**, 1284 (1996).

[4] C. Molteni, G. P. Francis, M. C. Payne, and V. Heine,in *Materials Theory, Simulations, and Parallel Algorithms*, edited by E. Kaxiras, J. D. Joannopoulos, P. Vashishta, and R. K. Kalia, MRS Symposia Proceedings No. 408 (Materials Research Society, Pittsburgh, 1996), pp. 277-282.

[5] M. R. Sorensen, K. W. Jacobsen, and P. Stoltze, Phys. Rev. B **53**, 2101 (1996).

[6] M. W. Finnis and M. Rühle, in *Materials Science and Technology*, edited by R. W. Cahn, P. Haasen, and E. J. Kramer (VCH, Weinheim, Germany, 1993), Vol. 1, pp. 533-605.

[7] D. I. Thomson, N. Marzari, V. Heine, and M. W. Finnis (to be published).

[8] A. F. Wright and S. R. Atlas, Phys. Rev. B **50**, 15 248 (1994).

[9] M. J. Mills, M. S. Daw, G. J. Thomas, and F. Cosandey, Ultramicroscopy **40**, 247 (1992).

[10] A. P. Sutton and V. Vitek, Philos. Trans. R. Soc. London A **309**, 1 (1983).

[11] M. J. Gillan, J. Phys. Cond. Matter **1**, 689 (1989).

[12] A. De Vita, Ph.D. Thesis, University of Keele (1992); A. De Vita and M. J. Gillan, J. Phys. Cond. Matter **3**, 6225 (1991).

[13] N. Marzari, Ph.D. Thesis, University of Cambridge (1996).

[14] N. Marzari, D. Vanderbilt, and M. C. Payne, Phys. Rev. Lett. (to be published).

[15] J. S. Lin, A. Qteish, M. C. Payne, and V. Heine, Phys. Rev. B **47**, 4174 (1993); M.-H. Lee, Ph.D. Thesis, University of Cambridge (1995).

[16] M. Methfessel and A. T. Paxton, Phys. Rev. B **40**, 3616 (1989).

[17] M. Hirano and K. Shinjo, Phys. Rev. B **41**, 11 837 (1990).

[18] W. Lojkowski, D. A. Molotov, G. Gottstein, and L. S. Shvindlerman, Mater. Sci. Forum **207–209**, 537 (1996).

[19] G. H. Bishop, Jr., R. J. Harrison, T. Kwok, and S. Yip, J. Appl. Phys. B **53**, 5596 (1982); L. Q. Chen and G. Kalonji, Philos. Mag. A **66**, 11 (1992).