

Dislocations in Complex Materials

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Deformation of metals and alloys by dislocations gliding between well-separated slip planes is a well-understood process, but most crystal structures do not possess such simple geometric arrangements. Examples are the Laves phases, the most common class of intermetallic compounds and exist with ordered cubic, hexagonal, and rhombohedral structures. These compounds are usually brittle at low temperatures, and transformation from one structure to another is slow. On the basis of geometric and energetic considerations, a dislocation-based mechanism consisting of two shears in different directions on adjacent atomic planes has been used to explain both deformation and phase transformations in this class of materials. We report direct observations made by Z-contrast atomic resolution microscopy of stacking faults and dislocation cores in the Laves phase Cr₂Hf. These results show that this complex dislocation scheme does indeed operate in this material. Knowledge gained of the dislocation core structure will enable improved understanding of deformation mechanisms and phase transformation kinetics in this and other complex structures.

Plastic deformation in a crystal occurs by the processes of slip and twinning. These processes are accomplished by the motion of dislocations whose character is closely related to the structure of the crystal. When these dislocations produce displacements that are less than a unit lattice translation vector in the crystal, they are called partial dislocations and they bound stacking faults. The motion of a partial dislocation can also produce certain types of phase transformations. The partial dislocation associated with the sliding of close-packed planes of atoms over each other during slip, twinning, or shear transformations in face-centered cubic (fcc) metals is the Shockley partial (1). In slip, a pair of partial dislocations bounding a stacking fault moves on the slip plane in response to an applied stress to produce plastic deformation. In twinning, a Shockley dislocation sweeps every slip plane, whereas when a Shockley dislocation sweeps alternate slip planes it converts an fcc structure into a hexagonal close-packed (hcp) structure (1). Observations on Laves phases (2) show that analogous mechanisms could operate in these more complex structures (3–7). Laves phases, compounds with the AB₂ stoichiometry where the large A atoms and the small B atoms have an ideal radius ratio of 1.225, are the most commonly occurring intermetallic compounds. Cubic, hexagonal, and rhombohedral structures have been imaged with the use of high-resolution electron microscopy (2–4, 8), and phase transformation mecha-

nisms based on dislocation motion have been proposed (2, 3, 5, 9).

On an atomic level, however, the shearing mechanisms in the Laves phases cannot be identical to those in simple metals because Laves phases are ordered structures with four different atomic planes parallel to the slip plane (10). A ball-and-stick model of the hexagonal C14 structure (the Laves phase with the shortest period along the basal plane normal) when viewed along a close-packed direction and with basal planes horizontal is illustrated (Fig. 1A). The alloy Cr₂Hf is used as the example. The structure, like all Laves phases, consists of alternating layers of single small (Cr) atom layers [in the form of a kagome (basket weave) net (11)] and three-layer stacks (Hf-Cr-Hf) that contain two low-density planes of large (Hf) atoms separated by a low-density plane of small (Cr) atoms. The great

number of possible Laves phases derives from the fact that there are two forms of these three-layer stacks that we designate as *t* and *t'*, which are rotated 180° in the layer plane to each other. In C14, these two arrangements of the three-layer stacks alternate (Fig. 1A) and the stacking sequence of single basal planes (*s*) and triple basal planes (*t*) is *s t s t'...*. All other Laves phases have longer stacking sequences than C14, and thus, during a transformation, some *t* layers must be changed to *t'* and vice versa; this may be accomplished by passage of the transforming Shockley dislocations, much like in the fcc structure.

An ideal technique for viewing the atomic structures in Laves phases is Z-contrast imaging in a high-resolution scanning transmission electron microscope (STEM) (12). With its sub-angstrom resolution (13), the positions of atom columns are revealed, and, because the atomic number [*Z*] values for Cr [24] and Hf [72] are very different, the light and heavy atoms may be distinguished. Figure 1B is a micrograph of C14 Cr₂Hf viewed along <11-20> in the same orientation as Fig. 1A.

It is known from conventional TEM observations that the slip planes for the Shockley dislocations in the C14 structure are the basal planes (4, 6), although atomic details remain unresolved. Slip, twinning, and shear transformations are believed, on geometric and energetic grounds, to occur inside the three-layer stack (rather than between the single Cr layer and the three-layer stack) by a mechanism called synchroshear (3, 4, 14) that consists of two shears in different directions on adjacent atomic planes. The dislocation description of synchroshear requires the passage of two Shockley dislocations through the three-layer stack, one gliding between the lower atom level and the center with one Burgers vector and the other gliding between the center and

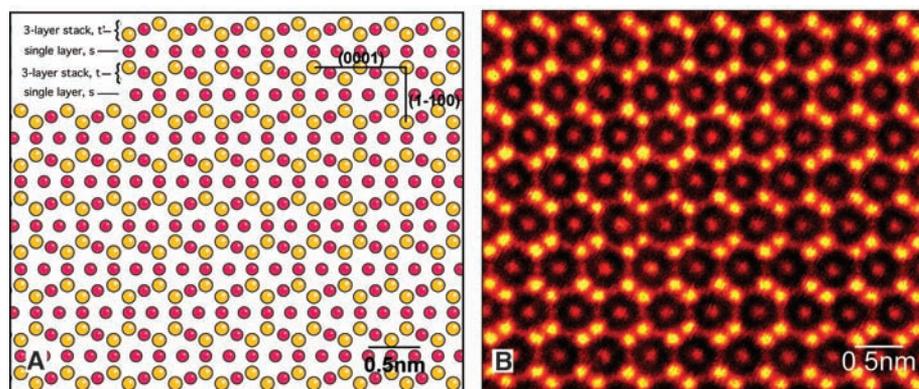


Fig. 1. (A) A schematic of the <11-20> projection of the C14 hexagonal structure showing the three-layer stack, *t*, and the 180°-rotated three-layer stack, *t'*, separated by the single layer, *s*. The large atoms (Hf) are in yellow and the small atoms (Cr) are in red. (B) A Z-contrast image of the <11-20> projection of the C14 variant of the Cr₂Hf Laves phase. The bright features (yellow) are Hf columns, and the less-intense features (red) are Cr columns.

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the upper level with a different Burgers vector. Figure 2 illustrates the sliding of two rigid blocks, whose faces terminate at the upper and lower Hf layers in the three-layer stack, past each other in response to an applied stress, with an intermediate Cr layer between the two blocks. If it is assumed that the bottom block is stationary, then in response to an applied shear stress the Hf atom in the top block moves in the plane of the paper in the direction shown by the bold black arrow to the position of the Cr atom labeled X . For this to happen, however, the Cr atom in the layer between the two rigid blocks needs to get out of the way, and it does so by moving out of the plane of the paper in the direction illustrated by the blue arrow to position X' , which was previously occupied by a Hf atom. These two coordinated movements can be described by the motion of two Shockley partial dislocations that for energetic reasons are closely coupled. For this reason, in the literature, the pair of Shockley dislocations has been treated as a single synchro-Shockley partial dislocation with its core spread on two adjacent planes (9). The effect of this synchronous translation of the two layers is to convert a t -type three-layer stack into a t' -type three-layer stack, thereby producing a stacking fault. In Fig. 2, the synchro-Shockley partial dislocation is an edge dislocation.

The Z-contrast image in Fig. 3 shows a stacking fault in Cr_2Hf that comes in from the right about halfway up the image (indicated by the arrow) and terminates in the center of the micrograph at the core of a synchro-Shockley dislocation. The construction of a Burgers circuit using the Hf atoms in the triple layer shows closure failure. In the core of the dislocation, a t layer (on the left) changes to a t' layer (on the right). Relative to the lower Hf atoms, the upper Hf atoms may move either to the right by $b/2$ (where b is the Burgers vector), signifying a 30° character for the dislocation, or to the left by b (as in Fig. 2), which would imply a pure edge dislocation (90° character). The closure failure of the Burgers circuit in Fig. 3 is $0.15 \text{ nm} = b/2$, implying that this dislocation has a 30° character. As may be seen in the figure, the core of the synchro-Shockley dislocation is compact, on the order of 0.5 nm in width and about 0.1 nm high.

A Laves phase transformation is illustrated (Fig. 4) where a strip of the cubic C15 Laves phase has formed in the C14 structure by repeated synchroshear. The C15 structure results by synchroshearing the C14 structure on alternate three-layer stacks; this is analogous to ordinary Shockley partial dislocations transforming a hcp structure to a fcc structure, by gliding on alternate close-packed planes. The stacking sequence in Fig.

Fig. 2. A schematic illustration of the motion of a synchro-Shockley partial dislocation. (A) The initial arrangement of the big (yellow) and small (red) atoms in the three-layer stack, shown with the same orientation as in Fig. 1. The kagome layers above and below the three-layer stack are represented by the rigid blocks, with the bottom block considered stationary and the top block responding to a shear stress by moving to the left. This representation is the motion of a synchro-Shockley partial dislocation with pure edge character. (B) The atomic arrangement after synchroshear. (C) The synchroshear process is illustrated where all the Hf atoms in the top layer of the three-layer stack move in the plane of the paper to the left by a distance b as shown by the bold black arrow, while the Cr atoms move out of the plane of the paper in the middle Cr layer (at 60° to the $-X$ direction) as shown by the blue arrow, producing the final configuration shown in (B).

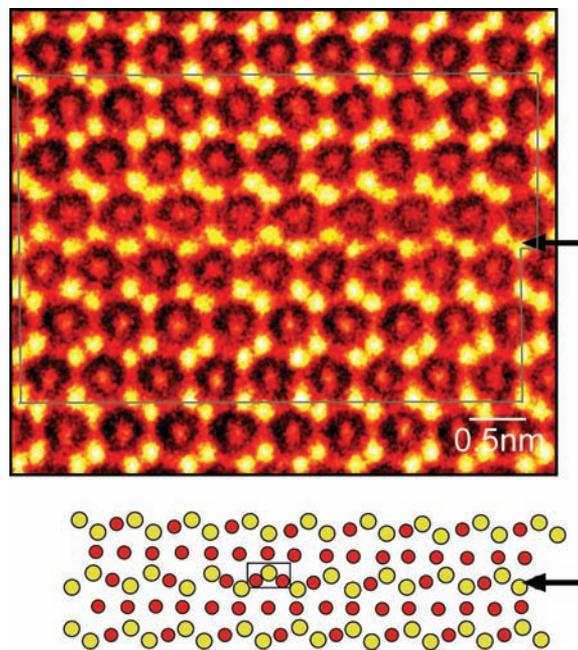
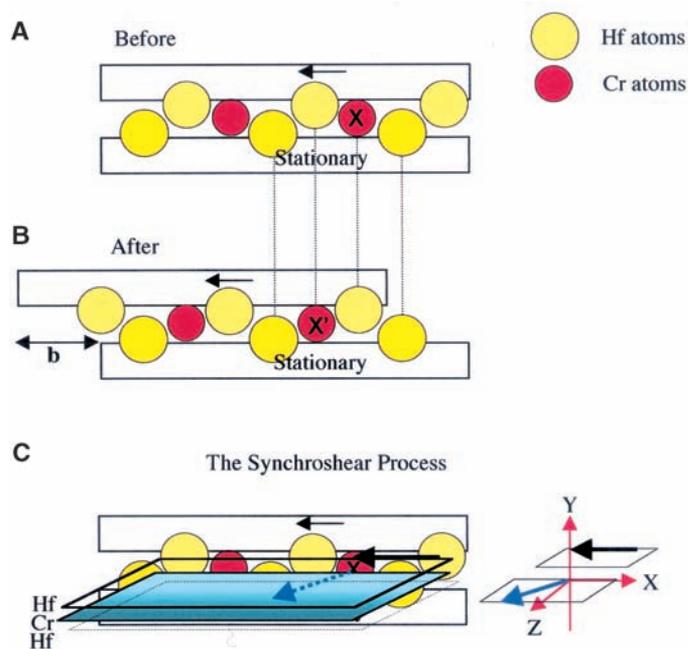


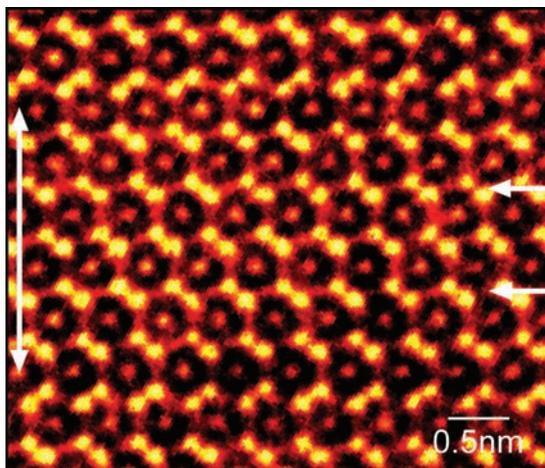
Fig. 3. A Z-contrast image of the $\langle 11\text{-}20 \rangle$ projection of a synchro-Shockley dislocation bounding a stacking fault in the C14 variant of the Cr_2Hf Laves phase. The fault comes in from the right (indicated by the arrows) and terminates at the dislocation core in the center of the image. The synchro-Shockley partial dislocation in this instance has a 30° character. The Burgers circuit made from Hf atoms failed to close. The schematic below the image, shows a proposed core structure. The indicated Cr columns in the small box in the schematic are included on the basis of the relatively large separation of the adjacent Hf columns.

4 is $\dots st'st'st'st'st'st'st'st' \dots$ instead of the unsheared $\dots st'st'st'st'st'st'st'st' \dots$.

The concept of synchroshear described above was originally introduced by Kronberg (14) to explain the deformation behavior of $\alpha\text{-Al}_2\text{O}_3$, although recent results (15–17) have confirmed that that is not the case. The Z contrast images of faults and dislocations presented here, however, demonstrate unambiguously that synchroshear [originally proposed by Allen, Delavignette, and Amelinckx

(4) for Laves phases] actually occurs in the Cr_2Hf Laves phase. Because all Laves phases are constructed from the same building blocks, there is good reason to believe that synchroshear occurs in the others as well. The motion of a single type of defect, a synchro-Shockley partial dislocation, is thought to be responsible for shear phase transformations as well as three mechanisms of deformation: slip, twinning, and stress-induced transformations. In this case, the

Fig. 4. A Z-contrast image of the $\langle 11\text{-}20 \rangle$ projection of a faulted region of the C14 variant of the Cr_2Hf Laves phase. This region (between the double arrow on the left) has the C15 cubic structure and could be formed by stacking faults in the C14 structure (indicated by the two short arrows on the right) that result from the passage of two synchro-Shockley dislocations.



kinetics of all four of these processes is controlled by the mobility of synchro-Shockley dislocations. Much understanding could be gained from atomistic simulations of the motion of this type of dislocation. Understanding the structure of the dislocation core and its influence on the ability of Laves phases to deform is central to designing alloys with optimized mechanical properties.

In addition, these concepts can be extended to other crystal structures where the slip planes have more than one spacing.

References and Notes

1. J. P. Hirth, J. Lothe, *Theory of Dislocations* (McGraw-Hill Series in Materials Science and Engineering, McGraw-Hill, New York, 1968).
2. F. Laves, H. Witte, *Metallwirtsch. Metallwiss. Metalltech.* **15**, 840 (1936).
3. J. D. Livingston, *Phys. Status Solidi A* **131**, 415 (1992).

4. C. W. Allen, P. Delavignette, S. Amelinckx, *Phys. Status Solidi A* **9**, 237 (1972).
5. Y. Liu, J. D. Livingston, S. M. Allen, *Metall. Mater. Trans. A* **23**, 3303 (1992).
6. K. S. Kumar, D. B. Miracle, *Intermetallics* **2**, 257 (1994).
7. Y. Liu, J. D. Livingston, S. M. Allen, *Met. Mat. Trans. A* **26**, 1441 (1995).
8. Y. Kitano, Y. Komura, H. Kajiwara, E. Watanabe, *Acta Crystallogr. A* **36**, 16 (1980).
9. P. M. Hazledine, P. Pirouz, *Scripta Metall. Mater.* **28**, 1277 (1993).
10. C. S. Barrett, T. B. Massalski, *Structure of Metals: Crystallographic Methods, Principles, and Data*, vol. 35 of International Series on Materials Science and Technology (Pergamon, Oxford, ed. 3, 1987).
11. K. Husimi, *Prog. Theor. Phys.* **5**, 177 (1950).
12. P. D. Nellist, S. J. Pennycook, *Phys. Rev. Lett.* **81**, 4156 (1998).
13. P. D. Nellist *et al.*, *Science* **305**, 1741 (2004).
14. M. L. Kronberg, *Acta Metall.* **5**, 507 (1957).
15. J. B. Bilde-Sørensen *et al.*, *Acta Mater.* **44**, 2145 (1996).
16. P. Pirouz *et al.*, *Acta Mater.* **44**, 2153 (1996).
17. T. Geipel *et al.*, *Acta Mater.* **44**, 2165 (1996).
18. This research was sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy at Oak Ridge National Laboratory, under contract no. DE-AC05-00OR22725. S.K. acknowledges the support from the NSF-sponsored Materials Research Science and Engineering Center on Micro- and Nano-Mechanics of Materials at Brown University (contract no. DMR-9632524), and P.H. acknowledges support from U.S. Air Force Research Laboratory contract no. F33615-01-5214 with UES, Incorporated.

4 October 2004; accepted 22 December 2004
10.1126/science.1105962

End States in One-Dimensional Atom Chains

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End states—the zero-dimensional analogs of the two-dimensional states that occur at a crystal surface—were observed at the ends of one-dimensional atom chains that were self-assembled by depositing gold on the vicinal Si(553) surface. Scanning tunneling spectroscopy measurements of the differential conductance along the chains revealed quantized states in isolated segments with differentiated states forming over end atoms. A comparison to a tight-binding model demonstrated how the formation of electronic end states transforms the density of states and the energy levels within the chains.

The break in translational symmetry at a crystal surface creates surface electronic properties that differ from those in the bulk crystal and localize at the surface layer (1, 2). The formation of surface states and resonances is a general property of solid surfaces, and the delicate interplay between the surface electronic structure and the atomic positions often leads to complex surface reconstructions in which the atoms in the top layer rearrange to minimize the surface energy.

In analogy to the surface of a bulk solid, we expect to observe similar physics in re-

duced dimensions at the edge or end of a nanostructure. Similar to a two-dimensional (2D) surface state formed at the surface of a bulk sample, an edge or step in a 2D structure breaks the 2D symmetry and can form a 1D edge state (3). Likewise, a finite 1D chain of atoms should exhibit zero-dimensional end states at its termini. An end state requires two criteria: (i) The wave function of the state must be localized to the end atoms, and (ii) it must decay exponentially into the chain (2). Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) enable the spatial mapping of differentiated electronic structure within a nanostructure. Thus, the local density of states (DOS) can be mapped in real space, providing direct access to electronic edge or end effects. Furthermore, questions of the spatial variation of the wave function

away from the end of a 1D structure can be answered directly.

So far, definitive spectroscopic evidence for the existence of end states in 1D structures has been lacking. Research has instead focused on the quantum mechanics of electrons confined to reduced dimensions within the surface layer. Electrons are partially reflected by step edges on metal surfaces and can exhibit refraction at the interface between two media (4–7). Electrons also exhibit quantum confinement when trapped within atomic “corrals” assembled by STM (8). At the 1D limit, finite atomic chains of Au on NiAl(110) (9, 10) and Cu on Cu(111) (11) constructed by STM exhibit quantized electronic states, and the observation of spectroscopic enhancement at or near the ends of these chains suggested the possibility of the formation of end states. However, the weakness of these effects in the systems studied, compounded with the possibility of experimental artifacts (10, 11), precluded unequivocal assignment. In the Si(553)-Au atom chains described below, end states are unequivocally manifested through a marked transfer of the DOS from the empty to the filled states above the end atoms. Furthermore, we found that quantized states within finite chains can no longer be described by a particle-in-a-box model, which has been successful in the previous studies (9–11), but rather require a model that includes end states.

To fabricate 1D chains, we used the self-assembly of chain reconstructions on stepped

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