

## Brief Reports

---

*Brief Reports are accounts of completed research which, while meeting the usual Physical Review standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

---

### *Ab initio* study of a grain boundary in gold

M. Needels,\* A. M. Rappe, P. D. Bristowe, and J. D. Joannopoulos

Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 2 June 1992)

The total energy of a grain boundary in a transition metal is calculated in an *ab initio* manner. Such calculations are now feasible using a plane-wave basis set provided that an optimally convergent pseudopotential is used. The investigation focuses on resolving two competing atomic models for the  $\Sigma=5$  [001] twist boundary in gold. It is found that the model of lower energy, which involves small atomic displacements, corresponds to a structure determined both experimentally, using quantitative x-ray-diffraction techniques, and theoretically, using the embedded-atom method.

It is now well established that *ab initio* molecular dynamics can be used effectively to study the bulk and defect properties of *sp*-bonded materials.<sup>1-6</sup> The principal reason for this success lies in the ability to describe these materials accurately using “soft” pseudopotentials and a limited plane-wave basis set. Clearly, it would be desirable to extend this technique to other materials while still retaining the advantages of pseudopotentials and plane waves. Transition metals are of interest because of their many metallurgical applications but, as is well known, they are difficult to describe using conventional pseudopotential theory. In particular, they require an extremely large number of plane waves for total-energy convergence because of the presence of *d* orbitals which are strongly localized but make an important contribution to the bonding.<sup>7</sup> Recently, however, an approach to constructing *ab initio* pseudopotentials has been proposed which minimizes these problems. In this approach, the freedom in constructing the pseudopotential is explicitly used to optimize the total-energy convergence of the solid.<sup>8</sup> Specifically, by optimizing the atomic kinetic energy and requiring the potential to be continuous, a soft pseudopotential can be constructed which is more rapidly convergent than a conventional pseudopotential. This has been demonstrated for the case of copper in which the lattice constant, cohesive energy, and bulk modulus of that metal have been computed efficiently and accurately.<sup>8</sup>

In the present paper, we apply the optimized pseudopotential approach in an *ab initio* molecular-dynamics calculation of a grain boundary in the transition metal, gold. Grain boundaries are important interfacial defects in metals and control many of the physical properties of the material. Our objective is twofold. First, we wish to show that large complex transition-metal systems can be investigated using plane-wave basis sets and, second, that an energetically preferred model for a specific twist grain

boundary can be determined and compared to previous experimental and theoretical studies. The results represent the first *ab initio* investigation of a grain boundary in a transition metal.

The computational methodology is as follows. We first tried using a preconditioned conjugate gradient algorithm.<sup>9</sup> However, this approach failed miserably since the total energy could not be converged to within 10 eV because it began to oscillate randomly. Therefore, we used a steepest-descent equation-of-motion algorithm.<sup>10</sup> We used an “optimized” nonlocal, norm-conserving, scalar-relativistic pseudopotential of the Kleinman-Bylander form.<sup>11</sup> We constructed the pseudopotential by solving the Dirac equation for the all-electron problem to obtain spin-up and spin-down pseudopotentials for the *s*, *p*, and *d* angular momentum wave functions.<sup>12</sup> The potentials are obtained by pseudizing the valence major components<sup>13,14</sup> and minimizing the kinetic energy beyond a cutoff<sup>6,15</sup> of 30 Ry. The scalar-relativistic potentials for each angular momentum are obtained by averaging the spin-up and spin-down potentials by their respective multiplicities.<sup>14</sup> These “averaged” potentials had the same level of convergence as the spin-dependent pseudopotentials.

The pseudopotential was tested in a number of ways. First, total-energy differences between the atomic ground-state configuration and several excited-state configurations were calculated for the all-electron atom using the Dirac and the pseudoatom using the Schrödinger equation. These energy differences agreed to within 1% in all cases. Second, the bulk properties of gold were calculated and are displayed in Table I. The lattice constant and bulk modulus agree well with experimental and other theoretical results.<sup>16</sup> The cohesive energy exceeds the experimental value, as expected for any local-density-approximation (LDA) calculation. Howev-

TABLE I. Comparison of the bulk properties of gold as calculated in the present work to experimental values (kinetic-energy cutoff = 30 Ry; number of  $k$  points is 110).

|                           | Experiment | Present | % Difference |
|---------------------------|------------|---------|--------------|
| Lattice constant (Å)      | 4.079      | 4.086   | +0.2         |
| Bulk modulus (Mbar)       | 1.732      | 1.95    | +12.6        |
| Cohesive energy (eV/atom) | 3.81       | 4.11    | +7.9         |

er, our result agrees well with other theoretical values.

The other aspects of the calculation were also tested. The supercell contained two grain boundaries to maintain periodicity in the direction normal to the boundary plane. Each grain consisted of six (002) planes of atoms with five atoms per plane. The separation of the grain boundaries was tested, using the embedded-atom method,<sup>17</sup> by comparing grain-boundary energies between the 12-layer supercell and an 80-layer cell. The energy difference was small. This can be understood in terms of the small intrinsic dislocation spacing of the boundary we are considering. Within elasticity theory, the dislocation strain field decays on a length scale approximately equal to this spacing. Convergence with respect to basis-set size was checked by increasing the cutoff from 30 Ry, which we used for the grain-boundary calculation (18 000 plane waves), to 50 Ry. The total energy of a one-atom unit cell of crystalline gold changed by less than 0.02 eV, indicating that the calculation was very well converged with respect to the basis-set size. Brillouin-zone averaging for the grain boundary was obtained by summing over three special  $k$  points in the irreducible  $\frac{1}{16}$  of the Brillouin zone. The possibility of partially filled and/or degenerate states occurring near the Fermi level was treated using a Gaussian spreading scheme<sup>4</sup> with a width of 0.05 eV. *A priori*, we estimated the accuracy of this  $k$  point set to be somewhere between that using 28 and 60  $k$  points in the bulk irreducible Brillouin zone. To compute the energy of the grain boundaries, we used a reference total energy of bulk gold obtained by using an identical  $k$  point sampling in a 10-atom unit cell of bulk gold, which gives 24  $k$  points in the irreducible  $\frac{1}{8}$  of the Brillouin zone, and an energy of  $-890.212$  eV/atom. As can be seen from Table II, with this level of  $k$  point sampling, the absolute total energy is converged to a few meV/atom.

The grain boundary of interest is the  $\Sigma=5$  ( $36.9^\circ$ ) [001] twist boundary in gold where  $\Sigma$  is the inverse density of coincidence sites.<sup>18</sup> The perfect geometrical

TABLE II. Bulk  $k$ -point convergence test (kinetic-energy cutoff = 30 Ry).

| No. of $k$ points in irreducible Brillouin zone | Energy/atom (eV) |
|---|------------------|
| 19  | -890.201         |
| 28  | -890.192         |
| 44  | -890.211         |
| 60  | -890.215         |
| 85  | -890.212         |
| 110   | -890.215         |

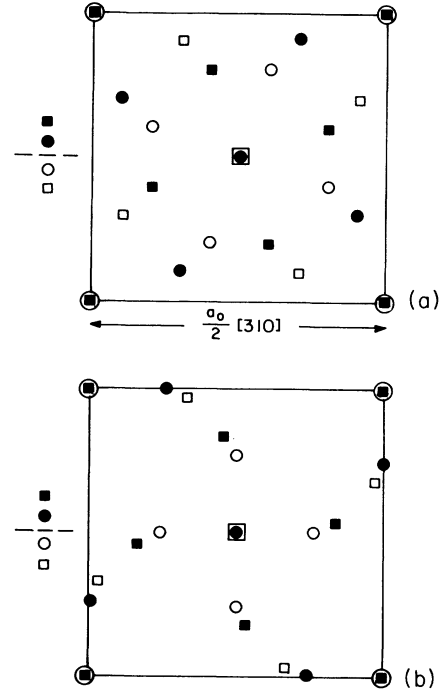


FIG. 1. Two models for the  $\Sigma=5$  ( $36.9^\circ$ ) [001] twist boundary in gold: (a) MBB model; (b) FS model. Structures are shown in projection along [001] with two planes on either side of the boundary. Stacking sequence of planes is indicated by the vertical column of open and closed symbols. Note that the MBB model is indistinguishable from the perfect unrelaxed geometry on the scale of this figure.

configuration for this boundary is formed by rotating one fcc crystal with respect to another by  $36.9^\circ$  about [001]. This boundary has been studied extensively using x-ray-diffraction techniques<sup>19,20</sup> and classical atomistic simulation methods.<sup>20,21</sup> The x-ray investigations have independently determined two distinct atomic models for the boundary which are shown in projection in Fig. 1. They are labeled the FS (Fitzsimmons-Sass) model and the MBB (Majid-Bristowe-Balluffi) model. Note that the MBB model is almost indistinguishable from the perfect geometrical configuration on the scale of this figure. Both models can be characterized by rotational-like relaxations around a symmetry axis passing through the center of the unit cell, but they differ in the magnitude of these relaxations. The maximum relaxation exhibited by the FS model (relative to the unrelaxed geometrical configuration) is about  $0.7$  Å, which is approximately seven times as large as the corresponding relaxation in

TABLE III. Computed twist boundary energies using the *ab initio* method and the EAM.

|                      |           | eV/Å <sup>2</sup> | ergs/cm <sup>2</sup> |
|----------------------|-----------|-------------------|----------------------|
| Present work         | MBB model | 0.031             | 510                  |
|                      | FS model  | 0.483             | 7731                 |
| Embedded-atom method | MBB model | 0.032             | 522                  |
|                      | FS model  | 0.236             | 3786                 |

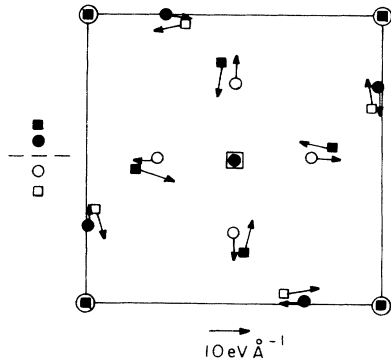


FIG. 2. Forces acting on atoms in the FS model determined from the pseudopotential calculation. Only forces parallel to the boundary are shown and are of order  $10 \text{ eV}/\text{\AA}$ . Forces normal to the boundary are of order  $1 \text{ eV}/\text{\AA}$ .

the MBB model. It is not immediately obvious which model should have the lower energy. However, it is noted that the FS model has 80 bond lengths that are distorted by more than 5% whereas the MBB model has only 12.

The computed energies for the two twist boundary models are shown in Table III. It is clear that the MBB model is energetically preferred over the FS model by more than a factor of 10. The forces on the atoms were also computed and found to be two orders of magnitude higher in the FS model compared to the MBB model. For the MBB model, the atomic forces in the plane of the boundary were all less than  $0.1 \text{ eV}/\text{\AA}$  and those normal to the boundary were less than  $0.26 \text{ eV}/\text{\AA}$ . This level of residual force is considered quite satisfactory for this kind of calculation and therefore the structure is thought to be relatively stable. On the other hand, the forces acting on the atoms in the FS model are so large that the structure must be unstable. In Fig. 2 we illustrate the direction and magnitude of these forces as vectors projected onto the model structure.

The energy of both model structures has been computed previously using semiempirical methods.<sup>20,22</sup> For comparison with the present calculations we present in Table III the results of the embedded-atom-method (EAM) calculations.<sup>20</sup> It is seen that these calculations also yield a much higher energy for the FS model (by a factor of about 7) compared to the MBB model. In addition, the magnitude of the MBB model energy is remarkably close to that computed using the *ab initio* method. However, the FS model energy computed using the EAM is smaller by a factor of 2 compared to the corresponding energy determined from the *ab initio* approach. This difference can be explained by the highly distorted nature of the FS model which results in large deviations in charge density. These deviations are accurately treated in the *ab initio* calculation but are poorly described using the EAM. Nevertheless, the vector map showing the EAM forces on the atoms in the FS model is very similar (at least in terms of the directions of the vectors) to that

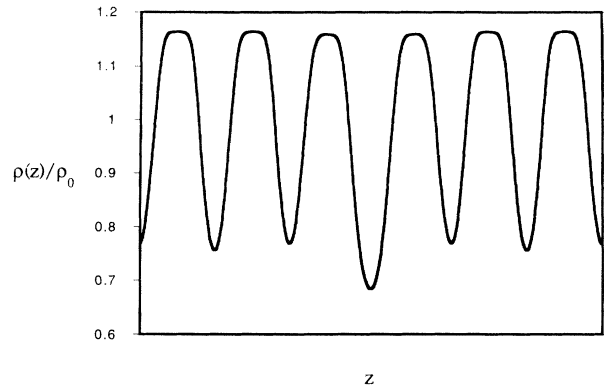


FIG. 3. Planar charge density, normalized to the average charge density in gold, as a function of distance from the grain boundary. The grain boundary is in the middle of the plot.

shown in Fig. 2. Since the FS model is known to relax back into the MBB model using the EAM, it is reasonable to assume that such relaxations would also occur in the *ab initio* calculation if the atoms were free to move.

In Fig. 3, we plot the planar charge density as a function of distance from the grain boundary. The charge density for half our unit cell is shown. The six atomic layers can be clearly identified as the six flat peaks. The grain boundary is at the middle of the plot and corresponds to the minimum in charge density. This minimum is broader than the other interlayer regions, as expected, because the interlayer distance is increased at the grain boundary to prevent the atoms in the two grains from being too close together. However, the minimum is also much deeper, being two-thirds the average charge density in the unit cell. Since there is a lack of fine structure in the charge density at the grain boundary, there are apparently no localized electronic states associated with it.

In conclusion, we have successfully performed an *ab initio* molecular-dynamics calculation of the total energy of a grain boundary in the transition metal, gold. The calculation was made possible through the application of an optimized pseudopotential and a plane-wave basis set. In addition, we have confirmed the low energy and stability of the MBB model for the  $\Sigma=5$  twist boundary in agreement with one of the previous studies.<sup>20</sup> We envision further applications of this technique to the study of other defects in transition-metal systems.

This work was supported in part by the U.S. Air Force Office of Scientific Research Contract No. 87-0098 and by the Department of Energy Grant No. DE-FG02-87ER-45310. A.M.R. acknowledges the support of the Joint Services Electronics Program. We wish to thank Dr. Sverre Froyen for the use of his relativistic atomic programs. Supercomputer time was provided by the National Science Foundation at the San Diego Supercomputer Center. Additional support was provided by the MIT Supercomputer Facility.

\*Present address: AT&T Bell Laboratories, Murray Hill, NJ 07974.

- <sup>1</sup>M. C. Payne, P. D. Bristowe, and J. D. Joannopoulos, *Phys. Rev. Lett.* **58**, 1348 (1987).
- <sup>2</sup>M. Needels, M. C. Payne, and J. D. Joannopoulos, *Phys. Rev. Lett.* **58**, 1765 (1987).
- <sup>3</sup>D. C. Allan and M. P. Teter, *Phys. Rev. Lett.* **59**, 1136 (1987).
- <sup>4</sup>G. W. Fernando, G-X Qian, M. Weinert, and J. W. Davenport, *Phys. Rev. B* **40**, 7985 (1989).
- <sup>5</sup>C. Woodward, B. I. Min, R. Benedek, and J. Garner, *Phys. Rev. B* **39**, 4853 (1989).
- <sup>6</sup>R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).
- <sup>7</sup>D. C. Allan and M. P. Teter, *J. Am. Cer. Soc.* **73**, 3247 (1990).
- <sup>8</sup>A. M. Rappe, K. M. Rabe, E. Kaxiras, and J. D. Joannopoulos, *Phys. Rev. B* **41**, 1227 (1990).
- <sup>9</sup>M. P. Teter, M. C. Payne, and D. C. Allan, *Phys. Rev. B* **40**, 12255 (1989).
- <sup>10</sup>M. C. Payne, J. D. Joannopoulos, D. C. Allan, M. P. Teter, and D. H. Vanderbilt, *Phys. Rev. Lett.* **56**, 2656 (1986).
- <sup>11</sup>L. Kleinman and D. M. Bylander, *Phys. Rev. Lett.* **48**, 1425 (1982).
- <sup>12</sup>The core radii are 2.25 bohrs for all three angular momentum states; the reference configuration is  $\{\text{Xe}\}5d^{10}6s^{0.5}6p^{0.5}$ .
- <sup>13</sup>D. R. Hamann, M. Schlüter, and C. Chiang, *Phys. Rev. Lett.* **43**, 1491 (1979).
- <sup>14</sup>G. B. Bachelet and M. Schlüter, *Phys. Rev. B* **25**, 2103 (1982).
- <sup>15</sup>A. M. Rappe and J. D. Joannopoulos (unpublished).
- <sup>16</sup>N. Takeuchi, C. T. Chan, and K. M. Ho, *Phys. Rev. B* **40**, 1565 (1989).
- <sup>17</sup>M. S. Daw and M. I. Baskes, *Phys. Rev. B* **29**, 6443 (1984).
- <sup>18</sup>W. Bollmann, *Crystal Defects and Crystalline Interfaces* (Springer, New York, 1970).
- <sup>19</sup>M. R. Fitzsimmons and S. L. Sass, *Acta Metall.* **36**, 3101 (1988).
- <sup>20</sup>I. Majid, P. D. Bristowe, and R. W. Balluffi, *Phys. Rev. B* **40**, 2779 (1989).
- <sup>21</sup>P. D. Bristowe and A. G. Crocker, *Philos. Mag. A* **38**, 487 (1978).
- <sup>22</sup>J. Budai, P. D. Bristowe, and S. L. Sass, *Acta Metall.* **31**, 699 (1983).