Tight-binding study of stacking fault energies and the Rice criterion of ductility in the fcc metals

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We have used the Naval Research Laboratory (NRL) tight-binding (TB) method to calculate the generalized stacking fault energy and the Rice ductility criterion in the fcc metals Al, Cu, Rh, Pd, Ag, Ir, Pt, Au, and Pb. The method works well for all classes of metals, i.e., simple metals, noble metals, and transition metals. We compared our results with full potential linear-muffin-tin orbital and embedded atom method (EAM) calculations, as well as experiment, and found good agreement. This is impressive, since the NRL-TB approach only fits to first-principles full-potential linearized augmented plane-wave equations of state and band structures for cubic systems. Comparable accuracy with EAM potentials can be achieved only by fitting to the stacking fault energy.

I. INTRODUCTION

The relationship between electronic structure and mechanical properties of materials has received considerable attention, with emphasis on the development of atomistic models of fracture and deformation.[1] The interfacial energetics under different modes of displacement, e.g., shear and cleavage, are often key factors in determining the mechanical response of a material to applied stress. The stability of stacking faults on the slip planes of a crystal is intimately connected to the mobility of dislocations on these planes. On the other hand, the ease for cleavage fracture is related to the ideal cleavage stress and the ideal cleavage energy (which is equal to the total surface energy γ_s of the two cleaved surface planes). Using a Peierls type of analysis, Rice and coworkers[2-4] developed a simple criterion for determining the intrinsic ductile versus brittle behavior of materials. Rice proposed that a simple rule to measure the brittle versus ductile behavior of materials is the ratio of two planar fault energies, γ_s/γ_{us}, which determines the competition between dislocation emission from a crack tip and crack cleavage. Dislocation nucleation is characterized by the unstable stacking fault energy γ_{us}, which corresponds to the lowest energy barrier encountered in sliding one half of a crystal relative to another along a slip plane.

In close-packed structures, both stable and unstable stacking faults are produced by the relative translation of two parts of a crystal through a fault vector $\vec{f}$, which is a rational fraction of a lattice vector. The fault is introduced by cutting a perfect crystal block along the fault plane and shifting the upper part with respect to the lower part by the vector $\vec{f}$. The energy surface obtained as a function of the fault vector $\vec{f}$ is called the generalized stacking fault (GSF) energy surface.[5] Stable intrinsic stacking faults are local energy minima on the GSF surface. For the (111) slip plane in fcc systems, the stable stacking fault configuration corresponds to a slip of $a/\sqrt{6}$ in the $\langle 121 \rangle$ direction resulting in the stacking $ABC|BCABC$; γ_{us} is the lowest energy barrier that needs to

be crossed for the slip from the ideal configuration to the intrinsic stacking fault in the $\langle 121 \rangle$ direction. Experimentally observed edge dislocations in fcc metals split and form an intrinsic stacking fault ribbon bounded by the two Shockley partials. The intrinsic stacking fault energy, γ_{is}, determines the equilibrium separation between the two partials.[6] In contrast to the rest of the GSF surface, the energies of the stable stacking fault configurations can be experimentally measured.

The GSF surface plays an important role in proposed models for the brittle-ductile transition[7,8] and they can also be used for calibration of model potentials for large-scale simulations and as input to quasi-continuum models.[9] At present, the GSF energies can be calculated using empirical potentials, such as the embedded-atom method (EAM) or electronic structure methods.[10,11] The empirical potentials are expedient but they are constructed by fitting physical properties obtained from experimental measurements or *ab initio* calculations. Moreover, these potentials may provide a good description of the energetics of a system when the density distribution of atoms in the system is close to equilibrium. When atoms move far away from equilibrium (such as in the case of stress) or when defects are present, these potentials meet their limitations. For example, the current formulation of the EAM method underestimates γ_{is} in Al compared to the corresponding *ab initio* value, thus yielding a dissociation for the edge dislocation in disagreement both with experiment and the *ab initio* calculations.[10] An improved EAM value for γ_{is} can be obtained by including this energy in the EAM database.[10,11] The more accurate first-principles electronic structure calculations, on the other hand, are computationally expensive. We would therefore like to find a method that is close in accuracy to first-principles methods, but computationally more efficient.

The NRL tight-binding method[12-16] meets this criterion for a large number of systems. The purpose of this work is to employ the tight-binding (TB) total-energy method to calculate the GSF energies for fcc metals and to compare them both with results of *ab initio* calculations based on the full-potential linear-muffin-tin-orbital (FLMTO) method[17,18] and experiment, when available. The fcc metals studied have a

wide range of unstable and stable stacking fault energy values. For example, Al and Cu have similar γ_{us} but quite different γ_{is}, while Ir (a brittle system) has very large γ_{us} and γ_{is}. We have also calculated the ratio γ_s/γ_{us} across the series. Overall, the good agreement found between the TB results and those of the *ab initio* calculations indicates that the TB method can be used for the study of fault energies accurately and expediently, and puts the TB method on firmer basis for future investigations of defects and fracture.

II. STACKING FAULT CALCULATIONS

We model the $\langle 121 \rangle$ slip on a (111) slip plane of an fcc solid by constructing a supercell which consists of nine close-packed (111) planes of atoms. One atom in each plane is part of the basis of the supercell. The primitive vectors of the supercell take the form

$$\mathbf{a}_1 = \frac{1}{2}a\hat{y} + \frac{1}{2}a\hat{z}$$

$$\mathbf{a}_2 = \frac{1}{2}a\hat{x} + \frac{1}{2}a\hat{z} \qquad (1)$$

$$\mathbf{a}_3 = \left(3 + \frac{q}{6}\right)a\hat{x} + \left(3 + \frac{q}{6}\right)a\hat{y} - \left(3 - \frac{q}{3}\right)a\hat{z} ,$$

where q represents the stacking fault variable, and represents a displacement of the atoms in the boundary layer along the fault vector $\vec{f}$ in the $\langle 11\bar{2} \rangle$ direction. When $q = 0$ the periodic crystal is a perfect fcc system. When $q = 1$, the atoms at the interface are in an hcp ordering, that is, the stacking at the interface is $ABCBCA$ rather than $ABCABC$.

Total energies were calculated using the NRL tight-binding (TB) total energy method.[12–16,19] In this method we simultaneously fit the energy bands and the total energy from first-principles full potential linearized augmented plane-wave (LAPW) calculations[20,21] to a nonorthogonal *spd* TB Hamiltonian containing density-dependent on-site terms and distance-dependent hopping and overlap parameters. The parameters for the transition and noble metals are determined by requiring that the TB method reproduce the first-principles total energies and electronic structures of fcc, and bcc as a function of volume. For Pb (Ref. 16) we add the simple cubic structure to the database, and for Al (Ref. 14) we included data from the simple cubic, diamond, and hcp structures. This method has been shown to give reliable structural behavior, elastic constants, phonon frequencies,[12] vacancy formation energies, and surface energies for the fcc metals, even for structures not included in the original database. We use the previously published parameters[13,16] for most elements. We have developed new parameters for Cu and Au by including the simple cubic structure in the fit along with the fcc and bcc structures, and by fitting to a wider range of lattice constants.[22] The parameters for Al differ from the published parameters[14] in that we have refit the parameters so that the d state t_{2g} and e_g on-site terms are identical, eliminating orientation effects seen in the older parameters.

As in all band structure total energy methods, the calculated total energy is determined by summing the eigenvalues
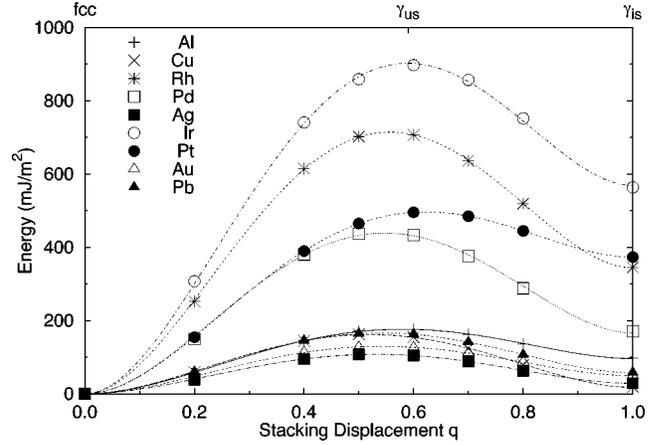

FIG. 1. Stacking fault energy as a function of the parameter q in Eq. (1) for the elemental *fcc* metals, determined by the NRL tight-binding method (Refs. 12–16 and 19). The labels γ_{us} and γ_{is} indicate positions of the unstable and intrinsic stacking faults, respectively, while *fcc* indicates the position of the ground state structure.

over the first Brillouin zone of the lattice. We perform this calculation using a regular, uniformly spaced, and symmetrized k-point mesh, including the origin. The tight-binding method is computationally very efficient, so to insure convergence we have used a large number of k points, 4730 in the irreducible part of the Brillouin zone of Eq. (1). This is equivalent to using a mesh of 1469 k points in the irreducible Brillouin zone of the fcc lattice. The total energy was calculated by weighting the eigenvalues with a Fermi distribution at a temperature of 5 mRy and then extrapolating to zero temperature.[23,24]

In Fig. 1 we show the stacking fault energies for all of our calculations as a function of the stacking fault variable q in Eq. (1). We note that the behavior of the stacking fault energies is quite reasonable. That is, the stacking fault energies for Ir are much larger than the corresponding energies for Au. We did not allow for relaxation in these systems, except for the case of the unstable stacking fault energy of Au and Ir. In this case, the relaxation reduced the unstable stacking fault energy by about 30% and 40%, respectively.

We then compared the results of the tight-binding parametrization to first-principles FLMTO calculations for Al, Ag, and Ir, using the same stacking fault geometry. In the FLMTO method no shape approximation is made to the potential and the charge density.[17,18] The basis set, charge density, and potential are expanded in cubic harmonics inside non-overlapping muffin-tin spheres and in Fourier series in the interstitial region. Spherical harmonic expansions were carried through $l_{max} = 8$ for the bases. Spin-orbit coupling was included self consistently. The volume in the muffin-tin spheres radius was kept constant for all deformations to make the basis set as consistent as possible in calculating energies for different deformations. Exchange and correlation were treated in the local-density approximation using the Ceperly and Alder[25] exchange-correlation functional as parametrized by Perdew and Zunger.[26] The calculations are performed at the theoretically determined in-plane lattice constant to eliminate the externally imposed stress associated with a nonequilibrium lattice constant. Multiple sets of energy parameters and tail parameters were used. The lower
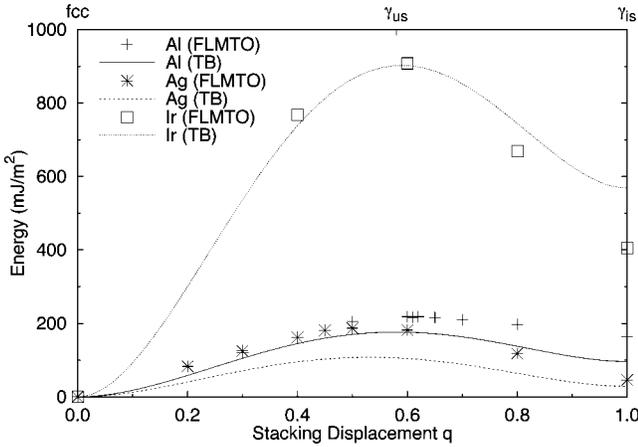
FIG. 2. Stacking fault energy as a function of the parameter q of Eq. (1), as determined by the NRL tight-binding method (Refs. 12–16 and 19) and from first-principles FLMTO calculations (Refs. 17 and 18). Tight-binding results are represented by the fitted curves from Fig. 1, and the first-principles results are marked by points.

energy is appropriate for semicore states and the higher for valence states. For the reciprocal space integration we used a uniform k-point grid of (15,15,3) divisions along the reciprocal lattice directions according to the special point method.[27]

Figure 2 compares the first-principles and tight-binding calculations. We see that the tight-binding results are qualitatively correct, that is, the stacking fault energies of the elements are ordered correctly. The results for Ir are particularly accurate, especially near the unstable stacking fault position. In addition, because of the reduced basis-set size and the elimination of the self-consistency cycle, the tight-binding method is approximately 1,000 times faster than FLMTO for comparable systems. Thus the tight-binding method can handle much larger systems than a first-principles calculation, with nearly the same accuracy.

The intrinsic ($q=1$ in equation 1) stacking fault energies γ_{is} are given in Table I, where they are compared to values derived from experimental observations of dislocation structure and isotropic elasticity theory.[28,29] Again, the results are qualitatively correct.

TABLE I. Intrinsic stacking fault energies γ_{is} (in mJ/m^2) of the nonmagnetic fcc transition metals, calculated from our tight-binding parameters, first-principles FLMTO (Refs. 17 and 18), and values derived from experiment. Unless otherwise noted, the experimental values are from Murr (Ref. 28).

Element	Tight-Binding	FLMTO	Experiment
Al	96	164	166
Cu	18		45 (Ref. 28), 78 (Ref. 29)
Rh	344		
Pd	166		
Ag	29	46	16
Ir	569	405	300
Pt	373		
Au	50		
Pb	58		

TABLE II. The unrelaxed (111) surface energy γ_s, unstable stacking fault energy γ_{us}, and the ductility parameter D from Eq. (2). The values of γ_s were obtained from previous calculations using our tight-binding parameters (Refs. 13 and 14). The γ_{us} were taken from the maximum of a polynomial fit to the points in Fig. 1. γ_s and γ_{us} are in units of mJ/m^2.

Element	γ_s (Refs. 13 and 14)	γ_{us}	D
Al	870	176	1.50
Cu	1730	162	3.24
Rh	2460	714	1.04
Pd	1570	439	1.08
Ag	1140	108	3.20
Ir	2590	902	0.87
Pt	2510	497	1.53
Au	1480	129	3.48
Pb	888	166	1.59

III. INTRINSIC DUCTILITY

Rice[3] has shown that under ''Mode I'' loading a metal is intrinsically ductile if the parameter

$$D = 0.3 \frac{\gamma_s}{\gamma_{us}} > 1 \ , \tag{2}$$

where γ_s is the surface energy of a freshly cleaved surface, and γ_{us} is the unstable stacking fault energy. This is a reasonable criterion. If the surface energy is small compared to the unstable stacking fault energy then under applied stress the metal will tend to form surfaces, i.e., crack, rather than shear so as to nucleate dislocations.

For our purposes we can take the unstable stacking fault energy γ_{us} to be the peak of the curve in Fig. 1. For surface energies, we take the unrelaxed (111) surface energies previously computed from our tight-binding parameters.[13,14] The results are shown in Table II. Since we have neglected relaxation of both the surface and the stacking fault the results can be only qualitatively correct, but the results are consistent with our expectations. The three noble metals, Cu, Ag, and Au, all have $D>3$. Of these, Au, the most ductile metal, has the largest ductility parameter. These are followed by Pt, Pb, and Al, all with $D \approx 1.5$. These metals are considerably less ductile than the noble metals, but substantially more ductile than the remaining metals, Rh, Pd, and Ir, which all have $D \approx 1$. These results indicate that the tight-binding Hamiltonian can be used to quickly estimate the ductility parameter of a metal.

IV. CONCLUSION

We have shown that the NRL tight-binding method is very successful in predicting both intrinsic and unstable stacking fault energies of the fcc metals on the right-hand side of the periodic table. This occurs without the introduction of any stacking fault configurations into the tight-binding database. Indeed, excepting Aluminum, the tight-binding parameters are determined by fitting to a first-principles database containing only electronic structure and total energy information for cubic systems. In contrast, the successful EAM schemes[10,11] must include γ_{is} in the database in order to correctly predict the stacking fault energies.

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