PHYSICAL REVIEW B VOLUME 46, NUMBER 21 1 DECEMBER 1992-I

Ab initio calculation of stacking-fault energies in noble metals

S. Schweizer, C. Elsässer, K. Hummler, and M. Fähnle
Institut für Physik, Max-Planck-Institut für Metallforschung, Heisenbergstrasse 1, 7000 Stuttgart 80, Federal Republic of Germany

(Received 17 April 1992; revised manuscript received 21 August 1992)

The defect energies for the intrinsic and extrinsic stacking faults and for the twin fault in Cu, Ag, and Au were calculated by supercell calculations based on the *ab initio* mixed-basis pseudopotential method and the linear-muffin-tin-orbital method in atomic-sphere approximation. The calculations correctly reproduced the experimentally observed trend, i.e., very low fault energies for all noble metals, being lower by a factor of about 2 for Ag than for Cu and Au. The physical mechanism (s-d hybridization) is discussed and illustrated by charge-density plots.

In the 1950's Seeger[1,2] pointed out that the energy of intrinsic stacking faults, γ_i, plays the role of a "hidden" parameter for the plastic deformation of fcc metals. In these materials the dislocations which mediate the plastic deformation are dissociated into partial (incomplete) dislocations[3,4] separated by a stacking-fault band, the width of the band being controlled by the stacking-fault energy γ_i. The activation energies for the processes occurring during plastic deformation depend strongly on the width of the extended dislocations and hence on γ_i, and therefore the paramount importance of the stacking-fault energy for the plastic deformation is obvious. The accurate experimental determination of γ_i, however, remains a highly delicate problem.[5] Because in many cases the uncertainties arise[5] from the application of less than adequate theoretical relationships between experimental measurables and γ_i, accurate *ab initio* calculations of the stacking-fault energies are of invaluable importance. It is the scope of this paper to demonstrate as an example for the case of noble metals that for an accurate determination of stacking-fault energies by *ab initio* electron theory one should not use a shape approximation for the self-consistent potential but should perform a full-potential calculation.

The uncertainties are especially large for the noble metals Cu, Ag, and Au where the stacking-fault energies are considerably lower than for instance in Ni, Pt, Ir, or Rh. Gallagher[5] critically reviewed all the results for γ_i up to 1970, yielding the following scatter in the experimental data: Cu(24–163 mJ/m^2), Ag(14–65 mJ/m^2), Au(10–61 mJ/m^2). By forming weighted mean values, he recommended the stacking-fault energies of 55, 21.7, and 50 mJ/m^2 for Cu, Ag, and Au, i.e., $\gamma_i^{\mathrm{Cu}} \approx \gamma_i^{\mathrm{Au}} \approx 2\gamma_i^{\mathrm{Ag}}$. This trend can be understood qualitatively by assuming that the stacking-fault energy is determined by covalent bonds between the hexagonal planes produced by s-d hybridization.[2] In Ag the d density of states at the Fermi level is smaller by a factor of 0.6 than in Cu or Au,[6] and hence the s-d hybridization is expected to be smaller. The question remains whether the experimentally observed trend can be reproduced also quantitatively by electron theory.

Early calculations on the basis of empirical interatomic model potentials[7–12] yielded stacking-fault energies depending critically upon the form of the interatomic potentials, sometimes even negative stacking-fault energies for noble metals.[8] Similarly, an effective medium theory,[13] including many-atom interactions, which is based on an *ab initio* calculation within the framework of the density-functional theory, gives γ_i values which depend critically on the assumed cutoff radius for the interatomic interactions, yielding stacking-fault energies between -17 and $+79$ mJ/m^2 for Cu. Considerably more successful were *ab initio* calculations within the framework of the fully self-consistent layer-Korringa-Kohn-Rostoker (LKKR) technique for a variety of metals,[14–17] including the noble metals, and within the framework of the linear-muffin-tin-orbital (LMTO) method for Al and Pd.[18] Both types of calculations are based on shape approximations for the potential, namely the muffin-tin geometry[14–16] or the atomic-sphere approximation.[17,18] It is well known that these potential approximations produce rather accurate results for ideal close-packed structures, but may fail badly[19,20] for the calculation of energies for defects which have a substantially larger free volume than the bulk material. Because the stacking faults in fcc metals remain close packed, the potential approximations may yield rather accurate quantitative results for γ_i, as demonstrated by the above discussed *ab initio* calculations.[14–18] To test for the absolute accuracy, comparison with full-potential calculations for some materials, especially for those with rather lower stacking-fault energies, is desirable.

We therefore have used for the whole series of noble metals an *ab initio* pseudopotential approach, within the local density approximation, which represents (apart from the frozen-core approximation) a full-potential method and which was already successfully applied for the calculation of the stacking-fault energy in silicon.[21,22] In a second step, we then performed the calculations within the LMTO theory in atomic-sphere approximation and compared the results of the two calculations.

In our pseudopotential calculations the atomic cores are represented by nonlocal, norm-conserving, scalar-relativistic ionic pseudopotentials constructed by the scheme of Vanderbilt.[23] These pseudopotentials are for the case of noble metals much softer than those according to Hamann, Schlüter, and Chiang,[24] especially for copper. The electronic wave functions and charge densities are represented by a mixed basis [25] of plane waves and five localized numerical d functions per atom, centered at the atomic sites. Total energies are calculated using a momentum space formalism.[26] The stacking-fault energy is defined by the difference of the total energies of a crystal with a stacking fault (calculated by a supercell method) and a perfect crystal. There are three cutoff parameters for the mixed basis method, the cutoff energy E_c for the plane waves, the cutoff $q_{\max}$ in Fourier space for the pseudopotential and the cutoff $c_{\max}$ in Fourier space for the representation of the charge density. Because of the small stacking fault energies γ_i, the convergence of γ_i with respect to these parameters had to be tested very carefully, and the parameters used in the final calculations are represented in Table I. It should be noted that the single total energies of the perfect crystal and of the crystal with a stacking fault themselves were not yet totally converged for these parameters, especially for Cu.

TABLE I. Cutoff parameters used for the calculations (see text).

	E_c (Ry)	$q_{\max}$ (1/a.u.)	$c_{\max}$ (1/a.u.)
Cu	16.5	15.9	28.0
Ag	13.5	11.9	16.0
Au	16.5	11.9	13.0

We considered the ideal fcc structure of the noble metals, an intrinsic stacking fault (γ_i), an extrinsic stacking fault (γ_e), and a twin fault (γ_t) by periodically repeated supercells according to the following stacking pattern of the hexagonal planes in $\langle 111 \rangle$ direction.

Ideal fcc crystal: 3-atom supercell, *ABC* .

Intrinsic stacking fault: 5-atom supercell, *AB ABC*; 8-atom supercell; *AB ABC ABC*;

11-atom supercell *AB ABC ABC ABC* .

Extrinsic stacking fault: 7-atom supercell, *ABCB ABC* .

Twin fault: 4-atom supercell, *AB AC*; 6-atom supercell, *ACB ABC* .

Our supercells consist of one atom out of each plane, respectively. Because these planes are hexagonal, we arrive at tubelike supercells with hexagonal axes. The point symmetry of the supercells is hexagonal for the twin fault and trigonal for the ideal crystal and the stacking faults. It should be noted explicitly that we did not use the primitive fcc supercell for the ideal crystal, because this supercell has a totally different convergence behavior with respect to the number of k points in the irreducible Brillouin zone. By using hexagonal axes both for the ideal and the defective crystal we obtained a much faster convergence for the fault energies. We thereby considered an equivalent number of k points in the irreducible Brillouin zones when comparing the ideal crystal and the faulted crystal. For instance, calculating the stacking-fault energy from a 5-atom supercell, we use in the ideal 3-atom supercell a number of k points which is a factor of $\frac{5}{3}$ larger than the number of k points in the 5-atom supercell. All calculations were performed for the theoretical lattice constant of the ideal crystal. The results for the fault energies are shown in Table II for supercells without structural relaxation. The empirical relation $\gamma_i \approx \gamma_e \approx 2\gamma_t$ is well fulfilled for the large supercells, and there is a remarkable agreement between our stacking fault energies and the recommended values of Gallagher.[5]

Comparing our results with those of the LKKR method in muffin-tin approximation[16] ($\gamma_i \approx 70$, 33, and 44 mJ/m^2 for Cu, Ag, and Au, respectively) shows that the potential approximation indeed yields the correct order of stacking-fault energies for the noble metals. Neverthe-

TABLE II. Results for the fault energies γ (in mJ/m^2) for Cu, Ag, and Au for the pseudopotential theory (PS) and the linear-muffin-tin-orbital method (LMTO). n_A and n_K denote the number of atoms in the supercell and the number of irreducible k points, respectively.

		Method	n_A	n_K	γ
	Cu	PS	5	75	46
	Ag	PS	5	108	23
	Au	PS	5	75	41
	Cu	PS	8	75	50
	Ag	PS	8	108	18
Intrinsic	Au	PS	8	75	45
	Cu	LMTO	8	133	58
	Ag	LMTO	8	133	43
	Au	LMTO	8	133	61
	Cu	LMTO	11	96	51
	Ag	LMTO	11	96	38
	Au	LMTO	11	96	52
	Cu	PS	4	75	31
	Ag	PS	4	108	9
	Au	PS	4	75	16
Extrinsic	Cu	PS	7	75	44
	Ag	PS	7	108	18
	Au	PS	7	75	41
	Cu	PS	6	75	29
Twin	Ag	PS	6	108	12
	Au	PS	6	75	21

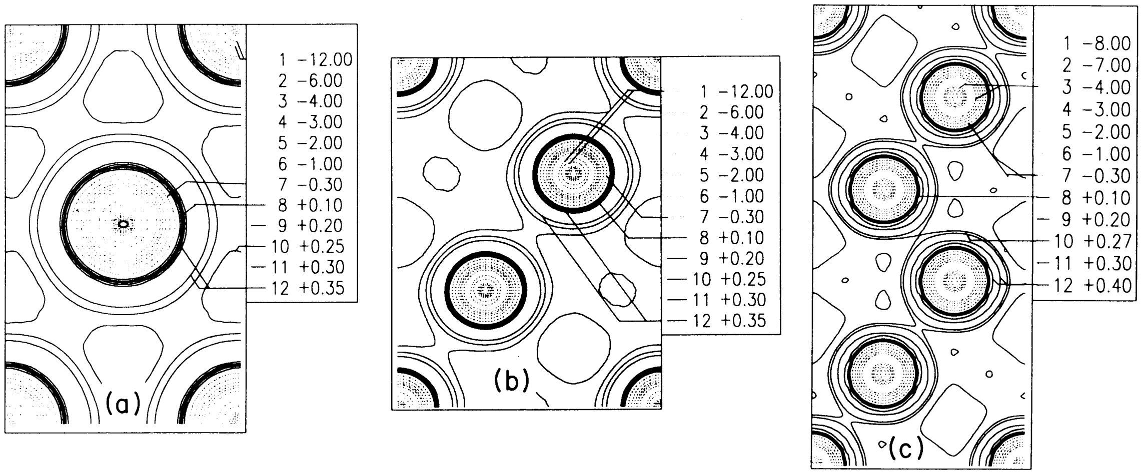

FIG. 1. Charge densities in different planes: (a) (100) plane of the ideal Cu crystal; (b) $(\bar{1}10)$ plane of the ideal Cu crystal; (c) $(\bar{1}10)$ plane with the intrinsic stacking fault in Ag. The charge densities of isolated atoms have been subtracted. The units for the contour lines are $1.34\times10^{-2}/(\mathrm{a.u.})^3$ for Cu and $9.05\times10^{-3}/(\mathrm{a.u.})^3$ for Ag.

less, considerable quantitative differences remain, especially for Ag, where the LKKR result is nearly twice our result from the 8-atom perpendicular calculation. We conclude that the muffin-tin approximation seems to be able to reproduce the general trends for the stacking-fault energies, but it has to be replaced by a full-potential method if highly accurate results are required.

As an example, we studied the influence of structural relaxations near the stacking fault (for fixed stacking fault volume) for the intrinsic 5-atom stacking-fault supercell, by vertical displacements of the planes along the hexagonal axis. It turned out that the displacements are smaller than 0.5% of the original distance between the planes, and the stacking-fault energies are affected by less than 10%. Such a small effect on the structural relaxation was also reported for silicon.[21] It is interesting to note that in Ag the planes at the stacking fault are attracted, whereas they are repelled for the case of Cu and Au.

Figure 1 represents the charge densities as obtained by the pseudopotential calculation. Thereby, the charge densities of the corresponding free atoms were subtracted to elucidate the subtle binding effects. Figure 1(a) shows that the charge densities in the closed packed (111) planes of the ideal fcc structure are nearly spherically symmetric. Figure 1(b) exhibits the $(\bar{1}10)$ plane which contains one atom out of each plane *A*, *B*, *C*, respectively. The enlarged charge densities between these atoms are responsible for the *ABC* stacking succession. From Fig. 1(c) it becomes obvious that at the stacking fault this accumulation of charge between the atoms is removed, and indeed the electron density in the middle between two atoms is lower for atoms at the stacking fault than for those in the bulk, resulting in an increase of the total energy due to the stacking fault.

Motivated by the success of the LMTO method in atomic-sphere approximation for the calculation of the large fault energies in Al and Pd,[18] we repeated the calculations by this method,[27] including partial waves up to $l_{\max}=3$ (Ref. 28) and the combined correction term. As shown in Table II, we obtained larger values than in the pseudopotential calculation, although the general trend, i.e., $\gamma_i^{\mathrm{Cu}}\approx\gamma_i^{\mathrm{Au}}\approx2\gamma_i^{\mathrm{Ag}}$, is fulfilled. Quantitatively, however, there remain considerable differences for the case of Ag, where the atomic-sphere approximation overestimates the stacking-fault energy by more than a factor of 2. (It should be noted that most recently there was another calculation based on the atomic-sphere approximation: Crampin, Vvedensky, and Monnier[17] applied a layer Green's function Korringa-Kohn-Rostocker method and used the force theorem[6] for the calculation of the stacking fault energy, yielding $\gamma_i=41$ mJ/m^2 for Cu.)

To conclude, we have shown that a full-potential electron theory is required to obtain accurate values for the stacking-fault energies even for close-packed fcc metals, if the stacking-fault energies are low. We think that for a reliable determination of defect energies for planar defects in non-close-packed systems (for instance bcc) a full-potential theory is absolutely essential.

The authors are indebted to A. Seeger for bringing this interesting subject to their attention. Our pseudopotential and LMTO programs are based on computer codes developed in the groups of K.-M. Ho (Ames Laboratory) and O. K. Anderson (University of Stuttgart).

[1] A. Seeger, in *Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 328.
[2] A. Seeger, in *Dislocations and Mechanical Properties of Crystals* (Wiley, New York, 1957), p. 243.
[3] R. D. Heidenreich and W. Shockley, in *Report Conference Strength of Solids* (The Physical Society, London, 1948), p. 57.
[4] F. C. Frank, Philos. Mag. **42**, 1014 (1951).
[5] P. C. J. Gallagher, Metall. Trans. **1**, 2429 (1970).

[6]A. R. Mackintosh and O. K. Andersen, in *Electrons at the Fermi Surface,* edited by M. Springborg (Cambridge Univ. Press, Cambridge, 1980), p. 149ff.
[7]R. M. J. Cotterill and M. Doyama, Phys. Rev. **145**, 465 (1966).
[8]A. Blandin, J. Friedel, and G. Saada, J. Phys. (Paris) Colloq. **27**, C3-128 (1966).
[9]H. R. Leribaux, Phys. Status Solidi (a) **31**, K27 (1975).
[10]J. F. Devlin, J. Phys. F **4**, 1865 (1974).
[11]A. Sugiyama, J. Phys. Soc. Jpn. **51**, 1243 (1982).
[12]R. H. Rautioaho, Phys. Status Solidi (b) **112**, 391 (1982).
[13]H. Häkkinen and M. Manninen, Phys. Scr. T **33**, 210 (1990).
[14]D. C. Chrzan, L. M. Falicov, J. M. MacLaren, X.-G. Zhang, and A. Gonis, Phys. Rev. B **43**, 9442 (1991).
[15]J. M. MacLaren, S. Crampin, D. D. Vvedensky, and M. E. Eberhart, Phys. Rev. Lett. **63**, 2586 (1989).
[16]S. Crampin, K. Hampel, D. D. Vvedensky, and J. M. MacLaren, J. Mater. Res. **5**, 2107 (1990).
[17]S. Crampin, D. D. Vvedensky, and R. Monnier (unpublished).
[18]J.-H. Xu, W. Lin, and A. J. Freeman, Phys. Rev. B **43**, 2018 (1991).
[19]P. H. Dederichs, T. Hoshino, B. Drittler, K. Abraham, and R. Zeller, Physica B **172**, 203 (1991).
[20]T. Beuerle, R. Pawellek, C. Elsässer, and M. Fähnle, J. Phys. Condens. Matter **3**, 1957 (1990).
[21]M. Y. Chou, M. L. Cohen, and S. G. Louie, Phys. Rev. B **32**, 7979 (1985).
[22]A. Gross and H. Teichler, Philos. Mag. B **64**, 413 (1991).
[23]D. Vanderbilt, Phys. Rev. B **32**, 8412 (1985).
[24]D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).
[25]S. G. Louie, K. M. Ho, and M. L. Cohen, Phys. Rev. B **19**, 1774 (1979); C. Elsässer, N. Takeuchi, K. M. Ho, C. T. Chan, P. Braun, and M. Fähnle, J. Phys. Condens. Matter **2**, 4371 (1990).
[26]J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979); **13**, 3095 (1980).
[27]O. K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984).
[28]Inclusion of f orbitals was so important for Au that we had to refrain from the downfolding procedure for the f orbitals.