

## First-principles calculation of stacking-fault energies in substitutionally disordered alloys

J. M. MacLaren

*Department of Physics, Tulane University, New Orleans, Louisiana 70118*

A. Gonis

*Department of Chemistry and Materials Science, Lawrence Livermore National Laboratory, Livermore, California 94550*

G. Schadler

*Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule, Zürich, Switzerland*

(Received 7 November 1991)

A generalization of the coherent-potential approximation to two-dimensional defects in substitutionally disordered alloys, based on the layer Korringa-Kohn-Rostoker method, is presented. We illustrate the method with *ab initio*, self-consistent total-energy calculations implemented within the muffin-tin approximation of intrinsic stacking-fault energies in various  $\text{Cu}_{1-x}\text{Zn}_x$  alloys ( $x=0, 0.1, 0.2, \text{ and } 0.3$ ). Excellent agreement is found between calculated fault energies and experimentally determined values.

It is well known that the energy of intrinsic stacking faults is an important factor controlling the separation of dislocations into partials, which in turn is crucial in characterizing the mechanical properties of metals and alloys.<sup>1</sup> The ability to understand, predict, and control the effects of stacking faults is a crucial step in rationalizing observed mechanical behavior and in attempting to design materials with desirable technological properties. To date there have been several calculations, using different electronic-structure methods, demonstrating that fault energies can be accurately determined from first principles. Most of these calculations model the planar defect by using a supercell construction,<sup>2</sup> although recent work using the layer Korringa-Kohn-Rostoker (LKKR) method has made possible the removal of this artificial boundary condition.<sup>3</sup> Control over the properties of the fault can be achieved by changing the electronic properties of the alloy by selective alloying. Hong and Freeman<sup>4</sup> considered the effects of impurities on the energy of an antiphase boundary in NiAl by constructing a periodic crystal containing the impurity atoms both with and without the defect. However, the impurities are more likely to be randomly distributed and therefore the ability to treat substitutionally disordered interfaces is of significant importance. In this Brief Report we present a technique capable of addressing properly the disordered nature of the system. We illustrate this method with *ab initio* calculations of the energies of an isolated intrinsic stacking fault in Cu/Zn alloys, which are found to agree well with experimental findings.

The technique presented here for calculating the electronic structure at a disordered interface is based upon the LKKR method<sup>5</sup> combined with the coherent-potential approximation (CPA).<sup>6-8</sup> The former circumvents the need for a supercell construction by correctly embedding the planar defect in an otherwise perfect crystal, while the latter approximation has had significant success in describing the electronic properties of bulk substitutionally disordered alloys.<sup>7</sup> The LKKR method has been described in detail elsewhere,<sup>5</sup> so in this pa-

per we will only give a brief outline, concentrating on the implementation of the CPA step within the layered geometry. A detailed account of the formalism of the LKKR-CPA will be given in a future publication.<sup>9</sup> In the LKKR method, the solid is broken down into layers of atoms within which two-dimensional (2D) translational symmetry is assumed. The electronic structure of the resulting system is found within the local spin-density approximation from the imaginary part of the one-electron site-diagonal Green function. This is obtained, within multiple-scattering theory (MST), by first considering the scattering of electrons within a single plane and then by appropriately combining the layers together to treat the scattering of electrons between the planes. Once the site-diagonal components of the Green function are obtained, the self-consistent charge density and total energy can be readily calculated. The calculation of the charge density involves integrals over the 2D Brillouin zone and over energy since the Green function is obtained at a specific energy and wave vector. The energy integration is achieved by a contour integral in the complex energy plane while the special point method is used for the 2D Brillouin-zone integration. This approach leads to rapidly convergent  $k$  space and energy integrals. The charge densities and potential can be obtained self-consistently by iterating the Kohn-Sham equations. The boundary condition for the Coulomb potential is found using the Ewald technique and assuming a compositionally averaged interstitial charge density. From the self-consistent charge density for each species, the kinetic, Coulomb, and exchange-correlation contributions to the total energy of each species are evaluated as in an ordered interface calculation. The assumption of a compositionally averaged interstitial charge density is used in evaluating the Madelung energy. The details of the construction of the muffin-tin total energy and self-consistent charge densities within the LKKR technique have been described in Ref. 5. The total energies for each species are configurationally averaged to give the alloy total energy, as described for bulk alloys by Johnson *et al.*<sup>12</sup>

In applications of the CPA to bulk alloys, an effective periodic medium is constructed<sup>7,8</sup> which has the property that the electron scatters on average in the disordered alloy as it would in the coherent potential. The usual implementation within MST of the CPA in bulk crystals<sup>7,8</sup> is based on a self-consistent condition applied to the site-diagonal components of the scattering path operator (SPO) (Ref. 10) of the coherent potential. This condition takes the form

$$\tau_c^{ii} = \sum_{\alpha} c_{\alpha} \tau_{\alpha}^{ii}, \quad (1)$$

where the superscript  $i$  refers to the site and  $\tau_c$  is the scattering path operator for the coherent medium. The quantity  $\tau_{\alpha}^{ii}$  is the SPO for an atom of type  $\alpha$  embedded in this medium at site  $i$ , and  $c_{\alpha}$  is the concentration of the  $\alpha$  species in the alloy. Within MST the site-diagonal components of the SPO for an atom type  $\alpha$  embedded at site  $i$  in the coherent medium is given by the expression

$$\tau_{\alpha}^{ii} = [(\tau_c^{ii})^{-1} + m_{\alpha} - m_c]^{-1}, \quad (2)$$

where  $m_c$  is the inverse of the single-site coherent-potential  $t$  matrix, and  $m_{\alpha}$  is the inverse of the  $t$  matrix of atom  $\alpha$ .

The concepts underlying the CPA can be readily generalized to treat two-dimensional extended defects, such as stacking faults, in substitutionally disordered alloys through the use of the LKKR method. The main difference to the case of bulk alloys is that the coherent medium is plane dependent with respect to the defect. To keep the notation transparent we shall assume only one atomic type per plane so that the site label is also the plane label. The extension to systems with many atoms per plane is straightforward. Thus, instead of a single effective (inverse) scattering matrix  $m_c$ , one must consider a number of distinct effective scattering matrices  $m_c^i$  for each plane away from the interface in the alloy. In the case of most systems it is necessary to distinguish between effective scattering matrices on either side of the interface. However, in the special case of the intrinsic fault the interface is symmetric about the fault plane. This procedure leads to a number of coupled, transcendental equations for the  $m_c^i$ . In a practical application, it is necessary to impose a restriction on the number of coherent scattering matrices to be determined independently. This can be done by assuming that the  $m_c^i$  approach the corresponding quantity  $m_c$  of the bulk alloy when the plane  $i$  lies sufficiently far from the interface. For metallic systems, one can expect from screening arguments that this occurs fairly close to the defect plane.

We now highlight the central equations of the LKKR-CPA reserving a more extended discussion for a later publication.<sup>9</sup> For materials containing two-dimensional defects, and within the LKKR formalism one obtains a self-consistent equation of the type of Eq. (1) for each plane characterized by a distinct  $m_c^i$ . For the sake of generality, one may allow also a planar dependence of the concentration so that Eq. (1) must be replaced with the equation

$$\tau_c^{ii} = \sum_{\alpha} c_{\alpha}^i \tau_{\alpha}^{ii}. \quad (3)$$

In this case, Eq. (2) must also be replaced with the equation

$$\tau_{\alpha}^{ii} = [(\tau_c^{ii})^{-1} + m_{\alpha}^i - m_c^i]^{-1} \quad (4)$$

since the scattering matrix of an atom of type  $\alpha$  may also have a layer dependence. Finally, the scattering path operators for the coherent medium can be calculated by means of an integral over the two-dimensional Brillouin zone defined by the periodicity of the defect,

$$\tau_c^{ii} = \frac{1}{\Omega} \int d\mathbf{k} [M^{ii} - \Delta^{ii}(\mathbf{k})]^{-1}. \quad (5)$$

Here,  $M^{ii}$  is the inverse of the layer scattering matrix and  $\Delta^{ii}$  describes the embedding of the layer  $i$  in the rest of the crystal. Equations (3)–(5) must be solved self-consistently at each energy just as in bulk KKR-CPA calculations. This solution proceeds in an iterative manner, with the initial approximation to the coherent scattering matrix set equal to the concentration average of the individual scattering matrices associated with the various species in the alloy (the average  $t$ -matrix approximation). The charge self-consistency loop can be completed since the site-diagonal Green function can be obtained from  $\tau_{\alpha}^{ii}$  and the appropriate wave functions. Equations describing the LKKR-CPA for an isolated layer have been given by Kaiser *et al.*<sup>11</sup> and can be obtained from the above equations by neglecting the coupling between the layer and the surrounding crystal, i.e.,  $\Delta^{ii}(\mathbf{k}) = 0$ .

We assume that electronic perturbations are localized around the fault and hence only the potentials on a certain number of planes are allowed to relax. The potentials for atoms further from the fault are assumed to be unperturbed from the bulk values. In the LKKR-CPA calculations this means that the site-diagonal components of  $\tau_c$  for these distant planes are assumed to be those of the disordered bulk alloy. Convergence in the stacking-fault energy with basis set size was checked. The LKKR basis set used in our self-consistent calculations included  $s$ ,  $p$ , and  $d$  partial waves, 13 plane waves, 36 special  $k$  points, and 24 energy points. The Ceperley-Alder local-density functional as parametrized by Perdew and Zunger was adopted<sup>13</sup> and electronic relaxations on eight planes of atoms surrounding the fault (four planes on either side) were taken into account. Owing to the reduced symmetry of the stacking fault it was found to be necessary to sample two wedges of the hexagonal Brillouin zone.

As an application of the LKKR-CPA method we have calculated the electronic properties of an intrinsic stacking fault in the fcc Cu/Zn alloy as a function of Zn concentration. The perfect fcc crystal structure is formed by the usual stacking of close-packed (111) planes denoted by  $\langle ABC \rangle$  (where the planes in the angle brackets are repeated). The intrinsic stacking fault in this notation is  $\langle ABC \rangle AB \langle ABC \rangle$ . In this initial study no account of Zn segregation to or from the fault was taken into consideration although this presents no difficulty for the method. Structural relaxations at the fault plane are expected to have a small effect on the fault energy and have been neglected in the calculations. The lattice constant for each different Zn concentration was taken

from the self-consistent bulk Cu/Zn calculations of Ref. 12. As a test of the accuracy of the method, calculations for bulk  $\text{Cu}_{0.5}\text{Zn}_{0.5}$  using the LKKR-CPA method gave a lattice constant with 0.5% of that obtained by the KKR-CPA method in Ref. 12. The Cu/Zn alloy has also been studied experimentally and the variation of fault energy as a function of Zn concentration obtained,<sup>14</sup> allowing a sensitive comparison of the calculations to experiment.

Figure 1 shows the variation of intrinsic fault energy calculated with the LKKR-CPA method and the experimental values.<sup>14</sup> The uncertainties in experimentally determined values are estimated to be about 10% though this may be conservative for the alloy faults. This estimate is based upon the different values for the intrinsic fault energy in pure Cu obtained by different groups. The largest difference between experimental and theoretical estimates of the fault energy is for the intrinsic stacking fault in the  $\text{Cu}_{0.7}\text{Zn}_{0.3}$  alloy. In fact, the calculations predict a negative energy for the fault suggesting that at this Zn concentration the hcp phase is more stable.<sup>15</sup> A calculation for this alloy in the hcp crystal structure was also performed. We find, within the approximations implicit in the LKKR-CPA method, that at this concentration the hcp phase also has a lower energy, the difference between hcp and fcc phases is  $-26 \text{ mJ/m}^2$ . If we assume that the energy to create a kink in the fcc structure (i.e., an *ABA* rather than *ABC* stacking sequence) is a constant and neglect the interactions between kinks,<sup>16</sup> then both the intrinsic fault and hcp unit cell have two kinks and we would expect the energies to be similar which is what we find (the energy of the intrinsic fault is  $-20 \text{ mJ/m}^2$ ). One possible reason for the discrepancy between calculated and measured fault energies lies in the approximations made in the LKKR-CPA method. These approximations include the muffin-tin approximation to the one-electron potential, the neglect of structural relaxations around the fault, and the assumption within the CPA of no correlation between the sites. Corrections to the LKKR part can in principle be made by using a full-potential multiple-scattering formalism, while a cluster CPA could take into account some degree of local segregation of Zn atoms. Non-muffin-tin corrections can be important when the energy differences are small. The statistical independence of sites is unlikely to be correct at high Zn concentrations though it is un-

clear how this will influence the fault energy. In fact, at Zn concentrations between 20% and 30% there is a phase transition from an fcc to a bcc crystal structure at low temperatures.<sup>15</sup> In addition, the fault energy, which is extracted from electron microscopy measurements by using continuum elasticity theory, requires a knowledge of the elastic constants. These are assumed to be the same for all the different alloys studied which is unlikely to be the case. Finally, unlike the case of pure Cu, there is only one set of experimental values and further there is uncertainty in the alloy composition as well as in the fault energy. Overall though, excellent agreement is obtained between calculated and experimental values, providing the first accurate theoretical determination of a stacking-fault energy in a disordered alloy. Applications of the LKKR-CPA technique to other alloy systems are in progress.

Structurally the intrinsic stacking fault is not a severe disruption of the fcc crystal. The coordination of atoms at the interface is still close-packed with the changes in bond lengths first occurring for third neighbors. This is reflected in the density of states (DOS) for atoms at the fault for pure Cu,  $\text{Cu}_{0.9}\text{Zn}_{0.1}$ ,  $\text{Cu}_{0.8}\text{Zn}_{0.2}$ , and  $\text{Cu}_{0.7}\text{Zn}_{0.3}$ , shown in Fig. 2. In these plots only the DOS for an atom at the fault, compared to an atom in the bulk, are displayed since the differences between the DOS profile on atoms further from the fault and that for an atom in the bulk is negligible. In all four plots the differences in the DOS between the different atoms are small and are localized at the fault plane and within the Cu *d* bands. The Zn *d* states appear as a peak 8 eV below the Fermi energy and only hybridize with the bottom of the Cu *sp* band. The position of Zn *d* states coincides exactly with the energy of the middle of the *d* bands in bulk Zn.<sup>17</sup> The atoms located on either side of the fault plane have first, second, and some third neighbor atoms at hcp lattice sites and the DOS profile shows marked similarities with that for hcp Cu (not shown). In particular the depletion of states at  $-2.5 \text{ eV}$  below the Fermi energy and the enhancement in either side of the peaks is seen in the Cu hcp DOS. This was also observed by Xu, Lin, and Freeman<sup>2</sup> for an intrinsic stacking fault in Al. As the concentration of Zn is increased, these perturbations, which reflect the influence of changes in the local symmetry at the fault, are significantly reduced, correlating with the reduced sensitivity to the local environment and therefore the smaller fault energy. The effect of alloying is to broaden the features in the DOS, and these changes in the electronic structure are an important mechanism for the lowering of the fault energy. A previous model based upon electron to atom ratio and a rigid-band model predicts a zero energy stacking fault at 36%.<sup>18</sup> This model would also predict a linear variation of fault energy with Zn concentration which is not observed in the calculations. The deviations from linearity reflect the significant changes in the electronic structure as a result of alloying.

In conclusion, the energy and electronic properties of an intrinsic stacking fault in a disordered Cu/Zn alloy have been calculated from first principles by combining the CPA and the LKKR approach. The calculated vari-

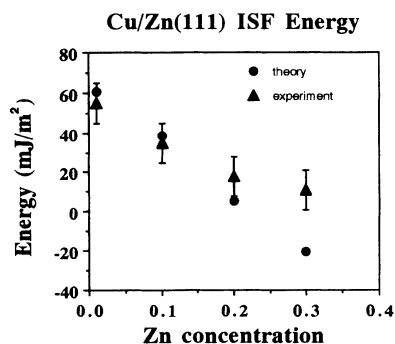


FIG. 1. Variation of both experimental and theoretical stacking fault energy in the Cu/Zn alloy as a function of Zn composition.

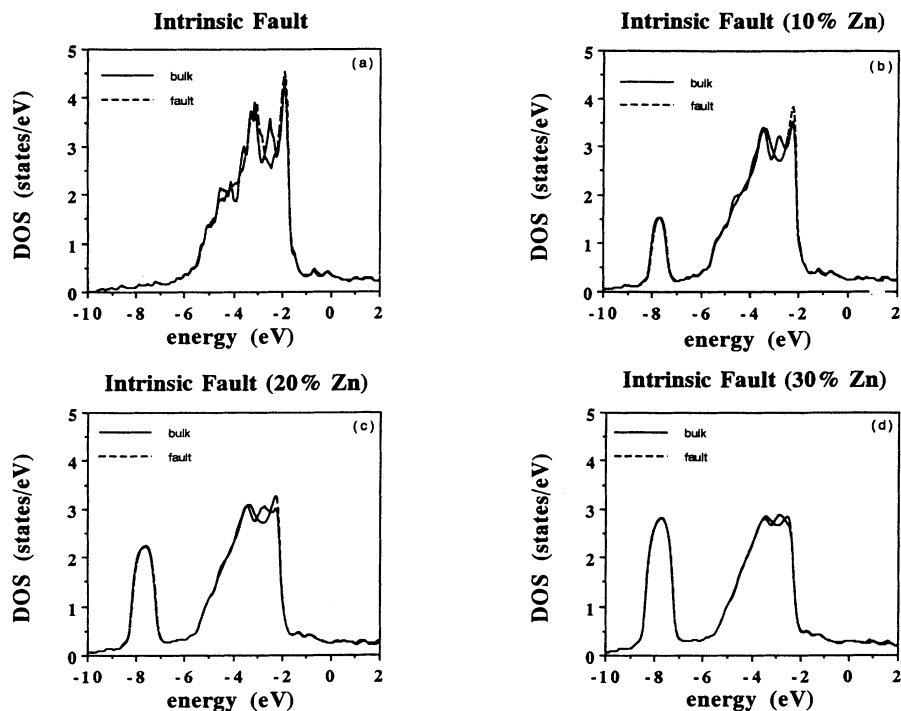


FIG. 2. Density of states for an atom in the bulk (solid line) and an atom at the fault plane (dotted line) for (a) pure Cu, (b)  $\text{Cu}_{0.9}\text{Zn}_{0.1}$ , (c)  $\text{Cu}_{0.8}\text{Zn}_{0.2}$ , and (d)  $\text{Cu}_{0.7}\text{Zn}_{0.3}$ .

ation of the fault energy agrees well with experimentally determined values. At low Zn concentrations the broadening in the electronic states resulting from the disorder reduces the sensitivity of the Cu  $d$  states to the local environment and thus to a reduction in the fault energy. At higher Zn concentrations the changes to the electronic structure are sufficient to produce a negative stacking-fault energy and suggest an hcp phase of lower energy. This should not be realized experimentally, however, be-

cause of the fcc-to-bcc phase transition. The mechanism at low impurity concentrations would also be expected to apply to other systems and indeed a reduction of fault energy upon alloying is observed in a wide variety of fcc alloys.<sup>1,14,18</sup>

This work was partly supported by the U.S. Department of Energy under Grant No. W-740-Eng-48 with Lawrence Livermore National Laboratory.

<sup>1</sup>L. E. Murr, *Interfacial Phenomena in Metals and Alloys* (Addison-Wesley, Reading, MA, 1975); J. P. Hirth and J. Lothe, *Theory of Dislocations* (Wiley Interscience, New York, 1982).

<sup>2</sup>M. Y. Chou and M. L. Cohen, *Phys. Rev. B* **32**, 7983 (1985); J. Xu, W. Lin, and A. J. Freeman, *ibid.* **43**, 2018 (1991).

<sup>3</sup>J. M. MacLaren, S. Crampin, D. D. Vvedensky, and M. E. Eberhart, *Phys. Rev. Lett.* **63**, 2586 (1989); S. Crampin, K. Hampel, D. D. Vvedensky, and J. M. MacLaren, *J. Mater. Res. B* **5**, 2107 (1990).

<sup>4</sup>T. Hong and A. J. Freeman, *Phys. Rev. B* **43**, 6446 (1991).

<sup>5</sup>J. M. MacLaren, S. Crampin, D. D. Vvedensky, and J. B. Pendry, *Phys. Rev. B* **40**, 12 164 (1989); J. M. MacLaren, S. Crampin, D. D. Vvedensky, R. C. Albers, and J. B. Pendry, *Comput. Phys. Commun.* **60**, 365 (1991).

<sup>6</sup>P. Soven, *Phys. Rev.* **156**, 809 (1967).

<sup>7</sup>B. L. Györfy, *Phys. Rev. B* **5**, 2382 (1972); J. S. Faulkner and G. M. Stocks, *ibid.* **21**, 3222 (1980).

<sup>8</sup>J. S. Faulkner, in *Progress in Materials Science*, edited by J. W. Christian, P. Hassen, and T. B. Massalski (Pergamon, New York, 1982), Vols. 1 and 2.

<sup>9</sup>J. M. MacLaren and A. Gonis (unpublished).

<sup>10</sup>B. L. Györfy and M. J. Stott, in *Band Structure Spectroscopy of Metals and Alloys*, edited by D. J. Fabian and L. M. Watson (Academic, New York, 1973), p. 385.

<sup>11</sup>J. H. Kaiser, P. J. Durham, R. J. Blake, and L. T. Wille, *J. Phys. C* **21**, L1159 (1988).

<sup>12</sup>D. D. Johnson, D. M. Nicholson, F. J. Pinski, B. L. Györfy, and G. M. Stocks, *Phys. Rev. B* **41**, 9701 (1990).

<sup>13</sup>D. Ceperley, *Phys. Rev. B* **18**, 3126 (1978); D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980); J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).

<sup>14</sup>P. C. J. Gallaher, *Metall. Trans.* **1**, 2429 (1970).

<sup>15</sup>Experimentally (see, for example, Ref. 18) a bcc phase is observed at a Zn concentration of about 30%. We did not examine this phase, since the stacking-fault energy is related to the relative stability of hcp and fcc phases.

<sup>16</sup>The empirical observation that the intrinsic and extrinsic faults (which both have two kinks) have approximately the same energy which is roughly twice that of the twin fault (which has only one kink) suggests that the kinks only interact weakly. The systematics of the interaction between kinks was investigated for Ni by D. C. Chrzan, L. M. Falicov, J. M. MacLaren, X.-G. Zhang, and A. Gonis, *Phys. Rev. B* **43**, 9442 (1991).

<sup>17</sup>V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

<sup>18</sup>P. J. Haasen, *Physical Metallurgy* (Cambridge University Press, Cambridge, UK, 1986).