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Model-Potential Calculations of Stacking-Fault Energies

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Calculations of stacking-fault energies in aluminum, magnesium, beryllium, copper, silver, and gold are reported. For the polyvalent metals it is shown, by means of comparisons of numerical results based on several different energy–wave-number characteristics, that exchange and correlation corrections are not as significant in the present context as they are in most other defect calculations. Nonlocal effects are quite important but can be approximately accounted for by empirical adjustments of the form factors based on simpler local models. Although stabilities against faulting and the relative magnitudes of stacking-fault energies are correctly predicted, quantitative agreement with experiment is not obtained. Possible reasons for this discrepancy are discussed. Results for the noble metals indicate a severe sensitivity to the detailed curvature of the energy–wave-number characteristic in the vicinity of the smallest reciprocal-lattice vector. Failure to obtain agreement with experiment in these cases may therefore be due to minor inaccuracies in the energy–wave-number characteristics for noble metals.

I. INTRODUCTION

Applications of the pseudopotential theory of metals to analyses of the energetics of most crystalline defects are made difficult by a number of factors. Among these are the questionable validity of a first-order perturbation treatment,[1] the sensitivity of interionic potentials to exchange and correlation corrections,[2,3] and the need to properly account for the nonlocal nature of the pseudopotential itself.[4] However, the calculation of stacking-fault energies in close-packed crystals is one class of problems that apparently does not suffer from the first mentioned difficulty, owing essentially, to the fact that close packing is preserved across the fault plane.[1] There is also reason to expect that stacking-fault-energy predictions are less sensitive than other defect calculations to uncertainties in exchange and correlation effects. This is because effective interionic potentials, which are always used at least implicitly in defect-energy calculations, are most sensitive to such many-body corrections at small interionic distances (or the order of the nearest-neighbor distance),[3] while the smallest distance involved in a stacking-fault-energy calculation is twice the distance between close-packed planes.[5] The effects of nonlocality, however, are more difficult to estimate because such effects persist, in the form of a reduction in magnitude of the oscillations in the interatomic potential, at large interatomic distances.[4] On the other hand, fully nonlocal treatments do exist,[2,6–8] so that it is now possible to avoid this difficulty altogether. Thus, if our suggestion that the stacking-fault energy is insensitive to many-body corrections is valid, it should be possible to proceed with reasonable confidence in the prediction of stacking-fault energies for at least a few close-packed metals.

In the present paper we examine the effects of both many-body corrections and nonlocality by means of comparisons of calculated stacking-fault energies. Our principal purpose in undertaking this work was to test the sensitivity of the result to such effects and thus to investigate the usefulness of the more rigorous models, and simple local potentials as well, for predicting trends in stacking-fault energies. A secondary objective was to explore possible advantages of the calculational method of Blandin, Friedel, and Saada,[5] in which the stacking-fault is expressed as a real-space sum, as opposed to the usual reciprocal-space formulation,[9] involving the effective interaction between close-packed planes.

A review of the method of calculation and a description of the scope of the work are presented in Secs. II and III. In Sec. IV we present numerical results for the interplanar potential in aluminum and gold, these results being typical of polyvalent and noble metals, respectively. Topics discussed here include the effects of nonlocality and many-body corrections in polyvalent metals, the asymptotic approximations of Blandin *et al.*,[5] the sensitivity of the gold potential to minor features of the energy–wave-number characteristic, and implications of this sensitivity as regards the relative stabilities of the two close-packed structures for noble metals. Section V contains the results of stacking-fault-energy calculations, comparisons with experiment, and an analysis based on the discussion in Secs. III and IV.

II. METHOD OF CALCULATION

The stacking-fault energy, which will be denoted by γ, is defined as the difference in energy per unit fault area between the faulted and perfect crystals. In the usual pseudopotential-perturbation approximation, the expression for γ is a sum over

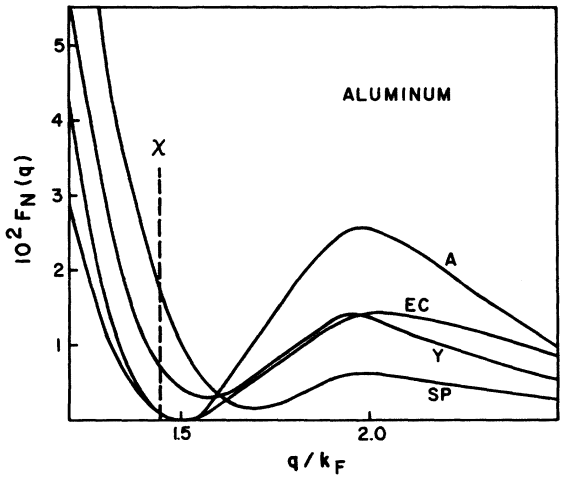

FIG. 1. Normalized energy–wave-number characteristics for aluminum. Stacking-fault energy calculations involve only those data for which q is greater than the smallest reciprocal-lattice vector, indicated here by the line labeled χ. Sources are as follows: A, Animalu (Ref. 12); Y, Yamamoto (Ref. 8); SP, Shaw and Pynn (Ref. 7); and EC, the empty-core model discussed in the text. The energy–wave-number characteristics of Shaw (Ref. 6) and Shyu *et al.* (Ref. 2) differ only slightly from the Shaw–Pynn curve.

wave-vector space of a factor that depends only on q, the electron wave number, multiplied by the difference in the absolute squares of the faulted- and perfect-crystal structure factors.[9] Blandin *et al.*,[5] have shown that this expression can be reduced to the simple form

$$\gamma = \sum_{n=2}^{\infty} N(n)\,\Delta\varphi(nh) \ , \tag{1}$$

where h is the distance between close-packed planes, $N(n)$ is a set of integral weights corresponding to a particular fault configuration, and $\Delta\varphi(nh)$ is an interplanar potential difference defined as follows: If the stacking sequence of close-packed planes is denoted in the usual way by a sequence of symbols (e.g., *ABABAB*... for the hcp structure), then $\Delta\varphi(nh)$ is the interaction energy of a pair of planes in nonequivalent (e.g., *A-B*) positions minus the energy of a pair of planes in equivalent (e.g., *A-A* or *B-B*) positions, the interplanar distance in both cases being nh. The reason that the sum in Eq. (1) begins with $n = 2$ is that in all of the stacking sequences considered here, nearest-neighbor planes are in nonequivalent positions in both the perfect and faulted crystals and their interaction energy therefore cancels in calculating the energy change due to faulting.

The function $\Delta\varphi(nh)$ is given by

$$\Delta\varphi(nh) = \frac{16z^2}{3k_F a^4} \sum_{\vec{g}} (\cos \vec{g}\cdot\vec{d} - 1) J(g, nh) \ , \tag{2}$$

where z is the effective valence,[1] k_F is the Fermi wave number, a is the lattice constant for the close-packed plane, $\vec{g}$ is a reciprocal lattice vector for the close-packed plane, $g = |\vec{g}|$, and $\pm\vec{d}$ is the parallel displacement of one plane relative to a second plane in a nonequivalent position.[1] The dimensionless function $J(g, nh)$ is the integral

$$J(g, nh) = \int_0^{\infty} \left[\frac{1 - F_N([\eta^2 + \chi^2]^{1/2})}{\eta^2 + \chi^2} \right] \cos k_F nh\eta \, d\eta \ , \tag{3}$$

where $\chi = g/k_F$ and $F_N(q/k_F)$ is the normalized energy–wave-number characteristic.[4] In practice the only significant terms in Eq. (2) are those for the smallest nonvanishing value of g. (By actual numerical test, higher-order terms contribute less than 1% to $\Delta\varphi$.) In all subsequent discussions we will therefore use

$$\Delta\varphi(nh) \approx -\frac{48z^2}{k_F a^4} J(nh) \ , \tag{4}$$

which is obtained by summing over the six smallest $\vec{g}$ vectors. The integral $J(nh)$, which is proportional to the interplanar potential, is, of course, given by the right side of Eq. (3) with χ equal to its minimum value. Actually, as the development of Eq. (2) reveals,[1] the interplanar potential is proportional to $+J(nh)$ for planes in equivalent positions and $-J(nh)$ for planes in nonequivalent positions.

From Eq. (3) it is evident that the only values of the argument of F_N that enter the calculation are those for which $q/k_F > \chi$. In Figs. 1 and 2 we show the location of χ with respect to the peaks and valleys in the energy–wave-number characteristics

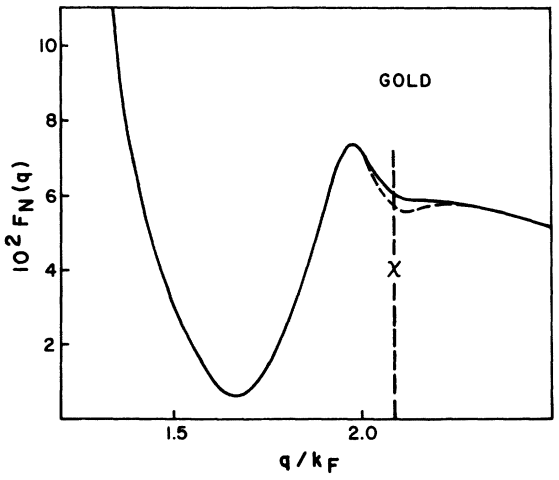

FIG. 2. Normalized energy–wave-number characteristics for gold. The line marked χ has the same significance as in Fig. 1. The solid curve is based on the tabulation of Moriarty (Ref. 16) and the dashed curve is an arbitrary alteration of that data as described in the text.

for aluminum and gold; these data are typical of polyvalent and noble metals, respectively. Since χ is of the order of, or greater than, the position of the first minimum in F_N, the large matrix elements of the pseudopotential that occur near $q/k_F = 0$ do not enter the calculation. Thus, as Heine and Weaire[1] point out, the first-order perturbation approximation on which the formalism is based is more likely to be valid for stacking-fault calculations than it is for other defect studies that do involve values of q/k_F near zero.

If $\chi < 2$, so that the integrand in Eq. (3) contains the logarithmic singularity at the point $q = 2k_F$ (i.e., $\eta^2 + \chi^2 = 4$), we can expect $J(nh)$ to exhibit a long-range oscillatory behavior similar to that of interionic potentials.[9] Blandin *et al.*,[5] showed that, in this case, the asymptotic form for $J(nh)$ is (with the usual assumption of a local pseudopotential)

$$J(nh) \approx -\frac{3a^4 k_F \nu [w(2k_F)]^2}{128\pi^2 z^2} \frac{\sin(2k_F \nu nh)}{n^2}, \quad (5)$$

where

$$\nu = [1 - (\chi/2)^2]^{1/2} \quad (6)$$

and $w(2k_F)$ is the screened-pseudopotential form factor evaluated at $q = 2k_F$. They also found that if this asymptotic approximation is used to calculate $\Delta\varphi(nh)$, the stacking-fault-energy sum given by Eq. (1) can be evaluated exactly for intrinsic, extrinsic, and twin faults in both fcc and hcp crystals. For $\chi > 2$ the poles in Eq. (3) occur at imaginary η and the resulting asymptotic form is a decaying exponential. In this case the sum in Eq. (1) converges quite rapidly.

In the present case, for $\chi < 2$, we used the asymptotic formulas of Blandin *et al.*, with numerically computed corrections to $\Delta\varphi(nh)$ for small n. Thus, if we let γ_A and $\Delta\varphi_A(nh)$ denote the asymptotic approximations described above, then the formula used in place of Eq. (1) is

$$\gamma = \gamma_A + \sum_{n=2}^{M} N(n)[\Delta\varphi(nh) - \Delta\varphi_A(nh)], \quad (7)$$

where M is a number large enough that the difference between $\Delta\varphi(Mh)$ and $\Delta\varphi_A(Mh)$ is small.

As it turned out, the most serious difficulty we encountered in applying Eq. (7) was in the numerical evaluation of the integral $J(nh)$ for large nh. Since preliminary tests showed that the mesh-point spacing in tabulated values of F_N is too coarse for the application of standard numerical-integration methods, it was necessary to interpolate the data to obtain estimates of F_N at intermediate values of q/k_F. After experimenting with various interpolation and integration schemes we finally settled on the Aitken interpolation method[10] for obtaining values of F_N at ten points within each tabulated interval. The integration over each subinterval was then done by fitting the quantity in brackets in Eq. (3) with a single exponential in η and evaluating the resulting integral exactly.

In an attempt to minimize the inevitable inaccuracy of interpolated values near the logarithmic singularity at $q = 2k_F$, we performed the interpolation on the function $\epsilon(q)F_N(q/k_F)/[\epsilon(q) - 1]$, where $\epsilon(q)$ is the Hartree dielectric function. The idea here was that in the local approximation with Hartree screening this function is smooth and, therefore, more easily interpolated than F_N itself. Even so, when we tested the method by applying it to such approximate functions we were not able to consistently reproduce the asymptotic oscillations in $J(nh)$ for n greater than about 4. This is illustrated in Fig. 3, where we show the asymptotic form of $J(nh)$, the curve obtained by evaluating F_N exactly at each mesh point, and the data obtained with an interpolated function. For the test shown here we used an exponentially damped, empty-core-model potential,[11] with parameters chosen to obtain an approximate fit to tabulated F_N data for magnesium. The lengths of the vertical lines drawn at integral values of n are proportional to the weights $-N(n)$ for an intrinsic fault in an hcp crystal. [From Eqs. (1) and (3) it follows that γ is proportional to the sum of the products $-N(n) \times J(nh)$.]

From the erratic behavior obtained with the interpolated F_N at large values of n, it is evident that when n is large the numerical integration is too sensitive to interpolation errors to be reliable. It is also evident that the interpolation procedure leads to some error for small n, as evidenced by results for n between 2 and 3. These errors, however, are not as important because the weights used in computing γ [the $N(n)$ in Eq. (7)] are greater

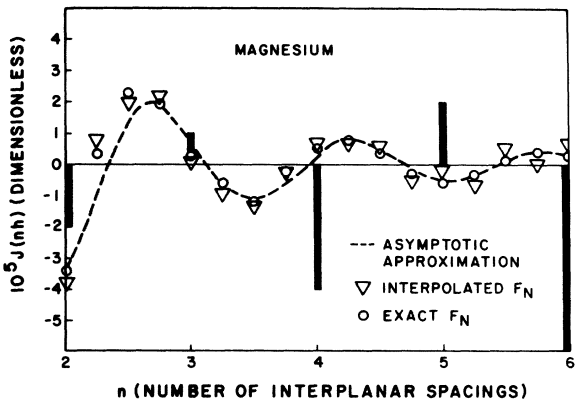

FIG. 3. Interplanar potential function for magnesium based on the local empty-core model described in the text. The lengths of the vertical bars are proportional to the weights involved in Eq. (1) in the calculation of the intrinsic fault energy in an hcp crystal.

for large n. Thus, if we use the data shown in Fig. 3 to compute the energy of an intrinsic fault in the hcp structure, we obtain 11.5 erg/cm^2 with the computed F_N and 13.2 erg/cm^2 with the interpolated function, if the sum in Eq. (7) is terminated at $M = 4$. With $M = 6$, however, we obtain 11.9 and 7.7 erg/cm^2 using the computed and interpolated functions, respectively. Similar results were obtained with empty-core models for aluminum and beryllium, although the errors in γ for these data were much smaller.

Since interpolation difficulties of this type undoubtedly exist with tabulated nonlocal F_N, the sum in Eq. (7) was terminated at $M = 4$ in all of the calculations reported here. Fortunately, this caused no serious problem in most of the computations because the agreement between computed and asymptotic approximations to J was generally quite good at $n = 4$. With some of the data for beryllium, however, the difference between the computed and asymptotic J was still significant at $n = 4$ and the fact that we could not handle larger interplanar distances prevented us from obtaining reliable results.

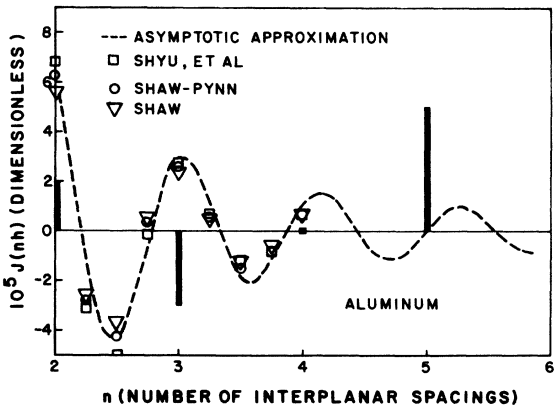

FIG. 4. Interplanar potential functions for aluminum based on the optimized model potential. The vertical bars correspond to weights for an fcc intrinsic fault.

III. SCOPE OF THE CALCULATIONS

The remaining sections of this paper are concerned with the results of calculations for aluminum, magnesium, beryllium, copper, silver, and gold. In all cases stacking-fault energies were computed for intrinsic, extrinsic, and twin faults in both the fcc and hcp structures, thus providing tests of the ability of the method to predict stability against faulting and the relative energies of different fault configurations.

The energy–wave-number data used in calculations for the polyvalent metals are indicated in Table I. In comparing the results of such calculations it is important to recall that there is an inherent arbitrariness in the construction of a model potential and that this arbitrariness leads, in a truncated perturbation expansion, to some unknown, model-sensitive error. Thus, as far as tests of sensitivity to many-body corrections are concerned, the most meaningful comparisons we can make are those involving the first three sets of data listed in Table I. All three sets were derived from the same ionic-model potentials and differ only in the treatment of electron exchange and correlation energies. Similarly, because they differ only in the way nonlocality is handled, the

TABLE I. Energy–wave-number characteristics used in calculations for polyvalent metals.

Data source	Model potential	Screening approximation	F_N calculation
Shaw–Pynn (Ref. 7)	Optimized[a]	Shaw–Pynn (Ref. 7)	nonlocal
Shaw (Ref. 6)	Optimized	Hartree	nonlocal
Shyu *et al.* (Ref. 2)	Optimized	SSTL[c]	nonlocal
Animalu (Ref. 12)	Heine–Abarenkov[b]	Hubbard–Sham[d]	semilocal
Yamamoto (Ref. 8)	Heine–Abarenkov	Hubbard–Sham	nonlocal
Empty-core model	Exponentially damped empty core	Hartree	local

[a]R. W. Shaw, Jr. and W. A. Harrison, Phys. Rev. 163, 604 (1967).
[b]References 13–15.
[c]K. S. Singwi, A. Sjölander, M. P. Tosi, and R. H. Land, Phys. Rev. B 1, 1044 (1970).
[d]L. J. Sham, Proc. R. Soc. Lond. A 283, 33 (1965).

next two sets of data, those based on the Heine–Abarenkov–model potential, provide a basis for investigating the importance of nonlocal effects. The primary reason for including calculations based on the empty-core model was to determine, through comparisons with results based on the more refined models, to what extent the simpler theory might be useful for estimating trends in stacking-fault energies.

The only nonlocal energy–wave-number characteristics available for the noble metals are those reported by Moriarty.[16] Although comparisons with results based on simpler local models could have been made, we did not do this because such models are obviously unrealistic for the noble metals, where the energy–wave-number characteristic is dominated by the highly nonlocal effects of resonant scattering. Our analysis for the noble metals is therefore limited to comparisons with experiment and a numerical test of the sensitivities of the interplanar potential and stacking-fault energies to minor alterations of the energy–wave-number characteristic.

IV. INTERPLANAR POTENTIALS

The interplanar potential function $J(nh)$ for aluminum, as determined from the energy–wave-number tabulations of Shaw[6] (Hartree approximation), Shaw and Pynn,[7] and Shyu *et al.*,[2] is plotted in Fig. 4 along with the asymptotic approximation based on the Shaw–Pynn form factor. The lengths of the vertical lines shown here are proportional to the negative of the weight factors for an intrinsic fault in an fcc crystal. Figure 5 is a similar plot, the tabulated F_N in this case being those of Animalu[12] and Yamamoto,[8] while the corresponding asymptotic curve was computed for the Heine–Abarenkov form factor.[13–15] The points and asymptotic curve for the empty-core model correspond to the energy–wave-number characteristic shown in Fig. 1. Potential functions for magnesium and beryllium were also computed but are not shown here because the main features we wish to consider are similar for all three polyvalent metals.

The first thing we should note regarding Fig. 4 is that it is very easy to see, from a plot such as this, how the interactions between various pairs of planes contribute to the stacking-fault energy. At the second nearest interplanar distance ($n = 2$) in aluminum, for example, J is positive and the weight $-N(2)$ is also positive. This indicates, according to Eqs. (1) and (4), that the interaction between second-nearest-neighbor planes is such as to oppose the formation of an intrinsic fault; i.e., this particular interaction leads to a positive contribution to the stacking-fault energy. At the next interplanar distance, however, the contribution is negative because J and $-N(3)$ are of opposite sign. The fourth- and fifth-neighbor planes are not important because $N(4) = 0$ and $J(5h) \approx 0$. Thus, neglecting possible contributions from larger n (which turns out to be valid in this case), we can see that the reason aluminum has a positive intrinsic fault energy, or equivalently, the reason that the fcc structure is stable against faulting, is because the positive contributions of second-nearest-neighbor planes outweigh the negative contributions of third-nearest-neighbor planes. The same kind of analysis can, of course, be applied to the magnesium plot shown in Fig. 3. Here the fact that the hcp structure is stable tells us that the positive stacking-fault-energy contributions from second- and third-nearest-neighbor planes must be greater than the negative contribution from more distant pairs.

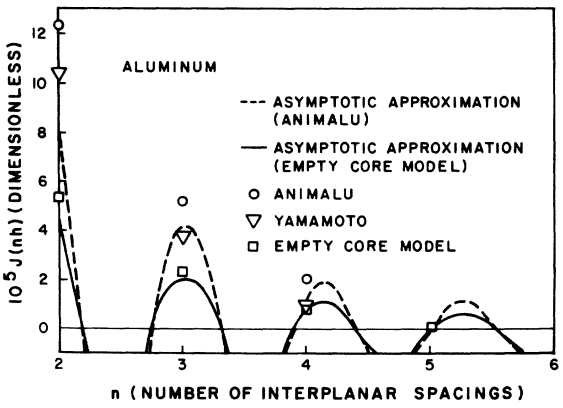

FIG. 5. Interplanar potential functions for aluminum based on the Heine–Abarenkov and empty-core-model potentials.

Another point illustrated in Fig. 4 is that at the interplanar distances of importance here, it makes very little difference whether we use the data of Shaw, Shaw and Pynn, or Shyu *et al.* in the calculation of J. Since the only difference among these three sets of data is the way in which exchange and correlation effects are handled in the screening calculation, the comparison shown here indicates that such effects are of little consequence in the present context. In fact, the good agreement of the results obtained with the other two characteristics with the result based on Shaw's data, which was calculated in the Hartree approximation, suggests that exchange and correlation corrections can safely be ignored in calculations of stacking-fault energies. The reason is, as we indicated earlier, that the effects of such corrections are observed at interplanar or interatomic distances somewhat shorter than those involved in the calculation of stacking-fault energies.

Figure 4 also illustrates the generally good

agreement experienced between the numerically computed value of J and the value obtained from the asymptotic approximation of Blandin *et al.* at separation distances of about four interplanar spacings. Further examples are provided by the Yamamoto and empty-core results shown in Fig. 5. Thus, as we indicated in Sec. III, it was possible to terminate the numerical-integration computations at $n = 4$ and, in effect, use the asymptotic curve for larger n without introducing serious errors in most applications.

An exception is illustrated in Fig. 5, where it is evident that computed values based on Animalu's semilocal energy–wave-number characteristic are significantly greater than the corresponding asymptotic curve. This difficulty was also observed with the Animalu calculation for magnesium and, to a much greater extent, with the beryllium calculation. In fact, with beryllium, the disagreement was so serious that we were not able to obtain even a reasonable estimate of the stacking-fault energy based on the Animalu data. Some difficulty was also experienced with the beryllium potentials based on the data of Shaw, Shaw–Pynn, and Shyu *et al.*, but not to such an extent as to completely invalidate the corresponding estimates of γ.

We can get some idea of the influence of nonlocality through a comparison of the Animalu and Yamamoto results shown in Fig. 5, since Yamamoto's data were obtained from a fully nonlocal treatment of the same model potential used in Animalu's calculations. The principal result is just what one would expect from Shaw's[4] investigation of similar effects on interionic potentials, namely, that a fully nonlocal treatment tends to diminish the amplitude while preserving the frequency and phase of the long-range oscillations of the potential function. It should be noted, however, that Animalu's energy–wave-number characteristic is semilocal, in the sense that he made use of certain simplifying approximations, usually invoked in the local theory, in performing the final integration to obtain F_N.[12] If a truly local approximation had been employed, Shaw's[4] studies indicate that the amplitude of the oscillations in J would be even greater than that obtained with the Animalu approximation. We conclude, therefore, in agreement with Shaw, that nonlocality must be accounted for in any accurate first-principles predictions of interionic or interplanar potentials.

This is not to say, however, that we cannot use simpler, empirically adjusted local models for the prediction of trends or even for obtaining rough estimates of the values of the stacking-fault energy itself, provided that we have some prior knowledge of the general features of the nonlocal energy–wave-number characteristic. This is illustrated by the fact that the empty-core calculations shown in Fig. 5 actually agree rather well with the more sophisticated first-principles results shown in Fig. 4. The energy–wave-number characteristic used here was of the usual form,[11]

$$F_N(q/k_F) = \{[\epsilon(q) - 1]/\epsilon(q)\} M^2(q/k_F), \tag{8}$$

where $\epsilon(q)$ is the Hartree dielectric function and

$$M(x) = \cos(\pi x/2x_0)\, e^{-Dx^2}. \tag{9}$$

The parameter x_0 was fixed by requiring that the first zero in F_N coincide with that in Animalu's tabulation, and the damping parameter D was chosen to bring the peak near $q = 2k_F$ down into rough agreement with tabulated nonlocal functions. The value used for all three polyvalent metals was $D = 0.12$, which is somewhat larger than the damping parameters usually employed in local-empirical-pseudopotential studies.[11] This value did, however, lead to rather good agreement with the nonlocal energy wavenumber characteristics and interplanar potential functions for all three polyvalent metals, the results shown in Figs. 1, 4 and 5 being typical.

Turning now to the noble metals we show a representative result in Fig. 6. This is the interplanar potential function for gold, as determined from Moriarty's energy–wave-number characteristic,[16] along with the corresponding asymptotic approximation. The second set of points shown here was obtained with the altered energy–wave-number characteristic shown in Fig. 2; the significance of these data will be discussed shortly. Again, the vertical lines are proportional to the weights $-N(n)$ for an intrinsic fault in an fcc crystal.

From these results, and those for copper and silver as well, it is evident that there is serious diagreement between the interplanar potential func-

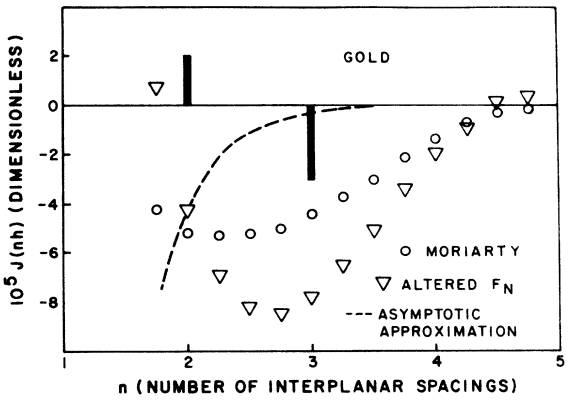

FIG. 6. Interplanar potential functions for gold. The corresponding energy–wave-number characteristics are shown in Fig. 2.

tion predicted by the asymptotic theory and that obtained by direct numerical integration. This is not surprising in view of the fact that the asymptotic approximation is based on the assumption that, as far as the long-range behavior of J is concerned, the logarithmic singularity at $q = 2k_F$ is the dominant feature of the energy–wave-number characteristic. Thus, when the asymptotic form resulting from this assumption turns out to be a rapidly decaying exponential, as it does here, there emerges the possibility that other features of F_N may dominate at large values of nh. Our results show that this is in fact the case for the noble metals and suggest that similar results might be expected for other monovalent metals as well.

One encouraging consequence of the radical departure of the numerically computed J from the asymptotic approximation is that the computed values lead to positive energies for fcc faults while the asymptotic theory incorrectly predicts negative fault energies.[5] As is evident from Fig. 6, this happens because the positive contribution from third-nearest-neighbor planes is strong enough to offset the negative contribution from $n = 2$ interactions. Thus, the strong negative dip in J between $n = 2$ and 3 seems to be essential to the correct prediction that the fcc noble metals are stable against faulting.

Unfortunately, the dip in J is not strong enough. In Sec. V we will present predictions of γ that show that although positive energies are obtained for fcc faults, these energies are low by about an order of magnitude for gold and silver. Furthermore, our calculations also indicate that noble-metal fault energies for the unstable hcp crystals, which one would expect to be negative, turn out to be positive and quite large. This indicates, of course, that the hcp structure is more stable than the fcc structure, an incorrect prediction that agrees with Moriarty's total-energy calculation.[16] The trouble is obviously due to some inaccuracy in the Moriarty F_N data, probably, as he suggests, to his neglect of the subtle effects of crystal field splitting on s-d hybridization.[16] However, whatever the basic reason may be, it is of interest to note that the correct interplanar potential function must have a more pronounced minimum than that obtained from the Moriarty data. This would produce a greater difference between the positive ($n = 3$) and the negative ($n = 2$) contributions to the fcc intrinsic-fault energy, while at the same time reducing the predicted values of fault energies in the hypothetical hcp structure.

An interplanar potential function having the desired characteristic is shown in Fig. 6. This curve was generated from the altered F_N data shown in Fig. 2. We wish to emphasize that this alteration is entirely arbitrary; it was obtained by trial-and-error manipulations of the data in the neighborhood of $q/k_F = \chi$, since J seems to be most sensitive to the detailed curvature of F_N in this region. We think the result is of interest, however, because it shows that for the noble metals at least, seemingly insignificant changes in the energy–wave-number characteristic can lead to major changes in the interplanar potential (Figs. 2 and 6) and in the predicted stacking-fault energy (the alteration shown here increased the fcc intrinsic-fault energy by about a factor of 7). Unfortunately this extreme sensitivity to detailed structure in the energy–wave-number characteristic also suggests that, in contrast to the situation for polyvalent metals, there is little hope for making useful estimates on the basis of simple models for the noble metals.

V. STACKING-FAULT ENERGIES

Table II is a listing of intrinsic-stacking-fault energies for the stable structures of aluminum, magnesium, and beryllium. Calculations were also performed for extrinsic and twin faults and, with few exceptions, the approximate relations for hcp crystals[10] $\gamma_{ext} \approx \frac{3}{2}\gamma_{int} \approx 3\gamma_{twin}$, were found to hold within about 10%. The exceptions were the twin-fault energies in magnesium, as determined from the energy–wave-number characteristics of Shaw and Pynn, Shaw, and Shyu *et al.*, where we

TABLE II. Intrinsic-stacking-fault energies in erg/cm^2 for aluminum (fcc), magnesium (hcp), and beryllium (hcp).

Data source	Al	Mg	Be
Shaw–Pynn	57.9	13.9	439
Shaw	52.1	8.54	390
Shyu *et al.*	69.2	16.6	468
Animalu	104	33.4	•••
Yamamoto	110	37.7	305
Empty-core model	43.1	11.5	128
Other calculations	195[a] 62[b] 142[c]	8.7[f] 30[a] 50[g]	225[f]
Experimental estimates	135[d] 135–280[e]	60–93[h] 100–150[d]	190[i]

[a]Reference 17; based on Animalu data.
[b]Reference 18; based on Shaw data.
[c]Reference 18; based on Animalu data.
[d]Reference 20.
[e]P. C. J. Gallagher, Met. Trans. 1, 2429 (1970).
[f]Reference 19; based on Shaw data.
[g]Reference 9; based on Harrison's pseudopotential.
[h]D. H. Sastry, Y. V. R. K. Prasad, and K. I. Vasu, Scripta Met. 3, 927 (1969).
[i]H. Conrad, Air Force Materials Laboratory Report No. AFML-IR-65-310 (1965) (unpublished).

TABLE III. Intrinsic-stacking-fault energies in erg/cm^2 for fcc copper, silver, and gold. Calculated values are based on the energy–wave-number characteristics of Moriarty (Ref. 16).

	Cu	Ag	Au
Calculated	44.8	1.7	4.8
Average experimental estimate[a]	55	21.7	50

[a]P. C. J. Gallagher, Met. Trans. 1, 2429 (1970).

found $\gamma_{ext} \approx 2.3\gamma_{twin}$. With fcc aluminum we obtained, to within about 25%, $\gamma_{ext} \approx \gamma_{int} \approx 2\gamma_{twin}$. For the unstable close-packed structures (hcp aluminum and fcc magnesium and beryllium) we obtained negative energies for all three types of fault, thus correctly indicating the instability of these structures against faulting.

Intrinsic-fault energies for fcc copper, silver, and gold, as determined from Moriarty's energy–wave-number data, are shown in Table III. As was noted in the Sec. IV, the hcp fault energies for these metals, rather than being negative as they should be, were calculated to be positive and quite large ($\gamma = 26$, 15, and 25 erg/cm^2 for the hcp intrinsic-fault energies in copper, silver, and gold, respectively). The good agreement with experiment obtained for the fcc intrinsic-fault energy in copper is therefore probably fortuitous.

When the energy–wave-number characteristic for gold was altered as shown in Fig. 2, we obtained 37 and 20 erg/cm^2 for the fcc and hcp intrinsic faults, respectively. We wish to emphasize again, however, that although this change is in the right direction, the alteration of F_N shown in Fig. 2 is entirely arbitrary, and serves only to illustrate the sensitivity of noble-metal results to rather minor features in the energy–wave-number characteristics. This being the case, there is not much more we can say about the noble metals except to note that the calculation of stacking-fault energies appears to be a very demanding test of the accuracy of the energy–wave-number characteristic in the vicinity of the smallest reciprocal-lattice spacing.

Returning now to the polyvalent metals we can see, as anticipated from the plots of the interplanar potential function shown in Fig. 4, that exchange and correlation effects are not particularly significant since little change was experienced in going from the Hartree approximation (Shaw) to calculations with such many-body corrections included (Shaw and Pynn and Shyu *et al.*). The only appreciable effect was that shown for magnesium, where there is roughly a factor of 2 spread in predicted intrinsic-fault energies.

Results based on the energy–wave-number data of Animalu and Yamamoto indicate that, in two cases at least, differences between fully nonlocal and semilocal calculations are not as great as one might expect from the data shown in Fig. 6. Apparently what has happened in aluminum is that the large differences between the Animalu and Yamamoto calculation of J at second- and third-nearest-neighbor planes are approximately canceled in performing the sum in Eq. (7) (recall that the second-nearest-neighbor plane gives a positive contribution to γ while the third-nearest-neighbor plane yields a negative contribution). A similar situation exists for magnesium, the cancellation in this case being between the positive contributions of the second- and third-neighbor pairs and the negative contribution of fourth-nearest-neighbor planes. For beryllium, however, the effect was quite marked because the Animalu data gave correction terms [those in the sum on the right side of Eq. (7)] that were about an order of magnitude greater than the corresponding values obtained with Yamamoto's data. As was mentioned previously, it is this large deviation of the numerically integrated J from the asymptotic approximation that prevented us from obtaining a meaningful estimate of γ for beryllium from Animalu's data. One should, of course, expect to encounter difficulties with the local or semilocal approximation for beryllium because the absence of p states in the core leads to a strongly nonlocal pseudopotential.[11]

It would appear, however, from results such as those illustrated in Figs. 1, 4, and 5, that in the present context the principal effect of a fully nonlocal treatment is the suppression of the peak in F_N near $q = 2k_F$ and the resulting reduction in the interplanar potential function J. Thus, given some prior knowledge of the magnitude of the peak in the nonlocal F_N, it should be possible to use empirically adjusted local-model potentials, even for such strongly nonlocal elements as beryllium, to obtain rough estimates of γ. To test this idea, we used the modified empty-core model described in the Sec. IV to compute the intrinsic-fault energies shown in Table II. Considering the fact that the model is extremely simple and that the same damping-factor adjustment was used for all three metals, the agreement with other predictions of γ is surprisingly good. Although improved agreement could probably be obtained by further adjustments of the model-potential parameters, we see little reason for doing so, particularly since there is still considerable uncertainty as to what one should assume for the correct value of γ. In any case, even if γ were known more accurately, the real merit of such simplified models lies in their ability to predict trends in relative magnitudes and,

perhaps, obtain rough estimates of γ itself, with minimum requirement for prior adjustment of the model-potential parameters. In this sense, then, the rough agreement shown here is actually quite encouraging.

As far as the more rigorous models are concerned, comparisons of our computations with those performed by other methods met with mixed results. With aluminum, for example, our value of 104 erg/cm^2 based on Animalu's data is significantly lower than Hodges[17] value of 195 erg/cm^2, which was computed from the same energy-wave-number characteristic using the reciprocal-space formulation. It is also lower than the value of 142 erg/cm^2 obtained by Wilkes and Sargent, [18] who used the same data in a real-space treatment involving the sums of interionic potentials over a large number of pairs of ions in the faulted and perfect structures. There is, unfortunately, reason to question the accuracy of both the Wilkes-Sargent result and our own. The Wilkes-Sargent calculation did not make use of the asymptotic theory of Blandin *et al.* and, therefore, suffers from a convergence difficulty typical of pairwise sums over the direct lattice. Our calculation in this case is also subject to a convergence uncertainty because, as we noted earlier, with the Animalu data it was not possible to carry the calculation out to distances large enough to obtain agreement with the asymptotic potential. We can be less certain of possible sources of error in Hodges result, although the fact that he had to perform a number of rather sensitive computations by hand could have resulted in some inaccuracy. The only other comparison we can make for aluminum is our value of 52 erg/cm^2, obtained from Shaw's data, with the Wilkes-Sargent value of 62 erg/cm^2. In view of the convergence difficulty experienced by Wilkes and Sargent this ageement is probably as good as can be expected.

For magnesium, our results based on the Shaw and Animalu energy-wave-number data are in excellent agreement with the values reported by Ducharme[19] (8.7 erg/cm^2 with Shaw's data) and Hodges[17] (30 erg/cm^2 with Animalu's data). Harrison's calculation of 50 erg/cm^2 was based on a different energy-wave-number characteristic[9] and is included here only as a further illustration of the rather significant differences that can result from the use of different potentials. The only comparison we can make for beryllium is our calculation of the fault energy with that of Ducharme, [19] both of which made use of Shaw's energy-wave-number characteristics. Here again, however, we experienced some convergence difficulty, which could account for the discrepancy.

Agreement with experimental results is generally rather poor. We are not particularly concerned that our results for beryllium seem to be too high, because of the convergence problem discussed earlier. The poor agreement for magnesium and aluminum, however, deserves further comment.

First we should point out that it is quite possible that the experimental values for these metals are too high, since experimental difficulties are usually encountered when γ is greater than about 20 erg/cm^2. [20] The source of this difficulty is that fault widths are roughly proportional to the inverse of the stacking-fault energy and are therefore too small for direct observation when γ is large. One must then resort to indirect methods, such as the observation of dislocation-loop annealing rates, [20] to obtain estimates of γ. Interpretations of such data necessarily involve the assumption of physical models and subsequent calculations to extract γ from the direct experimental results. The present situation is therefore one of considerable uncertainty, as evidenced by the spread in experimental data referenced in Table I. For this reason we are inclined to regard comparisons with experiment primarily as tests of the ability to predict trends, placing less emphasis on the achievement of absolute numerical agreement.

As for why the calculations might be inadequate, if indeed it is the calculations that are at fault, we cannot offer a completely satisfactory explanation. While it is certainly possible that the numerical problems discussed in Sec. II led to significant errors in the predictions, agreement with calculations performed by other methods seems to indicate that this is not the case. Nor does it seem likely that uncertainties in exchange and correlation corrections are responsible, because we can totally ignore such effects and still obtain about the same answers. Nonlocal effects can be ruled out because they are fully accounted for in some of the energy-wave-number characteristics of concern here. Although magnesium and aluminum are generally considered "simple" metals, in the sense that the matrix elements of their pseudopotentials are small, we cannot ignore the possibility that higher-order terms in the perturbation expansion, which would be structure dependent and therefore different in the faulted and perfect crystals, may have a greater effect in stacking-fault-energy calculations than they do in calculations of other properties. Still, if agreement with presently available experimental data is our goal, we are looking for a factor of about 2 or 3 increase in γ, and the possibility that a higher-order perturbation treatment would give us such a factor does seem remote.

Thus, because the major sources of error usually present in defect studies are of diminished importance in stacking-fault-energy calculations, it is difficult to identify any one uncertainty as being

most likely to cause disagreement with experiment. The best we can do at present is to simply note that there are still many approximations and idealizations present, both in the theory and in the derivation of stacking-fault energies from experimental observations and, for this reason, perhaps we should not expect much better agreement than that obtained here.

VI. SUMMARY AND CONCLUSIONS

We have applied the method of Blandin, Friedel, and Saada[5] to the calculation of stacking-fault energies in aluminum, magnesium, beryllium, copper, silver, and gold. Energy–wave-number characteristics representing various degrees of refinement of the theory were used in order that the sensitivity of the result to such refinements could be determined.

Our results for the polyvalent metals indicate that the stacking-fault energy is influenced by many-body and nonlocal effects, but not nearly so much as to invalidate the use of approximate model potentials. In fact, comparisons of results based on a simple local potential with those based on the more sophisticated nonlocal treatments suggest that, with certain semiempirical adjustments to account for the major effects of nonlocality, the simpler theory is entirely adequate for predicting trends and for obtaining rough estimates of the stacking-fault energy, as long as the use of such models is restricted to polyvalent metals. Calculations for copper, silver, and gold, on the other hand, show that the stacking-fault energies of these metals (and probably other monovalent metals as well) are quite sensitive to minor alterations in the energy–wave-number characteristic. The use of simplified semiempirical models for these metals could therefore lead to serious error.

The real-space formulation of Blandin *et al.* was found to have both its advantages and disadvantages. On the positive side, the fact that the method involves a sum of interplanar potentials over pairs of close-packed planes offers some interpretative advantages over the reciprocal-space treatment. It is very easy to see, for example, in terms of the amplitudes and oscillatory characteristics of the interplanar potentials, how interactions between various pairs of planes contribute to the stability or instability against faulting for a given close-packed structure.

The principal disadvantage of the method is that it presents some difficult computational problems, both in the sensitivity of the result to numerical-integration approximations and in the usual convergence problem associated with real-space lattice sums. Still, with the aid of the asymptotic approximations developed by Blandin *et al.*, the latter difficulty can be largely overcome, and the method therefore offers an instructive, though perhaps somewhat less accurate, alternative to the more familiar reciprocal-space treatment.

Comparisons of predicted stacking-fault energies with experimental results were disappointing, the calculated values in most cases being substantially lower than experimental values. Since the major uncertainties that one usually has to deal with in defect-energy calculations (the validity of perturbation theory, exchange and correlation corrections, and the importance of nonlocal effects) are of minimal significance in the present application, it is difficult to explain why this disagreement exists. Although this is an unsettling situation, and one that we think deserves further study, we can draw some satisfaction from the fact that the calculations do correctly predict the stabilities of close-packed structures against faulting, and, at least roughly, the relative magnitudes of stacking-fault energies for different metals. The calculations also indicate that trends such as these can be predicted with reasonable success with a local-model potential, provided that the major effects of nonlocality, the suppression of the peak in the energy–wave-number characteristics at $q = 2k_F$, is approximately accounted for by an empirical adjustment. This may well be the most important result of the present work because it suggests that in spite of quantitative difficulties that seem to persist in even the most refined version of the theory, there is still much that can be learned from the simplest local approximation.

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