# CALCULATION OF SURFACE ENERGY AS A FUNCTION OF ORIENTATION FOR CUBIC CRYSTALS 

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## Summary


#### Abstract

The surface energies of face-centred and body-centred cubic crystals have been calculated on the assumption that the atoms interact with pairwise potentials of either Morse or Mie type. The calculations take into account interactions between all neighbours and have been carried through for about 50 crystallographically distinct orientations of the surface. No allowance has been made for relaxation of the surface atoms. Stereographic contour plots of the surface energy are presented for four Morse and six Mie potentials in each structure. It is shown that, for all these potentials, a good approximation to the results can be obtained by counting only the numbers of nearest and next-nearest neighbour bonds that are broken and associating empirically determined energies with each of these.


## I. Introduction

In principle, if the atoms in a crystal can be regarded as interacting with a particular pairwise potential, then it is possible to calculate the energy involved in creating particular surfaces by summing the energies associated with all atomic pairs that are split up in this creation. The literature contains many calculations of this type, most of which have been limited to a few different surfaces (e.g. Stranski and Suhrmann 1947; Benson and Claxton 1964; Drechsler and Liepack 1965) and/or to an interatomic potential that has been neglected for all but the nearest few shells of neighbours (e.g. Stranski and Suhrmann 1947; Mackenzie, Moore, and Nicholas 1962; Drechsler and Liepack 1965).

The present paper reports calculations of the surface energy for 50-60 crystallographically distinct orientations in face-centred (f.c.c.) and body-centred (b.c.c.) cubic crystals, using potentials of both Mie (Lennard-Jones) and Morse types, and taking account of the interactions of all neighbours. No allowance has been made for any relaxation that may occur among the surface atoms to minimize the surface energy, but a study of this effect will be reported later.

## II. Method of Calculation

With pairwise interactions, it is convenient to say that each atom is linked to each other atom by a "bond" and to associate an energy with each such bond. When an infinite crystal is divided into two parts, a number of these bonds will be "broken", i.e. will be increased to infinite length, and the energy associated with each new surface can be computed as one-half of the increase in energy associated with the breaking of these bonds. If $\phi(r)$ is the chosen interaction potential for two atoms separated by a distance $r$ and a particular bond is specified by the interatomic vector

[^0]$\mathbf{u}_{i}$ of magnitude $u_{i}$, then the breaking of this bond will contribute to each surface an energy
\[

$$
\begin{equation*}
E_{i}=\frac{1}{2}\left\{\phi(\infty)-\phi\left(u_{i}\right)\right\} . \tag{1}
\end{equation*}
$$

\]

It is cústomary to choose the origin of $\phi$ so that $\phi(\infty)=0$ and we then have

$$
\begin{equation*}
E_{i}=-\frac{1}{2} \phi\left(u_{i}\right) . \tag{la}
\end{equation*}
$$

In the present work, the division is assumed to occur along a mathematical plane of a particular orientation specified by the normal vector $\mathbf{h}$ of magnitude $h$, and the energy computed is then treated as the surface energy $\gamma(\mathbf{h})$ for this orientation. If $n\left(\mathbf{u}_{i}\right)$ is the number of bonds with original vector $\mathbf{u}_{i}$ that are broken per unit area of surface, then

$$
\begin{equation*}
\gamma(\mathbf{h})=\sum E_{i} n\left(\mathbf{u}_{i}\right) \tag{2}
\end{equation*}
$$

where the summation is over all interatomic vectors within the crystal. Following Mackenzie, Moore, and Nicholas (1962), we can write

$$
\left.\begin{array}{rlrl}
n\left(\mathbf{u}_{i}\right) & =\mathbf{h} \cdot \mathbf{u}_{i} / \Omega h & & \text { if } \mathbf{h} \cdot \mathbf{u}_{i} \geqslant 0  \tag{3}\\
& =0 & & \text { if } \mathbf{h} \cdot \mathbf{u}_{i} \leqslant 0,
\end{array}\right\}
$$

where $\Omega$ is the volume of crystal per atom. Thus equation (2) can be rewritten as

$$
\begin{equation*}
\gamma(\mathbf{h})=(\mathbf{1} / \Omega h) \Sigma E_{i} \mathbf{h} \cdot \mathbf{u}_{i} \tag{4}
\end{equation*}
$$

where all terms are calculable for any given interaction potential and the sum covers all $\mathbf{u}_{i}$ with positive $\mathbf{h} . \mathbf{u}_{i}$.
(a) Potentials Used

The interacting potentials used, all having a minimum of $-\phi_{0}$ at a distance $r_{0}$, have been either
(1) of Morse type, that is,

$$
\begin{equation*}
\phi(r)=\phi_{0}\left[\left\{1-\exp a\left(1-r / r_{0}\right)\right\}^{2}-1\right], \tag{5}
\end{equation*}
$$

where $a$ is the dimensionless Morse constant, or
(2) of Mie (Lennard-Jones) type, that is,

$$
\begin{equation*}
\phi(r)=\phi_{0}\left\{n\left(r_{0} / r\right)^{m}-m\left(r_{0} / r\right)^{n}\right\} /(m-n), \tag{6}
\end{equation*}
$$

where $m$ and $n(>m)$ are the exponents of the attractive and repulsive parts of the potential.
As is usual in these calculations, the constants in the potential are adjusted in all cases to minimize, for a perfect infinite crystal, the total lattice energy computed as a sum of pairwise interactions. This means that for a given $a$ or $(m, n)$ the ratio of $r_{0}$ to the lattice parameter is determined by calculations of lattice energy. This is discussed in some detail in Drechsler and Nicholas (1967a), where values of this ratio are given for a variety of Morse and Mie potentials.

Figure 1 shows some of the potentials considered, plotted against the positions of various neighbours. This figure is drawn exactly for the f.c.c. structure, but the
scale added for b.c.c. is still accurate to within $0 \cdot 5 \%$ for the potentials considered here, since, if we write $r_{1}^{*}$ for the nearest neighbour distance in the perfect crystal,


Fig. 1.-Plots of some Morse potentials (full lines labelled with Morse constants) and some Mie potentials (dashed lines with $(m, n)$ ). Plots of the $(6,10)$ and $(6,14)$ potentials would lie to the right and left of the $(6,12)$ plot; the $(4 \cdot 5,8)$ potential is almost coincident with the $(5,7)$ potential, being one linewidth to the right for most of its length. The linear scale across the centre of the figure has a unit equal to the lattice parameter $\alpha$ of an f.c.c. crystal and the values of $r_{0}$ (the minimum of the interaction potential) have been chosen so as to minimize the lattice energy of such a crystal. The numbers at the bottom of the figure indicate the distances to the first 12 shells of neighbours in such an f.c.c. crystal and those at the top show the positions of the first 13 shells in a b.c.c. crystal.
we find, for example, that

$$
\left.\frac{\left(r_{1}^{*} / r_{0}\right)_{\text {f.c.c. }}}{\left(r_{1}^{*} / r_{0}\right)_{\text {b.c.c. }}}=\begin{array}{ll}
1 \cdot 029  \tag{7}\\
1 \cdot 026
\end{array} \quad \begin{array}{l}
\text { for } a=3, \\
\text { for } a=5, \\
1 \cdot 025
\end{array} \quad \begin{array}{l}
\text { for }(m, n)=(5,7), \\
\text { for }(m, n)=(6,14) .
\end{array}\right\}
$$

The b.c.c. scale is drawn for a value of this ratio of $1 \cdot 024$.

The constants $\phi_{0}$ and either $a$ or ( $m, n$ ) can be chosen in two ways. In the first, the surface energies are computed for a whole range of values of these constants and these are then compared with some experimental data to determine the appropriate values for a particular material. This approach has been adopted in Drechsler and Nicholas (1967b), where measurements of the equilibrium shape of annealed crystals have been used to predict possible values for $a$ or ( $m, n$ ). Naturally, an approach based on equilibrium shapes or any other property dependent only on relative values of surface energy can give no information about the scale factor $\phi_{0}$.

The second approach, which has been adopted in this paper, is to select appropriate values for the constants on the basis of other data before calculating the surface energy. Thus, for Mie potentials the calculations reported are those for the commonly used Lennard-Jones $(6,12)$ form of the Mie potential, for the closely related $(6,10)$ and $(6,14)$ potentials, and for a few potentials whose significance has been suggested elsewhere (Fürth 1945; Drechsler and Nicholas 1967b). For Morse potentials, Girifalco and Weizer (1959) have calculated values of $\phi_{0}$ and $a$ ( $D$ and $\alpha r_{0}$ in their notation) for a variety of metals using experimental values of sublimation energy and compressibility. Surface energy calculations have been carried through for all values of the constants given by Girifalco and Weizer, and a selection is reproduced here. In all these cases, the Morse constant is between 3 and 5.

## (b) Method of Summation

Equation (4) can be rewritten as

$$
\begin{equation*}
\gamma(\mathbf{h})=(\mathbf{l} / \Omega h) \sum_{j} E_{j}\left(\mathbf{h} \cdot \sum_{k} \mathbf{u}_{k}\right) \tag{8}
\end{equation*}
$$

where the sum over $k$ covers all bonds, with positive $\mathbf{h} . \mathbf{u}_{k}$, that have a particular magnitude $u_{j}$, and the sum over $j$ covers all possible interatomic distances in the crystal. Physically, this means first summing (with $k$ ) over all bonds linking an atom to the atoms in a particular shell of neighbours and then summing (with $j$ ) over all shells. For later use, it is convenient to rewrite equation (8) as

$$
\begin{equation*}
\gamma(\mathbf{h})=\sum_{j} \mu_{j}(\mathbf{h}) E_{j} \tag{9}
\end{equation*}
$$

where

$$
\begin{equation*}
\mu_{j}(\mathbf{h})=(\mathbf{l} / \Omega h) \mathbf{h} \cdot \sum_{k} \mathbf{u}_{k} \tag{9a}
\end{equation*}
$$

is a "multiplicity factor" for the surface energy term associated with a broken bond from the $j$ th shell.

For Morse potentials, the sums were evaluated directly using 300 shells of neighbours, which is sufficient to ensure that the neglected terms, even in the worst case of $a=3$, have no effect on the eighth significant digit in the energy values. This number of shells corresponds to considering all bonds whose length is less than 17-18 times the distance between nearest neighbours.

For Mie potentials, the sums were evaluated directly for the first 500 shells of neighbours, i.e. for bond lengths up to $22-23$ times the interatomic distance. The contribution from more distant neighbours was then estimated as an integral and
added to the direct sum. For the exponent 6, this integral correction was of the order of $10^{-3}$ of the direct sum but rapidly became negligible for higher exponents. In all cases, the sums including the integral correction may be expected to be accurate to at least four digits.

Some of the calculations were checked by evaluating the sums of type (4) in the order adopted by Benson and Claxton (1964), i.e. in the order of increasing size of $\mathbf{h} . \mathbf{u}_{i}$. This method is slower than that generally adopted here since it involves more frequent evaluation of $\phi\left(u_{i}\right)$, but it does provide the additional information that is essential for calculations in which the surface atoms are allowed to relax. It also allows the Mie sums to be transformed into rapidly convergent series for small exponents and for orientations where the lattice planes parallel to the surface are densely packed, namely (100), (110), and (111). However, since the convergence of the transformed series falls off seriously for surfaces with higher indices, direct summation has been preferred in the present work.

## (c) Consideration of Oscillatory Potentials

Friedel (1962), Harrison (1963, 1964, 1965), Johnson, Hutchinson, and March (1964), and Enderby and March (1965) have suggested that the real interatomic potential is described better by an oscillatory function rather than by one of either a simple Morse or Mie type. Although potentials proposed for solids are in general not available in a convenient analytic form, Johnson, Hutchinson, and March prescribe for liquid metals a pair potential of the form

$$
\begin{equation*}
\phi(r)=A\left(r_{0} / r\right)^{3} \cos \{2 k(r+\beta)\} \exp (-\alpha r), \tag{10}
\end{equation*}
$$

where $A, r_{0}, k, \beta$, and $\alpha$ are constants. They further specify the values of these constants for $\mathrm{Li}, \mathrm{Na}, \mathrm{K}, \mathrm{Rb}, \mathrm{Cs}, \mathrm{Al}$, and Pb ; thus making it formally possible to calculate surface energies by use of equations (8) or (9). However, such calculations showed that $\gamma$ would always be negative for Li , that $x$ was negative for Na thus making all sums divergent, and that the ratio $\gamma_{\max } / \gamma_{\min }$ would be more than 3 for Rb . Since such results appear physically unreasonable, no further calculations were carried out with oscillatory potentials. In fact, it would seem unprofitable to pursue such calculations further until much better forms for the appropriate interatomic potential in the solid are available.

## III. Results

The results of the calculations are most conveniently displayed as contour plots of $\gamma$ within a unit stereographic triangle. A selection of such plots is shown in Figure 2 for f.c.c. crystals and in Figure 3 for b.c.c. crystals. All results have been normalized to unity at (111) in Figure 2 and at (110) in Figure 3, the necessary normalization factors being shown in the tables to the figures.

Figures $2(j)$ and $3(j)$ show the orientations for which calculations were, in general, made and these give an indication of the accuracy with which the contours can be drawn. In order to define $\gamma$ more clearly near the corners of the triangle, subsidiary calculations were carried out for sets of 25 extra orientations within some $7^{\circ}$ of each corner. Such orientations are not marked on Figures $2(j)$ or $3(j)$, nor are the results used in the calculations described in the next section.


| Plot | Symbol | $\frac{\gamma(111)}{\phi_{0} / \alpha^{2}}$ | $\phi_{0} / \alpha^{2}$ <br> $\left(\mathrm{erg} / \mathrm{cm}^{2}\right)$ | Plot | Symbol | $\frac{\gamma(111)}{\phi_{0} / \alpha^{2}}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| $(a)$ | $\mathrm{F} 4 \cdot 419(\mathrm{~Pb})$ | $7 \cdot 1447$ | $154 \cdot 2$ | $(e)$ | $(4 \cdot 5,8) \mathrm{F}$ | $43 \cdot 294$ |
| $(b)$ | $\mathrm{F} 4 \cdot 265(\mathrm{Ag})$ | $7 \cdot 7902$ | $320 \cdot 1$ | $(f)$ | $(4 \cdot 5,14) \mathrm{F}$ | $23 \cdot 203$ |
| $(c)$ | $\mathrm{F} 3 \cdot 894(\mathrm{Cu})$ | $10 \cdot 092$ | $422 \cdot 0$ | $(g)$ | $(5$, | $7) \mathrm{F}$ |
| $(d)$ | $\mathrm{F} 3 \cdot 680(\mathrm{Ca})$ | $12 \cdot 453$ | $83 \cdot 96$ | $(h)$ | $(6,10) \mathrm{F}$ | $8 \cdot 4531$ |
|  |  |  |  | $(i)$ | $(6,12) \mathrm{F}$ | $7 \cdot 4309$ |
|  |  |  |  | $(j)$ | $(6,14) \mathrm{F}$ | $6 \cdot 8778$ |

Figs. 2(a)-2(j).—Contour plots of surface energy for f.c.c. crystals using (a)-(d) Morse potentials and $(e)-(j)$ Mie potentials. The full contours are drawn at intervals of $0 \cdot 01$ in $\gamma(\mathbf{h}) / \gamma(111)$, dashed contours at intervals of $0 \cdot 005$, and dotted contours at intervals of 0.0025 . Where a maximum occurs other than at a corner of the triangle, the value shown represents the highest value found in this region. The dots in ( $j$ ) show the particular orientations for which calculations were made. The above table gives for each plot (1) a symbol for the potential (Drechsler and Nicholas 1967b) consisting of the value of either $a$ or ( $m, n$ ) together with F to denote f.c.c. and, for Morse potentials, the metal for which this value of $a$ is appropriate (Girifalco and Weizer 1959), (2) a normalization factor in which $\alpha$ is the lattice parameter of the crystal, and (3) for the Morse potentials, the value of $\phi_{0} / \alpha^{2}$ given by Girifalco and Weizer (1959).


Figs. 2(e)-2( $j$ )

## IV. A Two-term Approximation

As Herring (1951) has pointed out, if the surface energy is calculated by the broken-bond method for any finite set of bonds, a polar plot of the energy will consist of portions of spheres through the origin. Since the present calculations involve the contributions from some thousands of different bonds, the final plots of energy will consist of small portions of so many spheres that the identity of each will be lost.


| Plot | Symbol | $\frac{\gamma(110)}{\phi_{0} / \alpha^{2}}$ | $\phi_{0} / \alpha^{2}$ <br> $\left(\mathrm{erg} / \mathrm{cm}^{2}\right)$ | Plot | Symbol | $\frac{\gamma(110)}{\phi_{0} / \alpha^{2}}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| $(a)$ | $\mathrm{B} 4 \cdot 488(\mathrm{Mo})$ | $4 \cdot 3620$ | 1304 | $(e)$ | $(4 \cdot 5,8) \mathrm{B}$ | $26 \cdot 894$ |
| $(b)$ | $\mathrm{B} 4 \cdot 279(\mathrm{~W})$ | $4 \cdot 8611$ | 1591 | $(f)$ | $(4 \cdot 5,14) \mathrm{B}$ | $14 \cdot 155$ |
| $(c)$ | $\mathrm{B} 3 \cdot 951(\mathrm{Fe})$ | $6 \cdot 0708$ | $817 \cdot 1$ | $(g)$ | $(5, r 7) \mathrm{B}$ | $16 \cdot 722$ |
| $(d)$ | $\mathrm{B} 3 \cdot 530(\mathrm{Ba})$ | $9 \cdot 4451$ | $90 \cdot 41$ | $(h)$ | $(6,10) \mathrm{B}$ | $5 \cdot 2246$ |
|  |  |  |  | $(i)$ | $(6,12) \mathrm{B}$ | $4 \cdot 5602$ |
|  |  |  |  | $(j)$ | $(6,14) \mathrm{B}$ | $4 \cdot 1868$ |

Figs. 3(a)-3(j).-Contour plots of surface energy for b.c.c. crystals using (a)-(d) Morse potentials and $(e)-(j)$ Mie potentials. The full contours are drawn at intervals of $0.01 \mathrm{in} \gamma(\mathbf{h}) / \gamma(110)$, dashed contours at intervals of $0 \cdot 005$, and dotted contours at intervals of 0.0025 . Where a maximum occurs other than at a corner of the triangle, the value shown represents the highest value found in this region. The dots in ( $j$ ) show the particular orientations for which calculations were made. The above table gives for each plot (1) a symbol for the potential (Drechsler and Nicholas 1967b) consisting of the value of either $a$ or ( $m, n$ ) together with $\mathbf{B}$ to denote b.c.c. and, for Morse potentials, the metal for which this value of $a$ is appropriate (Girifalco and Weizer 1959), (2) a normalization factor in which $\alpha$ is the lattice parameter of the crystal, and (3) for the Morse potentials, the value of $\phi_{0} / \alpha^{2}$ given by Girifalco and Weizer (1959).


Figs. 3(e)-3(j)
However, in practice, it appears that the final plots can usually be approximated, within one stereographic triangle, as portions of one sphere for f.c.c. or two spheres for b.c.c. crystals. The implications of this are discussed below.

In broken-bond calculations the first approximation is to assume that only nearest neighbour interactions are significant, i.e. that

$$
\left.\begin{array}{rl}
\infty & \text { for } r<r_{0}  \tag{11}\\
\phi(r)=-\phi_{0} & \text { for } r=r_{0} \\
0 & \text { for } r>r_{0}
\end{array}\right\}
$$

In this case, $r_{0}$ is both the spacing between nearest neighbours and the position of the minimum interaction energy, while the value of $\phi_{0}$, the energy of the nearest neighbour interactions, is irrelevant for calculations of relative energies. This case has been discussed in some detail by Mackenzie, Moore, and Nicholas (1962), and Figures $4(a)$ and $4(b)$ show contour plots of the surface energy for the two structures.


Fig. 4.-Theoretical contour plots of surface energy (1) when only nearest neighbour interactions are considered in (a) f.c.c. and (b) b.c.c. crystals and (2) when nearest and second-nearest neighbour interactions are considered in (c) f.c.c. crystals with $\rho=0 \cdot 5$, and (d) b.c.c. crystals with $\rho=1$. The dashed lines in the b.c.c. plots show where corners occur in the contours.

The next approximation is to include second-nearest neighbour interactions as well, i.e. to use a potential of the form

$$
\left.\begin{array}{cl}
\infty & \text { for } r<r_{1},  \tag{12}\\
-\phi_{1} & \text { for } r=r_{1}, \\
0(r)= & \text { for } r_{1}<r<r_{2} \\
-\rho \phi_{1} & \text { for } r=r_{2}, \\
0 & \text { for } r>r_{2},
\end{array}\right\}
$$

where $r_{1}$ and $r_{2}$ are the distances between nearest and second-nearest neighbours and $\rho$ measures the relative strengths of the two interactions. This case is also treated by Mackenzie, Moore, and Nicholas (1962), $\dagger$ where it is shown that
(1) for f.c.c. crystals, the polar plot within the unit triangle for which $h \geqslant k \geqslant l \geqslant 0$ consists of portion of the sphere through the origin $O$ with diameter from $O$ along $[2+\rho 1+\rho \rho]$; and
(2) for b.c.c. crystals, this plot consists of portions of two spheres through $O$ with diameters from $O$ along [111] and [ $2+\rho \rho \rho$ ], the intersection of the spheres being along the zone from (110) to (211), that is, the [111] zone.

Figures $4(c)$ and $4(d)$ show contour plots of $\gamma$ calculated from such potentials with $\rho=0 \cdot 5$ for f.c.c. and $\rho=1$ for b.c.c. crystals.

A striking feature of the results shown in Figures 2 and 3 is that, although all are markedly different from the nearest neighbour plots in Figures $4(a)$ or $4(b)$, many bear a strong similarity to the appropriate plot in Figures $4(c)$ or $4(d)$, or to a similar plot for a different value of $\rho$. Thus, it looks as if a good approximation to the results could have been obtained from some treatment involving nearest and second-nearest neighbours only. In other words, a good approximation to $\gamma(\mathbf{h})$ should be given by

$$
\begin{equation*}
\gamma^{*}(\mathbf{h})=\mu_{1}(\mathbf{h}) E_{1}^{*}+\mu_{2}(\mathbf{h}) E_{2}^{*}, \tag{13}
\end{equation*}
$$

with $E_{1}^{*}$ and $\rho=E_{2}^{*} / E_{1}^{*}$ appropriately chosen and $\mu_{1}(\mathbf{h})$ and $\mu_{2}(\mathbf{h})$ defined as in equation (9a).

This approximation has been investigated by minimizing the sum

$$
\begin{equation*}
S=\Sigma\left\{\gamma(\mathbf{h})-\gamma^{*}(\mathbf{h})\right\}^{2} \tag{14}
\end{equation*}
$$

taken over all $\mathbf{h}$ in the present set of orientations, by variation in $E_{1}^{*}$ and $\rho$. Table 1 lists the values found for $E_{1}^{*}$ and $\rho$ for the same potentials that were considered in Figures 2 and 3.

Figure 5 shows plots of the error in the approximation for two Morse and two Mie potentials. This figure and the errors listed in the last four columns of Table 1 indicate the accuracy of the approximation. For the steep Mie potentials with $m=6$ and Morse potentials with $a \gtrsim 3 \cdot 6$, the maximum error is of the order of $5 \%$, but for the shallower potentials with $m \leqslant 5$ or $a<3 \cdot 6$ the maximum error can rise to $10-12 \%$. However, in all cases, this maximum occurs only in very restricted regions near one or two corners of the stereographic triangle and the average error over the whole triangle is always less than $3 \%$.

Table 1 also lists values of $E_{1}, E_{2} / E_{1}$, and, for the simplest planes, the fractional contribution to $\gamma$ that arises from the first two terms in equation (9), namely

$$
\left\{\mu_{1}(\mathbf{h}) E_{1}+\mu_{2}(\mathbf{h}) E_{2}\right\} / \gamma(\mathbf{h}) .
$$

As the influence of second neighbours (measured by $E_{2} / E_{1}$ ) decreases, this contribution from the first two terms increases and, as would be expected, the errors in the
$\dagger$ The final paragraph of the Appendix to this paper contains an error that is most easily corrected by replacing the definition $E_{2}=\rho E_{1}$ by $E_{2}=2 \rho^{\prime} E_{1}$, and then replacing $\rho$ by $\rho^{\prime}$ throughout the rest of the paragraph.

Table 1
ENERGY RELATIONS FOR POTENTIALS USED IN FIGURES 2 AND 3, TOGETHER WITH PARAMETERS OF THE TWO-TERM APPROXIMATIONS
The last four columns show the percentage error in the approximation at various orientations, the first of these being the largest negative error and the last the largest positive error that is found

| Potential | $\left\{\mu_{1}(\mathbf{h}) E_{1}+\mu_{2}(\mathbf{h}) E_{2}\right\} / \gamma(\mathbf{h})$ |  |  | $E_{1}$ | $E_{2} / E_{1}$ | $\rho$ | $E_{1}^{*}$ | Error (\%) in Approximation at: |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | (100) | (111) |  |  |  |  |  | (100) | (111) | (110) | $\sim(531)$ |
| Face-centred Cubic Crystals |  |  |  |  |  |  |  |  |  |  |  |
| $(m, n)=(4 \cdot 5,8)$ | $0 \cdot 078$ | $0 \cdot 093$ | $0 \cdot 092$ | $0 \cdot 2687$ | $1 \cdot 1546$ | $0 \cdot 5680$ | $4 \cdot 2326$ | -11.6 | $-6 \cdot 6$ | $-0 \cdot 2$ | $3 \cdot 8$ |
| $(4 \cdot 5,14)$ | $0 \cdot 184$ | $0 \cdot 189$ | $0 \cdot 203$ | $0 \cdot 4418$ | $0 \cdot 4336$ | $0 \cdot 5000$ | $2 \cdot 1013$ | $-10 \cdot 3$ | $-5 \cdot 9$ | $-0 \cdot 2$ | $3 \cdot 3$ |
| $(5,7)$ | $0 \cdot 134$ | $0 \cdot 155$ | $0 \cdot 156$ | $0 \cdot 2952$ | 1.0409 | $0 \cdot 5662$ | $2 \cdot 3306$ | $-10 \cdot 8$ | $-5 \cdot 8$ | $0 \cdot 1$ | $3 \cdot 7$ |
| $(6,10)$ | 0.508 | $0 \cdot 519$ | $0 \cdot 542$ | $0 \cdot 4700$ | 0.3484 | $0 \cdot 3843$ | $0 \cdot 8543$ | $-6 \cdot 3$ | $-3 \cdot 1$ | $0 \cdot 4$ | $2 \cdot 3$ |
| $(6,12)$ | 0.571 | 0.578 | $0 \cdot 603$ | $0 \cdot 4817$ | $0 \cdot 2862$ | $0 \cdot 3390$ | $0 \cdot 7794$ | $-5 \cdot 5$ | $-2 \cdot 7$ | $0 \cdot 4$ | $2 \cdot 0$ |
| $(6,14)$ | $0 \cdot 610$ | 0.613 | 0.639 | $0 \cdot 4875$ | $0 \cdot 2488$ | 0.3083 | $0 \cdot 7400$ | $-5 \cdot 0$ | $-2 \cdot 5$ | $0 \cdot 3$ | $1 \cdot 8$ |
| $a=4.419$ ( Pb ) | $0 \cdot 606$ | $0 \cdot 636$ | $0 \cdot 649$ | $0 \cdot 4443$ | $0 \cdot 4771$ | $0 \cdot 4218$ | 0.7092 | $-5 \cdot 3$ | $-2 \cdot 2$ | $0 \cdot 8$ | $2 \cdot 1$ |
| $4 \cdot 265(\mathrm{Ag})$ | $0 \cdot 555$ | $0 \cdot 590$ | $0 \cdot 601$ | $0 \cdot 4278$ | $0 \cdot 5452$ | $0 \cdot 4559$ | $0 \cdot 7508$ | $-6 \cdot 0$ | $-2 \cdot 5$ | $0 \cdot 8$ | $2 \cdot 3$ |
| $3 \cdot 894(\mathrm{Cu})$ | $0 \cdot 402$ | $0 \cdot 450$ | $0 \cdot 451$ | 0.3564 | $0 \cdot 8385$ | $0 \cdot 5493$ | $0 \cdot 9091$ | $-7 \cdot 8$ | $-3 \cdot 3$ | $0 \cdot 9$ | $3 \cdot 0$ |
| $3 \cdot 680$ (Ca) | $0 \cdot 291$ | $0 \cdot 346$ | $0 \cdot 339$ | $0 \cdot 2731$ | 1-2792 | $0 \cdot 6102$ | 1-0724 | $-9 \cdot 1$ | $-3 \cdot 9$ | $0 \cdot 9$ | $3 \cdot 5$ |
|  | (110) | (100) | (111) |  |  |  |  | (110) | (100) | (111) |  |


| $(m, n)=(4 \cdot 5,8)$ | $0 \cdot 066$ | $0 \cdot 057$ | $0 \cdot 080$ | $0 \cdot 1280$ | $3 \cdot 9056$ | $0 \cdot 7824$ | $4 \cdot 6707$ | $-12 \cdot 4$ | $-2 \cdot 8$ | $5 \cdot 8$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $(4 \cdot 5,14)$ | $0 \cdot 164$ | 0.167 | $0 \cdot 194$ | 0.3732 | 1-1944 | $0 \cdot 7656$ | $2 \cdot 5185$ | $-11 \cdot 1$ | $-2 \cdot 4$ | $5 \cdot 2$ |
| $(5,7)$ | $0 \cdot 113$ | $0 \cdot 101$ | $0 \cdot 135$ | $0 \cdot 1671$ | $2 \cdot 9925$ | $0 \cdot 8170$ | $2 \cdot 8765$ | $-11 \cdot 6$ | $-2 \cdot 3$ | $5 \cdot 8$ |
| $(6,10)$ | $0 \cdot 462$ | $0 \cdot 474$ | 0.517 | $0 \cdot 4193$ | 1-0353 | $0 \cdot 8162$ | 0.9460 | $-7 \cdot 0$ | $-0.8$ | $4 \cdot 2$ |
| $(6,12)$ | 0.525 | 0.542 | 0.581 | $0 \cdot 4407$ | 0.9221 | $0 \cdot 7860$ | $0 \cdot 8470$ | $-6 \cdot 2$ | $-0.7$ | 3•7 |
| $(6,14)$ | $0 \cdot 565$ | $0 \cdot 585$ | $0 \cdot 619$ | $0 \cdot 4529$ | $0 \cdot 8467$ | $0 \cdot 7565$ | $0 \cdot 7950$ | $-5 \cdot 7$ | $-0 \cdot 6$ | 3-4 |
| $a=4 \cdot 488$ (Mo) | $0 \cdot 561$ | $0 \cdot 566$ | $0 \cdot 621$ | $0 \cdot 3887$ | 1-2243 | $0 \cdot 9110$ | $0 \cdot 7598$ | $-5 \cdot 9$ | $0 \cdot 0$ | $4 \cdot 4$ |
| $4 \cdot 279$ (W) | $0 \cdot 493$ | $0 \cdot 494$ | 0.554 | $0 \cdot 3596$ | $1 \cdot 3560$ | $0 \cdot 9217$ | $0 \cdot 8346$ | $-6 \cdot 7$ | $-0.2$ | $4 \cdot 9$ |
| $3 \cdot 951$ (Fe) | 0.369 | $0 \cdot 358$ | $0 \cdot 425$ | $0 \cdot 2813$ | 1-7767 | $0 \cdot 9324$ | 1.0195 | $-8 \cdot 2$ | $-0 \cdot 6$ | $5 \cdot 8$ $7 \cdot 1$ |
| $3 \cdot 530$ (Ba) | $0 \cdot 152$ | $0 \cdot 119$ | $0 \cdot 182$ | $0 \cdot 04076$ | $11 \cdot 4476$ | $0 \cdot 9229$ | 1-5509 | $-10 \cdot 7$ | $-1 \cdot 3$ | $7 \cdot 1$ |

approximation decrease. However, the approximation is still remarkably good even when the first two terms account for less than $10 \%$ of the total surface energy.

The accuracy of the approximation has implications for those problems where it is desired to calculate energies of particular atomic configurations in a semiquantitative way. The most common procedure is to take account of nearest neighbours only, despite the large errors that are introduced thereby. The present results suggest that the inclusion of second neighbours can lead to significantly more reliable


Fig. 5.-Contour plots of the percentage error in the two-term approximation for (a), (b) f.c.c. and (c), (d) b.c.c. crystals. The heavy contour is the zero error and others are drawn at intervals of $1 \%$ (full lines) or $0.5 \%$ (dashed lines). The symbols for the plots as defined for Figures 2 and 3 are
(a) $(6,12) \mathrm{F}$,
(b) F 3.894,
(c) $(6,12) \mathrm{B}$,
(d) $\mathrm{B} 4 \cdot 279$.
results, provided the energies associated with the interactions are treated as adjustable parameters. The differences found here between $E_{1}$ and $E_{1}^{*}$ and between $E_{2} / E_{1}$ and $\rho$ show that it is profitless to calculate these energies from a given potential function. However, when only relative energy values are needed, Table 1 suggests that a good estimate should be obtained by taking $\rho$ between $\frac{1}{3}$ and $\frac{1}{2}$ for f.c.c. and between $\frac{3}{4}$ and 1 for b.c.c. crystals.

## V. Discussion

The present work has shown how the surface energy will depend on orientation if a pairwise potential of a given form operates in an unrelaxed crystal. The calculations are exact within the limits of this assumption and the results in Table 1 show that the effects of distant neighbours can be highly significant. However, for potentials of the type considered, quite a good approximation can be obtained by counting only first and second neighbours and associating empirically determined energies with each of these. This may account for the success of various arguments (e.g. Sundquist 1964) based on only these two groups of neighbours. When the calculations are extended to include the effect of surface relaxation, which will allow a reduction in the surface energy, the detailed results will change but no qualitative changes are to be expected in the orientation dependence of $\gamma$.

The most detailed experimental evaluation of a surface energy contour plot is that derived for gold by Winterbottom and Gjostein (1966). Normalizing their results to make $\gamma(111)=1$, they find $\gamma(100)=1.072$ and $\gamma(110)=1.047$ and the contour plot shows a maximum of $1 \cdot 077$ at about ( 1010 ) with a minimum at (111). The degree of anisotropy $\gamma_{\max } / \gamma_{\min }$ corresponds best to that given by a Mie potential with $m=6$ or a Morse potential with $a \simeq 4$. However, none of the pairwise potentials considered here predict a maximum close to (100) nor, in consequence, do they predict $\gamma(100)>\gamma(110)$. Indeed, as pointed out above, all predict that for f.c.c. crystals the maximum lies close to the zone from (210) to (111). Thus, any explanation of a maximum elsewhere in the triangle must be based on pair potentials significantly different from those used here or on a completely different approach. It may be worth noting in passing that the oscillatory potentials for lead and aluminium (Johnson, Hutchinson, and March 1964) do predict maxima near to (100) but the degree of anisotropy is around $1 \cdot 35-1 \cdot 4$.

## VI. References

Benson, G. C., and Claxton, T. A. (1964).—J. Phys. Chem. Solids 25, 367.
Drechsler, M., and Liepack, H. (1965).-Colloque Internat. du Centre National de la Recherche Scientifique No. 152, p. 49. (Paris.)
Drechsler, M., and Nicholas, J. F. (1967a).-Distribution of the lattice energy in cubic crystals and its variation with compression or expansion. J. Phys. Chem. Solids 28 (in press).
Drechsler, M., and Nicholas, J. F. (1967b).-On the equilibrium shape of cubic crystals. J. Phys. Chem. Solids 28 (in press).

Enderby, J. E., and March, N. H. (1965).-Adv. Phys. 14, 453.
Friedel, J. (1962).-J. Phys. Radium, Paris 23, 501.
Fürtif, R. (1945).-Proc. R. Soc. A 183, 87.
Girifalco, L. A., and Weizer, V. G. (1959).—Phys. Rev. 114, 687.
Harrison, W. A. (1963).-Phys. Rev. 129, 2512.
Harrison, W. A. (1964).-Phys. Rev. 136, All07.
Harrison, W. A. (1965).-Phys. Rev. 139, Al79.
Herring, C. (1951).-Phys. Rev. 82, 87.
Johnson, M. D., Hutchinson, P., and March, N. H. (1964).-Proc. R. Soc. A 282, 283.
Mackenzie, J. K., Moore, A. J. W., and Nicholas, J. F. (1962).—J. Phys. Chem. Solids 23, 185.
Stranski, I. N., and Suhrmann, R. (1947).—Annln Phys. 1, 153.
Sundquist, B. E. (1964).-Acta metall. 12, 67.
Winterbottom, W. L., and Gjostein, N. A. (1966).-Acta metall. 14, 1041.


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