ENERGY OF INTERFACES BETWEEN CRYSTALS: AN AB INITIO APPROACH

N. H. Fletcher and K. W. Lodge

Department of Physics
University of New England
Armidale, Australia

I. Introduction

For many purposes it is helpful to distinguish between two different approaches to problems involving distortions of crystals: the atomic and the metric. An atomic view is generally a pictorial one that takes account of individual atoms or molecules, their arrangements, and their interactions with one another; it is useful in making first-order models but is difficult when even semiquantitative calculations are required. A metric approach concentrates attention on the crystal lattice and often regards it as embedded in a uniform elastic medium, with certain limitations being placed upon the types of lattice discontinuity that are permitted. The degree of abstraction is thus higher than for an atomic approach and leads to some sacrifice in visualizing the physical situation, but at the same time certain patterns become much more explicit and semiquantitative calculations are quite readily possible.

In the discussion of crystal interfaces these two approaches can be fairly readily recognized. The pioneering work of Burgers (1940) and Bragg (1940) began with an atomic picture in which each crystal was supposed to be continuous up to the interface. They then abstracted this to a metric model in which the connections between the two parts of the bicrystal were provided by an array of dislocations. This abstraction provides an excellent description of the interface for small mismatches between the two crystals—orientation differences up to about 15° or lattice-parameter differences up to about 20%—but for boundaries of greater mismatch than this the dislocations begin to overlap and the picture is no longer clear.

The classic work of Read and Shockley (1950) showed how this dislocation model could be made into a semiquantitative theory and yielded the well-known result

$$E(\theta) = \tau\theta(A - \ln\theta) \qquad (1)$$

for the energy E per unit area of an interface with misorientation angle θ. The elastic coefficient τ was given explicitly in terms of the known elastic parameters of the crystal material, while the quantity A, which was related to the unknown "core energy" of a dislocation, was chosen to give best fit with experiment. Quite similarly, for a boundary between two crystals with fractional lattice-parameter difference δ, we find (Fletcher, 1971)

$$E(\delta) = \tau'\delta(A' - \ln\delta) \qquad (2)$$

This simple model was extended to orientations for which a row of equally spaced dislocations appears inadequate by the introduction of hierarchies of dislocations (Read and Shockley, 1950; du Plessis and van der Merwe, 1965), but while this artifice gives a successful numerical result it constitutes something of a bar to the visualization of the model in atomic terms. Further

important extensions of this approach to deal more particularly with epitaxial systems were introduced by Frank and van der Merwe (1949) and further developed by van der Merwe (1950) and his co-workers and by Fletcher (1964). These matters have been discussed in detail in earlier chapters and their considerable contribution to our understanding set out. The method suffers limitations because of the uncertainty of its application to interfaces of large mismatch, the necessity of making a further ad hoc introduction of crystal symmetry, and the somewhat artificial treatment of dislocation cores. We shall not, however, discuss these points here (see Fletcher, 1971).

Among treatments of interfaces that we might classify as primarily atomic are those based upon a simplified picture of atomic arrangements in the interface—"island" models (Mott, 1948), coincidence-lattice models (Brandon, 1966), and the like. A recent survey has been given by Gifkins (1969), and some of these matters are also discussed in the present volume. The 0-lattice concept introduced by Bollmann (1967) serves to formalize many of these ideas and to provide a basic means of describing and predicting atomic relationships across an interface.

Attractive and useful as these models are, they provide very little more than qualitative information about interface energy, even when they are extended to include some of the features of a dislocation description of the interface (Brandon, 1966; Bollmann, 1967). This is understandable, since the reasons for the development of the models were generally to provide a physical picture rather than to serve as an aid to computation.

The only basically atomic approach to a direct calculation of interface energy that has so far been developed appears to be that of Fletcher and his students (Fletcher, 1964, 1967; Fletcher and Adamson, 1966; Lodge 1970). The purpose of this chapter is to describe that method, to show its relationship to the various atomic and metric models mentioned above, and to show how it can be used to calculate interface energy in a real situation. Finally we shall make some remarks about interfacial entropy and interfacial free energy at a finite temperature.

II. The Interface Problem from First Principles

Before we begin to make any sort of calculation about an interface we must decide exactly what we are trying to calculate. Interfaces between real crystals will generally tend to modify their structure with time, so that the free energy of the system of which they are a part is minimized. This minimization will, however, generally be subject to one or more constraints governing the relative orientations of the two crystals (as when two grains grow together in a solidifying melt) or of the boundary relative to one of the crystals (as when an epitaxial film is deposited on a substrate of high melting point). We shall also generally assume that the two crystals are mutually insoluble.

We seek therefore, to be realistic, a minimum in the free energy of the system through variation of the interface configuration subject to the given constraints. Fortunately many of the systems in which we are interested are at temperatures well below the melting points of the crystalline components or of any possible grain-boundary eutectic, so that we may reasonably minimize the energy, thus calculating effectively the configuration and energy of the boundary at $0°K$. This is the approach we shall take, returning in the last section of the chapter to consider the effect of finite temperature on the calculation.

Because we are concerned in this book with the epitaxial growth of one crystalline material upon another, we can usefully restrict the range of possible problems to those in which we are given one semiinfinite crystal possessing a plane surface of known orientation. We then seek to determine the structure and energy of the interface between this crystal and another, which may be of finite thickness, growing upon it with arbitrary orientation. The actual preferred growth orientations will then be those that yield minima in the interfacial energy.

III. Symmetry Considerations and Coincidence Lattices

Naive ideas about epitaxial growth place emphasis upon the principle that coherent overgrowth of crystal material B on crystal A is likely to occur if some undistorted crystal plane of B can be laid down on top of the exposed face of A in such a way that a large fraction of the B atoms can be made to coincide with the sites of A atoms. We might go further and say that the greater the number of coincidences per unit area, the lower will be the energy of the resulting interface. Both these principles are correct and must find expression in any complete theory of interface energy. They obviously rest heavily on consideration of the symmetry and structure of the two crystals involved, and the geometrical working out of these ideas constitutes the theory of coincidence lattices. We shall take a little time to consider this before going on to the main development of our ideas.

Consider two crystals of quite general structure and imagine that the lattice of each is extended to fill all space so that these two lattices interpenetrate. Let us then translate one lattice relative to the other so that they have one lattice point as a common origin. For two arbitrary crystals there will in general be no other lattice point in common, but there will always be pairs of lattice points between which the spacing is arbitrarily small, if we go far enough away from the origin. We can therefore, by infinitesimal adjustment of orientation angle and lattice parameter, bring three other pairs of lattice points into coincidence with negligible change in the physics of the situation. If these pairs of points are chosen so that they are not collinear, and not coplanar

with the origin, then this action will have generated a three-dimensional grid of common lattice points that is called the "coincidence lattice." Its properties have been investigated by Friedel (1926) and more recently by Ranganathan (1966).

From our present point of view, possible low-energy boundaries between these two crystals in the given relative orientation are geometric planes containing a high density of coincidence-lattice points, and the reciprocal of the density of these points in the selected plane gives a measure of the grain-boundary energy. It is possible to extend these ideas to include dislocated coincidence boundaries (Brandon, 1966) but this need not concern us here.

Once we have established a coincidence lattice between two crystals we can proceed one step further, following the analysis of Bollmann (1967). Choosing one of the coincidence-lattice points as origin we can define a homogeneous linear transformation $\mathscr{A}$ performed about the point that establishes a one-to-one correspondence between the lattice points $\mathbf{r}$ of one crystal and the lattice points $\mathbf{r}'$ of the other by

$$\mathbf{r}' = \mathscr{A}\mathbf{r} \tag{3}$$

The transformation $\mathscr{A}$ will generally involve a rotation, a change in scale, and perhaps an angular distortion as well. In Fig. 1, for example, if we consider this to be an (001) section through two interpenetrating simple cubic lattices, $\mathscr{A}$ represents a relative rotation of $\tan^{-1}(1/2) = 26°34'$ about the [001] axis together with a uniform expansion by a factor $5^{1/2}$.

Looking again at Fig. 1 and remembering that the transformation $\mathscr{A}$ was applied about any one of the coincidence-lattice points, we see that we could have achieved exactly the same result by applying the same transformation $\mathscr{A}$
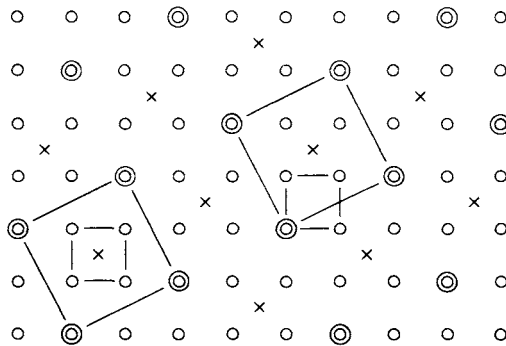

FIG. 1. A (001) section through two interpenetrating cubic lattices, represented by ○ and ◯, respectively, related by a transformation $\mathscr{A}$, showing points of the coincidence lattice and with points of the 0-lattice marked by ×.

about any one of the set of points marked ×. The set of all these points together with the coincidence-lattice points constitutes what Bollmann has called the "0-lattice" in the plane. In fact the 0-lattice, like the coincidence lattice, is a three-dimensional concept and consists of the complete set of points about which the transformation $\mathscr{A}$ could have been applied to achieve the same result. For the particular case shown in Fig. 1, the 0-lattice really consists of a set of lines running parallel to [001] and passing through the 0-lattice points in the (001) plane. For a more general transformation the 0-lattice is a discrete three-dimensional grid of points.

The 0-lattice has an analytical significance that we shall consider later. For the present we simply note the symmetry of both crystals about the points of the 0-lattice, which means that, no matter what elastic relaxation may take place when the physical interface is formed, the 0-lattice points will remain stationary. It can also be shown, though this is most useful for situations more complex than that shown in Fig. 1, that the 0-lattice gives directly the intensity maxima in the moiré pattern obtained by superposing the interface atoms of the two crystals (Bollmann, 1967).

IV. Interface Energy as a Variational Problem

Following this apparent digression, let us return to the program outlined in Section II: that we should write down an expression for the total energy of our bicrystal system and then minimize this with respect to the atomic configuration of the interface, subject to the constraints assumed for the physical problem. Formally we might proceed as follows.

Consider the potential energy $V_0(\mathbf{r})$ of a B atom at a point $\mathbf{r}$ just outside the plane surface of a crystal of A atoms located at points $\mathbf{R}_i$. If the interaction potential between individual A and B atoms is $v_{AB}(\mathbf{r})$, then

$$V_0(\mathbf{r}) = \sum_i{}^- v_{AB}(\mathbf{r} - \mathbf{R}_i) \tag{4}$$

where the minus on the summation indicates that it extends only over the lower half-space. If the B atom is actually part of a semiinfinite crystal of B with atom positions $\mathbf{r} = \mathbf{R}_i{}'$, then the energy of the entire system can be written

$$E_0{}^T = \sum_i{}^+ \sum_j{}^- v_{AB}(\mathbf{R}_i{}' - \mathbf{R}_j) + \tfrac{1}{2} \sum_{i \neq j}{}^- v_{AA}(\mathbf{R}_i - \mathbf{R}_j) + \tfrac{1}{2} \sum_{i \neq j}{}^+ v_{BB}(\mathbf{R}_i{}' - \mathbf{R}_j{}') \tag{5}$$

the last two terms representing the self-energies of the two semiinfinite crystals.

So far this formulation contains no variational parameters, but in principle we could simply vary all the atomic positions $\mathbf{R}$ and $\mathbf{R}'$ within small limits so

as to keep the interface position fixed and thus determine the configuration giving minimum energy. This is, of course, quite impracticable because of the number of atoms involved, so that we must devise some simplification.

To do this we note two things. In the first place, the interactions $v_{AB}(\mathbf{r})$ are generally of reasonably short range so that they should extend over only a few atomic layers on either side of the interface. In the second place, the variations of the self-energy terms describe essentially the elastic behavior of two semiinfinite crystals subject to stresses on their free surfaces. Provided these stresses are not too large, we should then be able to use continuum elasticity theory to approximate the variation of these last two terms.

To this end, let us suppose that all the atoms near the interface are varied in position so that $\mathbf{R}_i$ moves to $\mathbf{R}_i + \mathbf{F}_i - \mathbf{F}_0$, etc., where $\mathbf{F}_0$ is a small translation of the whole semicrystal and the $\mathbf{F}_i$ are small individual atomic displacements. The total energy then becomes

$$E^{\mathrm{T}} = \sum_i^+ \sum_j^- v_{AB}(\mathbf{R}_i' + \mathbf{F}_i' - \mathbf{R}_j - \mathbf{F}_j + \mathbf{F}_0)$$
$$+ E_{A_0}^{\mathrm{T}} + E_A^{\mathrm{T}}(\mathbf{F}_1, \mathbf{F}_2, \ldots) + E_{B_0}^{\mathrm{T}} + E_B^{\mathrm{T}}(\mathbf{F}_1', \mathbf{F}_2', \ldots) \qquad (6)$$

where $E_{A_0}^{\mathrm{T}}$ and $E_{B_0}^{\mathrm{T}}$ are the self-energies of the two undistorted semicrystals, $E_A^{\mathrm{T}}(\mathbf{F}_1, \mathbf{F}_2, \ldots)$ is the elastic strain energy in semicrystal A resulting from the displacement of the surface atom at $\mathbf{R}_i$ by an amount $\mathbf{F}_i$, etc., and similarly for B.

In this form the problem is now solvable in principle, although the number of independent parameters $\mathbf{F}$ and $\mathbf{F}'$ would still make a practical calculation prohibitively tedious. However, a great simplification is possible in special cases when there is a high density of coincidence-lattice points in the interface. When this happens, we note that symmetry requires the coincidence-lattice points to remain fixed during elastic relaxation and also requires the pattern of atomic displacements to repeat in each coincidence-lattice cell. The constancy of 0-lattice points during relaxation imposes further symmetry requirements on the distortions $\mathbf{F}$. In these special cases then, the variational formulation given in (6), together with explicit forms for $E_A^{\mathrm{T}}(\mathbf{F}_i)$ and $E_B^{\mathrm{T}}(\mathbf{F}_i)$ should make calculation relatively simple, since the number of independent variational parameters is small.

However, two problems with this approach have meant that it has not been seriously followed up. In the first place, the assumption of simple linear elastic behavior implied by the form of (6) is not justified for the individual atomic displacements implied in the variational problem. This necessarily introduces errors of unknown magnitude into the result. Second, there seems to be no simple way in which results of general utility can be derived from the variational function given in (6); all we can do is to calculate specific cases and then attempt to generalize.

In the next section we shall see that, by adhering to the general philosophy of the variational method but by carrying out all the operations in reciprocal space, we can overcome both these objections and derive valid and useful general results.

V. The Coincidence Boundary in Reciprocal Space

Returning to Eq. (4), we can write the potential energy of a B atom at position $\mathbf{r}$ outside a plane face of an A crystal with atomic positions $\mathbf{R}$ as

$$V_0(\mathbf{r}) = \sum_i{}^- v_{AB}(|\mathbf{r} - \mathbf{R}_i|) \equiv \sum_{\mathbf{R}}{}^- v(\mathbf{r} - \mathbf{R}) \tag{7}$$

where we shall adopt now the simplified notation on the right. This potential can be written in terms of its Fourier components $V_0(\mathbf{k})$ as

$$V_0(\mathbf{r}) = (N/8\pi^3) \int V_0(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}) \, d\mathbf{k} \tag{8}$$

where N is the (infinite) number of atoms in the crystal,

$$V_0(\mathbf{k}) = (1/N) \sum_{\mathbf{R}}{}^- v(\mathbf{k}) \exp(-i\mathbf{k} \cdot \mathbf{R}) \tag{9}$$

and $v(\mathbf{k})$, the Fourier transform of the atomic potential, is given by

$$v(\mathbf{k}) = \int v(\mathbf{r}) \exp(-i\mathbf{k} \cdot \mathbf{r}) \, d\mathbf{r} \tag{10}$$

With this artifice we can now write down the total interaction energy between the two crystals by summing $V_0(\mathbf{r})$ over all the atomic positions $\mathbf{R}'$ of the B crystal, assumed undistorted, to give

$$E_0^{\mathrm{T}} = \sum_{\mathbf{R}'}{}^+ V_0(\mathbf{R}') = (1/8\pi^3) \sum_{\mathbf{R}'}{}^+ \sum_{\mathbf{R}}{}^- \int v(\mathbf{k}) \exp[i\mathbf{k} \cdot (\mathbf{R}' - \mathbf{R})] \, d\mathbf{k} \tag{11}$$

Now we know that a sum like $\sum_{\mathbf{R}} \exp(i\mathbf{k} \cdot \mathbf{R})$, taken over an infinite crystal, vanishes unless $\mathbf{k}$ is a vector of the reciprocal lattice of that crystal. The sums over $\mathbf{R}$ and $\mathbf{R}'$ in (11) are only over semiinfinite crystals, so we cannot make exactly this statement. We can, however, reexpress the crystal geometry if necessary so that, instead of using a normal primitive cell, we use a cell of the same volume having two of its primitive translations lying in the plane of the interface so as to define a surface lattice for each crystal. We denote the surface lattice vectors by $\mathbf{R}_s, \mathbf{R}_s'$, respectively, and the areas of the surface unit cells by A, A'. We can also define a surface reciprocal lattice for each crystal, following the usual rules, and denote the vectors of this lattice by $\mathbf{G}_s, \mathbf{G}_s'$, respectively. Similarly, $\mathbf{k}_s$ is the component of $\mathbf{k}$ parallel to the surface.

Since the sums in (11) over $\mathbf{R}_s$ and $\mathbf{R}_s'$ are infinite, we can perform these in one of two equivalent ways to write either

$$\sum_{\mathbf{R}_s} \exp(i\mathbf{k}_s \cdot \mathbf{R}_s) = (4\pi^2/A)\,\delta(\mathbf{k}_s - \mathbf{G}_s) \tag{12}$$

or

$$\sum_{\mathbf{R}_s'} \exp(i\mathbf{k}_s \cdot \mathbf{R}_s') = N_s'\,\delta_{\mathbf{k}_s,\,\mathbf{G}_s'} \tag{13}$$

where N_s' is the total number of B atoms in the interface. Substituting (12) and (13) into (11), integrating with respect to $\mathbf{k}_s$, and dividing by the interface area $N_s'A'$, we can write the interface energy per unit area as

$$E_0 = (1/2\pi AA')\,\delta_{\mathbf{k}_s,\,\mathbf{G}_s}\,\delta_{\mathbf{k}_s,\,\mathbf{G}_s'}\,\mathscr{V}_0(\mathbf{k}_s, B_3)\exp(i\mathbf{k}_s \cdot \mathbf{B}_s) \tag{14}$$

with a sum over all $\mathbf{G}_s$ and $\mathbf{G}_s'$ being understood and with

$$\mathscr{V}_0(\mathbf{k}_s, B_3) = \sum_{R_3'}^{+} \sum_{R_3}^{-} \int v(\mathbf{k})\exp[ik_3(R_3' - R_3 + B_3)]\,dk_3 \tag{15}$$

where the subscript 3 represents the component of a vector normal to the interface, and we have redefined $\mathbf{R}$ and $\mathbf{R}'$ so that each is measured from an origin fixed on a lattice point of its respective crystal and $\mathbf{B}$ is the vector joining these two origins.

If we remember that so far we are dealing with two completely undistorted semicrystals, then (14) has a specially simple significance. The two Kronecker deltas require that the only nonvanishing terms have $\mathbf{G}_s = \mathbf{G}_s' = \mathbf{k}_s$, which means that they arise from the points of coincidence of the two reciprocal surface lattices $\mathbf{G}_s$ and $\mathbf{G}_s'$, each point of coincidence contributing an energy $\mathscr{V}_0$, which depends on the $\mathbf{G}_s$ involved and also on the relative displacement of the two crystals. Now the reciprocal surface lattices of two crystals will have points of coincidence only if the direct surface lattices have coincidences, so that what we have evaluated is the energy of a coincidence boundary before any elastic relaxation takes place. Notice that this energy is quite explicitly given and that it depends upon the interatomic interaction potential $v(\mathbf{r})$ through its Fourier components $v(\mathbf{k})$, upon the extent of the coincidence through the deltas, which select only the coincidence terms in reciprocal space, and upon the relative displacement of the two crystals through the vector $\mathbf{B}$.

Actual evaluation of the interface energy is relatively straightforward, since the sums in (15) need to be taken over only a few pairs of layers on either side of the interface, the vector $\mathbf{B}$ being appropriately chosen for each pair to agree with the specified physical situation. If only the orientations of the two crystals and of the boundary are fixed, then we have the three components of

a single vector **B** that can serve as variational parameters. The minimum-energy configuration will possess certain symmetry, generally corresponding to $\mathbf{k}_s \cdot \mathbf{B}_s = n\pi$. There may, however, also be energy maxima or subsidiary minima corresponding to other symmetric configurations. This situation is illustrated in Fig. 2. The true minimum-energy configuration will depend upon the form of $v(\mathbf{r})$ and on the lattice geometry.
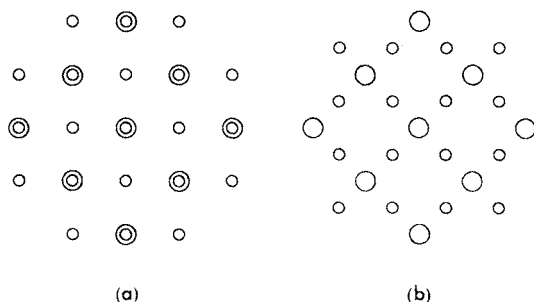
FIG. 2. An example of generalized matching between (100) faces of two fcc crystals with lattice parameters in the ratio $2^{1/2}:1$ and relative orientation $45°$. Depending upon the form of the interaction potential either one of the configurations (a) or (b) might represent the minimum energy.

An important thing that we should point out about this approach is that not only is it quantitative and related to a priori atomic interaction potentials, but it also includes considerations of crystal symmetry automatically. In fact, the analysis of terms contributing to E_0 in (14) is formally very similar to the 0-lattice analysis discussed in Section III, the distinction being that here the whole treatment is carried out in reciprocal space so that there is a duality rather than a direct correspondence between the geometry in the two cases.

VI. The Interface Problem in Reciprocal Space

To treat a more general interface, and indeed to treat a coincidence boundary to a better approximation, it is necessary to allow for elastic displacement of atoms near the interface and for the effect of this upon more distant parts of the crystals. The method of approach is essentially that of Section IV, except that again the analysis is performed in reciprocal space.

The displacements that we will include in the theory are those in which a surface A atom, initially at **R**, moves to $\mathbf{R} + \mathbf{F}(\mathbf{R})$ and the B atom at $\mathbf{R}'$ moves to $\mathbf{R}' + \mathbf{F}'(\mathbf{R}')$. Atoms deeper in the crystal will also move, but we may suppose this to be largely as a result of elastic interactions with their nearest-neighbor atoms of like kind rather than because of interactions across the interface.

While the vectors $\mathbf{F}$ are confined to describing the displacement of surface atoms, they are not necessarily parallel to the interface.

Now we have seen that for a general interface we can always define a coincidence lattice, although its primitive vectors may be extremely large. We can therefore construct the reciprocal lattice $\mathbf{K}$ of this superlattice with all vectors $\mathbf{K}$ lying parallel to the interface and, because of the periodicity in real space, it is necessary that all possible displacements $\mathbf{F}(\mathbf{R})$ can be written as a Fourier series

$$\mathbf{F}(\mathbf{R}) = -\sum_{\mathbf{K}} \mathbf{F}_{\mathbf{K}} \exp(i\mathbf{K} \cdot \mathbf{R}) \tag{16}$$

or, since $\mathbf{F}(\mathbf{R})$ is necessarily real,

$$\mathbf{F}(\mathbf{R}) = -\sum_{\mathbf{K}}^{+} 2[\mathbf{D}_{\mathbf{K}} \sin(\mathbf{K} \cdot \mathbf{R}) + \mathbf{C}_{\mathbf{K}} \cos(\mathbf{K} \cdot \mathbf{R})] - \mathbf{C}_0 \tag{17}$$

where $\mathbf{C}$ and $\mathbf{D}$ are real vectors. The corresponding expansion for the B crystal is

$$\mathbf{F}'(\mathbf{R}') = \sum_{\mathbf{K}}^{+} 2[\mathbf{D}_{\mathbf{K}}' \sin(\mathbf{K} \cdot \mathbf{R}') + \mathbf{C}_{\mathbf{K}}' \cos(\mathbf{K} \cdot \mathbf{R}')] + \mathbf{C}_0' \tag{18}$$

The change in sign relative to (17) is for reasons of symmetry and clearly

$$\mathbf{C}_0 + \mathbf{C}_0' = \mathbf{B} \tag{19}$$

If we substitute these distortions into (11), then the interaction part of the total interface energy becomes

$$E_i^{\mathrm{T}} = \frac{1}{8\pi^3} \sum_{\mathbf{R}'}^{+} \sum_{\mathbf{R}}^{-} \int v(\mathbf{k}) \exp[i\mathbf{k} \cdot (\mathbf{R}' + \mathbf{F}' - \mathbf{R} - \mathbf{F})] \, d\mathbf{k} \tag{20}$$

To reduce this rather complicated expression we can make use of a Bessel function expansion (Watson, 1944; Fletcher and Adamson, 1966) to write

$$\exp[2i\mathbf{k} \cdot \mathbf{C}_{\mathbf{K}} \cos(\mathbf{K} \cdot \mathbf{R})] = \sum_{m=-\infty}^{\infty} i^m J_m(2\mathbf{k} \cdot \mathbf{C}_{\mathbf{K}}) \exp(im\mathbf{K} \cdot \mathbf{R}) \tag{21}$$

and

$$\exp[2i\mathbf{k} \cdot \mathbf{D}_{\mathbf{K}} \sin(\mathbf{K} \cdot \mathbf{R})] = \sum_{m=-\infty}^{\infty} J_m(2\mathbf{k} \cdot \mathbf{D}_{\mathbf{K}}) \exp(im\mathbf{K} \cdot \mathbf{R}) \tag{22}$$

Similar expressions arise in the theory of sidebands in frequency-modulated radio transmissions, although the analysis is usually carried out in a rather more limited way than has been done here. The significant thing about these two expansions is that, when they are substituted into (20), along with similar expressions for $\mathbf{F}'$, the sums over $\mathbf{R}_s$ and $\mathbf{R}_s'$ no longer have forms like (12) and (13) but rather like

$$\sum_{\mathbf{R}_s} \exp[i(\mathbf{k}_s - m\mathbf{K}_1 - n\mathbf{K}_2) \cdot \mathbf{R}_s] = N_s \delta_{\mathbf{k}_s, \mathbf{G}_s + m\mathbf{K}_1 + n\mathbf{K}_2} \tag{23}$$

so that when we come to calculate the energy per unit area, as in (14), we have contributions not just from those $\mathscr{V}_0(\mathbf{k}_s)$ for which $\mathbf{k}_s = \mathbf{G}_s = \mathbf{G}_s'$, but also from those with $\mathbf{k}_s = \mathbf{G}_s = \mathbf{G}_s' + m\mathbf{K}_1 + n\mathbf{K}_2$ and $\mathbf{k}_s = \mathbf{G}_s' = \mathbf{G}_s + m\mathbf{K}_1 + n\mathbf{K}_2$ for all possible vectors $\mathbf{K}_1$ and $\mathbf{K}_2$ corresponding to allowed distortion components and for all integers n and m. The Fourier components of the distortion have thus coupled together potential components $\mathbf{G}_s$ and $\mathbf{G}_s'$ that are not coincident.

If we follow the same sort of procedure that led from (11) to (14), then we find from (20) that the interaction energy per unit area of interface can be written

$$E_i = (1/2\pi A A') \sum_{\mathbf{k}_s} \mathscr{V}_0(\mathbf{k}_s, B_3) \exp(i\mathbf{k}_s \cdot \mathbf{B}_s)$$

$$\times \left\{ \prod_{\mathbf{K}}{}^+ J_0(2\mathbf{k} \cdot \mathbf{D}_\mathbf{K}) J_0(2\mathbf{k} \cdot \mathbf{C}_\mathbf{K}) \right\} \left\{ \prod_{\mathbf{K}}{}^+ J_0(2\mathbf{k} \cdot \mathbf{D}_\mathbf{K}') J_0(2\mathbf{k} \cdot \mathbf{C}_\mathbf{K}') \right\}$$

$$\times \left\{ \delta_{\mathbf{k}_s, \mathbf{G}_s}\, \delta_{\mathbf{k}_s, \mathbf{G}_s'} + \sum_{n=1}^{\infty} \sum_{\mathbf{K}}{}^+ [\ ]_1\, \delta_{\mathbf{G}_s + n\mathbf{K}, \mathbf{G}_s'}\, \delta_{\mathbf{k}_s, \mathbf{G}_s'} \right.$$

$$\left. + \sum_{n=1}^{\infty} \sum_{\mathbf{K}}{}^+ [\ ]_{1'}\, \delta_{\mathbf{G}_s + n\mathbf{K}, \mathbf{G}_s'}\, \delta_{\mathbf{k}_s, \mathbf{G}_s} + \cdots \right\} \tag{24}$$

The bracket $[\ ]_1$ is defined by

$$[\ ]_1 \equiv \left[\frac{J_n(2\mathbf{k}_s \cdot \mathbf{D}_\mathbf{K})}{J_0(2\mathbf{k}_s \cdot \mathbf{D}_\mathbf{K})} + i^n \frac{J_n(2\mathbf{k}_s \cdot \mathbf{C}_\mathbf{K})}{J_0(2\mathbf{k}_s \cdot \mathbf{C}_\mathbf{K})} \right] \tag{25}$$

and similarly for $[\ ]_{1'}$ with $\mathbf{C}_\mathbf{K}$ and $\mathbf{D}_\mathbf{K}$ replaced by $\mathbf{C}_\mathbf{K}'$ and $\mathbf{D}_\mathbf{K}'$. There are further terms in expansion (24), involving the coupling of $\mathbf{G}_s$ and $\mathbf{G}_s'$ by two vectors $\mathbf{K}$, but we need not be concerned with these here. Explicit expressions for these second-order coupling terms are given by Fletcher and Adamson (1966) and a numerical error in these expressions is corrected by Lodge (1970).

These expressions (24) and (25) look forbiddingly complex, but in fact $\mathbf{k}_s \cdot \mathbf{C}_\mathbf{K}$ and $\mathbf{k}_s \cdot \mathbf{D}_\mathbf{K}$ are generally small quantities so that only terms with $n = 1$ or 2 need usually be considered and the second-order coupling terms are also small. We have therefore succeeded in expressing the interaction energy E_i across the interface in a relatively simple form involving a set of variational parameters $\mathbf{C}_\mathbf{K}$, $\mathbf{D}_\mathbf{K}$, $\mathbf{C}_\mathbf{K}'$, and $\mathbf{D}_\mathbf{K}'$. Their number is potentially the same as the number of variational parameters $\mathbf{F}$ shown in (6) for the same problem in direct space but we shall see that it is possible to reduce the number of significant $\mathbf{K}$-values to a quite small set so that the variational problem then becomes tractable. In addition, the elastic problem for each semicrystal is soluble in simple terms and does not do violence to our physical assumptions, as we shall see in the next section.

VII. The Elastic Problem

In our initial formulation we agreed to treat interactions across the interface on an atomic basis, as we have done, and to approximate the energy behavior of the two homogeneous semicrystals by continuum elasticity theory. Since the basis distortions envisaged in the theory are sinusoidal surface waves with wavevector $\mathbf{K}$ and amplitudes and polarizations specified by $\mathbf{C_K}$ and $\mathbf{D_K}$, this elastic problem can be fairly readily solved and, because of the continuous nature of the surface displacements, no reasonable physical assumptions are violated. In addition, since these elementary distortions for the elastic problem are all orthogonal, their contributions to the elastic energy can be individually evaluated and then simply summed.

A detailed discussion of the elastic problem has been given by van der Merwe (1950, 1963) both for the case of a semiinfinite crystal and for a crystal of finite thickness. A more recent investigation has been made by Lodge (1970). Without going into details of the analysis we can fairly easily see that, if the surface of a semiinfinite crystal is distorted by the imposition of a sinusoidal displacement

$$\mathbf{F_K} \exp(i\mathbf{K} \cdot \mathbf{r}) = 2[\mathbf{D_K} \sin(\mathbf{K} \cdot \mathbf{r}) + \mathbf{C_K} \cos(\mathbf{K} \cdot \mathbf{r})] \tag{26}$$

where we have now replaced the discrete variable $\mathbf{R}$ by the continuous variable $\mathbf{r}$, then the amplitude of the displacement decays more or less expotentially away from the surface with a characteristic penetration depth of order $2\pi/K$. If we take the smallest allowed $\mathbf{K}$ for the problem, then this distance is equal to the largest of the primitive vectors of the surface coincidence lattice. Any crystal overgrowth that is much thicker than this is essentially infinite from an energy point of view, while for thinner overgrowths their finite thickness must be taken into account.

For the case of a semiinfinite A crystal subject to surface displacements $\mathbf{F_K}$, Lodge (1970) shows that the elastic energy per unit area is

$$E_e^A = \mu \sum_{\mathbf{K}}{}^{+} K \left[C_{K_2}^2 + D_{K_2}^2 + \frac{4(1-\sigma)}{3-4\sigma} (C_{K_1}^2 + D_{K_1}^2 + C_{K_3}^2 + D_{K_3}^2) \right.$$

$$\left. + \frac{4(1-2\sigma)}{3-4\sigma} (D_{K_1} C_{K_3} - C_{K_1} D_{K_3}) \right] \tag{27}$$

where subscript K_1 refers to the component of a displacement in the direction of $\mathbf{K}$, the K_3-component is normal to the interface, and K_2 is chosen so that the $1, 2, 3$ directions form a right-handed set. The quantities μ and σ are, respectively, the shear modulus and the Poisson's ratio for the crystal material A, assumed isotropic for simplicity. An exactly similar expression with μ, σ replaced by μ', σ' applies to crystal B.

From (27) we can see that elastic displacements with different wavevectors $\mathbf{K}$ are in fact independent but that for any given $\mathbf{K}$ the longitudinal displacements (subscript K_1) and the normal displacements (subscript K_3) are coupled, as is clearly necessary on physical grounds. The distortion components of the two crystals A and B could be taken as independent variational parameters, but a considerable simplification occurs if we instead apply the simple mechanical condition that elastic stresses must balance across the interface when it is in its equilibrium configuration. Again components with different $\mathbf{K}$-vectors are orthogonal and a set of six relations between the twelve components of $\mathbf{C_K}$, $\mathbf{D_K}$, $\mathbf{C_K'}$, and $\mathbf{D_K'}$ can be derived. Because of the K_1, K_3 distortion coupling, these relations are also coupled, their explicit form being given by Lodge (1970) as

$$\mu C_{K_2} = \mu' C'_{K_2} \tag{28}$$

$$\mu D_{K_2} = \mu' D'_{K_2} \tag{29}$$

$$\mu(C_{K_3} + D_{K_1}) = [\mu'/(3 - 4\sigma')](C'_{K_3} + D'_{K_1}) \tag{30}$$

$$\mu'(C'_{K_3} - D'_{K_1}) = [\mu/(3 - 4\sigma)](C_{K_3} - D_{K_1}) \tag{31}$$

$$\mu(C_{K_1} - D_{K_3}) = [\mu'/(3 - 4\sigma')](C'_{K_1} - D'_{K_3}) \tag{32}$$

$$\mu'(C'_{K_1} + D'_{K_3}) = [\mu/(3 - 4\sigma)](C_{K_1} + D_{K_3}) \tag{33}$$

Rather similar treatment could be given to the case of an overgrowth crystal of finite thickness following the lead given by van der Merwe (1963) but this has not yet been done. Following his discussion and that given above we should expect the semiinfinite results to be approximately applicable to all but the very thinnest layers.

VIII. The Variational Problem in Reciprocal Space

We can now put together all the information contained in (24) and (27) to write for the total interface energy per unit area

$$E = E_i + E_e^A + E_e^B = E_i + E_e \tag{34}$$

The variational parameters in the problem are the $\mathbf{C_K}$, $\mathbf{D_K}$, $\mathbf{C_K'}$, and $\mathbf{D_K'}$ for all the allowed values of $\mathbf{K}$ but these can be reduced simply to the $\mathbf{C_K}$ and $\mathbf{D_K}$ by use of the relations (28)–(33). Let us now look at the totality of possible $\mathbf{K}$-vectors and their associated distortions to see how they can be enumerated.

One of the great attractions of the variational approach is the opportunity it provides for simplification. An approximate result can always be obtained by considering just a few of the variational parameters that are judged on physical or mathematical grounds to be most important and, if one's intuition is good, this result may approach quite closely to the fuller treatment achieved with many more parameters.

To derive a simple criterion for this choice let us remember that distortions for different $\mathbf{K}$-vectors are independent and then consider the form of E for a single $\mathbf{D_K}$ only, such that $\mathbf{G_s} = \mathbf{G_s'} + \mathbf{K}$. From (24), (25), (27), and (34) if we expand the Bessel functions and keep first-order terms only, we find

$$E \simeq E_0(\mathbf{B}) + Q(\mathbf{B}) D_\mathbf{K} + PKD_\mathbf{K}{}^2 \tag{35}$$

where E_0 is the coincidence part (if any) of the boundary energy, $Q(\mathbf{B})$ contains the atomic interactions across the interface, $\mathscr{V}_0(\mathbf{G_s})$ and $\mathscr{V}_0(\mathbf{G_s'})$, P represents the elastic coefficients, and $\mathbf{B}$ is, of course, the displacement of one crystal relative to the other. Clearly $P > 0$, and $\mathbf{B}$ can be chosen so that $Q < 0$.

If we minimize with respect to $D_\mathbf{K}$ and $\mathbf{B}$, we find

$$E \simeq E_0 - (Q^2/4PK) \tag{36}$$

with

$$D_\mathbf{K} = -Q/2PK \tag{37}$$

Clearly the approximation is valid only for $\mathbf{G_s} \cdot \mathbf{D_K} \lesssim 1$ but from it we can deduce two things: the contribution of a given $D_\mathbf{K}$ to the energy is greatest if $\mathbf{K}$ is very small, and the contribution is large if the potential components $\mathscr{V}_0(\mathbf{G_s})$ and $\mathscr{V}_0(\mathbf{G_s'})$ for the two points are large. The energy (36) actually appears to have an infinite negative value as we approach $\mathbf{K} = 0$, the coincidence-boundary configuration, but the real situation is that the coincidence boundary of any order represents a cusped minimum in the energy, the depth of this minimum depending on the strength of the potential components $\mathscr{V}_0(\mathbf{G_s})$ brought into coincidence. This already tells us a great deal about interface behavior and makes it plain that it is not only the geometry that is important but also the detailed form of the interaction potential $v(\mathbf{r})$.

To select the distortion wavevectors to be included in the calculation we therefore examine the pattern of the interface in reciprocal space and select a suitable number of short $\mathbf{K}$-vectors joining reciprocal lattice points where the potential is large. There is an upper limit to the magnitude of any physically significant $\mathbf{K}$-vector set by the criterion that it must lie within the first Brillouin zone of both the crystals concerned, but we may often select vectors that are limited to being much smaller than this. The choice will also be determined to some extent by the range of the interaction potential $v(\mathbf{k})$ in reciprocal space. An example of such an initial choice of $\mathbf{K}$-vectors is shown in Fig. 3.

When it comes to second-order terms, the most important and therefore the only ones worth including are those made up from combinations of first-order $\mathbf{K}$-vectors. Thus, for example, if $\mathbf{K}$ and $\mathbf{K}'$ link pairs of reciprocal lattice
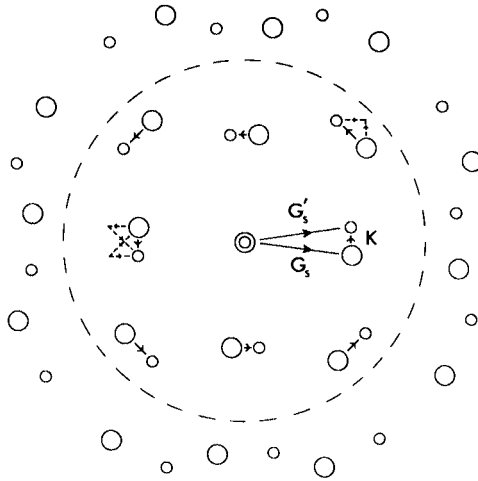
FIG. 3. Portion of the reciprocal lattice, near the origin, for two similar cubic crystals related by a twist boundary of small angle. The dashed circle represents either the range of the potential $v(k)$ or the arbitrary region inside which distortion vectors K are considered. The principal distortion K-vectors are shown, together with the way they can combine to give second-order terms.

points in first-order, we can always find a pair of points linked by $K \pm K'$, and this term in E_i should be included since it requires no additional contribution to the elastic energy E_e.

The practical feasibility of this whole scheme depends on the possibility of selecting a sufficiently small set of important K-vectors so that the computation becomes tractable. This in turn depends partly on the range of $v(k)$ in reciprocal space and partly on the geometry of the interface. The method becomes difficult for very small-angle boundaries because of the many small K involved, but this is not of much importance since it is just this region that is simply and validly covered by the dislocation theory.

One of the main contributions of the formalism itself is to place on a firm quantitative basis the energy considerations relating to coincidence and near-coincidence boundaries. The coincidence boundaries are shown to represent local cusped minima in the interface energy and their behavior is shown to be critically related to the actual form of the interatomic potential. Crystal symmetry is automatically taken into account and there is no necessity for any artificial picture involving hierarchies of dislocations. A simple dislocation is, in fact, represented by the distortions associated with a single set of vectors nK, where K is the first-order distortion wavevector for a particular set of reciprocal lattice points. Inclusion of alternate couplings of the type $n(K + K')$ is equivalent to the introduction of another dislocation set of higher order.

IX. The Interaction Potential

In many problems in metal-crystal physics it is usual to assume a simple analytic form for the interaction potential $v(\mathbf{r})$, both the Lennard–Jones potential

$$v(\mathbf{r}) = v_0 [(r/r_0)^{-12} - 2(r/r_0)^{-6}] \qquad (38)$$

and the Morse potential

$$v(\mathbf{r}) = v_0 \{\exp[-2a(r-r_0)] - 2\exp[-a(r-r_0)]\} \qquad (39)$$

being common choices. In either case the parameters v_0 and r_0 are chosen to match as well as possible the lattice parameters, the cohesive energy, and the elastic properties derived from experiment. Similarly in the treatment of ionic crystals we might usefully assume a Coulombic or shielded Coulombic attraction or repulsion together with a hard-sphere or other appropriate repulsion at short distance.

These potentials are particularly useful in direct lattice calculations because of their simple analytical form. Apart from this and the r^{-6} term in (38) they have no particular physical significance. In the present situation what we need for a simple model calculation is a potential that has a simple analytical form for $v(\mathbf{k})$ in reciprocal space and that adequately represents the real interatomic potential. Since there is a dual relation between $v(\mathbf{k})$ and $v(\mathbf{r})$, in the sense that if $v(\mathbf{r})$ has a short range then the range of $v(\mathbf{k})$ is long and vice versa, it is rather difficult to find a suitable model potential for trial calculations. For real calculations, of course, we must try to use the real form of $v(\mathbf{r})$ derived as accurately as possible from calculations and experimental data, so that this difficulty cannot be avoided. Even for a real potential, however, we shall see that there is some freedom of choice associated with the exact form of the potential within the inaccessible repulsive core, and we may use this freedom to advantage in real calculations.

A suitable model potential for exploratory calculations introduced by Fletcher (1967) has the form

$$v(\mathbf{k}) = H[(a+b)/a]^3 \{\exp[2.5k(a+b)-4]+1\}^{-1} \qquad (40)$$

where H is a scale constant. This potential is designed for the case where the atoms of crystals A and B have radii proportional to a and b, respectively, so that the lattice parameters of the two crystals vary in the same way. The form of the potential in real and in reciprocal space for the case $a = b$ is shown in Fig. 4. It can be seen that the potential $v(\mathbf{k})$ has an appreciable value only for $\mathbf{k} \lesssim 3\pi/a$, while $v(\mathbf{r})$, its form in real space, has a physically reasonable shape and is small for $\mathbf{r} \gtrsim 1.5a$. With the particular form given by (40), $v(\mathbf{r})$ has a minimum at $r = \frac{1}{2}(a+b)$, the depth of which is independent of b/a. The potential is, of course, spherically symmetrical.
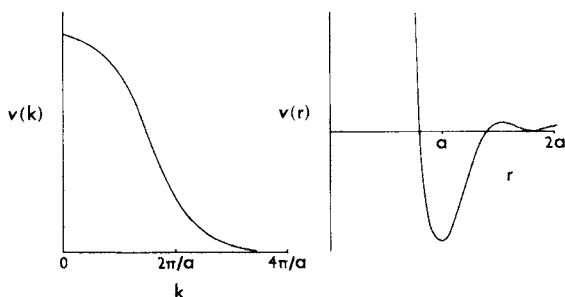
FIG. 4. (a) The Fourier transform $v(\mathbf{k})$ and (b) the direct potential $v(\mathbf{r})$ used in the model calculation, both drawn for the case $b = a$.

In the next section we shall detail the results of some calculations with this potential, which show the general features expected from the formal development. We must remember, however, that a model calculation with such a potential, instructive though it may be, has only a limited resemblance to reality. We can improve the resemblance by choosing the few available parameters to give agreement with important physical data but we cannot be sure how valid are the other predictions of the model.

It is more satisfying, from a physical point of view, to derive a more realistic potential from first principles and then to perform our best calculation without the aid of any adjustable parameters. This we shall try to do in Section XI.

X. Calculations with a Model Potential

A set of survey calculations with the model potential (40) was carried out by Fletcher (1967) to check the general feasibility of the method for interface-energy calculations and to examine quantitatively its predictions for misfit boundaries of various types. The system chosen for analysis was a twist boundary between (100) faces of two fcc crystals A and B having atomic potential parameters a and b, respectively. The cubic-lattice parameters thus turn out to be about $2.5a$ and $2.5b$ for the two crystals, and the surfaces are simple square lattices with parameters slightly less than a and b.

For the purposes of the calculation several additional simplifications were made: integral (15) for $\mathscr{V}_0$ was evaluated as a sum over a relatively small number of equally spaced k_3-values, only one atomic layer on either side of the interface was taken into account in evaluating E_i, and a simplified elastic analysis was used. This last involved neglect of the interaction term in (27) and replacement of the other terms by

$$E_e^A = (M/a^3) \sum_K{}^+ \sum_i (C_{K_i}^2 + D_{K_i}^2) \tag{41}$$

With the choice of 5.8 for the constant H in (40) to give a convenient arbitrary energy scale, a value of 500 for M made the various elastic moduli of the order expected physically. In retrospect this oversimplification was probably undesirable, but it is hardly worthwhile to recompute the results with less crude approximations.

Figure 5 shows the energy of the twist boundary as a function of angle θ for various values of the ratio b/a. When $b = a$ there is a deeply cusped energy minimum at the orientation of exact fit, $\theta = 0$, and the interface energy then rises smoothly in the same manner as predicted by the dislocation theory result (1). Instead of decreasing for $\theta > 20°$ and then becoming unphysically negative, however, the interface energy reaches a plateau for $\theta > 20°$. The predicted energy is also symmetrical about $\theta = 45°$ and shows a cusp for $\theta = 90°$ identical with that at $\theta = 0°$, as is physically necessary.

The behavior of interface energy as a function of misfit ratio $b/a = 1 + \delta$ is shown more explicitly in Fig. 6. For $\theta = 0$ there is a logarithmic cusp of the
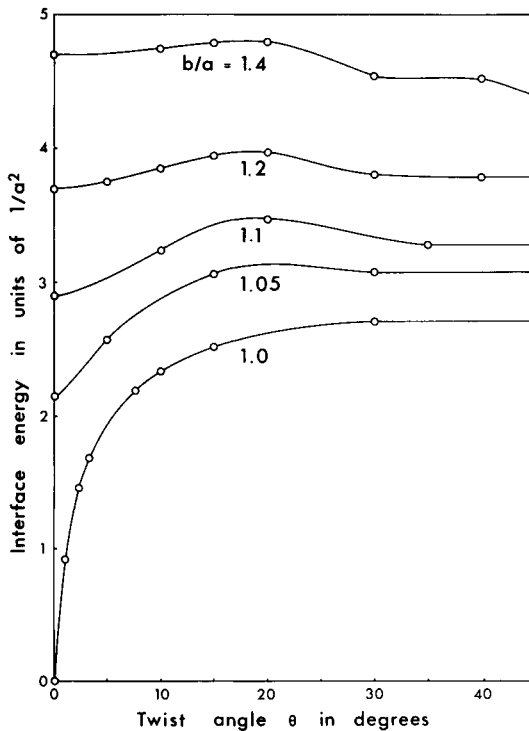

FIG. 5. Energy, in units of $1/a^2$, of a twist boundary of angle θ between two crystals with lattice-potential parameters a and b, respectively (Fletcher, 1967).
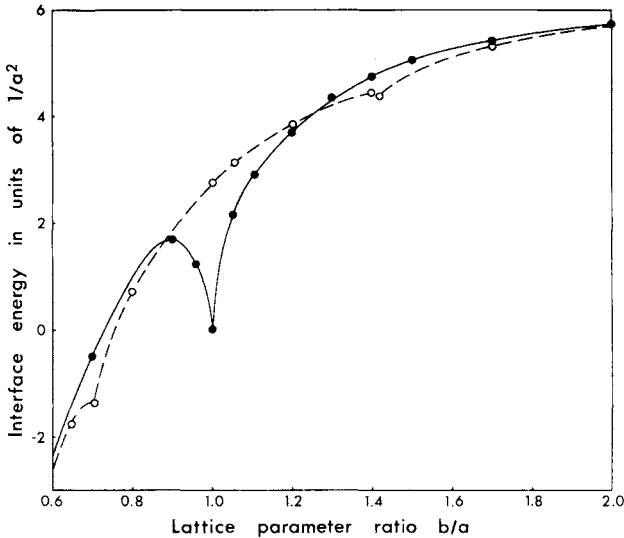
FIG. 6. Energy, in units of $1/a^2$, of a twist boundary between two crystals, with lattice-potential parameters a and b, respectively, for boundary twist angles of 0 (●) and 45° (○) (Fletcher, 1967).

type predicted by dislocation theory (2) for $b = a$, although this is superposed on a general rising trend of interface energy with parameter b which is a result of the particular form of the potential (40).

The theory also predicts the existence of subsidiary minima at points $\theta = 45°$, $b = 2^{1/2}a$, and $\theta = 0$, $b = 2a$, corresponding to more general coincidence boundaries. The first of these cusps is clearly visible in Fig. 6 but the second is not, presumably because the magnitude of the relevant Fourier components of the potential is too small.

From the results of the computation for the distortion vectors $\mathbf{C_K}$ and $\mathbf{D_K}$ it is also possible to determine atomic positions in the elastically relaxed interface. This is generally of little practical interest but there is a possibility of identifying the major $\mathbf{K}$-vectors by electron-diffraction methods applied to thin films.

Using the theory with a simple model potential like this we are thus able to reproduce the results of the dislocation theory for small misfits and to make an estimate of interface energy for large misfits. For the particular potential chosen the number of variational parameters was only small and the calculation only involved quite a small amount of computer time. The more difficult cases of real potentials and of tilt boundaries, however, may no longer be simple computational problems.

As a second example of the use of the model potential (40), let us apply it to estimate the grain-boundary energy in aluminum. To this end we use the full treatment of the elastic problem set out in Section VII and choose the constant H in the potential (40) for $b = a$ to give best agreement with the experimental elastic moduli used in (27). To do this, the total energy of an fcc crystal with interaction potential (40) is evaluated and, upon minimization with respect to the lattice constant a_0, including interactions up to fourth neighbors, we find

$$a_0 = 1.3838a \qquad (42)$$

The same minimization gives the bulk modulus in terms of H and thus allows H to be evaluated. This is considered to be a better procedure in the present case than to use the sublimation energy, because of the importance of relatively small atomic displacements in the theory. The value of H and the experimental values used for μ and σ are

$$H = 4.25 \times 10^{-35} \text{ erg cm}^3, \quad \mu = 2.62 \times 10^{11} \text{ dyne cm}^{-2}, \quad \sigma = 0.345 \qquad (43)$$

The assumption of isotropic elastic properties for aluminum is a reasonable approximation but by no means exact.

Once more in this calculation only one atomic layer on either side of the interface was taken into account, since this is a reasonably good approximation when the interface plane is of low index. The results of the model calculation are shown in Fig. 7. The calculated energy of a high-angle twist boundary relative to the zero-angle (no grain-boundary) energy is 1014 erg cm^{-2}. The only available experimental value is 630 ± 100 erg cm^{-2}, determined by Astrom (1957) using a calorimetric method. The agreement is reasonable but not very close.

XI. An Ab Initio Potential for Aluminum

To illustrate the problems encountered in a calculation based upon a potential derived from ab initio physical argument, rather than on a criterion of calculational simplicity, we shall consider the case of aluminum. There are two reasons for this choice: aluminum is a metallurgically important material so that it is of value to understand its properties as fully as possible, and there is a reasonable body of theoretical work on which we can base our calculations. The argument we follow is essentially that given by Lodge (1970).

Aluminum is a metal, and the effective interaction between its atoms is therefore composed of two parts: the repulsive interaction between the aluminum ion cores and the shielding effect of the conduction electrons on this interaction. The shielding effect of the electrons is complicated by the
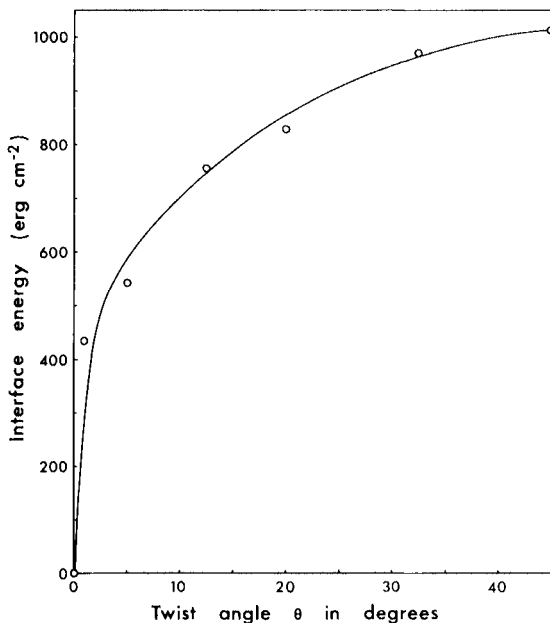
FIG. 7. Energy of a twist boundary in aluminum as calculated using a model potential.

electronic band structure of the metal, and the sharp decrease to zero of the electron density above the Fermi energy limits its shielding effectiveness at short wavelengths so that the total atomic-interaction potential resembles an exponentially shielded repulsion with, superposed upon it, an oscillation related to the shielding cutoff at the Fermi energy. It is the principal minimum produced by these oscillations that is responsible for the overall attractive potential between atoms. The matter has been discussed in detail by Ziman (1964) and by Harrison (1966).

It would be out of place to enter into a detailed discussion of this matter here and we content ouselves with reproducing, as the solid line in Fig. 8, the interaction potential calculated by Harrison (1966). At small distances the potential has the form of a simple Coulomb repulsion Z^2e^2/r, where Ze is the effective ionic charge.

One of the principal difficulties with using Harrison's potential in a calculation of grain-boundary energy arises from this highly repulsive core potential at short distances. The infinity in the potential at $r = 0$ leads to a large spread of $v(\mathbf{k})$ in reciprocal space, and any truncation of the expansion leads to large oscillations in $v(\mathbf{r})$ that completely mask the true form of the potential.

It is possible, however, to reduce this difficulty by a simple artifice. We note that, because of the limited energy available, ion cores are never forced to overlap appreciably, and it is therefore quite immaterial what is the form of $v(\mathbf{r})$ at very small $\mathbf{r}$, so long as it is large and positive. We may therefore use the modified core potential.

$$v'(\mathbf{r}) = \begin{cases} (Z^2 e^2/R)\,[2-(r/R)], & r < R \\ Z^2 e^2/r, & r > R \end{cases} \qquad (44)$$

where R is chosen small enough (actually 3.5 a. u. or about 1.9 Å) that overlap to the altered region never occurs. These two potentials join smoothly as shown in Fig. 9 and the effect on the range of $v(\mathbf{k})$ is very great, as shown in Fig. 10. Using the modified potential it now becomes possible to truncate $v(\mathbf{k})$ in k-space without doing violence to its representation of the important part of the potential, as shown in Fig. 8. We see that a cutoff at $k_M = 4.64$ a.u. (8.8 Å^{-1}) represents the potential quite well, although somewhat under-estimating the depth of the primary minimum, while a cutoff at $k_M = 2.7$ a.u. (5.1 Å^{-1}) gives the correct overall behavior but overestimates the depth of this minimum by about a factor of two.

Here we arrive at the prime difficulty of the variational method when applied to real potentials, and this is simply computational. For the aluminum structure a cutoff in the potential $v(\mathbf{k})$ at $k_M = 2.7$ a.u. is found to include 20 pairs of reciprocal lattice points with $G_s < k_M$, which would coincide
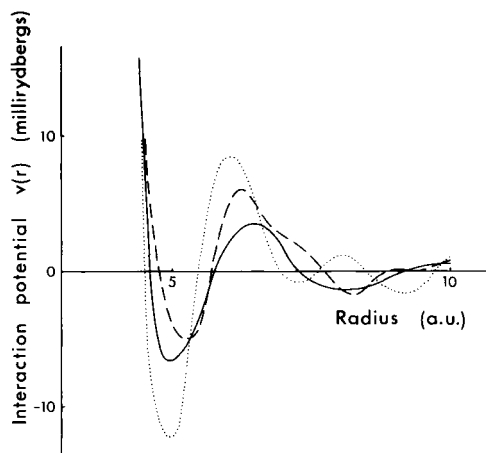

FIG. 8. Effective interaction potential between ions in aluminum as calculated by Harrison (solid line) and the modifications introduced by using k_M cutoffs of 4.6365 a.u. (dashed line) and 2.7 a.u. (dotted line) (Lodge, 1970).
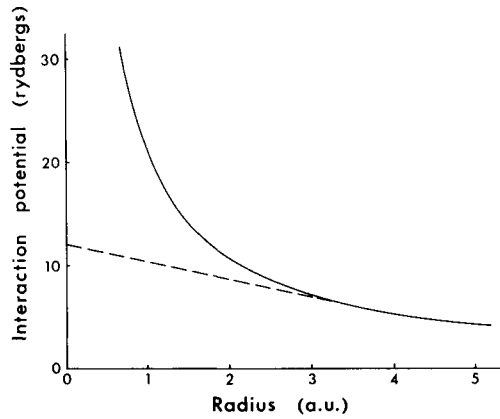
FIG. 9. The direct Coulomb interaction (solid line) compared with the altered direct interaction used in the calculation (dashed line) (Lodge, 1970).

at $\theta = 0$. This implies 20 primary **K**-vectors and 120 distortion components, although symmetry considerations reduce the number of independent components to 15. For a potential cutoff at $k_M = 4.64$ a.u., this number is increased by about a factor of 3. At small twist angles θ, the primary **K**-vectors
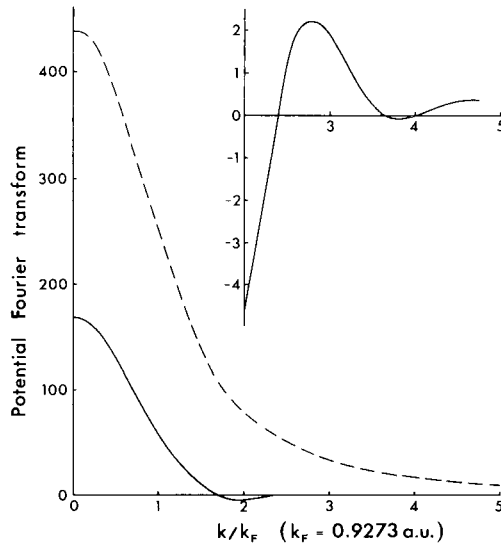

FIG. 10. Comparison between the Fourier transform of Harrison's potential for aluminum (dashed line) and the Fourier transform of the modified interaction potential. The units are rydbergs (Bohr radius)^3. The tail of the modified potential is shown on an expanded scale in the inset (Lodge, 1970).

are all small, convergence is slow, and second-order terms are important so that the calculation, while feasible, is computationally difficult. For larger twist angles, K-vectors joining reciprocal lattice points that are not equivalent at $\theta = 0$ become more important but, generally speaking, the second-order contributions are much smaller and the energy depends primarily on those few distortions for which K happens to be small.

Lodge (1970) has carried out calculations for a twist boundary in aluminum using a potential truncated at $k_M = 2.7$ a.u. and trying various simplifications and extensions. The convergence was poor for $\theta < 5°$, except for the identical-fit case $\theta = 0$, but the familiar cusped minimum was apparent. The boundary energy was found to have a plateau for θ between about 10 and 45° with an energy of about 1700 erg cm^{-2}, which does not accord very well with the experimental value of 630 $\pm$ 100 erg cm^{-2} found by Astrom (1957).

In retrospect the reasons for this descrepancy are clear. In his calculation, Lodge truncated the potential itself at $k_M = 2.7$ a.u., and this, as is plain from Fig. 8, has the effect of deepening the primary potential minimum by about a factor of two with a consequent increase by this factor in the binding energy across the interface at $\theta = 0$. In the spirit of our variational method it should not be that we truncate the potential at a particular value of k_M but rather that only distortion vectors K joining reciprocal lattice points G_s with $G_s < k_M$ should be included. All coincident reciprocal-lattice points should always be included in the energy summation.

It is actually quite easy to revise Lodge's calculation in this way since, in general, there are no coincidences besides $k = 0$ except for special coincidence-boundary configurations. Ideally the coincidence sum should be taken over all values of k but in fact, from Fig. 8, a sum to $k = 4.64$ a.u. is fairly adequate. When this revised calculation is performed and another error in the computer program corrected, the high-angle grain-boundary energy is found to be about 590 erg cm^{-2}. This is in excellent agreement with experiment, although this may be fortuitous.

XII. Surface Entropy and Free Energy

As we discussed in Section II, the quantity that we have considered and attempted to calculate has, so far, been the interfacial energy, whereas the quantity that is relevant in most physical problems is actually the interfacial free energy. For a liquid–vapor interface the surface free energy is identical with the surface tension, but for solid boundaries or interfaces these two quantities are physically and numerically quite distinct. The surface free energy is a scalar quantity (although its value depends in general on surface orientation) and it must always be positive, or the solid will spontaneously

disintegrate to create extra surface. The surface tension, on the other hand, is generally a tensor describing surface stress and may have either positive or negative components, depending on the nature of the forces between atoms in the crystal. The same distinction applies to crystal interfaces.

If we denote the surface energy by ε, the surface free energy by γ, and the surface entropy by σ, then at temperature T we have as usual

$$\gamma = \varepsilon - T\sigma \tag{45}$$

so that γ and ε are equal at 0°K and

$$\sigma = -\partial\gamma/\partial T$$

For liquid–vapor interfaces we know that the surface entropy σ is positive so that γ decreases with rising temperature and vanishes at the critical point. For the interface between a crystal and its supercooled melt, however, there is indication from nucleation experiments that γ increases with rising temperature so that σ is negative. This behavior accords with the experimental fact that there does not appear to be any critical point associated with the solid–liquid transition.

If we consider a simple grain boundary, then the thermodynamic properties of the material on either side of the boundary are identical, while the boundary region itself is characterized by having a higher energy per atom than the bulk material and a less ordered configuration. We should thus expect both the surface energy and surface entropy to be positive in this case. It is more difficult to make the same assertion about an interface between two different crystals without detailed thermodynamic and statistical analysis, but it seems likely that it is still true. This conclusion implies that the free energy of a crystalline interface should decrease as the temperature is raised, so that all our calculated energies will be overestimates if they are taken to represent the free energy at a finite temperature.

It is difficult to estimate the numerical magnitude of the surface entropy without a very detailed analysis. In the first place there are vibration modes that differ in frequency from those of the bulk crystal and therefore contribute to surface entropy; there are also configurational terms that depend on the degree of disorder in the interface. It is tempting to assume simply, in the case of grain boundaries, that the free energy goes to zero at the melting point, but this is much too extreme a variation since melting is a phase change of first order rather than the higher order associated with a liquid–vapor critical point. It seems likely, rather, that the interface free energy near the melting point has probably at least half the magnitude it has at 0°K. Part of this change will be associated with configurational entropy terms, and part will be due to the effect of the decrease in shear modulus μ as the temperature is raised.

XIII. Relation to Epitaxial Growth

In our discussion we have seen that it is possible to calculate, quite generally, the energy of an interface between two materials provided that the interaction potential between pairs of atoms is known together with the elastic moduli of the two bulk crystals. In practice the calculation is feasible provided that the interface constitutes a low-index crystallographic face for each of the two crystals and that the interaction potential can be reduced to a form that does not have too large an extension in reciprocal space.

Extension of this treatment to the case where one of the crystals is of small thickness is relatively straightforward, since this only involves modification of the elastic energy component. If, however, we consider a further extension to the case where one of the crystals is of finite lateral extent, then we encounter more fundamental difficulties because the lattice sums parallel to the interface are no longer infinite. If the patch of overgrowth is finite but sufficiently large to contain several periods of the shortest distortion wavevector $\mathbf{K}$, then it is legitimate to use the results for an overgrowth of infinite lateral extent as a good approximation. If this condition is not fulfilled, then the overgrowth island will be relatively small and an energy calculation in real space along the lines indicated in Section IV is probably the best way to proceed. Bearing these limitations in mind, we can now proceed to draw some general conclusions from our treatment, which will be of use in considering epitaxial growth problems.

Oriented overgrowth of one crystal upon another can occur when there is a well-defined minimum in the interfacial free energy for some particular orientational relationship of the two crystals relative to the specified boundary. Generally the boundary will be fixed relative to the substrate crystal and the orientational freedom will be that of the overgrowth.

For two arbitrary crystals of different materials there will not, in general, be any exact coincidence boundaries so that, instead of a cusped minimum as for the case $b/a = 1.0$ in Fig. 5, we are more likely to find a simple minimum as for the case $b/a = 1.05$ in the same figure. This means that, because of the finite curvature at the trough of the minimum, we should expect to find a small distribution in angle for different overgrowth islands rather than a precise orientation.

To estimate the expected spread we might reasonably evaluate the total interfacial free energy F for an island nucleus of critical size and we should then expect to find a distribution $\Delta\theta$ in orientation angle such that $\Delta F(\theta) \sim kT$. Applying this criterion to the case of $b/a = 1.05$ in Fig. 8 and assuming the reasonable value of 100 erg cm^{-2} for the plateau value of interface energy, a critical island embryo of 1000 atoms and a substrate temperature of 400°K, we find a spread in orientation of $\Delta\theta \simeq \pm 2°$. If deposition were carried out

at a lower substrate temperature under the same deposition conditions, then the size of the critical embryo would decrease much more rapidly than kT so that the spread $\Delta\theta$ would increase. This calculation is, of course, simply for illustration and quite different values may be appropriate in physical situations of interest.

Another important possibility is that there may be more than one possible orientation of the overgrowth that approximates to a coincidence boundary of some order and therefore represents a local minimum in the interfacial free energy. Generally there will be one of these minima that is substantially deeper than the others, but occasionally we may find two minima of comparable depth. An example is the epitaxial growth from the vapor of ice onto an (001) face of iodine (Bryant *et al.*, 1959) where growth is observed with either the (0001) or the (2$\bar{1}$10) planes of ice parallel to the interface. The growth habit of the ice islands either as hexagons or rectangles makes distinction between the two growth modes obvious.

Examination of the interface geometry shows that each of these configurations differs by about 6% from a simple coincidence boundary. It does not, of course, immediately follow that the interface energies are nearly equal in the two cases, since this may depend on details of the interaction potential, but it is not surprising that this is so. If we can calculate the interface energy in the two configurations, then it is possible to apply standard heterogeneous nucleation theory (e.g., Fletcher, 1963) to evaluate nucleation rates for the two crystal habits as a function of temperature and supersaturation. The critical embryos in this case are certainly large enough for our interface theory to be applied with good approximation.

This last remark has introduced the subject of nucleation theory, and it may be appropriate to conclude with a few comments on this topic. Broadly speaking, we are here concerned only with heterogeneous nucleation on a plane substrate, and it is useful to distinguish two extreme cases representing high and low supersaturations, respectively.

In the high-supersaturation regime we are concerned with the deposition of a relatively nonvolatile material, such as a metal, onto a substrate whose temperature is very much less than that of the vapor source. The effective supersaturation at the substrate surface is therefore very high and the critical embryo for epitaxial growth contains only a few atoms. It would be pointless to try to apply any of our techniques to this case since the assumptions from which they were derived are not even approximately valid. Even the application of classical nucleation theory represents an extrapolation that can hardly be justified, and the problem should properly be treated by straightforward cluster statistical techniques.

In the low-supersaturation regime, on the other hand, we are concerned with deposition of a relatively volatile material onto a substrate at a temperature

nearly equal to that of the source so that the supersaturation is only of the order of a few percent. Alternatively, the situation may involve deposition from a solution with only a small supersaturation. In such cases the critical embryo typically contains thousands or even millions of atoms, the interface area may be of order 10^{-10} cm^2 or larger, and the embryo may be many molecular layers in thickness. Under these circumstances classical nucleation theory can be applied with a good deal of confidence and the techniques outlined above can be used to evaluate the interface energy, which plays such a critical role in determining the manner of the epitaxial growth.

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