General Principles Governing the Structure and Energy of Interfaces between Crystals

by

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Synopsis: The general principles governing the structure and energy of crystal interfaces are reviewed, particular emphasis being laid upon the coincidence lattice and O-lattice concepts, on models involving dislocation grids and on variational calculations. Important common ground between these different approaches is pointed out and the generally agreed features of the structure of simple intercrystalline boundaries are summarized.

1 Introduction

Most practical applications of solid materials involve polycrystalline aggregates, rather than large single crystals. In some cases the individual grains in such an aggregate are chemically and crystallographically similar, but often this is not so and the variety of combinations encountered is enormous. Many physical properties, like density or specific heat, depend relatively little upon such structural details but others, like certain mechanical properties, are critically affected by grain size, purity, etc.

For this reason if no other it is important that we should have as good an understanding as possible of the properties of intercrystalline boundaries and one of the first steps to be taken is to study theoretically the very simplest kinds of boundary—those between two simple, pure and mutually insoluble crystals. Only against such a background can more complex situations usefully be discussed.

This paper aims to survey some of the general principles which guide such studies and to set out some of the main conclusions which have so far been reached. The emphasis will be on structure and energy, since these are the two most fundamental aspects involved. We shall not attempt to survey any of the other properties of interfaces, since Amelinckx and Dekeyser [1] have given an authoritative review of work before 1959 and the collected papers of the present Conference will bring the account up to date.

2 General Principles

The structure achieved by a crystalline interface is governed by the general principle that adjustments will occur until the free energy of the system is a minimum. This is indeed a powerful approach to the problem,

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as we shall see later, but we must recognize at the outset that the minimum attained is not generally absolute but rather a conditional minimum subject to certain constraints placed upon the system as a whole. This means that the sort of interface we may find in practice will generally depend to some extent upon the nature and history of the larger system of which it forms a part.

To be more explicit, suppose we cleave an ionic crystal at room temperature and then evaporate onto it a layer of pure metal. The metal atoms are moderately free to take up their configuration of lowest free energy but, at ordinary temperatures, the ionic substrate is immobile and cannot adjust its configuration except for minor elastic strain. On the other hand, suppose we examine the solidification of a eutectic alloy or of a pure metal; as two crystallites grow together their relative orientations remain fixed but the location and orientation of the grain boundary is a disposable parameter, which may even change by solid-state diffusion after solidification has occurred. We cannot, therefore, hope to develop models completely suitable for all occasions but must ask, in each case, the nature of the relevant constraints.

3 The Coincidence Lattice

A most useful concept in the treatment of intercrystalline boundaries is that of the coincidence lattice, the geometrical basis of which has been discussed by Ranganathan [2], following a method put forward by Frank in 1958.

The idea is simple. Suppose we have two crystals of given structure and relative orientation and let their lattices interpenetrate to fill all space, as illustrated for a two-dimensional case in Fig. 1. Then if we bring a lattice point of one crystal into coincidence with a lattice point of the other, as at O in Fig. 1, we will in general generate a whole three-dimensional array of such coincidences which we may call the coincidence lattice for the problem. A unit cell of this coincidence lattice is shown as OABC in Fig. 1. (Strictly speaking, the set of cases for which a coincidence lattice of finite size exists has measure zero relative to the set of possible lattices and orientations. However, there always exists such a finite case arbitrarily close to any given configuration so that, from continuity arguments, we may always treat instead this finite case.)

The degree of matching between the two crystals can be measured by the density of coincidence lattice sites relative to lattice sites in the individual lattices. The possibilities in the general case are numerous, but systematic relations exist when the two crystal lattices are identical [2]. If Σ is the reciprocal density of coincidence lattice sites, then Friedel [3] has shown that Σ has only odd values for the cubic system, $\Sigma=1$ corresponding to exact coincidence and $\Sigma=3$ to the simplest twin relationship between the two crystals.

If the orientations of the two crystals are fixed but the position of the boundary is determined by energy considerations, then it is clear that it will lie along a closely packed plane of the coincidence lattice. If for some reason the boundary is constrained so that it must make a small angle to this plane, then one would expect the boundary to be stepped [4]. These

factors should be most important for determining boundary direction when Σ is small (say $\Sigma < 20$), for then the most closely packed plane of the coincidence lattice will contain a fairly large density of lattice points. If Σ is large then other factors may become increasingly important. In particular, since small values of Σ are bordered by very large values, we might expect some sort of near-coincidence phenomenon in such a case, and indeed, as we shall see later, this does occur [5].

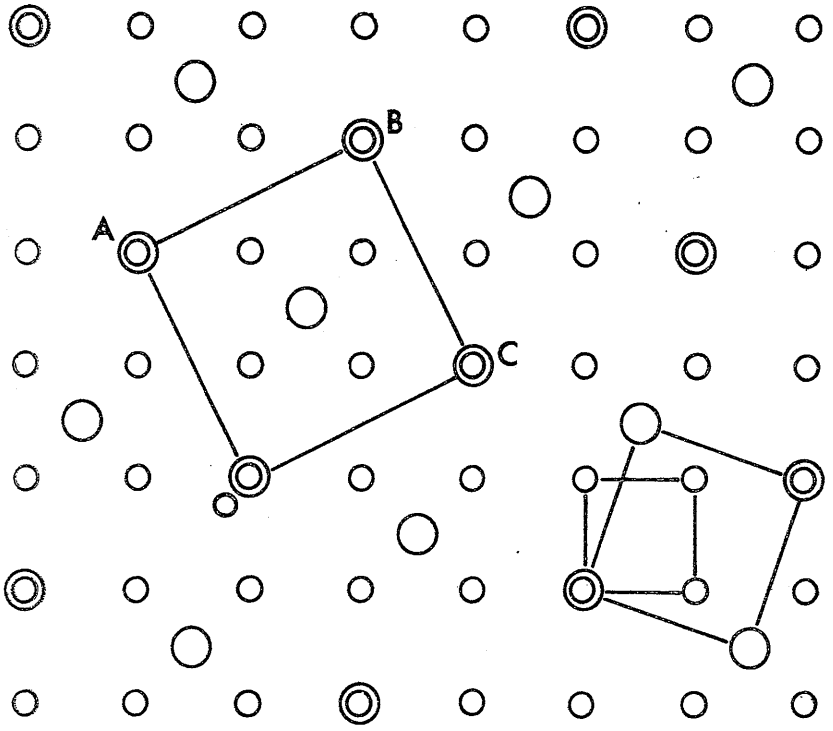

Fig. 1.—The coincidence lattice formed by interpenetration of two different crystals. OABC . . . are points of this coincidence lattice. The linear transformation relating the two lattices is shown at the right.

The coincidence lattice concept is also fruitful in discussion of the growth of one crystal upon a substrate surface provided by another, as in the formation of epitaxial films. Here the boundary direction is not a disposable parameter, but only the orientation of the growing crystal. We can immediately state that the orientation giving minimum interface energy, and therefore the one which will be favoured in normal growth, will be that which gives a maximum density of coincidence lattice sites in the boundary.

For a pair of arbitrary real crystals it is, of course, impossible to produce a rigorous coincidence lattice of finite size, but we have already remarked that, by a very small change in the parameters involved, this can generally be accomplished. By continuity arguments then, the real situation will differ very little from this adjusted model and we can make predictions about preferred growth orientations and epitaxial relations. In the next section we shall return to consider these deviations from exact matching in greater detail.

Recently Bollman [6] has extended the concept of the coincidence lattice to a new sort of lattice relation between two interpenetrating structures which he terms the O-lattice. For a wide class of pairs of lattices having a common point like O in Fig. 1, we can regard each point $\mathbf{r}'$ of one lattice as having been derived from a point $\mathbf{r}$ of the other lattice by a linear transformation $\boldsymbol{L}$ referred to O as origin

$$\mathbf{r}' = \boldsymbol{L}\mathbf{r} \tag{1}$$

Thus, in Fig. 1, $\boldsymbol{L}$ involves a relative rotation about O of $\tan^{-1}(1/3) = 18° 25'$ and an expansion of one lattice relative to the other by a factor $\sqrt{(5/2)} = 1.5811$, while in Fig. 2 the rotation is $\tan^{-1}(9/16) = 26° 51'$ and there is no change in relative lattice dimension.

This relation between the two lattices is not unique, however, and it is an important property of the points of the coincidence lattice that the same result is obtained by applying the same transformation $\boldsymbol{L}$ about any point of the coincidence lattice. It may, however, be possible to transform one lattice into the other by applying $\boldsymbol{L}$ about points other than those belonging to the coincidence lattice. This is not the case in Fig. 1 but, in Fig. 2, points like O′ serve in this way, as is easily seen by inspection. The totality of points having this property is called the O-lattice; the coincidence lattice is a superlattice of the O-lattice.

Whilst the coincidence lattice is of simple Bravais form, it is important to realize that the O-lattice may degenerate into some sort of continuum. For example, if Fig. 2 represents a (100) plane of two cubic crystals which have been rotated about a common [100] axis, then the O-lattice consists of a set of parallel lines running in the [100] direction (normal to the plane of the diagram) through the set of points O and O′.

The important thing about the O-lattice is that, as shown by Bollman [6], there is a direct correspondence between the pattern of the O-lattice in a given plane and the fringes of the moiré pattern produced by superposing the atomic position maps of the two crystals in that plane. The O-lattice therefore defines regions of good fit between the two crystals and hence regions of minimum elastic strain. Its geometry thus tells us a good deal about the structure of the interface and this can be derived by elegant formal manipulations without going into details of atomic displacements.

4 Dislocation Models

Burgers [7] and Bragg [8] seem to have been the first to suggest that small angle grain boundaries can be considered as arrays of dislocations and the familiar picture of a simple tilt boundary is shown in Fig. 3. If θ is the

angle of relative tilt and b the Burgers vector of the dislocations, then their spacing D is given, for small θ, by

$$D = b/\theta \tag{2}$$

this relation has been verified, for example, by direct counting of dislocations, made visible by etching, in germanium crystals [9], so that the model rests on a firm physical basis.

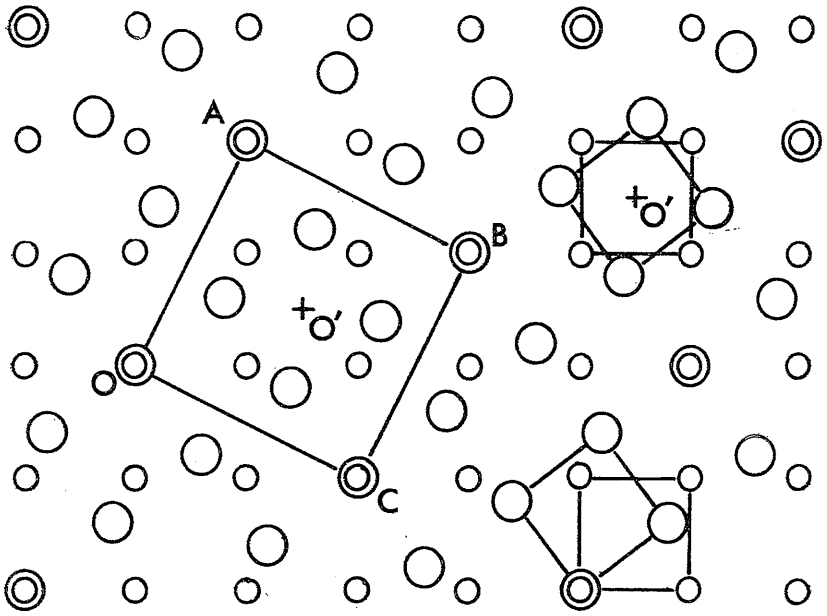

Fig. 2.—The coincidence lattice points OABC . . . are supplemented by other special points like O′ to form the O-lattice. The two possible linear transformations relating the lattices are shown at the right.

Description of a more general grain boundary in terms of a dislocation model is necessarily more complex. Frank [10] has derived a relation for the total dislocation content of an arbitrary grain boundary between two similar crystals in the form

$$\mathbf{B} = 2(\mathbf{u} \times \mathbf{v}) \sin(\theta/2) \simeq \theta(\mathbf{u} \times \mathbf{v}) \tag{3}$$

where $\mathbf{v}$ is any arbitrary unit vector lying in the plane of the boundary, $\mathbf{u}$ is a unit vector parallel to the axis of relative rotation between the crystal parts separated by the boundary, θ is the angle of rotation and $\mathbf{B}$ is the vector sum of the Burgers vectors of all dislocations cutting $\mathbf{v}$, the unit of length used in defining $\mathbf{v}$ being very much greater than the lattice spacing. Two arbitrary directions for $\mathbf{v}$ give all the available information about the boundary from this relation so that, if only one or two kinds of dislocation are present, their distribution is uniquely determined. If three or more dislocation types occur in the boundary, then there are

many possible geometrically consistent solutions and the physically applicable one must be that with lowest energy.

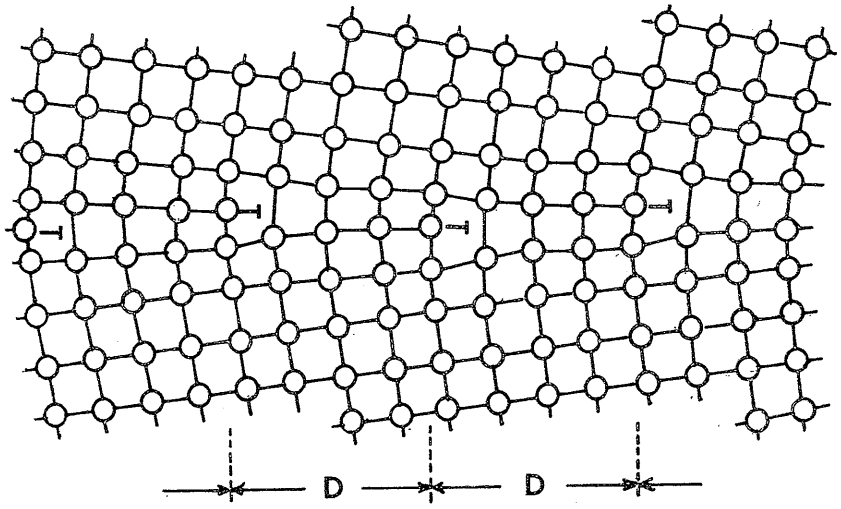

Fig. 3.—Dislocation model of a small-angle tilt boundary.

Kuhlmann-Wilsdorf [11] has considered the application of Frank's result in some detail. From this and other work we can see that boundaries consist in general of intersecting grids of parallel dislocations. If there is only one grid, then the boundary must be a tilt boundary of the type discussed before. A twist boundary has two intersecting grids of screw dislocations as shown in Fig. 4 and any more complex boundary requires at least two grids of dislocations of mixed type. It can be stated in general that the vector sum of the edge components, in the plane of the boundary, of all Burgers vectors contributing to the network, multiplied by the respective dislocation densities, must vanish; the corresponding sum of the screw components is equal to twice the negative angle of twist.

The validity of the dislocation model depends upon the dislocations being far enough apart that they may preserve their separate identity. This can only be the case if their separation is greater than about four atomic spacings which, from Equation (2), implies a misorientation angle less than about 15°. For greater angles of misorientation some other sort of model must be used.

One such possibility has been suggested by Brandon [5] and represents an extension of the coincidence lattice model. We have already seen that, at particular relative orientations, the reciprocal density Σ of coincidence lattice sites is small and favoured boundaries are then the most closely packed planes of the coincidence lattice. For closely neighbouring orientations, Σ is very large, but it may be energetically favourable to strain the crystals slightly near the interface to force a coincidence lattice of small Σ over neighbouring regions of crystal. Because of the slight misfit,

however, this coincidence lattice will then contain arrays of dislocations separating these well-aligned lattice blocks. The intercrystalline boundary can then follow the close-packed planes of the coincidence lattice but will be disturbed at intervals by the dislocations.

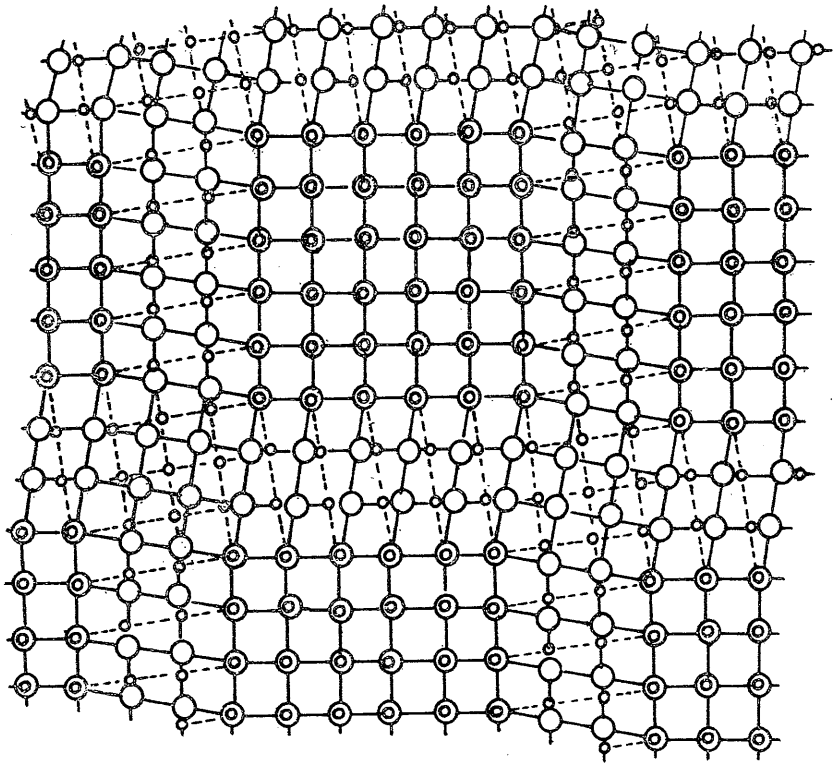

Fig. 4.—A twist boundary of small angle, showing the crossed grid of screw dislocations which comprise it. Atoms in planes immediately above and below that of the paper are shown.

This sort of picture is valid provided, again, that the dislocations in the coincidence lattice are far enough apart that their cores do not begin to overlap. For an orientation difference close to zero, the coincidence lattice becomes identical with the real lattice and $\Sigma = 1$. In this case the orientation range over which the dislocation model applies is roughly $\theta_0 = \pm 15°$, as follows from Equation (2). For a more general boundary Brandon therefore suggests the criterion

$$\theta < \theta_0(\Sigma)^{-\frac{1}{2}} \tag{4}$$

Figure 5 shows the range of orientations over which this sort of model is applicable in the face-centred cubic system. The stereographic plot shows the crystallographic orientation of the twinning direction involved and the circle around each particular orientation suggests its range of validity. Only cases with $\Sigma < 19$ have been plotted, but even for these there is considerable overlap. It is plain, however, that quite a large fraction of possible boundary orientations might be treated in this way.

When we come to consider boundaries between crystals of differing structures, the same sort of principles apply. In general, there will not exist any strict coincidence lattice, but one can be forced by introducing elastic distortions and it will then contain dislocations. The one case exceptional to this rule is that of a very thin film of material growing upon a substrate, for it may then be energetically possible to strain this film macroscopically so that its lattice parameter is changed and an undislocated coincidence lattice is formed over the whole interface [12]. For any film much thicker than a monolayer, however, this cannot occur and the resulting coincidence lattice will contain dislocations [13].

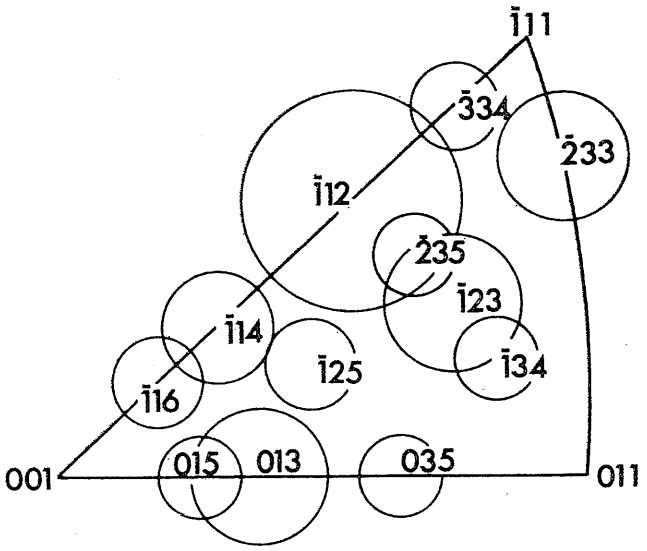

Fig. 5.—Stereographic plot of the twinning directions for which simple coincidence-lattice boundaries occur in a f.c.c. metal, together with an indication of the range of validity of each boundary model (after Brandon [5]).

From our previous discussion we may therefore expect to find oriented overgrowth (epitaxy) of one material upon another provided one can produce a reasonably large density of coincidence sites in the interface with a relatively small strain. To be more explicit, if Σ' is the density of coincidence sites in the interface, then the allowable fractional deviation from fit should be of order $0.2\ (\Sigma')^{-\frac{1}{2}}$. There may, of course, be several orientations which simultaneously satisfy this criterion, so that there is the possibility of several different epitaxial orientations.

5 Energy Considerations

So far our discussion has only been concerned with geometrically reasonable solutions to the interface problem, and the selection of the appropriate boundary has been made on the intuitive ground that the most symmetrical configuration will generally have the lowest energy. Let us now consider the energy in more detail.

Once again, the background calculation relates to grain boundaries in homogeneous materials and here it is the well-known treatment of Read and Shockley [15]. We have already seen that simple grain boundaries can be regarded as made up of grids of dislocations, and the problem is simply to calculate the energy of such an array. This energy is basically elastic strain energy and, for the purposes of the calculation, it can be divided conveniently into two parts: that contained in the dislocation cores, which can only be evaluated by detailed calculation of atomic interactions, and that in the rest of the crystal, which can be treated to good approximation by elastic continuum theory.

Provided the dislocations are far enough apart that their cores do not begin to overlap (about four atom spacings) then the first contribution is simply proportional to the density of dislocations and hence to the boundary angle θ. The continuum contribution can be evaluated in several ways [14, 15], all of which are equivalent to an integration of the stress-strain product for the combined elastic fields of the dislocations over the region outside the cores. The final result is

$$E = E_0\theta\,(A - \ln\theta) \tag{5}$$

with

$$E_0 = Ga/4\pi\,(1-\sigma) \tag{6}$$

where G is the rigidity modulus, a the lattice constant and σ Poisson's ratio for the crystal material (neglecting anisotropy). The constant A, which contains the core contribution, is found to have a value near 0.23 for many metals.

The shape of this theoretical curve is shown, as the full curve, in Fig. 6, but it must be remembered that its validity is restricted to values of θ small enough that the cores do not overlap, say θ less than 15°, or at most 20°. Despite this restriction, some metals such as iron actually show an energy maximum near $\theta = 30°$ as calculated, though they tend towards a behaviour independent of angle for larger θ [1]. Rather more commonly, however, in lead and tin [1], in germanium [16] and in AgCl [17] the energy increases steadily until it becomes independent of angle for $\theta \gtrsim 30°$. The correctness of Equation (5) is therefore limited to $\theta \lesssim 20°$, which is what would be expected from its derivation. The extension necessary in this model when the core regions begin to overlap has been examined by Li [18]. In outline, one expects the core regions to be highly distorted so that, once overlap occurs, the boundary is nearly amorphous and has an energy independent of θ. The detailed argument is, of course, rather more specific than this.

Although the theoretical curve plotted in Fig. 6 is shown as smooth, this is really an oversimplification, for it assumes that the spacing of dislocations can have any arbitrary value, while the dislocation model requires that dislocation cores be directly upon atomic planes. Thus, for example, for $\theta = 9°\ 24'$ in a simple cubic tilt boundary, a dislocation is required in every sixth lattice plane. If the angle is increased slightly, by $\delta\theta$ say, then the average dislocation spacing will be somewhat less, and occasionally dislocations will be separated by five rather than six planes. For small values of $\delta\theta$ these "five" spacings will occur at separations of $a/6\delta\theta$ and can be thought of as arising from a superimposed set of dislocations at this spacing [14]. These additional dislocations have an

associated elastic energy, so that the special point $\theta = 9° 24'$ is located at a small cusp of the form $-E'\delta\theta \ln\delta\theta$, where E' in the present case is of order $E_0/6$. The smooth curve given by Equation (5) is therefore really the locus of cusps such as this, and the true behaviour is as suggested by the broken line in Fig. 6.

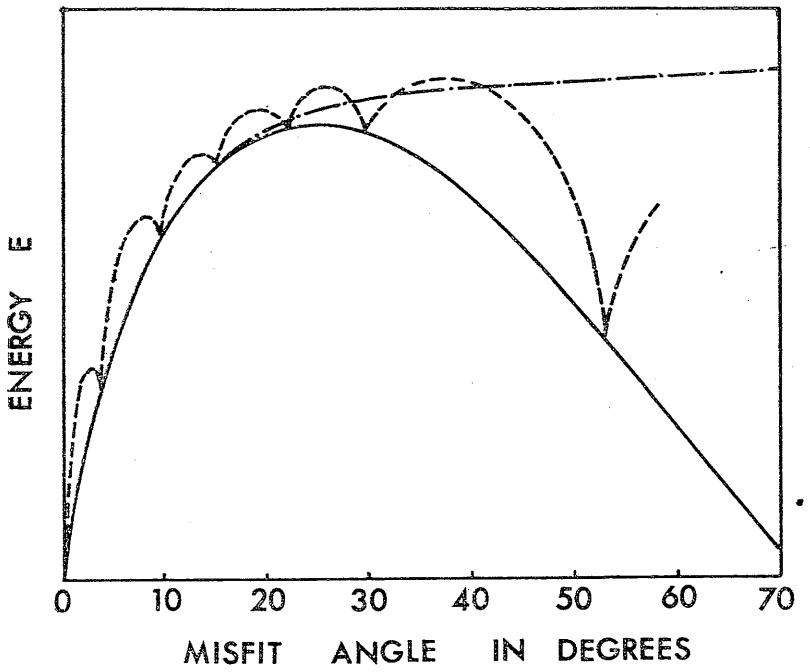

Fig. 6.— ——— The Read-Shockley Equation (5) for interface energy.
– – – – Qualitative addition of cusped subsidiary minima.
– · – · Energy calculated from the theory of Van der Merwe

It is immediately clear that this is simply another manifestation of the coincidence lattice idea and the stability of boundaries containing a high density of coincidence lattice sites. The strength E' of the cusp near any preferred orientation increases as the site density Σ^{-1} increases, so that simple twin boundaries, like that at 53° in Fig. 6, are located at particularly deep cusps. This calculation can, however, only be suggestive, since the dislocation model is not valid in detail for $\theta > 20°$.

It is not possible to apply this sort of treatment to boundaries between crystals of different materials since the elastic properties change continuously across the boundary. Frank and Van der Merwe [12], however, have investigated the detailed nature of dislocations in this case and Van der Merwe [19, 20] has applied the results to a discussion of such interfaces.

Basically we can divide the problem into two parts: the interaction and dislocation problem at the interface itself and the treatment of elastic strain energy in the two separate half-crystals. Except in the case where one of the half-crystals is a monomolecular layer so that it can be homogeneously strained, it will be necessary for the interface to contain dislocations to accommodate the lattice misfits, for example as shown in Fig. 7. Treatment of these dislocations is difficult because the adhesive forces across the interface are different from the cohesive forces within the crystals.

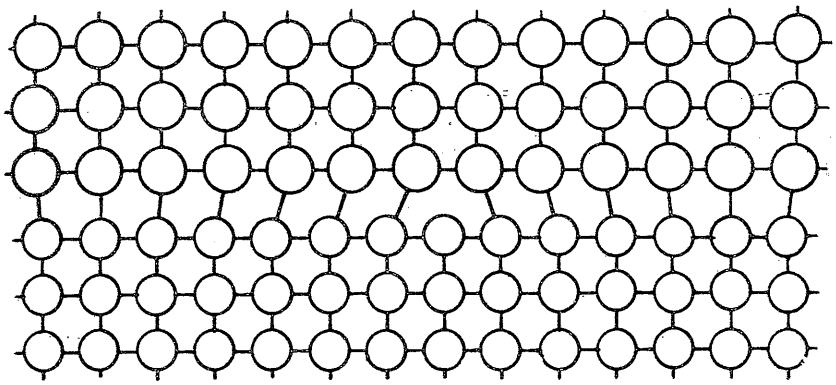

Fig. 7.—Dislocations in a simple misfit boundary between two crystals.

Van der Merwe avoids this difficulty by replacing the real boundary potential by either a simple sinusoidal potential or by a set of periodically arranged parabolic wells. His treatment is basically one-dimensional but the results are then superposed to give a reasonable approximation for a real two-dimensional boundary. With this assumption, the atomic positions at the boundary can be determined to quite good approximation, so that it is no longer necessary to separate out the dislocation cores. Since the real misfit regions are confined to the crystal boundary, it is then reasonable to treat each half-crystal by simple elasticity theory, matching stresses across the boundary to connect the two regions.

This model is really a generalization of the treatment of Read and Shockley, since dislocations are still quite explicitly involved. We therefore expect the two treatments to agree, at least for small angles in the case of simple twist boundary which can be discussed in either formalism. This is, in fact, the case, and the model of Van der Merwe shows the familiar $-\theta\ln\theta$ cusp for $\theta = 0$. For $\theta > 20°$, however, the new curve continues to rise in energy, as shown in Fig. 6, rather than falling, as does the Read-Shockley result. This tends to give better agreement with experiment in

many cases but brings its own region of invalidity, for the energy of a cubic (100) twist boundary, for example, continues to rise as θ approaches 90°, whereas $\theta = 90°$ is really equivalent to $\theta = 0$. This situation can be alleviated by combining the curve centred on $\theta = 0$ with another centred on $\theta = 90°$, but this is not very satisfactory.

Van der Merwe's original treatment [19, 20] gives a curve with no subsidiary cusps, but this is a product of the simplifications built into the model. A later calculation [21] using a hierarchy of dislocations, similar to those proposed by Read and Shockley, leads to the same sort of subsidiary cusped minima.

The new information which comes from Van der Merwe's calculation relates not to simple grain boundaries but rather to interfaces between differing crystals. The simplest case is that of two crystals with a fractional difference

$$\delta = 2 \left| \frac{a_1 - a_2}{a_1 + a_2} \right| \qquad (7)$$

in lattice parameter, meeting on similar crystallographic planes. It is not possible to write a simple expression for the energy but the curve of E vs δ is very similar to the E vs θ curve given by the theory in Fig. 6. There is a cusp of approximate form $-\delta \ln \delta$ at $\delta = 0$, where the fit is exact, and the curve then rises continuously as the lattice parameters differ increasingly.

This discussion also allows an evaluation to be made of the relative contributions made to boundary energy by interactions across the boundary and by elastic energy stored in the bulk of the crystal. Generally speaking, if the dislocation separation in the boundary is D, then most of the elastic strain energy is localized within a distance D of the boundary, with a predominance of energy in the softer crystal, as measured by the effective surface modulus $G/(1-\sigma)$. This allows definition of an effective thickness of order 2D for the interface zone, and this is of particular importance in cases where the growth of one material in the form of a thin film upon a crystal of macroscopic dimensions is being considered [13].

Whilst this sort of treatment can be extended [22] to show that there are subsidiary cusped minima for cases when the lattice parameters of the two crystals are in the ratio of two small integers, corresponding again to a surface coincidence lattice of small Σ, the approach suffers from the fundamental defect that the true interface potential is replaced by an arbitrary and rather artificially simplified potential. We shall see in the next section how this restriction can be removed.

6 Variational Methods

At the beginning of this paper we remarked that the interface problem is essentially variational in nature—we seek that interface which will minimize the free energy of the system subject to such constraints as may be applied. All the approaches so far discussed have essentially attempted this, but they have done so by combining together elements, such as dislocations, for which the energy solutions for the strain field and re-

lated quantities were already known. They have also all dealt with energy rather than free energy, corresponding to the solution expected at very low temperatures. This is not a serious approximation and we shall return to it later. The point we now take up is whether some more direct variational procedure might lead more conveniently, or more generally, to information about crystal interfaces.

The variational method is simple in principle—if the interaction potentials between all the atoms involved are known, then we just vary the positions of all the atoms, subject to constraints like that defining the relative orientations of the two crystals at large distances, until the energy is a minimum. This is, of course, too large a programme to be feasible in practice, so that we may simplify matters by noting that each bulk crystal behaves, to a good approximation, like an elastic continuum. We may, therefore, confine our atomic interaction calculation to the region very near the interface and adopt some artifice to couple this variational problem to the continua representing the bulk crystals.

Before discussing this further, let us examine the sorts of potential functions which characterize the interactions between atoms, for the nature of these may affect our approach to the problem. For simple insulators like solid argon, the potential consists of an r^{-6} attraction, due to dispersion forces, and a short range repulsive term due to electron overlap. This can be reasonably represented by a potential of Lennard-Jones form

$$V(r) = V_0[(r/r_0)^{-12} - 2(r/r_0)^{-6}] \tag{8}$$

or by the analytically more tractable Morse potential

$$V(r) = V_0\{\exp[-2a(r-r_0)] - 2\exp[-a(r-r_0)]\} \tag{9}$$

where the potential has the value $-V_0$ at the equilibrium distance r_0. In ionic crystals the r^{-6} attractive potential is replaced by the r^{-1} Coulomb interaction which makes matters much more difficult because of its extremely long range, though, by taking plane-wise summations, the interaction of a single ion with the crystal is more nearly exponential [23, 24].

In metals the interaction is primarily that between ion cores, shielded by the charge distribution of the valence electrons. A simple discussion would lead to a potential of the form

$$V'(r) = A\, r^{-1}\exp(-ar) \tag{10}$$

which has no attractive part at all if the volume is kept constant. A more careful treatment of the shielding, however, shows that the sharp cut-off in electron density at the Fermi surface can give rise to potential oscillations of considerable magnitude [25], the so-called Friedel oscillation. The total cohesive energy is a combination of this interaction potential which, though of complex origin, can be treated very nearly in the same way as an ordinary potential [26], together with an electronic term which depends mainly upon the total volume per atom and so can usually be considered as constant in an interface problem. Because of the collective nature of these metallic potentials, however, they can only be applied in detail to discussions of grain boundaries in otherwise homogeneous material. The interactions between two metal atoms across an interface separating two crystals of the pure metals may be quite different.

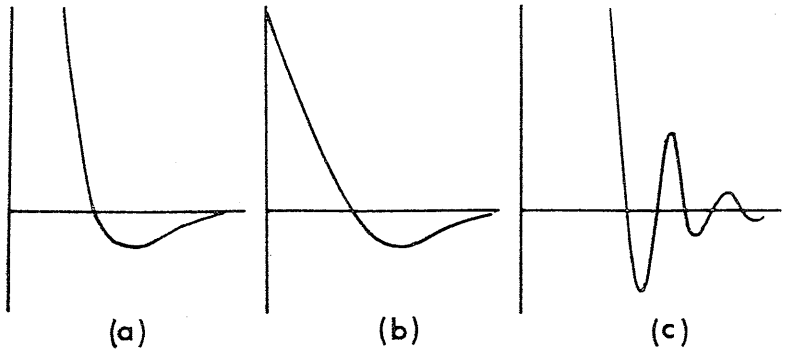

Fig. 8.—Different forms of atomic interaction curves: (a) Lennard-Jones potential; (b) Morse potential; (c) Harrison calculation for aluminium.

Curves showing the general form of these interactions are drawn in Fig. 8. Apart from their obvious differences, one of the main things to note is their moderately long range. Any calculation must therefore extend to at least second-nearest neighbours, in general, to be a reasonable approximation to reality.

There is one further type of interaction potential which we have not yet discussed. This is the sort of interaction found in materials with a high degree of covalent bonding, such as diamond or germanium, for example. These interactions are not simple central forces but involve three-body correlations and have strong angular dependence. An analytical treatment of such materials is extremely difficult but, as a compensation, the concept of valence bonds in particular directions assumes good physical reality so that useful boundary models can be built which probably have a high degree of validity [27].

Once the interatomic potential has been evaluated, it becomes marginally possible, using modern computers, to perform a direct variational calculation of interface structure and energy. Such a calculation might consider the positions of atoms in the two layers on either side of the boundary as variational parameters and use some simple method to connect their displacements to associated elastic strains in the crystal bodies, approximated by continua. This does not, however, seem yet to have been attempted.

An alternative approach which achieves the same result has been developed by the present author and his students [28, 29]. The basis is still that outlined in the preceding paragraph but, by dealing with the Fourier transform of the interaction potential, the whole manipulation can be carried out in reciprocal space. This leads to important simplifications, since the Fourier components of the atomic displacements are much more nearly independent, in the expression for the energy, than are the displacements themselves and, in addition, several formal results directly related to the coincidence lattice and O-lattice concepts arise.

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

$$V_0(\mathbf{r}) = \sum_{\mathbf{R}} v_{AB}(|\mathbf{r}-\mathbf{R}|) \equiv \sum_{\mathbf{R}} v(\mathbf{r}-\mathbf{R}) \tag{11}$$

where we shall now keep to the simplified notation at the right. This potential can be written as a Fourier series

$$V_0(\mathbf{r}) = \sum_{\mathbf{k}} V_0(\mathbf{k}) \exp(i\mathbf{k}.\mathbf{r}) \tag{12}$$

where the Fourier components $V_0(\mathbf{k})$ are given by

$$V_0(\mathbf{k}) = \sum_{\mathbf{R}} v(\mathbf{k}) \exp(-i\mathbf{k}.\mathbf{R}) \tag{13}$$

and $v(\mathbf{k})$ is the transform of the interatomic potential $v(\mathbf{r})$.

If the B atom is one of a whole crystal with lattice positions $\mathbf{R}'$, then the total interaction energy across the interface is

$$E_0 = \sum_{\mathbf{R}'} V_0(\mathbf{R}') = \sum_{\mathbf{R}} \sum_{\mathbf{R}'} \sum_{\mathbf{k}} v(\mathbf{k}) \exp[i\mathbf{k}.(\mathbf{R}'-\mathbf{R})] \tag{14}$$

Since the $\mathbf{R}$ and $\mathbf{R}'$ summations are over crystals which are infinite in directions parallel to the interface and semi-infinite in the normal direction, the sum in Equation (14) vanishes except for values of $\mathbf{k}$ whose components parallel to the interface are vectors of both the reciprocal lattice of the surface layer of crystal A and of the reciprocal lattice of the surface layer of crystal B. Expressing this differently, the only Fourier components contributing to the energy are those belonging to the coincidence lattice of the two-dimensional reciprocal lattices of the surfaces of the two crystals. There are various phase factors involved in Equation (14), representing the normal separation of the two crystals, but the interaction energy will generally be large (corresponding to a low-energy boundary) if the density of these reciprocal coincidence lattice sites is high. This is the exact dual of our earlier statement about the density of ordinary coincidence lattice sites in direct lattices, but is now formulated in such a way as to allow direct evaluation of interface energy.

The next thing to be included is some allowance for relaxation of atomic positions near the interface. This can be done by displacing the A atom at $\mathbf{R}$ to a position $\mathbf{R} + \mathbf{F}(\mathbf{R})$ where

$$\mathbf{F}(\mathbf{R}) = \sum_{\mathbf{K}} \mathbf{F}_{\mathbf{K}} \exp(i\mathbf{K}.\mathbf{R}) \tag{15}$$

and the $\mathbf{F}_{\mathbf{K}}$ are now the Fourier components of the displacement. The atoms of the B crystal are similarly displaced from $\mathbf{R}'$ to $\mathbf{R}' + \mathbf{F}'(\mathbf{R}')$. This is quite general, but it is convenient to consider only displacements of atoms right at the interface, the displacement associated with Fourier component $\mathbf{F}_{\mathbf{K}}$ falling off with distance z from the interface as $\exp(-Kz)$, from the standard elastic solution. The components $\mathbf{F}_{\mathbf{K}}$ and $\mathbf{F}'_{\mathbf{K}}$ in the two crystals are matched across the interface by requiring continuity of stress. The allowed Fourier components $\mathbf{K}$ are controlled by the requirement that the boundary configuration be periodic with the period of the coincidence lattice between the two crystals at the interface and, in addition,

there must be displacement nodes at all points of the O-lattice. The allowed **K** are thus the vectors of the reciprocal lattice of this coincidence lattice. For twin boundaries the allowed **K** will be rather large in magnitude and there will be only few of them, but for a general boundary **K** will approximate a continuous variable.

When the displacements (15) are made, the energy E_0 given by (14) becomes more complicated [28], but the leading terms have the form

$$E \simeq \sum_{\mathbf{k}} v(\mathbf{k}) \prod_{\mathbf{K}} J_0(2\mathbf{k}.\mathbf{F}_\mathbf{K}) \{\delta_{\mathbf{k},\mathbf{g}}\, \delta_{\mathbf{k},\mathbf{g}'} + \sum_{\mathbf{K}} \frac{J_1(2\mathbf{k}.\mathbf{F}_\mathbf{K})}{J_0(2\mathbf{k}.\mathbf{F}_\mathbf{K})} \delta_{\mathbf{k},\mathbf{g}}\, \delta_{\mathbf{g}'-\mathbf{K},\mathbf{g}}\} + \sum_{\mathbf{K}} GK|\mathbf{F}_\mathbf{K}|^2 \quad (16)$$

where **g** is a surface reciprocal lattice vector of crystal A and **g′** of crystal B and the $J_n(x)$ are Bessel functions. Briefly, the first term $\delta_{\mathbf{k},\mathbf{g}}\, \delta_{\mathbf{k},\mathbf{g}'}$ represents the undistorted energy E_0, modified by the Debye-Waller-like distortion factor $\prod J_0$. The second term represents a coupling between nearly-coincident reciprocal points **g** and **g′** by the distortion component **K** and gives an energy contribution nearly linear in $\mathbf{F}_\mathbf{K}$. The final term takes account of the elastic energy stored as distortions in the crystal. There are higher order terms representing compound coupling between **g** and **g′** involving several different **K**, which have been omitted.

Equation (16) can be minimized with respect to the distortions $\mathbf{F}_\mathbf{K}$ and exhibits cusped minima whenever two reciprocal vectors **g** and **g′** coincide. Near such coincidences the prominent $\mathbf{F}_\mathbf{K}$, which are those with smallest **K**, produce a distortion of the lattice near the interface which is equivalent to a dislocation. The dislocation "core", however, is treated in a straightforward manner rather than being separated off as an unknown quantity.

No calculations applying this approach to real materials have yet been published, but a trial calculation using a simple short-range potential shows the expected behaviour [30]. The case treated was that of a (100) twist boundary between two face-centred cubic crystals of lattice parameters a_1 and a_2. There is, as expected, a deep cusped minimum at $a_1 = a_2$, $\theta = 0$ and a much shallower minimum at $a_1 = \sqrt{2}a_2$, $\theta = 45°$. No other minima were apparent but this may have been because of the particular form of potential chosen. Calculations using Harrison's potential for aluminium [25] are now in progress [29]. The actual variational calculation using a real potential like that for aluminium is, unfortunately, not as simple as the abbreviated Equation (15) might suggest, but the minimization, when taken to second order, can be performed in about 10 minutes on a CDC 3600 computer.

One particularly attractive feature of this approach, in addition to the use of realistic potentials, is the fact that crystal symmetry is automatically included, which is not the case for most other methods.

As a final comment, something should be said about the effects of temperature, since at finite temperatures it is the free energy, rather than the energy, which must be minimized. Little work seems to have been done on this in the case of crystal-crystal interfaces, attention being concentrated on the solid-liquid and solid-vapour cases. The same principles, however, apply. As the temperature is raised, the entropy term becomes increasingly important and there is a general blurring of sharp

lines. We thus expect dislocations to become more diffuse and steps less well defined. The interface energy must be supplemented by an entropy term, deriving from the difference between the vibrational spectrum of modes which can be localized at the interface and those which are characteristic of the bulk crystal. All this is important but probably has little effect on interface properties, except at temperatures approaching the melting point.

7 Discussion

This paper has reviewed what appear to be some of the most promising approaches to the theoretical treatment of the structure and energy of simple interfaces between crystals. The word simple should perhaps be stressed because it is clear, from experimental work using electron microscopy, that rather complicated structures can arise at general interfaces. None the less, the two key concepts involved are those of the coincidence lattice and the dislocation grid. Together they allow simple pictures to be drawn up for various lattice structures and these pictures are substantiated by energy calculations using a sufficiently general formalism.

References — see p. 18.

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