

Crystal Interface Models — A Critical Survey

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I. INTRODUCTION

For many practical reasons we are often concerned with the properties of the interfaces between crystals of the same or different materials, and the problem of devising a model for the structure of such interfaces has received a good deal of attention over the past 20 years. Many techniques have been used to obtain experimental information about interface structure and behavior and the range of properties to be studied is immense. We shall not attempt to survey this wide field in the present paper but rather concentrate on a comparison and interrelation of the models that have been put forward to describe the structure and allow calculation of the energy of various rather simple types of interface. A more general overview can be obtained from the reviews by McLean(1) and by Amelinckx and Dekeyser(2).

The various models and theoretical approaches that we shall discuss are superficially distinct and can be given different names — dislocation models, coincidence lattice models, island models, etc. — but we shall see that they have many features in common and that the distinctions

arise because, in different physical situations, one or the other pictorial feature may be most prominent.

Rather than attempt a grand synthesis, let us begin with the simplest sort of model and then see how it must be modified for more complex situations. We shall see that, in fact, some interface configurations can be described in a variety of ways, depending upon the degree of emphasis given to the occurrence of specific atomic groupings. The equilibrium configuration is, however, determined by one single requirement, that the free energy of the system be a minimum. This minimum is not generally an absolute minimum, for this would require that the boundary migrate out of the crystal, but rather a conditional minimum subject to certain constraints. Thus we might fix the orientations of the two crystals and allow the interface to assume its equilibrium direction, this being a situation generally found in the solidification of a melt. Alternately, we might consider a situation common in growth from the vapor in which the orientations of one crystal and of the interface are fixed and the second crystal may take up any relative orientation so as to minimize the free energy. It is not to be expected that the results will be the same in each case.

A complication, from a theoretical point of view, arises from the fact that it is the free energy, rather than the energy, that must be minimized. These two quantities are, of course, equal at 0°K, but evaluation of the entropy term in the free energy at a finite temperature requires not only a knowledge of atomic positions in the boundary but also of the way in which vibrational modes localized on the interface modify the total vibrational spectrum of the crystal. This latter consideration is probably of no great significance in determining the equilibrium configuration, since the total effect of the interface modes should depend little upon interface orientation. The detailed atomic structure of the interface will, however, depend to some extent upon temperature, configurations of greater disorder being preferred at higher temperatures. No detailed calculations have apparently been made, and we shall not attempt this here, being content rather to minimize energy instead of free energy and so to determine interface structure at low temperatures.

II. DISLOCATION MODELS

A. A Simple Tilt Boundary

While early studies of the behavior of grain boundaries suggested that they might present an amorphous transition region between the

two crystals, it soon became evident that this could not be the true state of affairs, at least for small-angle boundaries. In 1940 Burgers(3) and Bragg(4) proposed a model in which each crystal was continuous up to the interface, the necessary connection between the two crystals being provided by an array of dislocations. This model is illustrated in Fig. 1 for the case of a simple tilt boundary in which one half-crystal has been rotated with respect to the other about an axis lying in the plane of the interface. It is clear that, except at the dislocation lines, there is little distortion of atomic environments across the grain boundary, so that the energy should be low. For the case shown, if θ is the angle between the two crystals and a the lattice parameter, which is also the Burgers vector of the edge dislocations, then the dislocation separation D is given by

$$D = a/(2 \sin \theta/2) \approx a/\theta \quad (1)$$

Clearly, though it might always be a reasonable approximation to consider the crystal lattices to extend right up to the interface, the concept of a wall of dislocations can only apply if $D \gg a$. Taking a dislocation separation $D \approx 4a$ as representing a reasonable limit, this restricts the model to boundaries with $\theta \lesssim 15^\circ$. For very small-angle boundaries the points of emergence of dislocations can often be made visible by etching, as for example in the case of germanium(5), and Eq. (1) has been verified exactly.

The energy problem for such an array of dislocations was first solved in classic paper by Read and Shockley(6) and we now consider this in some detail, since its conclusions are important and form the basis of much more recent work.

From standard dislocation theory, the elastic stress field at a point with coordinates (r, θ) near a single edge dislocation of Burgers vector

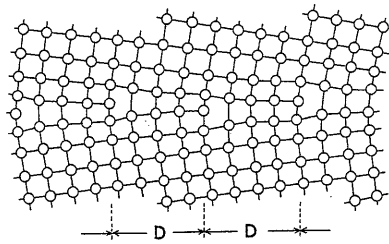


Fig. 1. Section through a simple small-angle tilt boundary between two cubic crystals. The boundary consists of a grid of edge dislocations, of separation D , running normal to the plane of the figure.

\mathbf{b} , lying along the z axis is given by

$$\sigma_{rr} = \sigma_{\theta\theta} = -2\tau_0 \sin \theta/r \quad (2)$$

$$\sigma_{r\theta} = 2\tau_0 \cos \theta/r$$

where

$$\tau_0 = G\mathbf{b}/4\pi(1-\nu) \quad (3)$$

G being the shear modulus and ν the Poisson's ratio for the material, assumed isotropic. This stress field is based on continuum theory and clearly becomes invalid near the origin where the continuum approximation is no longer valid. We might therefore use Eq. (2) and the associated expression for elastic energy only for r greater than some small value r_c , for which the continuum model is acceptable, and treat the "core" region $r < r_c$ by more explicit means. Alternately Eq. (2) might be used to some smaller radius r_0 , so chosen that the energy in the region $r_0 < r < r_c$ is equal to the core energy, eliminating the region $r < r_0$ from consideration. It is this difficulty, which lies near the heart of the dislocation model, that so drastically restricts its region of applicability. The core radius r_c is approximately two interatomic spacings, so that the results we now consider can only apply for dislocation spacings greater than about $4a$.

The energy density derived from Eq. (2) behaves as r^{-2} . We have already discussed the singularity at the origin, but there is also a logarithmic divergence in the total elastic energy when this density is integrated over an infinite crystal. This need not concern us, however, since we wish rather to compute the energy of a whole wall of parallel dislocations of equal spacing, as in Fig. 1. In this case the angular factors in Eq. (2) remove the divergence and a finite result emerges. The integration of the elastic energy density, using the r_0 artifice discussed above, has been carried out by Read and Shockley and, for a boundary of the type in Fig. 1, leads to the result

$$E = \tau_0 \theta (A_0 - \ln \theta) \quad (4)$$

where τ_0 is given by Eq. (3) with $\mathbf{b} = \mathbf{a}$ and the constant A_0 has the value

$$A_0 = 1 + \ln(\mathbf{a}/2\pi r_0) \quad (5)$$

The boundary of Fig. 1 is not, however, of the most general type, even for a simple tilt relation between the two crystals, for it lies along a principal crystal axis. If, instead, we let the boundary make an angle ϕ with a (100) plane, then Eq. (4) is generalized to

$$E = \tau\theta(A - \ln \theta) \quad (6)$$

where

$$\tau = \tau_0(\cos \phi + \sin \phi) \quad (7)$$

and

$$A = A_0 - \frac{\sin 2\phi}{2} \frac{\sin \phi \ln \sin \phi + \cos \phi \ln \cos \phi}{\sin \phi + \cos \phi} \quad (8)$$

The variation of A with ϕ over the range of θ validity of Eq. (6) is not large compared with the rapid variation of $\ln \theta$. However, τ does vary by about 30% over the range of validity of Eq. (7), $0 < \phi < \pi/2$, and is a minimum for $\phi = 0$.

There are various other ways of deriving the form of Eq. (6) for the energy [see, e.g., ref. (7)] which make it plain that the result holds for much more general types of boundary than the tilt boundary between simple cubic crystals discussed in the original paper, though Eqs. (7) and (8) are explicit in this case. We shall return to consider these more general boundaries presently and give a simple derivation of Eq. (6).

Let us now look at the angular dependence predicted by Eq. (6) which is plotted as a full line in Fig. 2. In this figure a value $A = 0.23$ has been used, since this is found to give good agreement with experiment for a number of metals. We see that the grain boundary energy has a sharply cusped minimum for $\theta = 0$ and an energy maximum near 30° . This maximum is, however, outside the region of validity of the result which should not extend as far as 20° . This breakdown is

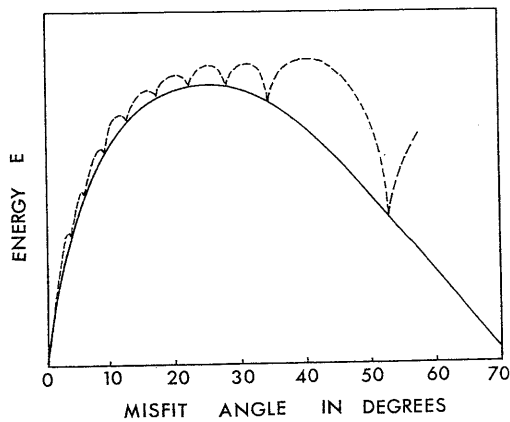


Fig. 2. Predictions of the Read-Shockley dislocation model for small-angle tilt boundaries. The full curve shows the form of the simple relation (6), while the broken curve shows the cusped energy minima predicted by the hierarchical dislocation model and Eqs. (11) and (12).

evident at larger angles, since the calculated E becomes negative for $\theta > 70^\circ$, while it is physically obvious, in the case of a symmetrical tilt boundary about an [001] axis, that $\theta = 90^\circ$ is exactly equivalent to $\theta = 0^\circ$, so that the figure should be symmetric about $\theta = 45^\circ$. One might reasonably take account of this symmetry by centering another cusped minimum at $\theta = 90^\circ$ and interpolating hopefully between the two curves but this is not really justified in the region $20^\circ < \theta < 70^\circ$.

This simple theory, treating A as an adjustable parameter or using the dimensionless form

$$\frac{E}{E_m} = \frac{\theta}{\theta_m} \left(1 - \ln \frac{\theta}{\theta_m} \right) \quad (9)$$

where E_m is the interface energy at the position θ_m of its maximum, gives a very good description of the energy behavior of many interfaces for $\theta < \theta_m$. For $\theta > \theta_m$, the energy generally ceases to depend on θ , for example, in lead and tin(2) in germanium(8) and in AgCl(9). Silicon iron does, however, show a tendency toward a maximum near $\theta = 30^\circ$, in accord with Eq. (6) (ref. 2).

B. More General Grain Boundaries

The simple tilt boundary discussed in the previous section had two degrees of freedom—the angles θ , specifying the relative orientation of the two crystals, and ϕ , specifying the orientation of the boundary. The general grain boundary problem is specified by five parameters—three to fix the orientation of one crystal relative to the other and two to fix the orientation of the boundary (since rotation of a plane about its normal has no significance). Despite this complexity, a simple description of such a boundary in terms of grids of dislocations is possible.

Before considering the general case, let us look at a simple twist boundary in which one half-crystal is rotated relative to the other about an axis normal to the interface. Atomic planes immediately above and below the grain boundary are shown superposed in Fig. 3. Again, following the principles expressed by Burgers and Bragg, we may expect slight distortions in these two layers, so that as many atoms as possible take up nearly normal relative positions and the strain is concentrated into dislocations. In this case, however, instead of a single grid of parallel edge dislocations as for the tilt boundary, the pattern resolves itself into two perpendicular grids of screw dislocations, as is easily seen from the figure. A single dislocation grid

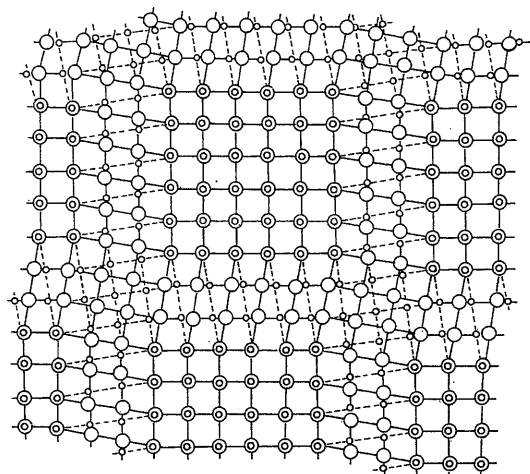


Fig. 3. Atomic pattern parallel to a simple, small-angle, twist boundary between two cubic crystals. Atoms above and below the boundary are shown as circles of different sizes. Islands of good fit are apparent and the boundary can be described in terms of two perpendicular grids of parallel screw dislocations.

is insufficient in this case, since it would lead to macroscopic shear distortions in each crystal.

An interesting pictorial feature of Fig. 3 is the occurrence of "islands," in which the fit between the two grains is good, separated by channels of highly distorted material forming the dislocation cores. This sort of island concept has had a long history in the discussion of crystal interfaces (10) and we shall see its recurrence in various forms at later stages of our present exposition.

The energy of an array of screw dislocations has also been considered by Read and Shockley (6), with the conclusion that here again the grain boundary energy has the form of Eq. (6), though the values of τ and A are somewhat different from those given previously.

Returning to the general case, we find that this can be analyzed by a method due to Frank (11). The final result, which has been treated in some detail by Brooks (12), has the form

$$\mathbf{B} = 2(\mathbf{u} \times \mathbf{v}) \sin(\theta/2) \approx \theta(\mathbf{u} \times \mathbf{v}) \quad (10)$$

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 of the two crystal parts separated by the boundary, θ is the angle of rotation about

\mathbf{u} 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} should be 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 at most 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 one physically applicable must be that with lowest energy.

Kuhlmann-Wilsdorf(13) has considered the application of Frank's result in some detail. From the invariance of Eq. (10) with origin, 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 shown in Fig. 1. A twist boundary has two intersecting grids of pure screw dislocations, as shown in Fig. 3, while any more complex boundary requires at least two grids of dislocations of mixed type. It can be stated quite generally 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 general form of the energy formula(6) also clearly applies to arbitrary boundaries, provided once again that the dislocations in each grid are far enough apart so that there is no overlap of core regions. This implies that the minimum at $\theta = 0$, for exact fit between the two grains, is a cusp with respect to any arbitrary angular misorientations away from this coincidence.

In many cases of interest, reasonably detailed atomic maps can be drawn for such general boundaries on the basis of Frank's formula(10) and the qualitative criterion that atomic positions should be adjusted so that nearest neighbor distances are roughly equal. A rather important special case arises with the diamond cubic and related structures; for, in these, interatomic forces are highly directional and it is physically plausible to talk of "bonds" between atoms. For these structures there are only four nearest neighbors and their arrangement must be closely tetrahedral, otherwise a bond becomes "broken" and these "dangling bonds" have significance for the electrical properties of these materials, which are electronic semiconductors. The geometry of such boundaries has been investigated in some detail by Hornstra(14) and by Holt(15).

C. Hierarchies of Dislocations

When the angle θ of a simple grain boundary is very small, the dislocation model meets no difficulties and provides a completely valid description of the interface structure. When θ becomes greater than about 5° , however, several difficulties arise. We shall leave the problem of the proximity of the dislocation cores to the next section and take up another point.

The dislocation model and associated energy calculation discussed above make one important assumption, which is that the dislocations in any one grid are uniformly spaced. Since dislocations must occur on atomic planes, this means that, for the simple case illustrated in Fig. 1, only angles θ such that

$$\tan \theta/2 = 1/n, \quad n = 1, 2, 3, \dots \quad (11)$$

can be considered, which restricts θ to the values 90° , $53^\circ 8'$, $36^\circ 52'$, $28^\circ 4'$, $22^\circ 37'$, $18^\circ 55'$, ... The configuration $\theta = 90^\circ$ actually represents exact fit and there are no dislocations, $\theta = 36^\circ 52'$ is a twin boundary on a (210) plane, $\theta = 28^\circ 4'$ a twin on a (310) plane, etc. It is true that the angles listed are so large that the overlap between dislocation cores is appreciable, so that the energy calculation may not be reliable, but at least the model is consistent. For larger values of n , say $n = 12$ corresponding to $\theta = 9^\circ 32'$, all conditions for validity are met, since the dislocation spacing is almost $6a$.

What happens, however, at a neighboring slightly larger value of θ ? The obvious configuration seems to be one in which most dislocations are spaced at $6a$ from their neighbors, but there is an occasional spacing of only $5a$. Read and Shockley suggest that this problem may be thought of as a regular dislocation grid of spacing $6a$, together with a superposed grid of dislocations of effective Burgers vector $a/6$, spaced so that one such dislocation occurs in each $5a$ -spaced region. If the deviation from the symmetrical position $\theta = 9^\circ 32'$ is $\delta\theta$, then the approximate spacing of these second-order dislocations is $a/6\delta\theta$. There is obvious difficulty in treating the core of these second-order dislocations but, provided that their spacing is large, most of their energy will reside in their elastic strain fields and will contribute an additional interface energy of order

$$\delta E_6 = -(\tau/6) \delta\theta \ln \delta\theta \quad (12)$$

which is a simple cusp of form like that near the coincidence point

$\theta = 0$ but of less depth. Similar cusps should occur around each of the orientations given by Eq. (11).

It is difficult to make any very precise calculations on the basis of this treatment, but its general implications are clear. The smooth curve of Fig. 1 represents a line drawn through the cusp orientations given by Eq. (11), while a more realistic angular dependence for the energy is that given by the cusped curve, shown as a broken line. The whole figure has been extended to rather large angles to show the behavior to be expected, but it must be remembered that its real validity does not extend past about 15–20°.

D. Large-angle Boundaries

It is obvious that the simple dislocation treatment must be modified to some extent if it is to serve for an analysis of large-angle boundaries. Much of this modification is most easily accomplished with the aid of some new concepts which we shall introduce in a later section. For the present, let us take up the question of what happens when the boundary angle θ is so large that dislocation cores begin to overlap but not so large that a simple twin boundary configuration is approached.

This problem has been discussed by Li(16) who extended the simple r^{-1} form of the stress field around an edge dislocation, by adding an r^{-3} term of opposite sign. The stress in the slip plane then has the form

$$\sigma_{r,\theta=0} = 2\tau \left(\frac{1}{r} - \frac{r_0^2}{r^3} \right) \quad (13)$$

where τ is given by Eq. (3). This stress vanishes for $r = r_0$ and, if we assume it to vanish for all smaller r , represents properly the field round a dislocation with a stress-free core of radius r_0 . It is thus an improvement on the simple representation used before and is a moderately good approximation to reality if $r_0 \lesssim a/2$.

With this form of elastic model, Li finds that, when $r_0 = a/2$, the dislocation cores begin to overlap when θ in a simple tilt boundary exceeds 37°. For smaller angles the behavior is very similar to that of the Read-Shockley model, with small modifications because of the r^{-3} terms; but for larger angles the cores unite to produce a slab of virtually amorphous material and, instead of decreasing continuously, the energy becomes independent of angle.

While this model certainly contains an element of realism and some of its features represent an improvement on the earlier model, it suffers from some grave defects. In the first place it fails to give any descrip-

tion of atomic positions within the core region and so is incomplete in this regard; in fact, the grain boundary energy in the angle-independent region cannot be determined directly from the theory. Secondly, though the model has a certain attraction in the region where the dislocation cores begin to overlap, it fails to predict the occurrence of low-energy twin boundaries at higher angles.

III. EXTENSION OF THE DISLOCATION MODEL

A. Intercrystalline Boundaries

The dislocation models that we have so far considered have been limited to a treatment of the grain boundary between two crystals of the same material. While this represents a very important practical and theoretical case, any complete theory must be able to deal also with the structure and energy of interfaces between quite different crystals.

The principal difficulties in this more general class of problems are that atomic interactions across the boundary must now be treated much more explicitly than before and that the elastic properties differ in the two semiinfinite crystal regions. The discussion is essentially that of Van der Merwe (17, 18) based on earlier work by Frank and Van der Merwe (19). Three particular simple cases can be recognized:

1. Two crystals of identical structure but different lattice parameters meeting in parallel orientation across a common low-index plane.
2. A simple twist boundary between identical crystals.
3. A simple tilt boundary between identical crystals.

Case (1) represents the extension made in the theory and, when combined with an appropriate treatment of cases (2) and (3), which have already been discussed, provides an analysis of quite general interfaces.

Van der Merwe's treatment does not set out to be completely rigorous but relies upon two simplifying approximations. We have already seen that boundaries can be described in terms of intersecting grids of dislocations; the first simplification is to treat each of these grids independently, thus reducing the problem to a superposition of a set of one-dimensional problems. This approximation is exact in the region of linear elastic behavior but becomes inexact in the nonlinear regions that represent dislocation cores. The second simplification is to split the atomic interaction problem into three parts: two elastic continua representing the crystals and an atomic interaction across

the boundary which is assumed to have a simple sinusoidal form. One half-crystal acts upon the other through the shear stresses produced by the effect of this sinusoidal potential upon the atoms at the interface, and these stresses extend into the crystal by the ordinary laws of linear elastic theory.

To illustrate the analysis as applied to case (1), consider the situation shown in Fig. 4, which represents a section normal to the interface of two crystals differing in lattice parameter. It is clear that there is an edge dislocation near the center of the figure. In the lower part of the figure is shown the sinusoidal potential experienced by the atoms of the upper crystal due to their interaction with the lower crystal. It is clear that these interactions produce shear stresses that tend to give the best possible fit between the two crystals and to concentrate the strain very close to the dislocation.

Since the elastic interactions are symmetrical between the two crystals, it is best to carry out the analysis with respect to an average crystal lattice. Suppose that the upper crystal has lattice parameter a and the lower b and that they are related by

$$D = (N + 1)a = Nb = (N + \frac{1}{2})c \quad (14)$$

where N is an integer. Then the average lattice used for reference has parameter c , defined by Eq. (14). If axes are chosen with origin at the dislocation, x axis along the interface and z axis into the crystal, then

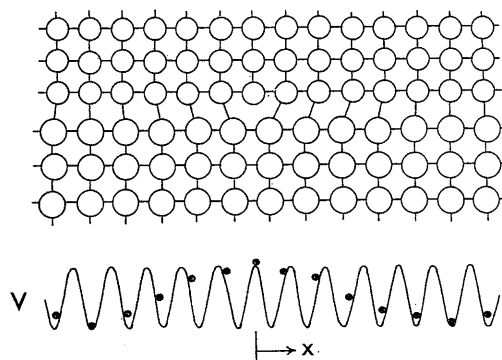


Fig. 4. Section normal to the interface between two simple crystals of different lattice parameters. The misfit is taken up by an edge dislocation at the center of the figure. Below is shown the potential V of the atoms of the upper crystal at the interface through interaction with those of the lower crystal, assuming a simple sinusoidal force law.

the shear stress at the boundary due to the interaction has the form

$$p_{zx}(0, x) = (\mu/2\pi) \sin(2\pi u/c) \quad (15)$$

where u is the relative displacement of two atoms across the interface at position x . Thus u increases by c in the distance D given by Eq. (14), but the increase is not necessarily linear in x if the crystals are distorted. The quantity μ determines the strength of the interaction across the boundary. Because these tangential stresses are coupled elastically to normal stresses through an effective surface Poisson's ratio, the normal stresses $p_{zz}(0, x)$ at the surface do not vanish. They must therefore be included in the general theory but, for simplicity, we neglect them here.

These surface stresses produce elastic strains at the crystal surfaces whose effects extend into the interior in a way that can be treated by ordinary elasticity theory (17). The general state of strain in such a semiinfinite body can be analyzed in terms of an Airy stress function χ that, for the half-crystal with $z > 0$, has the form

$$\chi = \sum_n \frac{1}{m^2} (B_n + mzC_n) e^{-mz} \sin mx \quad (16)$$

where $m = 2\pi n/D$ and $n = 1, 2, 3, \dots$. The stresses in the material are derived from χ by the relations

$$p_{xx} = \partial^2 \chi / \partial z^2, \quad p_{zz} = \partial^2 \chi / \partial x^2, \quad p_{zx} = -\partial^2 \chi / \partial x \partial z \quad (17)$$

and it can be seen that they all fall off exponentially with distance from the interface. From Eqs. (16) and (17) the general form of the atomic displacements at $z = 0$ is easily found, and hence the relative displacements u across the interface. Substitution into the shear stress relation (15) and the equations specifying the continuity of stress across the interface then provides equations from which the Fourier components B_n and C_n can be uniquely determined.

The sort of general solution found is illustrated in Fig. 5. The relative atomic displacements u are seen not to vary linearly with x , as in the undistorted case, but to concentrate their change near the dislocation region $x = 0$. From Fig. 5 it can be seen that the core of the dislocation, where u differs significantly from 0 or c , extends about $2a$ on either side of the dislocation line, in agreement with our earlier discussion. The width of the dislocation could, however, be substantially modified if the interaction force parameter μ in Eq. (15) were taken to differ considerably from the shear modulus of the crystals, as

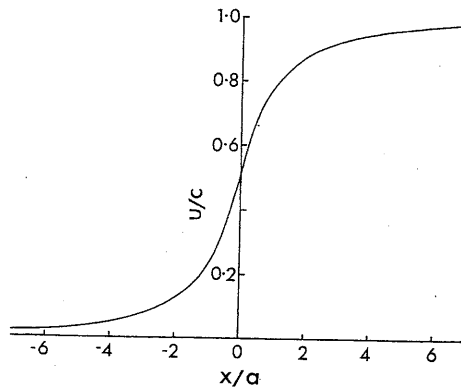


Fig. 5. The relative displacement, u , in terms of mean lattice parameter c , across a simple one-dimensional dislocation of misfit $\delta = 0.05$, x measures the distance in the interface (ref. 17).

is physically possible if the crystals bond only weakly to each other for chemical reasons.

It should, perhaps, be pointed out that there is no difficulty, in the present case, in treating core regions that overlap, since the cores are treated to the same approximation as the rest of the problem. Despite this, we shall still find other difficulties for large angles.

The results of a typical calculation of this type are shown in Fig. 6. There is a cusped energy minimum for exact matching, $b = a$; the energy then rises smoothly as the misfit $\delta = (b - a)/a$ increases. The energy dependence very near the cusp, depending as it does simply on the dislocation spacing that varies as $1/\delta$, has a form essentially equivalent to that derived by Read and Schockley for grain boundaries, Eq. (6). It should be noted that the energy scale is in units proportional to $c \approx (a + b)/2$ and its overall rising form depends upon this choice.

The formalism of Van der Merwe provides a simple and instructive way of deriving the $-\delta \ln \delta$ or $-\theta \ln \theta$ form of the energy cusp (20, 21). From Eqs. (16) and (17) we can derive all the components of the elastic stress; for example, the principal shear stress is

$$p_{zx} = \sum_n [(B_n - C_n) + mzC_n] e^{-mz} \cos mx \quad (18)$$

The elastic strains have the same form, differing only by a constant elastic modulus factor, say η , whose exact value depends on which strain component is being considered. The elastic strain energy in each half-crystal can now be evaluated by integrating half the product

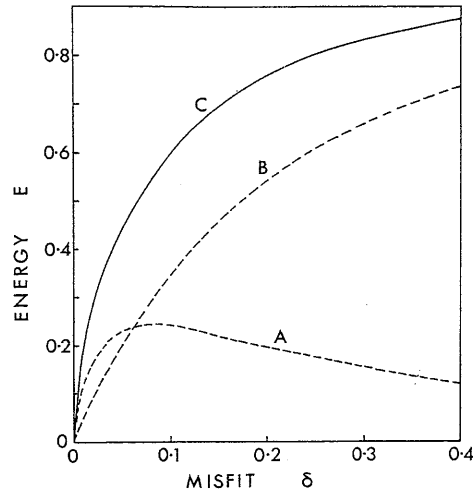


Fig. 6. Interfacial energy E , in units of $\mu c/4\pi^2$ per unit area, for a simple interface with misfit δ in one direction only. Curve A shows the elastic strain energy in the two half-crystals, curve B the energy of misfit due to the sinusoidal potential at the interface, and curve C the total energy (17).

of stress and strain over the half space. Reducing this to the energy per unit area, we find, for these shear strains,

$$E_s = \eta_s^{-1} \sum_n (B_n - \frac{1}{2}C_n)^2/4m \quad (19)$$

Other distortion components can be treated similarly.

Now, if we assume a simple dislocation model, the two crystal interfaces are in exact registry across the $z = 0$ plane, except at the dislocation lines. To achieve this, the interface displacements must be of saw-tooth form with a maximum amplitude $a/2$ for each half-crystal. For a dislocation spacing D , such a displacement has the Fourier resolution

$$u_s = (a/\pi) \sum_n (-1)^n n^{-1} \sin mx \quad (20)$$

We differentiate this, and multiply by the modulus η_s . A comparison with Eq. (18) for $z = 0$ shows that

$$B_n - C_n = 2(-1)^n a\eta_s/\pi D \quad (21)$$

which is independent of n in magnitude. Using similar arguments for the other elastic distortion components, we find that Eq. (19) then

gives the total elastic energy per unit of interface area in the form

$$E = A(\eta a^2/D) \sum_n (1/n) \quad (22)$$

where A is a numerical constant.

Now the series plainly diverges if carried to infinity; but physically this should not be done, since it implies an infinitesimally narrow dislocation, while the nature of the crystal lattice requires a dislocation width of at least a . Putting this another way, wavelike crystal distortions having wave numbers lying outside the first Brillouin zone have no physical significance. We must therefore truncate the series in Eq. (22), so that

$$n \leq N = D/a \quad (23)$$

The series $\sum_{n=1}^N (1/n)$ has the asymptotic form $K + \ln N$, where K is a constant lying between 0.577 and 1.0, so that Eq. (22) becomes

$$E = (A\eta a^2/D)[K + \ln(D/a)] \quad (24)$$

By Eqs. (1) or (14), however, a/D simply measures the interface misfit θ or δ , so that Eq. (24) has the form

$$E \sim \tau\theta(K - \ln \theta) \quad \text{or} \quad \tau\delta(K - \ln \delta) \quad (25)$$

and the exact point of truncation of the series, and hence the width of the dislocation, are seen to have their effect through the value of K .

Van der Merwe (17) has also used this approach to discuss the energy behavior of simple tilt and twist boundaries, again using a sinusoidal approximation for interactions across the interface. In the case of a twist boundary, as for the Read-Shockley model, the two sets of dislocations must be treated separately and then superposed. The results are shown in Fig. 7. Both curves show a cusp of $-\theta \ln \theta$ form at $\theta = 0$, but, in contrast to the results of Read and Shockley, the curves rise continuously with increasing θ , rather than reach a maximum or even a plateau. This does not agree well with experiment, and the curves have the additional fault, in common with the Read-Shockley model, of not showing the required symmetry between $\theta = 0$ and $\pi/2$. This may be remedied, in a fashion, by writing a symmetrical expression

$$E_s(\theta) = E(\theta) + E\left(\frac{\pi}{2} - \theta\right) - E\left(\frac{\pi}{2}\right) \quad (26)$$

which gives a flatter curve, but this cannot really be regarded as satisfactory.

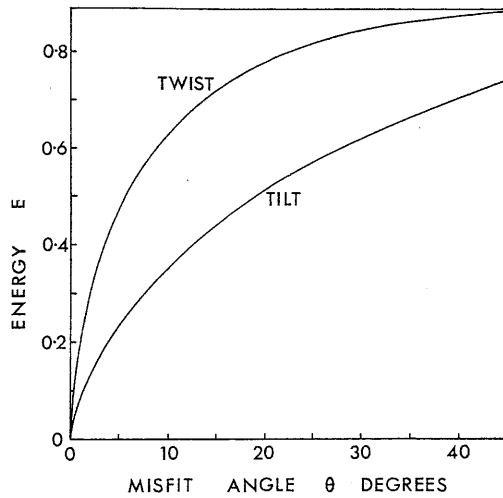


Fig. 7. The dependence of interface energy E upon misfit angle θ for twist and tilt boundaries in a cubic crystal, from the calculations of Van der Merwe(17). Energy for twist is in units of $\mu a/2\pi^2$ and for tilt in units of $\mu a/2\pi^2 (1-2\nu)$.

B. Finite Overgrowths

One very useful feature of this approach is that it lends itself very easily to treatment of the case in which the thickness of one of the crystals is small, a case of practical interest for many problems of heterogeneous nucleation and of epitaxial growth. This extension has been treated by Van der Merwe(22). The procedure is simple in principle and only requires the inclusion of terms in $\exp(+mz)$ in the stress function (16), so that the stresses may vanish at the free surface.

For thick crystals this finiteness has little effect because, from Eqs. (16) and (17), the strain fields decay exponentially away from the interface with a decay length $1/m$ for the lowest Fourier component equal to $D/2\pi$, where D is the spacing between dislocations. Higher components decay more rapidly. We therefore think of the interface region as having a thickness of the order $D/2\pi$ on either side of the dividing plane; the effect of crystal thickness will be small until the free surface begins to penetrate this zone.

The analysis of this case shows an interesting possibility for very thin films which may, if the misfit is small enough, have a minimum energy configuration in which the film is homogeneously strained into exact conformity with the substrate, rather than develop interfacial

dislocations. This sort of behavior is practically limited to monolayers, or perhaps double layers, which are elastically rather soft and are bound tightly to the substrate. In such cases homogeneous strain may occur up to a limiting misfit δ of about 0.13, in agreement with an earlier estimate by Frank and Van der Merwe(19). For thicker, harder, or less closely matching layers, however, the misfit is always taken up in dislocations.

C. Subsidiary Minima

Since the analysis of Read and Shockley(6), when carried out in full, suggests that there should be subsidiary energy minima associated with particular misfit orientations, it is natural to enquire whether or not such effects are predicted by the present theory. This question was first taken up by Fletcher(21) on the basis of a model rather similar to that of Van der Merwe but using repeating parabolic wells, instead of a sinusoidal potential, to represent the interface. The analysis was, however, rather different and used a variational method to establish the configuration of minimum energy. We shall reserve discussion of this technique to a later section, where it is treated more generally, and simply point out the conclusion that, in the one-dimensional misfit case, there are cusped energy minima wherever the two lattice parameters are in the ratio of two small integers, like 3:2 or 2:1. The depth of these subsidiary minima is related to the amplitude of particular Fourier components in the assumed interface potential, and a sinusoidal potential gives minima only for lattice ratios $n:1$, where n is an integer.

These conclusions, which have been more rigorously investigated by du Plessis and Van der Merwe(23) using a simpler physical model, form a fairly obvious generalization of the work of Read and Shockley for grain boundaries; the solution of du Plessis and Van der Merwe makes use of similar ideas involving dislocation hierarchies. We shall see later, however, that they have a wider and rather more fundamental significance than this.

IV. COINCIDENCE LATTICES

A. The Coincidence Lattice Concept

A most useful concept, which antedates the various dislocation treatments of grain boundaries, is that of the coincidence lattice. It is at once a simple and a general concept.

Consider two crystals of quite general structure whose interface

properties we wish to examine, and imagine that the lattice of each is extended to fill all of space. In general there will be no common points between the two lattices; but it will always be possible, by infinitesimal adjustments of positions and lattice parameter, to bring into coincidence four pairs of points of the two lattices such that the four are not coplanar and no three are collinear. Because these adjustments have been infinitesimal, the physics of the problem is unchanged.

Now, because of the translational symmetry inherent in crystals, the existence of these four points of coincidence between the two lattices implies the existence of a whole three-dimensional lattice of common points; this we call the coincidence lattice. In general the unit cell of the coincidence lattice will be very large but, for certain relations between the two crystals, it may become small. It is these cases that will be of particular interest to us later. A particular example in two dimensions is shown in Fig. 8, the common points such as $O, A, B, C \dots$ forming the coincidence lattice. It is easy to picture similar structures in three dimensions.

It is useful to measure the degree of matching between two such crystals by specifying the reciprocal density Σ of coincidence lattice points in terms of the density of ordinary lattice points. The possibilities in the general case are numerous but systematic relations exist when the two crystal lattices are identical. No general relation giving possible values of Σ is known even in this case, but Friedel(24) has shown that all Σ values are odd in the cubic system and Ranganathan (25) has extended earlier work to derive a generating function capable of giving possible Σ values for two cubic crystals related by a rotation

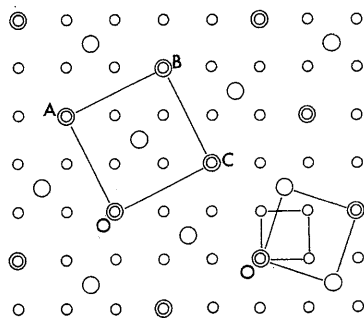


Fig. 8. A two-dimensional coincidence relation between two cubic crystals of different lattice parameters. $OABC \dots$ are points of the coincidence lattice and the linear transformation \mathcal{A} relating the two crystals is shown in the lower right-hand corner.

about an $[hkl]$ axis. His result is

$$\Sigma = x^2 + (h^2 + k^2 + l^2)y^2 \quad (27)$$

where x and y are integers having no common divisor, and any even values given by Eq. (27) should be divided successively by two until odd. The angle of rotation for a particular boundary described by Eq. (27) is given by

$$\theta = 2 \tan^{-1} [(y/x)(h^2 + k^2 + l^2)^{1/2}] \quad (28)$$

Some results are shown in Table I for the particular cases of rotation about $[111]$ and $[210]$ axis directions. It is clear that $\Sigma = 1$ corresponds to exact coincidence between the two crystals, while $\Sigma = 3$ refers to the simplest kinds of twin relationship.

For cases in which the two crystals have different structures or lattice constants, the orientations yielding coincidence lattices of small Σ , if any exist, can usually be determined by inspection.

B. Interface Models

A model for a quite general class of crystal interfaces can be constructed on the basis of the coincidence lattice concept. To see how this can be done, let us first consider the case of a grain boundary between two similar crystals, following the method of Brandon (26).

Suppose that we have constructed an interpenetrating model for the two crystals; then we ask how the boundary between them should be oriented so that its energy is a minimum. Clearly, if we find a plane boundary passing through a large number of coincidence lattice points,

TABLE I
Coincidence Lattice Relationships
[after Ranganathan (25)]

		[111] axis				[210] axis			
		x	y	Σ	θ (degree)	x	y	Σ	θ (degree)
1	0	1	0	1	0	1	0		
1	1	1	120	1	1	3	131.8		
0	1	3	180	0	1	5	180		
3	1	3	60	3	1	7	73.4		
2	1	7	81.8	2	1	9	96.4		

then the number of bonds that are broken across the boundary is smaller than for a general interface, so that the energy is lower and this "coincidence boundary" is preferred. This conclusion is only true if the density of coincidence lattice points in the boundary is large, for only then will this consideration dominate over more subtle points of atomic fitting, so that such boundaries are restricted to reasonably small values of Σ , say $\Sigma < 20$.

These possible coincidence boundaries are easily identified by the method discussed in the previous section, taking account of the particular crystal structure involved. The first few such boundaries are listed in Table II for body-centered and face-centered cubic structures.

It is plain, however, that coincidence boundaries will rarely be exactly achieved. What can be said about slight deviations from such exact relationships? The first case to consider is that in which the two crystals are correctly oriented to establish the coincidence lattice, but for some reason the boundary is constrained to lie at some angle to a densely packed coincidence lattice plane. If this angle is small, then the boundary will take up a stepped configuration with the long faces of the steps lying along coincidence planes. The energy of such a configuration will be low, provided that the density of steps is small, a criterion which probably applies for angular deviations up to 15° or so.

The second and more generally important case is that in which the relative orientation of the two crystals is not exactly that required to establish a coincidence lattice of small Σ . Brandon points out that it is possible, in such a case, to distort the crystals slightly to achieve the required exact coincidence over regions of moderate size, but the coincidence lattice in these regions will be separated from that in neighboring regions by grids of dislocations. This is exactly analogous to the situation that we met in treating simple grain boundaries; the

TABLE 2
Simple Coincidence Boundaries
[after Brandon (26)]

Σ	Twinning direction		Densely packed plane	
	bcc	fcc	bcc	fcc
3	111	112	112	111
5	012	013	013	012
7	123	123	123	123
9	122	114	114	122
11	113	233	233	113

energy may be calculated similarly, the exact coincidence configuration corresponding to a cusped minimum in the energy.

In the same way as for a simple boundary, we may expect such a model to be valid as long as the dislocations in the coincidence lattice are sufficiently far apart to maintain their identity. Since the point of invalidity for a simple lattice occurs for $\theta > \theta_0 \approx 15^\circ$, Brandon suggests for the coincidence lattice the generalized validity criterion

$$\delta\theta < \theta_0 (\Sigma)^{-1/2} \quad (29)$$

where $\delta\theta$ is the angular deviation from the coincidence relationship. From this relation and an extended version of Table II it is possible to determine the total region of relative configuration over which this sort of generalized coincidence boundary model is applicable. This is shown pictorially in Fig. 9, only boundaries with $\Sigma < 20$ being included.

Two things are apparent from these stereograms. First, there are regions in which two possible boundary configurations may exist. Here the relevant solution will be determined by the constraints on the boundary or, if it is free to reorient itself, by the configuration having lowest energy. Second, the angular ranges over which some sort of coincidence boundary model is applicable comprise a moderate fraction of the total of possible orientations. Even allowing for certain double counting in Brandon's original estimate, roughly 40% of relative crystal orientations can be connected by boundaries of this kind if the boundary orientation is free. If the boundary orientation is also

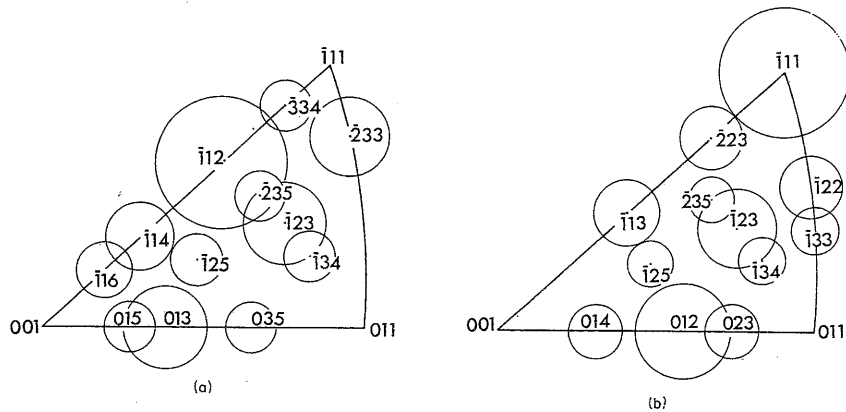


Fig. 9. Stereographic plot of the range of orientations over which coincidence boundaries can exist: (a) is for face-centered and (b) for body-centered cubic crystals (26).

arbitrarily fixed, then the fraction of boundaries properly described is probably about 10%.

As well as treating grain boundaries, however, the coincidence lattice approach is a valuable conceptual aid in dealing with interfaces between different crystalline materials, e.g., in situations of epitaxial growth of a crystal upon a substrate. Here the geometry of the substrate surface is fixed and the preferred overgrowth orientation will be that with the lowest energy. From the argument above, we should expect this orientation to be that which establishes a maximum density of coincidence lattice points in the interface, allowing slight deviations from exact coincidence to be taken up in dislocations.

It is immediately clear that this is a simple generalization of the conclusions reached in the last section on the basis of the one-dimensional analyses of Fletcher and of Van der Merwe. The cusped minima at points of simple integer relations between lattice parameters are the exact one-dimensional analogs of the coincidence lattice relations. The three-dimensional picture provides the necessary extra concepts to deal with preferred orientations and similar generalizations. We shall return to a more detailed discussion of energy relations in a later section.

C. The O-Lattice Concept

We have seen that the coincidence lattice provides a powerful aid to the description of a wide variety of crystalline interfaces. We now turn to a generalization of this idea which provides still further insight into the geometry of interfaces.

Consider two crystal lattices having one point O in common and interpenetrating to fill all of space, as in our original introduction of the coincidence lattice. Then, for a wide class of lattices, we can regard one as having been formed from the other by a homogeneous linear transformation \mathcal{A} performed about the point O as origin. To be explicit, we can regard each point \mathbf{r}' of one lattice as derived from a corresponding point \mathbf{r} of the other lattice by the relation

$$\mathbf{r}' = \mathcal{A}\mathbf{r} \quad (30)$$

Thus, in Fig. 8, \mathcal{A} involves a relative rotation of about O of $\tan^{-1}(1/3) = 18^\circ 25'$ and an expansion of one lattice relative to the other by a factor $\sqrt{(5/2)} = 1.5811$, again keeping O fixed. This particular choice of \mathcal{A} is seen to generate an infinity of coincidences A, B, C, \dots between the two lattices; these coincidence lattice points have the important property that we could have reached the same final configuration by

applying the transformation \mathcal{A} about any one of them as origin instead of O . The particular atoms brought into coincidence would have been different, but this is immaterial.

Now consider the case shown in Fig. 10, in which \mathcal{A} represents a relative rotation of $\tan^{-1} (9/16) = 26^\circ 51'$ and there is no change in lattice parameters. The coincidence lattice points A, B, C, \dots are generated as before, but it is also obvious that there is another set of points like O' which also have the property that the transformation applied about any one of them converts one lattice into the other. Following Bollmann(27), we define the O -lattice to be the totality of points possessing this property. Clearly, the coincidence lattice points are a subset of the O -lattice points or, equivalently, the coincidence lattice is a superlattice of the O -lattice. The O -lattice for a particular relation between the two crystal lattices is not completely unique; in general, there will be at least two different O -lattices, defined by two different relations \mathcal{A} and \mathcal{A}' , and involving different pairings between lattice points in the two crystals for any particular situation. This does not create any difficulty and it is generally the O -lattice with the largest spacing that has physical significance, as we shall see later.

In one important property the O -lattice may differ greatly from an ordinary crystal lattice. This is in the matter of degenerate forms. Figure 10 shows the O -lattice for a particular two-dimensional case. A little thought shows that, if this is considered as a projection of a three-dimensional problem in which the crystals are rotated about an [001] axis, then, with our definition of the O -lattice, this actually consists of continuous lines through the points O, O', \dots , parallel to the

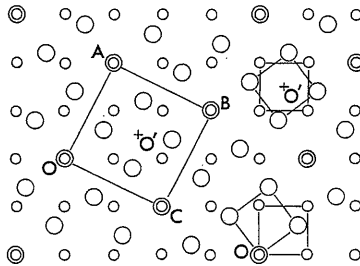


Fig. 10. A two-dimensional coincidence relation between two cubic crystals, yielding the coincidence lattice points $OABC \dots$. The linear transformation \mathcal{A} illustrated in the lower right-hand corner, when applied about O , transforms one crystal lattice to the other. The same transformation applied about points like O' , as illustrated in the upper right-hand corner, has the same effect. The totality of points like O and O' comprise the O -lattice.

[001] direction. A similar degeneracy to sets of parallel lines in the boundary plane can also occur and then has greater physical significance.

Bollmann(27) has derived the algebraic relations determining the O -lattice and has used these to investigate in detail the specific case of two body-centered cubic structures related by a rotation θ about a common $[1\bar{1}0]$ axis, the boundary of interest being the $(1\bar{1}0)$ plane perpendicular to this axis. The two possible computed O -lattices for various values of θ are shown in Fig. 11. Also shown is the moiré pattern obtained by superposing atomic layers of the two crystals from immediately on either side of the boundary.

The result is immediately startlingly evident: there is an almost exact pictorial correspondence between the moiré pattern and one of the two O -lattices, that derived from transformation \mathcal{A} for $\theta = 10^\circ$ and that from \mathcal{A}' for the larger angles. The reason for this correspondence is fairly obvious from a consideration of Fig. 10. The O -lattice points are points of particular symmetry and are either at coincidence lattice points surrounded by more than average amounts of empty space or are themselves at the centers of such empty spaces. The O -lattice points or lines thus correspond to the light features of the moiré pattern. The physical significance of the light parts of these patterns is that they correspond to nodes in the displacement pattern when elastic relaxation is allowed. The O -lattice formalism thus allows these nodes to be analytically described.

Bollmann has extended this analysis to investigate the effect of small relative translations of the two crystals and has shown how dislocation networks can be introduced, in the same way as suggested by Brandon, to simplify the patterns and reduce the energy.

V. ENERGY CONSIDERATIONS

A. Atomic Interactions

At the beginning of this chapter we remarked that the interface problem is essentially variational in nature—we seek that interface which will minimize the free energy (or, approximately, the 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 elements such as dislocations for which the minimum energy solutions for the strain field and related quantities were already known. The point we now take up is whether some

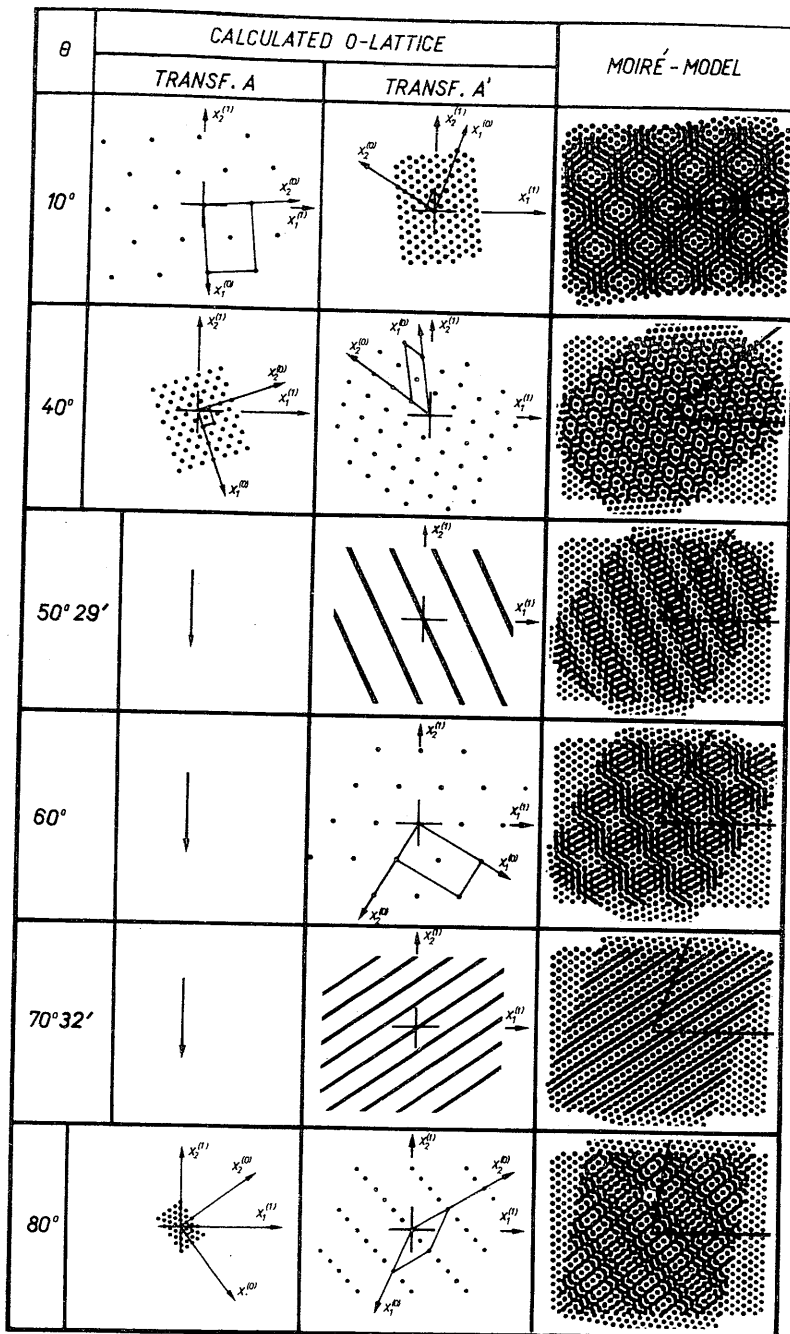


Fig. 11. The relation between the two possible O-lattices, for rotation of a body-centered cubic crystal about a [110] axis, and the moiré pattern of the boundary. For $\theta = 10^\circ$, the moiré pattern is represented by the transformation \mathcal{A} and for higher values of θ by \mathcal{A}' (27).

direct variational procedure might lead more conveniently or more generally to information about the crystalline interface.

The variational approach is simple to formulate in general terms if the interaction potentials between all the atoms involved are known. We have only to vary the positions of all the atoms, subject to whatever constraints may be applied, such as those defining the relative orientations of the two crystals, until the total energy is a minimum. This is too big a program to be feasible in practice, and various simplifying assumptions must be made. The most obvious simplification is to recall that, except in the immediate vicinity of the boundary, it is a valid approximation to regard each crystal as an elastic continuum with appropriately anisotropic elastic moduli. If we adopt this, then the approach reduces to an atomic-scale variational problem for a few atomic layers on either side of the interface joined, by stress continuity conditions, to a simple elastic problem represented by stress functions of the type of Eq. (16). This is now a tractable situation using modern computers, though the labor may be long. Such explicit computer solutions, though valuable in their way, shed no particular light upon the interface problem itself. However, we shall see that, when properly formulated, the variational approach can serve to make more quantitative some of the ideas about coincidence boundaries set out in the previous section.

Before discussing this further, let us examine the sorts of potential functions that characterize the interactions between atoms. These will vary with the type of material and may radically affect some of the approximations we can make.

In ionic crystals the dominant interaction is of electrostatic origin and may be of either sign. In addition, there is a short-range repulsive potential, due to quantum effects when ion cores begin to overlap, which can be reasonably represented as r^{-n} with n about 12. The universal attractive dispersion force can be neglected in comparison with these other forces, and we may write the total interaction potential as

$$V(r) = ar^{-12} \pm br^{-1} \quad (31)$$

The Coulombic term is only conditionally convergent over an infinite crystal but leads to no difficulty when summed to give the Madelung energy. In fact, though the potential of an individual ion has such a long range, the potential outside a complete crystal face falls off almost exponentially with distance (28).

For the interactions between uncharged atoms, such as in inert-gas crystals, the dispersion forces are important and the interaction can

reasonably be represented by the Lennard-Jones potential

$$V(r) = V_0[(r/r_0)^{-12} - 2(r/r_0)^{-6}] \quad (32)$$

or by the analytically more tractable Morse potential

$$V(r) = V_0 \{ \exp[-2a(r-r_0)] - 2 \exp[-a(r-r_0)] \} \quad (33)$$

where $V(r)$ has a minimum value $-V_0$ at the equilibrium distance r_0 . These potentials are shown in Fig. 12.

In a metal the interaction is primarily that between ion cores, shielded by the charge distribution of the valence electrons and bound together by a simple volume-dependent electrostatic interaction. If the volume is kept constant, then the two-body interaction potential might be expected to have a simple, shielded Coulombic form

$$V(r) = Ar^{-1} \exp(-ar) \quad (34)$$

A more careful treatment of the shielding, however, shows that the sharp cutoff in electron density at the Fermi surface can give rise to potential oscillations of considerable magnitude, the so-called Friedel oscillations [see (29) for a recent treatment]. A typical potential, in this case for aluminium, is shown in Fig. 12c. Although this sort of potential is strictly nonlocal, since it depends on collective electron effects, it is valid for many cases to treat it in the same way as an ordinary potential. For isolated misplaced atoms or for dislocations, this is probably satisfactory (30). For a grain boundary this approximation is less clearly valid because of other effects but is unlikely to be very much in error. For interfaces between different metals, however, we may be very much astray because of different densities for electron states in the two metals. The potential shown in Fig. 12c has, how-

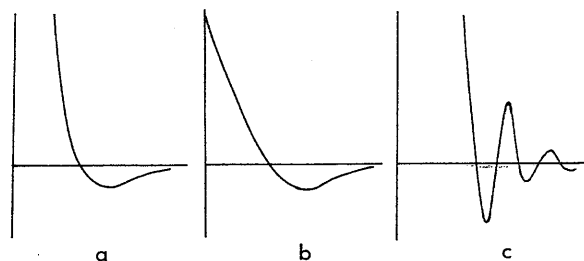


Fig. 12. a—Lennard-Jones potential; b—Morse potential; c—Friedel oscillations.

ever, not been fully investigated; for many purposes a Morse potential is often used for metallic interactions.

Finally, for materials like diamond or germanium, where bonding is by covalent forces, we recognize that we no longer deal with simple central potentials but rather with interactions involving strong three-body correlation effects. Such potentials are usefully pictured in terms of naïve tetrahedral bonds; but, while this is of great importance and good validity for constructing interface models, it helps little if we wish to evaluate interface energy. We shall leave such classes of substance out of our present discussion.

B. A Variational Formulation

The only attempt at a general variational treatment of crystal interfaces seems to be that of Fletcher and Adamson(31) and, because it yields results closely related to our present discussion, we shall treat it in some detail. The method is essentially that outlined above, the two crystals being treated as elastic continua, except for atoms near the interface; instead of dealing directly with the displacements of individual atoms as variational parameters, however, the whole operation is carried out in reciprocal space, with important simplifications.

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

$$V_0(\mathbf{r}) = \sum_{\mathbf{R}} v_{AB}(|\mathbf{r} - \mathbf{R}|) \equiv \sum_{\mathbf{R}} v(\mathbf{r} - \mathbf{R}) \quad (35)$$

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

$$V_0(\mathbf{r}) = \sum_{\mathbf{k}} V_0(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (36)$$

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

$$V_0(\mathbf{k}) = \sum_{\mathbf{R}} v(\mathbf{k}) \exp(-i\mathbf{k} \cdot \mathbf{R}) \quad (37)$$

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

If the B atom is a member of a whole crystal with lattice positions \mathbf{R}' , then the total interaction energy across the interface is, by Eqs. (36) and (37),

$$E_0 = \sum_{\mathbf{R}'} V_0(\mathbf{R}') = \sum_{\mathbf{R}'} \sum_{\mathbf{k}} v(\mathbf{k}) \exp[i\mathbf{k} \cdot (\mathbf{R}' - \mathbf{R})] \quad (38)$$

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 Eq. (38) are only over semi-infinite crystals but the component sums parallel to the interface are fully infinite. The sum over \mathbf{R}, \mathbf{R}' in Eq. (38) thus vanishes except for values of \mathbf{k} such that the component of \mathbf{k} parallel to the interface is equal to a projection of a reciprocal lattice vector of both crystals upon this interface. Expressing this differently, the only Fourier components contributing to the energy are those belonging to the projections onto the interface of the coincidence lattice points of the reciprocal lattices of the two crystals. There are various phase factors involved in Eq. (38), representing the three degrees of translational freedom of one crystal relative to the other. When the energy has been minimized with respect to these parameters (which have no effect upon the reciprocal lattices) then it will be large and negative if there is a high density of coincidence reciprocal lattice points in space. Furthermore, the \mathbf{R}, \mathbf{R}' sums in the directional normal to the interface, while not giving delta function behavior, do have a maximum when the component of \mathbf{k} normal to the interface vanishes. Thus the interface of lowest energy will be that oriented so as to pass through a maximum density of coincidence reciprocal lattice points.

It is immediately apparent that these statements are simply the duals, expressed in terms of reciprocal lattices, of the coincidence boundary criteria discussed before. In the present form they have the advantage, through Eq. (38), of giving an explicit value for the boundary energy before any elastic distortions are included.

Now we must allow for the possibility of elastic relaxation of atomic positions near the interface. To do this, let the A atom at \mathbf{R} move to a new position $\mathbf{R} + \mathbf{F}(\mathbf{R})$ where the displacement $\mathbf{F}(\mathbf{R})$ is given by the Fourier series

$$\mathbf{F}(\mathbf{R}) = \sum_{\mathbf{K}} \mathbf{F}_{\mathbf{K}} \exp(i\mathbf{K} \cdot \mathbf{R}) \quad (39)$$

and the $\mathbf{F}_{\mathbf{K}}$ are now the Fourier coefficients of the displacement. The atoms of crystal B are similarly displaced from \mathbf{R}' to $\mathbf{R}' + \mathbf{F}'(\mathbf{R}')$. The displacements $\mathbf{F}'(\mathbf{R}')$ are given by a series similar to Eq. (39). So far this is quite general, but we must now make a junction with the rest of each crystal, represented by an elastic continuum, across the interface. To do this, we relate the displacements of Eq. (39) to elastic distortions in the continua through the stress function (16) and, to match the two crystals across the interface, require that the stress components associated with $\mathbf{F}_{\mathbf{K}}$ and $\mathbf{F}'_{\mathbf{K}}$ for the same \mathbf{K} must balance.

Returning to Eq. (39), we note that the existence of a coincidence lattice between the two crystals may impose limitations upon the values of \mathbf{K} that occur, since, in terms of our previous discussion, there must be displacement nodes at all points of the O -lattice. It is the pattern on the interface plane that is important here and we can see that, if there exists in this plane a two-dimensional coincidence lattice between the direct lattices of the two crystals, then the only \mathbf{K} values which can occur are those belonging to the two-dimensional reciprocal of this coincidence lattice. Except for boundaries with a high degree of coincidence, the mesh of this superlattice will be very small and \mathbf{K} will approximate a continuous variable, though its magnitude is limited because of the general limitation of meaningful magnitude for crystal-line wave vectors.

When the displacements of Eq. (39) are included in the energy expression (38), together with the contribution from elastic strain energy in the bulk crystals, the expression becomes much more complicated. Fuller details are given by Fletcher and Adamson(31), but the leading terms have the form

$$\begin{aligned}
 E \approx & \sum_{\mathbf{k}} v(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{d}) \prod_{\mathbf{K}} J_0(2\mathbf{k} \cdot \mathbf{F}_{\mathbf{K}}) \\
 & \left\{ \delta_{\mathbf{k},\mathbf{g}} \delta_{\mathbf{k},\mathbf{g}'} + \sum_{\mathbf{K}} \frac{J_1(2\mathbf{k} \cdot \mathbf{F}_{\mathbf{K}})}{J_0(2\mathbf{k} \cdot \mathbf{F}_{\mathbf{K}})} \delta_{\mathbf{k},\mathbf{g}} \delta_{\mathbf{g}'-\mathbf{K},\mathbf{g}} \right\} \\
 & + \sum_{\mathbf{K}} \tau_0 K |\mathbf{F}_{\mathbf{K}}|^2
 \end{aligned} \tag{40}$$

where \mathbf{g} is a reciprocal lattice vector of the surface of crystal A and \mathbf{g}' of crystal B, the J_n are Bessel functions, and τ_0 is the elastic modulus given by Eq. (3). Here \mathbf{d} is a small vector representing the displacement of the origin of one crystal relative to that of the other. 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 lattice points \mathbf{g} and \mathbf{g}' by the distortion component \mathbf{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 crystals. There are higher terms representing compound coupling between \mathbf{g} and \mathbf{g}' , involving several different \mathbf{K} , which have been omitted.

It is easy to see that the minimization of Eq (40) with respect to the $\mathbf{F}_{\mathbf{K}}$ leads to cusped minima about the coincidence boundary configurations. Consider the case in which \mathbf{g} and \mathbf{g}' are nearly equal. Then,

keeping only leading terms in the expansion of the Bessel functions, (40) becomes

$$E \sim \text{const} + 2v(\mathbf{g}) \mathbf{g} \cdot \mathbf{F}_K + \tau_0 K |\mathbf{F}_K|^2 \quad (41)$$

which, when minimized by varying \mathbf{F}_K , gives

$$E \sim \text{const} - v^2 g^2 / \tau_0 K \quad (42)$$

This form is not, of course, valid as $K \rightarrow 0$, for then the approximations used in Eq. (41) fail, but the sharp minimum at $K = 0$, corresponding to $\mathbf{g} = \mathbf{g}'$, is evident. A more detailed analysis is required to elucidate the $-\theta \ln \theta$ form of the cusp.

It is useful to note that, in this formulation, there is no difficulty in treating the dislocation core, since atomic positions and interactions are considered explicitly. It is also possible to extend the formalism easily, so that several atomic layers on either side of the interface are treated explicitly.

The important thing arising from this approach is, however, the ability to make quantitative estimates of interface energies and energy cusp depths based on realistic interaction potentials. The depth of any cusp is determined by the value of the sum involving just the first term of Eq. (40), the coincidence term $\mathbf{g} = \mathbf{g}'$. Its maximum value, ignoring the ΠJ_0 term that is somewhat less than unity, is

$$\delta E \sim \sum_{\mathbf{g}=\mathbf{g}'} v(\mathbf{g}) \exp(i\mathbf{g} \cdot \mathbf{d}) \leq \sum_{\mathbf{g}=\mathbf{g}'} |v(\mathbf{g})| \quad (43)$$

where the sum is over just the reciprocal lattice coincidence sites $\mathbf{g} = \mathbf{g}'$ on the boundary. Since $v(\mathbf{k})$ generally decreases as \mathbf{k} increases, it is evident that boundaries with $\mathbf{g} = \mathbf{g}'$ for small g have prominent cusps. Equation (43) yields the interesting conclusion that the magnitude of particular cusps depends quite largely upon the form of the potential, and particular cusps may be completely absent in some cases. This conclusion was reached for the one-dimensional case that we discussed before on the basis of an analysis by Fletcher (21), but we now see its greater generality. It is an effect not comprehended in simple hierarchical dislocation models.

No explicit calculations for real materials have yet been made, using this formalism. Fletcher (32), however, has published calculations based on a simple interatomic potential, chosen so as to minimize the computation time required, while at the same time representing a reasonable approximation to reality. The case treated was that of a twist boundary on a (100) plane between two face-centered cubic crystals of lattice parameters a_1 and a_2 . There is, as expected,

a deeply cusped minimum at $a_1 = a_2$, $\theta = 0$, and a much shallower minimum at $a_1 = \sqrt{2}a_2$, $\theta = 45^\circ$. No other minima are apparent, but this may be because of the particular form of potential chosen.

It is worth commenting upon some further features of the present approach. Like all methods based upon coincidence lattices and proceeding with sufficient rigor, it takes automatic account of crystal symmetry and has no failure at large angles. This is of quite fundamental importance. The treatment is, however, limited, in its present form, to the treatment of plane boundaries. Within this limitation it is able to deal satisfactorily with a wide variety of cases such as the epitaxial growth of a metal upon an ionic crystal, to yield both useful general results and specific calculations for particular cases. For large-angle grain boundaries in homogeneous materials, however, where the boundary is likely to be closely terraced, a still more general formalism is required.

VI. CONCLUSION

The models of crystal interfaces that we have discussed are rather varied; we hope, however, that the close interrelations between them have been made clear. All the features have observational significance under different conditions—dislocations can be seen in several ways and periodic elastic distortions show up in some diffraction experiments—but they are all manifestations of the same basic structural relations.

We have not attempted to give such experimental evidence here or to comment on the significance of the structures observed for other aspects of interface behavior. We have scarcely referred to experimental determinations of grain boundary energy. All of these are of importance, but a discussion of them has been sacrificed in the interests of unity of treatment. It is hoped that, by reconciling and unifying a number of the important approaches to interface theory at present in use, a clearer background will evolve against which to examine more complex phenomena.

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