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STRUCTURE OF HIGH ANGLE GRAIN BOUNDARIES IN
METALS AND CERAMIC OXIDES *

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ABSTRACT

A critical review is given of the state of our current knowledge of the structure of high angle grain boundaries in metals and in ceramic oxides. Particular attention is given to effects due to differences in the bonding and crystal structure in these solid types. The results of recent experimental work and efforts to model grain boundary structure using computer simulation methods are described. Important characteristic features of boundaries in these materials are discussed. Difficulties which are presently being encountered in efforts to determine their structure are pointed out.

I. INTRODUCTION

In the present paper we attempt a review and comparison of the state of our current knowledge of the structure of high angle** grain boundaries in metals and ceramic oxides.

We begin (in Section II) with a brief description of a number of general aspects of grain boundary structure which are expected to hold true for any crystalline material and which are central to much of the present paper. Specific discussions of modeling and experimental work on grain boundaries in fcc metals (Section III) and ceramic oxides (Section IV) are then given. Particular attention is given to effects due to differences in the bonding and crystal structure of these solid types, and important characteristic features of boundaries in these materials are described. Difficulties which are presently being encountered in efforts to determine their structure are pointed out. Finally (Section V), a number of general remarks regarding the state of the field are given.

Our attention is primarily focused throughout on the basic problem of the structure of grain boundaries in pure materials even though it is recognized that impurities may play dominant roles in certain cases, especially in common ceramic materials. However, a brief discussion of impurity effects is attempted at the end of Section V. This procedure seems justified at the present time, since it is clear that a sound knowledge of grain boundary structure in pure materials must precede any adequate understanding of the complex phenomena which are associated with impurities.

** "High angle" grain boundaries are taken to be boundaries possessing sufficiently large crystal misorientations ($> 15^\circ$) so that the cores of the primary dislocations of which they are composed overlap. The cores of such boundaries are therefore continuous slabs of bad material.

II. GENERAL ASPECTS OF THE STRUCTURE OF HIGH ANGLE GRAIN BOUNDARIES IN CRYSTALLINE SOLIDS

In considering the structure of a grain boundary in any pure crystalline solid it is useful to visualize the construction of the boundary by the following process. Place the two misoriented crystals (which will adjoin the boundary) together along the desired grain boundary plane rigidly in a standard reference position [as in Fig. 1(a)] and then let the entire ensemble relax. In this process the atoms in the boundary region will relax their positions to minimize the total energy, and at the same time Crystal 2 will find a minimum energy position relative to Crystal 1 by a rigid body translation without rotation, i.e., $\vec{t}$ in Fig. 1(b).

In general, eight geometric parameters are then required in order to give a complete macroscopic specification of a given boundary. These include three parameters to describe the crystal misorientation, two parameters to describe the orientation of the boundary plane, and three parameters to describe the rigid body translation of Crystal 2 with respect to Crystal 1. We note that the rigid body translation must be defined in certain cases in order to avoid ambiguities which arise when the boundary structure possesses symmetry elements which allow different $\vec{t}$'s to exist which can produce a degeneracy involving structurally similar boundaries.^{1,2} Besides these geometric parameters the temperature

should be specified, since it is conceivable that the boundary may undergo a first order phase transformation.^{3,4} Also, in ionic solids there will exist at any finite temperature a direct coupling between the point defect distribution in the lattice in equilibrium with the boundary and the detailed structure of the boundary [see Section IV (4)].

On the other hand, the microscopic structure of the grain boundary can only be specified completely by describing the positions of all the atoms in the entire bicrystal ensemble. However, this is usually not practicable, and an adequate description can usually be given in terms of:

- (i) the positions of the atoms in the "bad material" in the relatively narrow grain boundary core region [Fig. 1(b)] which includes all of those atoms which are appreciably displaced from their normal positions in either Crystal 1 or Crystal 2. (We note that this core region may contain line and point defects as described below.)

- (ii) the displacement vector, $\vec{t}$.

- (iii) the long range strain fields in Crystals 1 and 2 of any line or point defects which might be present in the core. In the case of ionic solids it would also be necessary to specify the long range equilibrium point defect distribution (and associated electrical space charge distribution) which might be present as mentioned above.

The core region is expected to possess a number of general geometric (or "crystalline") properties since it is the locus where the two

adjoining crystal lattices, which are themselves periodic structures, meet.[‡] First of all, we expect the core structure to be periodic in the plane of the boundary. As shown elsewhere^{4,5,6}, the periodicity is expected to correspond to that of the plane of the Coincidence Site Lattice[†] which lies parallel to the boundary. Secondly, we expect the two lattices to exhibit periodic registry at points in the core. As shown elsewhere^{4,5,6}, these points are described by lattice points in the plane of the O-Lattice[§] which lies parallel to the boundary. Thirdly, in view of the periodic structures of Lattices 1 and 2 and the grain boundary core, rigid body translations of Lattice 2 with respect to Lattice 1 should exist which have the property that the structure of the grain boundary core is preserved. As shown elsewhere^{4,5,6}, the vector translations which possess

‡ We note that this may not be true at elevated temperatures near the melting point if the boundary undergoes complete disordering as a result of a transformation upon heating.^{3,4} However, there is no clear evidence available at present that such a transformation generally occurs^{3,4}, and, in fact, it has been shown⁷ that grain boundaries in at least copper remain ordered all the way up to the melting point.

† The CSL may be constructed by imagining that Lattices 1 and 2 both extend throughout all of space. The three-dimensional lattice made up of all points in space which possess the same atomic environment is then the CSL.^{4,5,6} (CSLs are often described in terms of the quantity Σ which is defined as the reciprocal of the fraction of atoms associated with CSL lattice points.)

§ The O-Lattice is defined as the array of points in space where points in Lattices 1 and 2 with the same internal unit cell coordinates coincide if it is again assumed that both lattices extend throughout all of space.^{4,5,6}

this property are vectors of the DSC-Lattice.^{††}

The "crystalline properties" of the core just described make it possible for line defects corresponding to perfect grain boundary dislocations (GBDs) to exist in the core. Such GBDs may be produced in a formal way by making a suitable cut along the boundary and introducing a displacement corresponding to a vector of the DSC-Lattice as described elsewhere.⁸

We also note that point defects may be created in the core by removing atoms (to make vacancies) or adding atoms (to make interstitials) and allowing the surrounding atoms to relax. As shown elsewhere,⁹ such a defect may relax (dissociate) over a considerable volume, at least in a metal. Nevertheless, the resulting configuration involves either a "missing" or an "extra" atom and therefore may be considered to be a bona fide point defect.

III. HIGH ANGLE GRAIN BOUNDARIES IN METALS

Essentially all of our information about the detailed atomic structure of grain boundaries has come from computer modeling and the comparison of the computer modeling with selected experimental results. In this type of work it is assumed that the atoms interact via pair potentials, and the minimum energy configuration of the ensemble making up the boundary is found by computer calculation.

^{††} The DSC-Lattice for a particular grain boundary defines all the vector displacements of Lattice 1 and Lattice 2 relative to each other which are possible under the condition that the overall pattern of atoms produced by the two interpenetrating lattices remains unchanged.

We therefore begin with a general discussion of the nature of metallic bonding and the basis for representing the energy of a metallic system in terms of pair potentials. Some of the basic methods which have been used to model grain boundary structures are then reviewed with special emphasis placed upon some of the difficulties which have been encountered. The main results of the calculations are then summarized and are compared with relevant experimental results.

(1) Bonding and Interatomic Potentials

In a simple metal the positive ions can be thought of as immersed in a cloud of negative charge with the conduction electrons contributing most to the binding energy. This form of bonding is non-localized and originates from the overlap of the electron distribution of each atom. The effective interaction between atoms is composed of the Coulomb interaction between ion cores and the shielding effect and mutual interaction of the conduction electrons. The complexity of the bonding is increased further in the transition and noble metals where additional overlap of the inner electron shells occurs.

The rigorous quantum mechanical treatment of the many-body problem for determining the atomic interactions in most perfect solids is quite intractable. Solid state theory involves making a number of assumptions and approximations, the validity of which can be tested by comparison with various physical properties of the solid that are known to be directly related to the interatomic forces. It is common to make the simplifying assumption that atoms interact via two-body central forces which can be separated into short and long range components. An example of a

simple interatomic two-body potential is shown in Fig. 2(a) and is seen to consist of an attractive interaction for r greater than the equilibrium separation and an increasingly repulsive interaction for small r as closed shells of electrons overlap.

For many practical purposes, such as the atomic modeling of grain boundaries, two main types of atomic interaction have been developed which employ the two-body approximation. Historically the first of these was the empirical potential which assumes a definite functional form and contains coefficients which are found by matching to experimentally determined physical constants. Examples of these include the Born-Mayer, Lennard-Jones and Morse potentials, none of which were originally developed for metals but all of which have now been applied at least in part to metallic systems. A further example of this class of potential, which is shown in Fig. 2(b), is the spline fitted polynomial function which has greater capability for parametric adjustment. None of these empirical potentials necessarily satisfy lattice stability criteria, and it is often essential to add extra volume dependent energy terms to the total interaction. This ensures correct matching to the lattice parameter and effectively simulates the cohesive energy of the free electron gas.

The second basic type of interaction is the pseudopotential where the interactions between the ions and conduction electrons are assumed to be weak. Since the ion cores are not allowed to overlap, the theory can only be applied successfully to the simple alkali metals and aluminum. A pseudopotential for aluminum is shown in Fig. 2(c) which features characteristic long range oscillations. In practice a cut-off radius is chosen to

ease computational problems. A similar procedure is adopted for the empirical potentials, and while there is no theoretical justification for this procedure it probably has little detrimental effect if it is assumed that positive and negative oscillations cancel at large distances. We note that besides the empirical and pseudopotentials for metals mentioned above there also exist potentials derived from liquid metal data, atomic collision theory, Thomas-Fermi theory and other quantum mechanical models.

If the development of reliable interatomic interactions from first principles is intractable for perfect metal lattices then their derivation in the neighborhood of lattice defects is just not possible. Clearly, in the vicinity of a grain boundary, especially a tilt boundary, there will be relatively large variations in the electron density which should somehow be accounted for. Although defects resulting in small ion displacements can be accounted for within the framework of the pseudoatom model, it is not clear how larger redistributions of electrons will affect the real structure of a boundary. It is clear, however, that drastic relaxation effects, such as those presumed to occur due to charge mismatch in ionic solids, will not occur. In view of this it has been generally assumed that the effects of electron redistribution are of higher order and can be ignored. To some extent this assumption has been justified, since there has been good correlation between modeling and experiment in at least two instances [see Section III (2)]. Therefore, for the time being it seems reasonably satisfactory to treat the atoms in the vicinity of a grain boundary as interacting point nuclei using central pairwise potentials derived for the perfect lattice. Further confidence in the use of this method is obtained from the

observation that systematic variations in the cut-off radius of the pseudopotentials do not appear to change significantly the calculated equilibrium structure of the boundary.

(2) Modeling of Grain Boundary Structure

The computational models which allow three-dimensional relaxation are generally of either the molecular dynamics or statics type.¹⁰ In the molecular dynamics type the atoms possess both potential and kinetic energy, and Newton's laws of motion are satisfied for each vibrating atom. In the molecular statics type the atoms possess only potential energy and obey the laws of static mechanical equilibrium. Molecular dynamics calculations involving large numbers of atoms are complex and expensive, and, therefore, most of the more recent progress has been made using static procedures. This has occurred despite the fact that the dynamical simulation is more general and powerful and is capable of studying grain boundary kinetics at a finite temperature. In most of what follows, reference is made to grain boundary calculations using static simulation. Despite the apparent simplicity of this technique, a number of difficulties is frequently encountered. Included are the following:

- i) Selection of the appropriate border conditions in order to avoid unintended constraints on the relaxed configuration.
- ii) Use of proper relaxation procedures to insure that a true minimum energy configuration is reached and that possible intermediate metastable configurations are avoided.
- iii) The need to use large computational cells for boundaries possessing large CSLs.

Imposing border conditions which do not interfere with the relaxation is relatively simple in the case of pure tilt or twist grain boundaries. Cyclic border conditions may be used along the directions in which the structure repeats itself, i.e., parallel to the tilt axis (tilt boundaries) or perpendicular to the twist axis (twist boundaries). Provided large enough computational cells are used, fixed borders can be used in the other directions although some normal strains may still be present and affect the grain boundary structure.¹¹ Ideally, free (or flexible) borders should be used in these directions. The situation becomes more complicated if boundaries of mixed character are to be simulated or if the interactions of other defects (such as vacancies or dislocations) with the boundary are to be studied. In such cases flexible borders using large models have to be used especially if, for example, a repetition of the interacting defect is to be avoided.

It is never possible to locate all minima on a multi-dimensional potential energy "surface" created by the many interacting point nuclei within the computational cell containing the grain boundary. Molecular statics using gradient methods of minimization can locate metastable configurations which, although in themselves can be interesting, should in general be avoided. Usually this can be done by simply using several slightly perturbed starting configurations as a check that the true minimum energy configuration has been reached. From this point of view the dynamical or quasi-dynamical methods of relaxation are preferred to the static since they are more likely to locate the global minimum.

As the need to simulate more general grain boundaries of longer wavelength increases [see Section III (4)], so it becomes necessary to use larger computational cells which, unfortunately, increases the

computational time. This problem is unavoidable unless it can be established that longer period grain boundary structures actually consist of a variety of much shorter repeating structural units.

Despite these difficulties computer modeling has led to a number of important results which include the following:

- a) In general, the boundary cores are very narrow, and crystallinity (i.e., the existence of "good" material) is maintained almost up to the boundary plane. A typical computed structure is shown in Fig. 3.
- b) Relatively high atomic densities are maintained in the cores, and lattice-like nearest neighbor configurations appear to be preserved frequently. As pointed out by Harrison et al.,¹² this result must be due to the simple fact that the interatomic potentials are strongly repulsive and relatively short-ranged. Many atoms undergo only relatively small displacements from their ideal lattice positions in Lattice 1 or Lattice 2. Some rather simple displacement rules which seem to apply to many tilt boundaries have been stated by Harrison et al.¹²
- c) Ordered arrays of characteristic interlocking groups of nearly closely packed atoms occur¹³ in a number of boundaries of relatively short period as seen, for example, in Fig. 3. These results have led to the suggestion that these characteristic groups, i.e., polyhedra, may also exist in boundaries of longer periodicity as well. The structure of many boundaries would therefore consist of arrays of a relatively small number of types of distinguishable atomic polyhedral groups of atoms.

Such a model would resemble Bernal's¹⁴ model for liquid structures in certain respects.

- d) In the minimum energy configuration Crystal 2 is usually translated with respect to Crystal 1 by the vector $\vec{t}$ so that the two crystals do not both lie on the CSL.^{15,16} The $\vec{t}$ translation forms a major component of the relaxation in tilt boundaries. In twist boundaries local atomic relaxations are of equal importance, and the magnitude of the translation tends to decrease as Σ increases.
- e) In certain cases of fixed crystal misorientation and fixed boundary plane orientation it has been found^{15,16} that several boundary structures can exist either (i) with crystallographically different $\vec{t}$'s and slightly different energies, or (ii) with crystallographically equivalent $\vec{t}$'s and the same energy. The latter boundaries may be considered as symmetry related degenerate structures. This result opens up the possibility that certain actual boundaries may consist of a number of patches possessing different $\vec{t}$'s. In such cases the patches would be separated from their neighbors by partial GBDs possessing Burgers vectors given by the differences of the $\vec{t}$'s of the adjoining patches. It is noted that these Burgers vectors would not be the same as the Burgers vectors of perfect GBDs which are given by the vectors of the DSC-Lattice (Section II).
- f) GBDs have been introduced into boundaries and their structures have been calculated.¹⁷ For the cases investigated, the dislocation cores have been reasonably narrow and well defined and have also contained distorted polyhedra of the type

described above in (c).

- g) The calculated boundary energy tends to be relatively low for many relatively short wavelength (small Σ) boundaries (Fig. 4). However, no simple monotonic relationship between boundary energy and periodicity has been found, and in fact, numerous cases have been found¹⁵ where longer wavelength (higher Σ) boundaries have lower energies than shorter wavelength (lower Σ) boundaries (Fig. 5). In addition, the energy does not seem to scale simply with other general geometrical properties of boundaries such as, for example, the density of O-Lattice points.¹⁸

(3) Comparison with Experiment

The calculated result that the width of the bad material in the core is quite narrow is in good general agreement with the direct observation of the apparent widths of grain boundaries in the field ion microscope.^{19,20}

The predicted existence of $\vec{t}$ translations has been confirmed by direct experiments^{21,22} using transmission electron microscopy (TEM). Annealing twins in aluminum were observed using TEM, and the relative translation, $\vec{t}$, between the adjacent crystals was deduced from the observation of interference fringe contrast. The structures of the twin related boundaries were also simulated¹⁵ using molecular statics and a pseudopotential suitable for aluminum. For two types of boundary good agreement was achieved between modeled and experimentally measured values of $\vec{t}$. The relaxed structure of one type of boundary is shown in Fig. 3. The relatively good agreement achieved here lends credence to the simulated boundary structures and the method which was used to calculate them.

Recently, further information about the detailed atomic arrangement in grain boundaries has been obtained by using electron and x-ray diffraction techniques. It has been shown^{23,24} that the ordered structure of a grain boundary causes it to act essentially as a diffraction grating and that it produces a unique diffraction pattern. In principle, it should therefore be possible to obtain information about the structure from an analysis of the intensities of the scattered beams. In general, the diffracted intensity from the thin grain boundary region in reciprocal space is concentrated in the form of narrow relrods which run perpendicular to the grain boundary plane and have lengths which are reciprocally related to the "thickness" of the grain boundary as might be expected. In recent work²⁵ the x-ray diffraction from a $\Sigma = 13$ (22.6°) [001] twist boundary in gold was studied, and the reflections from the grain boundary in the $L = 0$ plane of reciprocal space (oriented parallel to the grain boundary plane) were measured. Also, a $\Sigma = 377$ (23.8°) boundary was observed²⁵, and the relrod profiles for certain grain boundary reflections along the L direction were measured. The $\Sigma = 13$ boundary was modeled by molecular statics using various empirical polynomial potentials representing gold. The structure factors of these structures in the $L = 0$ plane of reciprocal space and along the L direction were then calculated. By comparing the computed structure via the calculated structure factors to the x-ray observations it was found²⁵ that for one particular potential the correlation was excellent. This computed structure is shown in Fig. 6 which also illustrates a basic polyhedral structural unit which was present in this boundary, i.e., an Archimedian Antiprism.¹³ A striking feature of the boundary structure is the large

displacement toward the boundary plane of the atoms nominally in "good" match. The distortion of the nearest neighbor spacing in the vicinity of the region of "good" match is only slightly smaller than in the vicinity of the region of "bad" match. Also the full width at half maximum of the calculated relrod profiles, which is related to the grain boundary thickness, compared well with the experimental value. Again in this work, the relatively good agreement between the calculated results for the simulated structure and experimental observations lend credence to the calculated structures.

In other experiments numerous observations of perfect GBDs have been made by TEM in various grain boundaries.²⁶⁻²⁸ An example is shown in Fig. 7 where a lattice dislocation enters a boundary and dissociates into several perfect GBDs. This structure can be understood by noting that all lattice vectors of Crystals 1 and 2 are also vectors of the DSC-Lattice, and, therefore, all lattice dislocations can dissociate in the boundary into an integral number of perfect GBDs according to a reaction of the type

$$\vec{b} = \sum_i n_i \vec{b}_i, \quad (1)$$

where $\vec{b}$ = Burgers vector of lattice dislocation, $\vec{b}_i$ = Burgers vector of i^{th} GBD, and the n_i are integers.²⁹ In general, the diffraction contrast produced by the GBDs indicates that they are line defects with localized cores which possess displacement fields approximating those of lattice dislocations. The calculated structural characteristics of the GBDs obtained to date by means of molecular statics seem to be reasonably consistent with these observations. Partial GBDs have also been observed

by electron microscopy¹ in boundaries which consist of patches possessing symmetry related degeneracy. In such cases the partial GBDs separate patches of the boundaries possessing different $\vec{t}$'s as described in Section III (2).

Considerable experimental evidence has been found that short wavelength (ordered) boundaries often possess relatively low energies, in qualitative agreement with the results shown in Figs. 4 and 5 calculated by molecular statics. In one type of experiment³⁰ a large number of initially randomly oriented single crystal spheres has been distributed on a single crystal plate of the same metal, and the ensemble has been heated to an elevated temperature in order to sinter the spheres to the plate. During the sintering a grain boundary generally formed in the necked region between each sphere and the plate, and each sphere generally tended to rotate in order to reduce the energy of the grain boundary. In the final state the rotations ceased, and the orientations of essentially all of the spheres were found to be collected into a relatively small number of discrete orientations which apparently corresponded to cusped minima in the energy versus crystal misorientation function such as those present in the calculated curve of Fig. 4.

In a large number of other TEM experiments²⁶⁻²⁸ it has been found that boundaries with crystal misorientations which deviate slightly from misorientations corresponding to high density (low Σ) CSL misorientations often relax into a structure which consists of a GBD network embedded in the high density CSL (short wavelength) boundary. The Burgers vectors of the GBD network are then vectors of the corresponding DSC-Lattice. In this relaxation the boundary preserves as much of the low energy configuration characteristic of the nearby short wavelength

CSL boundary as possible. The role of such networks is therefore very similar to that of networks of lattice dislocations in low angle boundaries which act to preserve the perfect crystal lattice structure. Such GBDs have been termed "secondary GBDs", since it is easily shown³¹ that they may be regarded as line defects produced by periodic irregularities in the spacings of the primary GBDs (i.e., lattice dislocations) which can be thought to make up the boundary as described, for example, by Read and Schockley³². ***

As an example, a well-defined series of such networks has been observed by Tan et al.³³ and Schober and Balluffi³⁴ in [001] twist boundaries in gold, as shown in Figs. 8 and 9. Three particularly high density CSL's with $\Sigma = 13, 17$ and 5 are formed by cubic crystals as a result of rotations around [001] of $\theta = 22.6^\circ, 28.1^\circ$ and 36.9° , respectively. Square networks of secondary screw GBDs (Fig. 8) were found in the angular vicinity of each of these CSL misorientations where the network spacing (Fig. 9) varied as expected³⁴ according to

$$d = \frac{|\vec{b}|}{2 \sin \Delta\theta/2}, \quad (2)$$

where $\vec{b}$ = secondary GBD Burgers vector, and $\Delta\theta$ = twist deviation from the exact high density CSL misorientation.

The observation of secondary relaxations of the type described above provides support for the so-called secondary GBD model for grain boundary structure.^{5,6,26,31,32} In this model the crystal misorientation

*** GBDs of this type have also been termed "intrinsic" GBDs, since they are part of the equilibrium structure of the boundary in contrast to extra intruding GBDs of the type shown in Fig. 7 which have been termed "extrinsic" GBDs.

across any grain boundary is described as either a relatively high density CSL misorientation or as a deviation from such a misorientation. The boundary structure can then be described formally as either a relatively short wavelength structure or as a relatively short wavelength structure containing an array of embedded secondary GBDs. The question of whether such a description is physically realistic for all boundaries is still not answered. As seen above, the model has been experimentally verified for many boundaries with misorientations close to high density CSL misorientations. However, the Burgers vectors of the GBDs corresponding to a given CSL tend to decrease as the density of the CSL decreases. Also, the spacings of the GBDs tends to decrease as the Burgers vector decreases and/or the misorientation from the nearby CSL misorientation increases [see Eq. (2)]. It therefore is difficult to detect such structures experimentally, and it is not clear at the present time whether all boundary structures can be described in terms of the CSL secondary GBD model in physically realistic terms. Extensive discussion of this problem may be found elsewhere.^{4,9,26}

(4) Discussion

It is evident that considerable progress has been made in the modeling and understanding of grain boundary structure in pure metals. The computer simulation technique using two-body potentials has produced structures which appear to be generally consistent with experiment. In several cases rather satisfactory agreement between the details of calculated structure and experimental observations has been obtained.

Nevertheless, a number of important problems remain. A major question is the extent to which the secondary GBD model is applicable to

all grain boundaries, particularly those long wavelength boundaries with crystal misorientations relatively far away from reasonably dense CSL misorientations. Also, the significance of describing elements of the core structure in terms of nearly close packed polyhedral units is not entirely clear at present. These units are always distorted to at least some extent, and there are often ambiguities in the choice of the units. In addition, the existence of specific types of these units in various boundaries has not been uniquely correlated with the macroscopic parameters which specify the boundaries (Section II).

The study of the detailed structure of line defects (GBDs) and point defects in boundaries is still in its infancy. Line defects are difficult to model reliably, and only a few specific examples have been studied. Of particular current interest is the detailed atomic structure of GBDs, since controversy¹⁷ has developed about the degree to which GBDs may spread out in the boundary in order to relax their elastic strain energies. Recently, some work has been carried out^{9,35} on molecular statics calculations of the structure of point defects in boundaries. In this work atoms were either removed or added at sites in the boundary core (to produce vacancies or interstitials, respectively) and the relaxed atomic configuration at the defect was calculated. So far, the results indicate that the point defects are rather widely dissociated, i.e., the defect is considerably de-localized, and local atomic restructuring of the boundary in its vicinity occurs.

At present, no simple rules connecting the grain boundary energy with the structure have been established which go beyond the rule that short wavelength (low Σ) boundaries are generally of relatively low

energy. Essentially all of the conceptual grain boundary modeling (e.g., the secondary GBD model) has been based on this simple geometrical concept. There is therefore a need to develop further and more fundamental approaches to the problem.

We may therefore conclude that while much has been accomplished with grain boundaries in metals, much work still needs to be done. It seems likely that present approaches (with logical extensions) should result in continued rapid progress in many areas. However, in certain areas (e.g., the understanding of the relationship between structure and energy) new approaches seem required.

IV. HIGH ANGLE GRAIN BOUNDARIES IN CERAMIC OXIDES

(1) Bonding and Interatomic Potentials

In ionic solids almost complete transfer of one or more electrons from one atomic component to another takes place, producing a set of positive and negative ions approaching noble gas configurations. Such bonding is therefore predominantly electrostatic, possessing little directed chemical bonding or discrete molecules and is characteristic of the ceramic oxides.

Many ceramic oxides, at least at elevated temperature, have the rocksalt structure (Fig. 10). Examples include the transition metal oxides and MgO. The coordination number for this structure is six so that, for instance, in MgO each Mg^{2+} ion has six O^{2-} nearest neighbors and twelve Mg^{2+} next nearest neighbors. The structure is fcc for each ion, and the Bravais lattice is also fcc. To maintain lattice stability between the

like and unlike charges the dominant Coulomb interaction is opposed by a strong repulsive force when the ions overlap. The relatively large short-range overlap energy is responsible for the low compressibility of ionic solids. Therefore, to a first approximation the ions can be represented as rigid spheres. The ionic bond is stronger than the metallic bond so that metals are more easily deformed. X-ray diffraction methods show that the ions are not perfectly spherical, however, and that there is often a significant electron density between the ions. Thus, the ionic interaction in a perfect crystal can be incomplete, and some covalent bonding, in which electrons are shared by pairs of atoms, may exist. The covalent bond is stronger than either the ionic or metallic bonds. The degree of covalency varies from one ionic solid to another, but for the most part, the ceramic oxides, and especially MgO, are predominantly ionic. The effective charge on an ion can also be reduced by polarization as a result of ion displacement in the lattice. Thus, the dynamical properties and defect properties of the lattice can alter the ionicity of an otherwise perfect static ionic crystal as discussed further below.

It is common in calculations for ionic solids to assume two-body central forces, as was seen to be the case with metals. In fact, the two-body approximation probably has greater validity in ionic crystals. However, the central force approximation is not as easily justified, as many ionic crystals exhibit significant deviations from the Cauchy relation $C_{12} = C_{44}$. The ceramic oxides, particularly MgO, deviate from this relationship (more significantly than the alkali halides), and non-central forces in these solids therefore become important.³⁶

The total energy of the interaction consists of four terms: the

Coulombic interaction; the closed shell repulsion; the Van de Waals interaction; and the zero point energy. Several models of varying complexity have been developed to describe this interaction. These include the point ion, shell, and breathing shell models in order of increasing sophistication. Potentials based on these models have been developed for many ceramic oxides³⁷ and have been used to calculate crystal defect properties. For example, in MgO, point defect formation energies and volumes³⁶, lattice dislocation core structures³⁸, and interaction energies between point defects and dislocations³⁹ have been calculated.

In developing these potentials the Van der Waals and zero point energy terms, which contribute less than 10% to the total, are often neglected. The form of the closed shell repulsion is generally assumed to be exponential, a form preferred to the inverse power law Born expression.⁴⁰ The exponential takes the form $a \cdot \exp(-r_{ij}/\rho)$ where the constants a, ρ are determined empirically from equilibrium crystal data. The point ion model neglects non-central forces, polarization effects, and the need to reproduce the dielectric response, and furthermore, assumes that the ions possess integer charges. The shell model neglects non-central forces but accounts for polarization in the form of a Buckingham potential³⁷ where the constants a, ρ are estimated using a quantum mechanical molecular orbital calculation. The ions consist of independent shells with shell charge Y and cores with core charge X coupled to each other by a spring with constant K . There is no Coulomb interaction between the core and shell of the same ion. Since the interionic forces act through the shells, the short-range forces are modified by ionic polarization. In the case of the oxide potentials it

has been assumed that the cations have negligible polarizability and that the anion polarization contribution to the energy takes the form $a \cdot \exp(-r/\rho) - b/r^6$. The constants a , b and ρ are estimated using the Hartree-Fock calculation and crystal data. The breathing shell model takes into account both polarization and non-central forces. In this model the shell radius responds harmonically to the total effective overlap pressure of all surrounding ions. The potential then depends on the position of neighboring ions and thereby incorporates many-body forces. The potential parameters for the polarized anions are adjusted to the observed elastic constants.

It is noted that the two-body calculational approaches described above are not capable of coping with varying degrees of ionicity which might conceivably occur in the direct vicinity of a crystal defect such as a grain boundary. For example, if ions of like charge tend to be close together in the unrelaxed defect structure it may be possible to reduce the high Coulomb energy which would be associated with such an arrangement by changing the nature of the local bonding in a direction to reduce the degree of ionic bonding and increase the degree of covalent bonding. This could presumably be accomplished by reducing the degree of electron transfer and increasing the degree of covalent electron-sharing. This behavior is more likely to occur in an ionic solid that is already partially covalent which is not the case for the ceramic oxides. However, there is some speculation⁴¹ that the (100) surface of MgO is more covalent than the bulk, mainly due to the instability of the O^{2-} ion in the free state. This would result in surface states and

increased directional bonding. Unfortunately, at the present time there appears no way of introducing such bond perturbations into an inter-atomic potential either from first principles or experimentally.

(2) Modeling of Grain Boundary Structure

It may be anticipated at the onset that the realistic modeling of grain boundary structure in even pure ceramic oxides will be considerably more complex and difficult than in metals, since two charged species are intrinsically present (i.e., the cations and the anions) which interact strongly via their Coulomb interaction. In order to construct an acceptable boundary in such a material it is necessary to join the two crystals together as in Fig. 1 and relax the ions in the core structure in such a way as to avoid high energy situations where larger numbers of like ions are juxtaposed. As will be shown below, there is probably a variety of ways in which this can be achieved, and we therefore expect, on this basis alone, that any realistic modeling procedure will be inherently complicated.

Besides dealing with the fundamental problem of arranging charges at the interface, any computer simulation of grain boundary structure must sum correctly the long-range Coulomb interaction and also enforce proper border conditions. In past simulations of point defects and lattice dislocations the border conditions have varied from the simple rigid border to the more sophisticated and mathematically complicated elastic displacement field and harmonic continuum. When the outer region is treated as a harmonic continuum the border ions are displaced so that the polarization induced by the charged defect matches the observed

dielectric behavior of the solid. Flexible border conditions have also been used in which the border ions respond to the relaxation of the free inner ions within the constraints of linear elasticity. Additionally, cyclic borders are used in cases where the defect structure periodically repeats in one direction, for example, along a dislocation line. The application of any of the above border conditions to the simulation of grain boundaries is not straightforward, since the degree of symmetry of the defect is lower, and in general the elastic displacement field is not known.

The summation of the long range Coulomb interaction is also not simple. Usually the symmetry of the defect needs to be utilized in order to ensure rapid convergence. Rapidly convergent sums have been formulated for point defects (spherical symmetry) and the Madelung method of summing strings of charges has been used for lattice dislocations (translational symmetry along the dislocation line). In the most recent grain boundary simulation⁴² described below the interaction energy of an ion with a semi-infinite crystal is calculated using an expression by Lennard-Jones and Dent, and the summation of the energy of the ions within the relaxable slab is performed using Ewald's method.⁴³

So far, only two approaches (one of which is very rudimentary) have been used in attempts to model grain boundaries in ionic solids. These are: (1) what we shall call the simple "inspection" method; and (2) the molecular statics technique.

The inspection technique, which is purely schematic, has been useful in developing simple ideas about how ions may be arranged or rearranged near an interface in order to reduce the electrostatic potential energy.

In considering this problem it quickly recognized that in the rocksalt structure (Fig. 10) two types of crystallographic plane can be distinguished with regard to charge: the "layer" plane in which all ions are of the same sign and each plane as a whole alternates in sign, e.g., (111); and the "checkerboard" plane in which equal numbers of like and unlike charges are intermixed in a regular pattern and where successive planes of the family are periodically displaced with respect to each other, i.e., (100) and (110). Clearly, it would be easier from an electrostatic point of view to form an interface in which layer type planes were parallel to the boundary because then the charge mismatch in the initial unrelaxed configuration would be across two planes in the boundary region instead of one. Twist boundaries on (111), for example, would have a lower unrelaxed Coulombic energy than those on (100). However, the charge mismatch energy would undoubtedly still be considerable, and further rearrangement using some or all of the relaxation modes discussed below in Section IV (4) would be required. Twin boundaries and stacking faults on (111) planes are additional examples of such boundaries.

Kingery⁴⁴ has used the simple inspection method to produce a conceivable $\Sigma = 5$ [001] symmetric tilt boundary in the rocksalt structure (Fig. 11), but he offers no explanation for the fact that like charges are still in relatively close proximity at the interface. (It is conceivable, however, that the charge concentrated at the interface is partially balanced by the equal and opposite charge concentration that alternates every other plane down the tilt axis.) Rice⁴⁵ has considered the closely related problem of the structure of the cores of lattice

dislocations which, for example, might be present in low angle boundaries in the rocksalt structure. He proposed three relaxation mechanisms (illustrated in Fig. 12) which could conceivably reduce the charge mismatch energy. These include: (1) bond stretching with a jump to a second plane of atoms; (2) bond compression and vacancy creation; and (3) bond stretching and no bonding to one row of atoms. (We note that charge mismatch is reduced by vacancy creation by simply removing an offending ion.) In addition, Rice considered a [001] low angle tilt boundary in the rocksalt structure (see Fig. 13) and suggested that in this case the problem of matching charges at the boundary would only be resolved by creating vacancies.

The computer simulation of ionic grain boundaries by the molecular statics method has been confined entirely to [001] twist boundaries. Chaudhari and Charbnau⁴⁶, using the exponential Born-Mayer potential to represent the overlap repulsive energy for MgO, calculated the energy required to produce four high density CSL boundaries ($\Sigma = 5, 13, 17, 25$) for the situation where the boundary was constructed by simply bringing two rigid crystals together face-to-face. Energy minima were found when the spacing between crystals was varied, but, despite this result, their relaxation technique of merely varying the spacing between two semi-infinite rigid crystals, without relaxing any individual ions, must be considered as too simple to produce meaningful results. Moreover, it has recently been suggested⁴² that there is reason to believe that their calculation of the Coulomb energy is incorrect. Recently, Wolf⁴² has carried out an improved simulation of the same four CSL boundaries in NiO using a point-ion model. In this work relaxation of all ions

within a boundary slab sandwiched between two semi-infinite adjoining rigid crystals was allowed, and the distance between the two crystals was varied. However, it was found that the energy of all the relaxed boundaries was always higher than that of the two free (001) surfaces, as shown in Fig. 14. This result predicts that these (001) type boundaries are unstable in an ionic solid, and this is attributed to the high-energy charge mismatch across the interface (which was not relieved to any great extent by the relaxation procedures used). This result disagrees with experiment (see below) and it was therefore concluded that the approach which was employed did not incorporate all possible modes of relaxation, some of which are discussed below in Section IV (4).

(3) Comparison with Experiment

Recently, a lengthy series of [001] twist boundaries in relatively pure MgO with twist misorientations very close to the high density $\Sigma = 5, 13, 17, 25$ and 29 CSL misorientations has been prepared⁴⁷ by welding single crystals together in an argon atmosphere under pressure at an elevated temperature. Stable grain boundaries were obtained in all cases which were subsequently examined by TEM. Square networks of screw GBDs were found in all of these boundaries (Fig. 15) which were evidently secondary GBDs of the same type as those observed in similar [001] twist boundaries in gold as described previously in Section III (3). The measured spacings of the GBDs in the MgO boundaries are shown in Fig. 16 as a function of the twist deviation, $\Delta\theta$, and appear to be consistent with Eq. (2) as expected. These results for twist boundaries

in MgO are therefore remarkably similar to those obtained for gold (see Figs. 8 and 9).

[001] twist boundaries in MgO have also been investigated in another manner by using small cubic MgO crystals which were produced in the form of a smoke by burning magnesium in air. In this work the small crystals in the smoke stuck to one another to form small bicrystals containing [001] twist boundaries⁴⁸ or else were deposited on a MgO [001] single crystal substrate to form similar boundaries.⁴⁹ Subsequent examination of the distribution of twist angles assumed by the crystals across the boundaries showed a marked preference for high density CSL orientations as seen, for example, in Fig. 17. This result therefore provides additional evidence that the high density CSL orientations are indeed of relatively low energy.

In other work Sun and Balluffi⁴⁷ have observed numerous examples of extrinsic GBDs in [001] twist boundaries in MgO (Fig. 15), and Yust and Roberts⁵⁰ and Yust⁵¹ (Fig. 18) have found examples of extrinsic GBDs in UO_2 boundaries. Again, these structures are remarkably similar in appearance to those observed in gold and other metals.^{6,26-29,52}

(4) Discussion

The above experimental results show that [001] twist boundaries which are produced by mating checkerboard planes together are actually stable, and, in fact, appear to have relatively low energy when they possess a short wavelength structure. We may therefore conclude that the modeling work carried out for these boundaries to date (Section IV (2)) has been inadequate and has not allowed proper relaxation of the core structure.

Relaxation mechanisms which could conceivably be of importance in pure material include some, or all, of the following:

- (a) Ionic reshuffling which might be accomplished by bond stretching and/or compression, rigid-body translations, ($\vec{t}$), or micro-faceting of the boundary plane.
- (b) Insertion or removal of self-ions of either polarity.
- (c) Polarization/reduction in ionicity/change in nature of bonding.

Bond stretching and/or compression has been discussed previously and in many cases will undoubtedly be coupled to the other atomistic relaxation modes suggested. This is evident from the fact that many of these modes operating by themselves seldom seem to produce a more favorable situation with regard to charge mismatch across the interface. Complex reshuffling of ions between the two crystals by itself, for instance, would cause considerable (and undesirable) charge disturbances throughout the bulk. Rigid-body in-plane translation of one crystal with respect to the other by itself might significantly lower the electrostatic energy for 'layer' structures but not for 'checkerboard' structures. In a 'checkerboard' structure, an example of which would be a [001] twist boundary, a decrease in the Coulomb repulsion between one pair of mismatched ions is generally opposed by a corresponding increase in Coulomb energy by another pair of mismatched ions within the CSL periodic unit cell of the boundary. In addition, we note that the magnitude, and hence the importance, of unique translations tends to decrease as Σ increases.

Since the boundary structure varies as the orientation of the

boundary plane is varied (at constant crystal misorientation) it may be possible in certain cases to reduce the energy by introducing micro-facets. This requires, of course, that any effect due to the increase in the number of ions in the core region which accompanies microfaceting is more than compensated for by a more favorable overall arrangement of the ions.

In some cases where like charges are in juxtaposition, the energy may be reduced by the insertion or removal of an appropriate self-ion. It seems conceivable that approximately equal numbers of like and unlike charges could often be inserted/removed in such a way as to avoid the buildup of an extensive space charge region. Also, a combined mechanism of self-ion insertion/removal and rigid body translation may be preferred in certain types of structure with the possibility that special translations would allow the insertion/removal of the minimum number of ions. We also note that a boundary may possess intrinsic local excess charges at various points in a manner similar to the excess charges which are associated with jogs on edge dislocations. In general, we would expect a coupling between such charges and the ionic structure of the boundary. Also, if the boundary acts as a source for thermally generated equilibrium point defects in the crystal during heating, and if the formation energies of the defects differ, it is known⁴⁴ that a space charge should develop. Effects of this nature clearly lead to a complicated coupling between the space charge, the point defects, and the detailed structure of the boundary under equilibrium conditions. So far, no efforts have been made to treat this difficult coupled problem.

Finally, we note that a reduction in the local degree of ionicity as a possible mechanism for relaxation has already been mentioned in Section IV (1). It is interesting to speculate that such an effect might lead to the formation of polyhedral groups of atoms in the boundary stabilized by localized covalent bonding.

The experimental results obtained to date with the ceramic oxides are seen to be similar in a number of respects to those obtained for metals. Boundaries with short wavelength structures often appear to be of relatively low energy, and networks of intrinsic secondary GBDs form in boundaries with misorientations close to high density CSL misorientations. Also, extrinsic GBDs appear in many boundaries which are generally similar in appearance to those observed in metals by transmission electron microscopy. It seems, therefore, that many aspects of grain boundary structure in relatively pure ceramic oxides may be interpreted in terms of the same geometrical framework which has been successfully employed in the case of the metals. It therefore follows that boundary cores in these ceramic oxides must bear certain geometrical resemblances to corresponding boundary cores in metals, e.g., it seems likely that the core must be relatively thin.

V. CONCLUDING REMARKS

The state of our knowledge of grain boundary structure in metals is seen to be considerably more advanced than in ceramic oxides. In the case of the metals, a relatively large number of experiments has been performed which has yielded critical information about boundary fine structure. In addition, the computer simulation of boundary structure has produced detailed models which seem to be consistent with experiment

in many respects. In contrast to this, only a limited number of useful experiments has been performed with relatively pure ceramic oxides, and, furthermore, no successful computer modeling has been accomplished.

The disparity in experimental results may be attributed, at least in part, to the fact that it is generally more difficult to produce and examine controlled grain boundaries in reasonably pure ceramic oxides than in metals. The disparity in the modeling results is undoubtedly due to the fact that the relaxation phenomena are more varied and complex in the ceramic oxides than in the metals.

However, a wide variety of modern research techniques is currently available which can be profitably applied to the determination of the structure and properties of grain boundaries in both metals and ceramic oxides. Further progress, particularly with ceramic oxides, will depend upon the completion of further high resolution experiments using carefully controlled boundaries in well-characterized specimens and further modeling efforts employing more realistic relaxation methods.

We conclude with a few remarks about impurity effects which we have essentially ignored up to this point. There is considerable evidence^{4,44,53} which indicates that important segregation effects may be expected in many common metal and ceramic oxide systems which may introduce entirely new grain boundary phenomena and behavior. As described elsewhere,⁴ a wide range of segregation behavior may be expected in metals depending upon the impurity concentration, the temperature, the nature of the interactions between the host atoms and the impurity atoms, and the type of host boundary. Conditions may be visualized which range from relatively simple situations where the segregating impurity atoms fit into

the basic structure of the host boundary to complex situations where the segregation produces a new structure in the boundary core.

In the case of the ceramic oxides, Kingery^{44,53} has emphasized that common ceramic oxides usually contain relatively large concentrations of allotropic impurities. Electrical charge effects of the type that we have already discussed should then make grain boundaries in the oxides particularly susceptible to strong segregation effects. The interaction of impurity ions with the boundary must therefore always be considered as a possible additional mode of relaxation and method of stabilizing the structure. As an interesting example, it has been shown recently⁵⁴ that twins formed in MgO smoke do not nucleate and grow in a dry atmosphere but they will nucleate and grow in the presence of water vapor. A conceivable structure of the boundary can then be modeled as consisting of a layer of $\text{Mg}(\text{OH})_2$ (brucite structure) with MgO growing on either side. In the MgO smoke particle experiments of Chaudhari and Matthews⁴⁸ [see Section IV (3)], it was found that the preference for twist angles at high density CSL misorientations was markedly reduced when the boundaries were produced under conditions which exposed them to impurities. Evidently, in these experiments, the impurities segregated in the various twist boundaries in such a way as to reduce the energy differences between them. Kingery⁵³ has described and discussed a wide range of additional experiments which indicate the existence of strong impurity segregation effects in ceramic oxides which under certain conditions can lead to the formation of relatively thick segregated layers and even precipitation at the boundaries. Our knowledge of these phenomena at the fundamental level is

essentially non-existent, and it is evident that a great deal of work needs to be done to understand them in terms of the structure of the boundary and the chemistry of the system.

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FIGURE CAPTIONS

- Fig. 1 Construction of bicrystal containing a grain boundary in its midplane. (a) Two crystals joined rigidly in standard reference position. (b) Bicrystal after relaxation. Crystal 2 has undergone a rigid body translation represented by $\vec{t}$.
- Fig. 2 Two-body central force interatomic potentials, $V(r)$, for metals. r = distance between ion cores; a = lattice parameter. (a) Typical simple potential. (b) Empirical potentials represented by spline fitted polynomials (from Ref. 16). (c) Pseudopotential (from Ref. 21).
- Fig. 3. Computer simulated $[110]$ symmetric tilt boundary (from Ref. 13). Tilt angle = 70.5° , $\Sigma = 3$. Structure viewed along tilt axis. Atoms in A and B type layers perpendicular to tilt axis indicated by filled and open circles respectively.
- Fig. 4 Computer calculated grain boundary energy, γ , versus tilt angle, θ , for symmetric $[001]$ tilt boundaries in aluminum (from Ref. 55). Characteristic cusps appear for (013) , (012) and (023) twin misorientations.
- Fig. 5 Computer calculated relative grain boundary energy of various short period $[001]$ symmetric tilt boundaries in aluminum (from Ref. 15). λ = boundary period in direction perpendicular to tilt axis; a = lattice parameter.

Fig. 6 (a) Perspective representation of atomic positions in [001] twist boundary in gold, as determined by computer simulation (from Ref. 25). Twist angle = 22.6° , $\Sigma = 13$. Two [001] planes below (i.e., Planes 1 and 2) and above (i.e., Planes 3 and 4) the midplane of the boundary region are shown with each plane containing four CSL unit cells. The atoms are shown as points with the nearest neighbor atoms in each plane joined by lines so as to form a contoured surface. For purposes of clarity the interplanar separation has been increased by a factor of about four. The shaded pyramids indicate the atoms in "good" match which have undergone large displacements normal to the boundary plane. (b) Further perspective representation of atomic positions in same boundary represented in (a). Planes numbered 1-4 correspond to those shown in (a). However, each plane contains one CSL unit cell plus additional atoms required to show the Archimedian Antiprism. Nearest neighbor atoms in each [001] plane joined by lines. Only one octahedron is shown in order to avoid confusion.

Fig. 7 Lattice dislocation (L) impinging on grain boundary and dissociating into five GBDs (1,2,3,4,5) (from Ref. 56). See Ref. 56 for details of the dissociation.

Fig. 8 Networks of screw GBDs in [001] twist boundaries in gold (from Ref. 34). (a) Boundary with small twist deviation

from exact $\Sigma = 5$ ($\theta = 36.9^\circ$) CSL misorientation.

(b) Boundary with small twist deviation from exact $\Sigma = 13$ ($\theta = 22.6^\circ$) CSL misorientation. θ = twist angle.

Fig. 9 Measured spacing of screw GBDs in networks in [001] twist boundaries as function of twist angle, θ , in gold (from Ref. 33). Curves calculated from Eq. (2). Note that primary and secondary GBDs are indistinguishable when $\Sigma = 1$.

Fig. 10 Rocksalt crystal structure. Larger spheres are anions; smaller spheres are cations.

Fig. 11 Conceivable model of $\Sigma = 5$ [001] symmetric tilt boundary in rocksalt structure obtained by simple inspection method (from Ref. 44).

Fig. 12 Three proposed mechanisms for relaxing charge mismatch in the cores of lattice dislocations in the rocksalt structure (from Ref. 45). In all cases the dislocation cores lie along $\langle 100 \rangle$ in the $\{100\}$ plane. (a) Bond stretching with a jump to the second plane of atoms. (b) Bond compression and vacancy creation. (c) Bond stretching and no bonding to one row of atoms (arrow).

Fig. 13 Illustration of the problem of relaxing charge mismatch

in the cores of edge dislocations in a 10° asymmetric tilt boundary in the rocksalt structure (from Ref. 45). Charge mismatch could presumably be relaxed by creating vacancies.

Fig. 14 Calculated energy of [001] twist boundaries in NiO as a function of the separation, d , of the two semi-infinite adjoining rigid crystals (e.g., Crystals 1 and 2 in Fig. 1) facing the boundary (from Ref. 42). Results given for $\Sigma = 1$ ($\theta = 0^\circ$), $\Sigma = 5$ ($\theta = 36.9^\circ$), $\Sigma = 17$ ($\theta = 28.1^\circ$), and $\Sigma = 25$ ($\theta = 16.3^\circ$). θ = twist angle; d_0 = equilibrium (001) interplanar spacing; σ = surface energy.

Fig. 15 (a) Intrinsic and extrinsic GBD structures in [001] twist boundary in MgO possessing a small twist deviation from the $\Sigma = 13$ ($\theta = 22.6^\circ$) misorientation (from Ref. 47). Intrinsic structure consists of grid of screw GBDs. Extrinsic structure consists of extra GBDs resulting from the impingement of a lattice dislocation. (b) Schematic diagram of extrinsic GBD structure in (a).

Fig. 16 Measured spacing of GBDs in networks in [001] twist boundaries as function of twist angle, θ , in MgO (from Ref. 47). Curves calculated from Eq. (2).

Fig. 17 Relative frequency of occurrence of twist angle, θ , for [001] twist boundaries produced by depositing MgO smoke particles on a MgO [001] single crystal substrate (from Ref. 49).

Fig. 18 Extrinsic GBDs in high angle grain boundary in UO_2 .
Note the addition of extrinsic GBDs at the points of impingement of the lattice dislocations (from Ref. 51).

(a)

(b)

Fig. 4

FIG. 5

FIG. 5

FIG. 6(a)

FIG. 6(a)

FIG. 6(b)

FIG. 7

FIG. 8

FIG. 9

FIG. 10

FIG. 11

FIG. 14

FIG. 14

FIG. 16

FIG. 16