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ON THE MORPHOLOGY OF INCLUDED CRYSTALS; BICRYSTALLINE KALEIDOSCOPES

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Abstract

The morphology of one crystal entirely surrounded by a different one, referred to here as an included crystal, is considered in this paper. It is shown that the morphology of such an included crystal can be profoundly affected by the presence of interfacial defects. On the basis of the Principle of Symmetry Compensation, it is shown that a cavity in the matrix crystal, which is bounded by degenerate surfaces, can always be filled by a contiguous included crystal in such a way that the initial surfaces become degenerate interfaces, provided the geometrically necessary defects are present. These defects can be predicted using a recently developed theory. Included crystals of this form exhibit symmetry consistent with that of the matrix crystal, and such morphologies are referred to as being fully compensated. Morphological forms exhibiting lower symmetry may also occur, and require fewer defects to be present. Experimental observations are presented illustrating an example of a fully compensated morphology, and other lower symmetry forms. It is also pointed out that the free energy of a system containing an included crystal with a given volume is not necessarily minimised for a defect free configuration, because the presence of defects can enhance the area of low energy interface.

1. INTRODUCTION

Crystallography is the experimental and theoretical investigation of the characteristic order, or symmetry, exhibited by crystals. Such order is manifested by the atomic arrangement in the crystal, the external morphology, and the crystal's physical properties. Bicrystallography is the extension of this subject where at least two crystals coexist, and are separated by an interface. The presence of interfaces in crystalline materials can influence physical properties so significantly that the study of the structure and properties of interfaces and bicrystallography have been active fields of research for many years.

Symmetry is specified in terms of geometrical operations, such as rotations, translations and inversions for example, and the permissible combinations of symmetry elements which can be exhibited by a crystal or bicrystal are concisely expressed by the various types of spacegroups. Historically speaking, the possible significance of the presence of symmetry in bicrystals has long been recognised, for example the idea that interfacial periodicity is related to specific interfacial free energy, \( \gamma \), is the basic premise of the coincidence-site-lattice theory. However, more recent assessments indicate that, in general, \( \gamma \) is probably not related in a simple way to geometrical parameters. On the other hand, valuable conclusions can be reached on the basis of purely geometrical considerations. In particular, a comprehensive theory of the topological properties of interfacial and crystal defects has been obtained by these means. The presence of defects in bicrystals is known to be important since these can mediate interfacial processes of technological significance. Naturally, a detailed understanding of the role of these defects in physical processes generally requires a more extensive knowledge than simply the topological properties of the defects concerned. One exception to this, however, is the influence of defects on the external morphology of bicrystals, and this is the principal topic of the present article. We shall show that the symmetry exhibited by one crystal which is entirely surrounded by another, referred to here as an included crystal, is profoundly influenced by the nature of defects which are present. Before presenting the treatment of bicrystal morphology, the geometrical theory of defects is briefly recalled. In particular, the crystallographic origin of defects is reviewed in terms of the fundamental relationship between symmetry and conservation principles. This relationship is referred to here as the Principle of Symmetry Compensation, and will be illustrated by kaleidoscopic figures. The relevance of these figures to the theory of defects, and their similarity to potential shapes of included crystals will be explained. Finally, after discussing the mathematical formulation of the symmetry of included crystals, experimental observations of precipitates will be presented, and compared with...
2 - CRYSTAL AND INTERFACIAL DEFECTS

The geometrical characterisation of line defects in crystals and interfaces has been described in detail elsewhere /4/, and here we briefly review some of the principal issues relevant to the present article. The distinctive feature of perfect single crystals is, of course, that they exhibit translation and also (generally) point symmetry. Such objects can be host to line defects, which are characterised geometrically by proper symmetry operations; namely dislocations, disclinations and dispirations characterised respectively by translations, rotations, and combinations of these. Using the notation of the International Tables for Crystallography /5/, we represent a symmetry operator by the matrix \( \mathbf{W} = (\mathbf{W}, \mathbf{w}) \), where \( \mathbf{W} \) represents a rotation or inversion operation for example, and \( \mathbf{w} \) represents any translation component. Thus, a perfect dislocation is characterised by a translation operation, \( \mathbf{W} = (1, 1) \), where 1 represents the identity, and 1 the translation vector corresponding to the Burgers vector. A disclination is characterised by \( \mathbf{W} = (\mathbf{W}, 0) \) where \( \mathbf{W} \) is a pure rotation, and a dispiration by \( \mathbf{W} = (\mathbf{W}, \mathbf{w}) \) corresponding to a screw-rotation operation. In the case of nonholosymmetric crystals (i.e. where the crystal's symmetry is lower than that of its lattice) extended defects such as inversion domains can arise. Defects of this type are characterised by improper symmetry operations belonging to the lattice's spacegroup, but which do not also belong to that of the crystal. We refer to such operations as exchange operations, and designate them \( \mathbf{W}_E \).

Bicrystals are objects comprising two component crystals, which we designate white (\( \lambda \)) and black (\( \mu \)). Such composite objects may exhibit symmetry, and can be assigned a spacegroup depending on whether they exhibit zero, one or two-dimensional translation symmetry /2/. If the \( j \)th operation in the white crystal's spacegroup, \( \mathbf{W}(\lambda)_j \), and the \( k \)th black operation, \( \mathbf{W}(\mu)_k \), coincide so that the composite exhibits this symmetry, we designate such a coincident operation (which therefore belongs to the bicrystal spacegroup) \( \mathcal{W}(\lambda\mu)_j \). Proper operations in the set of coincident operations characterise line defects which can exist in the interface of the bicrystal, and also, of course, in either of the component crystals. However, the number of defects of this type which can arise in interfaces in general is very restricted. Nevertheless, interfaces can act as hosts to a wide range of defects, but the crystallographic origin of these is distinct from that described above. It has been shown elsewhere /4/ that the breaking of crystal symmetry when a bicrystal is created leads potentially to a variety of interfacial line defects. A treatment has been presented which enables defects of the two types mentioned above, which are admissible in a given interface, to be predicted, and this is summarised below.

Whereas line defects in single crystals are characterised by proper symmetry operations, admissible line defects in interfaces are characterised by proper combinations of symmetry operations, one from each of the adjacent crystals. Thus, choosing the white crystal's coordinate frame to be our reference frame, the inverse of the \( j \)th black operation is then given by \( \mathbf{P}^{-1} \mathbf{W}(\mu)_j \mathbf{P} \), where \( \mathbf{P} = (\mathbf{P}, \mathbf{p}) \) is the transformation relating the black and white frames /5/. Admissible defects are characterised by compound operations \( Q_{ij} = (Q, \mu) \) given by

\[
Q_{ij} = \mathcal{W}(\lambda)_j \mathcal{W}(\mu)_k \mathbf{P}^{-1} \mathbf{P}
\]

which are proper. When \( Q_{ij} \) corresponds to a translation, the associated defect is an interfacial dislocation, and when it is a rotation or screw operation, the defect is an interfacial disclination or dispiration respectively. The set of defects predicted by expression (1) includes all the admissible white crystal defects, as can be appreciated by substituting \( \mathbf{W}(\mu)_j \mathbf{P}^{-1} = (I, \mathbf{p}) \), and, similarly, all the black crystal defects. (This subset of defects includes defects characterised by coincident operations \( \mathcal{W}(\lambda\mu)_j \), discussed above.) In addition, further defects are predicted, and the range of these depends on the extent to which crystal symmetry is broken when a bicrystal is created; the greater the extent of crystal symmetry breaking, the wider is the range of interfacial defects that can arise in a given interface /4/. We also note that black or white (or both) exchange operators, \( \mathbf{W}_E(\mu)_j \) or \( \mathbf{W}_E(\lambda)_j \), can be substituted into expression (1). Provided \( Q_{ij} \) is proper, this compound operation characterises the line defect which delineates the intersection with the interface of an extended black, or white (or both) defect. Similarly, a twinning operation, corresponding to a mirror operation across some plane in the black crystal, \( T(\mu) \), for example, can be substituted into the expression in order to identify the nature of the line defect terminating this twin at the interface. The geometrical theory of defects, outlined above, can also be used to obtain approximate expressions for the topological features associated with interfacial discontinuities. In general, defects are associated with interfacial steps and/or facet junctions; these features are relevant to the present article, and the reader is referred to a previous publication /4/ for details.

3 - INCLUDED CRYSTAL MORPHOLOGY

In the previous section it was recalled that the crystallographic origin of many interfacial defects is the breaking of crystal symmetry when a bicrystal is created. The converse of this proposition is that crystal symmetry which is suppressed in the creation of a bicrystal can be re-established by the introduction into the bicrystal of appropriate defects. This point will be illustrated further below. In the context of included crystals, this appreciation leads to a most interesting result, namely, that an included crystal, bounded by sets of degenerate interfaces, residing in an otherwise perfect matrix crystal can exhibit a morphology consistent with that of the host, provided the appropriate interfacial defects are introduced. In other words, if an internal cavity is prepared in the host matrix, bounded by degenerate sets of surfaces, this cavity can be filled by the included crystal so that the sets of initially degenerate surfaces become sets of degenerate interfaces. This pleasing conclusion is, furthermore, independent of the symmetries and structures of the two crystals concerned and their relative orientation, although these factors would affect the nature
of the geometrically necessary defects. The fundamental principle underlying this conclusion is the Principle of Symmetry Compensation/1/, and can be illustrated in a simple manner by kaleidoscopic images.

In a kaleidoscope three reflecting surfaces are set along the axis of the instrument in the form of a hollow equilateral triangle. Coloured fragments trapped between these mirrors at one end form a pattern, as illustrated schematically by the region UVW in fig.1. The optical system is arranged so that this pattern, along with the five other mirror images, fall on the observer's retina, and a beautiful pattern is seen, as represented by fig.1. By rearranging the fragments, an endlessly changing pattern is observed, but, regardless of these changes, the symmetry of the pattern is invariant. Using crystallographic terminology, we would describe the assembly of six mirror images as a set of coexisting variants. The discontinuities between adjacent variants are analogous to extended defects, twin boundaries in the present instance. Moreover, the bounding hexagon in fig.1 can be regarded as analogous to a cavity in a medium exhibiting trigonal symmetry, and it can be seen that this cavity can be filled with twinned variants in a manner which conserves the trigonal symmetry irrespective of the arrangement of the fragments.

We can pursue the analogy further, without loss of generality, by requiring that the fragments become ordered, similar to the atoms in a crystal. The arrangement of atoms (fragments) will then exhibit symmetry, possibly identical to that of the cavity, as depicted in fig.2. In such a situation, no defects are necessary since the 'variants' have identical structures. However, if the symmetry of the primary variant, UVW, is different, or not coincident with, that of the cavity, as illustrated in fig.3, defects (twin boundaries) must arise which separate the variants. However, irrespective of this symmetry breaking, the set of interfaces between the cavity and the included crystal remain crystallographically equivalent (energetically degenerate). On the other hand, the structure (and hence energy) of these interfaces, and also that of the twin boundaries, will depend on the actual crystal structures and their relative orientation and position.

The discussion above indicates how defects can be regarded as agents which, by separating crystallographic variants, compensate for (re-establish), the initially broken symmetry. Mirror-related optical variants can, of course, coexist without interaction. On the other hand, coexisting material variants will interact, and an excess free energy would be associated with the twin boundaries in the above example. The interaction between variants may not necessarily take the form of an extended defect, but can for example be brought about by the displacement field of dislocations or disclinations. Fig.4 is a schematic illustration of a square lattice (symmetry 4 mm) filling a hexagonal cavity (symmetry 6 mm). Again, it can be seen that the symmetry of the complete ensemble is fully compensated, i.e. 6 mm, and that all the interfaces are crystallographically equivalent. However, the interfacial defects lying along the vertices of the hexagon (i.e. perpendicular to the page in a three-dimensional extension), as can be determined using expression (1), are 30° disclinations. The six interfacial disclinations are balanced by a 180° crystal disclination running along the centre of the figure. Clearly, the square unit cells are considerably distorted in the displacement field of these line defects, but they remain recognisable except along the core of the crystal disclination. A more complicated example is shown in fig.5; in this case a rectangular lattice (symmetry 2 mm) is shown filling a hexagonal cavity (symmetry 6 mm), and the relative orientation of the two lattices leads to the breaking of all the initial symmetry. In this configuration twelve variants co-exist, separated by twin boundaries parallel to (2110), and interfacial disclinations located at the vertices and running parallel to [0001]. Despite the increased structural complexity, the compensated nature of the symmetry of the ensemble, and the degenerate nature of the cavity interfaces are evident.

4 - FORMAL TREATMENT

The account given above introduces and illustrates the principal ideas involved in the demonstration that an included crystal can conform to a cavity in the matrix material. We now consider the formal crystallographic proof of this possibility. This involves two distinct aspects: first the totality of variants must be identified for the case in question, and secondly, the nature of the geometrically necessary defects must be determined.

Let the matrix crystal be white, and the included crystal be black, and let their spacegroups be designated $\mathcal{I}(\lambda)$ and $\mathcal{I}(\mu)$ respectively. Consider next the dichromatic complex $/2/ formed by imagining the black and white structures to interpenetrate with the relative orientation and position defined by $\mathcal{P} = (\vec{p},g)$. (For convenience we choose that value of $\mathcal{p}$ which leads to the highest symmetry.) The spacegroup of the resulting complex, $\mathcal{I}(c)$, is given by $\mathcal{I}(\lambda) \wedge \mathcal{I}(\mu)$, and the elements in the group $\mathcal{I}(c)$ are the coincident black and white symmetry operations $\mathcal{W}(c), \mathcal{W}(c)\mathcal{W}(c)$ etc. (We take the black and white crystals to be chemically and/or structurally different in the present work, so that antisymmetry need not be considered /6/.) In general, the formation of the dichromatic complex leads to the suppression of back and white crystal symmetry operations, and thus a multiplicity of equivalent complexes exists inter-related by the suppressed operations. Consider the subset of equivalent complexes, which are inter-related by suppressed white operations; this set can be found by decomposing $\mathcal{I}(\lambda)$ with respect to $\mathcal{I}(c)$, i.e.

$$\mathcal{I}(\lambda) = \mathcal{I}(c) \cup \mathcal{I}(c) \mathcal{W}(\lambda)_q \cup \mathcal{I}(c) \mathcal{W}(\lambda)_q$$

where $\mathcal{W}(\lambda)_q, \mathcal{W}(\lambda)_q$,... are coset representatives, and correspond to white operations which do not belong to $\mathcal{I}(c)$.

We now consider the creation of a bicrystal from the primary complex, and let the interfacial orientation be represented by the unity vector $\mathcal{g}$ which is perpendicular to the chosen interface and points into the white crystal. The symmetry of the resulting bicrystal is designated $\mathcal{I}(b)$. If coincident symmetry exhibited by the complex is suppressed by the creation of this bicrystal, a multiplicity of equivalent bicrystals can be formed from that complex, and these can be identified by decomposing $\mathcal{I}(c)$ with respect to $\mathcal{I}(b)$ i.e.
Fig. 1 - Kaleidoscopic figure showing six mirror-related variant patterns. The primary variant, UVW, is a pattern created by coloured fragments, and exhibits no symmetry, but the symmetry of the ensemble is the same as that of the arrangement of mirrors in the instrument, i.e. 3m, irrespective of the configuration of the fragments. The bounding hexagon is analogous to an internal crystal cavity, and the discontinuities between adjacent variants are analogous to twin boundaries.

Fig. 2 - A kaleidoscopic figure where the fragments are identical and exhibit crystalline symmetry. In this case the symmetry of the primary variant is coincident with that of the bounding cavity, and hence no multiplicity of variants arises, and hence no discontinuities (defects) are required.

Fig. 3 - A kaleidoscopic figure similar to fig. 2, but where the orientation of the included crystal leads to symmetry breaking. The variant configurations coexist contiguously by virtue of twin boundaries, and the symmetry of the ensemble is consistent with that of the cavity. The interfaces between the included crystal and the surrounding matrix are also crystallographically equivalent.
Fig. 4 - A kaleidoscopic figure showing a square lattice included in a hexagonal cavity. The six variants of the square lattice coexist by virtue of 30° disclinations at the vertices of the hexagon, and a 180° disclination in the centre of the included lattice. The symmetry of the ensemble is 6 mm, and all the interfaces are equivalent. This figure is also a schematic projection of a tetragonal TiH crystal included in a hexagonal Ti matrix; the lines drawn in the hydride correspond to traces of \{110\} planes in order to represent the experimentally observed orientation relationship (see text).

Fig. 5 - A kaleidoscopic figure showing a rectangular lattice included in a hexagonal cavity. Twelve variants of the rectangular lattice coexist, separated by disclinations at the hexagon's vertices and twin boundaries; the ensemble exhibits compensated symmetry, 6 mm. This figure is also a schematic projection of a tetragonal rutile crystal included in a sapphire matrix (see text).
The total set of equivalent bicrystals obtained from the multiplicity of dichromatic complexes can now be enumerated. There will be \( x \) such bicrystals which can be created from the primary complex, and these have normals \( n \), \( W(c)_1 \), \( W(c)_2 \), etc. In addition, \( x \) equivalent bicrystals can be obtained from each of the \( y \) equivalent complexes, these having normals given by \( W(\lambda)_1 n \), \( W(\lambda)_2 n \), \( W(\lambda)_3 n \), ..., \( W(\lambda)_y n \), ..., etc. leading to a total of \( x y \) bicrystals. Now, for the general case, we chose \( n \) such that the resulting bicrystal exhibits no point symmetry, i.e. \( \Xi(b) = 1 \) or \( 2 \) (the existence of any translation symmetry in the interface will not affect the morphology of the included crystal). Thus, the coset representatives in expression (3) will include all the operations \( W(c)_n \), \( W(c)_m \), ..., in the group \( \Xi(c) \). It therefore follows that the total set of \( x y \) bicrystals will have interfacial orientations given by \( W(\lambda)_1 n \), \( W(\lambda)_2 n \), ..., where the set \( W(\lambda)_m n \), \( W(\lambda)_m n \), etc. comprises all the point symmetry operations (mirror-glide and screw-rotation operations included) in the group \( \Xi(\lambda) \). In other words, in addition to the chosen bicrystal with orientation \( n \), there will be \((g-1)\) further bicrystals (where \( g \) is equal to the order of the point group of the white crystal), each one of these being related to the initial bicrystal by a distinct white point symmetry operation.

The set of \( g \) bicrystals has been obtained from equivalent dichromatic complexes inter-related by white symmetry operations. It is therefore possible to join the white components of this set into a contiguous assembly without distortion. In fact, we can arrange these components so that they create a closed cavity within the white crystal. The black components however, cannot in general be joined contiguously without the introduction of defects. Before the nature of the necessary defects is considered, we mention the possibility that the set of \( g \) interfacial orientations described above does not enclose a volume. This can arise in cases where the white crystal exhibits low symmetry (monoclinic or triclinic for example). In such circumstances further sets of bicrystals must be introduced; thus, if bicrystals with interfacial orientations \( n_1, n_2, ... \) are created from the primary complex, \((g-1)\) equivalent sets can be obtained from the equivalent complexes. By appropriate choice of \( n_2 \) etc., it will always be possible to ensure that closed figures can be obtained. Furthermore, it is not necessary to require that \( n_2 \) etc. correspond to general bicrystals, i.e. \( \Xi(b) \) may exhibit any degree of point symmetry. As long as at least one of the sets of interfacial orientations \( n_1 \) by convention in this work) is general, then the cavity within the white crystal will have a morphology exhibiting the general form consistent with the white crystal's symmetry. On the other hand, if none of the interfacial orientations chosen in the primary complex correspond to general bicrystals, then the resulting cavity in the white crystal may exhibit a special morphological form (though not necessarily), and this may exhibit higher symmetry than the white crystal.

5 - GEOMETRICALLY NECESSARY DEFECTS

Consider again the situation mentioned earlier where the set of \( g \) bicrystals, including the one characterised by the interfacial orientation \( n \), in the primary complex, can be arranged so that the white components can be joined to form a closed cavity. Associated with each white component is a black crystal component, and, as mentioned, these cannot in general be joined contiguously without distortion. We consider in particular a pair of bicrystals, one created from the primary complex with interfacial orientation \( n_1 \), and a second one adjacent to the first in the connected assembly. The second bicrystal is related to the first by a white symmetry operation \( W(\lambda)_1 n \Xi(c) \), and hence the white crystal component, the interfacial orientation and the black crystal component of the second bicrystal are related to their counterparts in the first by this operation. A defect must be introduced in order to bring the two black components into contiguous contact, and, following the method of Volterra developed for interfacial defects by Pond \( A / 4 \), the necessary defect is characterised by the operation required to bring the first black component into coincidence with the second. As explained above, this operation is \( W(\lambda)_1 n \), but we are at liberty to precede this by any appropriate black symmetry operation, say \( W(\mu)^{\perp} \). Thus, appropriate defects are characterised by (using the white coordinate frame) \( Q_{ij} = W(\lambda)_i \cdot W(\mu)^{\perp}_j \), which is seen to be identical to expression (1). In this way we can determine the character of the line defect delineating the facet junction separating the interfaces with orientations \( n \) and \( W(\lambda)_1 n \). Furthermore, we can, if necessary, employ a black exchange operation \( W(\mu)^{\perp} \), or tumbling operation, \( T(\mu) \), instead of a black symmetry operation. The resulting line defect, characterised by \( Q_{ij} = W(\lambda)_i \cdot T(\mu) \cdot W(\mu)^{\perp}_j \), respectively, may be more favourable energetically, although it must be kept in mind that an \( \perp \) extended defect or twin boundary must now emanate from the facet junction.

Two additional points need to be covered next regarding, first, the total defect content of an included crystal, and secondly, whether the argument advanced above for the geometrically necessary defects needs modification if more than one set of degenerate interfaces is present. Concerning the first point, it is clear that the total dislocation and disclination content of the included crystal system must be zero, because we have assumed that the matrix is otherwise perfect. Thus, the configuration of line-defects introduced must be arranged in the form of closed loops around the particle, as indicated schematically in figs. 4 and 5. In addition, if one constructs a closed path starting from an arbitrarily chosen black component crystal, and progressing through any sequence of other black components, the series of exchange and tumbling operations corresponding to the extended faults and twins crossed in the circuit, must combine to be equal to the identity. These conditions are not modified if more than one set of degenerate interfaces is present. This arises...
because no defects are present at junctions between interfacial facets created from any given dichromatic complex. Defects are only required at junctions between facets created from different dichromatic complexes. Thus, since the multiplicity of dichromatic complexes is fixed (for a given pair of black and white crystals with specified relative orientation and position), and does not depend on the number of interfacial orientations invoked, the geometrically necessary defect content is also independent of this latter number.

6 - DISCUSSION AND ANALYSIS OF SELECTED EXPERIMENTAL OBSERVATIONS

The foregoing discussion has demonstrated that the morphology of an included crystal can be profoundly influenced by the presence of interfacial and extended defects. Geometrically speaking, it is possible at one extreme that an included crystal, bounded by energetically degenerate interfaces, can exhibit a morphology consistent with the symmetry of the surrounding material. Such configurations, referred to as exhibiting fully 'compensated' symmetry, will require the presence of defects (unless the spacegroups of the two crystals are identical). Lower symmetry configurations, requiring fewer defects, can also arise. In particular, a configuration requiring no defects at all, referred to as exhibiting 'intersection' symmetry and discussed previously by Kalonji and Cahn /7, 8/, can occur. Included crystals in this class exhibit a morphology consistent with \( \mathcal{H}(c) \), and can be regarded as having been created from a single dichromatic complex. (We note that in practice defects may arise at facet junctions in such cases as a result of relaxation processes, but these latter processes cannot be predicted using geometrical arguments). Morphologies exhibiting symmetry even lower than intersection symmetry can in principle arise if, for example, the mechanisms involved in the early stages of precipitate growth suppress the development of certain symmetries.

It might seem at first sight that the presence of defects in an included crystal would increase the free energy of the total system. However, it must be kept in mind that the presence of defects can optimise the area of low-energy interfaces bounding the particle. Thus, it is not necessarily the case that the free energy per unit volume of an included crystal is minimised for a defect free configuration. It seems probable that the free energy of the system is a function of the size of the included crystal, particularly as the stored elastic energy associated with defects such as disclinations depends strongly on this parameter. In the remainder of the present article we present a preliminary analysis of some previously published works in order to demonstrate that defects do sometimes enhance the morphological symmetry of included crystals. In particular, we shall illustrate one case where the fully compensated configuration does arise, presumably because the formation energies of the necessary defects are not prohibitive. On the other hand, we shall show that lower symmetries also arise, especially where disclinations would be required for the fully compensated form. One example of the role of dispirations, and one of internal twinning will be shown.

7 - NiSi\(_2\) PRECIPITATION IN Si.

NiSi\(_2\) exhibits the fluorite structure, and hence its spacegroup is \( \mathcal{H}(\mu) = Fm\overline{3}m \). The spacegroup of Si, which has the diamond structure, is \( \mathcal{H}(\lambda) = Fd\overline{3}m \). The lattice parameters of these two cubic materials are very similar, and, for present purposes, we shall take them as being equal. Silicide precipitation occurs in two different orientations with respect to the matrix; in the type A orientation, the two crystals have parallel orientations, and in type B the silicide is rotated with respect to the Si by 60° about [111]/9. The intersection symmetry, \( \mathcal{H}(c) \), for the type A and B orientations is \( F4\overline{3}m \) and \( P\overline{3}m \) respectively, whereas the fully compensated symmetry for both cases is \( \mathcal{H}(\lambda) = Fd\overline{3}m \). For type B precipitates, the fully compensated morphology would require large angle disclinations, which are presumably very unfavourable since the observed morphology is consistent with the intersection symmetry. A dark field micrograph showing a trigonal platelet with large faces parallel to (111) and (TTT), taken from the work of Augustus /9/, is shown in fig. 6. On the other hand, octahedral morphology, consistent with the fully compensated form is exhibited by type A precipitates, as shown by the micrograph fig. 7, again taken from the work of Augustus /9/. The geometrically necessary defects in the latter case are dislocations with \( \mathcal{h} = 1/4<111> \), which delineate all the edges of the octahedral precipitate. This Burgers vector can be obtained by substituting into expression (1) any pair of corresponding operations in \( \mathcal{H}(\lambda) \) and \( \mathcal{H}(\mu) \), provided \( \mathcal{W}(\lambda) - \mathcal{Y}(c) \) and \( \mathcal{W}(\mu) \neq \mathcal{Y}(c) \), or vice versa /4/. Although the individual dislocations of this type are not seen in fig. 7, they have been studied in detail by other workers /4/.

8 - RUTILE PRECIPITATION IN SAPPHIRE.

Rutile (TiO\(_2\)), which has the spacegroup \( \mathcal{H}(\mu) = P4_2/m nm \), is observed to precipitate in sapphire (α-Al\(_2\)O\(_3\)), which has the spacegroup R3c. The relative orientation of these crystals is found to be (011)/(12\(\overline{1}\)0), (01\(\overline{1}\))/(10\(\overline{1}\)0), (and hence [100]/(0001)]/10/). The intersection symmetry in this case is \( \mathcal{H}(c) = T \), and the fully compensated morphology would be consistent with \( \mathcal{H}(\lambda) \). However, precipitates exhibiting this latter morphology would require unfavourable defects such as disclinations; fig. 5 is a schematic projection along [0001] of such a configuration. It can be seen that disclinations delineate the facet junctions, and the rutile is internally twinned on (011) parallel to the (2\(\overline{1}\)0) c-mirror glide planes in the sapphire matrix. The precipitate morphology actually observed exhibits symmetry lower than that for full compensation, but is higher than intersection symmetry. Needle precipitates, with their long axes parallel to <10\(\overline{1}\)0> are observed, with internal twinning of rutile on (011) forming 'mid-rib' twins. It is interesting to note that the symmetry exhibited by these needles, 2\(\overline{1}\)m, is intermediate between the fully compensated and intersection symmetries. It can be seen that conically joined needles would require the formation of disclinations, but this appears to be unfavourable in the present case. The line defect delineating the intersection of a mid-rib twin with the rutile-sapphire interface must be a dislocation. The \( \mathcal{h} \) of this defect can be obtained by substituting into expression (1) the white c-mirror.
Fig. 6 - Electron micrographs showing NiSi$_2$ precipitates in Si; the orientation relationship is type B, and the large faces of the precipitates are parallel to (111). The included crystal exhibits a morphology consistent with the 'intersection' symmetry, 3m. (a) Dark-field micrograph with beam direction parallel to [111], and (b) bright-field micrograph with beam direction inclined to the platelet. (Courtesy of P. Augustus and Plessey Co.)

Fig. 7 - Electron micrographs showing NiSi$_2$ precipitates in Si matrix; the orientation relationship is type A, and the precipitates have octahedral form with {111} interfaces. The included crystal exhibits a morphology of the 'fully compensated' form consistent with the symmetry of Si. (a) Sequence of micrographs with beam directions parallel to different {111} faces of the precipitate, and (b) with beam direction parallel to [111].
glide operation \( \mathcal{W}(\lambda) = (m(2\overline{1}0), \overline{1}2\overline{2}) \), where \( c \) is a lattice parameter of sapphire, and the black twinning operation \( T(\mu) = (m(011), d) \), where \( d \) represents any rigid body displacement across the twin, which yields \( Q_{ij} = (\mathbb{I}, \mathbb{h}) \), where \( \mathbb{h} = \overline{1}2\overline{2} \cdot d \) (modulo any black or white translation vector).

9. HYDRIDE PRECIPITATION IN TITANIUM.

\( \text{TiH} \) is thought to have the same structure as \( \text{p}-\text{ZrH}_2 \), and its spacegroup is \( \text{P4}_2/\text{mcm} \), and \( \text{Ti} \) is an example of an hcp metal with spacegroup \( \text{P6}_3/\text{mc} \). The relative orientation of these crystals has been observed \cite{12} to be \( [\text{T}10]//[0\overline{1}0\overline{1}0], [\overline{1}10]//[2\overline{2}0\overline{0}] \) (and hence \( [001]//[0001] \)). The intersection symmetry, \( \mathbb{S}(c) \), for such non symmorphic crystals depends on the relative position, \( p \), chosen but will be of low order, e.g. \( \mathbb{S}(c) = m \) for one particular choice. The compensated symmetry will, of course, be consistent with \( \mathbb{S}(\lambda) \), and fig.4 is a schematic view along \( [001] \) for such a configuration, but where the planes indicated within the tetragonal hydride precipitate are \( \{110\} \) planes. The reason for including this example is in order to consider the nature of the line defects delineating the facet junctions. By substitution of the appropriate symmetry operations (i.e. \( \mathcal{W}(\lambda) = (6+\overline{4}, 1/2\overline{2}) \) representing the six-fold screw axis parallel to \( [001] \), and \( \mathcal{W}(\mu) = (4+, 1/2\overline{2}) \) representing the four-fold screw axis parallel to \( [001] \), and where \( c \) and \( c' \) represent \( [0001] \) and \( [001] \) respectively), expression (1) yields \( Q_{ij} = (30+, 1/2(c-c')) \), which is a dispiration (actually, the displacement component will also depend on \( p \)). Thus, the defect includes 30° disclination character, which might be expected to be very unfavourable. The precipitate morphology actually observed is platelets parallel to \( [0\overline{1}0\overline{1}]1/2/ \), which is clearly a lower symmetry than the fully compensated form. However, some of the platelets are found to be joined contiguously, and the formation of the 30° disclination component of the line defect necessary at the facet junction observed has been directly using HREM \cite{12}. In fact, since defects are necessary at both facet junctions in the chevron shaped precipitate, the defect is a dispiration dipole. Thus, the chevron configuration can be regarded as a portion of the fully compensated form shown in fig.4.

CONCLUSIONS

Using arguments based on geometrical symmetry theory, it has been shown that the morphology of an included crystal, bounded by degenerate interfaces, can exhibit symmetry consistent with that of the surrounding crystal. In general, such fully compensated configurations require interfacial line defects delineating facet junctions, and, possibly, the presence of extended defects within the included crystal. Moreover, the possibility that such configurations can arise is independent of the structure and symmetry of the two crystals, and their relative orientation, but the nature of the geometrically necessary defects will depend on these parameters. Morphological forms exhibiting lower symmetries can also exist. For example, included crystals exhibiting intersection symmetry do not require the presence of any defects (except those that might arise as a result of relaxation processes). Other morphological forms, exhibiting intermediate symmetries and requiring only a subset of the defects necessary for the fully compensated form can also exist.

A preliminary analysis of published experimental observations has been presented illustrating included crystal morphologies corresponding to fully compensated, intersection, and intermediate forms. It has been suggested that the formation energy of certain defects, particularly those including disclination character, may be a significant contributing factor leading to morphologies exhibiting lower than the fully compensated symmetry. It has also been pointed out that the total free energy for an inclusion of given volume is not necessarily minimised for the defect free form, because the presence of defects can enhance the area of favourable interfaces.

The conclusions described here for bicrystals are analogous to the situation for single crystals. In the case of nonholosymmetric crystals, external morphologies can be consistent with the spacegroup of the crystal's lattice, rather than that of the crystal, provided the necessary defects are introduced \cite{13}.

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REFERENCES