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Crystallographic classification of special grain boundaries

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Abstract

Object of research: Special grain boundaries in centrosymmetric crystals.

The aim of this work is to classify special grain boundaries in centrosymmetric crystals of all syngonies based on the symmetric properties of plane lattices that are the crystallographic planes of these crystals.

Conclusions: It is shown that the set of geometric parameters identifying special boundaries consists of elements of the symmetry of the plane formed by coinciding atoms that preserve the atomic structure of this plane. Possible misorientations of contacting crystals are found depending on the symmetry of the crystallographic plane for different crystallographic syngonies.

Keywords: Lattice of matching nodes, Interfaces, Crystal, Special grain boundaries

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1. Introduction

Special grain boundaries are flat boundaries exhibiting a biperiodic atomic structure. Unlike general-type grain boundaries that do not have a periodic atomic structure, their energy is relatively low, which leads to their thermodynamic stability with respect to various rearrangements [1–4]. Therefore, despite the discreteness of many geometric parameters of these boundaries, they can occupy a large share in polycrystalline samples [3]. An important property of the boundaries of this class is their relatively simple atomic structure, which simplifies the construction of theoretical models for interpreting various properties and phenomena in polycrystalline samples associated with the presence of grain boundaries in crystals [5–11]. Progress in the field of experimental studies of grain boundaries is largely associated with the development of methods for the purposeful preparation of the grain boundary structures of samples (Grain Boundary Engineering, [12–18]). Studies of grain boundaries in metals were mainly carried out to study their influence on the mechanical characteristics of materials [19]. Similar studies in ionic crystals containing two or more chemical elements were carried out in order to understand the effect of their structure on the domain structure, electronic and ionic electrical conductivity [19], characteristics of the Schottky barrier [20], and solar cells [21]. The study of boundaries and their totality in polycrystalline samples in these aspects is currently relevant.

Methods for calculating possible geometric parameters and atomic structures of special grain boundaries were initially based on representations of lattices of coinciding nodes [22] and were designed for the boundaries of various crystallographic syngonies: cubic [23], tetragonal [24], rhombohedral [25], and hexagonal [26]. In [27, 28], a method for classifying grain boundaries based on the consideration of coordination polyhedra was developed and applied to one-component and ionic crystals of a cubic structure.

In this paper, we propose a single method that allows us to specify possible special boundaries for crystals of any syngony. This method is based on the crystallographic classification of planar periodic structures.

2. Results and discussion

Since the atomic structure of a flat special boundary has a periodic structure, its primitive cell has five possible shapes: a parallelogram with sides of different lengths, a rectangle, a rhombus, a rhombus with an angle of 60°, and a square. Further, various rotations will be considered as symmetry operations of the boundary cell; generalization to the case of reflections from possible planes of symmetry is not difficult.

Crystallographic planes that have cells in the form of a parallelogram can be found in crystals of any crystallographic syngony. These planes form an infinite discrete set on the sphere of directions. Let's call these planes general-type planes. Only such planes are present in the crystals of triclinic syngony. The only non-trivial rotation for such a border is a 180° rotation around the normal. Since this rotation is not a symmetry for the entire crystal, by rotating half of the crystal and bringing the resulting halves into contact, we obtain a 180° torsion boundary. Therefore, all boundaries of the general type in all crystallographic syngonies will be 180° torsion boundaries. Note that if we take into account the presence of other symmetry elements of the crystallographic plane, namely, the reflection from the plane coinciding with this plane, and the inversion center located at the intersection of the diagonals of the parallelogram, then in general, other atomic configurations of the atoms of the grain boundary are obtained. In the first case, the specular boundary is obtained, and in the second case, the inverse boundary is obtained. Moreover, if the crystal as a whole is centrosymmetric, then the inversion transformation does not generate a grain boundary. An example of an inverse boundary is any plane in a polarized ferroelectric that is a 180° inter-domain boundary.

Crystallographic planes with rectangular cells are present in all other syngonies. In monoclinic syngony, they form a discrete one-dimensional set of rotations around *the z-axis*. The symmetry group of a rectangle generated by 180° rotations around the normal and edges of a cell in the crystallographic plane consists of three nontrivial operations that are not elements of crystal symmetry. Therefore, they lead to three different atomic configurations of the intergranular boundary. In the rhombic syngony, there are three

one-dimensional families of boundaries with rectangular cells; in the rhombohedral one, there are similar planes passing through the third-order axis and lying perpendicular to this axis.

Crystallographic planes having rhombic cells are present in crystals of rhombohedral syngony, in particular, in the basic planes of the crystal cell and sublattices perpendicular to the third-order axis. The symmetry group includes 180° rotations around the normal to the rhombus plane and around its diagonals. Therefore, in crystals belonging to the orthorhombic syngony, three atomic configurations are possible at the grain boundaries, which have a rhombic lattice structure of matching atoms.

In tetragonal syngony crystals, the crystallographic planes with rectangular cells are defined by the normals lying in two planes passing through the sides of the base square and the fourth-order *z axis*. The normals to planes with rhombic cells are located in vertical planes passing through the diagonals of the square. In addition, grain boundaries obtained by rotations at angles other than 180° around the fourth-order axis can be realized in crystals of this syngony. The totality of these rotation angles is obtained by considering square sublattices in the (*xy*) plane. Provided that the edge length of the square is taken as one and the origin is located at one of the lattice nodes, the sides of the square sublattices have coordinates (*m*,*n*, 0), where *m*,*n* are positive and negative coprime integers. In particular cases, when $m = 0, n = 1$ and $m = 1, n = 1$, squares are obtained. In a typical case, they generate a coordination octagon, which can be represented as the sum of squares expanded with respect to each other at an angle φ, determined by the relation:

$$\mathrm{tg}(\varphi/2) = m/n, \quad (1)$$

or an additional angle. Turning the upper part of the crystal by this angle and then bringing it into contact generates the special torsion boundary in the z = 0 plane. A three-dimensional lattice of matching nodes appears in the volume of the bicrystal. Any crystallographic plane in this lattice can serve as a basis for constructing a grain boundary. At the same time, the variants of multiplication of atomic structures of the grain boundary, depending on the cell shape, are preserved.

In some special cases, the coordinate polygon may have more than eight vertices. This requires that the distance between atoms, whose positions are defined by different sets $(m_1,n_{1,0})$, $(m_2,n_{2,0})$, be equal. As an example, we consider a coordination dodecagon defined by the vertices of the (3, 4, 0) and (5, 0, 0) types. The two square sublattices defined by these vectors are superposed by a rotation determined by the formula:

$$\cos\varphi = 3/5, \quad (2)$$

or an additional angle.

For crystals of hexagonal syngony, in general, the same regularities are observed as for tetragonal crystals, with the only difference being that instead of a square cell in the base plane, we need to consider a hexagonal one.

In crystals of cubic syngony, a special feature is fulfilled that distinguishes this syngony from the rest, namely, that any crystallographic plane generates a spatial lattice of coinciding atoms, which in general has a monoclinic structure. This conclusion follows from the obvious regularity that the coordinates of the vector product of two vectors with integer coordinates are also integer coordinates. In particular cases, a sieve of matching atoms can have tetragonal and cubic symmetry.

All the regularities for the characteristics of possible grain boundaries arising from the presence of high-order symmetry axes occur in crystals with a cubic syngony. Furthermore, these crystals contain nontrivial planes with square and hexagonal sublattices. As an example, we consider a crystallographic plane with the following basis vectors of the cell: (−1, 2, 2) and (2, −1, 2). The normal to this plane has coordinates (2, 2, −1), so the lattice of matching atoms is a simple cubic one. Rotations of the crystal around the normal leave the lattice invariant in the plane, but change the positions of the atoms in the crystal, since these rotations are not elements of the crystal's symmetry. Thus, these rotations give rise to different atomic configurations at the grain boundary. Other atomic configurations are obtained by performing operations of 180°rotation around the edges of the square and one of its diagonals (1,1,4). The other diagonal (−1, 1, 0) is the second-order axis of the crystal, so rotating around it will not result in a new atomic configuration of the grain boundary.

An example of a hexagonal sublattice in a plane that does not coincide with the cell faces of a crystal with cubic syngony is given by a set of basis vectors (4, 1, 1), (1, 4, 1), (3, –3, 0). It is not difficult to check that these vectors have the same lengths, lie in the same plane, and the angle between them is 60°. The common normal to these vectors has coordinates (–1, 1, 5). Since this normal is not the axis of symmetry of the crystal, rotations around it while preserving any hexagonal sublattice will lead to new atomic configurations in the region of the torsion boundary. The second-order axes that leave the above-mentioned hexagonal structure invariant are defined by the vectors (4, 1, 1), (1, 4, 1), (7, –2, 1), (5, 5, 2), (–2, 7, 1), (1, –1, 0). Rotations around the first five axes, which are not elements of crystal symmetry, will also lead to other atomic configurations at the intergranular boundary. The last axis (1, –1, 0) is the second-order axis of the crystal and therefore will not lead to a new atomic configuration.

3. Conclusion

1. A grain boundary can be constructed on a general-type crystallographic plane in crystals of all syngonies by the 180° rotation of half of the crystal around the normal to this boundary.

2. In crystals with second-order axes, the grain boundaries passing through this axis can have three different atomic configurations.

3. In crystals with high-order symmetry axes, grain boundaries with different misorientation angles and atomic configurations can be present. A lattice of matching nodes appears in the region of contacting crystals.

4. In crystals of cubic syngony, there are crystallographic planes that do not coincide with the basic planes, which contain plane sublattices with high-order symmetry axes. Such planes allow several misorientations of contacting crystals and atomic configurations.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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