SYMMETRY CONSTRAINTS ON THE ORIENTATION DEPENDENCE OF INTERFACIAL PROPERTIES : THE GROUP OF THE WULFF PLOT

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Résumé – Nous présentons le groupe de la représentation de Wulff qui décrit la variation en fonction de l'orientation des propriétés physiques des interfaces, telles que les joints de grains, entre deux cristaux d'orientation spatiale arbitraire. A partir du groupe de la représentation de Wulff, nous obtenons les contraintes de symétrie sur la forme des cristaux croissant dans un environnement cristallin. Des exemples d'autres applications sont aussi donnés.

Abstract – We present the group of the Wulff plot, which describes the orientation dependence of physical properties of interfaces, such as grain boundaries, between two crystals of arbitrary spatial relationship. From the group of the Wulff plot, symmetry constraints upon the forms of crystals grown in crystalline enviroments are derived. Examples of other applications are given.

1. Introduction – It is well-known that crystals growing in isotropic media are constrained to adopt forms compatible with their point symmetries [1]. In this paper we derive symmetry constraints on the orientation dependence of of physical properties of interfaces between crystals, and hence upon the morphologies of crystals grown in crystallographic environments. The case in which the two crystals are of different phases reduces to a restatement of Curie's principle of symmetry [2], which states that the group of symmetries of two or more objects regarded as a whole is the highest common subgroup of the symmetry groups of these objects. However, for grain boundaries, stacking faults and antiphase boundaries, where the two crystals are of the same phase, symmetry operations relating the two crystals can arise which lead to new and unexpected results.

2. Procedure – A concept that has been found useful in interfacial symmetry problems when the two crystals are of the same phase is the dichromatic pattern, or dcp [3, 4]. The dichromatic pattern consists of two infinite crystals interpenetrated and exhibiting the relative misorientation and relative translation that will characterize their spatial relationship at distances beyond the range of the local distortions at the interface. We will denote the rigid body rotation and translation which describe the relationship between the crystals by $(R|\tau)$, using the Seitz notation. In our analysis, we employ the black and white, or Shubnikov, symmetry groups. One crystal is called white and the other black. Symmetry operations of the dcp which relate atoms equivalent in every respect except color are called colored symmetry operations. Operations relating black atoms to black atoms and white atoms to white atoms are termed classical symmetry operations. The structure of the Shubnikov point groups is well-known [5]. They consist of three types. The

first type consists of the 32 classical point groups, containing no colored
operations. In all cases in which the two crystals belong to different
phases, the dcp group belong to this class, as well as some cases where the
two crystals are of the same phase. The second type consists of the 32 grey
groups, which describe structures in which every site is simultaneously black
and white. They are of no interest for our purpose since these correspond to
symmetry groups of superimposed single crystals. The third type consists of a
set of classical elements which themselves form an halving subgroup, and a set
of colored elements. The groups thus have the form

$$M = \{H\} \cup \{(G-H)\}'$$

Brackets denote all the operations of the cosets, and the prime indicates
symmetry operations that are combined with the color change operation, which
is equivalent to interchanging the grains. G is a group from which the black
and white group M is derived and H is a halving subgroup of G. Because
rotations of one crystal by $\pi/4$ and $\pi/6$ about 4 and 6-fold rotation axes
common to both crystals yield colored 8 and 12-fold rotation axes
respectively, G is not restricted to crystallographic point groups. H must,
however, be crystallographic. For all type I Shubnikov groups M = H as there
are no colored operations.

The problem of determining the symmetry of the dcp as a function of the
two crystal symmetries and the imposed rigid body rotation and translation of
one of the crystals with respect to the other is addressed in other
papers (4,6). To create the bicrystal, a mathematical surface having the
shape of the desired interface is introduced into the dcp. Black atoms are
rejected from one side of the surface and white atoms from the other.

We approach the problem of morphological constraints in the following
manner. Consider two crystals B and W meeting at a planar interface of
arbitrary location. The spatial relationship between crystals B and W is
fixed, i.e., the symmetry group M of the dcp is given. We adopt the
convention that the boundary normals point from B to W. Now we wish to solve
for the set of interfaces that are physically equivalent to the first. This
will give us the symmetry group W of the Wulff plot, or the variation of
interfacial energy with crystallographic orientation of the boundary plane and
hence the morphological constraints upon crystalline inclusions. Clearly if
we operate on the entire bicrystal with one of the symmetry operations common
to both crystals and superimposed in the dcp, holding the interface plane
fixed, we will generate an identical interface. These common operations from
the classical subgroup H of M since this subgroup is obtained by a procedure
of taking the intersection of symmetry operations of B and W, taking account
of their relative orientation and location, which may be written as
$H = G_w \cap (R|\tau)G_B(R|\tau)^{-1}$ where G_w and G_B are symmetry groups of the black and
white crystals and $(R|\tau)$ is the operation generating the relative
misorientation and translation of the crystals.

If we instead operate on the bicrystal with one of the colored
operations, i.e., those present in the coset $\{(G-H)\}$, and subsequently invert
the boundary plane normal n, we will have again generated a physically
equivalent interface. Combining these two sets of operations we obtain a
group of symmetry operations that generate equivalent interfaces.
This means that for the type III Shubnikov point groups the set W of symmetry
operations that generate equivalent interfaces is found by

$$W = \{H\} \cup \{(G-H)\} I \qquad (1)$$

where I is the inversion operator.

We can now make use of the well-known group theoretical properties of
cosets. Since H is a halving subgroup of G, its number of cosets is two [5].
Cosets of a given subgroup contain either all elements in common or none.

This makes it simple to divide the various cases we will observe in the
morphological problem into three categories.

Case 1: $\bar{I} \in \{(G-H)\}$. The inversion center is among the colored symmetry elements of the dcp. Thus it cannot be contained in the classical subgroup H. Since the inversion is its own inverse, $E \in \{(G-H)\} \bar{I}$ where E is the identity. Because the two cosets $\{H\}$ and $\{(G-H)\} \bar{I}$ contain the common element E, we know that all their elements are identical. Then:
$$W = \{H\} \cup \{H\} = H \qquad (2)$$
The morphological set W thus reduces, in this case, to the classical subgroup H in spite of the presence of additional symmetries.

Case 2: $\bar{I} \in \{H\}$. Since the inversion is present in $\{H\}$ it cannot be included in $\{(G-H)\}$. Therefore the identity can't be in $\{(G-H)\} \bar{I}$. Since there is one element not shared by both cosets, then no elements can be shared.

All elements, classical and colored, then yield invariances, i.e.,
$$W = G \qquad (3)$$
Again, the set W is a group. Although, in this case, the bicrystal symmetry will be at most H, for the morphological group, W, all operations of the coset $\{(G-H)\}$ are included.

Case 3: $\bar{I} \notin G$. Inversion is present in neither $\{H\}$ nor $\{(G-H)\}$. In this case the morphology is constrained by a group which will be given by equation (1) and which is not contained in the dcp symmetry. That this group will be of the same order as G is evident from the fact that its halving subgroup is unchanged.
The dcp group $M = \{H\} \cup \{(G-H)\}'$ has the following properties:
1) $H_i \cdot H_j \in \{H\}$, 2) $(G-H)_i \cdot (G-H)_j \in \{H\}$, and 3) $(G-H)_i \cdot H_j \in \{(G-H)\}$.
Here $(G-H)_i$ and H_i are arbitrary colored or classical operations of the group respectively. Since the inversion commutes with all point symmetry operations and is its own inverse, the new group set W will be an isomorphic to the original group G. In all four cases the set W has been found to be a group.
Table 1 gives the morphological group W both for the 58 type III crystallographic black and white point groups, and for the additional groups containing colored 8 and 12-fold rotation axes. It is interesting to note from examination of Table I, that some of the crystallographic point groups never represent type III groups of the Wulff plot symmetry. These are point groups $\bar{1}$, $\bar{3}$ and m3.

3. Discussion – The point group M of a dcp is fully determinable from the relative orientation and translation of two crystals. The group of symmetry operations that generate equivalent orientations of interfaces between these two crystals have been shown to be simply derived from M. When M is either a type I Shubnikov group or a type III case 1, in which the inversion is one of the colored operations of M, those interface properties which are a function of its crystallographic orientation must conform to the classical subgroup H of M, which is M itself for the type I. These two cases are equivalent to Curie's principle of symmetry.
For the other two cases of Shubnikov type III groups, the morphological group W contains H as a halving subgroup. If inversion is present in H, W becomes G, which is simply the group of the dcp disregarding color. If inversion is not present in G, W is a new group isomorphic with G.
As an example of the application of our procedure consider antiphase boundaries in Fe_3Al, which has the DO_3 structure, with space group Fm3m [7]. There exist two different APB's in this system. The dcp's for both interfaces are generated by pure translations, i.e., $(R|\tau) = (E|\tau)$. The translations are, in the crystal coordinate system, 1/2[100] and 1/4[111]. Fig. 1 illustrates the dcp structures resulting from these translations. For this example the determination of the symmetry of the resulting dcp's is simple enough to be accomplished by direct inspection. A relative shift of two interpenetrated lattices having space group Fm3m of $\tau = 1/2$ [100] yields the

NaCl structure. A shift of 1/4[111] gives ZnS. Thus the dcp resulting from the 1/2[100] translation has m3m for its morphological group. The 1/4[111] APB, on the other hand, has as its space group Fd'3m and colored point group m'3m. This group falls into case 1, and its morphological group W becomes its classical subgroup, i.e., $\bar{4}$3m. This means that for the 1/2(100) APB a plot of interfacial scalar properties can be condensed into a spherical triangle with corners at (001), (101) and (111). For the 1/4(111) APB however, a larger triange (001), (1$\bar{1}$1) and (111) is required because (hkl) and ($\bar{h}k\bar{l}$) are no longer equivalent by symmetry.

In examining stacking faults and stacking fault inclusions we found that the 1/4[111] shift in fcc crystals is at a symmetry dictated extremum in energy. As with the Fe$_3$Al example this has the morphological group $\bar{4}$3m. We have found that 1/4[111] shifts lead to a simpler description of the morphology and energy of stacking fault tetrahedra.

The idealized 90° antiphase boundary in CuAu leads to a dcp with black and white point group symmetry 4'/mmm'. The classical subgroup is only mmm. This is as expected. The 4-fold axes in the two domain are at right angles. No 4-fold axis survives the intersection. The 4' originates from a 90° rotation and color change about a 2-fold axis. The symmetry of W is 4/mmm, which includes a 4-fold axis that was present in neither domain.

Finally, it is worth pointing out that while operations in W yield equivalent interfaces, they are generally not symmetry operations of bicrystals. The shape of an interface imposes a symmetry constraint. A bicrystal consisting of a crystalline inclusion within a matrix crystal with a shape that conforms to the group W has a symmetry belonging only to H. An operation in (W-H) will superimpose interfaces with equivalent properties but will convert the matrix into the orientation of the inclusion and vice versa.

In conclusion, the procedure developed in the previous section allows one to make rigorous statements about morphologies permitted to crystals growing in crystalline environments. The crystallographic form adopted must include the point symmetry operations of the group W as must a plot of interfacial scalar properties as a function of interfacial orientation. Definitive statements may now be made about allowable morphologies in phenomena such as precipitation and eutectic solidification.

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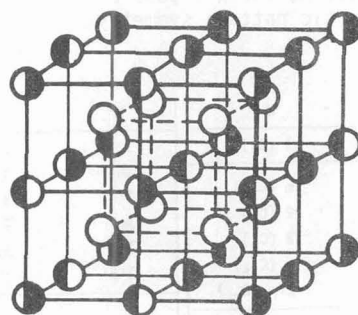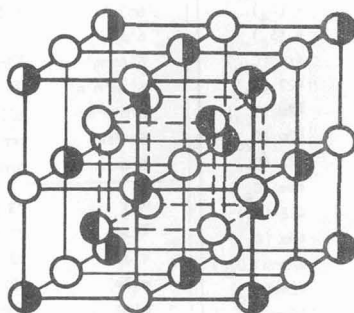
Fig. 1 - a) Dichromatic pattern for the 1/2[100] APB in Fe₃Al. Its colored space group is F_m3m, with classical point symmetry m3m. b) Dichromatic pattern for the 1/4[111] APB in Fe₃Al. Its colored space group is Fd'3m, with classical point symmetry 43m.

Table 1: The group of the Wulff plot, W, and its classical subgroup, H, for all possible groups, M, desribing dichromatic pattern symmetry.

M	H	W
$1'$	1 (C_1)	1 (C_1)
$2'$	1 (C_1)	m (C_{1h})
m'	1 (C_1)	2 (C_2)
$2/m'$	2 (C_2)	2 (C_2)
$2'/m$	m (C_{1h})	m (C_{1h})
$2'/m'$	$\bar{1}$ (C_1)	$2/m$ (C_{2h})
$2'2'2$	2 (C_2)	$mm2$ (C_{2v})
$m'm'2$	2 (C_2)	222 (D_2)
$m'm2'$	m (C_{1h})	$mm2$ (C_{2v})
$m'm'm$	$2/m$ (C_{2h})	mmm (D_{2h})
$m'm'm'$	222 (D_2)	222 (D_2)
mmm'	$mm2$ (C_{2v})	$mm2$ (C_{2v})
$4'$	2 (C_2)	$\bar{4}$ (S_4)
$\bar{4}'$	2 (C_2)	4 (C_4)
$42'2'$	4 (C_4)	$4mm$ (C_{4v})
$4'22'$	222 (D_2)	$\bar{4}2m$ (D_{2d})
$4/m'$	4 (C_4)	4 (C_4)
$4'/m'$	$\bar{4}$ (S_4)	$\bar{4}$ (S_4)
$4'/m$	$2/m$ (C_{2h})	$4/m$ (C_{4h})
$4m'm'$	4 (C_4)	422 (D_4)
$4'mm'$	$mm2$ (C_{2v})	$\bar{4}2m$ (D_{2d})
$\bar{4}2'm'$	$\bar{4}$ (S_4)	$\bar{4}2m$ (D_{2d})
$\bar{4}'2m'$	222 (D_2)	422 (D_4)
$\bar{4}'m2'$	$mm2$ (C_{2v})	$4mm$ (C_{4v})
$4/m'm'm'$	422 (D_4)	422 (D_4)
$4/m'mm$	$4mm$ (C_{4v})	$4mm$ (C_{4v})
$4'/mmm'$	mmm (D_{2h})	$4/mmm$ (D_{4h})
$4'/m'm'm$	$\bar{4}2m$ (D_{2d})	$\bar{4}2m$ (D_{2d})
$4/mm'm'$	$4/m$ (C_{4h})	$4/mmm$ (D_{4h})
$8'$	4 (C_4)	$\bar{8}$ (S_8)
$\bar{8}'$	4 (C_4)	8 (C_8)
$8'/m$	$4/m$ (C_{4h})	$8/m$ (C_{8h})
$8'mm'$	$4mm$ (C_{4v})	$\bar{8}2m$ (D_{4d})
$\bar{8}'m'2$	422 (D_4)	822 (D_8)
$\bar{8}'m2'$	$4mm$ (C_{4v})	$8mm$ (C_{8v})
$8'22'$	422 (D_4)	$\bar{8}2m$ (D_{4d})
$8'/mmm'$	$4/mmm$ (D_{4h})	$8/mmm$ (D_{8h})

M	H	W
$32'$	3 (C_3)	$3m$ (C_{3v})
$3m'$	3 (C_3)	32 (D_3)
$\bar{3}'$	3 (C_3)	3 (C_3)
$\bar{3}m'$	$\bar{3}$ (C_{3i})	$\bar{3}m$ (D_{3d})
$\bar{3}'m$	$3m$ (C_{3v})	$3m$ (C_{3v})
$\bar{3}'m'$	32 (D_3)	32 (D_3)
$\bar{6}'$	3 (C_3)	6 (C_6)
$\bar{6}m'2'$	$\bar{6}$ (C_{3h})	$\bar{6}2m$ (D_{3h})
$\bar{6}'m2'$	$3m$ (C_{3v})	$6mm$ (C_{6v})
$\bar{6}'m'2$	32 (D_3)	622 (D_6)
$6'$	3 (C_3)	$\bar{6}$ (C_{3h})
$62'2'$	6 (C_6)	$6mm$ (C_{6v})
$6'2'2$	32 (D_3)	$\bar{6}2m$ (D_{3h})
$6/m'$	6 (C_6)	6 (C_6)
$6'/m'$	$\bar{3}$ (C_{3i})	$6/m$ (C_{6h})
$6'/m$	$\bar{6}$ (C_{3h})	$\bar{6}$ (C_{3h})
$6m'm'$	6 (C_6)	622 (D_6)
$6'm'm$	$3m$ (C_{3v})	$\bar{6}2m$ (D_{3h})
$6'/mmm'$	$\bar{6}2m$ (D_{3h})	$\bar{6}2m$ (D_{3h})
$6'/m'm'm$	$\bar{3}m$ (D_{3d})	$6/mmm$ (D_{6h})
$6/m'm'm'$	622 (D_6)	622 (D_6)
$6/m'mm$	$6mm$ (C_{6v})	$6mm$ (C_{6v})
$6/mm'm'$	$6/m$ (C_{6h})	$6/mmm$ (D_{6h})
$m'3$	23 (T)	23 (T)
$\bar{4}'3m'$	23 (T)	432 (O)
$4'32'$	23 (T)	$\bar{4}3m$ (T_d)
$m'3m'$	432 (O)	432 (O)
$m'3m$	$\bar{4}3m$ (T_d)	$\bar{4}3m$ (T_d)
$m3m'$	$m3$ (T_h)	$m3m$ (O_h)
$12'$	6 (C_6)	$\overline{12}$ (S_{12})
$\overline{12}'$	6 (C_6)	12 (C_{12})
$12'/m$	$6/m$ (C_{6h})	$12/m$ (C_{12h})
$12'mm'$	$6mm$ (C_{6v})	$\overline{12}2m$ (D_{6d})
$\overline{12}'m2$	622 (D_6)	1222 (D_{12})
$\overline{12}'m2'$	$6mm$ (C_{6v})	$12mm$ (C_{12v})
$12'22'$	622 (D_6)	$\overline{12}2m$ (D_{6d})
$12'/mmm'$	$6/mmm$ (D_{6h})	$12/mmm$ (D_{12h})

DISCUSSION

R.C. POND :   I would like to comment on the elegance of your work, and to men-
tion that Pond and Vlachavas have carried out an investigation of
dichromatic symmetry (communicated to Phil. Trans. Roy. Soc.)
using a different methodology. We have used the theory of the
symmetry of composite objects, and have identified the nature of
crystallographic variants produced as a result of each stage of
dissymmetrisation (modifications which reduce symmetry) starting
from an initial configuration which exhibits the highest possible
symmetry for the case in question.
This methodology emphasizes the differences which can arise bet-
ween interfacial structures in materials with different symmetries.
For example, quite distinct consequences arise as a result of
dissymetrisation due to the existence of non-holosymmetric as com-
pared to non-symmorphic symmetry. In the latter case, for example
[100] rotations in diamond-structure materials, modifications to the
set of dsc (structure-conserving) displacements arise .