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Some Problems on Interfaces, in Homogeneous Materials, Related to Transformation or Deformation

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Two-dimensional defects in homogeneous materials are the subjects of many investigations. Many properties are related to the nature of the surface, to the grain (or domain, or variant) structure, and to the presence of stacking faults, shear planes etc. Some remarks on the nature of interfaces from a geometric and eventually chemical point of view are reported.

I. Interface Characterization

In this paper I do not consider the shape and position of the interface itself but only emphasize the geometrical relation between crystals separated by an interface, which is one important characteristic of the interface.

I.1. The Interface Relation

Two equivalent points r_1 and r_2 in two crystals I and II separated by an interface are related by (Seitz notation)

$$(R|\boldsymbol{\tau})\mathbf{r}_1 = \mathbf{r}_2 = R\mathbf{r}_1 + \boldsymbol{\tau},$$

where R is the point operation leaving the chosen origin unchanged and $\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates in each crystal of points where the potential energy, the electron density, and any other scalar quantities are the same.

$$V_{\mathrm{I}}(\mathbf{r}_1) = V_{\mathrm{II}}(\mathbf{r}_2).$$

I.2. Coset of the Interface

Let us call $(h_i|\mathbf{t}_i)$ a symmetry operation of crystal I (including translations $(E|\mathbf{T}_n)$, where E is the identity and $\mathbf{T}_n$ is a primitive translation). $(h_i|\mathbf{t}_i)$ is defined in the same way as $(R|\boldsymbol{\tau})$. The interface operation $(R|\boldsymbol{\tau})$ is strictly equivalent to any other operation of the coset

$$(R|\boldsymbol{\tau})(h_i|\mathbf{t}_i) = \{(R|\boldsymbol{\tau})\}.$$

I.3. What to Call an Interface

The name of an interface must be chosen arbitrarily. If there is a (nonprimitive) translation $(E|\boldsymbol{\tau}_0)$ in the coset $\{(R|\boldsymbol{\tau})\}$ the interface is generally called a stacking fault, an antiphase boundary or a shear plane.

For describing grain boundaries, it is common to choose rotations around crystallographic directions. Even in this case an arbitrary choice is needed. For example, a rotation of 12° around a fourfold axis is the same as a rotation of $90+12=102°$ around the same fourfold axis.

Some grain boundaries cannot be described by rotations, and one needs a mirror or a center, as in inversion boundaries of lithium ferrospinel, $\mathrm{LiFe_5O_8}$.

I.4. Location of the Boundary Operation and Reducibility of the Associated Translation

If the operation $(R|\boldsymbol{\tau})$ is referred to an origin O' other than the previous origin, $(R|\boldsymbol{\tau})$ is changed into $(R|\boldsymbol{\tau}+R\mathbf{OO'}-\mathbf{OO'})$.

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The point operation is then moved to another origin O', and the translation is increased by $R\mathbf{OO}'-\mathbf{OO}'$. A judicious choice of the origin may lead to a pure point operation if

$$(R-E)\mathbf{OO}'+\boldsymbol{\tau}=0.$$

It is easily seen that this is always impossible for translations because $(R-E)\mathbf{OO}'=0$. On the contrary the inversion is essentially a pure operation always reducible.

In the case of rotations reducibility is possible if τ is perpendicular to the rotation axis (and for mirrors if the translation is perpendicular to the mirror). Actually a more careful inspection of the problem shows that the origin O_n' giving pure operations is given by the equation

$$(R-E)\mathbf{OO}'+\boldsymbol{\tau}+R\mathbf{T}_n=0$$

or the equivalent equation

$$(R-E\mathbf{OO}'-R^{-1}\boldsymbol{\tau}+\mathbf{T}_n=0.$$

There are solutions if the component of the translation $R\mathbf{T}_n$ of the second lattice along the rotation axis is the same as the component of τ along the same axis.

A similar approach is used for mirrors. It is thus possible to study such equations for every operation of the coset $\{(R|\boldsymbol{\tau})\}$ and eventually to find a complicated set of such points.

We have followed the same reasoning, but in a more general way, as that followed by Bollman when he defined his O-lattice.

Some misunderstanding may arise from the confusion between the plane of the boundary and the operation of the boundary. Donnay *et al.* (*1*), in an excellent paper on the twin boundary in pyrite, state that "on atomic scale the twin operation is a glide reflexion with glide component equal to $(\mathbf{a}_1+\mathbf{a}_2)/2$ in a $(1\bar{1}0)$ plane passing through point 0, $\frac{1}{2}$,.0." This is possibly true, but, if so, the operation is a pure mirror passing through the origin.

The model of the twin is a plane interface parallel to the mirror, and *if one chooses to locate the operation on the plane interface* the mirror is a glide mirror, but, of course, the twin crystals are related only by a pure mirror.

I.5. Determination of the Nature of the Interface

It is possible to find extinction conditions of the interface in TEM. They have been given elsewhere and are valid in multidiffraction conditions (zero layer approximation). The set of g vectors of the diffracted pattern must follow the relations

$$Rh_i\mathbf{g}=\mathbf{g}$$

and

$$\mathbf{g}(R\mathbf{t}_i+\boldsymbol{\tau})=n.$$

An example of a twin of Yb_2O_3 is given here, and the location of the mirror is such that the Yb ions are at the nodes of an invariant sublattice of the twin and oxygen-12 and are also invariant. High-resolution images also lead to the determination of the interface operation, but the boundary conditions may give an "artefact" in the image, and we have suggested for the location of the surface boundary by such images the use of a set of g beams satisfying the previous extinction conditions—at least the first one, $Rh_i\,\mathbf{g}=\mathbf{g}$.

II. Twins

Following an earlier idea of Georges Friedel, we call twins interfaces conserving one or several sublattices. Let us call R the invariant sublattice, whose space group is G_R, with G_0 the group of the structure. The intersection of G_R and G_0 is a group $G_I = G_R \cap G_0$ whose elements leave both R and the structure invariant.

II.1. Numbering of Interfaces

The symmetry operations leaving R invariant, but not the structure, are the twin operations (leaving R invariant) we attempt to number. That number is the index p of G_I in G_R.

There are equivalent twins leaving the k sublattices equivalent to R invariant. This number k is the index of G_I into G_0. Thus the number of twins leaving an R sublattice invariant or their equivalent is

$$n \leqslant k(p-1),$$

where n is equal to $k(p-1)$ if each twin leaves only one R lattice unchanged. (A more detailed study shall be published.) This is the number of twins adjacent to a given variant. The number of variants in the material is not infinite if there is a common supergroup G of G_0 and G_R. This is always the case for R sublattices whose nodes are occupied by the entire Wyckoff family of the structure.

II.2. Twin Interface Operations and Mechanism of Twinning

If for simplicity one examines a $\{10\bar{1}2\}$ twin in hexagonal metals in a case with a c/a ratio equal to $3^{1/2}$, it is possible to find an atomic model describing the movement of atoms without shear. The relative movement of atoms consists in a permutation of the distances from an atom of a pair of nearest and next-nearest neighbors.

It is possible to choose two types of coincidence lattice sites: occupied sites or octahedral interstices. The movements of atoms are slightly different in the two hypotheses. [A detailed description of these and other twins will soon be published by Le Lann and Dubertret (*8*).]

It is interesting to note that in the first case, the mirrors' planes are not equivalent: If $(10\bar{1}\bar{2})$ is a pure mirror $(10\bar{1}2)$ is a glide mirror. In the second case, however, the $10\bar{1}2$ and $10\bar{1}\bar{2}$ planes can be pure mirrors simultaneously. These situations may be distinguished experimentally.

III. Ordering Materials

If the space group H of the ordered phase is a subgroup of the disordered group G_0 it is possible to classify and to number the interfaces and the variants.

One decomposes group G_0 into cosets of group H referred to the first chosen variant.

$$G_0 = H + g_1H + g_2H_2 \cdots + g_{n-1}H,$$

where g_1 is one operation $(R|\boldsymbol{\tau})$ and H is the group of operators $(h_i|\mathbf{t}_i)$ modulo the unit cell. The index n of H in G_0 is the number of variants. In some cases the numbering is easy (4 variants in $AuCu_3$; 8 in $LiFe_5O_8$), whereas in other cases it is more difficult (64 variants in V_8C_7; 84 variants in Au_5Mn_2.

III.1. Equivalent Boundaries

Two variants V_2 and V_3 deduced from each other by a symmetry operation $(h_i|\mathbf{t}_i)$ of a variant V_1 are separated from this variant by equivalent interfaces. It is mathematically easy to see that in this case the cosets of the boundaries V_1/V_2 and V_1/V_3, say g_2H and g_3H, are conjugated by an operation $(h_i|\mathbf{t}_i)$ of V_1.

Generally it is easy to classify the boundaries: In $LiFe_5O_8$ there are two families, 12 antiphase boundaries, and 16 inversion boundaries. Sometimes one must classify the antiphase boundaries whose vectors are not equivalent. In vanadium carbide there are vectors which, like the antiphase vectors $\frac{1}{2}\langle 110\rangle$ of ordered $L1_2$ structures ($AuCu_3$ Ni_3Fe), are not related by the rotations of the cube.

A complete analysis of the boundaries requires a number of diffraction experiments, which can be carried out by group theory considerations. If k is the number of variants whose space groups are deduced from each other by identity, translation, or inversion, n is the total number of variants ($n = pk$). The number N of distinguishable extinction conditions (in a zero layer approximation) is given by

$$N = p(n-1) - \tfrac{1}{2}(p-1)N.$$

If all variants are inversion or translation related $(p-1)$ as in the case of $AuCu_3$ or $LiFe_5O_8$, there are $n-1$ extinction conditions.

III.3. Coarsening of Domains and Nonstoichiometry

It is commonly thought that domain coarsening follows quite well the law $D^2 = D_0^2 + kt$ of the evolution of mean thickness D of domains as a function of time t. In permalloy systems, Ni_3Fe, the results of Smallman confirm this law, as did those of Calvayrac previously. But this result is due only to the way in which these authors measured the sizes of the domains. Carefully studying the profile of the superstructure X-ray diffraction line 100, Bley *et al.* (*9, 10*) found that the law was

$$D^n = A + kt.$$

The exponent n varies with temperature.

This equation shows that the phenomenon of domain coarsening is not a simple thermally activated phenomenon. As in grain coarsening the variation of the composition near the boundary and the dragging of these "impurities" are surely responsible for this deviation from the law in D^2.

In small-domain materials one has to take into account the effect of boundaries on stoichiometry, "equilibrium" properties, and thermodynamic quantities.

References

1. G. Donnay, J. D. H. Donnay, and S. Iijima, *Acta Crystallogr.* **33**, 622 (1977).

2. D. Gratias, M. Guymont, R. Portier, and M. Fayard, *Phil. Mag.* **35**, 1199 (1977).

3. R. Portier, D. Gratias, and M. Fayard, *Phil. Mag.* **36**, 421 (1977).

4. G. van Tendeloo, R. Wolf, and S. Amelinckx, *Phys. Status Solidi A* **40**, 531 (1977).

5. M. Guymont, D. Gratias, R. Portier, and M. Fayard, *Phys. Status Solidi A* **38**, 629 (1976).

6. W. Bollmann, "Crystal Defects and Crystalline Interfaces," Springer-Verlag, Berlin (1970).

7. M. Fayard, D. Gratias, R. Portier, and M. Guymont, *in* "Proceedings, 50th Anniversary of the Discovery of Electron Diffraction," London Institute of Physics.

8. A Le Lann and A. Dubertret, to be published.

9. F. Bley and M. Fayard, *Acta Met.* **34**, 575 (1976).

10. H. Ferjani and F. Bley, to be published.