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Twin Domains and Antiphase Domains

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Displacive phase transitions and phase transitions of the type disorder–order usually result in symmetry changes such that the space groups of both structures are related as group and subgroup. The subgroups of a space group always belong to one of the following three types: they have either the same primitive cell as the original space group (they are *translationengleich*), or they belong to the same crystal class (*klassengleich*), or they are general (*allgemein*), *i.e.* they do not belong to either one of the previous categories exclusively and thus have lost translations as well as other symmetry operations with respect to their higher-symmetry (parent) space group. Twin domains are expected whenever the derived structure belongs to a lower-symmetry crystal class. Antiphase domains are possible whenever the derived structure has lost translational symmetry operations. The usefulness of these considerations is demonstrated and discussed for several materials with derivative structures.

Introduction

Derivative crystal structures can be defined as structures which are derived from a parent (=basic) structure by the suppression of one or more sets of symmetry operations of the space group of the parent structure (Buerger, 1947). Usually the parent structure is also a high-temperature form of the derived structure. The phase transition from the high-temperature structure to the low-temperature structure results in the formation of domains. Two fundamentally different kinds of domains can be distinguished: twin domains and antiphase domains. The axis system of twin domains ('twins') are at least partially nonparallel or antiparallel. Antiphase domains have parallel axis systems.‡

From a kinetics point of view two kinds of derivative crystal structures can be distinguished: (1) those which derive from the higher-symmetry 'disordered' (=parent) structure by an ordering process (a well known example is the disorder–order transition in Cu_3Au); and (2) those which derive from the higher-symmetry structure by small atomic displacements (*e.g.* the displacive phase transitions in $BaTiO_3$). Empirically it is known that antiphase domains occur frequently in alloy structures derived by an ordering process, whereas twin domains are usually observed in structures derived by a displacive phase transition. From a group-theory point of view, however, the distinction between order–disorder and displacive phase transitions is not relevant. Recently antiphase domains were also observed in β-$Gd_2(MoO_4)_3$ (Barkley & Jeitschko, 1973) which has a displacive phase transition. This has led us to examine the subject (Jeitschko & Wondratschek, 1974) in the light of earlier group-theory considerations (Hermann, 1929; Neubüser & Wondratschek, 1966). In the present paper we give a full account of that study. The derivation of twin and antiphase domains in derivative structures from group-theory considerations was treated recently also by Tendeloo & Amelinckx (1974). Our approach is different and perhaps more accessible from a geometric point of view.

Prediction of twin and antiphase domains from space group relationships

In accordance with the common usage of the terms we define a crystal to be made up of *twin domains* if they transform into each other by a point symmetry operation which does not belong to their (common) crystal class. *Antiphase domains* transform into each other by a translational operation which does not belong to the space group of the domains, but which is present in their common parent space group. A third kind of domains can be defined as *general domains*. They transform into each other neither by a point symmetry operation (alone), nor by a translational operation (alone), but a combination of the two (Fig. 1). These

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‡ The term 'antiphase domain' seems to be generally accepted now, although strictly speaking it applies only for domains with doubled translation periods. The somewhat clumsy term 'out-of-step domain' is more appropriate for domains with translation periods of higher multiplicity. For the early literature on superstructures in alloy phases and the concept of antiphase domains the reviews by Nix & Shockley (1938) and Lipson (1950) may be consulted.

latter domains will in many respects (for instance in their optical behaviour under polarized light) behave like their corresponding twin domains and may therefore be called *general twin domains*.

According to Hermann (1929) the subgroup *R* of a space group *S* belongs always to one of the following three types: (*a*) *R* has the same (primitive) cell as *S* (*translationengleich**) but the crystal class of *R* is of lower symmetry than that of *S*; or (*b*) the crystal class of *R* and *S* is the same (*klassengleich*) but *R* has lost translational symmetry operations, and thus the primitive cell of *R* is larger than the primitive cell of *S*; or (*c*) *R* is general (*allgemein*), *i.e.* *R* is neither translationengleich nor klassengleich and thus when compared with *S*, has lost translational operations as well as crystal class operations. Hermann's theorem (Hermann, 1929) states that for every subgroup *R* of a space group *S* there is a space group *Z* which contains *R* as a klassengleiche subgroup and at the same time is also a translationengleiche subgroup of *S*: $S \geq Z \geq R$. Therefore we can limit our considerations to the first two categories and their subsequent combinations. A further discussion of space group relationships is given by Neubüser & Wondratschek (1966) who also prepared tables† of maximal subgroups of the space-groups.

We are now prepared to predict the possible occurrence of twin and antiphase domains in materials with derivative structures as long as the space group of the derived structure is a subgroup of the space group of the parent structure. Only twins are expected whenever the space group of the derived structure is a translationengleiche subgroup of the space group of the parent structure. Only antiphase domains can occur in the derived structure if its space group is a klassengleiche subgroup of the space group of the parent structure. Twins *and* antiphase domains are possible whenever the space group of the derived structure is a general (allgemeine) subgroup of the space group of the parent structure.

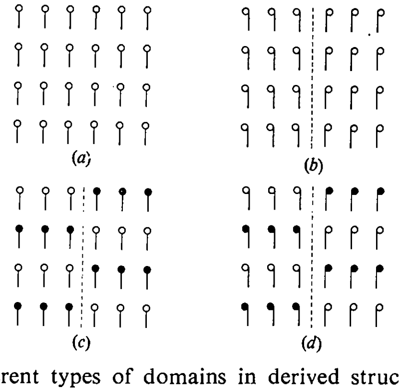

Fig. 1. Different types of domains in derived structures; (*a*) parent structure, plane group *pm*, (*b*) twin domains, the single domain has symmetry *p*1, (*c*) antiphase domains, the symmetry of a single domain is *pm* with $a'=2a$, (*d*) domains which are neither twin nor antiphase domains but a combination of both; symmetry of a single domain *p*1 with $a'=2a$.

Examples

A few examples are discussed here to illustrate the usefulness of these considerations. High quartz has space group $P6_222$-D_6^4 and transforms on cooling to low quartz with space group $P3_221$-D_3^6 (Young & Post, 1962; Smith & Alexander, 1963; Zachariasen & Plettinger, 1965). $P3_221$ is a maximal translationengleiche subgroup of $P6_222$ and therefore only twin domains – but not antiphase domains – are expected in low quartz. The twin domains are the well known Dauphiné twins.

Cu_3Au is a classic example for antiphase domains (for references see Barrett, 1951; Pearson, 1958). At high temperature the atoms occupy randomly the positions of an f.c.c. structure. At low temperatures the atoms order with Au at the origin and Cu at the face centres of the cubic cell. The transformation is from $Fm3m$-O_h^5 to $Pm3m$-O_h^1 and therefore klassengleich. Therefore antiphase domains are expected in the low-temperature form, but twin domains are not possible.

β-$Gd_2(MoO_4)_3$ is tetragonal ($a_t \simeq 7$, $c_t \simeq 11$ Å) at high temperature and orthorhombic ($a \simeq b \simeq a_t\sqrt{2}$, $c \simeq c_t$) at room temperature (Prewitt, 1970; Jeitschko, 1972). The group–subgroup relationship is of the general type where $Cmm2$-C_{2v}^{11} is a maximal translationengleiche subgroup of $P\bar{4}2_1m$-D_{2d}^3 and also a minimal klassengleiche supergroup of $Pba2$-C_{2v}^8:

$$\begin{array}{ll} P\bar{4}2_1m & \\ \downarrow & \text{translationengleich} \rightarrow \text{twin domains} \\ Cmm2 & \\ \downarrow & \text{klassengleich} \rightarrow \text{antiphase domains.} \\ Pba2 & \end{array}$$

Twin and antiphase domains have been observed in the ferroelastic–ferroelectric form of β-$Gd_2(MoO_4)_3$ (Barkley & Jeitschko, 1973; Bohm & Kürsten, 1973; Capelle & Malgrange, 1973; Meleshina, Indenbom, Bagdasarov & Polkhovskaya, 1973; Yamamoto, Yagi & Honjo, 1974). As discussed above, general domains could also occur. Actually their existence must be inferred from the observation (see for instance Barkley & Jeitschko, 1973) that several antiphase domains end at the same ferroelastic–ferroelectric domain wall. A detailed analysis by Janovec (1975) shows that in this case there is no difference between twin domains and general twin domains.

$BaTiO_3$ has a displacive transition at −90°C from $R3m$-C_{3v}^5 ($a \simeq 4{\cdot}0$ Å, $\alpha \simeq 90°$) to $Amm2$-C_{2v}^{14} ($a \simeq 4{\cdot}0$,

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* Hermann designated space groups which have the same primitive cell as *zellengleich*. Since this term is somewhat misleading (for instance space groups *Fm*3*m* and *Pm*3*m* are not zellengleich but klassengleich), we use the term *translationengleich* instead.

† These tables will be published in the new edition of the *International Tables for Crystallography*.

$b \simeq c \simeq 5{\cdot}7$ Å) (Landolt–Börnstein, 1969). Neither space group is a subgroup of the other, however, both are subgroups of $Pm3m\text{-}O_h^1$ which is also the space group of $BaTiO_3$ at high temperature. Thus the relevant group–subgroup relationships are $Pm3m \to R3m$ and $Pm3m \to Amm2$. Both, $R3m$ and $Amm2$ are translationengleiche (though not maximal) subgroups of $Pm3m$ and therefore only twin domains and no antiphase domains are allowed in the $R3m$ and $Amm2$ forms of $BaTiO_3$.

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Analytic Approximations for the Incoherent X-ray and Electron Intensities of Light Atoms and Ions

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It has been found that the incoherent scattered X-ray and electron intensities of light atoms, with 2 to 18 electrons, and of light ions, with 2 to 28 electrons, can be accurately approximated by an analytical formula containing six parameters.

The incoherent intensities of the first 36 atoms calculated by Tavard, Nicolas & Rouault (1967) have been fitted analytically by Hajdu (1971, 1972), those of the atoms of higher atomic numbers (from Ca to Am) were approximated by Pálinkás (1973) with the numerical values of Cromer (1967, 1969).

In these works, the validity of the approximations had been tested in the scattering-variable range available for X-ray diffraction, $0 \le s = \sin\theta/\lambda \le 1{\cdot}5$ Å^{-1}.

In the present paper, a new analytical expression with six parameters is proposed for similar purposes. Its applicability is demonstrated in two somewhat different domains:

(1) for light atoms of atomic numbers 2 to 18 over a wide range of the scattering variable: $0 \le s \le 4{\cdot}0$ Å^{-1},

(2) for all the ions ($2 < Z \le 30$) for which numerical incoherent-intensity tables were available. The scattering-variable range of these published tables extends to $s = 1{\cdot}1$ Å^{-1}, so the fit could not be checked beyond this limit in the case of the ions.

We endeavoured to find an approximating formula with good analytic behaviour. By the use of such a function, physical quantities determined by the incoherent scattering function, *e.g.* the exchange energy, and the contribution to the electron–electron correlation function (Bartell & Gavin, 1964), can also be expressed analytically.

We have found that an expression meeting these conditions and yielding a good approximation can be composed of terms similar to the function describing