Twinning on the Unit Cell Level as a Structure-Building Operation in the Solid State

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Introduction

It is well known that a great number of structures are based on closest packing of atoms, cubic (*ccp*), hexagonal (*hcp*) or mixed, with interstices in the form of octahedra or tetrahedra occupied in various ways. Topological distortions (*1*), crystallographic slip (*CS*)[1] (*2*), swinging *CS* planes (*3*), rotation (*4*, *5*) and the stereochemical effect of the lone pair (*6*) simply relate such structures to many others.

[1] While the *CS* process called "crystallographic shear" may result in a macroscopic shear of the crystal, at the unit cell level the lattice is invariant and the process is actually one of *slip*. On the other hand, in topological distortion for example, the process *is* shear, involving lattice deformation, even at the unit cell level. It therefore seems necessary to change the significance of the term *CS* from crystallographic shear to crystallographic slip.

Another equally useful method for deriving a great number of structures from a few parent ones is regular, polysynthetic twinning on the unit cell level. This is obtained in the same way as macroscopic twinning, with the same definitions of twin plane and twin axis. Unit cell twinning simply means that the periodicity of the twin planes determines the size of the unit cell.

Unit Cell Twinning and *hcp*

We start with *hcp*, and choose the (11$\bar{2}$0) projection shown in Fig. 1, with the close-packed layers perpendicular to the plane of the paper. This kind of projection has been described in some detail earlier (*7*), and is useful for relating and depicting many structures. In Fig. 1, twinning is regularly repeated on (1$\bar{1}$02), producing a
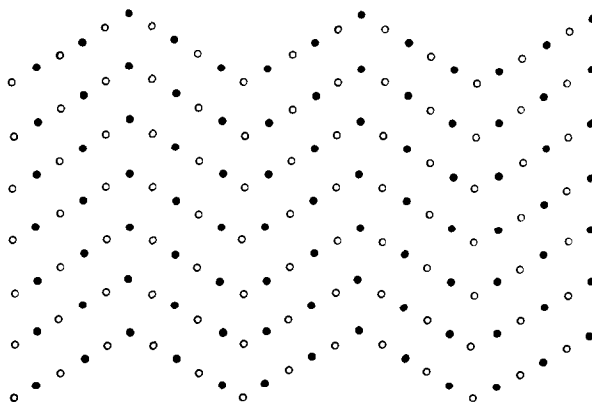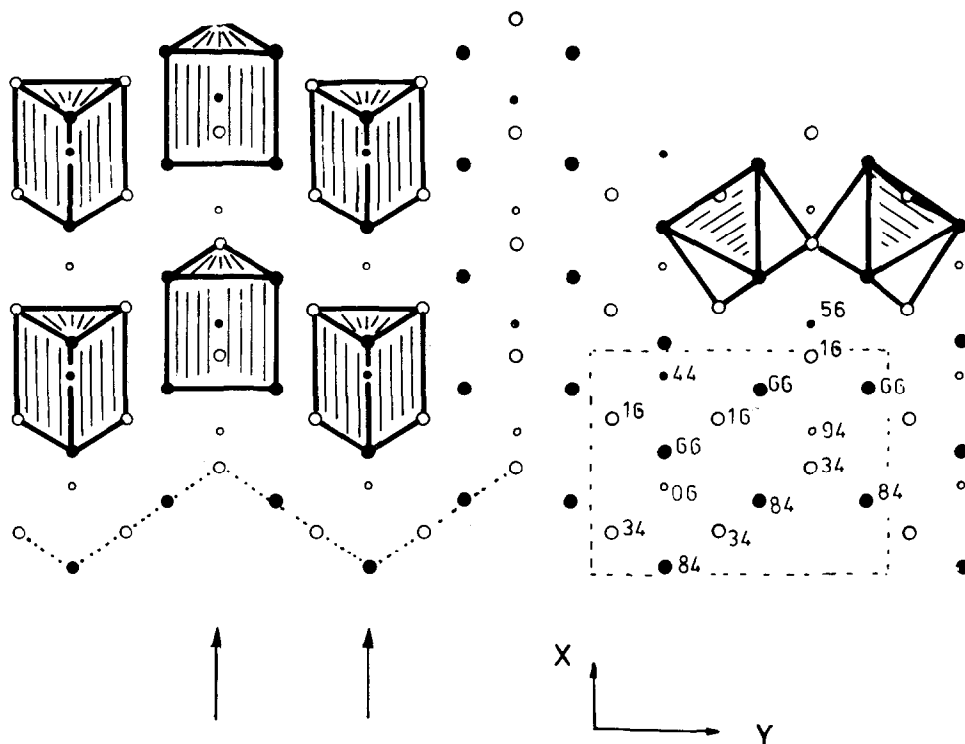

FIG. 1. Twinning and *hcp*.

FIG. 2. The structure of Fe_3C.

herring-bone pattern of atom planes. The *hcp* parts, or the *twin blocks*, are six atoms wide and the structure can be written symbolically as

$$6,6,6,6,\ldots$$

The same projection is utilized in Fig. 2 to describe the structure of Fe_3C or cementite (*8, 9*). The unit cell dimensions are $a = 5.0890$ Å, $b = 6.7428$ Å and $c = 4.5230$ Å. The trigonal prism of iron atoms surrounding each carbon is shown in the left part of Fig. 2, and the herring-bone pattern is indicated in the lower left. The $(1\bar{1}02)$ twin (= composition) planes are also perpendicular to the plane of the paper, and are indicated by arrows. The Fe_3C structure contains twinned *hcp* blocks of the size

$$4,4,4,4,\ldots$$

Within each block the iron atoms are very close to the positions for perfect closest packing, the z coordinates for ideal *hcp* being 1/6, 2/6, 4/6 and 5/6. The empty octahedra are shown in the right upper part of Fig. 2; clearly it is easy to build a model of the Fe_3C structure (and also the Pd_5B_2 or Fe_5C_2 structure described below) using ideal octahedra and tetrahedra. The *hcp* blocks are built separately, every second one is rotated 180°

around the twin axis, and the blocks are then joined exactly together across the twin planes. This idealized structure is indeed very close to the real one. By the twinning operation the trigonal prisms of iron atoms in the ideal model are given the same distortion as is observed in the real structure. Two edges are shorter than the others: they correspond to the short Fe–Fe distances observed in this structure.

It is obvious that the stoichiometry will change if the distance between the twin planes is varied. An example of this is given by the structure of Pd_5B_2 (*10*) shown in Fig. 3 (Fe_5C_2 is isostructural). It is monoclinic with $a = 12.786$ Å, $b = 4.955$ Å, $c = 5.472$ Å and $\beta = 97.2°$, and symbolically represented by

$$3,4,3,4,\ldots$$

The interval between twin planes alternates, as indicated by the zigzag dotted lines in the lower part of Fig. 3.

The structure antitype to Fe_3C is YF_3 but, to our knowledge, no antitype of the Pd_5B_2 structure has yet been found. However, it is interesting to note that the structure of the tetragonal form of $YbO(OH)$ (*11*) corresponds to the sequence
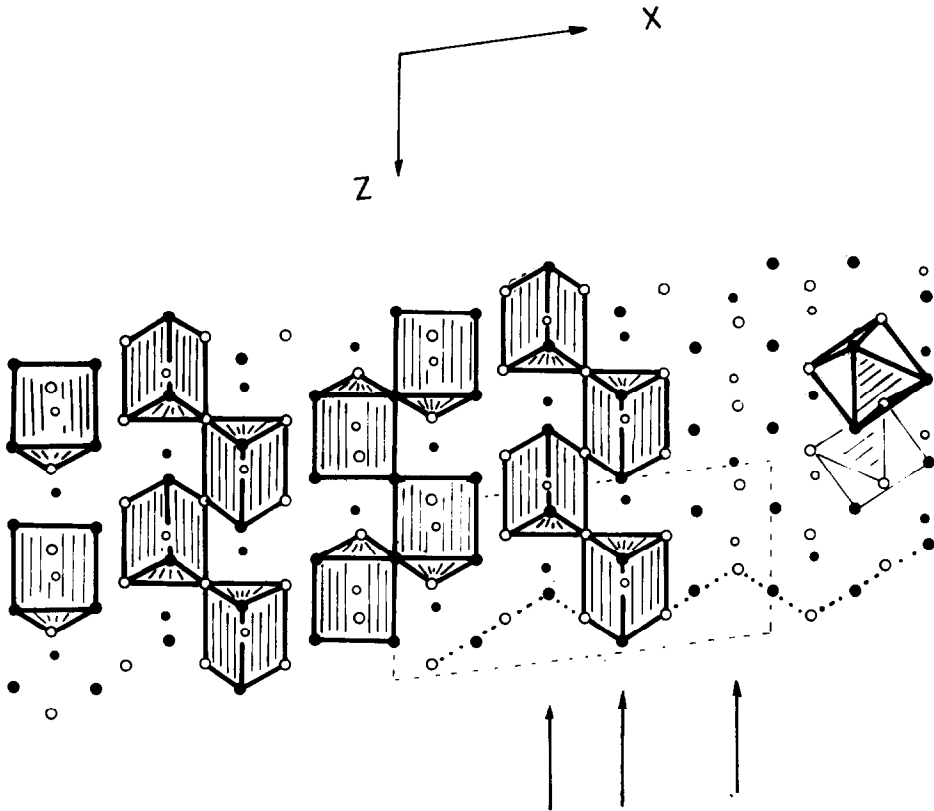
$$3,3,3,3,\ldots$$

X

Z

FIG. 3. The structure of Pd_5B_2.

This structure is shown, slightly idealized, in Fig. 4. The twin-plane interval is now so small that all the trigonal prisms share all their corners and four of their edges with adjacent trigonal prisms.

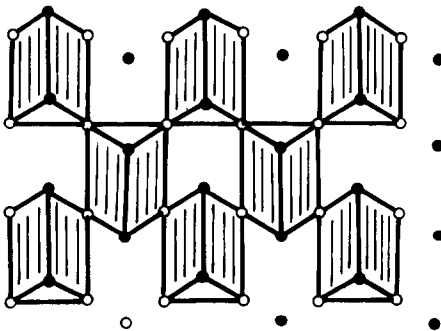Their size may be further reduced to the shortest possible sequence

2,2,2,2,...

FIG. 4. Idealized structure of tetragonal YbO(OH).

which obtains in FeB. The twin blocks are now united by face-sharing between the trigonal prisms.

c

a

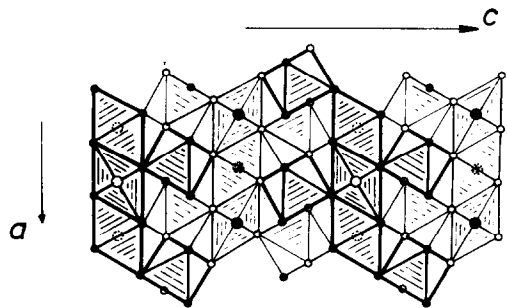FIG. 5. The structure of α-Sb_2O_4 somewhat idealized. Small circles are oxygens, larger circles are lone pairs. The rhombohedral shaped figures are the SbO_4 polyhedra in projection with lone pairs pointing upwards (filled or open circles) or downwards (dotted circles). The Sb^{3+} ions are above or below the lone pairs. The SbO_4 polyhedra form chains which are joined to the octahedral Sb^{5+} sheets by corner sharing.
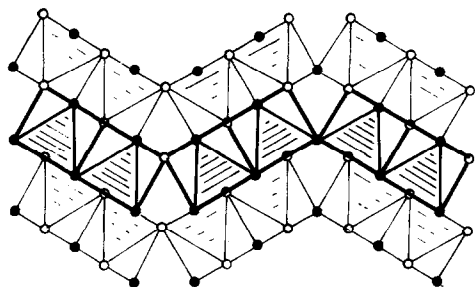
FIG. 6. A hypothetical M_2X_5 structure with the same anion packing as in Fig. 1.

The changes from Fe_3C, with unconnected layers of trigonal prisms, to Pd_5B_2, in which the layers are paired by edge-sharing, to YbO(OH), with the layers joined to both their neighbors by edge-sharing, to FeB, in which all adjacent layers are joined by face-sharing, constitute a sequence of CS operations. In each case the displacement vector is the edge of a trigonal prism base (equal to the edge of an octahedron in a twin block).

It is interesting to compare the structure of α-Sb_2O_4 (12) with the structures just described. The pentavalent antimony atoms are in octahedra and, if the lone pair and its trivalent antimony are assumed to take the space and position of an anion (6), it is easy to trace the herring-bone pattern in this structure also. Twin blocks, analogous to those in Fe_3C but now 6,6,6,... in size, build up the structure as shown in Fig. 5. The composition can be written Sb_2O_4E, where E stands for lone pair; and it is then easy to design a structure M_2X_5, which could be taken by Sb_2O_5, or by a new polymorph of Nb_2O_5 (Fig. 6).

Unit Cell Twinning and ccp

It is easy to find a number of compounds related by unit cell twinning in cubic close packing. An example is Re_3B, which has an orthorhombic unit cell whose dimensions are $a = 2.890$ Å, $b = 9.313$ Å and $c = 7.258$ Å (13) ($PuBr_3$ is the antitype). Its structure is normally described as a compact arrangement of rhenium atoms, forming columns of trigonal prisms which are centered by boron atoms. The picture
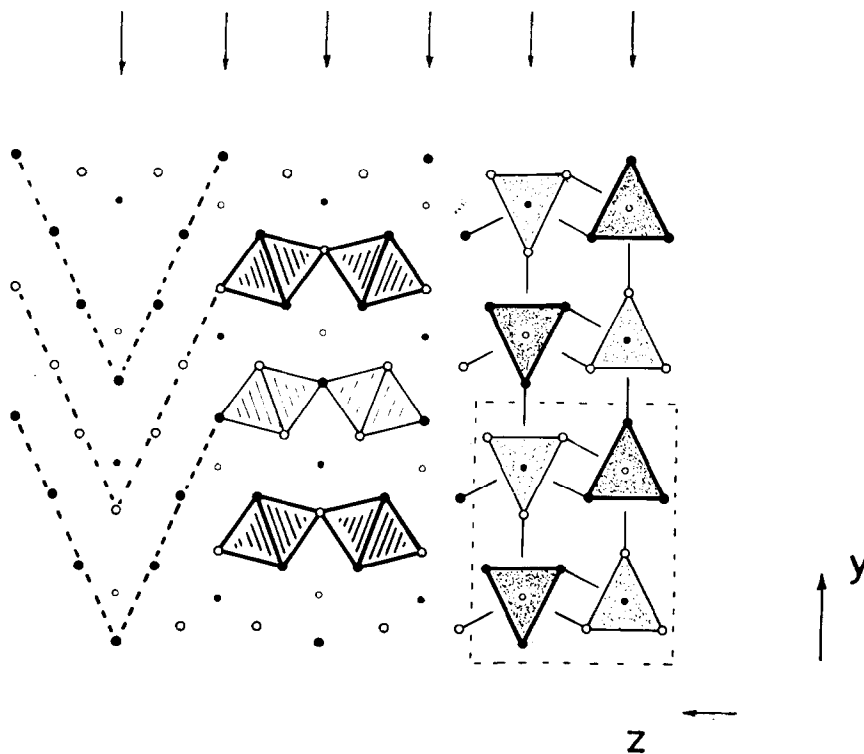

FIG. 7. The structure of Re_3B.

corresponding to this description is given in the right part of Fig. 7. In the left part, the herringbone packing of metal atoms is shown, and the twin blocks of ccp, 4,4,4,..., are situated between the arrows. The empty regular octahedra (which are filled in Cr_2VC_2) are shown in the middle of Fig. 7. Again the trigonal prisms are created by the twinning operation, and the same geometrical deviation from the ideal polyhedron occurs, as in the case of Fe_3C.

If the twin blocks are

$$5,5,5,5,...$$

the structure of $CaTi_2O_4$ (14), depicted in Fig. 8, is obtained; with Ca in the trigonal prisms and titanium in the octahedra. We would also like to add here that the important structure type of $CaFe_2O_4$ (15, 16) can be generated by means of unit cell twinning combined with a small distortion of the structure of hollandite.

With the sequence

$$6,6,6,6,...$$

we obtain a structure, shown in Fig. 9, which does not seem to correspond to any known oxide or alloy. Similar, but larger, twinned blocks of ccp occur in the mineral lillianite (17), 3PbS· Bi_2S_3:

$$7,7,7,7,....$$

In this structure, shown in Fig. 10, lead atoms are in trigonal prisms, while the octahedra are occupied by both lead and bismuth at random.

Table I summarizes the compounds belonging to this group of twinned ccp structures.

Another very interesting example of twinning on the unit cell level is found in the structure of Fe_2TiO_5, pseudobrookite (18), shown in Fig. 11. The ccp blocks are

$$6,6,6,6,...$$

but the twin plane is now different. It contains a metal atom squeezed into a rather distorted octahedron of oxygens. The geometry of this

TABLE I

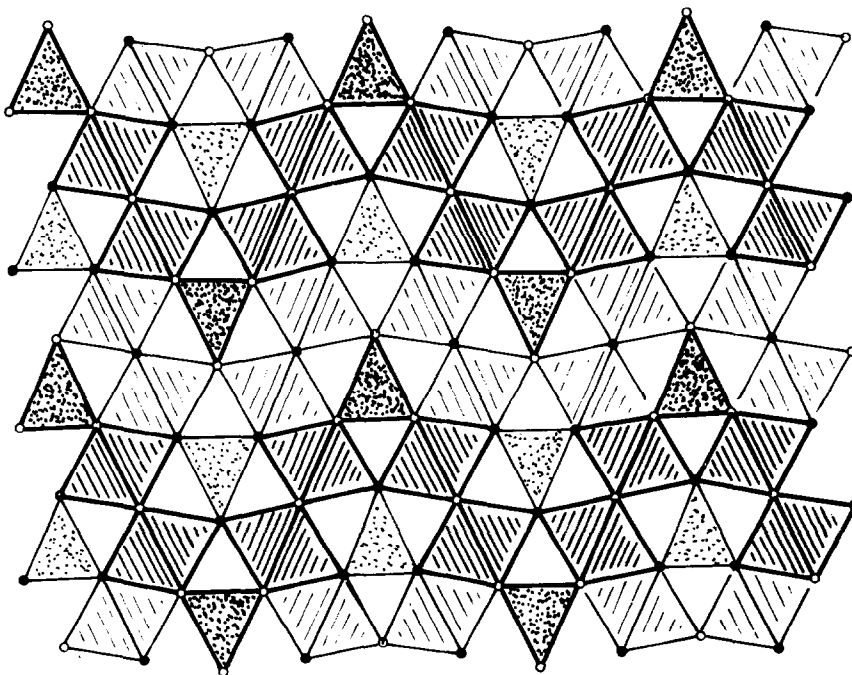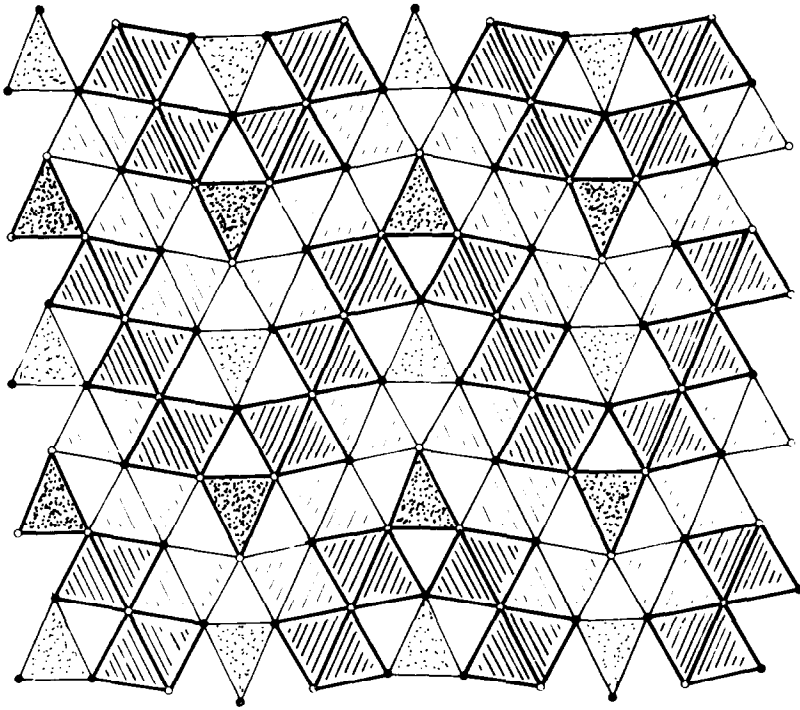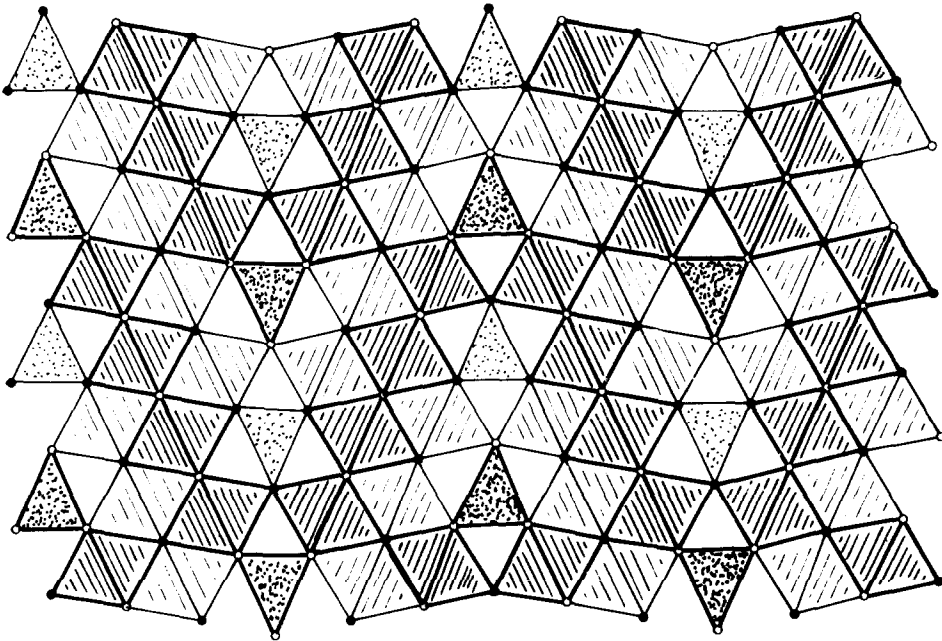| Twin block size	Alloy	Antiform	Filled antiform
4,4,4,4	Re_3B	$PuBr_3$	ABX_3
5,5,5,5	M_4X	MX_4	$CaTi_2O_4$
6,6,6,6	M_5X	MX_5	AB_3X_5
7,7,7,7	M_6X	MX_6	$PbPb_2Bi_2S_6$

FIG. 8. The structure of $CaTi_2O_4$, somewhat idealized.

FIG. 9. A hypothetical $A_2B_6X_{10}$ structure.

FIG. 10. The structure of 3 $PbS \cdot Bi_2S_3$, somewhat idealized.

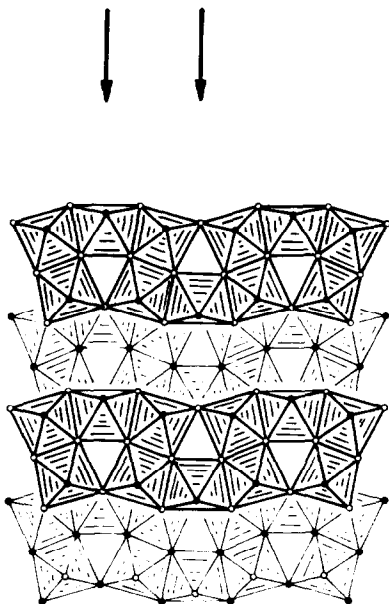FIG. 11. The structure of pseudobrookite, Fe_2TiO_5.

FIG. 13. A hypothetical M_2X_3 structure.

distortion is indeed more a result of the building principle than anything else! If the twin blocks grow to

$$8,8,8,8,\ldots$$

a hypothetical M_5X_8 structure is obtained. It is demonstrated in Fig. 12. A number of similar structures is easily designed, and the end member (parent structure), M_2X_3, is shown in Fig. 13.

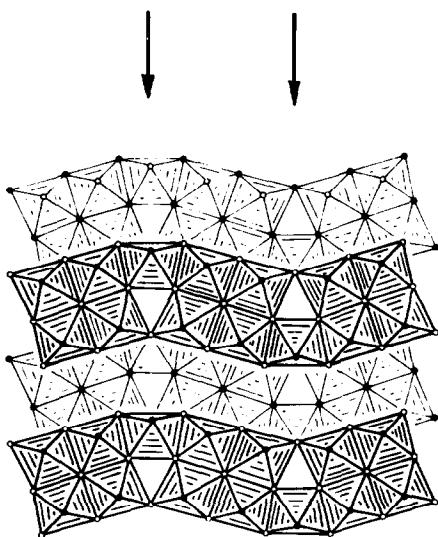Similarly, $BaTi_4O_9$ and KTi_3NbO_9 (19, 20) can be described as ccp twinned on the unit cell
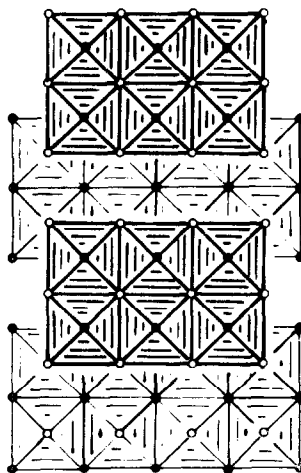

FIG. 12. A hypothetical M_5X_8 structure.

level but, in this structure, the blocks have a different geometry as shown in Fig. 14. Very similar to these, and related by an obvious CS operation, is the structure of $BaNb_2O_6$ (21).

Unit Cell Twinning and Primitive Cubic Packing

Structures with CsCl-type blocks twinned on the unit cell level are represented by the two structures Rh_5Ge_3 (22) and Ru_4Si_3 (23). The twin operation is here combined with a slip of $\frac{1}{2}a$. The two structures are shown in Figs. 15 and 16. The glide reflection operation creates trigonal prisms, with interstitial positions for extra Ge or Si atoms in the immediate neighborhood of the twin-slip planes. Other, related alloy structures such as Na_3As, etc., described by Edshammar (24), are easily comprehended as simple unit cell-twinned derivatives of primitive cubic metal atom arrays, with blocks of various widths. Some of these are interrelated by CS.

Further Comments

Normally, twinning is supposed not to change the stoichiometry of a crystal: and the composition plane is one of lowest energy—least misfit. However, all the structures discussed here are derived by the unit cell twinning operation, the very essence of which is the creation, in or close to the twin plane, of polyhedra of a kind different from those in the parent structure.[2] The

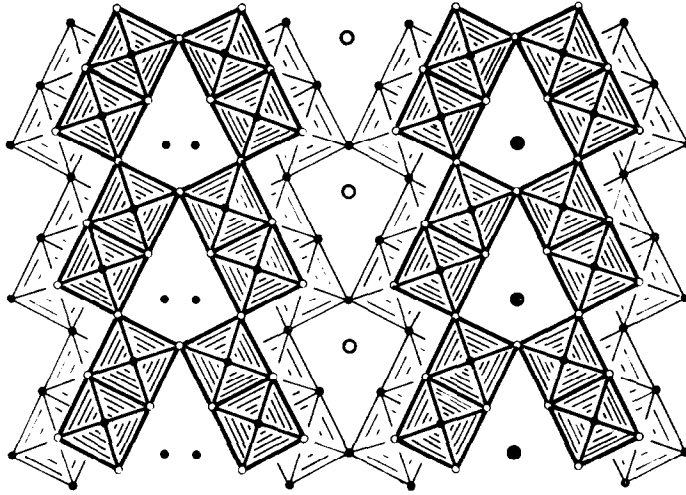[2] The pseudobrookite case appears to be an exception.

FIG. 14. The structure of $BaTi_4O_9$ (or KTi_3NbO_9), somewhat idealized. In the left part is shown how the twinning operation gives pairs of atoms, with impossible atomic distances. In the right part is shown that potassium atoms, drawn as large circles, formally substitute for such pairs.
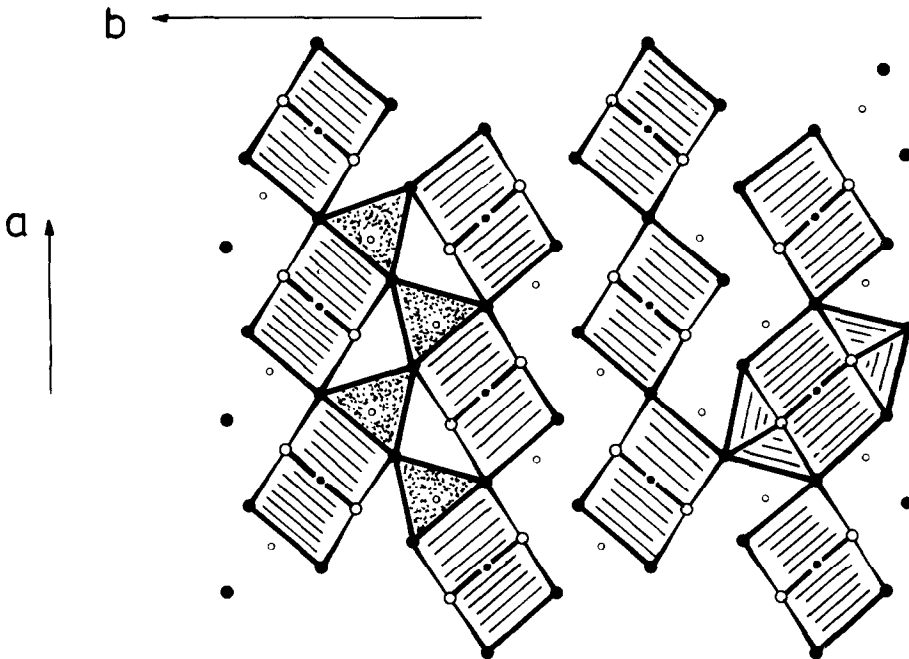

FIG. 15. The structure of Rh_5Ge_3.

new types of interstices thus provided are *occupied* in these structures. This immediately suggests the possibility that macroscopic twinning—in some cases at least—could simply be a natural way for a crystal to accommodate impurities, or interstitial atoms, down to a very low concentration. We suggest that *chemical twinning* (cf., for example, "mechanical

twinning") may be an appropriate term for the operation.

Clearly, the process offers two opportunities for nonstoichiometry: the composition of the crystal could be varied by fractional occupancy of these interstitial positions, or by changing, or breaking, the regular periodicity of the twin planes. The possibility that twin planes, such as
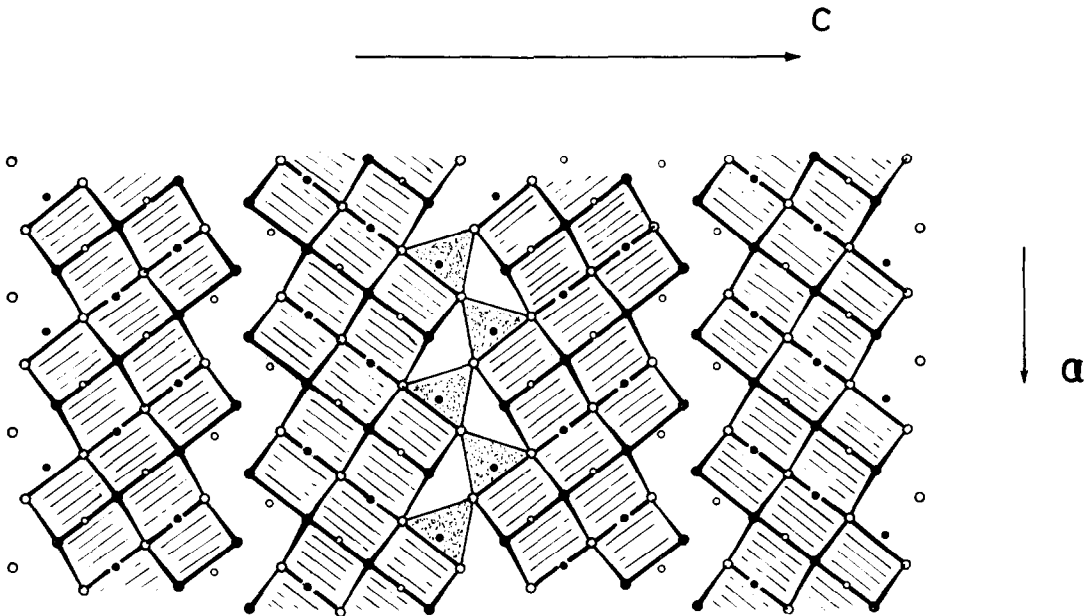
C

α

FIG. 16. The structure of Ru_4Si_3.

we have described, could act as extended defects should be studied experimentally, and we intend to do so. Superficially such a defect is similar to a Wadsley defect; geometrically and chemically it is fundamentally different. While Wadsley defects seem to be limited in their occurrence to certain chemical systems, unit cell twinning could (geometrically) occur in any solid state system.

For structures such as Fe_3C, Pd_5B_2 or Re_3B, it seems to us that the size factor forces their formation by the building principle of unit cell twinning. In the iron–carbon system, it is tempting to suggest a crystal growth mechanism for cementite. Due to the size ratio of iron and carbon atoms, the latter require a trigonal prismatic environment of iron atoms. When the crystal grows, blocks of perfect *hcp* iron are formed when the carbon activity is high enough (*25*), and carbon atoms order up along planes in order to achieve the coordination that they want. The growth of the crystal then continues in a zigzag way, giving the trigonal prisms for carbon atoms in twin planes or, as it may be as well described, giving the crystals a laminar twinning on the unit cell level. It may be that the stress of accommodating the carbon atoms stabilizes the high-pressure, *hcp*, allotrope of iron, ε-Fe (*26*). But the process that produces cementite in steels suggests a solid state transformation from the ε-carbide. This question will be considered elsewhere.

Conclusion

Unit cell twinning as a structure-building mechanism seems to us to be very useful in the classification, organization and understanding of structures. Certainly there are many more structures that can be visualized in this way, among them Cr_3C_2, Hf_3P_2 and Rh_4P_3. Finally we may add that, geometrically, it is easy to derive a mechanism for translating a twin plane by cooperative movements of atoms. We intend to take up these questions in a forthcoming paper.

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