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

JAN-OLOV BOVIN AND STEN ANDERSSON

Inorganic Chemistry 2, Chemical Centre, P. O. Box 740, S-220 07; LUND 7, Sweden

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Swinging twinning on the unit cell level is introduced as a structure-building operation in the solid state. If a parent structure can produce different twin units by swinging (changing the direction of) the twin planes, and each twin unit can be identified in different compounds, the compound can be described as a swinging twinning of the parent structure. The parent structure type of this presentation is the TlI (or CrB) type. It is shown that if the trigonal prisms of the TlI-structure type are alternatingly unoccupied there are three different isostructural AX_2-compounds, *viz*, YO(OH), $SrBr_2$, and α-$PdCl_2$. The Hf_3P_2 structure type (including the structures of Sb_2S_3, Th_2S_3, U_2S_3, Np_2S_3, K_2CuCl_3, Cs_2AgCl_3, Cs_2AgI_3, $(NH_4)_2CuBr_3$, $CuPbBiS_3$, and Ba_2ZnS_3) is described as a swinging twinning of the YO(OH) structure with one direction of the twin planes. Another direction of the twin planes of YO(OH) gives rise to the Cr_3C_2-structure type (including the structures of K_2AgI_3, Rb_2AgI_3, and $(NH_4)_2AgI_3$). A third direction of the twin planes in the structures of TlI produces the structure type of FeB if the twin units are only one trigonal prism broad instead of two.

Introduction

Swinging twinning on the unit cell level as a structure-building operation is easily understood if first the characteristics of two other operations, swinging crystallographic shear (*SCS*) (*1*, *2*) and chemical twinning on the unit cell level (*3*), are briefly recapitulated.

SCS was revealed as a new structural model when the nature of slightly reduced rutile was examined by means of electron microscopy and electron diffraction (*2*). Hyde and coworkers found that in TiO_x phases, having a continuous variation in composition over the $1.90 < x \leqslant 1.93$ range, the *CS* planes of the $[1\bar{1}1]$ zone of rutile were swinging from the (132) plane to the (121) plane via a large number of intermediate orientations. In principle, any composition in this range is accommodated by a perfectly ordered structure with *CS* planes of different orientation. Since then the *SCS* model has been used successfully in many systems, notably in the feldspar system.

A structure is described as a chemical twinning on the unit cell level if it contains units (the twin units) which are twin related to each other by reflection, glide reflection, and/or rotation. The definitions of twin plane and twin axis are the same as for macroscopic twins. The twin unit is usually a narrow band of atoms bounded in one direction by the twin planes. If every second of the twin bonds is rotated by π rad around the twin axis, which is either parallel or perpendicular to the twin plane, and joined across the twin planes, the resulting structure will show the same atom packing as the single twin unit. Chemical twinning is recognizable in a number of inorganic, metal, and mineral structures. It has been shown (*4*) that defects in crystals of Ru_4Si_3 depend on the variation of the spacing and periodicity of the twin planes. In view of *SCS* and chemical twinning it seems reasonable that in a given packing of atoms the set of parallel twin planes can vary their orientation (swing) and thus produce a new structure for each direction. An illustrative example of how swinging twinning, in one system of atom

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packing, gives birth to several well-known structures, follows.

The System of Atom Packing in the Structures of TlI, YO(OH), and $SrBr_2$

As the parent structure the structure chosen is the TlI (*5*) structure type, which is well known and reported for some 70 compounds (*6*). It has also been described as the CrB (*7*) or CaSi (*8*) structure type. In the lower part of Fig. 1 a drawing of the TlI (CrB)-structure type is projected onto the (001)-plane. The trigonal prisms share four faces, with each other, two square and two triangular. The infinite sheets formed are separated by empty square pyramids. Each trigonal prism is centered around one atom. The distances between such adjacent atoms are, of course, dependent on the size of the atoms situated in the corners of the trigonal prisms and can vary between 1.74 Å (as in CrB, with B–B bonding) and 4.32 Å (as in TlI).

The trigonal prisms in the TlI structure can be unoccupied alternatingly in at least three different ways and thus produce AX_2 compounds. The two structures of $SrBr_2$ (*9*) and YO(OH) (*10*) show this previously disregarded relationship to TlI. In the structure of YO(OH) the yttrium atom is coordinated to seven oxygen atoms in the form of a slightly distorted one-capped trigonal prism. If half of the thallium atoms in the TlI structure are removed, as the upper part of Fig. 1 illustrates, an isostructural configuration with the structure of YO(OH) is obtained. If, further, the yttrium atoms in every second pair of sheets in YO(OH) is transported one step in one direction to the next trigonal prism, an isostructural configuration with the structure of $SrBr_2$ (cf. Fig. 2) is obtained. The relationships are obvious by comparing Fig. 1 with Fig. 2. Some later works on the structure of $SrBr_2$ (*11–13*) have proposed that the structure determined by Kamermans (*9*) is doubtful. It seems reasonable, however, to believe that the structure determinations have been performed on different modifications of $SrBr_2$ because the crystals were synthesized under quite different conditions.

Nyman (*14*) has pointed out that the chromium atom packing of CrB(TlI) is identical with the chlorine atom packing of orthorhombic $PdCl_2$ (*15*). If half of the boron

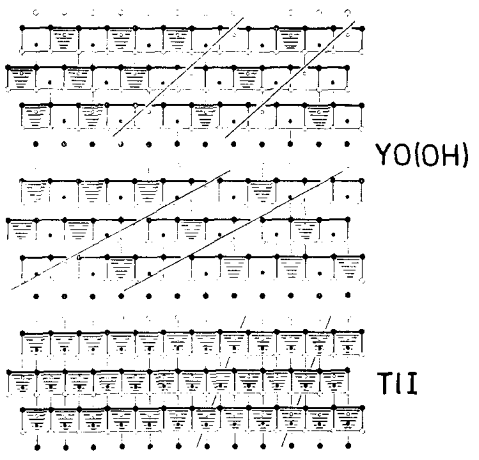

FIG. 1. An idealized projection of the TlI [or CrB, YO(OH)] structure type on the (001)-plane. Open and filled large circles indicate iodine (or chromium, oxygen) at $z=\frac{1}{4}$ and $z=\frac{3}{4}$, respectively. Open and filled small cirlces mark thallium (or boron, yttrium) at $z=\frac{1}{4}$ and $z=\frac{3}{4}$, respectively. In the lower part of the figure all the trigonal prisms are occupied contrary to the two upper projections of the structure YO(OH). Notice that the middle projection is in an opposite direction from the upper one. The twin planes are marked with parallel lines.

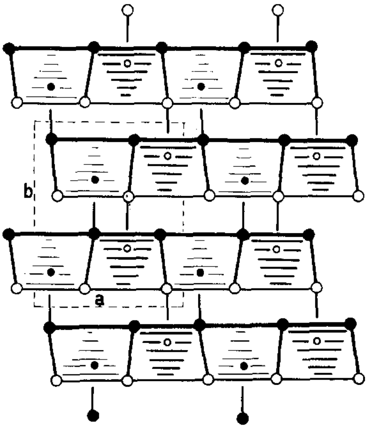

FIG. 2. The structure of $SrBr_2$ projected along its *c*-axis. Open and filled large circles indicate Br at $z=\frac{1}{4}$ and $z=\frac{3}{4}$, respectively. Open and filled small circles mark Sr at $z=\frac{1}{4}$ and $z=\frac{3}{4}$, respectively. Compare the structure with that of YO(OH) (cf. Fig. 1).

atoms are removed and the rest are shifted into the square face of two trigonal prisms (in fact in the center of a rhombic prism, as described by Nyman), an isostructural configuration with orthorhombic $PdCl_2$ is obtained.

The Hf_3P_2(K_2CuCl_3)-Structure Type as Swinging Twinning of YO(OH)

In the structure type of Hf_3P_2 the phosphorus atom is seven-coordinated to hafnium in the form of a one-capped trigonal prism which shares edges in the manner illustrated in Fig. 3. The structure could be considered a swinging twinning of the structure of YO(OH) because, if every second of the twin blocks between the twin planes (marked with arrows in Fig. 3) in the structure is rotated $\pi/2$ rad around its twin axis (which in this case is perpendicular to the twin planes) and then is joined together, the structure of YO(OH) is obtained (cf. middle part of Fig. 1 with the twin planes marked as lines). The Hf_3P_2 structure type (*16*) includes a large number of compounds. The first determined structure of this type was of the mineral stibnite, Sb_2S_3 (*17*, *18*) (cf. Fig. 4); later Zachariasen (*19*) solved the structures of Th_2S_3, U_2S_3, and Np_2S_3 and pointed out that they had the same type of structure as Sb_2S_3. Lundström (*16*) then found Hf_3P_2 to be the antitype of the Sb_2S_3 structure. Both Zachariasen and Lundström, however, mentioned that the parameters of the antimony atoms differed considerably from those found in the other structures because of the stereochemically active lone pair of electrons of antimony(III). The lone pairs usually require space comparable with that of the anion (*20*) and therefore push the antimony atom in the structure of Sb_2S_3 toward the one-capped square face of the trigonal prism (compare Figs. 3 and 4) in order to make enough space for the lone pair in the center of the trigonal prism.

Wyckoff (*21*) pointed out that the structures of K_2CuCl_3 (cf. Fig. 5), Cs_2AgCl_3, $CsAgI_3$ (*22*), $(NH_4)_2CuBr_3$ (*23*), $CuPbBiS_3$ (*24*), and Ba_2ZnS_3 (*25*) are also isostructural with Sb_2S_3 and Th_2S_3. In almost all chemical twinnings on the unit cell level, the twinning plan lodges coordination polyhedra which are different from those found in the parent structure (*2*). This is also the case in swinging twinnings, as can be illustrated by the K_2CuCl_2

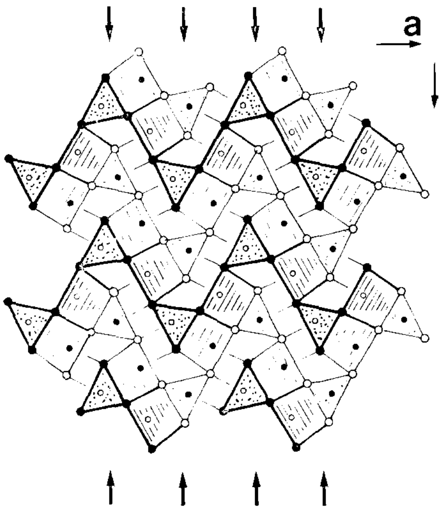

FIG. 3. The structure Hf_3P_2 projected along its *b*-axis. Small circles indicate phosphorus and large circles indicate hafnium. The atoms on $y = \frac{3}{4}$ (filled) and or $y = \frac{1}{4}$. Dotted triangles are trigonal prisms projected along its trigonal axis. The twin planes are marked with arrows. Compare the twin unit with that in the middle of Fig. 1.

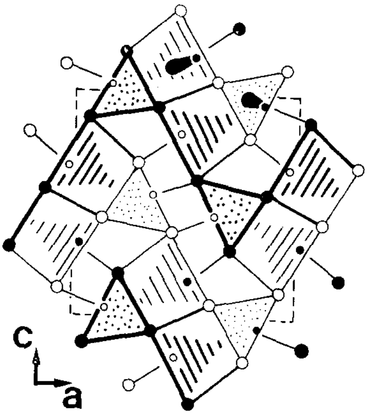

FIG. 4. The structure of stibnite, Sb_2S_3, projected along its *b*-axis. Large circles indicate sulfur. The atoms on $y = \frac{3}{4}$ (filled) and on $y = \frac{1}{4}$. The stereochemical active lone pair of antimony(III) are marked in the two upper trigonal prisms of the figure. Compare Fig. 3 with Fig. 4 and notice the effect of the lone pair.

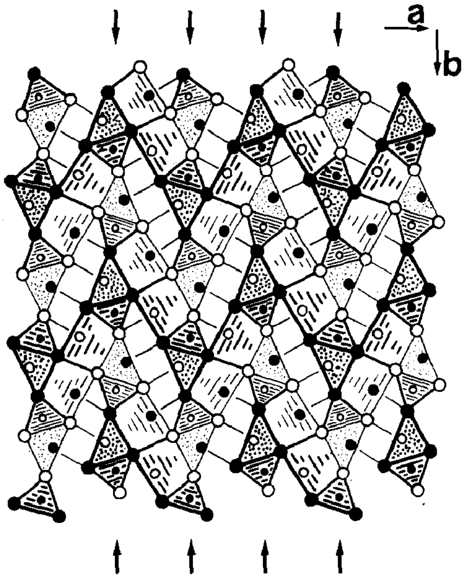

FIG. 5. The orthorhombic K_2CuCl_3 structure viewed along its c-axis. The copper atoms are the small, the potassium atoms are the medium, and the chlorine atoms are the large circles. The atoms on $z = \frac{3}{4}$ (filled) and on $z = \frac{1}{4}$. The triangles marked with lines are the $CuCl_4$-tetrahedra. The twin planes are marked with arrows. Compare Fig. 3 with Fig. 5.

structure type in which the twin planes contain the copper atoms (or silver in the other structures) in tetrahedral polyhedra (cf. Fig. 5). The $CuCl_4$-tetrahedra share corners to form a string parallel to the c-axis. Within such a string, ion transport could be possible in an electric field.

The $Cr_3C_2(K_2AgI_3)$-Structure Type as Swinging Twinning of YO(OH)

In the structure type of YO(OH) the twinning planes can be rotated (swinged) counterclockwise approximately 0.29 rad from the previous position of the Hf_3P_2-twin planes and thus produce a new type of twin block (cf. upper part of Fig. 1). The resulting twin block is found in the structure of Cr_3C_2 as can be seen in Fig. 6. The structure of Cr_3C_2 can thus be described as a swinging twinning of the structure type YO(OH). The twin operation applied on the structure proves this because, if every second of the twin block is rotated

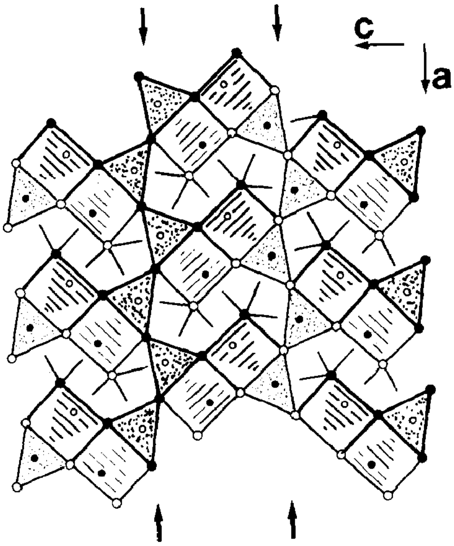

FIG. 6. The structure of Cr_3C_2 projected on the (010)-plane. Large circles indicate chromium. The atoms on $y = \frac{3}{4}$ (filled) and on $y = \frac{1}{4}$. The twin planes are marked with arrows. Dotted triangles are trigonal prisms projected along its trigonal axis. Compare the twin unit with that in the upper part of Fig. 1.

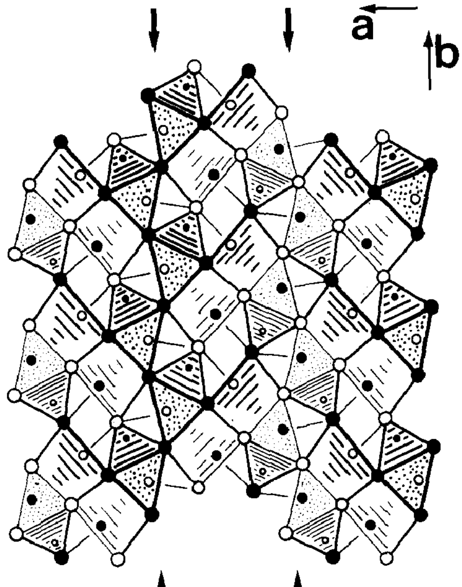

FIG. 7. The orthorhombic structure of K_2AgI_3 projected along its c-axis. The smallest circles are silver and the largest are iodine. The silver atom is coordinated to iodine in the form of a tretahedron (triangles marked with lines). The twin planes are marked with arrows. Compare Fig. 7 with Fig. 6.

around its twin axis, which in this case is parallel to the twin planes, and then joined, the YO(OH) structure type is obtained. The twin planes of Cr_3C_2 not only lodge trigonal prisms with an orientation differing from the parent structure but also empty tetrahedra. Such filled tetrahedra in the twin planes are to be found in the structure of K_2AgI_3 (*26*) (cf. Fig. 7). The iodine atoms are in the same positions as the chromium atoms and the potassium atoms correspond to the carbon atoms in Cr_3C_2. The silver atoms are coordinated in the form of tetrahedra to iodine atoms. The structure of K_2AgI_3 is isostructural with Rb_2AgI_3 and $(NH_4)_2AgI_3$ (*26*).

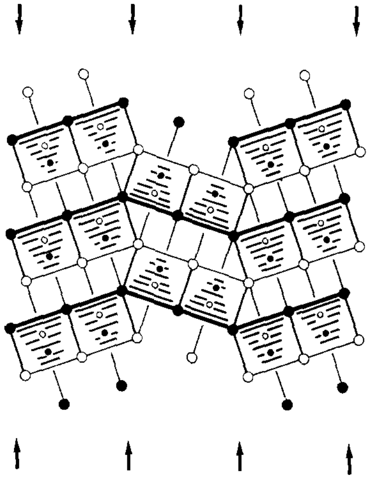

FIG. 8. A theoretical *xy*-compound. The twin units are the same as that in the lower part of Fig. 1.

The FeB-Structure Type as Swinging Twinning of TlI

A further counterclockwise swing of 0.72 rad from the starting position of the twin planes of Hf_3P_2 produces a new twin block type of the TlI packing (cf. the lower part of Fig. 1). Applying the twin operation, with the twin axis perpendicular to the twin planes, on every second of such blocks, gives rise to a theoretical compound *XY* (cf. Fig. 8). But it is, of course, conceivable to vary the spacing between the twin planes and, by bringing the

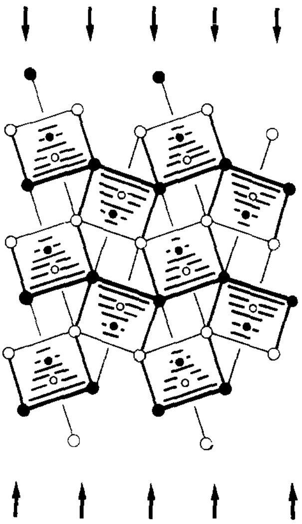

FIG. 9. The structure of FeB projected on the (001)-plane. Large circles indicate iron. The atoms on $z = \frac{3}{4}$ (filled) and on $z = \frac{1}{4}$. Twin planes are marked with arrows. Compare with Fig. 8 and Fig. 1.

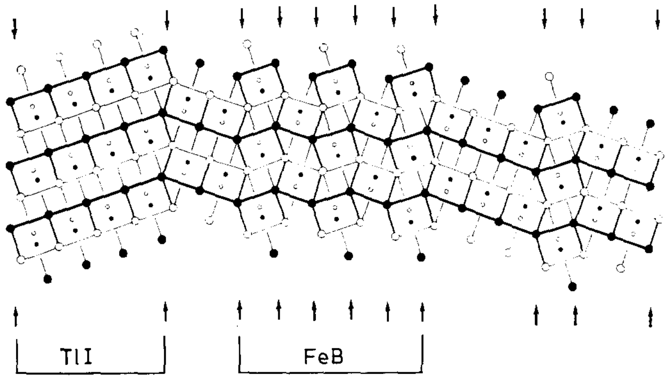

FIG. 10. A part of a theoretical crystal of Zr(Si,Al) which could contain TlI-units and FeB-units of different width.

twin planes near each other, produce a twin block type found in the FeB structure type (*27*, *28*) (cf. Fig. 9). It seems reasonable to believe that there must be some XY compounds which, under certain conditions, crystallize in both the TlI and FeB structure types. A promising example of this is the compound Zr(Si,Al) (*29*). The question of whether or not there exist crystals with both types of packing caused by nonregular spacing between the twin planes (cf. Fig. 10) now arises. If such defect crystals exist, it would be interesting to study the relations between the aluminum content and the periodicity of the twin planes by means of electron microscopy.

Conclusions

Swinging twinning on the unit cell level as a structure-building operation in the solid state is introduced here as a method of classification, description, organization, and understanding of structures like the earlier published methods such as topological distortions (*30*), intergrowth (*31*, *32*), the building block principle (*33*, *34*), crystallographic slip (*CS*) (*32*), swinging (*CS*) (*1*, *2*), rotation (*35*, *36*), the stereochemical effect of the lone pair of electrons (*20*, *37*, *38*), chemical twinning (*3*), the Vernier model (*39*), and chemical fourlings (*40*). Our intention has been to present only a few examples of structures which can be described as swinging twinnings. We believe many more examples must exist, in various systems of atom packing, not only in the TlI system. Work along these lines is being continued.

Acknowledgment

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