Chemical Fourling 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, Sweden

Chemical fourling on the unit-cell level is introduced as a structure-building operation in the solid state. A chemical fourling structure is achieved when two twin planes are perpendicular to each other. Each fourling unit has infinite extension in only one direction and can be related to a well-known structure type or packing of atoms. The structures of the tetragonal tungsten bronzes M_xWO_3 and $Pd(NH_3)_4Cl \cdot H_2O$ are presented as examples of chemical fourlings of cubic close packing. The structures of SeO_2, Mn_2Hg_5, and Zr_2F_7O are shown to be a sequence of chemical fourlings of primitive cubic packing. Chemical fourling units of hexagonal close packing are found in the structures of tetragonal Ti_3Sb, α-V_3S and $Sb_6O_7(SO_4)_2$. The structures of $CuAl_2$, $SeTl$, $NbTe_4$, Ti_3Sb, and MnU_6 all have the same chemical fourling unit. $Cr_{23}C_6$ is described as a bounded chemical fourling of cubic close packing.

"Nature hath framed strange fellows in her time"
W. Shakespeare (1600) in *The Merchant of Venice*

Introduction

Several structure-building operations such as topological distortions (*1*), intergrowth (*2, 3*), the building-block principle (*4, 5*), crystallographic slip (*CS*) (*2*), swinging *CS* (*6, 7*), rotation (*8, 9*), the stereochemical effect of the lone pair of electrons (*10–12*), chemical twinning (*13*), and the Vernier model (*14*) have been useful in the classification, organization, and understanding of structures.

Chemical twinning on the unit cell level was introduced (*13*) to derive a number of complicated structures from a few simple parent ones. Chemical twinning is achieved in the same way as macroscopic twinning, with the same definition of twin plane and twin axis. Among minerals not only are twins well-known, but also trillings and fourlings are found. On the unit-cell level the Ru_7B_3 structure was described as a chemical trilling (*14*), and we now wish to report some examples of chemical fourlings.

A chemical fourling on the unit-cell level is achieved in two ways: either when two twin planes are perpendicular to each other, giving rise to four parts (the fourling units) of the structure; or when the four parts of the structure could be repeated only by a fourfold axis (the fourling axis). Each part has infinite extension in only one direction. Both mirror planes and glide mirror planes can be twin planes. The periodicity of the twin planes determines the size of the fourling unit and consequently also determines the size of the unit cell. At present, it seems reasonable to describe a structure as a chemical fourling only when the fourling unit can be related to a well-known structure type of packing (hexagonal *hcp*, cubic *ccp*, or primitive packing) of atoms.

Chemical Fourlings of *ccp* and Primitive Cubic Packing

An illustrative example of chemical fourling with *ccp* is the tetragonal tungsten bronze (TTB) structure (*15*). The TTB structure contains a framework of corner-sharing WO_6

octahedra as illustrated in Fig. 1. By the chemical fourling operation, the TTB structures can be derived from the ReO_3 structure type. This is shown in Fig. 1, where the twin planes are indicated by arrows. The two sets of parallel twin planes are perpendicular to each other and circumscribe the fourling unit (seen in the lower right part of the figure). In almost all chemical twinnings on the unit-cell level, the twinning plane lodges coordination polyhedra which are different from those found in the parent structure (13). This is also the case in chemical fourlings, as can be illustrated by the TTB structures in which the twin planes contain potassium atoms in pentagonal prism polyhedra. The TTB structures can also be derived by a rotation operation (8, 16) from the ReO_3 structure type.

A string of cuboctahedra sharing square faces is a part of ccp. If such a string is repeated by the chemical fourling operation, a structure which is closely related to the structure of $Pd(NH_3)_4Cl_2 \cdot H_2O$ (17), is obtained and this structure is shown in Fig. 2. The palladium atoms are situated in the square faces. The center of the cuboctahedron is empty. The water oxygen is found at the
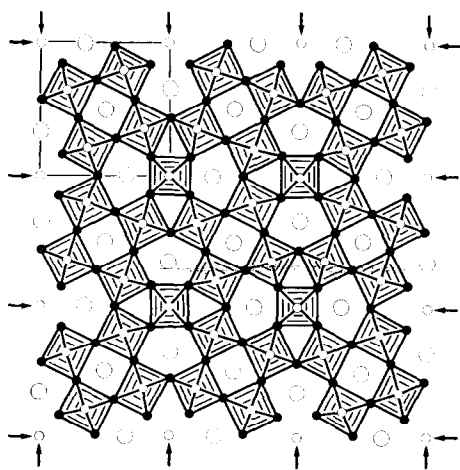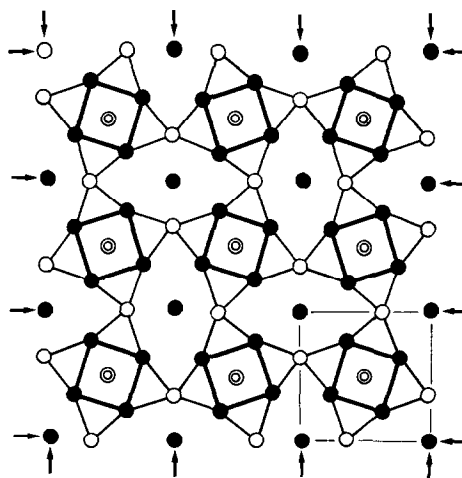

FIG. 2. The structure of $Pd(NH_3)_4Cl_2 \cdot H_2O$ projected on the (001) plane. Double rings indicate palladium atoms in the same plane as the four nitrogen atoms (filled circles). The chlorine atoms (open circles) are displaced from the former plane by one-half of c-axis. The water oxygen is situated in the corner of the fourling unit, which is marked in the lower right of the figure.

intersection line of the twin planes. This structure also can be obtained by a rotation operation on ccp.

The cuboctahedron of ccp can be topologically distorted to a four-capped cube resembling primitive cubic packing. A string of face-sharing four-capped cubes arranged through the chemical fourling operation in the same way as the cuboctahedra in $Pd(NH_3)_4Cl_2 \cdot H_2O$ (compare Figs. 2 and 3) produces the structure of the alloy Mn_2Hg_5 (18), which is isostructural with Pd_2Hg_5 (19). The mercury cube, four-capped by manganese atoms, is empty and one mercury atom is situated at the intersection line of the twinning planes in the structure of Mn_2Hg_5 (see upper left part of Fig. 3). The chemical fourling operation creates two different polyhedra in the twin plane of this type of structure, viz., a pentagonal bipyramid and a tri-capped trigonal prism. The structure of Zr_2F_7O (20) (see upper right part of Fig. 3) is an example where the centers of the pentagonal bipyramids are occupied. The lower left part of Fig. 3 shows the arrangement of the tri-capped trigonal prism in a hypothetical compound M_3X_{17}
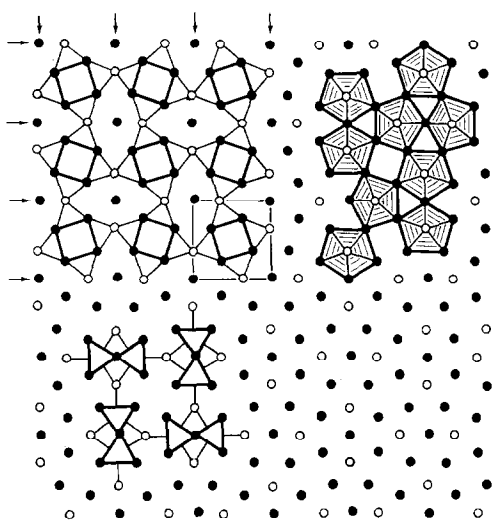

Fig. 1. The structure of the tetragonal tungsten bronze M_xWO_3. Small circles indicate oxygen atoms and large circles indicate M. The twin planes are marked with arrows. The fourling unit is marked in the lower right part of the figure.

FIG. 3. The upper left part of the figure shows the structure of Mn_2Hg_5 projected down (001). Filled circles indicate Hg atoms at $z = 0$ and open circles indicate Mn atoms at $z = \frac{1}{2}$. The twin planes are marked with arrows. The upper right part of the figure shows the structure of Zr_2F_7O illustrated with the zirconium atoms in the pentagonal prisms. The lower left part shows the hypothetical compound M_3X_{17} drawn with atoms in tri-capped trigonal prisms.

where M is an element which prefers a trigonal prism as coordination polyhedron.

It has been shown that lone pairs of electrons *(10, 11)* in compounds of ns^2-elements can be located in a structure in such a way that frameworks consisting of lone pairs of electrons and atoms correspond to a close packing of atoms or to a well-known structure type. Another structure fitting this scheme is found among the chemical fourlings, viz., the structure of SeO_2 *(21)* (cf. Fig. 4). The common oxygen coordination polyhedron of Se(IV) is the tetrahedron *(22)* with the lone pair of elections at one of the corners. In the structure of SeO_2 the centers of the lone pair electrons complete the frameworks of the atoms (cf. Fig. 4) in such a way that SeO_2 is almost isostructural with Mn_2Hg_5 (compare Figs. 3 and 4). The only differences are that the intersection line of the two twin planes does not contain any atom in the structure of SeO_2 and that the Se(IV) atoms fill a tetrahedral position which is empty in the structure of

Mn_2Hg_5. Indeed, this heterogeneous group of almost isostructural compounds comprising one alloy, one chloride, one oxide hydroxide fluoride, and one compound containing lone pairs of electrons constitutes a remarkable type of atom packing. One reason for the ability to accommodate such different elements in the same type of packing can be the special property of rigid column elasticity which this type of chemical fourling offers. The structure is elastic because a rotation around the fourfold axis of one fourling unit— or rigid column—causes a reverse rotation of the adjacent fourling units, thus generating a variable polyhedron with its center at the intersection line of the twin planes. This polyhedron has variable form or shape, depending on the degree of rotation of the fourling unit or rigid column which, in its turn, depends on the size of the atom lodged
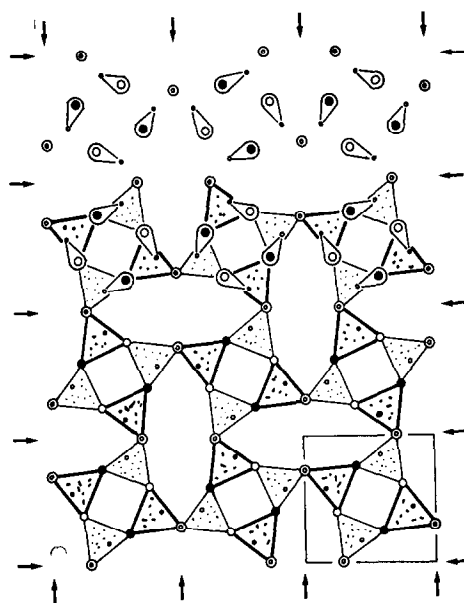

FIG. 4. The structure of SeO_2 projected on the (001) plane. Double rings indicate two superimposed oxygen atoms at $z = \frac{1}{4}, \frac{3}{4}$. Open and filled large circles indicate oxygen atoms at $z = 0$ and $x = \frac{1}{2}$, respectively. Small open and filled circles indicate selenium atoms at $z = 0$ and $z = \frac{1}{2}$, respectively. A lone pair of electrons (E) of selenium is marked with circle sectors in the upper part of the figure and their centers are found at the same height as the selenium atoms. The SeO_3E-tetrahedron is marked with dots.
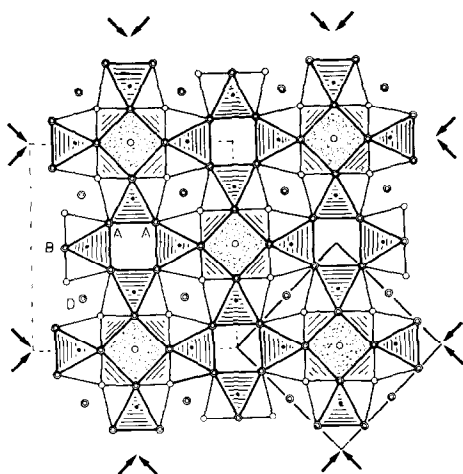
FIG. 5. Bounded projection, $\frac{1}{4} \leqslant z \leqslant \frac{3}{4}$, of the structure of $Cr_{23}C_6$. Double circles A ($z = 0.381$ and $z = 0.619$), B ($z = \frac{1}{4}$ and $z = \frac{3}{4}$), and D ($z = \frac{1}{4}$ and $z = \frac{3}{4}$) represent two superimposed chromium atoms. Single circles indicate chromium atoms on $z = \frac{1}{2}$ with one in the center of the cuboctahedron. D is surrounded by a distorted truncated tetrahedron. Small filled circles mark carbon atoms on $z = \frac{1}{2}$ situated in a square antiprism. The twin planes are marked with arrows.

in the center of the polyhedron. Similar relationships are found in the structures of the felspars when they are compared with

structures of zeolites belonging to the Phillipsite–Harmotome group.

All chemical fourlings have infinite extension in one direction. The introduction of the term *bounded chemical fourling*, which no longer has infinite extension in any direction, makes it possible to describe the structure of $Cr_{23}C_6$ (*23, 24*). In Fig. 5, the bounded projection ($\frac{1}{4} \leqslant z \leqslant \frac{3}{4}$) is shown and the chemical fourling unit (marked in the lower right part of the figure) is a cuboctahedron of chromium. The coordination polyhedra generated by the twin operation are empty cubes around the intersection line of the twin planes and a distorted truncated tetrahedron, with Cr in its center, in the twin planes. The cuboctahedron and the cube are connected by square antiprisms which contain carbon atoms. The whole structure is then generated from the bounded chemical fourling if it is rotated $\pi/4$ radians around its fourfold axis, then connected to the former one, and so on.

Chemical Fourling of *hcp*

The structure type of tetragonal Ti_3Sb (*25*) can be described as a chemical fourling of *hcp* with a string of face-sharing octahedra within the fourling unit (cf. right part of Fig. 6). All
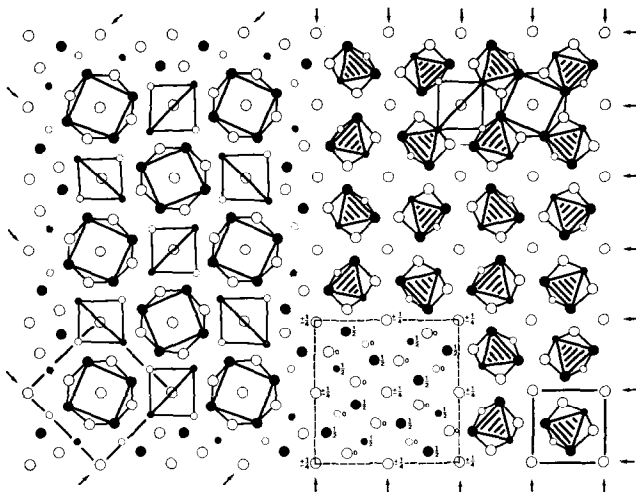

FIG. 6. A projection of the tetragonal modification of Ti_3Sb along its *c*-axis. Small circles indicate antimony atoms, and large circles indicate titanium atoms. The right part of the figure shows how one setting of the twin planes (marked with arrows) give rise to an *hcp* twin unit of octahedra with a large tetrahedron and a square antiprism in the twin planes. The left part shows the other setting of twin planes given with a twin unit containing a string of face-sharing square antiprisms (compare this figure with Figs. 9, 10, and 11).

of the twin planes used so far have been mirror planes, but in this structure they are glide mirror planes. The twin operations generate two different coordination polyhedra in this chemical fourling, viz., one square antiprism of Ti atoms containing another titanium atom in its center and one large tetrahedron with antimony atoms at the corners and a titanium atom in its center (cf. upper right part of Fig. 6). Three other compounds, viz. Si_3W_5, Si_3Mo_5 (26), and α-US_2 (27) resemble tetragonal Ti_3Sb closely, differing only in the stoichiometry. In the structure of α-US_2 the uranium atoms in the square antiprisms are statistically distributed, so that only half of the sites are occupied. The structure type of tetragonal Ti_3Sb is an example of how the orientation of twin planes can be arranged in two different directions (cf. the left part of Fig. 6). The other arrangement causes another fourling unit and it will be described in the next section.

In the α (high-temperature) modification of trivanadium sulfide, V_3S (28), the vanadium atoms are situated at the corners of an empty trigonal bipyramid (cf. Fig. 7). The trigonal bipyramids share corners with each other in such a way that a somewhat distorted hcp fourling unit is obtained (cf. the lower right part of Fig. 7). The fourling unit is repeated in the structure by two glide mirror planes to a chemical fourling with the sulfur atom situated in the twin planes. The polyhedron generated in the center of the chemical fourling is a tetrahedron, which in this structure is empty. A large number of compounds crystallize in the similar but more asymmetric structure type Fe_3P (29), viz., Ni_3P, Cr_3P, Mn_3P, Mo_3P, $(Fe,Ni,Co)_3P$, Pd_3P, Pd_3As, Zr_3Sb, and Hf_3Sb (30, 31). This structure type also can be described as a chemical fourling of distorted hcp. The relation of this structure type with $Ni_{12}P_5$ has been given by Rundqvist (32) as a topological distortion. It has been overlooked earlier that eight Ni atoms form a regular polyhedron of a new kind in the $Ni_{12}P_5$ structure. This polyhedron can be put together by two square pyramids (half octahedra) and four tetrahedra, all sharing faces. It has one hexagonal face slightly bent with its central atom
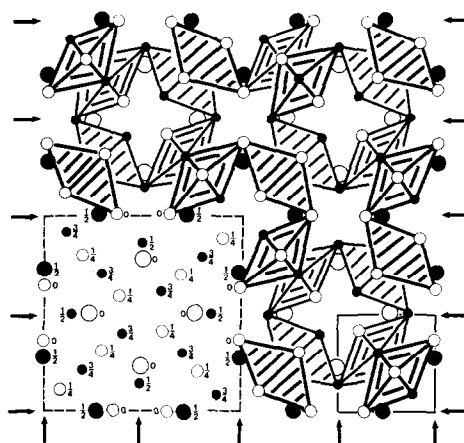

FIG. 7. A projection of the α (high-temperature) modification of V_3S along its c-axis. Small circles indicate vanadium atoms and large circles indicate sulfur atoms. The fourling unit, with its corner-sharing trigonal bipyramids, is marked in the lower right part of the figure. The twin planes are marked with arrows.
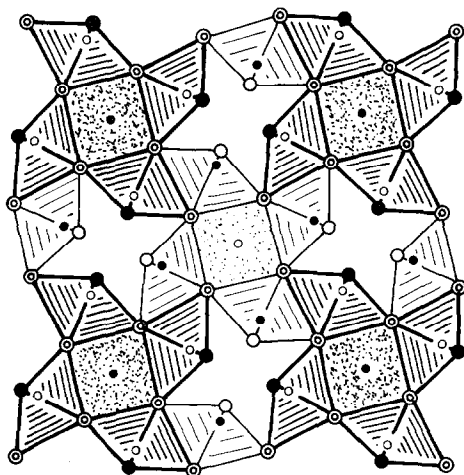

FIG. 8. A projection of the structure of $Ni_{12}P_5$ onto the (001) plane. Double rings indicate Ni atoms on $z = \frac{1}{4}$ and $z = \frac{3}{4}$. Open and filled large circles represent Ni atoms on $z = 0$ and $z = \frac{1}{2}$, respectively. Open and filled small rings indicate P atoms on $z = 0$ and $z = \frac{1}{2}$, respectively.

missing. If the central atom had been in the form of a Ni atom, the polyhedron would have been a perfect part of the hcp. However, the phosphorus atom is situated close to this central position in the hexagon, but of course
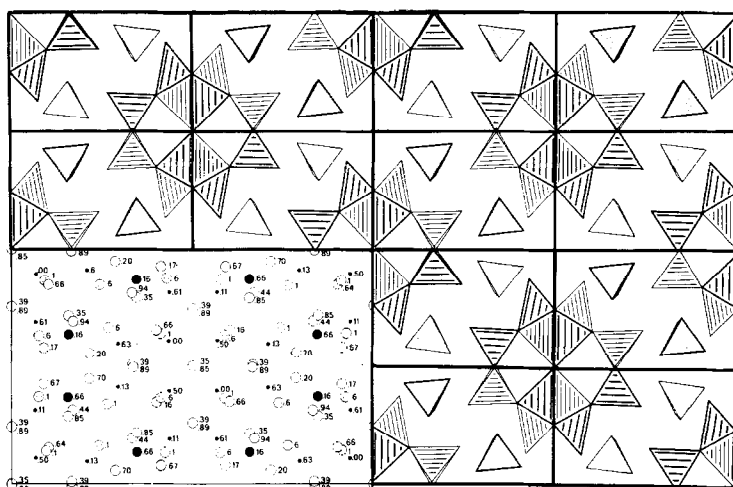
FIG. 9. A projection of the structure of $Sb_6O_7(SO_4)_2$ onto the (001) plane. The figures indicate the z coordinates Large open circles indicate oxygen atoms, large open circles with two dots are lone pair of electrons of antimony, small black circles indicate antimony atoms, and large black circles are sulfur atoms. The relative heights of the different SbO_3E tetrahedra and sulfate tetrahedra (shaded) are indicated by the thickness of the lines. The twin planes are heavily drawn.

moved into the polyhedron. The P atom can be said to substitute approximately for a nickel atom. The polyhedron becomes rather flat—this is compensated for by the fact that this hexagon face is capped by two Ni atoms belonging to other identical polyhedra. The total coordination number of Ni around P is thus 10. The structure is drawn in Fig. 8, and the particular polyhedron described here is shaded. This structure is an example of a chemical fourling without twin planes but with a fourling axis in the center of the figure perpendicular to the (001) plane.

A more complex example of chemical fourlings of *hcp* is found in the structure of $Sb_6O_7(SO_4)_2$ (*33*). Figure 9 shows how the two twin planes, which are glide mirror planes in this structure, divide the unit cell into four units. Each fourling unit consists in its turn of a left and a right half, containing distorted hexagonally close packed oxygens and lone pair of electrons (E) of antimony. The *hcp* part in each fourling unit is repeated in the center of the unit cell by the symmetry of the twin planes to give a cylindrically unit of SbO_3E-tetrahedra. Besides this cylindrical unit, the intersection line of the twin planes contains an empty distorted cube.

Chemical Fourlings of Square Antiprism Strings

In the present section our intention is to illustrate how the same twin unit can be found in a sequence of compounds but with the difference that the intersection line of the twin planes contains coordination polyhedra of different sizes. For this purpose we choose a chemical fourling unit which contains a string of face-sharing square antiprisms. The square antiprism is a common coordination polyhedron in alloys. Such strings of square antiprisms can be repeated by the chemical fourling mechanism in several ways.

In the structure of $CuAl_2$ (*34*), which is isostructural with more than 40 binary phases, the strings of square antiprisms share edges with each other (cf. Fig. 10). The coordination polyhedron generated in the center of the chemical fourling is an empty tetrahedron of the structure type of $CuAl_2$. Filling this tetrahedron produces the structure type of SeTl (*35*). This type of structure also could be considered as a chemical fourling with the same twin unit as the structure type of $CuAl_2$.

The structure of $NbTe_4$ (*36*) could be described as a $CuAl_2$-type of structure which

has half of the square antiprism strings empty (compare Figs. 10 and 11). In another way, it also could be seen as a chemical fourling with the same twin unit as before and with a somewhat large and empty square antiprism in the intersection line of the twin planes (here glide mirror planes).
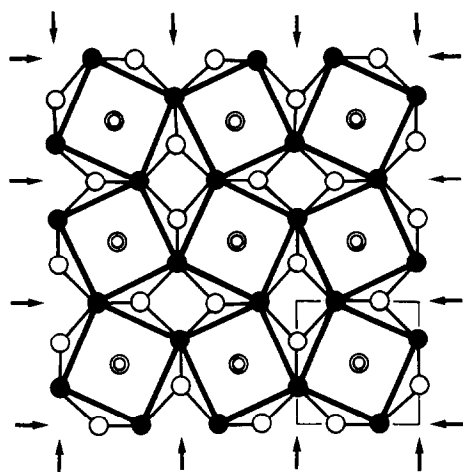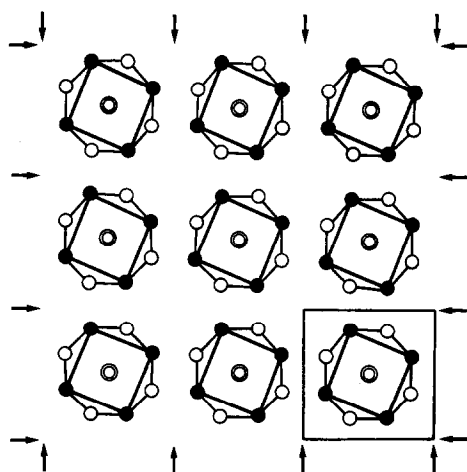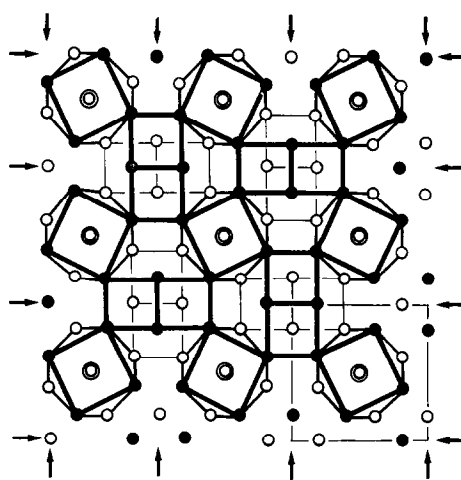

FIG. 10. A projection of the structure of $CuAl_2$ onto the (001) plane. Double rings indicate copper atoms on $z = \frac{1}{4}$ and $z = \frac{3}{4}$. Open and filled circles represent aluminium atoms on $z = 0$ and $z = \frac{1}{2}$, respectively.

FIG. 11. A projection of the structure of $NbTe_4$ onto the (001) plane. Double rings represent niobium atoms on $z = \frac{1}{4}$ and $z = \frac{3}{4}$. Open and filled circles represent tellurium atoms on $z = 0$ and $z = \frac{1}{2}$, respectively.

FIG. 12. A projection of the structure of MnU_6 onto the (001) plane. Double rings represent manganese atoms on $z = \frac{1}{4}$ and $z = \frac{3}{4}$. Open and filled circles represent uranium atoms at $z = 0$ and $z = \frac{1}{2}$, respectively.

In the former section we discussed the structure type of Ti_3Sb as a chemical fourling of *hcp* with one setting of the twin planes (cf. right part of Fig. 6). The other possible setting of twin planes (cf. left part of Fig. 6) produces a fourling unit containing the string of square antiprisms. The large tetrahedra of antimony atoms form strings in the center of the chemical fourling, which in a way could be considered as a string of cubic close packings, and are occupied by titanium atoms.

Instead of a narrow column of *ccp* as in the structure of Ti_3Sb it is possible to insert a larger column of *ccp* as into the structure of MnU_6 (*37*) (cf. Fig. 12). Also, in this structure the fourling unit is a string of square antiprisms with the manganese atoms in their centers and the uranium atoms in the somewhat distorted *ccp* framework.

Conclusion

Chemical fourling on the unit-cell level as a structure-building operation is introduced here as a method of classification, description, organization, and understanding of structures. Our intention has been to present a few examples of structures which can be described

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