THE FEDOROV GROUP (D\textsubscript{4h}) AS A GENERIC INDEX
OF A FAMILY OF CRYSTAL STRUCTURES
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In a Fedorov group with a large number of symmetry elements not containing translation components, there occur many particular positions, and around each of these is a "forbidden" zone, the free space for accommodating atoms in general positions thus being reduced to a minimum. As a result solved structures with a not very large number of parameters are greatly simplified, and, furthermore, these appear to be very close to one another, it being frequently possible to obtain one from another by the regular removal or insertion of certain atoms. These regularities are considered within the framework of the extremely widespread group D\textsubscript{4h} = P6\textsubscript{3}/mmc, to which such structures as hexagonal and topaz close packing, a number of intermetallic compounds, in particular Laves phases, etc., are subordinate.

In 1926 occurred the great sensation of the deciphering by Bragg and West [1] of the structure of beryl Be\textsubscript{2}Al\textsubscript{4}[Si\textsubscript{6}O\textsubscript{18}]. Despite the large number (88) of atoms in the unit cell, the structure was solved almost in one stroke. On account of the old (holohedral) Fedorov group D\textsubscript{4h} = P6/mcc, there was such a large number of overlapping symmetry elements and corresponding forbidden zones in the hexagonal cell that the atoms had simply nowhere to go but certain strictly determined positions. For very high symmetry and small numbers of different sorts of atoms, these have to be placed in a small selection of special positions with corresponding multiplicities. If any high symmetry group is subscribed to by a series of structures with small numbers of atoms, then, for a limited assortment of "special" positions without parameters, it is easy to visualize that some structures are "derived" from others as a result of the insertion of additional atoms into the earlier analyzed structure or, conversely, the removal of "excess" atoms from the latter. In the P6/mcc beryl group there are some few structures, but a large number of them fall under another holohedral group D\textsubscript{4h} = P6\textsubscript{3}/mcc, and here the operations of insertion and removal are demonstrated especially clearly.

Figure 1 reproduces the arrangement of space group D\textsubscript{4h} = P6\textsubscript{3}/mmc. For a multiplicity 24 of the general position points, the particular points with maximum symmetry 12 lie in particular points of the mirror \(\hat{6}\)-axis and inversion \(\hat{6}\)-axis. Only the former are multiplied (by translations) according to the six-fold axis law, so that the cell only contains two \(\hat{6}\) positions (their symmetry is increased to \(\hat{6}m\) owing to the vertical mirror planes passing through the \(\hat{6}a\)-axis), while there are three pairs of the special points \(\hat{6}\) (the vertical \(m\) also increase their symmetry to 12-fold, \(\hat{6}m2\)).

The best-known structure with symmetry group D\textsubscript{4h} is the hexagonal close-packed (two-layer) with two atoms in the cell, their positions being established from the simplest data with as little uncertainty as the Na and Cl in the structure of rock salt. A single pair of atoms cannot fall either at \(\hat{6}m\) points or at those \(\hat{6}m2\) points which lie on the \(\hat{6}a\)-axis, since this would create in the cell four horizontal mirror planes, halving the period along the \(c\) axis. The two atoms must be situated at the...
Fig. 2. Structure of graphite. On the horizontal mirror planes (levels \( \frac{1}{4} \) and \( \frac{3}{4} \)) are two pairs of crystallographically nonequivalent carbons, one on the \( \frac{6}{3} \) axes and the other on the \( \frac{3}{3} \) axes. The cell origin is in the center of symmetry (6) at level 0, where there is no atom (a - primitive cell; b - minimum, reflecting symmetry).

Fig. 3. Structure of americium: four-layer ("topaz") dense packing with crystallographically nonequivalent atoms in the symmetry centers at levels 0 and \( \frac{1}{2} \) and in the horizontal mirror planes at levels \( \frac{1}{4} \) and \( \frac{3}{4} \).

Fig. 4. Two aspects of the structure of NiAs (FeS); a) prisms formed from 6 As around an As are marked out; b) octahedra formed from 6 As around Ni. The Ni atoms are at the centers of symmetry, the As atoms in the mirror (horizontal) planes.

Intersections of the symmetry planes with the two ternary axes of the cell, i.e., in \( (\frac{2}{3}, \frac{1}{3}, \frac{2}{3}, \frac{1}{3}, \frac{2}{3}, \frac{2}{3}) \) or \( (\frac{1}{3}, \frac{2}{3}, \frac{1}{3}, \frac{2}{3}, \frac{1}{3}, \frac{2}{3}) \). Clearly, the choice of one pair or the other is immaterial.

If the cell contains two pairs of chemically identical but not crystallographically identical atoms, then these two pairs cannot simultaneously be disposed at two pairs of points on the ternary axes, for in that case the vertical translation would be shortened by a factor of two. One pair necessarily falls on the \( \frac{6}{3} \) axis (through the origin of coordinates), and two cases are possible. The first case is when here also the atoms lie at a pair of positions 6. This is the structure of graphite with all the atoms in two horizontal mirror planes (Fig. 2).

As we know, a physical analog (in respect of lubricating properties) of graphite is molybdenite MoS\(_2\). If, in this, in accordance with [2], Mo is assigned valence 2 and the two sulfur atoms are united in an S\(_2\) dumbbell, then in the MoS\(_2\) structure the Mo atoms occupy the pair of positions 6 on the \( \frac{6}{3} \) axis, and the S\(_2\) dumbbells (or their centers) the pair of positions \( \frac{6}{3} \) on the ternary axes. Thus, MoS\(_2\) is also a crystallographic analog of graphite.

The other case is when the second pair of atoms (on the \( \frac{6}{3} \)-axis) is situated at points 6, and then all four atoms are disposed on different levels. If the atoms have the same radius and the distances between them are the same, then we have a four-layer dense packing ABAC . . . = chch . . . , which is realized as such in the structure of metallic americium (Fig. 3).

For different pairs of atoms, structures of the NiAs type are formed with the Ni atoms in 6 (on the \( \frac{6}{3} \)-axes) and As atoms at points \( \frac{6}{3} \) (on the 3-axes). If we assign the Ni atoms larger radius than the As ("atomic" radii), we shall speak (Fig. 4a) of the prismatic coordination of the As among six Ni. If the large radius ("ionic") is fixed for the As atoms, then we obtain dense hexagonal (two-layer) packing of the As atoms, all the octahedral vacancies of this containing Ni "cations" (Fig. 4b).

After making the two sorts of crystallographically nonidentical atoms in the americium structure "physically" equivalent in a single four-layer dense packing, we may in this also separate out octahedra, four to the cell (which of course are all crystallographically identical as well). Populating these with cations, we arrive at the TiAs structure (Fig. 5) and the analogous Ta\(_3\)MnN\(_4\) [3]. In the latter the pair of positions \( \frac{8}{3} \) are occupied by the Ta, and in the pair of positions \( \frac{6}{3} \) we have Ta + Mn distributed statistically and all the octahedral vacancies occupied by N atoms.