# The Origin of the Crystallographic Pedigree 

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#### Abstract

The origin of the crystallographic pedigree [Haisa (1978). Acta Cryst. A34, 753-759] is shown to be the $F m 3 m$ family, by examining crystal structures of chemical elements and compounds. The family is maintained by making the most of the relevant symmetry sites over the structures of $a$ (Strukturbericht $A 1)$, $a b(B 1), a c(C 1), a b c\left(L 2_{1}\right), a b d, a e, a b e, a c e$ $\left(J 1_{1}\right)$, abce ( $J 2_{1}$ ), abcde, bcef ( $D 8_{9}$ ), abcef ( $H 5_{8}$ ), cdf, $b d e f\left(D 8_{a}\right), a b d e f, \operatorname{acefh}\left(D 8_{4}\right), a i\left(D 2_{f}\right), a b c g j, a b d f k$ and abcejl types in Wyckoff notation. The descent in site symmetry from $O_{h}$ to its subgroups may be caused by the balance of the interactions between the neighbors of atomic contents which can be estimated from the lifting of the degeneracy of the nearest-neighbor distances, or the coordination index. When the interactions become out of balance, a descent of the space group through $\operatorname{Pm} 3 m$, $\operatorname{Im} 3 m$ and $P 6_{3} / m m c$ to their subgroups occurs to form the crystallographic pedigree.


## 1. Introduction

Why the observed crystal structures exist is a fundamental problem of crystal chemistry, of which the first problem to be solved is why the observed crystal structures are not uniformly distributed among the 230 space groups but are concentrated on the particular space groups. This must be explained in terms of physical interactions between the atomic contents of the crystal. The theory of crystallographic pedigree (Haisa, 1978) has been proposed in order to throw light upon this problem on the basis of the principle of symmetry by unifying the concept of superposition of symmetries in crystal physics (Curie, 1884) and of morphotropism in crystal chemistry (Goldschmidt, 1929).

## 2. Space group as a faithful representation of crystal structure

The possible highest symmetry of the atomic contents would be $K_{h}-\infty / \infty / \mathrm{mmm}$ for a free atom with closed
shells. At a first approximation the perturbing influence of a crystalline environment is small enough to make it worthwhile to consider the free atom or ion as a starting point. When a free atom or ion is placed in a crystal lattice, the energy levels are split by its crystalline environment (Bethe, 1929). According to the Curie principle of superposition of symmetries, the group of symmetries of two or more objects, regarded as a whole, is the highest common subgroup of the symmetry groups of these objects. The subgroups of $K_{h}$ are the Curie ultimate symmetry groups as shown with rectangles in Fig. 1.
A crystal structure can be faithfully represented by a space group $S$ which is the full group of operations of


Fig. 1. Subgroup relations between the ultimate symmetry groups (enclosed within rectangles) and the crystallographic point groups. The $n$ stands for 6, 4 and 2 .
type $\{R \mid t\}$, rotation $R$ followed by translation $t$ (Seitz, 1935). We shall briefly designate $S=(\mathbf{R} / \mathbf{t})$ where $\mathbf{R}$ and $t$ are the set of rotational and translational operators respectively. These operators bring the crystal (i.e. atomic contents and space lattice) into self-coincidence (McWeeny, 1963). The rotation axis $n=\infty$ in $K_{h}$ is self-limited to be $n=6,4,3,2$ or 1 in $\mathbf{R}$ and then the 32 crystallographic point groups are realized as shown in Fig. 1. Every space group $S$ has a set of pure translations $\{E \mid t\}$, which forms an invariant subgroup $T$ of the space group $S$. This is simply the group of the translational operations of the Bravais lattice on which the crystal is based. The derivation of all possible space groups amounts to a systematic study of the reduction of the holohedry of each type of the 14 Bravais lattices to its subgroups, by the insertion of symmetrical contents in the lattice cells.

## 3. The crystallographic pedigree

We shall now rephrase the morphotropism by Paul von Groth (Goldschmidt, 1929) so as to include both isomorphism and polymorphism collectively as follows. Even if the physical (e.g. temperature or pressure) conditions or the chemical (e.g. atom or group) substitutions change the point group $G$ of the atomic contents to a new one $G^{\prime}$ which should be a subgroup or supergroup of $G$, so long as the space group $S$ remains the same, the same symmetry principle does determine the new crystal structure. This may be called the extended isomorphism or homomorphism. In other words, the change of $G$ to $G^{\prime}$ will be completely balanced by the change of the site symmetry $H$ to $H^{\prime}$ which are the subgroups of $\mathbf{R}$ in $S=(\mathbf{R} / \mathbf{t})$ as tabulated with Wyckoff's notation in International Tables for X-ray Crystallography (1969).

On the other hand, if the change of $G$ to $G^{\prime}$ does not allow the compatibility in ( $\mathbf{R} / \mathbf{t}$ ) to be maintained, then $S=(\mathbf{R} / \mathbf{t})$ passes into a new $S^{\prime}=\left(\mathbf{R}^{\prime} / \mathbf{t}^{\prime}\right)$. This may be called the extended polymorphism or heteromorphism. According to Hermann (1929), the transformations from $S$ to $S^{\prime}$ may be classified as the klassengleiche ( $k$ ) and the zellengleiche ( $z$ ) according as $\mathbf{R}^{\prime}=\mathbf{R}$ and $\mathbf{t}=\mathbf{t}^{\prime}$.

The restriction of the highest rotation axis $n=6$ in $\mathbf{R}$ results in the two geneses of symmorphic space groups, cubic $O_{h}^{1}-P m 3 m$ and hexagonal $D_{6 h}^{1}-P 6 / \mathrm{mmm}$ according as they adopt an improper and a proper rotation of order 6, that is, $S_{6}=C_{3 i}-3$ and $C_{6}-6$. All the other space groups can be derived from them by way of the $k$ and $z$ subgroups as illustrated in Fig. 2, where only the physically favourable routes are depicted by thick arrows directed to the $k$ subgroups and by thin arrows directed to the $z$ subgroups. The dashed arrow indicates the switching of $D_{3 d}$ into $D_{3 h}$ and connects the two
geneses of the observed crystal structures as discussed below. Some intricate routes are omitted for the sake of clarity.

The replacement of the primitive translations of the symmorphic space groups by the subtranslations, $t=$ $1 / n$ for the rotation $n$ and $t=1 / 2$ for the reflection $m$, gives rise to the asymmorphic space groups. These subtranslations play an important role in the pedigree and remove the severe conditions imposed by the pure rotation and reflection by increasing the number of adjustable coordinates of the atomic contents in the cell. In fact, they are frequently realized in the observed crystal structures as the screw, glide operations and $C$, $I$ or $F$ centering. Thus, the subtranslation facilitates the closer packing of the lower-symmetric atomic contents and the favourable arrays of dipoles and multipoles, but is accompanied by the descent of the higher $H$ to the lower $H$. This is an important factor of the preferential occurrence of the particular space groups of the crystal structures and hence the existence of the crystallographic pedigree.

## 4. Two geneses of the observed crystal structures

The physical requirement of the occurrence of two geneses of observed crystal structures is originated


Fig. 2. Main routes of the crystallographic pedigree. Thick and thin arrows are directed to the $k$ and $z$ subgroups respectively.

Table 1. Two geneses of observed crystal structures

| Substance | Cubic form | $(F m 3 m)$ | Hexagonal form | $\left(P 6_{3} / m m c\right)$ |
| :--- | :--- | :--- | :--- | :--- |
| Noble gases | He Ne Ar Kr Xe | $F m 3 m$ | He Ne Ar | $P 6_{3} / m m c$ |
| CaSr | low-temp. form | $F m 3 m$ | high-temp. form | $P 6_{3} / m m c$ |
| Zr Hf | high-temp. form | $I m 3 m$ | low-temp. form | $P 6_{3} / m m c$ |
| C | diamond | $F d 3 m$ | graphite | $P 6_{3} / m m c$ |
| SiC | $\beta$ form | $F \overline{4} 3 m$ | $\alpha$ form | $P 6_{3} m c$ |
| BN | borazon | $F \overline{4} 3 m$ | ordinary form | $P 6_{3} / m m c$ |
| ZrP | $a$ form | $F m 3 m$ | $\beta$ form | $P 6_{3} / m m c$ |
| ZnS | zinc blende | $F \overline{4} 3 m$ | wurtzite | $P 6_{3} m c$ |
| AgI | $\gamma$ form | $F \overline{4} 3 m$ | $\beta$ form | $p 6_{3} m c$ |
| $\mathrm{OH}_{2}$ | cubic ice | $F d 3 m$ | hexagonal ice | $P 6_{3} / m m c$ |
| $\mathrm{SiO}_{2}$ | cristobarite | $F d 3 m$ | tridymite | $P 6_{3} / m m c$ |
| $\mathrm{Al}_{2} \mathrm{O}_{3}$ | $\gamma$ corundum | $F d 3 m$ | $\beta$-corundum | $P 6_{3} / m m c$ |
| $\left(\mathrm{CH}_{2} \mathrm{CH}_{2}\right)_{3} \mathrm{~N}_{2}$ | phase I | $F m 3 m$ | phase II | $P 6_{3} / m$ |

from the closest packing of the like spheres with $G=$ $K_{h}$. The symmetry of the closest-packed layer is $D_{6 n}$ about each sphere and $C_{3 v}$ about each void. The stacking of the layers is efficiently realized by adoption of $G=D_{3 d}$ and $D_{3 h}$ which are subgroups of $D_{6 h}$ and yet supergroups of $C_{3 p}$, their adoption being called $c$ and $h$ stackings respectively by Belov (1939). Their infinite succession results in $O_{h}^{5}-F m 3 m$ and $D_{6 h}^{4}-P 6_{3} / m m c$ respectively, as exemplified by some polymorphs of chemical elements and compounds in Table 1.

## 5. The coordination index

In order to infer the reduction of $G$ from $K_{h}$ to its subgroups we shall now introduce the coordination index $\lambda$ defined as

$$
\lambda=\sum_{j}\left(d_{1} / d_{j}\right)^{6},
$$

where $d_{i}$ is the distance to the $j$ th nearest neighbor and the summation is taken over $d_{i} / d_{1}$ less than 1.40 . The limit of $d_{j} / d_{1}$ is chosen from the fact that the structure-sensitive interactions are rapidly diminished with increasing $d_{j} / d_{1}$ and hence the larger $d_{j} / d_{1}$ shows no significant contribution to the interactions. For example, the structure-determinative quadrupolequadrupole interactions decrease with $d_{j}^{-10}$, and the familiar van der Waals interactions decrease with $d_{j}^{-6}$. Thus, the coordination index $\lambda$ may be considered to be a measure of the effective coordination number expressed in the unit of the van der Waals potential between the neighboring atoms and can be computed from the atomic coordinates by X-ray structure analysis.

The genuine closest-packed Fm 3 m structure has the largest $\lambda=12,12$-fold degeneracy of $d_{1}$, corresponding to $G$ of the cuboctahedron (Wells, 1975). The lifting of this degeneracy begins with the $P 6_{3} / \mathrm{mmc}$ structure, where the degeneracy is lifted to sixfold $d_{1}$ and sixfold $d_{2}$. Only when $d_{2}=d_{1}$ with $c / a=\sqrt{8 / 3}$, since the interatomic distance $a$ within the hexagonal layer is associated with the distance $\left(a^{2} / 3-c^{2} / 4\right)^{1 / 2}$ between the successive layers, the structure being closest packed with $G=K_{h}$ and $\lambda=12$. However, the
$c / a$ deviates generally from $\sqrt{8 / 3}$, the $d_{2} / d_{1}$ increases from unity, and the $\lambda$ decreases from 12, according to the increasing distortion of $G$ from $K_{h}$ to its subgroups $D_{3 d}$ and $D_{3 h}$, corresponding to $G$ of the twinned cuboctahedron.

On the other hand, the $d_{2} / d_{1}$ of the $\operatorname{Im} 3 m$ structure is fixed to be $2 / \sqrt{3}=1 \cdot 154$, which gives a fixed $\lambda=10 \cdot 5$, corresponding to $G$ of the truncated cuboctahedron. This value is close to the weighted coordination number $Z^{*}=10.2$ proposed by O'Keeffe (1979) which has been derived from the Voronoi polyhedron (Carter, 1978). Thus, in a similar way to the lifting of the degeneracy of the energy levels of wave functions of atoms, the nearest-neighbor distances $d_{j}$ may be lifted in degeneracy with increasing interactions between neighbors in the crystal. The spacing between the $d_{2}$ and $d_{1}$ is variable for $P 6_{3} / m m c$ while it is fixed for $\operatorname{Im} 3 m$ as shown in Fig. 3.

## 6. Crystal structures of noble gases and metals

It is relevant to consider the crystal structures of noble gases as the most original structure from the Unsöld theorem. The noble gases have closed shells and behave as monoatomic molecules, showing a strong repulsion between the neighbors. Because of the central repulsive forces, the $G$ should be nearly $K_{h}$ and the crystal structure would be of the closest-packed structure of like spheres. In fact all the noble gases crystallize at high pressure into Fm 3 m , where the sites $4(a) O_{h}$ are occupied by monoatomic molecules and $d_{1}$ is 12 -fold degenerated with $\lambda=12$ as shown in Table 2. It is noted that the value of $d_{1}$ is much larger than that expected from the radius $r_{0}$ of the principal maximum of the outermost orbital by Waber \& Cromer (1965), indicating the effect of the strong repulsion. Thus, the effective $G$ of the noble gases seems to be near $K_{h}$ rather than $O_{h}$ as has been discussed by Henshaw (1958). The isotopes ${ }^{3} \mathrm{He}$ and ${ }^{4} \mathrm{He}$ crystallize only under higher than $2.5 \mathrm{~atm}(0.27 \mathrm{MPa})$ and transform from Fm3m through $P 6_{3} / m m c$ with $c / a=1.597$ and 1.634


Fig. 3. Lifting in the degeneracy of the nearest-neighbor distances for the $\operatorname{Fm} 3 m$ (f.c.c.), $P 6_{3} / m m c$ (h.c.p.) and $\operatorname{Im} 3 m$ (b.c.c.) structures.
respectively into $\operatorname{Im} 3 m$ with $a=3.963$ and $4.11 \AA$ with decreasing pressure (Schuch \& Mills, 1963). This corresponds to the decreasing $\lambda$. Ne and Ar transform into $P 6_{3} / m m c$ with $c / a=1.633$ (Barrett \& Meyer, 1964). These facts indicate that an application of a strain or perturbation may reduce the crystal symmetry from the original Fm 3 m to either $\mathrm{P6}_{3} / \mathrm{mmc}$ by switching of $D_{3 d}$ to $D_{3 h}$ or $\operatorname{Im} 3 m$, a subgroup of $F m 3 m$, and that the symmetry of the atoms in the crystal must be reduced and a certain degeneracy should be partially lifted.
Such a tendency develops also in the crystal structures of the metals with low electronegativity $x$ (Allred \& Rochow, 1958; Little \& Jones, 1960) as shown in Table 3. It is noted that the values of $d_{\mathrm{LI}} / d_{\mathrm{IF}}$ are close to $\left(\lambda_{I} / \lambda_{F}\right)^{1 / 6}=0.978$.
Transitions among these three structures have been discussed by Altmann, Coulson \& Hume-Rothery (1957) based on the bond hybrids, and by Johansson \& Rosengren (1975) based on the generalized phase diagram, and by many other authors. According to the pseudopotential theory (Heine \& Weaire, 1970), the structure-sensitive energy consists of the Ewald electrostatic energy $U_{E}=-\alpha Z^{2} e^{2} / 2 r_{a}$ and the bandstructure energy $U_{b}$, where the $r_{a}$ is the atomic radius in the crystal (Slater, 1964). $\alpha$ has been estimated to be 1.79175 for $\mathrm{Fm} 3 \mathrm{~m}, 1.79168$ for $\mathrm{Pb}_{3} / \mathrm{mmc}, 1.79186$ for $\operatorname{Im} 3 \mathrm{~m}, 1.77464$ for $P 6 / \mathrm{mmm}$ and 1.76012 for Pm 3 m . Accordingly, the metals with $x=1.1$ to 1.7 crystallize into two or one of these first three as seen from Table 4, their coordination indices ranging between 12 and 9.3. Table 4 shows the descent from the Fm 3 m structure which is indicated by the lattice constant $a$ in $\AA$ to four figures (Schubert, 1974) to the subgroup structures indicated by the highest space groups adopted. We shall call such a table 'the pedigree table'.

Table 2. The values of nearest-neighbor distances $d_{1}$ and atomic radii $r_{0}$ for noble gases

|  | $a(\AA)$ | $d_{1}(\AA)$ | $r_{0}(\AA)$ | Reference |  |
| :--- | :--- | :---: | ---: | :--- | :--- |
| He | 4.242 at 19 K | 3.000 | $0.291(1 s)$ | Schuch \& Mills (1963) <br> Ne | 4.429 |
| 4.2 | 3.132 | $0.354(2 p)$ | Henshaw (1958) |  |  |
| Ar | 5.256 | 4.2 | 3.717 | $0.659(3 p)$ | Henshaw (1958) |
| Kr | 5.721 | 58 | 4.034 | $0.795(4 p)$ | Cheesman \& Soane <br> (1957) |
| Xe | 6.197 | 58 | 4.220 | $0.986(5 p)$ | Cheesman \& Soane <br> $(1957)$ |

## 7. Crystal structures of radioactive and electronegative elements

The radioactive elements which are spontaneously in a high-energy state show a remarkable descent in symmetry from $F m 3 m$ through $\operatorname{Im} 3 m$ to its subgroups as shown in Fig. 4. The Fm 3 m form of Pu is stable between 724 and 592 K , but descends to $\operatorname{Im} 3 m$ and $I 4 / \mathrm{mmm}$ above 724 K and to $F d d d, C 2 / m$ and $P 2_{1} / m$ below 592 K . Po is the only element which adopts the $P m 3 m$ structure and descends to $R \overline{3} m$, a precursor of the chain structure of metallic Se and Te . The Fmmm form of Pa resembles $\gamma \mathrm{Pu}$ (Zachariasen, 1952; Donohue, 1959). The $\beta$ - U has a complicated coordination (Thewlis \& Steeple, 1954) and may be


Fig. 4. Crystallographic pedigree of radioactive elements.

Table 3. Transitions among $\mathrm{Fm} 3 m, P 6_{3} / m m c$ and $\operatorname{Im} 3 m$ structures of some electropositive metals

| Metal |  | Li | Sr | Na | Ca | Pr | Ce | La |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $x$ |  | 0.97 | 0.99 | 1.01 | 1.04 | 1.07 | 1.08 | 1.08 |
| $F m 3 m$ | $d_{1 F}(\AA)$ | 3.114 | 4.302 | 3.783 | 3.932 | 3.649 | 3.637 | 3.754 |
| $P 6_{3} / m m c$ | $d_{1 H}$ | 3.111 | 4.31 | 3.77 | 3.940 | 3.649 | 3.630 | 3.727 |
|  | $d_{2 H}$ | 3.116 | 4.32 | 3.77 | 3.955 | 3.669 | 3.650 | 3.754 |
| $I m 3 m$ | $d_{11}$ | 3.039 | 4.191 | 3.715 | 3.877 | 3.577 | 3.56 | 3.69 |
|  | $d_{21}$ | 3.507 | 4.836 | 4.287 | 4.474 | 4.124 | 4.11 | 4.26 |
| $r_{0}$ |  | 1.586 | 1.836 | 1.713 | 1.690 | 1.942 | 1.978 | 1.915 |
| $r_{a}$ |  | 1.45 | 2.00 | 1.80 | 1.80 | 1.85 | 1.85 | 1.95 |
| $d_{1 H} / d_{1 F}$ |  | 0.976 | 0.974 | 0.982 | 0.986 | 0.980 | 0.979 | 0.982 |

considered to be the prototype of the $\sigma$ phase of intermetallic compounds (Kasper \& Waterstrat, 1956).

Generally speaking, as the $x$ of elements increases, the descent in symmetry to the subgroups of Fm 3 m , $\operatorname{Im} 3 m$ and $P 6_{3} / m m c$ begins with $\operatorname{Sm}(\lambda=11 \cdot 6), \operatorname{Gd}(p)$ $(\lambda=11.6), W(\beta)(\lambda=12$ and 6.4$) \operatorname{Hg}(\alpha)(\lambda=8.6)$, $\operatorname{Hg}(\beta)(\lambda=6 \cdot 1), \operatorname{In}(\lambda=10 \cdot 3), \operatorname{Mn}(\alpha)(\lambda=15 \cdot 5,14 \cdot 9$, 117 and 10.6$), \operatorname{Mn}(\beta)(\lambda=7.9$ and 6.9$)$ as shown in Fig. 5. With increasing $x$, the coordination index decreases through $\lambda=4$ for the diamond structure, $\lambda=3$ for the molecular and layer structure and $\lambda=2$ for the ring and chain structure to $\lambda=1$ for the diatomic molecule structure.

## 8. The Fm 3 m structure with $\mathbf{4 ( a )} \mathrm{O}_{\boldsymbol{h}}$

As seen from Table 4, the basic $F m 3 m$ structure with the atoms in the symmetry sites $4(a) \mathrm{O}_{h}$ is predominantly adopted by noble gases and noble metals and some similar metals to them and is called the $a$ type ( $A_{1}$ type in Strukturbericht).

This structure is maintained by the interstitial compounds $M X_{x}$ with $X=\mathrm{H}, \mathrm{B}, \mathrm{C}$ and N for small $x$, irrespective of the inherent structure of the metal $M$. As $x$ reaches unity, they progressively transform to the $B 1$ type by filling the octahedral interstices $4(b) O_{h}$ and, as $x$ reaches 2 , to the $C 1$ type by filling the tetrahedral interstices 8(c) $T_{d}$ (Rundle, 1948; Pauling, 1947).

Many alloys adopt this structure with randomly occupied $4(a) O_{h}$ by various metals as follows: (Ag, Au ), $(\mathrm{Fe}, \mathrm{Ni}), \quad(\mathrm{Ir}, \mathrm{Os}), \quad(\mathrm{Fe}, \mathrm{Ni}, \mathrm{P}), \quad(\mathrm{Cu}, \mathrm{Al}, \mathrm{Mn}),(\mathrm{Ir}, \mathrm{Os}, \mathrm{Au})$, $\mathrm{AuCu}_{3}, \mathrm{CrIn}_{3}, \mathrm{Tl}_{2} \mathrm{H}_{5}, \mathrm{Zr}_{2} \mathrm{NiAl}_{5}, \mathrm{Zr}_{2} \mathrm{CuAl}_{5}$. $\mathrm{AuCu}_{3}$ descends to $\mathrm{Pm} 3 m$ with $a=3.7527 \AA$ as $\mathrm{Au}_{3} \mathrm{Cu}$ with $a=3.9525 \AA$, while AuCu descends to its subgroup $P 4 / \mathrm{mmm}$ with $c / a=1.3238$ ( $L 10$ type). Cd and Zr themselves adopt $P_{6} / m m c$ and $\operatorname{Im} 3 m$ respectively, whereas their alloys $\mathrm{Cd}_{x} \mathrm{Zr}_{1-x}$ adopt the disordered $A 1$ type up to $x=0.67$.

The $\mathrm{Cu}-\mathrm{Pt}$ alloys maintain the $A 1$ type all over the components ( $a=3.6148$ to $3.9237 \AA$ ), CuPt descends to its subgroup $R \overline{3} m$ ( $L 1_{1}$ type) (Schneider \& Esch, 1944).

The $M_{3} M^{\prime}$ alloys with rare earths $M^{\prime}$ randomly distributed in $4(a) O_{h}$ show the pedigree as shown in Table 5.*

There are many molecules which crystallize in the $A 1$ type with rotationally disordered molecules centered at $4(a) O_{h}$ (e.g. $\mathrm{DCl}, \mathrm{HCl}, \mathrm{HBr}, \mathrm{HI}$ (pseudocubic with $c / a=1.08$ near 100 K , Sándor \& Farrow, 1967), $\mathrm{CD}_{4}$, $\mathrm{CH}_{4}, \mathrm{CCl}_{4}, \mathrm{CBr}_{4}, \mathrm{Cl}_{4}, \mathrm{CMe}_{4}, \mathrm{CMe}_{3} \mathrm{Cl} . \mathrm{CMe}_{3} \mathrm{Br}$,

[^0]Table 4. The Fm 3 m pedigree of chemical elements
(a) Typical elements

| H | $\mathrm{Li}(\mathrm{c})$ | Be | B | C | N | 0 | $\begin{aligned} & \mathrm{H} \\ & P 6_{3} / m m c \end{aligned}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 4.242 | 4.38 | Im3m | $R \overline{3} m$ | Fd $3 m$ | Pa3 | Pm3n | Pm3n |
| Ne | $\mathrm{Na}(c)$ | Mg | Al | Si | P | S | Cl |
| 4.429 | 5.350 | $\mathrm{Pb}_{3} / \mathrm{mmc}$ | 4.050 | Fd3m | Pm3n | $R \overline{3} m$ | Cmea |
| Ar | K | $\mathrm{Ca}(a)$ | Ga | Ge | As | Se | Br |
| $5 \cdot 256$ | Im $3 m$ | $5 \cdot 588$ | Im $3 m$ | $5 \cdot 658$ | R ${ }^{\text {a }}$ m | Fd3m | Cmea |
| Kr | $\mathrm{Rb}(p)$ | $\mathrm{Sr}(\alpha)$ | In | Sn | Sb | Te | I |
| 5.721 | 5.63 | 6.085 | $14 / \mathrm{mmm}$ | Im 3 m | $\mathrm{Pb}_{3} / \mathrm{mmc}$ | $R \overline{3} m$ | Cmea |
| Xe | $\mathrm{Cs}(p)$ | Ba | $\mathrm{Tl}(\beta)$ | Pb | $\mathrm{Bi}(p)$ | Po | At |
| 6.197 | 5.80 | Im3m | 4.851 | 4.950 | 6.354 | Pm3m | - |

(b) Transition elements

| $\mathrm{Sc}(\beta)$ | Ti | V | Cr | $\mathrm{Mn}(\gamma)$ | $\mathrm{Fe}(\gamma)$ | $\operatorname{Co}(\beta)$ | $\mathrm{Ni}(q)$ | Cu | Zn |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $5 \cdot 541$ | Im $3 m$ | Im $3 m$ | 3.68 | 3.863 | 3.647 | 3.544 | 3.524 | 3.615 | $P 6_{3} / \mathrm{mmc}$ |  |
| Y | Zr | Nb (i) | Mo | Tc | Ru | Rh | Pd | Ag | Cd |  |
| Im $3 m$ | Im3m | 4.40 | $4 \cdot 16$ | $\mathrm{Pb}_{3} / \mathrm{mmc}$ | $\mathrm{Pb}_{3} / \mathrm{mmc}$ | $3 \cdot 804$ | 3.891 | 4.086 | $\mathrm{Pb}_{3} / \mathrm{mmc}$ |  |
| * | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg |  |
| $\dagger$ | $\operatorname{Im} 3 m$ | Im3m | Im $3 m$ | $\mathrm{Pb}_{3} / \mathrm{mmc}$ | $\mathrm{Pb}_{3} / \mathrm{mmc}$ | 3.839 | 3.924 | 4.078 | $R \overline{3} m$ |  |
| ${ }^{*} \mathrm{La}(\beta)$ | $\mathrm{Ce}(\mathrm{a})$ | $\operatorname{Pr}(\beta)$ | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho |
| $5 \cdot 296$ | 4.84 | $5 \cdot 161$ | Im3m | Im $3 m$ | Im $3 m$ | Im3m | Im $3 m$ | Im $3 m$ | Im3m | $P 6_{3} / m m c$ |
| Er | Tm | $\mathrm{Yb}(\alpha)$ | Lu |  |  |  |  |  |  |  |
| $\mathrm{Pb}_{3} / \mathrm{mmc}$ | $\mathrm{Pb}_{3} / \mathrm{mmc}$ | $5 \cdot 846$ | $P 6_{3} / m m c$ |  |  |  |  |  |  |  |
| $\dagger \mathrm{Ac}$ | $\mathrm{Th}(\alpha)$ | Pa | U | Np | $\mathrm{Pu}(\delta)$ | $\mathrm{Am}(i)$ | Cm |  |  |  |
| $5 \cdot 311$ | 5.085 | I4/mmm | Im $3 m$ | Im $3 m$ | $4 \cdot 637$ | 4.894 | 4.382 |  |  |  |

$\mathrm{CMe}_{3} \mathrm{COOH}, \mathrm{CMe}_{3} \mathrm{CH}_{2} \mathrm{OH}, \mathrm{CMe}_{2}\left(\mathrm{NO}_{2}\right)_{2}$, adamantane, 2 -adamantanone, 1 -cyanoadamantane, cyclohexane (form I), norbornane dodecafluorocyclohexane, quinuclidine, triethylenediamine (above 351 K ; Nimmo \& Lucas, 1976). These molecules may acquire $O_{h}$ symmetry by the rise of temperature.

It is noted that the $M \mathrm{~F}_{6}$ compounds with $M=\mathrm{S}$, Mo, $\mathrm{W}, \mathrm{Re}, \mathrm{Os}$, Ir and Pt acquire $G=O_{h}$ but descend to $\operatorname{Im} 3 m$ (Siegel \& Northrop, 1966) as the $\mathrm{C}_{2} X_{6}$ compounds with $X=\mathrm{H}, \mathrm{F}, \mathrm{Cl}, \mathrm{Br}$ and Me and $\mathrm{C}_{2} \mathrm{H}_{4}$ and $\left(\mathrm{CH}_{2} \mathrm{CN}\right)_{2}$ do (van Nes \& Vos, 1978).

## 9. The Fm 3 m structure with $4(a) O_{h}$ and $4(b) O_{h}$

The $M X$ compounds with $Z=4, M$ in $4(a) O_{h}$ and $X$ in $4(b) O_{h}$ are called the $a b$ type ( $B 1$ type) and maintained as shown in Tables 6 to 9 . As the temperature is lowered or the pressure increases, $\mathrm{RbF}, \mathrm{RbCl}, \mathrm{CsCl}$, $\mathrm{CsBr}, \mathrm{CsI}$ descend to a subgroup Pm 3 m , as expected from the ratio of radii of $X$ and $M$ ions. The $\mathrm{NH}_{4} X$


Fig. 5. Crystallographic pedigree of electronegative elements. Polymorphs of P are white $(w)$, black $(b)$ amd Hittorf's $(H) . \mathrm{Si}(I I)$ is a high-pressure form. The $m$ stands for metallic and the $g$ stands for graphitic.
halides descend through $\operatorname{Pm} 3 m$ to $P 4 / n m m$ and/or to $P \overline{4} 3 m$ according as the orientation of the $\mathrm{NH}_{4}$ ions is frozen.
The groups $X$ in Table 7 are rotating or disordered in $4(b) . \mathrm{KCN}$ and NaCN descend through Immm to Pmmm with lowering temperature (Rowe, Rush \& Prince, 1977). CsCN descends to $R \overline{3} m$, but TICN to Pm3m.

InTe in Table 8 descends to $14 / \mathrm{mcm}$ (Hogg \& Sutherland, 1976) and $\mathrm{In}_{4} \mathrm{Te}_{3}$ to Pnnm (Hogg \& Sutherland, 1973). MnO is a member with $n=\infty$ of the $\mathrm{Mn}_{n} \mathrm{O}_{n+1}$ compounds which show the following pedigree:
$n=3 \quad 2 \quad 1$
$\begin{array}{lllllllll}F d 3 m & I 4_{1} / a m d & I a 3 & R \overline{3} c & P 6_{3} / m m c & P 4_{2} / m n m & I 4 / m & P b n m .\end{array}$
Schubert (1977) has discussed the morphotropism in $(\mathrm{Ni}, \mathrm{Pd}, \mathrm{Pt})(\mathrm{S}, \mathrm{Se}, \mathrm{Te})$ system on the basis of the two-correlation model.
The solid solutions of CrN and VN in Table 9 maintain the $B 1$ type at room temperature but descend to $\operatorname{Pnmm}$ below a characteristic temperature (Eddine, Bertaut, Roubin \& Pâris, 1977).
$\mathrm{N}_{2} \mathrm{H}_{4} \cdot \mathrm{H}_{2} \mathrm{O}$ with $Z=4, a=6.76 \AA$, rotationally disordered $\mathrm{H}_{2} \mathrm{NNH}_{2}$ in $4(a), \mathrm{O}$ in $4(b)$ descends to $P 3{ }_{1} 21$ with $Z=3, c / a=2.2450$ at 108 K .

The $M_{3} \mathrm{C}$ compounds with $1 \cdot 6 \mathrm{C}$ in $4(a), 4 M$ in $4(b)$, $M=\mathrm{Y}, \mathrm{Sm}, \mathrm{Gd}, \mathrm{Tb}, \mathrm{Dy}, \mathrm{Ho}, \mathrm{Er}, \mathrm{Tm}, \mathrm{Yb}$ and Lu are called the $L 1^{\prime}$ type. $\mathrm{V}_{4} \mathrm{C}_{3}$ crystallizes with $Z=1, a=$ $4 \cdot 149 \AA, \mathrm{~V}$ in $4(a), \mathrm{C}$ deficient in $4(b)$, but the $M_{2} \mathrm{C}_{3}$ compounds descend to $I \overline{4} 3 d$ ( $D 5_{c}$ type) and the $M \mathrm{C}_{2}$ compounds to $14 / \mathrm{mmm}$ ( C 11 type).
$\mathrm{Ag}_{3} \mathrm{~N}$ takes $Z=4 / 3, a=4.378 \AA$, probably statistically distributed N atoms in the octahedral interstices. $\mathrm{PoBr}_{4}$ takes $Z=1, a=5.61 \AA$, 1 Po statistically distributed in $4(a), 4 \mathrm{Br}$ in $4(b)$.

The $M M^{\prime} X_{2}$ compounds with $Z=2, M$ and $M^{\prime}$ randomly in $4(a), X$ in $4(b)$ show a remarkable descent to $R \overline{3} m$ as shown in Table 10.

The $M_{n-1} M^{\prime} X_{n}$ compounds with $M$ and $M^{\prime}$ randomly in $4(a)$ and $X$ in $4(b)$ are $\mathrm{Li}_{2} \mathrm{TiO}_{3}, \mathrm{Na}_{2} \mathrm{CeO}_{3}$, $\mathrm{Na}_{2} \mathrm{PrO}_{3}, \quad \mathrm{Li}_{3} \mathrm{NbO}_{4}, \quad \mathrm{Li}_{3} \mathrm{TaO}_{4}, \quad \mathrm{Li}_{2} \mathrm{Mg}_{3} \mathrm{SnO}_{6}$ and $\mathrm{Na}_{1,9}, \mathrm{Pr}_{0.9}{ }_{9} \mathrm{La}_{0.2} \mathrm{O}_{3}$. Its anti-type is $\mathrm{Nd}_{4} \mathrm{O}_{3} \mathrm{C}$ and $\mathrm{In}_{4} \mathrm{Te}_{3} \mathrm{Sb}$ (Hauck, 1980).

## 10. The Fm 3 m structure with $\mathbf{4 ( a )} \mathrm{O}_{h}$ and $8(c) \mathrm{T}_{d}$

The $M X_{2}$ compounds with $Z=4, M$ in $4(a)$ and $X$ in $8(c)$ are called the $a c$ type ( $C 1$ type) and show the pedigree in Table 11. The $M M_{2}^{\prime}$ alloys with $M$ in $4(a)$ and $M^{\prime}$ in 8(c) show the pedigree in Table 12. The $M_{2} X$ compounds with $X$ in $4(a)$ and $M$ in $8(c)$ are the anti $C 1$ type and show the pedigree in Table 13.

The $M_{n} \mathrm{O}_{2 n-1}$ compounds with $M$ in $4(a)$ and O deficient in 8(c) occur for $\mathrm{Bi}_{2} \mathrm{O}_{3}, \mathrm{~Tb}_{4} \mathrm{O}_{7}$ and $\mathrm{Pr}_{6} \mathrm{O}_{11}$. $\mathrm{Sb}_{2} \mathrm{O}_{3}$ and $\mathrm{As}_{2} \mathrm{O}_{3}$ descend to Fd 3 m .

The MOF compounds with rare earths $M$ in $4(a)$, O and F randomly in $8(c)$ show the following pedigree:

$$
\begin{array}{rlllllll}
M= & \text { Sc } P 22_{1} / a & \text { Y } 5.363 & \text { La } 5.768 & \text { Ce } 5.697 & \text { Pr } 5.644 & \text { Nd } 5.595 \\
& \text { Sm } 5.519 & \text { Eu } R \overline{3} m & \text { Gd } R \overline{3} m & \text { Tb } R \overline{3} m & \text { Dy } R \overline{3} m & \text { Ho } 5.523 \\
& \text { Er } R \overline{3} m & \text { Yb } R \overline{3} m & \text { Ac } 5.943 & \text { Th } 5.68 & \text { Pu } 5.71 & \text { Cf } 5.561 \AA .
\end{array}
$$

The $M M^{\prime} X$ compounds with $X$ in $4(a), M$ and $M^{\prime}$ randomly in $8(c)$ show the pedigree in Table 14.

The $M M^{\prime} X_{4}$ compounds with $M$ and $M^{\prime}$ randomly in $4(a), X$ in $8(c)$ show the pedigree in Table 15.

The $\mathrm{Li}_{2 n-1} M X_{n}$ compounds with $X$ in $4(a), \mathrm{Li}$ and $M$ randomly in 8(c) adopt the superlattices as shown in Table 16.

There are some deficient variants of the C1 type as follows: $\mathrm{Cu}_{5} \mathrm{FeS}_{4}$ with $Z=1, \dot{a}=5.50 \AA, 4 \mathrm{~S}$ in $4(a)$, 5 Cu and 1 Fe in $192(1) C_{1}$ near 8(c) descends to $F d 3 m$ with $Z=8, a=10.94 \AA$ on rapid cooling, and to $R 3 m$ with $Z=3 / 2, c / a=4.897$ on slow cooling, and to $P \overline{4} 2{ }_{1} c$ with $Z=16, c / a=2 \cdot 000$, where the subcell is cubic with $a=5.47 \AA$ (Morimoto \& Kullerud, 1961).

The $M_{n} M^{\prime} \mathrm{O}_{2 n-1}$ compounds with $M$ and $M^{\prime}$ randomly in $4(a)$, O deficient in $8(c)$ are $\mathrm{Zr}_{3} \mathrm{MgO}_{7}$ with $Z=1, a=5.081 \AA$ and $\mathrm{Bi}_{4} \mathrm{MoO}_{9}$ with $Z=4 / 5, a=$ $5 \cdot 654$ A.

The $M \mathrm{Cl}_{6}\left(\mathrm{Me}_{4} \mathrm{~N}\right)_{2}$ compounds with $M=\mathrm{Ce}, \mathrm{Sn}$ and U and $\mathrm{Ni}\left(\mathrm{MeNH}_{2}\right)_{6} \mathrm{I}_{2}$ are the variants of the Cl type.

## 11. The $F m 3 m$ structure with $4(a) O_{h}, 4(b) O_{h}$ and $8(c) T_{d}$

The $M_{2} M^{\prime} M^{\prime \prime}$ alloys, including the Heusler alloys, with $M^{\prime}$ in $4(a), M^{\prime \prime}$ in $4(b), M$ in $8(c)$ are the $a b c$ type ( $L 2_{1}$ type) and show the pedigree in Table 17.

The $M_{3} M^{\prime}$ compounds with $M^{\prime}$ in $4(a), M$ in $4(b)$ and 8(c) show the following pedigree:

| $M=\mathrm{K}$ | Rb | Cs | Cu |
| :---: | :--- | :--- | :--- |
| $M^{\prime}=\mathrm{Sb} 8.493$ | $P 6_{3} / m m c$ | 9.184 | 6.01 |
| Bi 8.805 | 8.989 | $9.310 \AA$ | - |

$\mathrm{Fe}_{3} \mathrm{Al}$ crystallizes with $Z=4, a=5.79 \AA, 4 \mathrm{Fe}$ in $4(a)$, 4 Fe in $4(b), 4 \mathrm{Fe}$ and 4 Al in $8(c)$, while $\mathrm{Cu}_{3} \mathrm{Au}$ descends to $P m 3 m$ with $Z=1, a=3.74$ A.

The $\mathrm{Li}_{2} M M^{\prime}$ compounds with $4 M$ in $4(a)$, 4 Li in $4(b), 4 M^{\prime}$ and 4 Li in $8(c)$ show the pedigree in Table 18.

The ideal form of $\mathrm{BiF}_{3}$ with $Z=4, a=5.853 \AA, \mathrm{Bi}$ in $4(a), \mathrm{F}$ in $4(b)$ and $8(c)$ has been called the $D 0_{3}$ type (Hassel \& Nilssen, 1929), but the actual $\alpha$ form deviates slightly from the $F$ lattice and descends to $P \overline{4} 3 m$ with 8 F in $1(a) T_{d}, 1(b) T_{d}, 3(c) \mathrm{D}_{2 d}, 3(d) D_{2 d}, 4 \mathrm{~F}$ and 4 Bi in $4(e) C_{3 v}$ with $x=0.25$ and 0.74 respectively. Above 473 K , it descends to the $\beta$ form, Pnma, of the $\mathrm{YF}_{3}$ type.

It should be noted that the $\mathrm{Li}-\mathrm{Mg}-\mathrm{Pb}$ alloys maintain the Fm 3 m structure progressively as follows:

| $\mathrm{Mg}_{2} \mathrm{~Pb}$ | $Z=4$ | $a=6.813 \AA$ | Pb in $4(a)$ | vacant in $4(b)$ | Mg in $8(c)$ | (C1 type) |
| :--- | ---: | :---: | :---: | :--- | :--- | :--- | :--- |
| $\mathrm{Li}_{2} \mathrm{MgPb}$ | 4 | 6.781 | Pb | Li | Mg | $\left(L 2_{1}\right.$ type $)$ |
| $\mathrm{Li}_{3} \mathrm{~Pb}$ | 4 | 6.687 | Pb | Li | Li | ( $D 0_{3}$ type). |

The $\mathrm{Pb}_{1-x} \mathrm{Bi}_{x} \mathrm{~F}_{2+x}$ compounds with Pb and Bi randomly in $4(a), \mathrm{F}$ in $8(c)$, excess F in $4(b)$ maintain the Fm 3 m structure over the following range:
$\left.\begin{array}{lllll}x & = & 0 & 0.33 & 0.66 \\ a & = & 5.927 & 5.878 & 5.901\end{array}\right) 5.849 \AA$.
$\mathrm{Mo}_{3} \mathrm{O}$ has $Z=3, a=5.549 \AA$, 3 Mo in $4(a), 6 \mathrm{Mo}$ in $8(c), 3 \mathrm{O}$ in $4(b)$, but $\mathrm{Cr}_{3} \mathrm{O}$ and $\mathrm{W}_{3} \mathrm{O}$ descend to $\mathrm{Pm} 3 n$ (Hägg and Schönberg, 1954).
It is noted that the $M M_{x}^{\prime}$ alloys show an interesting pedigree as given in Table 19.

Mooser \& Pearson (1959) have shown that the descent of normal valence compounds occurs with a remarkably sharp separation in the average principal quantum number versus the electronegativity difference plot.

## 12. Descent in site symmetry to $24(d) D_{2 h}$

$\mathrm{GeCa}_{7}$ takes $Z=4, a=9.45 \AA, \mathrm{Ge}$ in $4(a), \mathrm{Ca}$ in $4(b)$ and $24(d)$ and the $\mathrm{GeCa}_{x}$ compounds show the following pedigree:

$$
x=33 \mathrm{Fd} 3 \mathrm{~m} \quad x=1 \mathrm{Cmcm} \quad x=2 \text { Pnma } .
$$

## 13. Descent in site symmetry to $24(e) C_{4 v}$

$\mathrm{Te}(\mathrm{OH})_{6}$ with $z=4, a=7.85 \AA, \mathrm{Te}$ in $4(a)$ and OH in $24(e)$ descends to $F d 3 c$ with $Z=32, a=15.51 \AA$ (Falck \& Lindqvist, 1978).
$\mathrm{CaPbF}_{6}$ takes $Z=4, a=8.476 \AA, \mathrm{~Pb}$ in $4(a), \mathrm{Ca}$ in $4(b), \mathrm{F}$ in 24(e), but $\mathrm{BaPbF}_{6}$ descends to $R \overline{3} m$ with $Z=3, c / a=1.0094$ and $\mathrm{SrPbF}_{6}$ to $\mathrm{P}_{2} / m m c$ with $Z=1, c / a=0.8599$.

The $M_{2} M^{\prime} X_{6}$ compounds with $Z=4, M^{\prime}$ in 4(a), $M$ in $8(c), X$ in $24(e)$ are called the ace type ( $J 1_{1}$ type) and show the pedigree in Table 20 to 22. The H atoms in $M=\mathrm{NH}_{4}$ occupy $32(f) C_{3 v}$ (Lisher, Cowlam \& Gillott, 1979). $\mathrm{NH}_{4} \mathrm{MnF}_{3}$ descends to $\operatorname{Pm} 3 m$ and $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{MnF}_{5}$ to Pmen.
$\mathrm{K}_{2} \mathrm{SnCl}_{6}$ in Table 21 shows the following pedigree with lowering temperature (Boysen \& Hewat, 1978):
below $\mathrm{Fm} 3 m \mathrm{Sn}$ in $4(a) O_{h} \mathrm{~K}$ in $8(c) T_{d} \mathrm{Cl}$ in $24(e) C_{4 v}$
$\begin{array}{llll}261 \mathrm{~K} \mathrm{P4/mnc} & 2(a) C_{4 h} & 4(d) D_{2} & 4(e) C_{4} \quad 8(h) C_{5} \\ 255 \quad P 2 / c & 2(a) C_{1} & 4(e) C_{1} & 4(e) C_{1} \times 3 .\end{array}$
$\left(\mathrm{NMe}_{4}\right)_{2} \mathrm{PtCl}_{6}$ and $\left[\mathrm{N}\left(\mathrm{CD}_{3}\right)_{4}\right]_{2} \mathrm{PtCl}_{6}$ descend to Fd 3 c but the distortion from $F m 3 m$ is probably small (Mackenzie, Berg \& Pawley, 1980).

The $M\left(\mathrm{NH}_{3}\right)_{6} X_{2}$ compounds with $M$ in 4(a), $X$ in $8(c), \mathrm{NH}_{3}$ in $24(e)$ show the pedigree in Table 23.

The $M_{2} M^{\prime}(\mathrm{CN})_{6}$ compounds with $Z=4,4 M^{\prime}$ in $4(a), 4 M$ in $4(b), 4 M$ deficient in $8(c), 24(\mathrm{CN})$ in $24(e)$ are called the $J 2_{5}$ type as follows:
$M=\mathrm{Cu} \quad M^{\prime}=\operatorname{Cr} \quad 10.24 \quad \mathrm{Mn} 10.16 \quad \mathrm{Fe} \quad 10.00$
$M^{\prime}=\mathrm{Fe} \quad M=\mathrm{Fe} \quad 10.2 \quad$ Co 10.14 Ni 10.02 $\AA$.
The $M_{3} M^{\prime} \mathrm{F}_{6}$ compounds with $M^{\prime}$ in $4(a), M$ in $4(b)$ and $8(c), \mathrm{F}$ in $24(e)$ are called the $J 2_{1}$ type as shown in Table 24. $\mathrm{Cs}_{2} \mathrm{AgAuCl}_{6}$ descends to metastable Pm 3 m form with $Z=1 / 2, a=5.29 \AA$, and to $I 4 / \mathrm{mmm}$ ( $K 7_{6}$ type) with $Z=2, c / a=1.4919$ as $\mathrm{Cu}_{2} \mathrm{Au}_{2} \mathrm{Cl}_{6}$ with $c / a=1.4513$.

The $M_{2} M^{\prime} M^{\prime \prime} \mathrm{O}_{6}$ compounds with $M^{\prime \prime}$ in $4(a), M^{\prime}$ in $4(b), M$ in $8(c), \mathrm{O}$ in $24(e)$ are perovskite-like as shown in Table 25. The variants $M_{2} M^{\prime} M^{\prime \prime} \mathrm{O}_{n} \mathrm{~F}_{6-n}$ are given in Table 26. $\mathrm{Sr}_{3} \mathrm{Fe}_{2} \mathrm{UO}_{\text {, }}$ has $Z=8 / 3, a=8.066 \AA, \mathrm{U}$ and Fe randomly in $4(a)$ and $4(b), \mathrm{Sr}$ in $8(c), \mathrm{O}$ deficient in 24(e).

The $M_{2} M^{\prime} M^{\prime \prime}(\mathrm{CN})_{6}$ compounds with $M^{\prime \prime}$ in 4(a), $M^{\prime}$ in $4(b), M$ in $8(c), \mathrm{CN}$ in 24(e) are shown in Table 27. $\mathrm{Cs}_{2} \mathrm{LiCr}(\mathrm{CN})_{6}$ descends to $P 4 / n m c$ with $Z=2$, $c / a=1.418$, the tetrahedral distortion of $\mathrm{CrC}_{6}$ and $\mathrm{LiN}_{6}$ octahedra having been discussed by Chowdhury, Wedgwood, Chadwick \& Wilde (1977) and by Ryan \& Swanson (1978).

The $M_{3}\left[\mathrm{Co}(\mathrm{CN})_{6}\right]_{2}$ compounds with Co in $4(a), M$ in $4(b)$ and $8(c), \mathrm{CN}$ in 24(e) are as follows:
$M=\operatorname{Co} 10.20 \mathrm{Cu} 9.90 \mathrm{Zn} 9.94 \mathrm{Cd} 10.37 \mathrm{Hg} 10.45 \mathrm{~Pb} 10.44 \AA$.
The $M_{3}\left[\mathrm{Co}(\mathrm{CN})_{6}\right]_{2} \cdot 12 \mathrm{H}_{2} \mathrm{O}$ compounds take $Z=$ $4 / 3,4 \mathrm{Co}^{\text {II }}$ in $4(a), 8 / 3 M^{\text {III }}$ disordered in $4(b), 16 \mathrm{CN}$ in $24(e), 16 \mathrm{H}_{2} \mathrm{O}$ near $8(c)$ and $24(e)$ or 32$) f$ ) for $M$ $=\mathrm{Mn}, \mathrm{Fe}, \mathrm{Co}, \mathrm{Ni}, \mathrm{Zn}$ and Cd .
$\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6} \mathrm{I}_{3}$ with $Z=4, a=10.82 \AA$, Co in $4(a)$, I in $4(b)$ and $8(c), \mathrm{NH}_{3}$ in $24(e)$ descends to $F \overline{4} 3 m$ with $Z=4, a=10.902 \AA$, while $\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6} \mathrm{I}_{2}$ belongs to the $J 1_{1}$ type.
$\mathrm{Li}_{6} \mathrm{NBr}_{3}$ takes $Z=4, a=8.895 \AA, \mathrm{Br}$ in $4(a)$ and $8(c), \mathrm{N}$ in $4(b), \mathrm{Li}$ in $24(e)$, while $\mathrm{Li}_{7} \mathrm{~N}_{2} \mathrm{I}$ descends to $F d 3 m$ with $Z=8, a=10.367 \AA$, and $\mathrm{Li}_{5} \mathrm{NI}_{2}$ descends to $F \overline{4} 3 m$ with $Z=5, a=9.540 \AA$.

The $M_{6} M^{\prime} X_{8}$ compounds with $Z=4, M^{\prime}$ in $4(a), X$ in $8(c)$ and $24(e), M$ in $24(d)$ and vacant $4(b)$ are $\mathrm{Mg}_{6} \mathrm{MnO}_{8}, \mathrm{Cu}_{6} \mathrm{PbO}_{8}$ and $\mathrm{Na}_{6} \mathrm{CdCl}_{8}$ and considered to be the prototype of the $M_{8} \mathrm{C}_{7}$ compounds.

## 14. Descent in site symmetry to $32(f) C_{3 v}$

The $M_{9} X_{8}$ compounds with $Z=4, M$ in $4(b)$ and $32(f), X$ in $8(c)$ and $24(e)$ are $\mathrm{Co}_{9} \mathrm{~S}_{8}, \mathrm{Co}_{9} \mathrm{Se}_{8}$ and $(\mathrm{Fe}, \mathrm{Ni})_{9} \mathrm{~S}_{8}$.
$2 \mathrm{Na}_{2} \mathrm{SO}_{4} \cdot \mathrm{NaCl} . \mathrm{NaF}$ crystallizes with $Z=4, a=$ $10.065 \AA, \mathrm{~F}$ in $4(a), \mathrm{Cl}$ in $4(b), \mathrm{S}$ in $8(c), \mathrm{Na}$ in $24(e), \mathrm{O}$ in $32(f)$.

The $M_{3}\left[M^{\prime}(\mathrm{CN})_{6}\right]_{2} .3 \mathrm{H}_{2} \mathrm{O}$ compounds with $Z=2$, $4 M^{\prime}$ in $4(a), 4 M$ in $4(b), 2 M$ randomly in $32(f), 24 \mathrm{CN}$ in $24(e), 6 \mathrm{H}_{2} \mathrm{O}$ randomly in $8(c)$ occur for $M=\mathrm{Mn}$, $\mathrm{Co}, \mathrm{Ni}, \mathrm{Cu}, \mathrm{Zn}$ and $\mathrm{Cd}, M^{\prime}=\mathrm{Fe}$ and Co .
$\mathrm{Zn}_{3}\left[\mathrm{Co}(\mathrm{CN})_{6}\right]_{2} \cdot 12 \mathrm{H}_{2} \mathrm{O}$ with $Z=4 / 3, a=$ 10.268 A , Co in $4(a), \mathrm{Zn}$ in $4(b), \mathrm{CN}$ in $24(e), \mathrm{O}$ disordered in $8(c)$ and $32(f)$ is isomorphous with the Mn and Cd compounds (Mullica, Milligan, Beall \& Reeves, 1978).
$\mathrm{Cu}_{3} \mathrm{SbS}_{4}$ with $Z=8, a=10.74 \AA$, Sb in $8(c), \mathrm{Cu}$ in $24(d), \mathrm{S}$ in $32(f)$, descends to $F d 3 m$ with $Z=1, a=$ $5.28 \AA$, all atoms being in $8(a) T_{d}$, the metals randomly in $000, S$ in $\frac{111}{44} . \mathrm{Cu}_{3} \vee \mathrm{~S}_{4}$ descends to $P \overline{4} 3 m$ with $Z=1$. $a=5.370 \AA, \mathrm{~V}$ in $1(a) T_{d}, \mathrm{Cu}$ in $3(d) D_{2 d}, \mathrm{~S}$ in $4(e) C_{3 v}$.
$\mathrm{Cu}_{5} \mathrm{FeS}_{4}$ shows the following pedigree:
$\mathrm{Fm} 3 m \quad \mathrm{Fd} 3 m \quad \mathrm{R} 3 m \quad P \overline{4}{ }_{1} c$
$a=5.50 \AA \quad a=10.94 \AA \quad c / a=4.8966 c / a=2.000$.
$\mathrm{Cu}_{12} \mathrm{Fe}_{2} \mathrm{~S}_{9}$ descends to $\operatorname{Pm} 3 m$ with $a=21.87 \AA$, and $\mathrm{CuFeS}_{2}$ to $I \overline{4} 3 m$ with $a=10.605 \AA$ and $I \overline{4} 2 d$ with $c / a=1.9656$.

The $M_{23} M_{6}^{\prime}$ compounds with $Z=4, M$ in $4(b), 24(d)$ and $32(f) \times 2, M^{\prime}$ in $24(e)$ show the pedigree in Table 28. It is noted that $\mathrm{Mg}_{4} \mathrm{Sr}$ and $\mathrm{Li}_{4} \mathrm{Ba}$ descend to $P 6_{3} / \mathrm{mmc}$ with $Z=18, c / a=2.698$ and 0.8064 respectively.

The $M_{16} M_{6}^{\prime} M_{7}^{\prime \prime}$ compounds with $Z=4, M^{\prime \prime}$ in $4(b)$ and $24(d), M$ in $32(f) \times 2, M^{\prime}$ in $24(e)$ in Table 29 and the $M_{15} M_{6}^{\prime} M_{8}^{\prime \prime}$ compounds with $M$ and $M^{\prime \prime}$ in $4(b)$, $24(d), 32(f) \times 2, M^{\prime}$ in $24(e)$ in Table 30 are the variants of the $M_{23} M_{6}^{\prime}$ type.

The $M_{4} M_{11}^{\prime}$ compounds with $Z=8, M$ in $4(a), 4(b)$ and $24(d), M^{\prime}$ in $24(e)$ and $32(f) \times 2$ for $M=\mathrm{Ir}$, Os and $\mathrm{Ru}, M^{\prime}=\mathrm{Sc}, \mathrm{Zr}$ correspond to $M_{16}^{\prime} M_{6}^{\prime} M_{8}$, the variants of the above with occupied 4(a) (Chabot, Cenzual \& Parthé, 1980).

## 15. Descent in site symmetry to $48(g) C_{2 v}, 48(h) C_{2 v}$ and 48(i) $C_{2 v}$

The $M_{23} X_{6}$ compounds with $Z=4, M$ in $4(a), 8(c)$, $32(f)$ and $48(h), X$ in $24(e)$ show the pedigree in Table 31.

The $M \mathrm{~B}_{12}$ compounds with $Z=4, M$ in $4(a), \mathrm{B}$ in 48(i) are maintained for $M=\mathrm{Sc}, \mathrm{Y}, \mathrm{Dy}, \mathrm{Ho}, \mathrm{Er}, \mathrm{Tm}$, $\mathrm{Lu}, \mathrm{Zr}$ and U .
$\mathrm{BaCaLu}_{2} \mathrm{~F}_{10}$ takes $Z=8, a=11 \cdot 366 \AA$, Ba in $8(c)$, Ca and Lu in 24(e), F in $32(f)$ and 48(i) (Védrine, Trottier \& Chevarier, 1979).

## 16. Descent in site symmetry to $96(j) C_{s}$ and $96(k) C_{s}$

$\mathrm{Ba}_{3}\left[\mathrm{Co}\left(\mathrm{NO}_{2}\right)_{6}\right]_{2}$ takes $Z=2, a=10.59 \AA, 6 \mathrm{Ba}$ deficient in $4(a)$ and $4(b), 4 \mathrm{Co}$ in $8(c), 24 \mathrm{~N}$ in $48(g)$, 480 in 96( $j$ ).
$\mathrm{Ag}_{7} \mathrm{NO}_{11}$ takes $Z=4, a=9.890 \AA, \mathrm{Ag}$ in $4(a)$ and $24(d), \mathrm{N}$ in $4(b), \mathrm{O}$ in $32(f)$ and $96(k)$, while $\mathrm{Ag}_{7} \mathrm{~F}_{3} \mathrm{O}_{9}$ takes $Z=4, a=9.842 \AA$ and a more disordered structure.
$\mathrm{Be}_{3} \mathrm{Ca}_{2} \mathrm{O}_{5}$ takes $Z=24, a=14.00 \AA$, Be in $4(b)$ and $32(f) \times 3, \mathrm{Ca}$ in 24(d) and 24(e), O in $8(c), 32(f)$ and 96(k).

## 17. Descent in site symmetry to $192(l) C_{1}$

The $M_{3} M^{\prime} \mathrm{F}_{m} \mathrm{O}_{n}$ compounds with $Z=4,4 M^{\prime}$ in $4(a)$, $12 M$ in $4(b)$ and $8(c), \mathrm{F}$ and O randomly in $24(e), 96(j)$ and $192(1) \times 2$ show the pedigree in Table 32. It is noted that there is a progressive descent for alkali metals $M$ from $M_{2} \mathrm{CoF}_{6}$ (ace type) through $M_{3} \mathrm{CoF}_{6}$ (abce type) to $M_{2} \mathrm{CoF}_{4}(I 4 / \mathrm{mmm})$.

## 18. Conciuding remarks

The electronic structure of the outer shells of atoms must be a controlling factor in deciding which crystal structure is assumed. Noble gases and noble metals have completely filled $s^{2}$ and $p^{6}$ and $d^{10}$ outer shells respectively, and hence $G=K_{h}$. The space groups with the highest site symmetry $H=O_{h}$ are limited to $\operatorname{Pm} 3 m$, $F m 3 m$ and $\operatorname{Im} 3 m$, their lattice points having the coordination indices $\lambda=6,12$ and $10 \cdot 5$ respectively. Thus, the Fm 3 m structure is most favorably close packed by the atomic contents with the highest
symmetry $G=K_{h}$, and hence will be the origin of the crystallographic pedigree. This structure is vastly maintained, firstly by noble gases and metals and even by ionic and molecular compounds as tabulated in the above pedigree tables, which may be summarized in Table 33.

Generally speaking, the point groups $G$ obtained by distortion of a cube or octahedron with $O_{h}$ along any of its symmetry axes are all subgroups of the $O_{h}$, because such an operation reduces the symmetry without introducing anything new. Emphasis must be placed on the facts that all the site symmetries $H$ of the Fm 3 m structure are uniquely determined by the $F 4 / m \overline{3} 2 / m$ symmetry principle to be the subgroups of the $O_{h}$ and that all the types of the $F m 3 m$ family obey faithfully this symmetry principle. In other words, the theory of the crystallographic pedigree is the symmetry principle of the crystal chemistry.

The basic $a(A 1)$ type has $M$ in 4(a) and consists of a regular cuboctahedron $M M_{12}$, the $M-M$ distances being $a / \sqrt{2}$, where $a$ is the lattice constant in $\AA$. This situation is commonly retained in all the Fm 3 m structures. An introduction of $X$ into $4(b)$ as in the $a b$ ( $B 1$ ) type results in the lifting in the degeneracy into the octahedra $M X_{6}$ and $X M_{6}$, the distances $M-X$ being the smaller $a / 2$, accompanying the decrease in $\lambda$. On the other hand, an introduction of $X$ into $8(c)$, as in the $a c$ (C1) type, results in the lifting into the cube $M X_{8}$ and the tetrahedron $M X_{6}$ with $M-X$ distances of $a / 2$. Proceeding to the $a b c\left(L 2_{1}\right)$ type of $M_{2} M^{\prime} M^{\prime \prime}$ with $M^{\prime}$ in $4(a), M^{\prime \prime}$ in $4(b)$ and $M$ in $8(c)$, the lifting into $M M_{4}^{\prime}$

Table 33. Descent in site symmetry of the Fm3m family

* Doubly occupied; - vacant.

| Site |  |
| :---: | :---: |
| Multiplicity |  |
| Point group |  |
| Compound type |  |
| $M$ (element) | A1 |
| MX | $B 1$ |
| M ${ }_{2}$ | C1 |
| $M_{2} M^{\prime} M^{\prime \prime}$ | $L 2_{1}$ |
| $\mathrm{BiF}_{3}$ | $\mathrm{DO}_{3}$ |
| $\mathrm{Mo}_{3} \mathrm{O}$ |  |
| $\mathrm{GeCa}_{7}$ |  |
| $\mathrm{Te}(\mathrm{OH})_{6}$ |  |
| $M M^{\prime} X_{6}$ |  |
| $M_{2} M^{\prime} X_{6}$ | $J 1{ }_{1}$ |
| $M_{3} M^{\prime} X_{6}$ | J2, |
| $M_{6} M^{\prime} X_{8}$ |  |
| $M_{9} X_{8}$ | D8, |
| $M_{3}\left(M^{\prime} X_{6}\right)_{2}$ |  |
| $M_{23} M_{6}^{\prime}$ | $D 8_{1}$ |
| $M_{16} M_{6}^{\prime} X_{7}$ |  |
| $M_{4} M_{11}^{\prime}$ |  |
| $M_{23}{ }^{\text {X }}$ | $D 8{ }_{4}$ |
| $M B_{12}$ | D2 ${ }_{\text {f }}$ |
| $\mathrm{Ba}_{3}\left[\mathrm{Co}\left(\mathrm{NO}_{2}\right)_{6}\right]_{2}$ |  |
| $\mathrm{Ag}_{7} \mathrm{NO}_{11}$ |  |
| $M_{3} M^{\prime} \mathrm{F}_{7}$ |  |


| (a) | (b) | (c) | (d) | (e) | (f) | (g) | (h) | (i) | (j) | (k) | (l) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ) | 4 | 8 | 24 | 24 | 32 | 48 | 48 | 48 | 96 | 96 | 192 |
| $O_{h}$ | $O_{h}$ | $T_{d}$ | $D_{2 h}$ | $C_{4 v}$ | $\mathrm{C}_{3 v}$ | $C_{2 v}$ | $\mathrm{C}_{2 v}$ | $C_{2 v}$ | $C_{s}$ | $C_{s}$ | $C_{1}$ |
| M |  |  |  |  |  |  |  |  |  |  |  |
| M | $X$ |  |  |  |  |  |  |  |  |  |  |
| M | - | $X$ |  |  |  |  |  |  |  |  |  |
| $M^{\prime}$ | $M^{\prime \prime}$ | M |  |  |  |  |  |  |  |  |  |
| Bi | F | F |  |  |  |  |  |  |  |  |  |
| Mo | 0 | Mo |  |  |  |  |  |  |  |  |  |
| Ge | Ca | - | Ca |  |  |  |  |  |  |  |  |
| Te | - | - | - | OH |  |  |  |  |  |  |  |
| $M^{\prime}$ | M | - | .- | $X$ |  |  |  |  |  |  |  |
| $M^{\prime}$ | - | M | - | $X$ |  |  |  |  |  |  |  |
| $M^{\prime}$ | $i_{i}$ | M | - | $X$ |  |  |  |  |  |  |  |
| $M^{\prime}$ | - | $X$ | M | $X$ |  |  |  |  |  |  |  |
| , | M | $X$ | - | $X$ | M |  |  |  |  |  |  |
| $M^{\prime}$ | M | - | - | $X$ | M |  |  |  |  |  |  |
| - | M | - | $M^{\prime}$ | M | $M^{*}$ |  |  |  |  |  |  |
| - | X | - | $X$ | $M^{\prime}$ | $M^{*}$ |  |  |  |  |  |  |
| M | M | - | M | $M^{\prime}$ | $M^{\prime *}$ |  |  |  |  |  |  |
| M | - | M | - | $X$ | M | - | M |  |  |  |  |
| M | - | - | - |  | - | - | - | B |  |  |  |
| Ba | Ba | Co | - | - | - | N | - | - | 0 |  |  |
| Ag | N | - | Ag | - | 0 | - | - | - | - | 0 |  |
| $M^{\prime}$ | M | M | - | F | - | - | - | - | F | - | F* |

and $M M_{4}^{\prime \prime}$ tetrahedra takes place, retaining the other degeneracy. In this way, the descent in symmetry of the $G$ of the atomic contents is reflected in the descent in the site symmetry $H$, accompanied by the lifting in degeneracy of the nearest-neighbor distances. Such a descent is effected by the directional covalent forces, instead of the central forces, between the atomic contents caused by chemical substitution, decreasing temperature or increasing pressure.

If the limit of maintenance of the Fm 3 m structure is surpassed by increasing distortion of the $G$ from $O_{h}$ into its subgroups owing to far stronger and directional


Fig. 6. Crystallographic pedıgree of the $\mathrm{Al}-\mathrm{Zr}$ system.


Fig. 7. Crystallographic pedigree of the $\mathrm{Ti}-\mathrm{O}$ system.
interactions between the neighbors, the descent in space group proceeds through $\operatorname{Pm} 3 m$ and $\operatorname{Im} 3 m$ or $\mathrm{P6}_{3} / \mathrm{mmc}$ to their subgroups to result in the crystallographic pedigree.

Representative examples of alloys, oxides and organics are given in Figs. 6-8, where the original structures consist of closest-packed metallic atoms, regular $\mathrm{TiO}_{6}$ octahedra and spherically disordered organic molecules respectively. In Fig. 8, monoclinic and anorthic systems are omitted for the sake of brevity; as the descent in space group proceeds, the ratio $x / y$ for $\mathrm{C}_{x} \mathrm{H}_{y}$ increases, corresponding to increasing $\pi$-electron nature. Thus, the crystallographic pedigree may serve to classify the crystal structures systematically under the symmetry principle.

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Fig. 8. Crystallographic pedigree of the $\mathrm{C}-\mathrm{H}$ system. The $x / y$ stands for $\mathrm{C}_{x} \mathrm{H}_{y}$. (1) $1 / 45 / 126 / 1210 / 16$, (2) $2 / 42 / 6$, (3) $9 / 16$ $10 / 16$, (4) $2 / 214 / 20$, (5) $2 / 618 / 24$, (6) $12 / 1818 / 16$, (7) $12 / 18$ $18 / 24$, ( 8 ) $8 / 614 / 22$, ( 9 ) $9 / 12$, (10) $8 / 810 / 1018 / 36$, (11) $28 / 34$, (12) $4 / 616 / 16$, (13) $24 / 18$, (14) $28 / 16$, (15) $10 / 1625 / 20$, (16) $18 / 20$, (17) 22/16, (18) 14/12, (19) 12/16 56/40, (20) $8 / 10$, (21) 12/18, (22) 18/24, (23) 22/16, (24 6/10, (25) $21 / 4423 / 48$ $\begin{array}{lllllll}25 / 52 & 27 / 56 & 29 / 60, & \text { (26) } & 18 / 24 \text {, (27) } & 6 / 6 & 12 / 12 \\ 15 / 12\end{array}$ 16/12 16/14 18/16 19/14 20/16 20/18 20/20 20/32 22/14 22/14
 $\begin{array}{llllllll}36 / 24 & 36 / 74, ~(28) & 11 / 8 & 13 / 10 & 14 / 10 & 19 / 12 & 24 / 30 & 30 / 62\end{array}$ $n /(2 n+2),(29) 5 / 1215 / 1016 / 1216 / 2420 / 1620 / 1626 / 16$ $26 / 1636 / 2442 / 24$, (30) $15 / 2819 / 24$, (31) $18 / 16$, (32) $17 / 14$, (33) $14 / 1018 / 12$, (34) $16 / 1417 / 1417 / 1618 / 16 \quad 18 / 1821 / 14$ $22 / 1422 / 1422 / 1842 / 28$, (35) $12 / 10$, (36) $12 / 8$, (37) $26 / 26$ $27 / 28$, (38) $14 / 817 / 18 \quad 18 / 1236 / 74$, (39) $18 / 12$ 18/18 $19 / 16$ $20 / 16$ 24/18 $32 / 2042 / 30$, (40) $7 / 812 / 8$ 28/16, (41) $2 / 414 / 14$ $\begin{array}{llllllllllllll}18 / 12 & 18 / 12 & 18 / 14 & 18 / 14 & 18 / 20 & 19 / 14 & 19 / 16 & 20 / 12 & 20 / 12\end{array}$
 27/44 28/48 28/48 29/50 30/20 30/52 34/24, (42) 8/10 27/48.

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[^0]:    * The pedigree tables 5 to 32 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36661 ( 14 pp .). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

