

Table 1. Two geneses of observed crystal structures

Substance	Cubic form	(<i>Fm3m</i>)	Hexagonal form	(<i>P6₃/mmc</i>)
Noble gases	He Ne Ar Kr Xe	<i>Fm3m</i>	He Ne Ar	<i>P6₃/mmc</i>
Ca Sr	low-temp. form	<i>Fm3m</i>	high-temp. form	<i>P6₃/mmc</i>
Zr Hf	high-temp. form	<i>Im3m</i>	low-temp. form	<i>P6₃/mmc</i>
C	diamond	<i>Fd3m</i>	graphite	<i>P6₃/mmc</i>
SiC	β form	<i>F43m</i>	α form	<i>P6₃/mc</i>
BN	borazon	<i>F43m</i>	ordinary form	<i>P6₃/mmc</i>
ZrP	α form	<i>Fm3m</i>	β form	<i>P6₃/mmc</i>
ZnS	zinc blende	<i>F43m</i>	wurtzite	<i>P6₃/mc</i>
AgI	γ form	<i>F43m</i>	β form	<i>p6₃/mc</i>
OH ₂	cubic ice	<i>Fd3m</i>	hexagonal ice	<i>P6₃/mmc</i>
SiO ₂	crystalbarite	<i>Fd3m</i>	tridymite	<i>P6₃/mmc</i>
Al ₂ O ₃	γ corundum	<i>Fd3m</i>	β -corundum	<i>P6₃/mmc</i>
(CH ₂ CH ₂) ₃ N ₂	phase I	<i>Fm3m</i>	phase II	<i>P6₃/m</i>

from the closest packing of the like spheres with $G = K_h$. The symmetry of the closest-packed layer is D_{6h} about each sphere and C_{3v} about each void. The stacking of the layers is efficiently realized by adoption of $G = D_{3d}$ and D_{3h} which are subgroups of D_{6h} and yet supergroups of C_{3v} , their adoption being called c and h stackings respectively by Belov (1939). Their infinite succession results in O_h^5 - $Fm3m$ and D_{6h}^4 - $P6_3/mmc$ 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 λ defined as

$$\lambda = \sum_j (d_j/d_1)^6,$$

where d_j is the distance to the j th nearest neighbor and the summation is taken over d_j/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 quadrupole-quadrupole interactions decrease with d_j^{-10} , and the familiar van der Waals interactions decrease with d_j^{-6} . Thus, the coordination index λ 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 $Fm3m$ 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 $P6_3/mmc$ 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 $(a^2/3 - c^2/4)^{1/2}$ 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 λ decreases from 12, according to the increasing distortion of G from K_h to its subgroups D_{3d} and D_{3h} , corresponding to G of the twinned cuboctahedron.

On the other hand, the d_2/d_1 of the $Im3m$ structure is fixed to be $2/\sqrt{3} = 1.154$, which gives a fixed $\lambda = 10.5$, 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 $P6_3/mmc$ while it is fixed for $Im3m$ 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 $Fm3m$, 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 ^3He and ^4He crystallize only under higher than 2.5 atm (0.27 MPa) and transform from $Fm3m$ through $P6_3/mmc$ with $c/a = 1.597$ and 1.634

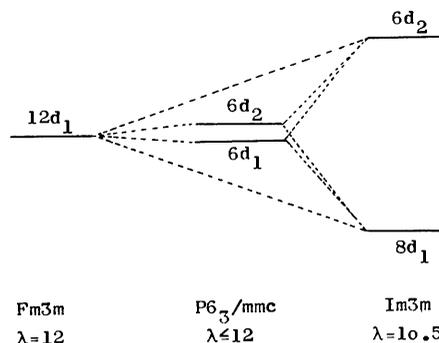


Fig. 3. Lifting in the degeneracy of the nearest-neighbor distances for the $Fm3m$ (f.c.c.), $P6_3/mmc$ (h.c.p.) and $Im3m$ (b.c.c.) structures.

respectively into $Im\bar{3}m$ with $a = 3.963$ and 4.11 \AA with decreasing pressure (Schuch & Mills, 1963). This corresponds to the decreasing λ . Ne and Ar transform into $P6_3/mmc$ 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 $Fm\bar{3}m$ to either $P6_3/mmc$ by switching of D_{3d} to D_{3h} or $Im\bar{3}m$, a subgroup of $Fm\bar{3}m$, 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_{1I}/d_{1F} are close to $(\lambda_I/\lambda_F)^{1/6} = 0.978$.

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 $U_E = -\alpha Z^2 e^2 / 2r_a$ and the band-structure energy U_b , where the r_a is the atomic radius in the crystal (Slater, 1964). α has been estimated to be 1.79175 for $Fm\bar{3}m$, 1.79168 for $P6_3/mmc$, 1.79186 for $Im\bar{3}m$, 1.77464 for $P6/mmm$ and 1.76012 for $Pm\bar{3}m$. 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 $Fm\bar{3}m$ 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 (1s)	Schuch & Mills (1963)
Ne	4.429 4.2	3.132	0.354 (2p)	Henshaw (1958)
Ar	5.256 4.2	3.717	0.659 (3p)	Henshaw (1958)
Kr	5.721 58	4.034	0.795 (4p)	Cheesman & Soane (1957)
Xe	6.197 58	4.220	0.986 (5p)	Cheesman & Soane (1957)

Table 3. Transitions among $Fm\bar{3}m$, $P6_3/mmc$ and $Im\bar{3}m$ 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
$Fm\bar{3}m$	d_{1F} (\AA)	3.114	4.302	3.783	3.932	3.649	3.637	3.754
$P6_3/mmc$	d_{1H}	3.111	4.31	3.77	3.940	3.649	3.630	3.727
	d_{2H}	3.116	4.32	3.77	3.955	3.669	3.650	3.754
$Im\bar{3}m$	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_{1I}/d_{1F}	0.976	0.974	0.982	0.986	0.980	0.979	0.982

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 $Fm\bar{3}m$ through $Im\bar{3}m$ to its subgroups as shown in Fig. 4. The $Fm\bar{3}m$ form of Pu is stable between 724 and 592 K, but descends to $Im\bar{3}m$ and $I4/mmm$ above 724 K and to $Fddd$, $C2/m$ and $P2_1/m$ below 592 K. Po is the only element which adopts the $Pm\bar{3}m$ structure and descends to $R\bar{3}m$, a precursor of the chain structure of metallic Se and Te. The $Fmmm$ form of Pa resembles γ -Pu (Zachariasen, 1952; Donohue, 1959). The β -U has a complicated coordination (Thewlis & Steeple, 1954) and may be

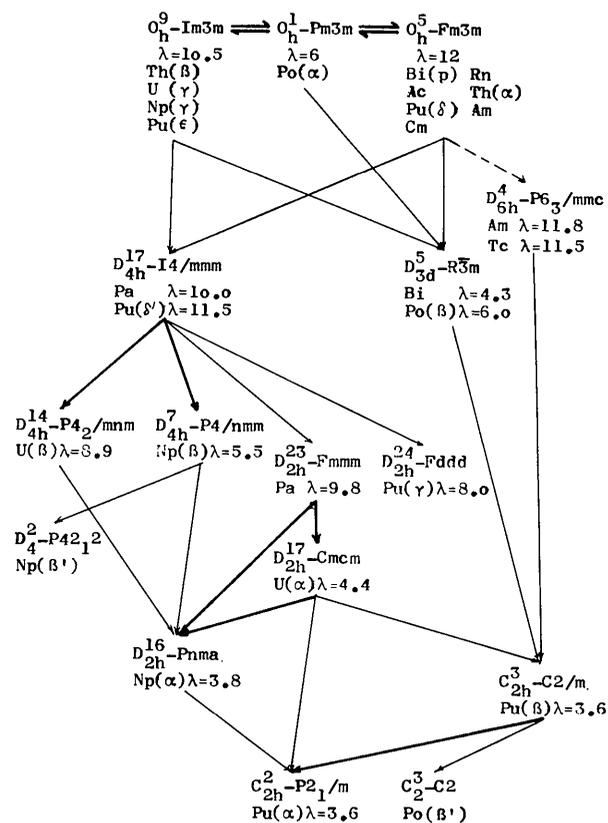


Fig. 4. Crystallographic pedigree of radioactive elements.

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

Generally speaking, as the x of elements increases, the descent in symmetry to the subgroups of $Fm\bar{3}m$, $Im\bar{3}m$ and $P6_3/mmc$ begins with Sm ($\lambda = 11.6$), Gd(p) ($\lambda = 11.6$), $W(\beta)$ ($\lambda = 12$ and 6.4) Hg(α) ($\lambda = 8.6$), Hg(β) ($\lambda = 6.1$), In ($\lambda = 10.3$), Mn(α) ($\lambda = 15.5, 14.9, 11.7$ and 10.6), Mn(β) ($\lambda = 7.9$ 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 $Fm\bar{3}m$ structure with $4(a)O_h$

As seen from Table 4, the basic $Fm\bar{3}m$ structure with the atoms in the symmetry sites $4(a)O_h$ is predominantly adopted by noble gases and noble metals and some similar metals to them and is called the a type ($A1$ type in *Strukturbericht*).

This structure is maintained by the interstitial compounds MX_x with $X = H, B, C$ and N for small x , irrespective of the inherent structure of the metal M . As x reaches unity, they progressively transform to the $B1$ type by filling the octahedral interstices $4(b)O_h$ and, as x reaches 2, to the $C1$ 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), (Fe,Ni), (Ir,Os), (Fe,Ni,P), (Cu,Al,Mn), (Ir,Os,Au), $AuCu_3$, $CrIn_3$, Tl_2H_5 , Zr_2NiAl_5 , Zr_2CuAl_5 , $AuCu_3$ descends to $Pm\bar{3}m$ with $a = 3.7527 \text{ \AA}$ as Au_3Cu with $a = 3.9525 \text{ \AA}$, while $AuCu$ descends to its subgroup $P4/mmm$ with $c/a = 1.3238$ ($L10$ type). Cd and Zr themselves adopt $P6_3/mmc$ and $Im\bar{3}m$ respectively, whereas their alloys Cd_xZr_{1-x} adopt the disordered $A1$ type up to $x = 0.67$.

The Cu - Pt alloys maintain the $A1$ type all over the components ($a = 3.6148$ to 3.9237 \AA), $CuPt$ descends to its subgroup $R\bar{3}m$ ($L1_1$ type) (Schneider & Esch, 1944).

The M_3M' alloys with rare earths M' randomly distributed in $4(a)O_h$ show the pedigree as shown in Table 5.*

There are many molecules which crystallize in the $A1$ type with rotationally disordered molecules centered at $4(a)O_h$ (e.g. DCl , HCl , HBr , HI (pseudocubic with $c/a = 1.08$ near 100 K, Sándor & Farrow, 1967), CD_4 , CH_4 , CCl_4 , CBr_4 , Cl_4 , CMe_4 , CMe_3Cl , CMe_3Br ,

* 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.

Table 4. The $Fm\bar{3}m$ pedigree of chemical elements

(a) Typical elements

H	Li(c)	Be	B	C	N	O	H		
4.242	4.38	$Im\bar{3}m$	$R\bar{3}m$	$Fd\bar{3}m$	$Pa\bar{3}$	$Pm\bar{3}n$	$P6_3/mmc$	F	
Ne	Na(c)	Mg	Al	Si	P	S		$Pm\bar{3}n$	
4.429	5.350	$P6_3/mmc$	4.050	$Fd\bar{3}m$	$Pm\bar{3}n$	$R\bar{3}m$		Cl	
Ar	K	Ca(α)	Ga	Ge	As	Se		Br	
5.256	$Im\bar{3}m$	5.588	$Im\bar{3}m$	5.658	$R\bar{3}m$	$Fd\bar{3}m$		$Cmca$	
Kr	Rb(p)	Sr(α)	In	Sn	Sb	Te		I	
5.721	5.63	6.085	$I4/mmm$	$Im\bar{3}m$	$P6_3/mmc$	$R\bar{3}m$		$Cmca$	
Xe	Cs(p)	Ba	Tl(β)	Pb	Bi(p)	Po		At	
6.197	5.80	$Im\bar{3}m$	4.851	4.950	6.354	$Pm\bar{3}m$		—	

(b) Transition elements

Sc(β)	Ti	V	Cr	Mn(γ)	Fe(γ)	Co(β)	Ni(g)	Cu	Zn	
5.541	$Im\bar{3}m$	$Im\bar{3}m$	3.68	3.863	3.647	3.544	3.524	3.615	$P6_3/mmc$	
Y	Zr	Nb(i)	Mo	Tc	Ru	Rh	Pd	Ag	Cd	
$Im\bar{3}m$	$Im\bar{3}m$	4.40	4.16	$P6_3/mmc$	$P6_3/mmc$	3.804	3.891	4.086	$P6_3/mmc$	
*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	
	$Im\bar{3}m$	$Im\bar{3}m$	$Im\bar{3}m$	$P6_3/mmc$	$P6_3/mmc$	3.839	3.924	4.078	$R\bar{3}m$	
†										
* La(β)	Ce(α)	Pr(β)	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho
5.296	4.84	5.161	$Im\bar{3}m$	$Im\bar{3}m$	$Im\bar{3}m$	$Im\bar{3}m$	$Im\bar{3}m$	$Im\bar{3}m$	$Im\bar{3}m$	$P6_3/mmc$
Er	Tm	Yb(α)	Lu							
$P6_3/mmc$	$P6_3/mmc$	5.846	$P6_3/mmc$							
† Ac	Th(α)	Pa	U	Np	Pu(δ)	Am(i)	Cm			
5.311	5.085	$I4/mmm$	$Im\bar{3}m$	$Im\bar{3}m$	4.637	4.894	4.382			

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

$M = \text{Sc}$	$P2_1/a$	Y	5-363	La	5-768	Ce	5-697	Pr	5-644	Nd	5-595	
	Sm	5-519	Eu	$R\bar{3}m$	Gd	$R\bar{3}m$	Tb	$R\bar{3}m$	Dy	$R\bar{3}m$	Ho	5-523
	Er	$R\bar{3}m$	Yb	$R\bar{3}m$	Ac	5-943	Th	5-68	Pu	5-71	Cf	5-561 Å.

The $MM'X$ compounds with X in 4(a), M and M' randomly in 8(c) show the pedigree in Table 14.

The $MM'X_4$ compounds with M and M' randomly in 4(a), X in 8(c) show the pedigree in Table 15.

The $\text{Li}_{2n-1}MX_n$ compounds with X in 4(a), 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: Cu_5FeS_4 with $Z = 1$, $a = 5.50$ Å, 4S in 4(a), 5Cu and 1Fe in $192(1)C_1$ near 8(c) descends to $Fd\bar{3}m$ with $Z = 8$, $a = 10.94$ Å on rapid cooling, and to $R\bar{3}m$ with $Z = 3/2$, $c/a = 4.897$ on slow cooling, and to $P\bar{4}2_1c$ with $Z = 16$, $c/a = 2.000$, where the subcell is cubic with $a = 5.47$ Å (Morimoto & Kullerud, 1961).

The $M_nM'O_{2n-1}$ compounds with M and M' randomly in 4(a), O deficient in 8(c) are Zr_3MgO_7 with $Z = 1$, $a = 5.081$ Å and Bi_4MoO_9 with $Z = 4/5$, $a = 5.654$ Å.

The $M\text{Cl}_6(\text{Me}_4\text{N})_2$ compounds with $M = \text{Ce}$, Sn and U and $\text{Ni}(\text{MeNH}_2)_6\text{I}_2$ are the variants of the $C1$ type.

11. The $Fm\bar{3}m$ structure with 4(a) O_h , 4(b) O_h and 8(c) T_d

The $M_2M'M''$ alloys, including the Heusler alloys, with M' in 4(a), M'' in 4(b), M in 8(c) are the abc type ($L2_1$ type) and show the pedigree in Table 17.

The M_3M' compounds with M' in 4(a), M in 4(b) and 8(c) show the following pedigree:

$M = \text{K}$	Rb	Cs	Cu
$M' = \text{Sb}$	8-493	$P6_3/mmc$	9-184
	Bi	8-805	8-989
			9-310 Å
			6-01
			—

Fe_3Al crystallizes with $Z = 4$, $a = 5.79$ Å, 4Fe in 4(a), 4Fe in 4(b), 4Fe and 4Al in 8(c), while Cu_3Au descends to $Pm\bar{3}m$ with $Z = 1$, $a = 3.74$ Å.

The Li_2MM' compounds with 4M in 4(a), 4Li in 4(b), 4M' and 4Li in 8(c) show the pedigree in Table 18.

The ideal form of BiF_3 with $Z = 4$, $a = 5.853$ Å, Bi in 4(a), F in 4(b) and 8(c) has been called the DO_3 type (Hassel & Nilssen, 1929), but the actual α form deviates slightly from the F lattice and descends to $P\bar{4}3m$ with 8F in 1(a) T_d , 1(b) T_d , 3(c) D_{2d} , 3(d) D_{2d} , 4F and 4Bi in 4(e) C_{3v} with $x = 0.25$ and 0.74 respectively. Above 473 K, it descends to the β form, $Pnma$, of the YF_3 type.

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

Mg_2Pb	$Z = 4$	$a = 6.813$ Å	Pb in 4(a)	vacant in 4(b)	Mg in 8(c)	($C1$ type)
Li_2MgPb	4	6-781	Pb	Li	Mg	($L2_1$ type)
Li_3Pb	4	6-687	Pb	Li	Li	(DO_3 type).

The $\text{Pb}_{1-x}\text{Bi}_x\text{F}_{2+x}$ compounds with Pb and Bi randomly in 4(a), F in 8(c), excess F in 4(b) maintain the $Fm\bar{3}m$ structure over the following range:

$x =$	0	0.33	0.66	1
$a =$	5.927	5.878	5.901	5.849 Å.

Mo_3O has $Z = 3$, $a = 5.549$ Å, 3Mo in 4(a), 6Mo in 8(c), 3O in 4(b), but Cr_3O and W_3O descend to $Pm\bar{3}n$ (Hägg and Schönberg, 1954).

It is noted that the MM'_x 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_{2h}

GeCa_7 takes $Z = 4$, $a = 9.45$ Å, Ge in 4(a), Ca in 4(b) and 24(d) and the GeCa_x compounds show the following pedigree:

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

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

$\text{Te}(\text{OH})_6$ with $z = 4$, $a = 7.85$ Å, Te in 4(a) and OH in 24(e) descends to $Fd\bar{3}c$ with $Z = 32$, $a = 15.51$ Å (Falck & Lindqvist, 1978).

CaPbF_6 takes $Z = 4$, $a = 8.476$ Å, Pb in 4(a), Ca in 4(b), F in 24(e), but BaPbF_6 descends to $R\bar{3}m$ with $Z = 3$, $c/a = 1.0094$ and SrPbF_6 to $P4_2/mmc$ with $Z = 1$, $c/a = 0.8599$.

The $M_2M'X_6$ compounds with $Z = 4$, M' in 4(a), M in 8(c), X in 24(e) are called the *ace* type ($J1_1$ type) and show the pedigree in Table 20 to 22. The H atoms in $M = \text{NH}_4$ occupy $32(f)C_{3v}$ (Lisher, Cowlam & Gillott, 1979). NH_4MnF_3 descends to $Pm\bar{3}m$ and $(\text{NH}_4)_2\text{MnF}_3$ to $Pm\bar{c}n$.

K_2SnCl_6 in Table 21 shows the following pedigree with lowering temperature (Boysen & Hewat, 1978):

below $Fm\bar{3}m$	Sn in 4(a) O_h	K in 8(c) T_d	Cl in 24(e) C_{4v}
261 K	$P4/mnc$	2(a) C_{4h}	4(d) D_2
255	$P2_1/c$	2(a) C_1	4(e) $C_1 \times 3$.

$(\text{NMe}_4)_2\text{PtCl}_6$ and $[\text{N}(\text{CD}_3)_4]_2\text{PtCl}_6$ descend to $Fd\bar{3}c$ but the distortion from $Fm\bar{3}m$ is probably small (Mackenzie, Berg & Pawley, 1980).

The $M(\text{NH}_3)_6X_2$ compounds with M in 4(a), X in 8(c), NH_3 in 24(e) show the pedigree in Table 23.

The $M_2M'(\text{CN})_6$ compounds with $Z = 4$, $4M'$ in 4(a), $4M$ in 4(b), $4M$ deficient in 8(c), $24(\text{CN})$ in 24(e) are called the J_2 type as follows:

$M = \text{Cu}$ $M' = \text{Cr}$ 10·24 Mn 10·16 Fe 10·00

$M' = \text{Fe}$ $M = \text{Fe}$ 10·2 Co 10·14 Ni 10·02 Å.

The $M_3M'F_6$ compounds with M' in 4(a), M in 4(b) and 8(c), F in 24(e) are called the J_2 type as shown in Table 24. $\text{Cs}_2\text{AgAuCl}_6$ descends to metastable $Pm3m$ form with $Z = 1/2$, $a = 5\cdot29$ Å, and to $I4/mmm$ ($K7_6$ type) with $Z = 2$, $c/a = 1\cdot4919$ as $\text{Cu}_2\text{Au}_2\text{Cl}_6$ with $c/a = 1\cdot4513$.

The $M_2M'M''O_6$ compounds with M'' in 4(a), M' in 4(b), M in 8(c), O in 24(e) are perovskite-like as shown in Table 25. The variants $M_2M'M''O_nF_{6-n}$ are given in Table 26. $\text{Sr}_3\text{Fe}_2\text{UO}_9$ has $Z = 8/3$, $a = 8\cdot066$ Å, U and Fe randomly in 4(a) and 4(b), Sr in 8(c), O deficient in 24(e).

The $M_2M'M''(\text{CN})_6$ compounds with M'' in 4(a), M' in 4(b), M in 8(c), CN in 24(e) are shown in Table 27. $\text{Cs}_2\text{LiCr}(\text{CN})_6$ descends to $P4/nmc$ with $Z = 2$, $c/a = 1\cdot418$, the tetrahedral distortion of CrC_6 and LiN_6 octahedra having been discussed by Chowdhury, Wedgwood, Chadwick & Wilde (1977) and by Ryan & Swanson (1978).

The $M_3[\text{Co}(\text{CN})_6]_2$ compounds with Co in 4(a), M in 4(b) and 8(c), CN in 24(e) are as follows:

$M = \text{Co}$ 10·20 Cu 9·90 Zn 9·94 Cd 10·37 Hg 10·45 Pb 10·44 Å.

The $M_3[\text{Co}(\text{CN})_6]_2\cdot 12\text{H}_2\text{O}$ compounds take $Z = 4/3$, 4Co^{II} in 4(a), $8/3M^{\text{III}}$ disordered in 4(b), 16CN in 24(e), $16\text{H}_2\text{O}$ near 8(c) and 24(e) or 32(f) for $M = \text{Mn}$, Fe , Co , Ni , Zn and Cd .

$\text{Co}(\text{NH}_3)_6\text{I}_3$ with $Z = 4$, $a = 10\cdot82$ Å, Co in 4(a), I in 4(b) and 8(c), NH_3 in 24(e) descends to $F\bar{4}3m$ with $Z = 4$, $a = 10\cdot902$ Å, while $\text{Co}(\text{NH}_3)_6\text{I}_2$ belongs to the $J1_1$ type.

Li_6NBr_3 takes $Z = 4$, $a = 8\cdot895$ Å, Br in 4(a) and 8(c), N in 4(b), Li in 24(e), while $\text{Li}_7\text{N}_2\text{I}$ descends to $Fd3m$ with $Z = 8$, $a = 10\cdot367$ Å, and Li_5NI_2 descends to $F\bar{4}3m$ with $Z = 5$, $a = 9\cdot540$ Å.

The $M_6M'X_8$ compounds with $Z = 4$, M' in 4(a), X in 8(c) and 24(e), M in 24(d) and vacant 4(b) are Mg_6MnO_8 , Cu_6PbO_8 and Na_6CdCl_8 and considered to be the prototype of the M_8C_7 compounds.

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

The M_9X_8 compounds with $Z = 4$, M in 4(b) and 32(f), X in 8(c) and 24(e) are Co_9S_8 , Co_9Se_8 and $(\text{Fe}, \text{Ni})_9\text{S}_8$.

$2\text{Na}_2\text{SO}_4\cdot \text{NaCl}\cdot \text{NaF}$ crystallizes with $Z = 4$, $a = 10\cdot065$ Å, F in 4(a), Cl in 4(b), S in 8(c), Na in 24(e), O in 32(f).

The $M_3[M'(\text{CN})_6]_2\cdot 3\text{H}_2\text{O}$ compounds with $Z = 2$, $4M'$ in 4(a), $4M$ in 4(b), $2M$ randomly in 32(f), 24CN in 24(e), $6\text{H}_2\text{O}$ randomly in 8(c) occur for $M = \text{Mn}$, Co , Ni , Cu , Zn and Cd , $M' = \text{Fe}$ and Co .

$\text{Zn}_3[\text{Co}(\text{CN})_6]_2\cdot 12\text{H}_2\text{O}$ with $Z = 4/3$, $a = 10\cdot268$ Å, Co in 4(a), Zn in 4(b), CN in 24(e), O disordered in 8(c) and 32(f) is isomorphous with the Mn and Cd compounds (Mullica, Milligan, Beall & Reeves, 1978).

Cu_3SbS_4 with $Z = 8$, $a = 10\cdot74$ Å, Sb in 8(c), Cu in 24(d), S in 32(f), descends to $Fd3m$ with $Z = 1$, $a = 5\cdot28$ Å, all atoms being in 8(a) T_d , the metals randomly in 000, S in $\frac{1}{4}\frac{1}{4}\frac{1}{4}$. Cu_3VS_4 descends to $P\bar{4}3m$ with $Z = 1$, $a = 5\cdot370$ Å, V in 1(a) T_d , Cu in 3(d) D_{2d} , S in 4(e) C_{3v} .

Cu_5FeS_4 shows the following pedigree:

$Fm3m$ $Fd3m$ $R3m$ $P\bar{4}2_1c$

$a = 5\cdot50$ Å $a = 10\cdot94$ Å $c/a = 4\cdot8966$ $c/a = 2\cdot000$.

$\text{Cu}_{12}\text{Fe}_2\text{S}_9$ descends to $Pm3m$ with $a = 21\cdot87$ Å, and CuFeS_2 to $I43m$ with $a = 10\cdot605$ Å and $I42d$ with $c/a = 1\cdot9656$.

The $M_{23}M'_6$ compounds with $Z = 4$, M in 4(b), 24(d) and 32(f) $\times 2$, M' in 24(e) show the pedigree in Table 28. It is noted that Mg_4Sr and Li_4Ba descend to $P6_3/mmc$ with $Z = 18$, $c/a = 2\cdot698$ and $0\cdot8064$ respectively.

The $M_{16}M'_6M'_7$ compounds with $Z = 4$, M'' in 4(b) and 24(d), M in 32(f) $\times 2$, M' in 24(e) in Table 29 and the $M_{15}M'_6M''_8$ compounds with M and M'' in 4(b), 24(d), 32(f) $\times 2$, M' in 24(e) in Table 30 are the variants of the $M_{23}M'_6$ type.

The $M_4M'_{11}$ compounds with $Z = 8$, M in 4(a), 4(b) and 24(d), M' in 24(e) and 32(f) $\times 2$ for $M = \text{Ir}$, Os and Ru , $M' = \text{Sc}$, Zr correspond to $M'_{16}M'_6M'_8$, the variants of the above with occupied 4(a) (Chabot, Cenzual & Parthé, 1980).

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

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 MB_{12} compounds with $Z = 4$, M in 4(a), B in 48(i) are maintained for $M = \text{Sc}$, Y , Dy , Ho , Er , Tm , Lu , Zr and U .

$\text{BaCaLu}_2\text{F}_{10}$ takes $Z = 8$, $a = 11\cdot366$ Å, 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 $96(k)C_s$

$\text{Ba}_3[\text{Co}(\text{NO}_2)_6]_2$ takes $Z = 2$, $a = 10\cdot59$ Å, 6Ba deficient in 4(a) and 4(b), 4Co in 8(c), 24N in 48(g), 480 in 96(j).

$\text{Ag}_7\text{NO}_{11}$ takes $Z = 4$, $a = 9.890 \text{ \AA}$, Ag in 4(a) and 24(d), N in 4(b), O in 32(f) and 96(k), while $\text{Ag}_7\text{F}_3\text{O}_9$ takes $Z = 4$, $a = 9.842 \text{ \AA}$ and a more disordered structure.

$\text{Be}_3\text{Ca}_2\text{O}_5$ takes $Z = 24$, $a = 14.00 \text{ \AA}$, Be in 4(b) and 32(f) $\times 3$, Ca in 24(d) and 24(e), O in 8(c), 32(f) and 96(k).

17. Descent in site symmetry to $192(I)C_1$

The $M_3M'F_mO_n$ compounds with $Z = 4$, $4M'$ in 4(a), $12M$ in 4(b) and 8(c), F and O randomly in 24(e), 96(f) 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 $M_2\text{CoF}_6$ (*ace* type) through $M_3\text{CoF}_6$ (*abce* type) to $M_2\text{CoF}_4$ (*I4/mmm*).

18. Concluding 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 $Pm3m$, $Fm3m$ and $Im3m$, their lattice points having the coordination indices $\lambda = 6, 12$ and 10.5 respectively. Thus, the $Fm3m$ 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 $Fm3m$ structure are uniquely determined by the $F4/m32/m$ symmetry principle to be the subgroups of the O_h and that all the types of the $Fm3m$ 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 ($A1$) type has M in 4(a) and consists of a regular cuboctahedron MM_{12} , the $M-M$ distances being $a/\sqrt{2}$, where a is the lattice constant in Å . This situation is commonly retained in all the $Fm3m$ structures. An introduction of X into 4(b) as in the ab ($B1$) type results in the lifting in the degeneracy into the octahedra MX_6 and XM_6 , the distances $M-X$ being the smaller $a/2$, accompanying the decrease in λ . On the other hand, an introduction of X into 8(c), as in the ac ($C1$) type, results in the lifting into the cube MX_8 and the tetrahedron MX_6 with $M-X$ distances of $a/2$. Proceeding to the abc ($L2_1$) type of $M_2M'M''$ with M' in 4(a), M'' in 4(b) and M in 8(c), the lifting into MM'_4

Table 33. Descent in site symmetry of the $Fm3m$ family

* Doubly occupied; – vacant.

Site	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)
Multiplicity	4	4	8	24	24	32	48	48	48	96	96	192
Point group	O_h	O_h	T_d	D_{2h}	C_{4v}	C_{3v}	C_{2v}	C_{2v}	C_{2v}	C_s	C_s	C_1
Compound type												
M (element)	$A1$	M										
MX	$B1$	M	X									
MX_2	$C1$	M	–	X								
$M_2M'M''$	$L2_1$	M'	M''	M								
BiF_3	DO_3	Bi	F	F								
Mo_3O		Mo	O	Mo								
GeCa_7		Ge	Ca	–	Ca							
$\text{Te}(\text{OH})_6$		Te	–	–	–	OH						
$MM'X_6$		M'	M	–	–	X						
$M_2M'X_6$	$J1_1$	M'	–	M	–	X						
$M_3M'X_6$	$J2_1$	M'	M'	M	–	X						
$M_6M'X_8$		M'	–	X	M	X						
M_9X_8	$D8_9$	–	M	X	–	X	M					
$M_3(M'X_6)_2$	$J2_5$	M'	M	–	–	X	M					
$M_{23}M'_6$	$D8_1$	–	M	–	M'	M	M^*					
$M_{16}M'_6X_7$		–	X	–	X	M'	M^*					
$M_4M'_{11}$		M	M	–	M	M'	M'^*					
$M_{23}X_6$	$D8_4$	M	–	M	–	X	M	–	M			
MB_{12}	$D2_f$	M	–	–	–	–	–	–	B			
$\text{Ba}_3[\text{Co}(\text{NO}_2)_6]_2$		Ba	Ba	Co	–	–	N	–	–	O		
$\text{Ag}_7\text{NO}_{11}$		Ag	N	–	Ag	–	O	–	–	–	O	
$M_3M'F_7$		M'	M	M	–	F	–	–	–	F	–	F^*

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