The Origin of the Crystallographic Pedigree

By Masao Haisa

Faculty of Science, Okayama University, Tsushima, Okayama 700, Japan

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Abstract

The origin of the crystallographic pedigree [Haisa (1978). Acta Cryst. A34, 753-759] is shown to be the Fm3m 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 A1), ab (B1), ac (C1), abc $(L2_1)$, abd, ae, abe, ace $(J1_1)$, abce $(J2_1)$, abcde, bcef $(D8_9)$, abcef $(H5_8)$, cdf, bdef $(D8_a)$, abdef, acefh $(D8_4)$, ai $(D2_f)$, abcgj, abdfk and *abceil* 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 Pm3m, Im3m and $P6_3/mmc$ 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 $K_{h} - \infty / \infty / mmm$ for a free atom with closed

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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.

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type $\{R|t\}$, 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 **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 $\{E|t\}$, 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' which should be a subgroup or supergroup of G, so long as the space group Sremains 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' will be completely balanced by the change of the site symmetry H to H'which are the subgroups of **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' does not allow the compatibility in (\mathbf{R}/\mathbf{t}) to be maintained, then $S = (\mathbf{R}/\mathbf{t})$ passes into a new $S' = (\mathbf{R}'/\mathbf{t}')$. This may be called the extended polymorphism or heteromorphism. According to Hermann (1929), the transformations from S to S' may be classified as the *klassengleiche* (k) and the *zellengleiche* (z) according as $\mathbf{R}' = \mathbf{R}$ and $\mathbf{t} = \mathbf{t}'$.

The restriction of the highest rotation axis n = 6 in **R** results in the two geneses of symmorphic space groups, cubic $O_h^1 - Pm3m$ and hexagonal $D_{6h}^1 - P6/mmm$ according as they adopt an improper and a proper rotation of order 6, that is, $S_6 = C_{3i} - 3$ 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_{3d} into D_{3h} 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.

| Substance | Cubic form | (Fm3m) | Hexagonal form | $(P6_3/mmc)$ |
|--|-----------------|--------|-------------------|--------------|
| Noble gases | He Ne Ar Kr Xe | Fm3m | He Ne Ar | P6,/mmc |
| Ca Sr | low-temp. form | Fm3m | high-temp. form | P6,/mmc |
| Zr Hf | high-temp. form | Im3m | low-temp. form | P6,/mmc |
| С | diamond | Fd3m | graphite | P6,/mmc |
| SiC | β form | F43m | α form | P6,mc |
| BN | borazon | F43m | ordinary form | P63/mmc |
| ZrP | a form | Fm3m | βform | P6,/mmc |
| ZnS | zinc blende | F43m | wurtzite | $P6_{1}mc$ |
| AgI | y form | F43m | β form | p6,mc |
| он, | cubic ice | Fd3m | hexagonal ice | P6,/mmc |
| SiO | cristobarite | Fd3m | tridymite | P63/mmc |
| Al,Ô, | y corundum | Fd3m | β -corundum | P6,/mmc |
| (CH ₂ CH ₂) ₃ N ₂ | phase I | Fm3m | phase II | P63/m |

Table 1. Two geneses of observed crystal structures

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 $C_{3\nu}$ 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 $C_{3\nu}$, 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 -P6₃/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

$$\lambda = \sum_{i} (d_1/d_j)^6,$$

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 quadrupolequadrupole 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 $4(a)O_{\mu}$ 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_{μ} 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





respectively into Im3m with a = 3.963 and 4.11 Å 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 Fm3m to either $P6_3/mmc$ by switching of D_{3d} to D_{3h} or Im3m, a subgroup of Fm3m, 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_{II}/d_{IF} 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 Fm3m, 1.79168 for P6,/mmc, 1.79186 for Im3m, 1.77464 for P6/mmm and 1.76012 for Pm3m. 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 Fm3m structure which is indicated by the lattice constant a in Å 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 (Å) | | $d_1(\dot{\mathbf{A}})$ | r_0 (Å) | Reference |
|----|----------|--------|-------------------------|---------------------|----------------------------|
| He | 4·242 at | t 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) |
| Кr | 5.721 | 58 | 4.034 | 0.795 (4 <i>p</i>) | Cheesman & Soane (1957) |
| Xe | 6.197 | 58 | 4.220 | 0·986 (5 <i>p</i>) | Cheesman & Soane (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 Fm3m through Im3m to its subgroups as shown in Fig. 4. The Fm3m form of Pu is stable between 724 and 592 K, but descends to Im3m 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 Pm3m 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.

Table 3. Transitions among Fm3m, P63/mmc and Im3m 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 |
| $Fm3m d_{1F}(\dot{A})$ | 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 |
| $Im3m d_{11}$ | 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 |

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

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Generally speaking, as the x of elements increases, the descent in symmetry to the subgroups of Fm3m, Im3m and P6₃/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, 117 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 Fm3m structure with $4(a)O_h$

As seen from Table 4, the basic Fm3m 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 (A 1 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).

(a) Typical elements

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), AuCu₃, CrIn₃, Tl₂H₅, Zr₂NiAl₅, Zr₂CuAl₅. AuCu₃ descends to *Pm3m* with a = 3.7527 Å as Au₃Cu with a = 3.9525 Å, while AuCu descends to its subgroup *P4/mmm* with c/a = 1.3238 (*L*10 type). Cd and Zr themselves adopt *P6₃/mmc* and *Im3m* respectively, whereas their alloys Cd_xZr_{1-x} adopt the disordered *A*1 type up to x = 0.67.

The Cu-Pt alloys maintain the A1 type all over the components (a = 3.6148 to 3.9237 Å), CuPt descends to its subgroup $R\bar{3}m$ (L1₁ 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), CD₄, CH₄, CCl₄, CBr₄, CI₄, CMe₄, CMe₃Cl. CMe₁Br,

| | | | | | | | Н | | | |
|---|---|--|---|--------------------------|------------------------------|------------------------------|----------------------------------|------------|--------------|----------------------------|
| | | | | | | | $P6_3/mmc$ | | | |
| н | Li(c) | Be | В | С | N | 0 | F | | | |
| 4.242 | 4.38 | Im3m | RĪm | Fd3m | Pa3 | Pm3n | Pm3n | | | |
| Ne | Na(c) | Mg | Al | Si | Р | S | Cl | | | |
| 4.429 | 5.350 | $P\bar{6_3}/mmc$ | 4.050 | Fd3m | Pm3n | R3m | Стса | | | |
| Ar | К | Ca(α) | Ga | Ge | As | Se | Br | | | |
| 5.256 | Im3m | 5.588 | Im3m | 5.658 | RŜm | Fd3m | Стса | | | |
| Kr | Rb(p) | $Sr(\alpha)$ | In | Sn | Sb | Te | I | | | |
| 5.721 | 5.63 | 6.085 | I4/mmm | Im3m | $P6_3/mmc$ | RĪm | Стса | | | |
| Xe | Cs(p) | Ba | Tl(β) | Pb | Bi(p) | Ро | At | | | |
| 6.197 | 5.80 | Im3m | 4.851 | 4.950 | 6.354 | Pm3m | - | | | |
| (b) Transi | ition element | S | | | | | | | | |
| $Sc(\beta)$ | Ti | v | Cr | Mn(y) | Fe(v) | $Co(\beta)$ | Ni(a) | Cu | Zn | |
| 5.541 | Im3m | Im3m | 3.68 | 3.863 | 3.647 | 3.544 | 3.524 | 3.615 | $P6_{3}/mmc$ | |
| Y | Zr | Nb(i) | Мо | Tc | Ru | Rh | Pd | Ag | Cď | |
| Im3m | Im3m | 4.40 | 4.16 | $P6_3/mmc$ | $P6_3/mmc$ | 3.804 | 3.891 | 4.086 | $P6_1/mmc$ | |
| * | Hſ | Та | W | Re | Os | Ir | Pt | Au | Hg | |
| | Im3m | Im3m | Im3m | $P6_3/mmc$ | P6 ₃ /mmc | 3.839 | 3.924 | 4.078 | RŠm | |
| † | | | | 5 | 5 | | | | | |
| * La(β) | $Ce(\alpha)$ | $\Pr(\beta)$ | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Но |
| 5.296 | 4.84 | 5.161 | Im3m | Im3m | Im3m | Im3m | Im3m | Im3m | Im3m | P6 ₃ /mmc |
| Er | Tm | Yb(a) | Lu | | | | | | | 5 |
| P6 ₃ /mmc | $P6_3/mmc$ | 5.846 | P6 ₃ /mmc | | | | | | | |
| † Ac | Th(a) | Ра | U | Np | $Pu(\delta)$ | Am(i) | Cm | | | |
| 5.311 | 5.085 | I4/mmm | Im3m | Im3m | 4.637 | 4.894 | 4.382 | | | |
| * La(β) 5·296 Er P6 ₃ /mmc † Ac 5·311 | Ce(α) 4.84 Tm P6 ₃ /mmc Th(α) 5.085 | Pr(β) 5·161 Yb(α) 5·846 Pa I4/mmm | Nd Im3m Lu P6 ₃ /mmc U Im3m | Pm Im3m Np Im3m | Sm Im3m Pu(δ) 4·637 | Eu Im3m Am(i) 4·894 | Gd <i>Im3m</i> Cm 4·382 | Tb Im3m | Dy Im3m | Ho P6 ₃ /mmc |

Table 4. The Fm3m pedigree of chemical elements

^{*} 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.

CMe₃COOH, CMe₃CH₂OH, CMe₂(NO₂)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 MF_6 compounds with M = S, Mo, W, Re, Os, Ir and Pt acquire $G = O_h$ but descend to Im3m (Siegel & Northrop, 1966) as the C_2X_6 compounds with X = H, F, Cl, Br and Me and C_2H_4 and $(CH_2CN)_2$ do (van Nes & Vos, 1978).

9. The Fm3m structure with $4(a)O_h$ and $4(b)O_h$

The MX compounds with Z = 4, M in $4(a)O_h$ and X in $4(b)O_h$ are called the *ab* type (B1 type) and maintained as shown in Tables 6 to 9. As the temperature is lowered or the pressure increases, RbF, RbCl, CsCl, CsBr, CsI descend to a subgroup *Pm3m*, as expected from the ratio of radii of X and M ions. The NH₄X



Fig. 5. Crystallographic pedigree of electronegative elements. Polymorphs of P are white(w), black(b) and Hittorf's(H). Si(II) is a high-pressure form. The *m* stands for metallic and the *g* stands for graphitic.

halides descend through Pm3m to P4/nmm and/or to $P\bar{4}3m$ according as the orientation of the NH₄ ions is frozen.

The groups X in Table 7 are rotating or disordered in 4(b). KCN and NaCN descend through *Immm* to *Pmmm* with lowering temperature (Rowe, Rush & Prince, 1977). CsCN descends to $R\bar{3}m$, but TICN to *Pm3m*.

InTe in Table 8 descends to I4/mcm (Hogg & Sutherland, 1976) and In₄Te₃ to *Pnnm* (Hogg & Sutherland, 1973). MnO is a member with $n = \infty$ of the Mn_nO_{n+1} compounds which show the following pedigree:

n = 3 2 1

 $Fd3m I4_1/amd Ia3 R\bar{3}c P6_3/mmc P4_2/mnm I4/m Pbnm.$

Schubert (1977) has discussed the morphotropism in (Ni,Pd,Pt) (S,Se,Te) system on the basis of the two-correlation model.

The solid solutions of CrN and VN in Table 9 maintain the B1 type at room temperature but descend to *Pnmm* below a characteristic temperature (Eddine, Bertaut, Roubin & Pâris, 1977).

 $N_2H_4.H_2O$ with Z = 4, a = 6.76 Å, rotationally disordered H_2NNH_2 in 4(a), O in 4(b) descends to $P3_121$ with Z = 3, c/a = 2.2450 at 108 K.

The M_3C compounds with 1.6C in 4(*a*), 4*M* in 4(*b*), M = Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu are called the *L*1' type. V₄C₃ crystallizes with Z = 1, a =4.149 Å, V in 4(*a*), C deficient in 4(*b*), but the M_2C_3 compounds descend to $I\bar{4}3d$ (*D*5_c type) and the MC_2 compounds to *I*4/*mmm* (C11 type).

Ag₃N takes Z = 4/3, a = 4.378 Å, probably statistically distributed N atoms in the octahedral interstices. PoBr₄ takes Z = 1, a = 5.61 Å, lPo statistically distributed in 4(a), 4Br in 4(b).

The $MM'X_2$ compounds with Z = 2, M and M'_1 randomly in 4(a), X in 4(b) show a remarkable descent to $R\bar{3}m$ as shown in Table 10.

The $M_{n-1}M'X_n$ compounds with M and M' randomly in 4(a) and X in 4(b) are Li_2TiO_3 , Na_2CeO_3 , Na_2PrO_3 , Li_3NbO_4 , Li_3TaO_4 , $\text{Li}_2\text{Mg}_3\text{SnO}_6$ and $\text{Na}_{1\cdot9}\text{Pr}_{0\cdot9}\text{La}_{0\cdot2}\text{O}_3$. Its anti-type is $\text{Nd}_4\text{O}_3\text{C}$ and $\text{In}_4\text{Te}_3\text{Sb}$ (Hauck, 1980).

10. The Fm3m structure with $4(a)O_h$ and $8(c)T_d$

The MX_2 compounds with Z = 4, M in 4(a) and X in 8(c) are called the *ac* type (C1 type) and show the pedigree in Table 11. The MM'_2 alloys with M in 4(a) and M' in 8(c) show the pedigree in Table 12. The M_2X compounds with X in 4(a) and M in 8(c) are the anti C1 type and show the pedigree in Table 13.

The $M_n O_{2n-1}$ compounds with M in 4(a) and O deficient in 8(c) occur for Bi_2O_3 , Tb_4O_7 and Pr_6O_{11} . Sb_2O_3 and As_2O_3 descend to Fd3m.

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

| $M = S_{0}$ | $P2_1/a$ | ı Y | 5.363 | La 5·768 | Ce 5.697 | Pr 5.644 | Nd 5-595 |
|-------------|----------|------|-------|---------------------|----------|----------|------------|
| S | n 5.519 |) Eu | R3m | Gd $R\overline{3}m$ | Tb R3m | Dy R3m | Ho 5-523 |
| E | : R3m | Yt | oR3m | 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 $\operatorname{Li}_{2n-1}MX_n$ 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: Cu₅FeS₄ with Z = 1, a = 5.50 Å, 4S in 4(a), 5Cu and 1Fe in 192(1)C₁ near 8(c) descends to Fd3m with Z = 8, a = 10.94 Å on rapid cooling, and to R3m 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 $M_n M'O_{2n-1}$ 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 $MCl_6(Me_4N)_2$ compounds with M = Ce, Sn and U and Ni(MeNH₂)₆I₂ are the variants of the C1 type.

11. The Fm3m 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:

$$M = K$$
 Rb
 Cs
 Cu

 $M' = Sb 8.493$
 $P6_3/mmc 9.184$
 6.01

 Bi 8.805
 8.989
 9.310 Å
 $-$

Fe₃Al crystallizes with Z = 4, a = 5.79 Å, 4Fe in 4(*a*), 4Fe in 4(*b*), 4Fe and 4Al in 8(*c*), while Cu₃Au descends to *Pm3m* 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 BiF₃ with Z = 4, a = 5.853 Å, Bi in 4(a), F in 4(b) and 8(c) has been called the D0₃ 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) $C_{3\nu}$ with x = 0.25 and 0.74 respectively. Above 473 K, it descends to the β form, *Pnma*, of the YF₃ type. It should be noted that the Li-Mg-Pb alloys maintain the *Fm3m* structure progressively as follows:

| Mg ₂ Pb | <i>Z</i> = 4 | a = 6.813 Å | Pb in 4(a) | vacant in $4(b)$ | Mg in 8(c) | (Cl type) |
|----------------------|--------------|-------------|------------|------------------|------------|-------------------------|
| Li ₂ MgPb | 4 | 6.781 | Pb | Li | Mg | $(L2_1 \text{ type})$ |
| Li ₃ Pb | 4 | 6.687 | Pb | Li | Li | (D0 ₃ type). |

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

| x | = | 0 | 0.33 | 0.66 | 1 |
|---|---|-------|-------|-------|----------|
| а | = | 5.927 | 5.878 | 5.901 | 5∙849 Å. |

Mo₃O has Z = 3, a = 5.549 Å, 3Mo in 4(a), 6Mo in 8(c), 3O in 4(b), but Cr₃O and W₃O descend to *Pm3n* (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 $24(d)D_{2h}$

GeCa₇ 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 Fd3m x = 1 Cmcm x = 2 Pnma.

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

Te(OH)₆ with z = 4, a = 7.85 Å, Te in 4(a) and OH in 24(e) descends to Fd3c with Z = 32, a = 15.51 Å (Falck & Lindqvist, 1978).

CaPbF₆ takes Z = 4, a = 8.476 Å, Pb in 4(a), Ca in 4(b), F in 24(e), but BaPbF₆ descends to $R\bar{3}m$ with Z = 3, c/a = 1.0094 and SrPbF₆ 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 $M = NH_4$ occupy $32(f)C_{3\nu}$ (Lisher, Cowlam & Gillott, 1979). NH_4MnF_3 descends to Pm3m and $(NH_4)_2MnF_5$ to *Pmcn*.

 K_2 SnCl₆ in Table 21 shows the following pedigree with lowering temperature (Boysen & Hewat, 1978):

below
$$Fm3m$$
Sn in $4(a)O_h$ K in $8(c)T_d$ Cl in $24(e)C_{4v}$ 261 K $P4/mnc$ $2(a)C_{4h}$ $4(d)D_2$ $4(e)C_4$ $8(h)C_s$ 255 $P2_1/c$ $2(a)C_1$ $4(e)C_1$ $4(e)C_1 \times 3$

 $(NMe_4)_2$ PtCl₆ and $[N(CD_3)_4]_2$ PtCl₆ descend to *Fd3c* but the distortion from *Fm3m* is probably small (Mackenzie, Berg & Pawley, 1980).

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

The $M_2M'(CN)_6$ compounds with Z = 4, 4M' in 4(a), 4M in 4(b), 4M deficient in 8(c), 24(CN) in 24(e) are called the $J2_5$ type as follows:

$$M = Cu$$
 $M' = Cr$ 10.24 Mn 10.16 Fe 10.00
 $M' = Fe$ $M = Fe$ 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 $J2_1$ type as shown in Table 24. Cs₂AgAuCl₆ descends to metastable *Pm3m* form with Z = 1/2, a = 5.29 Å, and to I4/mmm ($K7_6$ type) with Z = 2, c/a = 1.4919 as Cu₂Au₂Cl₆ with c/a = 1.4513.

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. Sr₃Fe₂UO₉ has Z = 8/3, a = 8.066 Å, U and Fe randomly in 4(*a*) and 4(*b*), Sr in 8(*c*), O deficient in 24(*e*).

The $M_2M'M''(CN)_6$ compounds with M'' in 4(*a*), M' in 4(*b*), M in 8(*c*), CN in 24(*e*) are shown in Table 27. Cs₂LiCr(CN)₆ descends to P4/nmc with Z = 2, c/a = 1.418, the tetrahedral distortion of CrC₆ and LiN₆ octahedra having been discussed by Chowdhury, Wedgwood, Chadwick & Wilde (1977) and by Ryan & Swanson (1978).

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

M = Co 10.20 Cu 9.90 Zn 9.94 Cd 10.37 Hg 10.45 Pb 10.44 Å.

The $M_3[Co(CN)_6]_2$. 12H₂O compounds take Z = 4/3, $4Co^{II}$ in 4(a), $8/3M^{III}$ disordered in 4(b), 16CN in 24(e), 16H₂O near 8(c) and 24(e) or 32)f) for M = Mn, Fe, Co, Ni, Zn and Cd.

Co $(NH_3)_6I_3$ with Z = 4, a = 10.82 Å, Co in 4(a), I in 4(b) and 8(c), NH₃ in 24(e) descends to $F\bar{4}3m$ with Z = 4, a = 10.902 Å, while Co $(NH_3)_6I_2$ belongs to the JI_1 type.

Li₆NBr₃ takes Z = 4, a = 8.895 Å, Br in 4(a) and 8(c), N in 4(b), Li in 24(e), while Li₇N₂I descends to Fd3m with Z = 8, a = 10.367 Å, and Li₅NI₂ descends to F43m with Z = 5, a = 9.540 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 Mg₆MnO₈, Cu₆PbO₈ and Na₆CdCl₈ and considered to be the prototype of the M_8C_7 compounds.

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

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 (Fe,Ni)₉S₈.

 $2Na_2SO_4$. NaCl. NaF crystallizes with Z = 4, a = 10.065 Å, F in 4(a), Cl in 4(b), S in 8(c), Na in 24(e), O in 32(f).

The $M_3[M'(CN)_6]_2$. $3H_2O$ compounds with Z = 2, 4M' in 4(a), 4M in 4(b), 2M randomly in 32(f), 24CN in 24(e), $6H_2O$ randomly in 8(c) occur for M = Mn, Co, Ni, Cu, Zn and Cd, M' = Fe and Co.

 $Zn_3[Co(CN)_6]_2$. $12H_2O$ with Z = 4/3, a = 10.268 A, 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).

Cu₃SbS₄ with Z = 8, a = 10.74 Å, Sb in 8(c), Cu in 24(d), S in 32(f), descends to Fd3m with Z = 1, a = 5.28 Å, all atoms being in 8(a) T_d , the metals randomly in 000, S in $\frac{111}{444}$. Cu₃VS₄ descends to $P\bar{4}3m$ with Z = 1. a = 5.370 Å, V in 1(a) T_d , Cu in 3(d) D_{2d} , S in 4(e) C_{3v} . Cu₅FeS₄ shows the following pedigree:

$$Fm3m$$
 $Fd3m$ $R3m$ $P\bar{4}2,c$

$$a = 5.50 \text{ Å}$$
 $a = 10.94 \text{ Å}$ $c/a = 4.8966 c/a = 2.000.$

 $Cu_{12}Fe_2S_9$ descends to Pm3m with a = 21.87 Å, and $CuFeS_2$ to $I\bar{4}3m$ with a = 10.605 Å and $I\bar{4}2d$ with c/a = 1.9656.

The $M_{23}M'_6$ compounds with Z = 4, M in 4(b), 24(d) and 32(f) × 2, M' in 24(e) show the pedigree in Table 28. It is noted that Mg₄Sr and Li₄Ba descend to $P6_3/mmc$ with Z = 18, c/a = 2.698 and 0.8064 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 =Ir, Os and Ru, M' = 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 $48(g)C_{2\nu}$, $48(h)C_{2\nu}$ and $48(i)C_{2\nu}$

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 = Sc, Y, Dy, Ho, Er, Tm, Lu, Zr and U.

BaCaLu₂F₁₀ takes Z = 8, a = 11.366 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 $96(k)C_s$

 $Ba_3[Co(NO_2)_6]_2$ takes Z = 2, a = 10.59 Å, 6Ba deficient in 4(a) and 4(b), 4Co in 8(c), 24N in 48(g), 480 in 96(j).

Ag₇NO₁₁ takes Z = 4, a = 9.890 Å, Ag in 4(a) and 24(d), N in 4(b), O in 32(f) and 96(k), while Ag₇F₃O₉ takes Z = 4, a = 9.842 Å and a more disordered structure.

Be₃Ca₂O₅ takes Z = 24, a = 14.00 Å, 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 $192(l)C_1$

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(j) and 192(1) × 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 $M_2\text{CoF}_4$ (14/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/msymmetry 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 Fm3mstructures. 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 (L2₁) 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) | (<i>b</i>) | (<i>c</i>) | (d) | (e) | (f) | (g) | (<i>h</i>) | (i) | (j) | (k) | (1) |
|----------------------------------|-------------------------|--------------|--------------|----------|------------|----------|------------|--------------|------------|---------|---------|------------------------|
| Multiplicity | 4 | 4 | 8 | 24 | 24 | 32 | 48 | 48 | 48 | 96 | 96 | 192 |
| Point group | O_h | O_h | T_d | D_{2h} | $C_{4\nu}$ | C_{3v} | $C_{2\nu}$ | C_{2v} | $C_{2\nu}$ | C_{s} | C_{s} | C_1 |
| Compound type | e | | _ | | | | | | | - | - | |
| M(element) A | l <i>M</i> | | | | | | | | | | | |
| MX BI | l M | Х | | | | | | | | | | |
| MX_{2} C | 1 <i>M</i> | - | X | | | | | | | | | |
| М,Ñ'М" L2 | $2_1 M'$ | M'' | М | | | | | | | | | |
| BiF, <i>D</i> (| D. Bi | F | F | | | | | | | | | |
| MojO | Мо | 0 | Мо | | | | | | | | | |
| GeČa₁ | Ge | Ca | - | Ca | | | | | | | | • |
| Te(OH) ₆ | Te | - | - | - | ОН | | | | | | | |
| MM'X ₆ | M' | М | | | Х | | | | | | | |
| $M,M'X_6 J1$ | 1 M' | _ | М | _ | Х | | | | | | | |
| $M_{3}M'X_{6}$ J2 | . M' | M | М | | Х | | | | | | | |
| $M_{6}M'X_{8}$ | | _ | Х | Μ | Х | | | | | | | |
| $M_{9}X_{8}$ D | 8, – | М | Х | - | Х | Μ | | | | | | |
| $M'_{3}(M'X_{6})_{2}$ J2 | . M' | Μ | - | - | Х | М | | | | | | |
| $M'_{23}M'_{6} = DS$ | B ₁ – | М | - | M' | М | M* | | | | | | |
| $M_{16}M_{6}X_{7}$ | - | X | - | X | M' | M* | | | | | | |
| $M_4 M'_{11}$ | М | М | - | М | M' | M'* | | | | | | |
| $M_{23}X_6$ D | B_4 M | - | М | - | X | М | | М | | | | |
| MB_{12} D2 | $2_f M$ | - | - | - | - | - | - | - | В | | | |
| $Ba_3[Co(NO_2)_6]$ | 2 Ba | Ba | Co | | - | - | Ν | - | - | 0 | | |
| Ag ₇ NO ₁₁ | Ag | Ν | - | Ag | - | 0 | - | _ | - | _ | 0 | |
| $M_{3}M'F_{7}$ | M' | М | М | - | F | - | - | - | - | F | - | F [∓] |

and MM''_4 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 Fm3m structure is surpassed by increasing distortion of the G from O_h into its subgroups owing to far stronger and directional



Fig. 6. Crystallographic pedigree of the Al-Zr system.



Fig. 7. Crystallographic pedigree of the Ti-O system.

interactions between the neighbors, the descent in space group proceeds through Pm3m and Im3m or $P6_3/mmc$ 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 TiO₆ 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 C_xH_y increases, corresponding to increasing π -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 C-H system. The x/ystands for C_xH_y, (1) 1/4 5/12 6/12 10/16, (2) 2/4 2/6, (3) 9/16 10/16, (4) 2/2 14/20, (5) 2/6 18/24, (6) 12/18 18/16, (7) 12/18 18/24, (8) 8/6 14/22, (9) 9/12, (10) 8/8 10/10 18/36, (11) 28/34, (12) 4/6 16/16, (13) 24/18, (14) 28/16, (15) 10/16 25/20, (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) 21/44 23/48 25/52 27/56 29/60, (26) 18/24, (27) 6/6 12/12 15/12 16/12 16/14 18/16 19/14 20/16 20/18 20/20 20/32 22/14 22/14 22/16 22/16 22/20 28/18 28/20 28/58 32/24 34/18 34/22 36/24 36/74, (28) 11/8 13/10 14/10 19/12 24/30 30/62 n/(2n + 2), (29) 5/12 15/10 16/12 16/24 20/16 20/16 26/16 26/16 36/24 42/24, (30) 15/28 19/24, (31) 18/16, (32) 17/14, (33) 14/10 18/12, (34) 16/14 17/14 17/16 18/16 18/18 21/14 22/14 22/14 22/18 42/28, (35) 12/10, (36) 12/8, (37) 26/26 27/28, (38) 14/8 17/18 18/12 36/74, (39) 18/12 18/18 19/16 20/16 24/18 32/20 42/30, (40) 7/8 12/8 28/16, (41) 2/4 14/14 18/12 18/12 18/14 18/14 18/20 19/14 19/16 20/12 20/12 20/14 20/30 20/32 20/32 20/32 21/18 22/16 26/16 27/18 27/44 28/48 28/48 29/50 30/20 30/52 34/24, (42) 8/10 27/48.

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