

Symmetry constraints and modularity: tools to model inorganic crystal structures

Giovanni Ferraris

Dipartimento di Scienze Mineralogiche e Petrologiche, Università di Torino – Istituto di Geoscienze e Georisorse, CNR – Via Valperga Caluso 35, 10125 Torino, Italy.

giovanni.ferraris@unito.it

Introduction

Modelling a crystal structure is a task harder for non-molecular than for molecular structures: in fact, in the latter case the process can often be reduced to the packing of known molecules. Coordination polyhedra in inorganic (i.e., non-molecular) structures are a kind of surrogate to molecules; however, apart simple structures, modelling a structure starting from coordination polyhedra is a hopeless task. In recent years, it has been recognized that a same module (fragment) consisting of several coordination polyhedra may be recurrent in different crystal structures. Classical examples are (i) polytypes, i.e. structures based on different stacking of a same basic layer, and (ii) layer silicates all based on tetrahedral (*T*) and octahedral (*O*) sheets grouped either as *TO* or *TOT* layers (See below Fig. 5).

Modelling structures by symmetry constraints

Given the cell parameters, chemical composition, density and space group, one can easily detect if some atomic species are constrained to special positions of the space group. If the symmetry of the structure is high, the symmetry constraints may be sufficient to fix the position of all the atomic species. The procedure will be illustrated by some classical examples.

CaF₂ (fluorite) (Fig. 1)

- *Chemical composition:* CaF₂
- *Cell parameter:* $a = 5.462 \text{ \AA}$
- *Density:* $\delta = 3.18 \text{ gr/cm}^3$

- *Space group*: hkl diffractions occur only if h, k, l are either all odd or all even; therefore, the lattice is cF ; from the morphology it is known that the point group of fluorite is $m\bar{3}m$, thus the space group is $Fm\bar{3}m$.

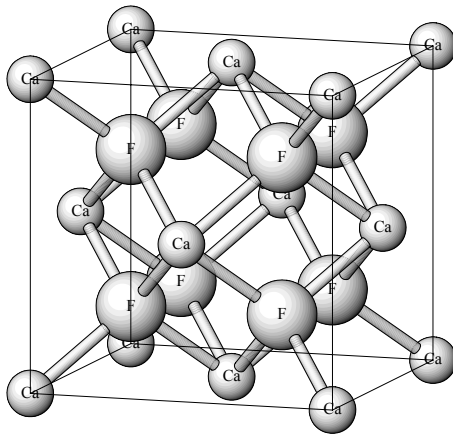


Figure 1 – Crystal structure of fluorite.

Number of unit formulae in the cell: $Z = (\delta VN)/M = (3.18 \times 162.95 \cdot 10^{-24} \times 6.022 \cdot 10^{23})/78.08 = 3.997$ (M = weight of the unit formula; V = cell volume; δ = density; N = Avogadro number).

$Z = 4$ means that 4 atoms of Ca and 8 of F occur in the unit cell. In the space group $Fm\bar{3}m$ only the Wyckoff site c ($1/4, 1/4, 1/4$) has multiplicity 8; therefore the 8 F atoms can only occupy the centres of the eight small cubes with edge $a' = a/2$. The four Ca atoms must stay in one of the two Wyckoff sites with multiplicity 4:

a ($0,0,0$) and b ($1/2, 1/2, 1/2$). The position a for Ca is coherent with F at $1/4, 1/4, 1/4$; the choice of b would imply a change of origin.

Note that:

1. F in c contributes only to the diffractions with even h, k, l (see the special systematic absences for the c site).
2. The site symmetry of the a ($m\bar{3}m$) and c ($\bar{4}3m$) sites constrains the symmetry of the coordination polyhedra: a cube for Ca and a tetrahedron for F.
3. For both Ca and F the site symmetry constrains the surface of thermal vibration to be a rotation ellipsoid with its rotation axis along the 3 axis.

TiO₂ (rutile) (Fig. 2)

- *Chemical composition*: TiO_2
- *Cell parameters*: $a = 4.594 \text{ \AA}$, $c = 2.958 \text{ \AA}$
- *Density*: $\delta = 4.25 \text{ gr/cm}^3$
- *Space group*: $0kl$ occur only if $k + l = 2n$; from the morphology it is known that the point group of rutile is mmm , thus the space groups is $P4_2/mnm$.
- $Z = (4.25 \times 79.90 \cdot 10^{-24} \times 6.022 \cdot 10^{23})/79.90 = 2.00$.

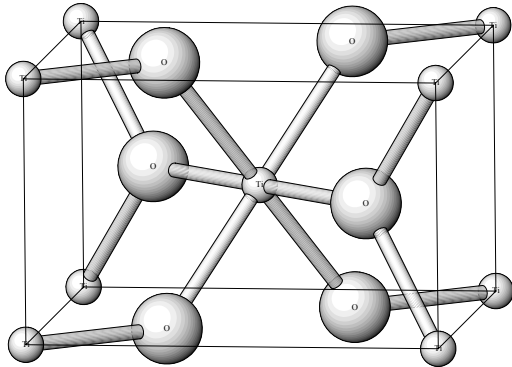


Figure 2 – Crystal structure of rutile.

$Z = 2$ implies that 2 atoms of Ti and 4 atoms of O occur in the unit cell. In the space group $P4_2/mnm$ the Wyckoff sites with multiplicity 2 are a and b ; the sites with multiplicity 4 are c, d, e, f and g . Choosing either a or b for Ti implies only a change of origin: a (0,0,0) is chosen. The assignment of O to one of the four sites with multiplicity 4 requires a further hypothesis: Ti is octahedrally coordinated by six O with $\text{Ti-O} \sim 2 \text{ \AA}$.

The site f ($xx0$) with $x = 0.305$ satisfies the hypothesis. Thus, a problem which without the theory of the space groups would require the determination of $6(\text{atoms}) \times 3 = 18$ coordinates, is reduced to a one-parameter problem: the x coordinate of the O atom.

MgAl₂O₄ (spinel) (Fig. 3)

- *Chemical composition:* MgAl_2O_4
- *Cell parameter:* $a = 8.09 \text{ \AA}$
- *Density:* $\delta = 3.58 \text{ gr/cm}^3$
- *Space group:* hkl diffractions occur only if h, k, l are either all odd or all even; therefore, the lattice is cF ; besides, $0kl$ occur only for $k + l = 4n$; from the morphology it is known that the point group of spinel is $m\bar{3}m$, thus the space group is $Fd\bar{3}m$.
- $Z = (3.588 \times 529.47 \cdot 10^{-24} \times 6.023 \cdot 10^{24}) / 142.27 = 8.04$.

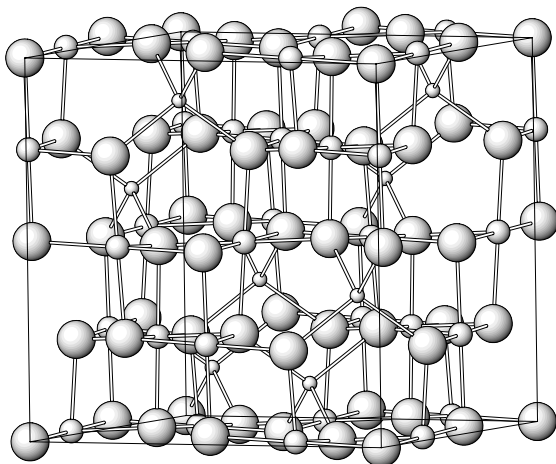
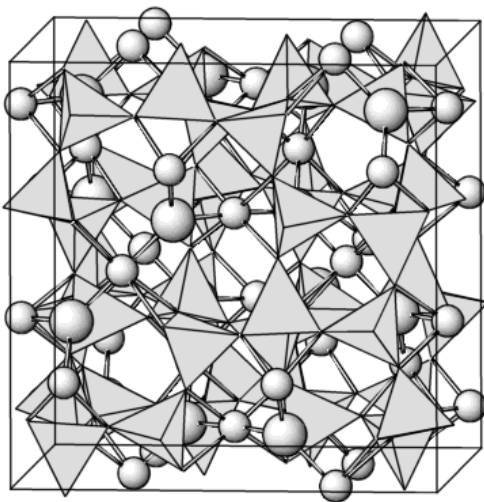


Figure 3 – Crystal structure of spinel. Small and intermediate spheres represent tetrahedral (Mg) and octahedral (Al) cations, respectively. Large spheres are oxygen atoms.

$Z = 8$ requires 8 Mg, 16 Al and 32 O atoms in the cell. Choosing either a or b Wyckoff sites for the 8 Mg implies only a change of origin: a (0,0,0) is chosen. On the hypothesis that Al is octahedrally coordinated, the 16 Al atoms are in d (5/8,5/8,5/8) and the 32 O atoms are in e (x,x,x). A value of $x \sim 3/8$ is obtained by the constraints of the Mg-O and Al-O bond distances. Without knowledge of the space group, $3 \times 56 = 168$ coordinates would be necessary to fix the 56 atoms in the unit cell.

NaAlSi₂O₆·H₂O (analcite, zeolite) (Fig. 4)

- *Chemical composition:* NaAlSi₂O₆·H₂O
- *Cell parameter:* $a = 13.73 \text{ \AA}$
- *Density:* $\delta = 2.28 \text{ gr/cm}^3$
- *Space group:* hkl diffractions occur only if $h+k+l = 2n$; therefore, the lattice is cI ; besides, $0kl$ occur only for k and l even and hhl occur only for $2h+l = 4n$; from the morphology it is known that the point group of analcrite is $m\bar{3}m$, thus the space group is $Ia\bar{3}d$.



$Z = 16$, thus in the unit cell there are: 16 Na, 16 Al, 32 Si, 96 anionic O (O1) and 16 water O (O2); the 32 atoms of H are ignored. Taking into account that in the aluminosilicates normally Si and Al statistically occupy the same crystallographic site, the following distribution of the atoms in the structure of analcrite is obtained: 48 (Si,Al) in $48f$ ($x,0,1/4$); 96 O1 in $96h$ (x,y,z); 16 O2 in $16b$ ($1/8,1/8,1/8$) and 16 Na statistically distributed in $24c$ ($1/8,0,1/4$). Finally, the problem of fixing the 176 atoms in the unit cell is reduced to a four-parameter problem: x,y,z of O1 and x of (Si,Al).

Figure 4 – Structure of analcrite. Large and small spheres are H₂O oxygens and Na, respectively

The modular approach

Several procedures useful to describe and model structures based on recurrent modules are reported in literature, as recently reviewed by Ferraris, G., Makovicky, E., Merlino, S. (2004):

Crystallography of Modular Materials, IUCr/Oxford University Press. Among several approaches, this lecture will focus on the so called *polysomatic series* which are a subclass of the *homologous series*.

All members of a polysomatic series share two or more modules that have definite chemical composition and lattice dimensions. Different modules (here supposed to be layers) must share the lattice dimensions at their common interface. For sake of simplicity, let us refer to the most common case of two modules (say A and B); a periodic stacking of intercalated mA and nB modules forms a crystal structure with chemical composition A_mB_n . The same symbol A_mB_n is used to represent the related series. The building principle of a polysomatic series implies that the chemical composition and the lattice dimensions of each member are linear functions of those of the single modules. Note that for a given composition A_mB_n , different sequences of the modules A and B , i.e. different polytypes, are possible.

Layers as building modules of a crystal structure have been used since long time (e.g., in phyllosilicates; Fig. 5), but only the work of J.B. Thompson (*Am. Min.*, 63, 239, 1978) on micas and amphiboles (biopyriboles) clearly showed the usefulness of the method.

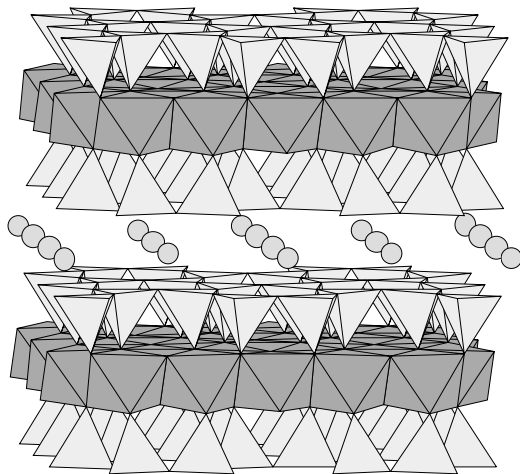


Figure 5 – TOT layers in phyllosilicates. According to the nature of the interlayer module, different phyllosilicates are obtained: talc (empty module), micas (alkaline cations), chlorites (octahedral sheet), smectites (H_2O).

Biopyriboles

Thompson (1978) proposed to describe the crystal structure of the amphiboles as built by alternating slices (modules) of micas (M) and pyroxenes (P) (Fig. 6). In principle, a series M_mP_n is possible with end members M_1P_0 (mica) and M_0P_1 (pyroxene); only the intermediate member M_1P_1 (pyroxene) was known. The following findings established a great success of the

modular interpretation of the amphiboles and of other structures:

1. Defects in the sequence M_1P_1 (e.g., $MPPMPMP\dots$) were soon discovered by transmission electron microscopy (TEM). Note that this type of defect implies a variation of chemical composition.
2. Two new minerals representing the members M_2P_1 (jimthompsonite) and M_3P_2 (chesterite) were discovered.

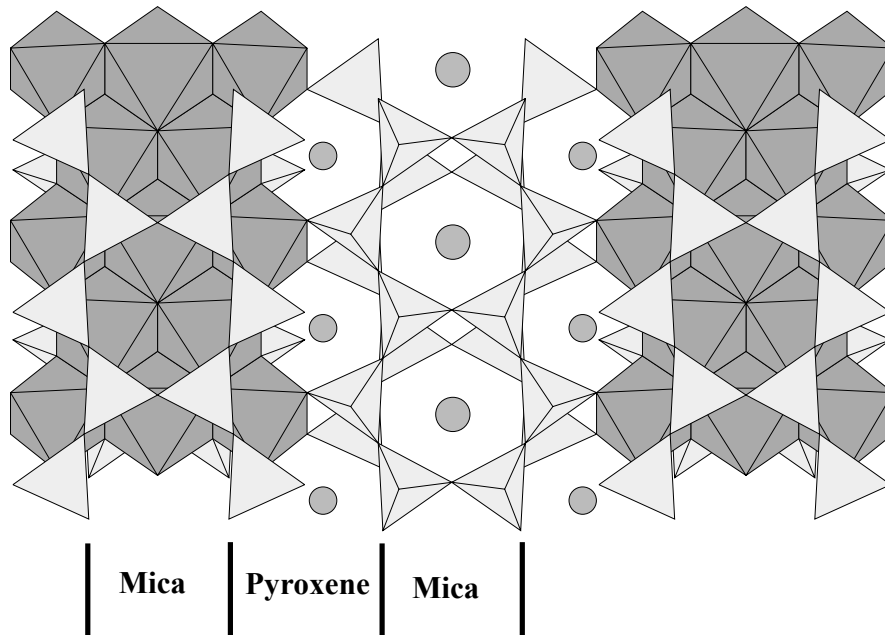


Figure 6 – Amphiboles can be described as built by alternating modules of mica (M) and pyroxene.

Modelling polysomatic structures

Hundreds of modular crystal structures are known: from minerals, to superconductors, organic-inorganic hybrid structures, etc.; in most cases these structures can be interpreted as members of a polysomatic series A_mB_n . In this lecture, we illustrate the use of the modular method to model unknown crystal structures that can be related to a polysomatic series. The main steps of the modelling process are as follows.

1. Determination of the chemical composition.
2. Determination of the lattice parameters and of the space group
3. Search of known structures with which, according to the chemical composition and lattice dimensions, the unknown structure likely shares structural modules. Of course, the

symmetry of the building modules must be compatible with the space group experimentally determined for the unknown structure.

4. Building of a structure model that matches the known chemical and crystallographic data of the unknown structure.
5. Assessment of the structure geometry (bonds and angles) via refinement procedures like Distance Least Squares (Baerlocher *et al.* (1978): *Manual DLS-76*, ETH, Zurich).
6. Validation of the structure model via crystal-chemical tests and comparison between calculated and observed diffraction patterns.
7. Refinement of the structure model against diffraction data, as far as the complexity of the structure and the quality of the experimental data allow it. Often, the best agreement between calculated and observed data can be assessed only by trial.

Nafertisite and the polysomatic series of the heterophyllosilicates

For **nafertisite** (*nfr*) $\{(\text{Na}, \text{K}, \square)_4(\text{Fe}^{2+}, \text{Fe}^{3+}, \square)_{10}[\text{Ti}_2\text{O}_3\text{Si}_{12}\text{O}_{34}](\text{O}, \text{OH})_6; A2/m, a = 5.353, b = 16.176, c = 21.95 \text{ \AA}, \beta = 94.6(2)^\circ\}$ a structure model was obtained (Fig. 7) by comparison with the crystal structures of **bafertisite** $\{bft; \text{Ba}_2(\text{Fe}, \text{Mn})_4[\text{Ti}_2\text{O}_4\text{Si}_4\text{O}_{14}](\text{O}, \text{OH})_2; P2_1/m, a = 5.36, b = 6.80, c = 10.98 \text{ \AA}, \beta = 94^\circ; \text{Fig. 7}\}$ and **astrophyllite** $\{ast; (\text{K}, \text{Na})_3(\text{Fe}, \text{Mn})_7[\text{Ti}_2\text{O}_3\text{Si}_8\text{O}_{24}](\text{O}, \text{OH})_4; P\bar{1}, a = 5.36, b = 11.63, c = 11.76 \text{ \AA}, \alpha = 112.1, \beta = 103.1, \gamma = 94.6^\circ; \text{Fig. 7}\}$ and noting the following.

1. Bafertisite, astrophyllite and nafertisite have a common value of $a \sim 5.4 \text{ \AA}$, which corresponds to the a value of mica.
2. $(b_{ast} - b_{bft}) \sim 1/2(b_{nfr} - b_{bft}) \sim 4.7 \text{ \AA}$ corresponds to $b/2$ in mica.
3. $(d_{002})_{nfr} = 10.94 \text{ \AA}$ matches the thickness of one structural layer in bafertisite and astrophyllite.
4. The difference in composition *between bafertisite and astrophyllite* and *between astrophyllite and nafertisite* is the same and ideally corresponds to $(I, \square)(Y, \square)_3[\text{Si}_4\text{O}_{10}](\text{OH}, \text{O})_2$ (I and Y are interlayer and octahedral cations, respectively), i.e. to the composition of **mica** (Fig. 5). That is confirmed by the comparison between the *layers of astrophyllite and bafertisite*: the first layer differs from the second one only by

the presence of a mica-like module (*M*) between two (010) slabs built up by Ti- and Si-polyhedra (Fig. 7, 8).

On the hypothesis that the difference between the unknown nafertisite layer and the known astrophyllite layer is the same mica slice which leads from the bafertisite structure to that of astrophyllite, a structural model of nafertisite has been built [Ferraris *et al.* (1996): *Eur. J. Mineral.*, **8**, 241-249] and successfully tested against the experimental X-ray powder-diffraction pattern.

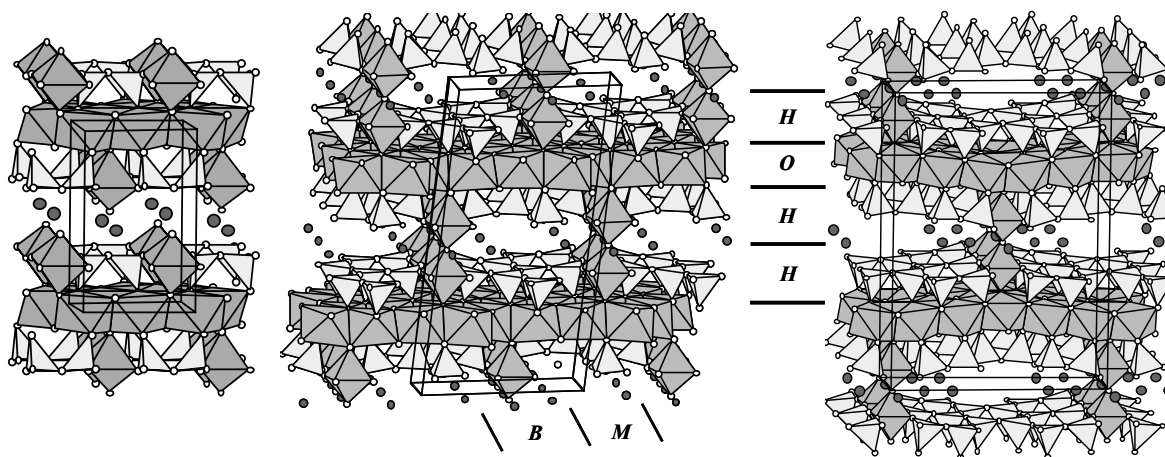


Figure 7 – From left to right side: perspective view of the structures of bafertisite, astrophyllite and nafertisite. The mica (*M*), bafertisite (*B*), mixed tetrahedral/octahedral (*H*) and octahedral (*O*) modules are shown (cf. Fig. 8).

One can note that the layers of the titanosilicates bafertisite, astrophyllite and nafertisite can be formally derived from the *TOT* layer (*T* and *O* stand for tetrahedral and octahedral, respectively) of the phyllosilicates (layer silicates) if a row of Ti-polyhedra periodically substitutes a row of disilicate tetrahedra in the *T* tetrahedral sheet (Fig. 8). *HOH* layers are thus obtained where *H* stands for *hetero* to indicate the presence of the rows of 5- or 6-coordinated Ti in a sheet corresponding to the *T* sheet of the layer silicates. Three types of *HOH* layers are known so far.

1. **Bafertisite-like (*HOH*)_B layer** - A bafertisite-like module $B = I_2Y_4[Ti_2(O)_4Si_4O_{14}](O,OH)_2$ is periodically repeated.
2. **Astrophyllite-like (*HOH*)_A layer** – Relative to the (*HOH*)_B layer, a one-chain-wide mica-like module $M = IY_3[Si_4O_{10}](O,OH)_2$ is present between two bafertisite-like modules.
3. **Bafertisite-like (*HOH*)_N layer** – A second *M* module is intercalated in the (*HOH*)_A layer.

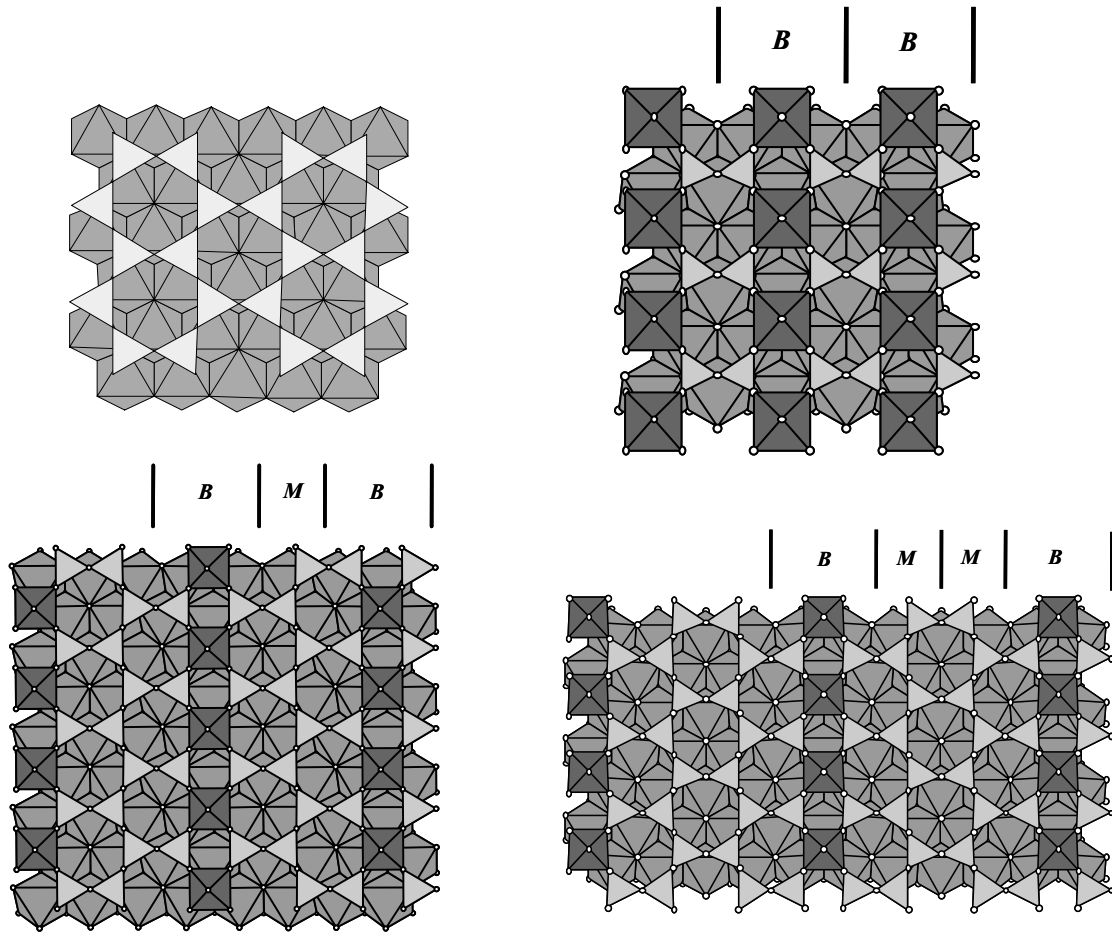


Figure 8 – From top to bottom and left to right side, orthogonal projection of the layers of mica, bafertisite, astrophyllite and nafertisite. The mica (M) and bafertisite (B) modules are shown. The *TOT* layer of mica is transformed to a *HOH* layer of heterophyllosilicates by periodic substitution of rows of octahedra for rows of tetrahedra.

Bafertisite, astrophyllite and nafertisite are members of a B_mM_n **polysomatic series** which is based on *B* (bafertisite-like) and *M* (mica-like) modules and has a general formula $I_{2+n}Y_{4+3n}[Ti_2(O')_{2+p}Si_{4+4n}O_{14+10n}](O'')_{2+2n}$. O' and O'' can be O, OH, F or H_2O ; the value of p (0, 1, 2) depends on the coordination of Ti.

Bornemanite and the series of bafertisite

The bafertisite module $B = I_2Y_4[Ti_2(O)_4Si_4O_{14}](O,OH)_2$ is the most common among heterophyllosilicates and more than 30 minerals are based on it. These minerals, apart details, differ

only for the composition of the interlayer (represented by I) which can be quite complex to include tetrahedral anions. All these compounds form a so called *merotype series* in the sense that they are based on modules of which at least one (a bafertisite-type in this case) is constant. The crystal structure of several members of this series has been modelled by matching the interlayer content, known from chemical analysis, with a bafertisite-type HOH layer.

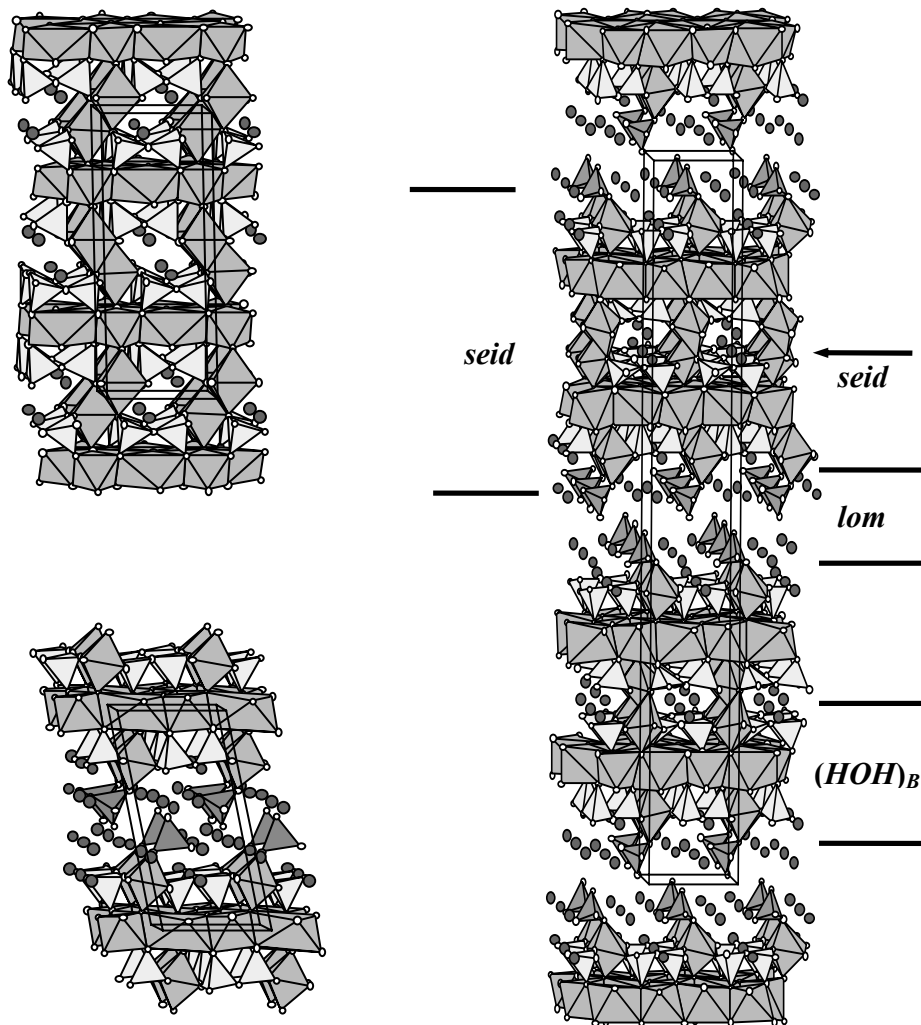


Figure 9 – The crystal structure of bornemanite (right side) contains modules of seidozerite (seid; top left) and lomonosovite (lom; bottom left).

A quite complex case is represented by the layered titanosilicate bornemanite ($\text{BaNa}_3\{(\text{Na},\text{Ti})_4[(\text{Ti},\text{Nb})_2\text{O}_2\text{Si}_4\text{O}_{14}](\text{F},\text{OH})_2\}\text{PO}_4$; $a = 5.498$, $b = 7.120$, $c = 47.95 \text{ \AA}$, $\gamma = 88.4^\circ$; space group $I11b$; Ferraris *et al.* (2001), *Can. Mineral.*, **39**, 1665). The values of the cell

parameters and the presence of the complex anion $[(\text{Ti,Nb})_2\text{O}_2\text{Si}_4\text{O}_{14}]$ in the chemical formula support a strong analogy between bornemanite and members of the bafertisite series. In particular, comparison with lomonosovite, $\text{Na}_8\{(\text{Na}_2\text{Ti}_2)[\text{Ti}_2\text{O}_2\text{Si}_4\text{O}_{14}](\text{O,F})_2\}(\text{PO}_4)_2$, and seidozerite, $\text{Na}_2\{(\text{Na,Mn,Ti})_4[(\text{Na,Ti,Zr})_2\text{O}_2\text{Si}_4\text{O}_{14}]\text{F}_2$, shows that:

1. $c/2$ (23.97 Å) of bornemanite corresponds to the sum in thickness of one lomonosovite-like module (14.5 Å) and one seidozerite-like module (8.9 Å).
2. Disregarding isomorphic substitutions (like Ba for Na and Nb for Ti), half the sum of the crystal chemical-formulae of lomonosovite and seidozerite corresponds to the simplified crystal-chemical formula of bornemanite given above.

On the basis of these indications, it has been possible to build a structure model for bornemanite based on alternating seidozerite-like and lomonosovite-like modules (Fig. 9). In practice, the structure of bornemanite can be described as a [001] stack of $(\text{HOH})_{\text{B}}$ heterophyllosilicate layers in which the lomonosovite and seidozerite interlayer contents alternate. The model has been tested against an X-ray powder-diffraction pattern.

Kalifersite and the palysepiole polysomatic series

The characterisation of the mineral **kalifersite** $\{(\text{K,Na})_5(\text{Fe}^{3+})_7[\text{Si}_{20}\text{O}_{50}](\text{OH})_6 \cdot 12\text{H}_2\text{O}; P\bar{1}, a = 14.86, b = 20.54, c = 5.29 \text{ \AA}, \alpha = 95.6, \beta = 92.3, \gamma = 94.4^\circ\}$ was achieved (Ferraris *et al.* (1998): *Eur. J. Mineral.*, **10**, 865-874) after noting a modular relationship relating it with **sepiolite** $\{\text{Mg}_8[\text{Si}_{12}\text{O}_{30}](\text{OH})_4 \cdot 12\text{H}_2\text{O}; Pncn, a = 13.40, b = 26.80, c = 5.28 \text{ \AA}\}$ and **palygorskite** $\{\text{Mg}_5[\text{Si}_8\text{O}_{20}](\text{OH})_2 \cdot 8\text{H}_2\text{O}; C2/m, a = 13.27, b = 17.868, c = 5.279 \text{ \AA}, \beta = 107.38^\circ\}$. In particular, it was noted:

1. Kalifersite, sepiolite and palygorskite have close values of their a and c parameters. The [001] direction corresponds to the fibre axis of these silicates and its value to the periodicity of a pyroxene chain.
2. The b value of kalifersite is intermediate between that of palygorskite and sepiolite.
3. The $[\text{Si}_{20}\text{O}_{50}](\text{OH})_6$ silicate anion of kalifersite corresponds to the sum of those of sepiolite, $[\text{Si}_{12}\text{O}_{30}](\text{OH})_4$, and palygorskite, $[\text{Si}_8\text{O}_{20}](\text{OH})_2$.
4. The crystal structures of sepiolite and palygorskite (Fig. 10) are based on a framework of interconnected [001] *TOT* ribbons which correspond to cuts with different width of the phyllosilicate 2:1 layer (Fig. 5). These ribbons are chess-board arranged and delimit [001]

channels. In the [010] direction, the $(TOT)_S$ ribbon of sepiolite is one chain wider than that, $(TOT)_P$, of palygorskite. This feature requires for sepiolite a b value about 9 Å longer than that of palygorskite, *i.e.* about 4.5 Å per T chain.

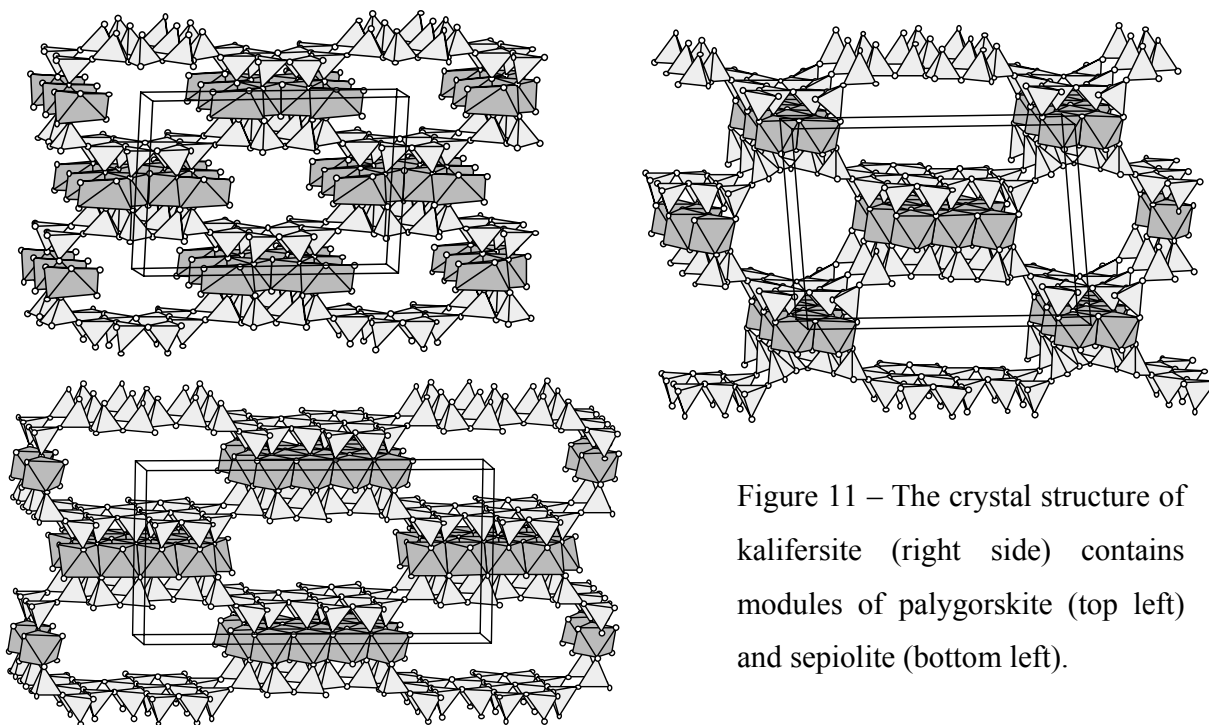


Figure 11 – The crystal structure of kalifersite (right side) contains modules of palygorskite (top left) and sepiolite (bottom left).

Taking into account the above chemical and crystallographic aspects, a structure model for kalifersite based on a 1:1 chess-board arrangement of $(TOT)_P$ and $(TOT)_S$ [001] ribbons and the filling of the channels with alkalis and water molecules was obtained (Fig. 10).

Palygorskite (P), and sepiolite (S) are the end members of the **palysepiole** (palygorskite + **sepiolite**) polysomatic series P_pS_s ; kalifersite is the P_1S_1 member.

Modeling the structure of seidite-(Ce)

The crystal structure of seidite-(Ce) $\{(\text{Na}_4(\text{Ce},\text{Sr})_2\text{Ti}[(\text{Si}_8\text{O}_{18})(\text{OH})_2](\text{O},\text{OH},\text{F})_4 \cdot 5\text{H}_2\text{O}; a = 24.61, b = 7.23, c = 14.53 \text{ \AA}, \beta = 94.6^\circ; C2/c; \text{Ferraris } et \text{ al. (2003): } \textit{Can. Min.}, \mathbf{41}, 1183\}$ can be modelled by comparison with rhodesite $\{\text{K}_2\text{Ca}_4[\text{Si}_8\text{O}_{18}(\text{OH})_2] \cdot 12\text{H}_2\text{O}; a = 23.416, b = 6.555, c = 7.050 \text{ \AA}, Pmam\}$ with which it shares the anion $[(\text{Si}_8\text{O}_{18})(\text{OH})_2]$ and shows similarity of cell parameters [$c/2$ for seidite-(Ce)].

Rhodesite (Fig. 12) and a group of related compounds share the same double silicate layer and differ by the composition of the “octahedral” layer that joins the silicate layer. Thus, these compounds are members of a merotype series where the silicate layer is constantly present.

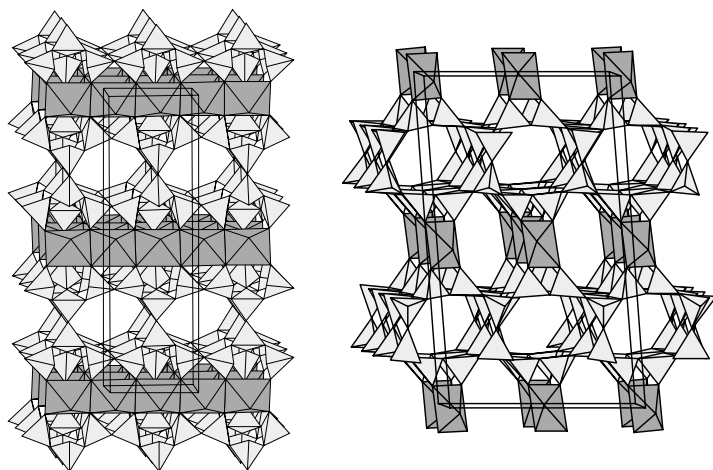


Figure 12 – The crystal structures of rhodesite (left side) and seidite-(Ce) share the same layer of eight-membered silicate channels and differ in the octahedral layer (grey polyhedra)

Practically, the crystal structure of seidite-(Ce) (Fig. 12) has been obtained by substituting the octahedral layer of rhodesite, which consists of chains of edge-sharing Ca octahedra, by an octahedral layer consisting of isolated Ti-octahedra. The channels are filled by (Ce,Sr), Na and H₂O in seidite-(Ce), and by K and H₂O in rhodesite.

The carlosturanite polysomatic series

Carlosturanite is a water- and magnesium-rich, silicon-poor serpentine-like asbestiform mineral; it shows rotational disorder about the [010] fibre axis. The modelling of the crystal structure of carlosturanite $\{(Mg_{21}[Si_{12}O_{28}(OH)_4](OH)_{30} \cdot H_2O; a = 36.7, b = 9.4, c = 7.3 \text{ \AA}, \beta = 101^\circ, \text{ space group } Cm; \text{ marked superlattice with } a' = a/7; \text{ Mellini } et al. (1985): \textit{Amer. Mineral. } 70, 773\}$ represents one of the first applications of polysomatism after the introduction of the biopyribole polysomatic series by Thompson (1978) (Fig. 6).

Comparison with lizardite, $Mg_6[Si_4O_{10}](OH)_8$, shows that carlosturanite has the same cell, except a which is 7 times the a parameter of lizardite, and a ratio $Si/Mg = 12/21 < 2/3$. This suggests that the structure of carlosturanite can be derived by inserting a silicon depleted module in a sevenfold lizardite cell. A model suitable to explain the observed data was obtained by preserving the octahedral sheet of lizardite and introducing a [010] row of tetrahedral vacancies at $x = 0$ and $1/2$ (Fig. 13). Precisely, starting from a sevenfold lizardite cell with $a = 5.2 \times 7 \text{ \AA}$ and

content $7\text{Mg}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$, two $[\text{Si}_2\text{O}_7]^{6-}$ ditetrahedral groups are replaced by two $[(\text{OH})_6\text{H}_2\text{O}]^{6-}$ groups (same tetrahedral arrangement), where H_2O and OH carry the bridging and non-bridging oxygen atoms, respectively. A structure model with composition $\text{Mg}_{42}[\text{Si}_{24}\text{O}_{56}(\text{OH})_8](\text{OH})_{60}(\text{H}_2\text{O})_2$ is thus obtained which fits the unit cell content of carlosturanite obtained from the chemical analysis.

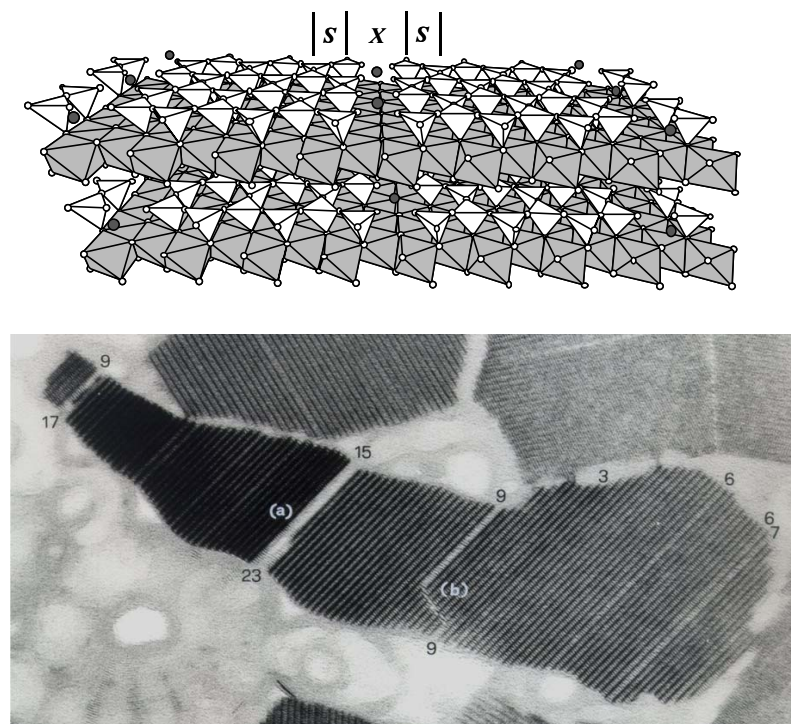


Figure 13 – The crystal structure of carlosturanite (top) consists of serpentine (S) and X (100) modules. It represents the member S_5X of a polysomatic series S_nX . In the shown (bottom) High Resolution Transmission Electron Microscopy (HRTEM) image the members $n = 3, 6, 7, 9, 15, 17, 23$ occur as polysomatic defects in a matrix of carlosturanite.

HRTEM images of carlosturanite (Fig. 13) show chain-multiplicity faults along $[100]$. The faults are explained as members of a polysomatic series S_nX (**inophite polysomatic series**) composed of two (100) modules: $S = \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ and $X = \text{Mg}_6\text{Si}_2\text{O}_3(\text{OH})_{14}\cdot\text{H}_2\text{O}$. The S module corresponds to a (100) slab of serpentine (lizardite) structure with thickness $a_s/2$ ($a_s = 5.2 \text{ \AA} = a$ of serpentine); the X slab has thickness a_s and corresponds to a hypothetical hydro-silicate. A generic S_nX member of the inophite series has: P lattice, $a = [(n + 2)/2]a_s$ and $Z = 1$ for n even; C lattice, $a = (n + 2)a_s$ and $Z = 2$ for n odd. Carlosturanite represents the S_5X member of the inophite series. As mentioned above, several polysomes with n in the range 1-23 have been observed as chain-width defects in a matrix of carlosturanite. This experimentally confirms the polysomatic interpretation of carlosturanite.

CONTINUED

No. 136

 $P4_2/mnm$ Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5); (9)

Positions

Multiplicity, Wyckoff letter, Site symmetry	Coordinates	Reflection conditions
General:		
16 <i>k</i> 1	(1) x, y, z (2) \bar{x}, \bar{y}, z (3) $\bar{y} + \frac{1}{2}, x + \frac{1}{2}, z + \frac{1}{2}$ (4) $y + \frac{1}{2}, \bar{x} + \frac{1}{2}, z + \frac{1}{2}$ (5) $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$ (6) $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z} + \frac{1}{2}$ (7) y, x, \bar{z} (8) $\bar{y}, \bar{x}, \bar{z}$ (9) $\bar{x}, \bar{y}, \bar{z}$ (10) x, y, \bar{z} (11) $y + \frac{1}{2}, \bar{x} + \frac{1}{2}, \bar{z} + \frac{1}{2}$ (12) $\bar{y} + \frac{1}{2}, x + \frac{1}{2}, \bar{z} + \frac{1}{2}$ (13) $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, z + \frac{1}{2}$ (14) $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$ (15) \bar{y}, \bar{x}, z (16) y, x, z	$0kl : k+l = 2n$ $00l : l = 2n$ $h00 : h = 2n$
Special: as above, plus		
8 <i>j</i> .. <i>m</i>	x, x, z \bar{x}, \bar{x}, z $\bar{x} + \frac{1}{2}, x + \frac{1}{2}, z + \frac{1}{2}$ $x + \frac{1}{2}, \bar{x} + \frac{1}{2}, z + \frac{1}{2}$ $\bar{x} + \frac{1}{2}, x + \frac{1}{2}, \bar{z} + \frac{1}{2}$ $x + \frac{1}{2}, \bar{x} + \frac{1}{2}, \bar{z} + \frac{1}{2}$ x, x, \bar{z} $\bar{x}, \bar{x}, \bar{z}$	no extra conditions
8 <i>i</i> <i>m</i> ..	$x, y, 0$ $\bar{x}, \bar{y}, 0$ $\bar{y} + \frac{1}{2}, x + \frac{1}{2}, \frac{1}{2}$ $y + \frac{1}{2}, \bar{x} + \frac{1}{2}, \frac{1}{2}$ $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, \frac{1}{2}$ $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, \frac{1}{2}$ $y, x, 0$ $\bar{y}, \bar{x}, 0$	no extra conditions
8 <i>h</i> 2... <i>m</i>	$0, \frac{1}{2}, z$ $0, \frac{1}{2}, z + \frac{1}{2}$ $\frac{1}{2}, 0, \bar{z} + \frac{1}{2}$ $\frac{1}{2}, 0, \bar{z}$ $0, \frac{1}{2}, \bar{z}$ $0, \frac{1}{2}, \bar{z} + \frac{1}{2}$ $\frac{1}{2}, 0, z + \frac{1}{2}$ $\frac{1}{2}, 0, z$	$hkl : h+k, l = 2n$
4 <i>g</i> <i>m</i> .2 <i>m</i>	$x, \bar{x}, 0$ $\bar{x}, x, 0$ $x + \frac{1}{2}, x + \frac{1}{2}, \frac{1}{2}$ $\bar{x} + \frac{1}{2}, \bar{x} + \frac{1}{2}, \frac{1}{2}$	no extra conditions
4 <i>f</i> <i>m</i> .2 <i>m</i>	$x, x, 0$ $\bar{x}, \bar{x}, 0$ $\bar{x} + \frac{1}{2}, x + \frac{1}{2}, \frac{1}{2}$ $x + \frac{1}{2}, \bar{x} + \frac{1}{2}, \frac{1}{2}$	no extra conditions
4 <i>e</i> 2.. <i>mm</i>	$0, 0, z$ $\frac{1}{2}, \frac{1}{2}, z + \frac{1}{2}$ $\frac{1}{2}, \frac{1}{2}, \bar{z} + \frac{1}{2}$ $0, 0, \bar{z}$	$hkl : h+k+l = 2n$
4 <i>d</i> $\bar{4}$..	$0, \frac{1}{2}, \frac{1}{4}$ $0, \frac{1}{2}, \frac{3}{4}$ $\frac{1}{2}, 0, \frac{1}{4}$ $\frac{1}{2}, 0, \frac{3}{4}$	$hkl : h+k, l = 2n$
4 <i>c</i> 2/ <i>m</i> ..	$0, \frac{1}{2}, 0$ $0, \frac{1}{2}, \frac{1}{2}$ $\frac{1}{2}, 0, \frac{1}{2}$ $\frac{1}{2}, 0, 0$	$hkl : h+k, l = 2n$
2 <i>b</i> <i>m</i> .. <i>mm</i>	$0, 0, \frac{1}{2}$ $\frac{1}{2}, \frac{1}{2}, 0$	$hkl : h+k+l = 2n$
2 <i>a</i> <i>m</i> .. <i>mm</i>	$0, 0, 0$ $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$hkl : h+k+l = 2n$

Symmetry of special projections

Along [001] $P4gm$ $a' = a$ $b' = b$ Origin at $0, \frac{1}{2}, z$ Along [100] $c2mm$ $a' = b$ $b' = c$ Origin at $x, 0, 0$ Along [110] $P2mm$ $a' = \frac{1}{2}(-a+b)$ $b' = c$ Origin at $x, x, 0$

Maximal non-isomorphic subgroups

I	[2] $P\bar{4}n2$ (118)	1; 2; 7; 8; 11; 12; 13; 14
	[2] $P\bar{4}2_1m$ (113)	1; 2; 5; 6; 11; 12; 15; 16
	[2] $P4nm$ (102)	1; 2; 3; 4; 13; 14; 15; 16
	[2] $P4_22_2$ (94)	1; 2; 3; 4; 5; 6; 7; 8
	[2] $P4_2/m11$ ($P4_2/m$, 84)	1; 2; 3; 4; 9; 10; 11; 12
	[2] $P2/m12/m$ ($Cmmm$, 65)	1; 2; 7; 8; 9; 10; 15; 16
	[2] $P2/m2_1/n1$ ($Pnmm$, 58)	1; 2; 5; 6; 9; 10; 13; 14

IIa none

IIb none

Maximal isomorphic subgroups of lowest index

IIc [3] $P4_2/mnm$ ($c' = 3c$) (136); [9] $P4_2/mnm$ ($a' = 3a, b' = 3b$) (136)

Minimal non-isomorphic supergroups

I none

II [2] $C4_2/mcm$ ($P4_2/mmc$, 131); [2] $I4/mmm$ (139); [2] $P4/mbm$ ($c' = \frac{1}{2}c$) (127)

CONTINUED

No. 227

$Fd\bar{3}m$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; $t(0, \frac{1}{2}, \frac{1}{2})$; $t(\frac{1}{2}, 0, \frac{1}{2})$; (2); (3); (5); (13); (25)

Positions

Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates

$(0,0,0)+ (0, \frac{1}{2}, \frac{1}{2})+ (\frac{1}{2}, 0, \frac{1}{2})+ (\frac{1}{2}, \frac{1}{2}, 0)+$

Reflection conditions

h, k, l permutable
General:

192	<i>i</i>	1	(1) x, y, z	(2) $\bar{x}, \bar{y} + \frac{1}{2}, z + \frac{1}{2}$	(3) $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, \bar{z}$	(4) $x + \frac{1}{2}, \bar{y}, \bar{z} + \frac{1}{2}$	$hkl : h + k = 2n$ and $h + l, k + l = 2n$ $0kl : k + l = 4n$ and $k, l = 2n$ $hhl : h + l = 2n$ $h00 : h = 4n$
			(5) z, x, y	(6) $z + \frac{1}{2}, \bar{x}, \bar{y} + \frac{1}{2}$	(7) $\bar{z}, \bar{x} + \frac{1}{2}, y + \frac{1}{2}$	(8) $\bar{z} + \frac{1}{2}, x + \frac{1}{2}, \bar{y}$	
			(9) y, z, x	(10) $\bar{y} + \frac{1}{2}, z + \frac{1}{2}, \bar{x}$	(11) $y + \frac{1}{2}, \bar{z}, \bar{x} + \frac{1}{2}$	(12) $\bar{y}, \bar{z} + \frac{1}{2}, x + \frac{1}{2}$	
			(13) $y + \frac{1}{2}, x + \frac{1}{2}, \bar{z} + \frac{3}{4}$	(14) $\bar{y} + \frac{1}{2}, \bar{x} + \frac{1}{2}, \bar{z} + \frac{1}{4}$	(15) $y + \frac{1}{2}, \bar{x} + \frac{1}{2}, z + \frac{3}{4}$	(16) $\bar{y} + \frac{1}{2}, x + \frac{1}{2}, z + \frac{1}{4}$	
			(17) $x + \frac{1}{2}, z + \frac{1}{2}, \bar{y} + \frac{3}{4}$	(18) $\bar{x} + \frac{1}{2}, z + \frac{1}{2}, y + \frac{1}{4}$	(19) $\bar{x} + \frac{1}{2}, \bar{z} + \frac{1}{2}, \bar{y} + \frac{1}{4}$	(20) $x + \frac{1}{2}, \bar{z} + \frac{1}{2}, y + \frac{3}{4}$	
			(21) $z + \frac{1}{2}, y + \frac{1}{2}, \bar{x} + \frac{3}{4}$	(22) $z + \frac{1}{2}, \bar{y} + \frac{1}{2}, x + \frac{1}{4}$	(23) $\bar{z} + \frac{1}{2}, y + \frac{1}{2}, x + \frac{1}{4}$	(24) $\bar{z} + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{x} + \frac{1}{4}$	
			(25) $\bar{x} + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z} + \frac{1}{4}$	(26) $x + \frac{1}{2}, y + \frac{1}{2}, \bar{z} + \frac{3}{4}$	(27) $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, z + \frac{1}{4}$	(28) $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, z + \frac{3}{4}$	
			(29) $\bar{z} + \frac{1}{2}, \bar{x} + \frac{1}{2}, \bar{y} + \frac{1}{4}$	(30) $\bar{z} + \frac{1}{2}, x + \frac{1}{2}, y + \frac{3}{4}$	(31) $z + \frac{1}{2}, x + \frac{1}{2}, \bar{y} + \frac{3}{4}$	(32) $z + \frac{1}{2}, \bar{x} + \frac{1}{2}, y + \frac{1}{4}$	
			(33) $\bar{y} + \frac{1}{2}, \bar{z} + \frac{1}{2}, \bar{x} + \frac{1}{4}$	(34) $y + \frac{1}{2}, \bar{z} + \frac{1}{2}, x + \frac{1}{4}$	(35) $\bar{y} + \frac{1}{2}, z + \frac{1}{2}, x + \frac{3}{4}$	(36) $y + \frac{1}{2}, z + \frac{1}{2}, \bar{x} + \frac{3}{4}$	
			(37) $\bar{y} + \frac{1}{2}, \bar{x}, z + \frac{1}{2}$	(38) y, x, z	(39) $\bar{y}, x + \frac{1}{2}, \bar{z} + \frac{1}{2}$	(40) $y + \frac{1}{2}, \bar{x} + \frac{1}{2}, \bar{z}$	
			(41) $\bar{x} + \frac{1}{2}, \bar{z}, y + \frac{1}{2}$	(42) $x + \frac{1}{2}, \bar{z} + \frac{1}{2}, \bar{y}$	(43) x, z, y	(44) $\bar{x}, z + \frac{1}{2}, \bar{y} + \frac{1}{2}$	
			(45) $\bar{z} + \frac{1}{2}, \bar{y}, x + \frac{1}{2}$	(46) $\bar{z}, y + \frac{1}{2}, \bar{x} + \frac{1}{2}$	(47) $z + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{x}$	(48) z, y, x	

Special: as above, plus

96	<i>h</i>	..2	$\frac{1}{2}, y, \bar{y} + \frac{1}{4}$	$\frac{7}{8}, \bar{y} + \frac{1}{2}, \bar{y} + \frac{3}{4}$	$\frac{5}{8}, y + \frac{1}{2}, y + \frac{3}{4}$	$\frac{3}{8}, \bar{y}, y + \frac{1}{4}$	no extra conditions
			$\bar{y} + \frac{1}{4}, \frac{1}{8}, y$	$\bar{y} + \frac{3}{8}, \bar{y} + \frac{1}{2}$	$y + \frac{3}{8}, \frac{7}{8}, y + \frac{1}{2}$	$y + \frac{1}{8}, \frac{5}{8}, \bar{y}$	
			$y, \bar{y} + \frac{1}{4}, \frac{1}{8}$	$\bar{y} + \frac{1}{2}, \bar{y} + \frac{3}{4}, \frac{7}{8}$	$y + \frac{1}{2}, y + \frac{1}{4}, \frac{3}{8}$	$\bar{y}, y + \frac{1}{4}, \frac{5}{8}$	
			$\frac{1}{8}, \bar{y} + \frac{1}{4}, y$	$\frac{3}{8}, y + \frac{3}{4}, y + \frac{1}{2}$	$\frac{7}{8}, \bar{y} + \frac{3}{4}, \bar{y} + \frac{1}{2}$	$\frac{5}{8}, y + \frac{1}{4}, \bar{y}$	
			$y, \frac{1}{8}, \bar{y} + \frac{1}{4}$	$y + \frac{1}{2}, \frac{3}{8}, y + \frac{3}{4}$	$\bar{y} + \frac{1}{2}, \frac{7}{8}, \bar{y} + \frac{3}{4}$	$\bar{y}, \frac{5}{8}, y + \frac{1}{4}$	
			$\bar{y} + \frac{1}{4}, y, \frac{1}{8}$	$y + \frac{3}{4}, y + \frac{1}{2}, \frac{7}{8}$	$\bar{y} + \frac{3}{4}, \bar{y} + \frac{1}{2}, \frac{7}{8}$	$y + \frac{1}{4}, \bar{y}, \frac{5}{8}$	

96	<i>g</i>	..m	x, x, z	$\bar{x}, \bar{x} + \frac{1}{2}, z + \frac{1}{2}$	$\bar{x} + \frac{1}{2}, x + \frac{1}{2}, \bar{z}$	$x + \frac{1}{2}, \bar{x}, \bar{z} + \frac{1}{2}$	no extra conditions
			z, x, x	$z + \frac{1}{2}, \bar{x}, \bar{x} + \frac{1}{2}$	$\bar{z}, \bar{x} + \frac{1}{2}, x + \frac{1}{2}$	$\bar{z} + \frac{1}{2}, x + \frac{1}{2}, \bar{x}$	
			x, z, x	$\bar{x} + \frac{1}{2}, z + \frac{1}{2}, \bar{x}$	$x + \frac{1}{2}, \bar{z}, \bar{x} + \frac{1}{2}$	$\bar{x}, \bar{z} + \frac{1}{2}, x + \frac{1}{2}$	
			$x + \frac{1}{2}, x + \frac{1}{2}, \bar{z} + \frac{3}{4}$	$\bar{x} + \frac{1}{4}, \bar{x} + \frac{1}{4}, \bar{z} + \frac{1}{4}$	$x + \frac{1}{2}, \bar{x} + \frac{3}{4}, z + \frac{3}{4}$	$\bar{x} + \frac{3}{4}, x + \frac{3}{4}, z + \frac{1}{4}$	
			$x + \frac{1}{2}, z + \frac{1}{4}, \bar{x} + \frac{3}{4}$	$\bar{x} + \frac{3}{4}, z + \frac{3}{4}, x + \frac{1}{4}$	$\bar{x} + \frac{1}{2}, \bar{z} + \frac{1}{2}, \bar{x} + \frac{1}{4}$	$x + \frac{1}{2}, \bar{z} + \frac{3}{4}, x + \frac{3}{4}$	
			$z + \frac{1}{4}, x + \frac{1}{4}, \bar{x} + \frac{3}{4}$	$z + \frac{1}{4}, \bar{x} + \frac{3}{4}, x + \frac{3}{4}$	$\bar{z} + \frac{3}{4}, x + \frac{3}{4}, x + \frac{1}{4}$	$\bar{z} + \frac{1}{4}, \bar{x} + \frac{1}{4}, \bar{x} + \frac{1}{4}$	

48	<i>f</i>	2. mm	$x, 0, 0$	$\bar{x}, \frac{1}{2}, \frac{1}{2}$	$0, x, 0$	$\frac{1}{2}, \bar{x}, \frac{1}{2}$	$0, 0, x$	$\frac{1}{2}, \frac{1}{2}, \bar{x}$	$hkl : h = 2n + 1$ or $h + k + l = 4n$
			$\frac{1}{4}, x + \frac{1}{4}, \frac{3}{4}$	$\frac{1}{4}, \bar{x} + \frac{1}{4}, \frac{1}{4}$	$x + \frac{1}{4}, \frac{1}{4}, \frac{3}{4}$	$\bar{x} + \frac{3}{4}, \frac{3}{4}, \frac{1}{4}$	$\frac{3}{4}, \frac{1}{4}, \bar{x} + \frac{3}{4}$	$\frac{1}{4}, \frac{3}{4}, x + \frac{3}{4}$	

32	<i>e</i>	. $3m$	x, x, x	$\bar{x}, \bar{x} + \frac{1}{2}, x + \frac{1}{2}$	no extra conditions
			$\bar{x} + \frac{1}{2}, x + \frac{1}{2}, \bar{x}$	$x + \frac{1}{2}, \bar{x}, \bar{x} + \frac{1}{2}$	
			$x + \frac{3}{4}, x + \frac{1}{4}, \bar{x} + \frac{3}{4}$	$\bar{x} + \frac{1}{4}, \bar{x} + \frac{1}{4}, \bar{x} + \frac{1}{4}$	
			$x + \frac{1}{4}, \bar{x} + \frac{3}{4}, x + \frac{3}{4}$	$\bar{x} + \frac{3}{4}, x + \frac{3}{4}, x + \frac{1}{4}$	

16	<i>d</i>	. $\bar{3}m$	$\frac{5}{8}, \frac{5}{8}, \frac{5}{8}$	$\frac{3}{8}, \frac{7}{8}, \frac{1}{8}$	$\frac{7}{8}, \frac{1}{8}, \frac{3}{8}$	$\frac{1}{8}, \frac{3}{8}, \frac{7}{8}$	$hkl : h = 2n + 1$ or $h, k, l = 4n + 2$ or $h, k, l = 4n$
			$\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$	$\frac{7}{8}, \frac{3}{8}, \frac{5}{8}$	$\frac{3}{8}, \frac{5}{8}, \frac{7}{8}$	$\frac{5}{8}, \frac{7}{8}, \frac{1}{8}$	
8	<i>b</i>	$\bar{4}3m$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{4}, \frac{3}{4}, \frac{1}{4}$	$hkl : h = 2n + 1$ or $h + k + l = 4n$		
			$0, 0, 0$	$\frac{3}{4}, \frac{1}{4}, \frac{3}{4}$			

Symmetry of special projections

Along [001] $p4mm$	Along [111] $p6mm$	Along [110] $c2mm$
$a' = \frac{1}{4}(a - b)$ $b' = \frac{1}{4}(a + b)$	$a' = \frac{1}{8}(2a - b - c)$ $b' = \frac{1}{8}(-a + 2b - c)$	$a' = \frac{1}{2}(-a + b)$ $b' = c$
Origin at 0, 0, z	Origin at x, x, x	Origin at x, x, $\frac{1}{2}$

CONTINUED

No. 230

$Ia\bar{3}d$

Symmetry operations

(given on page 715)

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; $t(\frac{1}{2},\frac{1}{2},\frac{1}{2})$; (2); (3); (5); (13); (25)

Positions

Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates
(0,0,0)+ $(\frac{1}{2},\frac{1}{2},\frac{1}{2})+$

Reflection conditions

h, k, l permutable
General:

96	h	1	(1) x, y, z	(2) $\bar{x} + \frac{1}{2}, \bar{y}, z + \frac{1}{2}$	(3) $\bar{x}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$	(4) $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z}$	$hkl : h + k + l = 2n$ $Ok l : k, l = 2n$ $hhl : 2h + l = 4n$ $h00 : h = 4n$
			(5) z, x, y	(6) $z + \frac{1}{2}, \bar{x} + \frac{1}{2}, \bar{y}$	(7) $\bar{z} + \frac{1}{2}, \bar{x}, y + \frac{1}{2}$	(8) $\bar{z}, x + \frac{1}{2}, \bar{y} + \frac{1}{2}$	
			(9) y, z, x	(10) $\bar{y}, z + \frac{1}{2}, \bar{x} + \frac{1}{2}$	(11) $y + \frac{1}{2}, \bar{z} + \frac{1}{2}, \bar{x}$	(12) $\bar{y} + \frac{1}{2}, \bar{z}, x + \frac{1}{2}$	
			(13) $y + \frac{1}{2}, x + \frac{1}{2}, \bar{z} + \frac{1}{2}$	(14) $\bar{y} + \frac{1}{2}, \bar{x} + \frac{1}{2}, \bar{z} + \frac{1}{2}$	(15) $y + \frac{1}{2}, \bar{x} + \frac{1}{2}, z + \frac{1}{2}$	(16) $\bar{y} + \frac{1}{2}, x + \frac{1}{2}, z + \frac{1}{2}$	
			(17) $x + \frac{1}{2}, z + \frac{1}{2}, \bar{y} + \frac{1}{2}$	(18) $\bar{x} + \frac{1}{2}, z + \frac{1}{2}, y + \frac{1}{2}$	(19) $\bar{x} + \frac{1}{2}, \bar{z} + \frac{1}{2}, \bar{y} + \frac{1}{2}$	(20) $x + \frac{1}{2}, \bar{z} + \frac{1}{2}, y + \frac{1}{2}$	
			(21) $z + \frac{1}{2}, y + \frac{1}{2}, \bar{x} + \frac{1}{2}$	(22) $z + \frac{1}{2}, \bar{y} + \frac{1}{2}, x + \frac{1}{2}$	(23) $\bar{z} + \frac{1}{2}, y + \frac{1}{2}, x + \frac{1}{2}$	(24) $\bar{z} + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{x} + \frac{1}{2}$	
			(25) $\bar{x}, \bar{y}, \bar{z}$	(26) $x + \frac{1}{2}, y, \bar{z} + \frac{1}{2}$	(27) $x, \bar{y} + \frac{1}{2}, z + \frac{1}{2}$	(28) $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, z$	
			(29) $\bar{z}, \bar{x}, \bar{y}$	(30) $\bar{z} + \frac{1}{2}, x + \frac{1}{2}, y$	(31) $z + \frac{1}{2}, x, \bar{y} + \frac{1}{2}$	(32) $z, \bar{x} + \frac{1}{2}, y + \frac{1}{2}$	
			(33) $\bar{y}, \bar{z}, \bar{x}$	(34) $y, \bar{z} + \frac{1}{2}, x + \frac{1}{2}$	(35) $\bar{y} + \frac{1}{2}, z + \frac{1}{2}, x$	(36) $y + \frac{1}{2}, z, \bar{x} + \frac{1}{2}$	
			(37) $\bar{y} + \frac{1}{2}, \bar{x} + \frac{1}{2}, z + \frac{1}{2}$	(38) $y + \frac{1}{2}, x + \frac{1}{2}, z + \frac{1}{2}$	(39) $\bar{y} + \frac{1}{2}, x + \frac{1}{2}, \bar{z} + \frac{1}{2}$	(40) $y + \frac{1}{2}, \bar{x} + \frac{1}{2}, \bar{z} + \frac{1}{2}$	
			(41) $\bar{x} + \frac{1}{2}, \bar{z} + \frac{1}{2}, y + \frac{1}{2}$	(42) $x + \frac{1}{2}, \bar{z} + \frac{1}{2}, \bar{y} + \frac{1}{2}$	(43) $x + \frac{1}{2}, z + \frac{1}{2}, y + \frac{1}{2}$	(44) $\bar{x} + \frac{1}{2}, z + \frac{1}{2}, \bar{y} + \frac{1}{2}$	
			(45) $\bar{z} + \frac{1}{2}, \bar{y} + \frac{1}{2}, x + \frac{1}{2}$	(46) $\bar{z} + \frac{1}{2}, y + \frac{1}{2}, \bar{x} + \frac{1}{2}$	(47) $z + \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{x} + \frac{1}{2}$	(48) $z + \frac{1}{2}, y + \frac{1}{2}, x + \frac{1}{2}$	

Special: as above, plus

48	g	$..2$	$\frac{1}{2}, y, \bar{y} + \frac{1}{2}$	$\frac{3}{2}, \bar{y}, \bar{y} + \frac{1}{2}$	$\frac{7}{2}, y + \frac{1}{2}, y + \frac{1}{2}$	$\frac{5}{2}, \bar{y} + \frac{1}{2}, y + \frac{1}{2}$	$hkl : h = 2n + 1$ or $h = 4n$
			$\bar{y} + \frac{1}{2}, \frac{1}{2}, y$	$\bar{y} + \frac{3}{2}, \frac{3}{2}, \bar{y}$	$y + \frac{1}{2}, \frac{7}{2}, y + \frac{1}{2}$	$y + \frac{1}{2}, \frac{5}{2}, \bar{y} + \frac{1}{2}$	
			$y, \bar{y} + \frac{1}{2}, \frac{1}{2}$	$\bar{y}, \bar{y} + \frac{3}{2}, \frac{3}{2}$	$y + \frac{1}{2}, y + \frac{1}{2}, \frac{7}{2}$	$\bar{y} + \frac{1}{2}, y + \frac{1}{2}, \frac{5}{2}$	
			$\frac{1}{2}, \bar{y}, y + \frac{1}{2}$	$\frac{3}{2}, y, y + \frac{1}{2}$	$\frac{7}{2}, \bar{y} + \frac{1}{2}, \bar{y} + \frac{1}{2}$	$\frac{5}{2}, y + \frac{1}{2}, \bar{y} + \frac{1}{2}$	
			$y + \frac{1}{2}, \frac{7}{2}, \bar{y}$	$y + \frac{1}{2}, \frac{5}{2}, y$	$\bar{y} + \frac{1}{2}, \frac{7}{2}, \bar{y} + \frac{1}{2}$	$\bar{y} + \frac{1}{2}, \frac{5}{2}, y + \frac{1}{2}$	
			$\bar{y}, y + \frac{1}{2}, \frac{7}{2}$	$y, y + \frac{1}{2}, \frac{5}{2}$	$\bar{y} + \frac{1}{2}, \bar{y} + \frac{1}{2}, \frac{7}{2}$	$y + \frac{1}{2}, \bar{y} + \frac{1}{2}, \frac{5}{2}$	
48	f	$2..$	$x, 0, \frac{1}{2}$	$\bar{x} + \frac{1}{2}, 0, \frac{3}{2}$	$\frac{1}{2}, x, 0$	$\frac{3}{2}, \bar{x} + \frac{1}{2}, 0$	$hkl : 2h + l = 4n$
			$\frac{3}{2}, x + \frac{1}{2}, 0$	$\frac{5}{2}, \bar{x} + \frac{3}{2}, \frac{1}{2}$	$x + \frac{3}{2}, \frac{1}{2}, \frac{1}{2}$	$\bar{x} + \frac{1}{2}, 0, \frac{1}{2}$	
			$\bar{x}, 0, \frac{3}{2}$	$x + \frac{1}{2}, 0, \frac{1}{2}$	$\frac{3}{2}, \bar{x}, 0$	$\frac{1}{2}, x + \frac{1}{2}, 0$	
			$\frac{1}{2}, \bar{x} + \frac{3}{2}, 0$	$\frac{3}{2}, x + \frac{1}{2}, \frac{1}{2}$	$\bar{x} + \frac{1}{2}, \frac{1}{2}, \frac{3}{2}$	$x + \frac{3}{2}, 0, \frac{1}{2}$	
32	e	$.3.$	x, x, x	$\bar{x} + \frac{1}{2}, \bar{x}, x + \frac{1}{2}$	$\bar{x}, x + \frac{1}{2}, \bar{x} + \frac{1}{2}$	$x + \frac{1}{2}, \bar{x} + \frac{1}{2}, \bar{x}$	$hkl : h = 2n + 1$ or $h + k + l = 4n$
			$x + \frac{1}{2}, x + \frac{1}{2}, \bar{x} + \frac{1}{2}$	$\bar{x} + \frac{3}{4}, \bar{x} + \frac{3}{4}, \bar{x} + \frac{3}{4}$	$x + \frac{1}{4}, \bar{x} + \frac{1}{4}, x + \frac{3}{4}$	$\bar{x} + \frac{1}{4}, x + \frac{3}{4}, x + \frac{1}{4}$	
			$\bar{x}, \bar{x}, \bar{x}$	$x + \frac{1}{2}, x, \bar{x} + \frac{1}{2}$	$x, \bar{x} + \frac{1}{2}, x + \frac{1}{2}$	$\bar{x} + \frac{1}{2}, x + \frac{1}{2}, x$	
			$\bar{x} + \frac{1}{2}, \bar{x} + \frac{3}{2}, x + \frac{3}{2}$	$x + \frac{1}{4}, x + \frac{1}{2}, x + \frac{1}{4}$	$\bar{x} + \frac{3}{4}, x + \frac{3}{4}, \bar{x} + \frac{1}{4}$	$x + \frac{3}{4}, \bar{x} + \frac{1}{4}, \bar{x} + \frac{3}{4}$	
24	d	$\bar{4}..$	$\frac{3}{2}, 0, \frac{1}{2}$	$\frac{1}{2}, 0, \frac{3}{2}$	$\frac{1}{2}, \frac{3}{2}, 0$	$\frac{3}{2}, \frac{1}{2}, 0$	$hkl : h, k = 2n, h + k + l = 4n$ or $h, k = 2n + 1, l = 4n + 2$ or $h = 8n, k = 8n + 4$ and $h + k + l = 4n + 2$
			$\frac{1}{2}, \frac{3}{2}, 0$	$\frac{3}{2}, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$	$\frac{3}{2}, 0, \frac{1}{2}$	
			$\frac{1}{2}, 0, \frac{1}{2}$	$\frac{3}{2}, 0, \frac{3}{2}$	$\frac{1}{2}, \frac{3}{2}, 0$	$0, \frac{1}{2}, \frac{3}{2}$	
			$\frac{3}{2}, 0, \frac{3}{2}$	$\frac{1}{2}, 0, \frac{1}{2}$	$\frac{3}{2}, \frac{3}{2}, 0$	$0, \frac{3}{2}, \frac{3}{2}$	
16	b	$.32$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$\frac{3}{2}, \frac{7}{2}, \frac{3}{2}$	$\frac{7}{2}, \frac{3}{2}, \frac{3}{2}$	$\frac{5}{2}, \frac{3}{2}, \frac{7}{2}$	$hkl : h, k = 2n + 1, l = 4n + 2$ or $h, k, l = 4n$
			$\frac{3}{2}, \frac{5}{2}, \frac{3}{2}$	$\frac{1}{2}, \frac{7}{2}, \frac{5}{2}$	$\frac{7}{2}, \frac{5}{2}, \frac{7}{2}$	$\frac{5}{2}, \frac{7}{2}, \frac{5}{2}$	
16	a	$.\bar{3}.$	$0, 0, 0$	$\frac{1}{2}, 0, \frac{1}{2}$	$0, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, 0$	$hkl : h, k = 2n, h + k + l = 4n$

(Continued on page 715)

CONTINUED

No. 225

$Fm\bar{3}m$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; $t(0, \frac{1}{2}, \frac{1}{2})$; $t(\frac{1}{2}, 0, \frac{1}{2})$; (2); (3); (5); (13); (25)

Positions

Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates

$(0,0,0)+$ $(0, \frac{1}{2}, \frac{1}{2})+$ $(\frac{1}{2}, 0, \frac{1}{2})+$ $(\frac{1}{2}, \frac{1}{2}, 0)+$

Reflection conditions

h, k, l permutable
General:

192	l	1	(1) x, y, z (5) z, x, y (9) y, z, x (13) y, x, \bar{z} (17) x, z, \bar{y} (21) z, y, \bar{x} (25) $\bar{x}, \bar{y}, \bar{z}$ (29) $\bar{z}, \bar{x}, \bar{y}$ (33) $\bar{y}, \bar{z}, \bar{x}$ (37) \bar{y}, x, z (41) \bar{x}, \bar{z}, y (45) \bar{z}, \bar{y}, x	(2) \bar{x}, \bar{y}, z (6) z, \bar{x}, \bar{y} (10) \bar{y}, z, \bar{x} (14) $\bar{y}, \bar{x}, \bar{z}$ (18) \bar{x}, z, y (22) z, \bar{y}, x (26) x, y, \bar{z} (30) \bar{z}, x, y (34) y, \bar{z}, x (38) y, x, z (42) x, \bar{z}, \bar{y} (46) \bar{z}, y, \bar{x}	(3) \bar{x}, y, \bar{z} (7) \bar{z}, \bar{x}, y (11) y, \bar{z}, \bar{x} (15) y, \bar{x}, z (19) $\bar{x}, \bar{z}, \bar{y}$ (23) \bar{z}, y, x (27) x, \bar{y}, z (31) z, x, \bar{y} (35) \bar{y}, z, x (39) \bar{y}, x, \bar{z} (43) x, z, y (47) z, \bar{y}, \bar{x}	(4) x, \bar{y}, \bar{z} (8) \bar{z}, x, \bar{y} (12) \bar{y}, \bar{z}, x (16) \bar{y}, x, z (20) x, \bar{z}, y (24) $\bar{z}, \bar{y}, \bar{x}$ (28) \bar{x}, y, z (32) z, \bar{x}, y (36) y, z, \bar{x} (40) y, \bar{x}, \bar{z} (44) \bar{x}, z, \bar{y} (48) z, y, x	$hkl : h + k, h + l, k + l = 2n$ $OkI : k, l = 2n$ $hhl : h + l = 2n$ $h00 : h = 2n$
-----	-----	---	---	--	--	--	---

Special: as above, plus

96	k	$\dots m$	x, x, z \bar{z}, \bar{x}, x x, x, \bar{z} $\bar{x}, \bar{z}, \bar{x}$	\bar{x}, \bar{x}, z \bar{z}, x, \bar{x} $\bar{x}, \bar{x}, \bar{z}$ x, \bar{z}, x	\bar{x}, x, \bar{z} x, z, x x, \bar{x}, z z, x, \bar{x}	x, \bar{x}, \bar{z} \bar{x}, z, \bar{x} \bar{x}, x, z z, \bar{x}, x	z, x, x x, \bar{z}, \bar{x} x, z, \bar{x} \bar{z}, x, x	z, \bar{x}, \bar{x} \bar{x}, \bar{z}, x \bar{x}, z, x $\bar{z}, \bar{x}, \bar{x}$	no extra conditions
96	j	$m \dots$	$0, y, z$ $\bar{z}, 0, y$ $y, 0, \bar{z}$ $0, \bar{z}, \bar{y}$	$0, \bar{y}, z$ $\bar{z}, 0, \bar{y}$ $\bar{y}, 0, \bar{z}$ $0, \bar{z}, y$	$0, y, \bar{z}$ $y, z, 0$ $y, 0, z$ $z, y, 0$	$0, \bar{y}, \bar{z}$ $\bar{y}, z, 0$ $\bar{y}, 0, z$ $z, \bar{y}, 0$	$z, 0, y$ $y, \bar{z}, 0$ $0, z, \bar{y}$ $\bar{z}, y, 0$	$z, 0, \bar{y}$ $\bar{y}, \bar{z}, 0$ $0, z, y$ $\bar{z}, \bar{y}, 0$	no extra conditions
48	i	$m . m 2$	$\frac{1}{2}, y, y$ $\bar{y}, \frac{1}{2}, y$	$\frac{1}{2}, \bar{y}, y$ $\bar{y}, \frac{1}{2}, \bar{y}$	$\frac{1}{2}, y, \bar{y}$ $y, y, \frac{1}{2}$	$\frac{1}{2}, \bar{y}, \bar{y}$ $\bar{y}, y, \frac{1}{2}$	$y, \frac{1}{2}, y$ $y, \bar{y}, \frac{1}{2}$	$y, \frac{1}{2}, \bar{y}$ $\bar{y}, \bar{y}, \frac{1}{2}$	no extra conditions
48	h	$m . m 2$	$0, y, y$ $\bar{y}, 0, y$	$0, \bar{y}, y$ $\bar{y}, 0, \bar{y}$	$0, y, \bar{y}$ $y, y, 0$	$0, \bar{y}, \bar{y}$ $\bar{y}, y, 0$	$y, 0, y$ $y, \bar{y}, 0$	$y, 0, \bar{y}$ $\bar{y}, \bar{y}, 0$	no extra conditions
48	g	$2 . mm$	$x, \frac{1}{2}, \frac{1}{2}$ $\frac{1}{2}, x, \frac{1}{2}$	$\bar{x}, \frac{1}{2}, \frac{1}{2}$ $\frac{1}{2}, \bar{x}, \frac{1}{2}$	$\frac{1}{2}, x, \frac{1}{2}$ $x, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, \bar{x}, \frac{1}{2}$ $\bar{x}, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, x$ $\frac{1}{2}, \frac{1}{2}, \bar{x}$	$\frac{1}{2}, \frac{1}{2}, \bar{x}$ $\frac{1}{2}, \frac{1}{2}, x$	$hkl : h = 2n$
32	f	$. 3 m$	x, x, x x, x, \bar{x}	\bar{x}, \bar{x}, x $\bar{x}, \bar{x}, \bar{x}$	\bar{x}, x, \bar{x} x, \bar{x}, x	x, \bar{x}, \bar{x} \bar{x}, x, x			no extra conditions
24	e	$4 m . m$	$x, 0, 0$	$\bar{x}, 0, 0$	$0, x, 0$	$0, \bar{x}, 0$	$0, 0, x$	$0, 0, \bar{x}$	no extra conditions
24	d	$m . mm$	$0, \frac{1}{2}, \frac{1}{2}$	$0, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, 0, \frac{1}{2}$	$\frac{1}{2}, 0, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, 0$	$\frac{1}{2}, \frac{1}{2}, 0$	$hkl : h = 2n$
8	c	$\bar{4} 3 m$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$					$hkl : h = 2n$
4	b	$m \bar{3} m$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$						no extra conditions
4	a	$m \bar{3} m$	$0, 0, 0$						no extra conditions

symmetry of special projections

long $[001] p4mm$
 $\mathbf{a}' = \frac{1}{2}\mathbf{a}$ $\mathbf{b}' = \frac{1}{2}\mathbf{b}$
origin at $0, 0, z$

Along $[111] p6mm$
 $\mathbf{a}' = \frac{1}{2}(2\mathbf{a} - \mathbf{b} - \mathbf{c})$ $\mathbf{b}' = \frac{1}{2}(-\mathbf{a} + 2\mathbf{b} - \mathbf{c})$
Origin at x, x, x

Along $[110] c2mm$
 $\mathbf{a}' = \frac{1}{2}(-\mathbf{a} + \mathbf{b})$ $\mathbf{b}' = \mathbf{c}$
Origin at $x, x, 0$