

Modelling Modular Inorganic Structures

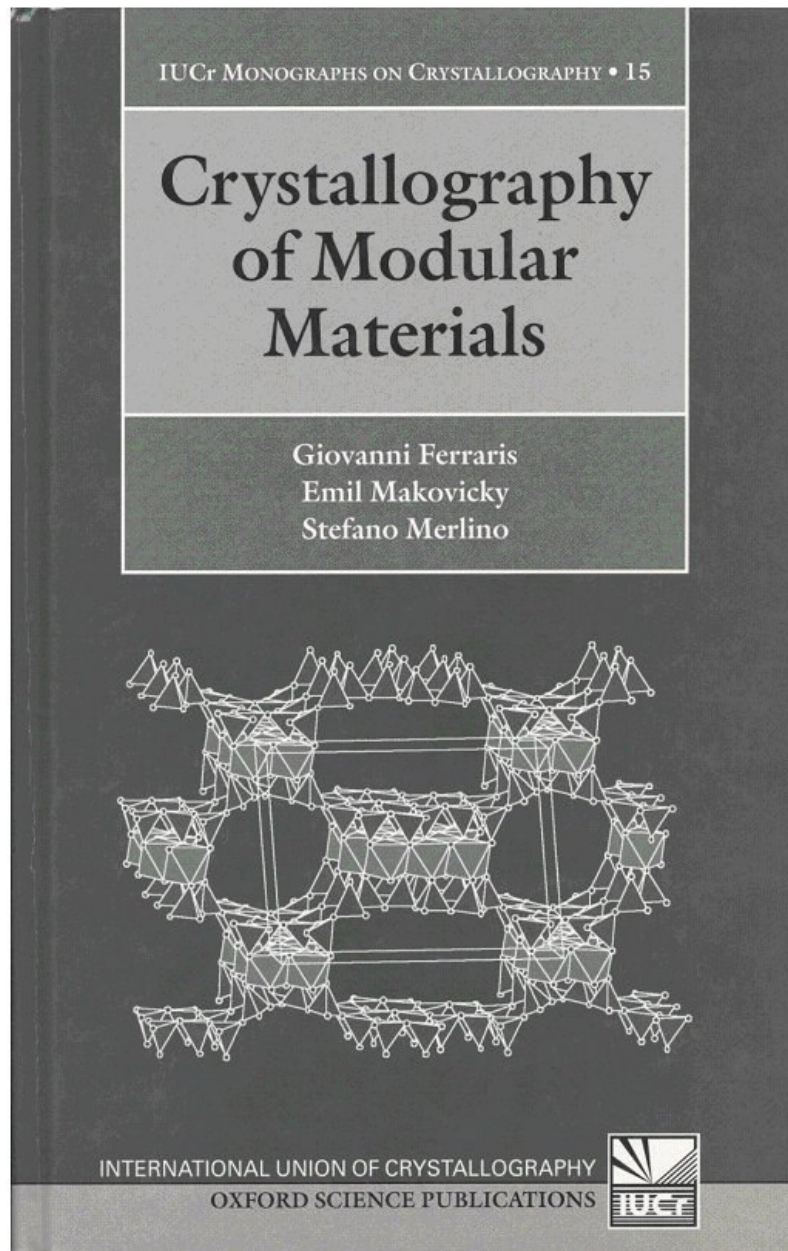
SOLUTION TO EXERCIZES

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Solution 1

CaF_2 (fluorite) (Fig. 1s)

- *Chemical composition:* CaF_2
- *Cell parameter:* $a = 5.462 \text{ \AA}$
- *Density:* $\delta = 3.18 \text{ gr/cm}^3$
- *Space group:* because of systematic absences the lattice is cF ; taking into account that the point group of fluorite is $m\bar{3}m$, the space group is $Fm\bar{3}m$.

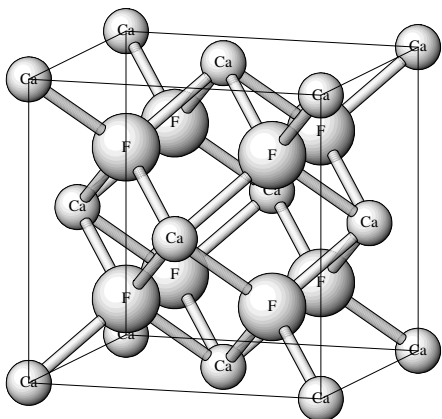


Figure 1s – Structure of fluorite.

$Z = 4$ 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 ($0, 0, 0$) or 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.

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).

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COMMENTS

Note that:

1. F in c contributes only to the diffractions with even h, k, l (see the special systematic absences for the c Wyckoff site).
2. The site symmetry of the a ($m\bar{3}m$) and c ($\bar{4}3m$) Wyckoff 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 threefold axis.

Solution 2

MgAl₂O₄ (spinel)

$$Z = (3.588 \times 529.47 \cdot 10^{-24} \times 6.023 \cdot 10^{24}) / 142.27 = 8.04.$$

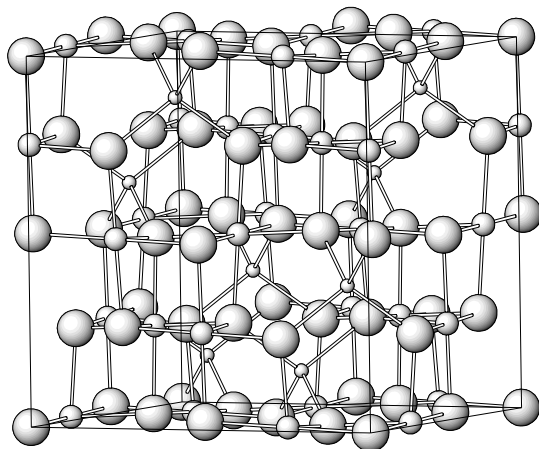
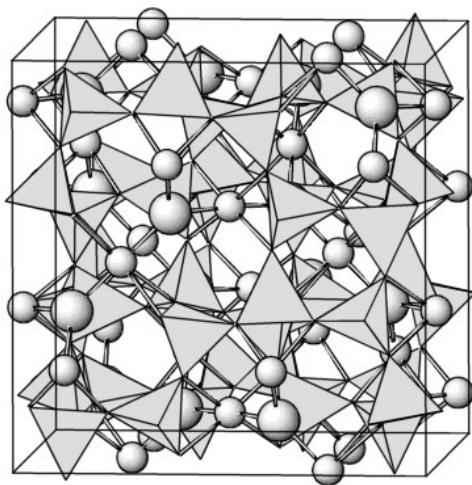


Figure 2s – Crystal structure of spinel. Small and intermediate spheres represent tetrahedral (Mg) and octahedral (Al) cations, respectively. Large spheres are oxygen atoms.

$Z = 8$ requires 8 Al, 16 Mg 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 (about 2 Å) and Al-O (about 1.9 Å) bond distances. Without knowledge of the space group, $3(\text{coordinates/atom}) \times 56(\text{atoms}) = 168$ coordinates would be necessary to fix the 56 atoms in the unit cell.

Solution 3

NaAlSi₂O₆·H₂O (analcite, zeolite) (Fig. 3s)



$Z = 16$, thus in the unit cell there are: 16 Na, 16 Al, 32 Si, 96 anionic O (O1) and 16 O belonging to H₂O (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 analcite 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 3s – Structure of analcite. Large and small spheres are H₂O oxygens and Na, respectively.

Solution 4

Kalifersite

Taking into account the chemical and crystallographic aspects one can note that a structure model based on a 1:1 chess-board arrangement of $(TOT)_P$ and $(TOT)_S$ [001] ribbons has cell dimensions and chemical composition corresponding to those of kalifersite (Fig. 4s).

Palygorskite (P), and sepiolite (S) are the end members of a cell named *palysepiole* (**p**alygorskite + **s**epiolite) *polysomatic series* P_pS_s ; kalifersite is the P_1S_1 member.

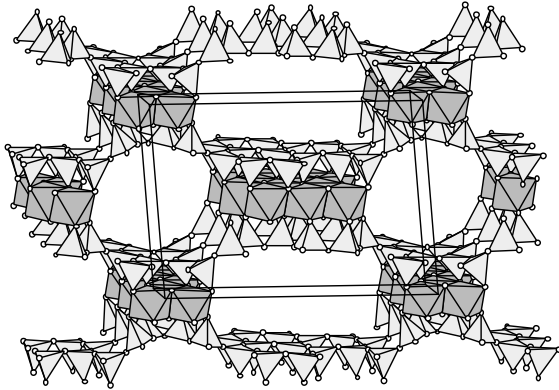


Figure 4s - Structure model of kalifersite. The content of the channels is not shown.

Solution 5

Seidite-(Ce)

By substituting the octahedral layer of rhodesite by a layer consisting of isolated Ti-octahedra, a structure model that has cell parameters and chemical composition of seidite-(Ce) is obtained. The channels are filled by (Ce,Sr), Na and H₂O in seidite-(Ce) instead of K and H₂O as in rhodesite.

Rhodesite and the mentioned 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, but the “octahedral” layer is typical of each member.

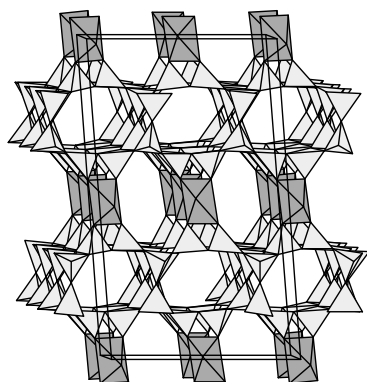


Figure 5s - Structure model of seidite-(Ce). Grey octahedra are centred on Ti. The content of the channels is not shown.