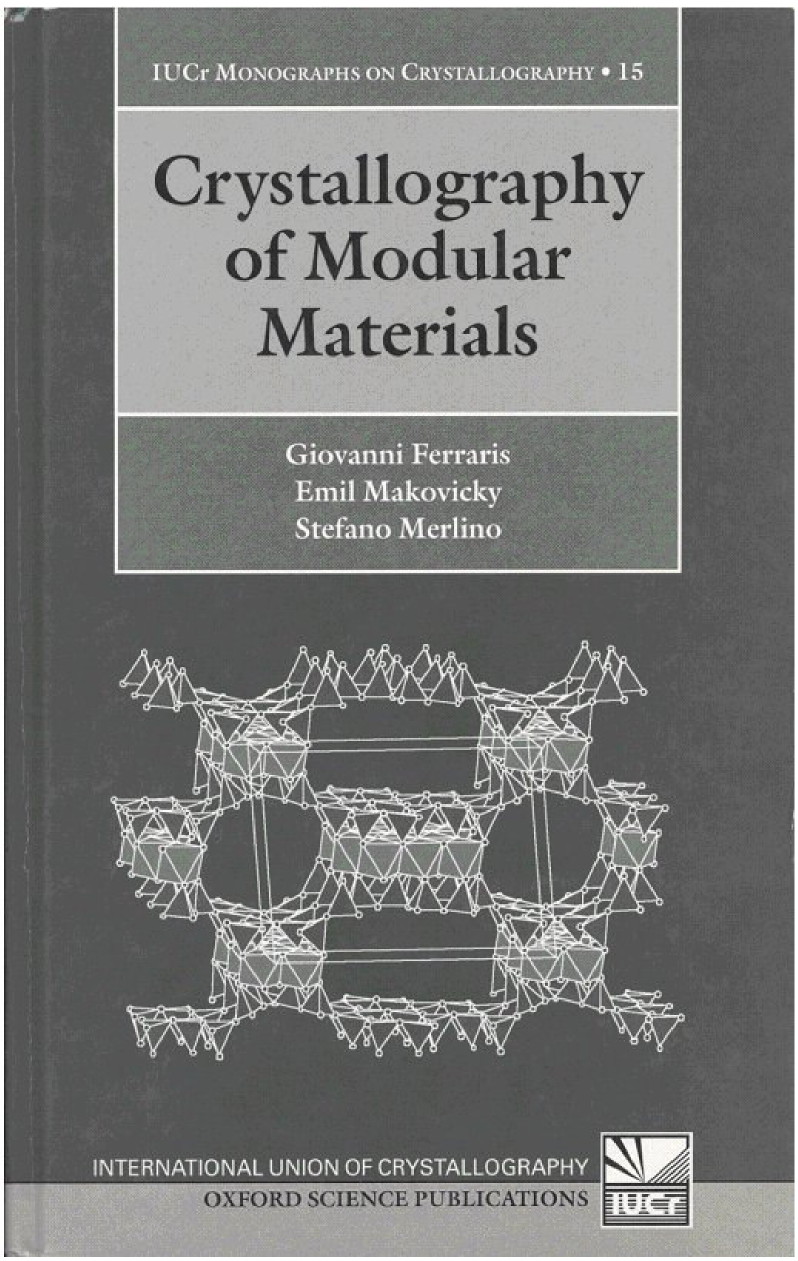
Modelling Modular Inorganic Structures

EXERCISES

Giovanni Ferraris
Dipartimento Scienze Mineralogiche e Petrologiche, Univ. Torino – IGG/CNR –
Via Valperga Caluso 35, 10125 Torino Italy
giovanni.ferraris@unito.it



Exercise 1

CaF_2 (fluorite) cubic (Fig. 1s see solution)

- *Chemical composition*: CaF_2 - *Cell parameter*: a = 5.462 Å
- *Density*: δ = 3.18 gr/cm^3 - *Atomic weights*: Ca 40.08, F 18.998
- *Symmetry*: *hkl* diffractions occur only if *h,k,l* are either all odd or all even; from morphology the point group of fluorite is $m\bar{3}m$; then, the space group is $Fm\bar{3}m$. Assign atoms to the Wyckoff positions.

Number of positions, Wyckoff notation, and point symmetry			Co-ordinates of equivalent positions $(0,0,0;\ 0,\frac{1}{2},\frac{1}{2};\ \frac{1}{2},0,\frac{1}{2};\ \frac{1}{2},\frac{1}{2},0)+$	Conditions limiting possible reflections
192	*l*	1	$x,y,z;\ z,x,y;\ y,z,x;\ x,z,y;\ y,x,z;\ z,y,x;$ $x,\bar{y},\bar{z};\ z,\bar{x},\bar{y};\ y,\bar{z},\bar{x};\ x,\bar{z},\bar{y};\ y,\bar{x},\bar{z};\ z,\bar{y},\bar{x};$ $\bar{x},y,\bar{z};\ \bar{z},x,\bar{y};\ \bar{y},z,\bar{x};\ \bar{x},z,\bar{y};\ \bar{y},x,\bar{z};\ \bar{z},y,\bar{x};$ $\bar{x},\bar{y},z;\ \bar{z},\bar{x},y;\ \bar{y},\bar{z},x;\ \bar{x},\bar{z},y;\ \bar{y},\bar{x},z;\ \bar{z},\bar{y},x;$ $\bar{x},\bar{y},\bar{z};\ \bar{z},\bar{x},\bar{y};\ \bar{y},\bar{z},\bar{x};\ \bar{x},\bar{z},\bar{y};\ \bar{y},\bar{x},\bar{z};\ \bar{z},\bar{y},\bar{x};$ $\bar{x},y,z;\ \bar{z},x,y;\ \bar{y},z,x;\ \bar{x},z,y;\ \bar{y},x,z;\ \bar{z},y,x;$ $x,\bar{y},z;\ z,\bar{x},y;\ y,\bar{z},x;\ x,\bar{z},y;\ y,\bar{x},z;\ z,\bar{y},x;$ $x,y,\bar{z};\ z,x,\bar{y};\ y,z,\bar{x};\ x,z,\bar{y};\ y,x,\bar{z};\ z,y,\bar{x}.$	General: *hkl*: $h+k,k+l,(l+h)=2n$ *hhl*: $(l+h=2n)$; ↻ *0kl*: $(k,l=2n)$; ↻
				Special: as above, plus
96	*k*	*m*	$x,x,z;\ z,x,x;\ x,z,x;\ \bar{x},\bar{x},\bar{z};\ \bar{z},\bar{x},\bar{x};\ \bar{x},\bar{z},\bar{x};$ $x,\bar{x},\bar{z};\ z,\bar{x},\bar{x};\ x,\bar{z},\bar{x};\ \bar{x},x,z;\ \bar{z},x,x;\ \bar{x},z,x;$ $\bar{x},x,\bar{z};\ \bar{z},x,\bar{x};\ \bar{x},z,\bar{x};\ x,\bar{x},z;\ z,\bar{x},x;\ x,\bar{z},x;$ $\bar{x},\bar{x},z;\ \bar{z},\bar{x},x;\ \bar{x},\bar{z},x;\ x,x,\bar{z};\ z,x,\bar{x};\ x,z,\bar{x}.$	no extra conditions (96*k*, 96*j*, 48*i*, 48*h*)
96	*j*	*m*	$0,y,z;\ z,0,y;\ y,z,0;\ 0,z,y;\ y,0,z;\ z,y,0;$ $0,\bar{y},\bar{z};\ \bar{z},0,\bar{y};\ \bar{y},\bar{z},0;\ 0,\bar{z},\bar{y};\ \bar{y},0,\bar{z};\ \bar{z},\bar{y},0;$ $0,y,\bar{z};\ \bar{z},0,y;\ y,\bar{z},0;\ 0,\bar{z},y;\ y,0,\bar{z};\ \bar{z},y,0;$ $0,\bar{y},z;\ z,0,\bar{y};\ \bar{y},z,0;\ 0,z,\bar{y};\ \bar{y},0,z;\ z,\bar{y},0.$	
48	*i*	*mm*	$\frac{1}{2},x,x;\ x,\frac{1}{2},x;\ x,x,\frac{1}{2};\ \frac{1}{2},x,\bar{x};\ \bar{x},\frac{1}{2},x;\ x,\bar{x},\frac{1}{2};$ $\frac{1}{2},\bar{x},\bar{x};\ \bar{x},\frac{1}{2},\bar{x};\ \bar{x},\bar{x},\frac{1}{2};\ \frac{1}{2},\bar{x},x;\ x,\frac{1}{2},\bar{x};\ \bar{x},x,\frac{1}{2}.$	
48	*h*	*mm*	$0,x,x;\ x,0,x;\ x,x,0;\ 0,x,\bar{x};\ \bar{x},0,x;\ x,\bar{x},0;$ $0,\bar{x},\bar{x};\ \bar{x},0,\bar{x};\ \bar{x},\bar{x},0;\ 0,\bar{x},x;\ x,0,\bar{x};\ \bar{x},x,0.$	
48	*g*	*mm*	$x,\frac{1}{4},\frac{1}{4};\ \frac{1}{4},x,\frac{1}{4};\ \frac{1}{4},\frac{1}{4},x;\ x,\frac{1}{4},\frac{3}{4};\ \frac{3}{4},x,\frac{1}{4};\ \frac{1}{4},\frac{3}{4},x;$ $\bar{x},\frac{1}{4},\frac{1}{4};\ \frac{1}{4},\bar{x},\frac{1}{4};\ \frac{1}{4},\frac{1}{4},\bar{x};\ \bar{x},\frac{1}{4},\frac{3}{4};\ \frac{3}{4},\bar{x},\frac{1}{4};\ \frac{1}{4},\frac{3}{4},\bar{x}.$	*hkl*: $h,(k,l)=2n$
32	*f*	$3m$	$x,x,x;\ x,\bar{x},\bar{x};\ \bar{x},x,\bar{x};\ \bar{x},\bar{x},x;$ $\bar{x},\bar{x},\bar{x};\ \bar{x},x,x;\ x,\bar{x},x;\ x,x,\bar{x}.$	no extra conditions (32*f*, 24*e*)
24	*e*	$4mm$	$x,0,0;\ 0,x,0;\ 0,0,x;\ \bar{x},0,0;\ 0,\bar{x},0;\ 0,0,\bar{x}.$	
24	*d*	mmm	$0,\frac{1}{4},\frac{1}{4};\ \frac{1}{4},0,\frac{1}{4};\ \frac{1}{4},\frac{1}{4},0;\ 0,\frac{1}{4},\frac{3}{4};\ \frac{3}{4},0,\frac{1}{4};\ \frac{1}{4},\frac{3}{4},0.$	*hkl*: $h,(k,l)=2n$ (24*d*, 8*c*)
8	*c*	$\bar{4}3m$	$\frac{1}{4},\frac{1}{4},\frac{1}{4};\ \frac{3}{4},\frac{3}{4},\frac{3}{4}.$	
4	*b*	$m3m$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}.$	no extra conditions (4*b*, 4*a*)
4	*a*	$m3m$	$0,0,0.$	

Exercise 2

$MgAl_2O_4$ (spinel) cubic (Fig. 2s, see solution)

- *Chemical composition*: $MgAl_2O_4$ - *Cell parameter*: a = 8.09 Å - *Density*: δ = 3.58 gr/cm^3
- *Atomic weights*: Mg 24.312, Al 26.982, O 15.999 - *Space group*: *hkl* diffractions occur only if *h,k,l* are either all odd or all even: thus, lattice is *cF*; besides, 0*kl* occur only for $k+l=4n$; from morphology the point group is $m\bar{3}m$, thus the space group is $Fd\bar{3}m$. Assign atoms to the Wyckoff positions.

Number of positions, Wyckoff notation, and point symmetry			Co-ordinates of equivalent positions $(0,0,0;\ 0,\frac12,\frac12;\ \frac12,0,\frac12;\ \frac12,\frac12,0)+$	Conditions limiting possible reflections
				General:
192	*i*	1	$x,y,z;\ z,x,y;\ y,z,x;\ x,z,y;\ y,x,z;\ z,y,x;$ $x,\bar{y},\bar{z};\ z,\bar{x},\bar{y};\ y,\bar{z},\bar{x};\ x,\bar{z},\bar{y};\ y,\bar{x},\bar{z};\ z,\bar{y},\bar{x};$ $\bar{x},y,\bar{z};\ \bar{z},x,\bar{y};\ \bar{y},z,\bar{x};\ \bar{x},z,\bar{y};\ \bar{y},x,\bar{z};\ \bar{z},y,\bar{x};$ $\bar{x},\bar{y},z;\ \bar{z},\bar{x},y;\ \bar{y},\bar{z},x;\ \bar{x},\bar{z},y;\ \bar{y},\bar{x},z;\ \bar{z},\bar{y},x;$ $\frac14-x,\frac14-y,\frac14-z;\ \frac14-z,\frac14-x,\frac14-y;\ \frac14-y,\frac14-z,\frac14-x;$ $\frac14-x,\frac14+y,\frac14+z;\ \frac14-z,\frac14+x,\frac14+y;\ \frac14-y,\frac14+z,\frac14+x;$ $\frac14+x,\frac14-y,\frac14+z;\ \frac14+z,\frac14-x,\frac14+y;\ \frac14+y,\frac14-z,\frac14+x;$ $\frac14+x,\frac14+y,\frac14-z;\ \frac14+z,\frac14+x,\frac14-y;\ \frac14+y,\frac14+z,\frac14-x;$ $\frac14-x,\frac14-z,\frac14-y;\ \frac14-y,\frac14-x,\frac14-z;\ \frac14-z,\frac14-y,\frac14-x;$ $\frac14-x,\frac14+z,\frac14+y;\ \frac14-y,\frac14+x,\frac14+z;\ \frac14-z,\frac14+y,\frac14+x;$ $\frac14+x,\frac14-z,\frac14+y;\ \frac14+y,\frac14-x,\frac14+z;\ \frac14+z,\frac14-y,\frac14+x;$ $\frac14+x,\frac14+z,\frac14-y;\ \frac14+y,\frac14+x,\frac14-z;\ \frac14+z,\frac14+y,\frac14-x.$	*hkl*: $h+k,k+l,(l+h)=2n$ *hhl*: $(l+h=2n)$; ↻ 0*kl*: $(k,l=2n)$; $k+l=4n$ ↻
				Special: as above, plus
96	*h*	2	$\frac18,x,\frac14-x;\ \frac18,\frac14-x,x;\ \frac38,x,\frac14+x;\ \frac38,\frac14+x,x;$ $\frac14-x,\frac18,x;\ x,\frac18,\frac14-x;\ \frac14+x,\frac38,x;\ x,\frac38,\frac14+x;$ $x,\frac14-x,\frac18;\ \frac14-x,x,\frac18;\ x,\frac14+x,\frac38;\ \frac14+x,x,\frac38;$ $\frac18,\bar{x},\frac34+x;\ \frac18,\frac34+x,\bar{x};\ \frac38,\bar{x},\frac34-x;\ \frac38,\frac34-x,\bar{x};$ $\frac34+x,\frac18,\bar{x};\ \bar{x},\frac18,\frac34+x;\ \frac34-x,\frac38,\bar{x};\ \bar{x},\frac38,\frac34-x;$ $\bar{x},\frac34+x,\frac18;\ \frac34+x,\bar{x},\frac18;\ \bar{x},\frac34-x,\frac38;\ \frac34-x,\bar{x},\frac38.$	no extra conditions
96	*g*	*m*	$x,x,z;\ z,x,x;\ x,z,x;\ \bar{x},x,\bar{z};\ \bar{z},x,\bar{x};\ \bar{x},z,\bar{x};$ $x,\bar{x},\bar{z};\ z,\bar{x},\bar{x};\ x,\bar{z},\bar{x};\ \bar{x},\bar{x},z;\ \bar{z},\bar{x},x;\ \bar{x},\bar{z},x;$ $\frac14-x,\frac14-x,\frac14-z;\ \frac14-z,\frac14-x,\frac14-x;\ \frac14-x,\frac14-z,\frac14-x;$ $\frac14-x,\frac14+x,\frac14+z;\ \frac14-z,\frac14+x,\frac14+x;\ \frac14-x,\frac14+z,\frac14+x;$ $\frac14+x,\frac14-x,\frac14+z;\ \frac14+z,\frac14-x,\frac14+x;\ \frac14+x,\frac14-z,\frac14+x;$ $\frac14+x,\frac14+x,\frac14-z;\ \frac14+z,\frac14+x,\frac14-x;\ \frac14+x,\frac14+z,\frac14-x.$	(no extra conditions, as for 96 *h*)
48	*f*	*mm*	$x,0,0;\ \bar{x},0,0;\ \frac14+x,\frac14,\frac14;\ \frac14-x,\frac14,\frac14;$ $0,x,0;\ 0,\bar{x},0;\ \frac14,\frac14+x,\frac14;\ \frac14,\frac14-x,\frac14;$ $0,0,x;\ 0,0,\bar{x};\ \frac14,\frac14,\frac14+x;\ \frac14,\frac14,\frac14-x.$	*hkl*: $h+k+l=2n+1$ or $4n$
32	*e*	3*m*	$x,x,x;\ \frac14-x,\frac14-x,\frac14-x;$ $x,\bar{x},\bar{x};\ \frac14-x,\frac14+x,\frac14+x;$ $\bar{x},x,\bar{x};\ \frac14+x,\frac14-x,\frac14+x;$ $\bar{x},\bar{x},x;\ \frac14+x,\frac14+x,\frac14-x.$	no extra conditions
16	*d*	$\bar{3}m$	$\frac58,\frac58,\frac58;\ \frac58,\frac78,\frac78;\ \frac78,\frac58,\frac78;\ \frac78,\frac78,\frac58.$	*hkl*: $h=2n+1$, $k=2n+1$, $l=2n+1$ or $4n+2$, $4n+2$, $4n+2$ or $4n$, $4n$, $4n$
16	*c*	$\bar{3}m$	$\frac18,\frac18,\frac18;\ \frac18,\frac38,\frac38;\ \frac38,\frac18,\frac38;\ \frac38,\frac38,\frac18.$	(as for 16 *d*)
8	*b*	$\bar{4}3m$	$\frac12,\frac12,\frac12;\ \frac34,\frac34,\frac34.$	*hkl*: $h+k+l=2n+1$ or $4n$
8	*a*	$\bar{4}3m$	$0,0,0;\ \frac14,\frac14,\frac14.$	(as for 8 *b*)

Exercise 3

***$NaAlSi_2O_6.H_2O$* (analcite, zeolite)** cubic (Fig. 3s, see solution)

- *Chemical composition*: $NaAlSi_2O_6.H_2O$ - *Cell parameter*: a = 13.73 Å - *Density*: δ = 2.28 gr/cm^3 - *Atomic weights*: Na 22.991, Al 26.982, Si 28.086, O 15.999.
- *Space group*: *hkl* diffractions occur only if $h+k+l = 2n$; therefore, the lattice is *cI*; besides, 0*kl* occur only for *k* and *l* even and *hhl* occur only for $2h+l = 4n$; from morphology the point group of analcite is $m\bar{3}m$, thus the space group is $Ia\bar{3}d$. Assign atoms to the Wyckoff positions.

Number of positions, Wyckoff notation, and point symmetry			Co-ordinates of equivalent positions $(0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2})+$	Conditions limiting possible reflections
				General:
96	*h*	1	$x,y,z;\ \frac{1}{2}+x,\frac{1}{2}-y,\bar{z};\ \bar{x},\frac{1}{2}+y,\frac{1}{2}-z;\ \frac{1}{2}-x,\bar{y},\frac{1}{2}+z;$ $z,x,y;\ \frac{1}{2}+z,\frac{1}{2}-x,\bar{y};\ \bar{z},\frac{1}{2}+x,\frac{1}{2}-y;\ \frac{1}{2}-z,\bar{x},\frac{1}{2}+y;$ $y,z,x;\ \frac{1}{2}+y,\frac{1}{2}-z,\bar{x};\ \bar{y},\frac{1}{2}+z,\frac{1}{2}-x;\ \frac{1}{2}-y,\bar{z},\frac{1}{2}+x;$ $\bar{x},\bar{y},\bar{z};\ \frac{1}{2}-x,\frac{1}{2}+y,z;\ x,\frac{1}{2}-y,\frac{1}{2}+z;\ \frac{1}{2}+x,y,\frac{1}{2}-z;$ $\bar{z},\bar{x},\bar{y};\ \frac{1}{2}-z,\frac{1}{2}+x,y;\ z,\frac{1}{2}-x,\frac{1}{2}+y;\ \frac{1}{2}+z,x,\frac{1}{2}-y;$ $\bar{y},\bar{z},\bar{x};\ \frac{1}{2}-y,\frac{1}{2}+z,x;\ y,\frac{1}{2}-z,\frac{1}{2}+x;\ \frac{1}{2}+y,z,\frac{1}{2}-x;$ $\frac{1}{4}+x,\frac{1}{4}+z,\frac{1}{4}+y;\ \frac{1}{4}+y,\frac{1}{4}+x,\frac{1}{4}+z;\ \frac{1}{4}+z,\frac{1}{4}+y,\frac{1}{4}+x;$ $\frac{3}{4}+x,\frac{1}{4}-z,\frac{3}{4}-y;\ \frac{3}{4}+y,\frac{1}{4}-x,\frac{3}{4}-z;\ \frac{3}{4}+z,\frac{1}{4}-y,\frac{3}{4}-x;$ $\frac{3}{4}-x,\frac{3}{4}+z,\frac{1}{4}-y;\ \frac{3}{4}-y,\frac{3}{4}+x,\frac{1}{4}-z;\ \frac{3}{4}-z,\frac{3}{4}+y,\frac{1}{4}-x;$ $\frac{1}{4}-x,\frac{3}{4}-z,\frac{3}{4}+y;\ \frac{1}{4}-y,\frac{3}{4}-x,\frac{3}{4}+z;\ \frac{1}{4}-z,\frac{3}{4}-y,\frac{3}{4}+x;$ $\frac{1}{4}-x,\frac{1}{4}-z,\frac{1}{4}-y;\ \frac{1}{4}-y,\frac{1}{4}-x,\frac{1}{4}-z;\ \frac{1}{4}-z,\frac{1}{4}-y,\frac{1}{4}-x;$ $\frac{3}{4}-x,\frac{1}{4}+z,\frac{3}{4}+y;\ \frac{3}{4}-y,\frac{1}{4}+x,\frac{3}{4}+z;\ \frac{3}{4}-z,\frac{1}{4}+y,\frac{3}{4}+x;$ $\frac{3}{4}+x,\frac{3}{4}-z,\frac{1}{4}+y;\ \frac{3}{4}+y,\frac{3}{4}-x,\frac{1}{4}+z;\ \frac{3}{4}+z,\frac{3}{4}-y,\frac{1}{4}+x;$ $\frac{1}{4}+x,\frac{3}{4}+z,\frac{3}{4}-y;\ \frac{1}{4}+y,\frac{3}{4}+x,\frac{3}{4}-z;\ \frac{1}{4}+z,\frac{3}{4}+y,\frac{3}{4}-x.$	*hkl*: $h+k+l=2n$ *hhl*: $(l=2n)$; $2h+l=4n$; ↻ 0*kl*: $k,(l)=2n$; ↻
				Special: as above, plus
48	*g*	2	$\frac{1}{8},x,\frac{1}{4}-x;\ \frac{3}{8},x,\frac{3}{4}+x;\ \frac{5}{8},\bar{x},\frac{1}{4}-x;\ \frac{7}{8},\bar{x},\frac{3}{4}+x;$ $\frac{1}{4}-x,\frac{1}{8},x;\ \frac{3}{4}+x,\frac{3}{8},x;\ \frac{1}{4}-x,\frac{5}{8},\bar{x};\ \frac{3}{4}+x,\frac{7}{8},\bar{x};$ $x,\frac{1}{4}-x,\frac{1}{8};\ x,\frac{3}{4}+x,\frac{3}{8};\ \bar{x},\frac{1}{4}-x,\frac{5}{8};\ \bar{x},\frac{3}{4}+x,\frac{7}{8};$ $\frac{1}{8},\bar{x},\frac{1}{4}+x;\ \frac{3}{8},\bar{x},\frac{3}{4}-x;\ \frac{5}{8},x,\frac{1}{4}+x;\ \frac{7}{8},x,\frac{3}{4}-x;$ $\frac{1}{4}+x,\frac{1}{8},\bar{x};\ \frac{3}{4}-x,\frac{3}{8},\bar{x};\ \frac{1}{4}+x,\frac{5}{8},x;\ \frac{3}{4}-x,\frac{7}{8},x;$ $\bar{x},\frac{1}{4}+x,\frac{1}{8};\ \bar{x},\frac{3}{4}-x,\frac{3}{8};\ x,\frac{1}{4}+x,\frac{5}{8};\ x,\frac{3}{4}-x,\frac{7}{8}.$	*hkl*: h or k or $l=2n+1$ or $4n$
48	*f*	2	$x,0,\frac{1}{4};\ \bar{x},\frac{1}{2},\frac{1}{4};\ \frac{1}{4}-x,0,\frac{1}{4};\ \frac{3}{4}+x,\frac{1}{2},\frac{1}{4};$ $\frac{1}{4},x,0;\ \frac{1}{4},\bar{x},\frac{1}{2};\ \frac{1}{4},\frac{1}{4}-x,0;\ \frac{1}{4},\frac{3}{4}+x,\frac{1}{2};$ $0,\frac{1}{4},x;\ \frac{1}{2},\frac{1}{4},\bar{x};\ 0,\frac{1}{4},\frac{1}{4}-x;\ \frac{1}{2},\frac{1}{4},\frac{3}{4}+x;$ $x,\frac{1}{2},\frac{3}{4};\ \bar{x},0,\frac{3}{4};\ \frac{1}{4}-x,\frac{1}{2},\frac{3}{4};\ \frac{3}{4}+x,0,\frac{3}{4};$ $\frac{3}{4},x,\frac{1}{2};\ \frac{3}{4},\bar{x},0;\ \frac{3}{4},\frac{1}{4}-x,\frac{1}{2};\ \frac{3}{4},\frac{3}{4}+x,0;$ $\frac{1}{2},\frac{3}{4},x;\ 0,\frac{3}{4},\bar{x};\ \frac{1}{2},\frac{3}{4},\frac{1}{4}-x;\ 0,\frac{3}{4},\frac{3}{4}+x.$	
32	*e*	3	$x,x,x;\ \frac{1}{2}+x,\frac{1}{2}-x,\bar{x};\ \bar{x},\frac{1}{2}+x,\frac{1}{2}-x;\ \frac{1}{2}-x,\bar{x},\frac{1}{2}+x;$ $\bar{x},\bar{x},\bar{x};\ \frac{1}{2}-x,\frac{1}{2}+x,x;\ x,\frac{1}{2}-x,\frac{1}{2}+x;\ \frac{1}{2}+x,x,\frac{1}{2}-x;$ $\frac{1}{4}+x,\frac{1}{4}+x,\frac{1}{4}+x;\ \frac{1}{4}-x,\frac{1}{4}-x,\frac{1}{4}-x;$ $\frac{3}{4}+x,\frac{1}{4}-x,\frac{3}{4}-x;\ \frac{3}{4}-x,\frac{1}{4}+x,\frac{3}{4}+x;$ $\frac{3}{4}-x,\frac{3}{4}+x,\frac{1}{4}-x;\ \frac{3}{4}+x,\frac{3}{4}-x,\frac{1}{4}+x;$ $\frac{1}{4}-x,\frac{3}{4}-x,\frac{3}{4}+x;\ \frac{1}{4}+x,\frac{3}{4}+x,\frac{3}{4}-x.$	*hkl*: If $h,k,(l)=2n$, then $h+k+l=4n$
24	*d*	$\bar{4}$	$\frac{3}{8},0,\frac{1}{4};\ \frac{1}{4},\frac{3}{8},0;\ 0,\frac{1}{4},\frac{3}{8};\ \frac{1}{8},0,\frac{3}{4};\ \frac{3}{4},\frac{1}{8},0;\ 0,\frac{3}{4},\frac{1}{8};$ $\frac{7}{8},0,\frac{1}{4};\ \frac{1}{4},\frac{7}{8},0;\ 0,\frac{1}{4},\frac{7}{8};\ \frac{5}{8},0,\frac{3}{4};\ \frac{3}{4},\frac{5}{8},0;\ 0,\frac{3}{4},\frac{5}{8}.$	*hkl*: $h=2n+1$, $k=2n+1$, $l=4n+2$ or $4n+2$, $4n+2$, $4n$ or $8n$, $8n+4$, $4n+2$ or $4n$, $4n$, $4n$
24	*c*	222	$\frac{1}{8},0,\frac{1}{4};\ \frac{1}{4},\frac{1}{8},0;\ 0,\frac{1}{4},\frac{1}{8};\ \frac{3}{8},0,\frac{3}{4};\ \frac{3}{4},\frac{3}{8},0;\ 0,\frac{3}{4},\frac{3}{8};$ $\frac{5}{8},0,\frac{1}{4};\ \frac{1}{4},\frac{5}{8},0;\ 0,\frac{1}{4},\frac{5}{8};\ \frac{7}{8},0,\frac{3}{4};\ \frac{3}{4},\frac{7}{8},0;\ 0,\frac{3}{4},\frac{7}{8}.$	h,k,l permutable
16	*b*	32	$\frac{1}{8},\frac{1}{8},\frac{1}{8};\ \frac{5}{8},\frac{3}{8},\frac{7}{8};\ \frac{7}{8},\frac{5}{8},\frac{3}{8};\ \frac{3}{8},\frac{7}{8},\frac{5}{8};$ $\frac{7}{8},\frac{7}{8},\frac{7}{8};\ \frac{3}{8},\frac{5}{8},\frac{1}{8};\ \frac{1}{8},\frac{3}{8},\frac{5}{8};\ \frac{5}{8},\frac{1}{8},\frac{3}{8}.$	*hkl*: $h=2n+1$, $k=2n+1$, $l=4n+2$ or $4n$, $4n$, $4n$ h,k,l permutable
16	*a*	$\bar{3}$	$0,0,0;\ 0,\frac{1}{2},\frac{1}{2};\ \frac{1}{2},0,\frac{1}{2};\ \frac{1}{2},\frac{1}{2},0;$ $\frac{1}{4},\frac{1}{4},\frac{1}{4};\ \frac{1}{4},\frac{3}{4},\frac{3}{4};\ \frac{3}{4},\frac{1}{4},\frac{3}{4};\ \frac{3}{4},\frac{3}{4},\frac{1}{4}.$	*hkl*: $h,k,(l)=2n$; $h+k+l=4n$

Exercise 4

Kalifersite and the palysepiole polysomatic series (Fig. 1e and 4s, see solution)

Kalifersite - $(K,Na)_5(Fe^{3+})_7[Si_{20}O_{50}](OH)_6 \bullet 12H_2O$; $P\bar{1}$, a = 14.86, b = 20.54, c = 5.29 Å, α = 95.6, β = 92.3, γ = 94.4°. Structure unknown.

Sepiolite - $Mg_8[Si_{12}O_{30}](OH)_4 \bullet 12H_2O$; *Pncn*, a = 13.40, b = 26.80, c = 5.28 Å. Structure known (Fig. 1e).

Palygorskite - $Mg_5[Si_8O_{20}](OH)_2 \bullet 8H_2O$; *C2/m*, a = 13.27, b = 17.868, c = 5.279 Å, β = 107.38°. Structure known (Fig. 1e).

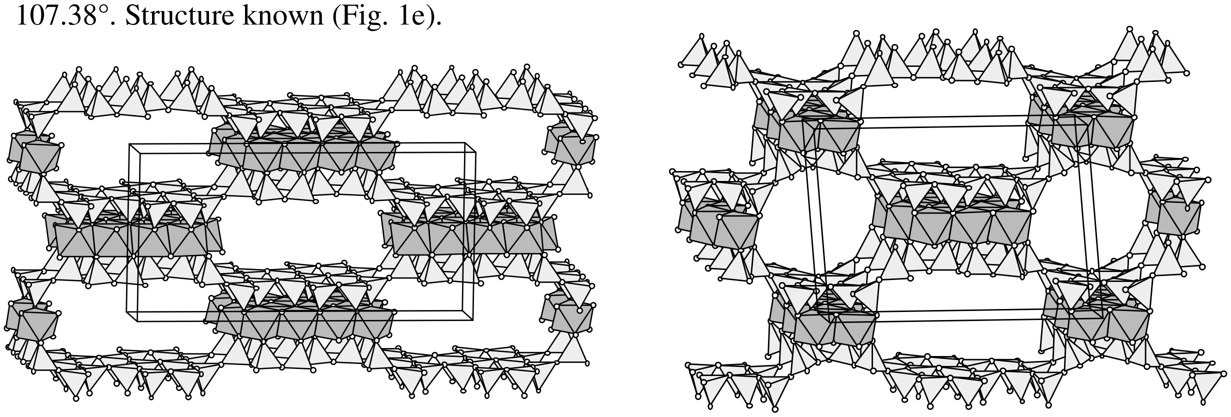


Figure 1e - Sepiolite (left) and palygorskite (right).

The following is 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 periodicity corresponds to that of a pyroxene chain.
2. The b value of kalifersite is intermediate between that of palygorskite and sepiolite.
3. The $[Si_{20}O_{50}](OH)_6$ silicate anion of kalifersite corresponds to the sum of those of sepiolite, $[Si_{12}O_{30}](OH)_4$, and palygorskite, $[Si_8O_{20}](OH)_2$.
4. The structures of sepiolite and palygorskite are based on a framework of interconnected [001] *TOT* ribbons which correspond to cuts with different width of the phyllosilicate 2:1 layer (Fig. 3 and 4). These ribbons are chess-board arranged and delimit channels. In the [010] direction, the $(TOT)_S$ ribbon of sepiolite is one chain wider than that, $(TOT)_P$, of palygorskite. That requires for sepiolite a b value about 9 Å longer than in palygorskite, *i.e.* about 4.5 Å per *T* chain. Mg and H_2O are in the channels delimited by the silicate ribbons.

Taking into account the above chemical and crystallographic aspects derive a structure model for kalifersite.

Exercise 5

Modelling the structure of seidite-(Ce) (Fig. 2e and 5s, see solution)

Seidite-(Ce) - $Na_4(Ce,Sr)_2Ti[(Si_8O_{18})(OH)_2](O,OH,F)_4$•$5H_2O$; *a* = 24.61, *b* = 7.23, *c* = 14.53 Å, β = 94.6°; *C*2/*c*. Structure is unknown.

Rhodesite - $K_2Ca_4[Si_8O_{18}(OH)_2]$•$12H_2O$; *a* = 23.416, *b* = 6.555, *c* = 7.050 Å, *Pmam*. The structure is known (Fig. 2e). Several compounds share with rhodesite the silicate double layer crossed by eight-membered channels delimited by Si-tetrahedra. The structures of these compounds differ instead in the content of the octahedral layer that is sandwiched between two silicate modules. In rhodesite, Ca is in the octahedral layer arranged in chains of edge-sharing Ca octahedra; K and H_2O are in the channels.

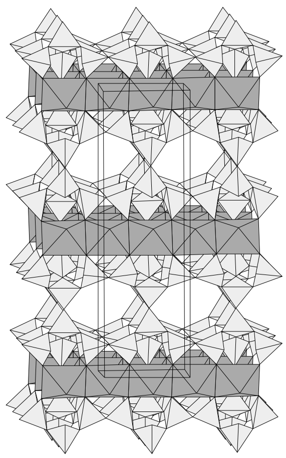


Figure 2e – The crystal structure of rhodesite.

The following is noted.

1. Seidite-(Ce) and rhodesite share the anion $[(Si_8O_{18})(OH)_2]$ which corresponds to the composition of the double layer mentioned above.
2. The two minerals show close values of the cell parameters [*c*/2 seidite-(Ce) to be compared with *c* of rhodesite].
3.

Table 1 – Members of the rhodesite group.

Name	Chemical formula	*a*, *b*, *c* (Å), β (°)
Seidite-(Ce)	$Na_4(Ce,Sr)_2\{Ti(OH)_2(Si_8O_{18})\}(O,OH,F)_4\cdot 5H_2O$	24.61, 7.23,14.53, 94.6
Rhodesite	$K_2Ca_4[Si_8O_{18}(OH)]_2\cdot 12H_2O$	23.416, 6.555, 7.050
Macdonaldite	$BaCa_4[Si_8O_{18}(OH)]_2\cdot 10H_2O$	14.081, 13.109, 23.560
Delhayelite	$K_7Na_3Ca_5[Si_7AlO_{19}]_2F_4Cl_2$	24.86, 7.07, 6.53
Hydrodelhayelite	$K_2Ca_4[Si_7AlO_{17}(OH)_2]_2\cdot 6H_2O$	6.648, 23.846, 7.073
Monteregianite-(Y)	$K_2Na_4Y_2[Si_8O_{19}]_2\cdot 10H_2O$	9.512, 23.956, 9.617, 93.85