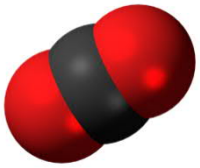
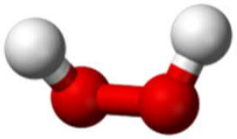
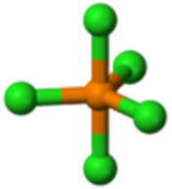
EXERCISE 2.1. Determine the point group for the following molecules/ions:

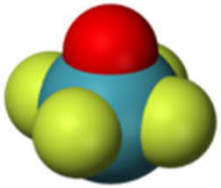
A. Carbon dioxide CO_2 

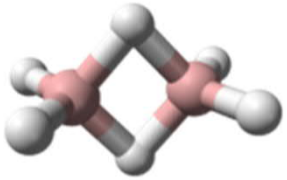
B. Hydrogen peroxide H_2O_2 

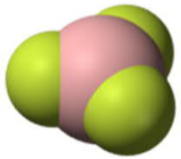
C. Benzene C_6H_6

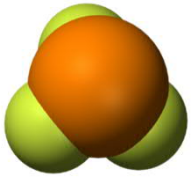
D. Phosphorus pentafluoride PF_5 

E. Hydrogenfluoride HF

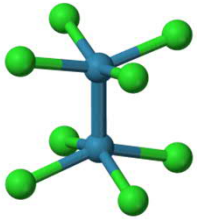
F. Xenon oxo tetrafluoride 

G. Diborane B_2H_6 

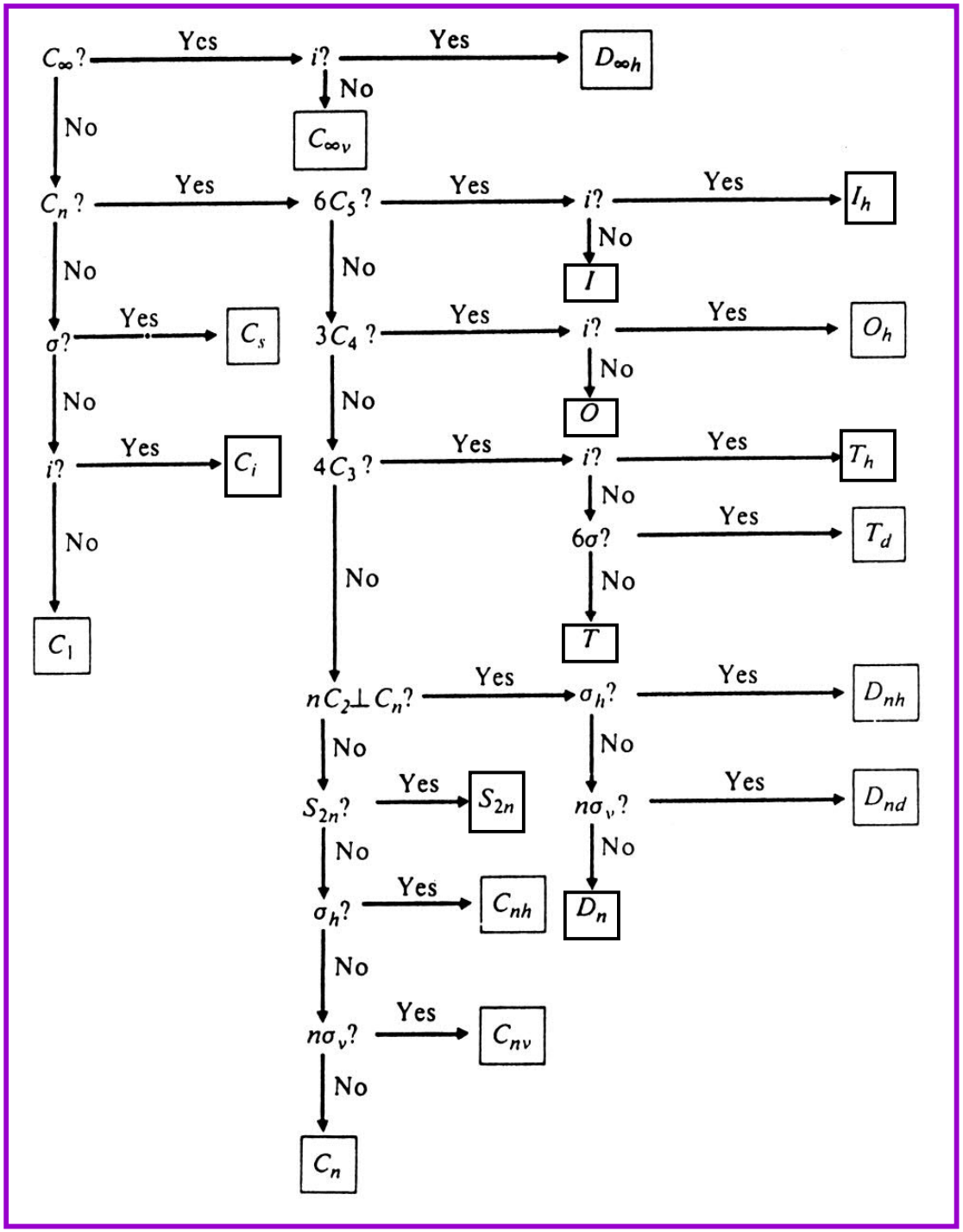
H. Boron trifluoride BF_3 (planar) 

I. Phosphorus trifluoride PF_3 

J. Sulfurhexafluoride SF_6

K. Octachlorodimolybdate 

L. SiFClBrI


C_∞?
Yes
i?
Yes
$D_{\infty h}$
No
$C_{\infty v}$
No
C_n?
Yes
$6C_5$?
Yes
i?
Yes
I_h
No
I
No
σ?
Yes
C_s
$3C_4$?
Yes
i?
Yes
O_h
No
O
No
i?
Yes
C_i
$4C_3$?
Yes
i?
Yes
T_h
No
6σ?
Yes
T_d
No
C_1
No
T
$nC_2 \perp C_n$?
Yes
σ_h?
Yes
D_{nh}
No
No
S_{2n}?
Yes
S_{2n}
$n\sigma_v$?
Yes
D_{nd}
No
No
σ_h?
Yes
C_{nh}
D_n
No
$n\sigma_v$?
Yes
C_{nv}
No
C_n

EXERCISE 2.2.

$Ni(CN)_4^{2-}$ ion has D_{4h} symmetry.

What can you tell about its structure based on that ?

EXERCISE 2.3.

What is the Bravais lattice type of perovskite $CaTiO_3$;

Please illustrate by a simple drawing.

EXERCISE 2.4.

In this structure grey balls are Ti atoms and red balls O atoms. The unit cell parameters are: a = 4.5937 Å, b = 4.5937 Å and c = 2.9587 Å; all angles are 90º.

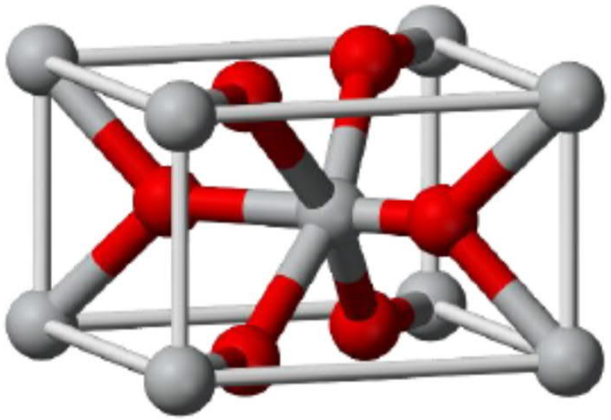
A. What is the crystal system?

B. What are the coordination numbers?

C. What is the chemical formula of the compound?

D. How many formula units in the unit cell, i.e. what is the value of Z?

E. Please calculate the density.

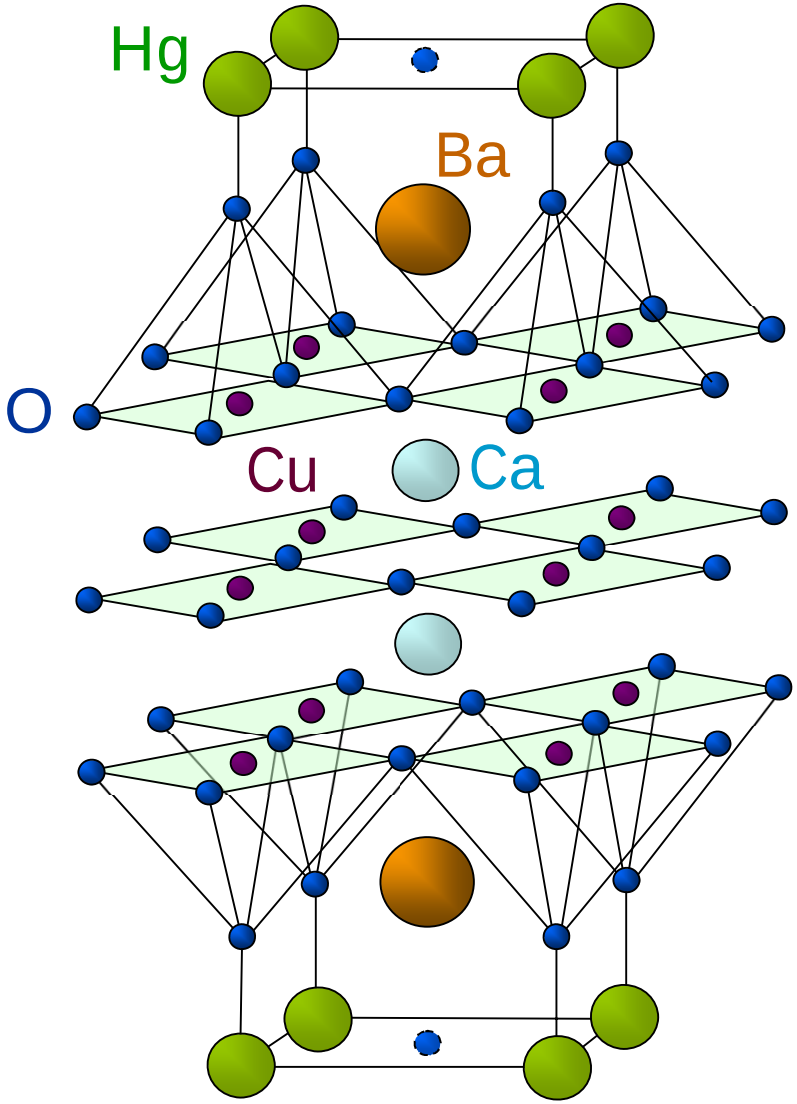


EXERCISE 2.5.

Here is the structure of the highest T_c superconductor Hg-Ba-Ca-Cu-O.

From this structure, derive the chemical formula of it.

How many formula units in the unit cell, i.e. what is the value of Z ?



Hg-Ba-Ca-Cu-O

EXERCISE 2.6.

The La-Ba-Co-O compound has a crystal structure with space group *P*4/*mmm* (No 123) and lattice parameters: *a* = 3.89 Å; *c* = 7.71 Å.

Atomic positions are:

Atomi	*x*	*y*	*z*
La	0	0	0
Ba	0	0	0.5
Co	0.5	0.5	0.248
O1	0.5	0.5	0
O2	0	0.5	0.2356
O3	0.5	0.5	0.5

A. Draw the unit cell.

B. What is the stoichiometry of the compound?

C. Do you see any correlation with the stoichiometry and site multiplicities ?

D. What is the name of the structure?

E. Calculate the theoretical density of the material.

(N_A = 6.022 x 10^{23}; atomic weights: La 138.9; Ba 137.3; Co 58.9; O 16.0)

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	u	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{y},x,z$	(4) $y,\bar{x},z$	no conditions
			(5) $\bar{x},y,\bar{z}$	(6) $x,\bar{y},\bar{z}$	(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) $y,\bar{x},\bar{z}$	(12) $\bar{y},x,\bar{z}$	
			(13) $x,\bar{y},z$	(14) $\bar{x},y,z$	(15) $\bar{y},\bar{x},z$	(16) y,x,z	
							Special:
8	t	$.m.$	$x,\frac{1}{2},z$	$\bar{x},\frac{1}{2},z$	$\frac{1}{2},x,z$	$\frac{1}{2},\bar{x},z$	no extra conditions
			$\bar{x},\frac{1}{2},\bar{z}$	$x,\frac{1}{2},\bar{z}$	$\frac{1}{2},x,\bar{z}$	$\frac{1}{2},\bar{x},\bar{z}$	
8	s	$.m.$	$x,0,z$	$\bar{x},0,z$	$0,x,z$	$0,\bar{x},z$	no extra conditions
			$\bar{x},0,\bar{z}$	$x,0,\bar{z}$	$0,x,\bar{z}$	$0,\bar{x},\bar{z}$	
8	r	$..m$	x,x,z	$\bar{x},\bar{x},z$	$\bar{x},x,z$	$x,\bar{x},z$	no extra conditions
			$\bar{x},x,\bar{z}$	$x,\bar{x},\bar{z}$	$x,x,\bar{z}$	$\bar{x},\bar{x},\bar{z}$	
8	q	$m..$	$x,y,\frac{1}{2}$	$\bar{x},\bar{y},\frac{1}{2}$	$\bar{y},x,\frac{1}{2}$	$y,\bar{x},\frac{1}{2}$	no extra conditions
			$\bar{x},y,\frac{1}{2}$	$x,\bar{y},\frac{1}{2}$	$y,x,\frac{1}{2}$	$\bar{y},\bar{x},\frac{1}{2}$	
8	p	$m..$	$x,y,0$	$\bar{x},\bar{y},0$	$\bar{y},x,0$	$y,\bar{x},0$	no extra conditions
			$\bar{x},y,0$	$x,\bar{y},0$	$y,x,0$	$\bar{y},\bar{x},0$	
4	o	$m\,2m.$	$x,\frac{1}{2},\frac{1}{2}$	$\bar{x},\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},x,\frac{1}{2}$	$\frac{1}{2},\bar{x},\frac{1}{2}$	no extra conditions
4	n	$m\,2m.$	$x,\frac{1}{2},0$	$\bar{x},\frac{1}{2},0$	$\frac{1}{2},x,0$	$\frac{1}{2},\bar{x},0$	no extra conditions
4	m	$m\,2m.$	$x,0,\frac{1}{2}$	$\bar{x},0,\frac{1}{2}$	$0,x,\frac{1}{2}$	$0,\bar{x},\frac{1}{2}$	no extra conditions
4	l	$m\,2m.$	$x,0,0$	$\bar{x},0,0$	$0,x,0$	$0,\bar{x},0$	no extra conditions
4	k	$m.2m$	$x,x,\frac{1}{2}$	$\bar{x},\bar{x},\frac{1}{2}$	$\bar{x},x,\frac{1}{2}$	$x,\bar{x},\frac{1}{2}$	no extra conditions
4	j	$m.2m$	$x,x,0$	$\bar{x},\bar{x},0$	$\bar{x},x,0$	$x,\bar{x},0$	no extra conditions
4	i	$2mm.$	$0,\frac{1}{2},z$	$\frac{1}{2},0,z$	$0,\frac{1}{2},\bar{z}$	$\frac{1}{2},0,\bar{z}$	$hkl: h+k=2n$
2	h	$4mm$	$\frac{1}{2},\frac{1}{2},z$	$\frac{1}{2},\frac{1}{2},\bar{z}$			no extra conditions
2	g	$4mm$	$0,0,z$	$0,0,\bar{z}$			no extra conditions
2	f	$mmm.$	$0,\frac{1}{2},0$	$\frac{1}{2},0,0$			$hkl: h+k=2n$
2	e	$mmm.$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,\frac{1}{2}$			$hkl: h+k=2n$
1	d	$4/mmm$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$				no extra conditions
1	c	$4/mmm$	$\frac{1}{2},\frac{1}{2},0$				no extra conditions
1	b	$4/mmm$	$0,0,\frac{1}{2}$				no extra conditions
1	a	$4/mmm$	$0,0,0$				no extra conditions

Symmetry of special projections

Along [001] $p\,4mm$
$\boldsymbol{a}'=\boldsymbol{a}$ $\boldsymbol{b}'=\boldsymbol{b}$
Origin at $0,0,z$

Along [100] $p\,2mm$
$\boldsymbol{a}'=\boldsymbol{b}$ $\boldsymbol{b}'=\boldsymbol{c}$
Origin at $x,0,0$

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

(*Continued on preceding page*)

EXERCISE 2.7.

$Cu(1)Ba_2YCu(2)_2O_{7-\delta}$ compound has a crystal structure with space group *Pmmm* (No 47) and lattice parameters: a = 3.8227 Å, b = 3.8872 Å, c = 11.6802 Å.

Atomic positions are:

Cu(1)	(0,0,0)	
Cu(2)	(0,0,z)	z = 0.3556
Ba	(½,½,z)	z = 0.1843
Y	(½,½,½)	
O(1)	(0,½,0)	
O(2)	(½,0,z)	z = 0.3779
O(3)	(0,½,z)	z = 0.3790
O(4)	(0,0,z)	z = 0.1590

A. Draw the unit cell.

B. Determine CN and bond lengths for both Cu(1) and Cu(2) atoms.

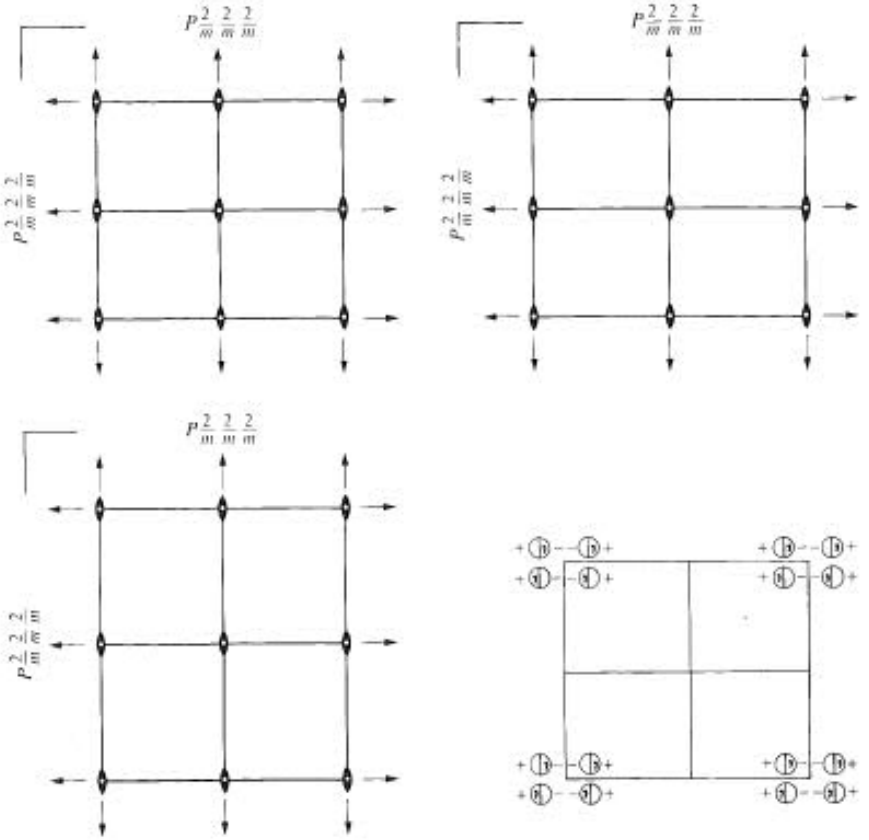
C. Calculate BVS for both Cu atoms [$R^0(Cu^{II}\text{-}O^{-II})$ = 1.679]

Reference:

J.D. Jorgensen, et al., *Physical Review B* **41**, 1863 (1990).

$Pmmm$ D_{2h}^{1} mmm Orthorhombic

No. 47 $P\,2/m\,2/m\,2/m$ Patterson symmetry $Pmmm$



Origin at centre $(m\,m\,m)$

Asymmetric unit $0\le x\le \frac{1}{4};\ 0\le y\le \frac{1}{4};\ 0\le z\le \frac{1}{4}$

Symmetry operations

(1) 1	(2) 2 $0,0,z$	(3) 2 $0,y,0$	(4) 2 $x,0,0$
(5) $\bar{1}$ $0,0,0$	(6) m $x,y,0$	(7) m $x,0,z$	(8) m $0,y,z$

Maximal non-isomorphic subgroups (*continued*)

IIa none

IIb $[2]Pccm(\boldsymbol{c}'=2\boldsymbol{c})$; $[2]Pcmm(\boldsymbol{c}'=2\boldsymbol{c})(Pmma)$; $[2]Pmcm(\boldsymbol{c}'=2\boldsymbol{c})(Pmma)$; $[2]Pbmb(\boldsymbol{b}'=2\boldsymbol{b})(Pccm)$; $[2]Pbmm(\boldsymbol{b}'=2\boldsymbol{b})(Pmma)$; $[2]Pmmb(\boldsymbol{b}'=2\boldsymbol{b})(Pmma)$; $[2]Pmaa(\boldsymbol{a}'=2\boldsymbol{a})(Pccm)$; $[2]Pmam(\boldsymbol{a}'=2\boldsymbol{a})(Pmma)$; $[2]Pmma(\boldsymbol{a}'=2\boldsymbol{a})$; $[2]Ammm(\boldsymbol{b}'=2\boldsymbol{b},\boldsymbol{c}'=2\boldsymbol{c})(Cmmm)$; $[2]Abmm(\boldsymbol{b}'=2\boldsymbol{b},\boldsymbol{c}'=2\boldsymbol{c})(Cmma)$; $[2]Bmmm(\boldsymbol{a}'=2\boldsymbol{a},\boldsymbol{c}'=2\boldsymbol{c})(Cmmm)$; $[2]Bmam(\boldsymbol{a}'=2\boldsymbol{a},\boldsymbol{c}'=2\boldsymbol{c})(Cmma)$; $[2]Cmmm(\boldsymbol{a}'=2\boldsymbol{a},\boldsymbol{b}'=2\boldsymbol{b})$; $[2]Cmma(\boldsymbol{a}'=2\boldsymbol{a},\boldsymbol{b}'=2\boldsymbol{b})$; $[2]Fmmm(\boldsymbol{a}'=2\boldsymbol{a},\boldsymbol{b}'=2\boldsymbol{b},\boldsymbol{c}'=2\boldsymbol{c})$

Maximal isomorphic subgroups of lowest index

IIc $[2]Pmmm(\boldsymbol{a}'=2\boldsymbol{a}$ or $\boldsymbol{b}'=2\boldsymbol{b}$ or $\boldsymbol{c}'=2\boldsymbol{c})$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (3); (5)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
8	α	1	(1) x,y,z (5) $\bar{x},\bar{y},\bar{z}$	(2) $\bar{x},\bar{y},z$ (6) $x,y,\bar{z}$	(3) $\bar{x},y,\bar{z}$ (7) $x,\bar{y},z$	(4) $x,\bar{y},\bar{z}$ (8) $\bar{x},y,z$	General: no conditions
4	z	$..m$	$x,y,\frac{1}{2}$	$\bar{x},\bar{y},\frac{1}{2}$	$\bar{x},y,\frac{1}{2}$	$x,\bar{y},\frac{1}{2}$	Special: no extra conditions
4	y	$..m$	$x,y,0$	$\bar{x},\bar{y},0$	$\bar{x},y,0$	$x,\bar{y},0$	
4	x	$.m.$	$x,\frac{1}{2},z$	$\bar{x},\frac{1}{2},z$	$\bar{x},\frac{1}{2},\bar{z}$	$x,\frac{1}{2},\bar{z}$	
4	w	$.m.$	$x,0,z$	$\bar{x},0,z$	$\bar{x},0,\bar{z}$	$x,0,\bar{z}$	
4	v	$m..$	$\frac{1}{2},y,z$	$\frac{1}{2},\bar{y},z$	$\frac{1}{2},y,\bar{z}$	$\frac{1}{2},\bar{y},\bar{z}$	
4	u	$m..$	$0,y,z$	$0,\bar{y},z$	$0,y,\bar{z}$	$0,\bar{y},\bar{z}$	
2	t	$mm2$	$\frac{1}{2},\frac{1}{2},z$	$\frac{1}{2},\frac{1}{2},\bar{z}$			
2	s	$mm2$	$\frac{1}{2},0,z$	$\frac{1}{2},0,\bar{z}$			
2	r	$mm2$	$0,\frac{1}{2},z$	$0,\frac{1}{2},\bar{z}$			
2	q	$mm2$	$0,0,z$	$0,0,\bar{z}$			
2	p	$m2m$	$\frac{1}{2},y,\frac{1}{2}$	$\frac{1}{2},\bar{y},\frac{1}{2}$			
2	o	$m2m$	$\frac{1}{2},y,0$	$\frac{1}{2},\bar{y},0$			
2	n	$m2m$	$0,y,\frac{1}{2}$	$0,\bar{y},\frac{1}{2}$			
2	m	$m2m$	$0,y,0$	$0,\bar{y},0$			
2	l	$2mm$	$x,\frac{1}{2},\frac{1}{2}$	$\bar{x},\frac{1}{2},\frac{1}{2}$			
2	k	$2mm$	$x,\frac{1}{2},0$	$\bar{x},\frac{1}{2},0$			
2	j	$2mm$	$x,0,\frac{1}{2}$	$\bar{x},0,\frac{1}{2}$			
2	i	$2mm$	$x,0,0$	$\bar{x},0,0$			
1	h	mmm	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$				
1	g	mmm	$0,\frac{1}{2},\frac{1}{2}$				
1	f	mmm	$\frac{1}{2},\frac{1}{2},0$				
1	e	mmm	$0,\frac{1}{2},0$				
1	d	mmm	$\frac{1}{2},0,\frac{1}{2}$				
1	c	mmm	$0,0,\frac{1}{2}$				
1	b	mmm	$\frac{1}{2},0,0$				
1	a	mmm	$0,0,0$				

Symmetry of special projections

Along [001] $p\,2m\,m$
$\boldsymbol{a}'=\boldsymbol{a}$ $\boldsymbol{b}'=\boldsymbol{b}$
Origin at $0,0,z$

Along [100] $p\,2m\,m$
$\boldsymbol{a}'=\boldsymbol{b}$ $\boldsymbol{b}'=\boldsymbol{c}$
Origin at $x,0,0$

Along [010] $p\,2m\,m$
$\boldsymbol{a}'=\boldsymbol{c}$ $\boldsymbol{b}'=\boldsymbol{a}$
Origin at $0,y,0$

Maximal non-isomorphic subgroups

I	[2]$P\,2\,2\,2$	1; 2; 3; 4
	[2]$P\,1\,1\,2/m$ ($P\,2/m$)	1; 2; 5; 6
	[2]$P\,1\,2/m\,1$ ($P\,2/m$)	1; 3; 5; 7
	[2]$P\,2/m\,1\,1$ ($P\,2/m$)	1; 4; 5; 8
	[2]$P\,m\,m\,2$	1; 2; 7; 8
	[2]$P\,m\,2m$ ($P\,m\,m\,2$)	1; 3; 6; 8
	[2]$P\,2m\,m$ ($P\,m\,m\,2$)	1; 4; 6; 7