1.17 Some important structure types

a) Rock salt (NaCl), zinc blende or sphalerite (ZnS), fluorite (CaF_2), antifluorite (Na_2F)

These structures all have ccp/fcc anions and differ only in cation positions.

Rock salt: O occupied; T_+ and T_- empty
Zinc blende: T_+ (or T_-) occupied; O, T_- (or T_-) empty
Antifluorite: T_+, T_- occupied; O empty
Unit cells are shown in Fig. 1.24, in oblique projection and as projections on the *ab* face.

Formula A_xX_y, the coordination numbers (CNs) of A and X must be in the ratio of y:x. For rock salt and zinc blende, x = y and anions and cations have the same CN.

In antifluorite (A_2X), since the cations occupy tetrahedral sites, the anion CN must be 8.

- A clear view: The cation at X($\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$) may be chosen as the new origin of the unit cell (Table 1.7 and Fig. 1.25a), which contains cations at corners, edge centers, face centers and body center.
- The unit cell may be divided into eight mini-cubes. The centers of the cubes are 8-coordinate sites (since cations at all 8 corners). These sites are alternately occupied by anions (4 occupied and 4 empty).
- Fig. 1.25b shows the eightfold coordination for one anion.

In rock salt and zinc blende structures, the cation and anion positions are interchangeable and it is immaterial whether the origin coincides with an anion or a cation.

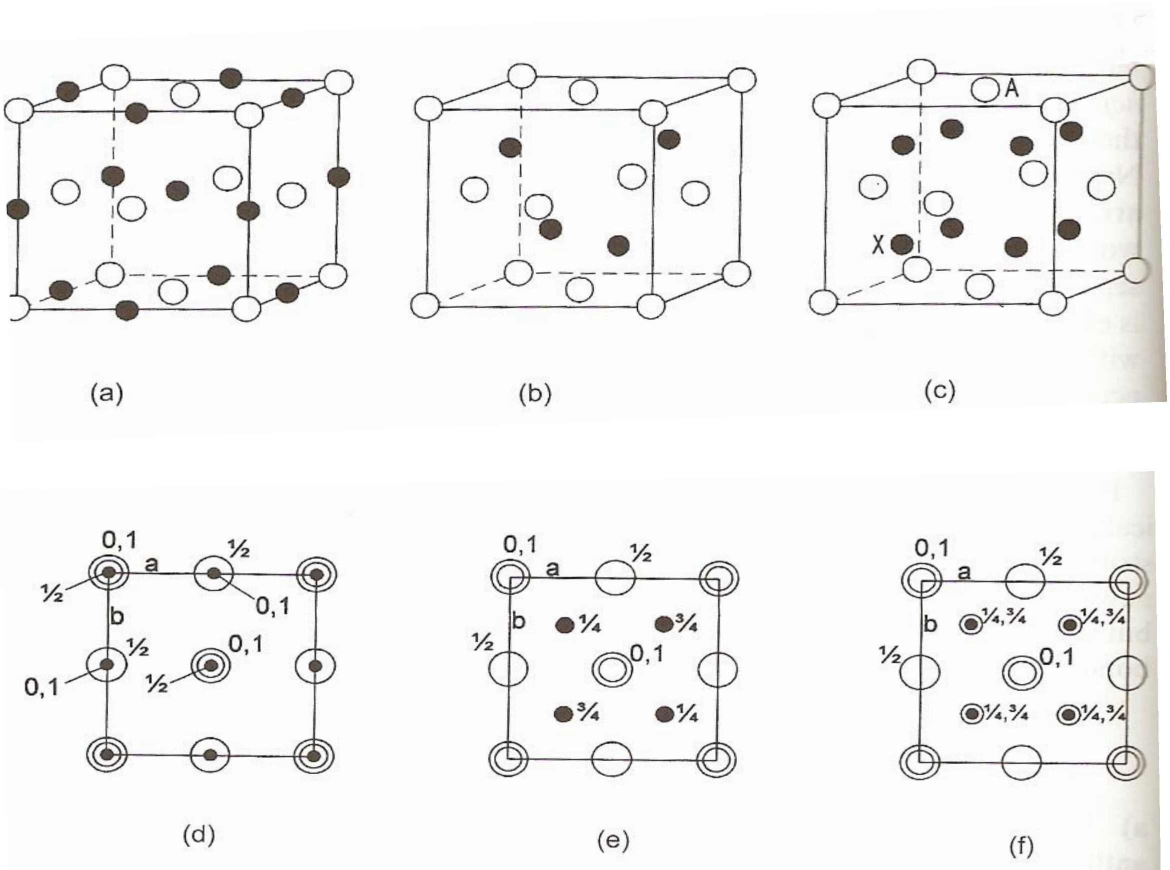


Fig. 1.24 Unit cell of (a,d) NaCl, (b,e) ZnS, sphalerite, and (c,f) Na_2O. Closed circles are cations; open circles are anions

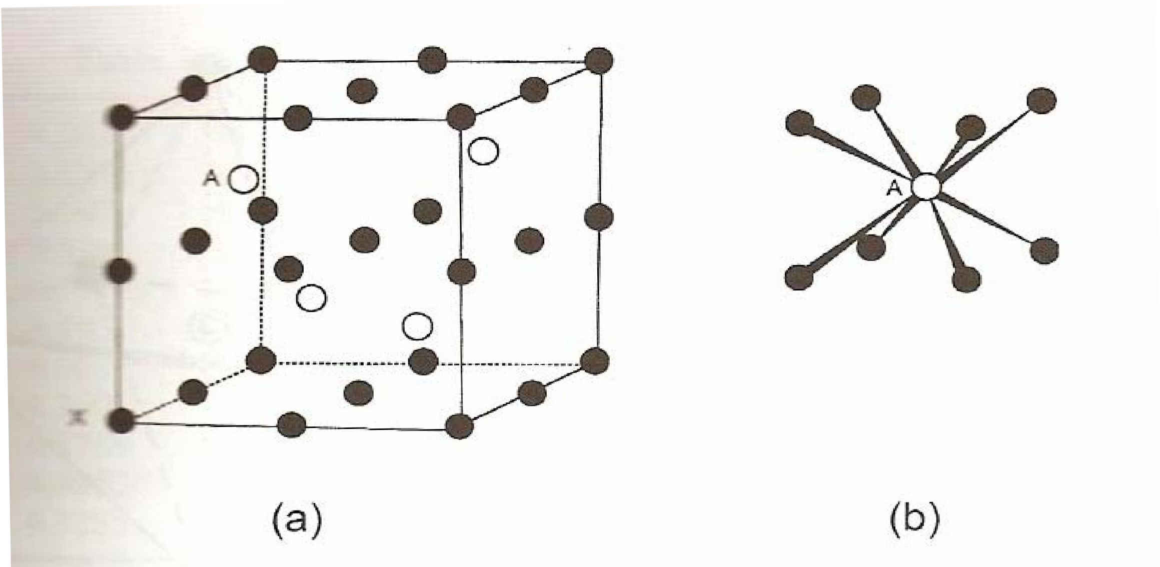


Fig. 1.25 Alternative view of the antifluorite structure

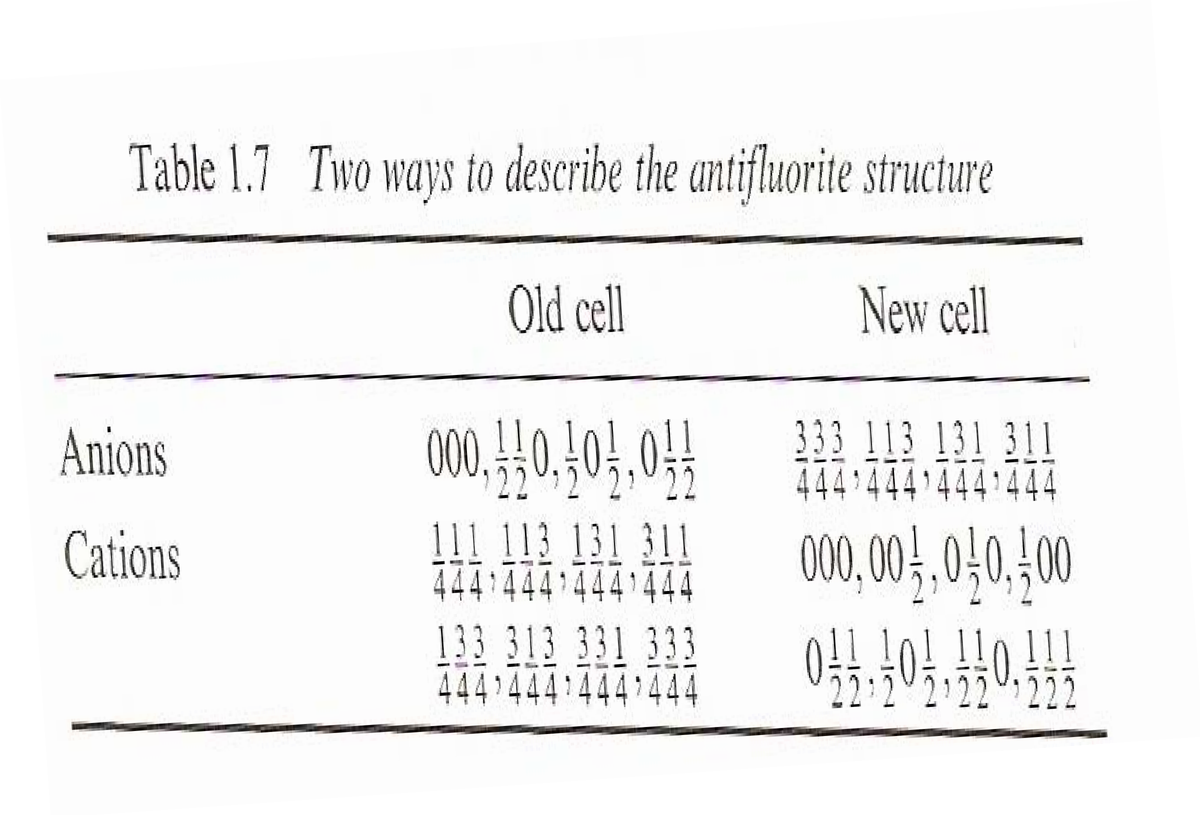


Table 1.7 *Two ways to describe the antifluorite structure*

	Old cell	New cell
Anions	$000, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}\frac{1}{2}$	$\frac{3}{4}\frac{3}{4}\frac{3}{4}, \frac{1}{4}\frac{1}{4}\frac{3}{4}, \frac{1}{4}\frac{3}{4}\frac{1}{4}, \frac{3}{4}\frac{1}{4}\frac{1}{4}$
Cations	$\frac{1}{4}\frac{1}{4}\frac{1}{4}, \frac{1}{4}\frac{1}{4}\frac{3}{4}, \frac{1}{4}\frac{3}{4}\frac{1}{4}, \frac{3}{4}\frac{1}{4}\frac{1}{4}$	$000, 00\frac{1}{2}, 0\frac{1}{2}0, \frac{1}{2}00$
	$\frac{1}{4}\frac{3}{4}\frac{3}{4}, \frac{3}{4}\frac{1}{4}\frac{3}{4}, \frac{3}{4}\frac{3}{4}\frac{1}{4}, \frac{3}{4}\frac{3}{4}\frac{3}{4}$	$0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}\frac{1}{2}\frac{1}{2}$

So far the NaCl, ZnS and Na_2O structure have been described in two ways: (a) as cp structures; (b) in terms of their unit cell. A third way is to regard them as built of space-filling polyhedral. It is then necessary to consider how neighboring polyhedra are linked in 3D.

i) Rock salt structure

* Each cation is surrounded by 6 anions and similarly, each anion is octahedrally coordinated by 6 cations (Fig. 1.26, consider the anion at the body center, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; it has 6 cation nearest neighbors at the 6 face centers).

* The $NaCl_6$ or $ClNa_6$ octahedra share common edges (Fig. 1.26). Each unit cell has 12 edges and each edge is common to two octahedra (Fig. 1.26 shows two such linkages).

* Fig. 1.27: a simplified perspective focusing on the 3D array of octahedra; the arrowed are the empty tetrahedral sites; each octahedron face is parallel to a cp layer of anions, as emphasized by the numbering or shading of coplanar faces (four cp orientations in a ccp/fcc array).

* Table 1.8: AB compounds possess the rock salt structure with the *a* dimension of the cubic unit cell; most halides and hydrides of the alkali

metals and Ag^+; a large number of chalcogenides (oxides, sulphites, etc) of divalent metals; many are ionic but others are metallic (TiO) or covalent (TiC).

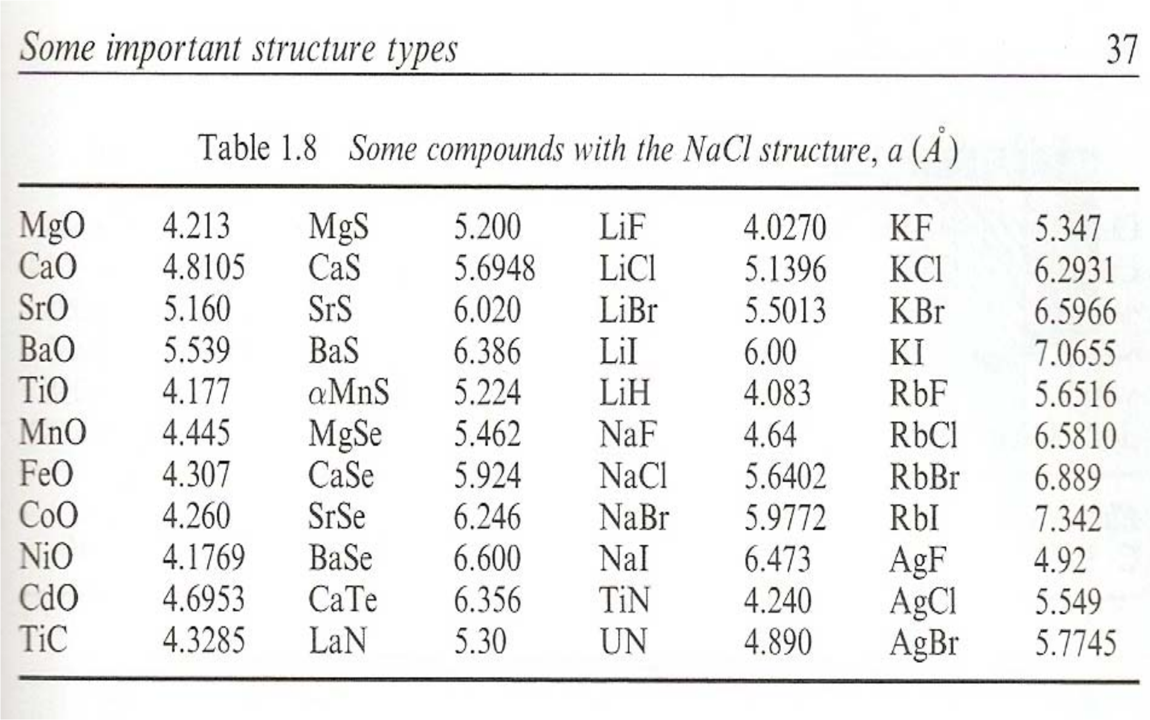


Table 1.8 *Some compounds with the NaCl structure, a (Å)*

MgO	4.213	MgS	5.200	LiF	4.0270	KF	5.347
CaO	4.8105	CaS	5.6948	LiCl	5.1396	KCl	6.2931
SrO	5.160	SrS	6.020	LiBr	5.5013	KBr	6.5966
BaO	5.539	BaS	6.386	LiI	6.00	KI	7.0655
TiO	4.177	αMnS	5.224	LiH	4.083	RbF	5.6516
MnO	4.445	MgSe	5.462	NaF	4.64	RbCl	6.5810
FeO	4.307	CaSe	5.924	NaCl	5.6402	RbBr	6.889
CoO	4.260	SrSe	6.246	NaBr	5.9772	RbI	7.342
NiO	4.1769	BaSe	6.600	NaI	6.473	AgF	4.92
CdO	4.6953	CaTe	6.356	TiN	4.240	AgCl	5.549
TiC	4.3285	LaN	5.30	UN	4.890	AgBr	5.7745

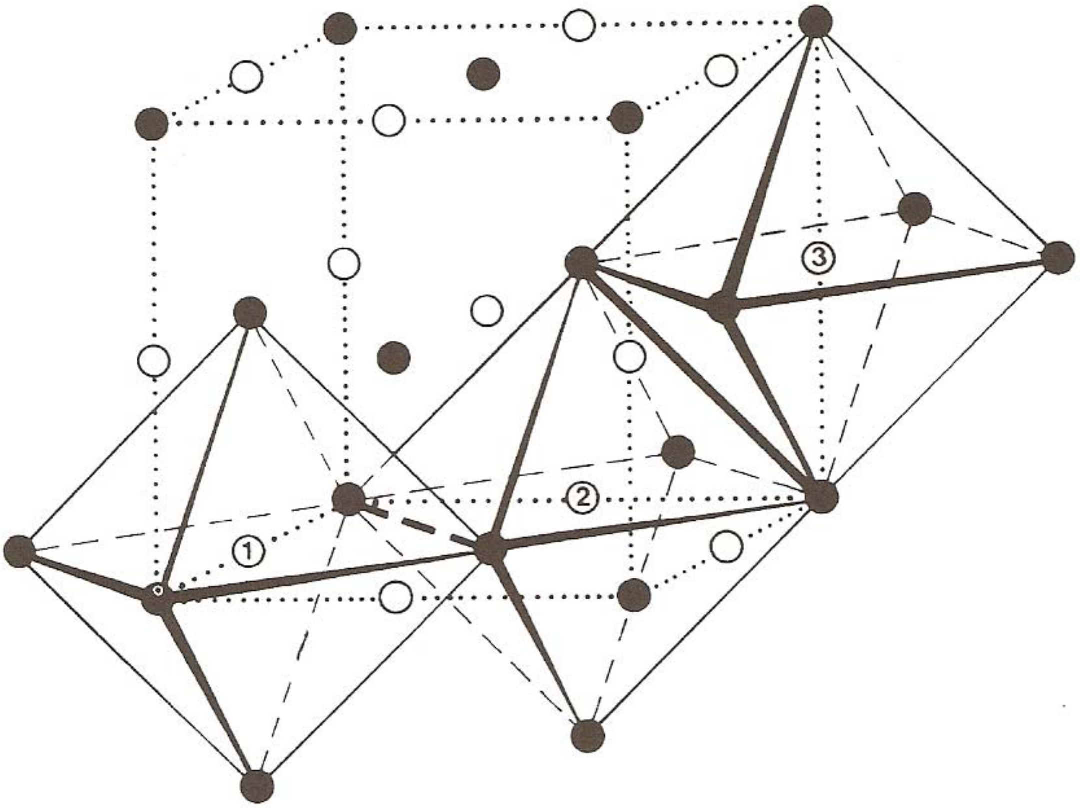


Fig. 1.26 Unit cell of the rock salt structure showing edge-sharing octahedra

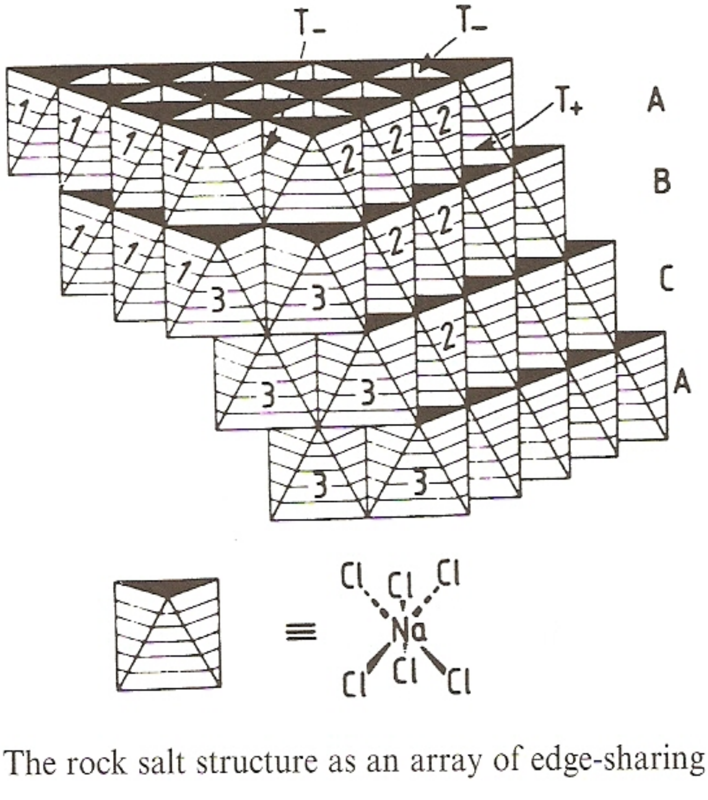


Fig. 1.27 The rock salt structure as an array of edge-sharing octahedra

ii) Zinc blende (sphalerite) structure

- The ZnS_4 tetrahedra are linked at their corners and each corner is common to four such tetrahedra.
- Fig. 1.24b is shown again in Fig. 1.28a, but in terms of corner-sharing ZnS_4 tetrahedra. The faces of the tetrahedra are parallel to the cp anion layers, i.e. the {111} planes.
- Fig. 1.28b: the model is oriented so that one set of tetrahedron faces is horizontal; the same structure is generated by interchanging the Zn and S.
- Table 1.9: the bonding is less ionic than in rock salt compounds, thus oxides usually do not have the zinc blende structure (ZnO is dimorphic with zinc blende and wurtzite polymorphs); chalcogenides of the alkaline earth metals (not Be) have the rock salt structure whereas the chalcogenides of Be, Zn, Cd and Hg have the zinc blende structure; copper(I) halides and γ-AgI; a range of III-V compounds (some are important semiconductors).

iii) Antifluorite/fluorite structure

- Antifluorite: a ccp <u>anion</u> array with tetrahedral (T_+ and T_-) <u>cations</u>
  Fluorite: a ccp <u>cation</u> array with tetrahedral <u>anions</u>
- In antifluorite, cation:anion = 2:1, CN of cation = 4 and CN of anion = 8
- Two distinct descriptions in a 3D network (Fig. 1.29)
  Fig. (a): a network of tetrahedra, corresponding to Fig. 1.24c
  Fig. (b): a network of cubes, corresponding to Fig. 1.25b. Fig. 1.29c shows an extended network of the corner- and edge-sharing cubes.
- Table 1.10
  Antifluorite: $A_2^+X^{2-}$ oxides and other chalcogenides of the alkali metals.
  Fluorite: $M^{2+}F_2$- fluorides of large, divalent cations
  $M^{4+}O_2$- oxides of large tetravalent cations
- An alternative description of the fluorite structure, Fig. 1.29b,c:
  a primitive cubic array of anions in which the 8-coordinate sites at the body centers are alternatively empty and occupied by a cation. However, fcc is still the true lattice type of fluorite (since the cubes represent only a small part of the fcc unit cell).

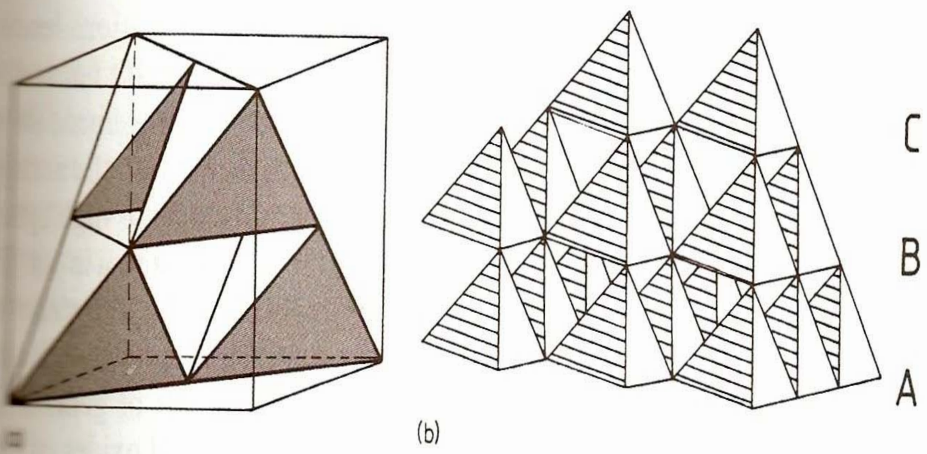


Fig. 1.28 The sphalerite (zinc blende) structure showing (a) the unit cell contents and (b) a more extended network of corner-sharing tetrahedra

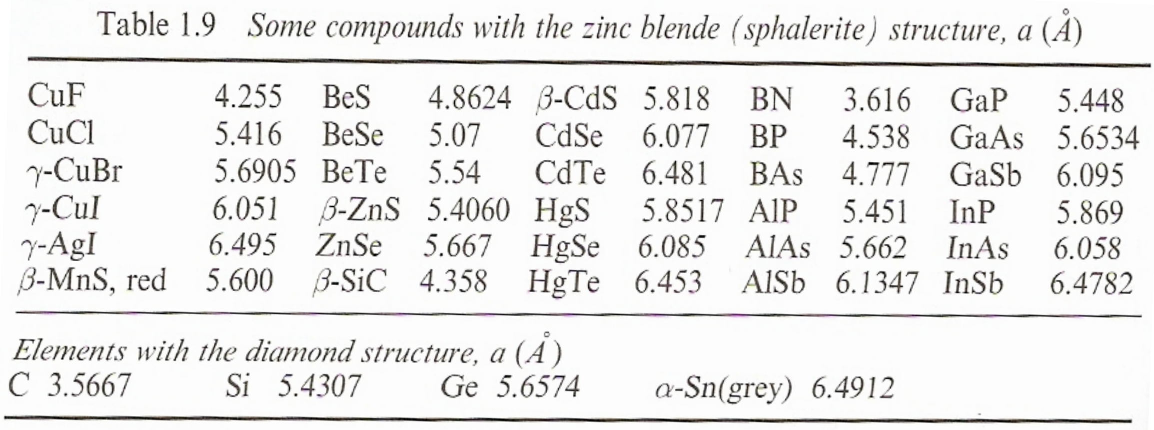


Table 1.9 *Some compounds with the zinc blende (sphalerite) structure, a (Å)*

CuF	4.255	BeS	4.8624	β-CdS	5.818	BN	3.616	GaP	5.448
CuCl	5.416	BeSe	5.07	CdSe	6.077	BP	4.538	GaAs	5.6534
γ-CuBr	5.6905	BeTe	5.54	CdTe	6.481	BAs	4.777	GaSb	6.095
γ-CuI	6.051	β-ZnS	5.4060	HgS	5.8517	AlP	5.451	InP	5.869
γ-AgI	6.495	ZnSe	5.667	HgSe	6.085	AlAs	5.662	InAs	6.058
β-MnS, red	5.600	β-SiC	4.358	HgTe	6.453	AlSb	6.1347	InSb	6.4782

Elements with the diamond structure, a (Å)

C	3.5667	Si	5.4307	Ge	5.6574	α-Sn(grey)	6.4912

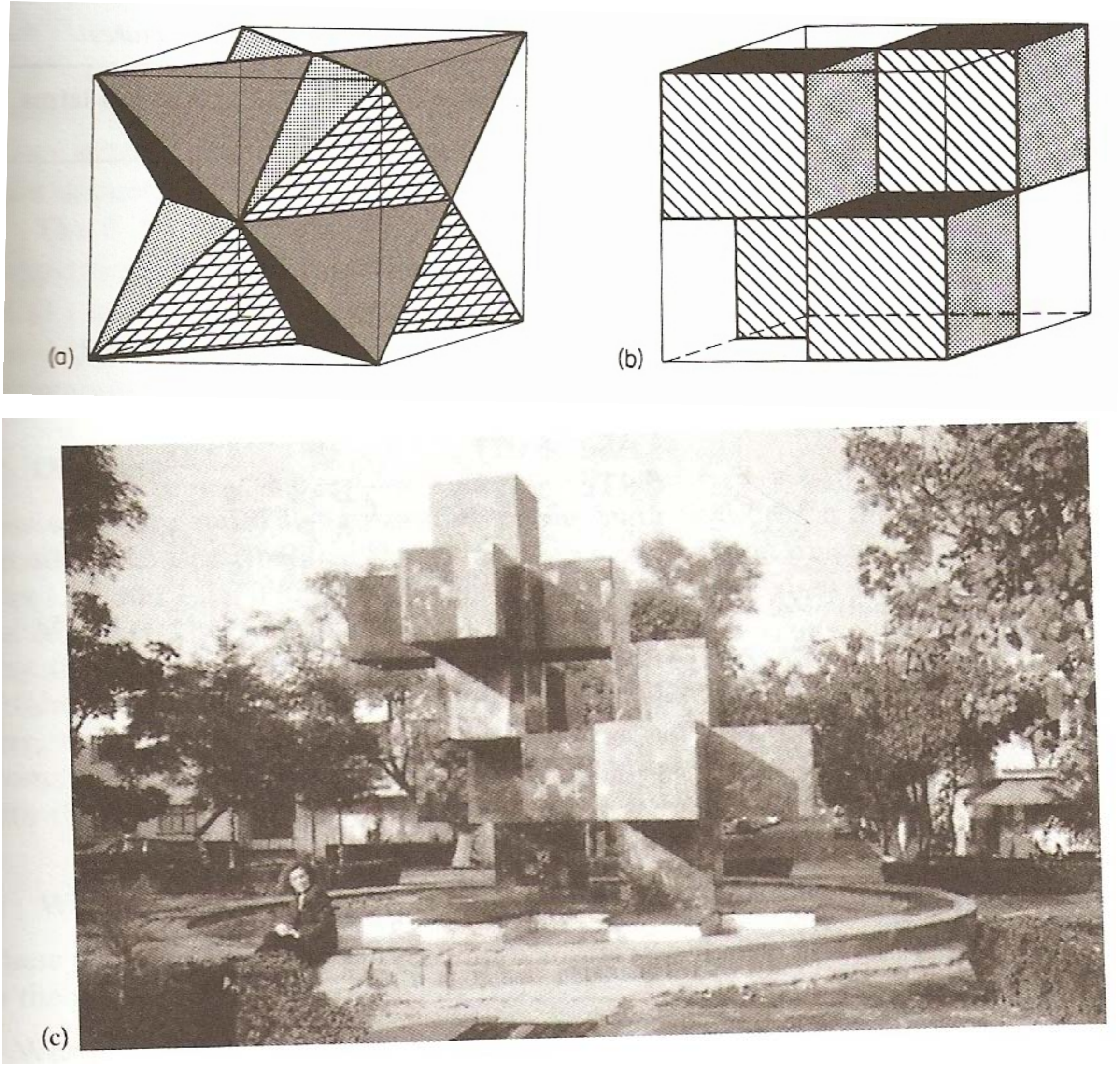


Fig. 1.29 The antifluorite structure showing the unit cell in terms of (a) NaO_4 tetrahedra or (b) ONa_8 cubes. A more extended array of cubes is shown in (c); this model resides on a roundabout in Mexico City

Table 1.10 *Some compounds with fluorite or antifluorite structure, a* (Å)

Fluorite structure				Antifluorite structure			
CaF_2	5.4626	PbO_2	5.349	Li_2O	4.6114	K_2O	6.449
SrF_2	5.800	CeO_2	5.4110	Li_2S	5.710	K_2S	7.406
$SrCl_2$	6.9767	PrO_2	5.392	Li_2Se	6.002	K_2Se	7.692
BaF_2	6.2001	ThO_2	5.600	Li_2Te	6.517	K_2Te	8.168
CdF_2	5.3895	UO_2	5.372	Na_2O	5.55	Rb_2O	6.74
β-PbF_2	5.940	NpO_2	5.4334	Na_2S	6.539	Rb_2S	7.65

iv) Bond length calculations

- * Simple trigonometric calculations for $\alpha=\beta=\gamma=90^\circ$ (orthogonal cells).
  e.g. rock salt, X–M = a/2, X–X = $a/\sqrt{2}$ (Fig. 1.21c)
- * Table 1.11: summary of the bond distance in terms of cell dimensions, which can be coupled with the a values shown in Tables 1.8–10 to determine the values of bond distances.
- * Appendix 4: summary of the bond distances of all metals with relevant CNs and oxidation states.
- * Some other consideration for fluorite:
  In CaF_2, Ca–Ca = 3.86 Å, which is much larger than the diameter of Ca^{2+} (2.2–2.6 Å). $\therefore$ Ca^{2+} ions have a eutectic ccp arrangement.
  F–F = 2.73 Å, which indicates the fluorines are approximately contacting (r_F = 1.2–1.4 Å). The array of F^- ions is not cp but is primitive cubic. This is perhaps a more realistic way of describing the CaF_2 structure by using F anions as the packing atoms and Ca as the interstitial ones.

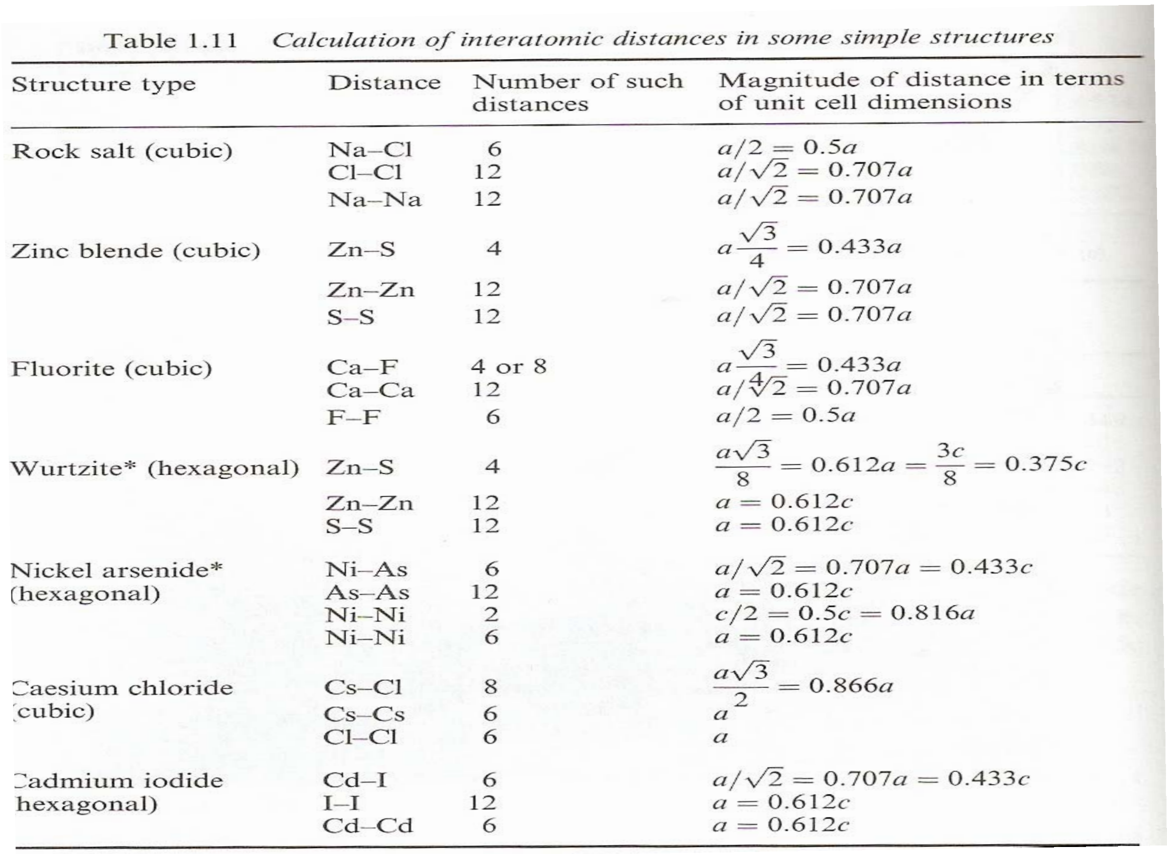


Table 1.11 *Calculation of interatomic distances in some simple structures*

Structure type	Distance	Number of such distances	Magnitude of distance in terms of unit cell dimensions
Rock salt (cubic)	Na–Cl	6	$a/2 = 0.5a$
	Cl–Cl	12	$a/\sqrt{2} = 0.707a$
	Na–Na	12	$a/\sqrt{2} = 0.707a$
Zinc blende (cubic)	Zn–S	4	$a\frac{\sqrt{3}}{4} = 0.433a$
	Zn–Zn	12	$a/\sqrt{2} = 0.707a$
	S–S	12	$a/\sqrt{2} = 0.707a$
Fluorite (cubic)	Ca–F	4 or 8	$a\frac{\sqrt{3}}{4} = 0.433a$
	Ca–Ca	12	$a/\sqrt{2} = 0.707a$
	F–F	6	$a/2 = 0.5a$
Wurtzite* (hexagonal)	Zn–S	4	$\frac{a\sqrt{3}}{8} = 0.612a = \frac{3c}{8} = 0.375c$
	Zn–Zn	12	$a = 0.612c$
	S–S	12	$a = 0.612c$
Nickel arsenide* (hexagonal)	Ni–As	6	$a/\sqrt{2} = 0.707a = 0.433c$
	As–As	12	$a = 0.612c$
	Ni–Ni	2	$c/2 = 0.5c = 0.816a$
	Ni–Ni	6	$a = 0.612c$
Caesium chloride (cubic)	Cs–Cl	8	$\frac{a\sqrt{3}}{2} = 0.866a$
	Cs–Cs	6	a
	Cl–Cl	6	a
Cadmium iodide hexagonal)	Cd–I	6	$a/\sqrt{2} = 0.707a = 0.433c$
	I–I	12	$a = 0.612c$
	Cd–Cd	6	$a = 0.612c$

b) Diamond

- The diamond structure is obtained when the two elements in zinc blende, ZnS, are identical, as in C; i.e. a ccp array of carbon atoms with one set of tetrahedral sites (either T_+ or T_-) occupied also by carbon atoms.
- Most Group IV elements crystallize with the diamond structure, Table 1.9.

c) Wurtzite (ZnS) and nickel arsenide (NiAs)

These structures all have hcp anions and differ only in cation positions.
Wurtzite: T_+ (or T_-) occupied; O, T_- (or T_-) empty
Nickel arsenide: O occupied; T_+ and T_- empty
The structures are hcp analogues of the ccp sphalerite and rock salt , respectively. No hcp equivalent of fluorite and antifluorite.

Both wurtzite and nickel arsenide have hexagonal symmetry and unit cells (Fig. 1.30a with hcp anions). The unit cell contains two anions: one at the origin and one inside the cell: 0,0,0 and $\frac{1}{3},\frac{2}{3},\frac{1}{2}$. Fig. 1.30b shows a projection down *c* (the basal planes at c = 0 (open), at c =1 and at c = $\frac{1}{2}$ (shaded)), with ABABA … layer stacking. Atoms 1–4 outline the base of the unit cell. Fig. 1.30c shows the content of one unit cell (dashed circles are the top four corners at c =1).

Assuming the anions are in contact (not eutectic), the hexagonal unit cell has a definite shape given by c/a = 1.633. This is because a = the distance X–X and c = twice the vertical height of a tetrahedron comprising 4 anions.

Fig. 1.30d shows the interstitial sites, two for each of T_+, T_- and O.
Fig. 1.30e shows the coordinates of the sites:

T_-(A) along the c edge at height $\frac{3}{8}$ above the origin (anion 1). This site is coordinated to 3 shaded (5–7) at c = $\frac{1}{2}$ and anion (1) at c = 0 and located at the center of gravity of this tetrahedron, which is at c = $\frac{3}{4} \times \frac{1}{2} = \frac{3}{8}$ = 0.375 ($\frac{3}{4}$ resulting from that the center is closer to the 3-anion base). The letter *u* represents the fractional c values. Table 1.11 shows that in wurtzite *u* ranges 0.345–0.385.

The 3 anions (5–7) forms the base of a T_+ at $0,0,\frac{5}{8}$ with the apex at 0,0,1. Another T_+(C), $\frac{1}{3},\frac{2}{3},\frac{1}{8}$, is coordinated to the base anions (1, 2 and 4) and the apex anion (5).

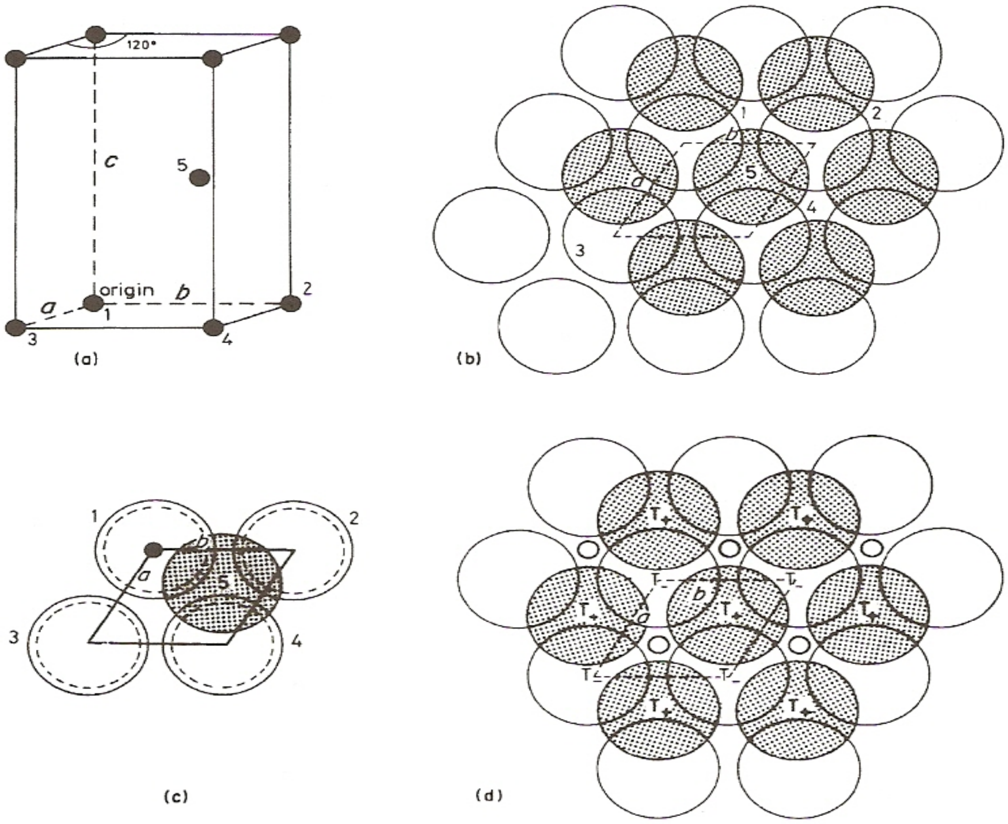
The octahedral site E is coordinated to anions 1, 3 and 4 at c = 0 and 5–8 at c = $\frac{1}{2}$. The center of gravity of the octahedron lies midway and the site has coordinates $\frac{2}{3},\frac{1}{3},\frac{1}{4}$. Another octahedral site lies above E at $\frac{2}{3},\frac{1}{3},\frac{3}{4}$.

Fig. 1.30f shows the cation environments in wurtzite. Zn is shown in T_+ sites and forms ZnS_4 tetrahedra, linked at their corners to form a 3D network (Fig. 1.30j). The tetrahedral environment of S(5) is also shown. The SZn_4 forms points down (S at T_- sites), in contrast to ZnS_4 tetrahedra which all point up.

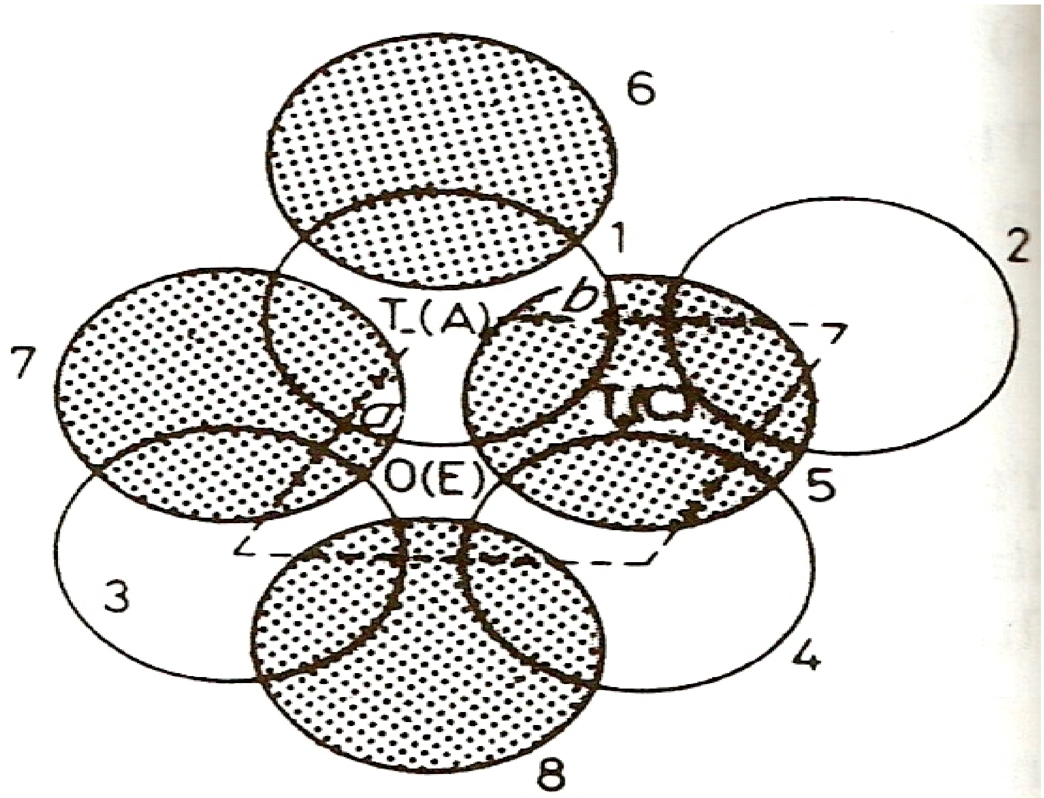
Comparison between zinc blende (Fig. 1.28b) and wurtzite (fig. 1.30j): They are similar and networks of tetrahedra. Zinc blende forms ABC stacking sequence with identical orientation of the tetrahedra. Wurtzite forms AB stacking with alternate layers rotated by 180° about c.

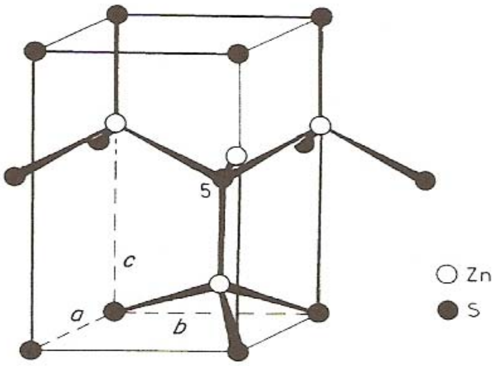
Fig. 1.30g shows the $NiAs_6$ octahedra in NiAs. One pair of opposite faces (As ions 5, 7 and 8) is shared to form chains of face sharing octahedral run parallel to c. In ac plane, the octahedra share edges (As ions 3 and 7) such that chains of edge-sharing octahedra form parallel to b. Similarly, chains of edge-sharing octahedra form parallel to a. See Fig. 1.30k.

The NiAs structure is unusual in that the anions and cations have the same coordination number but different coordination environment. The Ni coordination is octahedral, but As has 6 Ni neighbors arranged as in a trigonal prism and not octahedrally. Fig. 1.30h shows As at c = $\frac{1}{2}$ is coordinated to 3 Ni at c= $\frac{1}{4}$ and 3 at c= $\frac{3}{4}$. The two sets of Ni are superposed in projection down c and give trigonal prismatic coordination for As. The NiAs may also be regarded as built of $AsNi_6$ trigonal prisms, which link up by sharing edges to form a 3D array. In Fig. 1.30i each triangle represents a prism in projection down c. The prism edges parallel to c are shared by 3 prisms. Prism edges that lie in the ab plane are shared by two prisms (top and down). Fig. 1.30l shows the sharing details and the ABABA stacking.

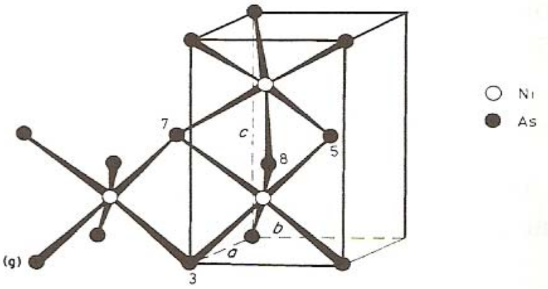


T_-	:	0 , 0 , 3/8	;	1/3 , 2/3 , 7/8
T_+	:	1/3 , 2/3 , 1/8	;	0 , 0 , 5/8
O	:	2/3 , 1/3 , 1/4	;	2/3 , 1/3 , 3/4
ANION	:	0 , 0 , 0		1/3 , 2/3 , 1/2





(f)



(e)

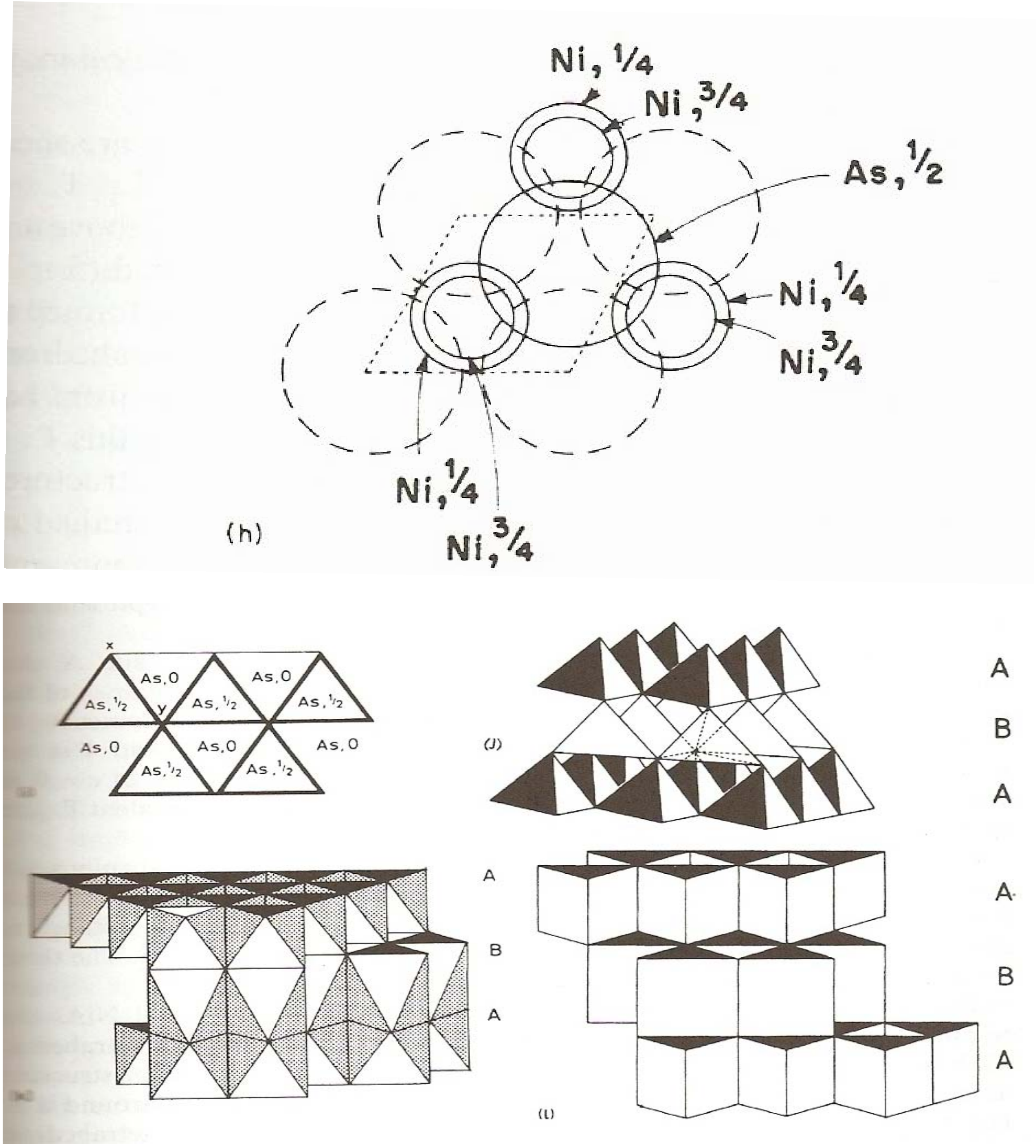


Fig. 1.30 The wurtzite and nickel arsenide structures: (a), (b), (c) the hexagonal unit cell of an *hcp* anion array; (d), (e) interstitial sites in an *hcp* array; (f), (g) structures of wurtzite and NiAs; (h), (i) trigonal prismatic coordination of arsenic in NiAs; (j), (k), (l) models of the ZnS and NiAs structures showing the arrangement and linkages of the polyhedra

Table 1.12 (wurtzite) and Table 1.13 (NiAs) gives values of hexagonal cell parameters *a* and *c*:

* The wurtzite structure is formed mainly by chalcogenides of divalent metals and is fairly ionic, with the ratio c/a approximately constant.

* The NiAs structure is more metallic and is adopted by a variety of intermetallic compounds and some transition metal chalcogenides (S, Se, Te). The c/a ratio varies in compounds with the NiAs structure. This is associated with the presence of metallic bonding which arises from metal-metal interactions in the c direction. For example, FeTe has c/a = 1.49 and Fe–Fe distance parallel to c is reduced to 0.745a (i.e. c/2 $=\frac{1}{2}$(1.49a); standard c/a = 1.633 with c/2 = 0.816a). Thereby, the Fe atoms are brought into contact and this increases the metallic bonding in the c direction.

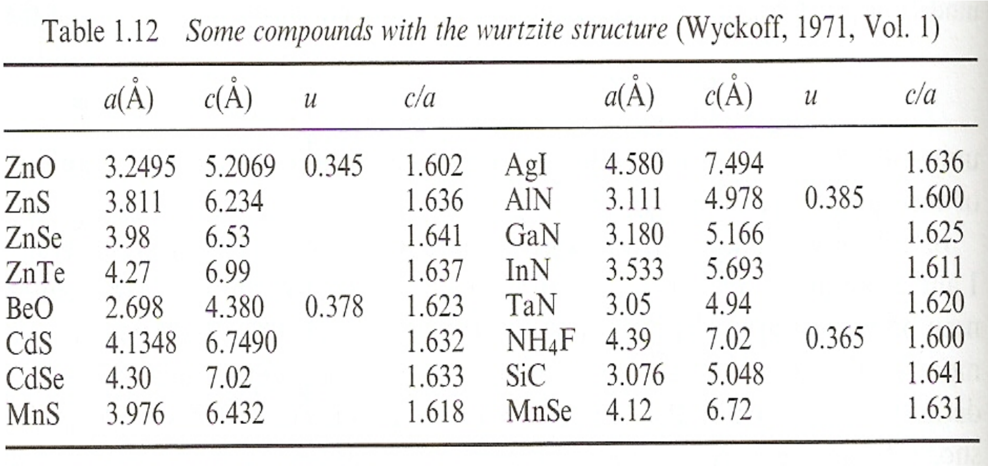


Table 1.12 *Some compounds with the wurtzite structure* (Wyckoff, 1971, Vol. 1)

	a(Å)	*c*(Å)	*u*	*c*/*a*		*a*(Å)	*c*(Å)	*u*	*c*/*a*
ZnO	3.2495	5.2069	0.345	1.602	AgI	4.580	7.494		1.636
ZnS	3.811	6.234		1.636	AlN	3.111	4.978	0.385	1.600
ZnSe	3.98	6.53		1.641	GaN	3.180	5.166		1.625
ZnTe	4.27	6.99		1.637	InN	3.533	5.693		1.611
BeO	2.698	4.380	0.378	1.623	TaN	3.05	4.94		1.620
CdS	4.1348	6.7490		1.632	NH_4F	4.39	7.02	0.365	1.600
CdSe	4.30	7.02		1.633	SiC	3.076	5.048		1.641
MnS	3.976	6.432		1.618	MnSe	4.12	6.72		1.631

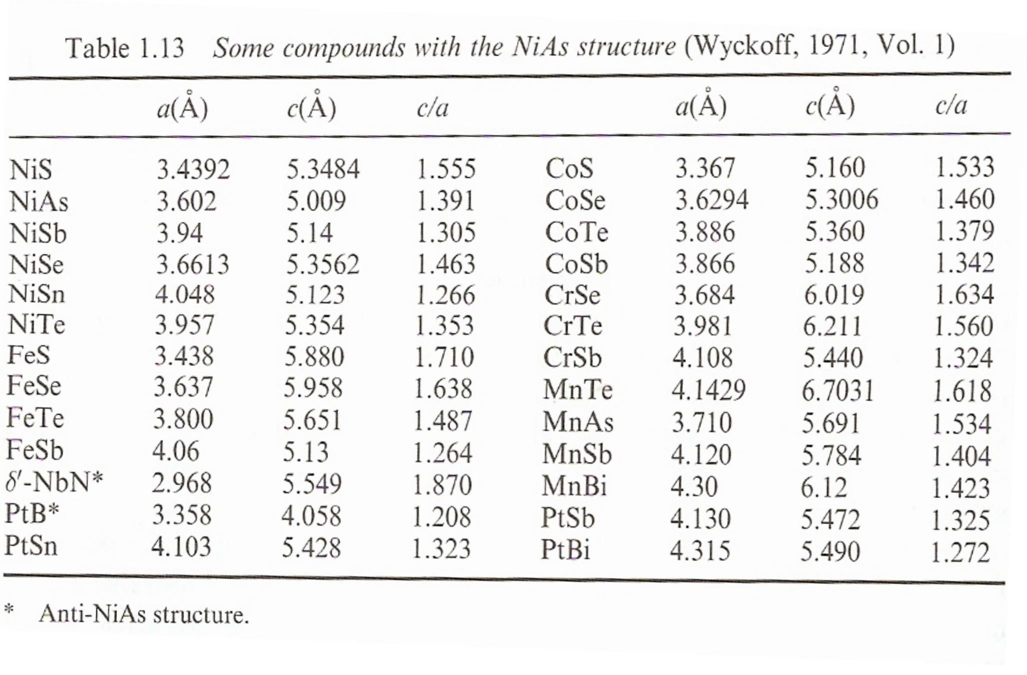


Table 1.13 *Some compounds with the NiAs structure* (Wyckoff, 1971, Vol. 1)

	a(Å)	*c*(Å)	*c*/*a*		*a*(Å)	*c*(Å)	*c*/*a*
NiS	3.4392	5.3484	1.555	CoS	3.367	5.160	1.533
NiAs	3.602	5.009	1.391	CoSe	3.6294	5.3006	1.460
NiSb	3.94	5.14	1.305	CoTe	3.886	5.360	1.379
NiSe	3.6613	5.3562	1.463	CoSb	3.866	5.188	1.342
NiSn	4.048	5.123	1.266	CrSe	3.684	6.019	1.634
NiTe	3.957	5.354	1.353	CrTe	3.981	6.211	1.560
FeS	3.438	5.880	1.710	CrSb	4.108	5.440	1.324
FeSe	3.637	5.958	1.638	MnTe	4.1429	6.7031	1.618
FeTe	3.800	5.651	1.487	MnAs	3.710	5.691	1.534
FeSb	4.06	5.13	1.264	MnSb	4.120	5.784	1.404
δ′-NbN*	2.968	5.549	1.870	MnBi	4.30	6.12	1.423
PtB*	3.358	4.058	1.208	PtSb	4.130	5.472	1.325
PtSn	4.103	5.428	1.323	PtBi	4.315	5.490	1.272

* Anti-NiAs structure.

d) Caesium chloride (CsCl)

Fig. 1.31 shows the unit cell of CsCl, which is a primitive cube of Cl containing Cs at the body center, or vice versa. The coordination numbers of both Cs and Cl are 8 with interatomic distance of 0.866a (Table 1.11). This structure is not cp since each Cl has only six Cl neighbors (12 for cp).

Table 1.14 show compounds with the CsCl structure: 1. Halides of large monovalent elements; 2. Intermetallic compounds.

3D structure of CsCl is similar to the fluorite in Fig. 1.29b, but all body centers are filled for CsCl.

e) Other AX structures

Five main AX structure types: rock salt, sphalerite, NiAs, wurtzite, CsCl. Each of them is found in a large number of compounds.

Several less common AX structures (distorted variants of the main structure types):
a. FeO at low temperatures (< 90 K), a rock salt structure with a slight rhombohedral distortion ($\alpha = 90.07^\circ$ by a compression along one threefold axis). This rhombohedral distortion is associated with magnetic ordering in FeO.
b. TlF has a rock salt structure in which the fcc cell is distorted into a face centered orthorhombic cell by changing the lengths of the axes.
c. NH_4CN has a distorted CsCl structure in which the CN^- ions are oriented parallel to face diagonals, leading to an increase in *a*/*c*.

Other AX compounds of completely different structures (Chapter 2):
a. compounds of d^8 ions (Pd^{2+}, Pt^{2+}, Ni^{2+}, …): PdO, PtS, …
b. compounds of heavy *p*-block atoms in their lower oxidation states (Sn^{2+}, Pb^{2+}, Bi^{3+}): SnO, PbO, InBi.

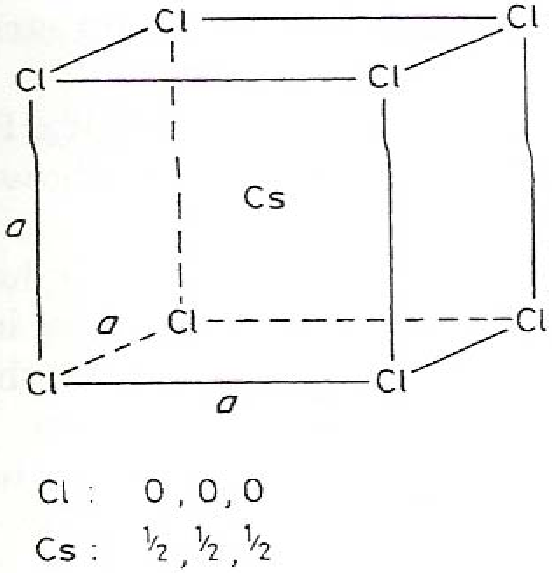


Fig. 1.31 The primitive cubic unit cell of CsCl

Table 1.14 *Some compounds with the CsCl structure*

	a(Å)		a(Å)
CsCl	4.123	CuZn	2.945
CsBr	4.286	CuPd	2.988
CsI	4.5667	AuMg	3.259
CsCN	4.25	AuZn	3.19
NH_4Cl	3.8756	AgZn	3.156
NH_4Br	4.0594	LiAg	3.168
TlCl	3.8340	AlNi	2.881
TlBr	3.97	LiHg	3.287
TlI	4.198	MgSr	3.900