Derivative and modular structures

Th_3P_4 , 2D perovskites, Half Heuslers

STRUCTURES DERIVING FROM THE ZnS-Type

ADAMANTINE STRUCTURES

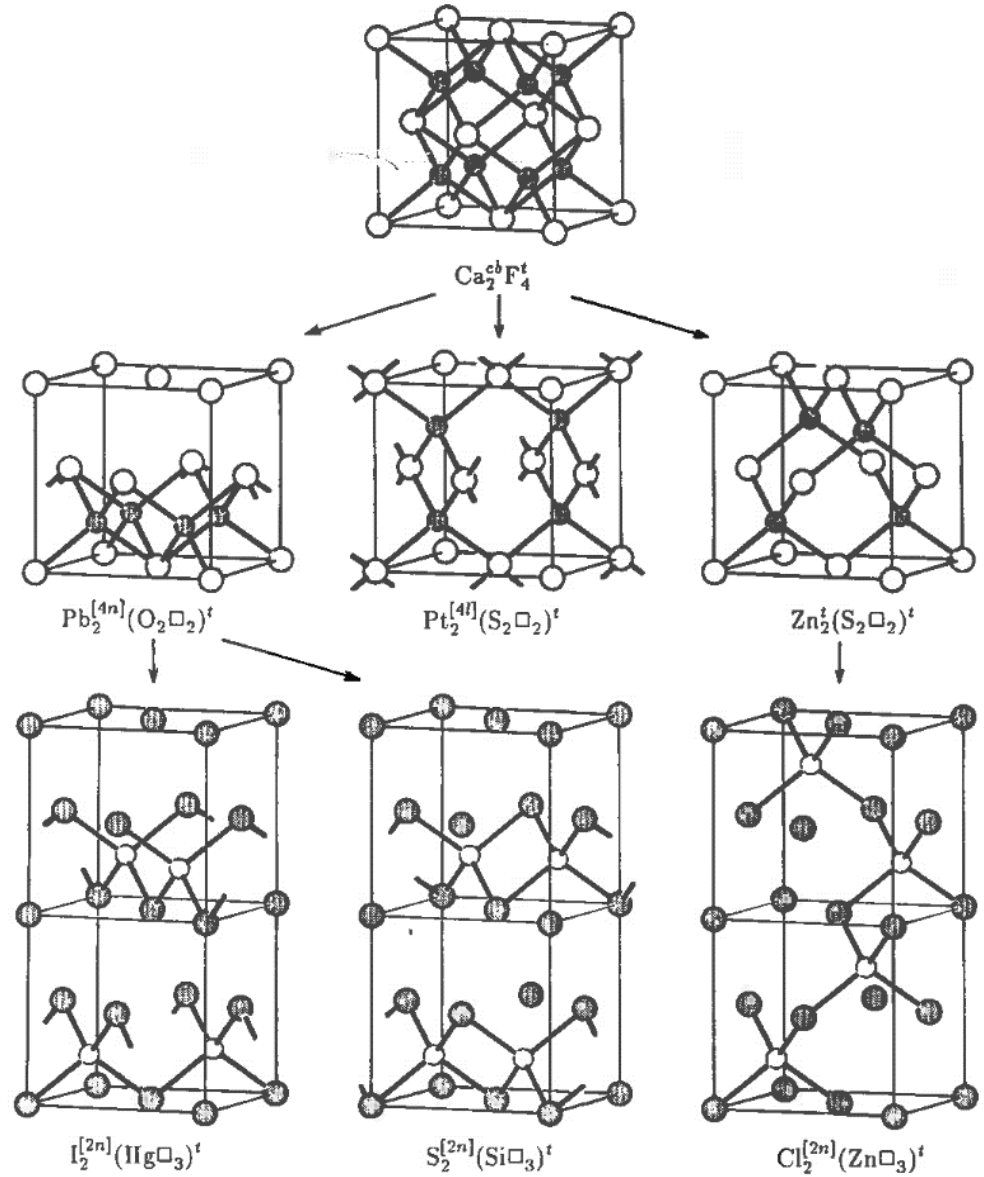
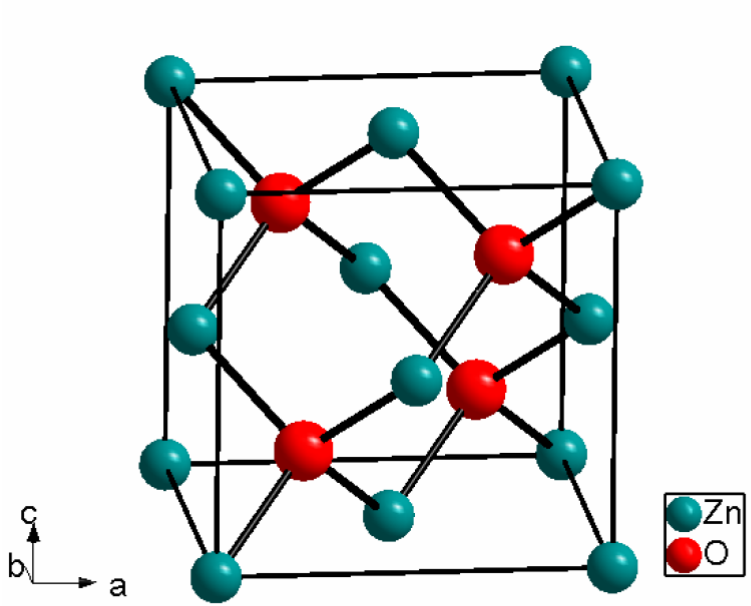
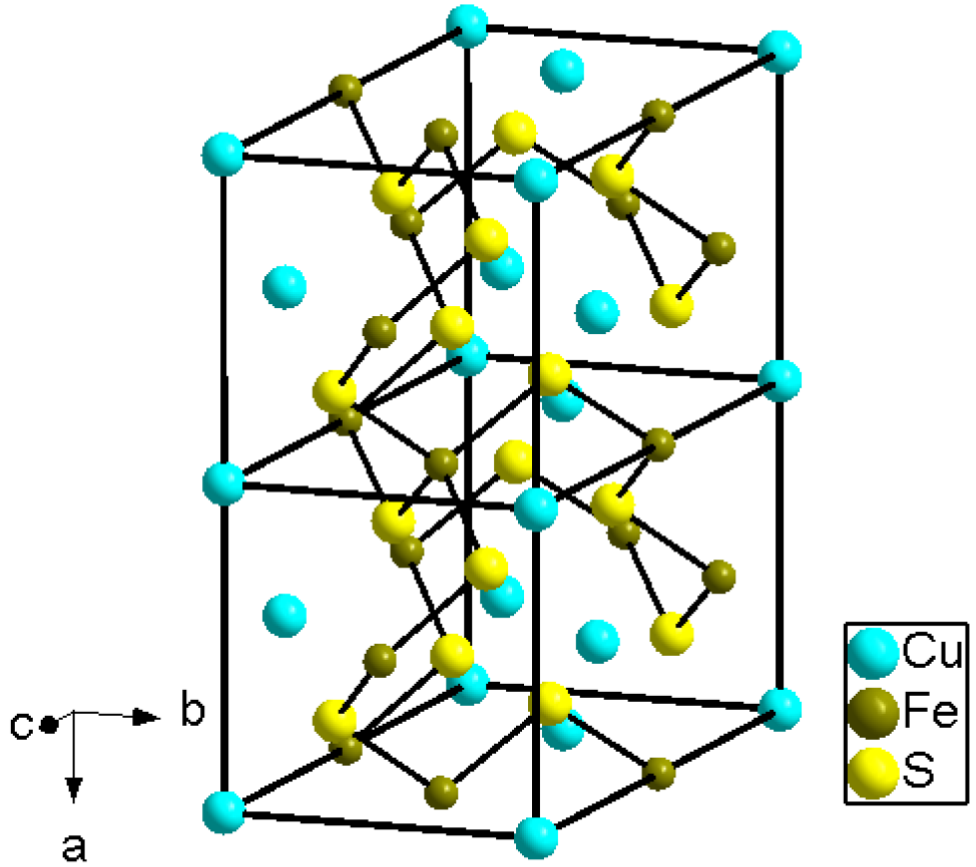


Fig. 128

Relationships among the structures of CaF_2, PbO, PtS, ZnS, HgI_2, SiS_2, and α-$ZnCl_2$. In the top row all tetrahedral interstices (= centers of the octants of the cube) are occupied. Every arrow designates a step in which the number of occupied tetrahedral interstices is halved; this includes a doubling of the unit cells in the bottom row. Light hatching = metal atoms, dark hatching = non-metal atoms. The atoms given first in the formulas form the cubic closest-packing

ADAMANTINE STRUCTURE





$CuFeS_2$

$ZnSiAs_2$

$CuInS_2$

$CuInSe_2$

Chalcopyrite

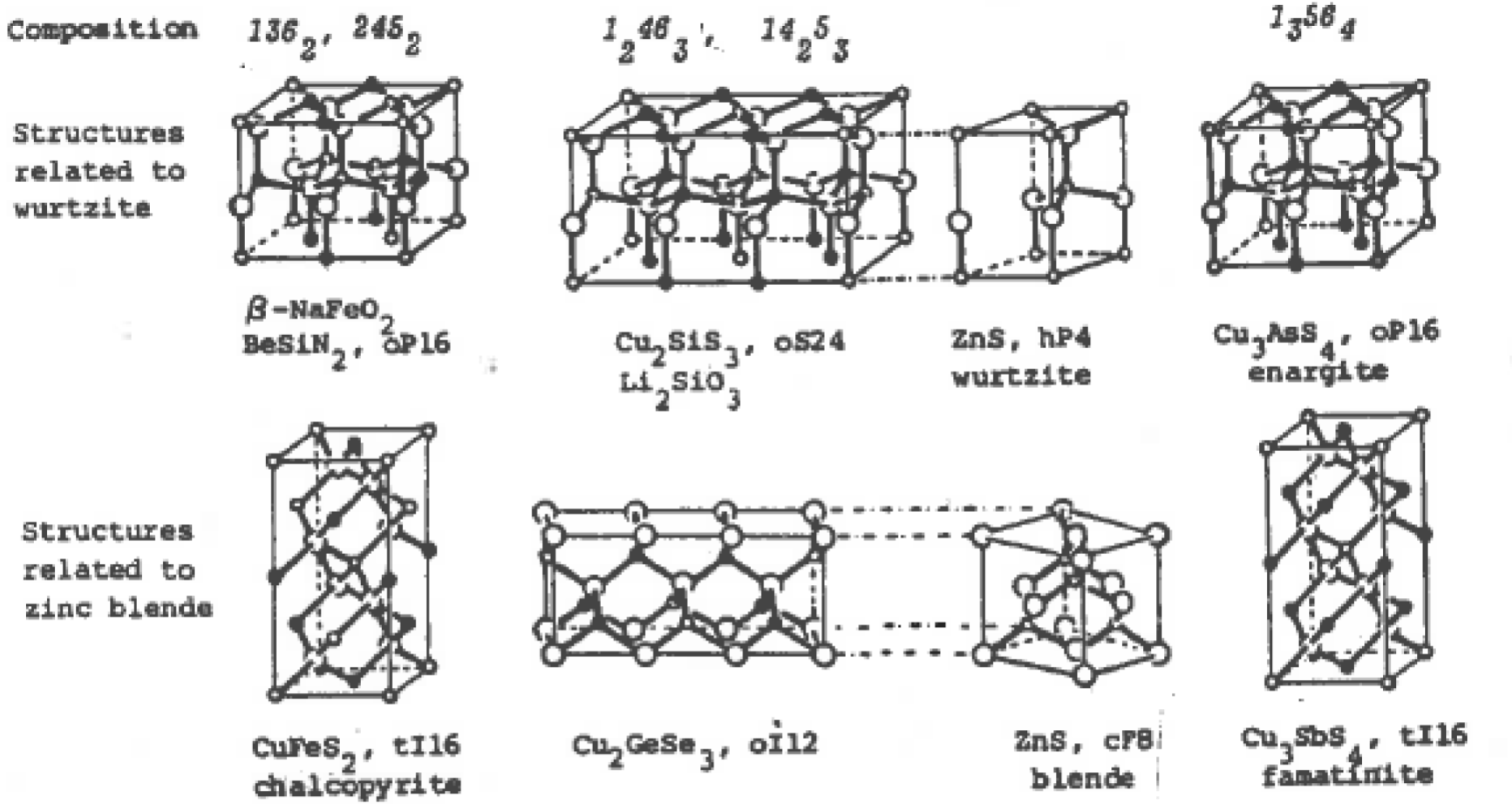
II VI V_2

I III VI_2

Zn Zn S_2

Cu In S_2

Structure derived by substitution

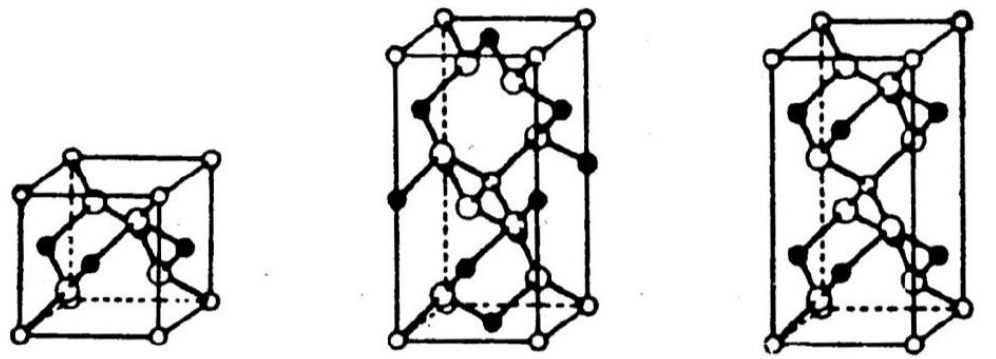


: Examples for ternary ordered normal adamantine structure types which can be related to the wurtzite or the zinc blende structure. Cations are presented by small circles.

Substitution must obey the octet rule!

Structure derived from defects

Examples of ternary ordered defect adamantine structure types with composition $C_2C'\square A_4$ which derive from the zinc blende structure are shown in Fig. 4. A comparison with Fig. 1 makes it evident where the unoccupied Zn sites are.



$Cd^{[4]}In_2^{[4]}Se_4$
tP7

$Cd^{[4]}Ga_2^{[4]}S_4$
$\beta Ag_2^{[4]}Hg^{[4]}I_4$
tI14

$\beta Cu_2^{[4]}Hg^{[4]}I_4$
tI14

Fig. ● : Three ternary ordered defect adamantine structure types of composition $C_2C'\square A_4$ which are substitution derivatives of the zinc blende structure. Cations are presented by small circles of which 1/3 are empty and 2/3 filled. $CdGa_2S_4$ and $CdGa_2Se_4$ have recently been refined [3,4].

Two more complicated binary ordered defect adamantine structures with general composition $C_2\square A_3$ have been found with α-Ga_2S_3 and β-Ga_2Se_3

$(Cu_{11.5}Zn_{23}Ga_{7.5}Ge_8)(As_{16}Se_{30}Br_4)$ was for three months in the furnace to assure a complete reaction. According to its Debye - Scherrer diagram, as shown in Fig. 8 practically identical with that of elemental germanium, in the heptenary normal adamantine structure compound the Cu, Zn, Ga and Ge atoms occupy the Zn sites and the As, Se and Br atoms the S sites of zinc blende in random fashion.

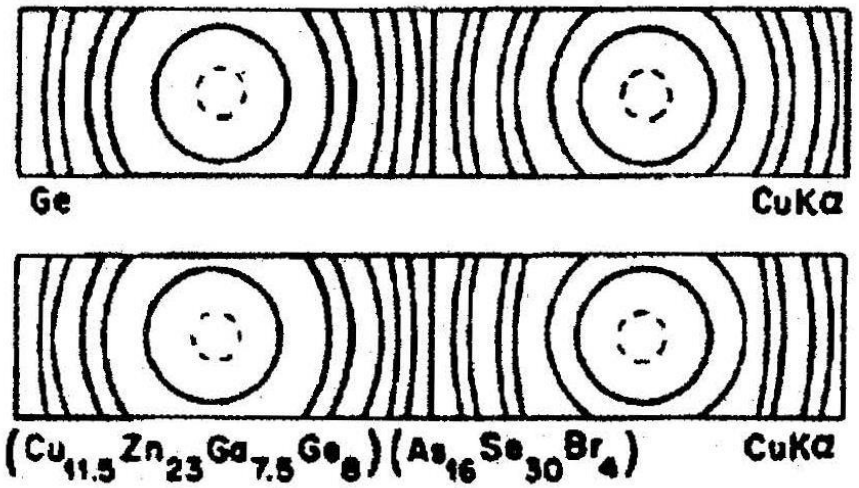
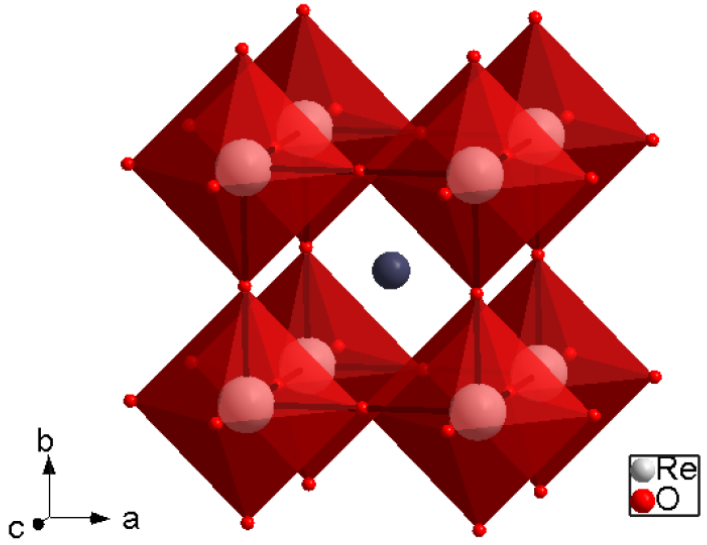


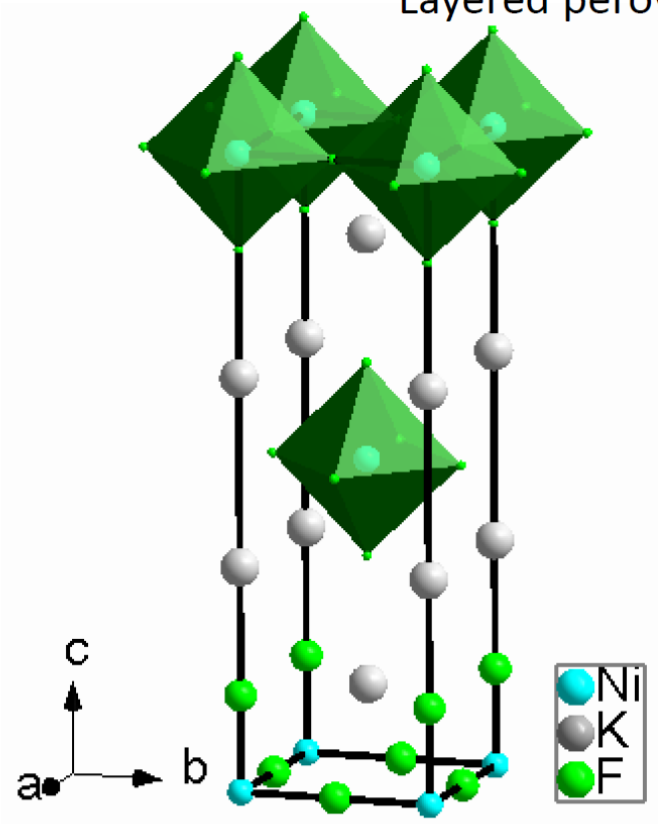
Fig. 8 : Debye - Scherrer diagram of Ge compared with that of $(Cu_{11.5}Zn_{23}Ga_{7.5}Ge_8)(As_{16}Se_{30}Br_4)$, a heptenary normal adamantine structure compound crystallizing with the zinc blende structure type.

Perovskite ABO_3

(a) The perovskite structure. Without the large A atom at the body center position, the structure becomes that of cubic ReO_3; (b) The K_2NiF_4 structure consisting of rocksalt (KF) and perovskite ($KNiF_3$) layers. The NiF_6 octahedral share equatorial corners restricting the Ni-F-Ni interaction to the xy-plane.



Layered perovskite



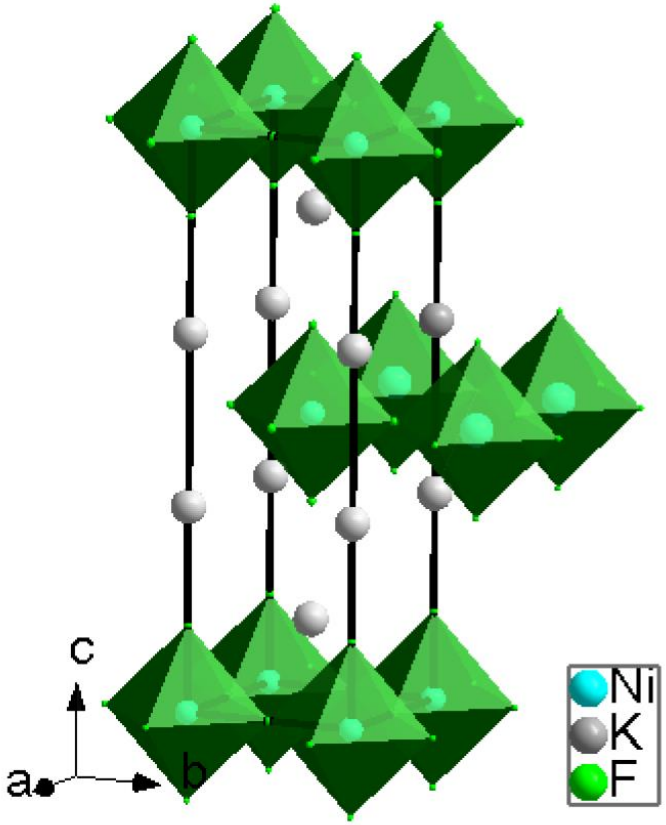
K_2NiF_4- type

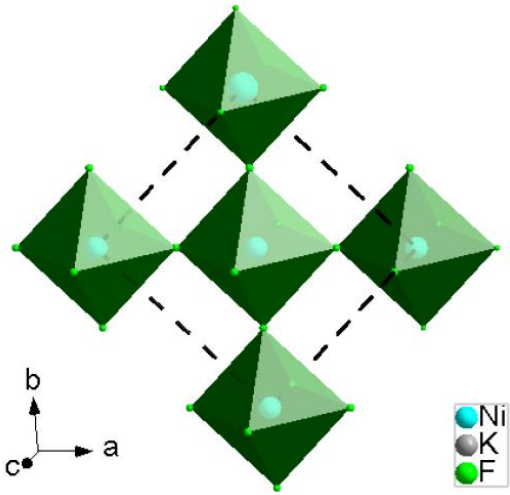
$La_{0.8}Ba_{0.2}CuO_4$

High T_c superconductor

$T_c \approx 40K$

K_2NiF_4-type





$A\,B\,O_3$

$A_3\,B_3\,O_9$

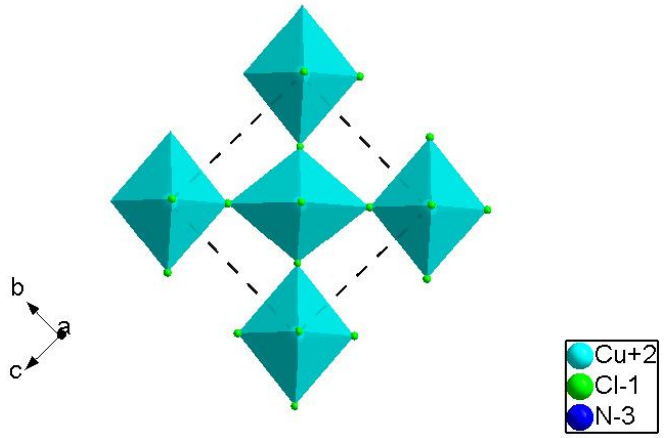
$Ba_2Y\,Cu_3O_9$

$Ba_2Y\,Cu_3\,O_{9-x}$ → $Ba_2YCu_3O_7$

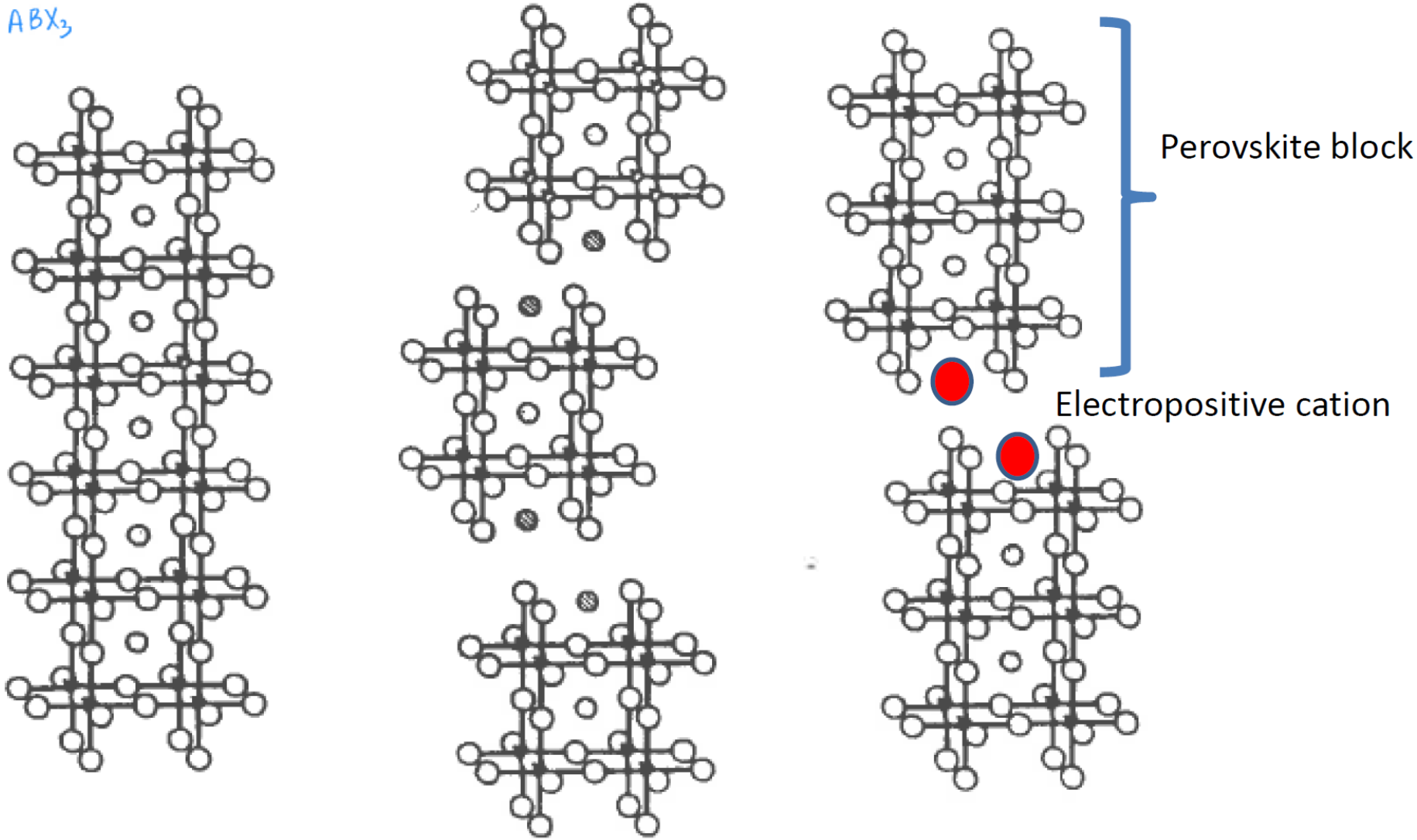
High Tc Superconductor
$T_c \simeq 92°K$

There are several derivatives of perovskite structure, e.g., K_2NiF_4. where the adjacent (100) planes of the perovskite are combined into a layer. In this structure, two neighboring K-F layers are situated in the same manner as in KF (NaCl structure). Other examples of this structure are Rb_2CoF_4, Na_2CuF_4, La_2CoO_4, Ca_2MnO_4 and Rb_2MnCl_4. SnF_4 and PbF_4 as well as $KAlF_4$ and $RbAlF_4$ also possess structures derived from perovskites.

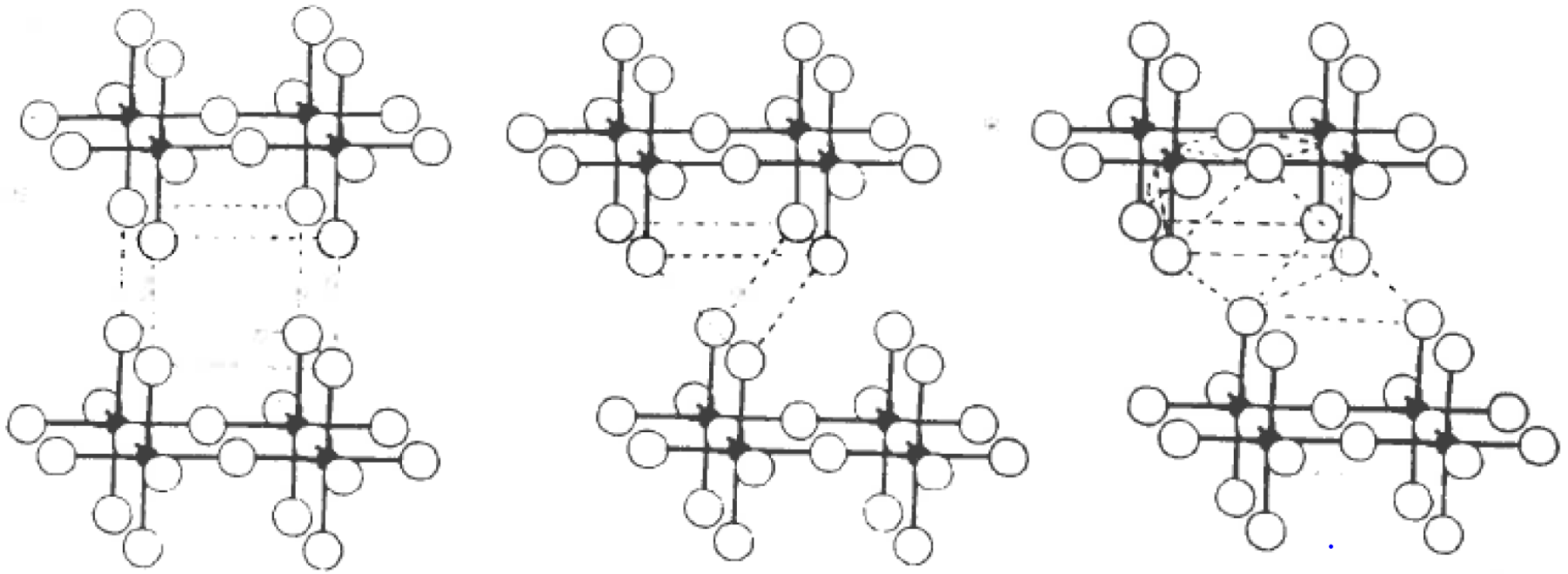
If the perovskite layers have a thickness of n unit cells (instead of one), compounds of the general formula $A_{n+1}\,B_n\,X_{3n+1}$ are formed, as in $Sr_3Ti_2O_7$ and $K_3Mn_2Cl_7$.



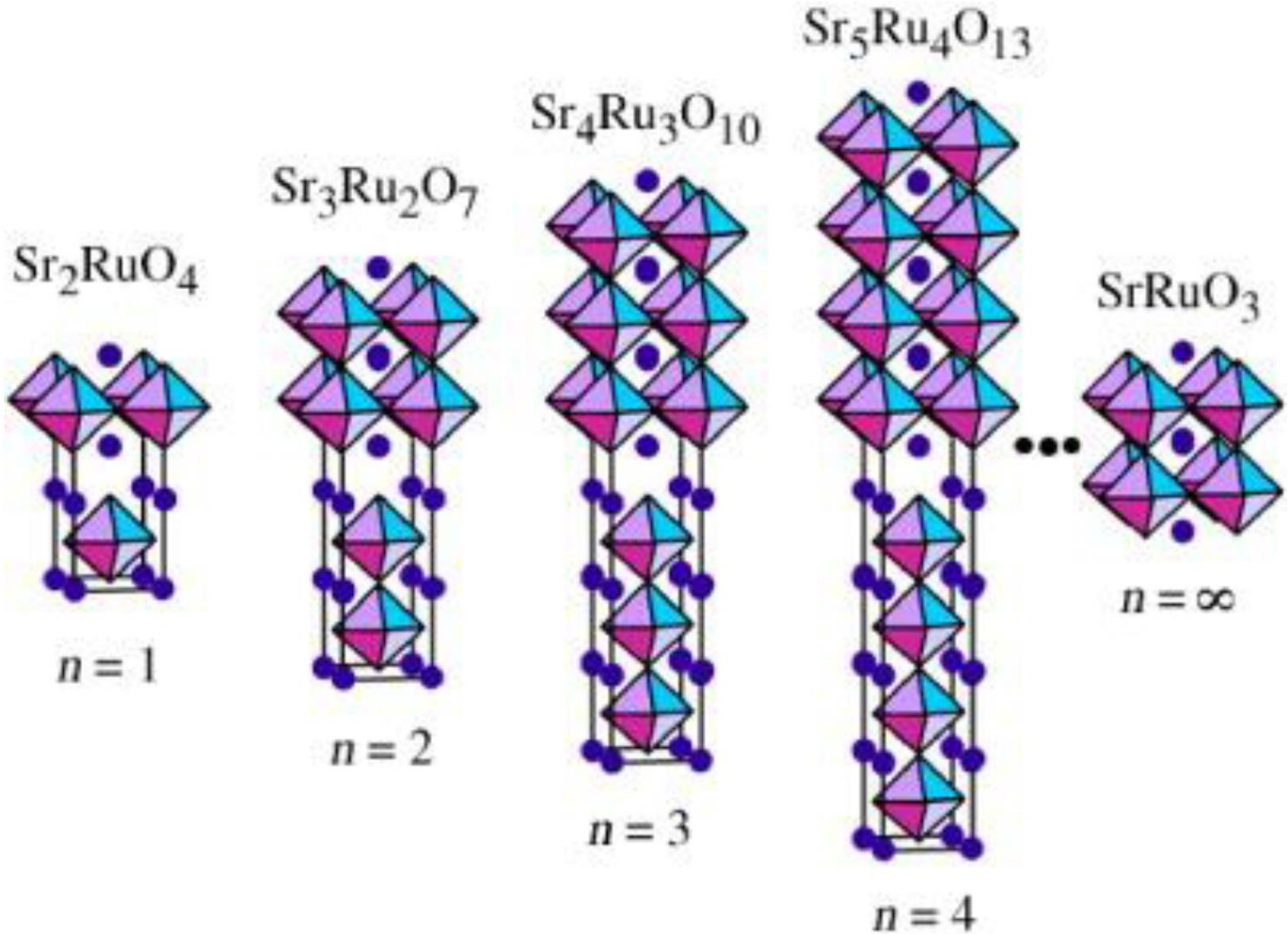
Ruddlesden-Popper (RP) phases are a form of layered perovskite structure consist of two-dimensional perovskite slabs interleaved with cations.



Ruddlesden Popper phases

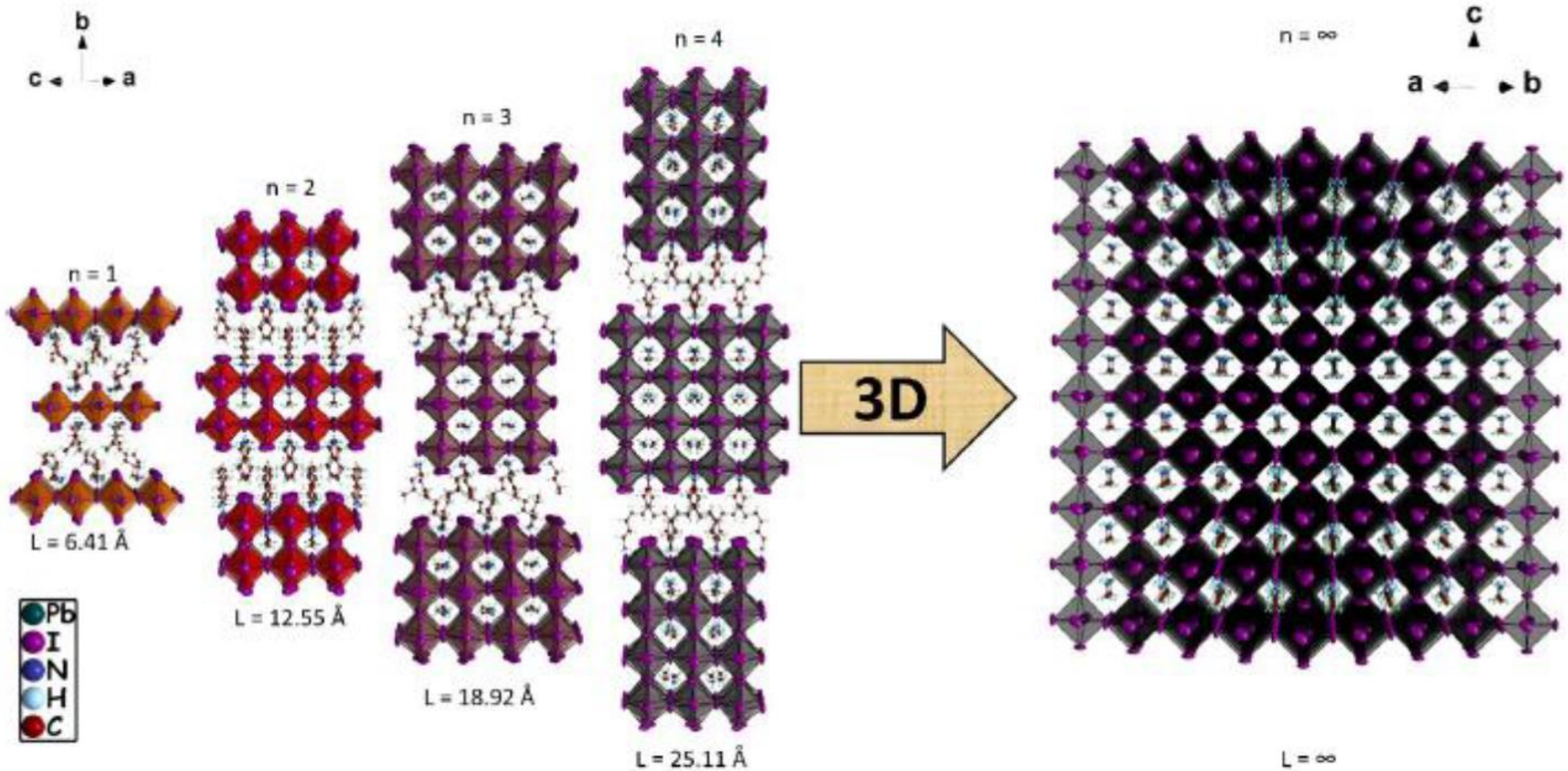


Ruddlesden Popper phases

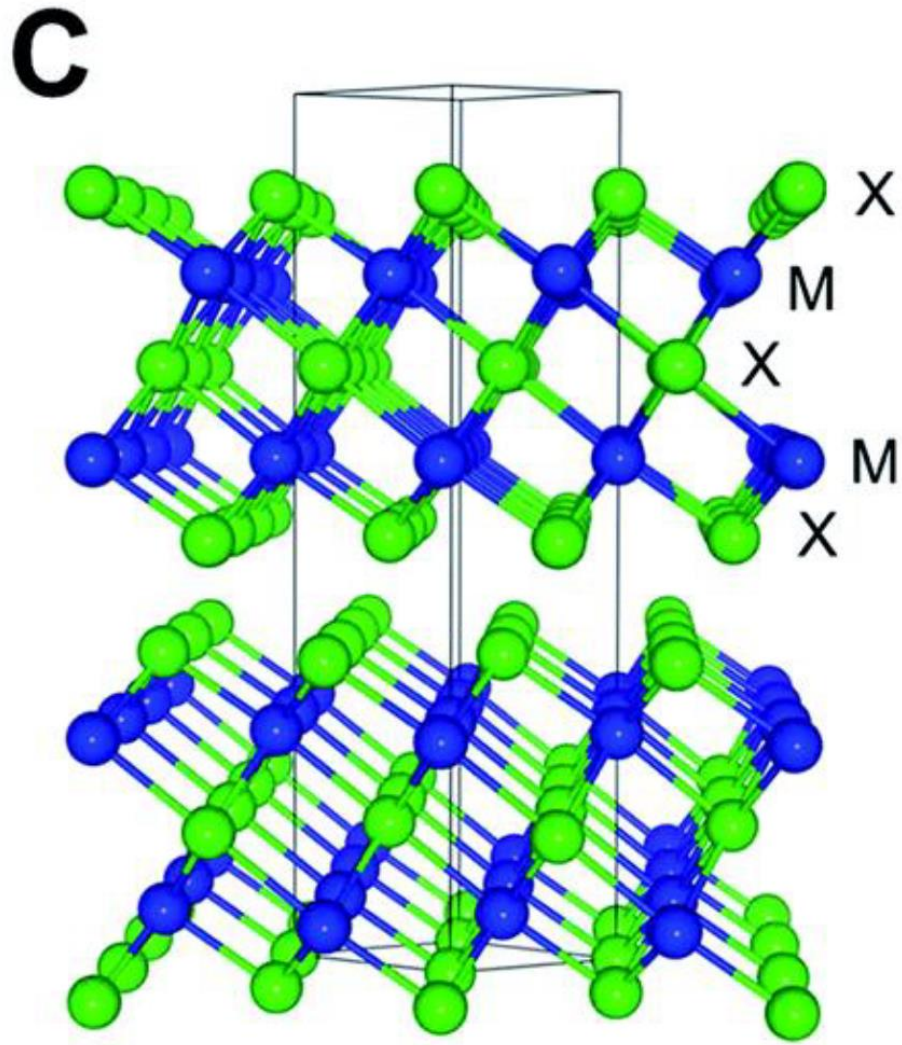


Organic-inorganic Ruddlesden Popper phases

$(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (n = 1, 2, 3, 4)



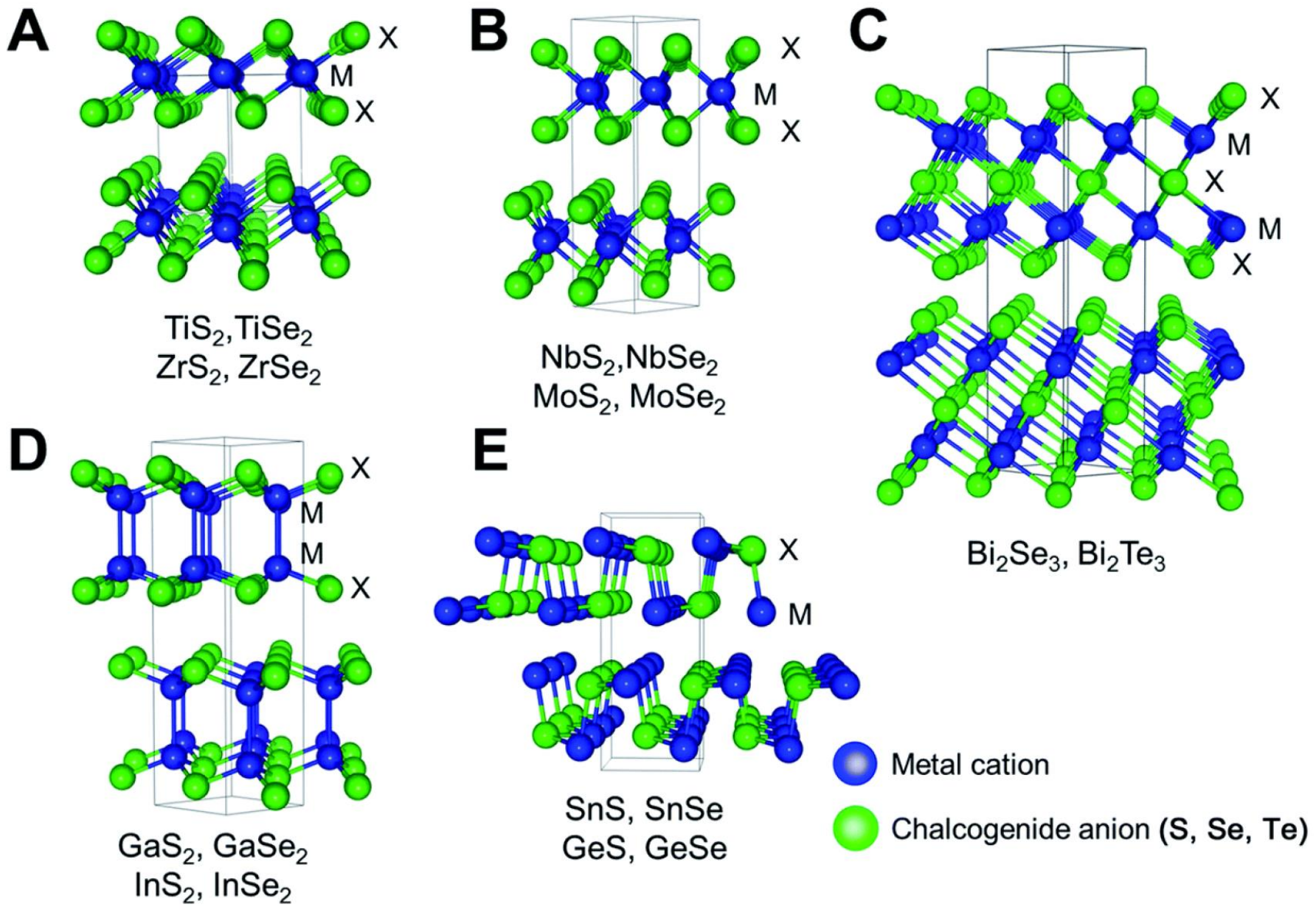
Bi_2Te_3 structure



Bi_2Se_3, Bi_2Te_3

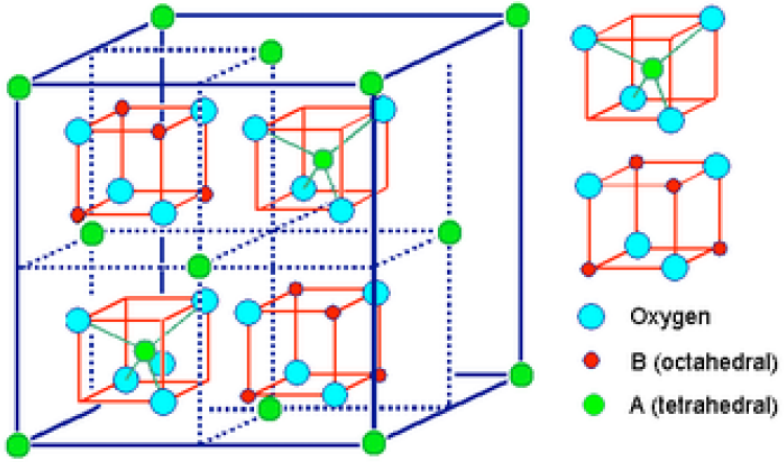
Sb_2Te_3

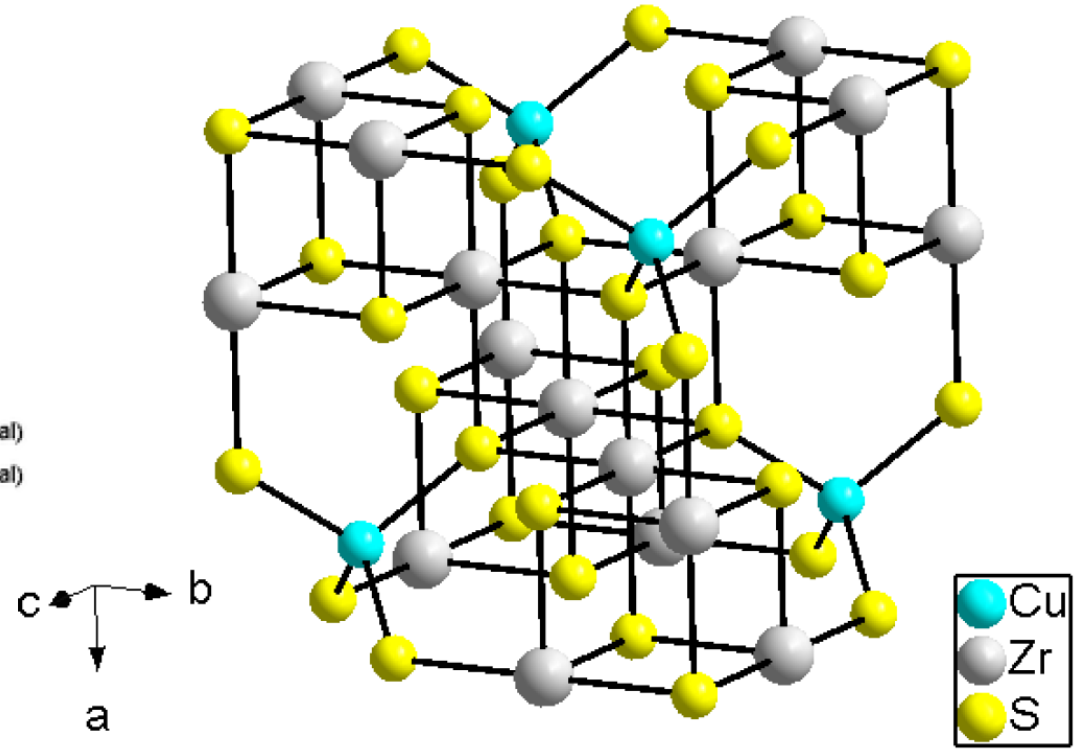
Important 2D materials



AB_2O_4 Structure (SPINEL)
$MgAl_2O_4$-Type

$A^{VI}B_2{}^{I}X_4$	$A^{I}B_2{}^{IV}X_4$	$A^{IV}B_2{}^{II}O_4$	$A^{II}B_2{}^{III}X_4$
K_2WO_4	$CuTi_2S_4$	Ni_2GeO_4	$MgFe_2O_4$



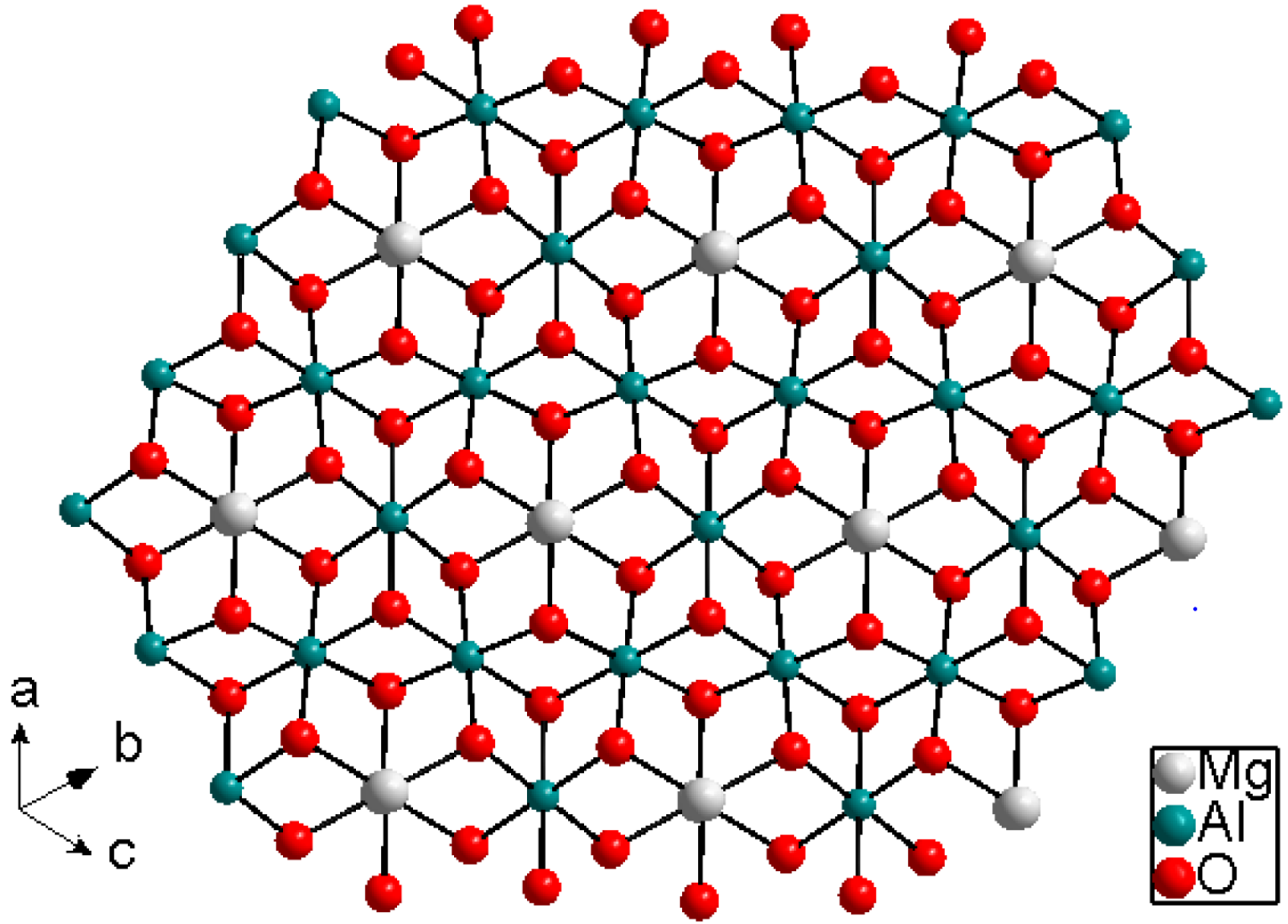


$MgZn_2Cl_4$

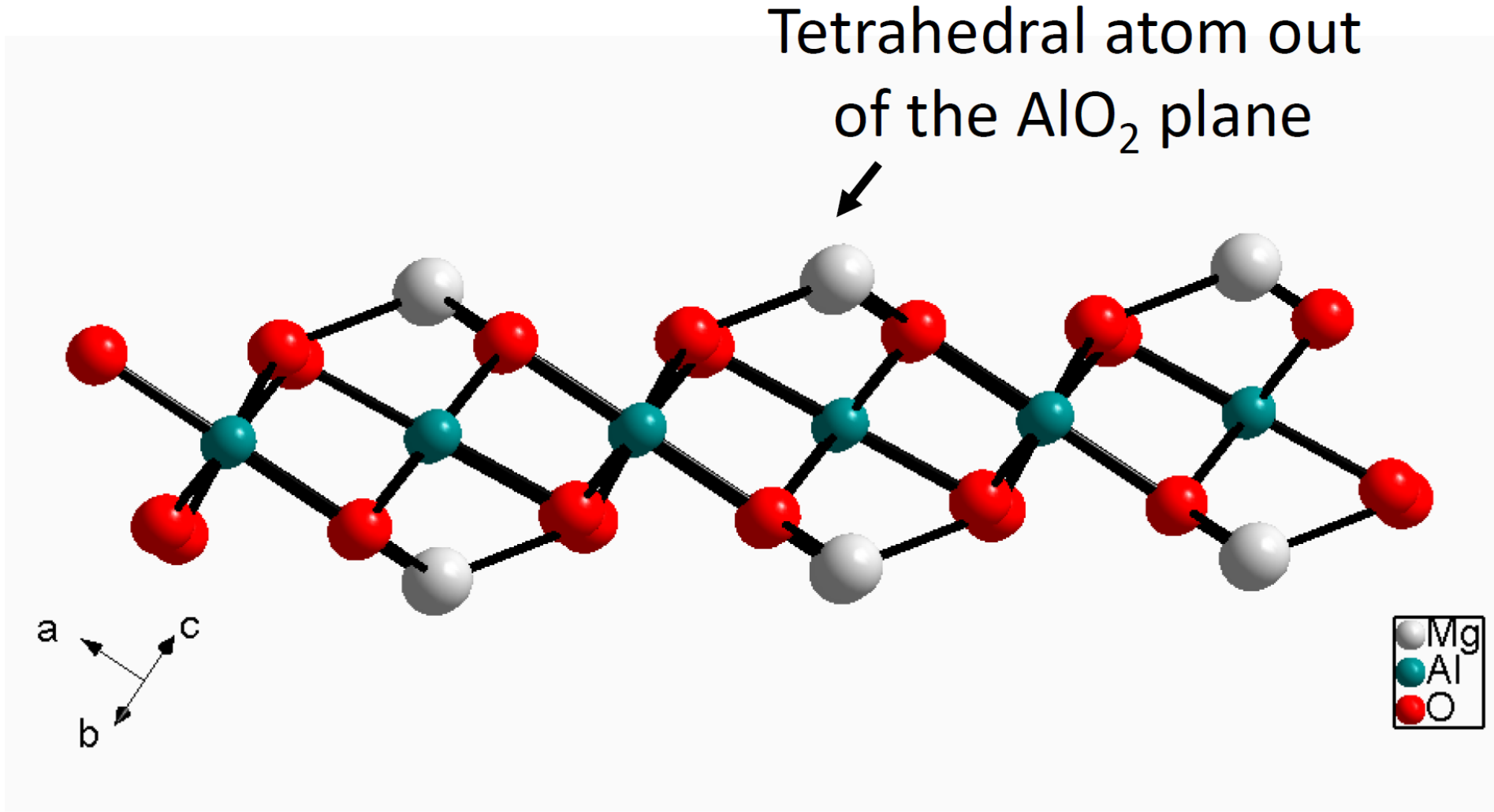
Li_2NiF_4 or $NiLi_2F_4$ "Inverse" spinel

$CuZr_2S_4$

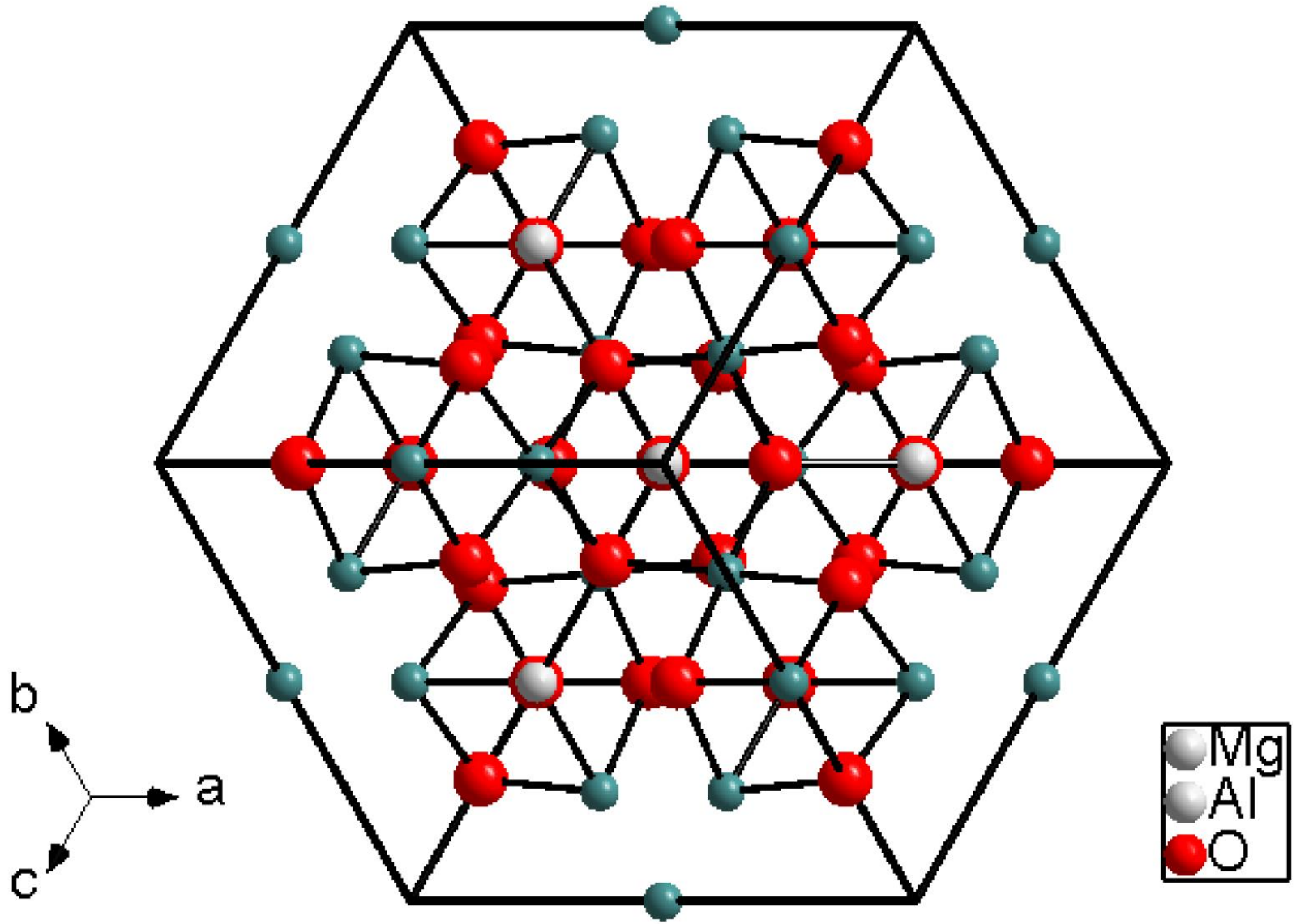
$MgAl_2O_4$-Spinel sheet



$MgAl_2O_4$-Spinel sheet



$MgAl_2O_4$-Spinel viewed down [111] direction of cube



Examples of spinel compounds

	STRUCTURE TYPE	SPACE GROUP	SPACE GROUP NUMBER
cF56	Al_2MgO_4	$Fd\bar{3}m$	227

REFERENCE

1968 13 P703 KRISTALLOGRAFIYA, N.G. Zorina et al.

Remarks: Origin at centre -3m, at 0.125, 0.125, 0.125 from -43m; also called Co_3O_4 type; mineral name spinel

a = 0.8075 b = c = [nm]

ALPHA = BETA = GAMMA = [DEGREE]

ORIGIN AT $\bar{3}m$

ATOMIC POSITIONS :

ATOMS	WYCKOFF NOTATION	SYMMETRY	x	y	z	OCCUPANCY
Al	16 (d)	$\bar{3}m$	0.5	0.5	0.5	1.00
Mg	8 (a)	$\bar{4}3m$	0.125	0.125	0.125	1.00
O	32 (e)	3m	0.251	0.251	0.251	1.00

$AgAlCr_4S_8$
$AgAl_5S_8$
$AgCr_4InSe_8$
$AgCrSe_4Sn$
$AgIn_5S_8$
$Ag_2MnS_8Sn_3$
Al_2CdS_4
$Al_2Cr_3CuS_8$
$Al_2Cr_3S_8Zn$
Al_4CuInS_8
$AlCuS_4Sn$
Al_2HgSe_4
$Al_3Mo_8S_{16}$
Al_2S_4Zn
As-Cr-Cu-Se
Cd-Co-Cr-S
Cd-Cr-In-S
$CdCr_2S_4$
$CdCr_2Se_4$
Cd-Cr-Se-Zn
$Cd_4EuS_{20}Yb_{10}$
$CdHo_2Se_4$
$CdLu_2S_4$
CdS_4Tm_2
$CdSe_4Sc_2$

$AgAl_4In_2S_8$
$Ag_2Cr_4GaS_8$
Ag-Cr-S-Se
$Ag_2FeS_8Sn_3$
Ag-In-S-Sn
$Ag_2NiS_8Sn_3$
Al-Cd-S-Zn
Al-Cr-Hg-Se
$AlCr_4CuS_8$
$Al_4CuInSe_8$
Al_5CuSe_8
Al_2MgO_4
Al_2O_3
Al_2Se_3
$AsIn_3S_3$
Cd-Cr-Cu-Se
Cd-Cr-In-Se
Cd-Cr-S-Se
$Cd_5Cr_9Se_{20}Sn$
$CdEr_2S_4$
Cd-Fe-S-Sn
$CdIn_2S_4$
$CdLu_2Se_4$
CdS_4Y_2
$CdSe_4Y_2$

$AgAl_4InSe_8$
$AgCr_4InS_8$
$AgCrS_4Sn$
Ag_2MgO_4
Ag_2InS_4Zr
Ag-S-Y-Zr
Al_2CdSe_4
Al_2CrS_4
$AlCr_4CuSe_8$
Al_5CuS_8
Al_2HgS_4
Al_2MnS_4
Al_2S_3
Al_2Se_4Zn
$CaIn_2S_4$
Cd-Cr-Fe-S
Cd-Cr-Mn-S
Cd-Cr-S-Zn
Cd-Cr-Se-Te
$CdEr_2Se_4$
$CdHo_2S_4$
$CdIn_2Se_4$
CdS_4Sc_2
CdS_4Yb_2
$CdSe_4Yb_2$

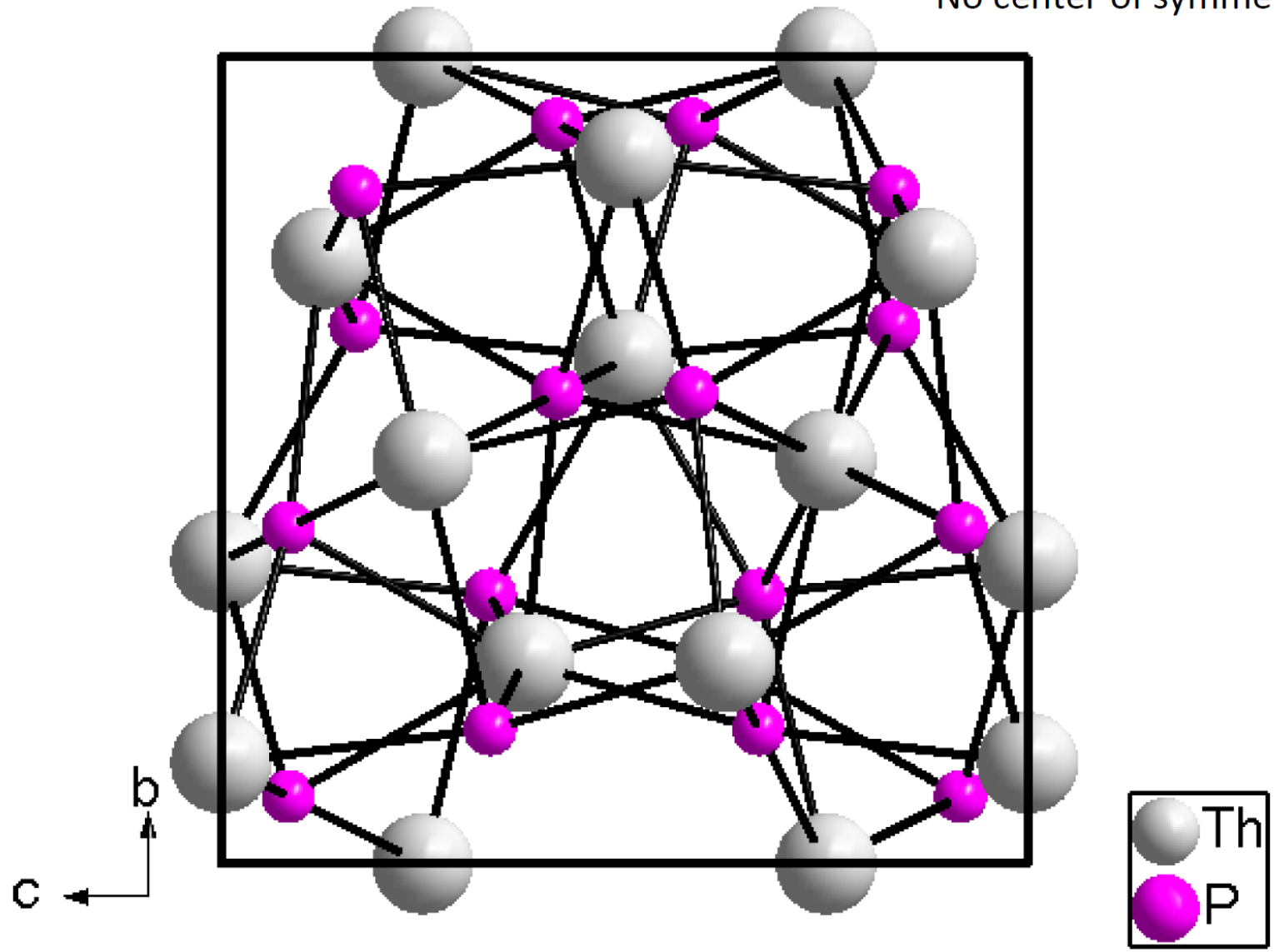
$CoCr_2S_4$
Co_2CuS_4
$CoIn_2S_4$
Co_2RhS_4
Cr-Cu-Fe-S
$Cr_4CuGaSe_8$
Cr-Cu-Hg-Se
Cr-Cu-Mn-S
Cr_2CuS_4
$CrCuS_4Ti$
$CrCuS_4Zr$
Cr-Cu-Se-Te
$CrCuSe_4Zr$
Cr-Fe-In-S
$CrFe_2S_4$
Cr-Fe-S-Zn
Cr-Hf-In-Se
Cr-Hg-S-Zn
$CrIn_2S_4$
Cr-Mn-S-Zn

Co-Cr-S-Se
$Co_3CuS_8Sn_2$
Co_2NiS_4
Co_3S_4
Cr-Cu-Fe-Se
$CrCuHfS_4$
Cr_4CuInS_8
Cr-Cu-Ni-S
Cr-Cu-S-Se
Cr-Cu-S-V
Cr_2CuSe_4
$CrCuSe_4Ti$
Cr_2CuTe_4
Cr-Fe-Ni-S
Cr_2FeS_4
Cr_4GaLiS_8
Cr_2HgS_4
Cr_2HgSe_4
Cr-In-S-Zn
Cr-S-Se-Zn

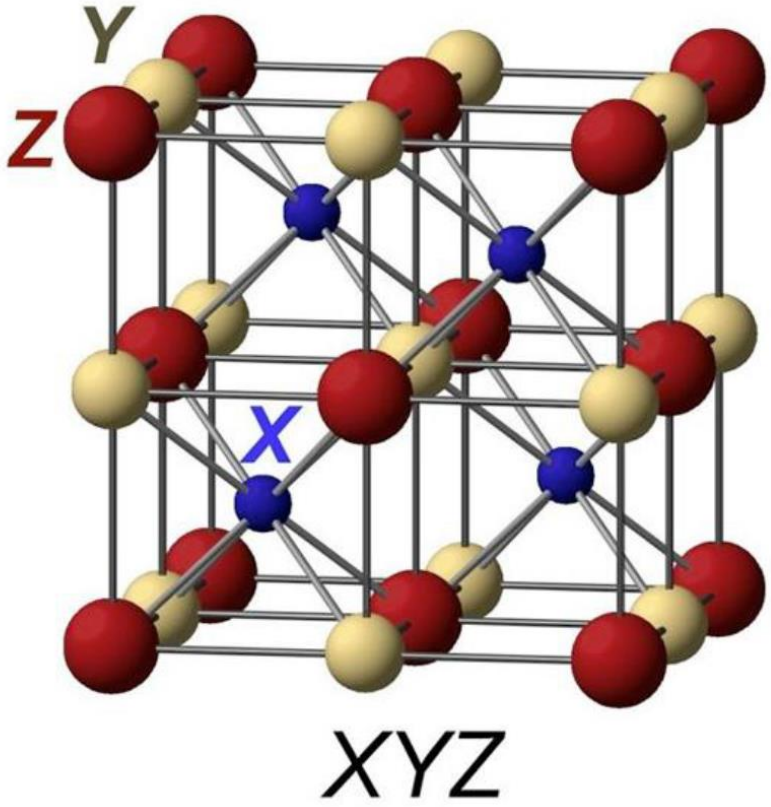
Co-Cr-S-Zn
$CoCuS_4Ti$
Co_3O_4
Co_3Se_4
Cr_4CuGaS_8
$CrCuHfSe_4$
$Cr_4CuInSe_8$
Cr-Cu-Rh-Se
$CrCuS_4Sn$
Cr-Cu-S-Zn
$CrCuSe_4Sn$
Cr-Cu-Se-Zn
Cr-Eu-Se-Zn
Cr-Fe-Rh-S
Cr-Fe-S-Se
Cr_3GaS_6
Cr-Hg-S-Se
Cr_4InLiS_8
Cr_2MnS_4
Cr_2S_4Zn

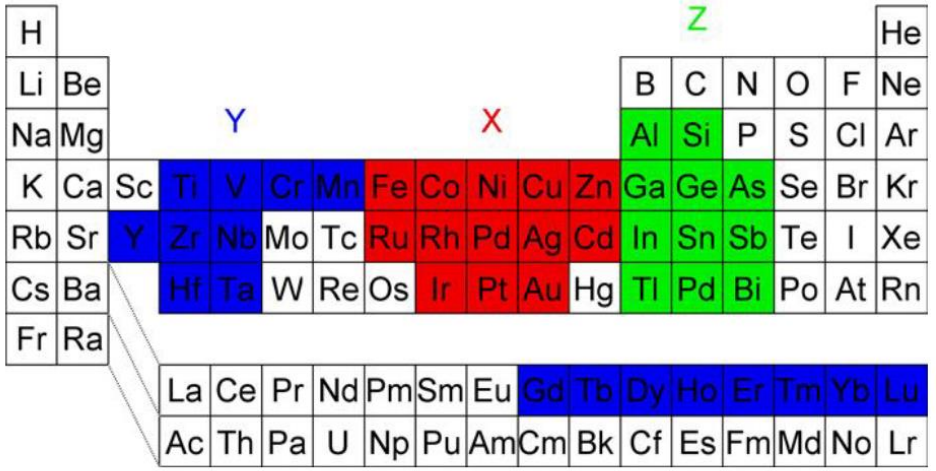
Th_3P_4: structure type

No center of symmetry



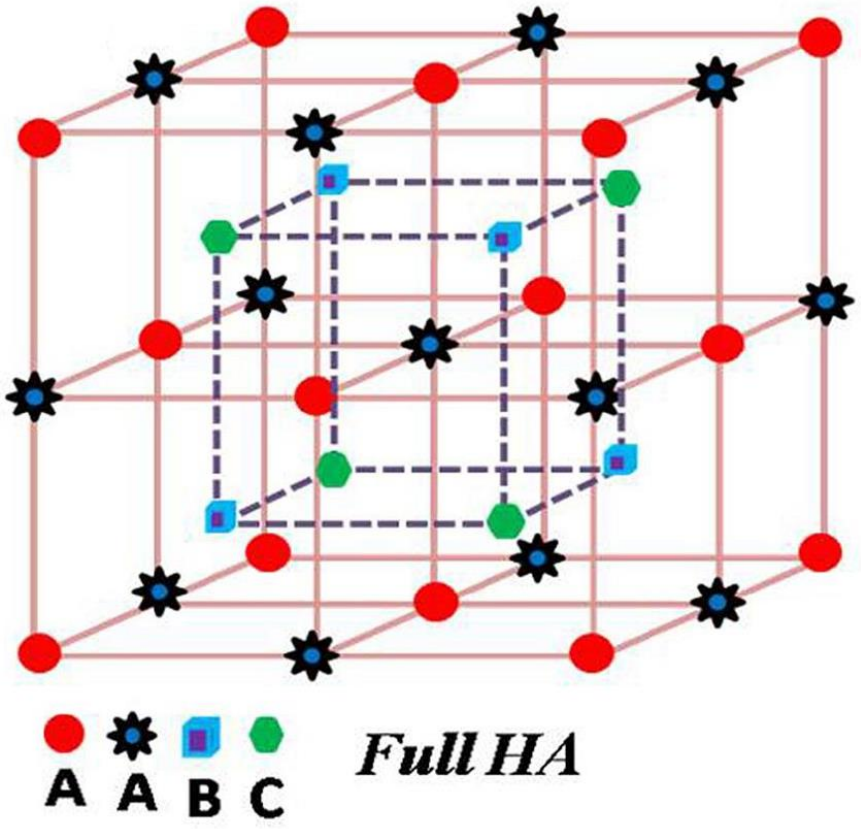
ABX (Half-Heusler alloys…ZrNiSn)





ZrNiSn
VFeSb
LaCoSb
LiZnAs

ABX (Half-Heusler alloys…ZrNiSn)



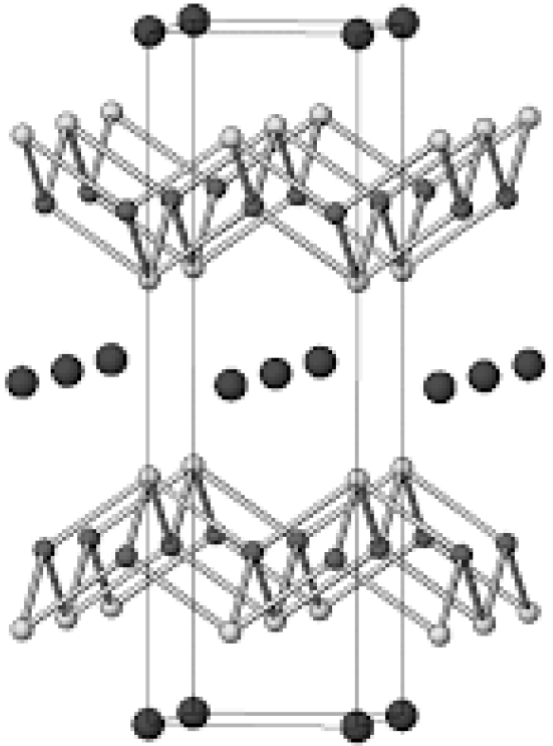
(a)

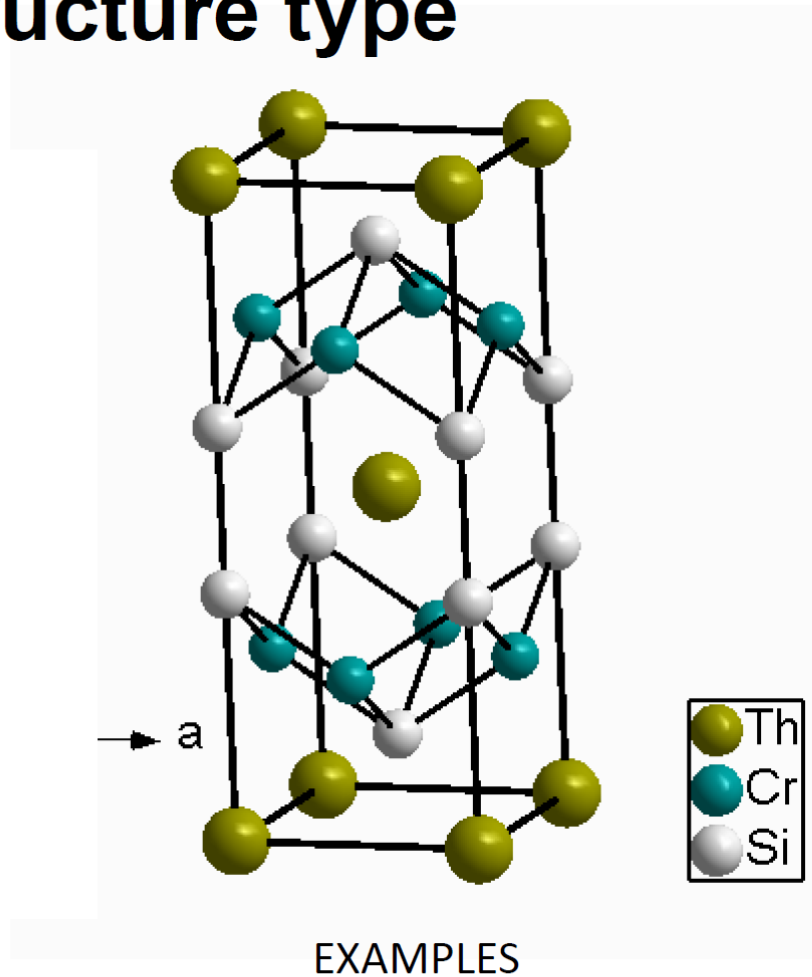
ZrNiSn
VFeSb
LaCoSb
LiZnAs

Full Heusler alloy: $ZrNi_2Sn$

$ThCr_2Si_2$, AB_2X_2 Structure type

$BaFe_2As_2$



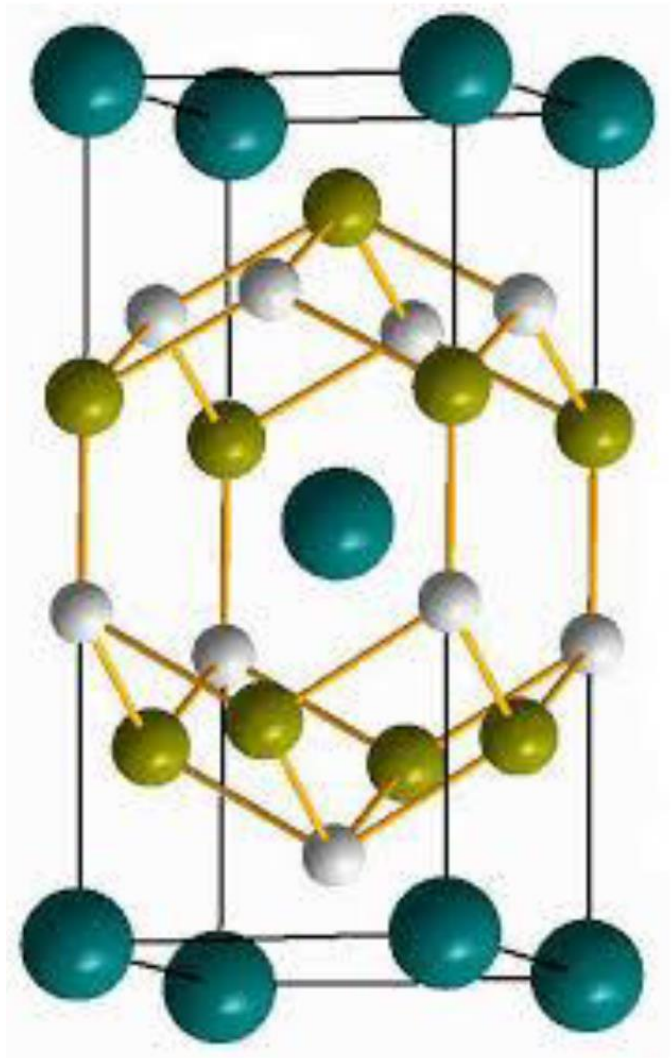


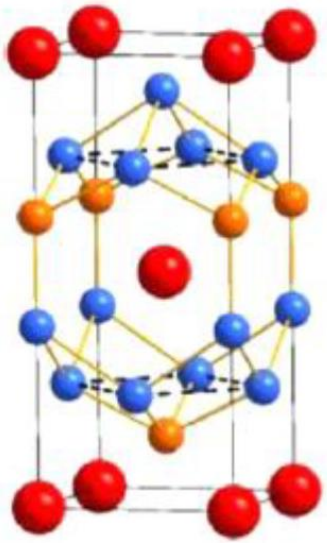
EXAMPLES

AM_2S_2, AM_2Se_2 (A=K, Rb, Cs; M = Co, Ni)

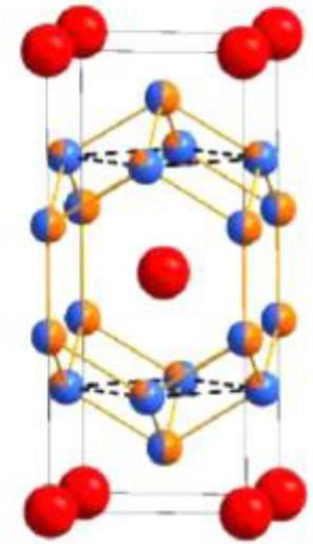
$BaCu_2S_2$

$CaBe_2Ge_2$, AB_2X_2 Structure type

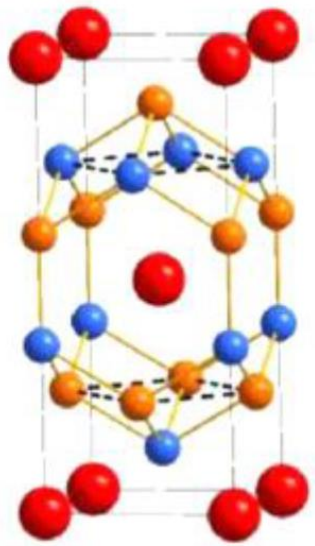




$BaNiSn_3$ type

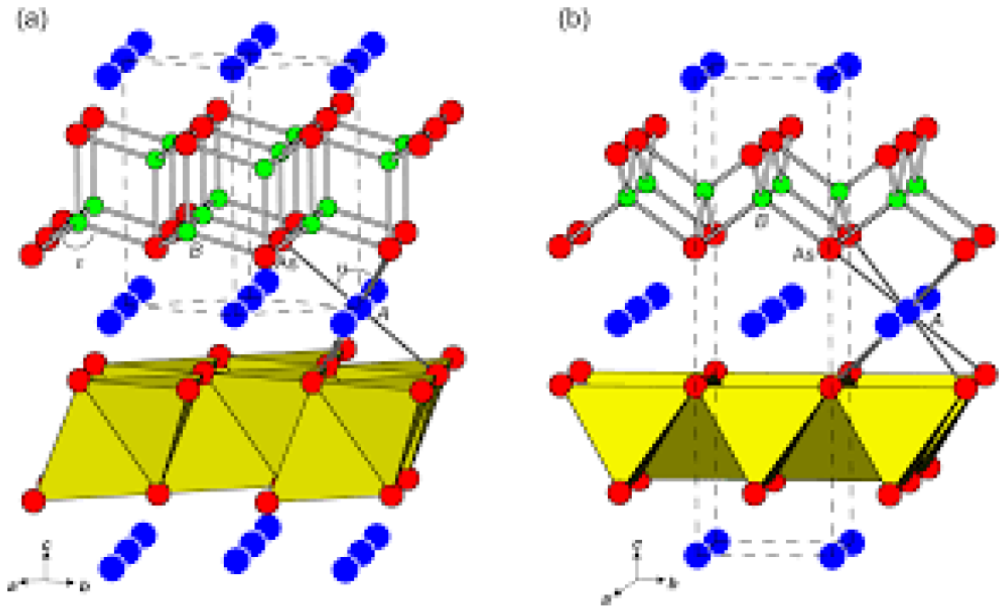


$ThCr_2Si_2$ type

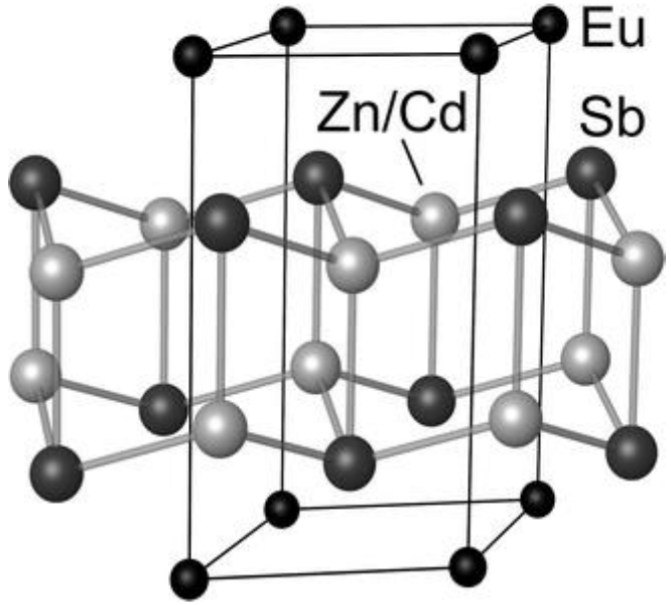


$CaBe_2Ge_2$ type

$CaAl_2Si_2$, AB_2X_2
Structure type



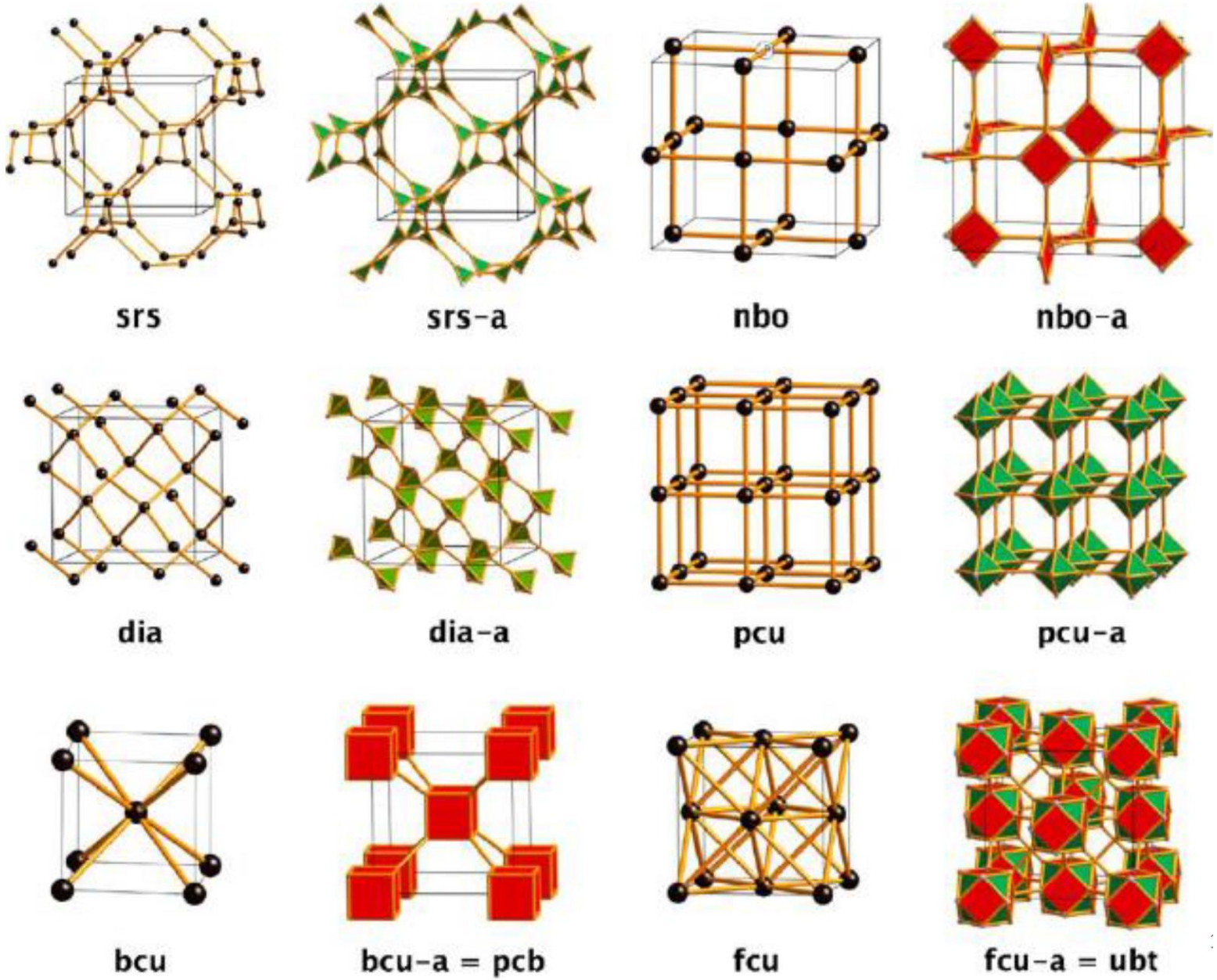
Comparison between CaAl2Si2 and ThCr2Si2



EXAMPLES

$CaZn_2Sb_2$

$MgAl_2Ge_2$


srs
srs-a
nbo
nbo-a
dia
dia-a
pcu
pcu-a
bcu
bcu-a = pcb
fcu
fcu-a = ubt