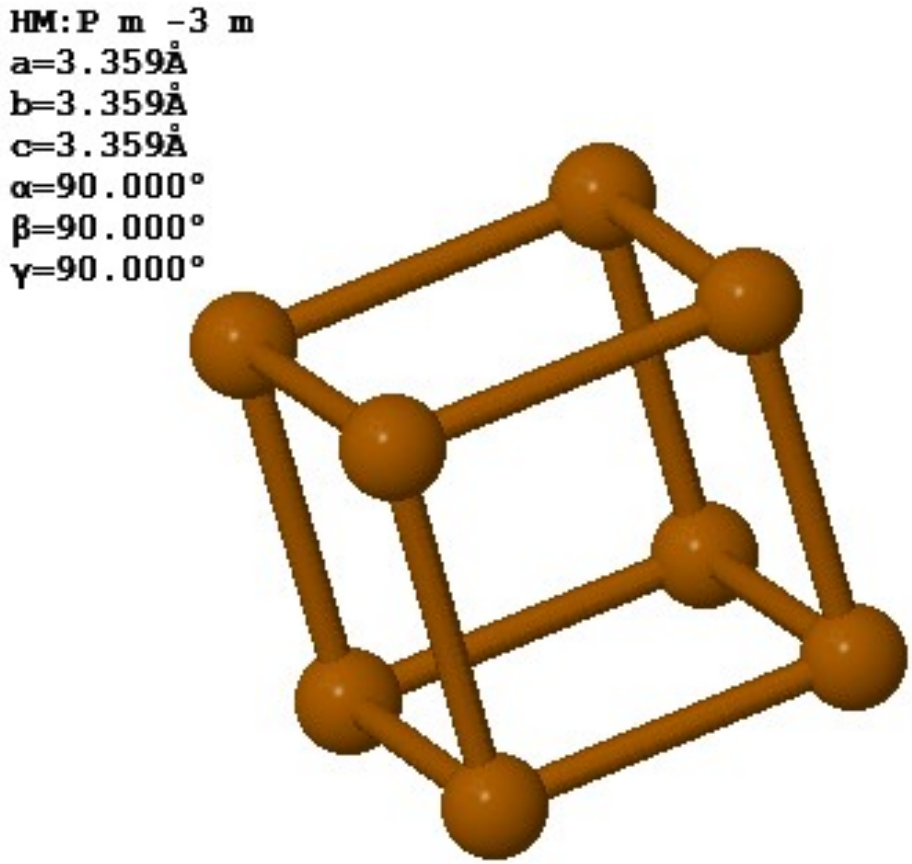
Crystal structures

Ionic crystals

simple cubic

Po



Number: 221

Primitive Vectors:

$$\vec{a}_1 = a\hat{x}$$

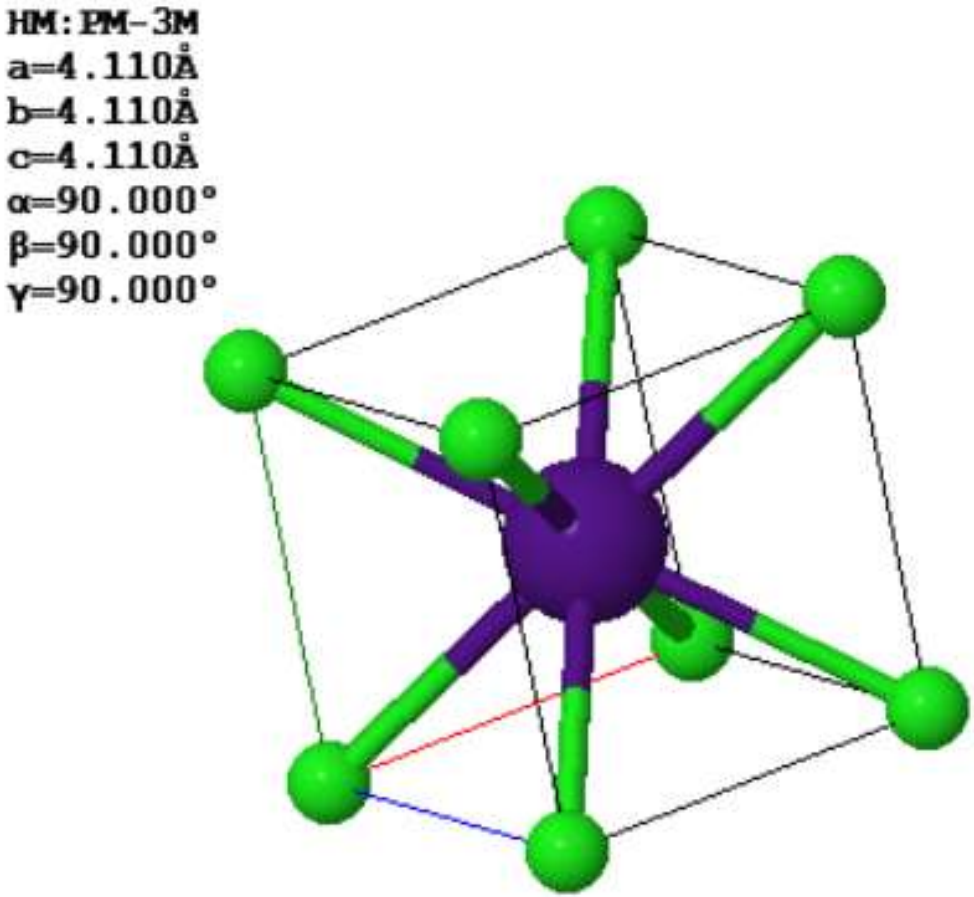
$$\vec{a}_2 = a\hat{y}$$

$$\vec{a}_3 = a\hat{z}$$

Basis Vector: $\vec{B}_1 = (0,0,0)$

CsCl

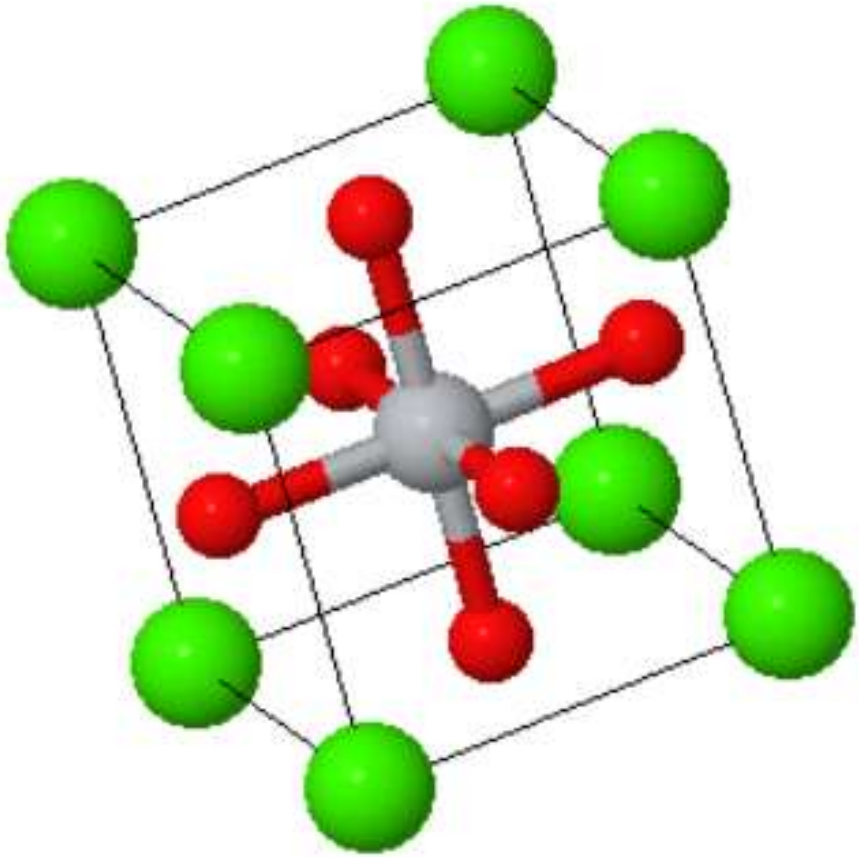
Number 221



perovskite

$SrTiO_3$
$LiNbO_3$
$BaTiO_3$
$Pb_xZr_{1-x}TiO_3$

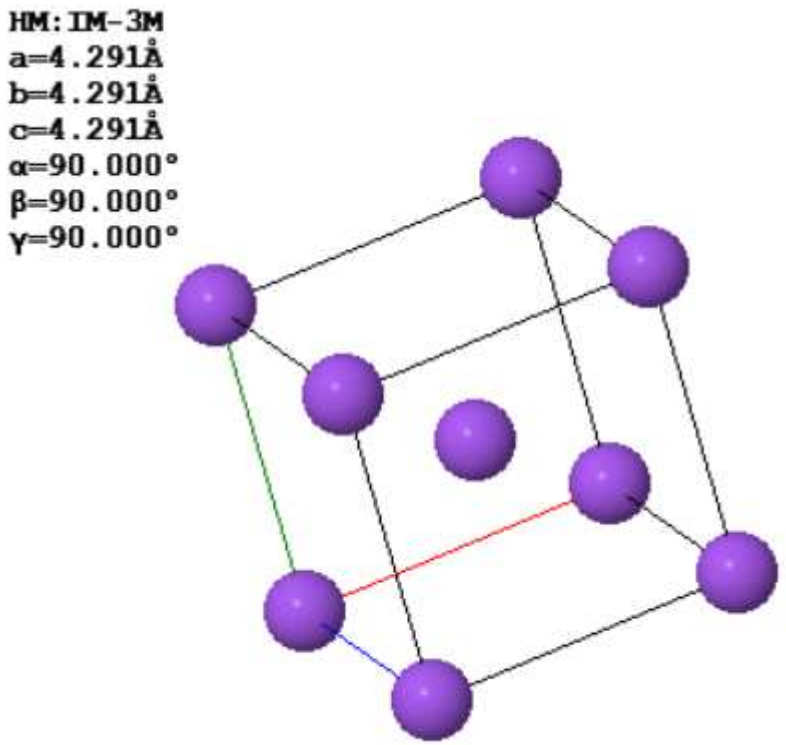
Number 221
simple cubic



bcc

W
Na
K
V
Cr
Fe
Rb
Nb
Mo
Cs
Ba
Eu
Ta

Number 229



Primitive Vectors:

$$\vec{a}_1 = -\frac{a}{2}\hat{x} + \frac{a}{2}\hat{y} + \frac{a}{2}\hat{z}$$

$$\vec{a}_2 = \frac{a}{2}\hat{x} - \frac{a}{2}\hat{y} + \frac{a}{2}\hat{z}$$

$$\vec{a}_3 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{y} - \frac{a}{2}\hat{z}$$

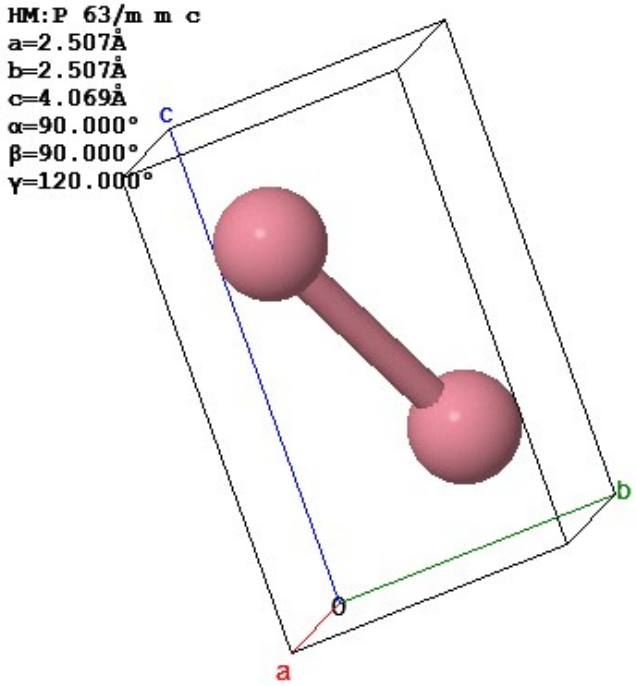
Basis Vector: $\vec{B}_1 = (0,0,0)$

hcp

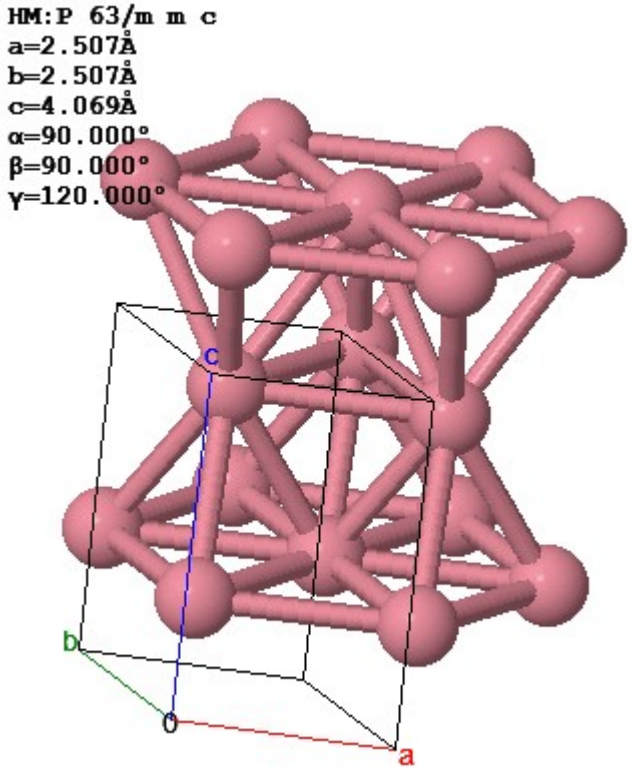
Space group 194

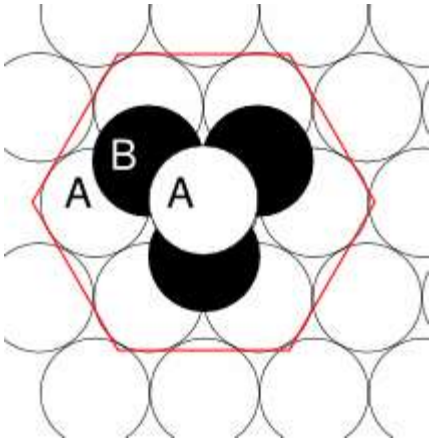
Mg, Be,
Sc, Ti,
Co, Zn,
Y, Zr, Tc,
Ru, Cd,
Gd, Tb,
Dy, Ho,
Er, Tm,
Lu, Hf,
Re, Os,
Tl

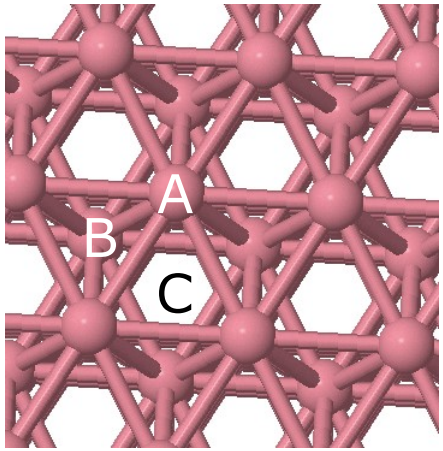
Crystallographic unit cell



Hexagonal unit cell







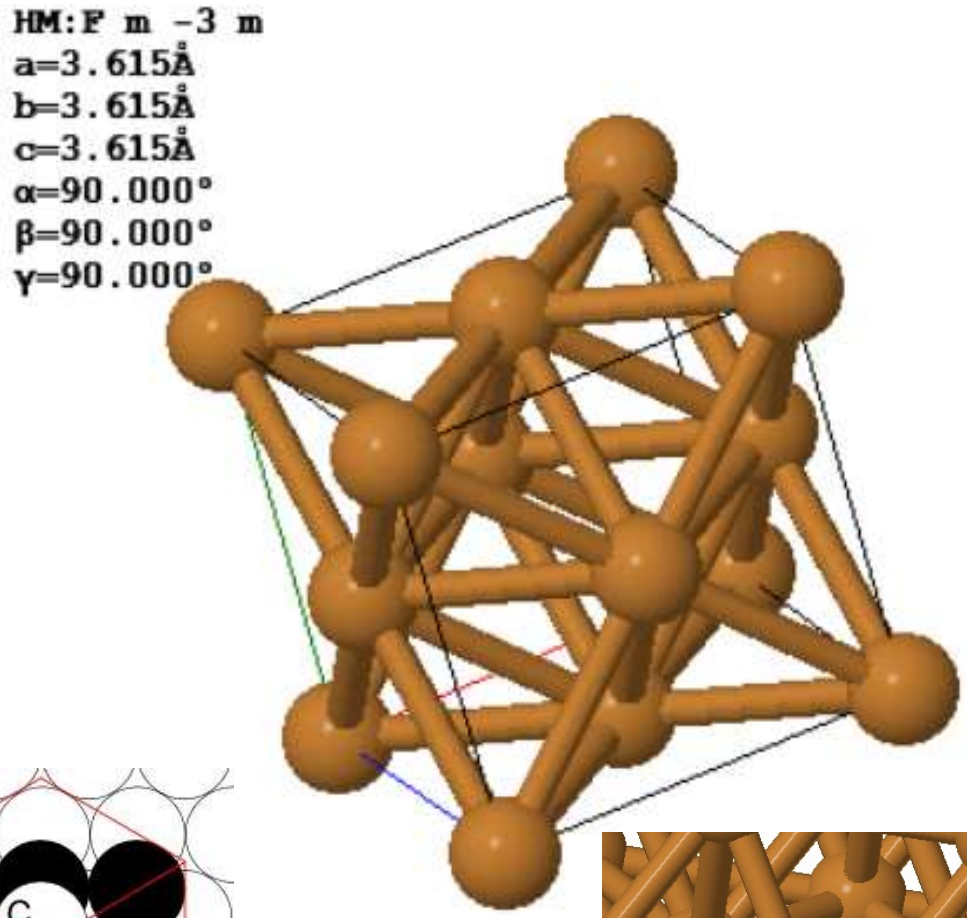
Hexagonal Bravais lattice
Basis vectors:

$$\vec{B}_1 = (0,0,0) \quad \vec{B}_2 = (\tfrac{2}{3},\tfrac{1}{3},\tfrac{1}{2})$$

fcc

Number 225

Al, Cu,
Ni, Sr,
Rh, Pd,
Ag, Ce,
Tb, Ir,
Pt, Au,
Pb, Th



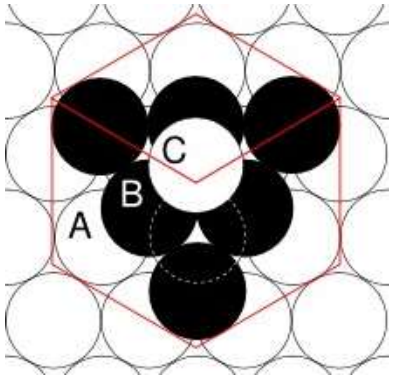
[111]

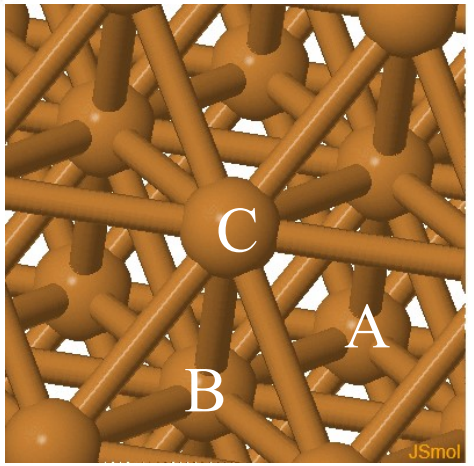
Primitive Vectors:

$$\vec{a}_1 = \frac{a}{2}\hat{y} + \frac{a}{2}\hat{z}$$

$$\vec{a}_2 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{z}$$

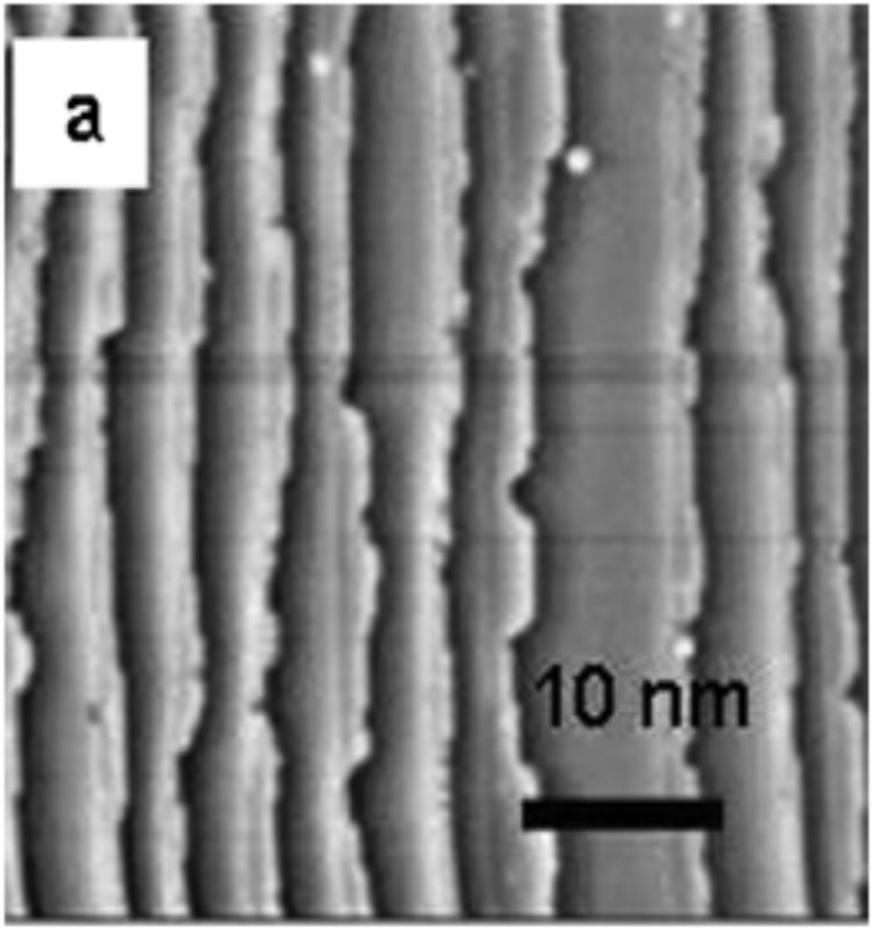
$$\vec{a}_3 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{y}$$



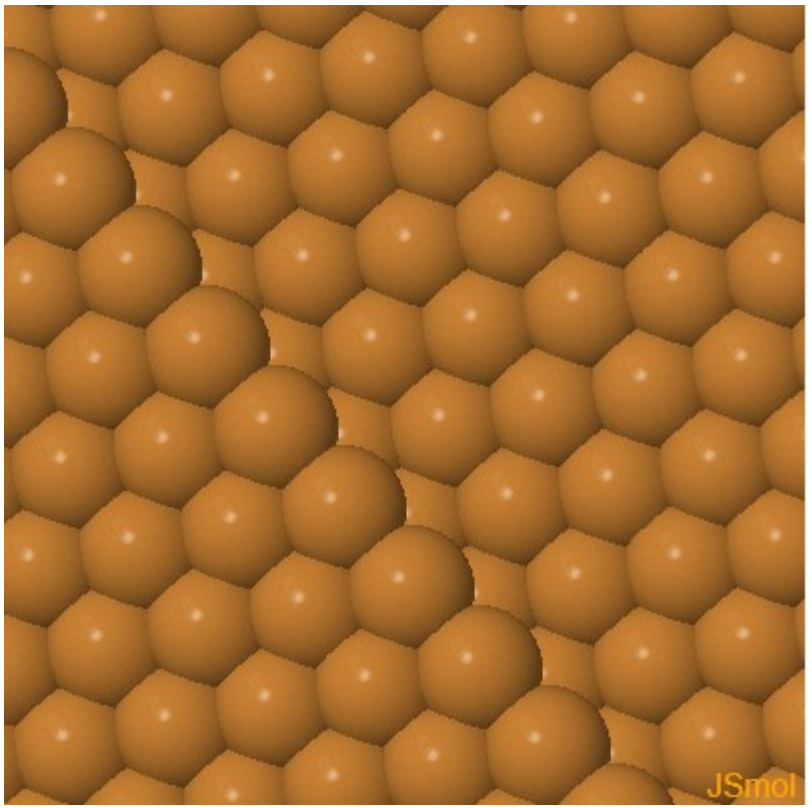


Basis Vector: $\vec{B}_1 = (0,0,0)$

Crystal planes: Miller indices



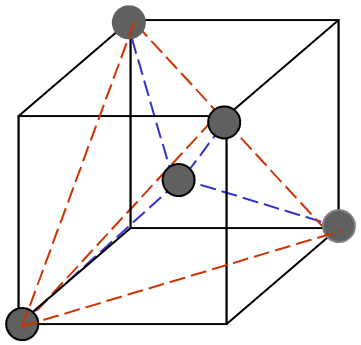
Rh(15,15,13) fcc



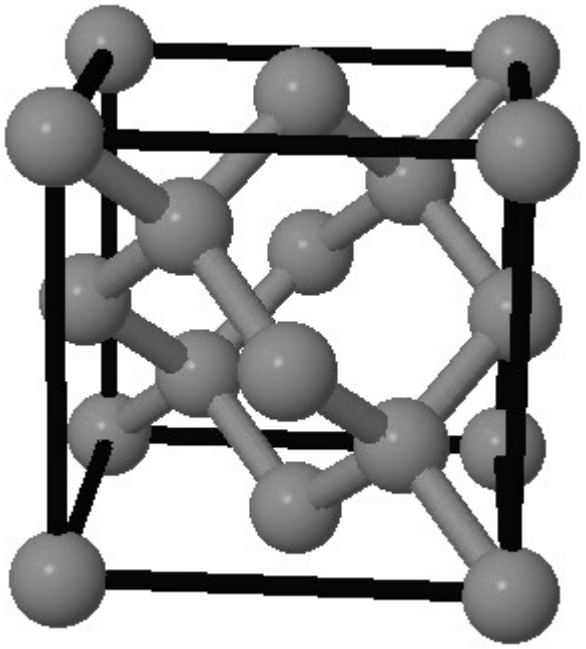
(15,15,13) fcc

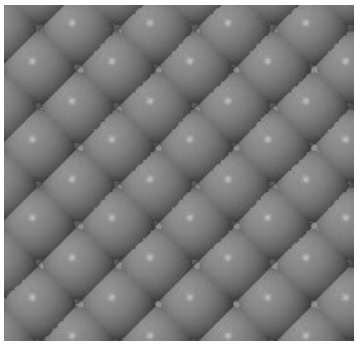
Reaction studies on nanostructured surfaces, Adolf Winkler, in *The Oxford Handbook of Nanoscience and Technology*, A. V. Narlikar and Y. Y. Fu ed., 2009.

Diamond

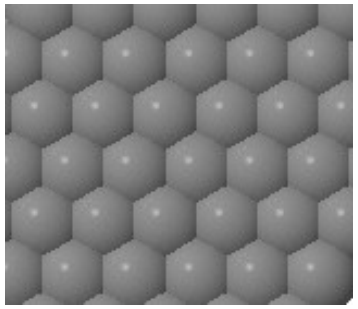


$$a = b = c, \quad \alpha = 90^\circ, \beta = 90^\circ, \gamma = 90^\circ$$





$$(100): \frac{2}{a^2}$$



$$(111): \frac{4}{\sqrt{3}a^2}$$

Space group: 227
point group: m3m

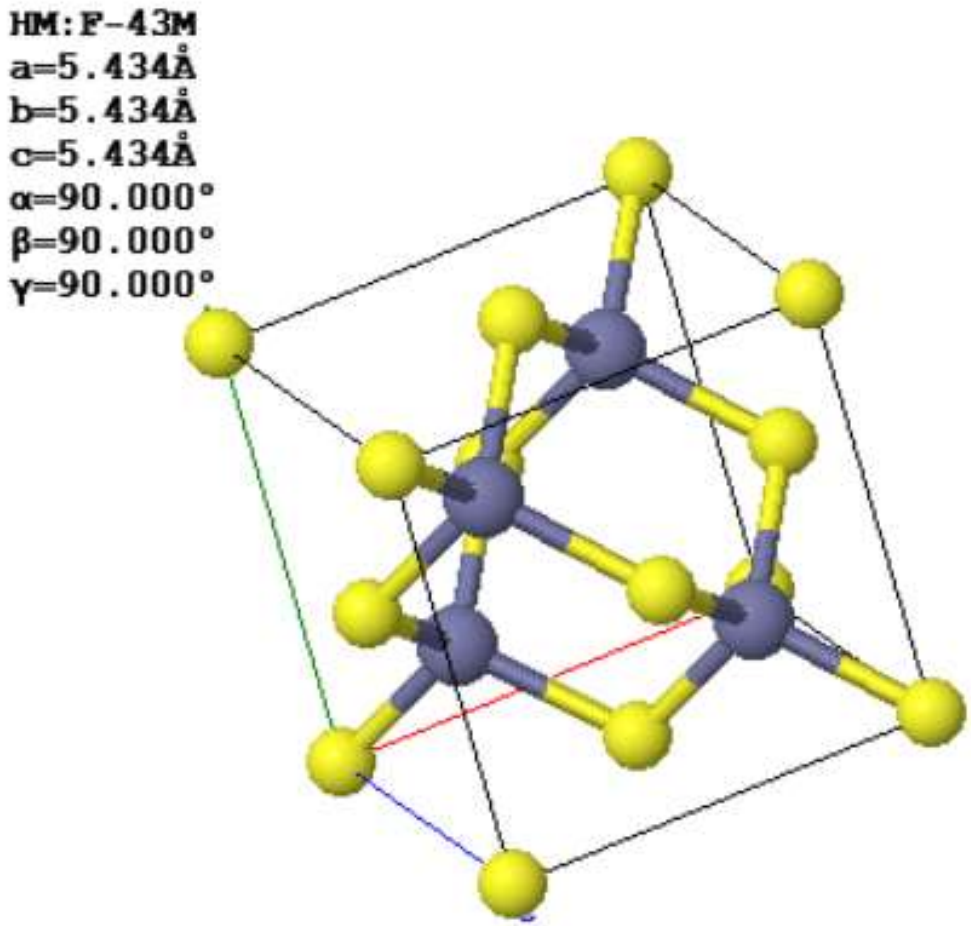
Primitive lattice vectors:

$$\vec{a}_1 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{y}, \qquad \vec{a}_2 = \frac{a}{2}\hat{x} + \frac{a}{2}\hat{z}, \qquad \vec{a}_3 = \frac{a}{2}\hat{y} + \frac{a}{2}\hat{z}.$$

Basis: $\vec{B}_1 = (0,0,0), \qquad \vec{B}_2 = (0.25, 0.25, 0.25).$

zincblende

ZnS
GaAs
InP

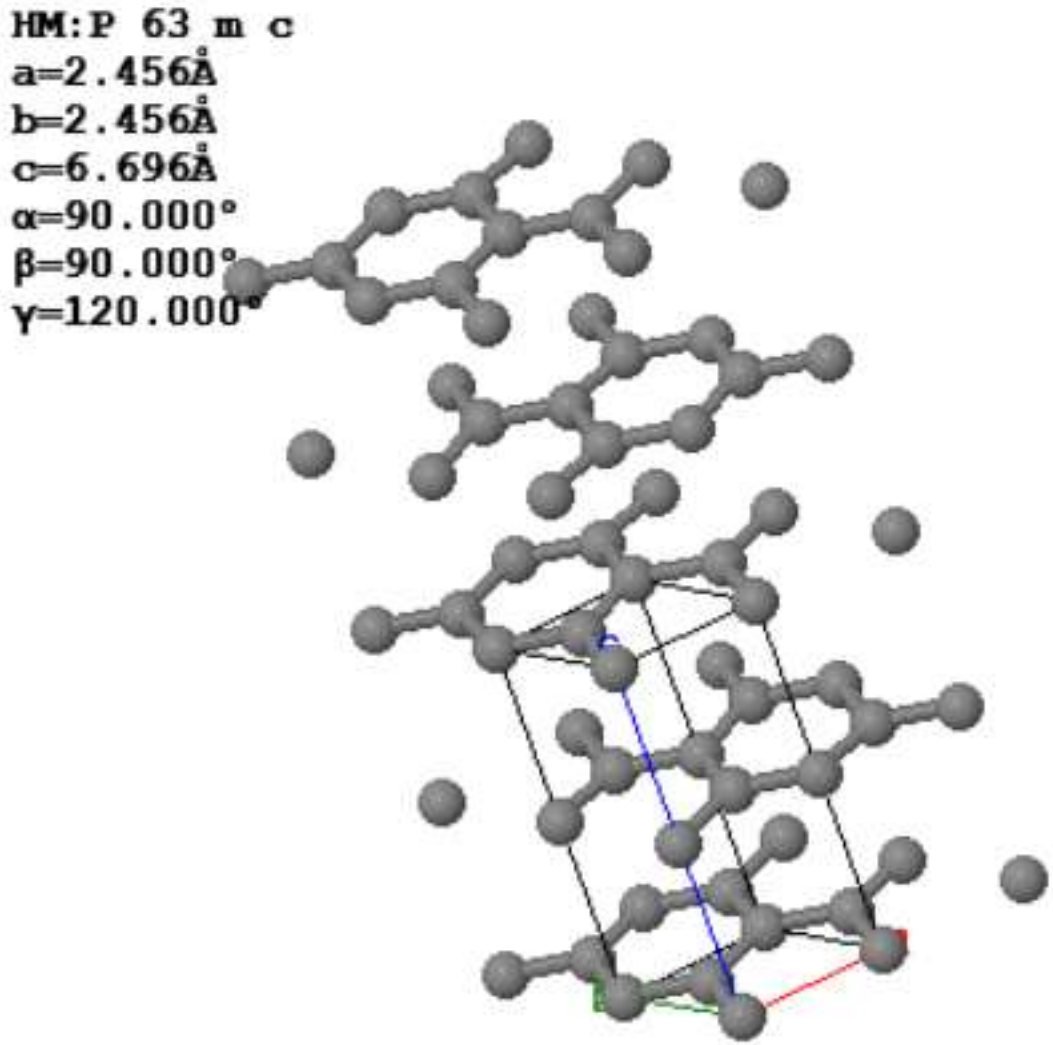


space group 216
F$\bar{4}$3m

graphite

Space group 194

4 inequivalent C atoms in the primitive unit cell

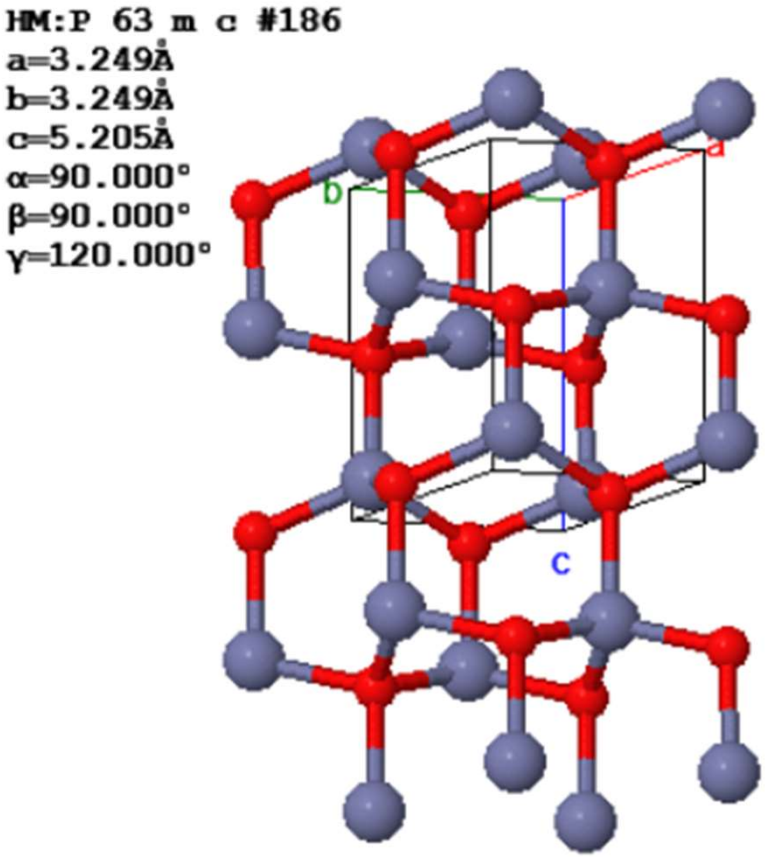


Polytypes of carbon
graphite (hexagonal)
carbon nanotubes
diamond
rhobohedral graphite
hexagonal diamond

wurtzite

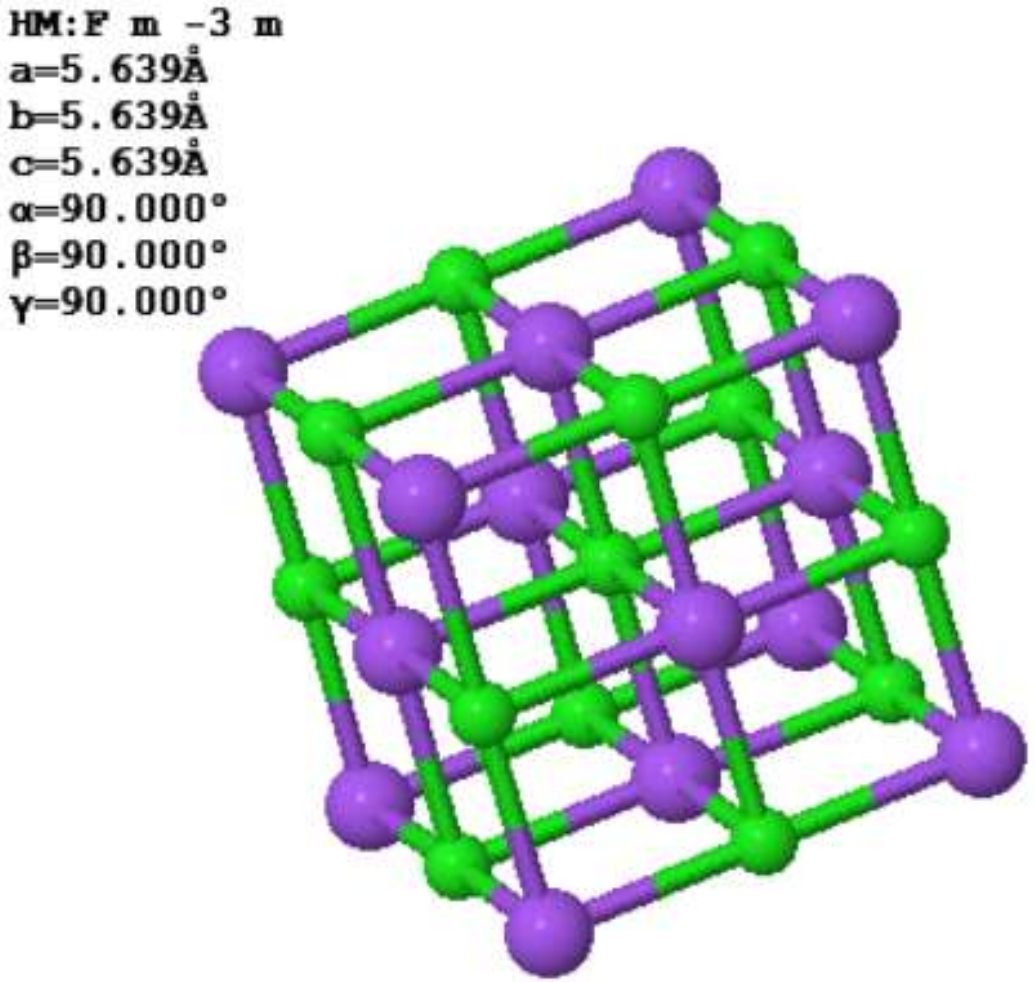
ZnS
ZnO
CdS
CdSe
GaN
AlN

Number 186



There are 2 polytypes of ZnS: zincblende and wurtzite

NaCl

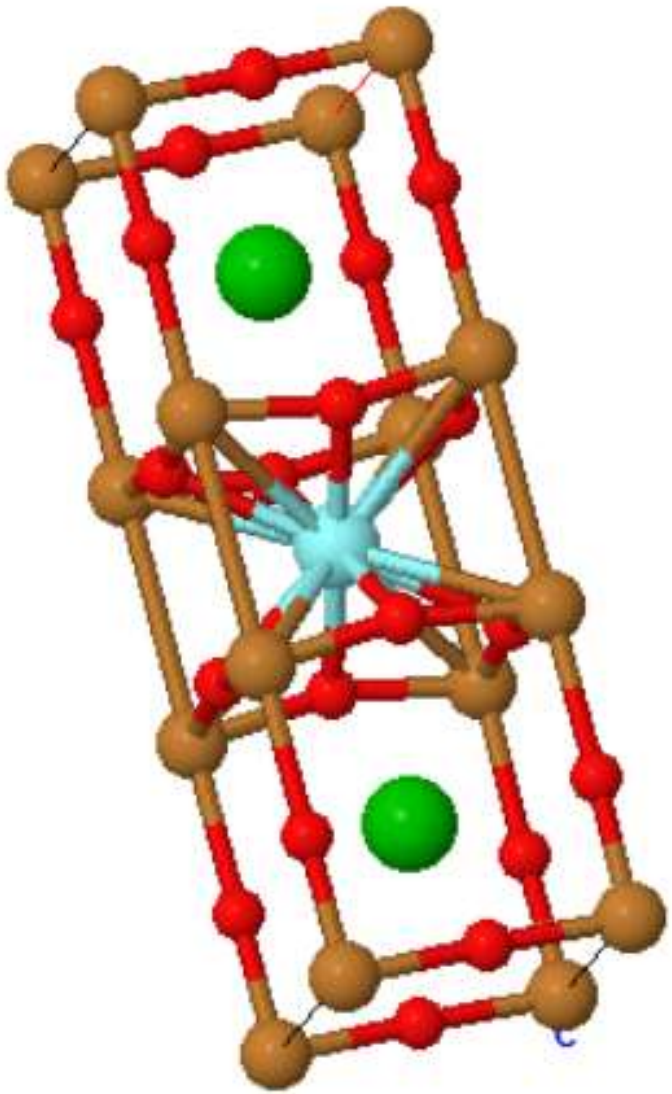


Number 225

Bravais: fcc

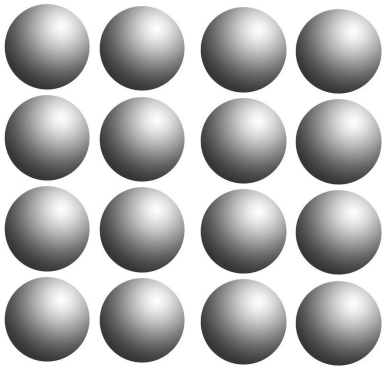
$YBa_2Cu_3O_7$

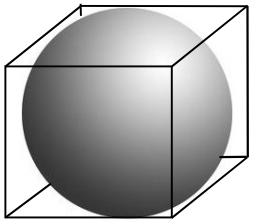
HM:P m m m
a=3.820Å
b=3.885Å
c=11.683Å
α=90.000°
β=90.000°
γ=90.000°



Number 47

atomic packing density



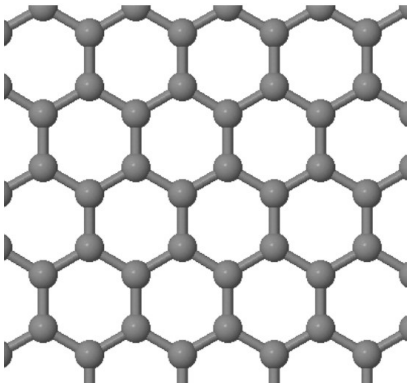


$$\frac{\frac{4}{3}\pi\left(L/2\right)^3}{L^3} = \frac{\pi}{6} \approx 0.52$$

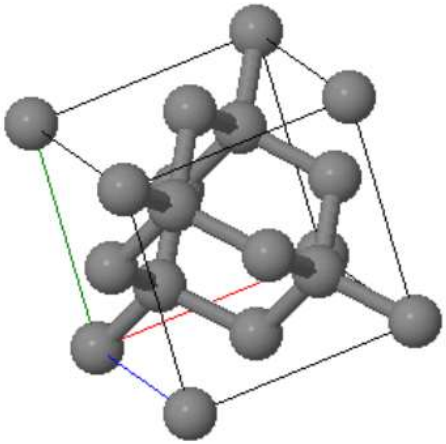
fcc, hcp = 0.74
bcc = 0.68
random close pack = 0.64
simple cubic = 0.52
diamond = 0.34

Coordination number

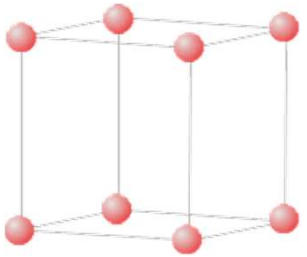
Number of nearest neighbors an atom has in a crystal



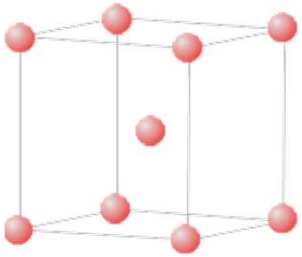
Graphene 3



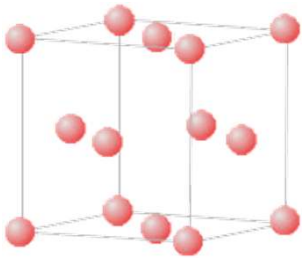
diamond 4



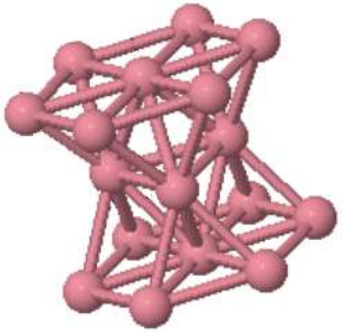
sc 6



bcc 8

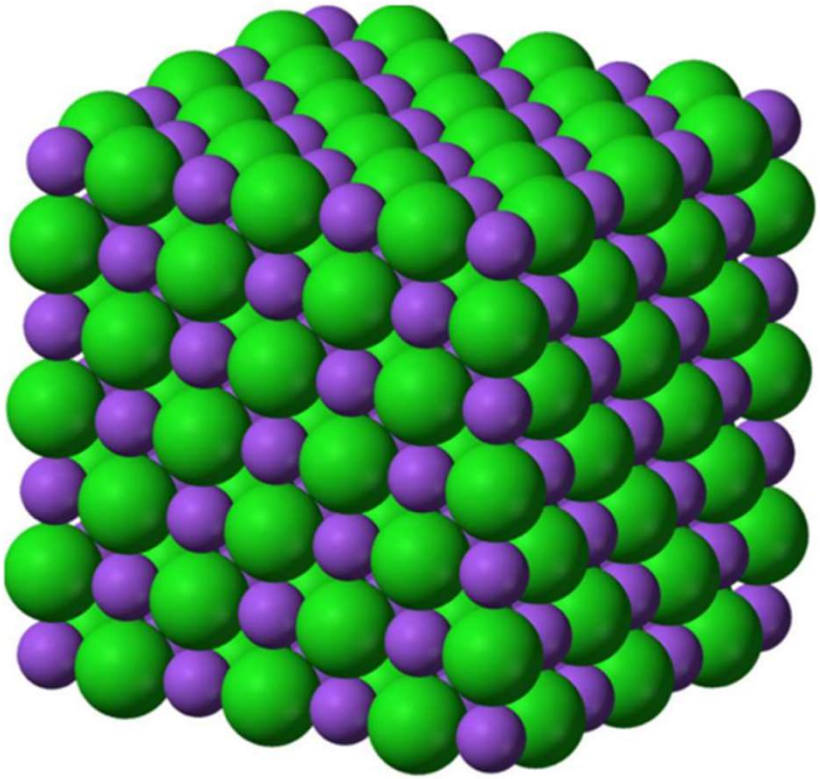


fcc 12



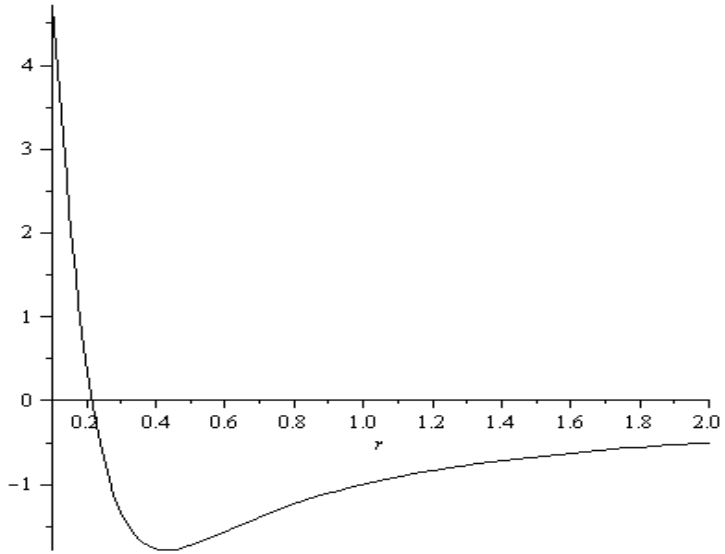
hcp 12

Ionic crystals



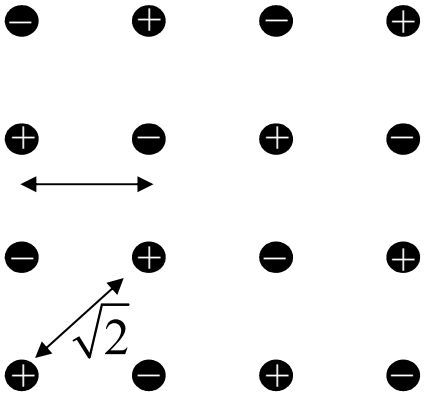
Ionic crystals

Nearest neighbors: $$U_{ij} = \lambda e^{-\frac{r_{ij}}{\rho}} - \frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$



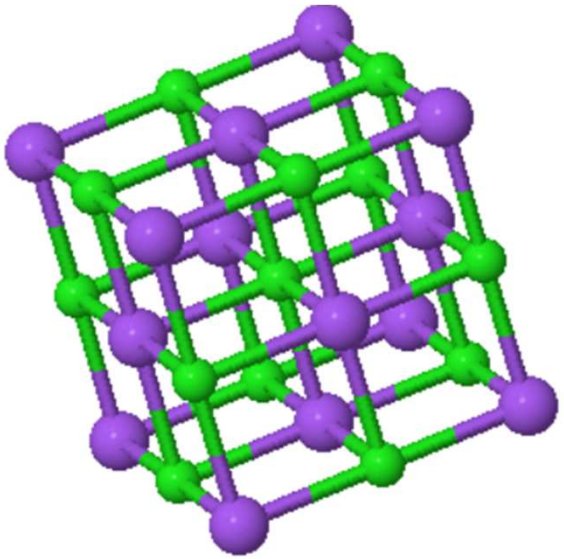
Distant neighbors: $$U_{ij} = \frac{\pm e^2}{4\pi\varepsilon_0 r_{ij}}$$

Ionic crystals



R = nearest neighbor separation

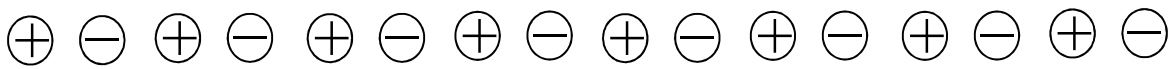
Ernst Madelung



α Madelung constant

$$U_{\text{ionic}} = -\frac{e^2}{4\pi\varepsilon_0 R}\left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \ldots\right)$$

Madelung constant in 1-D



$$\alpha = 2\left[1-\tfrac{1}{2}+\tfrac{1}{3}-\tfrac{1}{4}+\tfrac{1}{5}-\cdots\right]$$

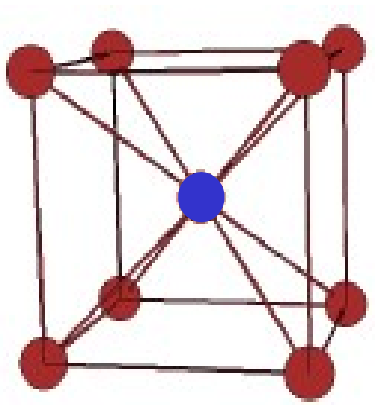
Taylor expansion: $\ln(1+x)=\left[x-\tfrac{x^2}{2}+\tfrac{x^3}{3}-\tfrac{x^4}{4}+\tfrac{x^5}{5}-\cdots\right]$

$$\ln(2)=\left[1-\tfrac{1}{2}+\tfrac{1}{3}-\tfrac{1}{4}+\tfrac{1}{5}-\cdots\right]$$

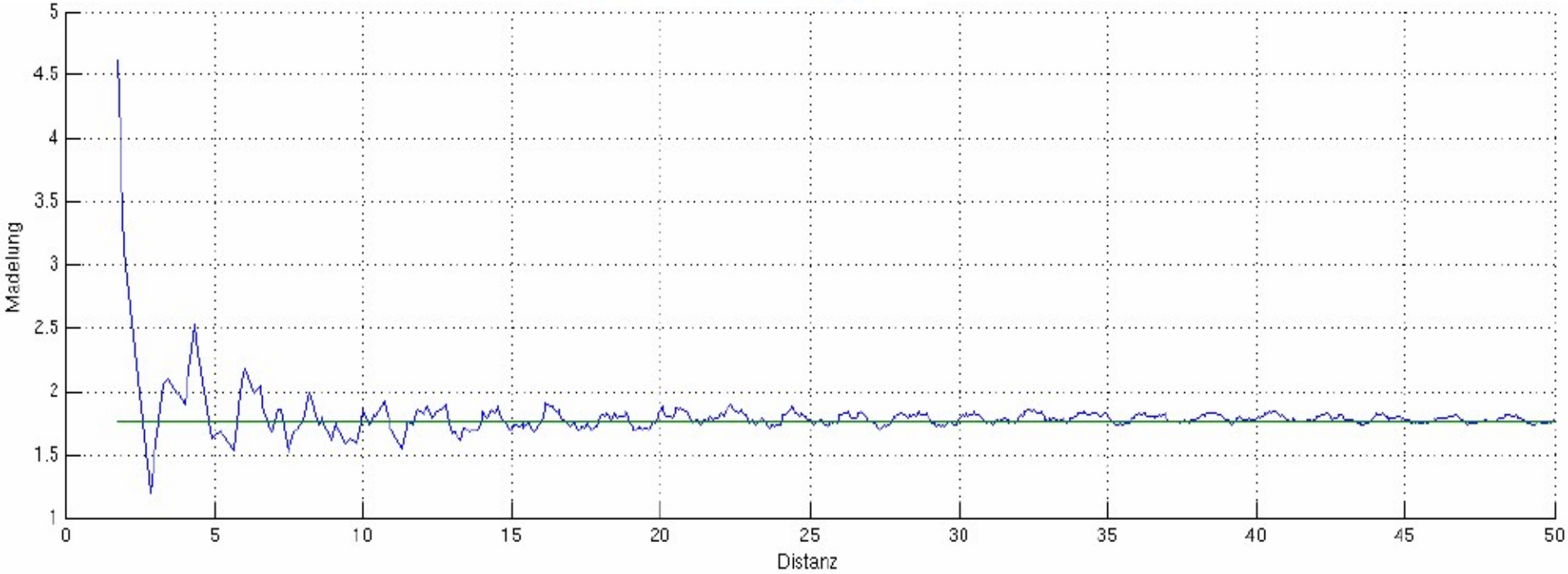
$$\alpha = 2\ln 2 = 1.38629436$$

Calculating the Madelung constant

CsCl
$z = 8$



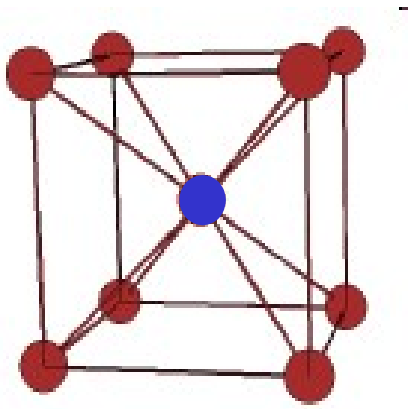
$\alpha = 1.767$



Iterative Bestimmung der Madelung-Konstante für CsCl - Yao Shan und Robert Krisper, 2010

Ionic Crystals

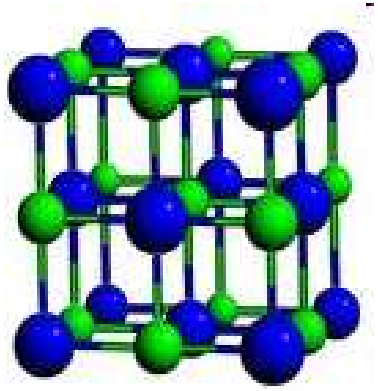
$\alpha = 1.767$



CsCl

$z = 8$

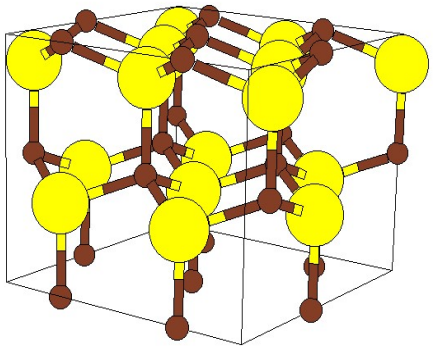
$\alpha = 1.747$



NaCl

$z = 6$

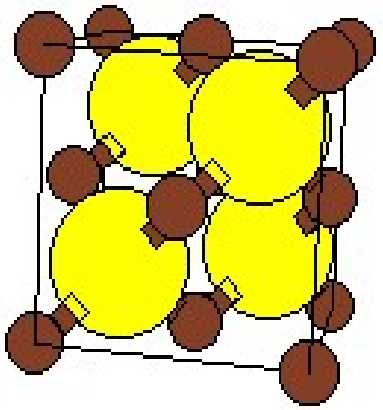
$\alpha = 1.641$



Wurtzite

$z = 4$

$\alpha = 1.638$

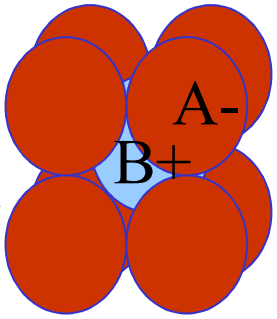


Zincblende

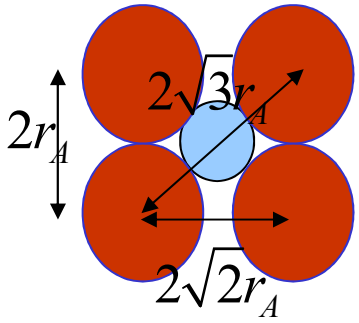
$z = 4$

Ionic radius

CsCl

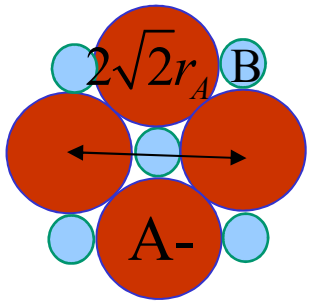


CsCl unstable: $\frac{r_A}{r_B} > \frac{1}{\sqrt{3}-1} = 1.366$



CsCl 110 plane

NaCl



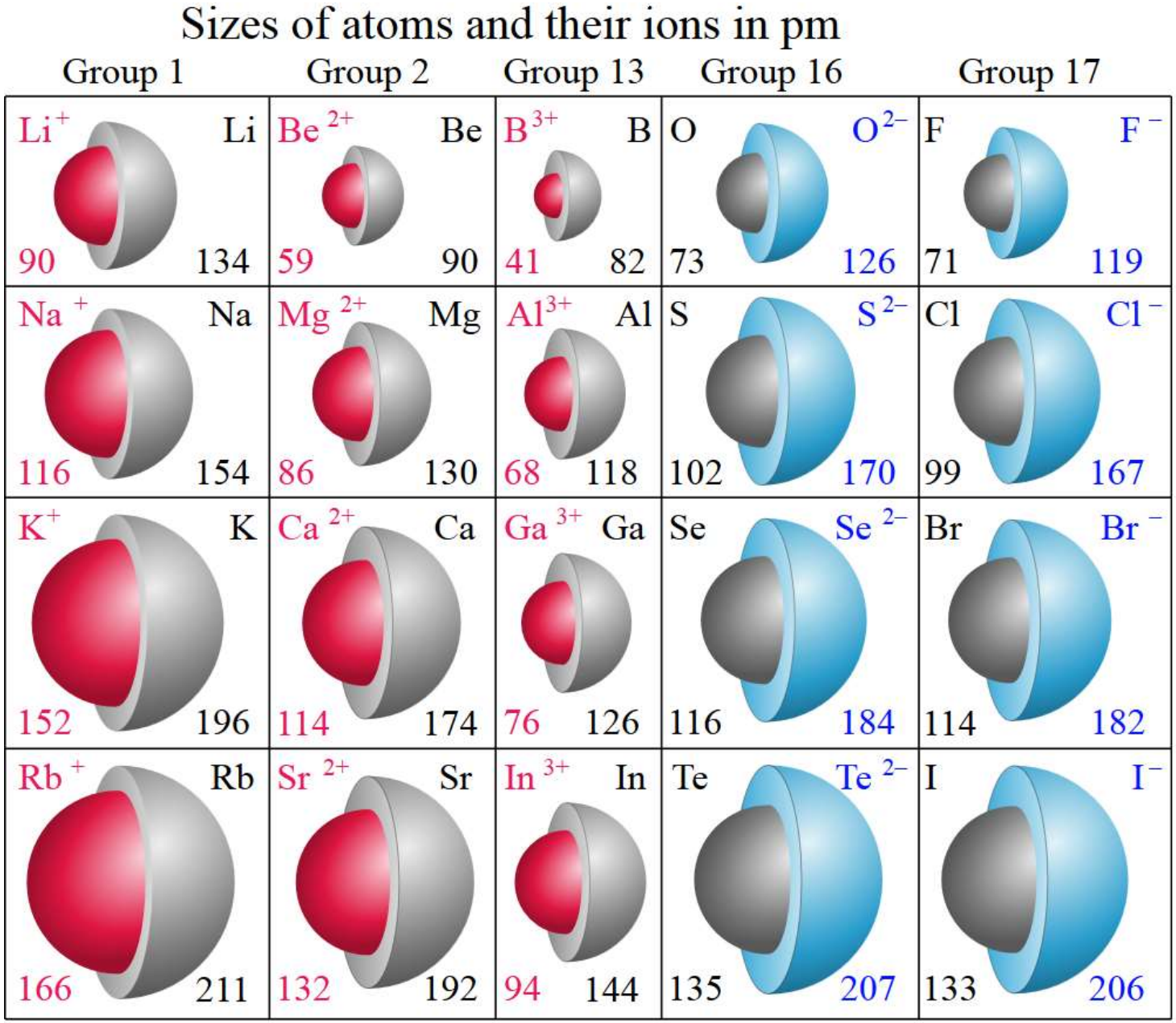
NaCl unstable: $\frac{r_A}{r_B} > \frac{1}{\sqrt{2}-1} = 2.41$

NaCl 100 plane

CsCl:

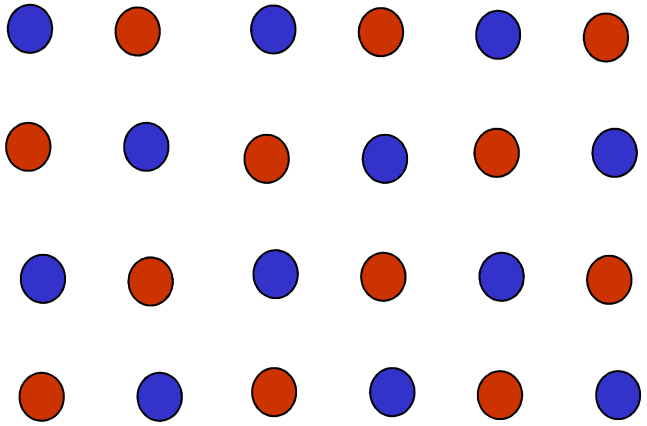
$\frac{r_A}{r_B} < 1.366$

$\frac{r_{Cl}}{r_{Na}} = 1.44$

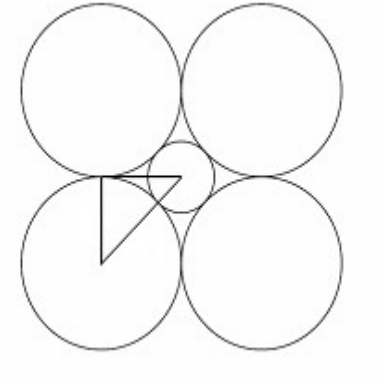


https://en.wikipedia.org/wiki/Ionic_radius#/media/File:Atomic_%26_ionic_radii.svg

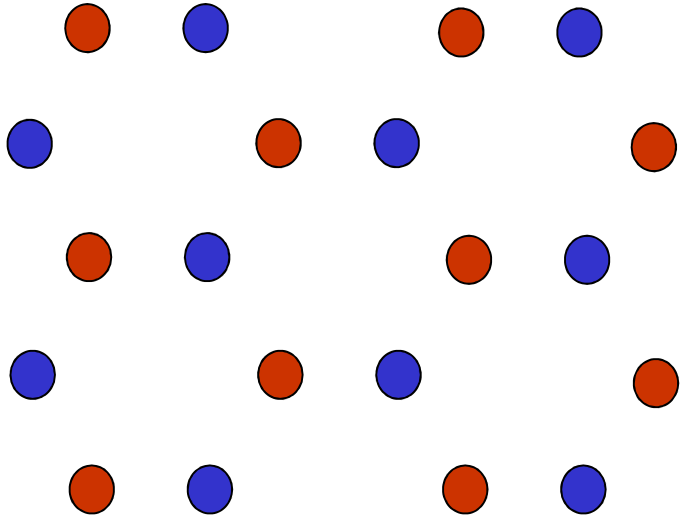
2-D crystals



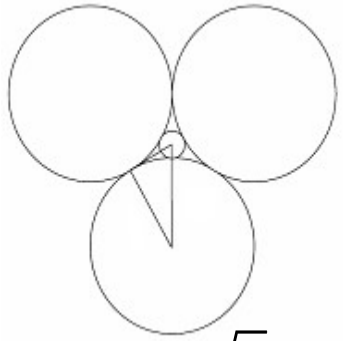
Checkerboard $\alpha = 1.616$



unstable: $\frac{r_A}{r_B} > \frac{1}{\sqrt{2}-1} = 2.41$



Boron nitride $\alpha = 1.542$



unstable: $\frac{r_A}{r_B} > \frac{\sqrt{3}}{2-\sqrt{3}} = 6.464$

Fit the constants ρ and λ

$$U_{tot} = N\left(z\lambda e^{-\frac{R}{\rho}} - \frac{\alpha e^2}{4\pi\varepsilon_0 R} \right)$$

$$\frac{dU_{tot}}{dR} = N\left(-\frac{z\lambda e^{-\frac{R}{\rho}}}{\rho} + \frac{\alpha e^2}{4\pi\varepsilon_0 R^2} \right) = 0$$

R_0 is the equilibrium separation

$$R_0^2 e^{-\frac{R_0}{\rho}} = \frac{\alpha e^2 \rho}{4\pi\varepsilon_0 z\lambda}$$

x-ray determination of atomic spacing is accurate to 1 part in 10^5

Elastic constant

Near the minimum, the potential energy is approximately a parabola.

$$U_{tot} \approx \tfrac{1}{2} k \left(R - R_0 \right)^2$$

$$\frac{dU_{tot}}{dR} \approx k\left(R - R_0 \right) = -F$$

$$k = \left. \frac{d^2 U_{tot}}{dR^2} \right|_{R=R_0} = \left(\frac{z\lambda e}{\rho^2} e^{-\frac{R_0}{\rho}} - \frac{\alpha e^2}{2\pi\varepsilon_0 R_0^3} \right)$$

spring constant of a bond

From the spring constant, the compressibility can be calculated.

Table 7 Properties of alkali halide crystals with the NaCl structure

All values (except those in square brackets) at room temperature and atmospheric pressure, with no correction for changes in R_0 and U from absolute zero. Values in square brackets at absolute zero temperature and zero pressure, from private communication by L. Brewer.

	Nearest-neighbor separation R_0 in Å	Bulk modulus B, in 10^{11} dyn/cm^2 or 10^{10} N/m^2	Repulsive energy parameter $z\lambda$, in 10^{-8} erg	Repulsive range parameter ρ, in Å	Lattice energy compared to free ions, in kcal/mol	
					Experimental	Calculated
LiF	2.014	6.71	0.296	0.291	242.3[246.8]	242.2
LiCl	2.570	2.98	0.490	0.330	198.9[201.8]	192.9
LiBr	2.751	2.38	0.591	0.340	189.8	181.0
LiI	3.000	(1.71)	0.599	0.366	177.7	166.1
NaF	2.317	4.65	0.641	0.290	214.4[217.9]	215.2
NaCl	2.820	2.40	1.05	0.321	182.6[185.3]	178.6
NaBr	2.989	1.99	1.33	0.328	173.6[174.3]	169.2
NaI	3.237	1.51	1.58	0.345	163.2[162.3]	156.6
KF	2.674	3.05	1.31	0.298	189.8[194.5]	189.1
KCl	3.147	1.74	2.05	0.326	165.8[169.5]	161.6
KBr	3.298	1.48	2.30	0.336	158.5[159.3]	154.5
KI	3.533	1.17	2.85	0.348	149.9[151.1]	144.5
RbF	2.815	2.62	1.78	0.301	181.4	180.4
RbCl	3.291	1.56	3.19	0.323	159.3	155.4
RbBr	3.445	1.30	3.03	0.338	152.6	148.3
RbI	3.671	1.06	3.99	0.348	144.9	139.6

Data from various tables by M. P. Tosi, Solid State Physics **16**, 1 (1964).

$$B = \frac{1}{V}\frac{dp}{dV} = \frac{1}{\kappa}$$

κ is the compressibility

from Kittel