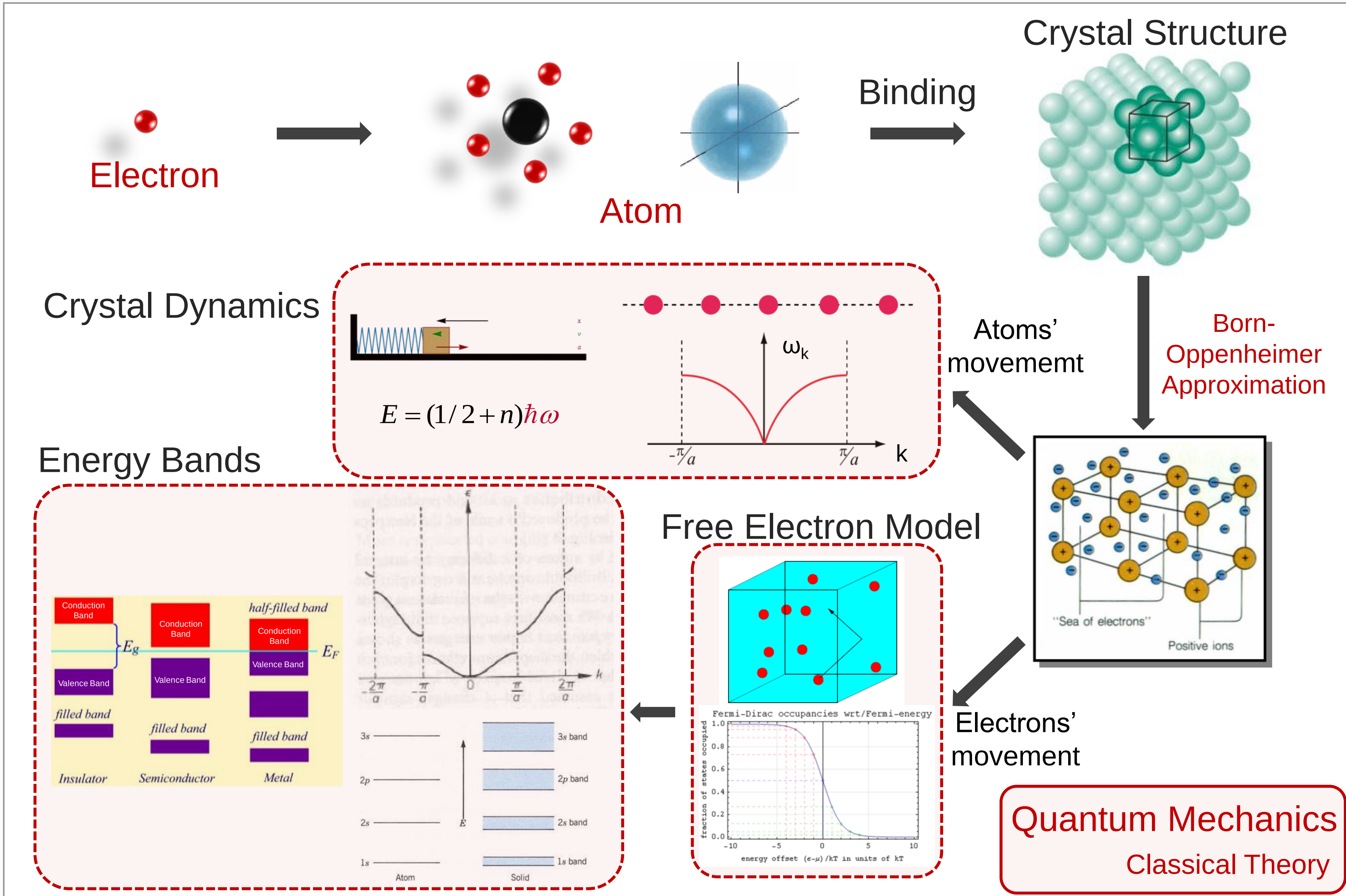
Chapter 1

Formation of Crystal

Today's lecture

Profile



Potential between Two Atoms

$$U(R) = \underbrace{\frac{-a}{R^m}}_{attraction} + \underbrace{\frac{b}{R^n}}_{repulsion}$$

$$a, b, m, n > 0 \quad and \quad n > m$$

$$F(R) = -\frac{\partial U(R)}{\partial R}$$

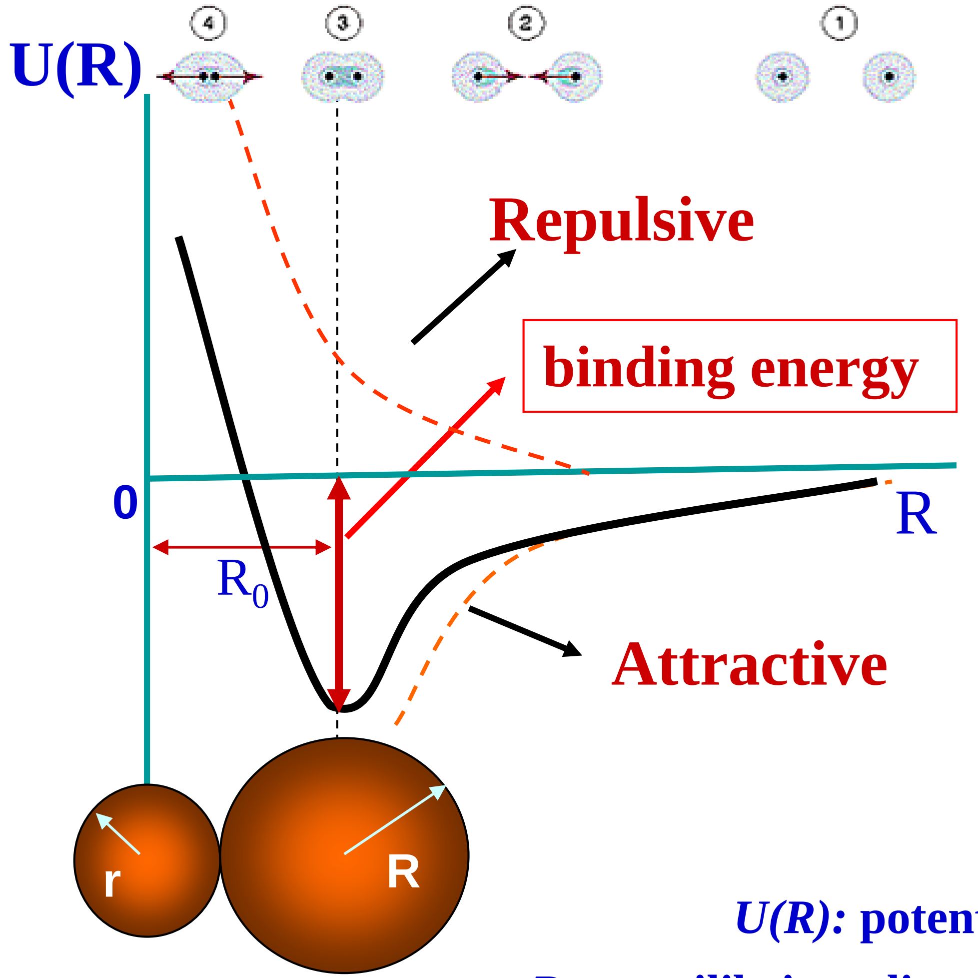
$$F(R) = F_a(R) + F_r(R)$$

R= R_0: F(R)=0.

R>R_0: F(R)>0, attractive

R<R_0: F(R)<0, repulsive

$$\left.\frac{\partial U(R)}{\partial R}\right|_{R=R_0} = 0 \Rightarrow R_0 \Rightarrow U(R_0)$$



***U(R)*: potential**

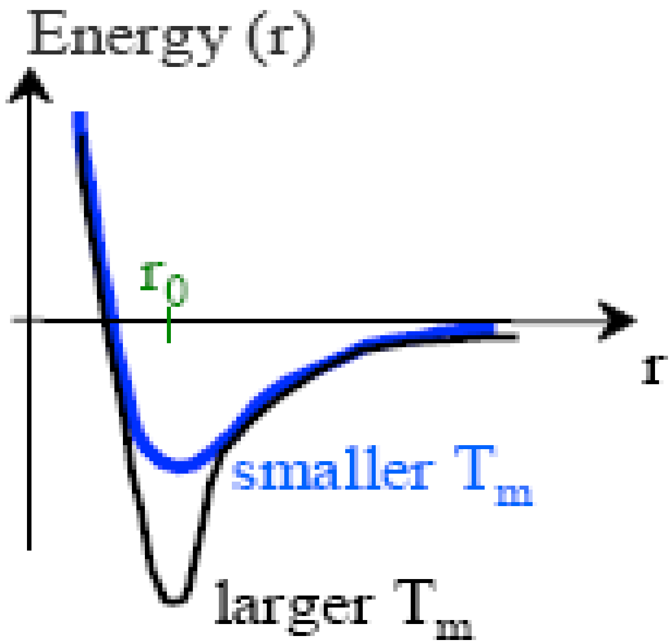
***R_0*: equilibrium distance**

***-U(R_0)*: binding energy or cohesive energy.**

Relationship Between Binding Energy and Melting Point

binding energies ↑

melting temperatures↑

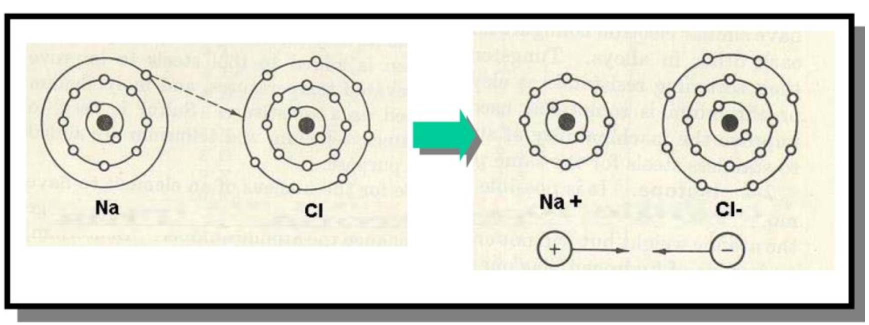


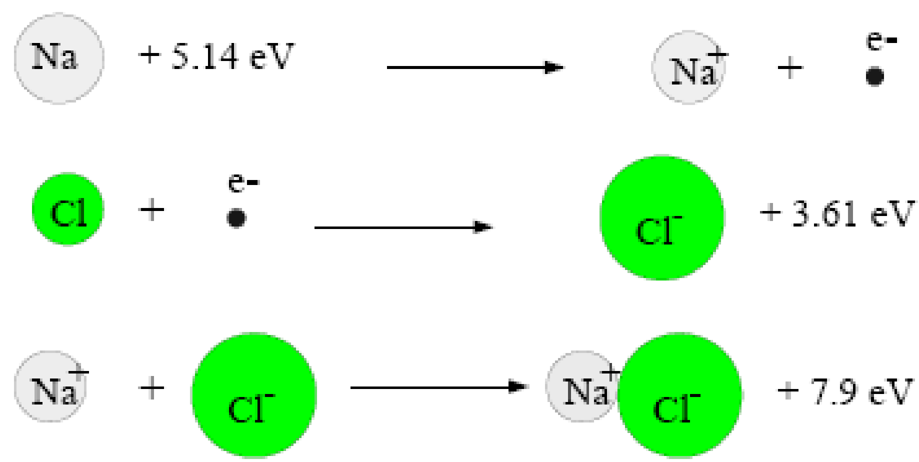
A higher binding energy means a higher melting point!

Ionic Crystal - Ionic Bond

Ionic bond is formed between atoms with large differences in electronegativity.
Group 1 alkali metals —— Li、Na、K、Rb、Cs
Group 7 halogen elements—— F、Cl、Br、I
A transfer of electrons between two atoms results the electrostatic force of attraction between positively and negatively charged ions

- **Binding Energy: 150~370 *kcal/mol***
- **Typical Crystal Structure：NaCl、CsCl 、ZnS**





Cohesive Energy in Ionic Crystals

The interaction between two ions can be described as:

$$U(R)=\frac{-a}{R^m}+\frac{b}{R^n} \qquad u(r)=-\frac{\delta q^2}{4\pi\varepsilon_0 r}+\frac{b}{r^n}$$

q: charges of ion,
δ= +1 for the unlike charges
δ= -1 for the like charges

For a crystal with N cations and N anions, the total cohesive energy are:

$$U=\frac{1}{2}(2N)\sum_{j=1}^{2N-1}\left(-\frac{\delta_j q^2}{4\pi\varepsilon_0 r_j}+\frac{b}{r_j^n}\right) \xrightarrow{r_j=\ell_j r} U(r)=-\frac{N\alpha q^2}{4\pi\varepsilon_0 r}+\frac{NB'}{r^n}$$

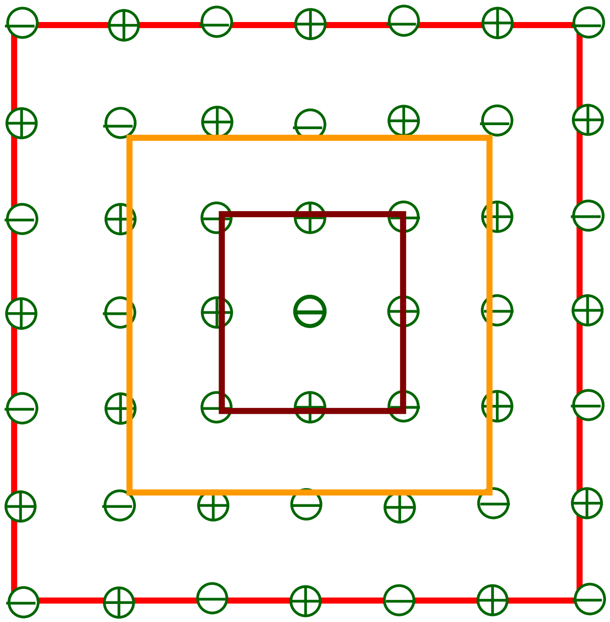
Here r : the nearest distance between two atoms

$$B'=\sum_{j=1}^{2N-1}\frac{b}{l_j^n} \qquad \alpha=\sum_{j=1}^{2N-1}\frac{\delta_j}{l_j} \longleftarrow \text{Madelung constant}$$

How to calculate a Madelung constant?

In 2-D ionic crystal,

$$\boxed{\alpha = \sum_{j \neq 0} \frac{\delta_j}{\ell_j}} \qquad r_j = \ell_j r$$



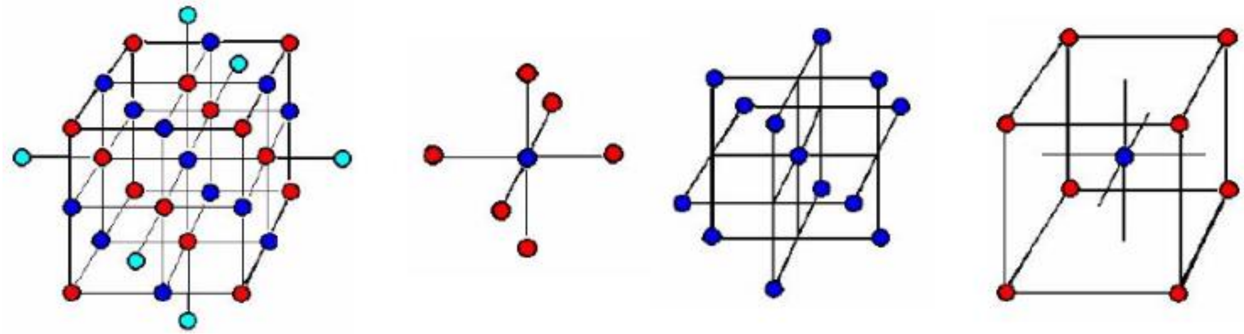
$$\alpha_1 = 4 \cdot \frac{1}{2} \cdot \frac{1}{1} - 4 \cdot \frac{1}{4} \cdot \frac{1}{\sqrt{2}} \approx 1.293$$

$$\alpha_2 = 4 - 4 \cdot \frac{1}{\sqrt{2}} - 4 \cdot \frac{1}{2} \cdot \frac{1}{2} + 8 \cdot \frac{1}{2} \cdot \frac{1}{\sqrt{5}} - 4 \cdot \frac{1}{4} \cdot \frac{1}{2\sqrt{2}} \approx 1.607$$

$$\alpha_3 \approx 1.6105$$

Example: Madelung Constant of NaCl Crystal

$$\alpha = \sum_{j \neq 0} \frac{\delta_j}{\ell_j}$$



Taking Na^+ as reference ion: First near: 6 Cl^-, r=1, R=1/2; Second near: 12 Na^+, $r=2^{1/2}$, R=1/4; Third near: 8 Cl^-, $r=3^{1/2}$, R=1/8

$$\alpha = \frac{1}{2}\times 6 - \frac{1}{4}\times\frac{1}{\sqrt{2}}\times 12 + \frac{1}{8}\times\frac{1}{\sqrt{3}}\times 8 = 1.457$$

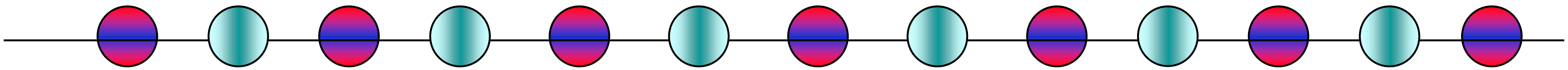
$$\alpha = \frac{1}{2}\times 6 - \frac{1}{4}\times\frac{1}{\sqrt{2}}\times 12 + \frac{1}{8}\times\frac{1}{\sqrt{3}}\times 8 + \ldots$$

The bigger the cell , the more exactness the Madelung constant is.

structure	NaCl	CsCl	Cubic ZnS
α	1.748	1.763	1.638

Practice

A chain consisting of univalent cations and anions is shown as follow, please calculate the Madelung constant.



$$\alpha = \sum_{j \neq 0} \frac{\delta_j}{\ell_j} = ?$$

How to calculate B' and n

$$U(r) = -\frac{N\alpha q^2}{4\pi\varepsilon_0 r} + \frac{NB'}{r^n}$$

$$B' = \sum_{j=1}^{2N-1} \frac{b}{l_j^n}$$

For B'

$$\left.\frac{\partial U}{\partial r}\right|_{r_0} = -\frac{N}{2}\left[-\frac{\alpha q^2}{4\pi\varepsilon_0 r^2} + \frac{nB'}{r^{n+1}}\right]_{r_0} = 0 \longrightarrow B' = \frac{\alpha q^2}{4\pi\varepsilon_0 n} r_0^{n-1}$$

$$\left.\begin{aligned} &U = f(B', n, r) \\ &B' = f_1(n) \\ &K = f_2(U, r) \end{aligned}\right\} \Rightarrow n = f_3(K)$$

K 由实验确定 $\to n \to B' \Rightarrow U$

How to calculate B' and n

$$U(r) = -\frac{N\alpha q^2}{4\pi\varepsilon_0 r} + \frac{NB'}{r^n}$$

$$B' = \sum_{j=1}^{2N-1} \frac{b}{l_j^n}$$

For B'

$$\left.\frac{\partial U}{\partial r}\right|_{r_0} = -\frac{N}{2}\left[-\frac{\alpha q^2}{4\pi\varepsilon_0 r^2} + \frac{nB'}{r^{n+1}}\right]_{r_0} = 0 \longrightarrow B' = \frac{\alpha q^2}{4\pi\varepsilon_0 n} r_0^{n-1}$$

For n

$V = N\gamma r^3$ γ -volume factor

$$\frac{\partial U}{\partial V} = \frac{\partial U}{\partial r}\frac{\partial r}{\partial V} = \frac{\partial U}{\partial r}\frac{1}{3\gamma N r^2}$$

$$\frac{\partial^2 U}{\partial V^2} = \frac{\partial}{\partial V}\left(\frac{\partial U}{\partial V}\right) = \ldots = \frac{1}{9\gamma^2 N^2 r^4}\frac{\partial^2 U}{\partial r^2} - \frac{2}{9\gamma^2 N^2 r^5}\frac{\partial U}{\partial r}$$

	γ
CsCl structure	$\frac{4}{3\sqrt{3}}$
ZnS structure	$\frac{8}{3\sqrt{3}}$
NaCl structure	1

$$K = -V\frac{\mathrm{d}p}{\mathrm{d}V} = V_0\left(\frac{\mathrm{d}^2 U}{\mathrm{d}V^2}\right)_{V_0} = N\gamma r_0^3 \frac{1}{9\gamma^2 N^2 r_0^4}\left(\frac{\partial^2 U}{\partial r^2}\right)_{r_0} = \frac{1}{9\gamma N r_0}\left(\frac{\partial^2 U}{\partial r^2}\right)_{r_0} \longrightarrow n = 1 + \frac{72\pi\varepsilon_0\gamma r_0^4}{q^2\alpha e^2}K$$

r_0 and K are decided by experiments, and γ is calculated according to the crystal structure.

How to calculate the γ of a crystal?

$$V = N\gamma R_0^3$$

CsCl structure

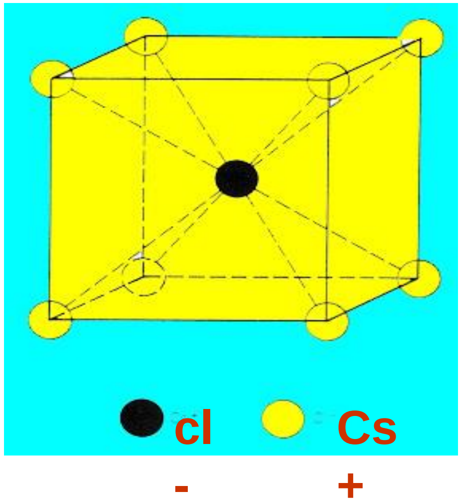
$$V = a^3, N = 2, R_0 = \frac{\sqrt{3}}{2}a,$$

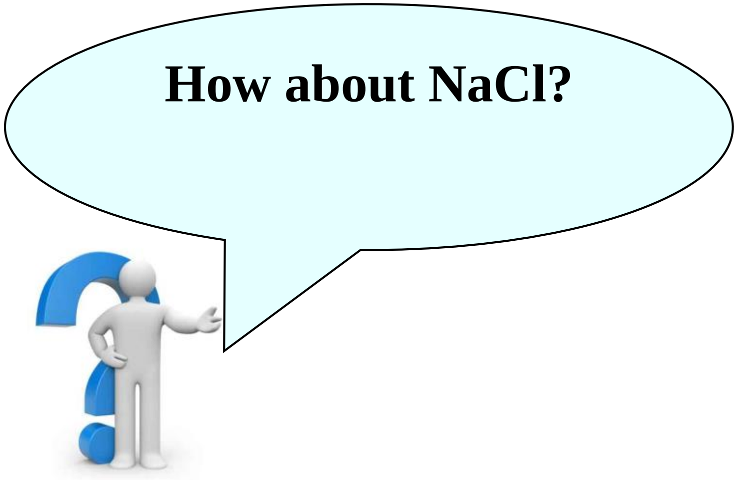
$$\gamma = \frac{4}{3\sqrt{3}}$$

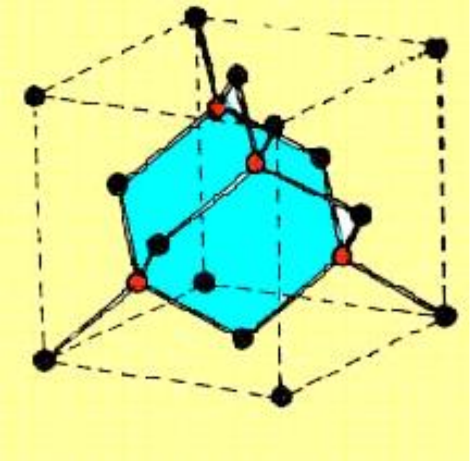
ZnS structure

$$V = a^3, \quad N = 8, R_0 = \frac{\sqrt{3}}{4}a$$

$$\gamma = \frac{8}{3\sqrt{3}}$$







Properties of Alkali Halide Crystal with NaCl Structure

Ionic Crystal	Nearest neighbor separation R_0(Å)	Bulk modulus $E(10^{10} N/m^2)$	Cohesive Energy $U_0(10^{-16}$J/ion pair)
LiF	2.014	6.71	-1.68
LiCl	2.570	2.98	-1.38
NaCl	2.82	2.40	-1.27
NaBr	2.989	1.99	-1.21
NaI	3.237	1.51	-1.13

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Profile