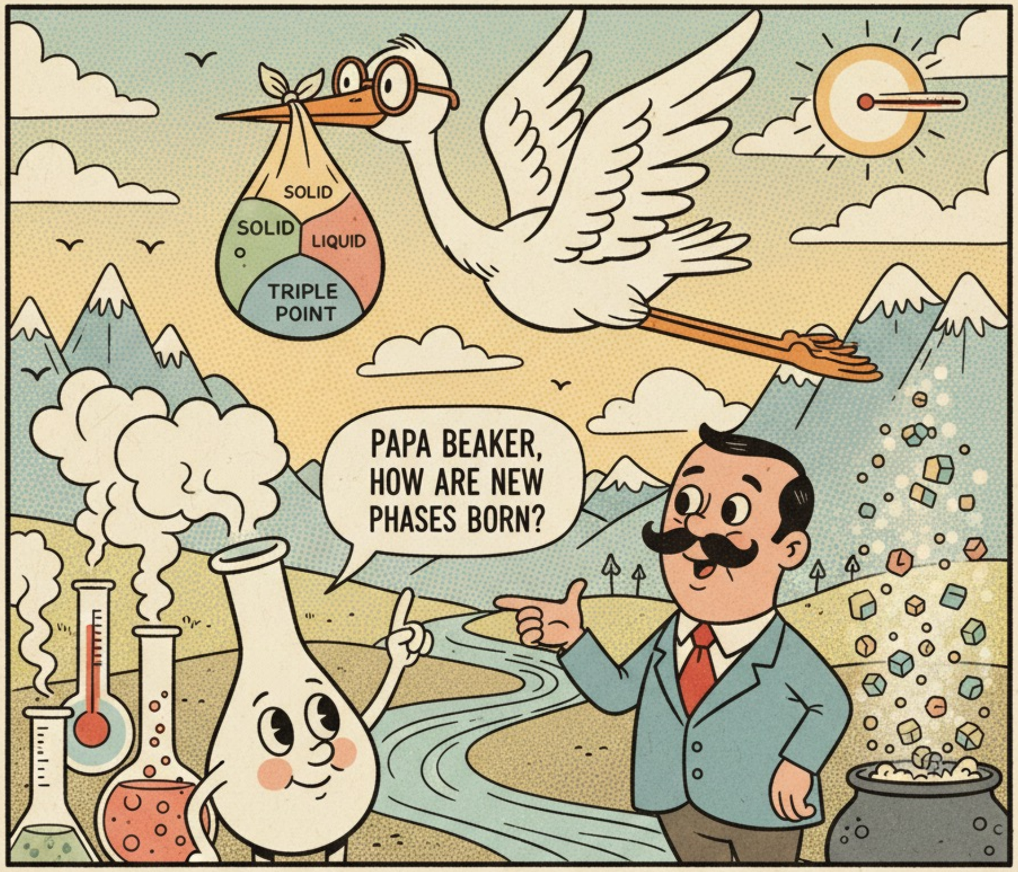
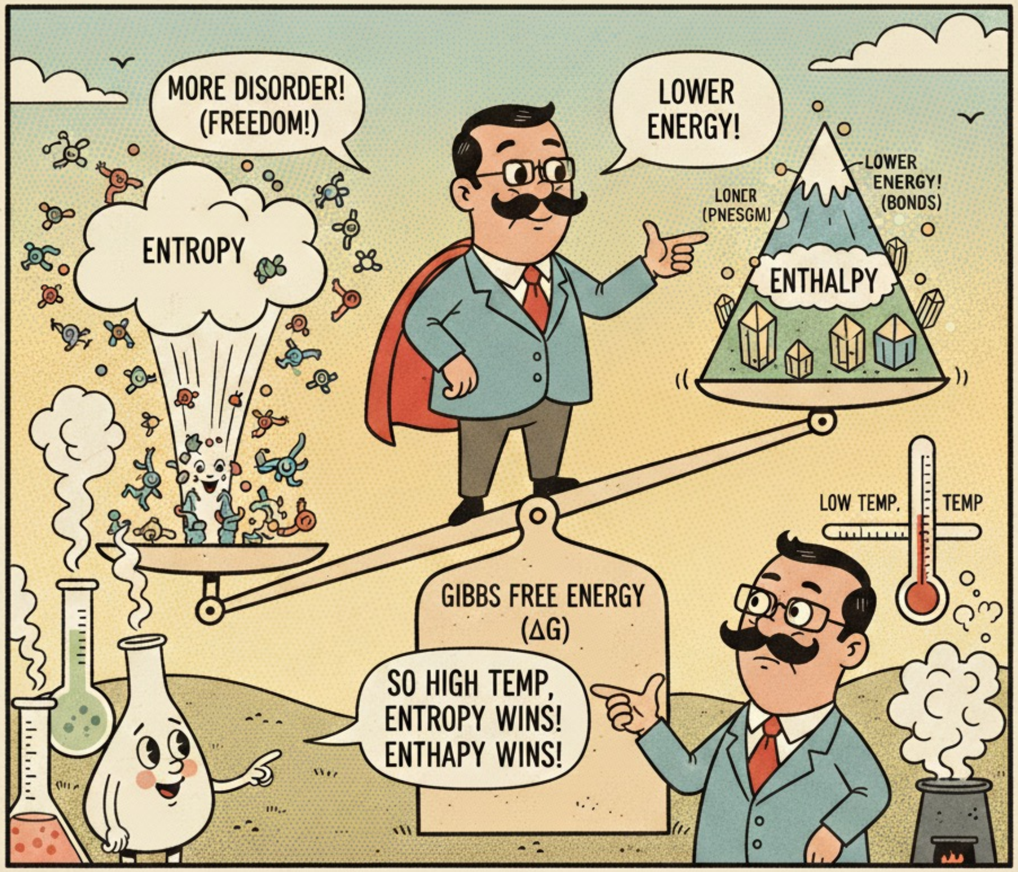
WHERE DO PHASE DIAGRAMS COME FROM?



A JOURNEY OF TEMPERATURE, PRESSURE & MOLEUCLAR LOVE

ENTROPY & ENTHAL Y: A LOVE-HATE STORY



PHASE TRANSITIONS: IT ALL DEPENDS ON THE TEMPERATURE!

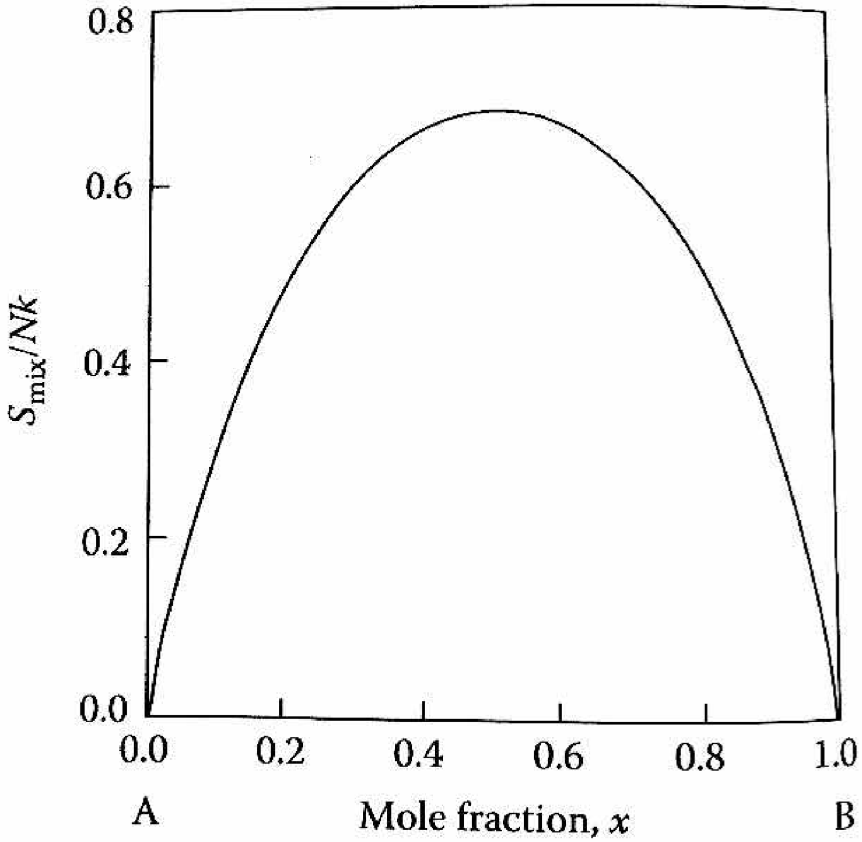
Where do Phase Diagrams Come From?

$F=U-TS$

Matter seeks to minimize the Helmoltz free energy at constant temp and Volume

$$S_{\text{mix}} = -Nk\left[\ln(1-x) + x\ln\left(\frac{1-x}{x}\right)\right]$$

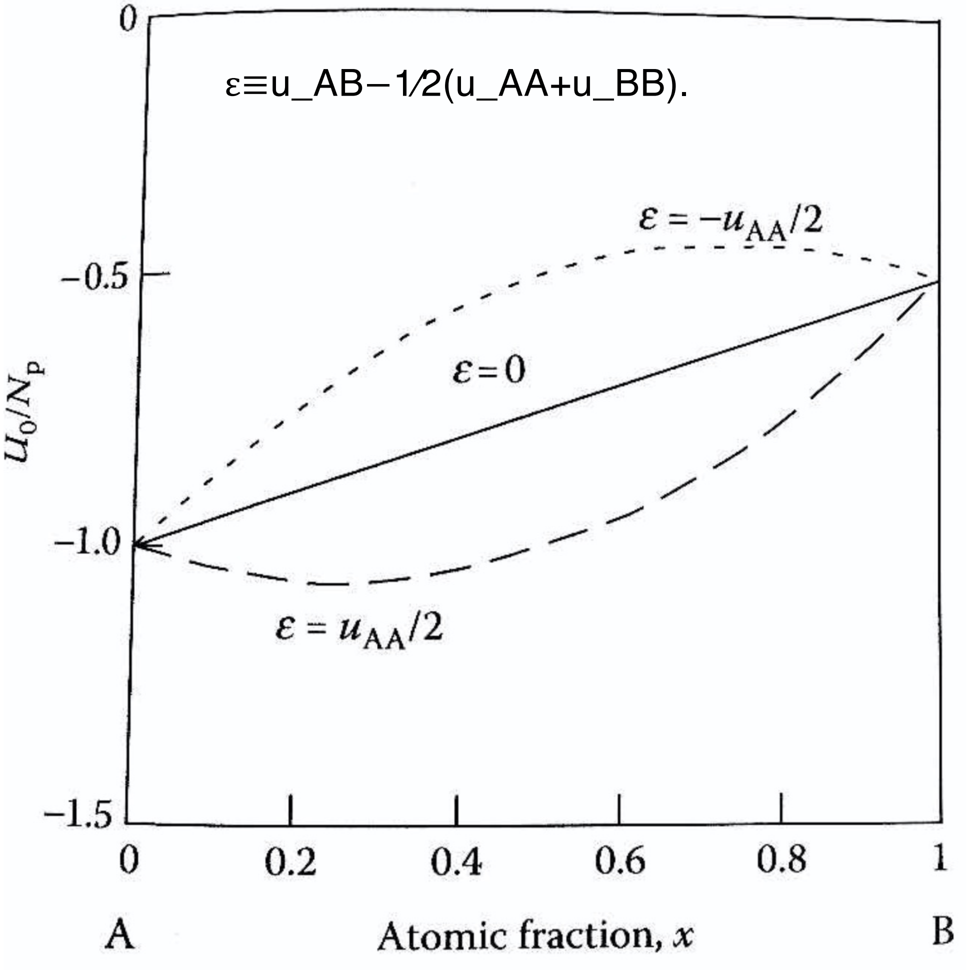
Entropy term is positive because there are more ways of rearranging 2 atoms in space then 1. Maximum at x=0.5.



$$U_{\text{tot}} = N\frac{p}{2}[(1-x)u_{AA} + xu_{BB} + 2x(1-x)\varepsilon]$$

Internal energy term is from bonding, which can be energetically favorable or unfavorable.

P is number of nearest neighbors.



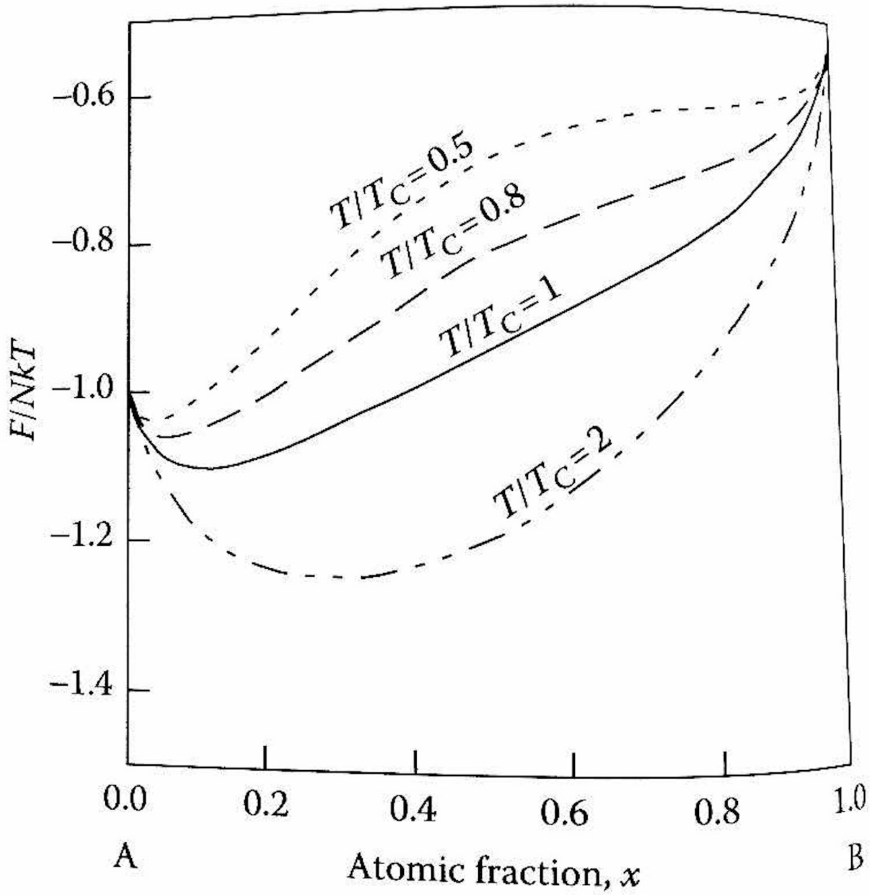
F(x,T)=ΔU(x)−T S_mix(x)

$$F(x,T) = \frac{Np}{2}[(1-x)\mu_{AA} + x\mu_{BB} + 2x(1-x)\varepsilon] + NkT[(1-x)\ln(1-x) + x\ln(x)]$$

At High T, Entropy Term dominates and mixing is favorable.

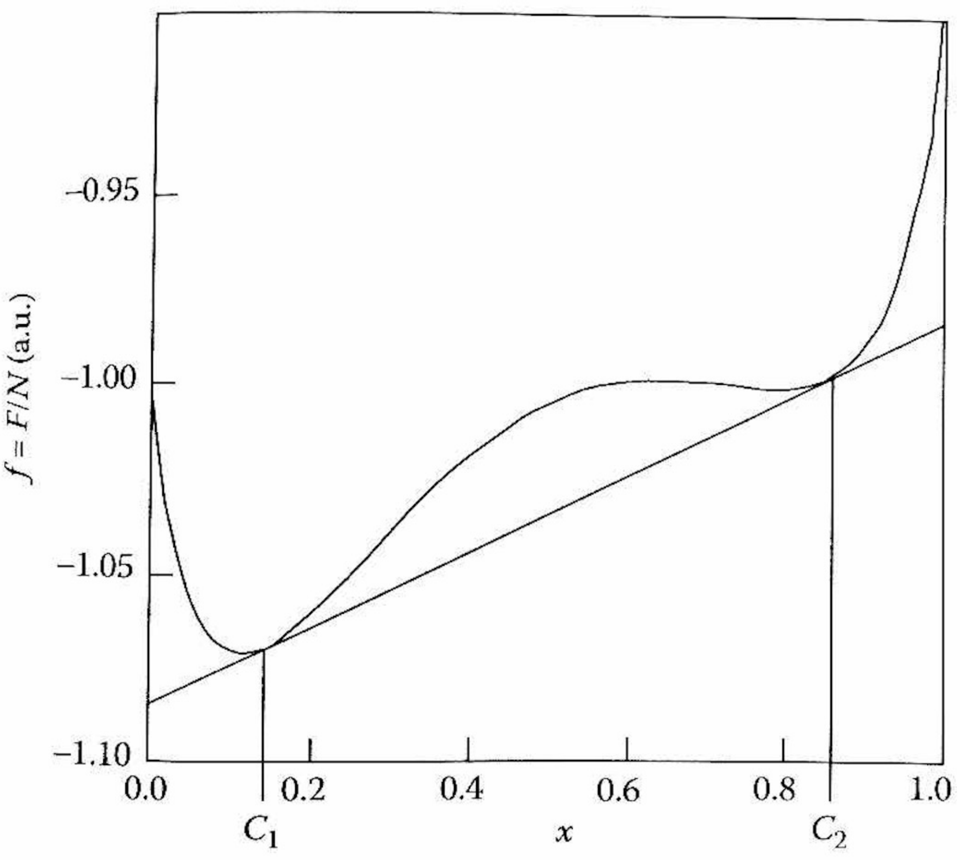
At low T, local minima appear, leading to phase segregation.

$T_c = p\varepsilon/2k$
p = #nearest neighbors
ε= energy penalty per unlike bond
k= Boltzmann constant

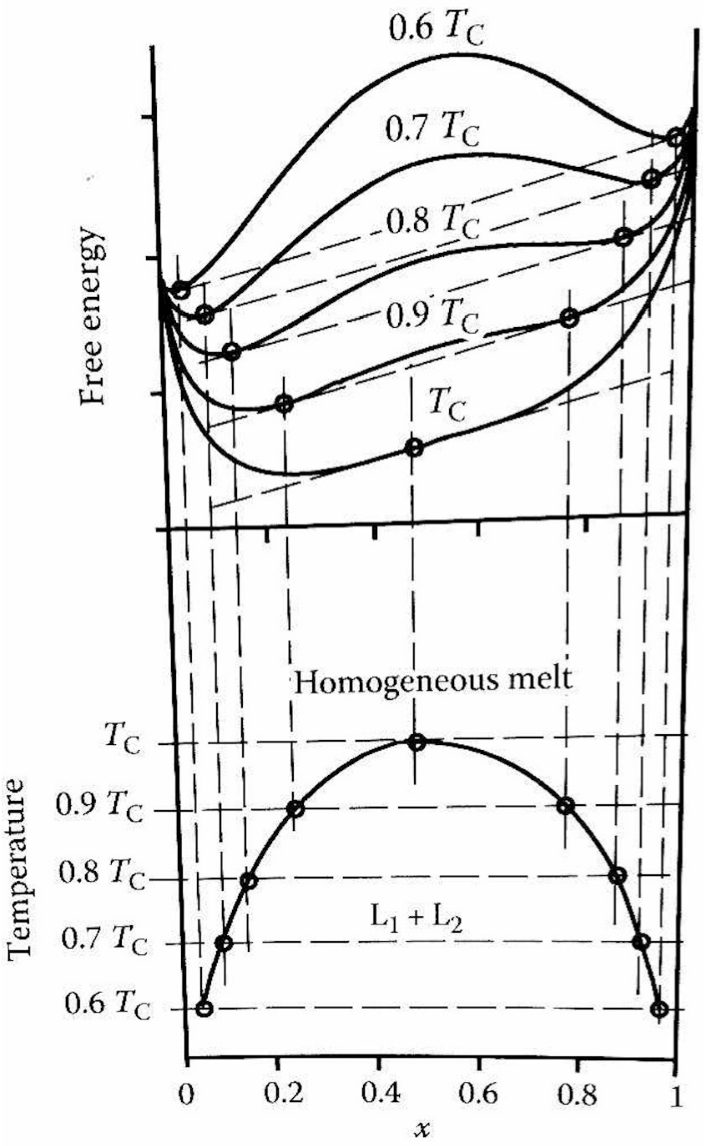


Method of Tangents

Method of Tangents can be used to find the compositions of each phase that are in equilibrium, in this case 13.2 % for alpha and 85.9 % for beta.



Applying the method of Tangents to free energy curves at different temperatures can be used to create a phase diagram.



Example of real ideal system (no heat of mixing)

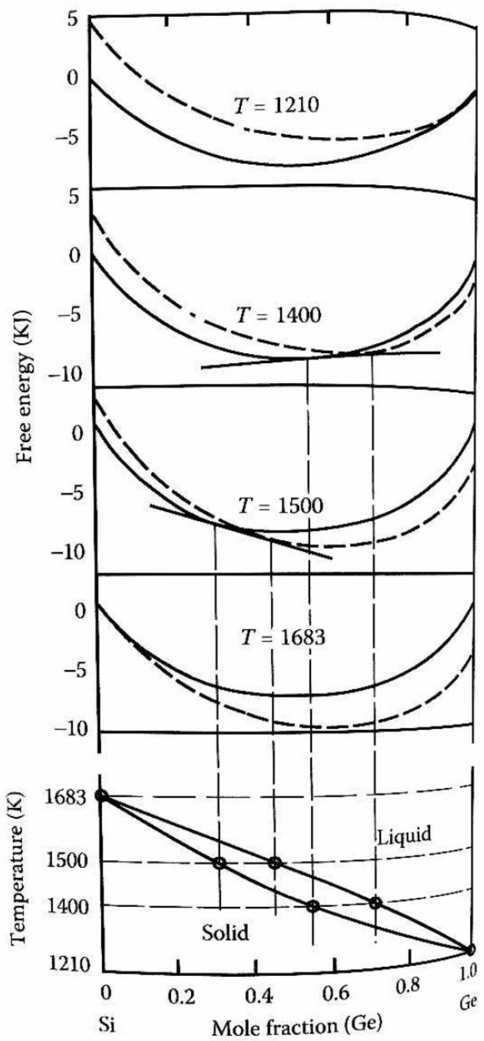


FIGURE 12.7

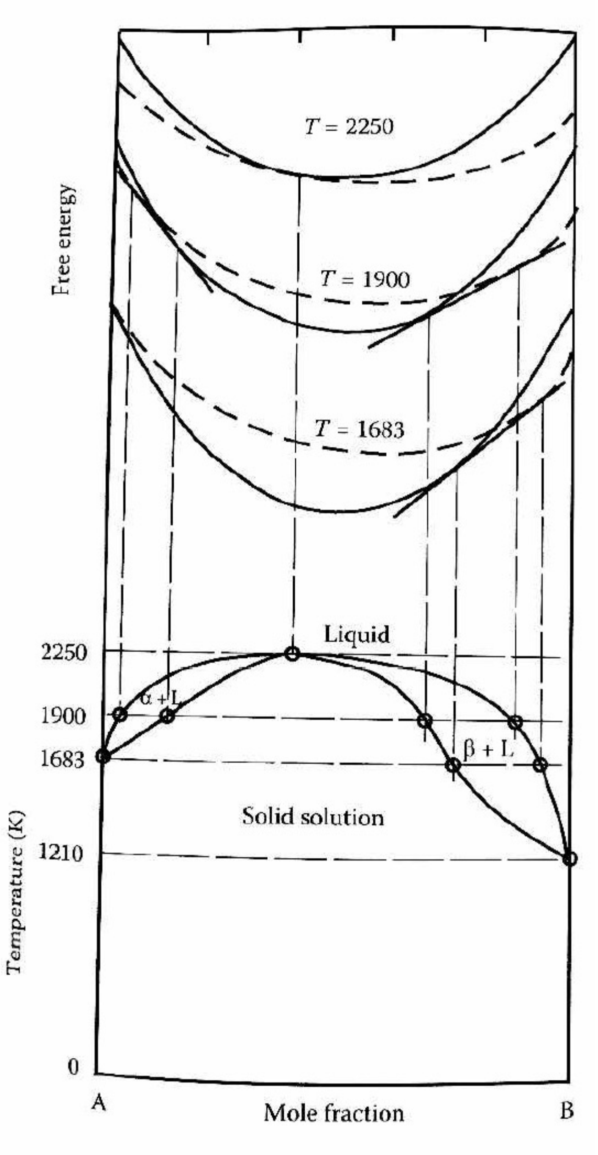
Construction of a phase diagram for the Si–Ge system, which is assumed to be isomorphic with no excess energy of mixing in either phase. The solid lines represent the free energy of the solid phase and the dashed line represent the free energies of the liquid phase. In the phase diagram, the line above which everything is liquid is the liquidus line. The line below which everything is solid is the solidus line. Liquid and solid coexist in the region between these two lines.

$$F_S(x \cdot T) = RT(x \ln(x) + (1 - x) \ln(1 - x))$$

$$F_L(x \cdot T) = RT(x \ln(x) + (1 - x) \ln(1 - x)) + \Delta S[x(T_B - T) + (1 - x)(T_A - T)].$$

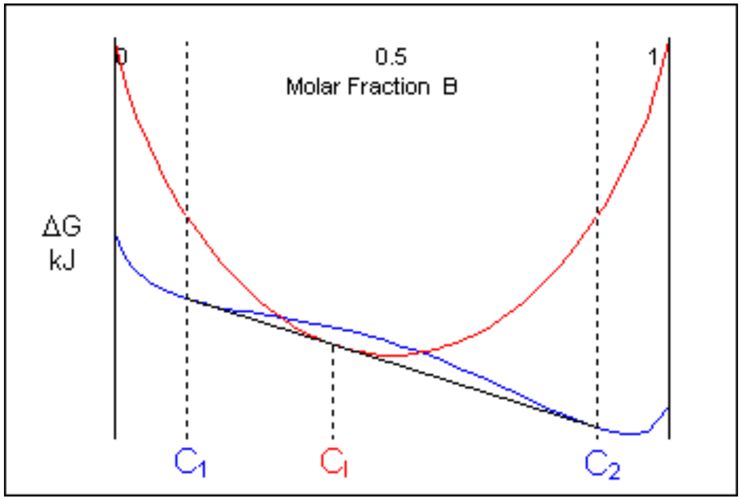
Example of system with heat of mixing of -30 kJ/mol

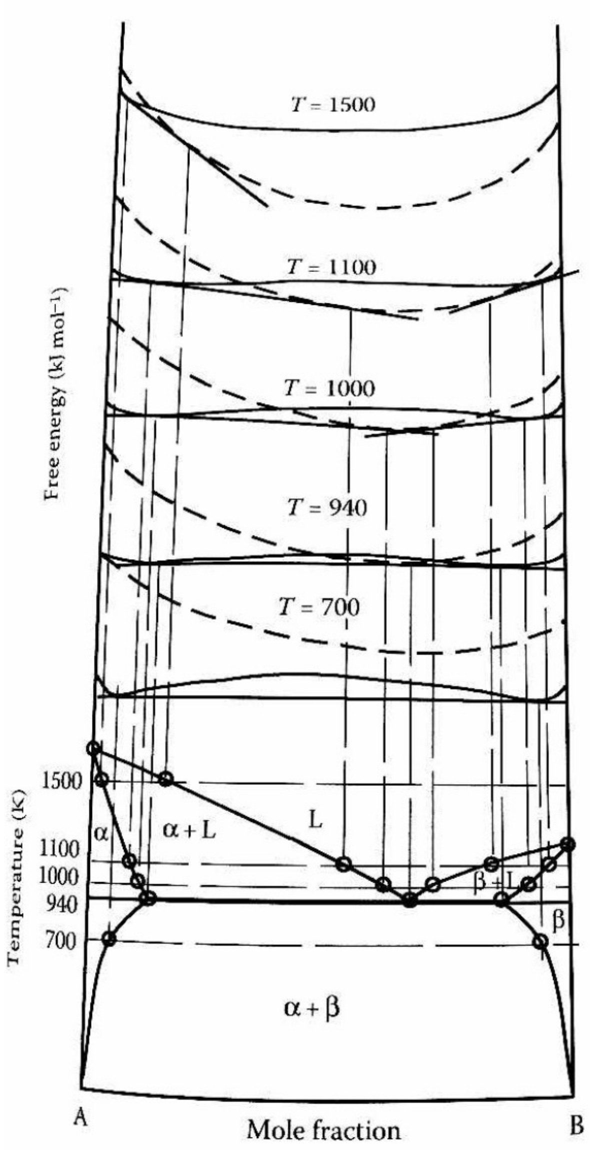
Positive heat of mixing means the melting point of the alloy is not higher than the melting point of the pure phases.



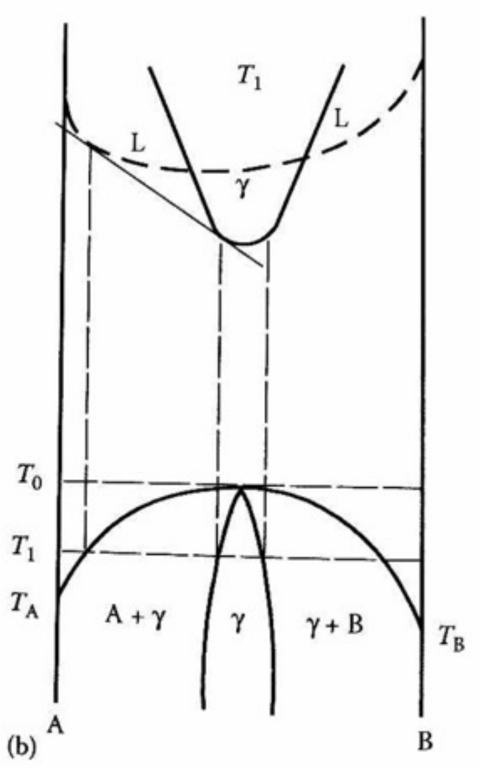
Example of system with Positive heat of mixing.

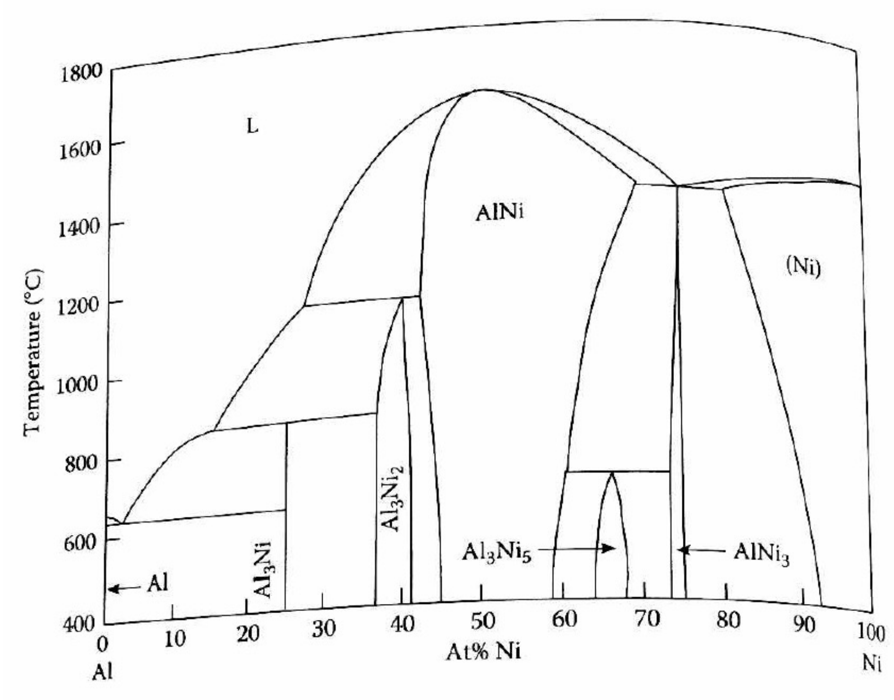
The point where the liquid line minima meets the tangents of the two solid phase minima leads to a lower melting point eutectic.



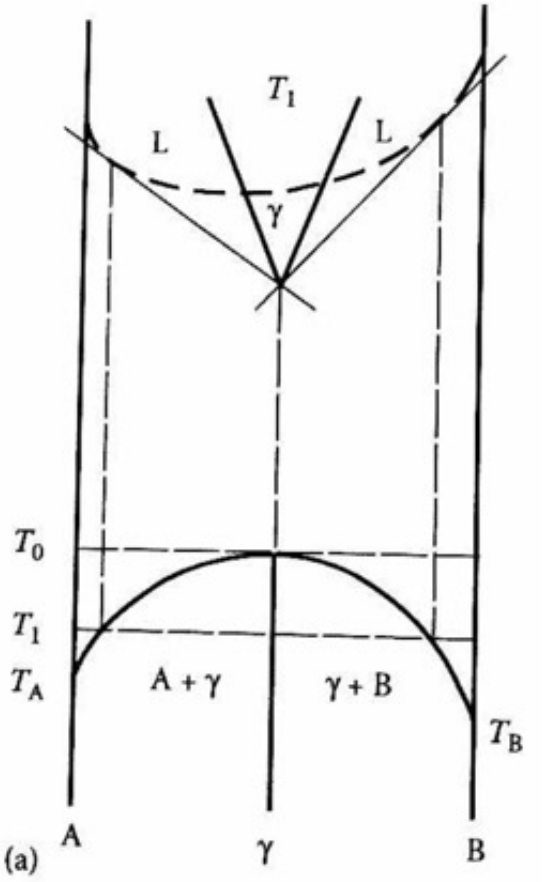


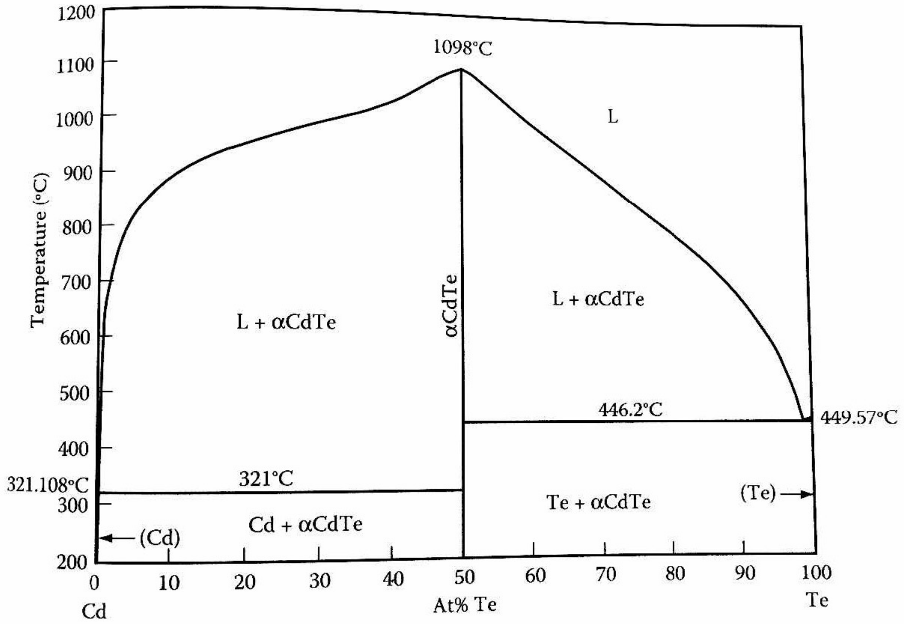
Example of solid solution intermediate phase



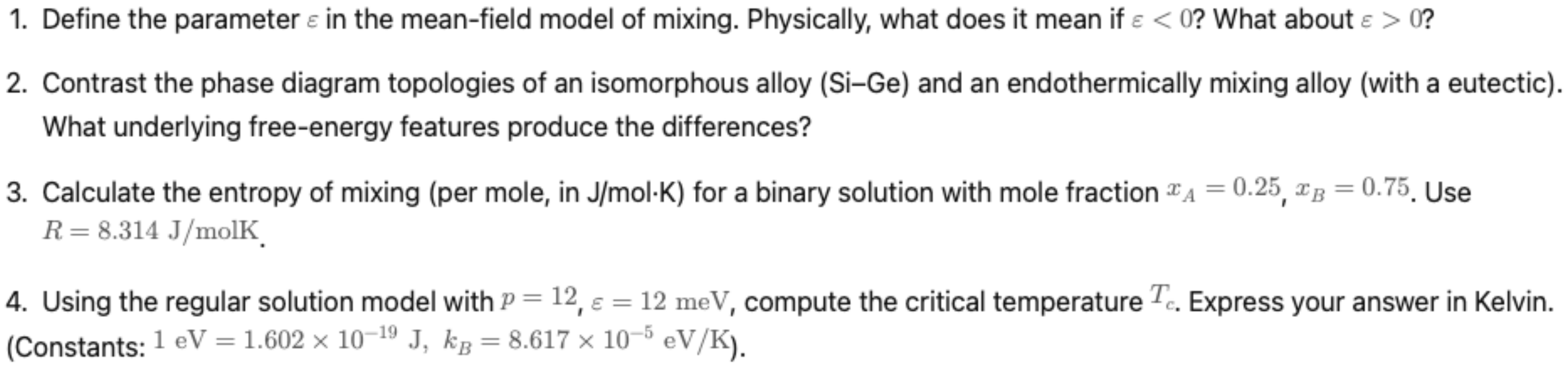


Example of Line compound.





Homework Questions



1. Define the parameter ε in the mean-field model of mixing. Physically, what does it mean if $\varepsilon < 0$? What about $\varepsilon > 0$?
2. Contrast the phase diagram topologies of an isomorphous alloy (Si–Ge) and an endothermically mixing alloy (with a eutectic). What underlying free-energy features produce the differences?
3. Calculate the entropy of mixing (per mole, in J/mol·K) for a binary solution with mole fraction $x_A = 0.25$, $x_B = 0.75$. Use $R = 8.314\ \mathrm{J/molK}$.
4. Using the regular solution model with $p = 12$, $\varepsilon = 12\ \mathrm{meV}$, compute the critical temperature T_c. Express your answer in Kelvin. (Constants: $1\ \mathrm{eV} = 1.602 \times 10^{-19}\ \mathrm{J},\ k_B = 8.617 \times 10^{-5}\ \mathrm{eV/K}$).

Ionic Bonding

By the end of this lecture, you should be able to:

- Explain why chemical bonding connects **structure** to **properties** of materials.
- Define **ionic bonding** as electrostatic interactions between point charges.
- Apply Coulomb's law to estimate attractive vs. repulsive interactions between ions.
- Describe how **coordination number** and **structure type** affect the **Madelung constant**.
- Explain what the **Madelung constant** represents and why it differs for NaCl, CsCl, ZnS, etc.
- Define **lattice energy** and distinguish between lattice **energy** and lattice **enthalpy**.
- Use the **Born–Mayer equation** to estimate lattice energies, recognizing the role of repulsive terms.

Coulomb Interaction

$$U_C = \frac{\overbrace{(z_1 e)\cdot(z_2 e)}^{\text{magnitude of the charges}}}{4\pi\varepsilon_0 d}$$

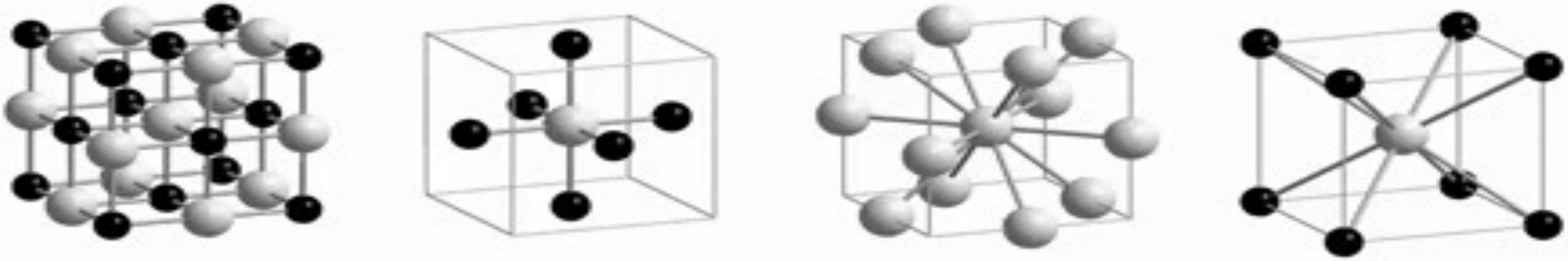
distance between charges

Cation-Anion Interaction - Attractive

Anion-Anion Interaction - Repulsive

Cation-Cation Interaction - Repulsive

Madelung Sum



1st nearest neighbors

2nd nearest neighbors

3rd nearest neighbors

$$V_{\mathrm{C}} = \frac{(z_1 e)\cdot(z_2 e)}{4\pi\varepsilon_0 d}\left(\frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}} - \frac{24}{\sqrt{6}} - \frac{12}{\sqrt{8}}\cdots\right)$$

If the shells are chosen in the right way (charge neutral shells) this sum converges to a value of **1.7476**. This is the Madelung constant, A for the NaCl structure type

Madelung Constants and Structure Type

Structure Type	*Coordination*	A	*Structure Type*	*Coordination*	A
Cesium chloride	$Cs^{[8]}\,Cl^{[8]}$	1.763	Fluorite	$Ca^{[8]}\,F_2^{[4]}$	2.519
Rock salt	$Na^{[6]}\,Cl^{[6]}$	1.748	Rutile	$Ti^{[6]}\,O_2^{[3]}$	2.408
Wurtzite	$Zn^{[4]}\,S^{[4]}$	1.641	Cadmium chloride	$Cd^{[6]}\,Cl_2^{[3]}$	2.244
Zinc blende	$Zn^{[4]}\,S^{[4]}$	1.638	Cadmium iodide	$Cd^{[6]}\,I_2^{[3]}$	2.192

Electrostatic interactions favor symmetric structures with close packing of anions and cations and high coordination numbers.

Lattice Energy

Lattice Energy (U_L):
The amount of energy that is released when one mole of a crystal is formed from its constituent ions at infinite separation in the gas phase at $T = 0$ K

$$a\,\mathrm{M}^{y+}(\mathrm{g}) + b\,\mathrm{X}^{z-}(\mathrm{g}) \rightarrow \mathrm{M}_a\mathrm{X}_b(\mathrm{s})$$

Lattice energy is exothermic

Lattice energy is approximately equal to lattice enthalpy, $U_L = H_L$

Lattice Energy

$$U_C = \frac{z_1 z_2 e^2 N_A}{4\pi\varepsilon_0 d} A$$

The lattice energy in the absence of repulsive forces

distance between ions

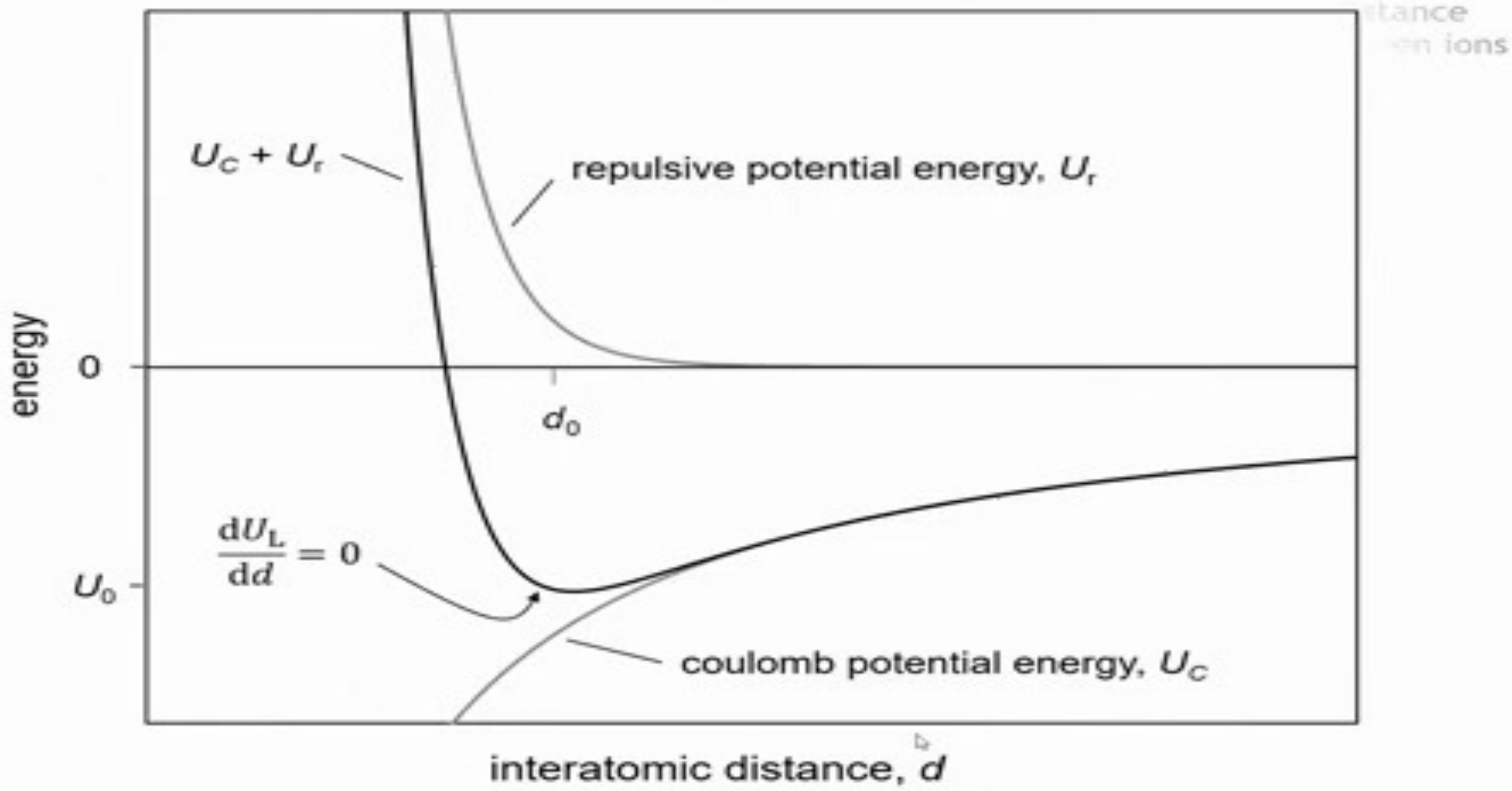
$$U_r = Be^{-\frac{d}{\rho}}$$

0.345 Å

Repulsive interactions, caused by overlap of core orbitals

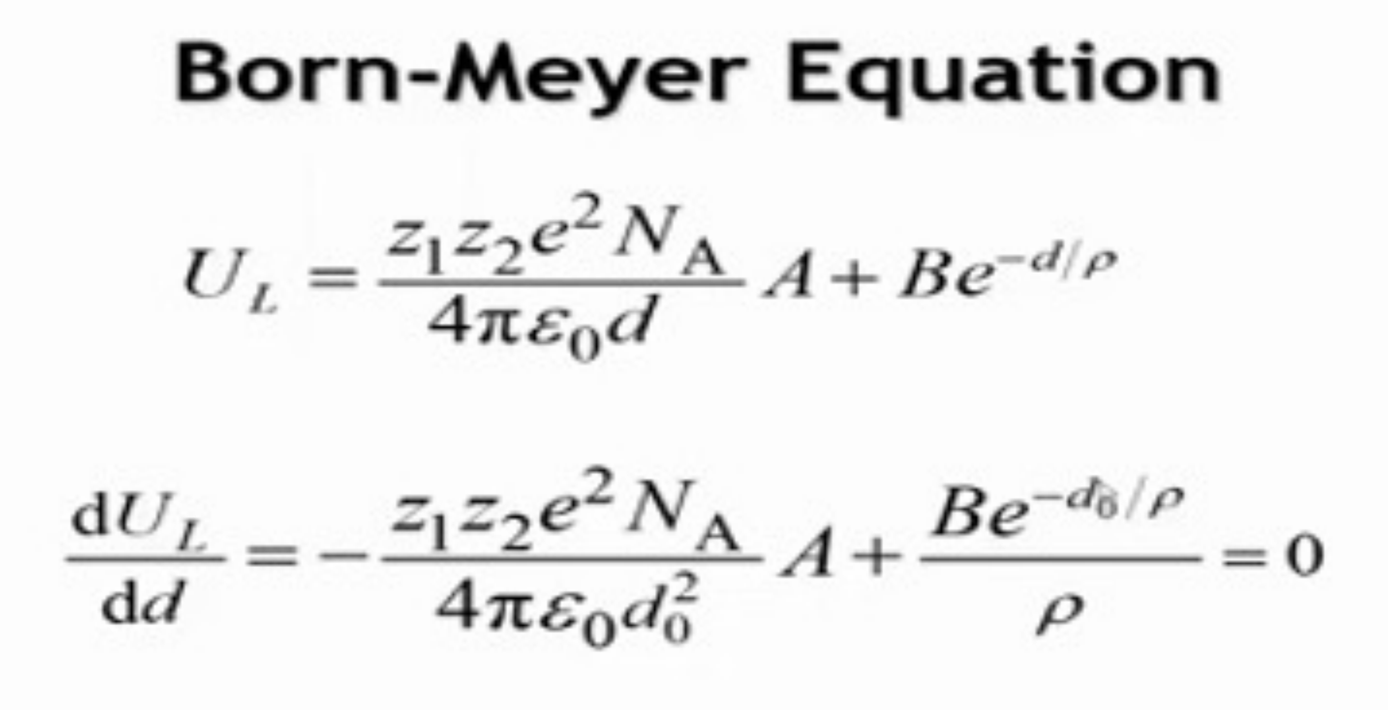
Combining these two gives the Born-Meyer equation

$$U_L = U_C + U_r = \frac{z_1 z_2 e^2 N_A}{4\pi\varepsilon_0 d} A + Be^{-d/\rho}$$


stance
en ions
$U_C + U_r$
repulsive potential energy, U_r
energy
0
d_0
$\frac{\mathrm{d}U_\mathrm{L}}{\mathrm{d}d} = 0$
U_0
coulomb potential energy, U_C
interatomic distance, d

Born-Meyer Equation

$$U_L = \frac{z_1 z_2 e^2 N_A}{4\pi\varepsilon_0 d} A + Be^{-d/\rho}$$



Born-Meyer Equation

$$U_L = \frac{z_1 z_2 e^2 N_A}{4\pi\varepsilon_0 d} A + Be^{-d/\rho}$$

$$\frac{dU_L}{dd} = -\frac{z_1 z_2 e^2 N_A}{4\pi\varepsilon_0 d_0^2} A + \frac{Be^{-d_0/\rho}}{\rho} = 0$$

Born-Meyer Equation

$$U_L = \frac{z_1 z_2 e^2 N_A}{4\pi\varepsilon_0 d} A + Be^{-d/\rho}$$

$$\frac{dU_L}{dd} = -\frac{z_1 z_2 e^2 N_A}{4\pi\varepsilon_0 d_0^2} A + \frac{Be^{-d_0/\rho}}{\rho} = 0$$

0.345 Å

$$U_L = -\frac{z_1 z_2 e^2 N_A}{4\pi\varepsilon_0 d_0} A\left(1 - \frac{\rho}{d_0}\right)$$

Equilibrium distance
between ions

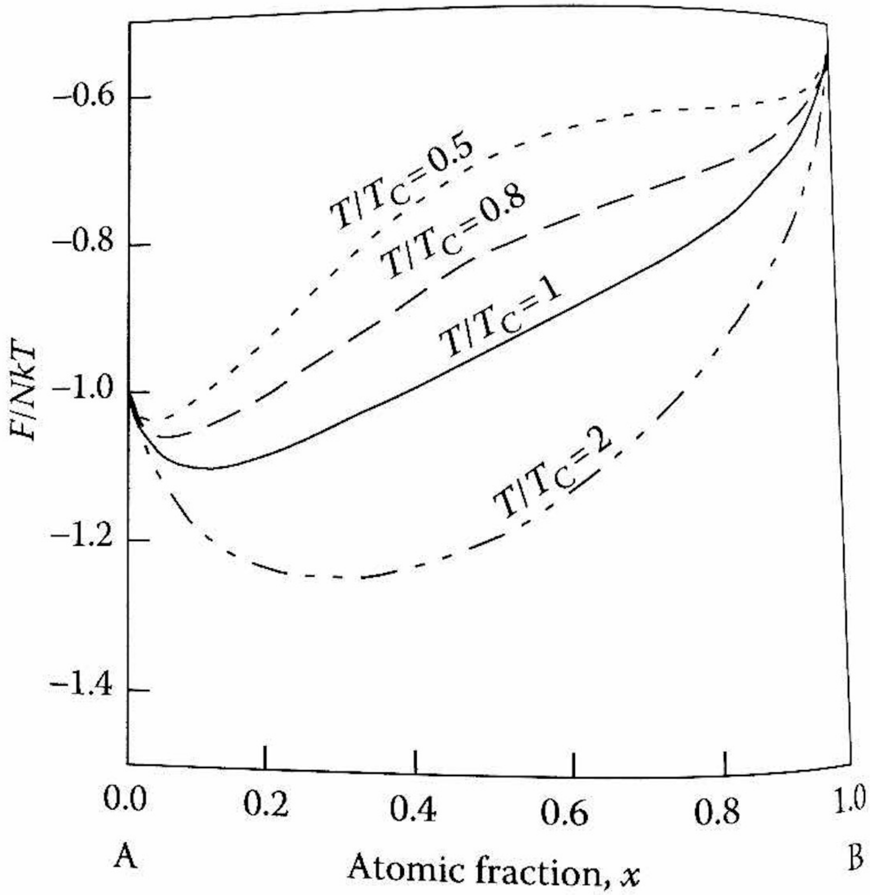
F(x,T)=ΔU(x)−T S_mix(x)

$$F(x,T) = \frac{Np}{2}\left[(1-x)\mu_{AA} + x\mu_{BB} + 2x(1-x)\varepsilon\right] + NkT\left[(1-x)\ln(1-x) + x\ln(x)\right]$$

At High T, Entropy Term dominates and mixing is favorable.

At low T, local minima appear, leading to phase segregation.

$T_c = p\varepsilon/2k$
p = #nearest neighbors
ε= energy penalty per unlike bond
k= Boltzmann constant

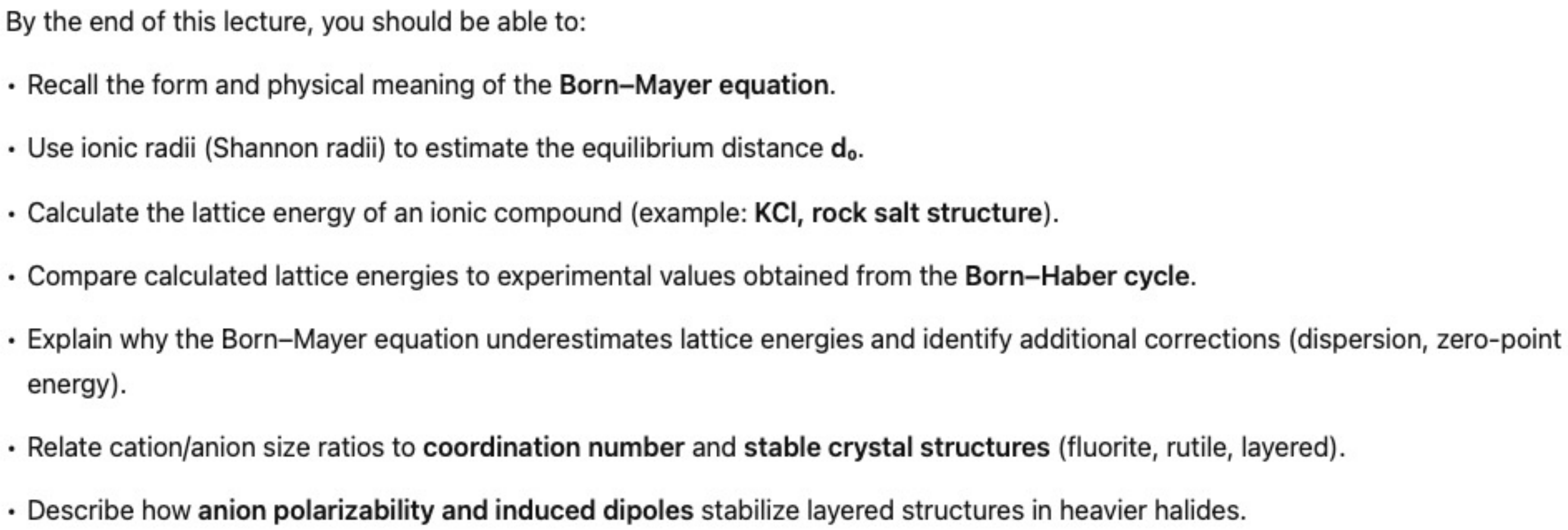


Summary – Chapter 5: Ionic Bonding

- **Bonding refresher** bridges earlier crystal structure topics to upcoming **band structure**.
- Ionic bonding model: treat ions as **point charges**; interaction energy from **Coulomb's law**.
- **Attractive vs. repulsive forces** depend on charge sign and distance.
- **Long-range nature** of Coulomb interactions requires summing over all shells of neighbors.
- Summation leads to the **Madelung constant** (e.g., 1.748 for NaCl rock salt).
    - Higher coordination → larger Madelung constant → stronger bonding.
    - Layered structures (e.g., $CdCl_2$, CdI_2) show reduced Madelung constants due to added cation–cation repulsions.
- **Lattice energy** = energy released when ions form a solid from infinite separation (exothermic).
- **Born–Mayer model** combines:
    - **Coulombic attraction** (favors collapse),
    - **Exponential repulsion** (prevents collapse),
    - Minimum → **equilibrium distance d_0**.
- **Born–Mayer equation** allows quantitative lattice energy estimates using charges, Madelung constant, and ionic radii.

Homework: 5.1 – 5.5

Part 2

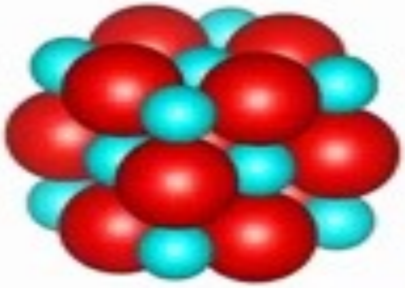


By the end of this lecture, you should be able to:

- Recall the form and physical meaning of the **Born–Mayer equation**.
- Use ionic radii (Shannon radii) to estimate the equilibrium distance **d_o**.
- Calculate the lattice energy of an ionic compound (example: **KCl, rock salt structure**).
- Compare calculated lattice energies to experimental values obtained from the **Born–Haber cycle**.
- Explain why the Born–Mayer equation underestimates lattice energies and identify additional corrections (dispersion, zero-point energy).
- Relate cation/anion size ratios to **coordination number** and **stable crystal structures** (fluorite, rutile, layered).
- Describe how **anion polarizability and induced dipoles** stabilize layered structures in heavier halides.

Lattice Energy - Example KCl

$$U_L = -\frac{z_1 z_2 e^2 N_A}{4\pi\varepsilon_0 d_0} A\left(1-\frac{\rho}{d_0}\right)$$



a = 629 pm

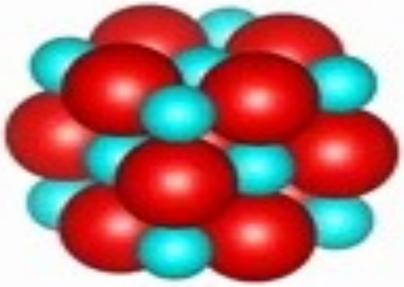
Shannon radii
http://www.knowledgedoor.com/2/elements_handbook
/shannon-prewitt_effective_ionic_radius.html

$$d_0 = r\left(\mathrm{K}^+\right) + r\left(\mathrm{Cl}^-\right) = 138\text{ pm} + 181\text{ pm} = 319\text{ pm}$$

$$U_L = -\frac{(1)(1)\left(1.602\times10^{-19}\,\mathrm{C}\right)^2\left(6.022\times10^{23}\right)}{4\pi\left(8.8542\times10^{-12}\,\frac{\mathrm{C}}{\mathrm{V\,m}}\right)\left(319\times10^{-12}\,\mathrm{m}\right)} 1.748\left(1-\frac{34.5\text{ pm}}{319\text{ pm}}\right)$$

Lattice Energy - Example KCl

$$U_L = -\frac{z_1 z_2 e^2 N_A}{4\pi\varepsilon_0 d_0} A\left(1-\frac{\rho}{d_0}\right)$$



a = 629 pm

Shannon radii
http://www.knowledgedoor.com/2/elements_handbook
/shannon-prewitt_effective_ionic_radius.html

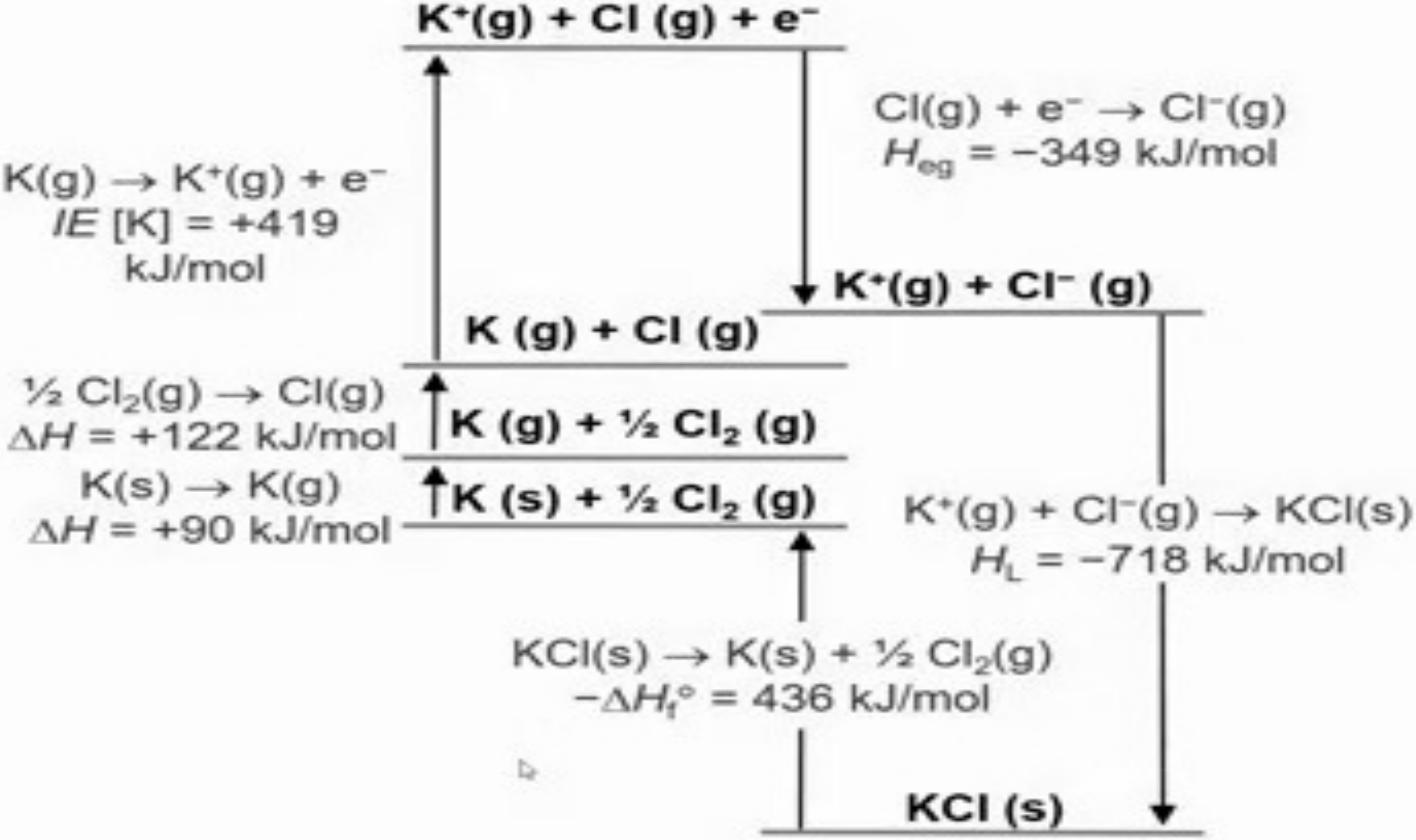
$$d_0 = r\left(\mathrm{K}^+\right) + r\left(\mathrm{Cl}^-\right) = 138\ \mathrm{pm} + 181\ \mathrm{pm} = 319\ \mathrm{pm}$$

$$U_L = -\frac{(1)(1)\left(1.602\times10^{-19}\,\mathrm{C}\right)^2\left(6.022\times10^{23}\right)}{4\pi\left(8.8542\times10^{-12}\ \frac{\mathrm{C}}{\mathrm{V\,m}}\right)\left(319\times10^{-12}\,\mathrm{m}\right)} 1.748\left(1-\frac{34.5\ \mathrm{pm}}{319\ \mathrm{pm}}\right)$$

$$U_L = -\left(7.61\times10^5\ \mathrm{J}\right)\left(1-0.108\right) = -6.79\times10^5\ \mathrm{J} = -679\ \mathrm{kJ}$$

Born-Haber Cycle

Experimental determination of Lattice Energy



$K^+(g) + Cl\ (g) + e^-$

$Cl(g) + e^- \rightarrow Cl^-(g)$
$H_{eg} = -349$ kJ/mol

$K(g) \rightarrow K^+(g) + e^-$
IE [K] = +419 kJ/mol

$K^+(g) + Cl^-\ (g)$

$K\ (g) + Cl\ (g)$

$\frac{1}{2}\ Cl_2(g) \rightarrow Cl(g)$
$\Delta H = +122$ kJ/mol

$K\ (g) + \frac{1}{2}\ Cl_2\ (g)$

$K(s) \rightarrow K(g)$
$\Delta H = +90$ kJ/mol

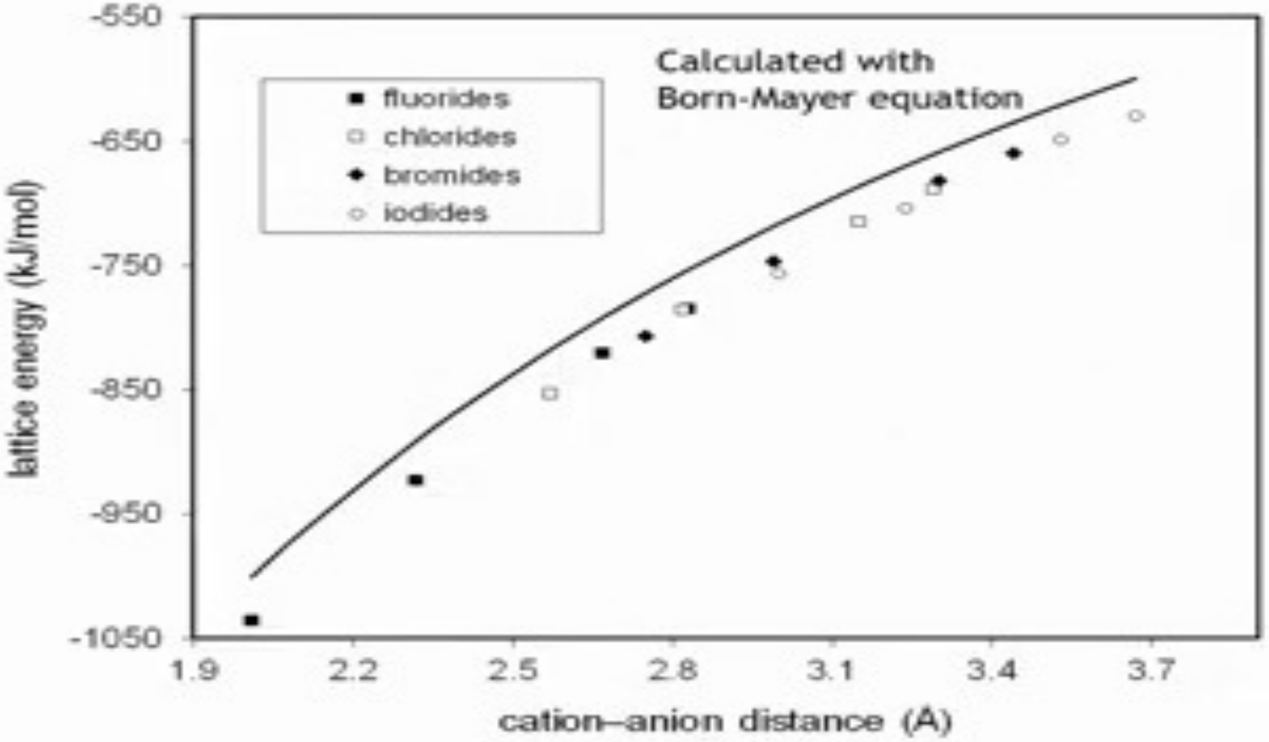
$K\ (s) + \frac{1}{2}\ Cl_2\ (g)$

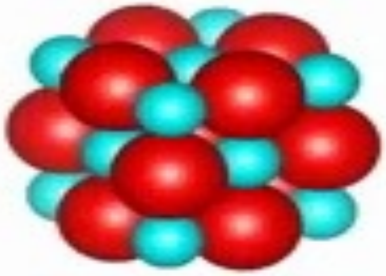
$K^+(g) + Cl^-(g) \rightarrow KCl(s)$
$H_L = -718$ kJ/mol

$KCl(s) \rightarrow K(s) + \frac{1}{2}\ Cl_2(g)$
$-\Delta H_f° = 436$ kJ/mol

$KCl\ (s)$

Calculated vs. Experimental Lattice Energy





Alkali metal halides

- Lattice energies drop off as ions get larger (d increases)
- Calculated values too small by 3-6%

Complete Lattice Energy Expression

$$U_L = \underbrace{-\frac{z_1 z_2 e^2 N_A}{4\pi\varepsilon_0 d_0} A}_{\text{[A] Coulomb energy}} \left(1 - \frac{\rho}{d_0}\right) - \frac{N_A C}{d_0{}^6} + 2.25 N_A h\upsilon_{\max}$$

[A] Coulomb energy

[B] Repulsive interaction (9-17%)

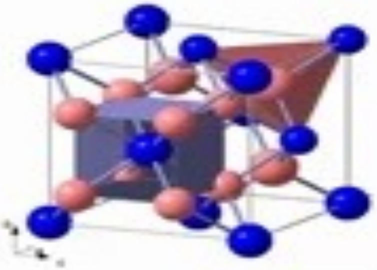
[C] Dispersion forces (0.1-5%)

[D] Zero point energy (<1.5%)

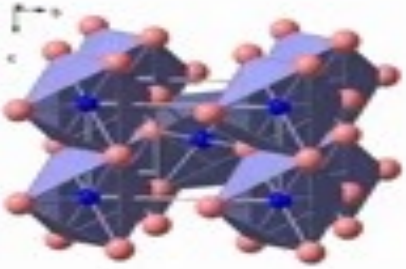
Substance	**[A] kJ**	**[B] kJ**	**[C] kJ**	**[D] kJ**
NaCl (U=−766)	−859	99	−12	7
MgO (U= −3921)	−4631	698	−6	18

Structures of MX_2 Halides

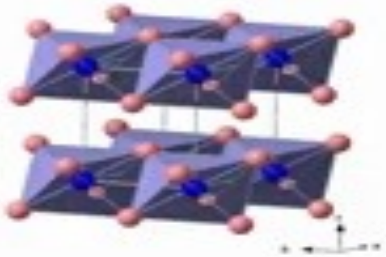
	F^- (133 pm)	Cl^- (181 pm)	Br^- (196 pm)	I^- (220 pm)
Mg^{2+} (72 pm)	rutile	$CdI_2/CdCl_2$	$CdI_2/CdCl_2$	$CdI_2/CdCl_2$
Zn^{2+} (74 pm)	rutile	$CdI_2/CdCl_2$	$CdI_2/CdCl_2$	$CdI_2/CdCl_2$
Mn^{2+} (83 pm)	rutile	$CdI_2/CdCl_2$	$CdI_2/CdCl_2$	$CdI_2/CdCl_2$
Ca^{2+} (100 pm)	fluorite	rutile	rutile	$CdI_2/CdCl_2$
Sr^{2+} (118 pm)	fluorite	fluorite	$PbCl_2$	SrI_2
Ba^{2+} (135 pm)	fluorite	fluorite	$PbCl_2$	$PbCl_2$



fluorite, $Ca^{[8]}F_2^{[4]}$
$A = 2.519$

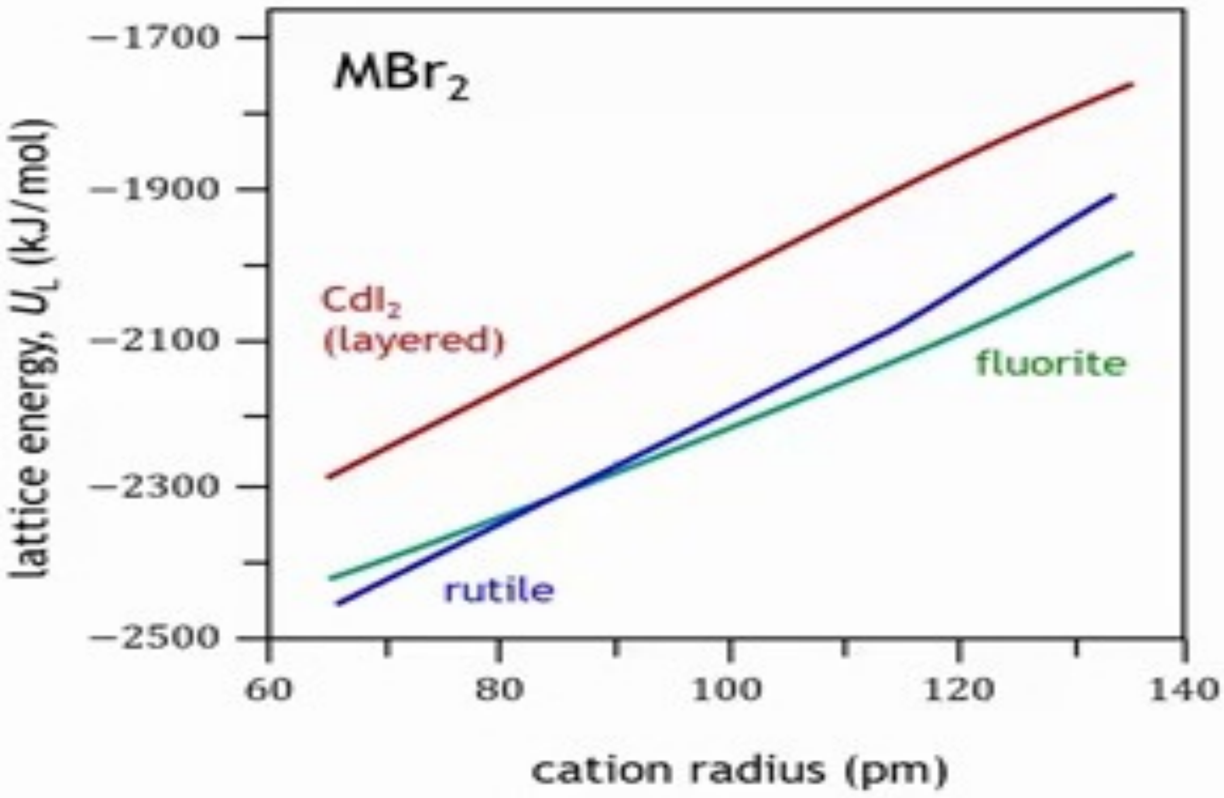


rutile, $Mg^{[6]}F_2^{[3]}$
$A = 2.408$



$Cd^{[6]}I_2^{[3]}$
$A = 2.192$

Calculated lattice energy



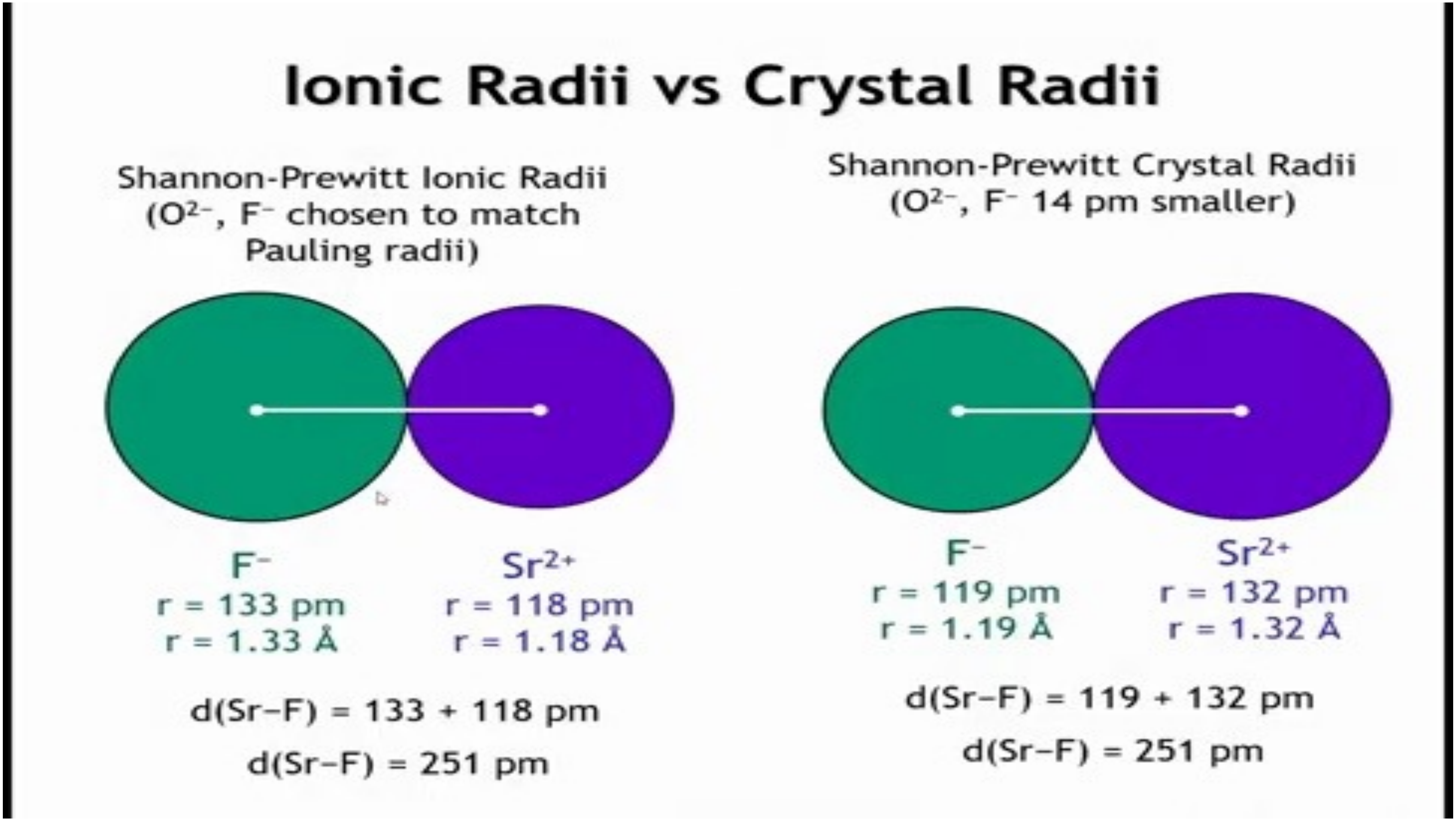
Calculations with a rigid ionic model (similar to Born-Meyer equation)

Fluorite structure has the lowest E when the cation is large

Rutile structure has the lowest E when the cation is small

CdI_2 layered structure not stable for any cation size

M. Wilson, P. A. Madden, *J. Phys. Cond. Matt.* **1994**, *6*, 159-170.



Ionic Radii vs Crystal Radii

Shannon-Prewitt Ionic Radii
(O^{2-}, F^- chosen to match
Pauling radii)

F^-
r = 133 pm
r = 1.33 Å

Sr^{2+}
r = 118 pm
r = 1.18 Å

d(Sr−F) = 133 + 118 pm

d(Sr−F) = 251 pm

Shannon-Prewitt Crystal Radii
(O^{2-}, F^- 14 pm smaller)

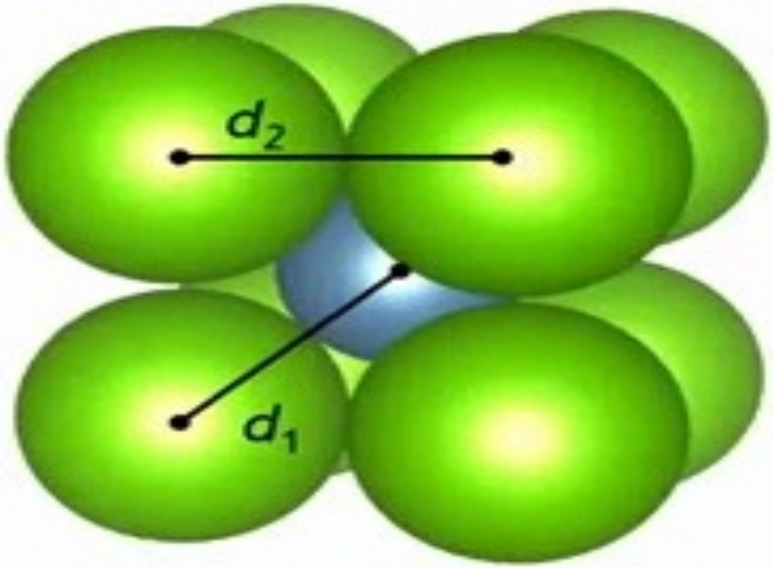
F^-
r = 119 pm
r = 1.19 Å

Sr^{2+}
r = 132 pm
r = 1.32 Å

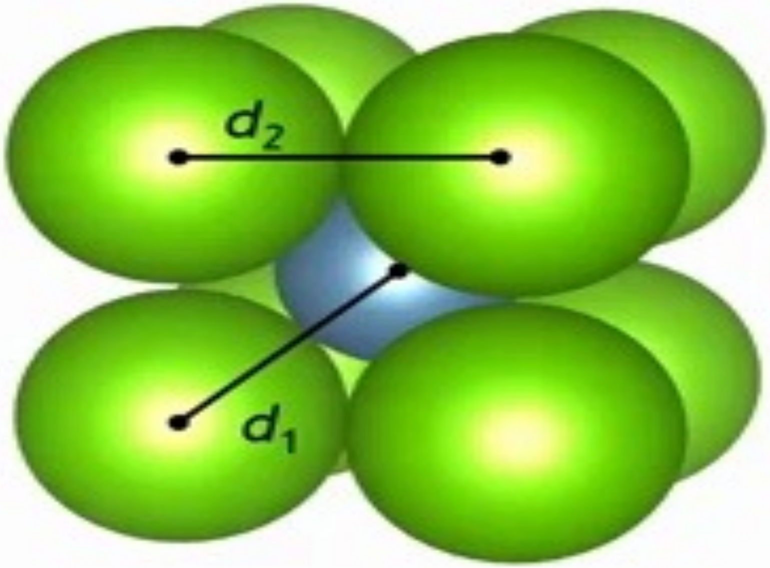
d(Sr−F) = 119 + 132 pm

d(Sr−F) = 251 pm

Ionic Size



Ionic Size

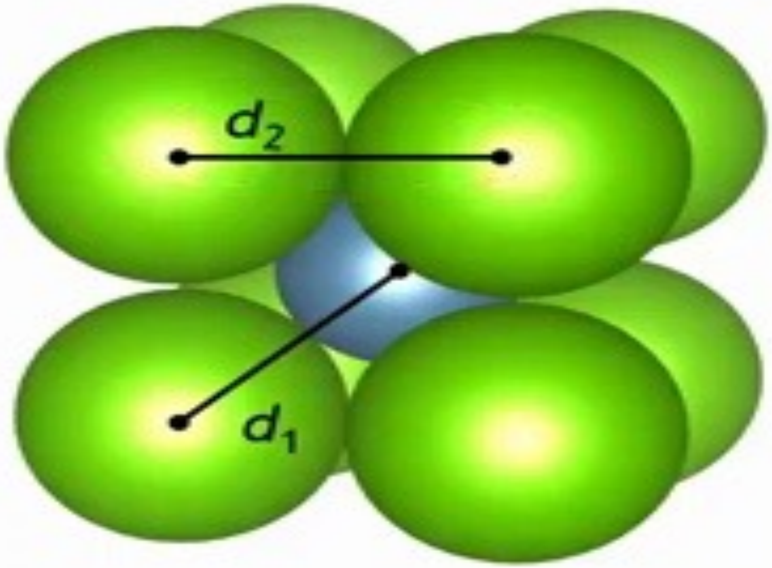


Mg–F distance, d_1

$d_1 = r\ (\mathrm{Mg^{2+}}) + r\ (\mathrm{F^-})$

$d_1 = 86\ \mathrm{pm} + 119\ \mathrm{pm} = 205\ \mathrm{pm}$

Ionic Size



Mg–F distance, d_1

$d_1 = r\ (\mathrm{Mg}^{2+}) + r\ (\mathrm{F}^-)$

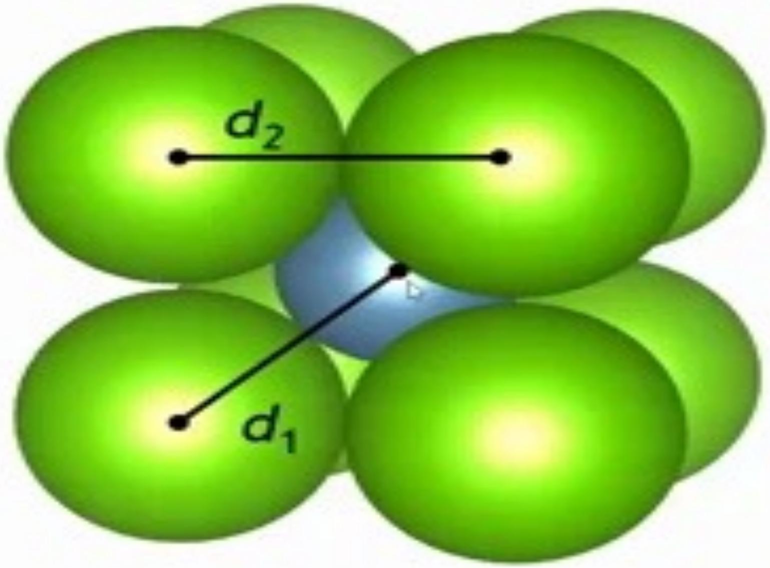
d_1 = 86 pm + 119 pm = 205 pm

F–F distance, d_2

$d_2 = 2d_1/\sqrt{3}$

d_2 = 237 pm

Ionic Size



Mg−F distance, d_1

$d_1 = r\,(\mathrm{Mg}^{2+}) + r\,(\mathrm{F}^-)$

$d_1 = 86\text{ pm} + 119\text{ pm} = 205\text{ pm}$

F−F distance, d_2

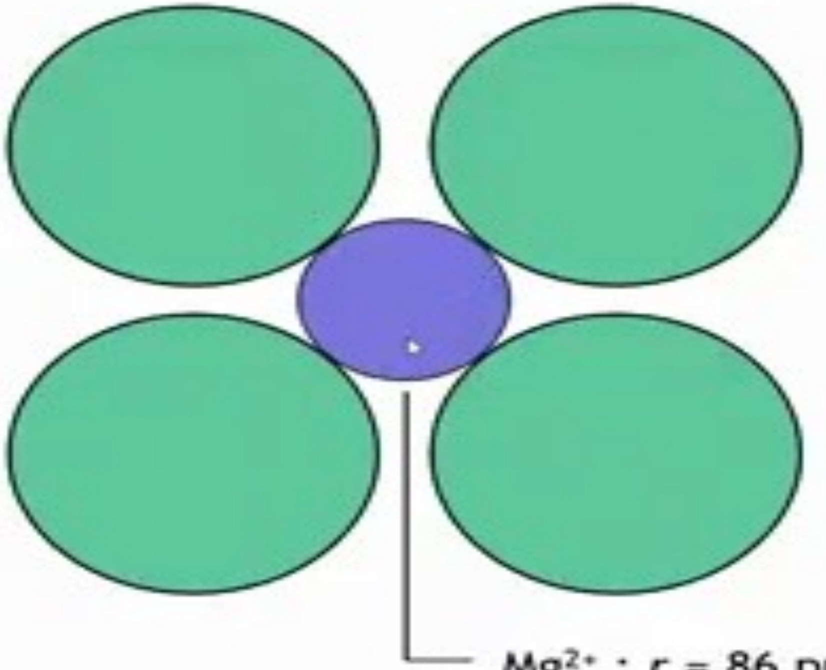
$d_2 = 2d_1/\sqrt{3}$

$d_2 = 237\text{ pm}$

$d_2 \approx 2r_{\mathrm{F}^-}$

$237\text{ pm} \approx 238\text{ pm}$

Ionic Size

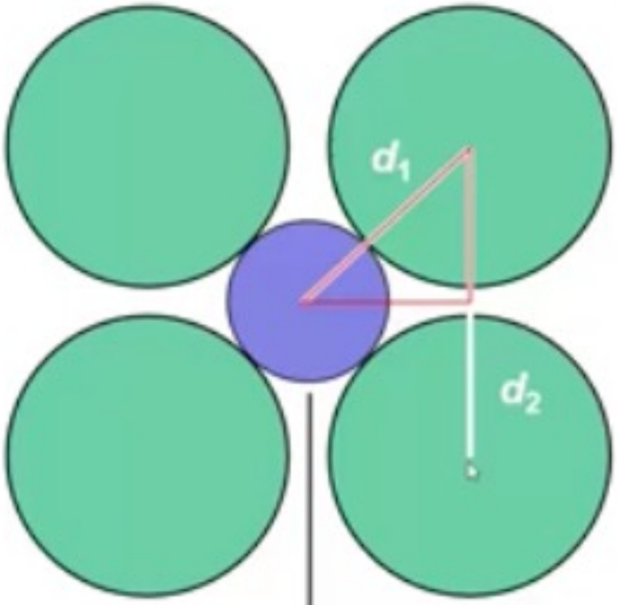


F^- : r = 119 pm

Mg^{2+} : r = 86 pm

Ionic Size

$F^- : r = 119$ pm



$Mg^{2+} : r = 86$ pm

Mg–F distance, d_1

$d_1 = r\,(Mg^{2+}) + r\,(F^-)$

$d_1 = 86\text{ pm} + 119\text{ pm} = 205\text{ pm}$

F–F distance, d_2

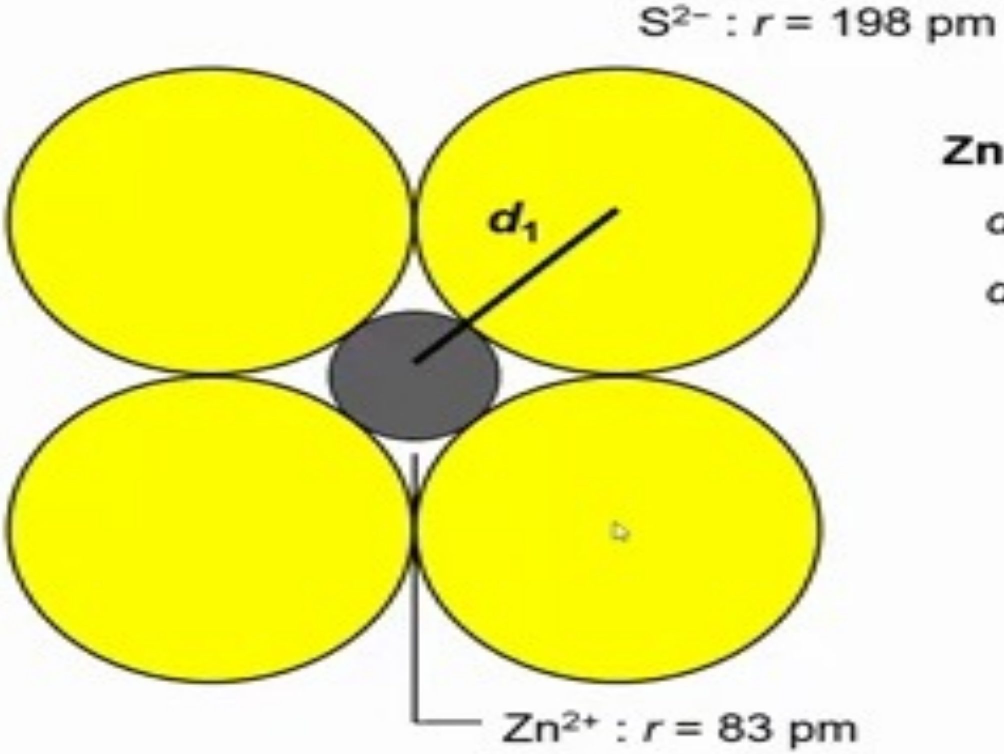
$d_2 = 2(d_1 \sin 45°)$

$d_2 = 290$ pm

$d_2 > 2r_{F-}$

$290\text{ pm} > 238\text{ pm}$

Ionic Size

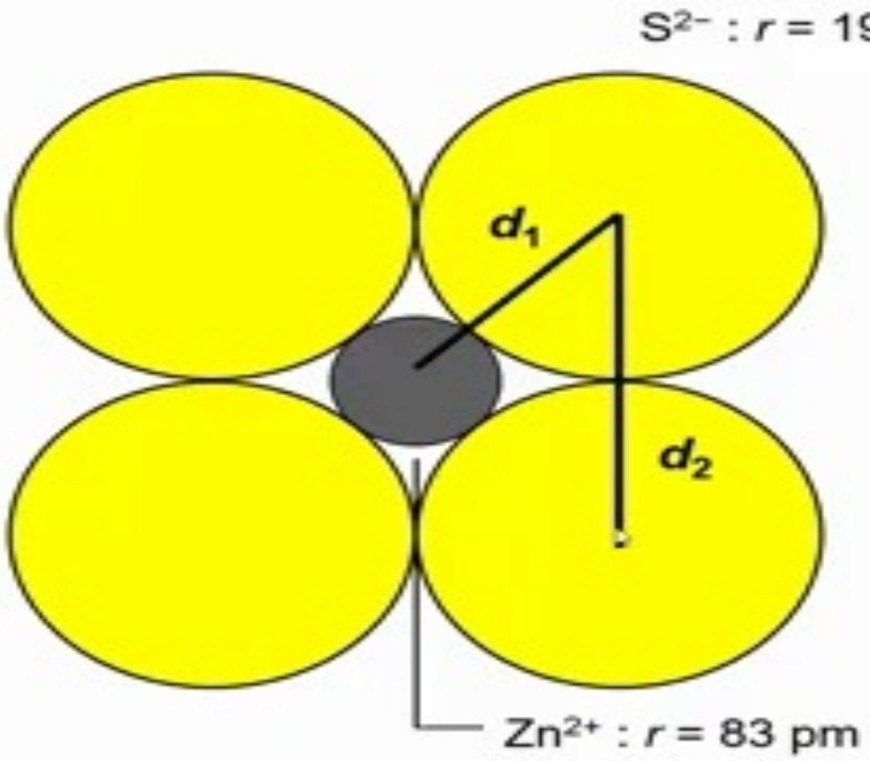


Zn-S distance, d_1

$d_1 = r(Zn^{2+}) + r(S^{2-})$

$d_1 = 83 \text{ pm} + 198 \text{ pm} = 281 \text{ pm}$

Ionic Size



Zn-S distance, d_1

$d_1 = r(Zn^{2+}) + r(S^{2-})$

d_1 = 83 pm + 198 pm = 281 pm

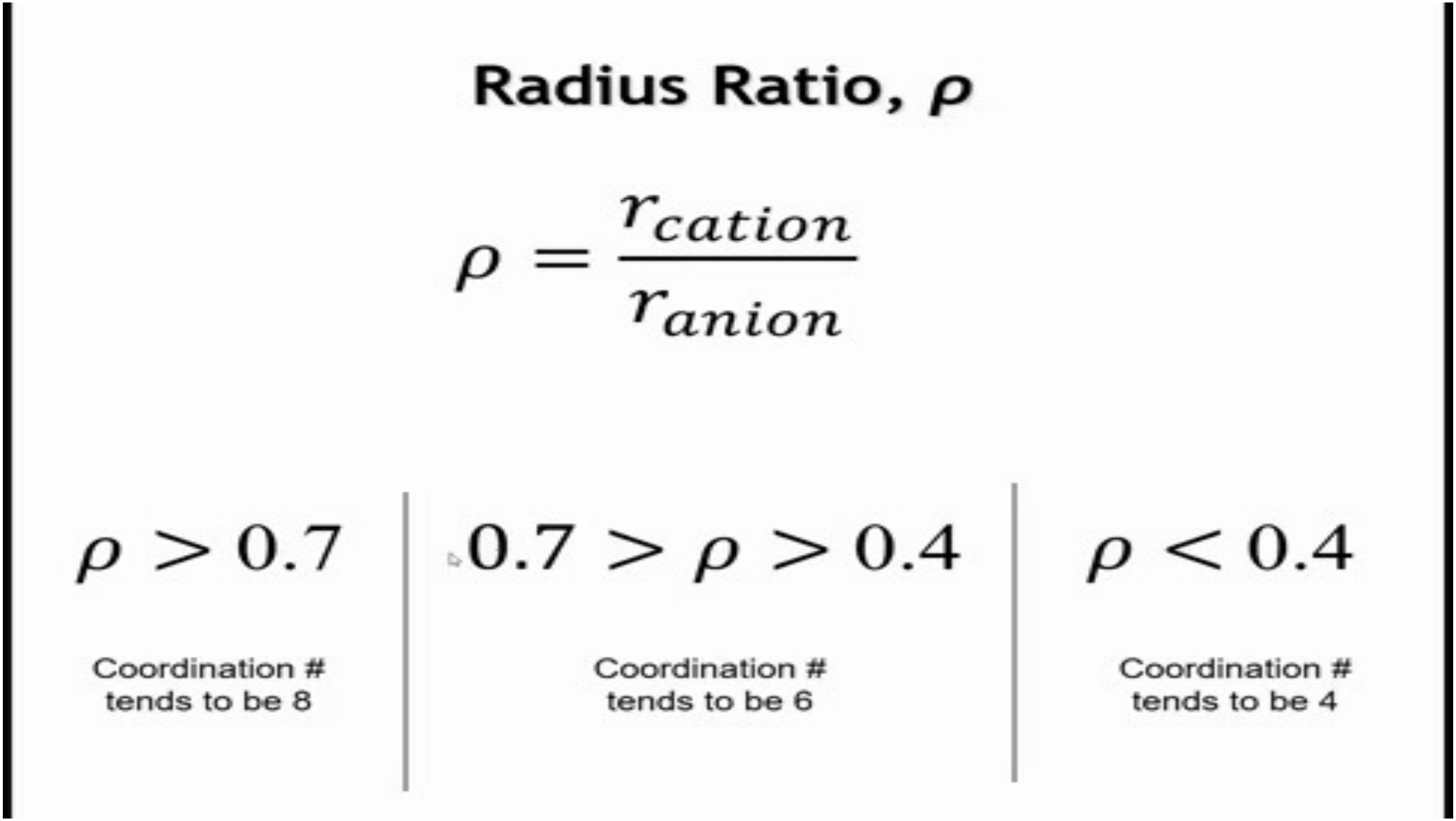
S-S distance, d_2

$d_2 = 2(d_1 \sin 45°)$

d_2 = 397 pm

$d_2 \approx 2r_{S2-}$

397 pm ≈ 396 pm



Radius Ratio, ρ

$$\rho = \frac{r_{cation}}{r_{anion}}$$

$$\rho > 0.7$$

Coordination #
tends to be 8

$$0.7 > \rho > 0.4$$

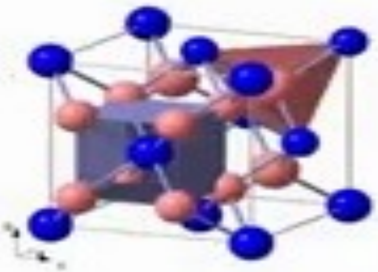
Coordination #
tends to be 6

$$\rho < 0.4$$

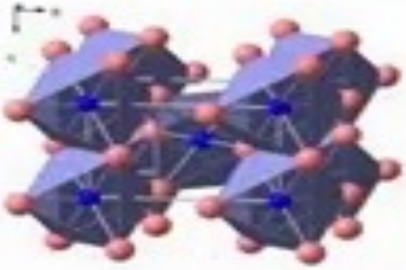
Coordination #
tends to be 4

Structures of MX_2 Halides

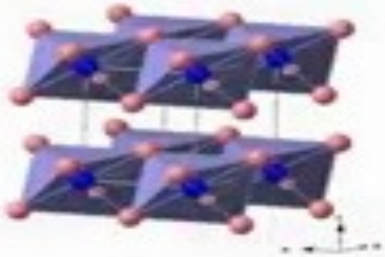
	F^- (119 pm)	Cl^- (167 pm)	Br^- (181 pm)	I^- (206 pm)
Mg^{2+} (86 pm)	rutile	$CdI_2/CdCl_2$	$CdI_2/CdCl_2$	$CdI_2/CdCl_2$
Zn^{2+} (88 pm)	rutile	$CdI_2/CdCl_2$	$CdI_2/CdCl_2$	$CdI_2/CdCl_2$
Mn^{2+} (97 pm)	rutile	$CdI_2/CdCl_2$	$CdI_2/CdCl_2$	$CdI_2/CdCl_2$
Ca^{2+} (114 pm)	fluorite	rutile	rutile	$CdI_2/CdCl_2$
Sr^{2+} (132 pm)	fluorite	fluorite	$PbCl_2$	SrI_2
Ba^{2+} (149 pm)	fluorite	fluorite	$PbCl_2$	$PbCl_2$



fluorite, $Ca^{[8]}F_2^{[4]}$
$A = 2.519$



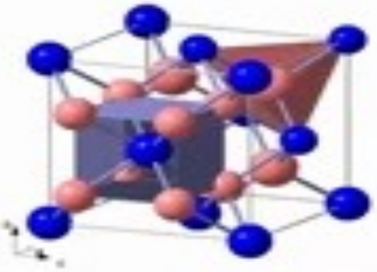
rutile, $Mg^{[6]}F_2^{[3]}$
$A = 2.408$



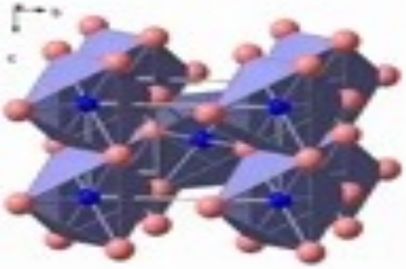
$Cd^{[6]}I_2^{[3]}$
$A = 2.192$

Structures of MX_2 Halides

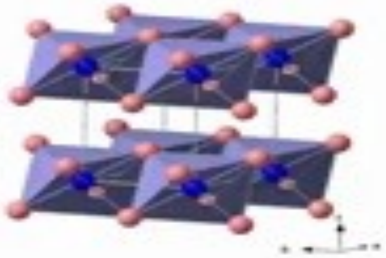
	F^- (119 pm)	Cl^- (167 pm)	Br^- (181 pm)	I^- (206 pm)
Mg^{2+} (86 pm)	$\rho = 0.72$	$\rho = 0.51$	$\rho = 0.48$	$\rho = 0.42$
Zn^{2+} (88 pm)	$\rho = 0.74$	$\rho = 0.53$	$\rho = 0.49$	$\rho = 0.43$
Mn^{2+} (97 pm)	$\rho = 0.82$	$\rho = 0.58$	$\rho = 0.54$	$\rho = 0.47$
Ca^{2+} (114 pm)	$\rho = 0.96$	$\rho = 0.68$	$\rho = 0.63$	$\rho = 0.55$
Sr^{2+} (132 pm)	$\rho = 1.11$	$\rho = 0.79$	$\rho = 0.73$	$\rho = 0.64$
Ba^{2+} (149 pm)	$\rho = 1.25$	$\rho = 0.89$	$\rho = 0.82$	$\rho = 0.72$



fluorite, $Ca^{[8]}F_2^{[4]}$
$A = 2.519$

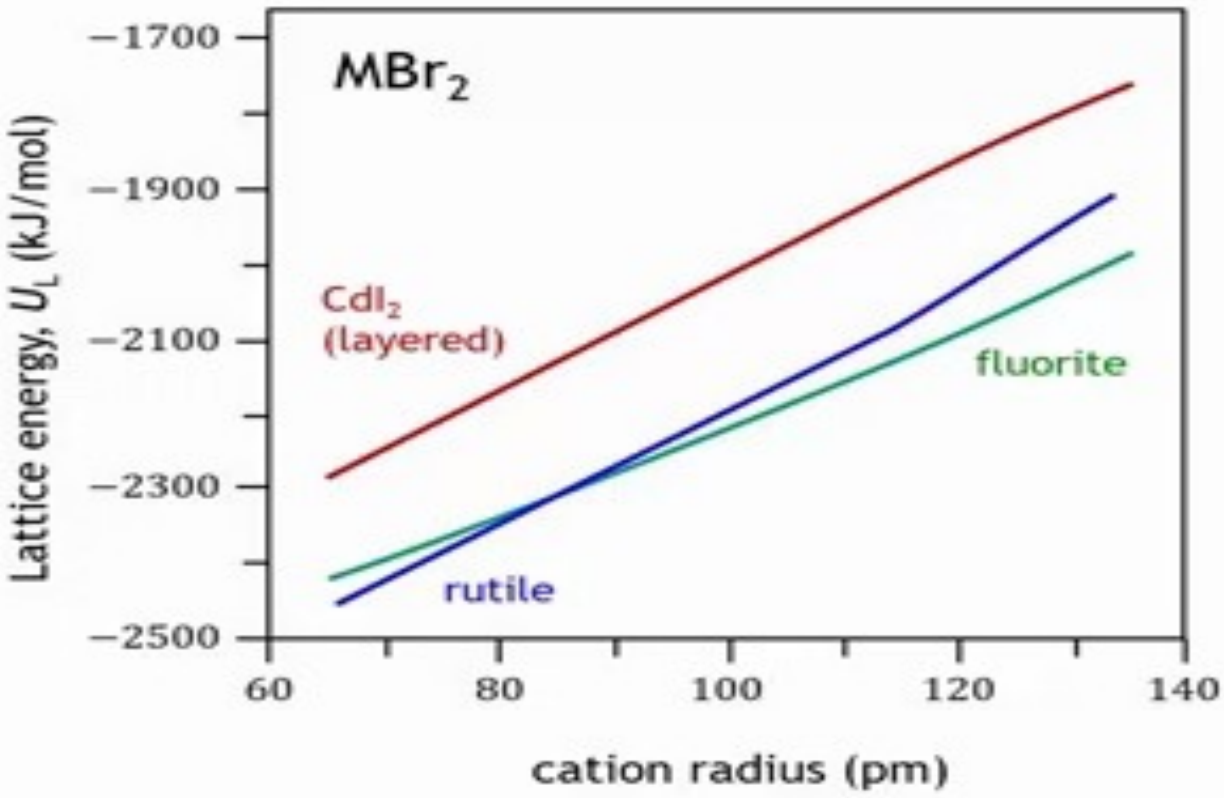


rutile, $Mg^{[6]}F_2^{[3]}$
$A = 2.408$



$Cd^{[6]}I_2^{[3]}$
$A = 2.192$

Calculated lattice energy



Calculations with a rigid ionic model (similar to Born-Meyer equation)

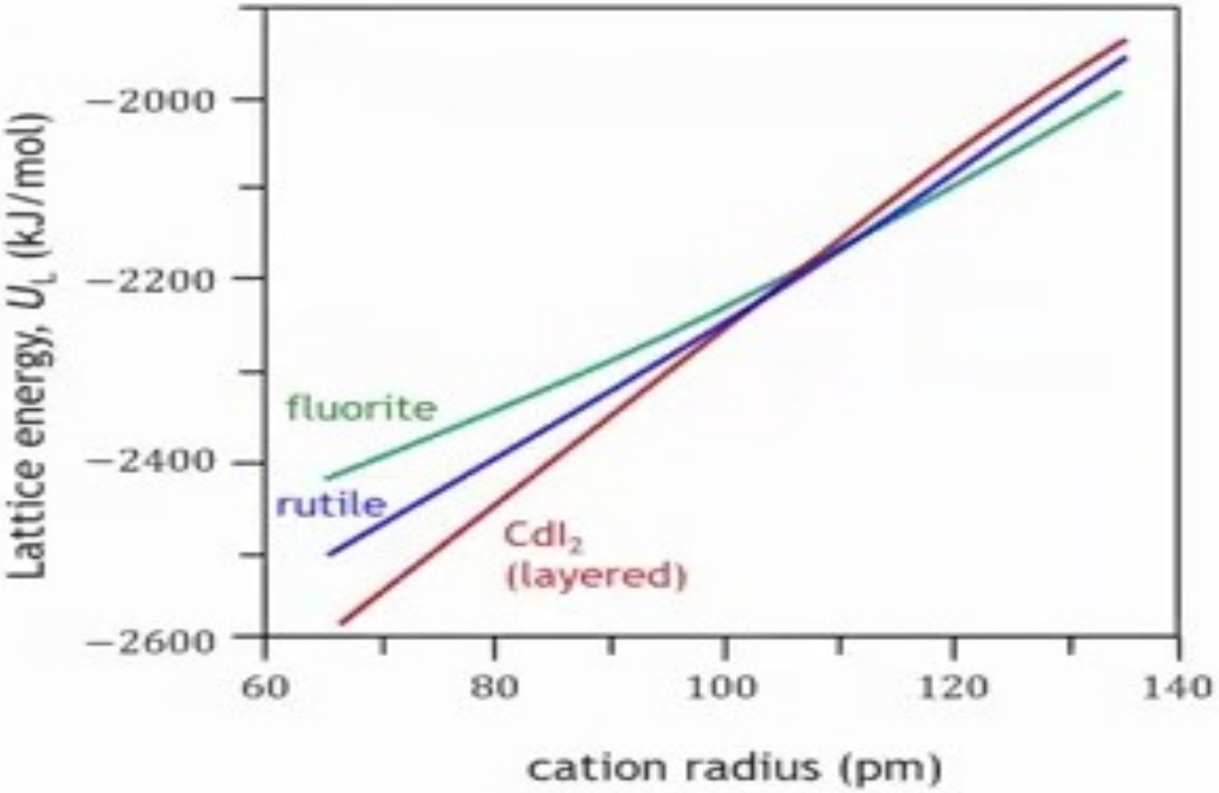
Fluorite structure has the lowest E when the cation is large

Rutile structure has the lowest E when the cation is small

CdI_2 layered structure not stable for any cation size

M. Wilson, P. A. Madden, *J. Phys. Cond. Matt.* **1994**, *6*, 159-170.

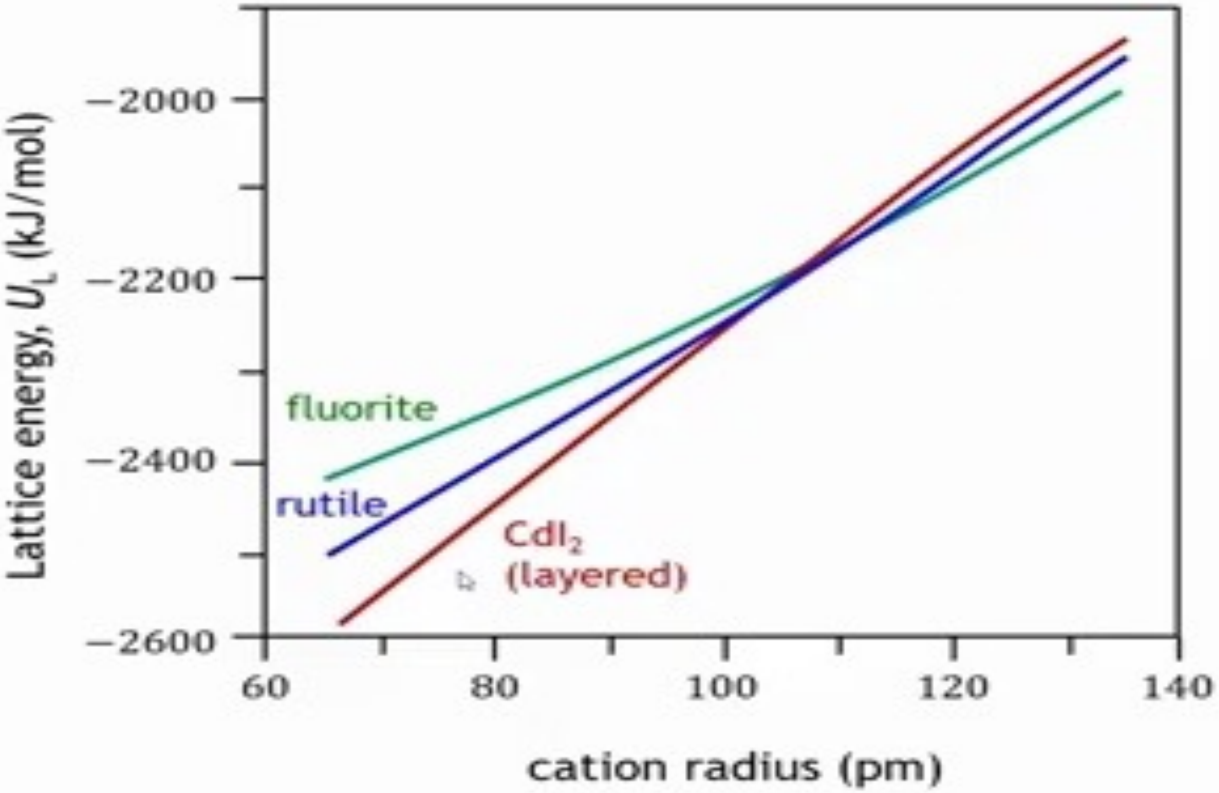
Calculated lattice energy MBr_2 halides



Introduce polarization of the electron cloud surrounding the anion (creating an induced dipole)

M. Wilson, P. A. Madden, *J. Phys. Cond. Matt.* **1994**, *6*, 159-170.

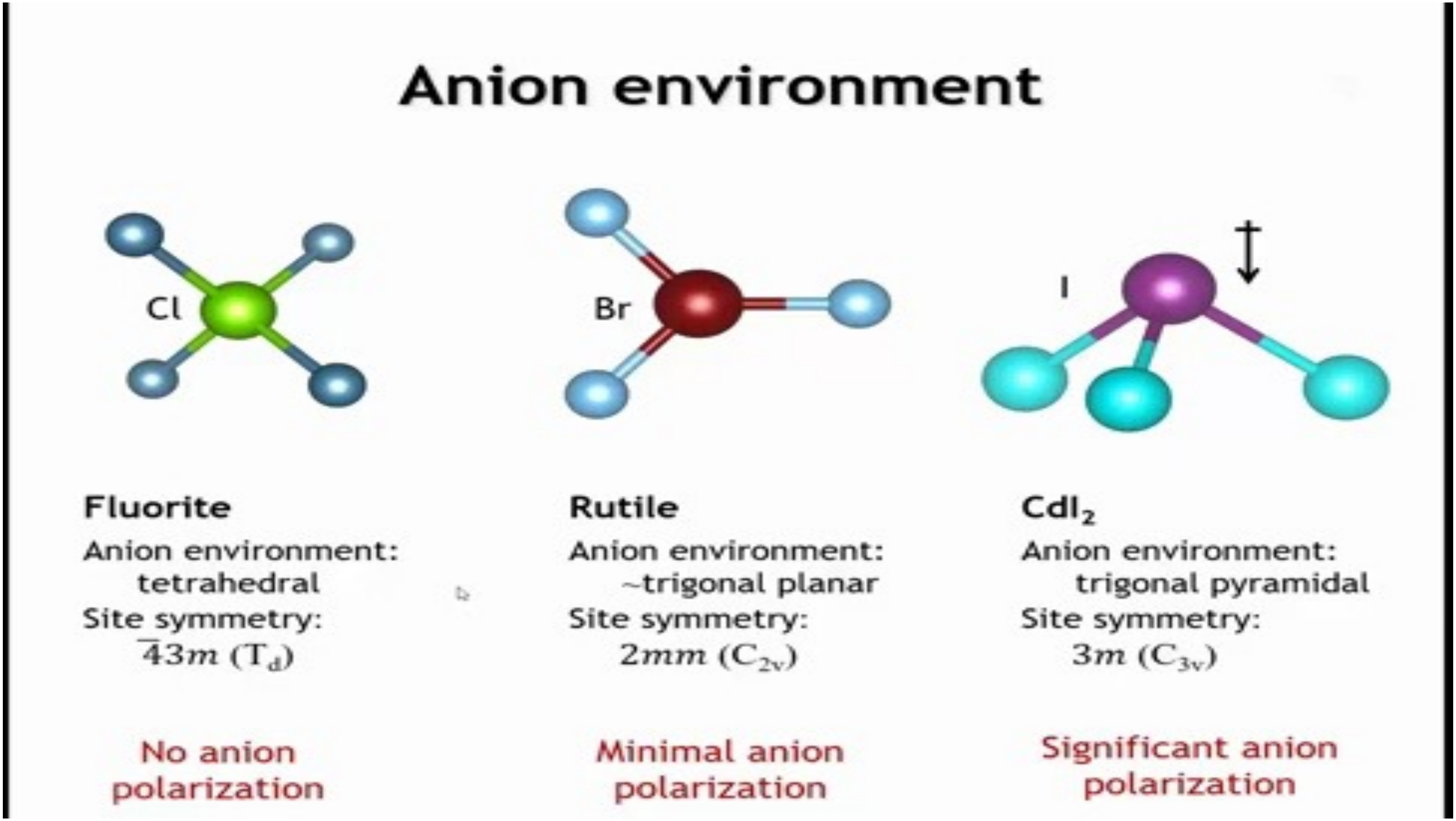
Calculated lattice energy MBr_2 halides



Introduce polarization of the electron cloud surrounding the anion (creating an induced dipole)

Now the layered CdI_2/$CdCl_2$ structures emerge as the lowest energy structure for small cations.

M. Wilson, P. A. Madden, *J. Phys. Cond. Matt.* **1994**, *6*, 159-170.



Anion environment

Fluorite

Anion environment:
tetrahedral
Site symmetry:
$\overline{4}3m$ (T_d)

No anion polarization

Rutile

Anion environment:
~trigonal planar
Site symmetry:
$2mm$ (C_{2v})

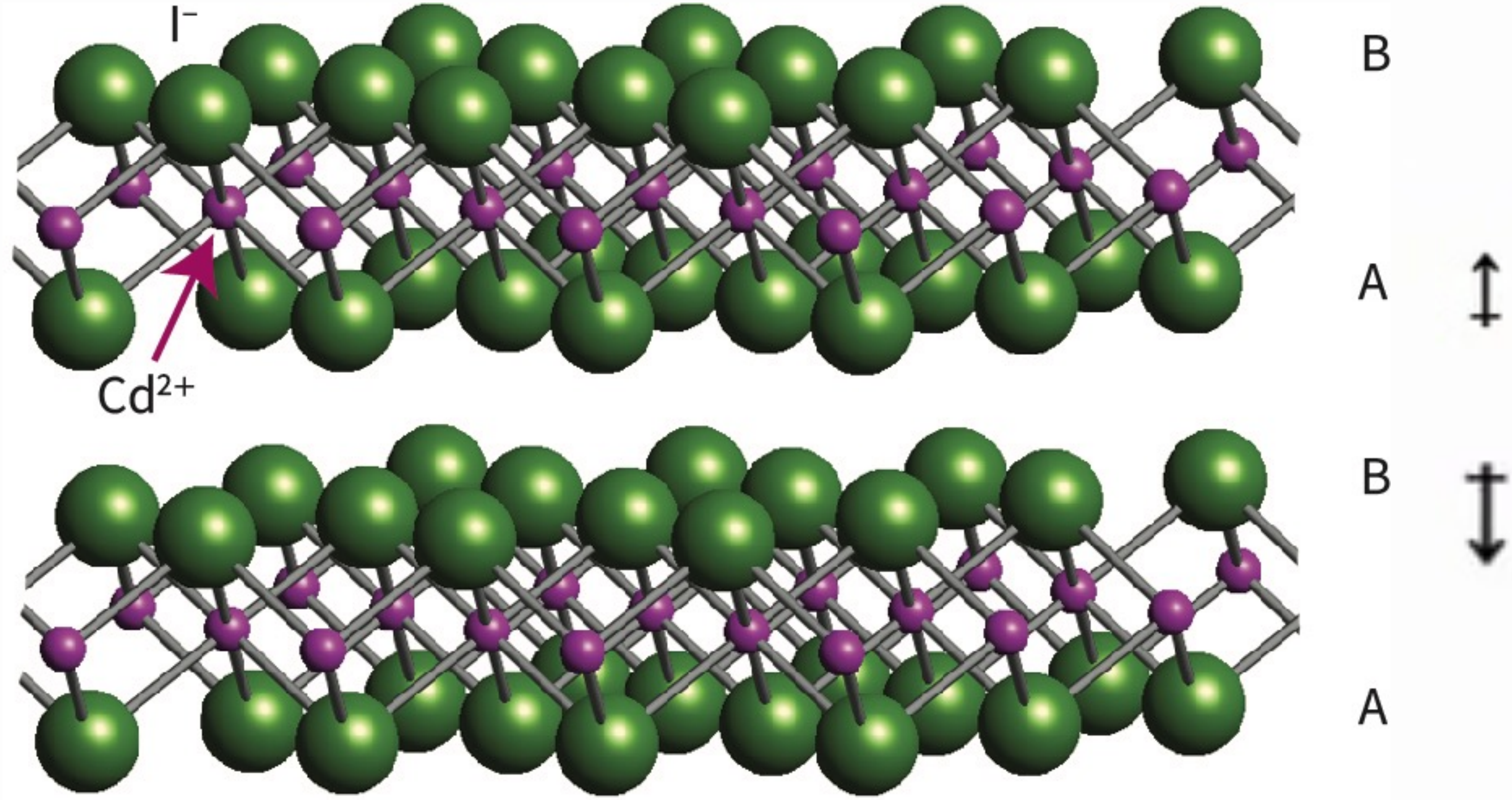
Minimal anion polarization

CdI_2

Anion environment:
trigonal pyramidal
Site symmetry:
$3m$ (C_{3v})

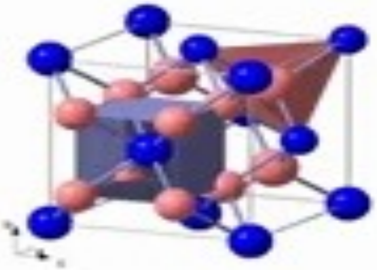
Significant anion polarization

Anion Polarization

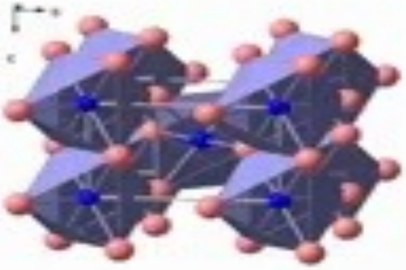


Structures of MX_2 Halides

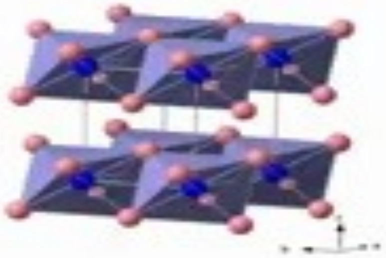
	F^- (119 pm)	Cl^- (167 pm)	Br^- (181 pm)	I^- (206 pm)
Mg^{2+} (86 pm)	rutile	$CdI_2/CdCl_2$	$CdI_2/CdCl_2$	$CdI_2/CdCl_2$
Zn^{2+} (88 pm)	rutile	$CdI_2/CdCl_2$	$CdI_2/CdCl_2$	$CdI_2/CdCl_2$
Mn^{2+} (97 pm)	rutile	$CdI_2/CdCl_2$	$CdI_2/CdCl_2$	$CdI_2/CdCl_2$
Ca^{2+} (114 pm)	fluorite	rutile	rutile	$CdI_2/CdCl_2$
Sr^{2+} (132 pm)	fluorite	fluorite	$PbCl_2$	SrI_2
Ba^{2+} (149 pm)	fluorite	fluorite	$PbCl_2$	$PbCl_2$



fluorite, $Ca^{[8]}F_2^{[4]}$
$A = 2.519$

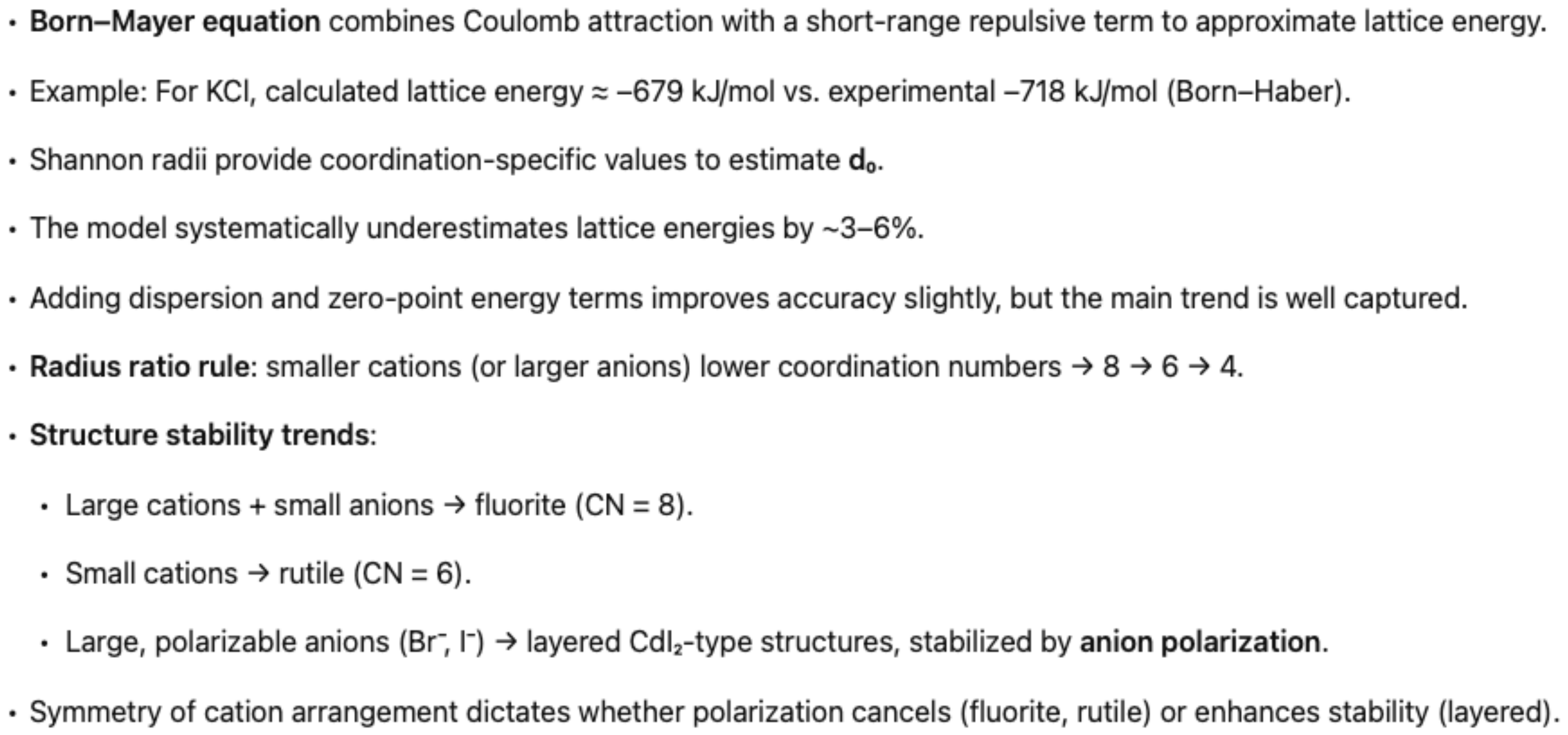


rutile, $Mg^{[6]}F_2^{[3]}$
$A = 2.408$



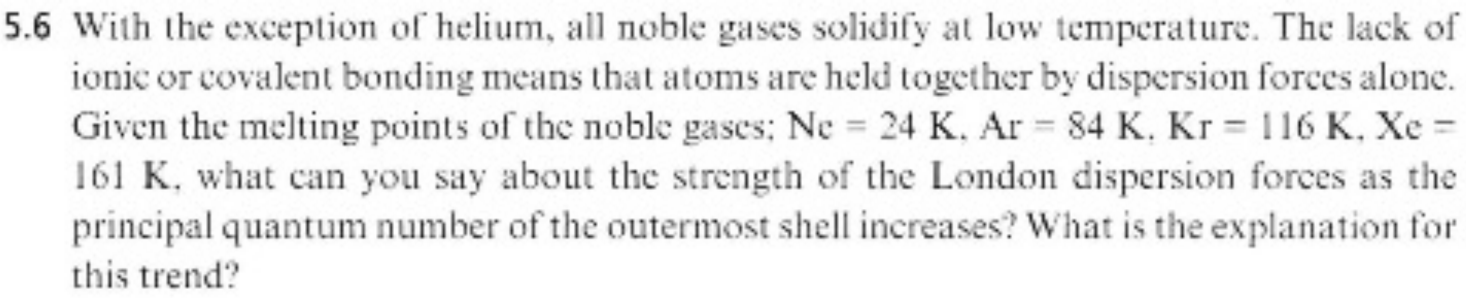
$Cd^{[6]}I_2^{[3]}$
$A = 2.192$

Summary



- **Born–Mayer equation** combines Coulomb attraction with a short-range repulsive term to approximate lattice energy.
- Example: For KCl, calculated lattice energy ≈ –679 kJ/mol vs. experimental –718 kJ/mol (Born–Haber).
- Shannon radii provide coordination-specific values to estimate $\mathbf{d_0}$.
- The model systematically underestimates lattice energies by ~3–6%.
- Adding dispersion and zero-point energy terms improves accuracy slightly, but the main trend is well captured.
- **Radius ratio rule**: smaller cations (or larger anions) lower coordination numbers → 8 → 6 → 4.
- **Structure stability trends**:
  - Large cations + small anions → fluorite (CN = 8).
  - Small cations → rutile (CN = 6).
  - Large, polarizable anions (Br^-, I^-) → layered CdI_2-type structures, stabilized by **anion polarization**.
- Symmetry of cation arrangement dictates whether polarization cancels (fluorite, rutile) or enhances stability (layered).

Homework



5.6 With the exception of helium, all noble gases solidify at low temperature. The lack of ionic or covalent bonding means that atoms are held together by dispersion forces alone. Given the melting points of the noble gases; Ne = 24 K, Ar = 84 K, Kr = 116 K, Xe = 161 K, what can you say about the strength of the London dispersion forces as the principal quantum number of the outermost shell increases? What is the explanation for this trend?