Bonding in crystals: Ionic

calorimetry and Born-Haber cycle

salt

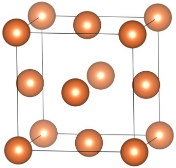
Linus Pauling

by Alexander Tsirlin, Leipzig University

Lecture 7: November 1, 2023

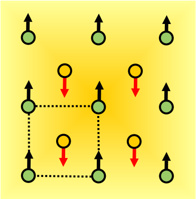
1. Structure of crystals

- direct lattice / reciprocal lattice
- symmetry
- crystal structure / structure factor



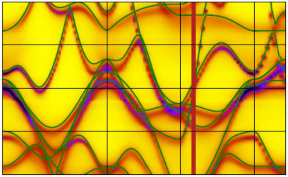
2. Atoms in crystals

- types of bonding
- elasticity and thermodynamics
- phonons (lattice vibrations)



3. Electrons in crystals

- free electron gas / Drude metal
- electronic band structure
- Fermi surface



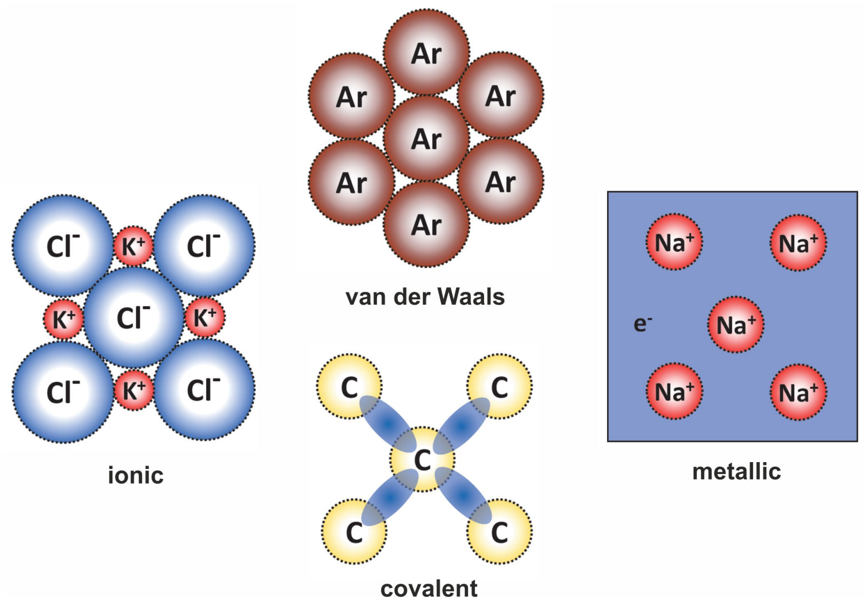
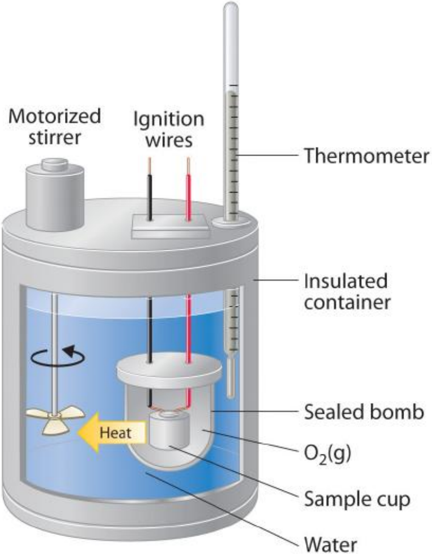


Image from Gross and Marx, Festkörperphysik

Experimental technique

calorimetry and Born-Haber cycle



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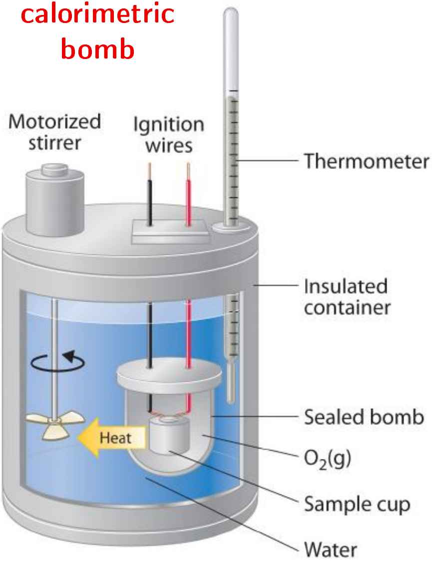
calorimetric bomb



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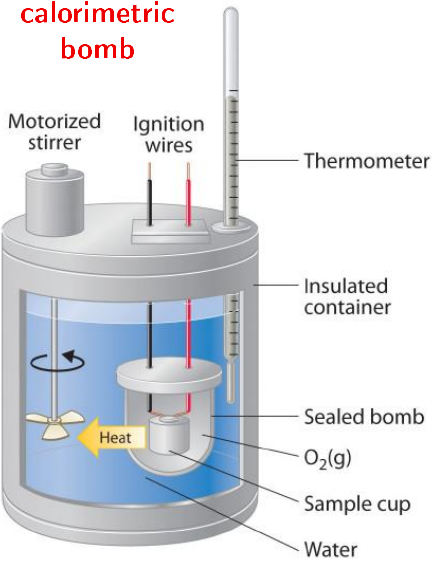
first calorimeter by Lavoisier

calorimetric bomb



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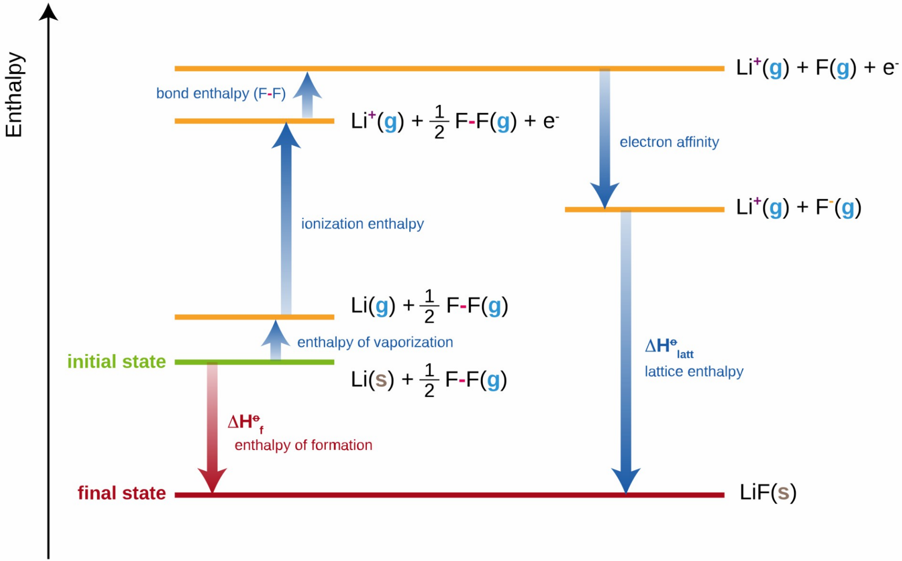
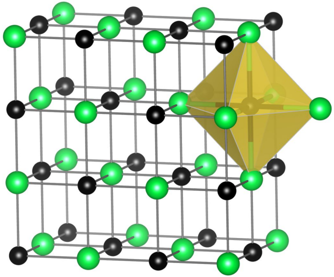

Enthalpy
bond enthalpy (F-F)
$Li^+(g) + F(g) + e^-$
$Li^+(g) + \frac{1}{2}$ F-F(g) + e^-
electron affinity
$Li^+(g) + F^-(g)$
ionization enthalpy
$Li(g) + \frac{1}{2}$ F-F(g)
enthalpy of vaporization
initial state
$Li(s) + \frac{1}{2}$ F-F(g)
ΔH°_{latt}
lattice enthalpy
ΔH°_f
enthalpy of formation
final state
LiF(s)

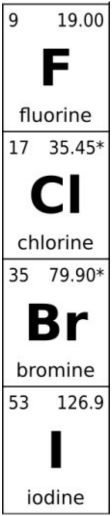
crystal	R_0 (Å)	$\widetilde{U}^{\text{theor.}}$ (eV)	$\widetilde{U}^{\text{exp.}}$ (eV)
		⟵ lattice energies	⟶
LiF	2.014	10.70	10.92
LiCl	2.570	8.55	8.93
NaCl	2.820	7.92	8.23
NaJ	3.237	6.96	7.35
KCl	3.147	7.17	7.47
KJ	3.533	6.43	6.75

Image from Gross and Marx, Festkörperphysik

	r_0 (Å)	T_m (K)	E_{lat} (eV/f.u.)
NaF	2.32	1269	9.43
NaCl	2.82	1074	7.97
NaBr	2.99	1020	7.59
NaI	3.24	933	7.07

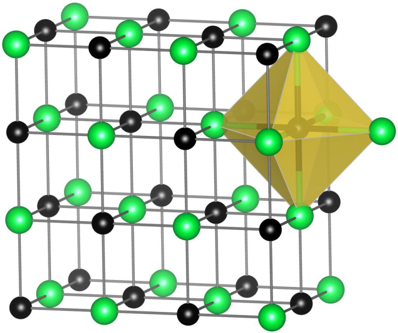


$$E = -\frac{\alpha e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{m}\right)$$



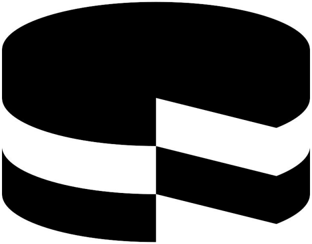
Data from CRC Handbook of Chemistry and Physics

	r_0 (Å)	T_m (K)	E_{lat} (eV/f.u.)
$Na^{+1}\,Cl^{-1}$	2.82	1074	7.97
$Ba^{+2}\,O^{-2}$	2.75	2196	31.7



$$E = -z^2 \frac{\alpha e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{m}\right)$$

Data from CRC Handbook of Chemistry and Physics



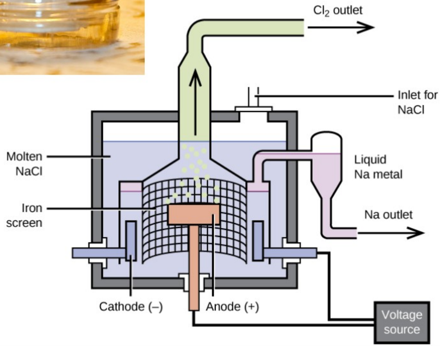
Material

Salt

Production: salt water or underground mining

Production: salt water or underground mining

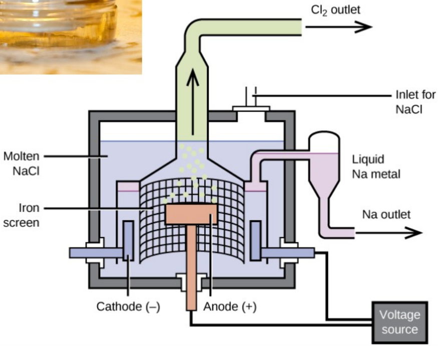
Applications: food industry, chemical industry...

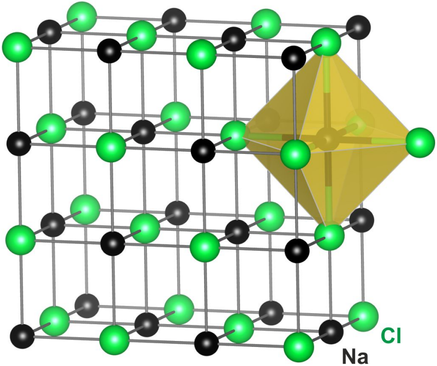


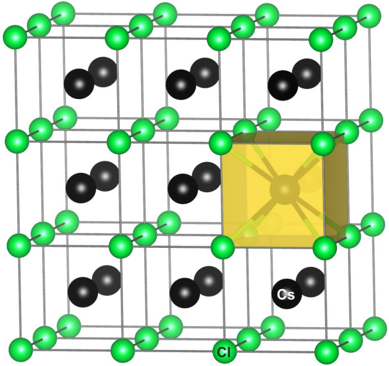
Production: salt water
or underground mining

200 million tons per year

Applications:
food industry,
chemical industry...





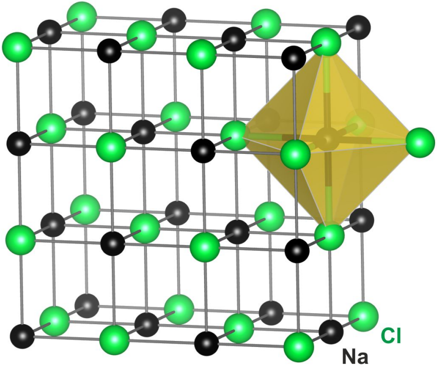


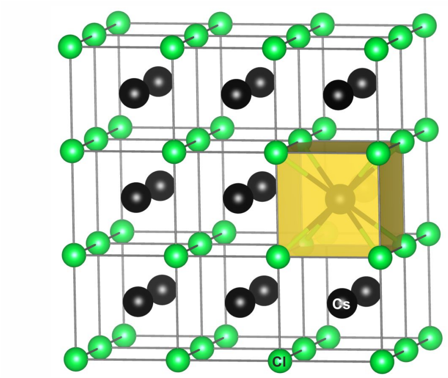
rocksalt-type

$\alpha = 1.7476$

CsCl-type

$\alpha = 1.7627$





rocksalt-type

$\alpha = 1.7476$

CN = 6

CsCl-type

$\alpha = 1.7627$

CN = 8

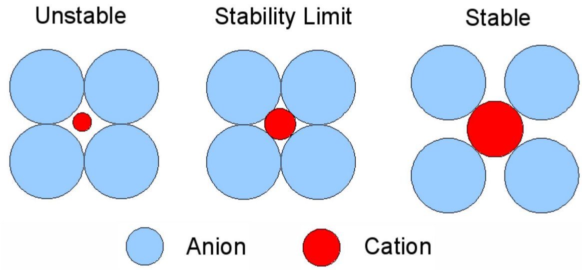
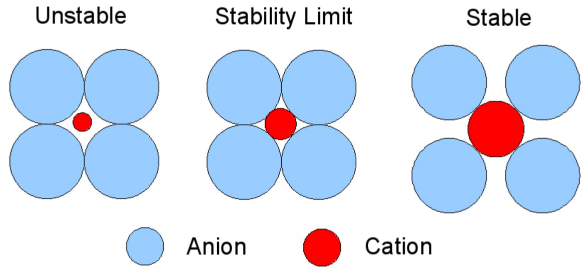
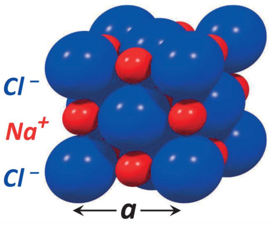


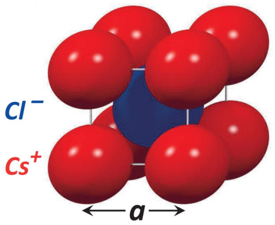
Image credit: Matthew Rollings (public domain); Gross and Marx, Festkörperphysik



only large Cs^{+}
is stable
with CN = 8

	H	F	Cl	Br	I
Li					
Na			NaCl		
K					
Rb					
Cs			CsCl		





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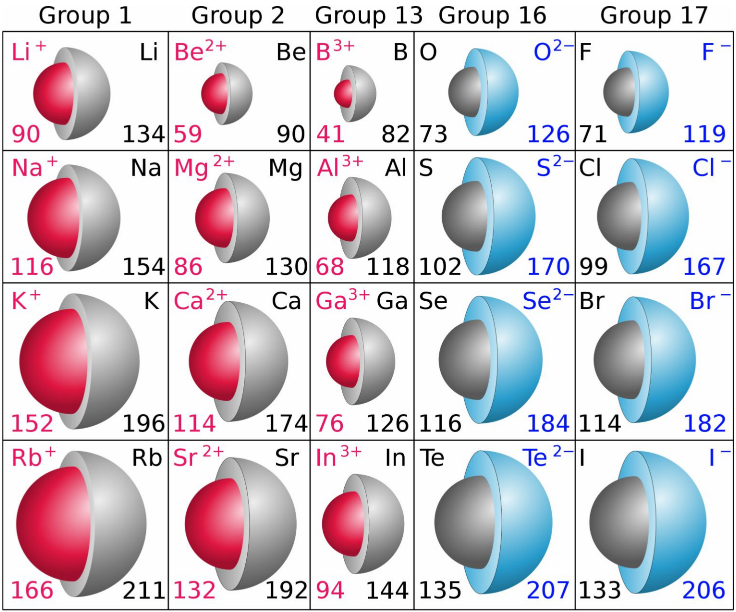

Group 1
Group 2
Group 13
Group 16
Group 17
Li+ Li 90 134
Be2+ Be 59 90
B3+ B 41 82
O O2− 73 126
F F− 71 119
Na+ Na 116 154
Mg2+ Mg 86 130
Al3+ Al 68 118
S S2− 102 170
Cl Cl− 99 167
K+ K 152 196
Ca2+ Ca 114 174
Ga3+ Ga 76 126
Se Se2− 116 184
Br Br− 114 182
Rb+ Rb 166 211
Sr2+ Sr 132 192
In3+ In 94 144
Te Te2− 135 207
I I− 133 206

values in pm!

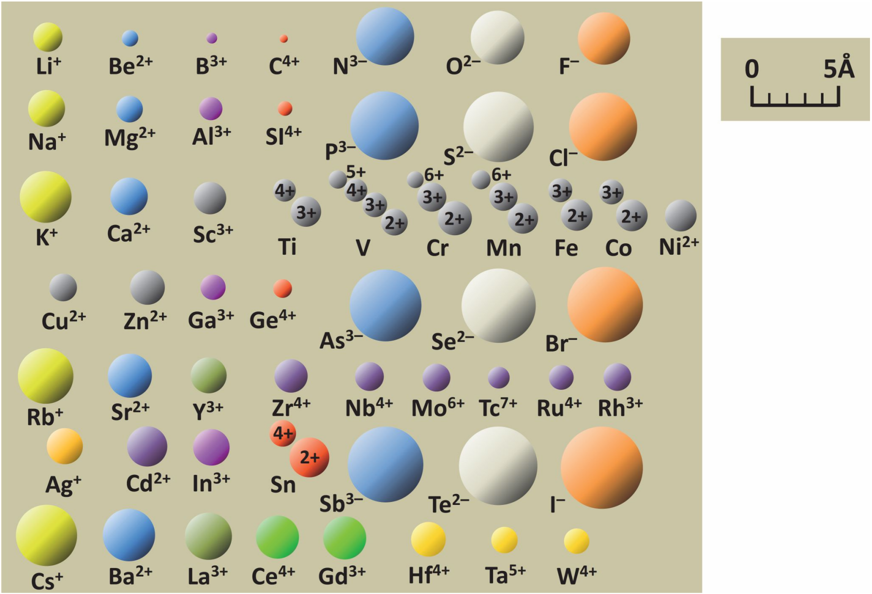


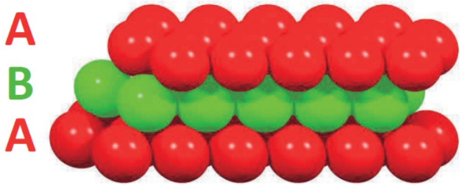
Image from Gross and Marx, Festkörperphysik

			coordination number	covalent (CR)	ionic (IR)	
NA+1	2P	6	IV	1.13	.99	
			V	1.14	1.00	
			VI	1.16	1.02	
			VII	1.26	1.12	
			VIII	1.32	1.18	
			IX	1.38	1.24	C
			XII	1.53	1.39	
NB+3	4D	2	VI	.86	.72	
NB+4	4D	1	VI	.82	.68	RE
			VIII	.93	.79	
NB+5	4P	6	IV	.62	.48	C
			VI	.78	.64	
			VII	.83	.69	C
			VIII	.88	.74	
ND+2	4F	4	VIII	1.43	1.29	
			IX	1.49	1.35	
ND+3	4F	3	VI	1.123	.983	R
			VIII	1.249	1.109	R*
			IX	1.303	1.163	R
			XII	1.41	1.27	E

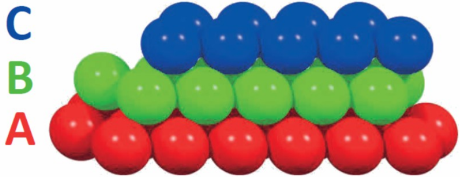
all values in Å !

R.D. Shannon

Acta Cryst. A32, 751 (1976)

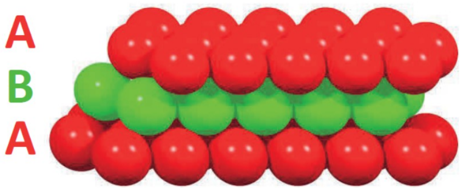


hexagonal close packing (hcp)



cubic close packing (ccp)

Image credit: LibreText Chemistry (CC-BY-NC); Gross and Marx, Festkörperphysik

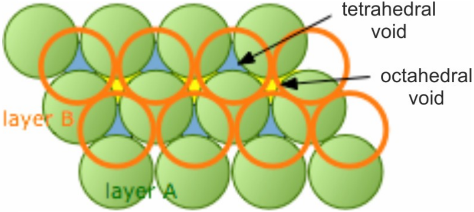


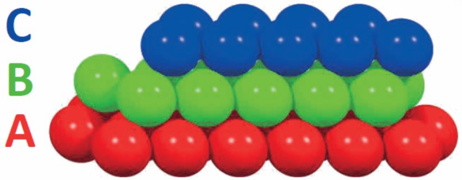
hexagonal close packing (hcp)

1 octahedral void

2 tetrahedral voids

per anion





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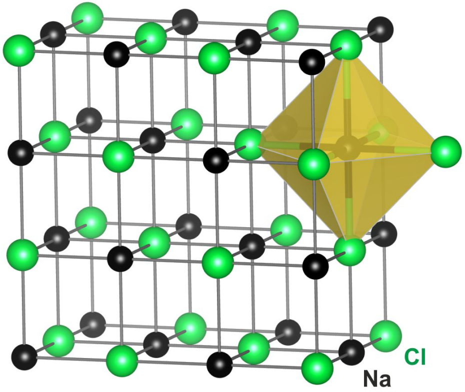
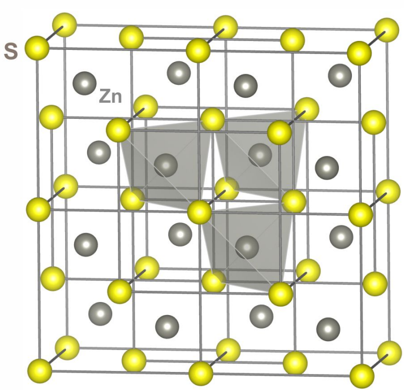


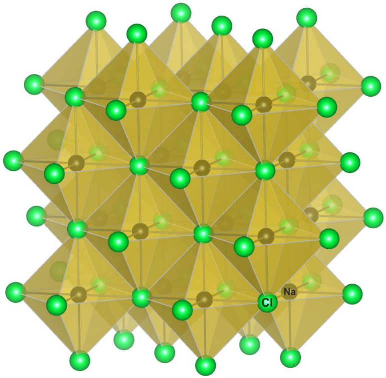


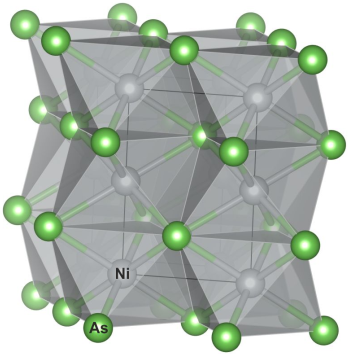
NaCl-type

(halite)

zinc blende type

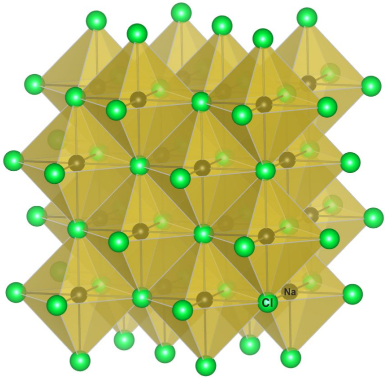
(sphalerite)





NaCl-type (ccp)
octahedra share edges

NiAs-type (hcp)
octahedra share faces



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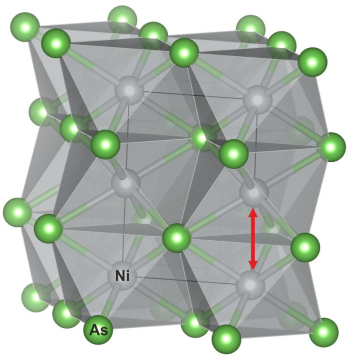


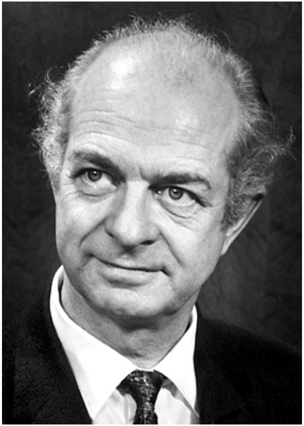
NiAs-type (hcp)
octahedra share faces

In ionic crystals, face-sharing should be avoided (third Pauling's rule)

Person

Linus Pauling

- 1917–22: undergraduate studies (chemical engineering) at Oregon State University
- 1925: PhD at Caltech, crystal structure determination using x-ray diffraction
- 1926: European trip, research stays with Sommerfeld, Bohr, and Schrödinger
- 1929: five Pauling's rules for ionic crystals
- 1930's: nature of chemical bond (electronegativity, hybridization, resonance)
- late 1940's: structures of biological molecules, α-helix
- **1954: Nobel prize in chemistry**
- 1950's: anti-nuclear campaign
- **1962: Nobel Peace prize**
- 1950-60's: structure of atomic nuclei
- 1970's: "Apostle of vitamin C"
- 1980's: denunciation of quasicrystals



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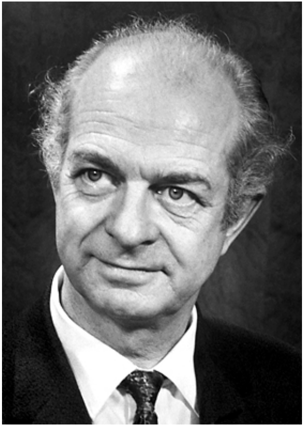

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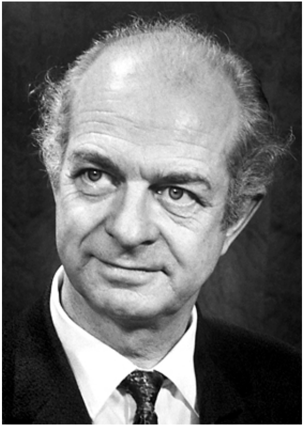

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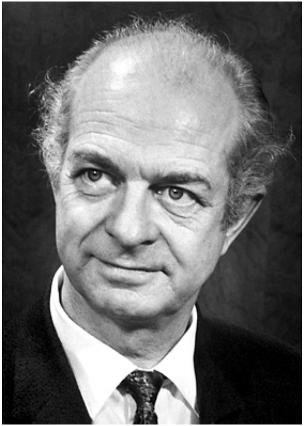

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