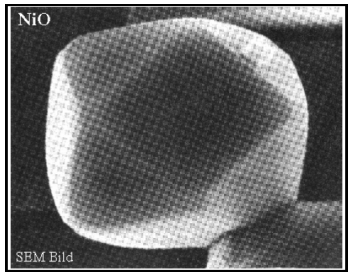
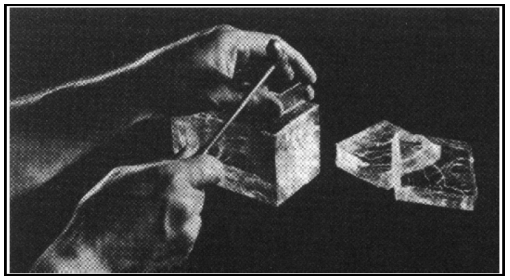
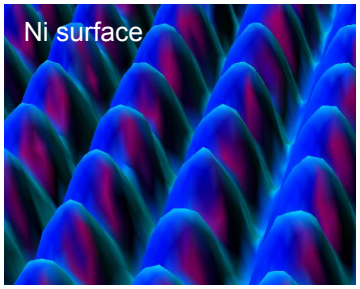


Scanning electron microscopy



Cleaved surface

ZnO, TiO_2, NiO, NaCl, Si, Ge, GaAs, InP



Scanning tunneling microscopy

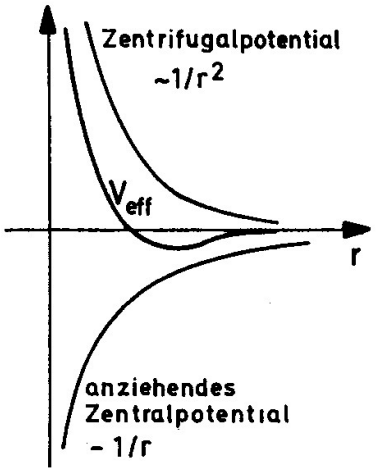
↳Crystals are build by „small“ repeating units (= basis) like atoms and molecules

1.1 Atoms

$$H = \frac{1}{2m}\,\vec{p}^{\,2} + V(r)$$
$$\vec{r} = r \cdot \hat{e}_r$$
$$\vec{L} = \vec{r} \times \vec{p} = const.$$
$$\Psi = R_{nl}(r) \cdot Y_{lm}(\vartheta, \varphi)$$

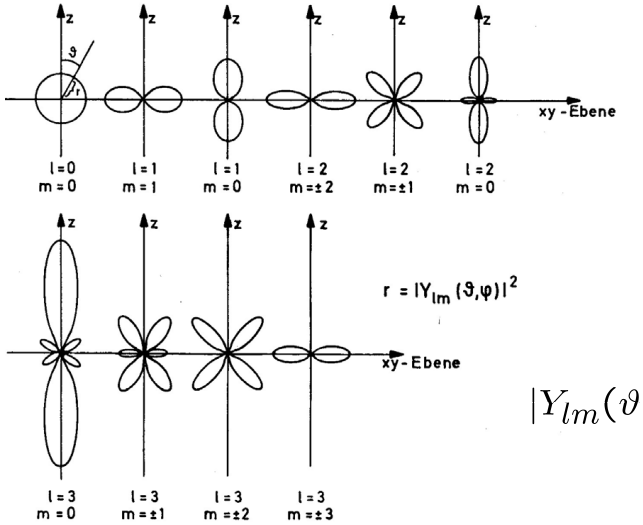
Hydrogen atom

$$V_l = \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r}$$



↳ only for s-waves (l=0)
$R_{n0}(r = 0) \neq 0$

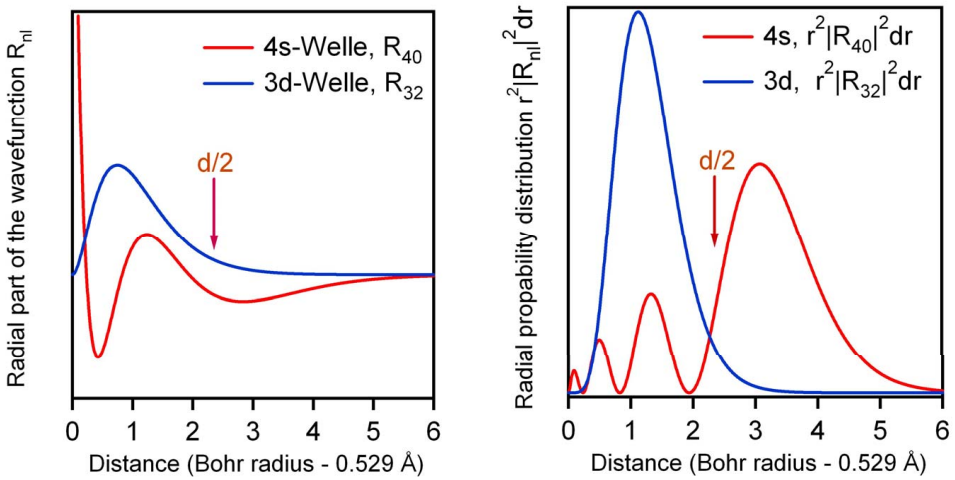
$$L^2 Y_{lm}(\vartheta, \varphi) = \hbar^2 l(l+1) Y_{lm}(\vartheta, \varphi)$$
$$L_z Y_{lm}(\vartheta, \varphi) = \hbar m_l Y_{lm}(\vartheta, \varphi)$$



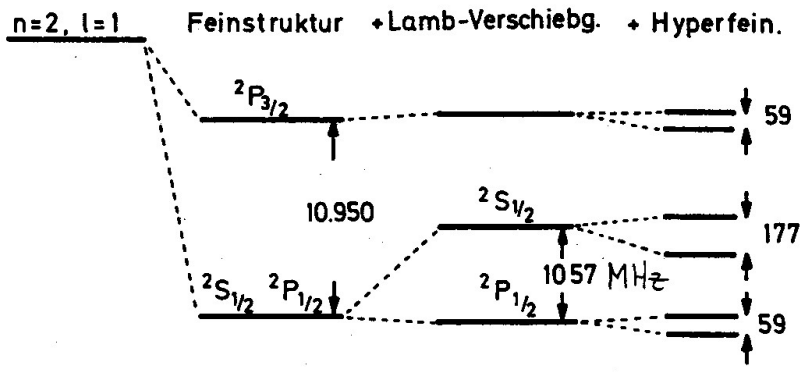
Polar plot

$$|Y_{lm}(\vartheta, \varphi)|^2 = |\Theta_{lm}(\vartheta)|^2$$

Ni (Z = 28), Z_{eff} = 8, d = 2.49 Å



Hydrogen atom



10950 MHz = 0.045 meV, beachte aber $\Delta E/E \sim Z^2\alpha^2$

Fine structure ($\alpha = e^2/4\pi\epsilon_0\hbar c = 1/137$)

corresponds to relativistic corrections which result from Dirac´s equation

i) Relativistic, kinetic energy
ii) Spin-orbit coupling (LS – coupling)
iIi) Darwin term

$$\Delta E_{rel}/E \propto \alpha^2 Z^2$$

(see, e.g., $p_{1/2}$ - $p_{3/2}$ splitting in Nickel)

i) Relativistic, kinetic energy

$$E = \sqrt{m^2c^4 + p^2c^2} =$$
$$mc^2(1 + p^2/m^2c^2)^{1/2} \simeq mc^2 + p^2/2m(1 - 1/4(v/c)^2 + \ldots)$$

Estimate of $(v/c)^2$ via uncertainty relation (a = Bohr radius):

$$\langle r\rangle_{nl} = an^2/Z$$
$$\Delta p \simeq \hbar/\Delta x = \hbar Z/a = Zme^2/(4\pi\epsilon_0\hbar)$$
$$(v/c)^2 = (p/mc)^2 = (Ze^2/(4\pi\epsilon_0 c\hbar))^2 = Z^2\alpha^2$$

ii) Classical Hamiltonian for the spin-orbit interaction

B field from the proton in the electron's rest frame is

$$\vec{B} = -(\vec{v}/c^2 \times \vec{E})$$

perturbation Hamiltonian

$$H = -\vec{\mu}\vec{B} = g\mu_B/\hbar\ \vec{S}\cdot\vec{B} = -g\mu_B/\hbar\ \vec{S}\cdot(v/c^2 \times E)$$

$$H = -\frac{g}{mc^2}\mu_B/\hbar\ \vec{S}\cdot(p\times\nabla V(r)) = -\frac{g}{mc^2}\mu_B/\hbar\ \vec{S}\cdot(p\times\hat{r}\frac{\partial}{\partial r}V(r))$$

$$H = \frac{g}{mc}\mu_B/\hbar\ \vec{S}\cdot\vec{L}\ \frac{1}{r}\frac{\partial}{\partial r}V(r)$$

$$H = \frac{1}{2}\frac{g}{2mc^2}\frac{e}{2m}\frac{Ze}{4\pi\epsilon_0 r^3}\ \vec{S}\cdot\vec{L}$$

recall $\vec{S}\cdot\vec{L} = (J^2 - L^2 - S^2)/2$

iii) Darwin term

Flickering motion of electron in nucleus leads to average potential

$$\langle V(x+\delta x)\rangle = V(x)+\langle\delta x\nabla V(x)\rangle+\langle 1/2\ \delta x^2\nabla^2 V(x)\rangle$$

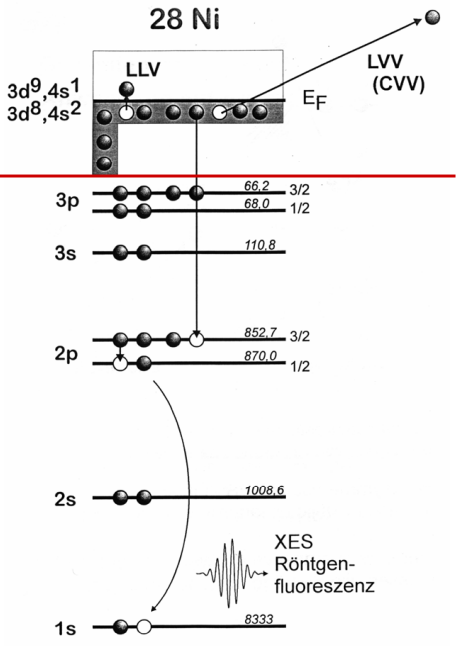
$$\langle H\rangle = E + \langle\Psi_{nl}|1/2\ \delta x^2\nabla^2 V(x)|\Psi_{nl}\rangle$$

contribution only for s-waves with finite amplitude at x = 0

Valenzniveaus

Nicht die Größe der Bindungsenergie sondern der Grad der Lokalisation der Wellenfunktion entscheidet.

Rumpfniveaus



Hund'sche Regeln für teilweise gefüllte Schalen (Valenzelektronen)

1. S maximal
2. L maximal
3. J = |L-S| für nicht mehr als halbgefüllte Schalen
4. J = L+S für mehr als halbgefüllte Schalen

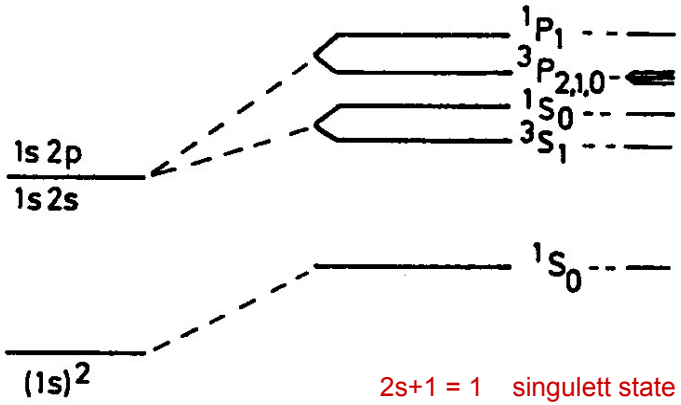
Ni: Ar $3d^8\,4s^2$

1. S = 1
2. L = 3
3. J = 4

$^{2S+1}L_J = {}^3F_4$

1.1 Atoms

He $1s^2$ – excited states $\quad {}^{2S+1}L_J$



attractive Coulomb interaction:

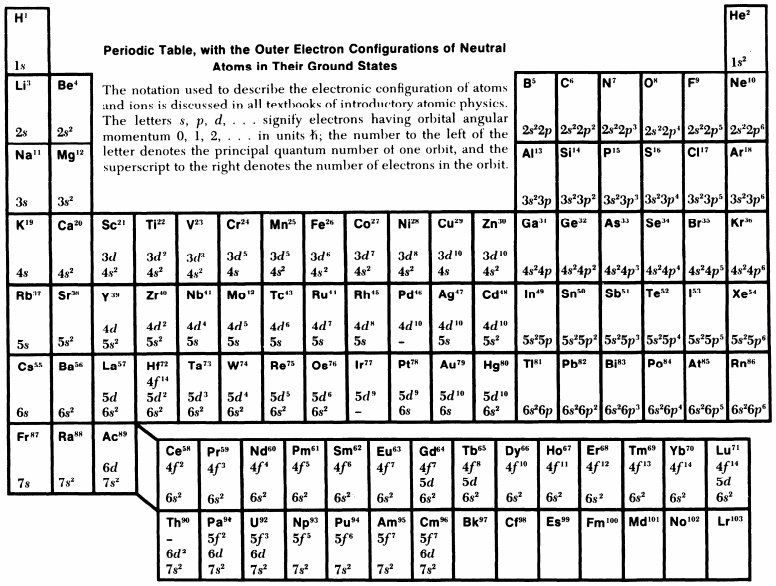
„s-wave in core, p-wave not“

2s+1 = 1 singulett state antisymmetric
2s+1 = 3 triplett state symmetric

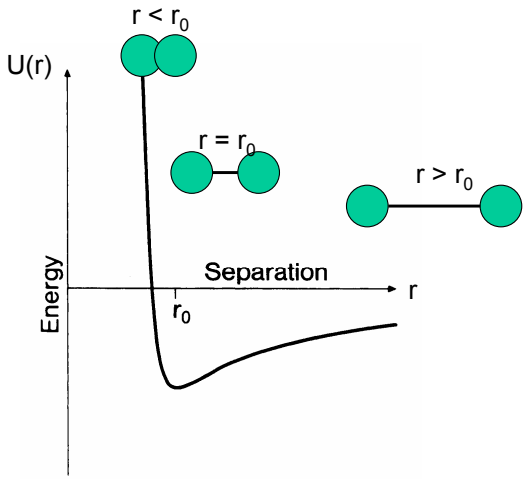
Spatial part accordingly (Hund‘s rules !)

1.1 Atoms

Aufbauprinzip



1.2 Molecules

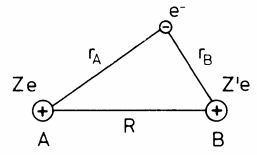


bonding (attraction) due to valence electrons
Pauli repulsion between neighbouring atoms

↳ equilibrium distance r_0 (related to lattice parameter)

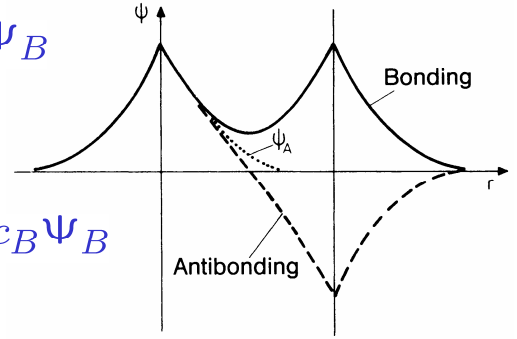
1.2 Molecules

Hydrogen ion H_2^-



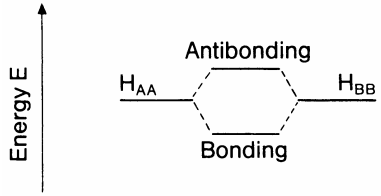
$$\Psi_{bonding} = c_A\Psi_A + c_B\Psi_B$$

$$\Psi_{antibonding} = c_A\Psi_A - c_B\Psi_B$$



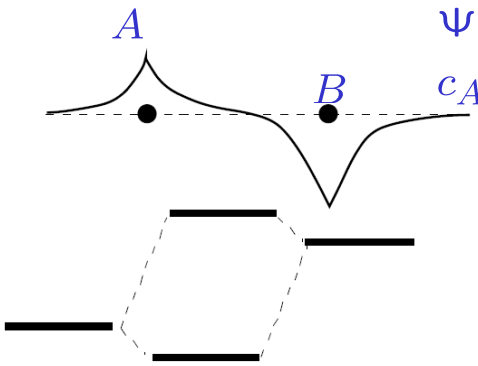
$\Psi_{A,B}$ = s-wave

$c_A = c_B$



LCAO – linear combination of atomic orbitals

$\Psi_{A,B}$ = s-wave



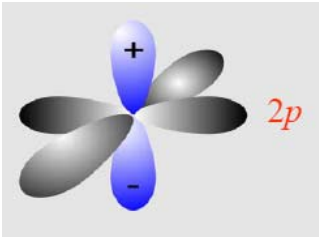
$\Psi_{antibonding} = c_A\Psi_A - c_B\Psi_B$

$|c_A| < |c_B|$

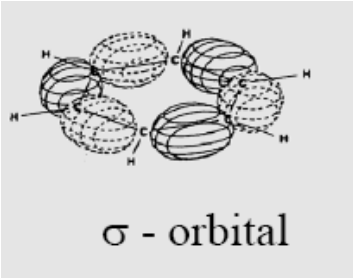
$\Psi_{bonding} = c_A\Psi_A + c_B\Psi_B$

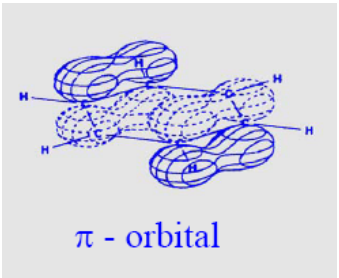
$|c_A| > |c_B|$

Molecular orbitals (e.g. benzene)

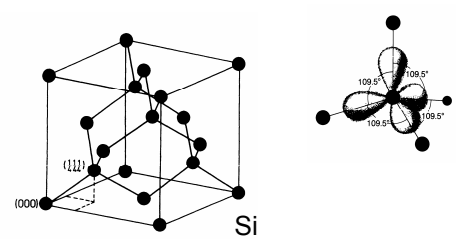


LCAO

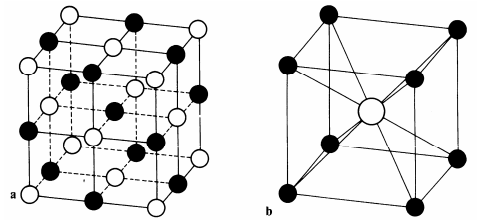




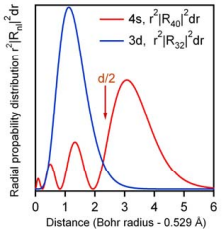
Covalent bonding (3-9 eV)

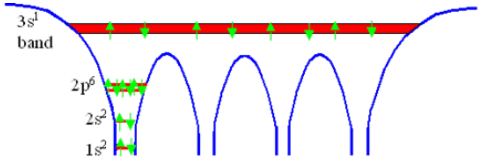


Ionic bonding (6 -10 eV)

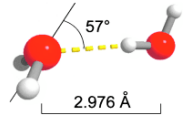


Metalic bonding (1-2 eV)

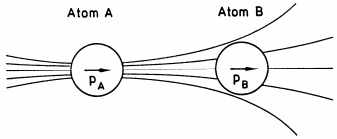




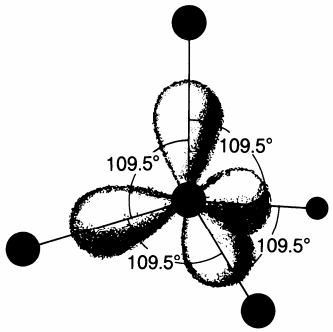
Hydrogen-bridge bonding (0.1 eV)



Van der Waals bonding (< 0.2 eV)

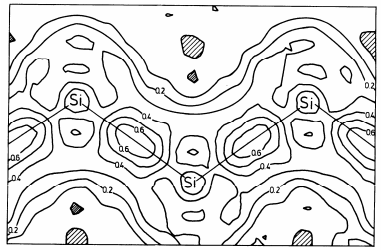


Covalent bonding

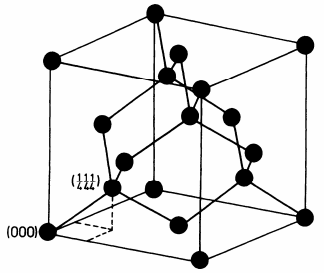


graphite: planar sp^2 structure

diamond, silicon: tetrahedral sp^3 structure



Electron density (contour plot)



Ionic bonding - energetics

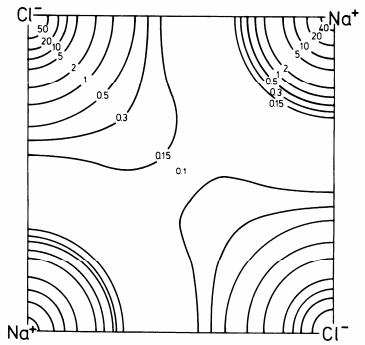
	ionization energy (eV)	electron affinity (eV)		ionization energy (eV)	electron affinity (eV)
Li	5.39	0.62	F	17.4	3.40
Na	5.14	0.55	Cl	13.0	3.61
K	4.34	0.5	Br	11.8	3.36
Rb	4.18		I	10.5	3.06

$Na + Cl \rightarrow Na^+ + Cl^- + 1.53$ eV

electrostatic interaction between ions Na^+ and Cl^-: 5.1 eV ($r_0 \sim 2.8$ Å)

total energy gain of 3.57 eV

Nearly spherical charge distributions (closed shell)



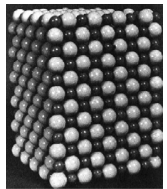
Electron density (contour plot)

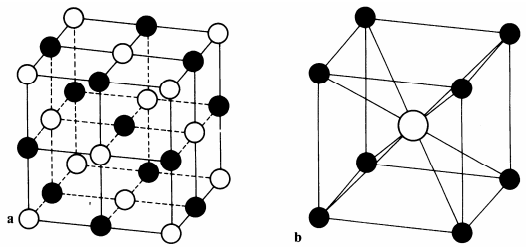
Ionic bonding - electrostatic energy (Born-Mayer potential)

$$U/N = zBe^{-r/\rho} - A\frac{e^2}{4\pi\epsilon_0 r}\ ,\ A = \sum_{i\neq j}\frac{\pm 1}{p_{ij}}$$

A Madelung constant, z coordination number

NaCl (z = 6): $A = 1.747565$





CsCl (z=8): $A = 1.762675$

	r_0 [Å]	κ [10^{-11} m^2/N]	ρ [Å]	B [eV]	$E_{Bind.}$ [eV] Theoretisch	$E_{Bind.}$ [eV] Experimentell
LiF	2,014	1,49	0,291	306	10,70	10,92
LiCl	2,570	3,36	0,330	509	8,55	8,93
NaCl	2,820	4,17	0,322	1090	7,92	8,23
NaBr	2,989	5,03	0,329	1360	7,50	7,82
NaJ	3,237	6,62	0,345	1655	6,96	7,35
KCl	3,147	5,75	0,327	2068	7,17	7,47
KJ	3,533	8,55	0,349	2936	6,43	6,75
RbF	2,815	3,82	0,301	1810	7,99	8,17

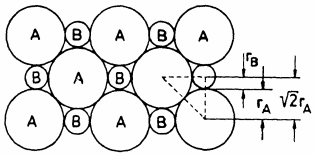
Parameters ρ and B of the repulsive potential determined by equilibrium distance r_0 and compressibility κ

Different structures of ionic crystals:

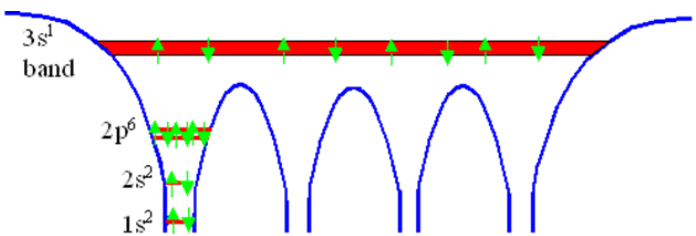
stability depends on the ratio r_A / r_B of ionic radii:

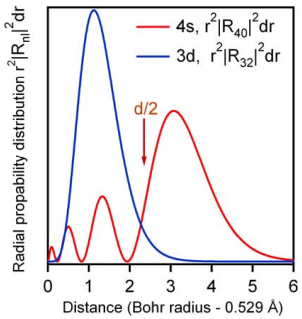
CsCl ↔ NaCl ↔ ZnS

$1.37 < r_A / r_B < 2.44$



Metallic bonding

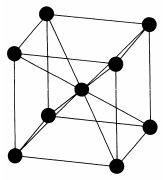




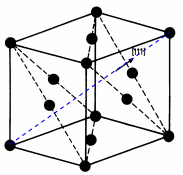
Overlapping wave functions form delocalized states (Bloch states)

- s – electrons of Alkali metals Li, Na, K, Cs, Rb (bcc)
- s,p – electrons of 3d metals Fe (bcc), Co (hcp), Ni (fcc), Cu (fcc)
  (d-electrons add covalent character)

bcc

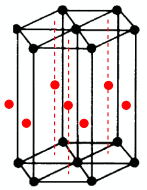


fcc



hexagonal

hcp

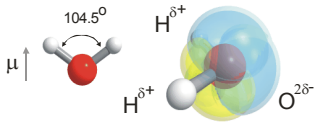


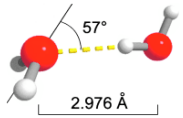
Hydrogen-bridge bonding

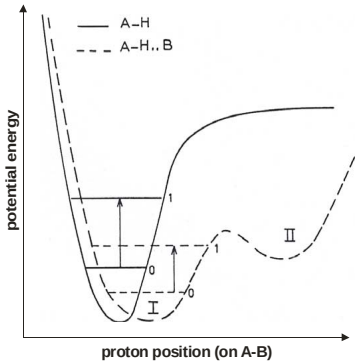
Hydrogen: $1s^1$, I_p = 15.6 eV, 'ion core' (proton) with radius ~10^{-15} m

- Electron transfer to strongly electronegative atoms (F, O, ...)
- Small size of proton leads to hydrogen bond A-H...B
  between two negatively charged atoms (double well potential)

Water

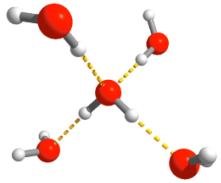


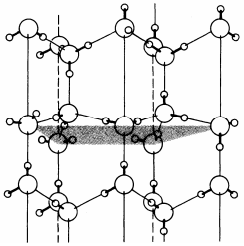




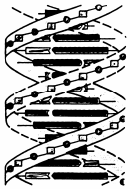
Hydrogen-bridge bonding

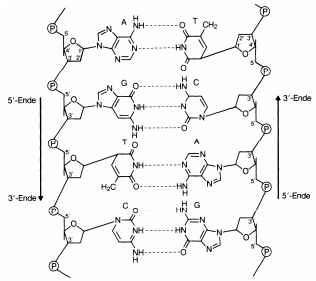
Ice

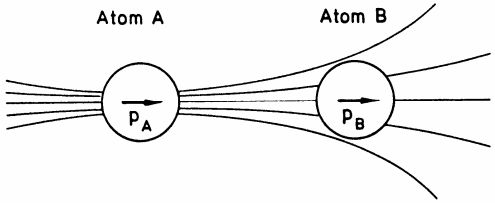




DNA





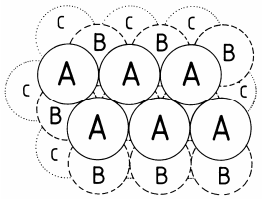


Origin: Interplay between attractive (van der Waals) and repulsive forces
- van der Waals interaction:
  zero point fluctuations of electrons lead to induced dipole forces
- Short range repulsive interaction due to Pauli exclusion principle

´Model potential: Lennard-Jones potential

$$U(r) = 4\epsilon\{(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}\}$$

$$U_{tot}(r) = 2N\epsilon\{A_{12}(\frac{\sigma}{r})^{12} - A_6(\frac{\sigma}{r})^{6}\};\ A_n = \sum_{i\neq j}(\frac{1}{p_{ij}})^n$$



closed packed
fcc (ABC – stacking)
A_{12} = 12.13; A_6 = 14.45
hcp (AB – stacking)

	Nearest-neighbor distance, in Å	Experimental cohesive energy kJ/mol	Experimental cohesive energy eV/atom	Melting point, K	Ionization potential of free atom, eV	
He	(liquid at zero pressure)				24.58	hcp
Ne	3.13	1.88	0.02	24	21.56	fcc
Ar	3.76	7.74	0.080	84	15.76	fcc
Kr	4.01	11.2	0.116	117	14.00	fcc
Xe	4.35	16.0	0.17	161	12.13	fcc

1.3 Crystal binding energy / atom

Table 1 Cohesive energies

Energy required to form separated neutral atoms in their ground electronic state from the solid at 0 K at 1 atm. The data were supplied by Prof. Leo Brewer in units kcal per mole, revised to May 4, 1977, after LBL Report 3720 Rev.

Li	Be											B	C	N	O	F	Ne
158.	320.											561	711.	474.	251.	81.0	1.92
1.63	3.32											5.81	7.37	4.92	2.60	0.84	0.020
37.7	76.5											134	170.	113.4	60.03	19.37	0.46
Na	Mg	← kJ/mol →										Al	Si	P	S	Cl	Ar
107.	145.											327.	446.	331.	275.	135.	7.74
1.113	1.51	← eV/atom →										3.39	4.63	3.43	2.85	1.40	0.080
25.67	34.7	← kcal/mol →										78.1	106.7	79.16	65.75	32.2	1.85
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
90.1	178.	376	468.	512.	395.	282.	413.	424.	428.	336.	130	271.	372.	285.3	237	118.	11.2
0.934	1.84	3.90	4.85	5.31	4.10	2.92	4.28	4.39	4.44	3.49	1.35	2.81	3.85	2.96	2.46	1.22	0.116
21.54	42.5	89.9	111.8	122.4	94.5	67.4	98.7	101.3	102.4	80.4	31.04	64.8	88.8	68.2	56.7	28.18	2.68
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
82.2	166.	422.	603.	730.	658	661.	650.	554.	376.	284.	112.	243.	303.	265.	211	107.	15.9
0.852	1.72	4.37	6.25	7.57	6.82	6.85	6.74	5.75	3.89	2.95	1.16	2.52	3.14	2.75	2.19	1.11	0.16
19.64	39.7	100.8	144.2	174.5	157.2	158.	155.4	132.5	89.8	68.0	26.73	58.1	72.4	63.4	50.34	25.62	3.80
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
77.6	183.	431.	621.	782.	859.	775.	788.	670.	564.	368.	65.	182.	196.	210.	144.		19.5
0.804	1.90	4.47	6.44	8.10	8.90	8.03	8.17	6.94	5.84	3.81	0.67	1.88	2.03	2.18	1.50		0.202
18.54	43.7	103.1	148.4	186.9	205.2	185.2	188.4	160.1	134.7	87.96	15.5	43.4	46.78	50.2	34.5		4.66
Fr	Ra	Ac															
	160.	410.															
	1.66	4.25															
	38.2	98.															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
417.	357.	328.		206.	179.	400.	391.	294.	302.	317.	233.	154.	428.
4.32	3.70	3.40		2.14	1.86	4.14	4.05	3.04	3.14	3.29	2.42	1.60	4.43
99.7	85.3	78.5		49.3	42.8	95.5	93.4	70.2	72.3	75.8	55.8	37.1	102.2
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
598		536.	456	347.	264.	385							
6.20		5.55	4.73	3.60	2.73	3.99							
142.9		128.	109.	83.0	63.	92.1							

metals: ~1 - 2 eV/atom
covalent: ~3 - 9 eV/atom
ionic: ~6-10 eV/atom

van der Waals: 20-200 meV/atom
hydrogen: ~100 meV/bond

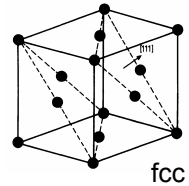
1.4 Bravais lattice

Table 3 Crystal structures of the elements

The data given are at room temperature for the most common form, or at the stated temperature in deg K. For further descriptions of the elements see Wyckoff, Vol. 1, Chap. 2. Structures labeled complex are described there.

H[1] 4K																	He[4] 2K
hcp																	hcp
3.75																	3.57
6.12																	5.83
Li 78K	Be											B	C	N 20K	O	F	Ne 4K
bcc	hcp											rhomb.	diamond	cubic	complex		fcc
3.491	2.27												3.567	5.66 (N_2)	(O_2)		4.46
	3.59																
Na 5K	Mg	← Crystal structure. →										Al	Si	P	S	Cl	Ar 4K
bcc	hcp	← a lattice parameter, in Å →										fcc	diamond	complex	complex	complex	fcc
4.225	3.21	← c lattice parameter, in Å. →										4.05	5.430			(Cl_2)	5.31
	5.21																
K 5K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr 4K
bcc	fcc	hcp	hcp	bcc	bcc	cubic	bcc	hcp	fcc	fcc	hcp	complex	diamond	rhomb.	hex.	complex	fcc
5.225	5.58	3.31	2.95	3.03	2.88	complex	2.87	2.51	3.52	3.61	2.66		5.658		chains	(Br_2)	5.64
		5.27	4.68					4.07			4.95						
Rb 5K	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn (α)	Sb	Te	I	Xe 4K
bcc	fcc	hcp	hcp	bcc	bcc	hcp	hcp	fcc	fcc	fcc	hcp	tetr.	diamond	rhomb.	hex.	complex	fcc
5.585	6.08	3.65	3.23	3.30	3.15	2.74	2.71	3.80	3.89	4.09	2.98	3.25	6.49		chains	(I_2)	6.13
		5.73	5.15			4.40	4.28				5.62	4.95					
Cs 5K	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
bcc	bcc	hex.	hcp	bcc	bcc	hcp	hcp	fcc	fcc	fcc	rhomb.	hcp	fcc	rhomb.	sc		
6.045	5.02	3.77	3.19	3.30	3.16	2.76	2.74	3.84	3.92	4.08		3.46	4.95		3.34	—	—
		ABAC	5.05			4.46	4.32					5.52					
Fr	Ra	Ac															
—	—	fcc															
		5.31															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
fcc	hex.	hex.	—	complex	bcc	hcp	hcp	hcp	hcp	hcp	hcp	fcc	hcp
5.16	3.67	3.66			4.58	3.63	3.60	3.59	3.58	3.56	3.54	5.48	3.50
	ABAC					5.78	5.70	5.65	5.62	5.59	5.56		5.55
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
fcc	tetr.	complex	complex	complex	hex.	—	—	—	—	—	—	—	—
5.08	3.92				3.64								
	3.24				ABAC								



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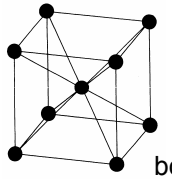
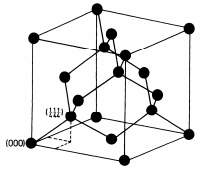
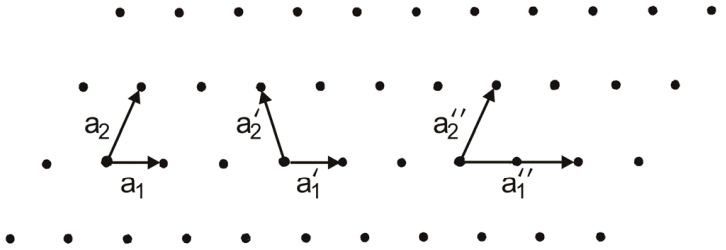

bcc



diamond

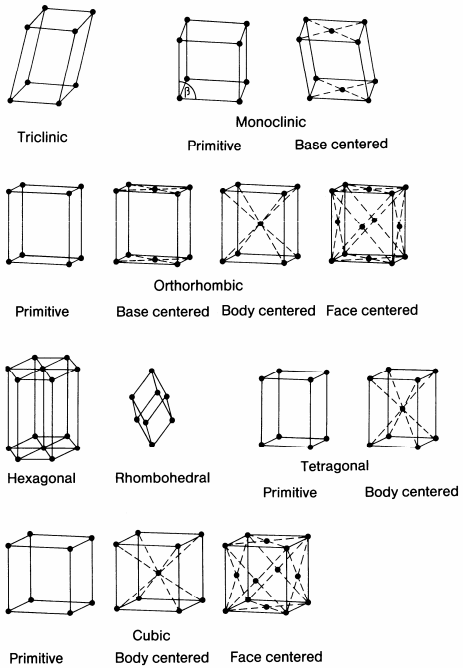
1.4 2d - Bravais lattice



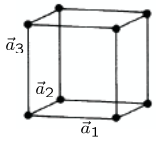
- choice of unit cell is not unique
- primitive unit cell contains only one point

1.4 14 Bravais lattices

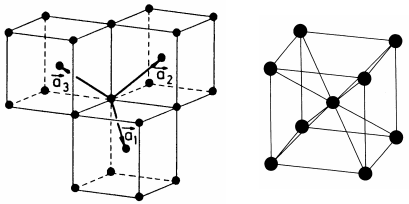
System	Number of lattices	Restrictions on conventional cell axes and angles
Triclinic	1	$a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2	$a_1 \neq a_2 \neq a_3$ $\alpha = \gamma = 90° \neq \beta$
Orthorhombic	4	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90°$
Tetragonal	2	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90°$
Cubic	3	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90°$
Trigonal	1	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < 120°, \neq 90°$
Hexagonal	1	$a_1 = a_2 \neq a_3$ $\alpha = \beta = 90°$ $\gamma = 120°$



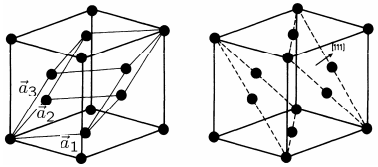
simple cubic



body-centered cubic

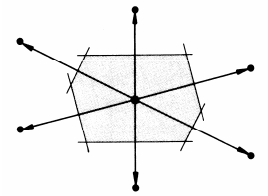


face-centered cubic

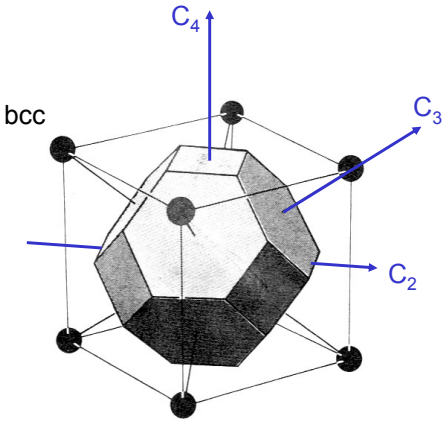


Wigner-Seitz cell

2 - dim.



bcc



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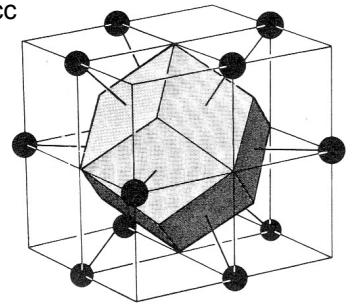
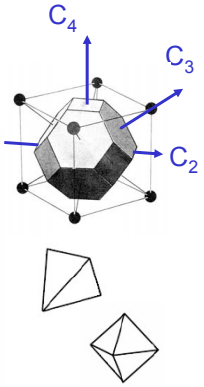


Wigner-Seitz cell reflects symmetry of point group

32 crystallographic point groups



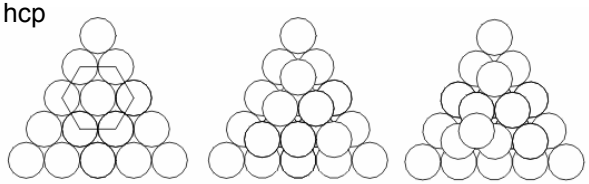
Schönflies symbols

	Symbol	Meaning
Classification according to rotation axes and principal mirror planes	C_j	(j=2, 3, 4, 6) j-fold rotation axis
	S_j	j-fold rotation-inversion axis
	D_j	j two-fold rotation axes ⊥ to a (j-fold) principal rotation axis
	T	4 three- and 3 two-fold rotation axes as in a tetrahedron
	O	4 three- and 3 four-fold rotation axes as in an octahedron
	C_i	a center of inversion
	C_s	a mirror plane
Additional symbols for mirror planes	h	horizontal = perpendicular to the rotation axis
	v	vertical = parallel to the main rotation axis
	d	diagonal = parallel to the main rotation axis in the plane bisecting the 2-fold rotation axes

Diamond point group T_d ; fcc and bcc point group O_h

Hexagonal close-packed

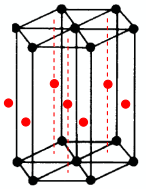
hcp



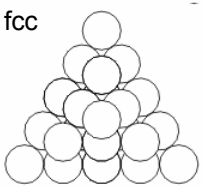
stacking ABABAB...

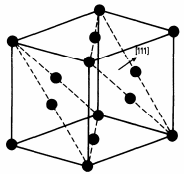
hexagonal

hcp



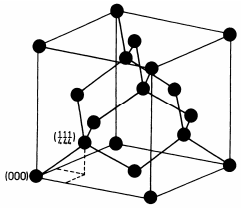
fcc



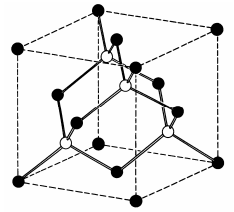


stacking ABCABC...

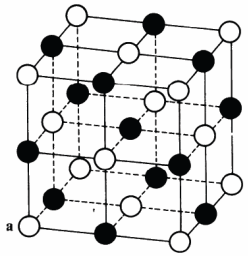
Diamond structure C, Si, Ge



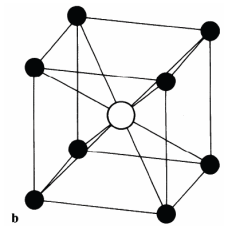
Zink sulfid structure ZnS, GaAs, AgI



NaCl

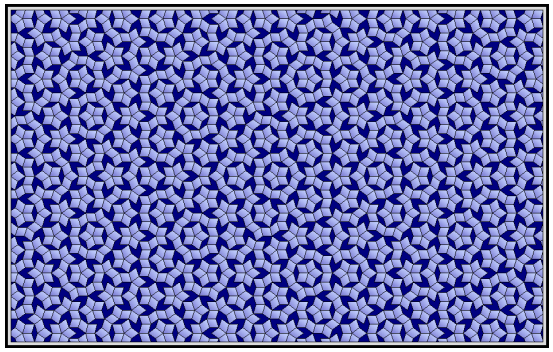


CsCl, NiAl, CuBe

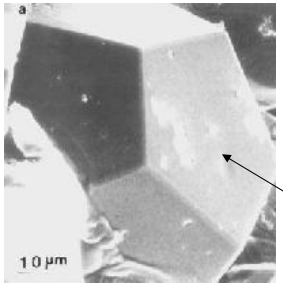


Quasicrystals

long-range orientational, but non-periodic order



Penrose tiles

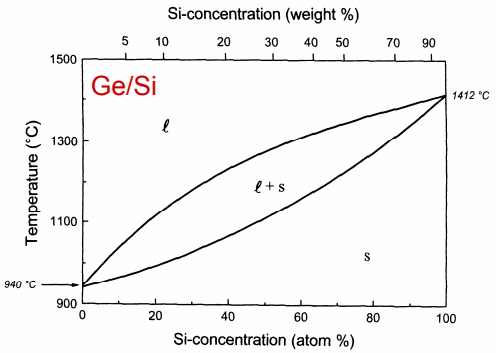


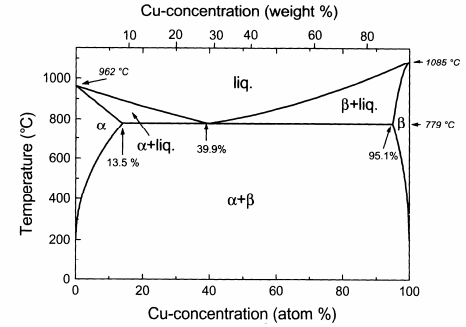
fivefold symmetry

$Al_{65}Cu_{20}Fe_{15}$
produced by cooling with 10^6 K/s

Substitutional binary alloys

Two elements crystallizing with the same structure

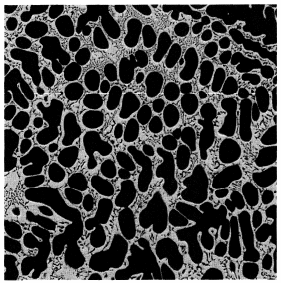




30% Ag/ 70% Cu

86 % Ag

95 % Cu



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