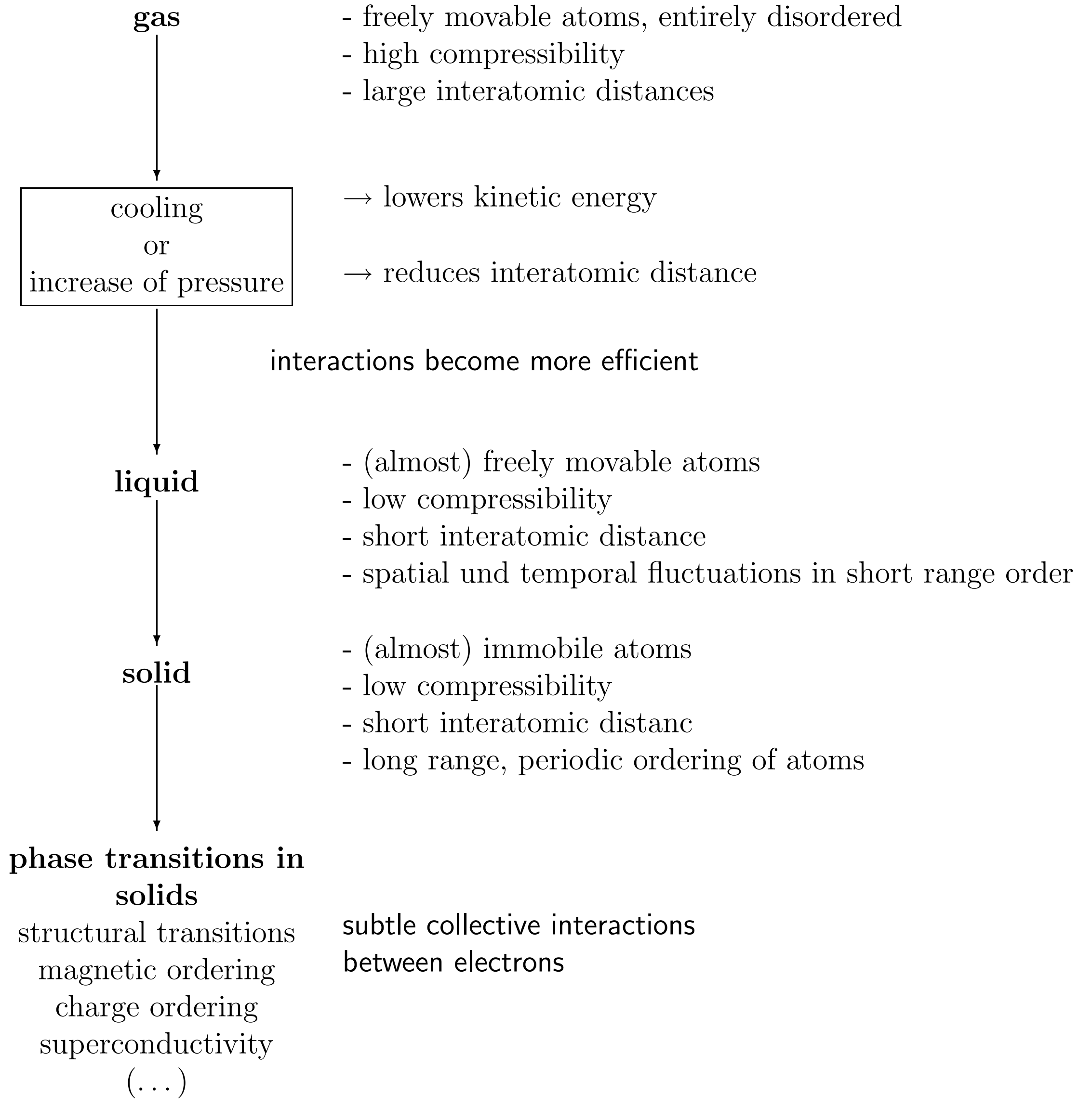
Chapter 2

Crystal Binding and some Crystal structures

From a gas to a solid



gas
- freely movable atoms, entirely disordered
- high compressibility
- large interatomic distances

cooling
or
increase of pressure

→ lowers kinetic energy

→ reduces interatomic distance

interactions become more efficient

liquid
- (almost) freely movable atoms
- low compressibility
- short interatomic distance
- spatial und temporal fluctuations in short range order

solid
- (almost) immobile atoms
- low compressibility
- short interatomic distanc
- long range, periodic ordering of atoms

phase transitions in solids
structural transitions
magnetic ordering
charge ordering
superconductivity
(...)

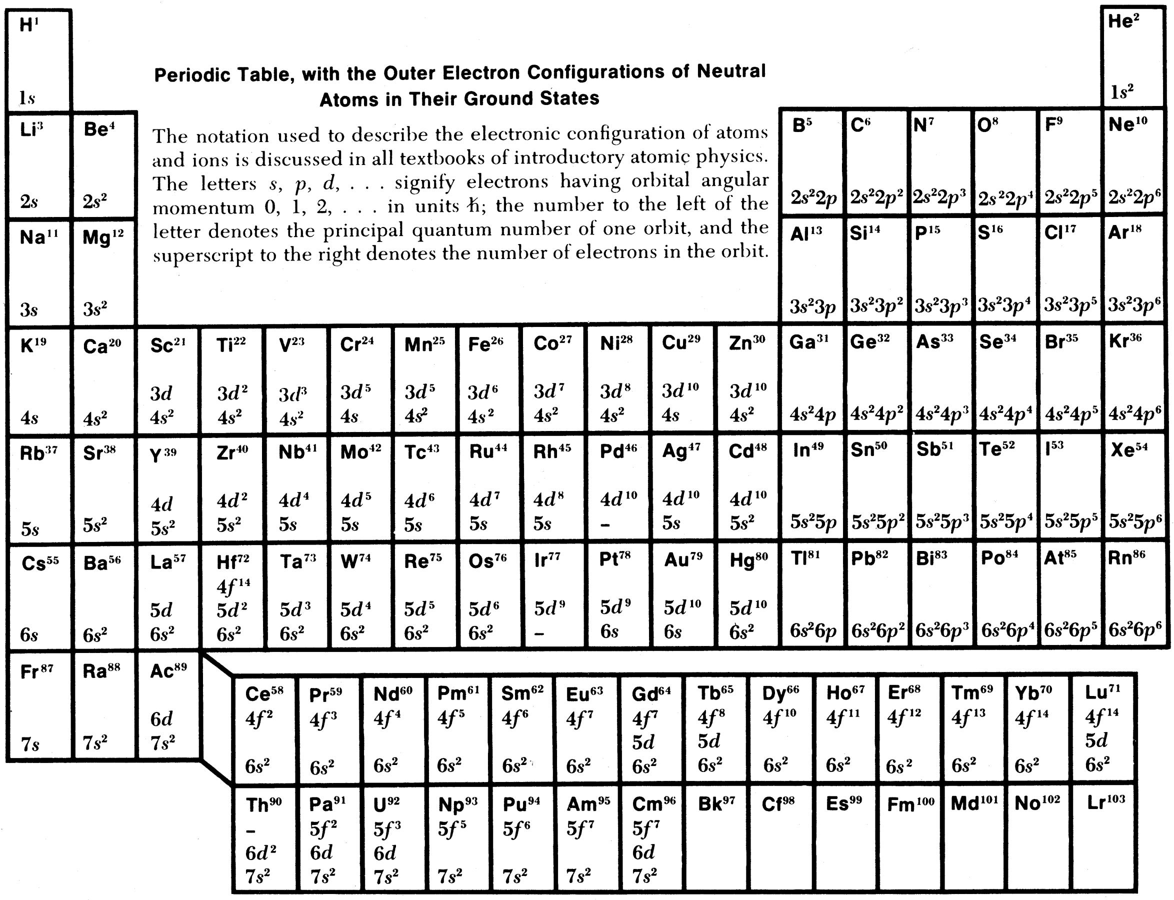
subtle collective interactions
between electrons

The arrangement of atoms in a solid (its 'structure') can be of many different types, even for the same material. Its formation depends on 'external' parameters like temperature T and pressure p and the 'route' in the $p - T$ phase diagram which is followed during transition, e.g. from a liquid to a solid. Important 'internal' parameters are the electronic configuration of the atoms, or the atomic/ionic radii, which also determine the nature and strength of binding between atoms.

Probably the most prominent state of condensed matter is the crystalline state, although other types like polycrystalline, amorphous or glassy states can be very important both for basic research and for various applications (e.g. amorphous superconductors with very small intrinsic pinning of flux lines or amorphous Si for solar cells).

Throughout this course we will focus on solids in the crystalline state, i.e. with a periodic arrangement of the atoms – the crystal lattice. Solid state physics is largely concerned with crystals and electrons in crystals. In the present chapter we will ask the basic question: **What holds a crystal together?**

We will answer this question by simultaneously introducing some typical crystal structures and types of crystal bonds, simply going through the periodic table of elements



Periodic Table, with the Outer Electron Configurations of Neutral Atoms in Their Ground States

The notation used to describe the electronic configuration of atoms and ions is discussed in all textbooks of introductory atomic physics. The letters s, p, d, . . . signify electrons having orbital angular momentum 0, 1, 2, . . . in units $\hbar$; the number to the left of the letter denotes the principal quantum number of one orbit, and the superscript to the right denotes the number of electrons in the orbit.

H^{1} $1s$																	**He**^{2} $1s^2$
Li^{3} $2s$	**Be**^{4} $2s^2$											**B**^{5} $2s^22p$	**C**^{6} $2s^22p^2$	**N**^{7} $2s^22p^3$	**O**^{8} $2s^22p^4$	**F**^{9} $2s^22p^5$	**Ne**^{10} $2s^22p^6$
Na^{11} $3s$	**Mg**^{12} $3s^2$											**Al**^{13} $3s^23p$	**Si**^{14} $3s^23p^2$	**P**^{15} $3s^23p^3$	**S**^{16} $3s^23p^4$	**Cl**^{17} $3s^23p^5$	**Ar**^{18} $3s^23p^6$
K^{19} $4s$	**Ca**^{20} $4s^2$	**Sc**^{21} $3d$ $4s^2$	**Ti**^{22} $3d^2$ $4s^2$	**V**^{23} $3d^3$ $4s^2$	**Cr**^{24} $3d^5$ $4s$	**Mn**^{25} $3d^5$ $4s^2$	**Fe**^{26} $3d^6$ $4s^2$	**Co**^{27} $3d^7$ $4s^2$	**Ni**^{28} $3d^8$ $4s^2$	**Cu**^{29} $3d^{10}$ $4s$	**Zn**^{30} $3d^{10}$ $4s^2$	**Ga**^{31} $4s^24p$	**Ge**^{32} $4s^24p^2$	**As**^{33} $4s^24p^3$	**Se**^{34} $4s^24p^4$	**Br**^{35} $4s^24p^5$	**Kr**^{36} $4s^24p^6$
Rb^{37} $5s$	**Sr**^{38} $5s^2$	**Y**^{39} $4d$ $5s^2$	**Zr**^{40} $4d^2$ $5s^2$	**Nb**^{41} $4d^4$ $5s$	**Mo**^{42} $4d^5$ $5s$	**Tc**^{43} $4d^6$ $5s$	**Ru**^{44} $4d^7$ $5s$	**Rh**^{45} $4d^8$ $5s$	**Pd**^{46} $4d^{10}$ –	**Ag**^{47} $4d^{10}$ $5s$	**Cd**^{48} $4d^{10}$ $5s^2$	**In**^{49} $5s^25p$	**Sn**^{50} $5s^25p^2$	**Sb**^{51} $5s^25p^3$	**Te**^{52} $5s^25p^4$	**I**^{53} $5s^25p^5$	**Xe**^{54} $5s^25p^6$
Cs^{55} $6s$	**Ba**^{56} $6s^2$	**La**^{57} $5d$ $6s^2$	**Hf**^{72} $4f^{14}$ $5d^2$ $6s^2$	**Ta**^{73} $5d^3$ $6s^2$	**W**^{74} $5d^4$ $6s^2$	**Re**^{75} $5d^5$ $6s^2$	**Os**^{76} $5d^6$ $6s^2$	**Ir**^{77} $5d^9$ –	**Pt**^{78} $5d^9$ $6s$	**Au**^{79} $5d^{10}$ $6s$	**Hg**^{80} $5d^{10}$ $6s^2$	**Tl**^{81} $6s^26p$	**Pb**^{82} $6s^26p^2$	**Bi**^{83} $6s^26p^3$	**Po**^{84} $6s^26p^4$	**At**^{85} $6s^26p^5$	**Rn**^{86} $6s^26p^6$
Fr^{87} $7s$	**Ra**^{88} $7s^2$	**Ac**^{89} $6d$ $7s^2$															

Ce^{58} $4f^2$ $6s^2$	**Pr**^{59} $4f^3$ $6s^2$	**Nd**^{60} $4f^4$ $6s^2$	**Pm**^{61} $4f^5$ $6s^2$	**Sm**^{62} $4f^6$ $6s^2$	**Eu**^{63} $4f^7$ $6s^2$	**Gd**^{64} $4f^7$ $5d$ $6s^2$	**Tb**^{65} $4f^8$ $5d$ $6s^2$	**Dy**^{66} $4f^{10}$ $6s^2$	**Ho**^{67} $4f^{11}$ $6s^2$	**Er**^{68} $4f^{12}$ $6s^2$	**Tm**^{69} $4f^{13}$ $6s^2$	**Yb**^{70} $4f^{14}$ $6s^2$	**Lu**^{71} $4f^{14}$ $5d$ $6s^2$
Th^{90} – $6d^2$ $7s^2$	**Pa**^{91} $5f^2$ $6d$ $7s^2$	**U**^{92} $5f^3$ $6d$ $7s^2$	**Np**^{93} $5f^5$ $7s^2$	**Pu**^{94} $5f^6$ $7s^2$	**Am**^{95} $5f^7$ $7s^2$	**Cm**^{96} $5f^7$ $6d$ $7s^2$	**Bk**^{97}	**Cf**^{98}	**Es**^{99}	**Fm**^{100}	**Md**^{101}	**No**^{102}	**Lr**^{103}

Figure 2.1: Periodic table of the elements [from Kittel, *Introduction to Solid State Physics* (1996); Fig.Front02] (see also http://www.webelements.com).

2.1 Hydrogen

electronic configuration: $1s$

the "simplest" and by far the most abundant element in the solar system

forms molecular hydrogen H_2
→ gas at R.T.[1] ($p = 1\,\text{bar}$)
→ liquid below $T_{boil} = 20.4$ K ($p = 1$ bar)
→ solid below $T_{melt} = 14$ K ($p = 1$ bar)

Properties of solid diatomic molecular Hydrogen:

- strong covalent molecular bonds (→ box on next page)
- molecules are in (almost) free rotational states
- complex, slightly anisotropic, weak intermolecular interaction
- filled valence band with large band gap → good insulator
- charge distribution is almost spherical → behavior is similar to a noble-gas[2] solid → (isotropic) parametrization of the intermolecular interaction potential

$$\Phi(R) = 4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right] \qquad \text{Lenard} - \text{Jones potential} \tag{2.1}$$

1. term: repulsion at short intermolecular distance R (Pauli principle)
2. term: attraction at large distance R
(induced dipole-dipole interaction = Van der Waals interaction)

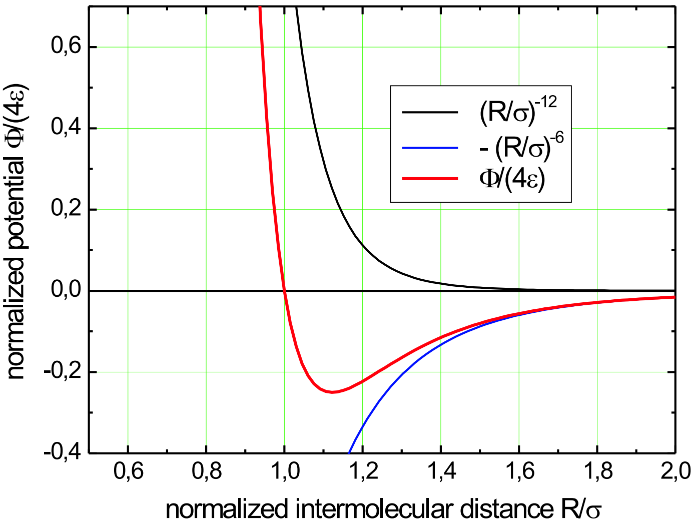


Figure 2.2: Lenard-Jones potential calculated from (2.1).

Parametrization is also used for other molecules.
For H_2: $\varepsilon \approx 3.2\,\text{meV} \rightarrow \varepsilon/k_B \approx 37$ K (k_B: Boltzmann constant $\approx 1\,\text{meV}/11.6\,\text{K}$)
$\sigma \approx 3$ Å
→ minimum $\Phi(R_0) = -\varepsilon$ at $R_0 = 2^{1/6} \cdot \varepsilon \approx 1.12 \cdot \varepsilon \approx 3.3$ Å

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[1] R.T. ≡ room temperature
[2] rare gas = inert gas = 'Edelgas'

covalent bond:

- usually formed from two electrons,
  one from each atom participating in the bond
  (the 'classical' electron pair bond of organic chemistry)
- the covalent bond is strong:
  e.g. bond between two Carbon atoms in diamond is comparable in strength to the bond strength in ionic crystals (e.g. sodium chloride – Na^+Cl^-)
- the covalent bond is strongly directional
  ⇒ gives typically low filling of space
  (see more below → diamond structure)
- electrons forming the bond tend to be partly localized in the region between the two atoms joined by the bond;
  important: antiparallel spin configuration lowers energy due to **Pauli principle**
  The Pauli principle modifies the distribution of charge according to the spin orientation
  ⇒ spin-dependent Coulomb energy ⇔ **exchange interaction**

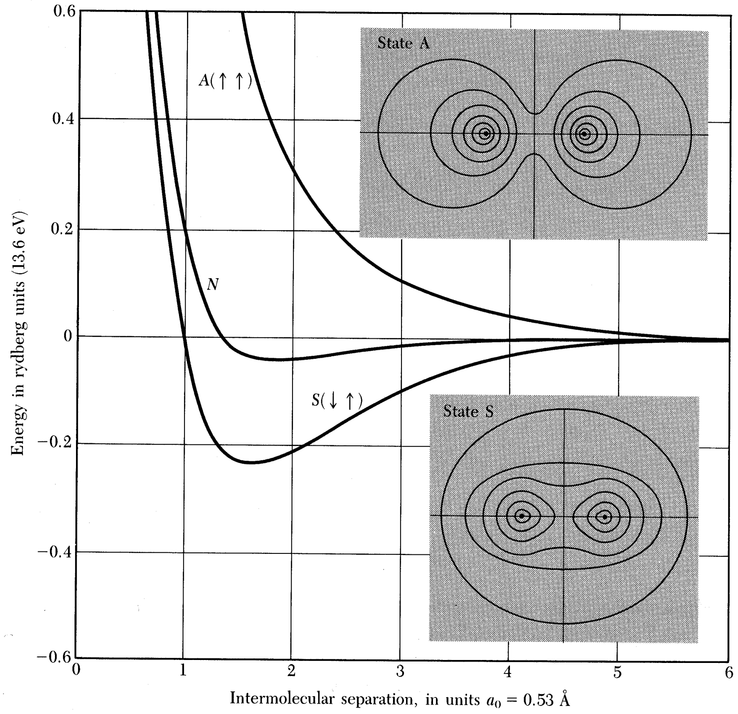

Figure 2.3: Energy of molecular hydrogen (H_2) referred to separated neutral atoms. A negative energy corresponds to binding. The curve N refers to a classical calculation with free atom charge densities; A is the result for parallel electron spins, taking the Pauli exclusion principle into account, and S (the stable state) for antiparallel spins. The density of charge is represented by contour lines for the states A and S [from Kittel, *Introduction to Solid State Physics* (1996); Fig.3.12].

Crystal structure of solid molecular hydrogen:
hexagonal close packed (hcp), compare Kittel, Fig. 1.21 – 1.23)
(**"Hexagonal dichteste Kugelpackung"**)

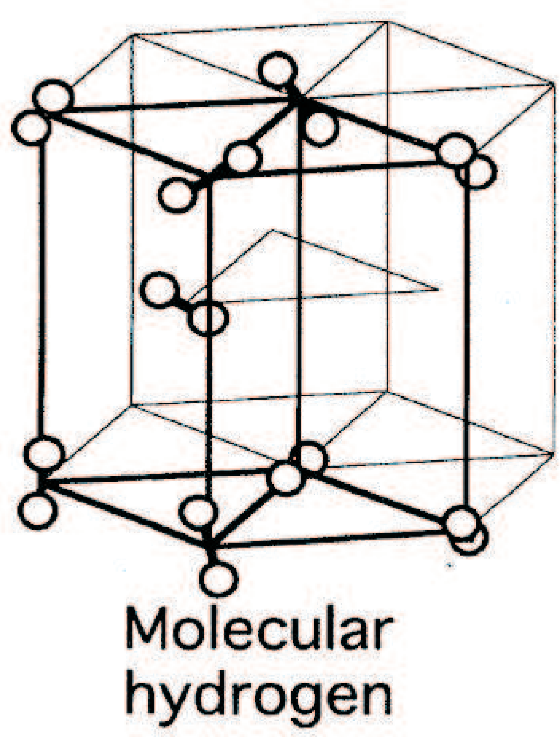

Figure 2.4: Idealized structure of solid molecular hydrogen (disordered hexagonal-close packed) [from Mao and Hemley, *Ultrahigh pressure transitions in solid hydrogen*, Rev. Mod. Phys. **66**, 671 (1994); Fig.1a].

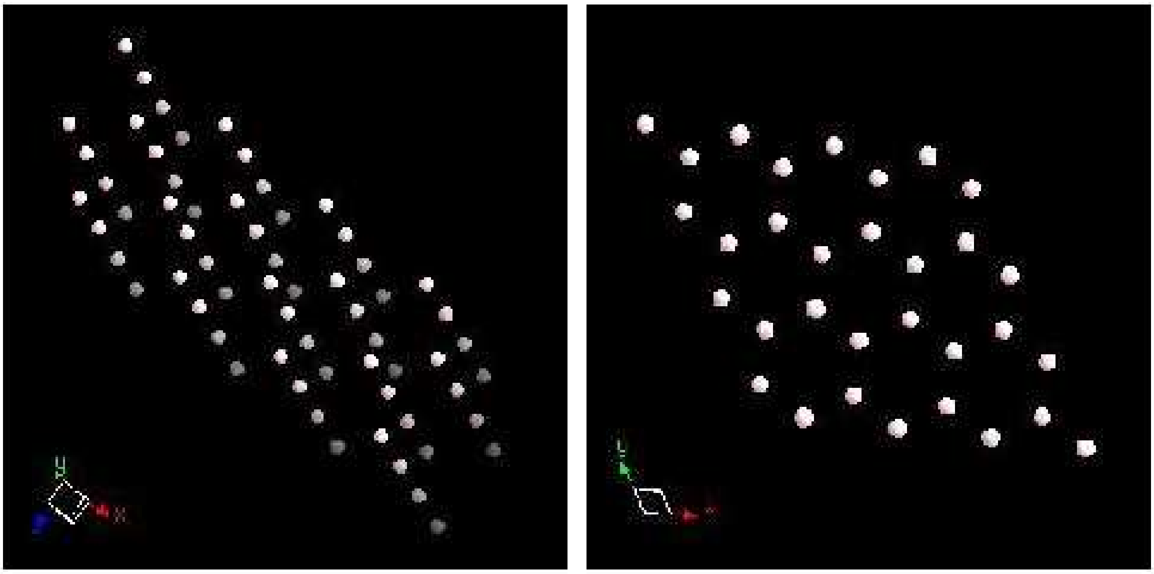

Figure 2.5: hcp structure of a molecular hydrogen crystal (view from different directions); each dot corresponds to a H_2 molecule [from http://www.webelements.com].

some remarks on H_2

- hydrogen is the lightest element,
  undergoes even at $T = 0$ strong oscillations about its equilibrium coordinate r_0
  → "zero point fluctuations" ("Nullpunktsschwingungen")
  (→ quantum mechanical effect)

$$E_{\text{zero point}} = \frac{1}{2}\hbar\omega$$

with ω = oscillation frequency,
$\hbar = \frac{h}{2\pi} = 1.0546 \cdot 10^{-34}$ Js: Planck constant.

→ kinetic energy contribution $E_{kin} = p^2/(2M)$
for particle with momentum p and mass M.

With quantum wavelength $\lambda = h/p$ (defined by boundaries):
$E_{kin} = (h/\lambda)^2/2M \propto M^{-1}$

Zero point fluctuations contribute an additional positive energy
to the (negative) cohesive energy of the crystal [3]

→ act as effective repulsive force

→ increase nearest-neighbor separation r_0 (or lattice constant) in equilibrium.

⇒ the lighter the atom, the larger is the amplitude of the oscillation.

Properties of solid molecular hydrogen are strongly affected by zero point fluctuations ('quantum crystal')

H_2 forms the only "quantum **molecular** crystal"

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[3] The cohesive energy is obtained by summation of (2.1) over all atoms/molecules in a crystal (only significant contribution from nearest neighbors) yields $r_0/\varepsilon = 1.09$ instead of 1.12; is valid e.g. for the heavy noble gas Xe, but increases with reduction of mass M due to zero point fluctuations

- relatively large distance between the molecules ↔ strongly compressible

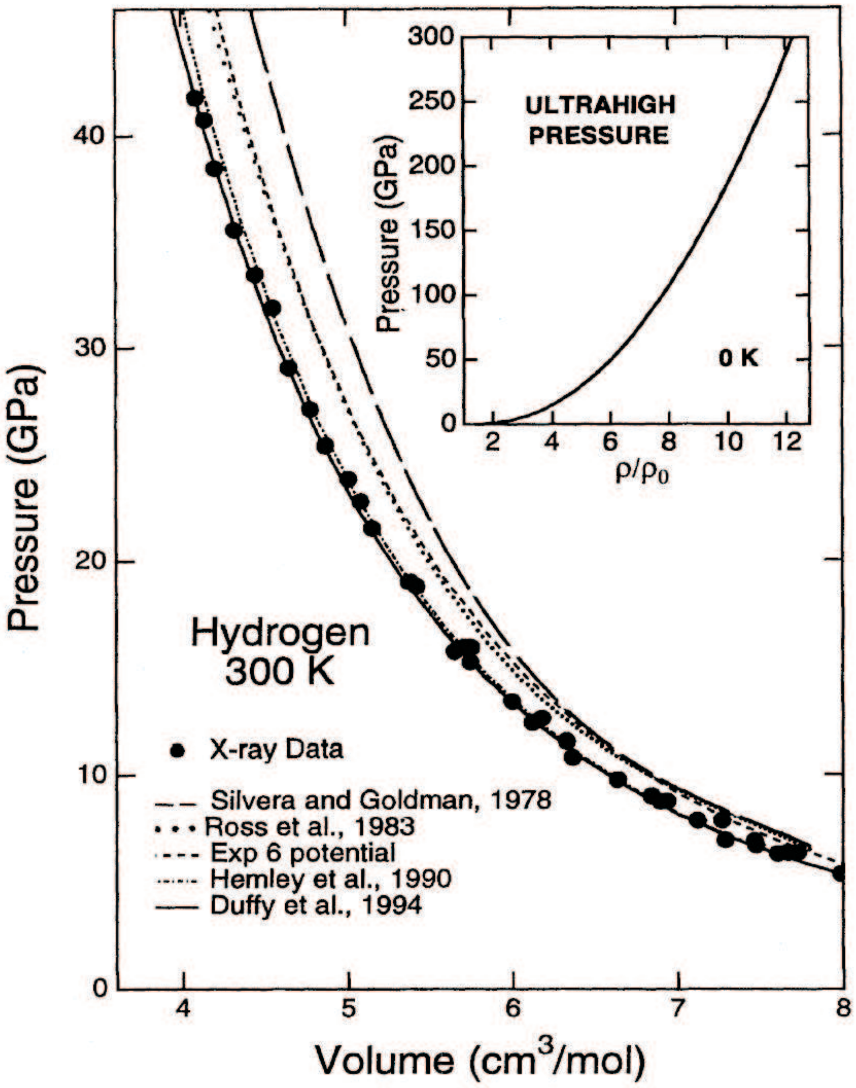

Figure 2.6: Pressure-volume relations for solid hydrogen determined from x-ray diffraction at 300 K, compared to equations of state calculated using lattice dynamics from effective pair, or two-body, intermolecular potentials [from, Mao and Hemley, *Ultrahigh pressure transitions in solid hydrogen*, Rev. Mod. Phys. **66**, 671 (1994); Fig.4].

- density at $T = 0$: $\rho = 23$ cm^3/mol for $p = 0$
  $\rho = 10$ cm^3/mol for $p = 0.25\,$kbar

- depending on pressure, H_2 can also form a **"cubic close-packed"** or **"face centered cubic" (fcc) lattice** (**"kubisch-flächenzentriertes Gitter"**)

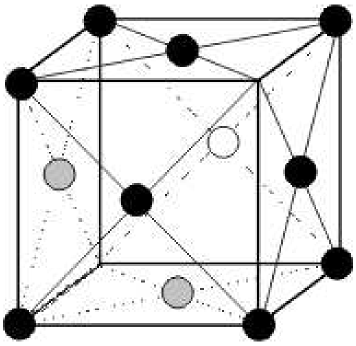

Figure 2.7: H_2 molecules on corners and diagonals of the surface of a cube [from Kleiner, *Lecture Notes* (2000); Abb.ExPIVb-P18-01].

... or even more complex crystallographic configurations

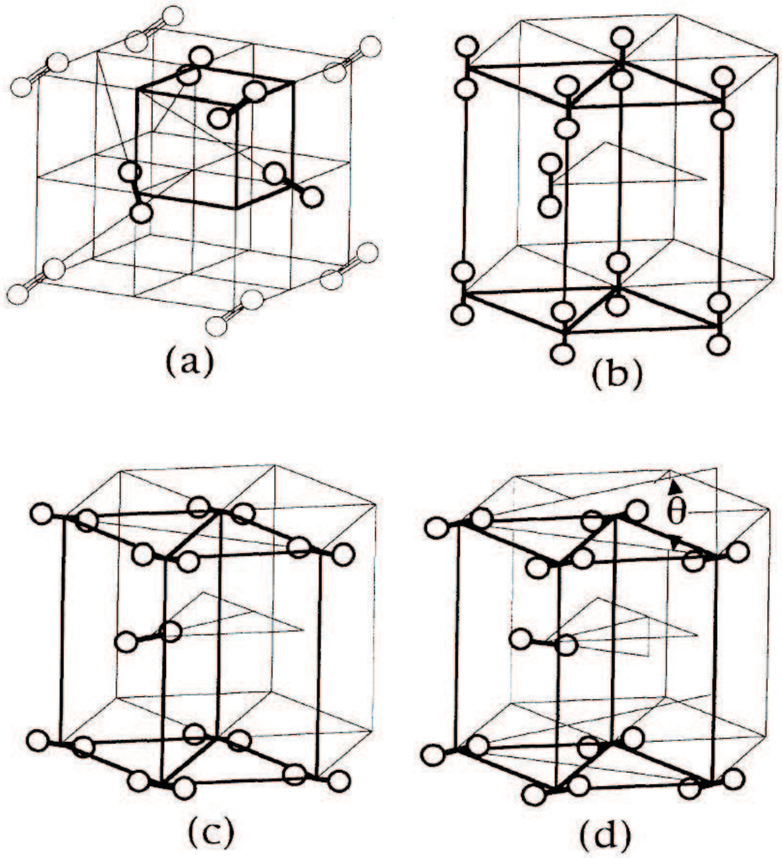

Figure 2.8: Predicted oriented crystal structures for hydrogen. (a) cubic *Pa*3 (Silvera, 1989). (b) c-axis oriented hcp-type structure (Abrikosov, 1954; Barbee *et al.*, 1989. (c) herringbone structure derived from hcp (Kaxiras *et al.*, 1991). (d) tilted herringbone-structure (Ashcroft, 1991a; Kaxiras *et al.*, 1991; Nagara and Nakamura, 1992). Nagara and Nakamura (1992) also consider lower symmetry structures [from Mao and Hemley, *Review of Modern Physics,* **66**,*671* (1994); Fig 11].

- does **monatomic** crystalline hydrogen exist?

  → Predictions: Yes, at very high ambient pressure
  in the Mbar (100 GPa) [4] regime

  In this case: Electrons should delocalize
  and
  hydrogen should form a monatomic **metallic** solid,[5]
  probably even superconducting at room temperature [6]

  → Experiments: strong efforts to realize very-high-pressure cells ≈ 3 Mbar

$$\boxed{\text{not successful up to now !}}$$

→ crystal structure: probably "body centered cubic (bcc)"
("Kubisch raumzentriert")

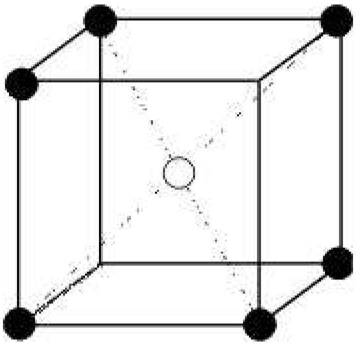

Figure 2.9: Possible crystal structure of atomic metallic hydrogen (body-centered-cubic structure, bcc): H atoms are located on the corners and in the center of a cube [adapted from Mao and Hemley, *Review of Modern Physics,* **66**,*671* (1994); Fig 1].

conclusion on H: → 'simplest' atom,
nevertheless reveals very rich crystallography.
→ search for metallic hydrogen is a currently active field of research.

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[4] 1 atm ≈ 1 bar = 10^5 Pa

[5] Wigner and Huntington J. Chem. Phys. **3**, 764 (1935)

[6] N. W. Ashcroft, Phys. Rev. Lett. **21**, 1748 (1968)

diamond pressure cell:

sample in the center of a ring-shaped gasket which is pressed by two diamonds.

Single crystal diamonds are used because they are
(i) the strongest known material.[a]

(ii) transparent to radiation from a wide range of the electromagnetic spectrum
– from high-energy x and γ radiation above 10 keV (wavelength $\lambda < 1.25\,\mathring{A}$)
– to lower-energy UV-visible-IR radiation below 5 eV ($\lambda > 250\,\mathrm{nm}$)

→ numerous diffraction, scattering and absorption techniques can be employed for investigating the electronic, molecular and crystallographic structure of samples under pressure.

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[a] a typical diamond size corresponds to 0.4 carat (1 ct.=0.2 g) which costs ~1000 USD

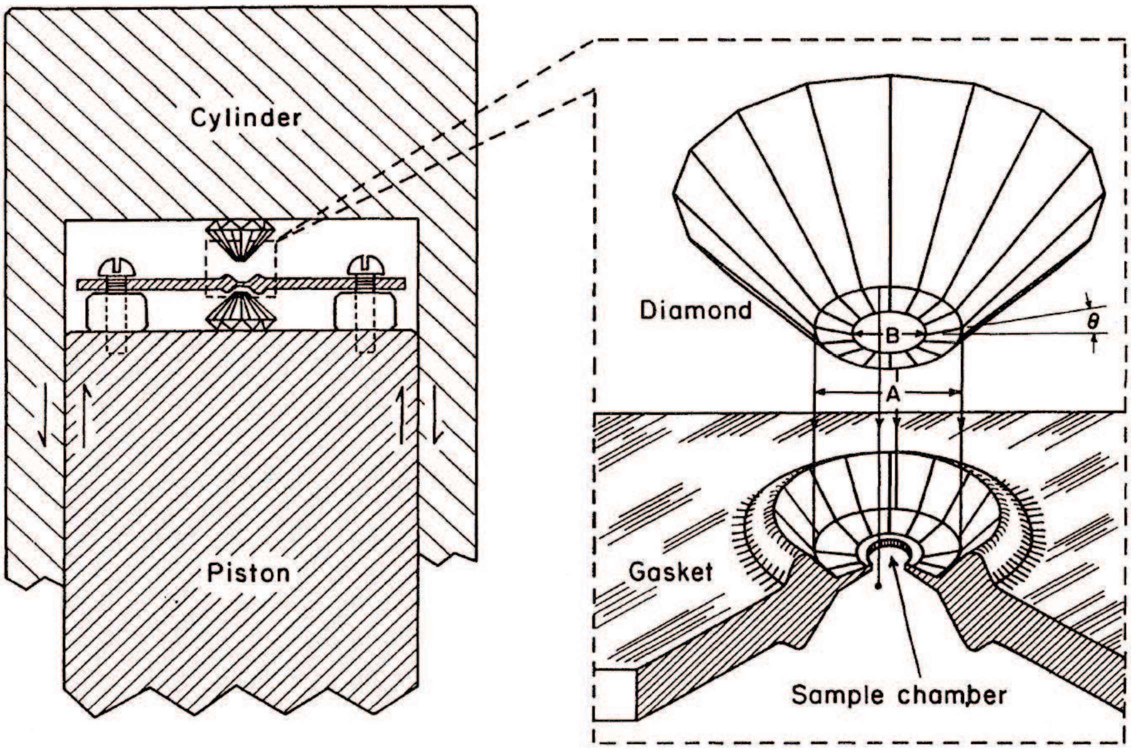

Figure 2.10: Schematic drawing of a megabar diamond-anvil cell. Critical design parameters for use of the cell to multimegabar pressures is the diameter of the central flat B of the diamond cullet (typically 20 to 600 μm) and the bevel angle θ. [from Mao and Hemley, *Review of Modern Physics,* **66**,*671* (1994); Fig.2].

2.2 Helium

electronic configuration: $1s^2$

completely filled 'outermost' electron shell → inert gases

- weak interaction, mediated by Van-der-Waals forces
- liquifies at $T = 4.2$ K ($p = 1$ bar) → LHe is frequently used as cooling medium.
- remains liquid at $T = 0$ ($p = 1$ bar) due to zero-point-fluctuations
- solid (insulating for $p > 30$ bar), forms cubic close-packed (fcc) lattice

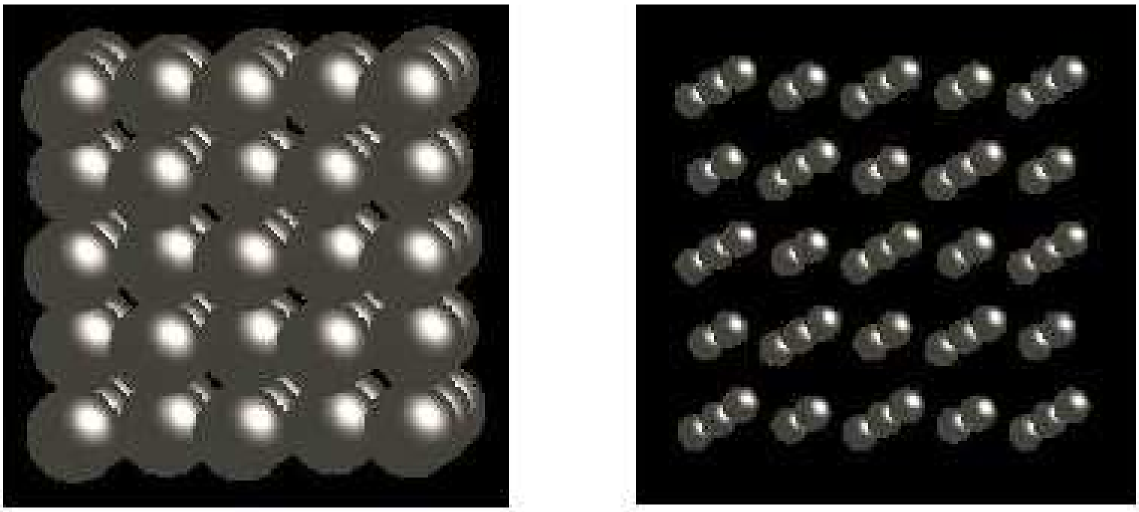

Figure 2.11: Cubic-close packed (fcc) structure of a helium crystal (view from different directions); [from http://www.webelements.com].

van-der-Waals interaction in crystals of inert gases:
= induced dipole-dipole-interaction → Lenard-Jones-Potential

- outermost shells of atoms are completely filled
  with spherically symmetric distribution of electron charges
- electron distribution in crystal is very close to that of free atoms
  → crystals are transparent insulators
- bonds are weak ($\varepsilon \approx 1 \ldots 20\,\mathrm{meV}$)
- isotropic interaction
  ⇒ in the crystal the atoms pack together as closely as possible:
  → fcc structure

van-der-Waals interaction in crystals of inert gases (continued):

equilibrium lattice constants:

cohesive energy $U_{tot}(R)$ of an inert gas lattice is obtained by summing the Lenard-Jones potential (2.1) over all pairs of atoms at distance $p_{ij}R$:
(R : nearest neighbor distance)

$$U_{tot}(R) = \frac{1}{2} N \cdot 4\varepsilon \cdot \left[\sum_{j \neq i} \left(\frac{\sigma}{p_{ij}R} \right)^{12} - \sum_{j \neq i} \left(\frac{\sigma}{p_{ij}R} \right)^{6} \right] \tag{2.2}$$

(factor $\frac{1}{2}$, to count each atom only once; N: number of atoms in the crystal)
For fcc or hcp structure (12 nearest neighbors):

$$\sum_j p_{ij}^{-12} \approx 12.13; \qquad \sum_j p_{ij}^{-6} \approx 14.45 \tag{2.3}$$

i.e. nearest neighbors contribute most of the interaction energy of inert gas crystals.

$U_{tot}(R)$ has a minimum for $\partial U_{tot}/\partial R = 0 \Rightarrow$ equilibrium value $R_0 = 1.09\,\sigma$ or

$$R_0/\sigma = 1.09 = const \tag{2.4}$$

(for all elements with fcc or hcp structure)

From experimental determination of the Lenard-Jones parameters:[7]

Table 2.1: Properties of inert gas crystals (extrapolated to 0 K and zero pressure)

Element	Helium	Neon	Argon	Krypton	Xenon
ε[meV]	0.87	3.1	10.4	14.0	20.0
σ[Å]	2.56	2.74	3.40	3.65	3.98
R_0[Å]	liquid	3.13	3.76	4.01	4.35
R_0/σ		1.14	1.11	1.00	1.09
u_0[meV/atom]		20	80	110	170

⇒ excellent agreement in R_0/σ with (2.4) for Xe
– increasing deviation with decreasing mass is due to zero-point fluctuations (neglected in deviation of (2.4)).

equilibrium cohesive energy:

At $T = 0$ (atoms at rest) and $p = 0$ one finds by substitution of (2.3) and (2.4) in (2.2)

$$U_0 \equiv U_{tot}(R_0) = -2.15 \cdot (4N\varepsilon) \quad \text{or} \quad u_0 \equiv \frac{U_0}{N} = -8.6\,\epsilon \tag{2.5}$$

Experimental data (table 2.1) show reduced binding by 28, 10, 6 and 4 % (quantum fluctuations – also seen as isotope effect in the lattice constants of Ne^{20}, Ne^{22}).

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[7] ε and σ obtained from gas-phase data

2.3 Lithium

group 1 (IA) element → alkali metal

electronic configuration: $2s^1$ → contains just one valence electron

solid at R.T.

- metallic
- body-centered cubic (bcc) crystal structure ("kubisch raumzentriert")
  (as all other alkali metals under normal conditions)
  In the bcc lattice, every Li atom is surrounded by eight other nearest neighbor lithium atoms organized into a cubic array.
  One way to visualize the bcc lattice is as two interlocked infinite cubic arrays of atoms.
- cubic cell parameter ≈3.5 Å

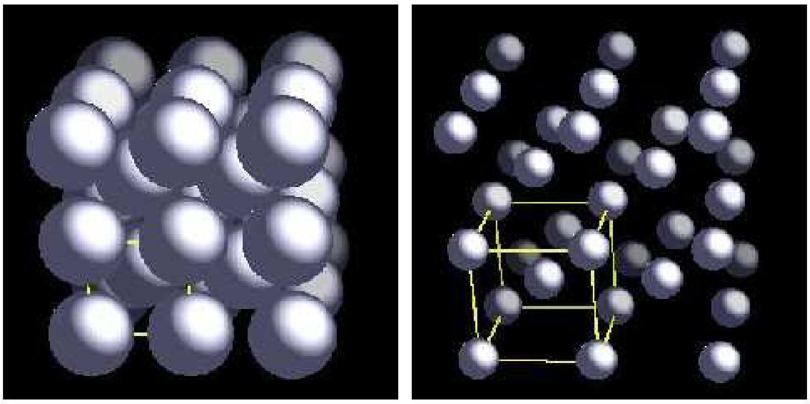

Figure 2.12: bcc structure of lithium [from http://www.webelements.com].

metallic bond:

- some fraction of the electrons of the atoms *delocalize* in the solid
  (typically one or two per atom – the valence electrons in the outermost shells)
  → 'freely' movable conduction electrons (→ high electric conductivity)
- electronic structure changes strongly by formation of a solid crystal
  ⇒ lowering in energy of the conduction electrons,
  as compared to the energy of the valence electrons in the free atoms
  (quantum effect)
- moderately strong and isotropic bond:
  → (relatively low) melting point (180°C for Li), ductile materials
  strong distortion of the valence electron configuration by transition to a solid
  → does not allow to obtain the cohesive energy within a simple model
  (as e.g. for the noble gases)
  → requires computation of the energy levels of the valence electrons
  in the presence of the periodic potential of the ion cores
  (see chapter on 'Fermi gas')

2.4 Beryllium

group 2 (IIA) element → alkaline earth metal ('Erdalkalimetall')

electronic configuration: $2s^2$ → contains two valence electrons

solid at R.T.

- metallic
- hexagonal close-packed (hcp) crystal structure (”hexagonal dichteste Kugelpackung”)
- melting point 1287 °C
- a-, b-axis parameter ≈2.3 Å; c-axis ≈ 3.6 Å

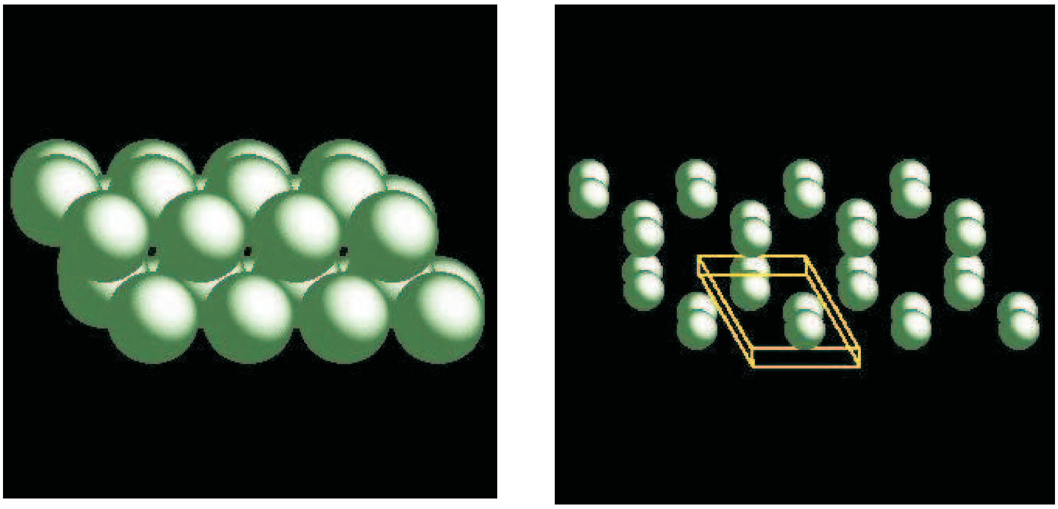

Figure 2.13: hcp structure of beryllium [from http://www.webelements.com].

2.5 Boron

group 13 (III) element

electronic configuration: $2s^2 2p$

solid at R.T.

- semi-metal/semiconductor
  Boron has properties which are at the borderline between metals and non-metals. It is a semiconductor rather than a metallic conductor.
- strong covalent bond
- melting point 2076 °C
- rhombohedral crystal structure
  → (58 ° angles)
  → cell parameters a = b = c ≈ 5.1 Å

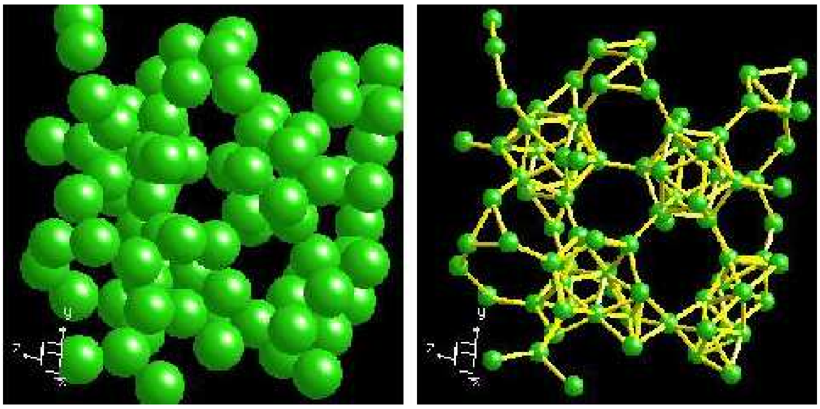

Figure 2.14: rhombohedral crystal structure of Boron [from http://www.webelements.com].

covalent bond: [see 2.1 Hydrogen]

- ”classic” chemical bond, electron-pair bond
- strong bond (comparable to ionic bond)
- directed (anisotropic)
  → low space filling
  → hard and brittle solids
  → often high melting point

2.6 Carbon

group 14 (IV) element

electronic configuration: $2s^2 2p^2$

- solid at R.T.

- strong covalent bond
- melting point 3550 °C
- different crystalline modifications:
  amorphous, graphite, diamond, buckeyballs, C-nanotubes
- electric properties depend on crystal structure

Graphite:
- layered structure (hcp),
- is one of the softest material known
- semi-metal (Halbmetall)

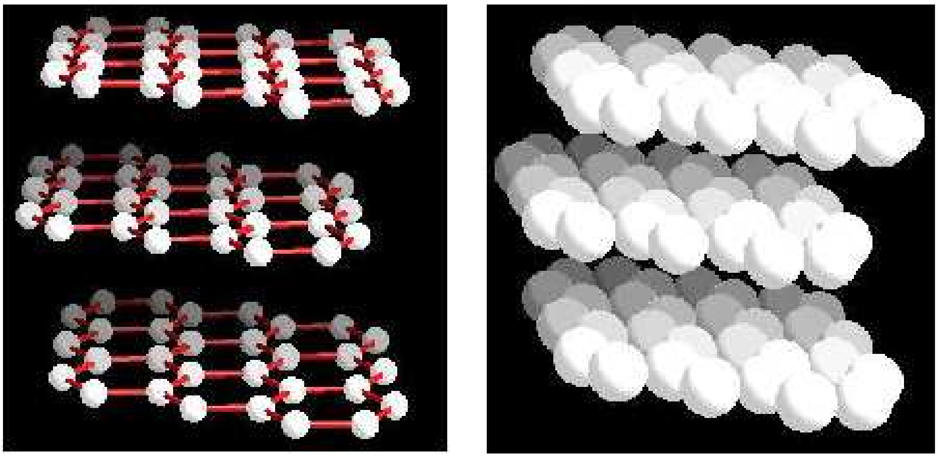

Figure 2.15: hcp structure of graphite [from http://www.webelements.com].

Diamond:
- grows under very high pressure
- fcc structure (2 atoms form primitive basis),
- tetrahedral bonding characteristics - is the hardest material known
- insulating

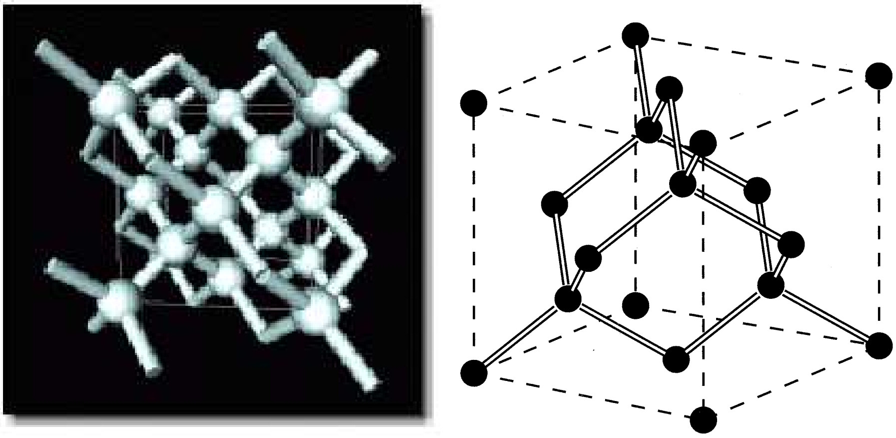

Figure 2.16: fcc structure of diamond [from http://www.ill.fr/dif/3D-crystals/index.html (left) and Kittel (1999) (right)].

C60 and **C-nanotubes**

- discovered only recently; related systems: ”carbon nanotubes”

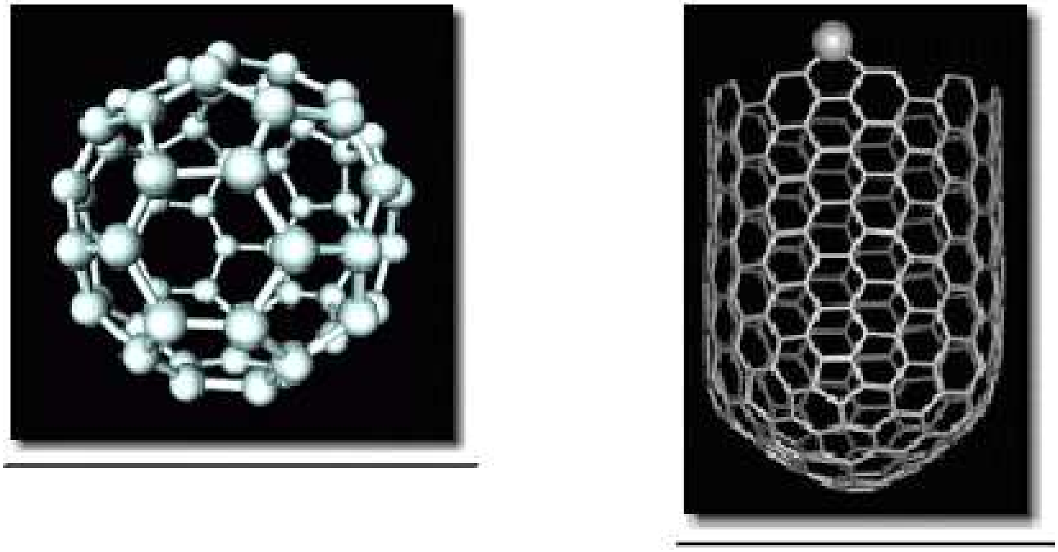

Figure 2.17: crystal structure of C60 and C-nanotubes [from http://www.ill.fr/dif/3D-crystals/index.html].

2.7 Nitrogen

group 15 (V) element → Pnictogen

electronic configuration: $2s^2 2p^3$

forms molecular nitrogen N_2:

→ gas at R.T. ($p = 1\,\mathrm{bar}$)
→ liquid below $T_{boil} = 77$ K ($p = 1$ bar)
→ solid below $T_{melt} = 63$ K ($p = 1$ bar)

molecular crystal N_2:
- crystal structure: hcp
- insulator

2.8 Oxygen

group 16 (VI) element → Chalcogen

electronic configuration: $2s^2 2p^3$

forms molecular oxygen O_2:

→ gas at R.T. ($p = 1\,\mathrm{bar}$)
→ liquid below $T_{boil} = 90$ K ($p = 1$ bar)
→ solid below $T_{melt} = 55$ K ($p = 1$ bar)

molecular crystal O_2:
- insulator
- crystal structure: monoclinic
  cell parameters: a=5.403 Å, b=3.429 Å, c=5.086 Å
  $\alpha = \gamma = 90°$, $\beta = 132.5°$

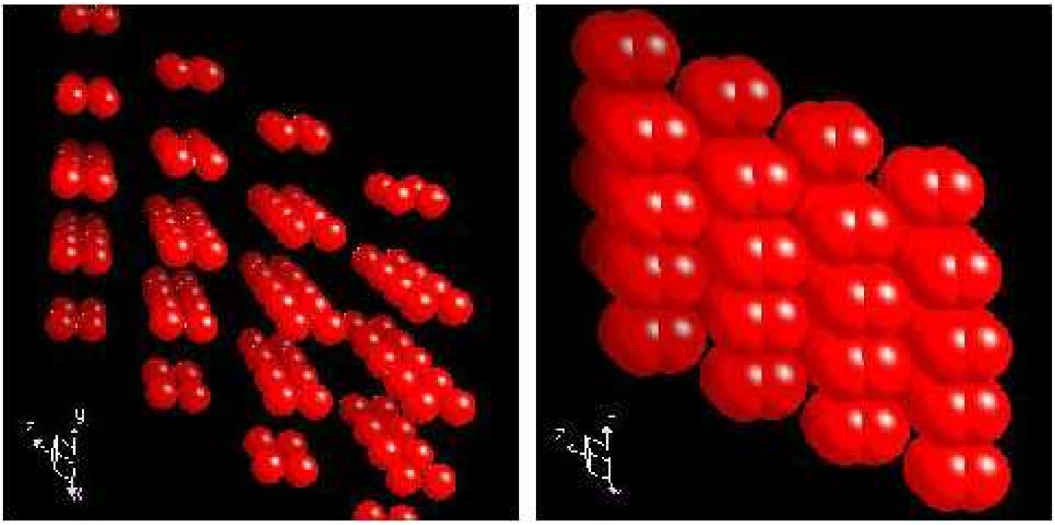

Figure 2.18: Monoclinic crystal structure of molecular oxygen crystal [from http://www.webelements.com].

2.9 Fluorine

group 17 (VII) element → Halogen

electronic configuration: $2s^2 2p^4$

forms molecular oxygen F_2:

→ gas at R.T. ($p = 1\,\text{bar}$)
→ liquid below $T_{boil} = 85$ K ($p = 1$ bar)
→ solid below $T_{melt} = 54$ K ($p = 1$ bar)

molecular crystal F_2:
- insulator
- crystal structure: monoclinic
  cell parameters: a=5.50 A,, b=3.28 Å, c=7.28 Å;
  $\alpha = \beta = \gamma = 90°$

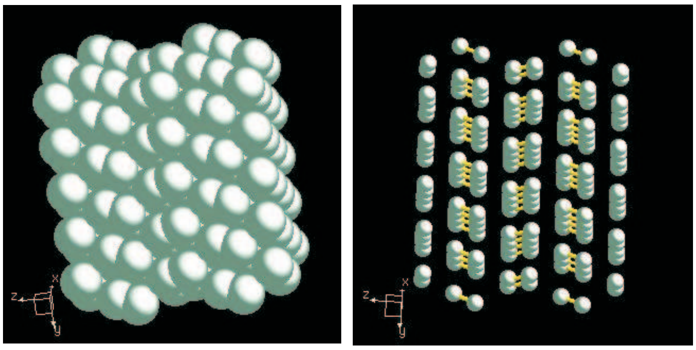

Figure 2.19: Monoclinic structure of fluorine [from http://www.webelements.com].

2.10 Neon

group 18 (VIII) element → noble gas

electronic configuration: $2s^2 2p^6$

- inert gas crystal for $T < 25$ K
- crystal structure: fcc

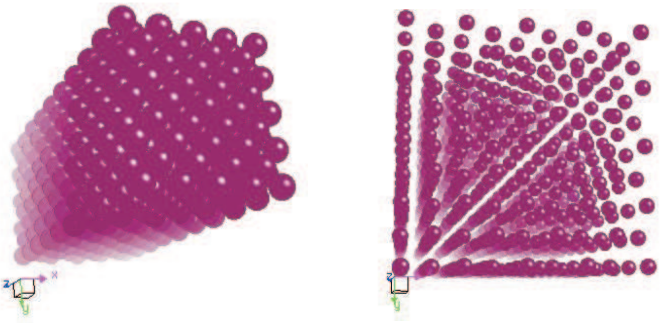

Figure 2.20: fcc structure of neon [from http://www.webelements.com].

(etc. . . .)

2.11 Sodium chloride: NaCl

'Rock salt' (NaCl) is a typical **ion crystal** ('Ionenkristall').

Ion crystals are typically formed in alkali halides ('Alkalihalogenide').

- the (single) valence electron of the alkali metal
  fills the outermost electron shell of the halogen
  $\Rightarrow$ e.g. in NaCl the solid consists of singly charged Na^+ ions and Cl^- ions
  $\rightarrow$ have electronic configurations of the inert gases (Ne, Ar),
  i.e. with closed shells and spherically symmetric charge distribution.
- crystal structure:
  face centered cubic (fcc);
  basis has one Cl^- ion at 000 and one Na^+ ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$

  We may construct the sodium chloride crystal structure by arranging Na^+ and Cl^- ions alternately at the lattice points of a simple cubic lattice.

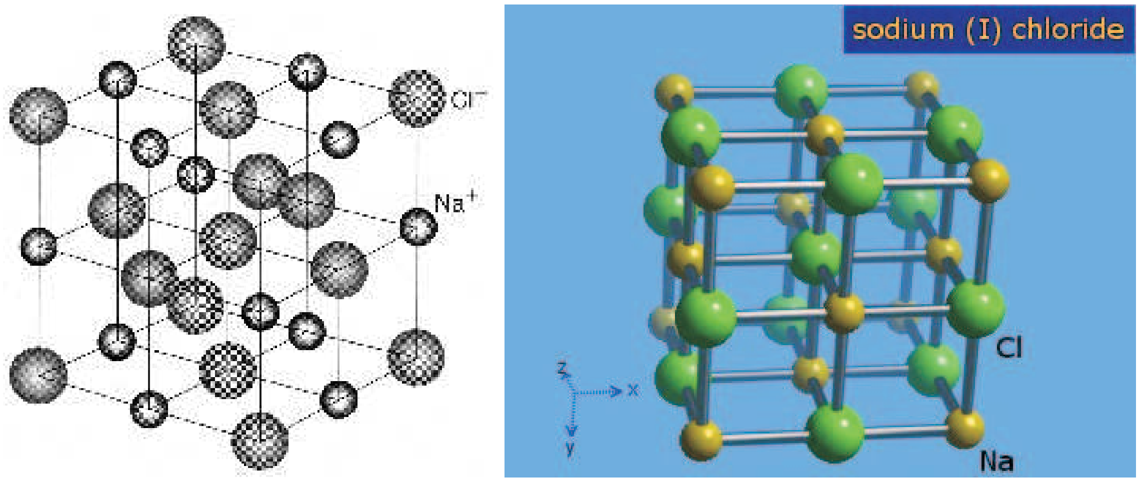

Figure 2.21: Crystal structure of NaCl. The figure shows one conventional cubic cell. The ionic diameters here are reduced in relation to the cell in order to clarify the spatial arrangement. [from Kittel, *Introduction to solid state physics* (1996); Fig.1.17 (left) and http://www.webelements.com (right)].

In the crystal each ion is surrounded by six nearest neighbors of the opposite charge $\rightarrow$ attractive Coulomb interaction $\Rightarrow$ ionic bond

Ionic bond
The long range electrostatic interaction $\pm q^2/r$ between ions with charge $\pm q$ at distance r accounts for the major part of the binding energy in an ionic crystal

Repulsive interaction at short distance is similar to the one of inert gas atoms.

The van der Waals part of the attractive interaction in ionic crystals makes only a small contribution ($\sim$ 1 to 2 %) to the cohesive energy.

Interaction energy between ions i, j at distance $r_{ij} \equiv p_{ij} R$:

$$U_{ij}(R) = \begin{cases} \lambda \exp\{\frac{-R}{\rho}\} - \frac{q^2}{4\pi\varepsilon_0 R} & \text{nearest neighbors} \\ \\ \pm\frac{q^2}{4\pi\varepsilon_0 p_{ij} R} & \text{otherwise} \end{cases} \tag{2.6}$$

(R: nearest-neighbor separation in the crystal)

- short range repulsive interaction
  - is modelled by exponential dependence with empirical parameters λ and ρ (better representation as R^{-12} form used for inert gases)
  - for simplicity only considered among nearest neighbors
- "±" accounts for like (−) and unlike (+) charges

With the sum $U_i \equiv \sum_j U_{ij}$ including all interactions of ion i, and neglecting surface effects, we can write the total lattice energy of a crystal with N molecules (or $2N$ ions) as $U_{tot} = N \cdot U_i$.[8]

Thus

$$U_{tot} = NU_i = N\left(z\lambda \exp\left\{\frac{-R}{\rho}\right\} - \alpha\frac{q^2}{4\pi\varepsilon_0 R}\right) \tag{2.7}$$

where z is the number of nearest neighbors of any ion and

$$\alpha = \sum_{j\neq i} \frac{\pm 1}{p_{ij}} = \textbf{Madelung constant}\,. \tag{2.8}$$

At the equilibrium separation R_0 we have $\partial U_{tot}/\partial R = 0$, so that

$$N\frac{\partial U_i}{\partial R} = N\left(-\frac{z\lambda}{\rho}\exp\left\{\frac{-R}{\rho}\right\} + \frac{\alpha q^2}{4\pi\varepsilon_0 R^2}\right) = 0 \quad , \tag{2.9}$$

or

$$R_0 \exp\left\{\frac{-R_0}{\rho}\right\} = \frac{\rho\alpha q^2}{4\pi\varepsilon_0}\frac{1}{z\lambda} \tag{2.10}$$

⇒ lattice parameter is determined by the crystal structure (via α/z) and the parameters ρ, λ of the repulsive interaction.

---

[8] N rather than $2N$ occurs, because we must count each bond only once.

Inserting (2.10) in (2.7) we obtain the total lattice energy of the crystal of $2N$ ions at their equilibrium separation R_0 as

$$U_{tot} = -\frac{N\alpha q^2}{4\pi\varepsilon_0 R_0}\left(1 - \frac{\rho}{R_0}\right) \tag{2.11}$$

The pre-factor is the so-called "Madelung energy".

The term $\frac{\rho}{R_0}$ can be interpreted as a correction of the lattice energy (reduction in $|U_{tot}|$) due to the repulsive interaction.

One typically finds that ρ is of the order of $0.1\,R_0$,
i.e. the repulsive interaction has very short range.

For comparison:
'experimental' determination of the binding energy
from the gain in energy by formation of the NaCl crystal from neutral gas:

Na(Gas) + 5.14 eV (ionization energy) → $\mathrm{Na}^+ + e^-$

e^- + Cl(Gas) → Cl^- + 3.61 eV (electron affinity)

$\mathrm{Na}^+ + \mathrm{Cl}^-$ → NaCl (crystal) + 7.9 eV

balance: Δ E = 7.9 eV - 5.1 eV + 3.6 eV = **6.4 eV**

Notes:

- ionic character of a bond is rarely complete;
  for NaCl ≈ 94 % ionic contribution to the total energy
- this is also valid for other types of bonds
- typical ionic crystals:
  - I-VII compounds ($\mathrm{A_I B_{VII}}$)
  - II-VI compounds ($\mathrm{A_{II} B_{VI}}$)
    → ionic character is weaker; e.g. 84 % for MgO

  in contrast

  - III- V compounds ($\mathrm{A_{III} B_V}$)
    → ionic character is even weaker; e.g. 34 % for GaAs

- in addition to the types of bonds mentioned above
  (ionic, metallic, covalent, Van der Waals-type)
  there exists the so-called **hydrogen bond** (”Wasserstoff-Brücken-Bindung”),
  e.g. in HF_2, HF_2, ferroelectric crystals.
  The hydrogen bond is largely ionic in character.

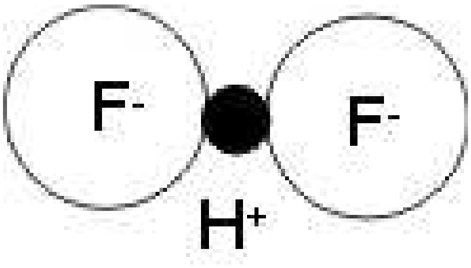

Figure 2.22: The hydrogen difluoride ion HF_2^- is stabilized by a hydrogen bond. The sketch is of an extreme model of the bond, extreme in the sense that the proton is shown bare of electrons [adapted from Kittel, *Introduction to solid state physics* (1996); Fig.3.13].