

Achievements

VESTA plotting of crystal structures

How to describe a crystal structure

- Crystal lattice
- Basis

How to resolve crystal structures

- Reciprocal space
- Scattering theory (Form and Structure Factor)
- Resolving the crystal structure of a superconductor

Lecture 5: How crystals bind together

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Tasks for Next week

(1) Read chapter 3: Crystal Binding (less than 20 pages)

Crystals of Inert Gases

Van der Waals-London Interaction

Repulsive Interaction

Equilibrium Lattice Constants

Cohesive Energy

Ionic Crystals

Electrostatic or Madelung Energy + Evaluation of Madelung Constant

Covalent Crystals

Metals

Atomic Radii + Ionic Crystal Radii

(2) Start Reading chapter 4: Phonons / Lattice Vibrations

(3) Solve next exercise sheets

(4) Summary:

Exercise 1 *Binding energy*

a) Show that for a potential of the form $U(R) = -\frac{A}{R^m} + \frac{B}{R^n}$ an equilibrium can only be reached if $n > m$.

b) For a pure van der Waals attraction the potential is often written as

$$U(R) = 4\epsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right].$$

Calculate the binding energy (cohesive energy) E_B and the equilibrium distance R_0 .

c) Calculate the effect of thermal expansion, $\Delta R_0(T)/R_0$, on a linear chain of atoms with the potential of part b. Assume that the thermal energy $k_B T \ll E_B$ allows motion of the atoms around the equilibrium position. Think about in what boundaries the atoms can move. From this deduce the average position and compare the result with R_0 .

Hint: Use the expansion $1/(1 \pm \epsilon) \approx 1 \mp \epsilon + \epsilon^2 + \dots$ up to the second order and $\sqrt[n]{1 + \epsilon} = 1 + \epsilon/n + \dots$ for $\epsilon \rightarrow 0$.

Exercise 2 *Madelung constant*

Calculate the Madelung constant for an infinitely long, evenly spaced, linear chain of ions with alternating anions and cations of charge $\pm e$.

Exercise 3 *Linear ionic crystal*

Consider a line of $2N$ ions of alternating charge $\pm q$ with a repulsive potential energy A/R^n between nearest neighbours.

a) Show that the expression for the potential energy can be approximated by

$$U(R) = N \left[\frac{2A}{R^n} - \frac{2 \ln 2 q^2}{4\pi\epsilon_0 R} \right].$$

b) Show that at the equilibrium separation

$$U(R_0) = -\frac{2Nq^2 \ln 2}{4\pi\epsilon_0 R_0} \cdot \left(1 - \frac{1}{n} \right).$$

c) Let the crystal be compressed so that $R_0 \rightarrow R_0(1 - \delta)$. Show that the work done in compressing a unit length of the crystal has the leading term $\frac{1}{2}C\delta^2$, where

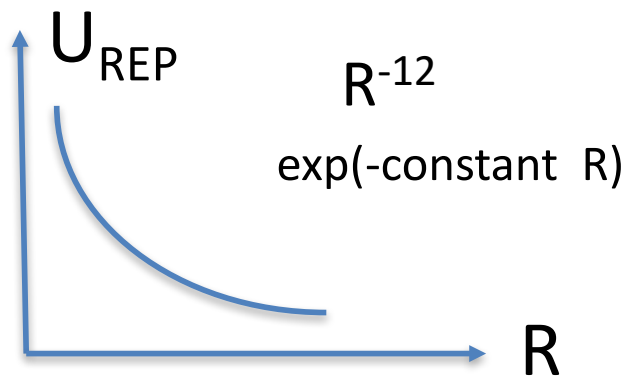
$$C = \frac{(n-1)q^2 \ln 2}{4\pi\epsilon_0 R_0}.$$

Note: Use the complete expression for $U(R)$ instead of $U(R_0)$.

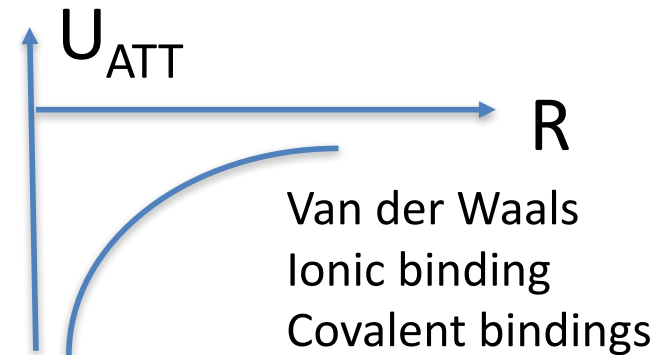
Crystal bindings

Total crystal potential: $U(R) = U_{\text{REP}} + U_{\text{ATT}}$

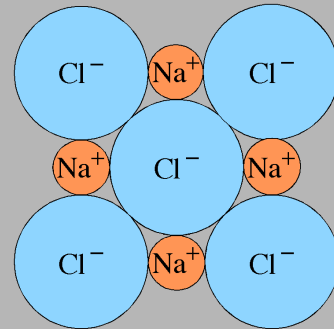
Repulsive Potential U_{REP}



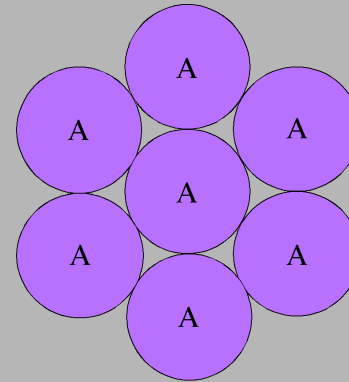
Attractive Potential U_{ATT}



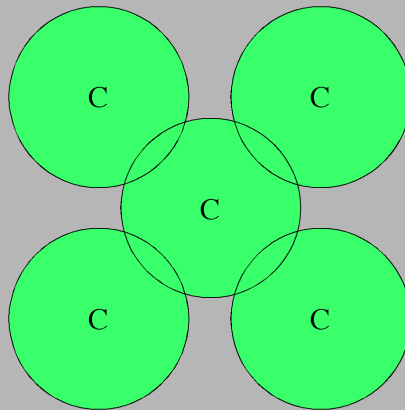
Today's lecture



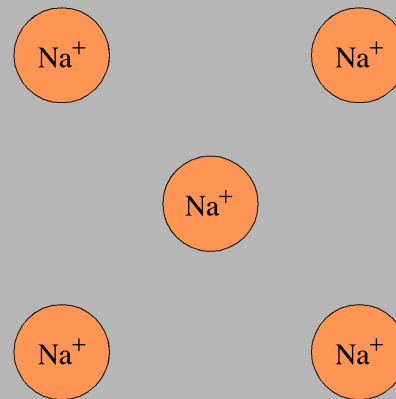
Natriumchlorid
(ionisch)



Kristallines Argon
(van der Waals)



Diamant
(kovalent)



Natrium
(metallisch)

Periodic Table

Periodic Table of the Elements

s
p
d
f

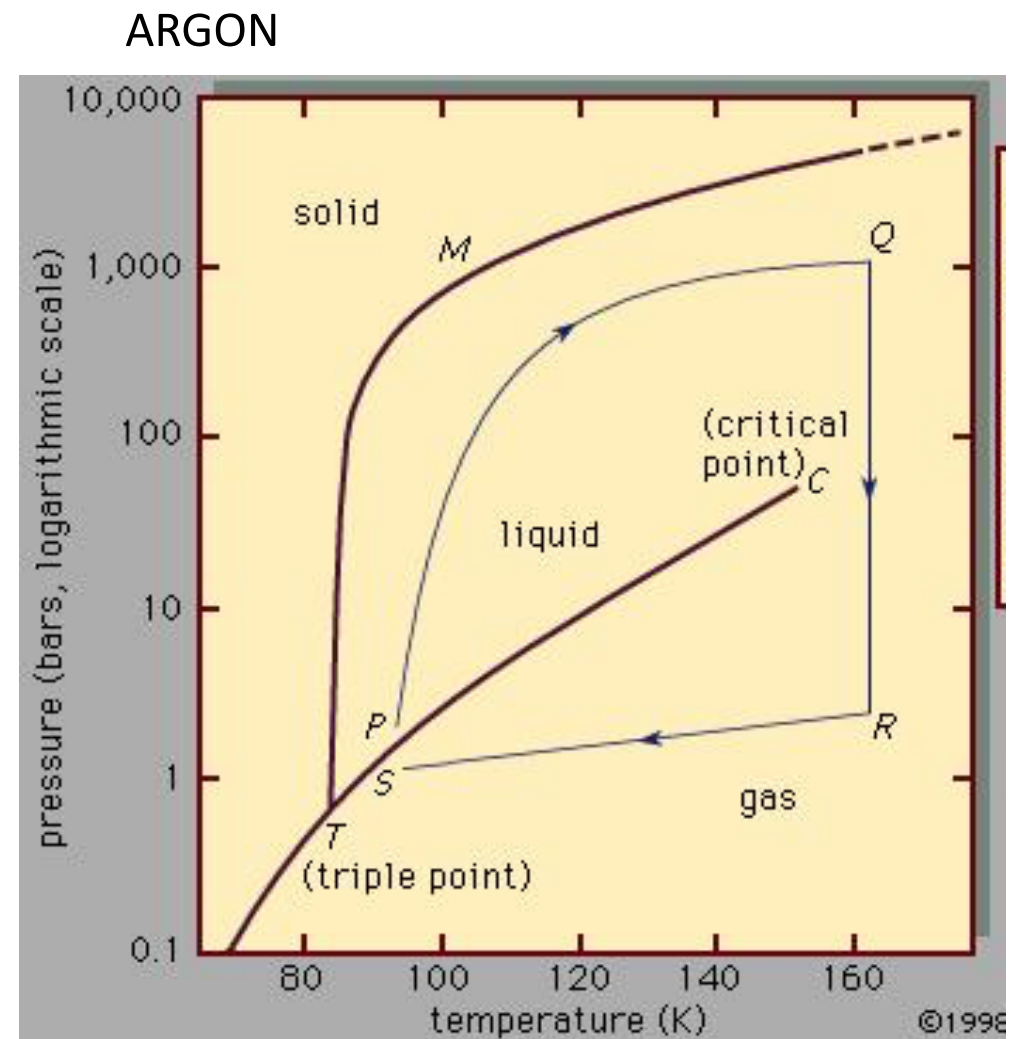
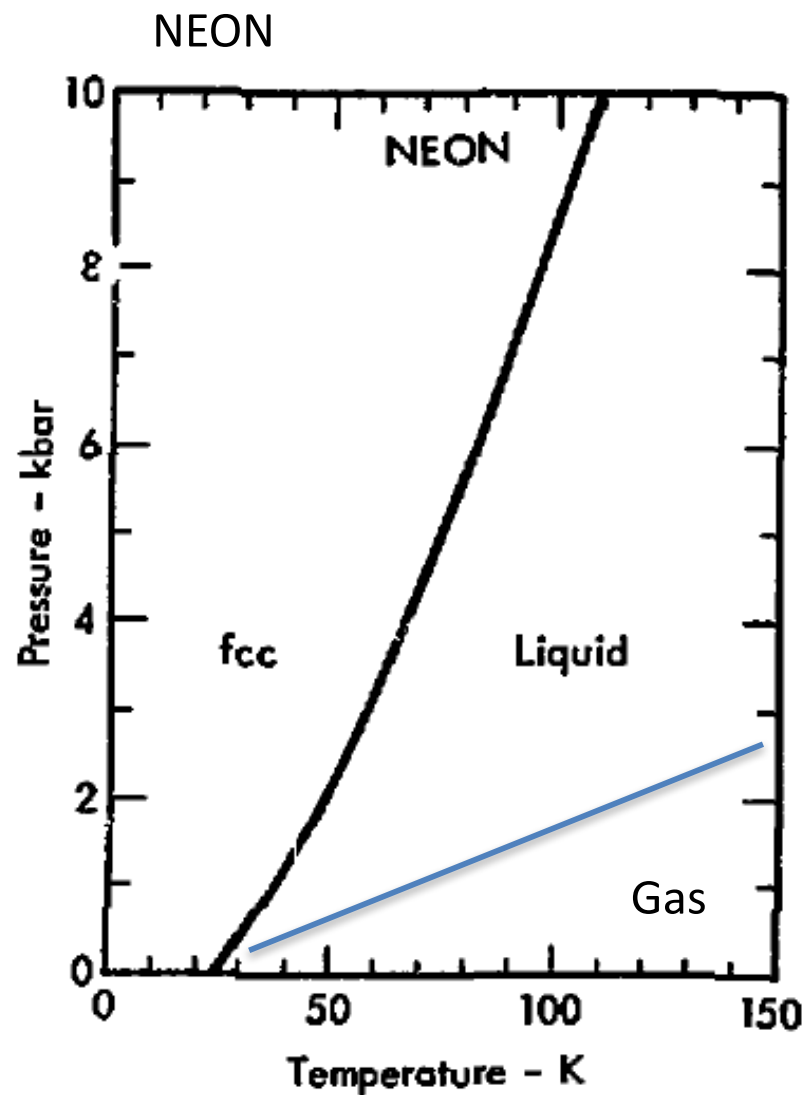
Atomic Number Atomic Mass
 Symbol
 Name
 Electron Configuration

1 IA 1A																	18 VIIIA 8A	
1 H Hydrogen 1s ¹	2 IIA 2A												13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	2 He Helium 1s ²
3 Li Lithium (He)2s ¹	4 Be Beryllium (He)2s ²											5 B Boron (He)2s ² 2p ¹	6 C Carbon (He)2s ² 2p ²	7 N Nitrogen (He)2s ² 2p ³	8 O Oxygen (He)2s ² 2p ⁴	9 F Fluorine (He)2s ² 2p ⁵	10 Ne Neon (He)2s ² 2p ⁶	
11 Na Sodium (Ne)3s ¹	12 Mg Magnesium (Ne)3s ²	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8		9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 Al Aluminum (Ne)3s ² 3p ¹	14 Si Silicon (Ne)3s ² 3p ²	15 P Phosphorus (Ne)3s ² 3p ³	16 S Sulfur (Ne)3s ² 3p ⁴	17 Cl Chlorine (Ne)3s ² 3p ⁵	18 Ar Argon (Ne)3s ² 3p ⁶
19 K Potassium (Ar)4s ¹	20 Ca Calcium (Ar)4s ²	21 Sc Scandium (Ar)3d ¹ 4s ²	22 Ti Titanium (Ar)3d ² 4s ²	23 V Vanadium (Ar)3d ³ 4s ²	24 Cr Chromium (Ar)3d ⁵ 4s ¹	25 Mn Manganese (Ar)3d ⁵ 4s ²	26 Fe Iron (Ar)3d ⁶ 4s ²	27 Co Cobalt (Ar)3d ⁷ 4s ²	28 Ni Nickel (Ar)3d ⁸ 4s ²	29 Cu Copper (Ar)3d ¹⁰ 4s ¹	30 Zn Zinc (Ar)3d ¹⁰ 4s ²	31 Ga Gallium (Ar)3d ¹⁰ 4s ² 4p ¹	32 Ge Germanium (Ar)3d ¹⁰ 4s ² 4p ²	33 As Arsenic (Ar)3d ¹⁰ 4s ² 4p ³	34 Se Selenium (Ar)3d ¹⁰ 4s ² 4p ⁴	35 Br Bromine (Ar)3d ¹⁰ 4s ² 4p ⁵	36 Kr Krypton (Ar)3d ¹⁰ 4s ² 4p ⁶	
37 Rb Rubidium (Kr)5s ¹	38 Sr Strontium (Kr)5s ²	39 Y Yttrium (Kr)4d ¹ 5s ²	40 Zr Zirconium (Kr)4d ² 5s ²	41 Nb Niobium (Kr)4d ⁴ 5s ¹	42 Mo Molybdenum (Kr)4d ⁵ 5s ¹	43 Tc Technetium (Kr)4d ⁵ 5s ²	44 Ru Ruthenium (Kr)4d ⁷ 5s ¹	45 Rh Rhodium (Kr)4d ⁸ 5s ¹	46 Pd Palladium (Kr)4d ¹⁰	47 Ag Silver (Kr)4d ¹⁰ 5s ¹	48 Cd Cadmium (Kr)4d ¹⁰ 5s ²	49 In Indium (Kr)4d ¹⁰ 5s ² 5p ¹	50 Sn Tin (Kr)4d ¹⁰ 5s ² 5p ²	51 Sb Antimony (Kr)4d ¹⁰ 5s ² 5p ³	52 Te Tellurium (Kr)4d ¹⁰ 5s ² 5p ⁴	53 I Iodine (Kr)4d ¹⁰ 5s ² 5p ⁵	54 Xe Xenon (Kr)4d ¹⁰ 5s ² 5p ⁶	
55 Cs Cesium (Xe)6s ¹	56 Ba Barium (Xe)6s ²	57-71	72 Hf Hafnium (Xe)4f ¹⁴ 5d ² 6s ²	73 Ta Tantalum (Xe)4f ¹⁴ 5d ³ 6s ²	74 W Tungsten (Xe)4f ¹⁴ 5d ⁴ 6s ²	75 Re Rhenium (Xe)4f ¹⁴ 5d ⁵ 6s ²	76 Os Osmium (Xe)4f ¹⁴ 5d ⁶ 6s ²	77 Ir Iridium (Xe)4f ¹⁴ 5d ⁷ 6s ²	78 Pt Platinum (Xe)4f ¹⁴ 5d ⁹ 6s ¹	79 Au Gold (Xe)4f ¹⁴ 5d ¹⁰ 6s ¹	80 Hg Mercury (Xe)4f ¹⁴ 5d ¹⁰ 6s ²	81 Tl Thallium (Xe)4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹	82 Pb Lead (Xe)4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	83 Bi Bismuth (Xe)4f ¹⁴ 5d ¹⁰ 6s ² 6p ³	84 Po Polonium (Xe)4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴	85 At Astatine (Xe)4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵	86 Rn Radon (Xe)4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁶	
87 Fr Francium (Rn)7s ¹	88 Ra Radium (Rn)7s ²	89-103	104 Rf Rutherfordium (Rn)5f ¹⁴ 6d ² 7s ²	105 Db Dubnium (Rn)5f ¹⁴ 6d ³ 7s ²	106 Sg Seaborgium (Rn)5f ¹⁴ 6d ⁴ 7s ²	107 Bh Bohrium (Rn)5f ¹⁴ 6d ⁵ 7s ²	108 Hs Hassium (Rn)5f ¹⁴ 6d ⁶ 7s ²	109 Mt Meitnerium (Rn)5f ¹⁴ 6d ⁷ 7s ²	110 Ds Darmstadtium (Rn)5f ¹⁴ 6d ⁸ 7s ²	111 Rg Roentgenium (Rn)5f ¹⁴ 6d ⁹ 7s ²	112 Cn Copernicium (Rn)5f ¹⁴ 6d ¹⁰ 7s ²	113 Uut Ununtrium (Rn)5f ¹⁴ 6d ¹⁰ 7s ² 7p ¹	114 Fl Flerovium (Rn)5f ¹⁴ 6d ¹⁰ 7s ² 7p ²	115 Uup Ununpentium (Rn)5f ¹⁴ 6d ¹⁰ 7s ² 7p ³	116 Lv Livermorium (Rn)5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁴	117 Uus Ununseptium (Rn)5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁵	118 Uuo Ununoctium (Rn)5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁶	
Lanthanide Series		57 La Lanthanum (Xe)5d ¹ 6s ²	58 Ce Cerium (Xe)4f ¹ 5d ¹ 6s ²	59 Pr Praseodymium (Xe)4f ³ 6s ²	60 Nd Neodymium (Xe)4f ⁴ 6s ²	61 Pm Promethium (Xe)4f ⁵ 6s ²	62 Sm Samarium (Xe)4f ⁶ 6s ²	63 Eu Europium (Xe)4f ⁷ 6s ²	64 Gd Gadolinium (Xe)4f ⁷ 5d ¹ 6s ²	65 Tb Terbium (Xe)4f ⁹ 6s ²	66 Dy Dysprosium (Xe)4f ¹⁰ 6s ²	67 Ho Holmium (Xe)4f ¹¹ 6s ²	68 Er Erbium (Xe)4f ¹² 6s ²	69 Tm Thulium (Xe)4f ¹³ 6s ²	70 Yb Ytterbium (Xe)4f ¹⁴ 6s ²	71 Lu Lutetium (Xe)4f ¹⁴ 5d ¹ 6s ²		
Actinide Series		89 Ac Actinium (Rn)6d ¹ 7s ²	90 Th Thorium (Rn)6d ² 7s ²	91 Pa Protactinium (Rn)5f ² 6d ¹ 7s ²	92 U Uranium (Rn)5f ³ 6d ¹ 7s ²	93 Np Neptunium (Rn)5f ⁴ 6d ¹ 7s ²	94 Pu Plutonium (Rn)5f ⁶ 7s ²	95 Am Americium (Rn)5f ⁷ 7s ²	96 Cm Curium (Rn)5f ⁷ 6d ¹ 7s ²	97 Bk Berkelium (Rn)5f ⁹ 7s ²	98 Cf Californium (Rn)5f ¹⁰ 7s ²	99 Es Einsteinium (Rn)5f ¹¹ 7s ²	100 Fm Fermium (Rn)5f ¹² 7s ²	101 Md Mendelevium (Rn)5f ¹³ 7s ²	102 No Nobelium (Rn)5f ¹⁴ 7s ²	103 Lr Lawrencium (Rn)5f ¹⁴ 6d ¹ 7s ²		

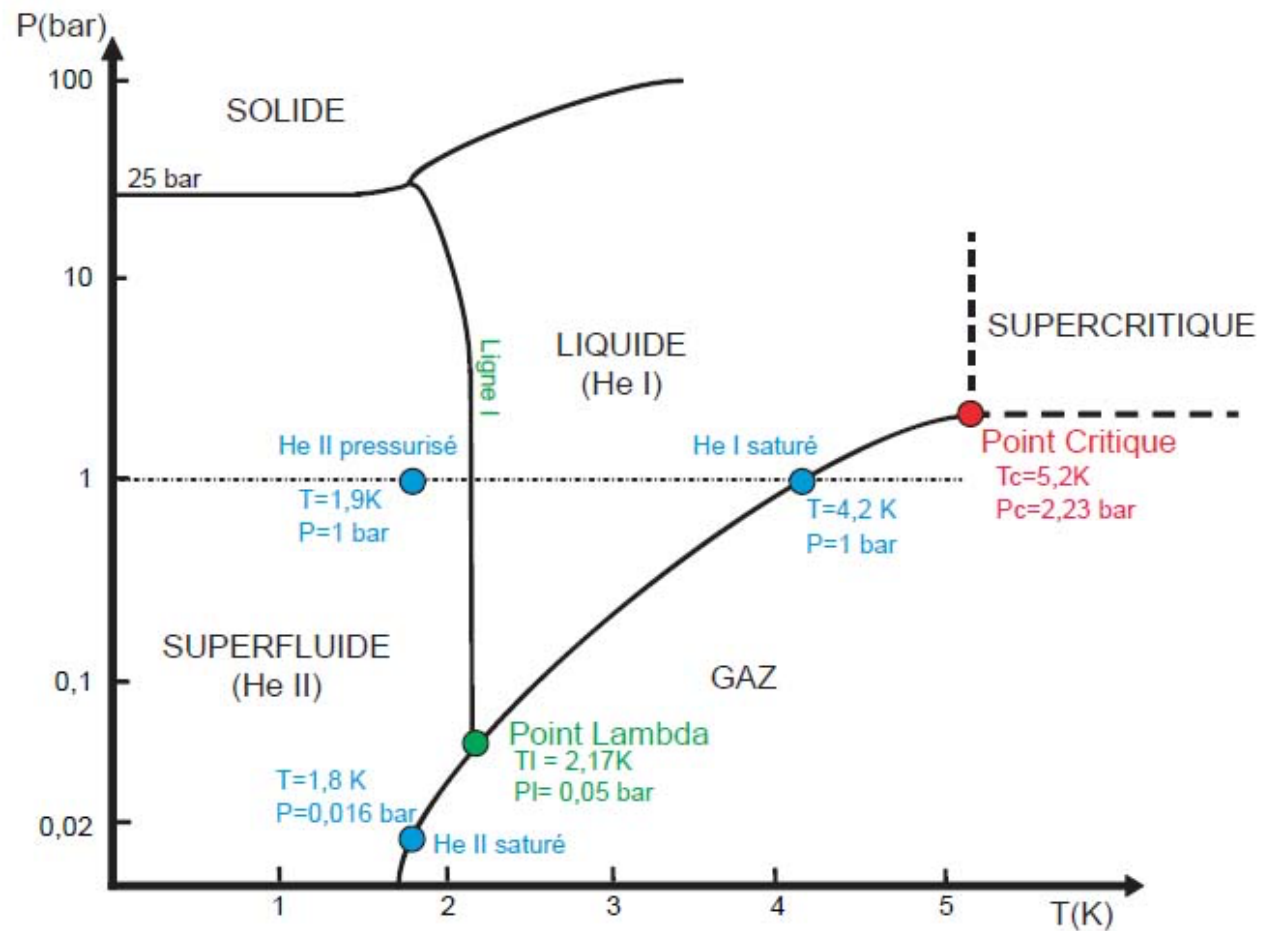
<http://sciencenotes.org/periodic-table-showing-shells/>

See also table 3 in Kittel.

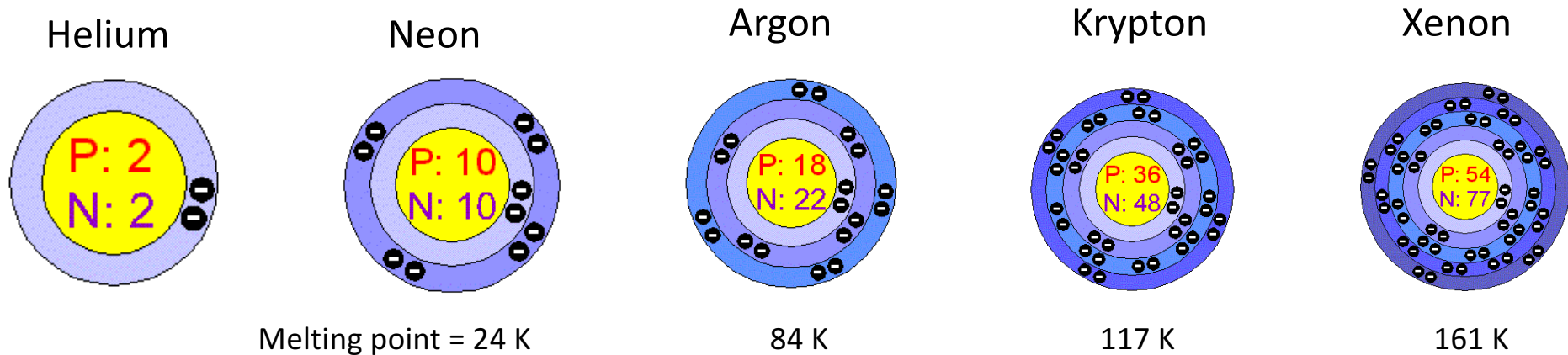
Phase diagrams:



Phase diagram of Helium



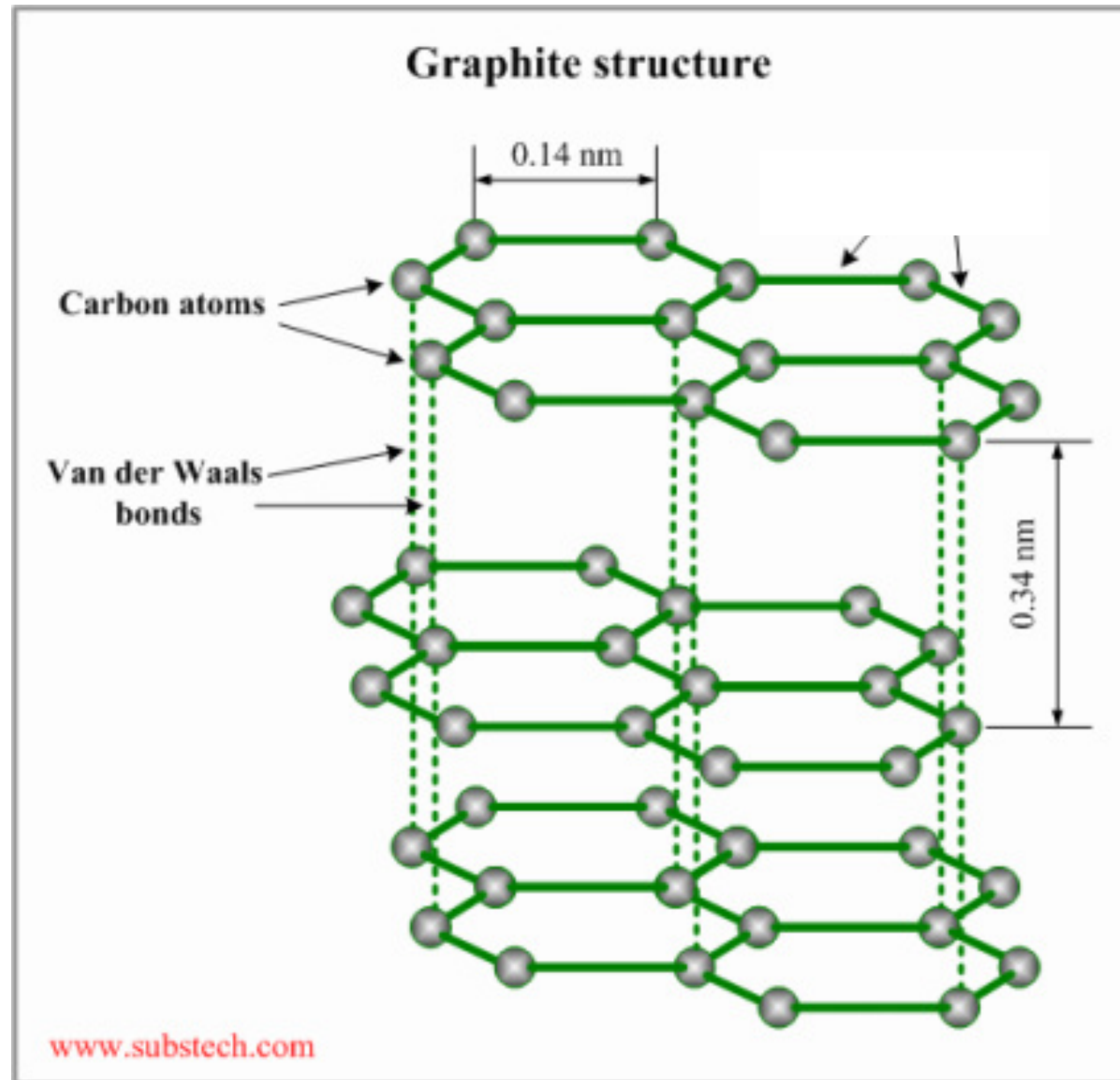
Inert gasses



Questions:

- (1) Why are these gasses solidifying in FCC rather than BCC?
- (2) What are the “glue” that binds these atoms together in the solid form?
- (3) Why are the melting point rather low?
- (4) Why are the inert gasses having different melting points?

Van der Waals bonds



Van der Waals bonds used Gecko's

