Exam

Structure at Macro, Meso and Nano Scale

Advanced Materials Track

January 30 2014, 9.00-12.00 uur

Write your name and student number clearly on every separate paper you hand in.
Write on the first paper the total number of separate papers you hand in.

Mark = 1 + 9*(sum of the number of points scored)/(max number of points that can be scored)

Exercise 1. (16 pts)

On the right a representation of the $\frac{4}{m}mm(D_{4h})$ point group is given.
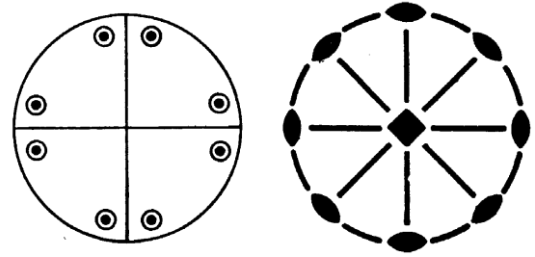
a. To which types of Bravais lattices is this point group connected? (1 pt)

b. Suppose we combine this point group with an I centered lattice type to obtain the space group I4/mcm. When we put one atom on the general x,y,z coordinate, how many equivalent atomic positions will be occupied by the same type of atom within the unit cell of this space group? Explain your answer in about two sentences (2 pts)

c. What do the different symbols 4/mcm in the space group exactly mean? (4 pts)

d. When we distort this lattice by changing the length of (only) one of the diagonals of the square faces by a factor $(1+\delta)$, what (new) Bravais lattice will be formed? What are the lattice parameters of the new Bravais lattice in relation to the ones of the initial lattice. (4 pts) (Hint: Do not try to solve this in your head, but draw a schematic representation of the initial lattice projected along a viewing direction perpendicular to the square face and then notify what will be the highest symmetry solution after the distortion.)

e. Suppose we have a(nother) point group (and thus also space group) that combines a 2-fold rotation axis with two 3-fold rotation axes. To which types of Bravais lattices is this point group connected? Which angles have to be present between these three different rotation axes? Note that this can be calculated using the so-called Euler equation:

$$\cos\left(\hat{AB}\right) = \frac{\cos\dfrac{\gamma}{2} + \cos\dfrac{\alpha}{2}\cos\dfrac{\beta}{2}}{\sin\dfrac{\alpha}{2}\sin\dfrac{\beta}{2}}. \qquad \text{(3 pts)}$$

f. Explain in a few words the close analogy between quasicrystals and Penrose tilings. (2 pts)

Exercise 2. (15 pts)

a. Calculate the ratio of the surface energies of {100} and {110} for the bcc (body-centered cubic) structure based on a nearest-neighbor broken bond model, where the maximum number of bonds (coordination) in the bulk is 8. The equilibrium shape of bcc particles based on these energies is the rhombic dodecahedron. (2 pts)

b. Use the result of a. to draw the 2D Wulff plot for bcc particles for viewing along a <100> (projection) direction. (3 pts)

c. The same as b., but now for viewing along the <111> (projection) direction. (3 pts)

d. Calculate for the octahedron the ratio of surface area to volume (A/V). (4 pts)

e. Derive the equation that relates the pressure inside nanoscale octahedrons as a function of their size. (3 pts)

Exercise 3. (17 pts)

a. III-V or II-VI semiconductors generally have a structure called Zinc-Blende or Sphalerite, which closely resembles the diamond structure. What is the Bravais lattice and what is the basis (motive) in case of this structure? (2 pts)

b. Another structure often occurring in case of III-V or II-VI semiconductors is the Wurtzite (Wz) structure, which is a hexagonal structure. InP nanowires can be grown with both the Zinc-Blende (ZB) or the Wz structure depending on the amount of Zn doping during the VLS growth method. In both cases the nanowires grow (with their long axis) in a direction parallel the normal of the close-packed planes in the structures, i.e. parallel to a <111> in case of ZB and parallel to [0001] in case of the Wz structure. So-called twinning superlattices were observed in the ZB structure above a certain Zn doping during the VLS growth process. Explain why it is possible that a twinning superlattice develops in the ZB structure, but that it can never develop in the Wz structure. (3 pts)

c. Single-wall carbon nanotubes are described on the basis of the vector in the graphene plane that exactly defines the circumference (i.e. perpendicular to the length) of the tube. i.e. the so-called chiral vector $\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \equiv (n,m)$, where the vectors a_1 and a_2 define the unit cell of graphene (see figure below). It can be derived that the reciprocal space vector $\vec{K}_1$ of this real space chiral vector remains parallel to $\vec{C}_h$ and can be described by:

$$\vec{K}_1 = (2\pi)\frac{2}{a}\frac{1}{4(n^2+nm+m^2)}\left(\sqrt{3}\vec{k}_x(n+m)+\vec{k}_y(n-m)\right)$$

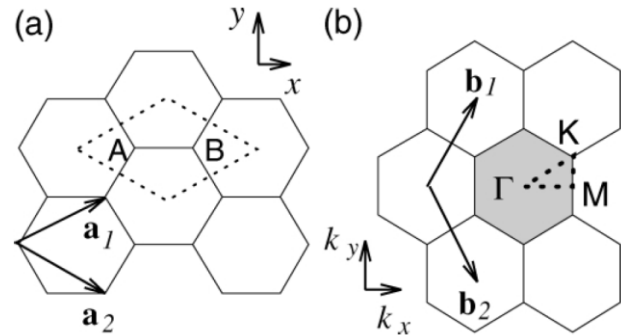In addition, the reciprocal space vectors b_1 and b_2 of the real-space vectors a_1 and a_2, which define the unit cell of graphene, are:

$\vec{b}_1 \perp \vec{a}_2$, and $\vec{b}_1 \cdot \vec{a}_1 = (2\pi)$

$\vec{b}_1 = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}\vec{k}_x + \vec{k}_y\right)$

$\vec{b}_2 \perp \vec{a}_1$, and $\vec{b}_2 \cdot \vec{a}_2 = (2\pi)$

$\vec{b}_2 = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}\vec{k}_x - \vec{k}_y\right)$

Now we have enough information in combination with the figure above to calculate whether an armchair or a zigzag nanotube is either metallic or semiconducting. Do this calculation in a transparent manner so to derive under what conditions (of *n* and *m*) an armchair or a zigzag nanotube is either metallic or semiconducting. (6 pts)

d. Explain why the bandgap of the semiconducting CNTs will be directly proportional to the reciprocal diameter of the CNT. A full derivation is not needed, but describe the (three) essential requirements that are fulfilled in order to arrive at this conclusion. (3 pts)

e. When in planar graphene we replace one or more (up to a maximum of 5) hexagon(s) by pentagons, like shown in the figure on the right for the shaded (yellow) hexagons, the planar graphene will be transformed into a cone with an opening angle θ like shown in figure f. Derive in a transparent manner the relation between the angle θ and the number of disclinations n (=1 to 5) introduced. (3 pts)
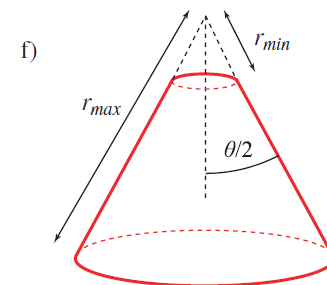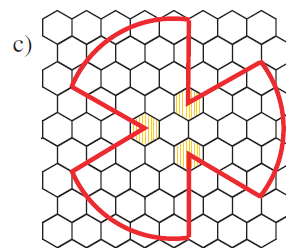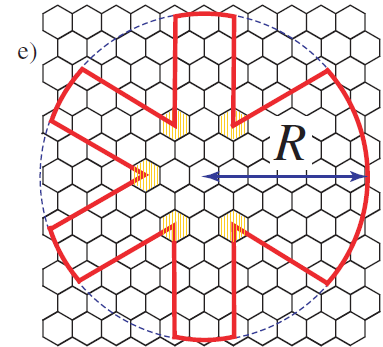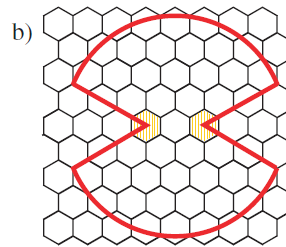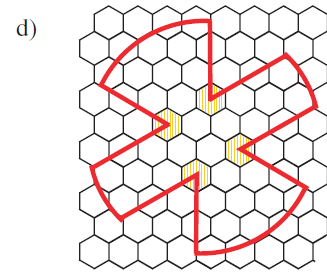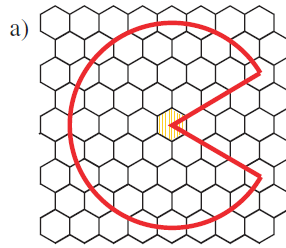
Exercise 4. (16 pts)

a. Draw in a so-called Angell plot, where $\log_{10}$(viscosity) versus T_g/T is given, with T_g the glass transition temperature (and T thus the variable temperature), the viscosity behaviour of (i) a strong liquid and (ii) a highly fragile liquid. It is required to also provide physically realistic values along the horizontal and vertical axes of the graph, i.e to properly scale the plot. (4 pts)

b. Which 5 requirement have to be fulfilled by phase-change materials, such that these materials become very suitable to be used in phase-change memories. (2.5 pts)

c. A phase-change memory cell loses its memory after (exactly) 15 hours at 120 °C and (exactly) 2 minutes at 150 °C. Compute the activation energy for crystal growth. The Boltzmann constant is 8.617 10^{-5} eV/K (= 1.38 10^{-23} J/K). How long is this memory cell then stable at 80 °C? (3.5 pts)

d. Phase-change materials have crystal structures that are prone to show (the so-called) Peierls distortion. Explain what a Peierls distortion is, when it can occur and why it can occur. (3 pt)

e. Phase transformations proceeding via nucleation and growth can generally be described by the following equation of the JMAK theory describing the fraction transformed x as a function of time t at at a constant temperature: $x(t) = 1 - \exp(-kt^n)$. When the isothermal transformation occurs at various temperatures generally only the factor k depends on temperature. The factor n is called the Avrami exponent. Derive the Avrami exponent within the framework of the JMAK theory for a constant nucleation rate and for isotropic crystal growth in a thin film, when the crystals have a size clearly larger than the film thickness (i.e. when growth is 2-dimensional). (3 pts)

Exercise 5. (20 pts)

Knowing that the energy of a spin with momentum m_s, in a magnetic field H, is $E = -\vec{m}_s \cdot \vec{H}$,

a) Calculate the partition function, Z(T,H), of a system of N paramagnetic spins, using the Ising model (6 pts).

   If you cannot calculate it, explain what is a system of paramagnetic spins and what is the Ising model? (3 pts)

b) Calculate the magnetization M(T,H) of the Ising system of N paramagnetic spins. (8 pts) . *For this you need a). If you could not get a), then explain how it should be done (4 pts)*

c) The Magnetization function M(T,H) of a system of N *ferromagnetic* Ising spins can be obtained

   from the paramagnetic M(T,H)(calculated in b) by substituting H by $H' = H + \dfrac{T_C M}{T M_S}$, where T_C

   is the Curie temperature of the ferromagnet and M_S is its saturation magnetization $M_S = M_{T=0K} = Nm_s$ and $M = Nm_s \langle s \rangle$, being $\langle s \rangle$ is the mean value of the Ising variable. Calculate the critical

   exponent β, using approximations valid for T close to T_C (that is $t = \dfrac{T - T_C}{T_C} \rightarrow 0$). (6 pts)

   For doing this, you need to know that for small enough x, one can approximate:
   tanh(x)= x- x^3/3 + 2x^5/15 -….
   $(1+x)^{-1}$= 1-x+x^2-x^3+…
   $(1+x)^{-3}$= 1-3x+6x^2-10x^3+..

   If you could not calculate b), then explain what is a ferromagnetic system of spins, what is the Hamiltonian of the ferromagnetic Ising model, what is T_C and why are the critical exponents relevant to describe second order phase transitions. (4 pts)