Examination CPS (11-01-2012)

Don't forget your name and student number
Write clearly your answers (*not readable = insufficient*)
Answer Part 1 and part 2 separately (both English and Dutch are acceptable)
Exam duration: 3 hours

Part 1:

1. Synthesis and preparation of solids:
   a) Eu-doped Yttria (Y_2O_3:Eu) is a red-emitting phosphor used in mercury discharge lamps and plasma displays. Traditionally Y_2O_3:Eu is made by solid state reaction from high melting Y_2O_3 and Eu_2O_3 powders. The reaction requires both high temperature (~1500 °C) and prolonged heat treatment. Why such conditions should be used? Argue your answer with reference to the reaction mechanism.
   b) Y_2O_3:Eu can also be prepared using the co-precipitation method. The mixture of Y_2O_3 and Eu_2O_3 is first dissolved in diluted HNO_3. By adding oxalic acid solution, the precipitation occurs. The precipitated solids, $(Y,Eu)_2(C_2O_4)_3 \cdot x\ H_2O$, are filtered out and calcinated at ~1000 °C for 1 h to yield the red phosphor. Explain why a much lower temperature is sufficient for reaction to occur in this case.
   c) The working principle of a halogen lamp is quite similar to that of metal purification using vapor phase transport method. In this case a halogen, e.g. I_2, is a transport agent that reacts with the evaporated W to form volatile WI_2. WI_2 is then decomposes at hot filament and release the metal. Write down the chemical reactions and indicate whether they are endothermic or exothermic.

2. Crystal structure and chemical bonding
   a) In crystallography the crystal structures of solids are often discussed in terms of lattices (Bravais lattices). What is a lattice? How many lattice types are there? Make schematic drawings for each of them.
   b) Not all Bravais lattices are possible for a given crystal system. For example, the tetragonal system can only have P- and I-type lattices. Show, using simple drawings, that a C- and an F-tetragonal lattice are equivalent to the P- and I-lattice.
   c) The lattice type determines the observable reflections. Give the reflection conditions for P-type, F-type, I-type and C-type lattice.
   d) The reciprocal lattice is a very useful concept to discuss single crystal diffraction and electronic structure of solids. Describe shortly how the reciprocal lattice is defined. In crystal chemistry there is an obscure statement "A body-centred lattice in real space gives rise to a face centred lattice in reciprocal space". How this statement can be understood?

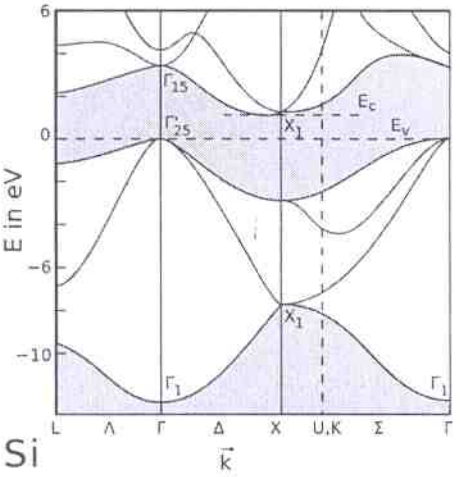
3. Electronic structure of solids

a) Electronic conductivity of solids depends on their band structures. What are the differences in band structures of an insulator, a conductor (metallic) and a semiconductor? Draw schematically their band structures.

b) The experimentally determined band-gaps (in eV) of the alkali metal fluorides are: LiF (13.6) – NaF (11.6) – KF (10.7) – RbF (10.3) – CsF (9.9). Give an explanation for this variation trend. A similar trend exists also in group IVa elements: C (5.47) - Si (1.12) - Ge (0.67) – Sn (~0.1). How do you explain?

c) The calculated band structure for silicon is shown at right. Does silicon have a direct band gap or an indirect band gap? Can silicon be used in LED device for infrared emission?

(The band gap of Si corresponds to an emission wavelength of 1107 nm)



Part 2:

1. What is a phonon? Write down the energy of the phonon, give the relation between ω and K, and explain this relationship. Are all wavelengths possible?
   If there are two atoms in a primitive cell, how many phonon branches are possible?

2. How is the heat capacity defined in relation to the phonons? Does the heat capacity depend on temperature (T)? If yes, how it depends on T in the case of an insulator and a metal. Which factors are responsible for the thermal expansion?

3. Give the expression of the thermal conductivity of a phonon gas. Draw schematically the thermal conductivity of a highly pure insulator as function of temperature. Explain.

4. What is ferrimagnetism? Fe_3O_4 and $NiFe_2O_4$ are ferrimagnetic spinels. Explain why they both show ferrimagnetism. Draw schematically the $1/\chi$ as function of temperature for them. Is spinel $ZnFe_2O_4$ ferrimagnetic or antiferromagnetic? Give an explanation.

5. How the electric cooling works using Peltier effect? Draw schematically the device and explain how it works in practice. What are the criteria of materials that can be used in such device?