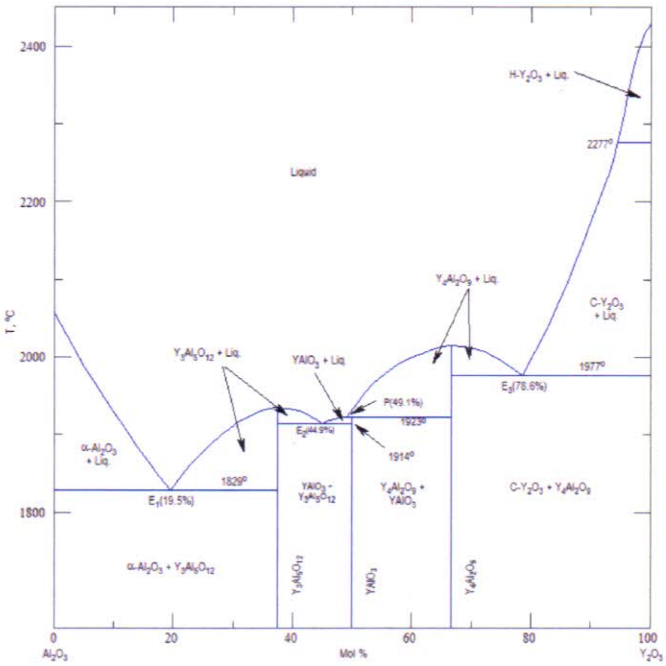
Examination CPS (16-06-2016)

Don't forget your name and student number
Write clearly your answers (*not readable = insufficient*)
Answers can be in either English or Dutch
Exam duration: 3 hours
Total points: 38

1. Synthesis and preparation of solids (**6p**)

   a) Ce(III)-doped garnet ($Y_3Al_5O_{12}$:Ce) is a yellow-emitting phosphor used in LED (light emitting diode) lamps. $Y_3Al_5O_{12}$:Ce is generally prepared by solid state reaction from Y_2O_3 CeO_2 and Al_2O_3 powders under reducing atmosphere. The reaction requires both high temperature (~1500 °C) and prolonged heat treatment. Why such conditions should be used? The co-precipitation method can significantly lower the reaction temperature (e.g. ~ 1000 °C) and duration. How to explain? Argue your answer with reference to the reaction mechanism. (**2p**)

   b) Both $Y_3Al_5O_{12}$ and $YAlO_3$ are promising host material for solid state laser when doped with Nd. For this application one needs single crystals. Consult the phase diagram of Al_2O_3-Y_2O_3 and describe how one can grow single crystals of these materials. Which compound is likely to be obtained as larger crystals? (**2p**)



   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 releases the metal (the halogen cycle). Write down the chemical reactions and indicate whether the reactions are endothermic or exothermic. (**2p**)

2. Crystal structure and chemical bonding (**8p**)

   a) In crystallography the crystal structures 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. (**2p**)

   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, respectively. (**1p**)

c) The lattice type determines the observable reflections. What are the reflection conditions for a face centred lattice (F-lattice)? KCl and KF have both the face-centred lattice (NaCl-type structure). In X-ray powder diffraction, some reflections of KCl have nearly zero intensity, whereas the same reflections are fairly strong in KF. Which reflections are they (give some exmples)? Explain why is it so? **(3p)**

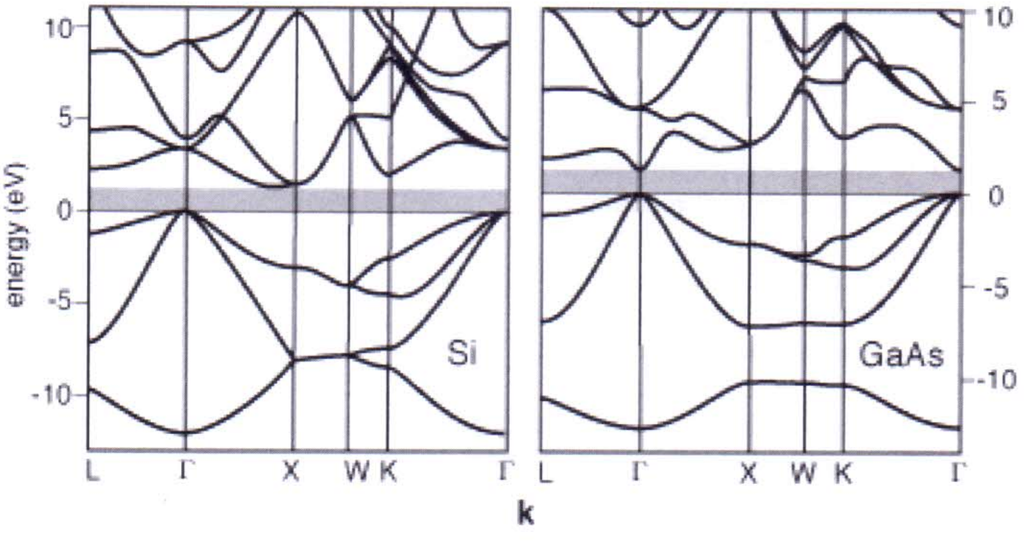
d) The reciprocal lattice is a very useful concept to discuss single crystal diffraction and electronic structure of solids. How the reciprocal lattice vectors ($\boldsymbol{a}^*$, $\boldsymbol{b}^*$ and $\boldsymbol{c}^*$) are defined from the vectors of the corresponding real lattice($\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$)? In crystal crystallography, 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? **(2p)**

3. Electronic structure of solids **(6p)**

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. **(2p)**

b) The band-gap (in eV) of the alkali metal fluorides varies as: LiF (13.6) – NaF (11.6) – KF (10.7) – RbF (10.3) – CsF (9.9). A similar, but more pronounced, trend exists also in group IVa elements: C (5.47) - Si (1.12) - Ge (0.67) – Sn (~0.1). Give an explanation for this variation trend. **(2p)**

c) The electronic band structure of Si (silicon) and GaAs (germanium arsenide) are shown below. Do they have the same type of band-gaps (i.e. direct or indirect banf-gap)? Which semiconductor is likely to be used in LED device for lighting? **(2p)**



4. Phonons and heat capacity **(4p)**

a) What is a phonon? How many phonon branches in NaCl which contains two different atoms per primitive cell (first Brillouin zone)? Draw schematically the dispersion relations of acoustic and optic phonons (angular frequency ω versus reciprocal lattice vector **k**). **(2p)**

b) What is the temperature dependence of heat capacity of an insulating solid at low and high temperature regimes according to the Debye theory? Make a schematic sketch of it. **(2p)**

c) The thermo-conductivity of pure solids increases initially with temperature to a maximum. It decreases then with increasing temperature. How do you explain this behaviour? **(2p)**

5. Magnetism **(6p)**

a) What is the origin of magnetism? What is the difference between diamagnetic and paramagnetic substances? **(2p)**

b) The formula of calculating the magnetic moment due to electron spin is given by: $\mu_S = g\sqrt{S(S+1)}$ (BM), where S is the sum of the spin quantum numbers of the individual unpaired electrons and $g \approx 2$. In case where the orbital moment makes its full contribution one uses: $\mu_{S+L} = g\sqrt{S(S+1) + 0.25 \cdot L(L+1)}$ (BM), where L is the total orbital angular momentum quantum number for the metal ion. Calculate the magnetic moment of Cr^{3+} in both cases. The observed value (μ) is ~ 3.8 (BM). What conclusion can you draw from it? **(2p)**

c) $ZnFe_2O_4$ is a normal spinel and $MgFe_2O_4$ is an inverse spinel. What do you predict their magnetic properties? Draw schematically the magnetic susceptibility (χ) as function of temperature for them. **(2p)**

6. Superconductivity **(4p)**

a) Superconductors have two unique properties that differ from other materials. What are these? What is difference between Type-I and type-II superconductors? **(2p)**

b) The occurrence of superconductivity in pure metals and alloys is explained by the BCS theory. The central idea of this theory is the existence of electron pairs (Cooper pairs). What is the origin of attractive force between two electrons that brought them together? **(1p)**

c) $YBa_2Cu_3O_7$ is the first superconductor with the critical temperature (T_c=93 K) surpass the boiling temperature of nitrogen. It is an oxygen deficient perovskite. Draw schematically the crystal structure of this compound. **(1p)**

7. Luminescence **(4p)**

a) What is luminescence? What are the activator and sensitizer? Give examples of them **(2p)**

b) Usual phosphor materials show Stokes shift, i.e. the emission wavelength is longer than the excitation wavelength. Explain why it is so. Anti-stokes phosphors emit light of shorter wavelength than that used for excitation. Explain how this may happen. **(2p)**