Materials Science and Engineering PhD Qualifying Exam

WRITTEN EXAM: Tuesday, May 21st, 2024 9:00AM-1:00PM, 15 Saint Mary's Street, Room 105

- NO ELECTRONIC DEVICES (smartphone, iPad, smartwatch) permitted
- Calculators and a ruler are allowed.
- CLOSED BOOK. Only the notes indicated below will be allowed.

INSTRUCTIONS:

- 1) Write your EXAM NUMBER on every sheet of paper
- 2) Write clearly and legibly as the exam may be scanned to faculty for grading.
- 3) **Answer 5 out of 6 questions** completely in the three required sections below:

Section I:

- **Problems 1 and/or 2:** Electrical, Optical and Magnetic Properties of Materials (MS 577/PY 543, Swan/Hu)
 - CLOSED BOOK, NO NOTES
- Section II: Problems 3 and/or 4: Thermodynamics and Statistical Mechanics (MS 505, Pal)

 CLOSED BOOK, 1-ONE-SIDED FORMULA SHEET & GRAPH PAPER
- Section III: Problems 5 and/or 6: Kinetic Processes in Materials (MS 503, Basu)
 - CLOSED BOOK, NO NOTES

*AM refreshments and grab n go lunch boxes served

ORAL EXAM: Thursday, May 23rd 9:00AM – 5:00PM Friday, May 24th 2024 10:00AM – 1:00PM 15 St. Mary's Street, Room 105

Oral Exam Schedule							
Thursday, May 23 rd							
Time Slot	Student	Committee					
9AM – 10AM							
10AM – 11AM							
11AM -12PM							
12PM – 1PM							
1PM – 2PM							
2PM – 3PM							
3PM – 4PM							
4PM – 5PM							

Friday, May 24 th							
Time Slot	Student	Committee					
10AM – 11AM							
11AM – 12PM							
12PM – 1PM							

1. Crystal structure and scattering.

NaCl has a rocksalt structure, where the conventional unit cell is shown in the figure. The atomic numbers are 11 (Na) and 17 (Cl).

- a) What lattice structure is the conventional unit cell? What is the basis?
- b) What lattice structure does the reciprocal lattice have? What is the reciprocal lattice constant?
- c) Consider the x-ray scattering peaks related to the 110 plane.
 - i. Draw the reciprocal lattice points in the 110 plane unit cell and label with their G vectors.
 - ii. What is the structure factor for each peak?
- d) If you were to observe the X-ray pattern, not knowing anything about the crystal, how would you be able to tell that the crystal has a basis beyond (000)?
- **2.** Electronic structure. Consider a simple cubic lattice with one atom per unit cell (highly unusual). The lattice constant is *a*. The figure shows the reciprocal unit cell, i.e. the 1st Brillouin Zone (BZ). Explore what happens to the electronic system as we vary the number of electrons per unit cell, as well as interaction strengths.



- a) Find the positions X, M,R, Γ in terms of the G vectors, $\frac{2\pi}{a}(h, k, l)$.
- b) Calculate and plot the free electron dispersion R- Γ -X- Γ -M for $G = \frac{2\pi}{a}(000)$. Set the energy at the X point as E_x, and give all other energies in terms of as E_x.
- c) Calculate the dispersion for one nonzero G vector for the-Γ-M direction that continue from the dispersion you already have. (pay attention to signs). If we considered a more realistic case of an FCC crystal, what differences would you have to consider?
- d) Find the Fermi vector for the case of 1 and 2 electrons per atom. Comment and sketch the shape of the Fermi surface relative to the reciprocal unit cell. Mark the Fermi level in the band diagram you drew above (label "1 el" and "2 el")
- e) Now consider gaps opening at X, R and M for the cases of two electrons/atom. All gaps are $E_{gap} = \frac{1}{4}E_x$. Sketch these cases for X- Γ -M- Γ -R. Is the material a metal or insulator? Discuss. If a metal, what does the Fermi- surface(s) look like? Will there be electron pockets in the 2nd BZ?



Formulas

Volume of sphere
$$V_{sphere} = \frac{4\pi r^3}{3}$$
Kinetic energy $E_{kin} = \frac{mv^2}{2} = \frac{\hbar^2 k^2}{2m}$ k-state density: reciprocal unit cell holds 2N states, N=# of unit cellsWave vector $\mathbf{k} - \mathbf{G}_{hkl} = (k_x - G_x)\hat{x} + (k_y - G_y)\hat{y} + (k_z - G_z)\hat{z}$ Structure factor $S_{hkl} = S_{lattice} \cdot S_{basis}$,
(cubic conventional cell) $S_{basis} = \sum_{i}^{N} f_i e^{2\pi i (h+k+l)}$
Form factor $f_i \sim Z$, N - number of basis points

Materials Ph.D. Qualifying Examination (May 2024) (Allowed 1-page open notes/formulae one-side) <u>No cell phones/laptops</u>

 a. A piece of copper (2 moles) at a uniform temperature of 273 K is initially placed in contact with another piece of copper (2 moles) at 373 K in an adiabatic enclosure. Calculate the temperature of the 2-piece (4 moles) copper system when thermal equilibrium is attained. Calculate the amount of heat transferred between the copper pieces and the total entropy change as a result of the heat transfer. The molar specific heat of copper at constant pressure is 22.64 + 6.28x10⁻³T J/mole-K.

b. Can a spontaneous process result in a decrease in the entropy of the system. Justify your answer.

c. While applying the phase rule what does degrees of freedom at equilibrium mean?

2. a. Lithium Boride vapors dissociate according to:

 $LiBr(g) = Li(g) + \frac{1}{2} Br_2(g)$

The standard free energy change of the above reaction is 333,900 – 42.09 T (K) J/mole.

The gas is heated at constant total pressure of 1 atmosphere. At what temperature does the partial pressure of Li (g) in the system reach 10^{-6} atm. and what is the partial pressure of Br (g) at that temperature?

b. If the total pressure in the system increases how will the equilibrium constant of the above reaction change? Will the above reaction move forward or backward as the pressure increases?

c. How many degrees of Freedom define the equilibrium for the $LiBr(g)/Li(g)/Br_2(g)$ system?

May 2024 MSE Qualifier Questions: MS 503

Closed book, NO additional notes

Some physical constants, equations and tables that may or may not be relevant:

Gas constant, R = 8.314 J/mole-K Avagadro's constant, N_{Av} = $6.023X10^{23}$ mole⁻¹ Plank's constant, h = $6.626X10^{-34}$ J-s Boltzman's constant, k = $1.381X10^{-23}$ J/K Charge of an electron, e = $-1.602X10^{-19}$ Coulombs $1 \text{ ev} = 1.602X10^{-19}$ J

Fick's Laws and solutions: $J = -D \frac{\partial c}{\partial x}, \quad \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right)$

Thin film solution: $c(x,t) = \frac{S}{\sqrt{4\pi Dt}} \exp(-x^2/4Dt)$, Leak test: tolerance = 1- $erf\left(\frac{l}{2\sqrt{Dt}}\right)$ Error function solution: $c(x,t) = A + Berf(x/2\sqrt{Dt})$, $erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-u^2} du$

Degassing solution:
$$c(x,t) = \frac{4c^0}{\pi} \sum_{j=0}^{\infty} \frac{1}{2j+1} \sin\left(\frac{(2j+1)\pi x}{l}\right) \exp\left(-\left(\frac{(2j+1)\pi}{l}\right)^2 Dt\right)$$

 $\overline{c}(t) = \frac{8c^0}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} \exp\left(-\left(\frac{(2j+1)\pi}{l}\right)^2 Dt\right), \quad \frac{\overline{c}}{c_0} = \exp\left(-\frac{t}{\tau}\right), \quad \tau = \frac{l^2}{\pi^2 D}$

Other general diffusivity relationships: $x \sim \sqrt{Dt}$, $D = D_0 exp\left(-\frac{Q}{RT}\right)$, $\frac{Q}{R} = \frac{q}{k}$

Broken bond model and nucleation: $\Delta G = V \Delta G_V + A \sigma$

Surface energy =
$$\frac{broken \ bonds}{atom} X \frac{atoms}{area} X \frac{energy}{broken \ bond}$$

 $\frac{\varepsilon}{2} = \frac{L_S}{ZN_{Av}}$
For FCC: $\sqrt{2}a = 4r$

For an equilateral triangle of side 'x', area of triangle = $\frac{\sqrt{3}}{4}x^2$

Error Function Table

					Hundredth	s digit of x				
x	0	1	2	3	4	5	6	7	8	9
0.0	0.00000	0.01128	0.02256	0.03384	0.04511	0.05637	0.06762	0.07886	0.09008	0.10128
0.1	0.11246	0.12362	0.13476	0.14587	0.15695	0.16800	0.17901	0.18999	0.20094	0.21184
0.2	0.22270	0.23352	0.24430	0.25502	0.26570	0.27633	0.28690	0.29742	0.30788	0.31828
0.3	0.32863	0.33891	0.34913	0.35928	0.36936	0.37938	0.38933	0.39921	0.40901	0.41874
0.4	0.42839	0.43797	0.44747	0.45689	0.46623	0.47548	0.48466	0.49375	0.50275	0.51167
0.5	0.52050	0.52924	0.53790	0.54646	0.55494	0.56332	0.57162	0.57982	0.58792	0.59594
0.6	0.60386	0.61168	0.61941	0.62705	0.63459	0.64203	0.64938	0.65663	0.66378	0.67084
0.7	0.67780	0.68467	0.69143	0.69810	0.70468	0.71116	0.71754	0.72382	0.73001	0.73610
0.8	0.74210	0.74800	0.75381	0.75952	0.76514	0.77067	0.77610	0.78144	0.78669	0.79184
0.9	0.79691	0.80188	0.80677	0.81156	0.81627	0.82089	0.82542	0.82987	0.83423	0.83851
1.0	0.84270	0.84681	0.85084	0.85478	0.85865	0.86244	0.86614	0.86977	0.87333	0.87680
1.1	0.88021	0.88353	0.88679	0.88997	0.89308	0.89612	0.89910	0.90200	0.90484	0.90761
1.2	0.91031	0.91296	0.91553	0.91805	0.92051	0.92290	0.92524	0.92751	0.92973	0.93190
1.3	0.93401	0.93606	0.93807	0.94002	0.94191	0.94376	0.94556	0.94731	0.94902	0.95067
1.4	0.95229	0.95385	0.95538	0.95686	0.95830	0.95970	0.96105	0.96237	0.96365	0.96490
1.5	0.96611	0.96728	0.96841	0.96952	0.97059	0.97162	0.97263	0.97360	0.97455	0.97546
1.6	0.97635	0.97721	0.97804	0.97884	0.97962	0.98038	0.98110	0.98181	0.98249	0.98315
1.7	0.98379	0.98441	0.98500	0.98558	0.98613	0.98667	0.98719	0.98769	0.98817	0.98864
1.8	0.98909	0.98952	0.98994	0.99035	0.99074	0.99111	0.99147	0.99182	0.99216	0.99248
1.9	0.99279	0.99309	0.99338	0.99366	0.99392	0.99418	0.99443	0.99466	0.99489	0.99511
2.0	0.99532	0.99552	0.99572	0.99591	0.99609	0.99626	0.99642	0.99658	0.99673	0.99688
2.1	0.99702	0.99715	0.99728	0.99741	0.99753	0.99764	0.99775	0.99785	0.99795	0.99805
2.2	0.99814	0.99822	0.99831	0.99839	0.99846	0.99854	0.99861	0.99867	0.99874	0.99880
2.3	0.99886	0.99891	0.99897	0.99902	0.99906	0.99911	0.99915	0.99920	0.99924	0.99928
2.4	0.99931	0.99935	0.99938	0.99941	0.99944	0.99947	0.99950	0.99952	0.99955	0.99957
2.5	0.99959	0.99961	0.99963	0.99965	0.99967	0.99969	0.99971	0.99972	0.99974	0.99975
2.6	0.99976	0.99978	0.99979	0.99980	0.99981	0.99982	0.99983	0.99984	0.99985	0.99986
2.7	0.99987	0.99987	0.99988	0.99989	0.99989	0.99990	0.99991	0.99991	0.99992	0.99992
2.8	0.99992	0.99993	0.99993	0.99994	0.99994	0.99994	0.99995	0.99995	0.99995	0.99996
2.9	0.99996	0.99996	0.99996	0.99997	0.99997	0.99997	0.99997	0.99997	0.99997	0.99998
3.0	0.99998	0.99998	0.99998	0.99998	0.99998	0.99998	0.99998	0.99999	0.99999	0.99999
3.1	0.99999	0.99999	0.99999	0.99999	0.99999	0.99999	0.99999	0.99999	0.99999	0.99999
3.2	0.99999	0.99999	0.99999	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000

Problem 1

The solubility limit of atomic H in Ta at 1000°C is 2wt%. A 5mm thick Ta sheet at 1000°C, is saturated with H. The sheet is coated on one side and all the edges with a TaN coating. Since H diffuses rapidly in Ta, the sheet is subjected to a degassing anneal by placing in a vacuum furnace at 1000°C. This causes H atoms in the sheet to diffuse to the only exposed (non-coated) surface, and quickly desorb as gas phase H₂ which is quickly removed by the pump (see figure on right, where the sheet is shown in cross-section).

Since the desorption step is much faster than the diffusion step, it can be assumed that the concentration of H atoms at the exposed surface of the sheet is maintained at 0wt% at all times. Further, assume that the diffusivity of H in TaN is many orders of magnitude slower than in Ta, so the coated surfaces can be considered to be effectively zero flux planes, making the H diffusion through the exposed surface a 1-D problem. The initial concentration profile in the sheet is shown in the figure to the right. Note that x = 0 is at the exposed surface of sheet. **Please use this axis system for all your answers**.



Ta sheet

➡ Vacuum

a) If the activation energy, Q, of diffusion of atomic H in Ta is 1eV/atom, and $D_0 = 0.913 \text{ cm}^2/\text{s}$, calculate diffusivity of hydrogen, D_H , at 1000°C.

b) Sketch qualitatively, the change in the concentration profile in the sheet as a function of time, assuming 1-D out-diffusion of H. The profile at t = 0 is shown.

c) How long will it take for the concentration at a depth of 1mm from the exposed surface to reach 1wt%? **Justify** which solution you have chosen. Assume error tolerance is 1%.

HINT: Always start with the simplest RELEVANT solution, and then check if the choice is valid.

d) How long will it take to remove 90% of the initial H in the Ta? **Justify** any assumption you make.

Problem 2.

a) During solidification of some metals with FCC crystal structure, the general shape of nuclei is shown in the figure on the right. The nuclei have six {100} faces and eight {111} faces. The relative areas of the two types of faces depend on their relative surface energies. Calculate $\sigma_{100}/\sigma_{111}$ for this FCC crystal based on the broken bond model. Clearly sketch out the geometry used to calculate the number of broken bonds/atom and atoms/area.



b) Based on the calculations above, do you think that the sketched shape of a nuclei is reasonable in terms of the relative areas of the two surfaces?

c) Can you explain qualitatively why the nuclei would not just be bounded by the lower energy faces, i.e., why would it not be a cube bounded by {100} faces if σ_{100} was lower, or a tetrahedron bounded by {111} if σ_{111} was lower?