State University of New York

University at Buffalo

Department of Mechanical and Aerospace Engineering

Ph.D. Qualifying Examination in Materials Science

May 28, 2008

This test includes 7 problems on 5 pages. Please answer any ***four*** of these problems in the blue book(s) provided. The Periodic Table of the Elements on the last page includes information on the atomic masses.

Avogadro's number = 6.02×10^{23}

Problem 1 (100%)

X-ray diffraction is conducted on aluminum (an FCC material with density 2.70 g/cm^3) with using an x-ray diffractometer and CuKα radiation of wavelength 1.542 Å. The specimen is in powder form. The melting temperature is 660^{0}C.

(a) (9%) What is the lattice constant (length of an edge of the conventional cubic unit cell) in Å?
(b) (3%) What is the number of atoms per conventional cubic unit cell?
(c) (3%) What is the number of lattice points per conventional cubic unit cell?
(d) (3%) What is the shape of the primitive (smallest) unit cell?
(e) (6%) What is the length (in Å) of an edge of the primitive unit cell?
(f) (12%) Sketch the reciprocal lattice and label each reciprocal lattice point with the Miller indices (with respect to the conventional cubic unit cell).
(g) (9%) What is the length (in Å^{-1}) of an edge of the conventional cubic unit cell in reciprocal space? Note that a unit cell must be a true unit cell.
(h) (6%) What is the length (in Å^{-1}) of an edge of the primitive unit cell in reciprocal space?
(i) (9%) Give the Miller indices (with respect to the conventional cubic unit cell) of the first three diffraction lines. List them in order of increasing diffraction angle.
(j) (6%) Calculate the diffraction angle (2θ, in degrees) of the lowest angle diffraction line.
(k) (6%) Is the satellite peak due to the CuKβ radiation at the lower angle side or the higher angle side of the corresponding main peak that is due to the CuKα radiation? Explain your answer.
(l) (6%) How would heating to a temperature below the melting temperature affect the diffraction pattern? The diffraction is conducted at the elevated temperature.
(m) (4%) How would heating to a temperature above the melting temperature affect the diffraction pattern? The diffraction is conducted at the elevated temperature.
(n) (6%) How would the diffraction pattern be affected by preferred orientation, which is such that the particles in the specimen powder preferentially have their (100) plane parallel to the diffraction plane?
(o) (6%) The mass absorption coefficient is 50.23 cm^2/g. Calculate the linear absorption coefficient.
(p) (6%) Describe the main principle behind how a copper x-ray tube produces CuKα radiation.

Problem 2 (100%)

(a) (16%) By consideration of equality of mechanical energy and electrical energy in the energy conversion, derive an equation that describes the direct piezoelectric effect. Use this equation to define the piezoelectric coupling coefficient. Give the unit for this coefficient.

(b) (6%) The piezoelectric coupling coefficient d_{33} is positive, whereas the coefficient d_{31} is usually negative. Why?

(c) (9%) Sketch the butterfly curve, i.e., the curve that describes the strain due to the converse piezoelectric effect during electric field variation.

(d) (6%) Piezoelectric materials are ceramics or polymers, but not metals. Why?

(e) (6%) Barium titanate is piezoelectric only below 120°C? Why?

(f) (6%) PZT is the most common piezoelectric material. What is meant by "PZT"?

(g) (6%) How is the piezoelectric effect utilized in scanning tunneling microscopy?

(h) (6%) How is the piezoelectric effect utilized in structural vibration control (active control)?

(i) (6%) How is the piezoelectric effect utilized in energy harvesting?

(j) (6%) How does the elastic modulus affect the piezoelectric effect?

(k) (6%) How does the relative dielectric constant affect the piezoelectric effect?

(l) (6%) Piezoelectric aging affects the direct piezoelectric effect much more than the converse piezoelectric effect. Why?

(m) (9%) Use a sketch to describe the structure and the components in a piezoelectric stack actuator.

(n) (6%) What is the main advantage of electrostrictive actuation compared to piezoelectric actuation?

Problem 3 (100%)

(20%) (a) $S = k \ln \Omega$

(i) which scientist established this relation?

(ii) identify the symbols S, k, Ω.

(iii) what two branches of thermodynamics are connected through this equation?

(40%) (b) Consider a system composed of N 'particles' in which a 'particle' may have either an energy of zero or an energy of ε. The total energy of the system is U.
Determine Ω when:

(i) the 'particles' are *distinguishable.*

(ii) the 'particles' are *indistinguishable.*

(40%) (c) When the 'particles' are atoms in a crystal and ε is the energy associated with a point defect in the lattice,

(i) are the particles *distinguishable* or *indistinguishable*? Why?

(ii) determine $S(U, \varepsilon, N)$ and simplify it using *Stirling's approximation*

(iii) consider $\varepsilon = \varepsilon(v)$, where $v = V/N$ (volume per mole of atoms); determine an expression for the pressure, P.

Problem 4 (100%)

(12%) (a) *True* or *False*:

(i) *Ideal Solid Solutions* and *Ideal Gas Solutions* have the same mixing behavior.

(ii) For an *Ideal Solution,* the entropy of mixing is *zero*.

(iii) For an *Ideal Solution,* the volume remains the same.

(iv) For an *Ideal Solution,* the Gibbs free energy of mixing is *zero*.

(v) The entropy of mixing for a *Regular Solution* equals that of an *Ideal Solution*.

(vi) The enthalpy of mixing for a *Regular Solution* equals that of an *Ideal Solution*.

(36%) (b) Define by giving an equation:

(i) activity

(ii) activity coefficient

(iii) fugacity

(iv) the partial molal differential operator

(v) a Gibbs-Duhem relation for a binary mixture

(vi) the Clausius-Clapeyron equation for a unary heterogeneous system

(52%) (c) Consider the *stability* of a *binary solution* for which:

$$\Delta G_{mix} = \alpha\, RT\, X_1 X_2 + RT\,(X_1 \ln X_1 + X_2 \ln X_2) \quad , \quad X = \text{mole fraction}$$

Determine the values of α for which the mixture is thermodynamically stable.

Problem 5 (100%)

(a) (50%) Demonstrate that the slope of the coefficient of compressibility β vs T is horizontal at T= 0 K.

(b) (50%) The ice of an outdoor skating rink is at ambient temperature of -1.5 °C. Calculate in atmospheres the minimum pressure (applied for example by a skate) necessary to melt the ice.

Data: At 0 °C, the specific volume of water is 1 cm^3/g and that of ice is 1.090 cm^3/g. The heat of fusion is 79.7 cal/g. 1 cal=41.3 cm^3 atm.

Problem 6 (100%)

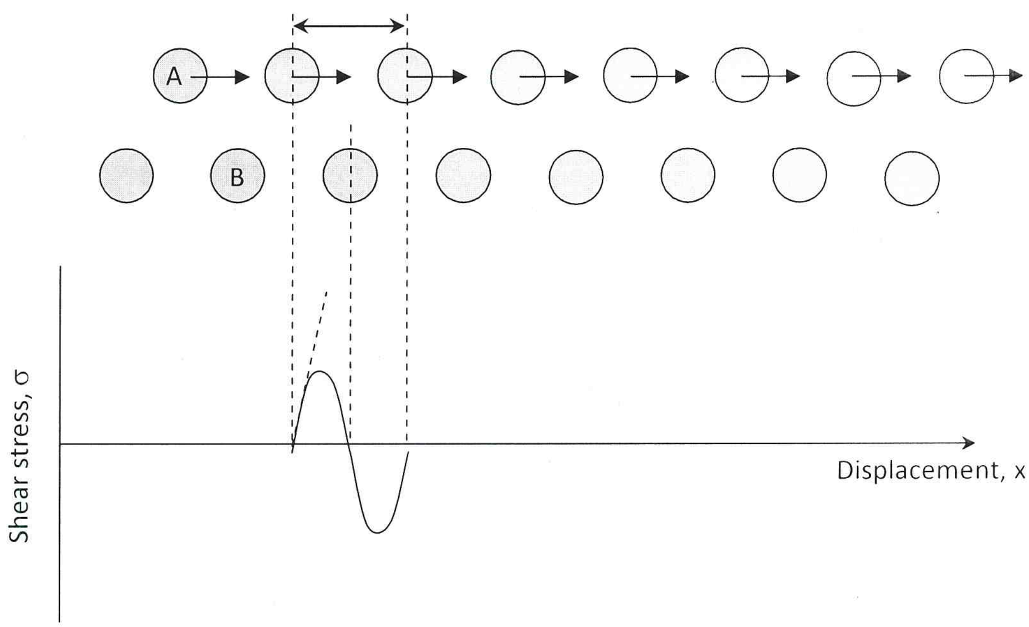

Figure above shows a simple method of estimating the theoretical shear strength of a perfect crystal. For small elastic strains, the stress σ is related to the displacement x by: σ=Gx/d, where d is the inter-planar distance between atom sin rows A and B, and G is the shear modulus (derived from the broken line in stress versus displacement at the initial slope). At first approximation, stress-displacement relation for large displacements may be written as:

$$\sigma=(Ga/2\pi d)\sin(2\pi x/d),$$

where 'a' is the inter-atomic spacing in the shear direction.

(a) (80%) What is the critical shear stress σ_c at which the lattice becomes unstable (that is when the atoms in row A are directly above B corresponding to zero stress)?

(b) (20%) What is the value of σ_c when a≈d?

Problem 7 (100%)

The fcc phase of the Al-Zn system exhibits a miscibility gap. The molar free energy of that phase may be described as

$G_m = X_1 G_1^o + X_2 G_2^o + RT(X_1 \ln X_1 + X_2 \ln X_2) + X_1 X_2 (3150 X_1 + 2300 X_2)[1-(T/4000)]$ cal, for which Al=1 and Zn=2. Calculate the composition and temperature of the miscibility gap's critical point.

Key: element name / atomic number / symbol / atomic weight (mean relative mass)

hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 **	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]				

*lanthanoids	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
**actinoids	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]