Engineering 45
Structure and Properties of Materials
Final Examinations: 1987-2001

1987

Problem 1:

(a) Draw the FCC crystal structure and identify the positions of all the atoms. How many atoms are there per unit cell?

(b) The ß-ZnS structure (the binary analogue of the diamond cubic) can be thought of as a derivative of the FCC. Describe the ß-ZnS structure. Let an AB compound have this structure. Show that either the A atoms or the B atoms can be put on the sites of an FCC lattice. Also show that each A atom has four equidistant B neighbors while each B atoms has four equidistant A neighbors.

(c) There is a hexagonal analogue of the ß-ZnS structure that is known as the wurtzite structure, and is commonly found in CdS, SiC and other binary compounds. It is based on the hexagonal close-packed structure in essentially the same way that ß-ZnS is based on the FCC. In a binary compound, AB, that has the wurtzite structure, either the A atoms or the B atoms may be taken to fill the sites of an HCP lattice. Each A atom has four equidistant B neighbors; each B atom has four equidistant A neighbors. Given this information, describe the atom positions in the wurtzite structure.

(d) Si normally has the diamond cubic structure and is a semiconductor. If it were made to have the NaCl structure, would you expect it to be a semiconductor, insulator or metal? Why?

Problem 2:

(a) A material that is made of atoms that have permanent magnetic moments must be paramagnetic, ferromagnetic or antiferromagnetic. Describe these three magnetic states. Which do you expect at high temperature?

(b) Describe the difference between a "hard" and a "soft" ferromagnet. Why is a hard magnet hard?

(c) If you were choosing a material for a magnetic disc to store information, would you prefer a hard or a soft ferromagnet? Would you want to coat the disc with small, discrete particles or with a continuous ferromagnetic film?

(d) Describe how you might make a material that has antiferromagnetic order at low temperature, nonetheless has a net magnetic moment and the engineering behavior of a ferromagnet.

Problem 3:

[withdrawn - too messy]

Problem 4:

(a) Describe the nucleation-and-growth mechanism of a structural phase transformation. Why is there a thermodynamic barrier to the formation of a nucleus?

(b) Let phase α transform to ß by nucleation and growth, where phase α is preferred at high temperature and ß at low temperature. It is often possible to suppress the transformation α → ß by cooling rapidly, but is almost never possible to suppress ß → α by heating rapidly. Why?

(c) A liquid phase will ordinarily solidify into a crystalline solid if cooled slowly, but may form a glass if cooled very rapidly. Explain this observation in terms of the relative kinetics of crystallization and glass formation (begin by showing that the crystalline solid <u>must</u> nucleate, while the glassy phase need not, but you must also explain why the glassy phase does not <u>always</u> form, if its kinetics are more favorable).

(d) If a typical crystalline semiconductor is melted and then quenched into a glassy state its conductivity increases significantly (it may even become metallic). However, if a typical crystalline metal is melted and quenched into a glassy state, its conductivity decreases significantly. Interpret this phenomenon.

Problem 5:

(a) Describe and distinguish between and extrinsic and an intrinsic semiconductor. Why are virtually all semiconducting devices based on extrinsic semiconductors?

(b) The development of semiconducting devices depended on the development of techniques to create very pure single crystals of semiconducting material such as Si. Why single crystals? Why very pure?

(c) When semiconducting Si is grown from the melt and purified, it usually contains a small residual concentration of boron (valence 3) which is very difficult to eliminate. The resulting crystal is p-type. Why? Assuming that you can implant atoms in the crystal at will, how would you create an n-type region within it?

(d) Draw a simple diagram illustrating the band structure of the semiconducting material near the n-p interface. Show that the interface easily passes current in one direction, but imposes a barrier to current flow in the other.

Problem 6:

It came to pass that the empress of Berkelia grew tired of her long-time lover, as is the way with empresses, and wished to make a change. Since the empire could hardly be cluttered with ex-lovers, it was, of course, necessary that he be put properly away. The empress retained a strong affection for her ex-paramour and was moved with gratitude for the many happy hours they had shared. She was determined that the execution be conducted with elegance and with due regard for all relevant traditions. To this end she convened the Royal Committee on Public Ceremonies to consult with the condemned on the appropriate etiquette for the occasion. The authorities agreed that there was only one proper procedure: the ex-lover should be quietly garroted with a silken cord. Unfortunately, the entire silken cord industry was in the midst of a protracted labor dispute, and there was not a single silken cord to be had in the empire. Desperate to satisfy the impatient empress, the Committee moved to high-tech, and decided to substitute a length of optical fiber that had been conveniently left behind by a TV crew filming a GTE commercial. However, when the optical fiber was proof-tested on a random undergraduate it proved a dismal failure and broke as it was being wound around his neck. The unfortunate undergraduate had to be bludgeoned to death, leaving a bloody mess in the foyer of the palace and infuriating the empress.

(a) What went wrong?

The concerned committee then retained a consulting engineer with impeccable credentials from a grossly expensive Junior University. "The tuition alone guarantees that he is an expert," they smugly assured one another. The expert promptly purchased a supercomputer, at an encouragingly exorbitant cost, and computed the stress imposed on the fiber during a proper strangulation. He then cut several very short specimens from the fiber and tested them in tension. Virtually all of the specimens had an ultimate tensile strength above the required value. "Your problem was simply a bad piece of fiber," concluded the expert. "My tests show that the inherent tensile strength of the fiber is more than adequate. It is very unlikely that another segment of the fiber will fail. Proceed with the execution." The result was a disaster. The fiber again broke on the first application of the strangulation load, thoroughly embarrassing both the empress and her ex-lover and forcing the committee to mass suicide.

(b) What went wrong?

In desperation, the empress offered a munificent reward for a suitable solution. The money attracted the interest of one Alvin Underfoot, a passing undergraduate possessed of a (cheap) public school education in Materials Science. "The solution is simple," he proclaimed. "One useful characteristic of glass is that when it breaks you can weld it by simply heating the broken ends until they fuse together. Therefore you should take the length of fiber you need for an proper strangulation and load it in tension. It will almost certainly break at a stress well below that calculated by my predecessor. Weld it back together and test it again. It will almost certainly be stronger. Repeat this procedure until it withstands a stress well above the strangulation load. You may then proceed with the execution with complete confidence." Alvin was, of course, correct. The ceremony was long remembered as a thing of grace and beauty. Alvin, now wealthy, lived happily for another year.

(c) Why was he right?

1988

Problem 1: (20 points)

Two common crystal structures of binary solids that have strong ionic bonding are the NaCl and CsCl structures.

(a) Describe the NaCl and CsCl structures.

(b) The CsCl structure is often adopted by binary compounds whose species differ significantly in ionic size. An example is AgBr (which is a common active compound in photographic film). In Pauling's picture the Ag^+ ion is very much smaller than Br^-, and the Br^- ions essentially touch one another in the CsCl lattice. This touching closes some of the octahedral voids in the BCC structure on which the CsCl structure is based. Show the positions of the octahedral voids in BCC, and indicate which remain open in a CsCl structure in which the Cl atoms touch.

(c) There are two kinds of intrinsic point defects in an ionic crystal: a vacancy of one specie accompanied by a vacancy of the other (Schottky defect) and a vacancy together with an interstitial of the same specie (Frenkel defect). Why are these the common intrinsic defects in ionic crystals?

(d) In AgBr, which has the CsCl structure, the mobile species is Ag^+, which diffuses via the motion of Ag^+ interstitials (Frenkel mechanism). To show that this is intuitively plausible, use the results of part (b) to show that a Ag^+ ion passes through an open octahedral void when it moves from one Ag^+ site in the CsCl lattice to the immediately adjacent site.

(e) In NaCl the mobile specie is Na^+, and the open interstitial sites are the tetrahedral sites of the FCC reference lattice. Na^+ diffuses by exchange with Na^+ vacancies (Schottky mechanism). To show that this is intuitively plausible, show that a Na^+ ion does not pass through an open interstitial site if it follows the most direct path of exchange with a vacancy on an adjacent Na^+ site.

Problem 2: (15 points)

Elements A and B form a binary system with a simple eutectic phase diagram.

(a) Draw the phase diagram and label the phase fields.

(b) It is desired to produce a solid that contains a microstructure of equiaxed grains of A-rich (α) solid solution with the grain interiors decorated by a dense distribution of B-rich (ß) precipitates. Given the phase diagram, design a heat treatment that should achieve this microstructure and describe why it would work.

(c) Assuming that the ß precipitates form within the grains of α during aging at constant temperature, describe the variation of the yield strength of the alloy with aging time, and explain the shape of the curve.

Problem 3: (20 points)

Those of you who are fortunate to survive so long will no doubt recall the vaporization of the Golden Gate Bridge. In the year ought-35 it will have happened, just two years before the centennial of the famous span. The event was conveniently attributed to an unfortunate misfiring of the space-based laser defense system during a routine readiness check. But local folks knew better. A red bridge affronts all true Californians.

(a) What property of steel makes it possible to vaporize a bridge with an intense burst of laser light?

It was, of course, decided to rebuild in appropriate blue and gold: pure gold for the Golden Gate with trimmings of sapphire and lapis lazuli. Humanists suggested solid gold. They were fortunately overruled.

(b) Why would a bridge of pure, solid gold be unlikely to stand, assuming that it could be erected?

The Golden Gate bridge was remade of gold-plated structural steel, highlighted with blue. The Californians looked on it and saw that it was good. They protected it with stringent environmental laws that proscribed the color red.

But not everyone was pleased. Even in those days the South Bay was home to a tribe of rich who revelled in red. Forbidden from the Golden Gate, they built submarines and desecrated it underwater. They scraped patches of the gold plating from the submerged portions of the pylons and engraved their arboreal insignia in the exposed steel with an axe they had tied for. Dressed in hideous colors and accompanied by scruffy individuals of uncertain function carrying musical instruments, they visited the structure annually in bubble subs and glass-bottomed boats for ritualistic exercises. And so it came to pass that on the day of the centennial, when the bridge was opened for the peaceful Californians to walk over, a main pylon collapsed sending thousands to their doom.

(c) Post-mortem metallurgical analysis showed that the pylon had corroded almost completely through in only two years. Why?

The Californians were distraught, but determined. They restored the bridge to its original strength and beauty, and waged incessant struggles underwater to protect it. But their resources, alas, were no match for the untold wealth of the red-men. Ultimately they realized that they must find a metallurgical solution that would protect the submerged pylons from desecration of the gold coat. To this end they climbed the hills of Berkeley to seek wisdom at the retirement home of the ancient sage, formerly random undergraduate Alvin Underfoot. "The solution is trivial," he advised them. "For a small fee I shall provide you with a secret polymeric formulation that completely wets steel and is wet by gold. Simply drain the Bay, peel off the gold, clean the steel surface, coat the steel with this magic substance, and replate with gold. Then if the gold coating is stripped the steel will not corrode. Even if the polymer coat is damaged the rate of corrosion will be so slow that vigilant Californians can easily find and repair the surface before serious damage occurs."

The Californians followed his advice. The avian submariners were frustrated, turning cardinal in their rage. Almost everyone lived happily ever after.

(d) Why did this solution succeed? What electrical property did the polymer have?

(e) Discuss the interfacial tensions of the polymeric coating with steel, gold and air.

Problem 4: (15 points)

(a) Draw a simple sketch of the band diagrams of an n-type and a p-type semiconductor. Indicate the position of the Fermi level relative to the center of the band gap in each material at moderate temperature.

(b) Roughly sketch the band structure of an n-p junction in which the two materials are joined and allowed to come to equilibrium.

(c) Explain qualitatively why the n-p junction conducts electricity much more easily in one direction than in the other.

Problem 5: (15 points)

(a) While the yield strength of an engineering material can be changed by as much as an order of magnitude by simple changes in the microstructure, the elastic modulus is relatively insensitive to microstructure. Why?

(b) Diamond has a relatively low value of Poisson's ratio, $\nu \sim 0.1$, while the Poisson's ratio of rubber is close to 0.5. Explain this observation in terms of the nature of bonding in the two materials.

(c) It is often good engineering practice to set the load limits on a metallic or polymeric structure on the basis of the ultimate tensile strength, s_u, but is often hazardous to set the load limits on a ceramic structure on the basis of a measurement of s_u. Why?

Problem 6: (15 points)

Alvin Underfoot, a random undergraduate, inadvertently transported himself in time and space to a famous Eastern university in the latter part of the nineteenth century. Strolling about the campus, he wandered into a introductory lecture on the mechanical properties of materials.

"To understand fatigue," lectured the professor, "imagine one man holding another by the arms suspended off a bridge. Eventually the holder tires and lets go. In a similar way the bonds that hold atoms together weaken under repeated loads and eventually break, causing fracture." Alvin was appalled, and interrupted the lecture to give an accurate description of the mechanism of fatigue. "Nonsense," replied the professor, who promptly had him removed from the room.

(a) While the professor's explanation is totally wrong, it was still being promulgated as an explanation of some kinds of wear fatigue as late as the 1970's (and may be still). It was not totally foolish, given the knowledge of the day. Explain why this explanation is consistent with the phenomenological behavior of high strength materials in fatigue, and describe an experiment that would prove it wrong.

Seeking some evidence of sound reasoning, Alvin wandered into a second lecture. The professor in this class was more subtle. "Cyclic stress causes a structural transformation in high strength metals," he explained. "After many cycles, the metal crystallizes. Since we know that crystals are brittle, the metal easily fractures after crystallization. It is easy to show this experimentally. If steel is fractured in tension the fracture surface is ductile and heavily deformed, like fracture in gold or wet mud. But if the steel is fatigued the fracture is flat and shiny in appearance, like the cleaved surface of quartz or diamond." Alvin sadly returned to the 1980's.

(b) The "crystallization" theory of fatigue should have died as soon as x-ray diffraction showed that common metals are already crystalline. But I ran into it as recently as two years ago in the testimony of an "expert" investigating an aircraft accident. The fractographic observations of the professor are true. Explain them in terms of the actual mechanisms of fracture and fatigue.

1989

[Problems 1,2 and 4 from this exam were lost. If you know of anyone who has a copy, ask them to contact me.]

Problem 3: (20 points)

(a) Suppose a one-component system has only three equilibrium phases: gas (g), liquid (l), and crystalline solid (s). At atmospheric pressure these phases are assumed in the sequence s → l → g as the temperature is raised at low pressure. Explain this behavior in terms of the expected relative energies and entropies of the three phases (assume the pressure is low enough that the pv term in the Gibbs free energy can be neglected), and provide a simple illustrative sketch of the variation of free energy with temperature.

(b) The liquid phase can be cooled some distance below its melting point, T_m, before crystallizing to (s). Explain this behavior in terms of the nucleation-and-growth mechanism of a structural phase transformation. Why is there a thermodynamic barrier to the formation of a nucleus?

(c) A liquid phase will ordinarily solidify into a crystalline solid if cooled slowly, but may form a glass if cooled very rapidly. Explain this observation in terms of the relative kinetics of crystallization and glass formation (begin by showing that the crystalline solid must nucleate, while the glassy phase need not, but you must also explain why the glassy phase does not always form, since its kinetics are more favorable).

(d) If a typical crystalline semiconductor is melted and then quenched into a glassy state its conductivity increases significantly (it may even become metallic). However, if a typical crystalline metal is melted and quenched into a glassy state, its conductivity decreases significantly. Interpret this phenomenon.

Problem 5: (15 points)

(a) Draw the engineering stress-strain curve of a typical ductile metal. Label the elastic region, the yield stress, the ultimate tensile strength, and the regions of stable and unstable plastic deformation. Explain (qualitatively or mathematically) why deformation becomes unstable at the ultimate tensile strength.

(b) Draw the engineering stress-strain curve of a brittle material. Explain why the ultimate tensile strength of a brittle material is not a well-defined property of the material.

(c) Describe four ways in which one can increase the yield strength of a typical ductile metal at ordinary temperatures. Why are these hardening mechanisms relatively ineffective at elevated temperature?

Problem 6: (15 points)

Wild Wally Wingwalker was on an island-hopping tour of the Pacific when he noticed a fatigue crack in the main spar (supporting member) of one of his wings. Since he did not want to interrupt his trip he jumped up and down on the wing several times to make sure that it would stay on and continued his trip. Shortly thereafter the wreckage of his plane was found on a desert atoll with the wing broken off at the position of the fracture. An accident investigation board examined the wreckage and quickly concluded that the accident was largely Wally's own fault.

(a) Why is their conclusion at least superficially reasonable? Why was Wild Wally's "safety inspection" particularly foolish?

Fortunately for Wild Wally's reputation, he had crashed on the particular atoll where Alvin Underfoot, a random undergraduate, was vacationing at the time. Employing the small scanning electron microscope and compact supercomputer he always carried with him, Alvin examined the fracture and made a few calculations. However dumb Wild Wally was, he immediately concluded, the fatigue fracture had nothing to do with the crash. Subsequent investigation showed that he was right. Wild Wally had been surreptitiously drugged by a jealous competitor.

(b) How did Alvin know?

(c) If the fatigue crack did not cause the accident, wasn't it a remarkable coincidence that the wing broke off at precisely the point of the crack?

1990

Problem 1: (20 points)

(a) Show how the ß-ZnS and NaCl crystal structures are derived from the FCC by filling selected interstitial sites in the FCC unit cell.

(b) Many compound semiconductors have the ß-ZnS structure, while the NaCl structure is common in ionic insulators. Explain in terms of the probable bond type.

(c) The plane of easiest cleavage for a material with the diamond cubic structure is usually {111}. Materials with the ß-ZnS structure cleave most easily along {111} or {110}. Materials with the NaCl structure cleave on {100}. Why might you expect this?

(d) Elements that crystallize in the ß-ZnS structure tend to have lower values of Poisson's ratio (ν), than those that crystallize in the NaCl structure. Why?

(e) The mineral calcium flourite has the stoichiometric formula CaF_2. The Ca atoms form an FCC array and each F atom has exactly four Ca neighbors. Suggest a possible crystal structure for CaF_2.

Problem 2: (15 points)

(a) Long-chain polymers and silica are relatively easily formed into glasses by cooling from the melt. Explain this in terms of their structure and bonding.

(b) Silica glasses are preferred to crystalline silica for windows and dinnerware because they are optically isotropic and are also relatively good thermal insulators. Relate these properties to their structure.

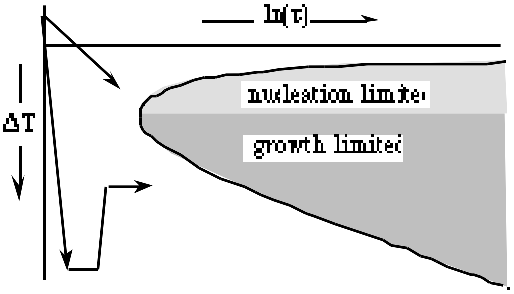
(c) It is very difficult to form a glass from a liquid of pure metal. Why? However, metallic glasses can be made by adding glass-forming solutes. What characteristics would you look for in selecting a solute to promote the formation of a metallic glass?

Problem 3: (20 points)

(a) Consider a binary system that contains two components, A and B. Component A has an FCC structure in its pure state while component B is BCC. The simplest possible binary phase diagram for the system is a eutectic diagram. Why? Sketch the phase diagram and label the phase fields.

(b) Given a temperature and composition (T,x) of the phase diagram in (a) it is possible to extract three pieces of information from the phase diagram: the phases present at (T,x), the compositions of the phases, and the fractions of the phases. Describe how.

(c) If a polygranular sample of the A-rich solution, α, is cooled into the two-phase, α+ß, region the kinetics of precipitation of ß are described by the kinetic diagram given below, where τ is the time required to initiate the transformation and ΔT is the undercooling below the temperature at which ß precipitation becomes thermodynamically possible.



If the material is cooled as indicated by the upper arrow, the final microstructure contains nuclei of ß almost exclusively in the grain boundaries of the α grains. Why might you expect this?

(d) If the material is cooled and then heated, as indicated by the lower path in the figure, the final microstructure consists of a dense distribution of ß precipitates in the interiors of the α grains. Why?

Problem 4: (15 points)

(a) Define the *Fermi energy,* E_F, of a material. Given its definition, show that a semiconductor behaves as an n-type extrinsic semiconductor if E_F is significantly greater than the energy at the midpoint of the band gap, and as a p-type extrinsic semiconductor if E_F is significantly below the mid-point of the band gap.

(b) Illustrate the behavior of the band structure at a junction between n-type and p-type semiconducting material and describe (briefly and qualitatively) how the band structure produces an asymmetry in the conduction characteristics of the junction.

(c) Some materials function as *photoconductors* in the sense that their normal conductivities are very low, but increase dramatically when they are illuminated with visible light. Explain how a semiconductor can behave as a photoconductor, and why a good photoconductor is opaque to visible light.

Problem 5: (15 points)

(a) In selecting an insulating material to isolate a conducting line you would ordinarily seek a material with a low dielectric constant and a high dielectric strength. Why?

(b) From the perspective of the properties listed in (a), many of the best insulators are non-polar polymeric solids. Why?

(c) The insulators selected for use in capacitors in microelectronic devices are often ferroelectric materials like $BaTiO_3$. What structural characteristic of a ferroelectric makes it attractive for this use?

Problem 6: (15 points)

(a) A good, ductile metal fails in tension when the applied tensile stress exceeds a critical value called the *ultimate tensile stress,* s_u, which is a reproducible material property. Describe the mechanism that produces the ultimate tensile stress. If you were assigned to improve the ultimate tensile stress, what material property would you attempt to change?

(b) Assume a small flaw in a ductile metal part that grows with time, for example, by fatigue. Describe and illustrate how the maximum tensile stress the part can withstand changes as the flaw grows. Suggest why it is often acceptable engineering practice to consider only the yield stress, s_y, and ultimate stress, s_u, when designing a part.

(c) Now consider a brittle material, such as a glass or structural ceramic. For these materials the "ultimate tensile stress" is also measured as the maximum engineering stress before fracture in a tensile test. Explain why the value of s_u ordinarily fluctuates widely and is a very iffy number to use for the design of mechanically reliable parts.

1993

Alvin Underfoot, a random undergraduate, was frustrated. He was furious. He had wasted his whole Thanksgiving vacation cramming for the upcoming E45 final, and he was getting nowhere. Angrily, he picked up the book that had most recently been the object of his attention, a tract called *The Principles of Material Science*, and threw it across the room. "This book is a sham! A hoax! A lie!" he exclaimed. "There are no principles of Materials Science. The whole subject is a collection of random facts. Every time I think I see a pattern in how materials behave, I end up finding more exceptions than examples. The prof who teaches this course is a sadist. There are hundreds of things he can ask about. I can't memorize all this random junk. I won't even be able to look it up in time on the final. I am cooked."

His comments were, of course, addressed to Maxwell, a demon of subatomic size with whom he often conversed. Maxwell had seen Alvin thrash like this before. He knew there was no simple way to calm him down. He could only wind him down by hearing him out. He fixed himself a long draught of the subatomic version of an adult beverage and sat back to listen.

Problem 1: (20 points)

"He may ask about crystal structure," bemoaned Alvin. "The way the crystal structures of even the simplest metals are chosen make no sense."

(a) "A number of elements, particularly including valence 1 metals like Na and K, have the BCC structure, but become close-packed at low temperature. From this I might conclude that close-packed structures are preferred at low temperature, while more open structures are preferred at high temperature" "You are at least partly right", responded Maxwell. "What you have described just reflects the natural balance between energy and entropy in determining the crystal structure." Explain.

(b) "But there are so many contradictions," continued Alvin. "Some metals, like Ba and Cr, are BCC even at the lowest temperatures, while others, like Cu, Au and Al, are always FCC." "Quite so," said Maxwell, "but there is no contradiction. Because of small differences in the details of metallic bonding, the relative energies of the BCC and FCC structures are different for different elements." How does this remove the contradiction?

(c) "I don't buy it," objected Alvin. "The example of Fe contradicts you. It is BCC at high temperature, FCC at intermediate T, and BCC again at low T. Gotcha!" "Got you," responded Maxwell. "Not only is the structural behavior of Fe relatively easy to reconcile with that of the other elements, but the reason for its anomalous behavior of was thoroughly discussed in E45 lecture. Since my memory is sub-atomic, it is undivided, so I easily retain all this information." Explain the behavior of Fe.

(d) But Alvin still wasn't convinced. "Even when we know the structure, we don't always know the structure. How does ß-brass fall into your scheme? At high temperature a 50-50 mixture of Cu and Zn has the BCC structure, while at low T the Zn atoms spontaneously order onto the sites in the center of the unit cell, so the structure becomes CsCl. There is no real reason to suspect a change in bonding with T, and the CsCl structure is essentially identical to BCC, so it is just as open. So why the change?" "Elementary, my dear Alvin," responded Maxwell. Explain.

Problem 2: (15 points)

In disgust, Alvin scattered a set of notes across the floor and uttered expletives that good taste prevents me from recording here. "The *#$@% may ask about the thermal properties of materials," he lamented. "The thermal properties of materials make no sense at all. They are contradictory. Look at this list of random facts."

(a) The valence electrons in a metal are energetic particles that wander throughout the metal at high velocity. Nonetheless, they contribute very little to the heat capacity of the metal.

(b) While they contribute very little to the heat capacity of a metal, the valence electrons are almost completely responsible for its thermal conductivity. The thermal conductivity increases with the electrical conductivity.

(c) But the highest room temperature thermal conductivity is found in diamond, which is an insulator with almost no electrical conductivity.

(d) When diamond transforms to the more stable form of carbon, graphite, its electrical conductivity rises dramatically, but its thermal conductivity decreases.

(e) But other good insulators, such as silica glass, have such low values of the thermal conductivity at room temperature that they are used as thermal insulators.

"Nonsense," responded Maxwell, "thermal properties make perfect sense to a subatomic being, like me, who has a good view of what the atoms and electrons are actually doing. If you will simply pay attention to the mechanisms of thermal behavior, which become so obvious when you study the material at the level I see it, these are not contradictions at all, but straightforward manifestations of the way the atoms and electrons respond to temperature." Explain.

Problem 3: (15 points)

"The chemical properties of materials are even worse," muttered Alvin. "He may ask about oxidation and corrosion. Physical obfuscation! I am not the least surprised that it took the whole human race two million years to invent stainless steel. Meditate on the following."

(a) "Gold doesn't oxidize or rust. I can cope with that. The oxides of gold are thermodynamically unstable at room temperature, so they wouldn't be expected to form spontaneously. But the other metals we use for their exceptional corrosion resistance are Al and Cr, which are among the strongest oxide formers known. Madness!"

(b) "Fe burns in air. I've seen it burn. When I machine a piece of steel the small filings that are thrown off burn immediately to form sparks. But the tools I use are also made of iron, and they don't burn. Why not?"

(c) "A solid piece of iron will not oxidize spontaneously even if I put it in pure oxygen at room temperature. But if I put it in water than contains a little bit of dissolved oxygen, it rusts right away. Water is relatively inert. So how does it cause oxygen to attack iron?"

(d) "If I put Au in tap water, nothing obvious happens. If I put Au in contact with Fe, nothing obvious happens. But if I put Au in contact with Fe and put the combination in tap water, the iron oxidizes fairly quickly. How can Au attack Fe in water?"

(e) "If I add Cr to Fe, and put the alloy in water, there is not a great effect on the corrosion rate until the Cr content exceeds about 8 atom percent. At that point, suddenly, the rate of corrosion drops to almost zero. Since the alloy is still almost entirely Fe, why doesn't it rust? And why the dramatic effect at about 8% Cr?"

"Corrosion is a little tougher for me," Maxwell responded. "Some of the most important things that are happening involve many atoms and reactions at sites that are very far from one another on the atomic scale. It it hard for me to see what is going on. But I do know something about the principles involved. Remember that thermodynamics govern what can happen, while kinetics govern what does happen, and how fast. When thermodynamics doesn't seem to lead you to the right answer, think kinetics, and the rates of the reactions that can go on." Using this hint, explain observations (a)-(e).

Problem 4: (15 points)

"I known damned well he's going to ask about electrical conductivity," moaned Alvin. "I know the basic kinds of conduction, and how they are determined by the band structure. But he asked about that on the midterm. What I can't get straight is how solutes affect conduction. There are so many contradictory effects. Madness!"

(a) "If I add just a little bit of N to Si, the conductivity of the Si goes up. Maybe this makes sense; since N has more valence electrons than Si, I am, perhaps, adding electrons. But if I push this theory, I only confuse myself. If I add B to Si the conductivity also goes up. B has fewer valence electrons than Si, so I seem to be subtracting electrons."

(b "So minor additions of N and B increase the conductivity of Si, right? Wrong. If I add a little B to Si that is doped with N, the conductivity goes down. If I add a little N to Si that is doped with B, the conductivity goes down."

(c) "But a minor addition of N or B alone does increases conductivity, right? Wrong. If I add N to Cu, the conductivity goes down. If I add B to Cu, the conductivity also goes down."

(d) "So N and B decrease the conductivity of Cu, right? Wrong. If I add a little B to Cu that contains a little N, the conductivity goes up."

"You are back at my level now," Maxwell enthused. "This one is easy." Explain.

Problem 5: (15 points)

"I think he's going to ask about optical properties," mused Alvin. "I just have a feeling. I know something about it. I understand why only electrical insulators are transparent to visible light. But there's so much more."

(a) "The common semiconductors are opaque to visible light. Not only that, they increase in conductivity when they are illuminated with visible light. But they are transparent to infrared radiation, which has a frequency just below the visible range."

(b) "Quartz is an insulator, and is transparent. Sand is often largely quartz. But if I make a thick plate by compacting quartz sand, the resulting material is an insulator, but it is opaque."

(c) "If I melt the sand and cast the liquid into a thick plate, it is an insulator, and it is transparent. If I cast the plate by cooling the melted sand very slowly, the images I see through it are distorted. If I cool it relatively quickly, the images I see through it are undistorted."

(d) "Water is transparent. Air is transparent. If I'm standing outside a body of water, it is relatively easy to see in, but if I am immersed in the water I can only see out if I am looking almost vertically upward."

Problem 6: (20 points)

(a) "He may ask about the mechanical properties of steel. But "steel" doesn't really have a particular set of mechanical properties. Even if the alloy is a simple, carbon steel (Fe-C) its yield strength can vary by almost a factor of ten, depending on how fast it is cooled. He may ask me to explain that." [He just did.]

(b) "The ultimate tensile strength is almost as confusing. I read somewhere that if you do a simple tensile test, using specimens of the same alloy, but with different heat treatments that cause them to have different strengths, the maximum strength of the specimen will be a function of its yield strength. For very high strength materials, the tensile strength actually decreases as the yield strength increases. "

(c) "To further the confusion, it seems to make a great deal of difference how the load is applied. A piece of ductile steel that has an ultimate tensile strength that is almost twice its yield strength will break if it is subjected to a cyclically repeated load that is actually less than its yield strength. Under this cyclic load the specimen does not deform significantly; it just breaks, usually with very little warning."

(d) "The same material may be used for purposes that appear totally incompatible with one another. Graphite, for example, is so weak that it is used as an easily deformable lubricant that minimizes friction between sliding surfaces, and is, at the same time, so strong that it is used as the strengthening fiber in some of the strongest composite materials known."

"I can't help you much with mechanical properties," said Maxwell. "Atoms don't bend and atoms don't break, so all the important things are happening on a scale much bigger than I am. But it's the last question on this exam. If you've gotten this far with time left you've probably already passed the course. Relax, and think microstructure, which does, after all, determine the properties of materials."

1994

Problem 1: (20 points)

Two common crystal structures of binary solids that have strong ionic bonding are the NaCl and CsCl structures.

(a) Describe the NaCl and CsCl structures.

(b) The CsCl structure is often adopted by binary compounds whose species differ significantly in ionic size. An example is AgBr (which is a common active compound in photographic film). In Pauling's picture the Ag^+ ion is very much smaller than Br^-, and the Br^- ions essentially touch one another in the CsCl lattice. This touching closes some of the octahedral voids in the BCC structure on which the CsCl structure is based. Show the positions of the octahedral voids in BCC, and indicate which remain open in a CsCl structure in which the Cl atoms touch.

(c) There are two kinds of intrinsic point defects in an ionic crystal: a vacancy of one specie accompanied by a vacancy of the other (Schottky defect) and a vacancy together with an interstitial of the same specie (Frenkel defect). Why are these the common intrinsic defects in ionic crystals?

(d) In AgBr, which has the CsCl structure, the mobile species is Ag^+, which diffuses via the motion of Ag^+ interstitials (Frenkel mechanism). To show that this is intuitively plausible, use the results of part (b) to show that a Ag^+ ion passes through an open octahedral void when it moves from one Ag^+ site in the CsCl lattice to the immediately adjacent site.

(e) In NaCl the mobile specie is Na^+, and the open interstitial sites are the tetrahedral sites of the FCC reference lattice. Na^+ diffuses by exchange with Na^+ vacancies (Schottky mechanism). To show that this is intuitively plausible, show that a Na^+ ion does not pass through an open interstitial site if it follows the most direct path of exchange with a vacancy on an adjacent Na^+ site.

Problem 2: (15 points)

(a) Distinguish between an intrinsic and an extrinsic semiconductor.

(b) Why is it that all semiconductors are extrinsic at sufficiently low temperature and intrinsic at sufficiently high temperature?

(c) Draw a band diagram that illustrates a simple p-n junction in a semiconductor. Indicate a plausible position for the Fermi level.

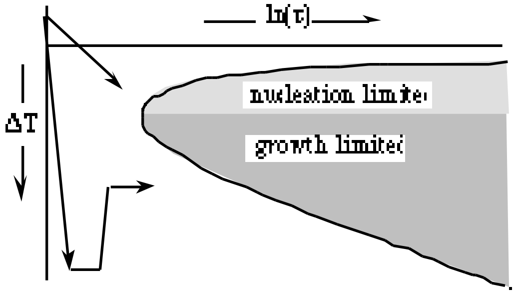
(d) Explain, qualitatively, why the current that is developed when a voltage difference is imposed across the junction depends on the direction of the voltage drop.

Problem 3: (20 points)

(a) Consider a binary system that contains two components, A and B. Component A has an FCC structure in its pure state while component B is BCC. The simplest possible binary phase diagram for the system is a eutectic diagram. Why? Sketch the phase diagram and label the phase fields.

(b) Given a temperature and composition (T,x) of the phase diagram in (a) it is possible to extract three pieces of information from the phase diagram: the phases present at (T,x), the compositions of the phases, and the fractions of the phases. Describe how.

(c) If a polygranular sample of the A-rich solution, α, is cooled into the two-phase, α+ß, region the kinetics of precipitation of ß are described by the kinetic diagram given below, where τ is the time required to initiate the transformation and ΔT is the undercooling below the temperature at which ß precipitation becomes thermodynamically possible.



If the material is cooled as indicated by the upper arrow, the final microstructure contains nuclei of ß almost exclusively in the grain boundaries of the α grains. Why might you expect this?

(d) If the material is cooled and then heated, as indicated by the lower path in the figure, the final microstructure consists of a dense distribution of ß precipitates in the interiors of the α grains. Why?

Problem 4: (15 points)

[The following is paraphrased from my recollection of the famous balcony scene from the movie, *Superman*, in which Lois Lane first encounters our hero. A portion of the dialogue runs roughly as follows:]

Lois Lane:	Is it true that you have x-ray vision, you can see through things?
Superman:	Yes, I can.
Lois Lane (blushing):	What color is my underwear?
Superman (blushing):	Pink.

(a) Alvin Underfoot, a random undergraduate, believes this exchange establishes that Superman is no gentleman; that he is, in fact, a Peeping Tom who should be indicted for sexual perversion. "It is obvious," he asserts, "that Superman has been using his flying abilities to spy on poor Lois while she is getting dressed." What evidence supports his position?

(b) Priscilla Pureheart defends the Man of Steel. "You underestimate Superman," she replies. "His eyes are capable of emitting and detecting radiation with incredible precision, and his brain contains a comprehensive catalogue of the properties of all known materials. He can "see" pink by analyzing the fabric of Lois' undergarments for colorants that make it pink." Does her argument make sense? Assuming that the color of the fabric is imparted by tiny, insulating crystals that adhere to the fibers of the fabric, what, qualitatively, would Superman be looking for? What is the nature of a colorant that would make an insulating crystal pink?

(c) "Nonsense," says Alvin. "If you were right Superman could see through lead, and he admits he can't." "But lead absorbs x-rays," Priscilla objects. "If his eyes are as good as you say," responds Alvin, "he would just raise the frequency until even lead became transparent." Is Alvin right?

(d) "You are fuzzy on the concept," responds PP. "If he did what you say he might be able to *look*, but he couldn't *see* ." Is she right?

Problem 5: (15 points)

(a) Draw the engineering stress-strain curve of a typical ductile metal. Label the elastic region, the yield stress, the ultimate tensile strength, and the regions of stable and unstable plastic deformation. Explain (qualitatively or mathematically] why deformation becomes unstable at the ultimate tensile strength.

(b) Draw the engineering stress-strain curve of a brittle material. Explain why the ultimate tensile strength of a brittle material is not a well-defined property of the material.

(c) Describe four ways in which one can increase the yield strength of a typical ductile metal at ordinary temperatures. Why are these hardening mechanisms relatively ineffective at elevated temperature?

Problem 6: (15 points)

Alvin Underfoot, a random undergraduate, supported himself, in part, from the modest profits of a small consulting business in which he applied what he had learned in E45 to solve the problems of the world. Since virtually no one had ever heard of him, his list of potential clients was not large. On the other hand, he was admirably qualified to offer complete confidentiality to those who made use of his services. For precisely this reason, Alvin's services were retained by a famous and accomplished superheroine with an unfortunate personal problem. She is, she tearfully confessed, an incurable exhibitionist. Even when flying on her many missions of mercy, she cannot bear to conceal herself from her admiring public, but insists on piloting transparent glass aircraft. These have an unfortunate proclivity to disintegrate in mid-air, a circumstance that has made her into an unusually proficient parachutist, but at considerable cost in bruises and broken bones. Since she is not, by training, a material girl, she needs a dedicated materialist to help her make her aircraft more reliable.

Her immediate problem concerned her available aircraft, made of the finest high-temperature glass, which were needed for immediate missions. How might they be made more resistant to fracture? In response, Alvin first explained why glass is brittle and, after thinking for some time, suggested that her planes might be improved by washing their surfaces with a certain acid that would chemically attack sharp surface cracks and blunt them into furrows. While she was doing that, he would consider more long-term solutions.

(a) Qualitatively, why is silica glass brittle, and why might Alvin's suggestion be of some help?

Alvin's client was pleased with his initial work, which increased the average lifetime of her aircraft from one flight to almost three, and returned for his suggestions for long-term solutions.

Alvin's first effort was to replace silica glass with a tough, transparent polymeric plastic. The resulting aircraft worked fine until his client accelerated to supersonic speeds, as was her practice, at which point aerodynamic heating caused the wings to droop like Dali's clocks, and caused our superheroine to practice skydiving.

(b) What difference in the basic mechanism of deformation makes it possible for transparent plastic (polymeric) to be tougher than transparent silica glass? Why might a tough plastic soften at high temperature?

Alvin's second effort was to build the aircraft of a fiber-reinforced plastic, in which fibers of transparent glass were used to strengthen a matrix of tough plastic. With some effort, he achieved a composite with very respectable mechanical properties at moderately high temperature. Unfortunately, the stuff was opaque.

(c) Why would a mixture of transparent materials be opaque?

Alvin's third effort was to return to a high-temperature glass, but to heat-treat it during forming so that the region near its surface had a high residual compressive stress. The resulting glass exhibited a high resistance to fracture, but, unfortunately, its fracture resistance disappeared when it was exposed to high temperature.

(d) Why would a compressive stress near the surface increase toughness? Why would the toughness disappear when the material was annealed at high temperature?

With this failure, Alvin conceded defeat. In desperation, he suggested that she steal an idea from Alaska Airlines, build her aircraft of aluminum, and paint a picture of herself on the outside. Our superheroine was last seen parachuting into the Caribbean, surrounded by fragments of glass.

1995

Problem 1: (20 points)

A material has the composition A_3B, and, at room temperature, has the Cu_3Au crystal structure. Provide brief explanations for the following observations.

(a) The material is a metallic conductor (show that it cannot be ionic or covalent in its bonding).

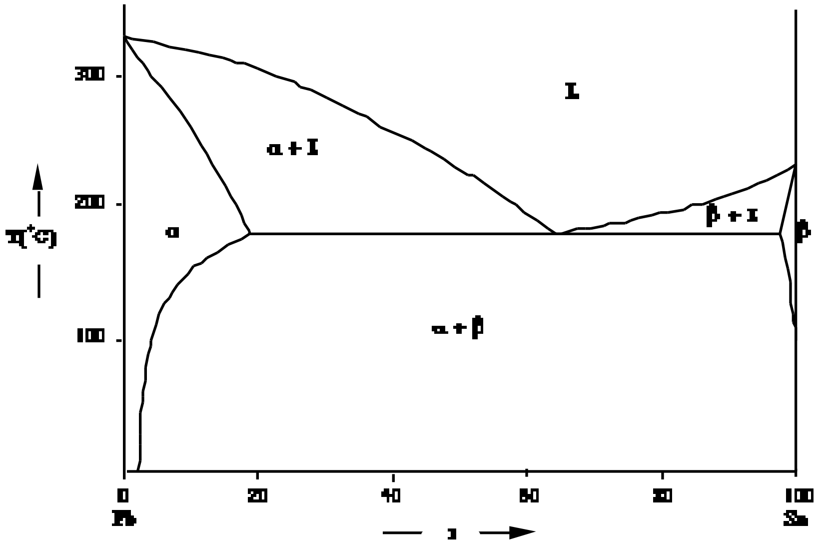
(b) Both its electrical and thermal conductivities decrease as temperature rises.

(c) The material is opaque to visible light. However, it is transparent to x-rays, unless the x-rays have energies very close to one of a few discrete values.

(d) At high temperature the structure becomes disordered; the material transforms into a random solid solution of A and B atoms on an FCC lattice.

(e) When the material disorders, its electrical resistance increases, its elastic modulus decreases, and its yield strength decreases.

Problem 2: (20 points)



The phase diagram of the Pb-Sn binary system is shown above.

(a) As reflected in the phase diagram, Pb and Sn can form solutions at all compositions in the liquid state, but not in the solid state. Why?

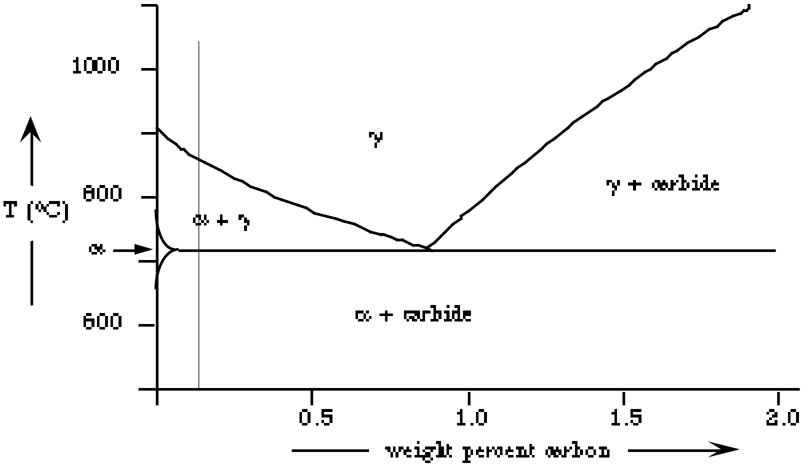
(b) The solubility of Sn in the Pb-rich α phase increases with temperature (at least a low temperature). Why would you expect this?

(c) Suppose you are given a sample that has composition 20Sn-80Pb, but need a sample that has precisely the eutectic composition. How could you obtain it?

(d) If material of precisely eutectic composition is solidified, it forms the classic eutectic microstructure. Describe this microstructure and explain, briefly, why it forms.

(e) Suppose you have a sample of Pb-Sn that has the eutectic composition, and need it to have a microstructure that has equiaxed grains of the α and ß phases. How might you obtain it?

Problem 3: (15 points)



A portion of the Fe-C phase diagram is shown above. Suppose you are given a sample with about 0.2 wt.% carbon (the composition of the vertical line drawn in the figure).

(a) If the alloy is homogenized in the γ (FCC) stability field, and cooled slowly to room temperature, the resulting alloy has relatively low strength, but reasonable ductility. Interpret this result in terms of the microstructure you expect.

(b) If the alloy is quenched rapidly to room temperature after homogenization in the γ field, the resulting alloy is a single-phase material with a body-centered tetragonal (BCT) structure. It is very hard, but is also relatively brittle, fracturing in a transgranular cleavage mode. Explain these observations in terms of the probable mechanism of phase transformation and the resulting microstructure.

(c) If the alloy in (b) is "tempered", that is, if it is reheated to an intermediate temperature (350-500°C) and held for some period of time, the structure of the matrix phase changes to BCC. The alloy strength initially decreases with tempering time, but then increases, eventually reaching a value close to that of the untempered material. The advantage of the tempered steel is that its fracture toughness at room temperature is much greater than that of the untempered material, even when it has similar strength. Explain these observations in terms of the probable change in microstructure during tempering.

Problem 4: (15 points)

Explain the following observations concerning oxidation and corrosion:

(a) If a sheet of iron is heated to a sufficiently high temperature to induce oxidation, the oxidation kinetics are initially parabolic (weight loss proportional to $\sqrt{t}$), but eventually become linear (weight loss proportional to t).

(b) If a sheet of iron is allowed to corrode in wet soil, the corrosion is most intense at crevices on the sheet surface.

(c) A sheet of iron can be protected from corrosion by plating it with Cu or Au. However, if the sheet is to be formed or handled roughly in service, it is better to protect it with a coating of zinc.

Problem 5: (15 points)

(a) If two extrinsic semiconductors are joined together, the electron energy levels on the two sides of the interface adjust so that the Fermi energy, E_F, is the same on both sides. Give a brief, qualitative explanation for why and how this happens.

(b) Sketch the band structure near an n-p junction.

(c) Explain, qualitatively, why an n-p junction has an asymmetric response to an imposed voltage: current flows relatively easily if the voltage imposes a forward bias, but saturates at a small value if the voltage imposes a reverse bias.

Problem 6: (15 points)

When I first came to Berkeley there was a major problem with bicycle theft on the campus (there probably still is, but I don't hear as much about it). The bicycle locks that were readily available at that time were the product of a more innocent age, and were made of reasonably tough steel. Motivated bicycle thieves discovered that they could be easily and quickly cut with long-handled bolt cutters (tools that resemble snub-nosed scissors, with long handles for leverage).

(a) In designing a bolt cutter for efficient bicycle theft, it is important that the blades of the scissors be made to be much harder than the chains or lock-bolts that are to be cut. Why?

An obvious defense against the bolt cutter was the use of chains and lock bolts that were themselves hardened to very high strength. However, this proved a temporary solution. Sophisticated thieves quickly learned that hardened chains and lock-bolts can be broken with a hammer, particularly if they are first swathed with a bit of the liquid nitrogen that is widely available on campus.

(b) Why does hardening risk fracture? Why would liquid nitrogen help?

The current solution is metallurgically more sophisticated, and involves the use of "case-hardened" chains and bolts. These are made of relatively soft steel, but have a surface layer (the "case") that is hardened to very high strength to protect the softer steel "core".

(c) Discuss how a "case-hardened" chain can provide an effective defense against both hammers and bolt-cutters, and suggest how you might make such a material.

1997

Problem 1: (15 points)

(a) Describe how the Cu_3Au, diamond cubic (DC), ß-ZnS and NaCl structures are derived from FCC.

(b) Of the structures above, only the ß-ZnS and NaCl can be ionic. Why?

(c) Suggest a plausible reason why some ionic compounds (e.g., silver halides) prefer the ß-ZnS structure over the NaCl structure.

(d) Of the structures above, only the DC and ß-ZnS are taken by covalent compounds. Why?

(e) Of the structures above, only the Cu_3Au commonly undergoes a disordering reaction on heating. Why would you expect and order-disorder transformation in Cu_3Au? Why not in NaCl or ß-ZnS?

Problem 2: (20 points)

To turn a piece of single crystal silicon into a functional semiconducting device, such as an n-p-n bipolar transistor, it is necessary to achieve a high-purity silicon starting material, add chemically appropriate dopants in the proper places, and keep them there.

(a) The silicon crystal that is the starting material for an n-p-n junction that is to be used at room temperature has a band gap of moderate size (1.1 eV), and can be made so that it is chemically very pure. Why are these properties important?

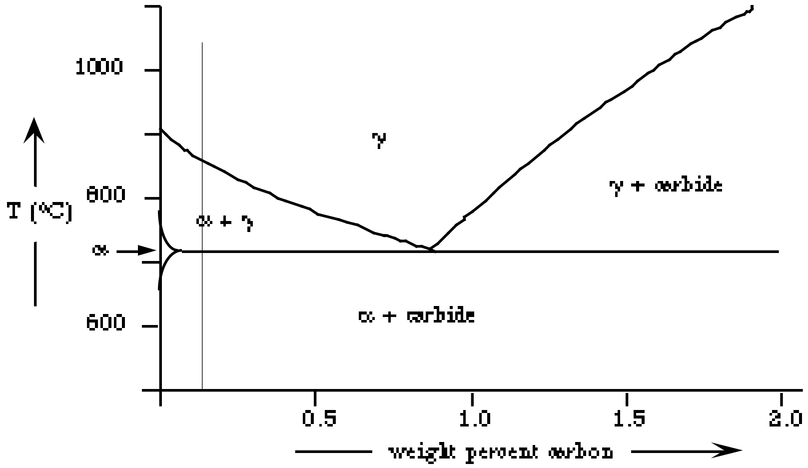
(b) Suppose that the Si starting material has an unacceptably high level of impurities. A much purer Si can usually be made by re-melting the starting material and re-solidifying it under controlled conditions. Why and how does this method work?

(c) To make an n-p-n junction device, one must use at least two different solutes, one that acts as a donor and one as an acceptor. B and P are common choices. Which is the donor and which the acceptor? Both are substitutional solutes. Why is this important?

(d) Since boron is difficult to extract from Si, Si crystals often contain a moderate boron content as-received. Assuming this makes them p-type, how can P be used to change the dominant carrier type in the regions that are to be n-type?

(e) Give a rough schematic drawing of the band structure of an n-p-n device, indicating the position of the Fermi level in each of the three regions when no external voltage is imposed. Explain why the band structure has the shape you have drawn.

Problem 3: (15 points)



Alvin Underfoot, a random undergraduate, is fascinated with the wonders of carbon steel, and the grand variety of microstructures and properties that can be achieved from a binary system whose phase diagram is, after all, fairly simple on the low-carbon side.

"The real secret to the wonders of steel," he declaimed, "follows from the fact that there are two very different ways to accomplish the phase transformation. If you take a low-carbon alloy that has the composition shown in the figure, and homogenize it in the γ-phase field, then you can make two totally different materials, depending on how you cool it back to room temperature. Slow cooling produces a mixture of relatively soft α-iron (ferrite) and an α-Fe$_3$C (carbide) eutectic. Since both the α phase and the eutectic are relatively soft, this steel is formable into complex shapes. Quenching the same alloy produces a very hard, martensitic structure that is useful for things like knives and hammer heads."

(a) Draw a simple schematic diagram that illustrates the kinetics of the transformations that lead to these two different structures. Explain why it is necessary to quench the alloy to produce the martensitic transformation, and why the martensitic microstructure is single-phase.

"But this is only the beginning." he exclaimed, "Suppose I anneal the alloy at a temperature in the upper part of the two-phase, α+γ field until it comes to equilibrium, and then quench it rapidly to room temperature. The result is a nearly 50-50 mixture of soft, low-carbon ferrite and hard, fresh, high-carbon martensite. The product is called 'dual-phase' steel, and has exceptional formability."

(b) Indicate the appropriate annealing temperature on the phase diagram, and describe the sequence of phase transformations that leads to the final microstructure.

"And even this does not begin to exhaust the possibilities," continued Alvin. "Suppose we anneal the same alloy at a relatively low temperature that is just inside the å+© field. Since the start temperature for the martensitic transformation decreases rapidly with carbon content, quenching this steel after annealing produces a microstructure that is mostly ferrite, with a relatively high carbon content, but with islands of retained © phase. The high carbon content of the å makes it relatively strong, and the retained © gives it a low ductile-brittle transition temperature, so it is a good steel for low-temperature uses."

(c) Indicate an appropriate annealing temperature on the phase diagram, and describe the sequence of phase transformations that leads to the final microstructure.

"And this does not begin to exhaust the possibilities," continued Alvin...

Problem 4: (20 points)

Visible light spans a range of wavelength between 0.4-0.7 µm, corresponding to a photon energy between « 2eV and « 4 eV.

(a) An old practical test says that if you can see through a piece of material, it is almost certainly a good insulator. Why?

(b) Why the modifier "almost"? How can a transparent material fail to be a good insulator? [Hint: you can see through NaCl if you squint, but it is not a very good insulator.]

(c) On the other hand, there are many good insulators that you cannot see through, including both opaque ceramics and brightly colored plastics. Describe at least one possible microstructure that creates an opaque insulator.

(d) Alvin Underfoot, a random undergraduate of great academic promise, accepted a summer job with Watergate Technologies. On arrival he was, naturally, assigned to the mail room. While inspecting incoming materials, he came across a package labeled "optical fibers". The fibers were metallic gray in color and totally opaque. Alvin sent them back as rejects. Shortly afterward, he was called in by his boss's boss, Priscilla Pureheart, PhD. Instead of commending him, she fired him. "Alvin," she said, "you are an imbecile. Instead of firing you, we should shoot you. The fibers you returned were super-high-tech fibers for use with our hot new semiconductor lasers, and were desperately needed. They are exceptionally clear and transparent." Alvin left, shaking his head in bewilderment. What was his mistake?

Problem 5: (15 points)

(a) Materials that have exceptionally high values of the shear modulus, G, are invariably hard at ordinary temperatures. Why?

(b) Materials that are not exceptionally hard can be strengthened for low-temperature service by adding solutes, particularly interstitial solutes. Why?

(c) The strength of many structural steels is controlled by adjusting the grain size. For high strength, should the grain size be large or small? Why?

Problem 6: (15 points)

(a) Materials that have exceptionally high values of the shear modulus, G, are invariably brittle at ordinary temperatures. Why?

(b) Materials that are tough at ambient temperature may behave in a brittle manner when used at temperatures only slightly below room temperature. Why?

(c) During the nineteenth century, high quality steel was difficult to procure or verify, and failures of steel railroad bridges were unfortunately common. In his brilliant design of the "Eads bridge" over the Mississippi river at St. Louis (completed in 1874 and still in use) James Eads addressed the problem in a particularly clever way. Wherever thick structural beams were to be subjected to heavy loads, he replaced them with bundles of thin plates, bound together to form laminates. These laminated beams proved to be reliable and very resistant to fracture. From the point of view of toughness, they have at least three advantages over monolithic beams. Identify and discuss at least one of these.

1998

Problem 1: (15 points)

A compound has the composition AB, and, at room temperature, has the NaCl crystal structure. Provide brief explanations for the following.

(a) The material may be ionic or metallic.

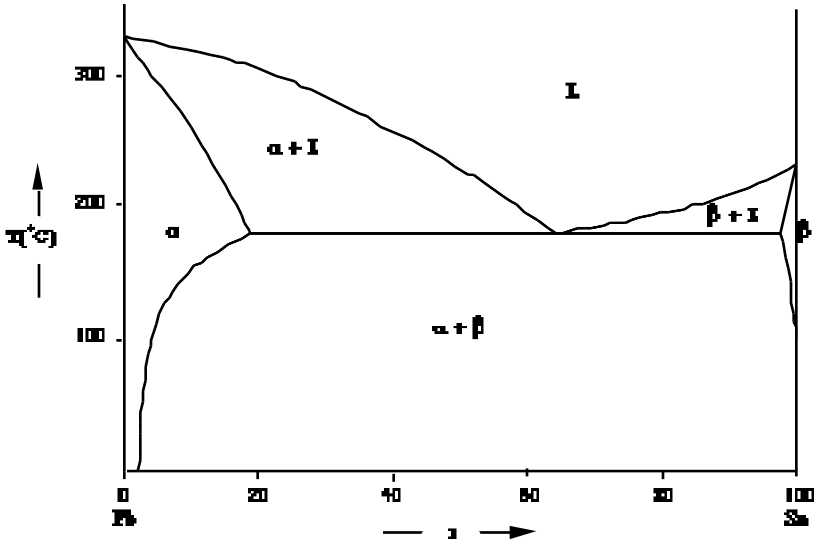
(b) If the material is transparent, it is ionic.

(c) On increasing the temperature, T, the conductivity increases if the material is ionic, but decreases if it is metallic.

(d) If the compound is metallic its conductivity decreases when a small amount of solute is added, whatever the nature of the solute.

(e) If the compound is an ionic conductor its conductivity may increase or decrease when a small amount of solute is added. Construct a plausible example in which the addition of a small quantity of a particular solute decreases the conductivity.

Problem 2: (20 points)



The phase diagram of the Pb-Sn binary system is shown above.

(a) Given an arbitrary point, (T,x), in this phase diagram, you can determine the phases present, their compositions, and their fractions. Explain how.

(b) Suppose you are given material that has composition 30Sn-70Pb, but need material that has composition 95Pb-5Sn. How could you obtain it?

(c) Let material with precisely the eutectic composition be solidified. At intermediate magnification its microstructure appears to be of the classic eutectic type, made up of grain-like "colonies" that contain alternate lamellae of the å and ∫ phases. On closer examination it is found that the å lamellae have dense distributions of fine, ∫-phase precipitates within them. Explain the microstructure.

(d) If the material of part (c) is heated to just below the eutectic temperature and held there for a long time, the microstructure evolves into a mixture of å and ∫ phases in coarse, equiaxed grains. Why?

Problem 3: (15 points)

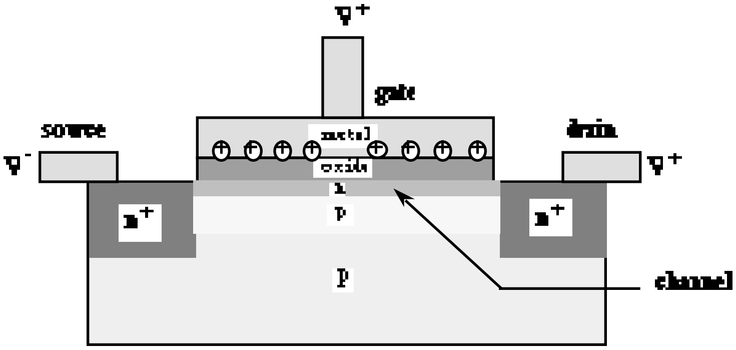
Explain the following observations concerning oxidation and corrosion:

(a) While very fine particles of iron can burn spontaneously in air (for example, the sparks thrown off during the machining of steel), a bulk sample of iron oxidizes at a negligible rate unless the temperature is very high.

(b) If the same bulk sample of iron is immersed in damp soil, it oxidizes (rusts) fairly quickly.

(c) If a bulk sample of iron is immersed in damp soil very near a piece of zinc, the iron corrodes just as it would if the zinc were not there. But if the iron is connected to the zinc by a thin metal wire, the iron immediately stops corroding, and is protected from further corrosion until the zinc has corroded away.

Problem 4: (15 points)



This figure shows a typical configuration of a metal-oxide-semiconductor field effect transistor (MOSFET). The drawing shows a positive voltage at the metal gate, which activates the inversion layer, or channel, in the underlying semiconductor.

(a) Using simple band diagrams, describe how a MOSFET works. In particular, explain why the current that flows between source and drain is negligible when the gate voltage is zero, but is significant when the gate voltage is large and positive.

(b) In the example shown the p-type semiconductor between source and drain is labeled p^- to indicate a very low concentration of acceptors. Why is this important?

(c) Suppose the semiconductor were a photoconductor, and the gate were replaced by a light source. Describe the behavior of the current from source to drain as the light is turned on and increased in intensity. What assumption must you make about the wavelength of the light?

Problem 5: (20 points)

(a) An isotropic, linear elastic material has two independent elastic constants. These are normally chosen from the set E (Young's modulus), ˆ (Poisson's ratio), ∫ (the bulk modulus), G (the shear modulus). Define each and describe how it could be measured.

(b) For a typical metal Poisson's ratio is about 0.3. Let a bar of the metal with a square cross-section (solely for simplicity in calculation) be loaded in tension along its axis. Show that the deformation of the bar is, in part, a hydrostatic tension.

(c) The yield strength of a ductile material tends to scale with its shear modulus, G. Why would you expect this?

(d) The shear modulus of Fe is about 3 times that of Al, and it is found that steels have about 3 times the yield strength of aluminum alloys with similar microstructures. Nonetheless, it is possible to make Al alloys that have yield strengths higher than those of many steels. Why might you expect this?

Problem 6: (15 points)

Given the phenomenal financial success of the recent movie, the tragedy of the *Titanic* has once again become a fashionable topic of conversation. I am always troubled when this happens since I am one of the very few living persons who know what really transpired, and I am sworn to secrecy. But nobody reads E45 exams anyway, so it shouldn't matter if I give a hint or two here.

The sinking of the *Titanic* was, in fact, one of the great crimes of the century, a vicious mass murder perpetrated by one Maples Pavilion, a scientist of enormous, though sadly perverted talent. The evil Pavilion coveted the fortune in jewels carried by the wealthy passengers on the *Titanic's* maiden voyage. While stealing the jewelry was child's play for a genius of Pavilion's caliber, it was not enough. To fence the loot for maximum profit, no one must know it was stolen. The jewels were to be filched and replaced with fakes, which would be sent to the bottom of the sea along with their owners and anyone else who happened to be on board at the time. The sinking would, of course, be "accidental" and, given the time of year, would naturally be blamed on poor seamanship leading to collision with an iceberg.

Pavilion was, of course, blessed with insights into mechanical metallurgy that were decades ahead of his time. An examination of samples of the steel plate intended for the ship's hull revealed that it was thick plate made to a strength unusually high for the time, with a coarse-grained microstructure. As a consequence, Pavilion was certain that the steel would fracture in a brittle manner in the cold waters of the North Atlantic.

(a) Each of the three factors, thick plate, high strength, and coarse grain size contributes to a high value of the ductile-brittle transition temperature. Why?

To verify this hypothesis, Pavilion invented fracture toughness testing, measured the fracture toughness (K_{Ic}) of the plate, and showed that it had a low value. He also measured the fatigue crack growth rate in the plate [dc/dn] as a function of the cyclic stress intensity (ÎK).

(b) Sketch the expected variation of dc/dn with ÎK . Explain why the crack growth rate [dc/dn] increases with crack length for a given cycle (Îß) of the applied stress.

There followed in rapid succession the invention of an appropriate supercomputer, the development of suitable stress analysis codes and the construction of viable oceanographic models, all leading to the calculation of projected hull stresses as a function of time. Given hull stresses, fracture toughness and crack growth rates, Pavilion computed a set of crack lengths and locations that would virtually guarantee that, with no prior warning, the Titanic hull would unzip like [politically sensitive simile deleted] at about the time the ship neared Newfoundland, and send it straight down before the first lifeboat could be launched.

(c) Given precise values of hull stress (as a function of time), fatigue crack growth rates, fracture toughness, and the mutual interaction of the cracks as they go unstable in a predictable sequence, describe how Pavilion could decide where and how big he should inscribe his hull cracks to ensure that the ship would crack like an egg after a given time at sea.

To complete the crime, Pavilion and his accomplices booked passage under assumed names. On the first night out they purloined the jewels, planted the fakes, inscribed the cracks, and escaped the ship by helicopter (another useful invention they brought on board disguised as a ceiling fan).

Still, the best-laid plans of mice and men oft go awry, and Pavilion spent anxious days at his satellite-linked video monitor watching the ship's progress, terrified that an unusually calm sea would permit the ship to reach harbor intact, or the crew would stumble onto his well-concealed hull cracks, or some lucky soul would survive the looming tragedy to tell what really happened.

But as many of you have already learned, life is not fair. Those who are truly evil are protected by a curious converse of Murphy's Law; for them, anything that can go wrong won't. And virtue was never at home in Maples Pavilion. He was, therefore, only mildly surprised when the captain of the *Titanic* actually did steer the ship smack into an iceberg. To be fair, it wasn't all that much of a smack. The survivors were shocked that a collision they described as a "slight shudder" could produce a fatal rip along the side of the hull. But by this time the poor *Titanic* didn't need much of a smack. Pavilion's cracks had grown almost to the point of instability under normal operating loads.

(d) Describe how and why the load required to propagate a crack to failure decreases with the length of the crack.

Maples Pavilion invested his ill-gotten gains and lived happily ever after. He was last sighted at a prestigious Junior University, where he had endowed a chair (in fact, quite a number of chairs) and enjoyed the congenial company of kindred souls.

1999

Problem 1: (20 points)

A particular material is a 50:50 mixture of Cu and Zn, and, at room temperature, has the CsCl structure. Provide brief explanations for the following:

(a) While the crystal structure permits ionic bonding, and many CsCl materials are ionic, CuZn is metallic.

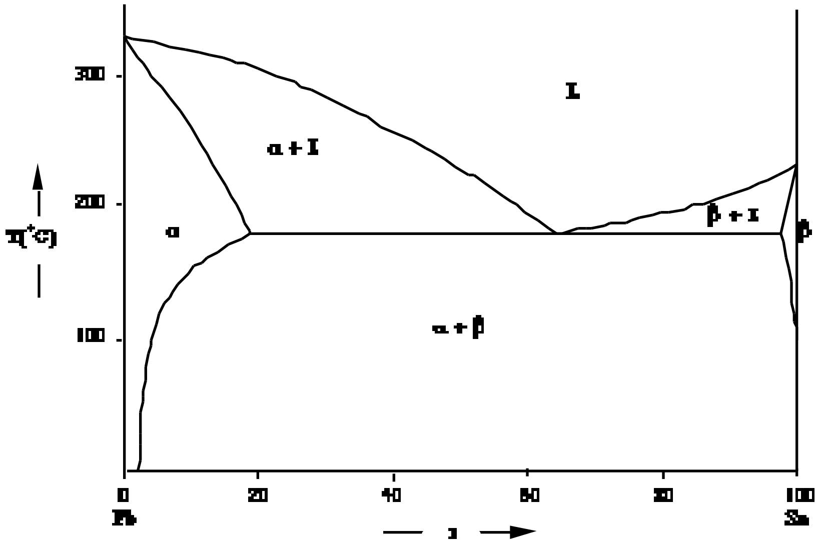
(b) Both its electrical and thermal conductivities decrease as temperature rises.

(c) The material is opaque to visible light. However, it is transparent to x-rays, unless the x-rays have energies very close to one of a few discrete values.

(d) At high temperature the structure becomes disordered; the material transforms into a random solid solution of A and B atoms on a BCC lattice.

(e) When the material disorders, its electrical resistance increases and its elastic modulus decreases.

Problem 2: (20 points)



The phase diagram of the Pb-Sn binary system is shown above.

(a) A eutectic phase diagram (at least qualitatively like the one shown above) is the simplest diagram the Pb-Sn binary system could possibly have. Why?

(b) If a material of precisely eutectic composition (62Sn-38Pb) is solidified, it forms the classic eutectic microstructure. Describe this microstructure and explain, briefly, why it forms.

(c) If a material of nominal composition 95Pb-5Sn is solidified, it tends to form a polygranular solid with a matrix of Pb grains that contain Sn-rich precipitates. Explain this microstructure, assuming the system stays reasonably close to equilibrium during cooling.

(d) Solders, that is, low-melting metals that join higher-melting components by melting and solidifying to form a joint between them, are widely used in microelectronic devices. Pb-Sn alloys are commonly used. In a simple device, a semiconductor chip is bonded to a chip carrier by soldering their respective metal contacts together, and a number of chip carriers are then soldered onto a circuit board. It is common to use a high-Pb solder, such as 95Pb-5Sn for the chip-to-carrier contact, and a eutectic solder for the carrier-to-board contact. From the perspective of manufacturing, what is the obvious advantage of this choice?

Problem 3: (15 points)

Explain the following observations concerning oxidation and corrosion:

(a) A sheet of iron exposed to dry air at room temperature does not oxidize to any appreciable degree. However, a sheet of iron heated red hot in dry air oxidizes fairly quickly. The oxide forms as a scale that flakes off of the surface.

(b) A small particle of iron that is freshly formed at room temperature and exposed to dry air (as, for example, in a grinding or machining operation) may actually burn, creating a spark.

(c) A small particle of gold that is freshly formed and exposed to dry air will not burn, even if its temperature is relatively high.

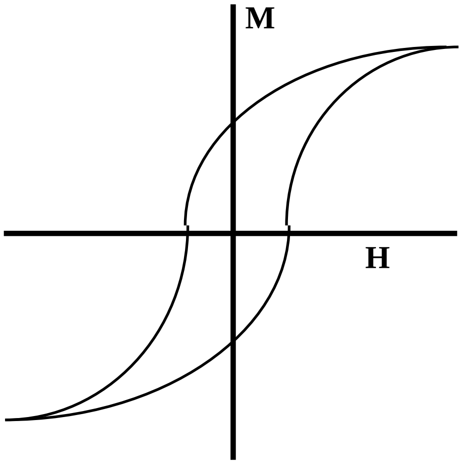
Problem 4: (15 points)

(a) If two extrinsic semiconductors are joined together, the electron energy levels on the two sides of the interface adjust so that the Fermi energy, E_F, is the same on both sides. Give a brief, qualitative explanation for why and how this happens.

(b) Sketch the band structure near an n-p junction.

(c) Explain, qualitatively, why an n-p junction has an asymmetric response to an imposed voltage: current flows relatively easily if the voltage imposes a forward bias, but saturates at a small value if the voltage imposes a reverse bias.

Problem 5: (15 points)



Simple ferromagnetic materials, like Fe, Ni and Co, are ferromagnetic at low temperature essentially because their atoms have net magnetic moments that align with one another.

(a) If a ferromagnetic material that has previously been magnetized is placed in a magnetic field, H, its magnetization, M, will trace out a "magnetic hysteresis loop" like that shown above as the field is cycled between large positive to large negative values. Explain the hysteresis in terms of the magnetic microstructure and its response to the magnetic field.

(b) How do the hysteresis curves of "hard" and "soft" magnetic materials differ? Identify a technological application for which one would want a "hard" magnet, and one for which one would want a "soft" magnet.

(c) How might you make a ferromagnetic material "harder"?

Problem 6: (15 points)

Structural materials that are used in shafts, bearings and other devices that are subject to abrasion and wear are often treated to harden their surfaces. One method that is widely used for steel is "nitriding". The steel is heated in a nitrogen-containing atmosphere so that nitrogen diffuses a short distance beneath the surface to form a hard layer, called the "case", that is usually about 1 mm thick.

(a) The case contains a high concentration of interstitial nitrogen and nitrogen-containing precipitates. Briefly describe how these harden, that is, increases resistance to plastic deformation.

(b) Because the added nitrogen has volume that must be squeezed into the case, the case is in a state of compressive stress. This compressive stress makes the case more resistant to fracture than it otherwise would be, that is, it increases its effective fracture toughness. Why?

(c) The chemical process that adds nitrogen to the case has the consequence that a thin, very brittle layer of nitride compounds is left on the surface. Since this layer is brittle, it may fracture in service. However, so long as it is very thin, its brittleness is of no great concern, since it does not make the hardened part more likely to fracture. Why not?