CHAPTER 1 CRYSTAL STRUCTURES AND INTERATOMIC FORCES

1.1 Introduction
1.2 The crystalline state
1.3 Basic definitions
1.4 The fourteen Bravais lattices and the seven crystal systems
1.5 Elements of symmetry
1.6 Nomenclature of crystal directions and crystal planes; Miller indices
1.7 Examples of simple crystal structures
1.8 Amorphous solids and liquids
1.9 Interatomic forces
1.10 Types of bonding

Good order is the foundation of all good things.
Edmund Burke
QUESTIONS

1. What is the reason for the fact that the tetrahedral bond is the dominant bond in carbon compounds?
2. Estimate the strength of the hydrogen bond in water (in electron volts per bond).
3. Show that two parallel electric dipoles attract each other.
4. Estimate the strength of the van der Waals bond for neon.

PROBLEMS

1. Given that the primitive basis vectors of a lattice are \( \mathbf{a} = (a/2)(i + j) \), \( \mathbf{b} = (a/2)(j + k) \) and \( \mathbf{c} = (a/2)(k + i) \), where \( i, j, \) and \( k \) are the usual three unit vectors along cartesian coordinates, what is the Bravais lattice?
2. Using Table 1.2 and the data below, calculate the densities of the following solids: Al, Fe, Zn, and Si, whose atomic weights are respectively 26.98, 55.85, 65.37, and 28.09.
3. Show that in an ideal hexagonal-close-packed (hcp) structure, where the atomic spheres touch each other, the ratio \( c/a \) is given by

\[
\frac{c}{a} = \left( \frac{8}{3} \right)^{1/2} = 1.633.
\]

(The hcp structure is discussed in Section 7.)
4. The packing ratio is defined as the fraction of the total volume of the cell that is filled by atoms. Determine the maximum values of this ratio for equal spheres located at the points of simple-cubic, body-centered-cubic, and face-centered-cubic crystals.
5. Repeat Problem 4 for simple hexagonal, and rhombohedral lattices.
6. Repeat Problem 4 for an hcp structure.
7. Consider a face-centered-cubic cell. Construct a primitive cell within this larger cell, and compare the two. How many atoms are in the primitive cell, and how does this compare with the number in the original cell?
8. a) Show that a two-dimensional lattice may not possess a 5-fold symmetry.
   b) Establish the fact that the number of two-dimensional Bravais lattices is five: Oblique, square, hexagonal, simple rectangular, and body-centered rectangular.
   (The proof is given in Kittel, 1970.)
9. Demonstrate the fact that if an object has two reflection planes intersecting at \( \pi/4 \), it also possesses a 4-fold axis lying at their intersection.
10. Sketch the following planes and directions in a cubic unit cell: (122), [122], (1\( \overline{1} \)2), [1\( \overline{1} \)2].
11. a) Determine which planes in an fcc structure have the highest density of atoms.
   b) Evaluate this density in atoms/cm\(^2\) for Cu.
12. Repeat Problem 11 for Fe, which has a bcc structure.
13. Show that the maximum packing ratio in the diamond structure is \( \pi \sqrt{3}/16 \). [Hint: The structure may be viewed as two interpenetrating fcc lattices, arranged such that each atom is surrounded by four other atoms, forming a regular tetrahedron.]
14. A quantitative theory of bonding in ionic crystals was developed by Born and Meyer along the following lines: The total potential energy of the system is taken to be

\[ E = N \frac{A}{R^n} - N \frac{\alpha e^2}{4\pi\varepsilon_0 R}, \]

where \( N \) is the number of positive-negative ion pairs. The first term on the right represents the repulsive potential, where \( A \) and \( n \) are constants determined from experiments. The second term represents the attractive coulomb potential, where \( \alpha \), known as the Madelung constant, depends only on the crystal structure of the solid.

a) Show that the equilibrium interatomic distance is given by the expression

\[ R_0^{-1} = \frac{4\pi\varepsilon_0 A}{\alpha e^2 n}. \]

b) Establish that the bonding energy at equilibrium is

\[ E_0 = -\frac{\alpha Ne^2}{4\pi\varepsilon_0 R_0} \left( 1 - \frac{1}{n} \right). \]

c) Calculate the constant \( n \) for NaCl, using the data in Table 1.2 and the fact that the measured binding energy for this crystal is 1.83 kcal/mole (or 7.95 eV/molecule). The constant \( \alpha \) for NaCl is 1.75.
CHAPTER 2 X-RAY, NEUTRON, AND ELECTRON DIFFRACTION IN CRYSTALS

2.1 Introduction  
2.2 Generation and absorption of x-rays  
2.3 Bragg's law  
2.4 Scattering from an atom  
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2.8 Scattering from liquids  
2.9 Experimental techniques  
2.10 Other x-ray applications in solid-state physics  
2.11 Neutron diffraction  
2.12 Electron diffraction

All things visible and invisible.  
The Book of Common Prayer
QUESTIONS

1. What is the justification for drawing the scattered rays in Fig. 2.2(a) as nearly parallel?

2. In the scattering of x-rays by electrons, there is a small probability that the photon may suffer Compton scattering by the electron—this in addition to the scattering considered in this chapter, which is known as Thompson scattering. Compton scattering is inelastic, and the photon loses some of its energy to the electron; the energy loss depends on the scattering angle. Would you expect Compton scattering to produce a diffraction pattern? Why or why not?

3. It was stated following Eq. (2.6) that the amplitude of the wave decreases as the inverse of the radial distance from the scattering center. Justify this on the basis of energy conservation.

4. The crystal scattering factor $f_{cr}$ of (2.19) is a complex number. What is the advantage of using complex representation?

5. Diamond and silicon have the same type of lattice structure, an fcc with a basis, but different lattice constants. Is the lattice structure factor $S$ the same for both substances?

6. A reciprocal-lattice vector has a dimension equal to the reciprocal of length, for example, cm$^{-1}$. Is it meaningful to compare the magnitudes of a direct-lattice vector $R$ with a reciprocal-lattice vector $G$? Is it meaningful to compare their directions? If the latter answer is yes, find the angle between $R$ and $G$ in terms of their components in a cubic crystal. What is the angle between $R = [111]$ and $G = [110]$?

7. Does a real lattice vector have a corresponding unique reciprocal vector?

8. Draw a figure illustrating momentum conservation in the Bragg reflection considered as a photon–crystal collision. Why is this collision elastic? Justify your answer with numerical estimates.
9. Why is the energy of a neutron so much smaller than that of an electron in radiation beams employed in crystal diffraction?

10. Can a light beam be used in the analysis of crystal structure? Estimate the lattice constant for a crystal amenable to analysis by visible light.

11. Why is the neutron more useful than the proton in structure analysis?

PROBLEMS

1. The minimum wavelength observed in x-ray radiation is \( \lambda = 1.23 \text{ Å} \). What is the kinetic energy, in eV, of the primary electron hitting the target?

2. The edge of a unit cell in a cubic crystal is \( a = 2.62 \text{ Å} \). Find the Bragg angle corresponding to reflection from the planes (100), (110), (111), (200), (210) and (211), given that the monochromatic x-ray beam has a wavelength \( \lambda = 1.54 \text{ Å} \).

3. A Cu target emits an x-ray line of wavelength \( \lambda = 1.54 \text{ Å} \).
   a) Given that the Bragg angle for reflection from the (111) planes in Al is 19.2\(^\circ\), compute the interplanar distance for these planes. Recall that aluminum has an fcc structure.
   b) Knowing that the density and atomic weight of Al are, respectively, 2.7 g/cm\(^3\) and 27.0, compute the value of Avogadro's number.

4. a) The Bragg angle for reflection from the (110) planes in bcc iron is 22\(^\circ\) for an x-ray wavelength of \( \lambda = 1.54 \text{ Å} \). Compute the cube edge for iron.
   b) What is the Bragg angle for reflection from the (111) planes?
   c) Calculate the density of bcc iron. The atomic weight of Fe is 55.8.

5. Establish the validity of (2.11) for an arbitrary origin.

6. Prove the result of (2.17).

7. Establish the result (2.20).

8. Establish the fact that Eq. (2.23) follows from (2.20) and the definitions (2.21) and (2.22).

9. The electron density in a hydrogen atom in its ground state is spherically symmetric, and given by
   
   \[ \rho(r) = e^{-\frac{2r}{a_0}} \frac{\alpha_0}{\pi a_0^3}, \]

   where \( a_0 \), the first Bohr radius, has the value 0.53 Å. Compute the atomic scattering factor \( f_a \) for hydrogen, and plot it as a function of \( s = 2k \sin \theta = 4\pi \sin \theta / \lambda \). Explain physically why the scattering factor is small for back reflection \( (\theta = \pi/2) \).

10. The crystal-structure factor \( f_{cr} \) depends on the origin of the coordinate system. Show that the intensity, which is the observed quantity, is independent of the choice of origin.

11. Evaluate the first subsidiary minimum of \( S^2 \) (Fig. 2.5b), and show that it is equal to 0.04N\(^2\), in the limit of large \( N \).

12. The geometrical structure factor \( F_{hkl} \) for a bcc lattice was evaluated in the text by assuming the cell to contain one atom at a corner and another at the center of the unit cell. Show that the same result is obtained by taking the cell to contain one-eighth of an atom at each of its eight corners, plus one atom at the center.

13. Evaluate the geometrical structure factor \( F_{hkl} \) for reflection from the (hkl) planes in an fcc lattice, and show that the factor vanishes unless the numbers \( h, k, \) and \( l \) are all even or all odd.
14. Which of the following reflections would be missing in a bcc lattice: (100), (110), (111), (200), (210), (220), (211)? Answer a similar question for an fcc lattice.

15. Diamond has an fcc structure in which the basis is composed of two identical atoms, one at the lattice point, and another at a point \((a/4, a/4, a/4)\) relative to the first atom, where \(a\) is the edge of the cube (see Fig. 2.15). Find the geometrical structure factor for diamond, and express it in terms of the factor corresponding to an fcc Bravais lattice. Which of the reflections in Problem 14 are missing in diamond?

16. Cesium chloride (CsCl) crystallizes in the bcc structure, in which one type of atom is located at the corners and the other at the center of the cell. Calculate the geometrical structure factor \(F_{100}\), assuming that \(f_{Cs} = 3f_{Cl}\). Explain why the extinction rule derived in the text is violated here.

17. Repeat Problem 15 for GaSb, which crystallizes in the zincblende structure (see Section 1.7), assuming that \(f_{S} = 2f_{Ga}\).

18. Show that the volume of the reciprocal cell is equal to the inverse of the real cell.

19. Construct the reciprocal lattice for a two-dimensional lattice in which \(a = 1.25\ \text{Å}, \ b = 2.50\ \text{Å}, \ \gamma = 120°\).

20. A unit cell has the dimensions \(a = 4\ \text{Å}, \ b = 6\ \text{Å}, \ c = 8\ \text{Å}, \ \alpha = \beta = 90°, \ \gamma = 120°\). Determine:
   a) \(a^*, \ b^*, \ c^*\) for the reciprocal cell.
   b) The volume of the real and reciprocal unit cells.
   c) The spacing between the (210) planes.
   d) The Bragg angle \(\theta\) for reflection from the above planes.

21. Show that if the crystal undergoes volume expansion, then the reflected beam is rotated by the angle

\[ \delta \theta = -\frac{\gamma}{3} \tan \theta, \]

where \(\gamma\) is the volume coefficient of expansion and \(\theta\) the Bragg angle.

22. Discuss the variation of the intensity with the half scattering angle \(\theta\). Include the effects of the lattice-structure factor, the geometrical-structure factor, and the electron scattering length.

23. Write an essay on the experimental aspects of x-ray diffraction.

24. Prove the result (2.52).

25. A beam of 150-eV electrons falls on a powder nickel sample. Find the two smallest Bragg angles at which reflection takes place, recalling that Ni has an fcc lattice with a cube edge equal to 3.25 Å.
CHAPTER 3  LATTICE VIBRATIONS: THERMAL, ACOUSTIC, AND OPTICAL PROPERTIES

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“We are no other than a moving row
Of visionary shapes that come and go
Round with this Sun-illumin’d Lantern held
In Midnight by the Master of the Show.

Omar Khayyam
134 Lattice Vibrations: Thermal, Acoustic, and Optical Properties


**Thermal conductivity**

H. M. Rosenberg, listed above under Specific Heat

**QUESTIONS**

1. Equation (3.11) gives the allowed values of $q$ in a continuous line under periodic boundary conditions. Plot a few of the corresponding wavelengths, and compare with results from elementary physics for, say, a vibrating string.

2. Determine the density of states for a two-dimensional continuous medium using periodic boundary conditions.

3. In the Einstein model, atoms are treated as independent oscillators. The Debye model, on the other hand, treats atoms as coupled oscillators vibrating collectively. However, the collective modes are regarded here as independent. Explain the meaning of this independence, and contrast it with that in the Einstein model.

4. Would you expect to find sound waves in small molecules? If not, how do you explain the propagation of sound in gaseous substances?

5. Explain qualitatively why the interatomic force constant diminishes rapidly with distance.

6. Show that the total number of allowed modes in the first BZ of a one-dimensional diatomic lattice is equal to $2N$, the total number of degrees of freedom.

7. Suppose that we allow two masses $M_1$ and $M_2$ in a one-dimensional diatomic lattice to become equal. What happens to the frequency gap? Is this answer expected? Compare the results with those of the monatomic lattice.

8. Derive an expression for the specific heat of a one-dimensional diatomic lattice. Make the Debye approximation for the acoustic branch, and assume that the optical branch is flat.

9. Figure 3.25(b) shows that the TA branches, as well as the TO branches, in Ge are degenerate in the [111] direction. Explain this qualitatively on the basis of symmetry.

10. Convince yourself that the BZ of an fcc lattice has the shape given in Fig. 3.26(b).

11. Give a physical argument to support the plausibility of (3.74) for thermal conductivity.

12. Explain the dependence of thermal conductivity on temperature as displayed in Fig. 3.32(b).

13. In the microwave generator of a miniature semiconductor, a considerable amount of undesirable heat is generated in the conversion of dc to ac power. Explain why diamond is being increasingly used as a heat sink to transport the heat away from the device.
14. Discuss two experimental techniques for measuring the mean free paths of phonons in solids.

15. Verify (3.91).


17. Draw a figure for a transverse oscillation in an ionic crystal and show that, unlike the case of longitudinal oscillations, no charge bunching takes place.

PROBLEMS

1. The longitudinal and transverse velocities of sound in diamond, a cubic crystal, along the [100] direction are, respectively, 1.76 and $1.28 \times 10^6$ cm/s. The longitudinal velocity in the [111] direction is $1.86 \times 10^6$ cm/s. From these data, and the fact that the density is $3.52 \text{ g/cm}^3$, calculate the elastic constants $C_{11}$, $C_{12}$, and $C_{44}$ for diamond.

2. In deriving (3.19) for the density of states for a continuous medium, it was assumed that the longitudinal and transverse velocities $v_l$ and $v_t$ were equal. Derive the density of states for a case in which this assumption is no longer true.

3. It is more convenient in practice to measure the specific heat at constant pressure, $C_p$, than the specific heat at constant volume, $C_v$, but the latter is more amenable to theoretical analysis.
   a) Using a thermodynamic argument, show that the two specific heats are related by
   \[ C_p - C_v = \alpha^2 TV/K, \]
   where $\alpha$ is the volume coefficient of thermal expansion and $K$ the compressibility.
   b) Show that $C_p - C_v = R$ for an ideal gas.
   c) Show that $C_p \simeq C_v$ for a solid at room temperature. (Look up the needed parameters in appropriate reference works, e.g., the *Handbook of Chemistry and Physics*.)

4. Using the Maxwell-Boltzmann distribution, show that the average energy of a one-dimensional oscillator at thermal equilibrium is \( \bar{\epsilon} = kT \).

5. Prove the result (3.26) for the average energy of a quantum oscillator.

6. a) If the classical theory of specific heat were valid, what would be the thermal energy of one mole of Cu at the temperature $T = \theta_D$? The Debye temperature for Cu is $340^\circ K$.
   b) Calculate the actual thermal energy according to the Debye theory (use Fig. 3.13), and compare with the classical value obtained above. (For the purpose of this calculation, you may approximate the Debye curve by a straight line joining the origin to the point on the Debye curve at $T = \theta_D$.)
   c) What is the order of magnitude of the maximum displacement of a Cu atom at the Debye temperature? Compare this displacement with the interatomic distance.

7. It was stated in the text that the Debye temperature $\theta_D$ is proportional to $(Y/M)^{1/2}$, where $Y$ is Young's modulus and $M$ the atomic mass. For solids of similar chemical and structural characteristics, the parameters $Y$ are nearly equal, and thus $\theta_D \sim 1/M^{1/2}$. Plot $\theta_D$ versus $M^{-1/2}$ for the alkali metals (Li, Na, K, Rb, Cs), the noble metals (Cu, Ag, Au), the covalent crystals (C, Si, Ge, Sn), and discuss how well this prediction is satisfied.
8. Verify the mathematical reasoning between (3.36) and (3.38).
9. a) Derive the expression for the specific heat of a linear continuous chain according to the Debye theory. Discuss the high and low temperature limits.
   b) Repeat part (a) for a continuous sheet.
10. Determine the phase and group velocities for a monatomic lattice. Plot the results versus the wave vector \( q \) and give a brief discussion of their significance.
11. When the frequency of a wave in a one-dimensional lattice is greater than the cutoff frequency \( \omega_m \), the wave is heavily attenuated. Assuming that the solution may still be expressed in the form (3.55), but with \( q \) being an imaginary number, calculate the attenuation coefficient, i.e., the coefficient governing the exponential decay of the intensity, and plot the result as a function of the frequency. \([Hint: Use the formula \( \sin iy = i \sinh y \).]\)
12. Verify (3.62) and (3.63).
13. Using the optical mode frequency for NaCl (Table 3.3), calculate the interatomic force constant and Young's modulus for this substance. From these data and the density (2.18 g/cm\(^3\)), calculate the velocity of sound in NaCl.
14. What is the minimum wavelength for a wave traveling in the [100] direction in an fcc structure? In the [111] direction? Use Fig. 3.26(a), and assume that the cube edge of the real unit cell is \( a = 5 \) Å.
15. Using the density of states (3.69) for a one-dimensional monatomic crystal, show that the total number of states is equal to \( N \).
16. Using data on thermal conductivity, calculate the velocity of sound in NaCl at \( T = 20^\circ\text{K} \) and \( T = 300^\circ\text{K} \). Compare your answer with that for Problem 13.
17. In discussing the behavior of the phonon's mean free path we treated the various collision processes separately. However, in most situations, several of these processes act simultaneously to scatter the phonon. Show that the effective path in that case is given by \( 1/l = \sum_i 1/l_i \), where the \( l_i \)'s refer to the mean free paths of the individual collision mechanisms. \([Hint: You may use a probabilistic argument. A similar approach is employed in Section 4.5 in connection with the scattering of electrons in metals.]\)
18. The text stated that the equations for the conservation of momentum and energy for the scattering of a photon by a phonon, Eqs. (3.75) and (3.76), may also be derived by treating the scattering process as a Doppler-shifted Bragg reflection. Prove this statement.
19. Brillouin scattering of a monochromatic light beam, \( \lambda_0 = 6328 \) Å, from water at room temperature leads to a Brillouin sideband whose shift from the central line is \( \Delta \nu = 4.3 \times 10^9 \) Hz at scattering angle of 90°. Knowing that the refractive index of water is 1.33, what is the velocity of sound in this substance at room temperature?
20. Fill in the entries left vacant in Table 3.3.
21. Solve for the two polariton dispersion relations from (3.86), and show that the dispersion curves are as shown in Fig. 3.45.
CHAPTER 4 METALS I: THE FREE-ELECTRON MODEL

4.1 Introduction
4.2 Conduction electrons
4.3 The free-electron gas
4.4 Electrical conductivity
4.5 Electrical resistivity versus temperature
4.6 Heat capacity of conduction electrons
4.7 The Fermi surface
4.8 Electrical conductivity; effects of the Fermi surface
4.9 Thermal conductivity in metals
4.10 Motion in a magnetic field: cyclotron resonance and the Hall effect
4.11 The AC conductivity and optical properties
4.12 Thermionic emission
4.13 Failure of the free-electron model

_Freedom has a thousand charms to show,
That slaves, how'er contented, never know._

William Cowper
QUESTIONS

1. Explain the distinction between localized and delocalized (or core) electrons in solids. Describe one experimental method of testing the difference between the two types.

2. The text said that the conduction electrons are better described as a plasma than an ordinary gas. In what essential ways does a plasma differ from a gas?

3. Trace the steps which show that the electrical current of the electrons is in the same direction as the field, even though the particles are negatively charged.

4. Assuming that the conduction electrons in Cu are a classical gas, calculate the rms value of the electron speed, and compare the value obtained with the Fermi velocity (see Problem 1).

5. Explain why electrons carry a net energy but not a net current in the case of thermal conduction.

6. Show that if the random velocity of the electrons were due to the thermal motion of a classical electron gas, the electrical resistivity would increase with the temperature as $T^{3/2}$.

7. In a cyclotron resonance experiment, part of the signal is absorbed by the electrons. What happens to this energy when the system is in a steady-state situation?

8. Explain qualitatively why the Hall constant $R_H$ is inversely proportional to the electron concentration $N$.

9. Demonstrate qualitatively that the Hall constant for a current of positive charges is positive.

10. Equation (4.54) shows that the skin depth $\delta$ becomes infinite at zero frequency. Interpret this result.

11. Describe the variation of skin depth with temperature.

12. According to the discussion in Section 4.11, free electrons make a negative contribution to the dielectric constant, while bound electrons make a positive contribution. Explain this difference in electron behavior.

PROBLEMS

1. Copper has a mass density $\rho_m = 8.95 \text{ g/cm}^3$, and an electrical resistivity $\rho = 1.55 \times 10^{-8} \text{ ohm-m}$ at room temperature. Assuming that the effective mass $m^* = m_0$, calculate:
   a) The concentration of the conduction electrons
   b) The mean free time $\tau$
   c) The Fermi energy $E_F$
   d) The Fermi velocity $v_F$
   e) The mean free path at the Fermi level $l_F$

2. Derive Eq. (4.19) for the mean free path.

3. The residual resistivity for 1 atomic percent of As impurities in Cu is $6.8 \times 10^{-8} \text{ ohm-m}$. Calculate the cross section for the scattering of an electron by one As impurity in Cu.

4. Sodium has a volume expansion coefficient of $15 \times 10^{-5} \text{ K}^{-1}$. Calculate the percentage change in the Fermi energy $E_F$ as the temperature is raised from $T = 0\text{ K}$ to $300\text{ K}$. Comment on the magnitude of the change.

5. Repeat Problem 4 for silver, whose volume coefficient of expansion is $18.6 \times 10^{-5} \text{ K}^{-1}$.
6. Calculate the Fermi temperatures \( T_F \) for Cu, Na, and Ag. Also calculate the ratio \( T/T_F \) in each case for \( T = 300^\circ \text{K} \). The effective masses of Cu and Na are 1.0 and 1.2 times \( m_0 \).

7. Estimate the fraction of electrons excited above the Fermi level at room temperature for Cu and Na.

8. Calculate the ratio of electrons to lattice heat capacities for Cu at \( T = 0.3^\circ, 4^\circ, 20^\circ, 77^\circ, \) and \( 300^\circ \text{K} \). The lattice heat capacity of Cu is given in Fig. 3.10.

9. Plot the Fermi–Dirac function \( f(E) \) versus the energy ratio \( E/E_F \) at room temperature \( T = 300^\circ \text{K} \). (Assume \( E_F \) independent of temperature.) If \( E_F = 5 \text{ eV} \), determine the energy values at which \( f(E) = 0.5, 0.7, 0.9, \) and 0.95.

10. Cyclotron resonance has been observed in Cu at a frequency of 24 GHz. Given that the effective mass of Cu is \( m^* = m_0 \), what is the value of the applied magnetic field?

11. Using Table 4.4, giving the Hall constants, calculate the electron concentrations in Na, Cu, Cd, Zn, Al, and In. Compare these results with those given in Table 1.1.

12. a) Using the appropriate values of \( \epsilon_{Lr}, \sigma_0, \) and \( \tau \) for Ag at room temperature, calculate the refractive index \( n \) and the extinction coefficient \( \kappa \) for Ag, and plot these versus \( \omega \) on the logarithmic scale.

b) Evaluate the optical reflectivity and plot it versus \( \omega \). (Data on Ag are found in Table 4.1.) The values of \( \omega \) may be confined to the range \( \omega < 10^{16} \text{ s}^{-1} \).

13. Evaluate the skin depth for Cu at room temperature, and plot the results versus the frequency on a logarithmic scale. (Data are given in Table 4.1.) The value of \( \omega \) may be confined to \( \omega < 10^{13} \text{ s}^{-1} \).

14. Carry out the integration which leads to (4.61).

15. Calculate the density of the thermionic emission current in Cs at 500, 1000, 1500, and 2000\(^\circ \text{K} \).
5.1 Introduction
5.2 Energy spectra in atoms, molecules, and solids
5.3 Energy bands in solids; the Bloch theorem
5.4 Band symmetry in k-space; Brillouin zones
5.5 Number of states in the band
5.6 The nearly-free-electron model
5.7 The energy gap and the Bragg reflection
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5.9 Calculations of energy bands
5.10 Metals, insulators, and semiconductors
5.11 Density of states
5.12 The Fermi surface
5.13 Velocity of the Bloch electron
5.14 Electron dynamics in an electric field
5.15 The dynamical effective mass
5.16 Momentum, crystal momentum, and physical origin of the effective mass
5.17 The hole
5.18 Electrical conductivity
5.19 Electron dynamics in a magnetic field: cyclotron resonance and the Hall effect
5.20 Experimental methods in determination of band structure
5.21 Limit of the band theory; metal–insulator transition

On the surface there is infinite variety of things; at base a simplicity of cause.

Ralph Waldo Emerson
QUESTIONS

1. It was pointed out in Sections 6.3 and 4.3 that an electron spends only a little time near an ion, because of the high speed of the electron there. At the same time it was claimed that the ions are "screened" by the electrons, implying that the electrons are so distributed that most of them are located around the ions. Is there a paradox here? Explain.

2. Figure 5.10(c) is obtained from Fig. 5.10(a) by cutting and displacing various segments of the free-electron dispersion curve. Is this rearrangement justifiable for a truly free electron? How do you differentiate between an empty lattice and free space?

3. Explain why the function \( \psi_0 \) in Fig. 5.18(b) is flat throughout the Wigner-Seitz cell except close to the ion, noting that this behavior is different from that of an atomic wave function, which decays rapidly away from the ion. This implies that the coulomb force due to the ion in cell \( A \) is much weakened in the flat region. What is the physical reason for this?

4. Band overlap is important in the conductivity of polyvalent metals. Do you expect it to take place in a one-dimensional crystal? You may invoke the symmetry properties of the energy band.

PROBLEMS

1. Figure 5.7 shows the first three Brillouin zones of a square lattice.
   a) Show that the area of the third zone is equal to that of the first. Do this by appropriately displacing the various fragments of the third zone until the first zone is covered completely.
   b) Draw the fourth zone, and similarly show that its area is equal to that of the first zone.

2. Draw the first three zones for a two-dimensional rectangular lattice for which the ratio of the lattice vectors \( a/b = 2 \). Show that the areas of the second and third zones are each equal to the area of the first.

3. Convince yourself that the shapes of the first Brillouin zones for the fcc and bcc lattices are those in Fig. 5.8.

4. Show that the number of allowed \( k \)-values in a band of a three-dimensional sc lattice is \( N \), the number of unit cells in the crystal.

5. Repeat Problem 4 for the first zone of an fcc lattice (zone shown in Fig. 5.8a).

6. Derive Eqs. (5.21) and (5.22).

7. Show that the first three bands in the empty-lattice model span the following energy ranges.

   \[
   E_1: \quad 0 \text{ to } \pi^2 \hbar^2/2m_0a^2; \quad E_2: \quad \pi^2 \hbar^2/m_0a^2 \text{ to } 2\pi^2 \hbar^2/m_0a^2; \quad E_3: \quad 2\pi^2 \hbar^2/m_0a^2 \text{ to } 9\pi^2 \hbar^2/2m_0a^2.
   \]

8. a) Show that the octahedral faces of the first zone of the fcc lattice (Fig. 5.8a) are due to Bragg reflection from the (111) atomic planes, while the other faces are due to reflection from the (200) planes.
   b) Show similarly that the faces of the zone for the bcc lattice are associated with Bragg reflection from the (110) atomic planes.
9. Suppose that the crystal potential in a one-dimensional lattice is composed of a series of rectangular wells which surround the atom. Suppose that the depth of each well is $V_0$ and its width $a/5$.

a) Using the NFE model, calculate the values of the first three energy gaps. Compare the magnitudes of these gaps.

b) Evaluate these gaps for the case in which $V_0 = 5$ eV and $a = 4 \, \text{Å}$.

10. Prove that the wave function used in the TB model, Eq. (5.27), is normalized to unity if the atomic function $\phi_v$ is so normalized. [Hint: For the present purpose you may neglect the overlap between the neighboring atomic functions.]

11. The energy of the band in the TB model is given by

$$E(k) = E_v - \beta - \gamma \sum_j e^{ik \cdot x_j},$$

where $\beta$ and $\gamma$ are constants, as indicated in the text, and $x_j$ is the position of the $j$th atom relative to the atom at the origin.

a) Find the energy expression for a bcc lattice, using the nearest-neighbor approximation. Plot the energy contours in the $k_x-k_y$ plane. Determine the width of the energy band.

b) Repeat part (a) for the fcc lattice.

12. a) Using the fact that the allowed values of $k$ in a one-dimensional lattice are given by $k = n(2\pi/L)$, show that the density of electron states in the lattice, for a lattice of unit length, is given by

$$g(E) = \frac{1}{2\pi} \left| \frac{dE}{dk} \right|.$$

b) Evaluate this density of states in the TB model, and plot $g(E)$ versus $E$.

13. Calculate the density of states for the first zone of an sc lattice according to the empty-lattice model. Plot $g(E)$, and determine the energy at which $g(E)$ has its maximum. Explain qualitatively the behavior of this curve.

14. a) Using the free-electron model, and denoting the electron concentration by $n$, show that the radius of the Fermi sphere in k-space is given by

$$k_F = (3\pi^2 n)^{1/3}.$$

b) As the electron concentration increases, the Fermi sphere expands. Show that this sphere begins to touch the faces of the first zone in an fcc lattice when the electron-to-atom ratio $n/n_a = 1.36$, where $n_a$ is the atom concentration.

c) Suppose that some of the atoms in a Cu crystal, which has an fcc lattice, are gradually replaced by Zn atoms. Considering that Zn is divalent while Cu is monovalent, calculate the atomic ratio of Zn to Cu in a CuZn alloy (brass) at which the Fermi sphere touches the zone faces. Use the free-electron model. (This particular mixture is interesting because the solid undergoes a structural phase change at this concentration ratio.)

15. a) Calculate the velocity of the electron for a one-dimensional crystal in the TB model, and prove that the velocity vanishes at the zone edge.

b) Repeat (a) for a square lattice. Show that the velocity at a zone boundary is parallel to that boundary. Explain this result in terms of the Bragg reflection.
c) Repeat for a three-dimensional sc lattice, and show once more that the electron velocity at a zone face is parallel to that face. Explain this in terms of Bragg reflection. Can you make a general statement about the direction of the velocity at a zone face?

16. Suppose that a static electric field is applied to an electron at time \( t = 0 \), at which instant the electron is at the bottom of the band. Show that the position of the electron in real space at time \( t \) is given by

\[
x = x_0 + \frac{1}{F} E(k = Ft/h),
\]

where \( x_0 \) is the initial position and \( F = -e\phi \) is the electric force. Assume a one-dimensional crystal, and take the zero-energy level at the bottom of the band. Is the motion in real space periodic? Explain.

17. a) Using the TB model, evaluate the effective mass for an electron in a one-dimensional lattice. Plot the mass \( m^* \) versus \( k \), and show that the mass is independent of \( k \) only near the origin and near the zone edge.

b) Calculate the effective mass at the zone center in an sc lattice using the TB model.

c) Repeat (b) at the zone corner along the [111] direction.

18. Prove Eq. (5.18).

19. a) Calculate the cyclotron frequency \( \omega_c \) for an energy contour given by

\[
E(k) = \frac{\hbar^2}{2m_1^*} k_x^2 + \frac{\hbar^2}{2m_2^*} k_y^2,
\]

where the magnetic field is perpendicular to the plane of the contour.

\[
\left[ \text{Answer: } \omega_c = \sqrt{\frac{e^2}{m_1^* m_2^*} B}. \right]
\]

b) Repeat (a) for an ellipsoidal energy surface

\[
E(k) = \frac{\hbar^2}{2m_1^*} (k_x^2 + k_y^2) + \frac{\hbar^2}{2m_3^*} k_z^2,
\]

where the field \( B \) makes an angle \( \theta \) with the \( k_z \)-axis of symmetry of the ellipsoid.

\[
\left[ \text{Answer: } \omega_c = \left[ \left( \frac{eB}{m_1^*} \right)^2 \cos^2 \theta + \frac{e^2 B^2}{m_1^* m_3^*} \sin^2 \theta \right]^{1/2} \right].
\]

20. In Section 5.19 we discussed the motion of a Bloch electron in \( k \)-space in the presence of a magnetic field. The electron also undergoes a simultaneous motion in \( r \)-space. Discuss this motion, and in particular show that the trajectory in \( r \)-space lies in a plane parallel to that in \( k \)-space, that the shapes of the two trajectories are the same except that the one in \( r \)-space is rotated by an angle of \(-\pi/2\) relative to the other, and expanded by a linear scale factor of \((\hbar/eB)\). [Hint: Use Eq. (5.108) to relate the electron displacements in \( r \) - and \( k \)-space.]

21. Prove Eq. (5.113) for the Hall constant of an electron–hole system.
CHAPTER 6 SEMICONDUCTORS I: THEORY

6.1 Introduction
6.2 Crystal structure and bonding
6.3 Band structure
6.4 Carrier concentration; intrinsic semiconductors
6.5 Impurity states
6.6 Semiconductor statistics
6.7 Electrical conductivity; mobility
6.8 Magnetic field effects: cyclotron resonance and Hall effect
6.9 Band structure of real semiconductors
6.10 High electric field and hot electrons
6.11 The Gunn effect
6.12 Optical properties: absorption processes
6.13 Photoconductivity
6.14 Luminescence
6.15 Other optical effects
6.16 Sound-wave amplification (acoustoelectric effect)
6.17 Diffusion

There be none of Beauty's daughters
With a magic like thee.

Lord Byron
QUESTIONS

1. In discussing the tetrahedral bond in the Group IV semiconductors (and other substances), we described the so-called bond model, in which each electron is localized along the covalent bond line joining the two atoms. Explain how this may be reconciled with the (delocalized) band model, in which the electron is described by a Bloch function whose probability is distributed throughout the crystal.

2. Do the bond orbitals of the above bonds correspond to the conduction band or the valence band? Why?

3. Describe the bond model associated with the electrons in the conduction band of the group IV semiconductors; i.e., state the spatial region(s) in which these electrons reside.

4. What does the breaking of a bond correspond to in the band model?

5. Give one (or more) experimental reason affirming that the electrons associated with the tetrahedral bond are delocalized.

6. The pre-exponential factor in Eq. (6.8), i.e., the factor preceding $e^{-E_g/k_BT}$, is frequently referred to as "the effective density of states of the conduction band." How do you justify this designation?

7. A cyclotron resonance experiment in $n$-type Ge exhibits only one electron line. In which direction is the magnetic field?

8. Is it possible for a cyclotron resonance experiment in Si to show only one electron line?

9. Does the fact that a sample exhibits intrinsic behavior necessarily imply that the sample is pure?

10. An experimenter measuring the Hall effect in a semiconductor specimen finds to his surprise that the Hall constant in his sample is vanishingly small even at room temperature. He asks you to help him interpret this result. What is the likely explanation?

11. In the expression for the electron temperature (6.53), the first power of the field $\delta$ is missing. Can you explain this by symmetry considerations? If the general expression for $T_e$ at an arbitrary field, which would be more complicated than Eq. (6.53), were to be expanded in powers of $\delta$, would you expect the terms $\delta$, $\delta^3$, $\delta^5$, etc., to appear? Why? Does your argument apply equally well to such materials as Ge and GaAs?

12. In discussing hot electrons, one finds that the temperature of the electron is greater than that of the lattice. Can you conceive of a situation in which the temperature of the electrons might be lower than that of the lattice?

13. Suppose that, in working with a given semiconductor, you use an incident optical beam which is very strong. Is it possible for a fundamental absorption to take place even at a frequency $\nu < E_g/h$?

14. In an intrinsic semiconductor, is the Einstein relation valid for electrons and holes individually?
PROBLEMS

1. Derive (6.13) for hole concentration.

2. a) Compute the concentration of electrons and holes in an intrinsic sample of Si at room temperature. You may take $m_e = 0.7 m_0$ and $m_h = m_0$.
   b) Determine the position of the Fermi energy level under these conditions.

3. Given that the pre-exponential factors in (6.8) and (6.13) are $1.1 \times 10^{19}$ and $0.51 \times 10^{19}$ cm$^{-3}$, respectively, in Ge at room temperature, calculate:
   a) The effective masses $m_e$ and $m_h$ for the electron and the hole.
   b) The carrier concentration at room temperature.
   c) The carrier concentration at 77°K, assuming the gap to be independent of temperature.

4. Gallium arsenide has a dielectric constant equal to 10.4.
   a) Determine the donor and acceptor ionization energies.
   b) Calculate the Bohr radii for bound electrons and holes.
   c) Calculate the temperature at which freeze-out begins to take place in an $n$-type sample.

5. A silicon sample is doped by arsenic donors of concentration $1.0 \times 10^{23}$ m$^{-3}$. The sample is maintained at room temperature.
   a) Calculate the intrinsic electron concentration, and show that it is negligible compared to the electron concentration supplied by the donors.
   b) Assuming that all the impurities are ionized, determine the position of the Fermi level.
   c) Describe the effect on the Fermi level if acceptors are introduced in the above sample at a concentration of $6.0 \times 10^{21}$ m$^{-3}$.

6. Given these data for Si: $\mu_e = 1350$ cm$^2$/volt-s, $\mu_h = 475$ cm$^2$/volt-s, and $E_g = 1.1$ eV, calculate the following.
   a) The lifetimes for the electron and for the hole.
   b) The intrinsic conductivity $\sigma$ at room temperature.
   c) The temperature dependence of $\sigma$, assuming that electron collision is dominated by phonon scattering, and plot log $\sigma$ versus $1/T$.

7. Repeat Problem 6 for Ge, using Tables 6.1 and 6.2.

8. A sample of extrinsic semiconductor is in the shape of a slab whose length is 5 cm, width 0.5 cm, and thickness 1 mm. When this slab is placed in a magnetic field of 0.6 Wb/m$^2$ normal to the slab, a Hall voltage of 8 mV develops at a current of 10 mA. Calculate: (a) the mobility of the carrier, (b) the carrier density.

9. A sample of $n$-type GaAs whose carrier concentration is $10^{16}$ cm$^{-3}$ has the same dimensions, is in the same field, and carries the same current as in Problem 8. Calculate: (a) the Hall constant in this sample, (b) the Hall voltage developed across the slab.

10. When we derived the Hall constant in Section 4.10, we assumed that the carrier mass is isotropic; the mobility of the carrier is therefore also isotropic. However, we have seen that carriers in some semiconductors have ellipsoidal masses.
   a) Show that when current in an $n$-type Si sample flows in the [100] direction, the Hall constant is given by
   
   $$ R = -\frac{3}{ne} \frac{\mu_i^2 + 2\mu_r^2}{(\mu_i + 2\mu_r)^2}, $$
where \( \mu_l = e\tau/\ell_l \) and \( \mu_t = e\tau/\ell_t \) are the longitudinal and transverse mobility, respectively.

b) Recalling that \( m_l/m_t \approx 5 \) in Si, evaluate the Hall constant for \( n = 10^{16} \text{ cm}^{-3} \).

c) What is the value of \( R \), given that the current flows in the [100] direction (with the orientation of the magnetic field appropriately rearranged)? [Hint: Note that the populations of the six valleys are equal to each other.]

11. a) Show that the density of states corresponding to an ellipsoidal energy surface is

\[
g(E) = \frac{1}{2\pi^2} \left( \frac{2}{\hbar^2} \right)^{3/2} (m_t^2 m_l^{1/2} E^{1/2},
\]

where \( m_t \) and \( m_l \) are the transverse and longitudinal masses, respectively. (The energy surface is taken to be an ellipsoid of revolution.)

b) If we make the replacement \( m_t^2 m_l = m_d^2 \) in the above expression, then \( g(E) \) would have the standard form for a spherical mass, (6.6), with \( m_d \) substituted for \( m_e \). For this reason, the mass \( m_d \) is usually called the density-of-states effective mass. Taking into account the many-valley nature of the conduction band in Ge, find \( m_d \) for this substance (expressing the results in units of \( m_0 \)).

12. When a carrier has an ellipsoidal mass, e.g., the electrons in Si, the mobility is also anisotropic. The longitudinal and transverse mobilities \( \mu_l \) and \( \mu_t \) are in inverse ratio to the masses, i.e., \( \mu_l/\mu_t = m_t/m_l \), as follows from (6.31). (The collision time is isotropic.) In tables such as Table 6.3, the so-called mobility \( \mu = (\mu_l + 2\mu_t)/3 \) is usually quoted. (This average is for an ellipsoid of revolution.)

a) Calculate \( \mu_l \) and \( \mu_t \) for silicon.

b) An electric field is applied in the [100] direction, and the field is so high that it heats the electrons (they become hot). But the valleys are heated at different rates because of the difference in carrier mobility in the longitudinal and transverse directions. Indicate which valleys become hotter than others.

c) Calculate the electric field at which the temperature of the hot valleys becomes 1000° K. (The lattice is at room temperature.) Take the energy relaxation time to be \( 2 \times 10^{-12} \text{ s} \). (Assume the mobility to be independent of the field.)

d) Suppose that the valleys are in quasi-equilibrium with each other; electrons then transfer from the hot to the cold valleys, and the valleys' populations are no longer equal. Find the fraction of the total electrons still remaining in the hot valleys at the field calculated in Problem 12(c).

e) Discuss the non-ohmic behavior resulting from this "intervalley transfer." Plot \( J \) versus \( \mathcal{E} \) up to a field three times the field calculated in Problem 12(c).

13. Estimate the value of the field for which an appreciable transfer of electrons takes place from the central to the secondary valleys in GaAs. [Hint: The energy absorbed by an electron in an interval of one lifetime must be of the order of the energy difference between valleys.]

14. a) Calculate the threshold photon energy for direct fundamental absorption of radiation in GaAs at room temperature.

b) Determine the corresponding wavelength.

c) At what wavelength is the absorption coefficient equal to 1000 cm\(^{-1}\)?

15. Suppose that you are a solid-state physicist, and a materials engineer asks you: Why should silicon exhibit metallic luster when viewed in visible light, yet be transparent when viewed in infrared light? What is your answer?
16. a) Determine the longest wavelength of light absorbed in ionizing an As donor in Si.
   b) Using data from Table 6.2, repeat Problem 16(a) for a Ga acceptor in Si.
17. A slab of intrinsic GaAs, 3 cm long, 2 cm wide, and 0.3 cm thick is illuminated by a
    monochromatic light beam, at which frequency the absorption coefficient is 500 cm$^{-1}$.
    The intensity of the beam is $5 \times 10^{-4}$ W cm$^{-2}$, and the sample is at room temperature.
   a) Calculate the photon flux incident on the slab.
   b) At what depth does the intensity decrease to 5% of its value at the surface?
   c) Calculate the number of electron–hole pairs created per second in the slab.
      (Assume that the beam entering is totally absorbed through fundamental transition.)
   d) Calculate the increase in the conductivity $\Delta \sigma$ due to the illumination. Take the
      recombination time to be $2 \times 10^{-4}$ s. [Data: The dielectric constant of GaAs is 10.4].
18. Establish the Einstein relation (6.81) between the mobility and diffusion coefficient.
    Consider a sample in the shape of a rod along which a voltage is applied, but no
    current may flow because the circuit is open. The sample has now both an electric
    field and a concentration gradient. Assume Maxwell–Boltzmann statistics for the
    carriers.
19. It is found experimentally that the mobility in Ge depends on the temperature as
    $T^{-1.66}$. The mobility of this substance at room temperature is 3900 cm$^2$/volt-s.
    Calculate the diffusion coefficient at room temperature (300°K) and at the
    temperature of liquid nitrogen (77°K).
20. Suppose that the concentration of electrons in $n$-type Ge at room temperature
    decreases linearly from $5 \times 10^{16}$ cm$^{-3}$ to zero over an interval of 2 mm.
   a) Calculate the diffusion current.
   b) What is the value of the electric field required to produce a drift current equal to the
      diffusion current of part (a)? Use the average value of the concentration in
      determining the drift current.
   c) Draw a diagram to show the direction of the field.
CHAPTER 7 SEMICONDUCTORS II: DEVICES

7.1 Introduction
7.2 The $p$-$n$ junction: the rectifier
7.3 The $p$-$n$ junction: the junction itself
7.4 The junction transistor
7.5 The tunnel diode
7.6 The Gunn diode
7.7 The semiconductor laser
7.8 The field-effect transistor, the semiconductor lamp, and other devices
7.9 Integrated circuits and microelectronics

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... The morality of art consists in the perfect use of an imperfect medium

Oscar Wilde
QUESTIONS

1. Show qualitatively the position of the Fermi level in a p-n junction at equilibrium. Use a figure similar to Fig. 7.2.

2. In the derivation of the rectification equation in Section 7.2 the approximation was made that the whole bias voltage appeared across the junction. Does this approximation hold better for forward or reverse bias? Explain.
3. Describe a metal-semiconductor junction at equilibrium (McKelvey, 1966).
4. Suppose that a p-n function at equilibrium is short-circuited with a metallic wire. Could the contact potential of the junction drive an electric current in the circuit? Explain. Draw the appropriate energy-band diagram for the whole circuit.
5. Show qualitatively the position of the Fermi level(s) in a biased p-n junction.
6. When the holes in a p-n-p transistor diffuse through the base, a certain fraction of them recombine with electrons and disappear. Does the fact that Si is an indirect-gap semiconductor improve or hamper the operation of a silicon transistor?
7. Suppose that the difference in energy between the bottoms of the central and secondary valleys in GaAs is gradually reduced until it vanishes. Do you expect the Gunn effect to be observed throughout this range? (Assume that the masses and mobilities of the various valleys remain unchanged.)
8. The wavelength of the coherent radiation emitted from a GaAs laser decreases from 9000 Å to 7000 Å as the substance is alloyed with phosphorus, producing the compound GaAsP. Explain why.

PROBLEMS

1. Establish Eq. (7.6) for the hole current in a forward-biased p-n junction.
2. The saturation current for a p-n junction at room temperature is $2 \times 10^{-6}$ amp. Plot the current versus voltage in the voltage range $-5$ to $1$ volt. Find the differential resistance at a reverse bias of $1$ volt and forward bias of $0.25$ volt, and compare the two values thus obtained.
3. Derive Eqs. (7.32) by solving the Poisson's equation (7.31), subject to the appropriate boundary conditions.
4. a) Determine the contact potential for a p-n junction of germanium at room temperature, given that the donor concentration is $10^{18}$ cm$^{-3}$ and the acceptor concentration is $5 \times 10^{16}$ cm$^{-3}$. Assume the impurities to be completely ionized.
   b) Calculate the widths of the depletion layer of the junction.
   c) Calculate the electric field at the center of the junction.
   d) The depletion double layer also acts as a capacitor, with the depletion regions on the opposite sides of the junction having equal and opposite charges. Evaluate the capacitance per unit area of the junction.
5. Repeat Problem 4 for silicon, whose dielectric constant is $12\epsilon_0$.
6. Using the rectifier equation, determine the differential resistance of a 1 mm$^2$ p-n junction of Ge (Problem 4) under a condition of forward bias at 0.25 volt. Take the recombination times $\tau_e = \tau_h = 10^{-6}$ s. Compare the answer with the resistance of an intrinsic sample of the same length as the depletion layer of the junction.
7. Draw the energy-band diagram for the p-n-p transistor at equilibrium. Plot the hole concentration versus the position along the length of the structure.
8. Repeat Problem 7 with the appropriate biases applied to the transistor.
9. Derive Eq. (7.38) for the voltage gain in a junction transistor.
10. Derive Eq. (7.39) for the power gain in a junction transistor.
11. Describe the operation of an n-p-n transistor, and derive expressions for the voltage and power gains in such a structure.
12. Read the description of the operation of the field-effect transistor given in Sze (1969). Summarize the physical processes involved and the characteristics of this device.
13. Estimate the dopings required for the operation of a GaAs tunnel diode. Take \( n_d = n_a \), and assume that tunneling becomes appreciable when the horizontal distance of the energy gap becomes 75 Å. You may employ the results developed in Section 7.3.

14. a) Using the continuity equation and Poisson’s equation, show that an excess localized charge in a semiconductor decays in time according to the equation
\[ \Delta \rho(t) = \Delta \rho(0) e^{-\tau_D}, \]
where \( \tau_D = \varepsilon/\sigma \) is the dielectric relaxation time and \( \Delta \rho(0) \) is the initial excess density.

b) Calculate \( \tau_D \) for GaAs at low field for a carrier concentration of \( 10^{21} \text{ m}^{-3} \).

15. Draw a Cartesian coordinate system in which the abscissa represents the product \( n_0L \) and the ordinate the product \( vL \). Mark the various regions in this plane corresponding to the Gunn mode and the LSA mode in GaAs.

16. Look up the derivation of (7.61) for the threshold current in an injection laser (Sze, 1969).

17. The lasing operation in a semiconductor laser may be influenced by several factors, such as temperature, pressure, magnetic field, etc. These effects are summarized in Chapter 10 of Pankove (1971). Read this chapter and give a brief summary.

18. Various procedures for population inversion in semiconductor lasers have been employed in addition to the injection technique in a \( p-n \) junction. Read the review of these procedures given in Pankove (1971), and give a brief summary of the results, including diagrams of experimental setups.
CHAPTER 8 DIELECTRIC AND OPTICAL PROPERTIES OF SOLIDS

8.1 Introduction
8.2 Review of basic formulas
8.3 The dielectric constant and polarizability; the local field
8.4 Sources of polarizability
8.5 Dipolar polarizability
8.6 Dipolar dispersion
8.7 Dipolar polarization in solids
8.8 Ionic polarizability
8.9 Electronic polarizability
8.10 Piezoelectricity
8.11 Ferroelectricity

When life is true to the poles of nature, the streams of truth will roll through us in songs.

Ralph Waldo Emerson


*Note*: Other relevant review articles in this volume are by M. Cordona, E. J. Johnson, J. O. Dimmock, H. Y. Fan, B. O. Seraphin, and H. E. Bennet.


**Piezoelectricity and ferroelectricity**


**QUESTIONS**

1. Let $A$ and $B$ refer to two different atoms. Using symmetry arguments, determine whether the following types of molecules are dipolar or not: $AA$, $AB$, $ABA$ (rectilinear arrangement), $ABA$ (triangular arrangement), $AB_3$ (planar arrangement with $A$ at center of triangle), $AB_4$ (tetrahedral arrangement). Give one example of each type.

2. The static dielectric constant of water is 81, and its index of refraction 1.33. What is the percentage contribution of ionic polarizability?

3. For a typical atom, estimate the field required to displace the nucleus by a distance equal to 1\% of the radius. [Refer to Eq. (8.79).]

4. Explain physically why ionic polarizability is rather insensitive to temperature. Do you expect a slight change in temperature to lead to an increase or a decrease in the polarizability as $T$ rises? Explain.

5. Referring to Table 6.4, one notes that the polarizabilities of the alkali ions are consistently lower than those of the halide ions. Give a physical, i.e., qualitative, explanation of this fact.

6. In the classical treatment of electronic ac polarizability, the restoring force on the electron is assumed to have a harmonic form. How do you justify this in view of the fact that the force due to the nucleus has a coulomb form which is very different from the harmonic form? Give an expression for the natural frequency $\omega_0$ in terms of the properties of the atom.

7. If one sets $\omega_0$ equal to zero in (8.85), one obtains the same electron dielectric constant found in Section 4.11. Explain why.
8. Suppose that a light beam passing through a semiconductor is absorbed either by
electrons excited from the valence band to the conduction band (fundamental
absorption), or by excitons. Describe an experimental electrical procedure for testing
which of these two mechanisms is the operative one.

PROBLEMS

1. Using Coulomb's law, derive the expression (8.2) for the field of an electric dipole.
Assume that \( d \ll r \).

2. a) Derive Eq. (8.3), that is, show that the torque exerted on a dipole \( \mathbf{p} \) by a uniform
field \( \mathbf{\boldsymbol{\mathcal{E}}} \) is given by

\[
\mathbf{\tau} = \mathbf{p} \times \mathbf{\boldsymbol{\mathcal{E}}}.
\]

b) Derive Eq. (8.4), that is, show that the potential energy of a dipole in a field is
given by

\[
V = -p \mathbf{\boldsymbol{\mathcal{E}}} \cos \theta,
\]

where \( \theta \) is the angle between the dipole and the field.

3. The dipole moment for a general distribution of charges is defined as the sum

\[
\mathbf{p} = \sum_i q_i \mathbf{r}_i,
\]

where \( q_i \) and \( r_i \) are the charge and position, respectively, of the \( i^{th} \) charge, and the
summation is over all the charges present. The choice of the origin of coordinates is
arbitrary.

a) Show that the above reduces to expression (8.1) for the special case of two equal
and opposite charges. (Take an arbitrary origin.)

b) Prove that if the charge system has an overall electrical neutrality, then the dipole
moment is independent of the choice of origin.

4. Determine the dipole moment for the following charge distributions: 1.5 \( \mu \)coul each at
the points (0,3), (0,5), where the coordinate numbers are given in centimeters.

5. A parallel-plate capacitor of area \( 4 \times 5 \) cm\(^2\) is filled with mica \( (\varepsilon_r = 6) \). The
distance between the plates is 1 cm, and the capacitor is connected to a 100-V battery.
Calculate:

a) The capacitance of this capacitor
b) The free charge on the plates

\( c) \) The surface charge density due to the polarization charges
d) The field inside the mica. (What would the field be if the mica sheet were
withdrawn?)

6. Prove that when a molecule is polarized by a field \( \mathbf{\boldsymbol{\mathcal{E}}} \), a potential energy is stored in this
molecule. The value of this energy is \( \frac{1}{2} \alpha \mathbf{\boldsymbol{\mathcal{E}}}^2 \), where \( \alpha \) is the molecular polarizability.

What is the value of this energy for an Ar atom in a field of \( 10^3 \) volt/m? The
polarizability of this atom is \( 1.74 \times 10^{-40} \) farad-m\(^2\).

7. a) Show that the surface charge density of the polarization charges on the outer
surface of a dielectric is given by

\[
\sigma_p = \mathbf{P} \cdot \mathbf{\hat{n}},
\]

where \( \mathbf{\hat{n}} \) is a unit vector normal to the surface.
b) Prove Eq. (8.25). That is, show that the depolarization field in an infinite slab, in which the field is normal to the slab, is given by

$$E_1 = -\frac{1}{\varepsilon_0} P.$$

c) The depolarization field $E_1$ depends on the geometrical shape of the specimen. When the shape is such that the polarization inside is uniform, the depolarization factor $L$ is defined such that

$$E_1 = -\frac{L}{\varepsilon_0} P.$$

Show that the depolarization factor for an infinite slab with field normal to the slab is 1, while for a slab in which the field is parallel to the face, $L = 0$. Also show that $L = \frac{1}{2}$ for a sphere, and $L = 0$ or $\frac{1}{2}$ for a cylinder, depending on whether the field is parallel or normal to the axis of the cylinder, respectively. Put these results in tabular form.

8. a) Prove Eq. (8.28), showing that the field $E_3$ due to the dipoles inside a spherical cavity vanishes in a cubic crystal.

b) Suppose that the Lorentz cavity is chosen to have a cubic shape. Calculate the field $E_2$ due to the charges on the surface of this cavity.

c) Does this new choice of cavity modify the value of the local field? Explain. Use your answer to evaluate the field $E_3$ due to the dipoles inside the cavity. (You may take the crystal to be cubic.)

9. The field $E_3$ of Eq. (8.24) due to the dipole inside a cavity depends on the symmetry of the crystal, and in general does not vanish in a noncubic crystal. Assuming that this field has the form

$$E_3 = \frac{b}{\varepsilon_0} P,$$

where $b$ is a constant, calculate the dielectric constant $\varepsilon_r$ in such a substance.

10. Show that Eq. (8.33) reduces to (8.18) in gaseous substances, i.e., substances in which $N\alpha/\varepsilon_0$ is very small.

11. Establish Eq. (8.40) by carrying out the necessary integration.

12. a) Expand the Langevin function $L(u)$ of (8.41) in powers of $u$ up to and including the third power in $u$, and show that

$$L(u) = u/3 - u^2/45 + \cdots, \quad u \ll 1.$$

b) Calculate the field required to produce polarization in water equal to 10% of the saturation value at room temperature.

13. a) Using Fig. 8.13 and Table 8.1, calculate the molecular concentration of CHCl₃, CH₂Cl₂, and CH₃Cl at which the measurements reported in the figure were made.

b) Calculate the electronic-ionic polarizability $\alpha_{ei}$ in each of these substances.

14. The molar polarizability of water increases from $4 \times 10^{-5}$ to $6.8 \times 10^{-5}$ m³ as the temperature decreases from 500°K to 300°K. Calculate the permanent moment of the water molecule.

15. Calculate the real and imaginary parts of the dielectric constant $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ for water at room temperature. Plot these quantities versus $\omega$ up to the frequency $10^{12}$ Hz. (Use semilogarithmic graph paper.)
16. We expressed the absorption in dipolar substances in terms of the imaginary dielectric constant, \( \varepsilon''(\omega) \). It is also frequently expressed in terms of the so-called loss angle \( \delta \), which is defined as
\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'},
\]
where the quantity \( \tan \delta \) is called the loss tangent.

a) Show that the electric displacement vector is
\[
D = \varepsilon_0 [\varepsilon'_r + \varepsilon''_r]^{1/2} e^{i\delta} \mathbf{E}.
\]

b) Calculate the loss tangent as a function of the frequency, and plot the result versus \( \omega \).

c) Show that the power absorbed by a dielectric (per unit volume) is
\[
Q = \frac{1}{2} \varepsilon_0 \varepsilon_r \omega \tan \delta \mathbf{E}^2.
\]
Express the loss angle \( \tan \delta \) in terms of the ratio of the dissipated energy to the energy stored in the dielectric.

d) Calculate the loss tangent in water at room temperature at frequency 10 GHz. Also calculate the energy dissipated per unit volume, given that the field strength is 5 volts/m.

17. Assuming that the jumping period \( \tau \) decreases exponentially with temperature as in (8.73), explain how the real and imaginary parts of the dielectric constant \( \varepsilon'_r \) and \( \varepsilon''_r \) vary with temperature. Plot the results versus \( 1/T \). (Assume that all quantities other than \( \tau \) are independent of temperature.) Does the loss tangent increase or decrease with temperature? Explain.

18. In deriving the result (8.74) for the dielectric constant involving ionic polarizability, it was assumed that the ions experience no collision or loss during their motion. Postulate the existence of a collision mechanism whose time is \( \tau_c \), and reevaluate the (complex) dielectric constant. Plot the real and imaginary parts \( \varepsilon'_r(\omega), \varepsilon''_r(\omega) \) versus \( \omega \), and compare with Fig. 8.20.

19. The crystal NaCl has a static dielectric constant \( \varepsilon_r(0) = 5.6 \) and an optical index of refraction \( n = 1.5 \).

a) What is the reason for the difference between \( \varepsilon_r(0) \) and \( n^2 \)?

b) Calculate the percentage contribution of the ionic polarizability.

c) Use the optical phonon for NaCl quoted in Table 3.3, and plot the dielectric constant versus the frequency, in the frequency range 0.1 \( \omega_s \) to 10 \( \omega_s \).

20. Using the data in the previous problem and Table 8.4, calculate the nearest distance between Na and Cl atoms. Calculate the lattice constant of NaCl, and compare the result with the value quoted in Table 1.2. (Sodium chloride has an fcc structure.)

21. Calculate the static polarizability for the hydrogen atom, assuming that the charge on the electron is distributed uniformly throughout a sphere of a Bohr radius. Also calculate the natural electron frequency \( \omega_0 \).

22. Show that expression (8.80) leads to a static susceptibility equal to that given by (8.77). Use elementary electrostatic arguments to find \( \omega_0 \) in terms of atomic characteristics.
23. Modify expression (8.80) for the electronic polarizability to include the presence of a collision mechanism of time \( \tau \). Evaluate the high-frequency dielectric constant, both real and imaginary parts.

24. Carry out the steps leading to the expression (8.86) for \( \varepsilon''(\omega) \) due to interband transition in solids.

25. The Kramers-Kronig relations, which lead to (8.88), are derived in Brown (1966). Read the discussion there and present your own summary.

26. a) An acoustic oscillator is made of a quartz rod. Explain why the resonant frequency of this oscillator is given by

\[
y = \frac{v_s}{2l},
\]

where \( l \) is the length of the rod and \( v_s \) the velocity of sound in the specimen.

b) Show that this frequency is also given by the expression

\[
y = \frac{1}{2l} \sqrt{\frac{Y}{\rho}},
\]

where \( Y \) is Young's modulus and \( \rho \) the mass density of the rod.

c) Taking \( Y = 8.0 \times 10^{11} \) dyne/cm\(^2\) and \( \rho = 2.6 \) g/cm\(^3\) for quartz, calculate the length of a 5-kHz-oscillator.

d) Calculate the potential difference across the rod for a strain of \( 2 \times 10^{-8} \). The piezoelectric coefficient \( P/S = 0.17 \) coul/m\(^2\).

27. Many applications of piezoelectric crystals are discussed in Mason (1950). Make a summary of these.

28. In evaluating the local field correction in (8.97), we neglected the electronic contribution. Reevaluate the correction including this contribution, and calculate the new optical phonon frequency \( \omega_l^* \) and the dielectric constant.

29. A dielectric has a very small electrical conductivity. However, if a very strong electric field is applied, the conductivity suddenly increases as the field reaches a certain high value. This phenomenon, known as dielectric breakdown, is due to the fact that a strong field ionizes the electrons from their atoms, and as these electrons are accelerated they ionize other atoms, etc. Read the discussion of dielectric breakdown presented in N. F. Mott and R. W. Gurney (1953), Electronic Processes in Ionic Crystals, second edition, Oxford University Press, and write your own review of this phenomenon.

30. The discussion of dielectric and optical properties in the text was limited to the linear region, i.e., the field is sufficiently small that polarization is a linear function of the field. Nonlinear effects become important at high fields, which are now conveniently available from laser sources. Read the discussion of such effects given in A. Yariv (1971), Introduction to Optical Electronics, Holt, Rinehart, and Winston, and write a brief summary.
CHAPTER 9 MAGNETISM AND MAGNETIC RESONANCES

9.1 Introduction
9.2 Review of basic formulas
9.3 Magnetic susceptibility
9.4 Classification of materials
9.5 Langevin diamagnetism
9.6 Paramagnetism
9.7 Magnetism in metals
9.8 Ferromagnetism in insulators
9.9 Antiferromagnetism and ferrimagnetism
9.10 Ferromagnetism in metals
9.11 Ferromagnetic domains
9.12 Paramagnetic resonance; the maser
9.13 Nuclear magnetic resonance
9.14 Ferromagnetic resonance; spin waves

Where order in variety we see,
    and where, though all things differ, all agree.

    Alexander Pope
QUESTIONS

1. The text stated that the diamagnetic response associated with the orbital motion of atomic electrons can be predicted on the basis of Lenz's law. Prove this statement.

2. Do you expect the constant $\lambda$ in (9.30) describing the susceptibility of the covalent bond to be positive or negative? Why?

3. Given that the total angular momentum quantum number $j$ for an atom is $j = \frac{1}{2}$, does this necessarily mean that the angular momentum is pure spin, and hence $g = 2$? Illustrate your answer with an example.

4. You may have realized, after reading Section 9.6, that the formula for paramagnetic susceptibility is valid only if one considers the ground state of the atom. But other excited atomic levels are also present. Explain the following.

a) Why is it usually permissible to disregard these higher levels when calculating the susceptibility?

b) How you would modify Eq. (9.42), or the original formula from which it is derived, if the temperature were high enough for some of the excited levels to be appreciably populated?

5. Given that the precession frequency due to spin–orbit interaction is 10 GHz, estimate the effective magnetic field experienced by the spin moment as a result of this interaction.

6. Referring to Questions 4 and 5, estimate the temperature above which the simple formula (9.42) breaks down for the strength of spin–orbit interaction given in Question 5.

7. Give a sufficient condition for the existence of paramagnetic susceptibility in terms of the number of electrons in the atom (or ion).

8. The spin paramagnetic susceptibility of conduction electrons is given in (9.47). What is its value for a full band? Is the answer surprising? Explain.

9. Neither Mn nor Cr are ferromagnetic by themselves, yet some of their alloys (with other elements) are. Explain how this may be possible. Refer to Fig. 9.17.

10. Solid-state theorists often conjecture that any spin system would eventually become ferromagnetic at sufficiently low temperature. Can you justify this conjecture in light of the discussion in Section 9.8? Given that the dipole–dipole electrostatic interaction is the one responsible for such a ferromagnetic transition, estimate the Curie temperature. (How would you account for the fact that only relatively few spin systems are observed in the ferromagnetic phase, even at very low temperatures?)
11. Can the domain structure in a ferromagnetic substance be detected by x-ray diffraction? By neutron diffraction?

12. Equation (9.80) shows that \( \chi'' \) decreases as the strength of the signal is increased, a phenomenon known as saturation. Explain the physical origin of this phenomenon. 

*Hint*: Think of \( \chi'' \) as it relates to the rate of absorption. Also note that the quantum picture of the EPR is more helpful in explaining this phenomenon than the classical picture.

13. Explain why the condition \( \tau_1 \tau_2 (\gamma b_0)^2 \ll 1 \) is necessary for the observation of EPR. Refer to Eqs. (9.78).


15. The condition of population inversion in a maser is often stated by ascribing a negative absolute temperature (\(!\)) to the system. Explain why this is meaningful; refer to Eq. (9.83). Calculate the temperature of the system, given that \( \Delta E = 1 \) GHz and \( N_2 / N_1 = 2 \).

16. Is the nuclear factor \( g_\text{n} \) positive or negative for the nucleus illustrated in Fig. 9.39?

17. The neutron has a magnetic moment (Table 9.10), and yet this particle is electrically neutral. Does the existence of this moment puzzle you? Explain. Also discuss how such a moment may be possible if one endows the neutron with a submicroscopic structure.

18. What is the precise physical meaning of the word adiabatic in connection with the technique of cooling by adiabatic demagnetization? Why are nuclear rather than electron spins used at very low temperatures?

19. The NMR technique is most useful in organic chemistry, due to the proton resonance of hydrogen. What are the two other commonest elements in this field of chemistry, and why are they not usually useful in NMR?

20. Another standard technique for observing ferromagnetic substances is by using a polarizing microscope. If a thin section is cut off the substance, and the plane of the section is normal to the easy-axis direction, then, when one adjusts the polarizing filter on the microscope, half the domains appear bright and the other half dark. Explain why.

21. Using the fact that the specific heat of the spin system is \( C \sim T^{3/2} \) at low temperature, give a physical derivation for the dependence of the magnon density of states \( g(\omega) \) on \( \omega \) in the long-wavelength region. Compare your result with the answer given in Problem 25.

**PROBLEMS**

1. Prove the validity of Eqs. (9.3) and (9.4).

2. Establish the result (9.6).

3. a) Prove the Larmor theorem, i.e., that a classical dipole \( \mu \) in a magnetic field \( \mathbf{B} \) precesses around the field with a frequency equal to the Larmor frequency \( \omega_L = eB/2m \).

b) Evaluate the Larmor frequency, in hertz, for the orbital moment of the electron in a field \( B = 1 \) W/m

There is a missing part for c) What is the precession frequency for a spin dipole moment in the same field?
4. The diamagnetic susceptibility due to the ion cores in metallic copper is \(-0.20 \times 10^{-6}\). Knowing that the density of Cu is 8.93 g/cm\(^3\) and that its atomic weight is 63.5, calculate the average radius of the Cu ion.

5. a) The susceptibility of Ge is \(-0.8 \times 10^{-5}\). Taking the radius of the ion core to be 0.44 Å, estimate the percentage of the contribution of the covalent bond to the susceptibility. Germanium has a density of 5.38 g/cm\(^3\) and an atomic weight of 72.6.

b) Given that the applied field is \(\mathcal{H} = 5 \times 10^4\) amp \(\cdot\) m\(^{-1}\), calculate the magnetization in Ge; also the magnetic induction.

6. A system of spins \((j = s = \frac{1}{2})\) is placed in a magnetic field \(\mathcal{H} = 5 \times 10^4\) amp \(\cdot\) m.

   a) The fraction of spins parallel to the field at room temperature \((T = 300^\circ K)\).
   b) The average component of the dipole moment along the field at this temperature.
   c) Calculate the field for which \(\mu_z = \frac{1}{2} \mu_B\).
   d) Repeat parts (a) and (b) at the very low temperature of 1\(^\circ\)K.

7. Establish the result (9.42) for an arbitrary value of \(j\). (This result is derived under the condition \(\mu_B B \ll kT\).) Estimate the field below which the result is valid at room temperature.

8. Prove that the average dipole moment of an atom, including the effect of the spin–orbit interaction, is given by \(\mu_{\text{avg}} = g(-e/2m)J\), where the Lande factor \(g\) is given by (9.45).

9. Verify the theoretical values of \(p\) given in the third column in Table 9.3.

10. Repeat Problem 9 for the third and fourth columns in Table 9.4.

11. a) The spin susceptibility of conduction electrons at \(T = 0^\circ\)K is given in Eq. (9.47). Express this result in terms of the electron concentration for an energy band of standard form.

   b) Calculate the spin susceptibility for K, whose density is 0.87 g/cm\(^3\) and whose atomic weight is 39.1.

   c) Calculate the diamagnetic susceptibility of the conduction electrons in K.

   d) Using the above results and Table 9.5, calculate the average radius of the K ion in the metallic state.

12. Iron has a bcc structure with a lattice constant \(a = 2.86\) Å.

   a) Using the value of the saturation magnetization in Table 9.6, show that the dipole moment of an Fe atom is equal to 2.22 \(\mu_B\). The density of Fe is 7.92 g/cm\(^3\), and its atomic weight is 55.6. (You may assume, for the present purpose, that the 3d electrons are completely localized.)

   b) Calculate the Weiss exchange constant \(\lambda\) and the molecular field in iron.

   c) Evaluate the Curie constant in iron.

   d) Estimate the exchange energy for a dipole interacting with its nearest neighbors.

13. Repeat Problem 12 for Co (hcp, \(a = 2.51\), \(c = 4.1\) Å), and Ni (hcp, \(a = 2.66\), \(c = 4.29\) Å). The densities of Co and Ni are 8.67 and 9.04 g/cm\(^3\), respectively.

14. a) Applying the Weiss model, with two exchange constants \(\lambda_1\) and \(\lambda_2\), to an anti-
ferromagnetic substance, derive the Néel formula for the susceptibility at high temperature [Eq. (9.59)].

b) Evaluate the exchange constants $\lambda_1$ and $\lambda_2$ for MnF$_2$.

c) Explain why $\lambda_2 > \lambda_1$.

15. Carry out the steps leading to Eq. (9.72).

16. a) Discuss the splitting of a Cr$^{3+}$ ion in a static magnetic field.

b) Calculate the field for which the electron resonance for this ion occurs at 10 GHz.

17. Solve the Bloch equations (9.66) and (9.67) in the presence of a static field $B_0$ but in the absence of the signal, and show that the magnetization spirals toward its equilibrium value as described in Fig. 9.33. Take the initial angle between magnetization and the field to be $10^\circ$, the longitudinal and transverse time to be $10^{-6}$ and $5 \times 10^{-7}$ s, respectively, and plot the longitudinal and transverse components of the magnetization versus time, in the interval $0 < t < 5 \times 10^{-6}$ s.

18. Carry out the steps leading to Eq. (9.78).

19. Nuclear magnetic resonance in water is due to the protons of hydrogen.

a) Find the field necessary to produce NMR at 60 MHz.

b) Find the maximum power absorbed per unit volume, given that the strength of the signal is such that $\tau_1 \tau_2 \gamma^2 b_0^2 = 1$ and $\tau_1 = \tau_2 = 3 \text{s}$.

20. Carry out the steps leading to (9.100).

21. Many microwave magnetic devices are discussed in Lax and Button (1962). Make a brief study of these devices, and present a review report.

22. The text said that spin waves are modes which describe the collective excitations of a spin system. It also pointed out the close analogy between spin waves (magnons) and lattice waves (phonons). What is the spin mode of excitation analogous to the Einstein mode in the lattice? That is, what are the localized spin excitation modes? Assuming that these are the only modes of excitation possible (which is incorrect), calculate the magnetization and spin specific heat for the system as functions of the temperature.

23. Discuss why spin waves are more favorable as modes of excitation than local spin modes, particularly at low temperatures.

24. Determine the expressions for the phase and group velocities of spin waves. Calculate the group velocity in iron at wavelength $\lambda = 1 \text{cm}$. (Use results of Problem 12.)

25. Show that the magnon density of states $g(\omega)$ in the long-wavelength limit is given by $g(\omega) = (\frac{1}{3} \pi^2) (\hbar / J' a^2)^{3/2} \times \omega^{1/2}$.

26. Many ferromagnetic, ferrimagnetic, and antiferromagnetic substances, such as the oxides and chalcogenides of the 3d transition metals, exhibit a small amount of electrical conductivity, i.e., they are semiconductors. Although we have not discussed this subject here, it is a lively area of research today and is reviewed in depth in J. P. Suchet, 1971, *Crystal Chemistry and Semiconduction*, New York: Academic Press. Study the highlights of this book and write a review report.
CHAPTER 10  SUPERCONDUCTIVITY

10.1 Introduction
10.2 Zero resistance
10.3 Perfect diamagnetism, or the Meissner effect
10.4 The critical field
10.5 Thermodynamics of the superconducting transition
10.6 Electrodynamics of superconductors
10.7 Theory of superconductivity
10.8 Tunneling and the Josephson effect
10.9 Miscellaneous topics

Take her up tenderly,
Lift her with care;
Fashion'd so slenderly
Young, and so fair!

Thomas Hood
QUESTIONS

1. What is the expected composition of a ZrNb alloy which has the highest $T_c$? Answer the same question for a NbSn alloy.

2. It was stated, following Eq. (10.12) that the critical field $H_c(0)$ is essentially proportional to the critical temperature $T_c$. (This will also be confirmed by your plot in Problem 3.) Yet the electron concentration $n$ also appears in (10.12), and this concentration differs from one superconductor to another. Why does the linear relationship still hold, nonetheless?

3. Discuss at least two different experimental methods for determining the critical temperature of a superconductor.

4. Experiments show that even though a superconductor exhibits zero static resistance, its ac resistance is finite, albeit very small. Explain how this is possible. [Hint: Use the two-fluid model. An electric circuit representation is also useful.]

5. Derive Eq. (10.29) for the surface current in a superconductor.

6. A footnote in Section 10.5 said that the gap $\Delta(T)$ decreases with temperature because of the collective nature of the superconducting transition. Explain this point more fully, relying on the concept of the Cooper pair.

7. Is the superconductor–normal junction of Fig. 10.19(a) electrically symmetric, or not?

8. A cylinder in the intermediate state is shown in Fig. 10.21(b). Describe one experimental electrical method for distinguishing this state from the superconducting state shown in Fig. 10.21(a).

PROBLEMS

1. Consider a lead solenoid wound around a doughnut-shaped tube. The total number of turns is 2500, and the diameter of the lead wire is 30 cm. The solenoid is cooled below the critical point, at which an electric current is induced in the coil. Assuming the lead resistivity in the superconducting state to be less than $10^{-25}$ ohm-m, calculate the minimum time interval needed for the current to damp out by 0.01%. (Assume the length of the wire to be sufficiently large for the infinite-length approximation to hold.)

2. a) Figure 10.7 indicates a discontinuity in specific heat at the transition point as the substance becomes superconducting. The size of the discontinuity can be calculated using a thermodynamical argument. Show that the size of the
Problems 525

The discontinuity per mole is given by

\[ C_s - C_n = V_m T_c \left( \frac{\partial \mathcal{H}_c}{\partial T} \right)_{T_c}^2, \]

where \( V_m \) is the molar volume.

b) Calculate this difference for tin, and compare your answer with the value given in Figure 10.7. The density and atomic weight of tin are 7.0 g/cm\(^2\) and 119, respectively. [Hint: In part (a), recall that

\[ C = T \frac{\partial S}{\partial T} \quad \text{and} \quad S = - \frac{\partial E}{\partial T}, \]

where \( S \) is the entropy and \( E \) the free energy of the system.]

3. Plot \( \mathcal{H}_c(0) \) versus \( T_c \) for a few superconductors using data from Tables 10.1 and 10.2, and verify the linear relationship predicted in Eq. (10.12).

4. The superconducting gap \( \Delta(T) \) decreases with temperature, as indicated in Fig. 10.12. The BCS theory shows that this decrease is given by \( \Delta(T)/\Delta_0 = \tanh (T/\Delta_0)/T \Delta_0 \), for \( T < T_c \). Using this relation and Table 10.4, plot \( \Delta(T) \) versus \( T \) for tin, in the range \( 0 < T < T_c \).

5. Section 10.5 said that the exponential behavior of the specific heat (10.5) implies the existence of an energy gap. This can be seen most readily by calculating the specific heat of an intrinsic semiconductor, in which the gap plays a very important role. Carry out this calculation, and establish the exponential behavior indicated above.

6. The London equation (10.21) is equivalent to the condition of perfect diamagnetism of a superconductor. A basic (and controversial) question often arises: Which is the more electrodynamic property of a superconductor, perfect conductivity or perfect diamagnetism? By this we mean: Does one of these two properties imply the other, or are they independent? Answer this question. [Hint: Note that the electric field and magnetic induction are related to each other by the Maxwell equations, in particular, \( \mathbf{E} = - \nabla \phi/\partial t \) and \( \mathbf{B} = \nabla \times \mathbf{A} \), where \( \mathbf{A} \) is the vector potential.]

7. Prove that the magnetic flux linking a superconducting ring is quantized according to \( \Phi = n(\hbar/2e) \), where \( \Phi \) is the flux and \( n \) an integer. This quantization was predicted by F. London (1950), and verified experimentally in 1961. [Hint: Use the Wilson-Sommerfeld quantization condition,\(^\dagger\) and take the path of integration in the interior of the ring. Recall also that the momentum of an electron in a magnetic field is given by \( p = m v + e A \).] (The quantization formula given by London was actually erroneous in one respect, because the concept of the Cooper pair was unknown in 1950. What do you expect the original London formula to have been?)

8. Discuss the Josephson tunneling current, given that, in addition to the static bias, an alternating voltage is also impressed across the junction. Enumerate the frequencies of the various modes of excitation.

\(^\dagger\) This condition is \( \oint \mathbf{p} \cdot d\mathbf{q} = nh \), where \( n \) is an integer, and \( q_i \) and \( p_i \) are a coordinate and its conjugate momentum. Thus the Bohr condition for quantizing the angular momentum, \( L = nh \), can be obtained from the integral by taking \( q_i = \theta \) and \( p_i = L \), where \( \theta \) is the angle and \( L \) the angular momentum.
9. The coherence length $\xi$ of a superelectron, which is the spatial extension of a super-electron (or of a Cooper pair), may be viewed as the quantum uncertainty in the position resulting from the uncertainty in the electron energy. Estimate the value of this coherence length for a typical superconductor.

10. Applications of superconductivity to the design of technical devices, including superconducting magnets, are discussed in Newhouse (1964) and Williams (1970). Study the highlights of these books and write a brief report.
CHAPTER 11 TOPICS IN METALLURGY AND DEFECTS IN SOLIDS

11.1 Introduction
11.2 Types of imperfections
11.3 Vacancies
11.4 Diffusion
11.5 Metallic alloys
11.6 Dislocations and the mechanical strength of metals
11.7 Ionic conductivity
11.8 The photographic process
11.9 Radiation damage in solids

*Truth is never pure, and rarely simple.*

Oscar Wilde
Dislocations
J. Friedel, 1964, Dislocations, Reading, Mass.: Addison-Wesley

Ionic conductivity: the photographic process

Radiation damage

QUESTIONS
1. The text said that vacancy concentration is normally measured in quenched samples, at room temperature.
   a) Why is it necessary to quench the sample, rather than to cook it slowly?
   b) Is the quenched sample in thermal equilibrium?
   c) If the vacancies in a quenched sample are annealed out under adiabatic conditions, will the solid heat up or cool down? And by how much?
2. What is the justification for calling Eq. (11.16) the "lever formula?"
3. What is the meaning of the fact that the solidus and liquidus lines in the phase diagram converge at the endpoints?

PROBLEMS
1. a) Calculate the atomic percentages of interstitials and vacancies at the melting point in Cu (1356°K). The formation energies for these defects in Cu are, respectively, 4.5 and 1.5 eV.
   b) Repeat the calculations at room temperature.
2. Verify that expression 11.7 satisfies both Fick's second law (11.6) and the initial conditions of the problem.
3. a) Carry out the integrations leading to the diffusion distance (11.8).
   b) Calculate the diffusion velocity, and explain physically why this velocity decreases in time, as it does.
4. The text estimated that an atom in a crystal diffuses a distance of about $1\mu$ in two years, if the lattice constant $d = 1\AA$ and the jump frequency is $1\text{ s}$. Estimate the distance the atom would travel in the same time interval if the atom were able to jump always in the same direction, e.g., to the right.

5. Other solutions to Fick's second law, besides the one reported in the text, are frequently quoted in the literature. These solutions correspond to boundary conditions different from those chosen here. Verify that the expression

$$c(x, t) = \frac{c_0}{2} \left[ 1 - \frac{2}{\sqrt{\pi}} \int_0^{x/2(Dt)^{1/2}} e^{-u^2} du \right]$$

is also a solution of Fick's law corresponding to the following initial conditions: $c(x,0) = c_0$, for $x < 0$, and $= 0$ for $0 < x$. Plot $c(x, t)$ versus $x$ at various instants $(0 < t)$, and show that $c(0, t) = \frac{1}{2}$ at all times. [The term in the brackets involving the integral is known as the error function, and denoted by erf $(x/2(Dt)^{1/2})$.]

6. The diffusion activation energy of carbon in $\gamma$-iron (austenite) is $3.38 \times 10^4 \text{ cal/mole}$, and $D_0 = 0.21 \text{ cm}^2/\text{sec}$. Calculate the diffusion coefficient at 800°C and 1100°C.

7. The carburizing of steel is accomplished by placing iron in a carbon-rich atmosphere, and allowing sufficient time for the carbon atoms to diffuse through the solid. If you want to achieve a carbon concentration of 1% (in weight) at a depth of $3 \text{ mm}$ after 10 hours of carburizing time at 1200°C, calculate the carbon concentration in weight per cent which must be maintained at the surface. Take the iron to be in the $\gamma$-phase, and use the data of Problem 6. [Hint: Use the solution given in Problem 5.]

8. The atomic size factor favors solid solubility for the following alloys. What is the effect of the relative valency factor in each case?

9. a) Construct the phase diagram for the Cu-Ni alloy, using the following data (Moffat, 1964).

<table>
<thead>
<tr>
<th>Weight% Ni</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquidus $T$</td>
<td>1083</td>
<td>1195</td>
<td>1275</td>
<td>1345</td>
<td>1410</td>
<td>1453</td>
</tr>
<tr>
<td>Solidus $T$</td>
<td>1083</td>
<td>1135</td>
<td>1205</td>
<td>1290</td>
<td>1375</td>
<td>1453</td>
</tr>
</tbody>
</table>

b) Starting with a liquid alloy of $60\%$ Ni and cooling it gradually, state the composition of the solid that forms first.

c) How much solid per kilogram can be extracted from the melt at $1300\text{°C}$?

10. Establish the validity of Eq. (11.20) for the free energy.

11. Find the derivative of the mixing entropy $(\partial S/\partial c)$, and show that it is infinite at $c = 0$.

12. Referring to Fig. 11.13(a), show that the free energy for a phase mixture (where the concentrations of the phases are given by $c'$ and $c''$) is given by the straight line $F' F''$ in the average concentration range $c'' < c < c'$.

13. Prove the lever formula for a phase mixture whose free-energy diagram has the shape shown in Fig. 11.13(b).
14. Confirm that the free-energy diagrams of Figs. 11.15(a)–11.15(d) lead to the phase diagram 11.15(f). Indicate on this latter figure suitable values for the temperatures $T$, $T'$, $T''$, and $T'''$ indicated in the former figures.

15. The phase diagram for the Cu-Ag alloy is shown in Fig. 11.15(f).
   a) Confirm that the atomic % and weight % scales indicated are consistent with each other.
   b) Determine the atomic percentage of the $\alpha$-phase at the eutectic concentration just after solidification.
   c) Determine the percentage of the same phase at the temperature 850°C, and the Cu concentration in atomic %.

16. a) Starting with a Cu-Ag alloy in the liquid phase and 60% weight Cu, indicate the various phases which appear as the system is cooled progressively from the liquid to the solid phase.
   b) What is the weight fraction of the $\beta$ phase at 850°C?

17. Prove that the Fermi surface begins to touch the boundaries of the Brillouin zone in the fcc and bcc structures when the electron/atom ratios are 1.36 and 1.48, respectively. [Refer to Fig. 5.8.]

18. Show that the shear strain on any crystal plane vanishes if the solid is placed under hydrostatic pressure.

19. a) Show that in an fcc lattice the (111) planes have the highest atomic concentration.
   b) Show that the $[100]$ direction in the (111) plane has the highest atomic concentration.
CHAPTER 12 MATERIALS AND SOLID-STATE CHEMISTRY

12.1 Introduction
12.2 Amorphous semiconductors
12.3 Liquid crystals
12.4 Polymers
12.5 Nuclear magnetic resonance in chemistry
12.6 Electron spin resonance in chemistry
12.7 Chemical applications of the Mössbauer effect

*Invention breeds invention.*

Ralph Waldo Emerson
QUESTIONs

1. For the magnetic fields used, the magnetic energy is too small compared to the thermal energy, and hence the field does not orient single molecules; yet the field does orient the director. How do you resolve this apparent paradox?
2. Suppose that you prepare a mixture of two cholesteric liquid crystals which rotate the polarization in opposite senses. What is the phase of the product?
3. Could expression (12.8) be valid for a cholesteric liquid crystal? If not, find a plausible expression.
4. Show that the asymmetry parameter $\eta$ (in a Mössbauer effect) vanishes for a solid which has a 3-fold axis of symmetry.

PROBLEMS

1. Read the articles by Adler (1971) and Owen (1970), and write a brief report.
2. Derive expression (12.3) for conductivity.
3. Prove that if the molecules in a nematic phase have random orientations, the order function $S$ vanishes.
4. Plot the intermolecular anisotropic potential in the nematic phase $V_{ij}$ versus the angle $\theta$ between the molecular axes of the two molecules involved, and point out the most favorable orientations.
5. Derive Eq. (12.9) for the orientational magnetic energy density.
6. Derive Eq. (12.11).
7. The molecular weight of a polyethylene molecule is 100,000. What is its length if the length of the C-C bond is 1.54 Å?
8. The monomer isoprene

$$\begin{align*}
\text{H}_2\text{C} = \text{C} - \text{C} = \text{CH}_2 \\
\text{CH}_3 & \quad \text{H}
\end{align*}$$

is the basic unit in natural rubber. Draw the complete molecular structure of rubber. What feature of this structure allows vulcanization to take place (the formation of sulfur cross links between adjacent chains)?
9. The difference in chemical shifts between two protons in a 60-MHz field is 700 Hz. What would be the difference in a 100-MHz field?
10. The proton resonance of a substance dissolved in TMS occurs at $-500$ Hz relative to the standard. Calculate $\delta$ and $\tau$ for the proton.
11. The NMR spectrum of $^{19}\text{F}$ ($I = \frac{1}{2}$) in olefin, $\text{C}_3\text{H}_4\text{F}_2$, consists of two sets of peaks: A doublet of doublets with coupling constants at 45 and 10 Hz, respectively. The other set of peaks consists of a quadruplet with coupling constants of 45 and 8 Hz, respectively.
a) Determine the structure of this compound.
b) Predict the proton NMR spectrum for olefin.

12. The frequency-shift formula (12.33), derived in the text on the basis of the Doppler effect, may also be obtained from the laws of conservation of energy and momentum. Carry out this derivation.