

# Contents

|   |           |
|---|-----------|
| Two Atoms per Primitive Unit Cell                             | 97        |
| Identification of Plane Waves                                 | 101       |
| <b>CHAPTER 1: CRYSTAL STRUCTURE</b>                           | <b>1</b>  |
| Periodic Arrays of Atoms                                      | 3         |
| Lattice Translation Vectors                                   | 4         |
| Basis and the Crystal Structure                               | 5         |
| Primitive Lattice Cell  | 6         |
| Fundamental Types of Lattices                                 | 6         |
| Two-Dimensional Lattice Types                                 | 8         |
| Three-Dimensional Lattice Types                               | 9         |
| Index Systems for Crystal Planes                              | 11        |
| Simple Crystal Structures                                     | 13        |
| Sodium Chloride Structure                                     | 13        |
| Cesium Chloride Structure                                     | 14        |
| Hexagonal Close-Packed Structure (hcp)                        | 15        |
| Diamond Structure   | 16        |
| Cubic Zinc Sulfide Structure                                  | 17        |
| Direct Imaging of Atomic Structure                            | 18        |
| Nonideal Crystal Structures                                   | 18        |
| Random Stacking and Polytypism                                | 19        |
| Crystal Structure Data  | 19        |
| Summary   | 22        |
| Problems  | 22        |
| <b>CHAPTER 2: WAVE DIFFRACTION AND THE RECIPROCAL LATTICE</b> | <b>25</b> |
| Diffraction of Waves by Crystals                              | 27        |
| The Bragg Law   | 27        |
| Scattered Wave Amplitude                                      | 28        |
| Fourier Analysis  | 29        |
| Reciprocal Lattice Vectors                                    | 31        |
| Diffraction Conditions  | 32        |
| Laue Equations  | 34        |
| Brillouin Zones   | 35        |
| Reciprocal Lattice to sc Lattice                              | 36        |
| Reciprocal Lattice to bcc Lattice                             | 38        |
| Reciprocal Lattice to fcc Lattice                             | 39        |

|   |           |
|---|-----------|
| Fourier Analysis of the Basis                           | 41        |
| Structure Factor of the bcc Lattice                     | 42        |
| Structure Factor of the fcc Lattice                     | 42        |
| Atomic Form Factor                                      | 43        |
| Summary   | 45        |
| Problems  | 45        |
| <b>CHAPTER 3: CRYSTAL BINDING AND ELASTIC CONSTANTS</b> | <b>49</b> |
| Crystals of Inert Gases                                 | 51        |
| Van der Waals–London Interaction                        | 55        |
| Repulsive Interaction                                   | 58        |
| Equilibrium Lattice Constants                           | 60        |
| Cohesive Energy   | 61        |
| Ionic Crystals  | 62        |
| Electrostatic or Madelung Energy                        | 62        |
| Evaluation of the Madelung Constant                     | 66        |
| Covalent Crystals                                       | 69        |
| Metals  | 71        |
| Hydrogen Bonds  | 72        |
| Atomic Radii  | 72        |
| Ionic Crystal Radii                                     | 74        |
| Analysis of Elastic Strains                             | 75        |
| Dilation  | 77        |
| Stress Components                                       | 77        |
| Elastic Compliance and Stiffness Constants              | 79        |
| Elastic Energy Density                                  | 79        |
| Elastic Stiffness Constants of Cubic Crystals           | 80        |
| Bulk Modulus and Compressibility                        | 82        |
| Elastic Waves in Cubic Crystals                         | 82        |
| Waves in the [100] Direction                            | 83        |
| Waves in the [110] Direction                            | 84        |
| Summary   | 87        |
| Problems  | 87        |
| <b>CHAPTER 4: PHONONS I. CRYSTAL VIBRATIONS</b>         | <b>91</b> |
| Vibrations of Crystals with Monatomic Basis             | 93        |
| First Brillouin Zone                                    | 95        |
| Group Velocity  | 96        |

---

|   |            |
|---|------------|
| Long Wavelength Limit                                 | 96         |
| Derivation of Force Constants from Experiment         | 96         |
| Two Atoms per Primitive Basis                         | 97         |
| Quantization of Elastic Waves                         | 101        |
| Phonon Momentum                                       | 102        |
| Inelastic Scattering by Phonons                       | 102        |
| Summary   | 104        |
| Problems  | 104        |
| <b>CHAPTER 5: PHONONS</b>                             | <b>107</b> |
| 11. THERMAL PROPERTIES                                |            |
| Phonon Heat Capacity                                  | 109        |
| Planck Distribution                                   | 109        |
| Normal Mode Enumeration                               | 110        |
| Density of States in One Dimension                    | 110        |
| Density of States in Three Dimensions                 | 113        |
| Debye Model for Density of States                     | 114        |
| Debye $T^3$ Law                                       | 116        |
| Einstein Model of the Density of States               | 116        |
| General Result for $D(\omega)$                        | 119        |
| Anharmonic Crystal Interactions                       | 121        |
| Thermal Expansion                                     | 122        |
| Thermal Conductivity                                  | 123        |
| Thermal Resistivity of Phonon Gas                     | 125        |
| Umklapp Processes                                     | 127        |
| Imperfections   | 128        |
| Problems  | 130        |
| <b>CHAPTER 6: FREE ELECTRON FERMI GAS</b>             | <b>133</b> |
| Energy Levels in One Dimension                        | 136        |
| Effect of Temperature on the Fermi-Dirac Distribution | 138        |
| Free Electron Gas in Three Dimensions                 | 139        |
| Heat Capacity of the Electron Gas                     | 143        |
| Experimental Heat Capacity of Metals                  | 147        |
| Heavy Fermions  | 149        |
| Electrical Conductivity and Ohm's Law                 | 149        |
| Experimental Electrical Resistivity of Metals         | 150        |
| Umklapp Scattering                                    | 153        |

---

|     |  |            |
|-----|--|------------|
| 60  | Motion in Magnetic Fields                                    | 154        |
| 62  | Hall Effect  | 155        |
| 78  | Thermal Conductivity of Metals                               | 158        |
| 101 | Ratio of Thermal to Electrical Conductivity                  | 158        |
| 201 | Problems   | 159        |
| 201 | <b>CHAPTER 7: ENERGY BANDS</b>                               | <b>163</b> |
| 201 | Nearly Free Electron Model                                   | 166        |
| 201 | Origin of the Energy Gap                                     | 167        |
| 201 | Magnitude of the Energy Gap                                  | 169        |
| 201 | Bloch Functions  | 169        |
| 201 | Kronig-Penney Model  | 170        |
| 201 | Wave Equation of Electron in a Periodic Potential            | 171        |
| 201 | Restatement of the Bloch Theorem                             | 175        |
| 201 | Crystal Momentum of an Electron                              | 175        |
| 201 | Solution of the Central Equation                             | 176        |
| 201 | Kronig-Penney Model in Reciprocal Space                      | 176        |
| 201 | Empty Lattice Approximation                                  | 178        |
| 201 | Approximate Solution Near a Zone Boundary                    | 179        |
| 201 | Number of Orbitals in a Band                                 | 182        |
| 201 | Metals and Insulators  | 183        |
| 201 | Summary  | 184        |
| 201 | Problems   | 184        |
| 201 | <b>CHAPTER 8: SEMICONDUCTOR CRYSTALS</b>                     | <b>187</b> |
| 201 | Band Gap   | 189        |
| 201 | Equations of Motion  | 193        |
| 201 | Physical Derivation of $\hbar\ddot{\mathbf{k}} = \mathbf{F}$ | 195        |
| 201 | Holes  | 196        |
| 201 | Effective Mass   | 199        |
| 201 | Physical Interpretation of the Effective Mass                | 200        |
| 201 | Effective Masses in Semiconductors                           | 202        |
| 201 | Silicon and Germanium  | 204        |
| 201 | Intrinsic Carrier Concentration                              | 207        |
| 201 | Intrinsic Mobility   | 210        |
| 201 | Impurity Conductivity  | 211        |
| 201 | Donor States   | 211        |
| 201 | Acceptor States  | 213        |
| 201 | Thermal Ionization of Donors and Acceptors                   | 215        |

---

|   |            |
|---|------------|
| Thermoelectric Effects                              | 216        |
| Semimetals  | 217        |
| Superlattices                                       | 218        |
| Bloch Oscillator                                    | 219        |
| Zener Tunneling                                     | 219        |
| Summary   | 219        |
| Problems  | 220        |
| <b>CHAPTER 9: FERMI SURFACES AND METALS</b>         | <b>223</b> |
| Reduced Zone Scheme                                 | 225        |
| Periodic Zone Scheme                                | 227        |
| Construction of Fermi Surfaces                      | 228        |
| Nearly Free Electrons                               | 230        |
| Electron Orbits, Hole Orbits, and Open Orbits       | 232        |
| Calculation of Energy Bands                         | 234        |
| Tight Binding Method for Energy Bands               | 234        |
| Wigner-Seitz Method                                 | 238        |
| Cohesive Energy                                     | 239        |
| Pseudopotential Methods                             | 241        |
| Experimental Methods in Fermi Surface Studies       | 244        |
| Quantization of Orbita in a Magnetic Field          | 244        |
| De Haas-van Alphen Effect                           | 246        |
| Extremal Orbita                                     | 250        |
| Fermi Surface of Copper                             | 251        |
| Magnetic Breakdown                                  | 253        |
| Summary   | 254        |
| Problems  | 254        |
| <b>CHAPTER 10: SUPERCONDUCTIVITY</b>                | <b>259</b> |
| Experimental Survey                                 | 261        |
| Occurrence of Superconductivity                     | 262        |
| Destruction of Superconductivity by Magnetic Fields | 264        |
| Meissner Effect                                     | 264        |
| Heat Capacity                                       | 266        |
| Energy Gap  | 268        |
| Microwave and Infrared Properties                   | 270        |
| Isotope Effect                                      | 271        |
| Theoretical Survey                                  | 272        |
| Thermodynamics of the Superconducting Transition    | 272        |
| London Equation                                     | 275        |

---

|  |            |
|--|------------|
| Coherence Length   | 278        |
| BCS Theory of Superconductivity                          | 279        |
| BCS Ground State   | 280        |
| Flux Quantization in a Superconducting Ring              | 281        |
| Duration of Persistent Currents                          | 284        |
| Type II Superconductors                                  | 285        |
| Vortex State   | 286        |
| Estimation of $H_{c1}$ and $H_{c2}$                      | 286        |
| Single Particle Tunneling                                | 289        |
| Josephson Superconductor Tunneling                       | 291        |
| Dc Josephson Effect                                      | 291        |
| Ac Josephson Effect                                      | 292        |
| Macroscopic Quantum Interference                         | 294        |
| High-Temperature Superconductors                         | 295        |
| Summary  | 296        |
| Problems   | 296        |
| Reference  | 298        |
| <b>CHAPTER 11: DIAMAGNETISM AND PARAMAGNETISM</b>        | <b>299</b> |
| Langevin Diamagnetism Equation                           | 301        |
| Quantum Theory of Diamagnetism of Mononuclear Systems    | 303        |
| Paramagnetism  | 304        |
| Quantum Theory of Paramagnetism                          | 304        |
| Rare Earth Ions  | 307        |
| Hund Rules   | 308        |
| Iron Group Ions  | 309        |
| Crystal Field Splitting                                  | 309        |
| Quenching of the Orbital Angular Momentum                | 310        |
| Spectroscopic Splitting Factor                           | 313        |
| Van Vleck Temperature-Independent Paramagnetism          | 313        |
| Cooling by Isentropic Demagnetization                    | 314        |
| Nuclear Demagnetization                                  | 316        |
| Paramagnetic Susceptibility of Conduction Electrons      | 317        |
| Summary  | 319        |
| Problems   | 320        |
| <b>CHAPTER 12: FERROMAGNETISM AND ANTIFERROMAGNETISM</b> | <b>323</b> |
| Ferromagnetic Order                                      | 325        |
| Curie Point and the Exchange Integral                    | 325        |

---

|   |            |
|---|------------|
| Temperature Dependence of the Saturation                | 324        |
| Magnetization   | 328        |
| Saturation Magnetization at Absolute Zero               | 330        |
| Magnons   | 332        |
| Quantization of Spin Waves                              | 335        |
| Thermal Excitation of Magnons                           | 336        |
| Neutron Magnetic Scattering                             | 337        |
| Ferrimagnetic Order                                     | 338        |
| Curie Temperature and Susceptibility<br>of Ferrimagnets | 340        |
| Iron Garnets  | 341        |
| Antiferromagnetic Order                                 | 342        |
| Susceptibility Below the Néel Temperature               | 345        |
| Antiferromagnetic Magnons                               | 346        |
| Ferromagnetic Domains                                   | 348        |
| Anisotropy Energy                                       | 350        |
| Transition Region Between Domains                       | 351        |
| Origin of Domains                                       | 353        |
| Coercivity and Hysteresis                               | 354        |
| Single-Domain Particles                                 | 356        |
| Geomagnetism and Biomagnetism                           | 357        |
| Magnetic Force Microscopy                               | 357        |
| Summary   | 359        |
| Problems  | 359        |
| <b>CHAPTER 13: MAGNETIC RESONANCE</b>                   | <b>363</b> |
| Nuclear Magnetic Resonance                              | 365        |
| Equations of Motion                                     | 368        |
| Line Width  | 372        |
| Motional Narrowing                                      | 373        |
| Hyperfine Splitting                                     | 375        |
| Examples: Paramagnetic Point Defects                    | 377        |
| F Centers in Alkali Halides                             | 378        |
| Donor Atoms in Silicon                                  | 378        |
| Knight Shift  | 379        |
| Nuclear Quadrupole Resonance                            | 381        |
| Ferromagnetic Resonance                                 | 381        |
| Shape Effects in FMR                                    | 382        |
| Spin Wave Resonance                                     | 384        |
| Antiferromagnetic Resonance                             | 385        |

|   |            |
|---|------------|
| Electron Paramagnetic Resonance                       | 388        |
| Exchange Narrowing                                    | 388        |
| Zero-field Splitting                                  | 388        |
| Principle of Maser Action                             | 388        |
| Three-Level Maser                                     | 390        |
| Lasers  | 391        |
| Summary   | 392        |
| Problems  | 393        |
| <b>CHAPTER 14: DIELECTRICS AND FERROELECTRICS</b>     | <b>395</b> |
| Maxwell Equations                                     | 397        |
| Polarization  | 397        |
| Macroscopic Electric Field                            | 398        |
| Depolarization Field, $\mathbf{E}_1$                  | 400        |
| Local Electric Field at an Atom                       | 402        |
| Lorentz Field, $\mathbf{E}_2$                         | 404        |
| Field of Dipoles Inside Cavity, $\mathbf{E}_3$        | 404        |
| Dielectric Constant and Polarizability                | 405        |
| Electronic Polarizability                             | 406        |
| Classical Theory of Electronic Polarizability         | 408        |
| Structural Phase Transitions                          | 409        |
| Ferroelectric Crystals                                | 409        |
| Classification of Ferroelectric Crystals              | 411        |
| Displacive Transitions                                | 413        |
| Soft Optical Phonons                                  | 415        |
| Landau Theory of the Phase Transition                 | 416        |
| Second-Order Transition                               | 417        |
| First-Order Transition                                | 419        |
| Antiferroelectricity                                  | 421        |
| Ferroelectric Domains                                 | 421        |
| Piezoelectricity                                      | 423        |
| Summary   | 424        |
| Problems  | 425        |
| <b>CHAPTER 15: PLASMONS, POLARITONS, AND POLARONS</b> | <b>429</b> |
| Dielectric Function of the Electron Gas               | 431        |
| Definitions of the Dielectric Function                | 431        |
| Plasma Optics   | 432        |
| Dispersion Relation for Electromagnetic Waves         | 433        |

---

|  |            |
|--|------------|
| Transverse Optical Modes in a Plasma                   | 434        |
| Transparency of Metals in the Ultraviolet              | 434        |
| Longitudinal Plasma Oscillations                       | 434        |
| Plasmons   | 437        |
| Electrostatic Screening                                | 439        |
| Screened Coulomb Potential                             | 442        |
| Pseudopotential Component $U(0)$                       | 443        |
| Mott Metal-Insulator Transition                        | 443        |
| Screening and Phonons in Metals                        | 445        |
| Polaritons   | 446        |
| LST Relation   | 450        |
| Electron-Electron Interaction                          | 453        |
| Fermi Liquid   | 453        |
| Electron-Electron Collisions                           | 453        |
| Electron-Phonon Interaction:                           |            |
| Polarons   | 456        |
| Peierls Instability of Linear<br>Metals                | 458        |
| Summary  | 460        |
| Problems   | 460        |
| <b>CHAPTER 16: OPTICAL PROCESSES AND EXCITONS</b>      | <b>465</b> |
| Optical Reflectance                                    | 467        |
| Kramers-Kronig Relations                               | 468        |
| Mathematical Note                                      | 470        |
| Example: Conductivity of Collisionless<br>Electron Gas | 471        |
| Electronic Interband Transitions                       | 472        |
| Excitons   | 473        |
| Frenkel Excitons                                       | 475        |
| Alkali Halides   | 478        |
| Molecular Crystals                                     | 478        |
| Weakly Bound (Mott-Wannier) Excitons                   | 479        |
| Exciton Condensation into Electron-Hole<br>Drops (EHD) | 479        |
| Raman Effect in Crystals                               | 482        |
| Electron Spectroscopy with X-Rays                      | 485        |
| Energy Loss of Fast Particles in a Solid               | 486        |
| Summary  | 487        |
| Problems   | 488        |

---

|  |            |
|--|------------|
| <b>CHAPTER 17: SURFACE AND INTERFACE PHYSICS</b>     | <b>491</b> |
| Reconstruction and Relaxation                        | 493        |
| Surface Crystallography                              | 494        |
| Reflection High-Energy Electron Diffraction          | 497        |
| Surface Electronic Structure                         | 498        |
| Work Function  | 498        |
| Thermionic Emission                                  | 499        |
| Surface States                                       | 499        |
| Tangential Surface Transport                         | 501        |
| Magnetoresistance in a Two-Dimensional Channel       | 502        |
| Integral Quantized Hall Effect (IQHE)                | 503        |
| IQHE in Real Systems                                 | 504        |
| Fractional Quantized Hall Effect (FQHE)              | 507        |
| p-n Junctions  | 507        |
| Rectification  | 508        |
| Solar Cells and Photovoltaic Detectors               | 510        |
| Schottky Barrier                                     | 510        |
| Heterostructures                                     | 511        |
| n-N Heterojunction                                   | 512        |
| Semiconductor Lasers                                 | 514        |
| Light-Emitting Diodes                                | 515        |
| Problems   | 517        |
| <b>CHAPTER 18: NANOSTRUCTURES</b>                    | <b>521</b> |
| Imaging Techniques for Nanostructures                | 525        |
| Electron Microscopy                                  | 526        |
| Optical Microscopy                                   | 527        |
| Scanning Tunneling Microscopy                        | 529        |
| Atomic Force Microscopy                              | 532        |
| Electronic Structure of 1D Systems                   | 534        |
| One-dimensional (1D) Subbands                        | 534        |
| Spectroscopy of Van Hove Singularities               | 535        |
| 1D Metals—Coulomb Interactions and Lattice Couplings | 537        |
| Electrical Transport in 1D                           | 539        |
| Conductance Quantization and the Landauer Formula    | 539        |
| Two Barriers in Series-Resonant Tunneling            | 542        |
| Incoherent Addition and Ohm's Law                    | 544        |

---

|  |            |
|--|------------|
| Localization                                       | 545        |
| Voltage Probes and the Büttiker-Landauer Formalism | 546        |
| Electronic Structure of 0D Systems                 | 551        |
| Quantized Energy Levels                            | 551        |
| Semiconductor Nanocrystals                         | 551        |
| Metallic Dots                                      | 553        |
| Discrete Charge States                             | 555        |
| Electrical Transport in 0D                         | 557        |
| Coulomb Oscillations                               | 557        |
| Spin, Mott Insulators, and the Kondo Effect        | 560        |
| Cooper Pairing in Superconducting Dots             | 562        |
| Vibrational and Thermal Properties                 | 563        |
| Quantized Vibrational Modes                        | 563        |
| Transverse Vibrations                              | 565        |
| Heat Capacity and Thermal Transport                | 567        |
| Summary  | 568        |
| Problems   | 568        |
| <b>CHAPTER 19: NONCRYSTALLINE SOLIDS</b>           | <b>573</b> |
| Diffraction Pattern                                | 575        |
| Monatomic Amorphous Materials                      | 576        |
| Radial Distribution Function                       | 577        |
| Structure of Vitreous Silica, $\text{SiO}_2$       | 578        |
| Glasses  | 581        |
| Viscosity and the Hopping Rate                     | 582        |
| Amorphous Ferromagnets                             | 583        |
| Amorphous Semiconductors                           | 585        |
| Low Energy Excitations in Amorphous Solids         | 586        |
| Heat Capacity Calculation                          | 586        |
| Thermal Conductivity                               | 587        |
| Fiber Optics                                       | 589        |
| Rayleigh Attenuation                               | 590        |
| Problems   | 590        |
| <b>CHAPTER 20: POINT DEFECTS</b>                   | <b>593</b> |
| Lattice Vacancies                                  | 595        |
| Diffusion  | 598        |
| Metals   | 601        |

---

|   |     |
|---|-----|
| CHAPTER 17: Color Centers                                   | 602 |
| F Centers   | 602 |
| Other Centers in Alkali Halides                             | 603 |
| Problems  | 605 |
| CHAPTER 21: DISLOCATIONS                                    | 607 |
| Shear Strength of Single Crystals                           | 609 |
| Slip  | 610 |
| Dislocations  | 611 |
| Burgers Vectors   | 614 |
| Stress Fields of Dislocations                               | 615 |
| Low-angle Grain Boundaries                                  | 617 |
| Dislocation Densities                                       | 620 |
| Dislocation Multiplication and Slip                         | 621 |
| Strength of Alloys  | 623 |
| Dislocations and Crystal Growth                             | 625 |
| Whiskers  | 626 |
| Hardness of Materials                                       | 627 |
| Problems  | 628 |
| CHAPTER 22: ALLOYS  | 631 |
| General Considerations                                      | 633 |
| Substitutional Solid Solutions—<br>Hume-Rothery Rules       | 636 |
| Order-Disorder Transformation                               | 639 |
| Elementary Theory of Order                                  | 641 |
| Phase Diagrams  | 644 |
| Eutectics   | 644 |
| Transition Metal Alloys                                     | 646 |
| Electrical Conductivity                                     | 648 |
| Kondo Effect  | 649 |
| Problems  | 652 |
| APPENDIX A: TEMPERATURE DEPENDENCE OF THE REFLECTION LINES  | 653 |
| APPENDIX B: EWALD CALCULATION OF LATTICE SUMS               | 656 |
| Ewald-Kornfeld Method for Lattice Sums<br>for Dipole Arrays | 659 |

---

|             |  |     |
|-------------|--|-----|
| APPENDIX C: | QUANTIZATION OF ELASTIC WAVES: PHONONS                         | 660 |
|             | Phonon Coordinates   | 661 |
|             | Creation and Annihilation Operators                            | 663 |
| APPENDIX D: | FERMI-DIRAC DISTRIBUTION FUNCTION                              | 664 |
| APPENDIX E: | DERIVATION OF THE $d\mathbf{k}/dt$ EQUATION                    | 667 |
| APPENDIX F: | BOLTZMANN TRANSPORT EQUATION                                   | 668 |
|             | Particle Diffusion   | 669 |
|             | Classical Distribution   | 670 |
|             | Fermi-Dirac Distribution                                       | 671 |
|             | Electrical Conductivity  | 673 |
| APPENDIX G: | VECTOR POTENTIAL, FIELD MOMENTUM,<br>AND GAUGE TRANSFORMATIONS | 673 |
|             | Lagrangian Equations of Motion                                 | 674 |
|             | Derivation of the Hamiltonian                                  | 675 |
|             | Field Momentum   | 675 |
|             | Gauge Transformation   | 676 |
|             | Gauge in the London Equation                                   | 677 |
| APPENDIX H: | COOPER PAIRS   | 677 |
| APPENDIX I: | GINZBURG-LANDAU EQUATION                                       | 679 |
| APPENDIX J: | ELECTRON-PHONON COLLISIONS                                     | 683 |
| INDEX       |  | 687 |
|             | 1. Tetrahedral angles  | 22  |
|             | 2. Nearest neighbour distance                                  | 22  |
|             | 3. Indices of planes   | 22  |
|             | 4. Indices of direction  | 22  |
|             | 5. Hop structure   | 23  |
|             | 6. Packing fraction  | 23  |
|             | 7. Interplanar spacing   | 23  |
|             | 8. Angle between planes  | 23  |