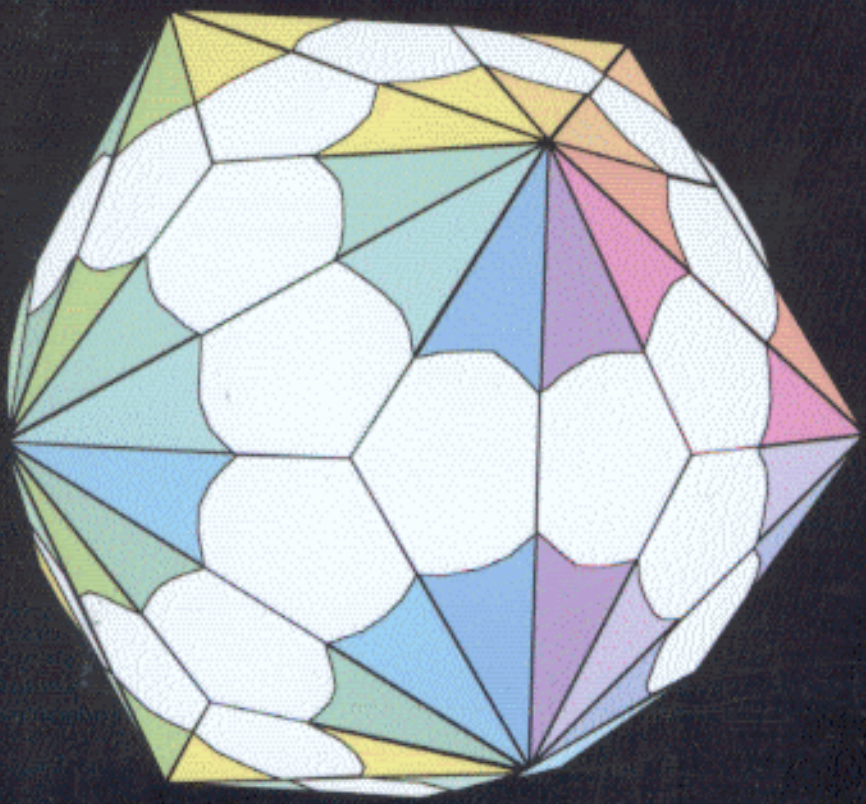
Introduction to the Electron Theory of Metals

Uichiro Mizutani



CAMBRIDGE

Contents

Preface *page* xi

1 Introduction 1
1.1 What is the electron theory of metals? 1
1.2 Historical survey of the electron theory of metals 3
1.3 Outline of this book 8
2 Bonding styles and the free-electron model 10
2.1 Prologue 10
2.2 Concept of an energy band 10
2.3 Bonding styles 13
2.4 Motion of an electron in free space 16
2.5 Free electron under the periodic boundary condition 18
2.6 Free electron in a box 20
2.7 Construction of the Fermi sphere 21
Exercises 28
3 Electrons in a metal at finite temperatures 29
3.1 Prologue 29
3.2 Fermi–Dirac distribution function (I) 29
3.3 Fermi–Dirac distribution function (II) 34
3.4 Electronic specific heat 37
3.5 Low-temperature specific heat measurement 40
3.6 Pauli paramagnetism 44
3.7 Thermionic emission 50
Exercise 53
4 Periodic lattice, and lattice vibrations in crystals 54
4.1 Prologue 54
4.2 Periodic structure and reciprocal lattice vectors 54
4.3 Periodic lattice in real space and in reciprocal space 57
4.4 Lattice vibrations in one-dimensional monatomic lattice 64

4.5 Lattice vibrations in a crystal 66
4.6 Lattice waves and phonons 69
4.7 Bose–Einstein distribution function 69
4.8 Lattice specific heat 72
4.9 Acoustic phonons and optical phonons 77
4.10 Lattice vibration spectrum and Debye temperature 80
4.11 Conduction electrons, set of lattice planes and phonons 81
Exercises 83
5 Conduction electrons in a periodic potential 86
5.1 Prologue 86
5.2 Cosine-type periodic potential 86
5.3 Bloch theorem 88
5.4 Kronig–Penney model 93
5.5 Nearly-free-electron model 97
5.6 Energy gap and diffraction phenomena 103
5.7 Brillouin zone of one- and two-dimensional periodic lattices 105
5.8 Brillouin zone of bcc and fcc lattices 106
5.9 Brillouin zone of hcp lattice 113
5.10 Fermi surface–Brillouin zone interaction 116
5.11 Extended, reduced and periodic zone schemes 121
Exercises 125
6 Electronic structure of representative elements 126
6.1 Prologue 126
6.2 Elements in the periodic table 126
6.3 Alkali metals 126
6.4 Noble metals 130
6.5 Divalent metals 132
6.6 Trivalent metals 135
6.7 Tetravalent metals and graphite 137
6.8 Pentavalent semimetals 141
6.9 Semiconducting elements without and with dopants 143
7 Experimental techniques and principles of electronic structure-related phenomena 148
7.1 Prologue 148
7.2 de Haas–van Alphen effect 148
7.3 Positron annihilation 155
7.4 Compton scattering effect 160
7.5 Photoemission spectroscopy 162
7.6 Inverse photoemission spectroscopy 169
7.7 Angular-resolved photoemission spectroscopy (ARPES) 172

7.8 Soft x-ray spectroscopy 176
7.9 Electron-energy-loss spectroscopy (EELS) 181
7.10 Optical reflection and absorption spectra 184
Exercises 188
8 Electronic structure calculations **190**
8.1 Prologue 190
8.2 One-electron approximation 190
8.3 Local density functional method 195
8.4 Band theories in a perfect crystal 199
8.5 Tight-binding method 200
8.6 Orthogonalized plane wave method 203
8.7 Pseudopotential method 204
8.8 Augmented plane wave method 207
8.9 Korringa–Kohn–Rostoker method 211
8.10 LMTO 215
Exercises 223
9 Electronic structure of alloys **224**
9.1 Prologue 224
9.2 Impurity effect in a metal 224
9.3 Electron scattering by impurity atoms and the Linde law 226
9.4 Phase diagram in Au–Cu alloy system and the Nordheim law 228
9.5 Hume-Rothery rule 232
9.6 Electronic structure in Hume-Rothery alloys 235
9.7 Stability of Hume-Rothery alloys 240
9.8 Band theories for binary alloys 245
10 Electron transport properties in periodic systems (I) **249**
10.1 Prologue 249
10.2 The Drude theory for electrical conductivity 249
10.3 Motion of electrons in a crystal: (I) – wave packet of electrons 254
10.4 Motion of electrons in a crystal: (II) 257
10.5 Electrons and holes 261
10.6 Boltzmann transport equation 264
10.7 Electrical conductivity formula 267
10.8 Impurity scattering and phonon scattering 270
10.9 Band structure effect on the electron transport equation 271
10.10 Ziman theory for the electrical resistivity 275
10.11 Electrical resistivity due to electron–phonon interaction 280
10.12 Bloch–Grüneisen law 284
Exercises 291

11 Electron transport properties in periodic systems (II) **293**
11.1 Prologue 293
11.2 Thermal conductivity 293
11.3 Electronic thermal conductivity 296
11.4 Wiedemann–Franz law and Lorenz number 299
11.5 Thermoelectric power 302
11.6 Phonon drag effect 307
11.7 Thermoelectric power in metals and semiconductors 309
11.8 Hall effect and magnetoresistance 312
11.9 Interaction of electromagnetic wave with metals (I) 317
11.10 Interaction of electromagnetic wave with metals (II) 321
11.11 Reflectance measurement 324
11.12 Reflectance spectrum and optical conductivity 325
11.13 Kubo formula 328
Exercises 333
12 Superconductivity **334**
12.1 Prologue 334
12.2 Meissner effect 335
12.3 London theory 338
12.4 Thermodynamics of a superconductor 341
12.5 Ordering of the momentum 343
12.6 Ginzburg–Landau theory 344
12.7 Specific heat in the superconducting state 346
12.8 Energy gap in the superconducting state 347
12.9 Isotope effect 347
12.10 Mechanism of superconductivity–Fröhlich theory 349
12.11 Formation of the Cooper pair 351
12.12 The superconducting ground state and excited states in the BCS theory 353
12.13 Secret of zero resistance 358
12.14 Magnetic flux quantization in a superconducting cylinder 359
12.15 Type-I and type-II superconductors 360
12.16 Ideal type-II superconductors 362
12.17 Critical current density in type-II superconductors 364
12.18 Josephson effect 368
12.19 Superconducting quantum interference device (SQUID) magnetometer 373
12.20 High-T_c superconductors 376
Exercises 382

13 Magnetism, electronic structure and electron transport properties in magnetic metals **383**
13.1 Prologue 383
13.2 Classification of crystalline metals in terms of magnetism 383
13.3 Orbital and spin angular momenta of a free atom and of atoms in a solid 386
13.4 Localized electron model and spin wave theory 390
13.5 Itinerant electron model 395
13.6 Electron transport in ferromagnetic metals 400
13.7 Electronic structure of magnetically dilute alloys 403
13.8 Scattering of electrons in a magnetically dilute alloy – "partial wave method" 405
13.9 Scattering of electrons by magnetic impurities 410
13.10 s–d interaction and Kondo effect 414
13.11 RKKY interaction and spin-glass 418
13.12 Magnetoresistance in ferromagnetic metals 420
13.13 Hall effect in magnetic metals 428
Exercises 431
14 Electronic structure of strongly correlated electron systems **432**
14.1 Prologue 432
14.2 Fermi liquid theory and quasiparticle 433
14.3 Electronic states of hydrogen molecule and the Heitler–London approximation 434
14.4 Failure of the one-electron approximation in a strongly correlated electron system 438
14.5 Hubbard model and electronic structure of a strongly correlated electron system 441
14.6 Electronic structure of 3d-transition metal oxides 444
14.7 High-T_c cuprate superconductors 447
Exercise 450
15 Electronic structure and electron transport properties of liquid metals, amorphous metals and quasicrystals **451**
15.1 Prologue 451
15.2 Atomic structure of liquid and amorphous metals 452
15.3 Preparation of amorphous alloys 462
15.4 Thermal properties of amorphous alloys 464
15.5 Classification of amorphous alloys 466
15.6 Electronic structure of amorphous alloys 467
15.7 Electron transport properties of liquid and amorphous metals 472

15.8 Electron transport theories in a disordered system 474
15.8.1 Ziman theory for simple liquid metals in group (V) 475
15.8.2 Baym–Meisel–Cote theory for amorphous alloys in group (V) 479
15.8.3 Mott s–d scattering model 482
15.8.4 Anderson localization theory 483
15.8.5 Variable-range hopping model 486
15.9 Electron conduction mechanism in amorphous alloys 488
15.10 Structure and preparation method of quasicrystals 494
15.11 Quasicrystals and approximants 495
15.12 Electronic structure of quasicrystals 500
15.13 Electron transport properties in quasicrystals and approximants 502
15.14 Electron conduction mechanism in the pseudogap systems 507
15.14.1 Mott conductivity formula for the pseudogap system 507
15.14.2 Family of quasicrystals and their approximants 509
15.14.3 Family of amorphous alloys in group (IV) 510
15.14.4 Family of "unusual" pseudogap systems 512
Exercises 515
Appendix 1 Values of selected physical constants 516
Principal symbols (by chapter) 517
Hints and answers 539
References 569
Materials index 577
Subject index 579