Site Symmetry in Crystals
Theory and Applications

Second Edition
With 42 Figures
## Contents

1. Introduction .................................................................................. 1

2. Finite Groups and Their Representations ..................................... 5
   2.1 Elements of Group Theory ....................................................... 5
      2.1.1 Groups. Generators and Generating Relations.
          The Factor Group ......................................................... 5
      2.1.2 Conjugate Elements and Classes. Factorization
          of Groups ........................................................................ 7
      2.1.3 Homomorphism and Isomorphism of Groups ............... 9
   2.2 Elements of Group Representation Theory ............................. 10
      2.2.1 Representations of a Group. Equivalent, Reducible
          and Irreducible Representations. Orthogonality Relations.
          Representation Characters ............................................. 10
      2.2.2 Decomposition of Representations.
          Complex Conjugate Representations ................................ 15
   2.3 Generation of Representations .............................................. 17
      2.3.1 Direct Product of Representations ................................. 17
      2.3.2 Subduction of Representations .................................... 20
      2.3.3 Induction of Representations ....................................... 22
      2.3.4 Little Group Method
          of Irreducible Representation Generation ........................ 26

3. Symmetry Groups and Their Representations ............................. 31
   3.1 The Euclidean Group and Its Subgroups ............................... 31
      3.1.1 Translation Group ..................................................... 31
      3.1.2 Rotation Group ........................................................ 32
      3.1.3 Inversion Group ....................................................... 35
      3.1.4 Full Orthogonal Group ............................................. 35
      3.1.5 Euclidean Group ...................................................... 36
   3.2 Point Symmetry Groups ....................................................... 39
      3.2.1 Symmetry Elements of Molecules
          and Crystallographic Point Groups ................................. 39
      3.2.2 Site Symmetry Subgroups of Point Groups ................. 40
   3.3 Space Groups .................................................................... 43
      3.3.1 Symmetry of a Model of an Infinite Crystal.
          Symmorphic and Nonsymmorphic Space Groups ............. 43
3.3.2 Symmetry of a Cyclic Model of a Crystal ................. 46
3.4 Site Symmetry in Space Groups .............................. 48
  3.4.1 Crystallographic Orbits. Wyckoff Positions ............... 48
  3.4.2 Oriented Site Symmetry Groups. Choice of Origin ......... 51
  3.4.3 Crystal Structure Types. Crystals with Space Group $D_{4h}^{14}$ 54
3.5 Symmetry Operations in Quantum Mechanics ................ 55
  3.5.1 Symmetry Group of a Quantum Mechanical System .......... 55
  3.5.2 Wigner’s Theorem ....................................... 56
  3.5.3 Time-Reversal Symmetry .................................. 57
3.6 Irreducible Representations of Rotation
  and Full Orthogonal Groups .................................... 59
3.7 Representations of Point Groups ............................ 62
3.8 Representations of Space Groups ............................. 70
  3.8.1 Irreducible Representations of the Translation Group.
    The Brillouin Zone ........................................... 70
  3.8.2 Stars of Wave Vectors. Little Group.
    Full Representations of Space Groups ....................... 76
  3.8.3 Small Representations of a Little Group.
    Projective Representations of Point Groups ................. 78
  3.8.4 Double-Valued Representations of Space Groups .......... 79
  3.8.5 Dependence of the Labeling of the Irreducible
    Representations of a Space Group on the Setting ........... 81
  3.8.6 Example: Irreducible Representations
    of Space Group $D_{4h}^{14}$. Compatibility Tables .......... 84

4. Site Symmetry and Induced Representations of Symmetry Groups 89
  4.1 Induced Representations of Point Groups.
    Correlation Tables ........................................... 89
  4.2 Induced Representations of Space Groups .................... 91
    4.2.1 Induction from Site Symmetry Subgroups
      of Space Groups ........................................... 92
    4.2.2 Induced Representations in the $k$-Basis.
      Band Representations .................................... 93
    4.2.3 Simple and Composite Induced Representations ......... 97
  4.3 Double-Valued Induced Representations ....................... 99
  4.4 Generation of the Simple Induced Representations
    of the Space Group $D_{4h}^{14}$ ............................ 100
  4.5 The Twenty-Four Most Common Space Groups: Crystal
    Structures and Tables of Simple Induced Representations .... 103
    4.5.1 Tables of Simple Induced Representations and Their Use 103
    4.5.2 Space Groups and Crystal Structures
      with Cubic Lattices ...................................... 106
    4.5.3 Space Groups and Crystal Structures
      with Hexagonal and Trigonal Lattices ..................... 111
    4.5.4 Space Groups and Crystal Structures
      with Tetragonal Lattices ................................ 114
4.5.5 Space Groups and Crystal Structures with Orthorhombic Lattices ........................................... 117
4.5.6 Space Group Setting and Simple Induced Representations for Monoclinic Space Groups .......................... 121

5. Application of Induced Representations in the Electron Theory of Molecules and Crystals .............................. 125

5.1 Adiabatic and One-Electron Approximations ................................................................. 125
  5.1.1 Space Symmetry of the One-Electron Approximation Hamiltonian ............................................. 129

5.2 Induced Representations in the Electron Theory of Molecules ................................................. 131
  5.2.1 Canonical, Localized and Hybridized Molecular Orbitals ......................................................... 131
  5.2.2 Localized Two-Center Bonds and Hybridized Orbitals in $AB_4$ and $AB_3$ Molecules ..................... 136
  5.2.3 Multicentered Bonds in the $1,6$-$C_2B_4H_8$ Molecule .............................................................. 139
  5.2.4 Canonical and Localized Orbitals in the $MnO_4$ Molecular Ion ................................................... 140
  5.2.5 Localized Orbitals in the Tetrahedral $Bi_4$ Molecule ............................................................... 142

5.3 One-Electron Approximation for Crystals ........................................................................... 144
  5.3.1 Crystalline Orbitals. Degenerate and Nondegenerate Energy Bands .............................................. 144
  5.3.2 Equivalent Hamiltonians for the Same Crystal Structures .......................................................... 146
  5.3.3 $k-p$ Perturbation Method in the Energy Band Theory ................................................................. 147
  5.3.4 Zero-Slope Points of Energy Bands ......................................................................................... 150
  5.3.5 Energy Bands in the Neighborhood of Degeneracy Points ......................................................... 152
  5.3.6 Additional Degeneracy of Energy Bands Due to the Reality of the Hamiltonian ......................... 155
  5.3.7 Density of States of an Energy Band ...................................................................................... 155

5.4 Induced Representations and the Theory of Chemical Bonding in Crystals ................................. 158
  5.4.1 Energy Band States and Localized Functions ........................................................................... 158
  5.4.2 Localized Orbitals and Atomic States in Crystals ..................................................................... 159
  5.4.3 Hybridized Orbitals in Crystals ............................................................................................... 160
  5.4.4 Crystals with Space Group $O_{h}^7$ .............................................................................................. 161
  5.4.5 Crystals with Space Group $O_{h}^{5}$ .............................................................................................. 162
  5.4.6 Crystals with Space Group $D_{4h}^{14}$ .......................................................................................... 163
  5.4.7 One-Electron States in High-$T_c$ Superconductors ................................................................. 165

5.5 Energy Bands and Localized States ...................................................................................... 173
  5.5.1 Localized Orbitals and Parameters of an Energy Band ............................................................. 173
  5.5.2 Generation of Localized Functions in Crystals ......................................................................... 174
  5.5.3 Interpolation Scheme Using Localized Functions ..................................................................... 175

5.6 Localized Orbitals in Molecular Models of Crystals ................................................................ 179
  5.6.1 Cluster Model of Perfect Crystals ............................................................................................. 179
  5.6.2 Cluster and Crystal Localized Orbitals ..................................................................................... 180
5.6.3 Energy Bands of AgBr from Cluster Calculations of [Ag$_{14}$Br$_{13}$]$^+$ ........................................ 181
5.6.4 Cyclic Model as a Molecular Model of Crystals ............................................... 182
5.6.5 Localized Orbitals in the Cyclic Model ............................................................... 183

6. Induced Representations in the Theory of Imperfect Crystals .......................... 185
6.1 Point Defects in Crystals ...................................................................................... 185
   6.1.1 Single Defect Model ..................................................................................... 186
   6.1.2 Cluster Model of Imperfect Crystals ............................................................ 188
   6.1.3 Cyclic Model of Imperfect Crystals ............................................................... 189
   6.1.4 Band Model of Imperfect Crystals ............................................................... 189
   6.1.5 Localized Orbitals in the Band Model of Point Defects .............................. 191
6.2 Diperiodic Space Groups. Surface Electron States ........................................... 192
   6.2.1 Diperiodic (Layer) Space Groups ............................................................... 192
   6.2.2 Site Symmetry in Layer Groups .................................................................. 195
   6.2.3 Irreducible Representations of Diperiodic Groups ...................................... 197
   6.2.4 Induced Representations of Diperiodic Groups .......................................... 199
   6.2.5 Use of Translational Symmetry in the Comparison of Bulk and Surface Crystalline States .......................................................... 201

7. Application of Induced Representations of Space Groups to Second Order Phase Transitions .............................................................. 205
7.1 Symmetry Rules in the Landau Theory of Second Order Phase Transitions .............................................................................. 205
7.2 Tensor Fields in Crystals and Induced Representations of Space Groups. Tensor Fields for Space Group $D_{4h}^{14}$ ........................................ 207
7.3 Vibrational Field Representation and Phase Transitions in High-Temperature Superconductors ...................................................... 210

8. Induced Representations of Space Groups in Phonon Spectroscopy of Crystals .............................................................. 213
8.1 Phonon Symmetry Analysis ............................................................................. 213
8.2 Infrared and Raman Spectra Selection Rules .................................................. 214
8.3 Phonon Symmetry and Optical Spectra Selection Rules in Semiconductor Superlattices .......................................................... 215
   8.3.1 (GaAs)$_m$(AlAs)$_n$ Superlattices .................................................................. 216
   8.3.2 (Si)$_m$(Ge)$_n$ Superlattices ........................................................................ 221
   8.3.3 Experimental Applications ......................................................................... 221
8.4 Phonon Symmetry in High-Temperature Superconductors ......................... 227
8.5 Phonon Symmetry in Diperiodic Systems .......................................................... 233

9. Site Symmetry in Magnetic Crystals and Induced Corepresentations ........... 237
9.1 Shubnikov Space Groups of Symmetry of Magnetic Crystals ..................... 237
9.2 Site Symmetry in Magnetic Crystals ................................................................. 238
9.3 Corepresentations of Shubnikov Space Groups ............................................. 241
9.4 Induced Corepresentations of Magnetic Space Groups ....... 244
9.5 Corepresentations of the Space Groups of Antiferromagnetic La$_2$CuO$_4$ ............................................. 247

10. Site Symmetry in Permutation – Inversion Symmetry Groups of Nonrigid Crystals ............................................. 251
10.1 Symmetry Groups of Nonrigid Crystals ......................... 252
  10.1.1 Labeling of Nuclei. Sampling of Coordinate Systems 252
  10.1.2 Description of Permutation – Inversion Symmetry Elements ................................................................. 253
  10.1.3 Coordinate Transformations Induced by Permutation – Inversion Symmetry Elements ... 255
  10.1.4 Site Symmetry Group of a Rotating Molecule in a Nonrigid Crystal ......................................................... 256
  10.1.5 Permutation – Inversion Group of a Nonrigid Sodium Nitrate Crystal ...................................................... 257
10.2 Irreducible Representations of a Nonrigid Crystal Symmetry Group ................................................................. 260
  10.2.1 Generation of Irreducible Representations .......... 260
  10.2.2 Irreducible Representations of a Site Symmetry Group ................................................................. 261
  10.2.3 Classification of States ...................................... 263
10.3 Generalized Symmetry of High-Temperature Phase of Fullerite C$_{60}$ .......................................................... 264
  10.3.1 Permutation – Inversion Symmetry Group of Fullerite C$_{60}$ in the High-Temperature Phase .... 265
  10.3.2 Irreducible Representations of the Groups [n] and P$_c$ ............................................................. 265
  10.3.3 Classification of States of Nonrigid Fullerite C$_{60}$ ... 266

References ................................................................. 269

Subject Index ............................................................. 277