# Table of Contents


1. Introduction . . . . . 1
   - 1.1 Structure of Point Defects . . . . . 2
   - 1.2 Basic Concepts of Defect Structure Determination by Electron Paramagnetic Resonance . . . . . 4
   - 1.3 Superhyperfine and Electronic Structures of Defects in Solids . . . . . 8

2. Fundamentals of Electron Paramagnetic Resonance . . . . . 11
   - 2.1 Magnetic Properties of Electrons and Nuclei . . . . . 11
   - 2.2 Electrons and Nuclei in an External Magnetic Field . . . . . 12
   - 2.3 Some Useful Relations for Angular Momentum Operators . . . . . 14
   - 2.4 Time Dependence of Angular Momentum Operators and Macroscopic Magnetization . . . . . 15
   - 2.5 Basic Magnetic Resonance Experiment . . . . . 17
   - 2.6 Spin–Lattice Relaxation . . . . . 20
   - 2.7 Rate Equations for a Two–Level System . . . . . 22
   - 2.8 Bloch Equations . . . . . 26
   - 2.9 Conventional Detection of Electron Paramagnetic Resonance and Its Sensitivity . . . . . 31

3. Electron Paramagnetic Resonance Spectra . . . . . 35
   - 3.1 Spin Hamiltonian . . . . . 35
   - 3.2 Electron Zeeman Interaction . . . . . 38
   - 3.3 $g$–Factor Splitting of EPR Spectra . . . . . 42
   - 3.4 Fine–Structure Splitting of EPR Spectra . . . . . 45
   - 3.5 Hyperfine Splitting of EPR Spectra . . . . . 53
   - 3.6 Superhyperfine Splitting of EPR Spectra . . . . . 62
   - 3.7 Inhomogeneous Line Widths of EPR lines . . . . . 72

4. Optical Detection of Electron Paramagnetic Resonance . . . . . 77
   - 4.1 Optical Transitions of Defects in Solids . . . . . 78



Bibliografische Informationen
http://d-nb.info/920899455

digitalisiert durch DEUTSCHE NATIONAL BIBLIOTHEK

4.2 Spectral Form of Optical Transitions of Defects in Solids . . . . . 80
4.3 EPR Detected with Magnetic Circular Dichroism of Absorption Method . . . . . 86
4.4 MCDA Excitation Spectra of ODEPR Lines (MCDA "Tagged" by EPR) . . . . . 96
4.5 Spatially Resolved MCDA and ODEPR Spectra . . . . . 102
4.6 Measurement of Spin–Lattice Relaxation Time $T_1$ with MCDA Method . . . . . 105
4.7 Determination of Spin State with MCDA Method . . . . . 106
4.8 EPR of Ground and Excited States Detected with Optical Pumping . . . . . 112
4.9 EPR Optically Detected in Donor–Acceptor Pair Recombination Luminescence . . . . . 122
4.10 Optically Detected EPR of Triplet States . . . . . 129
4.11 ODEPR of Trapped Excitons with MCDA Method . . . . . 133
4.12 Sensitivity of ODEPR Measurements . . . . . 135

5. Electron Nuclear Double Resonance . . . . . 139
5.1 The Resolution Problem, a Simple Model . . . . . 139
5.2 Type of Information from EPR and NMR Spectra . . . . . 141
5.3 Indirect Detection of NMR, Double Resonance . . . . . 143
5.4 Examples of ENDOR Spectra . . . . . 150
5.5 Relations Between EPR and ENDOR Spectra, ENDOR-Induced EPR . . . . . 154
5.6 Electron Nuclear Nuclear Triple Resonance (Double ENDOR) . . . . . 160
5.7 Temperature Dependence and Photo–Excitation of ENDOR Spectra . . . . . 163
5.7.1 Temperature Dependence of ENDOR Spectra . . . . . 163
5.7.2 Photo–Excitation of ENDOR Spectra . . . . . 166

6. Determination of Defect Symmetries from ENDOR Angular Dependences . . . . . 169
6.1 Definition of Neighbor Shells . . . . . 170
6.2 Neighbor Shells and Transformation of Interaction Tensors . . . . . 171
6.3 Interaction Tensor Symmetries and ENDOR Angular Dependence . . . . . 173
6.4 Neighbor Shell Symmetries and ENDOR Angular Dependences . . . . . 175
6.4.1 Simple Example . . . . . 175
6.4.2 General Case . . . . . 178

6.4.3 Defect Structure and Symmetry Matrices . . . . . 182
6.5 Low Symmetry Defects in Higher Symmetry Environments . . . . . 194
6.6 Ways to Distinguish Between High and Low Symmetry Defects . . . . . 200
6.7 Role of EPR Spectrum for an ENDOR Analysis . . . . . 204
6.8 Solution of the Spin Hamiltonian . . . . . 207
6.8.1 Concept of Effective Spin . . . . . 207
6.8.2 Nuclear Spin Hamiltonian . . . . . 208
6.8.3 Calculation of Effective Spin . . . . . 214
6.8.4 Mutual Interactions Between Neighbor Nuclei . . . . . 215
6.8.5 Large hf or shf Interaction for One Nucleus . . . . . 218
6.8.6 Numerical Calculation of EPR Angular Dependences . 218
6.8.7 Fitting of Free Parameters in a Simulated ENDOR Angular Dependence . . . . . 220
6.8.8 Examples of Results Obtained from Analysis of ENDOR Angular Dependences . . . . . 222
6.9 Software Treatment of ENDOR Spectra . . . . . 225

7. Theoretical Interpretation of Superhyperfine and Quadrupole Interactions . . . . . 231
7.1 Structures of Point Defects . . . . . 231
7.1.1 Impurities in Insulators . . . . . 232
7.1.2 Color Centers . . . . . 233
7.1.3 Defects in Semiconductors . . . . . 233
7.2 Origin of Zeeman, Hyperfine and Quadrupole Interactions . . . . . 234
7.2.1 Origin of the Hamiltonian . . . . . 234
7.2.2 Wigner–Eckart Theorem . . . . . 236
7.2.3 Zeeman Interaction . . . . . 236
7.2.4 Hyperfine Interaction . . . . . 237
7.2.5 Quadrupole Interaction . . . . . 238
7.2.6 Total Hamiltonian . . . . . 239
7.3 Central Ion Hyperfine Structure . . . . . 239
7.3.1 Free Ion Electronic Structure . . . . . 240
7.3.2 Crystal Field Splitting . . . . . 243
7.3.3 Spin Hamiltonian . . . . . 244
7.4 Covalency and Superhyperfine Interaction . . . . . 247
7.4.1 Molecular Orbitals and Configuration Mixing . . . . . 248
7.4.2 Superhyperfine Interaction . . . . . 249
7.4.3 Ligand Core Polarization . . . . . 253
7.4.4 Ligand Quadrupole Interaction . . . . . 254
7.4.5 Pseudopotentials . . . . . 256
7.4.6 Lattice Dynamical Effects . . . . . 258

7.5 Orthogonalized Envelope Functions . . . . . 258
7.5.1 Wannier's Theorem and Effective-Mass Theory . . . . 259
7.5.2 Continuum Models . . . . . 260
7.5.3 Point-Ion Model and Ion-Size Corrections . . . . . 261
7.5.4 Green's Function Method for Deep-Level Impurities . . 262
7.5.5 Orthogonalization to Core Orbitals . . . . . 263
7.6 Simple Approximations and Illustrations for Interpretation of shf and Quadrupole Interactions . . . . . 264
7.6.1 Point Dipole-Dipole Interaction . . . . . 265
7.6.2 Calculation of Isotropic shf Constants with Orthogonalized Envelope Function . . . . . 270
7.6.3 Transferred shf Interactions . . . . . 271
7.6.4 Calculation of Anisotropic shf Constant $b$ with Orthogonalized Envelope Function . . . . . 273
7.6.5 Dynamical Contributions to shf Interactions . . . . . 275
7.6.6 Quadrupole Interactions . . . . . 277

8. Technology of ENDOR Spectrometers . . . . . 281
8.1 Experimental Constraints for Conventional ENDOR . . . . . 282
8.1.1 Modulation Frequency . . . . . 282
8.1.2 Sensitivity . . . . . 282
8.1.3 Temperature . . . . . 282
8.1.4 Microwave and Radio-Frequency Field Intensities . . . 283
8.1.5 Microwave and ENDOR Frequency . . . . . 284
8.1.6 Static Magnetic Field . . . . . 285
8.1.7 Modulation of Parameters . . . . . 285
8.2 ENDOR Spectrometer Design . . . . . 286
8.3 Components of ENDOR Spectrometer . . . . . 291
8.3.1 Signal Pre-Amplifier . . . . . 291
8.3.2 Microwave Detector . . . . . 292
8.3.3 Microwave Sources . . . . . 297
8.3.4 ENDOR Microwave Cavities . . . . . 301
8.3.5 Radio-Frequency Generators . . . . . 306

9. Experimental Aspects of Optically Detected EPR and ENDOR . . 309
9.1 Sensitivity Considerations . . . . . 309
9.1.1 Magnetic Circular Dichroism of Absorption . . . . . 310
9.1.2 Optically Detected EPR . . . . . 311
9.2 ODMR Spectrometers Monitoring Light Emission . . . . . 312
9.3 ODMR Spectrometers Monitoring Magnetic Circular Properties of Absorption and Emission . . . 314
9.3.1 General Description of the Spectrometer . . . . . 314
9.3.2 Measurement of Magnetic Circular Dichroism of Absorption . . . . . 316

9.3.3 Measurement of Magnetic Circular Polarization of Emission . . . . . 319
9.4 Experimental Details of the Components of an MCDA/MCPE ODMR Spectrometer . . . . . 320
9.4.1 Light Sources . . . . . 321
9.4.2 Monochromators . . . . . 321
9.4.3 Imaging Systems . . . . . 322
9.4.4 Linear Polarizers . . . . . 322
9.4.5 Photo-Elastic Modulator . . . . . 322
9.4.6 Detectors . . . . . 323
9.4.7 Cryostat . . . . . 323
9.4.8 Magnet . . . . . 324
9.4.9 Microwave System and Cavity . . . . . 325
9.4.10 Radio-Frequency System for ODENDOR . . . . . 327
9.4.11 Control and Registration Electronics . . . . . 328

Appendices . . . . . 329
A. Nuclear $g$-Factors, Quadrupole Constants, NMR Frequencies . . 329
B. The Cayley Transformation Formula . . . . . 333
C. Algorithm for the Subtraction of an Unknown Background . . . 334
D. Digital Filters for Application in ENDOR Spectra . . . . . 335
E. Deconvolution of ENDOR Spectra . . . . . 336
F. Peak Search Algorithm . . . . . 337
G. Simulation of EPR Spectra . . . . . 338
H. Values of $\psi_{ns}(0)$ and $< r^{-3} >_{np}$ for Selected Ions . . . . . 340

References . . . . . 341

Subject Index . . . . . 357