

Contents

1. Introduction	1
1.1 Structure of Point Defects	2
1.2 Basic Concepts of Defect Structure Determination by EPR	4
1.3 Superhyperfine and Electronic Structures of Defects in Solids	9
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	13
2.3 Some Useful Relations for Angular Momentum Operators	15
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	46
3.5 Hyperfine Splitting of EPR Spectra	53
3.6 Superhyperfine Splitting of EPR Spectra	61
3.7 Inhomogeneous Line Widths of EPR Lines	70
4. Optical Detection of Electron Paramagnetic Resonance	75
4.1 Optical Transitions of Defects in Solids	76
4.2 Spectral Form of Optical Transitions of Defects in Solids	78
4.3 EPR Detected with Magnetic Circular Dichroism of Absorption Method	84
4.4 MCDA Excitation Spectra of ODEPR Lines (MCDA “Tagged” by EPR)	93

4.5	Spatially Resolved MCDA and ODEPR Spectra	99
4.6	Measurement of Spin-Lattice Relaxation Time T_1 with MCDA Method	101
4.7	Determination of Spin State with MCDA Method	103
4.8	EPR of Ground and Excited States Detected with Optical Pumping	109
4.9	EPR Optically Detected in Donor-Acceptor Pair Recombination Luminescence	118
4.10	Optically Detected EPR of Triplet States	125
4.11	ODEPR of Trapped Excitons with MCDA Method	129
4.12	Sensitivity of ODEPR Measurements	131
4.13	Structural Information from Forbidden Transitions in MCDA-EPR Spectra	134
4.14	Spatial Correlation Between Defects by Cross-Relaxation-Spectroscopy	144
4.15	High-Field ODEPR/ODENDOR	156
5.	Electron Nuclear Double Resonance	163
5.1	The Resolution Problem, a Simple Model	163
5.2	Type of Information from EPR and NMR Spectra	165
5.3	Indirect Detection of NMR, Double Resonance	167
5.4	Examples of ENDOR Spectra	174
5.5	Relations Between EPR and ENDOR Spectra, ENDOR-Induced EPR	176
5.6	Electron Nuclear Nuclear Triple Resonance (Double ENDOR)	183
5.7	Temperature Dependence and Photo-Excitation of ENDOR Spectra	186
5.7.1	Temperature Dependence of ENDOR Spectra	186
5.7.2	Photo-Excitation of ENDOR Spectra	188
5.8	Stochastic ENDOR	190
6.	Analysis of ENDOR Spectra	197
6.1	Qualitative Analysis of ENDOR Spectra	198
6.1.1	Spin Hamiltonian	198
6.1.2	Simple First Order Solution	199
6.1.3	Assignment of Nuclei	201
6.1.4	Angular Dependence of ENDOR Lines	204
6.1.5	Symmetry Considerations, Neighbor Shells	209
6.2	Quantitative Analysis of ENDOR Spectra	212
6.2.1	Higher Order Approximations	212
6.2.2	Large Anisotropic Hyperfine Interactions	213
6.2.3	Approximation with the Effective Electron Spin $\mathbf{S}_{\text{eff}}$..	223
6.2.4	Second Order Splittings of the Superhyperfine Structure	226

6.2.5	Sample Alignment	237
6.2.6	Reconstruction of the EPR Line Shape from ENDOR Data	243
6.2.7	Asymmetric Superhyperfine Tensors	247
6.2.8	Selection Rules and ENDOR Line Intensities	250
6.2.9	ENDOR Spectra in the Case of a Large Quadrupole Interaction and Axial Symmetry	253
6.2.10	Powder ENDOR Spectra	259
6.2.11	Final Results Obtainable from the Analysis of ENDOR Spectra	261
7.	Electrical Detection	
	of Electron Paramagnetic Resonance	265
7.1	Experimental Methods to Detect EDEPR	266
7.2	Experimental Observation of EDEPR	269
7.3	The Donor-Acceptor Pair Recombination Model	282
7.4	On the Role of the Electron Irradiation for the Donor EPR in Silicon	286
7.5	Spatial Resolution and Low Frequency EDEPR	289
7.6	Electrical Detection of ENDOR	293
7.7	Concentration and Temperature Dependence of the EDEPR Signals	295
7.8	Further Spin-Dependent Recombination Models	304
7.8.1	The <i>Lépine</i> Model	304
7.8.2	The Model of <i>Kaplan, Solomon</i> and <i>Mott</i>	305
7.8.3	The Spin-Dependent SRH Model	306
8.	Theoretical ab initio Calculations	
	of Hyperfine Interactions	309
8.1	Electron States in Solids	310
8.1.1	<i>Born–Oppenheimer</i> Approximation	311
8.1.2	<i>Hartree</i> and <i>Hartree–Fock</i> Approximations	312
8.1.3	Density Functional Theory and Local Density Approximation	314
8.1.4	Computational Methods for Energy Band Calculations	320
8.2	Computational Methods for Deep Point Defects	324
8.2.1	Cluster Methods	325
8.2.2	The Supercell Method	325
8.2.3	Green’s Function Methods	328
8.2.4	The Band Gap Problem and the Scissor Operator	332
8.3	Hyperfine Interactions	334
8.3.1	Non-relativistic Hyperfine Interactions	335
8.3.2	Scalar Relativistic Hyperfine Interactions	336
8.3.3	Magnetization Density for Many-Electron States	338

8.3.4	The Jahn–Teller Effect	341
8.3.5	The Core Polarization	343
8.3.6	Electrical Quadrupole Interaction	347
8.3.7	The Empirical LCAO Scheme	349
8.3.8	The Envelope Function Method	351
8.3.9	Point Dipole-Dipole Interaction	352
8.4	Deep Point Defects	
	in Semiconductors and Insulators	353
8.4.1	Substitutional Donors with $\Delta z = 1$	354
8.4.2	Substitutional Donors with $\Delta z = 2$	355
8.4.3	Interstitial Deep Donors	363
8.4.4	Shallow Acceptors with $\Delta z = -1$	367
8.4.5	Deep Acceptors with $\Delta z = -2$	368
8.4.6	Vacancies	370
8.4.7	Point Defects in Ionic Solids	377
8.4.8	3d Transition Metal Defects	384
8.4.9	Interstitial 3d TM Defects	393
8.5	Shallow Defects:	
	The Effective Mass Approximation and Beyond	399
8.5.1	The EMA Formalism	400
8.5.2	Simplest Case: Nondegenerate Band Edge	401
8.5.3	Conduction Band with Several Equivalent Minima . . .	405
8.5.4	Pseudopotential Calculations	407
8.5.5	Degenerate Valence Bands	411
8.6	Conclusions	411
9.	Experimental Aspects	
	of Optically Detected EPR and ENDOR	415
9.1	Sensitivity Considerations	415
9.1.1	Magnetic Circular Dichroism of Absorption	416
9.1.2	Optically Detected EPR	417
9.2	ODMR Spectrometers Monitoring Light Emission	418
9.3	ODMR Spectrometers Monitoring Magnetic Circular	
	Properties of Absorption and Emission	420
9.3.1	General Description of the Spectrometer	420
9.3.2	Measurement of Magnetic Circular Dichroism	
	of Absorption	422
9.3.3	Measurement of Magnetic Circular Polarization	
	of Emission	425
9.4	Experimental Details of the Components of an MCDA/MCPE	
	ODMR Spectrometer	426
9.4.1	Light Sources	426
9.4.2	Monochromators	427
9.4.3	Imaging Systems	427
9.4.4	Linear Polarizers	427

9.4.5	Photo-Elastic Modulator	427
9.4.6	Detectors	428
9.4.7	Cryostat	429
9.4.8	Magnet	430
9.4.9	Microwave System and Cavity	430
9.4.10	Radio-Frequency System for ODENDOR	432
9.4.11	Control and Registration Electronics	432
9.5	High Frequency ODEPR/ODENDOR Cavities	433
9.5.1	Cylindrical V-Band Cavity	433
9.5.2	Cylindrical Cavity for W-Band MCDA-EPR/ENDOR ..	434
9.5.3	Multimode W-Band <i>Fabry-Pérot</i> Cavity for MCDA-EPR/ENDOR	435
9.6	High Pressure Photoluminescence-Detected EPR	440
Appendices		443
A. Scalar Relativistic Hyperfine Interactions		443
A.1	Scalar Relativistic One-Electron Theory	443
A.2	Hyperfine Interactions for a One-Electron System	445
B. Perturbation Theory of the Spin Hamiltonian		449
B.1	Transformation of the Interaction Tensors	449
B.2	Hamilton Operator, Matrix Elements and Perturbation Theory for the Interaction with one Neighbor Nucleus	451
C. Electrical Detection of EPR		455
C.1	Standard Donor-Acceptor Recombination Model.....	455
C.2	Extended Donor-Acceptor Recombination Models	456
C.2.1	Symmetrical D^0-A^0 Recombination Model After Stich	456
C.2.2	Non-symmetrical D^0-A^0 Pair Recombination Model After Broise	460
C.2.3	Solutions of the Standard D^0-A^0 Pair Recombination Model After Stich for EDENDOR	463
References		467
Index		485

Point Defects in Semiconductors and Insulators
Determination of Atomic and Electronic Structure from
Paramagnetic Hyperfine Interactions

Spaeth, J.-M.; Overhof, H.

2003, XI, 492 p., Hardcover

ISBN: 978-3-540-42695-0