Contents

Preface *XIII*

Part One Materials Science and Raman Spectroscopy Background *1*

1 The sp^2 Nanocarbons: Prototypes for Nanoscience and Nanotechnology *3*
1.1 Definition of sp^2 Nanocarbon Systems *3*
1.2 Short Survey from Discovery to Applications *5*
1.3 Why sp^2 Nanocarbons Are Prototypes for Nanoscience and Nanotechnology *10*
1.4 Raman Spectroscopy Applied to sp^2 Nanocarbons *11*

2 Electrons in sp^2 Nanocarbons *17*
2.1 Basic Concepts: from the Electronic Levels in Atoms and Molecules to Solids *18*
2.1.1 The One-Electron System and the Schrödinger Equation *18*
2.1.2 The Schrödinger Equation for the Hydrogen Molecule *20*
2.1.3 Many-Electron Systems: the NO Molecule *21*
2.1.4 Hybridization: the Acetylene C_2H_2 Molecule *23*
2.1.5 Basic Concepts for the Electronic Structure of Crystals *24*
2.2 Electrons in Graphene: the Mother of sp^2 Nanocarbons *27*
2.2.1 Crystal Structure of Monolayer Graphene *27*
2.2.2 The π-Bands of Graphene *28*
2.2.3 The σ-Bands of Graphene *31*
2.2.4 *N*-Layer Graphene Systems *33*
2.2.5 Nanoribbon Structure *35*
2.3 Electrons in Single-Wall Carbon Nanotubes *37*
2.3.1 Nanotube Structure *38*
2.3.2 Zone-Folding of Energy Dispersion Relations *40*
2.3.3 Density of States *44*
2.3.4 Importance of the Electronic Structure and Excitation Laser Energy to the Raman Spectra of SWNTs *47*
2.4 Beyond the Simple Tight-Binding Approximation and Zone-Folding Procedure *48*

Raman Spectroscopy in Graphene Related Systems. Ado Jorio, Riichiro Saito, Gene Dresselhaus, and Mildred S. Dresselhaus
Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
ISBN: 978-3-527-40811-5

3 Vibrations in sp^2 Nanocarbons *53*
3.1 Basic Concepts: from the Vibrational Levels in Molecules to Solids *55*
3.1.1 The Harmonic Oscillator *55*
3.1.2 Normal Vibrational Modes from Molecules to a Periodic Lattice *56*
3.1.3 The Force Constant Model *59*
3.2 Phonons in Graphene *61*
3.3 Phonons in Nanoribbons *65*
3.4 Phonons in Single-Wall Carbon Nanotubes *66*
3.4.1 The Zone-Folding Picture *66*
3.4.2 Beyond the Zone-Folding Picture *67*
3.5 Beyond the Force Constant Model and Zone-Folding Procedure *69*

4 Raman Spectroscopy: from Graphite to sp^2 Nanocarbons *73*
4.1 Light Absorption *73*
4.2 Other Photophysical Phenomena *75*
4.3 Raman Scattering Effect *78*
4.3.1 Light–Matter Interaction and Polarizability: Classical Description of the Raman Effect *79*
4.3.2 Characteristics of the Raman Effect *81*
4.3.2.1 Stokes and Anti-Stokes Raman Processes *81*
4.3.2.2 The Raman Spectrum *82*
4.3.2.3 Raman Lineshape and Raman Spectral Linewidth Γ_q *82*
4.3.2.4 Energy Units: cm^{-1} *84*
4.3.2.5 Resonance Raman Scattering and Resonance Window Linewidth γ_r *85*
4.3.2.6 Momentum Conservation and Backscattering Configuration of Light *86*
4.3.2.7 First and Higher-Order Raman Processes *86*
4.3.2.8 Coherence *87*
4.4 General Overview of the sp^2 Carbon Raman Spectra *88*
4.4.1 Graphite *88*
4.4.2 Carbon Nanotubes – Historical Background *92*
4.4.3 Graphene *96*

5 Quantum Description of Raman Scattering *103*
5.1 The Fermi Golden Rule *103*
5.2 The Quantum Description of Raman Spectroscopy *108*
5.3 Feynman Diagrams for Light Scattering *111*
5.4 Interaction Hamiltonians *114*
5.4.1 Electron–Radiation Interaction *114*
5.4.2 Electron–Phonon Interaction *115*
5.5 Absolute Raman Intensity and the E_{laser} Dependence *116*

6 Symmetry Aspects and Selection Rules: Group Theory *121*
6.1 The Basic Concepts of Group Theory *122*
6.1.1 Definition of a Group *122*
6.1.2 Representations *123*
6.1.3 Irreducible and Reducible Representations *124*

6.1.4 The Character Table *126*
6.1.5 Products and Orthogonality *127*
6.1.6 Other Basis Functions *128*
6.1.7 Finding the IRs for Normal Modes Vibrations *128*
6.1.8 Selection Rules *130*
6.2 First-Order Raman Scattering Selection Rules *130*
6.3 Symmetry Aspects of Graphene Systems *132*
6.3.1 Group of the Wave Vector *132*
6.3.2 Lattice Vibrations and π Electrons *135*
6.3.3 Selection Rules for the Electron–Photon Interaction *138*
6.3.4 Selection Rules for First-Order Raman Scattering *140*
6.3.5 Electron Scattering by $q \neq 0$ Phonons *141*
6.3.6 Notation Conversion from Space Group to Point Group Irreducible Representations *141*
6.4 Symmetry Aspects of Carbon Nanotubes *142*
6.4.1 Compound Operations and Tube Chirality *143*
6.4.2 Symmetries for Carbon Nanotubes *145*
6.4.3 Electrons in Carbon Nanotubes *151*
6.4.4 Phonons in Carbon Nanotubes *151*
6.4.5 Selection Rules for First-Order Raman Scattering *152*
6.4.6 Insights into Selection Rules from Matrix Elements and Zone Folding *153*

Part Two Detailed Analysis of Raman Spectroscopy in Graphene Related Systems *159*

7 The G-band and Time-Independent Perturbations *161*
7.1 G-band in Graphene: Double Degeneracy and Strain *162*
7.1.1 Strain Dependence of the G-band *163*
7.1.2 Application of Strain to Graphene *165*
7.2 The G-band in Nanotubes: Curvature Effects on the Totally Symmetric Phonons *165*
7.2.1 The Eigenvectors *166*
7.2.2 Frequency Dependence on Tube Diameter *168*
7.3 The Six G-band Phonons: Confinement Effect *169*
7.3.1 Mode Symmetries and Selection Rules in Carbon Nanotubes *169*
7.3.2 Experimental Observation Through Polarization Analysis *170*
7.3.3 The Diameter Dependence of ω_G *172*
7.4 Application of Strain to Nanotubes *174*
7.5 Summary *175*

8 The G-band and the Time-Dependent Perturbations *179*
8.1 Adiabatic and Nonadiabatic Approximations *179*
8.2 Use of Perturbation Theory for the Phonon Frequency Shift *181*
8.2.1 The Effect of Temperature *181*
8.2.2 The Phonon Frequency Renormalization *183*

8.3 Experimental Evidence of the Kohn Anomaly on the G-band of Graphene *186*
8.3.1 Effect of Gate Doping on the G-band of Single-Layer Graphene *186*
8.3.2 Effect of Gate Doping on the G-band of Double-Layer Graphene *186*
8.4 Effect of the Kohn Anomaly on the G-band of M-SWNTs vs. S-SWNTs *187*
8.4.1 The Electron–Phonon Matrix Element: Peierls-Like Distortion *188*
8.4.2 Effect of Gate Doping on the G-band of SWNTs: Theory *191*
8.4.3 Comparison with Experiments *194*
8.4.4 Chemical Doping of SWNTs *196*
8.5 Summary *197*

9 Resonance Raman Scattering: Experimental Observations of the Radial Breathing Mode *199*
9.1 The Diameter and Chiral Angle Dependence of the RBM Frequency *200*
9.1.1 Diameter Dependence: Elasticity Theory *200*
9.1.2 Environmental Effects on the RBM Frequency *202*
9.1.3 Frequency Shifts in Double-Wall Carbon Nanotubes *206*
9.1.4 Linewidths *208*
9.1.5 Beyond Elasticity Theory: Chiral Angle Dependence *209*
9.2 Intensity and the Resonance Raman Effect: Isolated SWNTs *211*
9.2.1 The Resonance Window *211*
9.2.2 Stokes and Anti-Stokes Spectra with One Laser Line *214*
9.2.3 Dependence on Light Polarization *215*
9.3 Intensity and the Resonance Raman Effect: SWNT Bundles *216*
9.3.1 The Spectral Fitting Procedure for an Ensemble of Large Diameter Tubes *217*
9.3.2 The Experimental Kataura Plot *218*
9.4 Summary *220*

10 Theory of Excitons in Carbon Nanotubes *223*
10.1 The Extended Tight-Binding Method: σ–π Hybridization *224*
10.2 Overview on the Excitonic Effect *225*
10.2.1 The Hydrogenic Exciton *226*
10.2.2 The Exciton Wave Vector *227*
10.2.3 The Exciton Spin *228*
10.2.4 Localization of Wavefunctions in Real Space *229*
10.2.5 Uniqueness of the Exciton in Graphite, SWNTs and C_{60} *230*
10.3 Exciton Symmetry *231*
10.3.1 The Symmetry of Excitons *231*
10.3.2 Selection Rules for Optical Absorption *234*
10.4 Exciton Calculations for Carbon Nanotubes *234*
10.4.1 Bethe–Salpeter Equation *235*
10.4.2 Exciton Energy Dispersion *236*
10.4.3 Exciton Wavefunctions *237*
10.4.4 Family Patterns in Exciton Photophysics *241*
10.5 Exciton Size Effect: the Importance of Dielectric Screening *243*

10.5.1 Coulomb Interaction by the 2s and σ Electrons *243*
10.5.2 The Effect of the Environmental Dielectric Constant κ_{env} Term *245*
10.5.3 Further Theoretical Considerations about Screening *246*
10.6 Summary *248*

11 Tight-Binding Method for Calculating Raman Spectra *251*
11.1 General Considerations for Calculating Raman Spectra *252*
11.2 The (n, m) Dependence of the RBM Intensity: Experiment *253*
11.3 Simple Tight-Binding Calculation for the Electronic Structure *255*
11.4 Extended Tight-Binding Calculation for Electronic Structures *258*
11.5 Tight-Binding Calculation for Phonons *259*
11.5.1 Bond Polarization Theory for the Raman Spectra *260*
11.5.2 Non-Linear Fitting of Force Constant Sets *261*
11.6 Calculation of the Electron–Photon Matrix Element *263*
11.6.1 Electric Dipole Vector for Graphene *264*
11.7 Calculation of the Electron–Phonon Interaction *266*
11.8 Extension to Exciton States *269*
11.8.1 Exciton–Photon Matrix Element *270*
11.8.2 The Exciton–Phonon Interaction *271*
11.9 Matrix Elements for the Resonance Raman Process *272*
11.10 Calculating the Resonance Window Width *273*
11.11 Summary *274*

12 Dispersive G′-band and Higher-Order Processes: the Double Resonance Process *277*
12.1 General Aspects of Higher-Order Raman Processes *278*
12.2 The Double Resonance Process in Graphene *280*
12.2.1 The Double Resonance Process *280*
12.2.2 The Dependence of the $\omega_{G'}$ Frequency on the Excitation Laser Energy *284*
12.2.3 The Dependence of the G′-band on the Number of Graphene Layers *286*
12.2.4 Characterization of the Graphene Stacking Order by the G′ Spectra *288*
12.3 Generalizing the Double Resonance Process to Other Raman Modes *289*
12.4 The Double Resonance Process in Carbon Nanotubes *290*
12.4.1 The G′-band in SWNTs Bundles *292*
12.4.2 The (n, m) Dependence of the G′-band *294*
12.5 Summary *296*

13 Disorder Effects in the Raman Spectra of sp^2 Carbons *299*
13.1 Quantum Modeling of the Elastic Scattering Event *301*
13.2 The Frequency of the Defect-Induced Peaks: the Double Resonance Process *304*
13.3 Quantifying Disorder in Graphene and Nanographite from Raman Intensity Analysis *307*
13.3.1 Zero-Dimensional Defects Induced by Ion Bombardment *308*
13.3.2 The Local Activation Model *310*

13.3.3 One-Dimensional Defects Represented by the Boundaries of Nanocrystallites *313*
13.3.4 Absolute Raman Cross-Section *317*
13.4 Defect-Induced Selection Rules: Dependence on Edge Atomic Structure *317*
13.5 Specificities of Disorder in the Raman Spectra of Carbon Nanotubes *320*
13.6 Local Effects Revealed by Near-Field Measurements *321*
13.7 Summary *323*

14 Summary of Raman Spectroscopy on sp^2 Nanocarbons *327*
14.1 Mode Assignments, Electron, and Phonon Dispersions *327*
14.2 The G-band *328*
14.3 The Radial Breathing Mode (RBM) *330*
14.4 G′-band *332*
14.5 D-band *333*
14.6 Perspectives *334*

References *335*

Index *351*