Ado Jorio, Riichiro Saito, Gene Dresselhaus and Mildred S. Dresselhaus Raman Spectroscopy in Graphene Related Systems

The Authors



Ado Jorio is a Professor in the Physics Dept. of the Federal University of Minas Gerais, Brazil, where he also earned his PhD, in 1999. His Post-doctoral research was done at MIT, USA, where his collaboration with the Dresselhaus group and with Professor Saito started. He has authored and co-authored several book chapters and books on carbon science and has been active in science policy in Latin America.



Mildred Dresselhaus received her Ph.D. at the University of Chicago in 1958 and started research on carbon science in 1960 with Gene Dresselhaus while working at the MIT Lincoln Laboratory. She has been an MIT professor since 1967, and started working with Riichiro Saito in 1991 and with Ado Jorio since 2000.



Riichiro Saito received PhD degree from the University of Tokyo in 1985. After being a Research Associate at the University of Tokyo in 1985 and an Associate Professor at the University of Electro-Communication in Tokyo in 1990, he became Professor at Tohoku University in Sendai since 2003.



Gene F. Dresselhaus received his PhD degree from the University on California, Berkeley under the supervision of Charles Kittel. He has actively worked on a variety of problems in condensed matter physics. He has taught courses in condensed matter physics at the University of Chicago and at Cornell University. He currently holds a Research appointment at MIT and jointly leads a research group at the MIT Center for Materials Science and Engineering which studies graphite intercalation compounds, fullerenes, graphene, and carbon nanotubes. He has Co-authored or Co-edited six books on Carbon Science. Ado Jorio, Riichiro Saito, Gene Dresselhaus, and Mildred S. Dresselhaus

Raman Spectroscopy in Graphene Related Systems



WILEY-VCH Verlag GmbH & Co. KGaA

The Authors

Prof. Ado Jorio

Departamento de Física Universidade Federal de Minas Gerais Av. Antonio Carlos, 6627, CP 702 30.123-970 Belo Horizonte, MG Brazil

Prof. Riichiro Saito

Tohoku University Dept. of Physics 6-3 Aoba, Aramaki, Aoba-ku Sendai 980-8578 Japan

Prof. Mildred S. Dresselhaus Dr. Gene Dresselhaus

MIT Room 13-3005 77 Massachusetts Ave. Cambridge, MA 02139-4307 USA All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data: A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at http://dnb.d-nb.de.

© 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Boschstr. 12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Typesetting le-tex publishing services GmbH, Leipzig

Printing and Binding Fabulous Printers Pte Ltd, Singapore Cover Design Formgeber, Eppelheim

Printed in Singapore Printed on acid-free paper

ISBN 978-3-527-40811-5

A. J. and R. S. dedicate this book to the 80th birthday of Professor Gene Dresselhaus (born Nov. 7, 1929) and Professor Mildred S. Dresselhaus (born Nov. 11, 1930).

Contents

Preface XIII

Part One Materials Science and Raman Spectroscopy Background 1

1 The sp² 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 sp² 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 C₂H₂ 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

3 Vibrations in sp² 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 sp² 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 $\omega_{\rm G}$ 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

- X Contents
 - 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: $\sigma \pi$ 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 sp² 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

- XII Contents
 - 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

Preface

Raman spectroscopy is the inelastic scattering of light by matter. Being highly sensitive to the physical and chemical properties of materials, as well as to environmental effects that change these properties, Raman spectroscopy is now evolving into one of the most important tools for nanoscience and nanotechnology. In contrast to usual microscopy-related techniques, the advantages of using light for nanoscience relate both to experimental and fundamental aspects. Experimentally, the techniques are widely available, relatively simple to perform, possible to carry out at room temperature and under ambient pressure, and require relatively simple or no special sample preparation. Fundamentally, optical techniques (normally using infrared and visible wavelengths) are nondestructive and noninvasive because they use the photon, a massless and chargeless particle, as a probe.

For understanding Raman spectroscopy, a combination of experiments and theory is important because some concepts of basic solid state physics are needed for explaining the behavior of the Raman spectra as a function of many experimental parameters, such as light polarization, the energy of the photon, temperature, pressure and changes in the environment. In this book, starting from some known example of physics and chemistry, we will explain how to use the basic concepts of molecular and solid state physics, together with optics to understand Raman scattering. Graphene, nanographite and carbon nanotubes (sp² carbons) are selected as the materials to be studied, due to their importance to nanoscience and nanotechnology, and because the Raman technique has been extremely successful in advancing our knowledge about these nanomaterials. It is possible to observe Raman scattering from one single sheet of sp²-hybridized carbon atoms, the two-dimensional (2D) graphene sheet, as well as from a narrow strip of a graphene sheet rolled-up into a 1 nm diameter cylinder to form the one-dimensional (1D) singlewall carbon nanotube. These observations are possible simply by shining light on the nanostructure focused through a commonly available microscope. This book therefore focuses on the basic concepts of both Raman spectroscopy and sp^2 carbon nanomaterials, together with their interaction. The similarities and differences in the Raman spectra for different sp² carbon nanomaterials, such as graphene and carbon nanotubes, provide a deep understanding of the Raman scattering capabilities that are emphasized in this book.

There is a general feeling that Raman spectroscopy is too complicated for a nonspecialist. Often, common users of Raman spectroscopy as a characterization tool for their samples only touch the surface of the capabilities of the Raman technique. This book is aimed to be sufficiently pedagogic and also detailed to help the general nanoscience and nanotechnology user of Raman spectroscopy to better utilize their instrumentation to yield more detailed information about their nanostructures than before. Our challenge was writing a book that would build from the most basic concept, the Schrödinger equation for the hydrogen atom, going up to the highest level use and application of Raman spectroscopy to study nanocarbons in general.

The book was initially structured for use in a course for graduate students in the Federal University of Minas Gerais (UFMG), Brazil, and it is organized in two parts. The first part gives the basic concepts of Raman spectroscopy and nanocarbons, addressing why we choose nanocarbons as prototype materials for writing this Raman book. The text is suitable for physicists, chemists, material scientists, and engineers, building a link between their languages, a link that is necessary for the future development of nanoscience. The second part gives a detailed treatment of the Raman spectroscopy of nanocarbons, addressing both fundamental material science and the use of Raman spectroscopy towards material applications. Again nanostructured *sp*²-hybridized carbon materials are model systems, both due to the common interest that physicists, chemists, material scientists, and engineers have in these systems and because these systems are pertinent to the length scales where these fields converge. By giving more details, the second part gives examples of the large amount of physics one can learn from studying nanocarbons.

Even though the Raman effect was first observed in the early 1920s, we believe this book is the starting point for lots of new scientific perspectives that the "nano" generation is making possible. We hope the reader will be interested in Raman spectroscopy and will accept the challenges that many researchers are now trying to solve in applying this technique to study nanostructures. Problem sets are included at the end of each chapter, designed to provide a better understanding of the concepts presented in this book and to reinforce the learning process. We appreciate if the readers are willing to solve our problems and send the solutions to the authors to post on the web. The answers by the readers and students using this book can be posted on the following web page: http: //flex.phys.tohoku.ac.jp/book10/index.html.

Finally, we strongly acknowledge all students and collaborators who have contributed to the development of this book.

September, 2010

Ado Jorio, Belo Horizonte, MG, Brazil Riichiro Saito, Sendai, Japan Gene Dresselhaus and Mildred S. Dresselhaus, Cambridge, MA, USA