

## Contents

**Preface** XV

**List of Contributors** XVII

**Abbreviations** XIX

- 1 Thermodynamic Properties of Solids: Experiment and Modeling** 1  
*Samrath L. Chaplot, Ranjan Mittal, and Narayani Choudhury*
- 1.1 Introduction 1
- 1.2 Spectroscopic Techniques and Semiempirical Theoretical Methods 2
- 1.3 Thermal Measurement Techniques 3
- 1.4 First-Principles Quantum Mechanical Methods 3
- 1.5 Outlook 4
- References 4
- 2 Optical Spectroscopy Methods and High-Pressure–High-Temperature Studies** 7  
*Alain Polian, Patrick Simon, and Olivier Pagès*
- 2.1 Methods and Principles: Ambient Conditions 9
- 2.1.1 Semiconductors 9
- 2.1.2  $q \sim 0$  Optical Modes: Concept of Polaritons 10
- 2.1.2.1 Maxwell Equations 10
- 2.1.2.2 Mechanical Equations 11
- 2.1.2.3 Lorentz Approach 12
- 2.1.2.4 Effective Charge/Force Constant 13
- 2.1.2.5 Combined Electrical/Mechanical Equations: Dispersion of Polaritons Modes 14
- 2.1.3 Vibration Spectra 15
- 2.1.3.1 IR Spectroscopies: A Direct Light/Optical-Mode Interaction 15
- 2.1.3.2 Raman Scattering: An Indirect Light/Optical-Mode Interaction 16
- 2.1.3.3 Brillouin Scattering: An Indirect Light/Acoustical-Mode Interaction 19
- 2.1.4 Some Particular Cases 20

2.1.4.1	Multioscillator System	20
2.1.4.2	Multilayer System	21
2.1.4.3	Multicomponent System (Composite)	22
2.1.5	Selection Rules	23
2.1.5.1	Raman Scattering	23
2.1.5.2	IR Absorption	24
2.1.5.3	Brillouin Scattering	24
2.1.6	When Departing from Pure Crystals . . .	25
2.2	Optical Vibrational Spectroscopies Under Extreme Conditions	25
2.2.1	A Specific Impact/Identity in the Field	25
2.2.1.1	Solid-State Physics	26
2.2.1.2	Earth Sciences	28
2.2.2	Specificities and Instrumentation for High-Temperature and High-Pressure Investigations	29
2.2.2.1	Temperature and Emissivity	29
2.2.2.2	High-Pressure Optical Cells, Diamond–Anvil Cells	31
2.2.2.3	High-Temperature Instrumentation	34
2.2.2.4	Brillouin Devices	37
2.2.2.5	Raman Devices	38
2.2.2.6	Infrared Devices: Emissivity Measurements (Temperature and Pressure)	42
2.2.3	Acoustical Modes	44
2.2.3.1	General Presentation	44
2.2.3.2	Examples	47
2.2.4	Optical Modes	55
2.2.4.1	Pressure Aspect	55
2.2.4.2	Temperature Aspect	58
2.3	Perspectives	63
2.3.1	Instrumentation	63
2.3.1.1	Natural Development of Existing Setups	63
2.3.1.2	Innovative Combinations of X-ray and Vibrational Spectroscopies	64
2.3.2	Physical Phenomena	65
2.3.2.1	Phonons (Zone-Center): A Natural “Mesoscope” into the Alloy Disorder	65
2.3.2.2	Elucidation of the Mechanism of the Pressure-Induced Phase Transformations	68
2.3.2.3	Glasses	69
	References	70
<b>3</b>	<b>Inelastic Neutron Scattering, Lattice Dynamics, Computer Simulation and Thermodynamic Properties</b>	<b>75</b>
	<i>Ranjan Mittal, Samrath L. Chaplot, and Narayani Choudhury</i>	
3.1	Introduction	75
3.2	Lattice Dynamics	77

3.2.1	Theoretical Formalisms	77
3.3	Computational Techniques	80
3.4	Thermodynamic Properties of Solids	82
3.5	Theory of Inelastic Neutron Scattering	84
3.5.1	Inelastic Neutron Scattering from Single Crystals: Phonon Dispersion Relations	85
3.5.2	Inelastic Neutron Scattering from Powder Samples: Phonon Density of States	86
3.6	Experimental Techniques for Inelastic Neutron Scattering	88
3.6.1	Measurements Using Triple-Axis Spectrometer	89
3.6.1.1	Phonon Density of States	89
3.6.1.2	Phonon Dispersion Relations	91
3.6.2	Measurements Using Time-of-Flight Technique	91
3.6.2.1	Phonon Density of States	92
3.6.2.2	Phonon Dispersion Relations	93
3.7	Molecular Dynamics Simulation	93
3.8	Applications of Inelastic Neutron Scattering, Lattice Dynamics, and Computer Simulation	95
3.8.1	Phonon Density of States	95
3.8.2	Raman and Infrared Modes, and Phonon Dispersion Relation	97
3.8.3	Elastic Constants, Gibbs Free Energies, and Phase Stability	100
3.8.3.1	Zircon Structured Compound	101
3.8.3.2	Sodium Niobate	102
3.8.4	Negative Thermal Expansion from Inelastic Neutron Scattering and Lattice Dynamics	102
3.8.4.1	Negative Thermal Expansion Calculation	104
3.8.4.2	Thermal Expansion from Experimental High-Pressure Inelastic Neutron Scattering	105
3.8.5	Thermodynamic Properties	106
3.8.6	Phase Transitions in Magnesium Silicate, $\text{MgSiO}_3$	107
3.8.7	Fast Ion Diffusion in $\text{Li}_2\text{O}$ and $\text{U}_2\text{O}$	111
3.9	Conclusions	114
	References	115
<b>4</b>	<b>Phonon Spectroscopy of Polycrystalline Materials Using Inelastic X-Ray Scattering</b>	<b>123</b>
	<i>Alexei Bosak, Irmengard Fischer, and Michael Krisch</i>	
4.1	Introduction	123
4.2	Theoretical Background	125
4.2.1	Scattering Kinematics and Dynamical Structure Factor	125
4.2.2	IXS Cross Section	127
4.3	Instrumental Principles	130
4.4	IXS in the Low- $Q$ Limit	133
4.4.1	Scattering from (Quasi)Longitudinal Phonons	134
4.4.2	Scattering from Quasitransverse Phonons	136

4.4.3	The Aggregate Elasticity of Polycrystalline Materials	138
4.4.4	Effects of Texture	140
4.5	IXS in the High- $Q$ Limit: The Phonon Density of States	141
4.5.1	Magnesium Oxide	143
4.5.2	Boron Nitride	145
4.5.3	Clathrate $\text{Ba}_8\text{Si}_{46}$	148
4.6	IXS in the Intermediate $Q$ -Range	149
4.7	Concluding Remarks	153
	References	155
<b>5</b>	<b>Heat Capacity of Solids</b>	<b>159</b>
	<i>Toshihide Tsuji</i>	
5.1	Introduction	159
5.2	Principles and Experimental Methods of Calorimetry	160
5.2.1	Adiabatic Heat Capacity Calorimetry	160
5.2.2	Adiabatic Scanning Calorimetry	162
5.2.3	Direct Pulse-Heating Calorimetry	165
5.2.4	Laser-Flash Calorimetry	165
5.2.5	Temperature Jump Calorimetry	167
5.3	Thermodynamic Relation Between $C_p$ and $C_v$	168
5.4	Data Analysis of Heat Capacity at Constant Volume ( $C_v$ )	170
5.4.1	Lattice Heat Capacity ( $C_l$ )	170
5.4.1.1	Classical Theory of Lattice Heat Capacity	170
5.4.1.2	Einstein's Model of Lattice Heat Capacity	171
5.4.1.3	Debye's Model of Lattice Heat Capacity	173
5.4.1.4	Anharmonic Term of Lattice Heat Capacity	175
5.4.2	Other Terms Contributed to Heat Capacity at Constant Volume	176
5.4.2.1	Electronic Heat Capacity ( $C_{e,c}$ )	176
5.4.2.2	Schottky-type Heat Capacity ( $C_{e,sh}$ )	177
5.4.2.3	Magnetic Heat Capacity ( $C_m$ )	178
5.4.2.4	Heat Capacity due to Activation Process	179
5.5	Estimation of Normal Heat Capacity	179
5.5.1	Analysis of Heat Capacity Data	179
5.5.1.1	Heat Capacity Data at Low Temperatures	179
5.5.1.2	Heat Capacity Data of Metal Oxides with Fluorite-Type Crystal Structure	180
5.5.1.3	Heat Capacity Data of Negative Thermal Expansion Materials $\text{ZrW}_2\text{O}_8$	181
5.5.2	Kopp–Neumann Law	184
5.5.3	Estimation of Heat Capacity Data from Thermal Expansion Coefficient	185
5.5.4	Corresponding States Method	186
5.5.5	Volumetric Interpolation Schemes	186

5.6	Phase Transition	188
5.6.1	Second-Order Phase Transition	188
5.6.1.1	Order–Disorder Phase Transition due to Atomic Configuration	188
5.6.1.2	Order–Disorder Phase Transition due to Orientation in $ZrW_2O_8$	189
5.6.2	Magnetic Order–Disorder Phase Transition	191
5.7	Summary	192
5.7.1	Heat Capacity Measurement	192
5.7.1.1	Adiabatic Heat Capacity Calorimetry	192
5.7.1.2	Temperature Jump Calorimetry	193
5.7.2	Thermodynamic Relation Between $C_p$ and $C_v$	193
5.7.3	Estimation of Normal Heat Capacity	193
5.7.3.1	Nonmagnetic Metals and Alloys at Low Temperatures	194
5.7.3.2	Nonmetals and Non-Alloys Without Magnetic Transition at Low Temperatures	194
5.7.3.3	Ferromagnetic and Ferrimagnetic Materials at Low Temperatures	194
5.7.3.4	Antiferromagnetic Materials at Low Temperatures	194
5.7.3.5	Metal Oxides with Fluorite-Type Crystal Structure at High Temperatures	194
5.7.4	Second-Order Phase Transition	195
5.7.4.1	Order–Disorder Phase Transition due to Atomic Configuration	195
5.7.4.2	Order–Disorder Phase Transition due to Orientation in $ZrW_2O_8$	195
	References	196
<b>6</b>	<b>Diffraction and Thermal Expansion of Solids</b>	<b>197</b>
	<i>Avesh Kumar Tyagi and Srungaru Nagabhusan Achary</i>	
6.1	Introduction	197
6.2	Strain Analysis	199
6.3	Thermodynamics of Thermal Expansion	201
6.4	Origin of Thermal Expansion	203
6.5	Techniques for Measurement of Thermal Expansion	205
6.5.1	Dilatometer	206
6.5.2	Interferometer	207
6.5.3	Telescope Methods	208
6.5.4	Diffraction Methods	208
6.6	X-Ray Diffraction in Thermal Expansion	209
6.7	Positive and Negative Thermal Expansions	213
6.8	Factors Affecting the Thermal Expansion Coefficients	215
6.8.1	Melting Points	215
6.8.2	Bond Strengths	216
6.8.3	Compressibility and Packing Density	217
6.8.4	Defects and Impurities or Alloy Formation	217

6.8.5	Phase Transitions (Magnetic and Electronic Transitions)	218
6.9	Structure and Thermal Expansion	218
6.10	Examples	221
6.10.1	Fluorite-Type $\text{AO}_2$ Compounds	221
6.10.1.1	Isovalent Substituted $\text{AO}_2$ Lattices	222
6.10.1.2	Aliovalent Substituted $\text{AO}_2$ Lattice	228
6.10.2	Framework Materials	232
6.10.2.1	Cristobalite-Type $\text{APO}_4$ ( $A = \text{Al}^{3+}$ , $\text{Ga}^{3+}$ , and $\text{B}^{3+}$ )	233
6.10.2.2	Molybdates and Tungstates	239
6.10.3	Scheelite- and Zircon-Type $\text{ABO}_4$ Compounds	250
6.10.3.1	$\text{CaMoO}_4$ and $\text{CaWO}_4$	250
6.10.3.2	$\text{LuPO}_4$ , $\text{LuVO}_4$ , and $\text{GdVO}_4$ (Zircon Type)	253
6.11	Conclusion	259
	References	259
<b>7</b>	<b>Electronic Structure and High-Pressure Behavior of Solids</b>	<b>269</b>
	<i>Carlos Moysés Araújo and Rajeev Ahuja</i>	
7.1	Introduction	269
7.2	First-Principles Theory	269
7.2.1	Density-Functional Theory: Hohenberg–Kohn Theorems and Kohn–Sham Equation	270
7.2.2	Exchange–Correlation Functional	271
7.2.3	Plane Wave Methods	272
7.2.4	Linearized Muffin–Tin Orbitals Method	272
7.2.5	Hellman–Feynman Theorem and Geometry Optimization	273
7.3	Structural Phase Transition from First Principles	274
7.4	Alkali Metals	275
7.5	Alkaline Earth Metals	277
7.6	Transition Metals	280
7.7	Group III Elements	282
7.8	Group IV Elements	283
7.9	Group V Elements	285
7.10	Overview	286
	References	287
<b>8</b>	<b>Ab Initio Lattice Dynamics and Thermodynamical Properties</b>	<b>291</b>
	<i>Razvan Caracas and Xavier Gonze</i>	
8.1	Introduction	291
8.2	Phonons	292
8.3	Density-Functional Perturbation Theory	296
8.3.1	Perturbation Expansion	297
8.3.2	Response to Static Electric Fields	299
8.3.3	Mixed Perturbations	299
8.4	Infrared and Raman Spectra	300
8.4.1	Infrared	301

8.4.2	Raman	303
8.5	Thermodynamical Properties	306
8.6	Examples and Applications	307
8.6.1	Polymeric Nitrogen	307
8.6.2	Ice X	309
8.7	Conclusions	312
	References	313
	<b>Index</b>	<b>317</b>

