

# Contents

|                                           |    |
|-------------------------------------------|----|
| List of Frequently Used Symbols . . . . . | XV |
|-------------------------------------------|----|

## **1. From a Strange Effect to Mössbauer Spectroscopy. By U. GONSER (With 17 Figures)**

|                                                                                  |    |
|----------------------------------------------------------------------------------|----|
| 1.1. Introduction . . . . .                                                      | 1  |
| 1.2. The pre-Mössbauer Time . . . . .                                            | 3  |
| 1.3. Existence and Intensity of the Mössbauer Line . . . . .                     | 11 |
| 1.4. Line Width . . . . .                                                        | 18 |
| 1.5. Hyperfine Interaction . . . . .                                             | 21 |
| 1.5.1. Isomer Shift . . . . .                                                    | 22 |
| 1.5.2. Nuclear Zeeman Effect . . . . .                                           | 24 |
| 1.5.3. Quadrupole Splitting . . . . .                                            | 26 |
| 1.6. Perturbation and Combined Effects in the Hyperfine<br>Interaction . . . . . | 28 |
| 1.6.1. Magnetic Dipole and Electric Quadrupole Interaction . . . . .             | 28 |
| 1.6.2. Lattice Vibrational Anisotropy (Goldanskii-<br>Karyagin Effect) . . . . . | 28 |
| 1.6.3. Relaxation Effects . . . . .                                              | 31 |
| 1.6.4. Low Temperature Boltzmann Distribution of Nuclear<br>Levels . . . . .     | 32 |
| 1.7. Relativistic Effects . . . . .                                              | 32 |
| 1.8. Methodology . . . . .                                                       | 35 |
| 1.8.1. Source . . . . .                                                          | 36 |
| 1.8.2. Absorber . . . . .                                                        | 37 |
| 1.8.3. Drive Systems . . . . .                                                   | 38 |
| 1.8.4. $\gamma$ -Ray Detectors . . . . .                                         | 40 |
| 1.8.5. Scattering Technique . . . . .                                            | 41 |
| 1.8.6. Polarized Recoil-Free $\gamma$ -Rays . . . . .                            | 43 |
| 1.8.7. Mössbauer Polarimetry . . . . .                                           | 45 |
| 1.8.8. Measurements of Motions . . . . .                                         | 47 |
| References . . . . .                                                             | 48 |

## 2. Mössbauer Spectroscopy in Chemistry. By P. GÜTLICH (With 12 Figures)

|                                                                                                 |    |
|-------------------------------------------------------------------------------------------------|----|
| 2.1. Hyperfine Interactions and Mössbauer Parameters . . . .                                    | 53 |
| 2.1.1. Electric Monopole Interaction; Isomer Shift . . . .                                      | 55 |
| 2.1.2. Electric Quadrupole Interaction; Quadrupole<br>Splitting . . . . .                       | 58 |
| Electric Field Gradient (EFG) . . . . .                                                         | 59 |
| Quadrupole Splitting . . . . .                                                                  | 63 |
| 2.1.3. Magnetic Dipole Interaction; Magnetic Splitting . .                                      | 65 |
| 2.2. Chemical Information from Isomer Shift . . . . .                                           | 67 |
| 2.2.1. Correlation of Isomer Shift with Oxidation State and<br>Electron Configuration . . . . . | 67 |
| 2.2.2. Correlation of Isomer Shift with Bonding Properties                                      | 70 |
| Iodine Compounds . . . . .                                                                      | 70 |
| Tin(IV) Compounds . . . . .                                                                     | 72 |
| Iron(II) High Spin Compounds . . . . .                                                          | 73 |
| Intermetallic Compounds . . . . .                                                               | 73 |
| Covalent Transition Metal Complexes . . . . .                                                   | 75 |
| Partial Isomer Shift . . . . .                                                                  | 81 |
| 2.3. Chemical Information from Quadrupole Splitting . . . .                                     | 82 |
| 2.3.1. Effect of $(V_{zz})_{CF}$ ; Electronic Structure . . . . .                               | 83 |
| 2.3.2. Effect of $(V_{zz})_{MO}$ ; Bonding Properties . . . . .                                 | 88 |
| Iodine and Xenon Compounds . . . . .                                                            | 88 |
| Covalent Iron(II) and Ru(II) Compounds . . . . .                                                | 88 |
| 2.3.3. Effect of $(V_{zz})_L$ ; Molecular Symmetry . . . . .                                    | 91 |
| 2.4. Conclusion . . . . .                                                                       | 92 |
| References . . . . .                                                                            | 94 |

## 3. Mössbauer Spectroscopy in Magnetism: Characterization of Magnetically-Ordered Compounds. By R. W. GRANT (With 21 Figures)

|                                                                                 |     |
|---------------------------------------------------------------------------------|-----|
| 3.1. Introduction . . . . .                                                     | 97  |
| 3.2. Analysis of $Fe^{57}$ Hyperfine Structure . . . . .                        | 99  |
| 3.2.1. Mixed Magnetic Dipole and Electric Quadrupole<br>Interactions . . . . .  | 99  |
| 3.2.2. Isomer Shift Determination in Complex Spectra .                          | 105 |
| 3.2.3. Sign of the Internal Magnetic Field . . . . .                            | 106 |
| 3.3. Some Typical Magnetic Material Characterization Studies                    | 108 |
| 3.3.1. Magnetic Ordering Temperature and Type of Magnetic<br>Ordering . . . . . | 109 |
| 3.3.2. Phase Analysis . . . . .                                                 | 112 |

|                                                                                             |     |
|---------------------------------------------------------------------------------------------|-----|
| 3.3.3. Phase Transition . . . . .                                                           | 113 |
| 3.3.4. Site Distribution Determination . . . . .                                            | 115 |
| 3.4. Magnetic Structure Studies . . . . .                                                   | 117 |
| 3.4.1. $\text{Ca}_2\text{Fe}_2\text{O}_5$ —A Colinear Antiferromagnetic Structure . . . . . | 122 |
| 3.4.2. Spin Reorientation in $\text{ErFeO}_3$ . . . . .                                     | 125 |
| 3.4.3. $\text{FeOCl}$ —A Noncolinear Antiferromagnetic Structure . . . . .                  | 131 |
| References . . . . .                                                                        | 135 |

#### 4. Mössbauer Spectroscopy in Biology. By C. E. JOHNSON (With 16 Figures)

|                                                           |     |
|-----------------------------------------------------------|-----|
| 4.1. Biological Molecules . . . . .                       | 139 |
| 4.2. Mössbauer Spectroscopy . . . . .                     | 141 |
| 4.2.1. Preparation of Specimen . . . . .                  | 142 |
| 4.2.2. The Isomer (Chemical) Shift ( $\delta$ ) . . . . . | 142 |
| 4.2.3. Quadrupole Splitting ( $\Delta E_Q$ ) . . . . .    | 143 |
| 4.2.4. Magnetic Hyperfine Splitting . . . . .             | 144 |
| 4.3. Heme Proteins . . . . .                              | 147 |
| 4.3.1. Low Spin Ferrous . . . . .                         | 148 |
| 4.3.2. High Spin Ferrous . . . . .                        | 149 |
| 4.3.3. Low Spin Ferric . . . . .                          | 150 |
| 4.3.4. High Spin Ferric . . . . .                         | 151 |
| 4.4. Iron-Sulphur Proteins . . . . .                      | 153 |
| 4.4.1. 1-Iron Proteins (Rubredoxins) . . . . .            | 156 |
| 4.4.2. 2-Iron Proteins (Plant-Type Ferredoxins) . . . . . | 159 |
| 4.4.3. 4- and 8-Iron Proteins . . . . .                   | 163 |
| 4.5. Possible Applications in Medical Research . . . . .  | 165 |
| References . . . . .                                      | 165 |

#### 5. Mössbauer Spectroscopy in Lunar Geology and Mineralogy. By S. S. HAFNER (With 11 Figures)

|                                                             |     |
|-------------------------------------------------------------|-----|
| 5.1. Introduction . . . . .                                 | 167 |
| 5.2. The Lunar Regolith . . . . .                           | 170 |
| 5.3. The Lunar "Soil" . . . . .                             | 171 |
| 5.3.1. The Mössbauer Spectrum of the Soil . . . . .         | 172 |
| 5.3.2. The Oxidation State of the Soil . . . . .            | 175 |
| 5.3.3. Metallic Iron in the Soil . . . . .                  | 179 |
| 5.4. The Minerals from Lunar Rocks . . . . .                | 183 |
| 5.5. Pyroxene . . . . .                                     | 184 |
| 5.5.1. Crystal Structure . . . . .                          | 184 |
| 5.5.2. The Hyperfine Spectrum of $\text{Fe}^{57}$ . . . . . | 186 |

|                                                       |     |
|-------------------------------------------------------|-----|
| 5.5.3. Oxidation State of Iron . . . . .              | 188 |
| 5.5.4. Doublet Intensity and Site Occupancy . . . . . | 190 |
| 5.5.5. $Mg^{2+}$ , $Fe^{2+}$ Order-Disorder . . . . . | 191 |
| 5.5.6. Cooling History of Lunar Basalts . . . . .     | 192 |
| 5.6. Plagioclase . . . . .                            | 194 |
| 5.6.1. Crystal Structure . . . . .                    | 194 |
| 5.6.2. The Hyperfine Spectrum of $Fe^{57}$ . . . . .  | 194 |
| 5.6.3. Oxidation State of Iron . . . . .              | 196 |
| References . . . . .                                  | 197 |

**6. Mössbauer Spectroscopy in Physical Metallurgy.** By F. E. FUJITA  
(With 19 Figures)

|                                                                                     |     |
|-------------------------------------------------------------------------------------|-----|
| 6.1. Introduction . . . . .                                                         | 201 |
| 6.2. Fundamental Concepts and Principles of Spectrum<br>Analysis . . . . .          | 203 |
| 6.2.1. Four Important Parameters . . . . .                                          | 204 |
| Internal Magnetic Field (Hyperfine Field) . . . . .                                 | 204 |
| Isomer Shift . . . . .                                                              | 206 |
| Electric Quadrupole Splitting . . . . .                                             | 206 |
| Line Intensities . . . . .                                                          | 207 |
| 6.2.2. Statistical Calculations on the Atomic<br>Arrangements in Alloys . . . . .   | 208 |
| Substitutional Solid Solutions . . . . .                                            | 208 |
| Interstitial Solid Solutions . . . . .                                              | 211 |
| 6.3. Interstitial Alloys (Carbon Steel) . . . . .                                   | 213 |
| 6.3.1. Quenching and Tempering of Plain Carbon Steel . . . . .                      | 214 |
| 6.3.2. Low Temperature Martensite Phase and<br>Martensitic Transformation . . . . . | 218 |
| 6.4. Substitutional Alloys (Magnetic Perturbation) . . . . .                        | 221 |
| 6.5. Solid Solubility Limit . . . . .                                               | 223 |
| 6.6. Order-Disorder Alloys . . . . .                                                | 224 |
| 6.7. Precipitation . . . . .                                                        | 225 |
| 6.8. Invar . . . . .                                                                | 227 |
| 6.9. Texture . . . . .                                                              | 230 |
| 6.10. Amorphous Alloys . . . . .                                                    | 231 |
| 6.11. Oxidation . . . . .                                                           | 233 |
| 6.12. Diffusion . . . . .                                                           | 233 |
| 6.13. Dislocation and Point Defect . . . . .                                        | 234 |
| References . . . . .                                                                | 235 |

|                                |            |
|--------------------------------|------------|
| <b>Subject Index . . . . .</b> | <b>237</b> |
|--------------------------------|------------|