

Contents

Preface	page	xi
1. The Mössbauer Effect		1
Introduction		1
1.1 Energetics of free-atom recoil and thermal broadening		2
1.2 Heisenberg natural linewidth		5
1.3 Energy and momentum transfer to the lattice		6
1.4 Recoil-free fraction and Debye-Waller factor		9
1.5 Cross-section for resonant reabsorption		11
1.6 A Mössbauer spectrum		15
2. Experimental Techniques		17
2.1 Velocity modulation of gamma-rays		17
2.2 Constant-velocity drives		19
2.3 Repetitive velocity-scan systems		21
(a) Pulse-height analysis mode		23
(b) Time-mode (multiscalar-mode) spectrometers		25
(c) On-line computers		26
2.4 Derivative spectrometers		26
2.5 Scattering experiments		27
2.6 Source and absorber preparation		30
2.7 Detection equipment		35
2.8 Cryogenic equipment and ovens		38
2.9 Velocity calibration		39
2.10 Curve fitting by computer		41
3. Hyperfine Interactions		46
Introduction		46
3.1 Chemical isomer shift, δ		46
3.2 Second-order Doppler shift and zero-point motion		50
3.3 Effect of pressure on the chemical isomer shift		53
3.4 Electric quadrupole interactions		54

3.5	Magnetic hyperfine interactions	59
3.6	Combined magnetic and quadrupole interactions	63
3.7	Relative intensities of absorption lines	66
3.8	Relaxation phenomena	72
3.9	Anisotropy of the recoilless fraction	74
3.10	The pseudoquadrupole interaction	76
4.	Applications of the Mössbauer Effect	80
4.1	Relativity and general physics	80
4.2	Nuclear physics	82
4.3	Solid-state physics and chemistry	84
5.	^{57}Fe – Introduction	87
5.1	The γ -decay scheme	87
5.2	Source preparation and calibration	89
5.3	Chemical isomer shifts	90
5.4	Quadrupole splittings	96
5.5	Magnetic interactions	102
5.6	Polarised radiation studies	104
5.7	Energetic nuclear reactions	109
5.8	The 136-keV transition	110
6.	High-spin Iron Complexes	112
A.	HIGH-SPIN IRON(II) COMPLEXES	112
6.1	Iron(II) halides	113
6.2	Iron(II) salts of oxyacids and other anions	130
6.3	Iron(II) complexes with nitrogen ligands	140
B.	HIGH-SPIN IRON(III) COMPLEXES	148
6.4	Iron(III) halides	148
6.5	Iron(III) salts of oxyacids	155
6.6	Iron(III) complexes with chelating ligands	159
7.	Low-spin Iron(II) and Iron(III) Complexes	169
7.1	Ferrocyanides	169
7.2	Ferricyanides	173
7.3	Prussian blue	178
7.4	Substituted cyanides	182
7.5	Chelating ligands	187
8.	Unusual Electronic Configurations of Iron	194
8.1	Iron(II) compounds showing $^5T_2 - ^1A_1$ crossover	194
8.2	Iron(III) compounds showing $^6A_1 - ^2T_2$ crossover	202

8.3 Iron(II) compounds with $S = 1$ spin state	205
8.4 Iron(III) compounds with $S = \frac{3}{2}$ spin state	206
8.5 Iron 1,2-dithiolate complexes	212
8.6 Systems containing iron(I), iron(IV), and iron(VI)	216
9. Covalent Iron Compounds	221
9.1 Binary carbonyls, carbonyl anions, and hydride anions	222
9.2 Substituted iron carbonyls	226
9.3 Ferrocene and other π -cyclopentadienyl derivatives	233
10. Iron Oxides and Sulphides	239
10.1 Binary oxides and hydroxides	240
10.2 Spinel oxides AB_2O_4	258
10.3 Other ternary oxides	269
10.4 Iron(IV) oxides	280
10.5 Iron chalcogenides	283
10.6 Silicate minerals	286
10.7 Lunar samples	294
11. Alloys and Intermetallic Compounds	304
11.1 Metallic iron	305
11.2 Iron alloys	308
11.3 Intermetallic compounds	317
12. ^{57}Fe – Impurity Studies	329
12.1 Chemical compounds	330
12.2 Metals	340
12.3 Miscellaneous topics	344
13. Biological Compounds	352
13.1 Haemoproteins	353
13.2 Metalloproteins	365
14. Tin-119	371
14.1 γ -Decay scheme and sources	371
14.2 Hyperfine interactions	375
14.3 Tin(II) compounds	381
14.4 Inorganic tin(IV) compounds	390
14.5 Organotin(IV) compounds	399
14.6 Metals and alloys	417
15. Other Main Group Elements	433
15.1 Potassium (^{40}K)	433

15.2 Germanium (^{73}Ge)	434
15.3 Krypton (^{83}Kr)	437
15.4 Antimony (^{121}Sb)	441
15.5 Tellurium (^{125}Te)	452
15.6 Iodine (^{127}I, ^{129}I)	462
15.7 Xenon (^{129}Xe, ^{131}Xe)	482
15.8 Caesium (^{133}Cs)	486
15.9 Barium (^{133}Ba)	488
16. Other Transition-metal Elements	493
16.1 Nickel (^{61}Ni)	493
16.2 Zinc (^{67}Zn)	497
16.3 Technetium (^{99}Tc)	499
16.4 Ruthenium (^{99}Ru)	499
16.5 Silver (^{107}Ag)	504
16.6 Hafnium (^{176}Hf, ^{177}Hf, ^{178}Hf, ^{180}Hf)	504
16.7 Tantalum (^{181}Ta)	507
16.8 Tungsten (^{182}W, ^{183}W, ^{184}W, ^{186}W)	509
16.9 Rhenium (^{187}Re)	514
16.10 Osmium (^{186}Os, ^{188}Os, ^{189}Os)	514
16.11 Iridium (^{191}Ir, ^{193}Ir)	518
16.12 Platinum (^{195}Pt)	524
16.13 Gold (^{197}Au)	526
16.14 Mercury (^{201}Hg)	530
17. The Rare-earth Elements	536
17.1 Praseodymium (^{141}Pr)	537
17.2 Neodymium (^{145}Nd)	537
17.3 Promethium (^{147}Pm)	539
17.4 Samarium (^{149}Sm, ^{152}Sm, ^{154}Sm)	539
17.5 Europium (^{151}Eu, ^{153}Eu)	543
17.6 Gadolinium (^{154}Gd, ^{155}Gd, ^{156}Gd, ^{157}Gd, ^{158}Gd, ^{160}Gd)	558
17.7 Terbium (^{159}Tb)	563
17.8 Dysprosium (^{160}Dy, ^{161}Dy, ^{162}Dy, ^{164}Dy)	563
17.9 Holmium (^{165}Ho)	573
17.10 Erbium (^{164}Er, ^{166}Er, ^{167}Er, ^{168}Er, ^{170}Er)	574
17.11 Thulium (^{169}Tm)	579
17.12 Ytterbium (^{170}Yb, ^{171}Yb, ^{172}Yb, ^{174}Yb, ^{176}Yb)	585
18. The Actinide Elements	596
18.1 Thorium (^{232}Th)	596
18.2 Protactinium (^{231}Pa)	596
18.3 Uranium (^{238}U)	597

18.4 Neptunium (^{237}Np)	600
18.5 Americium (^{243}Am)	604
Appendix 1. Table of nuclear data for Mössbauer transitions	607
Appendix 2. The relative intensities of hyperfine lines	612
Notes on the International System of Units (SI)	619
Author Index	621
Subject Index	645

interactions to be measured more accurately than had been possible in 1960. This has led to the extension of Mössbauer spectroscopy rapidly towards and the continuing periodicity of the new techniques has led to its extension to a wide variety of compounds and solid-state problems. It is hoped that the results obtained by Mössbauer spectroscopy during the past decade will be of value to those who are interested in the structure of molecules and applications of the technique to solid-state problems in the future.

It has been attempted to write a simple and compact treatment which briefly reviews the basic principles underlying the phenomenon, outlines the experimental techniques used, and finally summarizes the variety of experimental and theoretical results which have been obtained. We have tried to give some idea for the physical basis of the Mössbauer effect without excessive use of mathematical formalism, and attempt a presentation of the experimental results in a logical sequence, endeavouring to relate discussions of electronic and magnetization. However, full references to the original literature are given and complete details can easily be pursued by reference to the detailed literature.

The last account of work which has been published using the Mössbauer resonance is the second in this series and again full references to the relevant literature are given. The objective has been to give a critical treatment which provides permanent value and loss of detail. The text has been updated to the beginning of 1970 and numerous references to important results after that time have also been included.

A similar approach has been adopted for tin-117 and for each of the four other elements for which Mössbauer resonances have been observed. Thus, the results here are much less complete than for iron, many new points of theory, energy and magnetic anomalies, applications have been discussed, and, one of the main advantages of Mössbauer spectroscopy is its applicability to a wide range of interesting problems. At all times we have