

# Contents

Foreword .....	v
Acknowledgements .....	xiii
1. Crystallography and the Importance of Structural Information .....	1
1.1 Single crystal diffraction – the basics .....	1
1.1.1 The crystal.....	1
1.1.2 The diffraction pattern .....	7
1.1.3 Measuring the diffraction pattern.....	12
1.1.4 Defining the molecular structure.....	14
1.2 Thermal motion and disorder in crystallography.....	14
1.2.1 Good crystallographic order.....	15
1.2.2 Thermal vibrational disorder.....	15
1.2.3 Static disorder .....	16
1.2.4 Thermal parameters and their chemical and physical importance	16
1.3 Chemical information from neutron crystallography.....	22
1.3.1 Examples.....	24
1.3.2 Areas of impact.....	27
1.3.3 Hydrogen bonding interactions .....	28
1.4 Biology - structure and function .....	31
1.5 Practical aspects of single crystal neutron diffraction experiments .....	32
1.5.1 Obtaining the sample .....	32
1.5.2 Collecting the data .....	33
1.5.3 Data resolution - desired and accessible .....	34
1.5.4 Solving the structure .....	35
1.5.5 Completing the structure - Fourier maps .....	37
1.5.6 Refining the structure.....	39
1.6 Summary.....	41
1.7 References .....	42

2. Neutron Scattering.....	53
2.1 Neutrons and their characteristics.....	53
2.2 Neutron production.....	57
2.2.1 The development of reactor sources .....	59
2.2.2 The development of spallation sources .....	60
2.3 The characteristics of neutron sources.....	62
2.3.1 Reactor sources .....	62
2.3.2 Spallation sources .....	63
2.3.3 Moderation.....	64
2.4 Two neutron sources.....	65
2.4.1 The ILL reactor source.....	65
2.4.2 The ISIS pulsed spallation neutron source.....	67
2.5 Neutron detection .....	69
2.5.1 Gas detectors.....	70
2.5.2 Scintillator detectors .....	70
2.5.3 Area neutron detectors .....	71
2.5.4 Image plates and Charge Coupled Devices (CCDs) .....	72
2.6 The complementarity of X-rays and neutrons in single crystal diffraction .....	74
2.6.1 Joint X-ray and neutron methods.....	75
2.6.2 Joint X+N refinements.....	75
2.6.3 The accuracy of X-ray and neutron determinations .....	77
2.6.4 Improving joint determinations: non-spherical X-ray form factors.....	78
2.6.5 Multipole refinement of X-ray data .....	79
2.6.6 Requirements for successful studies using both X-ray and neutron data .....	79
2.7 Other methods in neutron scattering.....	81
2.8 References .....	81
3. Techniques for Single Crystal Neutron Diffraction.....	86
3.1 Single crystal diffractometers .....	86
3.1.1 Basic principles of single crystal diffractometers .....	87
3.1.2 Automatic diffractometry.....	90
3.2 Data collection and intensity extraction.....	91
3.2.1 Basic procedures for single crystal data collection .....	91
3.2.2 Choice of scans for data collection .....	95
3.2.3 Peak Integration .....	97
3.2.4 Over-determination of data sets .....	99
3.3 Data reduction and correction.....	102
3.3.1 Normalisation.....	102
3.3.2 Absorption corrections.....	102

3.3.3	Extinction corrections .....	105
3.3.4	Thermal diffuse scattering .....	107
3.4	Laue methods.....	108
3.4.1	Time-of-flight Laue methods .....	109
3.4.2	The hedgehog detector .....	110
3.5	Structure solution from single crystal neutron data .....	111
3.5.1	Determination of absolute configuration .....	112
3.6	Structure refinement .....	114
3.6.1	Constrained refinements .....	114
3.6.2	Scattering length refinements.....	117
3.6.3	Hydrogen isotope effects on crystal structure .....	119
3.6.4	Comparing data sets and refinements: Half-normal probability plots and significance tests .....	121
3.7	Sample Environment .....	122
3.7.1	Low temperature devices for single crystal neutron diffraction.....	123
3.7.2	Calibrating data collection temperatures.....	124
3.7.3	Choosing and reaching data collection temperatures .....	124
3.8	Crystal sizes for single crystal neutron diffraction .....	126
3.9	Molecular structures and neutron single crystal diffraction.....	127
3.10	References .....	128
4.	Review of Applications I: The Accurate Location of Atoms .....	142
4.1	Accurate and complete molecular geometry.....	142
4.1.1	Chemical structure and tautomeric form.....	143
4.1.2	Proton transfer and disorder.....	147
4.1.3	Correcting bond lengths for thermal motion effects .....	147
4.1.4	Comparing atomic positions from X-ray and neutron data.....	150
4.1.5	Less well justified bond length corrections.....	153
4.2	Molecular conformation .....	154
4.2.1	The van der Waals and electrostatic surfaces of molecules .....	155
4.3	Hydrogen atom location in metal complexes: hydride and other ligands.....	159
4.3.1	First Row metal compounds .....	160
4.3.2	Second Row metal compounds .....	164
4.3.3	Third Row metal compounds .....	168
4.3.4	Fourth Row metal compounds .....	179
4.3.5	Di-hydrogen ligands.....	180
4.3.6	Agostic interactions .....	182
4.4	Combined X-ray and neutron studies .....	185
4.4.1	Deformation and difference density studies.....	186
4.5	Biological structures .....	188
4.5.1	Location of hydrogen atoms .....	189

4.5.2 Solvent structure .....	190
4.5.3 Hydrogen exchange .....	191
4.5.4 Low resolution studies .....	191
4.5.5 Other biologically relevant molecules .....	191
4.5.6 Recent developments .....	192
4.6 References .....	192
<b>5. Review of Applications II: Hydrogen Bonding and other</b>	
Intermolecular Interactions .....	211
5.1 Introduction to hydrogen bonds .....	211
5.1.1 Hydrogen bonds in organometallic complexes .....	215
5.1.2 Isotope effects .....	215
5.1.3 Computational methods .....	215
5.2 'Normal' hydrogen bonds .....	216
5.2.1 Intermolecular hydrogen bonds .....	216
5.2.2 Intramolecular hydrogen bonds .....	220
5.3 Very short hydrogen bonds: symmetric or asymmetric? .....	225
5.3.1 Short O...O hydrogen bonds - flat-bottomed potentials and proton disorder .....	225
5.3.2 Short N...N hydrogen bonds .....	229
5.4 Bifurcated and combined inter/intra- molecular hydrogen bonds .....	230
5.4.1 Carbohydrate structures .....	230
5.4.2 Other structures .....	233
5.5 Dimer motifs .....	235
5.6 Weaker hydrogen bonds .....	237
5.6.1 C-H...O and related types of hydrogen bond .....	237
5.6.2 Halides as acceptors .....	239
5.6.3 Other hydrogen bonds .....	240
5.7 Hydrogen bonding in water molecules .....	241
5.7.1 Clathrate hydrates .....	242
5.7.2 Cyclodextrins - complex hydrogen bonded networks .....	243
5.7.3 Hydrated proton systems .....	244
5.8 Novel hydrogen bonds and very weak interactions; non-bonded interactions .....	246
5.9 References .....	247
<b>6. Review of Applications III: Probing Vibrations and Disorder .....</b>	<b>262</b>
6.1 Principles of thermal motion analysis .....	262
6.1.1 Torsional motions .....	264
6.1.2 Validity of the simple model .....	264
6.1.3 Lattice dynamical calculations .....	265
6.2 Dynamics from statics - thermal motion analysis .....	266

6.2.1 Rigid body thermal motion analysis .....	267
6.2.2 Multiple temperature studies.....	268
6.2.3 Molecular structure and geometry changes with temperature....	272
6.3 Hydrogen atom motions in molecules .....	274
6.3.1 Hydrogen atoms in hydrogen bonds .....	275
6.3.2 Hydrogen atoms in covalent bonds: X-H stretches.....	278
6.3.3 Metal hydrides .....	279
6.4 Librating groups .....	280
6.5 The inadequacy of the ellipsoidal description of anisotropic displacement parameters.....	283
6.5.1 Examples of moving beyond the ellipsoid model in molecular systems .....	285
6.6 Mismatches between X-ray and neutron thermal parameters.....	286
6.6.1 Methods for correcting thermal parameters .....	288
6.7 Static atomic disorder in molecular structures.....	289
6.7.1 Disordered atoms .....	290
6.7.2 Configurational and orientational disorder .....	294
6.7.3 Plastic crystals.....	298
6.7.4 Phase transitions.....	299
6.8 The role of diffuse scattering in characterising molecular disorder....	303
6.9 References .....	304
<b>7. Impact on Material Properties and Design .....</b>	<b>317</b>
7.1 Pharmaceuticals and other bio-active small molecules.....	317
7.1.1 Ibuprofen.....	318
7.1.2 Acetylcholine .....	320
7.2 Optically-active materials.....	323
7.2.1 The importance of intermolecular interactions .....	325
7.3 Organic semi-conductors, conductors and superconductors.....	326
7.3.1 Structural studies of $\beta$ -(BEDT-TTF) <sub>2</sub> X organic superconductors.....	328
7.4 Crystal engineering and molecular design.....	329
7.4.1 Supramolecular concepts .....	330
7.4.2 The role of hydrogen atoms and hydrogen bonding.....	330
7.5 References .....	333
<b>8. The Future: New Instruments, New Sources, New Techniques, New Science .....</b>	<b>337</b>
8.1 The potential of Laue and time-of-flight Laue diffraction.....	338
8.1.1 LADI - steady state quasi-Laue diffractometer.....	339
8.1.2 SXD - Next generation time-of-flight Laue diffraction .....	341
8.2 Improvements in sources .....	342

8.3 Options in neutron powder diffraction.....	343
8.4 The present uses of neutrons and the future uses of more neutrons....	344
8.4.1 "Traditional" single crystal areas .....	344
8.4.2 "Novel" single crystal areas .....	345
8.5 Final word: whither single crystal neutron diffraction?.....	346
8.6 References .....	346
Appendix I. Absorption coefficients used in single crystal neutron diffraction experiments.....	348
Appendix II. Analyses of the librations of terminal groups.....	358
Index .....	365