to my parents
BIMETALLIC TRIS-OXALATE MAGNETS: SYNTHESIS, STRUCTURE AND PROPERTIES

by Christopher John Nuttall, of the Royal Institution London.


Abstract

In this thesis the series of compounds (cation)\(M^{II}Fe^{III}\)(ox)_3\) \(\{M^{II} = Mn\) and Fe, ox = \(C_2O_4^{2-}\)\} are studied for cation = NPr_4, NBu_4, Npent_4, PPh_4, AsPh_4, PBu_4 and PPN. X-ray diffraction reveals all 14 compounds crystallise with layer honeycomb structures. A linear correlation is found for both the inter-layer and the intra-plane unit-cell parameters between analogous MnFe and FeFe compounds. The profiles have been compared to single crystal structure models of (cation)MM'(ox)_3 in the form of partial refinement. For cation = Npent_4 the powders can be described by the C\(222(1)\) Npent_4Mn^{II}Fe^{III}(ox)_3 single crystal structure (solved at 120K). In the case of cation = NPr_4, NBu_4 and PBu_4, the compounds have found to be bi-phasic containing \(R3c\) and \(P6(3)\) phases, similar to the \(R3c\) NBu_4MnCr(ox)_3 and \(P6(3)\) NBu_4MnFe(ox)_3 single crystal structures. A stacking faulting model, allowing the layer sequence to vary between \(R3c\) and \(P6(3)\) structures, was found to explain the broadening apparent in the X-ray profiles.

(cation)\(M^{II}Fe^{III}\)(ox)_3\) \(\{M^{II} = Mn, Fe\}\) compounds present a variety of magnetic ordering phenomena. (cation)\(Mn^{II}Fe^{III}\)(ox)_3 compounds are nominally antiferromagnet with \(T_c\)'s in the range 24-27K. Neutron diffraction experiments on PPh_4(-\(d_{20}\))Mn^{II}Fe^{III}(ox)_3 reveal the magnetic structure to be well explained by antiparallel spin alignment along the c-axis with \(R3c\) magnetic Shubnikov symmetry. The low temperature uncompensated moments exhibited in the MnFe compounds were reasoned to be the result of sublattice disorder.

(cation)\(Fe^{II}Fe^{III}\)(ox)_3\) compounds are ferrimagnetic and have an unusual cation dependence. For cation = NPr_4, NBu_4, Npent_4, PBu_4 and PPN \(T_c = 43.5-45K\) and the temperature dependent magnetisation approximates a variant of Néel type N ferrimagnetic order, with a temperature of compensation \((T_{comp})\) and a low temperature negative magnetisation. For cation = PPh_4 and AsPh_4 compounds \(T_c = 34-37K\) and the magnetisation temperature dependence is similar to Néel type Q ferrimagnetic order, with low temperature positive magnetisation. The magnetic order in the FeFe series has been investigated by AC and DC SQUID magnetometry, MuSR spectroscopy, Mössbauer spectroscopy (experiments not performed by the author) and, in the case of PPh_4(-\(d_{20}\))FeFe(ox)_3, neutron diffraction. The compounds with low temperature
negative magnetisation exhibit evidence of a magneto-strictive transition ($T_{\text{comp}} < T < T_c$) which stabilises the negative remanence. The compounds with a low temperature positive magnetisation exhibit considerable evidence for only a glassy-type magnetic order developing at low temperature. This has been correlated to Fe and consequent Fe$^{II}$ deficiencies in the compounds.
Acknowledgements

I would like to thank my supervisor, Peter Day for his constant encouragement, support, open-mind and guidance throughout my PhD.
I am indebted to Corine Mathionière who worked in parallel on the (cation)M^{II}Fe^{III}(ox)_3 compounds and helped greatly in both their synthesis and the purification during my first year.
I would like to thank Mark Green for sharing his sharp insight into solid state structural chemistry and encouraging me to tackle 'impossible' data.
I would like to thank Professor Yakushi and Dr Nakasawa at the I.M.S. (Japan) for much help and support during my stay. Thanks to Hiroshi and Chihoko for making my stay very special and their friendship.
Thanks to Mo Kurmoo for assistance and encouragement early on.
Thanks to Simon Carling for accompanying me on numerous, sometimes embarrassing, Neutron diffraction experiments and also for some assistance on UNIX computers.
Thanks to Steven Bramwell (my UCL supervisor) and Kosmas Prassides for useful discussions; and again to Kosmas for letting me have-a-first-go at MuSR at PSI.
Thanks to Simon Carling and Dick Visser for their help during the MuSR experiments performed at ISIS.
Thanks to Richard Catlow for letting me use his computers (and his generosity) throughout my PhD - without me even asking.
Thanks to Jürgen Ensling for performing and interpreting the Mössbauer experiments.
Special thanks to Alan Hewat for his assistance during Neutron Diffraction experiments
Lastly, I would like to thank many people (past and present) at the R.I. (not just the Day group) who make it a special, sociable place.
Table of Contents

CHAPTER 1

Introduction .............................................................. 17-29
  1.1 Overview .............................................................. 17
  1.2 Strategies to molecular magnets ............................ 18
    1.2.1 Purely molecular magnets ................................ 18
    1.2.2 Molecular based magnets with extended lattices 20
  1.3 Scope of the research ............................................ 28

CHAPTER 2

Magnetic theory .......................................................... 30-39
  2.1 Susceptibility ....................................................... 30
  2.2 Magnetic interactions .......................................... 31
  2.3 Long range magnetic order ................................. 32
    2.3.1 Magnetic model hamiltonians ......................... 32
    2.3.2 Molecular field theory .................................. 34
    2.3.3 Spin canting ............................................... 39

CHAPTER 3

Experimental techniques .............................................. 40-61
  3.1 Diffraction .......................................................... 40
    3.1.1 Powder X-ray diffraction ............................... 42
    3.1.2 Neutron diffraction ....................................... 42
    3.1.3 Powder neutron diffraction instruments ............ 46
      (i) D1B instrument ............................................ 47
      (ii) D1A instrument .......................................... 47
      (iii) D2B instrument ......................................... 48
3.1.4 Fitting powder diffraction profiles ......................................................... 49
3.1.5 Diffraction from disordered layer compounds ...................................... 52
3.2 Magnetometry .............................................................................................. 53
  3.2.1 Low field DC SQUID measurements .................................................. 53
  3.2.2 High field DC SQUID measurements .................................................. 54
  3.2.2 Alternating current (AC) magnetometry .............................................. 54
3.3 The MuSR technique.................................................................................... 56

CHAPTER 4
Synthesis and structural properties of (cation)M^{II}Fe^{III}(ox)_3 compounds. ................................................................. 62-103

4.1 Synthesis and characterisation ................................................................. 62
  4.1.1 Synthesis of PPh_4(-d_{20})M^{II}Fe^{III}(ox)_3 ........................................ 65
    (i) Preparation of the Grignard reagent Ph(-d_3)MgBr ......................... 66
    (ii) Preparation of PPh_4(-d_{20})Br ......................................................... 66
    (iii) Preparation of PPh_4(-d_{20})M^{II}Fe^{III}(ox)_3 and PPh_4(-d_{20})Fe^{II}Fe^{III}(ox)_3 67
4.2 Powder X-ray diffraction ............................................................................ 68
  4.2.1 General X-ray profiles and unit cell extraction ................................... 68
4.3 Structural models ....................................................................................... 74
  4.3.1 N{pent}_4M^{II}Fe^{III}(ox)_3 ................................................................. 74
  4.3.2 (cation)M^{II}Fe^{III}(ox)_3 {cation = NPr_4, NBu_4, PBu_4} .............. 77
  4.3.3 PPh_4M^{II}Fe^{III}(ox)_3 and AsPh_4M^{II}Fe^{III}(ox)_3 ......................... 86
  4.3.4 Sample dependence of powder diffraction profiles ............................ 87
  4.3.5 (PPN)M^{II}Fe^{III}(ox)_3 compounds .................................................. 88
  4.3.6 Attempted preparation of single crystals ............................................ 90
4.4 Neutron diffraction .................................................................................... 91
  4.4.1 Neutron diffraction experiments on PPh_4(-d_{20})Mn^{II}Fe^{III}(ox)_3 ... 91
  4.4.2 Neutron diffraction experiments on PPh_4(-d_{20})Fe^{II}Fe^{III}(ox)_3 ... 100
CHAPTER 5
Magnetic characterisation of (cation)MIIFeIII(ox)3 compounds by AC and DC SQUID magnetometry............. 104-134
  5.1 Overview....................................................... 104
  5.2 FeIIFeIII oxalate salts................................. 104
    5.2.1 General behaviour.................................... 104
    5.2.2 Compounds with a negative low temperature magnetisation..... 107
      (i) Low field studies......................................... 107
      (ii) High field studies....................................... 112
      (iii) AC susceptibility measurements.................... 119
    5.2.3 Compounds with a positive low temperature magnetisation..... 119
      (i) Low field studies......................................... 119
      (ii) High field studies....................................... 124
      (iii) AC susceptibility measurements.................... 126
  5.3 MnIIFeIII oxalate salts................................. 129

CHAPTER 6
Investigation of (cation)FeIIFeIII(ox)3 compounds with local magnetic probes............................. 135-148
  6.1 MuSR spectroscopy............................................. 135
  6.2 Mössbauer spectroscopy.................................... 144

CHAPTER 7
Discussion............................................................ 149-164
  7.1 Structural considerations............................... 149
  7.2 Interpretation of the magnetic behaviour............ 152
    7.2.1 (cation)FeIIFeIII(ox)3.................................. 152
      (i) High temperature magnetic behaviour............... 152
(ii) Low temperature magnetic behaviour ............................................ 154

7.2.2 (cation)Mn$^{II}$Fe$^{III}$(ox)$_3$ .................................................. 161

(i) High temperature magnetic behaviour ........................................ 161

(ii) Low temperature magnetic behaviour ...................................... 162

7.3 Conclusions .................................................................................... 163

References ............................................................................................... 165-169

Appendix 1 Factors in Rietveld refinements ....................................... 170

Appendix 2 (cation)M$^{II}$Fe$^{III}$(ox)$_3$ fitted powder X-ray profiles ...... 171-172

Appendix 3 Example of a DIFFaX input file ..................................... 173-176

Appendix 4 Magnetisation plots for (cation)M$^{II}$Fe$^{III}$(ox)$_3$ compounds ... 177-180
Figure Captions

1.1: Structure of decamethylferrocenium tetracyanoethenide Fe(Me5C5)2TCNE. . . 19
1.2: (a) Structure of the organic radical para-Nitrophenyl Nitronyl Nitroxide
   
   \( (p^-\text{NPNN}) \) ................................................................. 20

   (b) Structure of the organic radical \( p\text{-NC-CF2-CNSSN}^* \) ............ 20
1.3: The structure of ferrimagnetic chain compound MnCu(pbaOH)(H2O)3. . . . 21
1.4: Illustration of the inter-chain registry in MnCu(pba) based compounds. . . . 21
1.5: The structure of ferrimagnetic chain compound Mn(hfac)2(NIT-isopropyl). . 22
1.6: The structure of three-dimensional lattice compound CsNiCr(CN)6. ........ 23
1.7: Inorganic anionic layer of the PPh4[MnCr(ox)]3 structure viewed parallel to the [001] plane. ................................................................. 24
1.8: The PPh4[MnCr(ox)]3 structure viewed parallel to the [100] plane (with one PPh4+ cation displayed per layer). ................................. 25
1.9: Inorganic anionic layer of the NBu4[MnCr(ox)]3 structure viewed parallel to the [001] plane. ................................................................. 26
1.10: The three-dimensional oxalate backbone of \([\text{Fe(bipy)}_3]^{2+}[\text{Fe}_2(\text{ox})_3]^{2-}\) in the \(P4_332\) enantiomeric space group. ....................................................... 27
2.1: Illustration of the principle Néel ferrimagnetic order types. .................. 36
2.2: The \((\alpha,\beta)\) Néel plot for \(\lambda/\mu = 2/3\). ................................. 37
2.3: Showing the relative magnetic sublattice ordering for Néel type N ferrimagnetic order. ................................................................. 38
3.1: The Ewald construction as a condition of elastic diffraction. ............... 41
3.2: The geometry of magnetic Bragg reflection. ...................................... 44
3.3: Schematic representation of the behaviour of spins upon symmetry operation . .................................................................................. 45
3.4: Typical constant wavelength powder neutron diffractometer set-up. . . . 46
3.5: The D1B constant wavelength diffractometer. .................................. 47
3.6: The D1A constant wavelength diffractometer .............................................. 48
3.7: The D2B constant wavelength diffractometer .............................................. 49
3.8: (a,b) Showing the instrumental arrangement and spatial distribution of positron emission in the longitudinal MuSR experiment .............................................. 58
3.9: Illustration of: (a) implantation; (b) precession and (c) decay in the MuSR experiment ................................................................. 59
4.1: Scheme of synthetic routes to (cation)M^{II}Fe^{III}(ox)_3 .................................. 63
4.2a: X-ray profile of NPr_4MnFe(ox)_3 with partial indexing on P6(5) cell ............ 69
4.2b: X-ray profile of Npent_4FeFe(ox)_3 with partial indexing on C222(1) cell .... 69
4.3: Fit of the NPr_4MnFe(ox)_3 X-ray profile in the two-theta region between 9 and 14 degrees ............................................................................................................. 70
4.4: Pattern matching for the Npent_4MnFe(ox)_3 X-ray profile using C222(1) cell. 71
4.5: (a) Inter-layer repeat distance in (cation)M^{II}Fe^{III}(ox)_3 \{M^{II} = Mn, Fe\} ........ 73
    (b) Hexagonal unit cell parameter \(a\) in (cation)M^{II}Fe^{III}(ox)_3 \{M^{II} = Mn, Fe\}. 73
4.6: (a) Layer stacking in the Npent_4MnFe(ox)_3 C222(1) structure. ................. 75
    (b) The two cation positions in the Npent_4MnFe(ox)_3 structure viewed parallel to the [001] plane. ............................................................ 75
4.7: Npent_4M^{III}Fe(ox)_3 powder X-ray profiles fitted to the Npent_4MnFe(ox)_3 C222(1) structural model for (a) Npent_4MnFe(ox)_3 and (b) Npent_4FeFe(ox)_3. 76
4.8: Layer stacking in (cation)MM'(ox)_3 with (a) R3c and (b) P6(3) structures .... 77
4.9: Two phase fits for NBu_4M^{III}Fe(ox)_3 powder X-ray profiles; fitting to R3c and P6(3) structural models for (a) NBu_4FeFe(ox)_3 and (b) NBu_4MnFe(ox)_3. .... 79
4.10: Two phase fits for NPr_4M^{III}Fe(ox)_3 powder X-ray profiles; fitting to R3c and P6(3) structural models for (a) NPr_4FeFe(ox)_3 and (b) NPr_4MnFe(ox)_3. ... 80
4.11: Illustration of the layer unit cell definition of R3c and P6(3) model structures and their stacking vectors. ......................................................... 83
4.12: (a-d) Simulated powder diffraction profiles of NPr_4MnFe(ox)_3 using the DIFFaX program. ............................................................... 84
4.12: (e-g) Simulated powder diffraction profiles of NPr₄MnFe(ox)₃ using the DIFFaX program and (h) the NPr₄MnFe(ox)₃ X-ray profile .......... 85

4.13: (a) PPh₄FeFe(ox)₃ powder X-ray profile fitted to the PPh₄MnCr(ox)₃ R3c structural model. .......................................................... 86

4.13: (b) PPh₄MnFe(ox)₃ powder X-ray profile fitted to the PPh₄MnCr(ox)₃ R3c structural model. .......................................................... 87

4.14: Preparation dependence of the PPh₄MnFe(ox)₃ X-ray profile for (a) a typical Ionic method precipitation and (b) a typical Block method precipitation. ... 88

4.15: (PPN)MᴵᴵFe(ox)₃ powder X-ray profiles partially indexed on a P6(3) cell for (a) (PPN)FeFe(ox)₃ and (b) (PPN)MnFe(ox)₃. ........................................ 89

4.16: Postulated conformation of the PPN cation within the interlamellar oxalate layer of (PPN)MᴵᴵFe(ox)₃ compounds. ........................................ 89

4.17: Neutron diffraction profile of PPh₄(-d₂O)MnFe(ox)₃ (D1A; 40K) fitted with pattern matching to a R3c cell. .................................................. 92

4.18: Neutron diffraction profile of PPh₄(-d₂O)MnFe(ox)₃ (D1A; 1.5K) with the most intense magnetic reflections marked. ........................................ 93

4.19: The D1B difference plot [I(1.7K) - I(30K)] for PPh₄(-d₂O)MnFe(ox)₃ with magnetic reflections (R3c cell) marked. ................................. 94

4.20: The integrated intensity of the [201] magnetic reflection of PPh₄(-d₂O)MnFe(ox)₃ (D1B) versus temperature. .................................................. 94

4.21: (a,b) Predicted magnetic diffraction patterns for antiferromagnetic alignment along c-axis in PPh₄MnFe(ox)₃ and (c) the observed [I(1.7K)-I(30K)]. ... 96

4.22: Predicted magnetic diffraction pattern for spin alignment along c-axis in a P6(3) phase with P6(3) magnetic symmetry (reflections are marked in P6(3) and R3c super cell as P6(3)(R3c)). .................................................. 97

4.23: Predicted magnetic diffraction pattern for a R3c magnetic structure with spin alignment at an angle to c-axis. .................................................. 98

4.24: An illustration of the magnetic order in PPh₄(-d₂O)MnFe(ox)₃ (Shubnikov R3c)
4.25: Neutron diffraction profile of PPh$_4$(-d$_{20}$)FeFe(ox)$_3$ (D2B; 50K) fitted with pattern matching to a $R3c$ cell.

4.26: (a) Low angle part of neutron diffraction profile of PPh$_4$FeFe(ox)$_3$ (D2B; 50K).

4.26: (b) Low angle part of neutron diffraction profile of PPh$_4$FeFe(ox)$_3$ (D2B; 1.5K) with the [201] magnetic reflection marked.

4.27: The D1B difference plot [I(1.7K) - I(30K)] for PPh$_4$(-d$_{20}$)FeFe(ox)$_3$ with the [201] magnetic reflection marked.

4.28: Integrated intensity of the [201] magnetic reflection of PPh$_4$(-d$_{20}$)FeFe(ox)$_3$ (D1B) versus temperature.

5.1: Inverse susceptibility (1/$\chi$) Curie-Weiss fits for (cation)FeFe(ox)$_3$.

5.2: The temperature dependence of the magnetisation of (cation)FeFe(ox)$_3$ after 100G field cooling.

5.3: The temperature dependence of the magnetisation of NBu$_4$FeFe(ox)$_3$ after zero and low field cooling (0G < H < 100G).

5.4: The temperature dependence of the ZFC magnetisation of (cation)FeFe(ox)$_3$ (cation = NBu$_4$, PPN and PBU$_4$).

5.5: The magnetisation of NBu$_4$FeFe(ox)$_3$ in 100G applied field during (a) slow cooling and (b) slow warming/cooling between 39.8 and 40.2K.

5.5: (b) Close-up of the magnetisation in NBu$_4$FeFe(ox)$_3$ during slow cooling/warming in 100G field, showing the magnetisation discontinuity at T = 40.0K.

5.6: The temperature dependence of the magnetisation of NBu$_4$FeFe(ox)$_3$ after 100G field cooling from different temperatures.

5.7: Temperature dependence of the magnetisation of NBu$_4$FeFe(ox)$_3$ after cooling in fields between 100G and 70,000G, measuring upon warming in 100G.

5.8: Hysteresis loops of NBu$_4$FeFe(ox)$_3$ at 5K after; (a) 100G FC, (b) 70,000G FC.
and (c) ZFC. .......................................................... 116

5.9: (a,b) The development of hysteresis of NBu$_4$FeFe(ox)$_3$ (100G FC) with
temperature. .......................................................... 118
(c) The development of hysteresis of NBu$_4$FeFe(ox)$_3$ (100G FC) with
temperature. .......................................................... 119

5.10: (a) AC and DC susceptibility behaviour of NBu$_4$FeFe(ox)$_3$. .............. 121
(b) $\chi''$ frequency dependence in NBu$_4$FeFe(ox)$_3$ over 0.1-1500Hz. ....... 121

5.11: Temperature dependence of the magnetisation of PPh$_4$FeFe(ox)$_3$ after zero and
low field cooling. ....................................................... 122

5.12: Comparison of ZFC magnetisation behaviour in (a) PPh$_4$FeFe(ox)$_3$ and (b)
AsPh$_4$FeFe(ox)$_3$. .................................................... 123

5.13: Hysteresis of PPh$_4$FeFe(ox)$_3$ at 5K after 100G FC. .......................... 125

5.14: The development of hysteresis of PPh$_4$FeFe(ox)$_3$ (100G FC) with temperature.
.................................................................................. 125

5.15: (a) AC and DC susceptibility behaviour of PPh$_4$FeFe(ox)$_3$. .............. 126
(b) $\chi''$ frequency dependence in PPh$_4$FeFe(ox)$_3$ over 0.1-1500Hz. ....... 127
(c) A test for Arrhenius magneto-dynamics in PPh$_4$FeFe(ox)$_3$ from AC
susceptibility measurements. ........................................... 128

5.16: Inverse susceptibility ($1/\chi$) Curie-Weiss fits for (cation)MnFe(ox)$_3$. ....... 129

5.17: Temperature dependence of the ZFC and 100G FC magnetisations in
Npent$_4$MnFe(ox)$_3$. ...................................................... 130

5.18: Magnetisation behaviour in (cation)MnFe(ox)$_3$ (100G FC) (cation = PPN,
PPh$_4$, AsPh$_4$ and PBu$_4$). ........................................... 132

5.19: Zero field and field cooling magnetisation behaviour in NBu$_4$MnFe(ox)$_3$. .. 133

5.20: Zero field and field cooling magnetisation behaviour in NPr$_4$MnFe(ox)$_3$. .. 133

5.21: The magnetisation in NBu$_4$MnFe(ox)$_3$ and NPr$_4$MnFe(ox)$_3$ at 5K as a function
of cooling field (100G measuring field). ................................. 134

6.1: ZF-MuSR of NBu$_4$FeFe(ox)$_3$ at (a) 100 and 45K, (b) 42K and (c) 4.5K. 137
6.2: ZF-MuSR of PPh₄FeFe(ox)₃ at (a) 80K, (b) 33K and (b) 4.5K. .... 138
6.3: The temperature dependence of fitted initial asymmetries of (cation)FeFe(ox)₃
ZF-MuSR experiments. ................................................................. 140
6.4: Temperature dependence of the fitted fast relaxation rate of NBu₄FeFe(ox)₃
ZF-MuSR. ................................................................. 141
6.5: Temperature dependence of the fitted fast relaxation rate of PPh₄FeFe(ox)₃
ZF-MuSR. ................................................................. 141
6.6: Longitudinal MuSR repolarisation curve of NBu₄FeFe(ox)₃ at 4.5K. .... 143
6.7: Temperature dependence of the fitted internal field at the Fe^{III} site in
(cation)Fe^{II}Fe^{III}(ox)₃. ................................................................. 146
6.8: Mössbauer spectra of NBu₄FeFe(ox)₃ between 1.9K and 46K. .... 147
6.9: Mössbauer spectra of PPh₄FeFe(ox)₃ between 1.9K and 60K. .... 148
7.1: The relative magnetic sublattice ordering in the ferrimagnet (cation)Fe^{II}Fe^{III}(ox)₃
required for a compensation point (type N Néel order). ........ 155
7.2: The temperature dependent hysteresis properties of NBu₄FeFe(ox)₃. .... 158
7.3: The temperature dependent hysteresis properties of PPh₄FeFe(ox)₃. .... 160
A2.1: Two phase fits for PBu₄M^{III}Fe^{III}(ox)₃ powder X-ray profiles; fitting to R3c and
P6(3) structural models for (a) PBu₄FeFe(ox)₃ and (b) PBu₄MnFe(ox)₃ ... 171
A2.2: Two phase fits for AsPh₄M^{III}Fe^{III}(ox)₃ powder X-ray profiles; fitting to R3c
and P6(3) structural models for (a) AsPh₄FeFe(ox)₃ and (b) AsPh₄MnFe(ox)₃ 172
A4.1: Inverse susceptibility (1/\chi) Curie-Weiss fits for (cation)FeFe(ox)₃ .... 177
A4.2: Inverse susceptibility (1/\chi) Curie-Weiss fits for (cation)MnFe(ox)₃ .... 178
A4.3: The magnetisation of Npent₄FeFe(ox)₃ in 100G applied field during (a) slow
cooling and (b) slow warming/cooling between 39.8K and 40.2K. .... 179
A4.4: AC and DC susceptibility behaviour of Npent₄FeFe(ox)₃. ........ 180
Table Captions

2.1: Spin and lattice dimensionalities exhibiting a transition to long-range magnetic order T > 0K. ......................................................... 33
2.2: Magnetic characteristics of the Néel ferrimagnetic ground states. ............. 37
4.1: (a) Elemental analyses of (cation)FeIIFeIII(ox)3 compounds. ................. 64
   (b) Elemental analyses of (cation)MnIIFeIII(ox)3 compounds. ............... 65
4.2: Refined unit cell parameters of PPh4(-d20)MIIFeIII(ox)3 \{MII = Mn, Fe\} ... 67
4.3: Refined unit cell parameters of (cation)MIIFeIII(ox)3 \{MII = Mn, Fe\}
   compounds at room temperature. ....................................................... 72
5.1: Magnetic characteristics of (cation)FeFe(ox)3 (100G FC). ..................... 107
5.2: Magnetisation saturation values at 5K in NBu4FeFe(ox)3 after cooling in
different fields between 100G and 70,000G, measuring in 100G. ......... 113
5.3: Magnetic remanence of NBu4FeFe(ox)3 at 5K from hysteresis loops recorded
   between +/-70,000G. ................................................................. 115
5.4: The temperature dependence of the magnetic coercivity and remanence of
   NBu4FeFe(ox)3 (100G FC) from hysteresis loops recorded between +/-10,000G. ................................................................. 117
5.5: Critical temperatures in (cation)FeFe(ox)3 from AC measurements. ....... 120
5.6: The temperature dependence of the magnetic coercivity and remanence of
   PPh4FeFe(ox)3 (100G FC) from hysteresis measurements. .................. 124
5.7: The frequency dependence of the $\chi''$ maximum in PPh4FeFe(ox)3. ....... 128
5.8: Magnetic characteristics of (cation)MnIIFeIII(ox)3 (100G FC). ............. 131
6.1: Mössbauer fitted parameters for NBu4FeFe(ox)3 and PPh4FeFe(ox)3 ....... 145
List of abbreviations

(not defined in the text)

(i) Chemical

\( \text{ox} = \text{oxalate} = C_2\text{O}_4^{2-} \)
\( \text{bipy} = \text{bipyridine} = N_2C_{10}H_8 \)

l.s. = low Spin
h.s. = high Spin

\( \Delta,A \) = chiral configurations of \( D_3 \) tris-bidentate complexes

(ii) Scientific

Magnetic units are given in C.G.S.; however, moments were converted to S.I. units to enable calculation of Bohr magnetons.

\( J \) = spin angular momentum quantum number
\( \mu_B \) = Bohr magneton
\( N \) = Avogadro number
\( k \) = Boltzmann constant
\( H \) = Hamiltonian
\( H \) = Field (given in Gauss i.e. as an induction)
\( S \) = classical vector spin
\( M \) = Magnetisation
\( e \) = coulomb charge of electron
\( c \) = speed of light

In general vector quantities have been marked in **Bold**.
CHAPTER 1

Introduction

1.1 Overview

The design and synthesis of new solid state materials with interesting physical properties is a contemporary challenge for chemists. A trend towards the use of molecules in the construction of novel systems is seen throughout solid state chemistry; examples including low dimensional conducting/semi-conducting materials, optical materials and magnets. The reasons for such an interest are manifold yet are often rooted in the flexibility inherent to molecular syntheses. Physical properties in the solid state are often crucially determined by subtle structural features. Hence, the synthetic flexibility within a molecular system can aid the elucidation of these factors through systematic structural variations.

Molecular solid state systems may be classified as either purely molecular systems (those that contain isolated molecular species) or as molecular based systems where recognisable molecular units are chemically linked. In purely molecular systems a controlled variation of structural parameters is sometimes difficult to achieve. Often many possible molecular packing arrangements are available with similar lattice energies. Chemical alterations of the molecular species can cause the interchange between possible phases from molecular packing/stacking energy considerations.

In molecular based systems structural control is effected by a number of factors. Primarily the connectivity and topology of the molecular units determine the possible structures available to lattice crystallisation. Successful lattice formation is also dependent on favourable steric and charge effects. Often a non-connecting component is used in the synthesis to enable charge neutralisation of the lattice. This species may also act as a structurally determining template when a number of possible lattice types exist. Subtle chemical changes in the non-connecting component e.g. \(-\text{CH}_3 \rightarrow \text{-CH}_2\text{-CH}_3\) may give systematic structural variations within a given lattice type.

In magnetism a move to the design of connected molecular based systems is the result of the desire to control structure, the magnetic interactions and hence magnetic ordering within compounds\(^1\). Connected molecular based magnets provide a controllable magnetic lattice environment in which magnetic exchange interactions between localised spins can be propagated by the efficient super exchange mechanism (§2.4).
The composite insulating nature of molecular based magnets promotes possibilities for the combination of magnetism with other physical phenomena. Optically induced magnetism is the most novel development in this sense. The ternary molecular based cyanide system \( K_{0.2}Co_{1.4}[Fe(CN)_{6}](H_{2}O)_{6.9}^2 \) was found to exhibit an increase in critical temperature from 12 to 16K upon red light illumination. The increase was attributed to the internal photochemical redox process \( \text{(l.s.)Fe}^{II} + (\text{l.s.})\text{Co}^{III} \xrightarrow{hv} (\text{h.s.)Fe}^{III} + (\text{h.s.)Co}^{II} \). The excited magnetic behaviour was found to be stable for a number of days and reversible via blue light illumination.

A molecular based approach to magnetism may eventually be a route to tailored magnetic materials where the magnetic characteristics; e.g. transition temperature, magnetic hardness and response to optical stimulus, are controlled by design. Molecular based magnets may also lead to new magnetic technologies e.g. molecular scale information storage devices\(^3,4,5\).

1.2 Strategies to molecular magnets

In the design of new magnetic materials from molecules a number of different factors to their design must be considered; for example, the selection of a suitable spin carrying molecule and its connectivity. The next section briefly describes various successful strategies that have yielded molecular and molecular based magnets. The discussion expands upon the molecular based metal tris-oxalate magnets which are subject of this thesis.

1.2.1 Purely molecular magnets

In 1986 Miller \textit{et al.}\(^6\) found that \( \text{Fe(Me}_5\text{C}_5)\text{C}_2\text{TCNE} \), the (1:1) charge transfer salt of decamethylferrocene donor and tetracyanoethenide (TCNE) acceptor molecules, exhibited a transition to long-range ferromagnetic order at 4.8K. The structure shown in Figure 1.1, consists of stacked alternating chains of \([\text{Fe(Me}_5\text{C}_5)\text{C}_2]^+ \) and \([\text{TCNE}^-] \) radicals of type \([\text{D-A-D-A}] \) (where D donates e\(^-\) donor and A an acceptor). Other compounds of this type have been synthesised and found to be low temperature ferromagnets; e.g. \( \text{Mn(Me}_5\text{C}_5)\text{C}_2\text{TCNE} \) (critical temperature, \( T_c = 8.5K \))\(^7\), \( \text{Cr(Me}_5\text{C}_5)\text{C}_2\text{(TCNE)} \) (\( T_c = 3.4K \))\(^8\) and \( \text{Mn(Me}_5\text{C}_5)\text{C}_2\text{(TCNQ)} \) \( (T_c = 6.2K) \). The McConnell-Breslow mechanism\(^9\), namely the mixing of an excited electronic triplet state \((D^2A)\) with the ground state stabilising parallel spin alignment, has met with considerable success in explaining the observed magnetic behaviour in these
compounds. A more general spin polarisation mechanism is now used to explain the magnetic order in purely molecular magnetic compounds\textsuperscript{11}.

![Figure 1.1: Structure of decamethylferrocenium tetracyanothenide Fe(Me\textsubscript{5}C\textsubscript{5})\textsubscript{2}TCNE](image)

Purely organic species have also been used successfully to synthesise bulk magnets. For example, the radical \textit{p-NPNN} (\textit{para}-nitrophenyl nitronyl nitroxide) (Figure 1.2(a)) exhibits a ferromagnetic transition at 0.6K in its \textit{\gamma} phase\textsuperscript{12}. The highest ferromagnetic ordering temperature for a nitronyl nitroxide organic magnet is currently 1.48K exhibited in N,N-dioxy-1,2,5,7-tetramethyl-2,6-diazaadamantane\textsuperscript{13}. Recently, a significant increase of ordering temperatures in purely organic radical magnets was achieved with the sulphur-nitrogen dithiadiazolyl radical \textit{p}-NC\textsubscript{6}F\textsubscript{4}CNSSN\textsuperscript{•} (Figure 1.2(b)) which exhibits weak ferromagnetism below \textit{T}_c = 36K in its \textit{\beta} phase\textsuperscript{14}.

The magnetic ground state in these purely molecular systems is very difficult to control as bulk magnetic order depends on the sign of magnetic interactions in three dimensions. Clearly, there is a preliminary requirement for the molecular packing...
arrangement to provide an efficient magnetic exchange pathway in at least one direction (§2.6.3).

Figure 1.2(a): Structure of the organic radical para-Nitrophenyl Nitronyl Nitroxide (p-NPNN)

Figure 1.2(b): Structure of the organic radical p-NC-CF\textsubscript{4}-CNSSN\textsuperscript{*}

1.2.2 Molecular based magnets with extended lattices

In molecular based magnets with chain lattices work has focussed on the control of magnetic order along the chain. The ferrimagnetic chain approach\textsuperscript{1}: propagating intra-chain antiferromagnetic exchange between uncompensating moments, has yielded many new magnets. The combination of [Cu(pbaOH)]\textsuperscript{2-} with hydrated Mn\textsuperscript{2+} ions in a (1:1) ratio precipitates the chain compound MnCu(pbaOH)(H\textsubscript{2}O)\textsubscript{3}\textsuperscript{15}, depicted in Figure 1.3 (pbaOH = 2-hydroxyl-1,3-propylenebis(oxamate)). The compound undergoes a ferrimagnetic transition at 4.6K. In contrast the almost identical chain compound MnCu(pba)(H\textsubscript{2}O)\textsubscript{3} orders antiferromagnetically at 2.3K. The difference in magnetic order between the two compounds is explained by the inter-chain registry in each compound. In MnCu(pbaOH)(H\textsubscript{2}O)\textsubscript{3} the nearest inter-chain neighbours are Mn-Cu as
opposed to Mn-Mn and Cu-Cu in MnCu(pba)(H₂O)₃. This results in an antiferromagnetic alignment of inter-chain moments in MnCu(pba)(H₂O)₃ and bulk antiferromagnetism (illustrated in Figure 1.4).

Figure 1.3: The structure of ferrimagnetic chain compound MnCu(pbaOH)(H₂O)₃.

Figure 1.4: Illustration of the interchain registry in MnCu(pba) based compounds.
In Mn(hfac)$_2$(NIT-isopropyl)$_{16}$ an alternative ferrimagnetic chain is realised (NIT-isopropyl = 2-isopropyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxy-3-oxide, hfac = hexafluoroacetylacetonate). Metal complexes are connected into a chain by ambidentate organic radical ligands, as shown in Figure 1.5. Intra-chain ferrimagnetism is propagated by a strong antiferromagnetic exchange interaction ($J \approx -100$K) between the radical ligands and the transition metal spins. The compound undergoes a ferrimagnetic transition at 7.6K.

![Figure 1.5: The structure of ferrimagnetic chain in Mn(hfac)$_2$(NIT-isopropyl).](image)

The analogous rare earth compounds Gd(hfac)$_2$NITR ($R =$ ethyl, isopropyl, methyl, and phenyl) provide interesting magnetic model compounds. The ratio of intra-chain nearest neighbour ($J_{nn}$) to next nearest neighbour ($J_{nnn}$) exchange interactions is found to be critical in determining the magnetic order in these compounds and for the $R =$ ethyl and isopropyl compounds results in the formation of chiral magnetic domains and a suppression of a transition to long-range magnetic order$^{17}$.

In general, magnetic ordering temperatures in one dimensional magnetic systems are restricted to low temperatures by the limiting strength of the inter-chain exchange interactions $J_{\text{intra-chain}} \gg J_{\text{inter-chain}}$. The design of molecular based materials that become bulk magnets at high temperatures has therefore been directed towards synthesising magnets with higher lattice dimensionalities. One approach is to use the cyanide ionic blocks [$M^{II}(CN)_6]^3-$ and $M^{II}$ ions. Many new magnets with structures similar to the classic Prussian Blue Fe$^{II}_3$[Fe$^{III}(CN)_3$]$_2$ compound$^{18,19}$ have been
prepared by this method. By choosing combinations of $M^ {II}$ and $[M^{III}(CN)_6]^{3-}$ in order to maximise the antiferromagnetic/ferromagnetic interactions (see §2.4)\cite{36,37} between adjacent spins high magnetic ordering temperatures have been achieved; for example, $CsNi^{II}[Cr^{III}(CN)_6]$ (Figure 1.6) becomes ferromagnetic at $T_c = 90K$, $Cr^{II}_3[Cr^{III}(CN)_6]_2$ is ferrimagnetic $T_c = 240K$\cite{20} and the room temperature magnet $(V^{2+},V^{3+})_n[Cr(CN)_6]_m.3H_2O$ $(n,m = \text{variable})$ $T_c = 315-340K$\cite{21}.

Figure 1.6: The structure of three-dimensional lattice compound $CsNiCr(CN)_6$.

Novel magnetic lattices have also been obtained \textit{via} a molecular based approach. The compound $(\text{rad})_2Mn_2[Cu(opba)_3(DMSO)].2H_2O\text{ }^{22,23} \text{ rad = 2-\{(1-methylpyridinium-4-yl)-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide\}}$, for example, is a unique lattice consisting of two equivalent perpendicular but interlocked honeycomb layers of connected molecular units. The compound undergoes a ferrimagnetic transition at 22.5K. Identical magnetic behaviour in the related \textit{simple} two-dimensional honeycomb layer compound $(NBu_4)_2Mn_2Cu_3(opba)_3$\cite{24} indicated that the magnetic lattice in the interlocked compound is essentially two-dimensional (§2.5) with only weak inter-network magnetic interactions.
The bimetallic tris-oxalate magnets (cation)[M^{II}M^{III}(ox)_{3}] were first reported by Tamaki et al. in the case of cation = NBu_{4}, M^{III} = Cr and M^{II} = Mn, Fe, Co, Ni and Cu. The compounds have two-dimensional honeycomb lattices and were found to undergo ferromagnetic phase transitions between 6 and 14K. The first crystal structure determination of these compounds was reported by Decurtins et al. on PPh_{4}MnCr(ox)_{3} and revealed crystallisation in R$ar{3}$c with the enormous cell a,b = 18.783Å, c = 57.283Å. The purely inorganic anionic [MnCr(ox)_{3}]_{n}^{n-} honeycomb layer (illustrated in Figure 1.7) exhibits an alternation of manganese and chromium M(ox)_{3} units which are connected through the ambidentate oxalate ligands. The connectivity of the layer requires that the M(ox)_{3} units have alternating configurations, A and A. The straightforward consequence of the connectivity is that within a given layer Cr(ox)_{3} and Mn(ox)_{3} units have single and opposing configurations. In PPh_{4}MnCr(ox)_{3} the layer is slightly distorted from an ideal hexagonal pattern which requires a doubled in-layer cell parameter.

Figure 1.7: Inorganic anionic layer of the PPh_{4}[MnCr(ox)_{3}] structure viewed parallel to the [001] plane.
Figure 1.8: The PPh$_4$[MnCr(ox)$_3$] structure viewed parallel to the (100) plane (with one PPh$_4^+$ cation displayed per layer).

The $R3c$ structure of PPh$_4$MnCr(ox)$_3$ denotes a six layer repeat, illustrated in Figure 1.8. As a consequence of the symmetry consecutive [MnCr(ox)$_3$]$_n$ layers contain alternating configurations for each metal. The six layer repeat can be defined as (a-b'-c-a'-b-c'), where ' refers to a reversal of M(ox)$_3$ configurations in the layer.

In PPh$_4$MnCr(ox)$_3$ the organic tetraphenylphosphonium cations are located between each inorganic layer, within the 9.5Å layer separation, such that each cation has one phenyl group penetrating the honeycomb vacancy. For clarity, in Figure 1.8 only one cation per layer has been included and in one conformation; in the structure
each honeycomb layer vacancy is filled, giving four cations per layer within the unit cell. Figure 1.7 shows the axial phenyl ligand that penetrates the honeycomb layer vacancy projected onto the [001] crystal plane. One phenyl ligand is disordered by the axial three-fold symmetry and lies in the non-distorted honeycomb site of the layer. The cation positions illustrated in Figure 1.8 exemplify the rhombohedral centering of the cell which generates layers 0, 2 and 4 and the layers 1, 3, 5 generated by the glide plane symmetry.

The compound NBu₄MnCr(ox)₃ was also found to crystallise in R3c with the reduced cell a,b = 9.414Å c = 53.66Å. The non-distorted hexagonal honeycomb inorganic layer of this compound is shown in Figure 1.9. The cell requires only one symmetry independent oxalate group. The tetrabutylammonium site is similar to that of the tetraphenylphosphonium cation in PPh₄MnCr(ox)₃ with one, approximately axial, butyl ligand axially penetrating the layer vacancy; however, in the structure the butyl groups are highly disordered and not exactly determined.

Figure 1.9: Inorganic zero layer of the NBu₄[MnCr(ox)₃] structure viewed parallel to the [001] plane

* the author wishes to thank Professor L.O. Atovymann and Dr. G.V. Shilov for their kind provision of a full set of atomic coordinates for the NBu₄MnCr(ox)₃ compound.
An alternative lattice built from connected tris-oxalate units was originally identified by Tamaki et al.\textsuperscript{25} In contrast to the honeycomb layers, consisting of alternating $\Delta$ and $\Lambda$ M(ox)$_3$ configurations, this structure contains only one configuration $\Delta$ or $\Lambda$ within the lattice. The connecting units now generate chiral helical nets in three dimensions. This lattice type has been realised in a number of different metal oxalate based magnetic materials; for example, $\{[\text{Fe}^{II}(\text{bipy})_3]^{2+}[\text{Fe}^{II}_2(\text{ox})_3]^{2-}\}_n$\textsuperscript{28,29} which becomes antiferromagnetic at around 15K. Figure 1.10 shows the oxalate backbone of this lattice. $\{[\text{Fe}^{II}(\text{bipy})_3]^{2+}[\text{Fe}^{II}_2(\text{ox})_3]^{2-}\}_n$ is cubic $\{a,b,c = 15.42\text{\AA}\}$ and crystallises in the chiral space groups $P4_332$ or $P4_132$ depending on which M(ox)$_3$ configuration is contained within the lattice ($\Delta = P4_332$ and $\Lambda = P4_132$).

Figure 1.10: The three-dimensional oxalate backbone of $\{[\text{Fe}(\text{bipy})_3]^{2+}[\text{Fe}_2(\text{ox})_3]^{2-}\}$ in the $P4_332$ enantiomeric space group.
It is interesting to note that a chiral oxalate crystal is formed with the molecular cation \([\text{Fe}^{II}(\text{bipy})_3]^{2+}\) which has the chiral point group \(D_3\) and that crystallisation from racemic mixtures of \([\text{M}(\text{ox})_3]^{3-}\) and \([\text{Fe}^{II}(\text{bipy})_3]^{2+}\) results in resolution of both components within the crystals: \(\Delta-[\text{Fe}^{II}(\text{bipy})_3]^{2+}\) enantiomers always crystallise with the \(\Delta-\text{M}(\text{ox})_3\) units and vice versa (\(\Lambda-\Lambda\)).

It can be concluded that the cation used in the synthesis of metal tris-oxalate magnets acts as a template to both two-dimensional and three-dimensional lattices depending upon its shape, charge and symmetry.

1.3 Scope of the research

The work reported in this thesis is concerned with the two-dimensional metal tris-oxalate molecular based magnets (cation)\(\text{M}^{II}\text{Fe}^{III}(\text{ox})_3\) with \(\text{M}^{II} = \text{Mn}\) and \(\text{Fe}\). These compounds were originally reported by Tamaki et al.\(^{30}\) for cation = \(\text{NBu}_4\) in a further paper to the original report on (cation)\(\text{M}^{II}\text{Cr}(\text{ox})_3\) compounds\(^{25}\); however, the magnetic characterisation was incomplete and the report included no structural characterisation. The magnets (cation)\(\text{M}^{II}\text{Fe}(\text{ox})_3\) present most interesting magnetic behaviours. In the case of \(\text{M}^{II} = \text{Mn}\) they can nominally be described as antiferromagnetic, as both \(\text{Mn}^{II}\) and \(\text{Fe}^{III}\) have \(S = 5/2\), with ordering temperatures around 24-27K. They also exhibit small ferromagnetic moments at low temperatures. In the case of \(\text{M}^{II} = \text{Fe}\) the compounds are ferrimagnetic (\(T_c = 35-45K\)). For \(\text{NBu}_4\text{Fe}^{II}\text{Fe}(\text{ox})_3\) a magnetic compensation temperature (\(T_{\text{comp}}\) see \(\S 2.6\)) is observed with a resultant negative magnetisation (\(T < T_{\text{comp}}\)) at low temperatures, whilst in contrast the compound \(\text{PPh}_4\text{Fe}^{II}\text{Fe}(\text{ox})_3\) displays apparently normal ferrimagnetism\(^{31}\). The synthetic work reported in this thesis has involved the extension of the series (cation)\(\text{M}^{II}\text{Fe}(\text{ox})_3\) through variation of the organic cation. Some of the compounds reported were first synthesised by Corine Mathonière within the same laboratory and original synthesis is noted (\(\S 4.1\)). Successful single crystal characterisation has been elusive during this study. Structural work has therefore focused on powder X-ray and powder neutron diffraction studies of the compounds (Chapter 4). Definitive structural solution was not possible from the powder diffraction data; however, a number of structural effects within the compounds were discerned from comparison with the available structural models of (cation)\(\text{M}^{II}\text{M}'(\text{ox})_3\) compounds provided by single crystal analyses. Indeed, during the period of thesis study, more single crystals have been have prepared and structures solved in the series. In particular, \(\text{Npent}_4\text{MnFe}(\text{ox})_3\)^{32} prepared by Corine Mathonière and also the most recently reported structures \(\text{NPr}_4\text{MnCr}(\text{ox})_3\) and \(\text{NBu}_4\text{MnFe}(\text{ox})_3\)^{33}. These structures are discussed in relation to the actual powder
diffraction data of the equivalent cation compounds (cation)\text{M}\text{III}Fe(ox)\text{3} in §4.2. Chapter 4 also includes an investigation of the magnetic order in compounds PPh\textsubscript{4}(-d\textsubscript{20})MnFe(ox)\text{3} and PPh\textsubscript{4}(-d\textsubscript{20})FeFe(ox)\text{3} by powder neutron diffraction.

Chapter 5 details a thorough investigation of the magnetisation behaviour of the compounds (cation)\text{M}\text{II}Fe(ox)\text{3}, particularly the (cation)FeFe(ox)\text{3} series, with SQUID AC and DC magnetometry techniques. Chapter 6 contains results of physical experiments carried out on the (cation)FeFe(ox)\text{3} compounds using the local magnetic probe methods; Mössbauer spectroscopy (experiments not performed by the author) and MuSR spectroscopy experiments performed on the EMU instrument at the ISIS pulsed muon facility.

Finally, Chapter 7 provides a general discussion of the results presented throughout the thesis, particularly, the magnetic information gained from each measuring technique is evaluated. In the (cation)FeFe(ox)\text{3} series the discussion focuses on possible mechanisms for the negative magnetisation behaviour seen in some of the series. In the case of (cation)\text{Mn}Fe(ox)\text{3} the magnetic structure information is compared to that gained from a single crystal magnetisation experiment performed on Npent\textsubscript{4}MnFe(ox)\text{3}\textsuperscript{32}. 
CHAPTER 2

Magnetic theory

'Few subjects are more difficult to understand than magnetism'

Despite the above, it is the purpose of this chapter to develop some theories of magnetism. The compounds examined in this thesis are two-dimensional insulating magnets and hence discussion focuses on superexchange effects between localised spins in layer lattices. Particular attention is given to ferrimagnetism and antiferromagnetism. Molecular field theory (§2.6) is developed to illustrate the variety of magnetic order in ferrimagnets (the Néel order types); however, the quantitative inaccuracies inherent in the approximation, especially with regard to low dimensional magnets, are noted.

2.1 Susceptibility

The electronic energies of all compounds are perturbed by a magnetic field and they acquire a magnetisation. The response of the magnetisation $M$ to a field $H$ is characterised by a magnetic susceptibility $\chi$.

$$\chi = \frac{\partial M}{\partial H} \quad (2.1)$$

The susceptibility behaviour of a compound denotes its magnetic classification. Diamagnetic materials, for example, expel lines of magnetic flux and have negative susceptibilities ($\chi < 0$). Diamagnetism arises from the interaction of a field with paired electrons and hence is present in all compounds. The susceptibility of a compound is usually corrected for its intrinsic diamagnetism ($\sim 10^{-6}$ emu mol$^{-1}$) by subtraction of its estimated value using the additive Pascal constants$^\dagger$.

Paramagnetic materials contain unpaired isolated electron spins and are attracted to magnetic fields ($\chi > 0$) because the Zeeman perturbation favours spin alignment with field. Statistical mechanical treatment of an ensemble of unpaired isolated spins in applied field yields paramagnetic bulk behaviour. The magnetisation behaviour of
Paramagnetic spins follows a Brillouin function\textsuperscript{3d} which in low fields gives susceptibility that follows the Curie Law of paramagnetism, Equation 2.2; where \( C \) is the Curie constant and is calculated as \( N g^2 \mu_B^2 J(J+1)/3k \).

\[
\chi = \frac{C}{T} \quad (2.2)
\]

Paramagnetic ions with thermally populated electronic states require a perturbation approach, used by Van Vleck\textsuperscript{34}, to derive their susceptibilities.

### 2.2 Magnetic interactions

In insulating solids, localised spins can interact by number of different mechanisms. The dominant interaction is usually magnetic superexchange which is covalent in origin. Isotropic (Heisenberg) superexchange in a dimer with spins \( S_A \) and \( S_B \) can be described by a Hamiltonian of type (2.3), where \( J \) is the exchange strength. Clearly, \( J = +\text{ve} \) favours ferromagnetic alignment and \( J = -\text{ve} \) an antiferromagnetic alignment of spins.

\[
H = -2JS_A \cdot S_B \quad (2.3)
\]

A theoretical calculation of \( J \) has been attempted by Anderson\textsuperscript{35}; however, qualitative interpretation is achieved via the Goodenough-Kanomori rules\textsuperscript{36,37}. To summarise, (i) magnetic orbitals with a large overlap have antiferromagnetic exchange; (ii) magnetic orbitals with an expected overlap due to proximity, but are non-overlapping (e.g. orthogonal orbitals) have ferromagnetic exchange and (iii) magnetic orbitals that overlap with empty orbitals give ferromagnetic exchange.

Unpaired magnetic spins also interact through their dipoles, according to Equation 2.4; where \( \mu_A \) and \( \mu_B \) are the magnetic moments of each spin and \( r_{AB} \) is the vector distance between the two atoms \( A \) and \( B \). The dipolar interactions in first row transition metals are weak in comparison to magnetic superexchange effects and, hence, play a secondary role in the magnetic order.

\[
H_{\text{dipole - dipole}} = \left[ \mu_A \cdot \mu_B / r_{AB}^3 - 3(\mu_A \cdot r_{AB})(\mu_B \cdot r_{AB}) / r_{AB}^5 \right] \quad (2.4)
\]
2.3 Long-range magnetic order

Magnetic superexchange interactions between spins in an extended lattice can result in a phase transition to long-range order at a critical temperature $T_c$. This can be followed by susceptibility, specific heat and neutron diffraction experiments (§3.1.2). Ferromagnetic transitions are characterised by local moments aligning spontaneously in the same direction within the lattice. Antiferromagnetic transitions occur when moments align in antiparallel directions, leading to zero spontaneous magnetisation. A ferrimagnetic state results when spins align antiferromagnetically but with non-compensating local moments. A further case of weak ferromagnetism or 'spin-canting' (§2.3.3) can occur in antiferromagnetic systems when ordered spins are canted at a small angle from exact antiparallel alignment, resulting in a non-zero spontaneous magnetisation in the direction of canting.

2.3.1 Magnetic model Hamiltonians

A system of interacting classical spins can be defined with respect to its spin dimensionality ($n$) and exchange dimensionality, $(J_x, J_y, J_z)$. The general case is described by the magnetic model Hamiltonian (2.5). Specifically; $J_x = J_y = J_z$ and $n = 3$ is known as the Heisenberg model; $J_x = J_y = 0$, $J_z = 0$ and $n = 2$ categorises the Planar model; whilst $J_x = J_y = 0$, $J_z 
eq 0$ and $n = 1$ corresponds to the Ising model.

$$H = -2 \sum_{i<j} (J_x S_i \cdot S_j + J_y S_i \cdot S_j + J_z S_i \cdot S_j) - D \sum_i S_i^2$$  \hspace{1cm} (2.5)

In the transition metal series superexchange interactions are usually isotropic. However, collective anisotropy arises from single ion anisotropy terms which manifest through spin-orbit coupling and crystal field effects; e.g. (h.s.)Fe$^{II}$ ions typically show Ising behaviour. The anisotropy of the system may best be described by a second term in the model Hamiltonian as in (2.5), where $D$ describes the anisotropy in a uniaxial system. If $D \to +\infty$ moments lie along the $z$-axis whilst for $D \to -\infty$ they are constrained to the plane.

Spin ($n$) and lattice dimensionalities ($d$) of a spin system are critical in determining whether a transition to long-range order occurs. This is summarised in Table 2.1. One-dimensional spin systems are always unstable to spin reversal and
hence do not exhibit transitions to long-range order. Two-dimensional systems are on the border of order and disorder with only the Ising 2-D model exhibiting a transition to long-range order. The two-dimensional XY model ($J_x = J_y \neq 0$, $J_z = 0$ and $n = 3$) exhibits a transition to a state with infinite susceptibility but without a spontaneous magnetisation.

Table 2.1: Spin and lattice dimensionalities exhibiting a transition to long-range magnetic order $T > 0K$.

<table>
<thead>
<tr>
<th></th>
<th>$d = 1$</th>
<th>$d = 2$</th>
<th>$d = 3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ising</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>XY</td>
<td>no</td>
<td>$\xi \rightarrow \infty$</td>
<td>yes</td>
</tr>
<tr>
<td>Heisenberg</td>
<td>no</td>
<td>no</td>
<td>yes</td>
</tr>
</tbody>
</table>

Real layer lattice magnets are best described as quasi two-dimensional spin systems because weak inter-layer exchange interactions $J'$, such that $J' \ll J$, act to couple the layers. A transition to long-range magnetic order in any quasi two-dimensional lattice will occur when two-dimensional spin correlations (characterised by a correlation length $\xi$) become large enough that the inter-layer coupling, which scales as $J'(\xi)^2$, can overcome thermal effects.

The anisotropy in real crystals is often only an approximation of the model Hamiltonians (discussed above). For example, finite $D = +ve$ and $D = -ve$ values in (2.5) describe respectively Ising and Planar type anisotropies to Heisenberg spins. A finite Ising type anisotropy in a quasi two-dimensional magnet will cause a transition to long-range magnetic order when anisotropic energy overcomes the thermal energy. This is classified as an anisotropy crossover. Indepth discussion of critical phenomena in two-dimensional magnets e.g. lattice and anisotropy crossovers is beyond the scope of this thesis. For more information see for example [De Jongh L. J.; 1990]38.

Exact solutions to the Hamiltonian (2.5) have been limited to the two-dimensional Ising model. For a general interpretation of magnetic properties approximations have to be made. Molecular field theory is a drastic approximation in magnetic theory and is detailed in the next section.
2.3.2 Molecular field theory

Molecular field theory or Weiss mean field theory is a powerful approximation to exchange Hamiltonians of type (2.5). In essence the sum of the exchange terms acting on a single spin site are approximated to a mean exchange field, which acts to orient spins below the bulk ordering temperature $T_c$. Considering only the $z$-spin components of a ferromagnet in an axial field $H$, the Hamiltonian (2.6)

$$H = -2 \sum_{i,j} J_{ij} S_i \cdot S_j - g \mu_B H \cdot \sum S_i$$  \hspace{1cm} (2.6)

becomes for each spin $S_i$,

$$H_{M.F} = -2 \sum_i J \langle S^z \rangle + g \mu_B H \rangle S^z_i$$  \hspace{1cm} (2.7)

Where $\langle S^z \rangle$ is the mean $z$-spin component of all spins interacting with $S_i$. The single ion Hamiltonian (Equation 2.7) is that of a paramagnetic spin perturbed by an effective field $H_{eff} = H + H_{M.F}$ which simplified to include only nearest neighbour ($z$) terms becomes,

$$H_{MF} = 2 \sum_i J \langle S^z \rangle / g \mu_B = 2 z J \langle S^z \rangle / g \mu_B = \lambda M_s \hspace{1cm} (2.8)$$

The Weiss molecular field constant $\lambda = 2zJ / g^2 \mu_B^2$ relates the molecular field to the spontaneously induced magnetisation, $M_s$, observed in ferromagnets below $T_c$. Hence, the spontaneous magnetisation is exactly that induced in a paramagnet by an external field equal to the molecular field $H_{M.F}$ (i.e. the magnetisation follows a Brillouin function).

The two sublattice model of Weiss mean field theory was first used by Néel to explain magnetic behaviour in antiparallel antiferromagnets. Each sublattice, A and B, has independent sublattice magnetisations $M_A$ and $M_B$. The molecular field acting on
sublattice A, to a first approximation, is that from exchange effects with the B magnetic sublattice and vice-versa (Equation 2.9).

\[ H_A = H_{\text{ext}} + \lambda_{AB} M_B \]  
\[ H_B = H_{\text{ext}} + \lambda_{BA} M_A \]  

(2.9)

Extending the two sublattice model to the case where the spins on each sublattice are uncompensating, Néel postulated the ferrimagnetic ground state in 1948^40^1. Néel’s model case was based on the general spinel A[B]_2O_4 lattice containing (for simplicity) only one magnetic ion distributed between the two magnetic sublattices. In zero external field the internal fields (now in Néel notation) are,

\[ H_A = n(\alpha \lambda M_A + \epsilon \mu M_B) \]  
\[ H_B = n(\beta \mu M_B + \epsilon \lambda M_A) \]  

(2.10)

Where \( \lambda \) and \( \mu \) are the fractional occupancies of the magnetic ion in the A and B sublattice sites respectively (\( \lambda + \mu = 1 \)); \( \alpha \) and \( \beta \) represent the Weiss field ratios \( \lambda_{AA}/\lambda_{AB} \) and \( \lambda_{BB}/\lambda_{BA} \) (\( \lambda_{AB} = \lambda_{BA} \)), \( n \) is the proportionality constant \( 1/\lambda_{AB} \), \( M_A \) and \( M_B \) are the magnetisations of the A and B sublattices when fully occupied, whilst \( \epsilon = +/-1 \) (= -1 for ferrimagnetism and antiferromagnetism). Solving for a minimum in molecular field energy (Equation 2.11) at absolute zero gives four possible solutions for the saturated spontaneous magnetisation \( M_s = |M_A - M_B| = |\lambda M_A + \epsilon \mu M_B| \) (see Table 2.2). A further consideration of both the variation in magnetisation near \( T_c \) (by expansion of the Brillouin function) and around absolute zero gives in total six possible ferrimagnetic ordering types (M, N, P, Q, R and V). The forms of the magnetisation curves are illustrated in Figure 2.1. The variation of \( \alpha \) and \( \beta \) i.e. the relative inter and intra sublattice exchange coupling determines the ordering type. The Néel plot \((\alpha, \beta)\) for the case \( \lambda/\mu = 2/3 \) is illustrated in Figure 2.2.

\[ W = -\frac{1}{2} \lambda M_A H_A - \frac{1}{2} \mu M_B H_B \]  

(2.11)
Figure 2.1: Illustration of the principle Néel ferrimagnetic order types
Figure 2.2: The $(\alpha, \beta)$ Néel plot for $\lambda/\mu = 2/3$

Table 2.2: Magnetic characteristics of the Néel ferrimagnetic ground states

<table>
<thead>
<tr>
<th>Plot region</th>
<th>Solution</th>
<th>$M_\alpha$</th>
<th>$M_\beta$</th>
<th>$M_r$</th>
<th>Néel type</th>
</tr>
</thead>
<tbody>
<tr>
<td>GSB</td>
<td>I</td>
<td>paramagnetism</td>
<td>G</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ACF</td>
<td>IV</td>
<td>$-\mu/\alpha \mu (1-1/\alpha)$</td>
<td>M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FCE</td>
<td>II</td>
<td>$\lambda \mu \mu-\lambda$</td>
<td>P,Q,N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ECSH</td>
<td>III</td>
<td>$\lambda \mu -\lambda(1+1/\beta)$</td>
<td>R,V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HSB</td>
<td>III</td>
<td>$\lambda (1+1/\beta)$</td>
<td>M</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The temperature evolution of magnetisation in Néel types M, R and V have a finite slope at \( T = 0 \text{K} \) \( (\partial M / \partial T \neq 0) \) which violates the third law of thermodynamics and hence they are not realised in experimental ferrimagnets.

The Néel types N, P and Q have many experimental examples. Type Q has a conventional magnetisation curve following a Brillouin function below \( T_c \). Type N exhibits a temperature of compensation (\( T_{\text{comp}} \)) where the magnetisation on each sublattice is equal and opposite and hence \( M_s (T = T_{\text{comp}}) = |M_A - M_B| = 0 \). Figure 2.3 illustrates the relative temperature dependence of each sublattice magnetisation that will give rise to a type N magnetic order.

![Figure 2.3: Showing the relative magnetic sublattice ordering for Néel type N ferrimagnetic order](image)

Figure 2.3 illustrates two possible forms of the spontaneous magnetisation curve for type N order. Either the magnetisation curve bounces at \( T_{\text{comp}} \) or the magnetisation changes sign and becomes negative above \( T_{\text{comp}} \). The bouncing type N curve (also illustrated in Figure 2.1) occurs when the magnetic pole reverses at the compensation temperature, i.e. the measured magnetisation changes from \( M_s = M_B - M_A \)
to $M_s = M_A - M_B$ above $T_{\text{comp}}$. It is a feature of molecular field theory that the exact form of the type N magnetisation curve can not be determined.

The high temperature susceptibility behaviour of magnets may be shown via molecular field theory to follow the Curie-Weiss law (Equation 2.12).

$$\chi = \frac{C}{T - \theta}$$

(2.12)

Generally, the Curie-Weiss law is used as an interpretation of the magnetic interactions in a spin system above $T_c$; where $\theta = +ve$ indicates ferromagnetic interactions and $\theta = -ve$ antiferromagnetic interactions. Molecular field theory predicts that $|T_c/\theta| = 1$ for ferromagnets, antiferromagnets and ferrimagnets. Hence, the measured experimental deviation of $|T_c/\theta|$ from unity in a magnet is a measure of its deviation from molecular field theory.

It can easily be shown that, in a system with $z$ nearest neighbours with exchange coupling strength $J$, the Weiss constant and hence $T_c$ are given by (2.13).

$$\theta = T_c = \frac{2J(J+1)zJ}{3k}$$

(2.13)

The quantitative inaccuracy of molecular field theory is particularly apparent for low dimensional magnets. For example, the assumption of uniform exchange clearly breaks down in two-dimensional systems. Short-range magnetic order effects above $T_c$ are critical in determining their behaviour and are not accounted for within molecular field theory.

2.3.3 Spin canting

Weak ferromagnetism or 'spin-canting' occurs when antiferromagnetic spins align in non exactly antiparallel, directions to one another. In a two-sublattice antiferromagnet, canting results in a small ferromagnetic moment measurable in the direction of canting below $T_c$. The canting can originate from a variety of effects e.g. spin-orbit coupling, dipolar interactions or single ion anisotropy.

An antisymmetric Dzyaloshinkii-Moriya exchange Hamiltonian $^{41}$ (Equation 2.14) may be used to describe some interactions that lead to canting. Where the vector $\hat{d}$ acts to cant spins from the antiparallel minimum implicit in symmetric exchange. The exchange can only exist when there is no centre of symmetry between spins.

$$H_{DM} = -2 \sum_{i<j} \hat{d} \cdot (S_i \times S_j)$$

(2.14)
CHAPTER 3

Experimental techniques

3.1 Diffraction

A crystal structure is composed of both a lattice, an infinite array of lattice points generated by the primitive vectors \( a, b \) and \( c \) according to Equation 3.1, and a basis, a chemical array located on each lattice point, such that (3.1) has translational invariance. A unit cell of a crystal structure is a convenient volume used to generate the structure purely by translational symmetry. The primitive unit cell contains only one lattice point and hence its translational symmetry is exactly that of (3.1).

\[
\mathbf{t}_n = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} \quad (3.1)
\]

\( \{n_i = \text{any integer} \} \)

Bravais lattices are the fourteen distinct crystal lattices which are derived from the seven crystal systems available to lattice arrays.

The reciprocal lattice is a useful concept in diffraction theory. Each lattice \( (a, b, c) \) has an associated reciprocal with vectors \( (a^*, b^*, c^*) \) related to the direct lattice by Equation 3.2.

\[
\begin{align*}
    a^* &= \frac{b \times c}{a \cdot (b \times c)} , \quad b^* = \frac{c \times b}{a \cdot (b \times c)} , \quad c^* = \frac{a \times b}{a \cdot (b \times c)} \\
    (a^* \cdot a &= b^* \cdot b = c^* \cdot c = 1, \quad a^* \cdot b = a^* \cdot c = etc = 0)
\end{align*}
\]

As a consequence of the reciprocal lattice definition, every set of Miller \((h,k,l)\) planes within the direct lattice corresponds to a perpendicular reciprocal lattice vector \( \tau \), as in Equation 3.3. The modulus of a reciprocal lattice vector \( |\tau| \) is in fact the reciprocal of the shortest distance between the associated Miller planes \((d_{hkl})\), \(|\tau| = 1/d_{hkl}\).

\[
\tau = ha^* + kb^* + lc^* \quad (3.3)
\]
Elastic scattering of X-rays or neutrons in crystals results from constructive interference or Bragg reflection from the set of lattice planes (h,k,l) at a direction where there is zero phase change between beams reflected from adjacent planes. This can be expressed qualitatively as Bragg’s law and geometrically, in reciprocal space, by means of the Ewald construction (Figure 3.1). Bragg reflection is therefore expected when the Ewald sphere crosses a reciprocal lattice point P associated with the direct planes (h,k,l) parallel to IP at \( \sin \theta_b = \frac{1}{2} \lambda \), i.e. at the Bragg angle.

\[ n\lambda = 2d_{hkl}\sin \theta_b \]  

\( (3.4) \)

Figure 3.1: The Ewald construction as a condition of elastic diffraction

The lattice of a compound determines the positioning and possibility of Bragg reflection. Diffraction experiments measure the position and intensity of the diffraction intensities, \( I_{hkl} \). The reflection intensities are dependent on the constituent atoms and their relative arrangement within the unit cell and are proportional, within the kinematical approximation, to the square modulus of the structure factors \( I_{hkl} = |F_{hkl}|^2 \). Equation 3.5 gives the structure factor \( F_{hkl} \) summing over all “i” atoms within the unit cell. The factor \( f_i \) is the scattering amplitude in X-ray diffraction and the scattering
length in neutron diffraction (more commonly referred to as $b_i$). $(x_i, y_i, z_i)$ refer to the partial coordinates of the atoms within the cell. $W_i$ are Debye-Waller isotropic temperature factors which result in a reduction in scattered intensity from thermal motions.

\[ F_{hkl} = \sum_i f_i \exp(-2\pi i(hx_i + ky_i + kz_i)) \exp(-W_i) \tag{3.5} \]

In some cases systematic absences occur ($F_{hkl} = 0$) where the lattice planes of a crystal are arranged so that reflection from them results in a total destructive interference of the diffracted beam.

### 3.1.1. Powder X-Ray Diffraction

In X-ray diffraction elastic scattering results from the coherent emission of X-rays from electrons accelerated by the incident X-ray beam. The atomic structure factor $f_i$ is therefore a summation over all the electrons in an atom. This results in a monotonic increase in the structure factor with atomic number and a fall-off of scattering with $(\sin \theta)/\lambda$, the X-ray form factor.

In this thesis powder X-ray profiles were collected on a Siemens D500 diffractometer, set in Bragg-Brentano reflection geometry, using CuK$\alpha$ doublets \{CuK$\alpha_1 = 1.54051\text{Å}, \text{CuK} \alpha_2 = 1.54433\text{Å}\} with a K$\text{ratio} \{K \alpha_1/K \alpha_2\}$ of 0.5. The X-ray beam slits were kept constant at 0.3mm for all experiments. During the experimentation period the X-ray source was replaced a number of times. Samples were mounted on a flat plate ceramic, such that the full beam area 3x15mm$^2$ was directed at the sample. Profiles were recorded as step scans at intervals of 0.02 in two-theta. Initial characterisation scans were carried out with a total collection time of 45 minutes, corresponding to a count time of one second. Profiles presented in Chapter 4 are from long scans with a count time of 10 seconds giving a total collection time of around 12 hours (generally performed overnight).

### 3.1.2. Neutron diffraction

Nuclear neutron scattering is as a result of the interaction of neutrons with scattering nuclei. This results in a number of differences between coherent elastic diffraction of neutrons and that of X-rays. In particular, the scattering lengths $b_i$ are only weakly dependent on atomic number, although often large fluctuations occur between isotopes.
Also the nucleus behaves effectively as a point scatterer to incident neutrons and hence does not incur a form factor effect.

Neutrons are spin-1/2 particles and interactions between the neutron's magnetic moment and unpaired spins on atoms results in elastic magnetic scattering. Coherent magnetic diffraction (magnetic Bragg reflection) will occur if there is long-range magnetic order between scattering spins. In magnetically ordered materials neutron diffraction structure factors, must therefore be described as a sum of contributions from nuclear and magnetic scattering. In an unpolarised neutron diffraction experiment the diffraction intensities \( I_{hkl} \) simplify to the sum of the squared moduli of the two terms (Equation 3.6).

\[
I_{hkl} = |F_{hkl}|^2 = |F_{Nhkl}|^2 + |F_{Mhkl}|^2 \quad (3.6)
\]

The magnetic structure factor \( F_{Mhkl} \) is given in Equation 3.7. The term \( p_i \) is the magnetic counterpart to the nuclear scattering length equal to \( (e^2\gamma/2mc^2)gJ(\tau) \), with \( \gamma \) the neutron magnetic moment and \( gJ \) the effective magnetic moment of the scattering atom. The magnetic form factor \( f(\tau) \) arises as a result of the atomic moment's spatial distribution.

\[
F_{Mhkl} = \sum_i q_i p_i \exp(-2\pi i (hx_i + ky_i + lz_i)) \exp(-W_i) \quad (3.7)
\]

The magnetic structure factor is dependent upon the spin orientations within the unit cell. It is therefore a vector quantity and this is reflected in the magnetic interaction vectors \( q_i \) within the structure factor summation. The general magnetic interaction vector \( q \) is defined as in Equation 3.8, where the scattering vector \( \hat{\tau} \) is the unit reciprocal lattice vector perpendicular to the scattering planes and \( \hat{M} \) is a unit vector parallel to the spin direction.

\[
q = \hat{\tau}(\hat{\tau} \cdot \hat{M}) - \hat{M} \quad (3.8)
\]

This is shown graphically in Figure 3.2. \( q^2 \) can be simply related to the angle between the scattering and spin vectors, \( \eta \), as

\[
q^2 = 1 - (\hat{\tau} \cdot \hat{M})^2 = 1 - \cos^2 \eta \quad (3.9)
\]
In a diffraction experiment domain effects within an ordered magnetic material can cause a variety of $q_i$ for each spin and the measured diffraction intensity is then proportional to the average $<q_i^2>$.

The description of a magnetic unit cell requires information on spin directions and the configurational symmetry between them. It is often the case that the magnetic symmetry is not the same as the nuclear symmetry. Indeed in the case of a second order phase transition\(^{43}\), we expect 'broken symmetry' with the appearance of the order parameter and therefore the magnetic group to be a subgroup of the nuclear group. The magnetic cell may also be altered with respect its nuclear counterpart. It can be described with respect to a propagation vector $\kappa$; Equation 3.10, which relates the moment at the direct lattice origin $M_0$ to the moment $M_n$ at the lattice point $t_n$.

$$M_n = M_0 \exp(2\pi it_n \cdot \kappa) \tag{3.10}$$

Here $\kappa = (0,0,0)$ describes an unaltered cell whilst $\kappa = (1/2,0,0)$ corresponds to a magnetic cell that is doubled along the $a$-axis with respect to the nuclear cell.

The magnetic space groups or 'Shubnikov groups'\(^{44}\) approach to magnetic structure defines the character of spins with respect to the symmetry operations of the group. The characters can readily be discerned when considering the effect of a given operation on the current associated with a magnetic spin. This is shown graphically in Figure 3.3. To summarise, (i) spins are invariant through a translation or an inversion centre; (ii) spin components parallel to a two-fold axis are invariant, and inverted

![Figure 3.2: The geometry of magnetic Bragg reflection](image)

\[^{43}\] Reference to a specific source or citation.
\[^{44}\] Reference to a specific source or citation.
through a mirror plane; (iii) spin components perpendicular to a mirror plane are invariant, and inverted through a two-fold axis. In the magnetic space group definition, anti-symmetry operations are further defined when the spin character change is opposite to that expected from the operation. In total, 1651 Shubnikov groups are generated.

Alternatively, Bertaut used group representation analysis to identify possible spin structures, which have to be linear combinations of irreducible representations of the group. This approach has met with success in interpreting magnetic structures which cannot be described by the Shubnikov groups. Indeed the Shubnikov magnetic space groups are only one dimensional representations of the group.

<table>
<thead>
<tr>
<th>Translation</th>
<th>Rotation 2</th>
<th>Inversion</th>
<th>Reflection</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Translation" /></td>
<td><img src="image2.png" alt="Rotation 2" /></td>
<td><img src="image3.png" alt="Inversion" /></td>
<td><img src="image4.png" alt="Reflection" /></td>
</tr>
</tbody>
</table>

Figure 3.3: Schematic representation of the behaviour of spins upon symmetry operations

In this thesis the approach to the interpretation of magnetic structure data has been one of trial and error. Purely magnetic neutron diffraction patterns have been generated using the FULLPROF program with structural models that previously had been found to explain the available structural data. The generated patterns have then been compared with the observed magnetic diffraction from neutron diffraction difference profiles, \([I(T_{base}) - I(T>T_c)]\). In the FULLPROF program the Fourier components of magnetic moments, when acted upon by each symmetry operation of the space group, are described along the x, y and z directions. This method allows the generation of a number of magnetic structures consistent with the space group. The program also facilitates the use of propagation vectors in the magnetic cell description.
3.1.3 Powder Neutron Diffraction Instruments

There are two common sources of neutrons used in neutron diffraction experiments: reactor sources and spallation sources. The powder neutron diffraction experiments reported in this thesis were performed at the Institut Laue Langevin (ILL) Grenoble, a reactor source\textsuperscript{47}. Neutrons are produced constantly in the reactor with a Maxwellian spread of wavelengths centred around the thermal energy of the modulating graphite rods and coolant D\textsubscript{2}O. Diffraction is performed at constant wavelength and a typical neutron powder diffractometer set-up\textsuperscript{48} is that of Figure 3.4. Generally the neutrons are guided by collimators, controlling the beam divergence and monochromation is by a single crystal set at Bragg scattering angle for a particular wavelength, known as the take-off angle $2\theta_{M}$.

![Diagram of typical constant wavelength powder neutron diffractometer set-up.](image)

Figure 3.4: Typical constant wavelength powder neutron diffractometer set-up.
(i) **D1B instrument**

The D1B diffractometer is a high intensity, medium resolution, powder diffractometer located in the guide hall at the I.L.L. The wavelength is fixed at 2.52Å, by a graphite focusing monochromator. High count rates are achieved with a fixed position sensitive detector (PSD), with 400 cells, covering a angular two-theta range of 80 degrees (see Figure 3.5). The data are collected in steps of 0.2 degrees, as defined by the distance between adjacent detector cells in the PSD bank.

![Diagram of D1B diffractometer](image)

Figure 3.5: The D1B constant wavelength diffractometer

(ii) **D1A instrument**

D1A is situated adjacent to D1B in the neutron guide hall (Figure 3.6). It has a high take-off angle of 122° giving a good resolution over 6°-160°. The detector now covers 150° solid two-theta angle with 25 cells. Scans are taken step-wise every 0.05 degrees,
via rotation of the detector bank. Monochromation is via 30 oriented Ge single crystals. A variety of wavelengths are available via rotation of the monochromator to a selected Bragg reflection plane. In the reported experiments the maximum wavelength of 2.9811Å has been used corresponding to the Ge[113] reflection. A special graphitic filter was inserted between the monochromator and the sample, which significantly reduced higher order wavelength contaminations ($\lambda/3 < 0.1\%$).

Figure 3.6: The D1A constant wavelength diffractometer

(iii) D2B instrument

D2B is a very high resolution constant wavelength diffractometer situated in the reactor hall (only 5m from the reactor face) at the I.L.L. The high take-off angle ($2\theta_{M} = 135^\circ$) of the, 300mm high, focusing Ge single crystal monochromator gives its high
resolution and high intensity\textsuperscript{49}. The focusing converges the beam to 40cm high at the sample position, some 3 meters from the monochromator. The multi-detector bank of 64 detectors covers a solid angle in two-theta of 160 degrees. Collection is by step scans of 0.05°. The new option of a graphitic filter similar to that of D1A allowed collection at the relatively high wavelength of 2.398Å (Ge[331]) without significant contamination from higher order wavelengths. During the measurements made in this thesis the instrument was set in its high intensity mode.

![Diagram of the D2B constant wavelength diffractometer](image_url)

**Figure 3.7:** The D2B constant wavelength diffractometer

### 3.1.4 Fitting powder diffraction profiles

In a powder diffraction experiment, with a random orientation of crystallites, lattice planes give Deybe-Scherer cones of scattering at directions determined by the Bragg condition, Equation 3.4. The three dimensional reciprocal lattice is projected onto one dimension, resulting in overlapping scattering from planes with similar \(d_{hkl}\) separations. The successful interpretation of a powder diffraction pattern relies on accurately measuring positions and intensities from a maximum number of reflections.

Partial pattern decomposition, the fitting of positions and intensities of single and non-severely overlapped peaks, has been used extensively in this thesis as a primary method for fitting of powder diffraction patterns using the WinFIT\textsuperscript{50} peak fitting program. Unit cell refinements have then been carried out using the indexed peak
positions with the linear squares refinement program REFCEL. It was not feasible to use integrated intensities from partial pattern decomposition to solve structures, in this case, as the number of reflections that could be assigned was limited.

The Rietveld method of structural refinement avoids the a priori attribution of intensities to reflections and attempts to fit the entire powder profile. In the Rietveld method the residual function $S_y$ between observed and calculated patterns, Equation 3.11, is minimised by non-linear least squares methods. Where the summation $S_y$ is over all observed points "i" in the profile with $y_i$(obs) and $y_i$(calc) the observed and calculated intensities of the profile at each point. The weighting function $w_i$ is equal to $1/y_i$(obs).

$$S_y = \sum_i w_i (y_i(\text{obs}) - y_i(\text{calc}))^2$$

(3.11)

The intensities $y_i$(calc) are calculated as:

$$y_i(\text{calc}) = s \sum_{hkl} L_{hkl} |F_{hkl}|^2 A_i \Omega(2\theta_i - 2\theta_{hkl}) P_{hkl} T + y_{bi}$$

(3.12)

where $s$ is the scale factor, $L_{hkl}$ is the Lorentz correction (inclusive of polarisation and multiplicity factors), $A_i$ is the asymmetry parameter, $\Omega$ is the peak shape function, $P_{hkl}$ is the preferred orientation function, $T$ is due to absorption and $y_{bi}$ is the background contribution.

Peak shapes are a result of convolution of sample and instrument effects. The most simple peak shape function is a Gaussian with a Full Width at Half Maximum (FWHM), defined by the model parameters $u$, $v$ and $w$, Equation 3.13.

$$(\text{FWHM})^2 = u \tan^2 \theta + v \tan \theta + w$$

(3.13)

Often, as a result either of sample or instrument effects, peaks have a Lorentzian component to their shape. In this case the pseudo-Voigt function, a linear combination of Lorentzian and Gaussian functions (Equation 3.14) is often a good description of the peak shape, where $\eta$ defines the fractional Lorentzian contribution:

$$\text{pseudo-Voigt('pV')} = \eta L + (1 - \eta)G$$

(3.14)

Further peak shapes are now available within Rietveld programs, e.g the Split-Pearson VII function, and these are discussed elsewhere.
Asymmetric peak shapes can arise from a number of other effects, most commonly being the result of diffraction geometry. This is caused by the cutting of the curved Debye-Scherer scattering cone with a finite width detector. The asymmetric contribution $A_i$ is modelled below a certain limiting Bragg angle, where asymmetry becomes noticeable. The expression for asymmetry $A_i$ used in the FULLPROF program is that introduced by Berar and Baldinozzi with four angle dependant refinable parameters.$^5$

Preferred orientation effects occur when powder crystallites align preferentially with respect to their crystal habit. In planar structures preferential alignment of crystallites is along their [001] planes, especially in flat plate geometry, which results in increasing relative intensity from [001] reflections, to the detriment of those from [hk0]. The preferred orientation function $P_{hkl}$ can be modelled by a number of expressions within the Rietveld approach,$^46$ however, the addition of such arbitrary parameters hinders successful refinement.

Minimisation of the residual $S_y$ does not necessarily indicate a successful structural solution and there are a number of factors which characterise refinement results: the structural factor $R_f$, Bragg Factor $R_B$, Pattern factor $R_p$, Weighted pattern factors $R_{wp}$ and the 'goodness' of fit $\chi^2$ are all defined in Appendix 1. Successful Rietveld refinement depends on, i) a good starting model for the structure; ii) an adequate description of the peak shape and its two-theta dependence, and iii) sufficient information in the diffraction profile to support the structural solution. In cases where i) ii) and iii) are not all met, Rietveld refinement must be used with extreme caution.

For a variety of reasons full structural refinement from the powder diffraction data in this thesis was not possible. In particular the peaks exhibited two-theta dependent broadening and asymmetry characteristics that could not be modelled using the Rietveld program FULLPROF.$^46$ However, the program's functionality has been used extensively to fit profiles to starting structural models and including features such as peak asymmetry and preferred orientation effects in refinement, so that structural information could be inferred from the powder profiles.

The pattern matching mode within the FULLPROF program minimises the residual $S_y$ by iterative fitting of $|F_{hkl}|^2$ values for a given symmetry and cell without a starting structural model and with a fixed correlated structure factor $s$. This type of refinement allows fitting of the profile parameters and that of the unit cell, even when a structural model is not available, and hence provides a best fit of the pattern that could be reasonably expected from full Rietveld refinement.
3.1.5 Diffraction from disordered layer compounds

Layered materials often exhibit structural disorder resulting from a poorly defined inter-planar lattice, despite a rigidly defined in-plane lattice. Two limiting cases of inter-layer disorder may be identified:

Case i) Layers stack in a completely random fashion with a complete loss in inter-planar registry. This results in crystalline diffraction intensities only being observed for [001] reflections, [hk0] reflections exhibiting weak two-dimensional diffraction and [hkl] reflections having no coherent intensity. This case has been dealt theoretically by Warren.\(^5\)

Case ii) Layers stack with a finite number of possible translational vectors between successive layers. This type of layer disorder, more commonly known as stacking faulting, manifests in many crystal structures and the resulting streaking in the reciprocal lattice gives [hkl] dependent broadening of peaks in the powder diffraction pattern.

The diffraction theory for stacking faulted crystals has been developed by a number of authors.\(^5\)\(^6\)\(^7\)\(^8\). A crystal can be described as that built-up by sheets of unit cells within a layer with successive layers and their displacements determined by probability. The diffracted intensity is then the weighted incoherent sum for each possible sequence of layers in each crystallite. Treacy and Newsham\(^5\)\(^7\)\(^8\) considerably simplified the problem of generating diffraction intensities by adopting a recursive approach to the layer stacking sequences. Essentially, similar partial stacking sequences occur many times within a crystallite and the diffraction intensity from each need only to be calculated once.

In the case of two layer \((i\) and \(j)\) stacking, the ensemble average of scattering wave functions \(\Psi_i\) from sequences beginning with the \(i\) layer at the scattering vector \(\tau\) is given by,

\[
\Psi_i(\tau) = F_i(\tau) + \sum_{j=1,2} \alpha_{ij} \exp(-2\pi i \tau \cdot R_{ij}) \Psi_j(\tau) \quad (3.15)
\]

where \(F(\tau)\) is the scattering contribution from the layer at the origin, \(\alpha_{ij}\) is the transition probability between layers, and \(R_{ij}\) is the translational vector displacement of layer origins.

It can be shown that the reflection intensity at \(\tau\) is given by the incoherent sum

\[
I(\tau) / N = \frac{1}{2} \sum_i (F_i^*(\tau)\Psi_i(\tau) + F_i(\tau)\Psi_i^*(\tau) - |F_i(\tau)|^2) \quad (3.16)
\]
The Diffraction Intensities From Faulted Crystals (DIFFaX) program\textsuperscript{58} has been used in Chapter 4 to simulate X-ray patterns. A sample input file for the program is given in Appendix 3.

3.2 Magnetometry

The magnetic measurements reported in this thesis were performed on SQUID (Super conducting QUantum Interference Device) magnetometers. DC magnetic measurements were recorded on the MPMS7 Quantum Design SQUID Magnetometer equipped with a 7 Tesla magnet\textsuperscript{59}. Measurements were carried out in the temperature range 2-300K. In SQUID magnetometers the dipole field of the magnetised sample and its holder are measured as they are moved through detector coils. In order to avoid sample holder contributions to the measured magnetisation the sample holder must, therefore, maintain a constant susceptibility along the length of measurement (>4cm). Sample mounting was as follows; Powder samples of around \(~30\text{mg (~3x3x6mm}^3\)) were loaded into gel caps and then placed in tight fitting transparent straws, which had been periodically punctured with tiny holes along their length. The straws were then loaded with three compensatory empty gel caps on either side of the sample containing gel cap. The loaded straws were then firmly fixed to the SQUID sample mount with Quantum Design magnetic (non-magnetic) tape.

3.2.1 Low field DC SQUID measurements

SQUID devices exhibit time dependent remnant fields and therefore it was necessary to first reduce and calibrate the remanent field present in the SQUID magnetometer before (and often after) measurement. Large remanent fields (~1-10G) were reduced when possible via the system magnet reset option, quenching the super conducting magnet in a high field (>10000G). Calibration of persistent remanance was carried out by measuring samples known to be in a paramagnetic regime, in a range of fields above and below zero applied field (+10G ↔ -10G). The remanent field could then be estimated as equal and opposite to the field at which the SQUID response became zero. Zero effective field in the magnetometer could then be accurately achieved at \(t = 0\) down to +/-0.05G. Measurements requiring zero applied field, for zero field cooling etc, were then carried out immediately after a calibration. The possibility of remanent field creep occurring during a prolonged measurement was investigated by a recalibration of remanence, after the completion of the measurement. Low field measurements were carried out with the magnet in its oscillation field setting mode, where the set field is
approached via an oscillation around the set value. A typical low field measurement procedure was adopted as follows: i) zero field calibration, ii) cooling in zero field, iii) measurement in a small field (\(-100\text{G}\)) during sample warming, iv) progressive sequences of cooling in higher fields, measurement being made in the same low field (\(-100\text{G}\)) during warming. In this way the low temperature magnetisation induced by the zero field/field cooling is measured in a weakly perturbing but constant measuring field. Measurements in a constant field also provided a check on remanant field changes at temperatures above the magnetic ordering transition.

3.2.2 High field DC SQUID measurements

High field (\(>10,000\text{G}\)) hysteresis measurements were carried out with the magnet set in the no-overshoot field setting mode using the hysteresis option. This avoided the field cycling procedure of the oscillation mode which would affect the hysteresis. In all high field measurements it was necessary to ensure that samples were rigidly held in the sample mount in order to avoid sample torquing effects in the applied field. Samples were mounted as detailed in §3.2.1. However, the samples were pressed and placed into an inverted sample gel cap to secure the powder orientations. For these measurements magnet remanance effects can not be accounted for and this causes a possible error in the exact field value of around +/-20G. However, even with this error the hysteresis curves are not significantly affected.

3.2.3 Alternating current (AC) magnetometry

AC susceptibility measurements were performed at the Institute of Molecular Science in Okazaki National Science Park, Japan on a MPMS2 SQUID magnetometer fitted with an A.C. measurement option. Measurements were recorded on samples at frequencies between 0.01Hz and 1500Hz, the limits of the instrument, and in the temperature region 2-100K. The driving field was maintained at 5G for all measurements and zero DC field was rigorously maintained in the low field SQUID magnetometer. Sample mounting was analogous to that used in the DC SQUID magnetometry studies (§3.2).

Principles of AC susceptibility measurement.

In AC susceptibility measurement the applied field, or driving field \(H(t)\), oscillates sinusoidally with a fixed magnitude \(h\) and angular frequency \(\omega\) according to Equation 3.17. A sample, when exposed to the driving field, has an induced magnetisation \(M(t)\) which oscillates with the field according to Equation 3.18.
\[ H(t) = \Re^\omega t \]  
\[ M(t) = m(\omega) e^{\omega t} \]  

The driving field is kept sufficiently small so that a linear response in magnetisation is induced and the exact differential or AC susceptibility \( \chi_{AC} = \partial M / \partial H = m(\omega)/h \) is measured. A spin system cannot always exactly precess with the oscillating field and exhibits a phase lag between the magnetisation and driving field. In this case the differential susceptibility becomes a complex quantity (Equation 3.19), resulting from the requirement that energy be exchanged between the spin system and the lattice.

\[ \chi_{AC} = \chi' + i\chi'' \]  

Here \( \chi' \) is defined as the dispersion and \( \chi'' \) the absorption, representing the energy exchange between the spin and lattice system.

The quantities measured during an AC experiment can be related to thermodynamic quantities using equations derived by Casmir and Du Pre\(^6\). The spin and lattice have their own temperatures \( T_s \) and \( T_l \) and it is assumed that a single relaxation time constant \( \tau \) exists for their equilibration, proportional to their temperature difference. The thermodynamic quantities measured with an oscillating field are the isothermal susceptibility \( \chi_T = (\partial M / \partial H)_T \) measured at thermal equilibrium \((T_s = T_l)\) when \( \omega \tau \ll 1 \), and the adiabatic susceptibility \( \chi_S = (\partial M / \partial H)_S \) measured when the spin assembly is effectively uncoupled from its surrounding lattice \( \omega \tau \gg 1 \). It can be shown that:

\[ \chi_{AC} = \chi_S + \frac{\chi_T - \chi_S}{1 + i\omega \tau} \]  

which then separates out into the real and imaginary parts.

\[ \chi' = \chi_S + \frac{\chi_T - \chi_S}{1 + \omega^2 \tau^2} \quad \text{and} \quad \chi'' = \frac{\omega \tau (\chi_T - \chi_S)}{1 + \omega^2 \tau^2} \]  

In real spin systems many temperature dependant relaxation processes are often active. In the paramagnetic regime \( \omega \tau \ll 1 \) \( \chi_{AC} = \chi' = \chi_T \) (\( \chi'' = 0 \)) and approximates the measured \( \chi_{DC} \). At magnetic ordering transitions \( \omega \sim \tau \) and \( \chi'' \neq 0 \) (provided \( M_{spont} \neq 0 \)). A sharp peak is generally observed at \( T_c \) from a large number of relaxation
processes operating around this temperature. At temperatures significantly lower than \( T_c \) relaxation processes are retarded and \( \omega \tau >> 1 \). In this limit \( \chi' = \chi_S \) and \( \chi'' = 0 \).

The relaxational processes acting in a spin system are generally investigated through frequency dependant AC measurements. An Argand diagram of \( \chi'(\omega) \) versus \( \chi''(\omega) \) susceptibilities at any temperature yields information on the range of \( \tau \) acting at that temperature, provided the range of frequencies used spans \( \omega \sim \tau \).

**DC investigations of relaxational processes**

The field step method of investigating relaxational behaviour provides another experimental tool; relaxational times that can be investigated greatly exceed those available in the AC measurement. The procedure used in Chapter 5 is one of, i) zero field cooling to temperature \( T \), ii) a small field (~100G) is applied at \( t = 0 \), iii) measurement of the time dependence of the relaxation of the magnetisation to its new equilibrium value\(^6^1\). For these measurements DC SQUID scans were set up for one scan instead of the usual 4 averaged scans. In this way a magnetisation measurement was completed in only ~10secs, increasing the accuracy of the time \( t \) of measurement. Also the field was ramped via the quick non-oscillation method; \( t = 0 \) was estimated as the exact time of field setting.

### 3.3 The MuSR technique

The MuSR technique involves the implantation of spin polarised muons into a sample and the observation of the anisotropy of subsequent positron decay.

Spin polarised muon beams are available both at medium energy particle accelerators (ISIS Rutherford Appleton Laboratory (R.A.L.) UK) and the so-called Meson Factories (Paul Scherrer Institute (P.S.I.) Switzerland). The MuSR experiments reported in this thesis have been performed at the ISIS accelerator on the EMU instrument.

At ISIS a beam of protons (800MeV) is accelerated at a graphite target and nuclear collisions result in the production of positive pions \((\pi^+)\). Pions are unstable and decay by the two-body parity violating process (Equation 3.22), producing a neutrino \((\nu_\mu)\) and a muonium ion \((\mu^+)\), with half-life \( \tau_\pi \sim 26\text{ns} \).

\[
\pi^+ \longrightarrow \mu^+ + \nu_\mu \tag{3.22}
\]
Neutrinos have negative helicity (spin and momentum vectors opposed) and conservation of momentum in their decay results in the emitted muon having longitudinal spin polarisation, with respect to the pion rest frame. Muons emitted from decaying pions at, or near, rest produce the so-called surface muon beam with a low momentum of ≈ 29.8MeV/c. In this case the spin and momentum vectors of the emitted muon are antiparallel and the beam has 100% polarisation. At ISIS the surface Muon beam is steered and focussed towards the sample by dipole and quadrupole magnets (Figure 3.8). The surface muon beam has an energy of ≈ 4MeV and is stopped and thermalised in samples in around ~ 10^{-13} secs with a stopping range of ~ 0.15gcm^{-2}. Typically the initial muon polarisation is maintained in the sample during thermalisation; however, a fraction of muons may experience prompt depolarisation during thermalisation, from spin-flip collisions with radiolysis products. The lost polarisation from such occurrences is assigned as the missing fraction intrinsic to the sample.

Muons decay (τ^μ ~ 2.2μs) according to a three body parity breaking process (Equation 3.23), emitting a positron (e^+), a neutrino (ν^μ) and an anti-neutrino (\overline{ν}_e).

\[ \mu^+ \rightarrow e^+ + \overline{ν}_e + ν^μ \]  

(3.23)

A consequence of this decay mechanism is that the positron is emitted preferentially along the direction of muon polarisation at the instant of decay. The spacial anisotropy distribution of the emitted positron W(θ) is given by Equation 3.24, where θ is the angle between positron direction and the muon spin direction and A is the asymmetry parameter.

\[ W(θ) = 1 + A\cos(θ) \]  

(3.24)

A is dependent upon the energy of the emitted positron and averaging over all energies gives A = 1/3. The asymmetry of the positron decay beam is recorded with scintillation detector telescopes. The use of forward and backward detector as illustrated in Figure 3.8 is known as the 'longitudinal geometry' set-up.

After thermalisation the implanted muons experience the local field at their site which can be either intrinsic or extrinsic to the sample. Larmour precession of the muon will occur around any static field perpendicular to their spin direction at a frequency \( γ^μ/2π = 136kHzmT^{-1} \). Hence the muon polarisation becomes time dependent, as illustrated in Figure 3.9. A distribution in local fields at the muon site (whether from static or temporal variations) results in a time dependent loss in muon polarisation and a corresponding loss in asymmetry of the emitted positrons. The time dependence of the positron asymmetry is characterised by a relaxation function G(t).
Figure 3.8(a,b): Showing the instrumental arrangement and spatial distribution of positron emission in the longitudinal MuSR experiment.
Figure 3.9: Illustration of (a) implantation, (b) precession and (c) decay in the MuSR experiment.

The forward and backward detector telescopes experience the positron count rates,

\[ N(t)_F = N_0 \exp(-t / \tau_\mu)(1 + a_0 G(t)\cos \omega t) \]

\[ \alpha N(t)_B = N_0 \exp(-t / \tau_\mu)(1 - a_0 G(t)\cos \omega t) \]  

(3.26)

where \( \alpha \) is a measure of the differences in efficiency and solid angle coverage of the detectors. It is calculated by a calibration experiment performed in a small transverse field (20G), at a temperature where G(t) is uncomplicated. Hence, the time dependence of the muon polarisation is extracted as,

\[ a_0 G(t)\cos(\omega t) = \frac{N_F - \alpha N_B}{N_F + \alpha N_B} \]  

(3.27)
Zero field (ZF) MuSR experiments provide insights into both the size and the variation, static and temporal, of the local field at the muon site(s) within a magnetic material. A precession of the positron asymmetry \( A \) demonstrates the existence non-zero static moments on the time scale of the MuSR experiment (= 10 - 20 \( \mu \)secs).

In the limit of static moments (correlation time \( \tau_c \to \infty \)) a variation of the local field experienced by the muon will cause depolarisation through dephasing of precession signals. If an isotropic Gaussian distribution of local fields is assumed, with the mean square field \( \sigma^2 \), the Fourier transform of the distribution yields the Gaussian relaxation function (Equation 3.28). In fact a distribution of fields such that \( \sigma^2 > \gamma^2_\mu \langle B^2_\mu \rangle \) results in over-damping and precession is not observed.

\[
G(t) = \exp\left(-\frac{1}{2} \sigma^2 t^2\right) \quad (3.28)
\]

\[
\sigma^2 = \gamma^2_\mu \langle B^2_\mu \rangle = \gamma^2_\mu \langle B^2_x \rangle = \gamma^2_\mu \langle B^2_y \rangle = \gamma^2_\mu \langle B^2_z \rangle
\]

In a polycrystalline sample only 2/3 of stopped muons will contribute to the precession as 1/3 of muons will have their spin directions parallel to the internal field, hence, 1/3 of the initial asymmetry \( A_0 \) will be retained at \( t \to \infty \). In this case with a Gaussian distribution of fields and \( \gamma^2_\mu \langle B^2_\mu \rangle = 0 \) the relaxation becomes the Kubo-Toyabe function (Equation 3.29).

\[
G(t) = \frac{1}{3} + \frac{2}{3}(1 - \sigma^2 t^2) \exp\left(-\frac{1}{2} \sigma^2 t^2\right) \quad (3.29)
\]

The existence of a persistent 1/3\( A_0 \) tail in the MuSR histogram can also be used as a characteristic of static random moments on the MuSR time scale. Applied longitudinal fields increase the persisting asymmetry by forcing more local fields along the initial muon spin direction, known as repolarisation. Slow fluctuations in the local fields (\( \tau_c \neq \infty, \tau_c \sigma \gg 1 \)) results in a slow decay of the ZF 1/3\( A_0 \) asymmetry tail. At high fluctuation rates (\( \tau_c \sigma \ll 1 \)) the muon experiences only the average of the field distribution and motional narrowing causes the cross over to a Lorentzian relaxation function (Equation 3.30).

\[
G(t) = \exp(-\lambda t) \quad (3.30)
\]

(\( \lambda = \sigma^2 \tau_c \))
A fuller discussion of MuSR relaxation functions lies out of the scope of this thesis and the reader is directed elsewhere\textsuperscript{62,63}.

In the reported experiments the calibration and fitting of the positron decay histograms has been carried out with the standard mUon Data Analysis program (UDA) which is provided locally at ISIS.

\textit{Features of pulsed MuSR}

The pulsed nature of the muon beam at ISIS introduces a number of additional features to the MuSR experiment. The ISIS proton beam is of double pulse character containing two pulses separated by 325nsecs repeating at 50Hz. The produced muon beam is converted into a single pulse by a fast electrostatic kicker device (the UPPSET kicker) which removes the second pulse before implantation\textsuperscript{64}. Each muon pulse represents a high number of muons implanted in the sample over 80nsecs. It is therefore not practical to measure individual muon arrival times and the approximate arrival time is taken as that corresponding to the centre of each pulse. In the limit of high precession frequencies there will be appreciable phase differences between precessing muons from the start and from the end of the pulse. This results in a loss of asymmetry and places an upper limit to measurable frequencies of approximately the inverse of the pulse width. Similarly fast relaxation processes that decay quickly with respect to the pulse width cannot be measured accurately. Therefore pulsed muon beams are not suitable for measuring high precession frequencies and relaxation processes compared with continuous muon sources where the exact implantation time is recorded. However, the pulsed muon source is advantageous for measuring slow relaxation rates as the statistics and background of the decay histogram are improved as a result of the greater flux of muons and long times (\( > 1000\tau_\mu \)) between each implantation.
CHAPTER 4

Synthesis and structural properties of (cation)M(II)Fe(III)(ox)₃ compounds

This chapter details the synthesis, characterisation, and structural investigations of powder samples of (cation)M(II)Fe(III)(ox)₃ {M(II) = Fe(II), Mn(II)} compounds. The compounds AsPh₄M(II)Fe(ox)₃, PBu₄M(II)Fe(ox)₃ and (PPN)M(II)Fe(ox)₃ have been synthesised as new compounds, whilst compounds with cations Npent₄, NBu₄, NPr₄ and PPh₄ have been synthesised and further optimised for the purposes of a comparative study. The reported elemental analyses are those obtained on the optimised compounds. Structural characterisation has mostly made use of laboratory powder X-ray diffraction methods. A further temperature dependent powder neutron investigation of PPh₄(d₂₀)M(II)Fe(ox)₃ compounds is reported with an interpretation of the magnetic diffraction observed in the compounds.

4.1 Synthesis and characterisation

The compounds (cation)M(II)Fe(III)(ox)₃ were precipitated in powder form using two general methods classed as the (1) Block and (2) Ionic methods. A representation of the two methods is given in Figure 4.1:

(1) The Block method; An aqueous solution of K₃Fe(ox)₃ (100mM) was mixed with an equal molar quantity of M(II) (100mM) ionic solution {for M(II) = Fe(II) preparations salt = Fe(SO₄)·6H₂O, for M(II) = Mn(II) salt = MnCl₂·6H₂O}. The solution was left standing for approximately one hour and then filtered to remove precipitated M(II)ox.2H₂O. A water/methanol solution containing an equi-molar quantity of organic cation (~100mM) was then slowly added to the filtrate, during stirring. After approximately 12hrs the precipitated (cation)M(II)Fe(III)(ox)₃ was filtered from solution, dried and stored under vacuum.

(2) The Ionic method; A solution of Fe(III)(NO₃)₃·6H₂O (50mM), M(II) ions (50mM) and oxalic acid (150mM) was prepared in a (1:1:3) molar ratio {for M(II) = Fe(II) preparations salt = Fe(SO₄)·6H₂O, and a few drops of 1M HCl(aq) were added upon Fe(II) dissolution, for M(II) = Mn(II) preparations salt = MnCl₂·6H₂O}. After approximately one hour any precipitated M(II)ox.2H₂O was removed by filtration. A molar quantity of
organic cation equal to that of the metal ions was then added to the filtrate and dissolved with addition of the minimum volume of methanol. The precipitated (cation)M^{II}Fe^{III}(ox)_3 was filtered after 24hrs, dried and stored under vacuum.

(1) The Block Method.

\[
\begin{align*}
\text{Fe}^{III} + M^{II} + 3.\text{H}_2\text{O} & \rightarrow M^{II}, \\
\text{Fe}^{III} & \rightarrow \text{Fe}^{III}, \\
\text{Fe}^{III} & \text{Fe}^{III} \\
\end{align*}
\]

+ cation

\[
\text{filter 1hr.}
\]

\[
- M^{II}(ox).2\text{H}_2\text{O}
\]

(2) The Ionic Method.

\[
\begin{align*}
\text{Fe}^{III} + M^{II} + 3.\text{H}_2\text{O} & \rightarrow M^{II}, \\
\text{Fe}^{III} & \rightarrow \text{Fe}^{III}, \\
\text{Fe}^{III} & \text{Fe}^{III} \\
\end{align*}
\]

+ cation

\[
\text{in-situ- } [\text{Fe}(ox)_3^{3-}]
\]

\[
\text{filter 1hr.}
\]

\[
- M^{II}(ox).2\text{H}_2\text{O}
\]

\[
\text{ox} = \begin{pmatrix}
\text{O} \\
\text{O}
\end{pmatrix}
\]

Figure 4.1: Scheme of synthetic routes to (cation)M^{II}Fe^{III}(ox)_3.
The competing bi-product phase $\text{M}^\text{II}\text{ox.2H}_2\text{O}$ was initially identified in X-ray diffraction scans of the compounds, and was visible as a yellow powder in green (cation)$\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3$ samples. The primary filtration step was necessary to remove this impurity and was found to reoccur when the precipitation of (cation)$\text{M}^\text{II}\text{Fe}^{\text{III}}(\text{ox})_3$ was extended beyond 1-2 days. The Block method was the initial preparative route to the (cation)$\text{M}^\text{II}\text{Fe}^{\text{III}}(\text{ox})_3$ compounds\(^{27}\), however, it was found to be disadvantageous in comparison to the Ionic method for a number of reasons. Firstly the quantity of $\text{M}^\text{II}\text{ox.2H}_2\text{O}$ precipitated was greater in the Block preparations than that in the Ionic preparations. This was probably a result of the acidic reaction conditions in the Ionic method \(\{\text{pH}_{(\text{ionic})} = 3, \text{pH}_{(\text{block})} = 6\}\) retarding the formation of $\text{M}^\text{II}\text{ox.2H}_2\text{O}$. The addition of a few drops of 1M HCl(aq) was observed to further reduce $\text{M}^\text{II}\text{ox.2H}_2\text{O}$ precipitation (in the Ionic procedure detailed $\text{M}^\text{II}\text{ox.2H}_2\text{O}$ precipitation was estimated as $\sim 10\%$). Highly acidic conditions \(\{\text{pH}<1\}\) stopped precipitation of both $\text{M}^\text{II}\text{ox.2H}_2\text{O}$ and (cation)$\text{M}^\text{II}\text{Fe}^{\text{III}}(\text{ox})_3$. The Block method precipitation reactions were also more rapid with the precipitation of (cation)$\text{M}^\text{II}\text{Fe}^{\text{III}}(\text{ox})_3$ practically complete in one hour whilst, in comparison, the Ionic preparations gave a gradual precipitation of (cation)$\text{M}^\text{II}\text{Fe}^{\text{III}}(\text{ox})_3$ over several hours. This is probably a result of the requirement, in the Ionic preparation to form $[\text{Fe(ox)}_3]^3-$ species or similar in solution during reaction. The slower precipitation of the Ionic method also gave more crystalline powder diffraction profile. The elemental analyses of the optimised ionic preparations are given in Tables 4.1(a,b).

Table 4.1(a): Elemental analyses of (cation)$\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3$ compounds.

<table>
<thead>
<tr>
<th>(cation)$\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3$</th>
<th>C exp(calc)</th>
<th>H exp(calc)</th>
<th>N/P/As exp(calc)</th>
<th>Fe exp(calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPr$_4\text{FeFe(ox)}_3$</td>
<td>39.03(38.48)</td>
<td>5.23(4.98)</td>
<td>N 2.84(2.49)</td>
<td>19.56(19.88)</td>
</tr>
<tr>
<td>NBu$_4\text{FeFe(ox)}_3$</td>
<td>43.2(42.7)</td>
<td>5.79(5.89)</td>
<td>N 2.23(2.27)</td>
<td>17.91(18.07)</td>
</tr>
<tr>
<td>NPent$_4\text{FeFe(ox)}_3$</td>
<td>46.18(46.33)</td>
<td>6.65(6.53)</td>
<td>N 2.08(2.00)</td>
<td>16.65(16.57)</td>
</tr>
<tr>
<td>PPh$_4\text{FeFe(ox)}_3$</td>
<td>51.93(50.39)</td>
<td>2.88(2.80)</td>
<td>P 4.68(4.332)</td>
<td>14.47(15.62)</td>
</tr>
<tr>
<td>AsPh$_4\text{FeFe(ox)}_3$</td>
<td>48.71(47.5)</td>
<td>2.91(2.64)</td>
<td>As 9.87(8.07)</td>
<td>11.82(14.72)</td>
</tr>
<tr>
<td>PBu$_4\text{FeFe(ox)}_3$</td>
<td>42.09(41.62)</td>
<td>5.88(5.62)</td>
<td>P 4.98(4.88)</td>
<td>17.91(17.6)</td>
</tr>
<tr>
<td>(PPN)$\text{FeFe(ox)}_3$</td>
<td>55.32(55.19)</td>
<td>3.68(3.28)</td>
<td>P 6.44(6.78)</td>
<td>11.34(12.22)</td>
</tr>
</tbody>
</table>
Table 4.1(b): Elemental analyses of (cation)Mn$^{II}$Fe$^{III}$(ox)$_3$ compounds.

<table>
<thead>
<tr>
<th>(cation)Mn$^{II}$Fe$^{III}$(ox)$_3$</th>
<th>C exp(calc)</th>
<th>H exp(calc)</th>
<th>N/P/As exp(calc)</th>
<th>Mn exp(calc)</th>
<th>Fe exp(calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPr$_4$MnFe(ox)$_3$</td>
<td>38.10(38.52)</td>
<td>5.02(5.00)</td>
<td>N 2.53(2.50)</td>
<td>9.42(9.80)</td>
<td>9.47(9.96)</td>
</tr>
<tr>
<td>NBu$_4$MnFe(ox)$_3$</td>
<td>42.79(42.80)</td>
<td>5.83(5.84)</td>
<td>N 2.31(2.27)</td>
<td>8.46(8.91)</td>
<td>9.05(8.43)</td>
</tr>
<tr>
<td>NPent$_4$MnFe(ox)$_3$</td>
<td>46.34(46.37)</td>
<td>6.44(6.54)</td>
<td>N 2.16(2.08)</td>
<td>8.49(8.17)</td>
<td>8.62(8.30)</td>
</tr>
<tr>
<td>PPh$_4$MnFe(ox)$_3$</td>
<td>50.61(50.44)</td>
<td>2.85(2.80)</td>
<td>-(-)</td>
<td>6.81(7.77)</td>
<td>7.03(7.82)</td>
</tr>
<tr>
<td>AsPh$_4$MnFe(ox)$_3$</td>
<td>47.98(47.51)</td>
<td>2.70(2.4)</td>
<td>-(-)</td>
<td>6.22(7.25)</td>
<td>6.58(7.25)</td>
</tr>
<tr>
<td>PBu$_4$MnFe(ox)$_3$</td>
<td>41.68(41.66)</td>
<td>5.68(5.68)</td>
<td>-(-)</td>
<td>8.27(8.67)</td>
<td>8.60(8.81)</td>
</tr>
<tr>
<td>(PPN)MnFe(ox)$_3$</td>
<td>5.40(6.12)</td>
<td>1.64(1.53)</td>
<td>N 1.64(1.53)</td>
<td>5.40(6.02)</td>
<td>5.78(6.12)</td>
</tr>
</tbody>
</table>

The elemental analyses are quite accurate for C, H, N, P and As, however, the Mn and Fe analyses vary for each cation with significant deficiencies in the PPh$_4$ and AsPh$_4$ compounds of around 10-20%. This is discussed fully in Chapter 7.

4.1.1 Synthesis of PPh$_4$(-d$_{20}$)Mn$^{II}$Fe$^{III}$(ox)$_3$

The deuterated tetraphenylphosphonium cation [PPh$_4$(-d$_{20}$)]$^+$ was prepared as its bromide salt, by a method modified from that proposed by Michealis$^{65}$ and Dodanova.$^{66}$ Bromobenzene(-d$_3$) (Ph(-d$_3$)Br) and triphenylphosphine(-d$_{15}$) (PPh$_3$(-d$_{15}$)) were used as purchased from Aldrich Chemicals Ltd. (deuteration >99.8%).

**Synthetic Scheme**

(i) $\text{Ph}(-d_3)\text{Br} + \text{Mg} \xrightarrow{\text{Et}_2\text{O}} \text{Ph}(-d_3)\text{MgBr}$

(ii) $\text{Ph}(-d_3)\text{MgBr} + \text{PPh}_3(-d_{15}) \xrightarrow{[0] \text{Et}_2\text{O}} \text{PPh}_4(-d_{20})\text{OH} + 2\text{HBr} \xrightarrow{\text{Et}_2\text{O/H}_2\text{O}} \text{PPh}_4(-d_{20})\text{Br}$

$\text{MgBrOH} \quad \text{MgBr}_2 + 2\text{H}_2\text{O}$

(iii) $\text{Fe}^{III} + \text{M}^{II} + 3\text{H}_2\text{O} \xrightarrow{M^{II}.2\text{H}_2\text{O}} [\text{M}^{II}\text{Fe}(\text{ox})_3] + \text{PPh}_4(-d_{20})\text{Br} \longrightarrow \text{PPh}_4(-d_{20})\text{Mn}^{II}\text{Fe}(\text{ox})_3$
All glassware in (i) and (ii) was heated prior to use in a drying oven at 100°C. The ether solvent used was dried over KOH prior to use.

(i) Preparation of the Grignard reagent Ph(-ds)MgBr

A three neck 250ml round bottomed conical flask, equipped with an equal pressure dropping funnel, reflux condenser and nitrogen inlet was loaded with 1.48g of magnesium turnings and flushed with a strong flow of dry-nitrogen (anh. CaCl₂) for 5 minutes. The apparatus was heated thoroughly throughout this period with a hair drier. The flow of nitrogen was then reduced, and the apparatus allowed to cool. 50ml of dry ether was then added to the flask through the dropping funnel with a few crystals of iodine catalyst. The dropping funnel was then charged with 9.96g of Ph(-ds)Br in 20ml ether; 2-3ml of liquid from the dropping funnel was then added to the reaction vessel during magnetic stirring. After a short period of between 2 to 10 minutes the Grignard reaction began, noticeable by a discolouration of the iodine and the appearance of a milky emulsion in the reaction mixture. The remaining Ph(-ds)Br was added drop-wise to the reaction vessel over 30 to 45 minutes retaining a gentle ether reflux. After the reaction was completed the stirring was continued for a further 30 minutes without heating.

(ii) Preparation of PPh₄(-d₂₀)Br

The reaction vessel containing the Grignard reagent (from (i)) was cooled in an ice bath and 4g of PPh₃(-d₁₅), dissolved in 50ml ether, was added via the dropping funnel. The nitrogen supply was then replaced by a rapid oxygen flow. The mixture was stirred and after approximately 5 minutes a gluey brown residue congealed. Stirring soon became impossible and agitation of the solid residue was continued manually with a glass stirrer rod, under a constant oxygen flow. During the reaction period the ice bath was maintained at 0°C and further 10ml aliquots of ether were added to the solution, replenishing that lost by evaporation. The brown dough-like material gradually became white and powdery with complete conversion to PPh₄(-d₂₀)OH after ~90 minutes. The oxygen flow and stirring were then ceased. A solution of fresh (9.5ml HBr(49%)/20.5ml H₂O) was then added drop-wise to the vessel, resulting in vigorous quenching of remaining Grignard reagent and the production of bright white crystals of PPh₄(-d₂₀)Br. The conical flask was then removed from the apparatus and stoppered. The ether layer was decanted and discarded; 100ml aliquots of washing ether were added to the reaction vessel, shaken and decanted until the ether layer was colourless. The remaining aqueous layer was cooled overnight in an ice bath, filtered and washed.
with dry ether. Recrystallisation was carried out in boiling D$_2$O (Yields 30-40%). The prepared PPh$_4$(-d$_{20}$)Br was confirmed to be >99% deuterated by mass spectrometry (performed by John Hill at UCL).

(iii) Preparation of PPh$_4$(-d$_{20}$)Mn$^{II}$Fe$^{III}$(ox)$_3$ and PPh$_4$(-d$_{20}$)Fe$^{II}$Fe$^{III}$(ox)$_3$

The deuterated compounds PPh$_4$(-d$_{20}$)MnFe(ox)$_3$ and PPh$_4$(-d$_{20}$)FeFe(ox)$_3$ were prepared by the "Ionic" method described in §4.1.

PPh$_4$(-d$_{20}$)MnFe(ox)$_3$: A solution containing 3.344g Fe(NO$_3$)$_3$.6H$_2$O (9.56mmol) and 1.885g MnCl$_2$.6H$_2$O (9.56mmol) in 64ml H$_2$O was prepared. 3.671g of H$_2$ox.2H$_2$O was dissolved in the solution. After 1hr the solution was filtered and 2.65g of PPh$_4$(-d$_{20}$)Br (6.38mmol), dissolved in 11ml of 70:30 MeOH/H$_2$O, was added drop-wise to the filtrate. The precipitated PPh$_4$(-d$_{20}$)MnFe(ox)$_3$ was removed by filtration and dried (Yield = 3.55g (80%)}.X-ray diffraction profiles of the two compounds verified that they were free of M$^{II}$ox.2H$_2$O peaks. The refined unit cells using a similar procedure to that detailed in §4.2.1 are recorded in Table 4.2.

PPh$_4$(-d$_{20}$)FeFe(ox)$_3$: A solution containing 2.271g Fe(NO$_3$)$_3$.6H$_2$O (6.5mmol) and 1.804g FeSO$_4$.6H$_2$O (6.5mmol) in 50ml H$_2$O was prepared. 2.496g of H$_2$ox.2H$_2$O was dissolved in the solution. After 1hr the solution was filtered and 1.9g of PPh$_4$(-d$_{20}$)Br (4.329mmol), dissolved in 11ml of 70:30 MeOH/H$_2$O, was added drop-wise to the filtrate. The precipitated PPh$_4$(-d$_{20}$)FeFe(ox)$_3$ was removed by filtration and dried (Yield = 2.05g (71.7%).

X-ray diffraction profiles of the two compounds verified that they were free of M$^{II}$ox.2H$_2$O peaks. The refined unit cells using a similar procedure to that detailed in §4.2.1 are recorded in Table 4.2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a,b (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPh$<em>4$(-d$</em>{20}$)MnFe(ox)$_3$</td>
<td>18.948(6)</td>
<td>57.30(17)</td>
</tr>
<tr>
<td>PPh$<em>4$(-d$</em>{20}$)FeFe(ox)$_3$</td>
<td>18.948(6)</td>
<td>57.42(20)</td>
</tr>
</tbody>
</table>
4.2 Powder X-ray diffraction

Powder X-ray diffraction profiles were collected using a Siemens D500 X-ray diffractometer providing CuKα doublet radiation (details in §3.1.1). The profiles discussed are those obtained after long 12 hour step scans with a step size of 0.02 degrees in two-theta. The long collection time was required as the compounds were found to be weakly diffracting with relatively high background intensities. Prolonged X-ray exposure also caused some sample surface discolouration and a commensurate loss in Bragg scattering intensity in a number of peaks. For this reason scan collection times were not extended beyond 12 hours. §4.3 details the general features of the profiles, their primary indexation and unit cell extraction. In §4.2.2 the X-ray profiles are discussed with respect to the published single crystal structural models of compounds (cation)MM'(ox)$_3$.

4.2.1 General X-ray profiles and unit cell extraction

Figures 4.2(a) and (b) show the powder profiles obtained on compounds NPr$_4$MnFe(ox)$_3$ and Npent$_4$FeFe(ox)$_3$ respectively. It is clear from the profiles that the compounds do not have an ideal set of crystalline Bragg diffraction peaks. The reflections are rather broad, their shapes have unusual (hkl) dependencies and exhibit considerable asymmetry at low angle. These diffraction effects are indicative of layer-disorder in the compounds and will be discussed later. There is also a sharp fall off in peak intensities with two-theta which indicates that the compounds are not fully crystalline.

A primary indexing of the diffraction peaks in the profiles of (cation)M$^{	ext{II}}$Fe(ox)$_3$ with cations NPr$_4$, NBu$_4$, PBu$_4$ and PPN was possible using the rhombohedral $R\overline{3}c$ cell (hexagonal setting) of the NBu$_4$MnCr(ox)$_3$ structure described in (§1.3). Compounds with cations AsPh$_4$ and PPh$_4$ were indexed using a doubled in-layer $R\overline{3}c$ cell from the PPh$_4$MnCr(ox)$_3$ structure (see again §1.3). A number of reflections formally forbidden by symmetry in $R\overline{3}c$ were indexed by relaxing the reflection conditions of $R\overline{3}c$ to those of $P6(5)$. The Npent$_4$M$^{	ext{II}}$Fe(ox)$_3$ profiles were indexed using the orthorhombic C222(1) cell, which a previous single crystal study of Npent$_4$MnFe(ox)$_3$ had revealed. The profiles see e.g. Figures 4.2(a) and (b) also show very weak and broad asymmetric reflections at low two-theta corresponding to lower order [001] reflections than those allowed by the reduced. These satellite type reflections are attributable to layer disorder effects and no further relaxation of symmetry was made to account for them.
Figure 4.2(a): X-ray profile of NPr₄MnFe(ox)₃ with partial indexing on P6(5) cell.

Figure 4.2(b): X-ray profile of Npent₄FeFe(ox)₃ with partial indexing on C222(1) cell.
Each profile was partially decomposed by peak fitting non-severely overlapped regions using the WinFit program\textsuperscript{50}. The diffraction peaks for each profile were best fitted using the Split-Pearson VII peak shape function with both asymmetric half widths (FWHM) and exponents\textsuperscript{46}. It was necessary to use this peak shape because the pseudo-Voigt function with asymmetry was incapable of adequately fitting the full peak intensity of the, highly asymmetric, low angle peaks. An example of a fitted region for NPr\textsubscript{4}MnFe(ox)\textsubscript{3} is given in Figure 4.3. The peak positions from each fit with an unambiguous reflection index (approximately 10 for each profile) were then used to extract a unit cell using the REFCEL program\textsuperscript{51}. The initial refined unit cell parameters were then used to further index each pattern and the positions added into the refinement. This method, accounting for the asymmetry in the reflections, gives more accurate unit cell parameters. The final refined unit cells are recorded in Table 4.3.

![Graph showing peak fitting](image)

**Figure 4.3:** Fit of the NPr\textsubscript{4}MnFe(ox)\textsubscript{3} X-ray profile in the two-theta region between 9 and 14 degrees.
Figure 4.4: Pattern matching for the Npent₄MnFe(ox)₃ X-ray profile using C222(1) cell.

Full pattern matching of the X-ray profiles using the refined unit cell parameters was carried out with the FULLPROF Rietveld program in pattern matching mode (see §3.1.3). An example of the best match for the Npent₄Mn²⁺Fe³⁺(ox)₃ profile is given in Figure 4.4 using the pseudo-Voigt peak shape function with an asymmetry correction below 20 degrees. The fit exemplifies the difficulty in adequately fitting the unusual peak shapes and their two-theta dependance within standard Rietveld description of two-theta dependent peak shapes $(u,v,w)$. Low angle peak asymmetry is clearly also underestimated. Whilst the $\chi^2$ for the displayed match is quite low at 9, the fit does not converge to one satisfactory minimum but rather many local minima are reached dependent on the starting parameters. Figure 4.4 shows the limitations of the Rietveld technique with respect to the type of powder X-ray data presented. The FULLPROF program has, hence, only been used further as a profile generating tool for structural models of the compounds $(\text{cation})\text{M}^{II}\text{Fe}^{III}(\text{ox})_3$. 
Table 4.3: Refined unit cell parameters of (cation)M$^{II}$Fe$^{III}$(ox)$_3$ at room temperature.

<table>
<thead>
<tr>
<th>(cation)Fe$^{II}$Fe$^{II}$(ox)$_3$</th>
<th>Space group used for refinement</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPr$_4$FeFe(ox)$_3$</td>
<td>$P 6(5)$</td>
<td>9.32(2)</td>
<td>9.32(2)</td>
<td>49.3(1)</td>
</tr>
<tr>
<td>NBu$_4$FeFe(ox)$_3$</td>
<td>$P 6(5)$</td>
<td>9.39(1)</td>
<td>9.39(1)</td>
<td>53.75(5)</td>
</tr>
<tr>
<td>Npent$_4$FeFe(ox)$_3$</td>
<td>$C 2 2 2(1)$</td>
<td>9.57(1)</td>
<td>16.1(1)</td>
<td>20.32(1)</td>
</tr>
<tr>
<td>PPh$_4$FeFe(ox)$_3$</td>
<td>$P 6(5)$</td>
<td>18.76(2)</td>
<td>18.76(2)</td>
<td>57.1(1)</td>
</tr>
<tr>
<td>AsPh$_4$FeFe(ox)$_3$</td>
<td>$P 6(5)$</td>
<td>18.75(5)</td>
<td>18.75(5)</td>
<td>57.9(1)</td>
</tr>
<tr>
<td>PBu$_4$FeFe(ox)$_3$</td>
<td>$P 6(5)$</td>
<td>9.41(2)</td>
<td>9.41(2)</td>
<td>55.3(1)</td>
</tr>
<tr>
<td>PPNFeFe(ox)$_3$</td>
<td>$P 6(5)$</td>
<td>9.38(1)</td>
<td>9.38(1)</td>
<td>86.6(2)</td>
</tr>
<tr>
<td>(cation)Mn$^{II}$Fe$^{II}$(ox)$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NPr$_4$MnFe(ox)$_3$</td>
<td>$P 6(5)$</td>
<td>9.42(1)</td>
<td>9.42(1)</td>
<td>49.1(1)</td>
</tr>
<tr>
<td>NBu$_4$MnFe(ox)$_3$</td>
<td>$P 6(5)$</td>
<td>9.47(1)</td>
<td>9.47(1)</td>
<td>53.5(1)</td>
</tr>
<tr>
<td>Npent$_4$MnFe(ox)$_3$</td>
<td>$C 2 2 2(1)$</td>
<td>9.68(1)</td>
<td>16.23(1)</td>
<td>20.21(1)</td>
</tr>
<tr>
<td>PPh$_4$MnFe(ox)$_3$</td>
<td>$P 6(5)$</td>
<td>18.87(2)</td>
<td>18.87(2)</td>
<td>56.84(5)</td>
</tr>
<tr>
<td>AsPh$_4$MnFe(ox)$_3$</td>
<td>$P 6(5)$</td>
<td>18.90(2)</td>
<td>18.90(2)</td>
<td>57.54(6)</td>
</tr>
<tr>
<td>PBu$_4$MnFe(ox)$_3$</td>
<td>$P 6(5)$</td>
<td>9.50(1)</td>
<td>9.50(1)</td>
<td>54.95(6)</td>
</tr>
<tr>
<td>PPNMnFe(ox)$_3$</td>
<td>$P 6(5)$</td>
<td>9.41(1)</td>
<td>9.41(1)</td>
<td>87.1(2)</td>
</tr>
</tbody>
</table>

Figure 4.5(a) plots the inter-layer distance for equivalent cation MnFe and FeFe compounds, corresponding to $c/6$ in $P6(5)$ ($R3c$ based profiles) and $c/2$ in $C222(1)$. The linear correlation between FeFe and MnFe indicates that the cation is determining the interlayer separation similarly for both compounds. A plot of the hexagonal intralayer repeat distance $a$ for each cation (see Figure 4.5(b)) shows only little variation; however, a linear correlation is apparently exhibited.

(N.B. in the $C222(1)$ cell for Npent$_4$M$^{II}$Fe(ox)$_3$ compounds the hexagonal repeat is equivalent to both $a$ and $b/\sqrt{3}$ . For PPh$_4$M$^{II}$Fe(ox)$_3$ and AsPh$_4$M$^{II}$Fe(ox)$_3$ compounds the plot uses the reduced hexagonal cell $a/2$)
Figure 4.5(a): Inter-layer repeat distance in (calion)MnFeyO3

<table>
<thead>
<tr>
<th>Layer distance</th>
<th>Key</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Npp</td>
</tr>
<tr>
<td>11</td>
<td>Np</td>
</tr>
<tr>
<td>6</td>
<td>Npp</td>
</tr>
<tr>
<td>11</td>
<td>Npp</td>
</tr>
<tr>
<td>15</td>
<td>Npp</td>
</tr>
</tbody>
</table>

Figure 4.5(b): Hexagonal unit cell parameter a in (calion)MnFeyO3

\[ W_1 = W_n \]
4.3 Structural models

In this section the X-ray laboratory profiles of each (cation)M\textsuperscript{II}Fe\textsuperscript{III}(ox)\textsubscript{3} compound are compared to the published crystal structures of (cation)MM'(ox)\textsubscript{3}. Previously (§4.2.1, Figure 4.4) profile matching has shown the data to not support full Rietveld structure refinement because of unusual peak shape effects. The comparison is, hence, presented in the form of partial refinement (refining; unit cell, peak shape (asymmetric pseudo-Voigt function §3.1.3)) and provides structural insights into the effects occurring in bulk powder samples. The possibility of preferred orientation effects altering relative reflection intensities has also been included into the refinement (see again §3.1.3). For each structural model the adaptations made to the (cation)MM'(ox)\textsubscript{3} structures are detailed.

4.3.1 \textit{Npent}_4\textit{M}^{\text{II}}\textit{Fe}^{\text{III}}(\text{ox})_3

The structure of the compound \textit{Npent}_4\textit{M}^{\text{II}}\textit{Fe}(\text{ox})_3 has been solved at 120K in \textit{C222(1)} with \textit{a} = 9.707Å, \textit{b} = 16.140Å and \textit{c} = 19.883Å\textsuperscript{3}. The room temperature refined lattice parameters of powder samples \textit{Npent}_4\textit{M}^{\text{II}}\textit{Fe}(\text{ox})_3 and \textit{Npent}_4\textit{FeFe}(\text{ox})_3 (Table 4.3) correspond well with this structure with an expansion of the \textit{c}-axis with temperature. The orthorhombic space group implies a distortion in the hexagonal oxalate layer array. The ratio \textit{b}/\textit{a} can be used to characterise this distortion since for an ideal hexagonal arrangement we have \textit{b}/\textit{a} = \sqrt{3} = 1.732. The ratios from the room temperature lattice parameters are: \textit{b}/\textit{a} = 1.676 for \textit{Npent}_4\textit{M}^{\text{II}}\textit{Fe}(\text{ox})_3 (cf. single crystal at 120K \textit{b}/\textit{a} = 1.663) and \textit{b}/\textit{a} = 1.682 for \textit{Npent}_4\textit{FeFe}(\text{ox})_3.

Using the coordinates from the structure the best fits for the powder data, including possible preferred orientation, are given in Figures 4.7(a) and (b). {\textit{Npent}_4\textit{M}^{\text{II}}\textit{Fe}(\text{ox})_3 \chi^2 = 9.71; \textit{Npent}_4\textit{FeFe}(\text{ox})_3, \chi^2 = 13.4.} (In the \textit{Npent}_4\textit{FeFe}(\text{ox})_3 case Fe\textsuperscript{II} was placed at the Mn\textsuperscript{II} site). It is clear from the fits that despite some intensity errors the powder samples can be described as monophasic with structures very similar to the model.

The structure corresponds to an [a-b'] type two-layer stacking of the bis-metal oxalate, [M\textsuperscript{II}Fe(ox)\textsubscript{3}], layer as shown in Figure 4.6(a), with an alternation in relative configuration of the M(ox)\textsubscript{3} and Fe(ox)\textsubscript{3} units between adjacent layers. The structure also has a highly disordered \textit{Npent}_4 position at 120K\textsuperscript{3}. The powder fits were generated using the two cation orientations (see Figure 4.6(b)) identified in the structural solution, with 0.5 occupancy of each orientation.
Figure 4.6(a): Layer stacking in the Npent$_4$MnFe(ox)$_3$ C222(1) structure.

Figure 4.6(b): The two cation positions in the Npent$_4$MnFe(ox)$_3$ structure viewed parallel to the [001] plane.
Figure 4.7: Npent₄MnFe(ox)₃ powder X-ray profiles fitted to the Npent₄MnFe(ox)₃ C222(1) structural model for (a) Npent₄MnFe(ox)₃ and (b) Npent₄FeFe(ox)₃.
4.3.2 \((\text{cation})\text{M}^{II}\text{Fe}^{III}(\text{ox})_3 \) \((\text{cation} = \text{NP}_4, \text{NBu}_4, \text{PBu}_4)\)

The structure of \(\text{NBu}_4\text{MnCr(ox)}_3\)\(^{27}\) (see §1.3) was solved in \(R3c\) with \(a,b = 9.414\text{Å}\) and \(c = 53.662\text{Å}\) and provided the first structural model for the compounds.

Figure 4.8: Layer stacking in \((\text{cation})\text{MM’(ox)}_3\) with (a) \(R3c\) and (b) \(P6(3)\) structures.
(cation)M^{II}Fe(ox)_3 with cation = NPr_4, NBu_4, and PBu_4. In §4.2.1 this cell with relaxed symmetry was used to index the X-ray powder data and refine unit cells of the compounds. Crystal structures of NPr_4MnCr(ox)_3 and NBu_4MnFe(ox)_3 have been published^33. NPr_4MnCr(ox)_3 was solved in the R3c cell with \(a, b = 9.363\,\text{Å} \text{ and } c = 49.207\,\text{Å}\), whilst NBu_4MnFe(ox)_3 was solved in P6(3) with \(a, b = 9.482\,\text{Å} \text{ and } c = 17.827\,\text{Å}\). Figure 4.8 illustrates the metal oxalate layer stacking in the six-layer R3c and the two-layer P6(3) structures. All three structures apparently exhibited disorder of the organic cation and only in the P6(3) NBu_4MnFe(ox)_3 structure was the disorder resolved into two possible conformations of NBu_4.

From the three available crystal structures, structural models of NPr_4M^{II}Fe(ox)_3, NBu_4M^{II}Fe(ox)_3 and PBu_4M^{II}Fe(ox)_3 in both R3c and P6(3) were generated*. A comparison of the powder X-ray profiles with those generated using the R3c and P6(3) structural models revealed that the reflections previously indexed by reducing symmetry from R3c were, in fact, those of the P6(3) phase. Figures 4.9, 4.10 and Appendix 2 show the best fits of the X-ray data using two phases for each compound. Examining the fits, it becomes clear that within the powder samples there are varying phase contributions from R3c and P6(3) phases. The data did not support the refinement of two independent unit cells for each phase. However, the previous single phase cell refinement indicates that the R3c and P6(3) cells must be similar with \(a(R3c) = a(P6(3)) +/-0.01\,\text{Å} \text{ and } c(R3c) = 3xc(P6(3)) +/-0.1\,\text{Å}\).

Figures 4.9 and 4.10 show some intensity errors between the observed and calculated patterns despite the inclusion of preferred orientation parameters. The reflections attributed to be fully from the P6(3) phase appear to be broader, with larger Lorentzian contributions to their line shape, than those from the R3c phase. A possibility, given the similarity of layer stacking in the R3c and P6(3) structures (Figure 4.8), is that within each powder-crystallite there are a portions of each stacking type, i.e. the compounds suffer from stacking faults.

* Notes on generating model structures:
(i) R3c structure models; R3c models of NBu_4MnFe(ox)_3 and NBu_4FeFe(ox)_3 were generated by using the coordinates of the NBu_4MnCr(ox)_3 structure and replacing Cr^{III} by Fe^{III}. R3c models of NPr_4MnFe(ox)_3 and NPr_4FeFe(ox)_3 were generated similarly using the coordinates of NPr_4MnCr(ox)_3.
(ii) P6(3) structure models; P6(3) NBu_4FeFe(ox)_3 was generated from the P6(3) NBu_4MnFe(ox)_3 structure by replacing Mn^{II} by Fe^{II}. P6(3) structural models for compounds with the NPr_4 cation were generated by placing NPr_4 on the NBu_4 site of the P6(3) NBu_4MnFe(ox)_3 structure, and displacing its position along \(c\) so that NPr_4 sat at a similar displacement from the oxalate layer to that in R3c NPr_4MnCr(ox)_3. (iii) PBu_4MFe(ox)_3 structure models were generated from those of NBu_4MFe(ox)_3 by replacing N by P.
Figure 4.9: Two phase fits for NBu$_4$M$^{II}$Fe(ox)$_3$ powder X-ray profiles; fitting to $R3c$ and $P6(3)$ structural models for (a) NBu$_4$FeFe(ox)$_3$ and (b) NBu$_4$MnFe(ox)$_3$. 
4.10: Two phase fits for NPr$_4$M$^{III}$Fe(ox)$_3$ powder X-ray profiles; fitting to $R3c$ and $P6(3)$ structural models for (a) NPr$_4$FeFe(ox)$_3$ and (b) NPr$_4$MnFe(ox)$_3$. 
Layer stacking faults are expected to cause (hkl) dependent broadening of Bragg reflections depending on which reciprocal lattice points become ill-defined by the layer disorder. Diffraction intensities in stacking faulted crystals can be generated using the Diffraction Intensities in Faulted Xtals (DIFFaX) program\(^{58}\) (see §3.1.4). X-ray powder diffraction patterns for R3c and P6(3) type layer stacking and cases where the stacking is faulted between each type have been generated for NPr\(_4\)MnFe(ox)\(_3\) using DIFFaX, between 5 and 40 degrees two-theta.

*Powder diffraction simulation using the DIFFaX Program*

The DIFFaX program works by defining a crystal as infinite sheets of layer unit cells stacked in sequence with defined stacking vectors (\(R_{ij}\)) between adjacent layers. Faulting in a structure is simulated by introducing alternative layers and/or stacking vectors within a layer sequence by using stacking probabilities (\(\alpha_{ij}\)) for each possible \(R_{ij}\) (see §3.1.4).

The R3c NPr\(_4\)MnFe(ox)\(_3\) structural model was rendered in to DIFFaX form by dividing the cell into six layer P1 unit cells \(a,b = 9.416\,\text{Å} \quad \text{and} \quad c = 8.18\,\text{Å}\). The P1 cells of layers 1, 3 and 5 are related by the rhombohedral centering of R3c whilst layers 2, 4 and 6 are generated from the c-glide plane in R3c. The full structure may therefore be described by two P1 layer cells stacking alternately with a six layer repeat. This is graphically illustrated in Figure 4.10 where the \(R_{ij}\) vectors are defined in terms of the layer unit cell. Setting the transition probabilities between each successive layer to unity (\(\alpha_{i\rightarrow i+1} = 1\)), the program was run to generate the R3c structure powder pattern\(^*\) (see Appendix 3 for an example sample input file). The simulated pattern (Figure 4.12(a)) using this 6-layer definition was identical to that generated by a FULLPROF pattern calculation using the R3c NPr\(_4\)MnFe(ox)\(_3\) structural model. The P6(3) NPr\(_4\)MnFe(ox)\(_3\) structural model was defined as two P1 layer unit cells, of identical size to the R3c layer cells, stacked as in Figure 4.10. The calculated DIFFaX profile for this two layer repeat (Figure 4.11(b)) was identical to the P6(3) profile generated with FULLPROF.

\* Note: The Molecular Simulations Incorporated (MSI) software suite Insight II\(^{79}\), with modules Solids Builder and Solids Adjuster was to be used in order to achieve the layer P1 definition of the NPr\(_4\)MnFe(ox)\(_3\) structure. DIFFaX is provided as freeware with the MSI Catalysis suite.

\# Note Diffax profiles were calculated with a pseudo-Voigt shape \(\mu = 0.4, \nu = -0.109, \omega = 0.026, \eta = 0.78\).
Inspection of layer cells (see also Figure 4.8) revealed that layer 2 in $R3c$ is identically displaced to layer 1 of $P6(3)$, with respect to the metal ion positioning, {layers in $P6(3)$ will now on be referred to as layer 7 and 8 corresponding to 1 and 2 in $P6(3)$ respectively}. Faulting between the two structures was simulated by generating an 8-layer DIFFaX input file with non-zero stacking probabilities for the stacking vectors $R_{17}$ and $R_{73}$ ($\alpha_{17} = \alpha_{73} \neq 0$) (see Appendix 3).

Profiles of the faulted layer structure were calculated for different faulting probabilities, $n$, $\alpha_{17} = \alpha_{73} = n$ {with $\alpha_{17} = \alpha_{73}$ the phase fractions of $R3c$ and $P6(3)$ are kept equal}. The calculated DIFFaX patterns are displayed in Figure 4.12 for (c) $n = 0.01$ a 1% faulting chance, (d) $n = 0.2$ 20% faulting chance, (e) $n = 0.3$ 30% faulting chance, (f) $n = 0.4$ 40% faulting chance and (g) $n = 0.5$ 50% faulting chance. The actual X-ray profile for NPr$_4$MnFe(ox)$_3$ is displayed for comparison in Figure 4.12(h).

A faulting chance of 1% between $P6(3)$ and $R3c$ gives a calculated X-ray profile equivalent to the sum of $R3c$ and $P6(3)$ phases. This might be expected as it corresponds to an average of 100 similar stacking sequences before faulting (~4,800Å in the $R3c$ structure). High faulting chances $\geq$20% results in significant changes in the simulated profile. Reflections, in general, become broadened. Reflections purely from the $P6(3)$ phase become, apparently, relatively weaker with increasing faulting chance and exhibit large Lorentzian broadening of their shapes. This effect is also seen in the NPr$_4$MnFe(ox)$_3$ data. Within the DIFFaX program the stacking probability cannot be varied as in a least square minimisation; however, the best comparison between real and simulated data appears to occur at around 20-30% faulting chance. The stacking faulted pattern simulation with DIFFaX does not model the X-ray peak asymmetry of the real profile. This may arise from the instrumental effects mentioned in §3.1.3.

The simulated DIFFaX patterns give strong indications that the broadening observed in the X-ray profiles is a result of layer stacking faulting disorder. Further calculations to include different phase fractions of $P6(3)$ and $R3c$ in NPr$_4$MnFe(ox)$_3$ or calculations for the other structures were not carried out due to computer time and real time constraints.
Figure 4.11: Illustration of the layer unit cell definition of $R3c$ and $P6(3)$ model structures and their stacking vectors.

i) $R3c$ simulation; \( \alpha_{12} = \alpha_{23} = \alpha_{34} = \alpha_{45} = \alpha_{56} = \alpha_{61} = 1 \), all other \( \alpha_{ij} = 0 \).

ii) $R3c \leftrightarrow P6(3)$ stacking faulting simulation (probability of faulting n);
\[
\alpha_{12} = 1-n, \quad \alpha_{17} = n, \quad \alpha_{78} = 1-n, \quad \alpha_{73} = n,
\]
\[
\alpha_{23} = \alpha_{34} = \alpha_{45} = \alpha_{56} = \alpha_{61} = \alpha_{87} = 1, \quad \text{all other } \alpha_{ij} = 0.
\]
Figure 4.12: (a-d) Simulated powder diffraction profiles of NPr$_4$MnFe(ox)$_3$ using the DIFFaX program.
Figure 4.12: (e-g) Simulated powder diffraction profiles of $\text{NP}r_4\text{MnFe(ox)}_3$ using the DIFFaX program and (g) the $\text{NP}r_4\text{MnFe(ox)}_3$ X-ray profile.
4.3.3 $\text{PPh}_4\text{M}^{II}\text{Fe}^{III}(\text{ox})_3$ and $\text{AsPh}_4\text{M}^{II}\text{Fe}^{III}(\text{ox})_3$

Compounds $\text{PPh}_4\text{M}^{II}\text{Fe}(\text{ox})_3$ and $\text{AsPh}_4\text{M}^{II}\text{Fe}(\text{ox})_3$ have a single structural model in the single crystal structure of $\text{PPh}_4\text{MnCr}(\text{ox})_3$ which was solved in $R3c$ with $a,b = 18.783\text{Å}$ and $c = 57.283\text{Å}$ (discussed in §1.3). This structure is distinct from the previous $R3c$ structures (discussed in §4.3.3) in that the hexagonal layer $[\text{MnCr}(\text{ox})_3]$ is distorted from an ideal hexagonal arrangement necessitating the doubled in-plane cell parameter. The best fit to $\text{PPh}_4\text{FeFe}(\text{ox})_3$ using this model is given in Figure 4.13(a). Similar broadening of reflections and intensity errors such as those occurring in other $(\text{cation})\text{M}^{II}\text{Fe}(\text{ox})_3$ profiles are apparent in the fit despite the inclusion of preferred orientation parameters. Evidence for a $P6(3)$ type stacking phase in the profile is minimal.

In the $\text{PPh}_4\text{MnFe}(\text{ox})_3$ profile weak intensity reflections characteristic of a $P6(3)$ type stacking phase are apparent (see Figure 4.13(b)). A $P6(3)$ structural model for $\text{PPh}_4\text{MnFe}(\text{ox})_3$ has not been generated to fit these reflections as adaptation of the $P6(3) \ 	ext{NBu}_4\text{MnFe}(\text{ox})_3$ structure is not obvious. Fits for $\text{AsPh}_4\text{M}^{II}\text{Fe}(\text{ox})_3$ are in Appendix 2.

Figure 4.13(a): $\text{PPh}_4\text{FeFe}(\text{ox})_3$ powder X-ray profile fitted to the $\text{PPh}_4\text{MnCr}(\text{ox})_3$ $R3c$ structural model.
4.3.4 Sample dependence of powder diffraction profiles

In §4.3.3. and §4.3.4. powder samples of (cation)MnFe(ox)₃ were found to contain two phases R3c and P6(3) corresponding to different stacking sequences of the oxalate layers. The subject of preparation dependence was not discussed. The effect of sample preparation on the X-ray profile for PPh₄MnFe(ox)₃ is now described.

The X-ray profile of a PPh₄MnFe(ox)₃ sample obtained by the quick 'Block' method precipitation (ppt in <1 hour) of PPh₄MnFe(ox)₃ is compared to that obtained by the slower 'Ionic' method (ppt in 24 hours) in Figure 4.14. The quicker precipitation clearly shows a larger contribution from reflections that can be attributed to the P6(3) phase than the slower 'Ionic' method. It seems that a slowing down of precipitation rate favours crystallisation in R3c over P6(3). However, examining profiles for all the compounds that suffer from this effect (Figure 4.9(a,b), 4.10(a,b) and 4.13(a,b)) indicates that the tendency to crystallise in P6(3) is also compound dependent.

Figure 4.13(b): PPh₄MnFe(ox)₃ powder X-ray profile fitted to the PPh₄MnCr(ox)₃ R3c structural model.
Figure 4.14: Preparation dependence of the PPh₄MnFe(ox)₃ X-ray profile for (a) a typical Ionic method precipitation and (b) a typical Block method precipitation.

4.3.5 \((PPN)M^{III}Fe(ox)_3\) compounds

There is no suitable structure model on which to model the powder diffraction profiles of the compounds \((PPN)M^{III}Fe(ox)_3\). The X-ray profiles for both \(M^{III} = \text{Mn and Fe}\) are isomorphous (see Figure 4.15) indicating that the PPN cation determines a similar structure (or structures) for both compounds. Partial indexing of the profiles was achieved as described in §4.2.1 based on an \(R3c\) model giving the unit cell \(a, b = 9.41\AA\) and \(c = 87.1\AA\) for \((PPN)\text{MnFe(ox)_3}\) and \(a, b = 9.38\AA\) and \(c = 86.6\AA\) for \((PPN)\text{FeFe(ox)_3}\). The \(c\)-lattice parameter corresponds to a large inter-layer separation of \(-14.5\AA\) in both compounds. Considering the size of the PPN cation it is tempting to postulate its orientation, within the inter-lamellar space, to be similar to that depicted in Figure 4.16. However, using the InsightII program to place the PPN cation at a number of inter-lamellar sites and orientations within expanded \(R3c\) metal oxalate layer stacking arrangements always gave predicted X-ray profiles, unlike the observed profiles.
Figure 4.15: (PPN)\textsuperscript{II}Fe(ox\textsubscript{3}) powder X-ray profiles partially indexed on a R3c cell for (a) (PPN)FeFe(ox\textsubscript{3}) and (b) (PPN)MnFe(ox\textsubscript{3}).

Figure 4.16: Postulated conformation of the PPN cation within the inter-lamellar oxalate layer of (PPN)\textsuperscript{II}Fe(ox\textsubscript{3}) compounds.
4.3.6 Attempted preparation of single crystals

Numerous single crystal growing experiments were attempted for (cation)M\textsuperscript{III}Fe(ox)\textsubscript{3} compounds using the techniques of slow-diffusion, slow-evaporation and gel-diffusion. Unfortunately, despite the production of small, apparently single crystallites for a number of (cation)M\textsuperscript{III}Fe(ox)\textsubscript{3} structural solution was not successful. Crystallographers at the Cardiff Crystallography Service and at Daresbury laboratories\textsuperscript{67} reported broad and weak reflections from the crystals on a position sensitive X-ray diffraction plate. The data obtained are not presented; however, it is tempting to postulate that crystals were suffering from layer stacking faults, as evidenced in their powder X-ray profiles, as an explanation to their broad diffraction spots. Crystals of the (PPN)M\textsuperscript{III}Fe(ox)\textsubscript{3} compounds prepared by an evaporation method had a flat diamond-like morphology; however, a single crystal diffraction experiment at Daresbury could not reveal the unit cell of the compound with the crystallographer concluding that the crystal was possibly exhibiting a complicated incommensurate structure\textsuperscript{67}.
4.4 Neutron diffraction

The compounds (cation)M\textsuperscript{ill}Fe(ox\textsubscript{3}) have been further investigated by powder neutron diffraction using the instruments D1B, D1A and D2B at the ILL Grenoble (see §3.2.1 for a description of each instrument). Neutron diffraction provides complementary structural information to that from X-ray diffraction studies. Also the occurrence of neutron magnetic diffraction in magnetically ordered compounds (§3.1.2) enables the elucidation of their microscopic magnetic structure. It is hence a valued tool for the investigation of (cation)M\textsuperscript{ill}Fe(ox\textsubscript{3}) compounds. The large incoherent neutron scattering length of the hydrogen nucleus necessitates the synthesis of deuterated analogues to (cation)M\textsuperscript{ill}Fe(ox\textsubscript{3}). Neutron diffraction experiments have been limited to compounds PPh\textsubscript{4}(d\textsubscript{20})M\textsuperscript{ill}Fe(ox\textsubscript{3}) (M\textsuperscript{ill} = Mn and Fe) because only for the tetraphenylphosphonium cation was a feasible deuteration route identified (§4.1.2).

The X-ray diffraction experiments and interpretations discussed above (§3.4.4) applies to the deuterated compounds whose X-ray profiles showed similar effects.

4.4.1 Neutron Diffraction experiments on PPh\textsubscript{4}(d\textsubscript{20})MnFe(ox\textsubscript{3})

PPh\textsubscript{4}(d\textsubscript{20})MnFe(ox\textsubscript{3}) was primarily investigated with the high intensity D1B fixed detector instrument, in a search for magnetic scattering. An initial 5 minute profile was recorded as the sample was cooled towards the base temperature of 1.7K during which time the sample temperature varied between 200-50K. At 1.7K 5 minute profiles were collected and summed using local programs and compared to the initial cooling scan. A number of new peaks in the low temperature profiles were immediately prominent. The temperature dependence of the profile was investigated with scans at a variety of temperatures through the magnetic ordering temperature (T\textsubscript{c} ~25K) (see §5.3) and above. The collection time at each temperature of the scans was set to 90 minutes due to the weak diffraction, both structural and magnetic.

The compound was further investigated with the high resolution diffractometer D1A. Profiles were recorded using the high wavelength option (λ = 2.9811\textsubscript{Å}) over the two-theta range 0-150° at 1.5K and 40K with a collection time of 22 hours per profile. The long wavelength was chosen in order to separate out the large number of overlapping reflections found in the D1B profiles.

The profile recorded on D1A at 40K is displayed in Figure 4.17. Using profile matching it was fitted with a purely Gaussian peak shape and the R3c cell. The fit gave lattice parameters of \(a,b = 18.831(4)\text{Å}\) and \(c = 55.511(8)\text{Å}\) which correspond well with
those obtained by room temperature X-ray diffraction (Table 4.2) with an expected
contraction in c (~2 Å) and a,b (~0.5 Å) on decreasing the temperature. The intensity not
fitted by the profile match may be attributed to the small amount of P6(3) type stacking
phase identified in the X-ray scan. Attempts to use the R3c structural model of
PPh₄MnCr(ox)₃ to fit the data were not successful, probably due to the data quality.
The 1.5K profile (Figure 4.18) revealed no significant change in lattice parameters
between 1.5K and 40K. A number of reflections had increased intensity in the 1.5K
profile. The extra scattering intensity arises from magnetic diffraction indicating long
range magnetic order. The indices of the most intense magnetic reflections are marked
in Figure 4.18 as [201] and [205] of the R3c cell.

Figures 4.17 and 4.18 also reveal a high background which is around 40-50%
of the most intense Bragg reflection. The background appears to exhibit a wave-like
modulation with two-theta and is temperature independent over the range
1.5K<T<40K. The background must therefore arise from both the sum of incoherent
scattering from the nuclei and also from structural disorder in the compound. The
background was estimated by interpolation between the bases of Bragg peaks in the
fitting.

Figure 4.17: Neutron diffraction profile of PPh₄(-d₂₀)MnFe(ox)₃ (D1A; 40K) fitted
with pattern matching to an R3c cell.
The magnetic diffraction peaks of $\text{PPh}_4(\text{d}_{20})\text{MnFe(ox)}_3$ were more apparent in the low temperature D1B profiles since the higher effective neutron flux of D1B on each fixed detector (§3.1.2) yields better statistics. Difference plots were generated by subtracting the profile intensity at 30K ($I(30\text{K})$) from lower temperature profiles in order to isolate the magnetic diffraction pattern. The difference plot between scans at 1.7K and 30K ($[I(1.7\text{K}) - I(30\text{K})]$) is plotted in Figure 4.19. The magnetic reflections are quite weak compared to the large fluctuations in the difference background; however, indexing is possible using a $R3c$ cell. The most intense magnetic reflection [201] was manually integrated, between $16.46 \leq 2\theta \leq 18.46$, for all difference plots [$I(T) - I(30\text{K})$] and its temperature dependence is plotted in Figure 4.20 (errors were calculated from the sum of neutron counts in the fitting region (N) as $[\sqrt{N(T)} + \sqrt{N(30\text{K})}]$). The sharp decrease of attributed magnetic intensity at around 24K compares favourably the with the ordering temperature estimated by bulk susceptibility measurements (see §5.3).
Figure 4.19: The D1B difference plot \([I(1.7K) - I(30K)]\) for \(\text{PPh}_4(-d_{30})\text{MnFe(ox)}_3\) with magnetic reflections \((R3c\text{ cell})\) marked.

Figure 4.20: The integrated intensity of the [201] magnetic reflection of \(\text{PPh}_4(d-2_{0})\text{MnFe(ox)}_3\) (D1B) versus temperature.
The indices of the magnetic reflections (Figure 4.19) indicate that the chemical and magnetic cells are coincident, i.e. the magnetic structure has the propagation vector \( \kappa = 0 \), and also that the moments lie along the \( c \)-axis, since no intensity is found for [001] reflections \( (q^2 = 0 \text{ for } [001] \text{ if } \eta = 0) \). In the \( R3c \) cell both antiferromagnetic and ferromagnetic magnetic ordering models can be envisaged with spin alignment parallel to the \( c \)-axis. Ferromagnetic ordering can be discounted immediately as susceptibility measurements have indicated an antiferromagnetic ordering in the hydrogenous analogue compound \( \text{PPh}_4\text{MnFe(ox)}_3 \) (§5.3). Possible antiferromagnetic ordering models parallel to the \( c \)-axis may be further defined by consideration of the character of axial spins with respect to the symmetry operations of the group. Two models are generated by considering the spin characters associated with the \( c \)-glide plane operation in \( R3c \), namely antiferromagnetism with and without inversion of axial spin components along the \( c \)-glide plane; respectively these are \( R3c \) and \( R3c' \) magnetic structures according to the Shubnikov definition (§3.1.2).

Using the FULLPROF program, patterns were generated for the antiferromagnetic models \( R3c \) and \( R3c' \) using the metal positions from the \( R3c \) structural solution of \( \text{PPh}_4\text{MnCr(ox)}_3 \) and the fitted low temperature cell constants from the D1A data. For each model a moment of \( 5\mu_B \) was placed antiparallel along the \( c \)-axis on the Mn\(^{2+}(\uparrow)\) and Fe\(^{3+}(\downarrow)\) sites. The predicted patterns are plotted in Figures 4.21(a) and (b). The observed difference pattern \( [I(1.7K) - I(30K)] \) is replotted in Figure 4.21(c) for a direct comparison with the predicted patterns.

Comparing the observed and predicted patterns we find that the \( R3c \) Shubnikov group, provides the best representation of the low temperature magnetic order in \( \text{PPh}_4(-d_{20})\text{MnFe(ox)}_3 \). There are, however, a few reflections which are not predicted by this model but are in the magnetic profile, the most prominent is indexed as [206]. The extra magnetic reflection intensity could result from either (i) the error in using the metal coordinates from the \( \text{PPh}_4\text{MnCr(ox)}_3 \) room temperature structure, (ii) magnetic intensity from a \( P6(3) \) stacking phase previously identified in the compound or (iii) from a magnetic order in \( R3c \) with moments not exactly aligned along the \( c \)-axis. Case (i) cannot be verified because the D1A profiles do not support Rietveld refinement. Case (ii) was investigated by constructing a cell in \( P6(3) \) using the metal atom positions from the \( P6(3) \) half cell structure of \( \text{NBu}_4\text{MnFe(ox)}_3 \).

---

# (iv) or even from the metal deficiency which has been identified in the analogous hydrogenated compound (see §7.2) introducing a disorder among the magnetic sublattices. This has not been investigated as metal analysis on the \( \text{PPh}_4(-d_{20})\text{MnFe(ox)}_3 \) sample has not been performed.
Figure 4.21(a,b): Predicted magnetic diffraction patterns for antiferromagnetic alignment along c-axis in PPh₄MnFe(ox)₃ and (c) the observed [I(1.7K)-I(30K)].
Predicted patterns for this structure, with antiferromagnetic alignment along the c-axis for $P6(3)'$ type alignment are given in Figure 4.22 ($P6(3)'$ here corresponds to axial spin inversion along the 6(3) screw rotation axis). The labelled indices in Figure 4.22 are in both the $P6(3)$ and the $R3c$ super cell and are indicated in the plot as $[P6(3)(R3c)]$. The $P6(3)$ models do predict a high intensity for the $[102(206)]$ reflection; however, $[100(200)]$ has a higher intensity and is not evident in the difference profile of $\text{PPh}_4(-d_{20})\text{MnFe(ox)}_3$. Case (ii) can therefore be discounted; however, the magnetic profiles generated by this method can not simulate the effects of stacking faults which may cause changes in relative magnetic reflection intensities (c.f. with X-ray's using the DIFFaX program see §4.3.3).

The possibility of an antiparallel antiferromagnetic ordering with spins lying off the c-axis (case(iii)) was investigated by generating magnetic profiles with spins on Mn($\uparrow$) and Fe($\downarrow$) inclined at various angles to the c-axis (using the $R3c$ Shubnikov group), with non-axial spin components parallel to the a-axis (altering the non-axial spin direction between the a and b axes caused little change in the predicted pattern because of the almost exact hexagonal arrangement of the metal atoms in the (a,b) plane). Figure 4.23 illustrates the effect of varying the inclination angle between 0 and 30 degrees. The change in the $[206]$ magnetic reflection intensity is not significant, whilst those of $[006]$ and $[204]$ increase greatly. The refinement of the moment directions and/or size was not attempted on the data due to the large fluctuating background.

![Figure 4.22: Predicted magnetic diffraction pattern for spin alignment along c-axis in a P6(3) phase with P6(3)' Shubnikov symmetry (reflections are marked in P6(3) and R3c super-cell.)](image-url)
In conclusion, despite the apparent unattributed magnetic reflection intensities in the powder neutron diffraction difference plot of $\text{PPh}_4(-d_{20})\text{MnFe(ox)}_3$ we can say that the observed magnetic diffraction is well explained by an antiferromagnetic alignment of spins along the $c$-axis with Shubinikov $R3c$ symmetry. The actual similarities between the observed and predicted patterns for this magnetic structure are unequivicable in this respect with the model accurately predicting the correct relative intensities for the four most intense magnetic reflections. Indeed, weaker intensities observed in the difference plot are also predicted in the model; however, the limitations of the fluctuating difference background hinders extra indexing. An illustration of the moment alignment for the model is given in Figure 4.24.
\( \downarrow \) = 5\( \mu_n \) Fe\(^{3+} \) site

\( \uparrow \) = 5\( \mu_n \) Mn\(^{3+} \) site

Figure 4.24: An illustration of the magnetic order in PPh\(_4\)(-d\(_{20}\))MnFe(ox)\(_3\) (Shubnikov R3c).

(N.B. The R3c Shubnikov magnetic ordering in the compound results in the alteration of Mn(\( \uparrow \)) and Fe(\( \downarrow \)) moments between adjacent layers in the cell. In comparison a R3c' ordering corresponds to Mn(\( \uparrow \)) and Fe(\( \downarrow \)) moments lying in the same direction throughout all the layers of the compound.)
4.4.2 Neutron Diffraction experiments on \( \text{PPh}_4(-d_{20})\text{Fe}^{II}\text{Fe(ox)}_3 \)

\( \text{PPh}_4(-d_{20})\text{FeFe(ox)}_3 \) was investigated in a similar manner to \( \text{PPh}_4(-d_{20})\text{MnFe(ox)}_3 \) by carrying out temperature dependent scans on D1B; however, the magnetic scattering was much weaker than in the MnFe compound and the number of temperatures examined was commensurately smaller, with a profile collection time of around 120 minutes.

\( \text{PPh}_4(-d_{20})\text{FeFe(ox)}_3 \) was also investigated using the high resolution diffractometer D2B. Profiles at 1.5K and 50K were collected over a two-theta range 0-160° using a wavelength of 2.398Å. Pattern matching the 50K data with an \( R3c \) cell gave a good fit (Figure 4.25) and the unit cell parameters \( a,b = 18.674(8)\text{Å} \) and \( c = 56.289(14)\text{Å} \). Attempted Rietveld fitting using the \( \text{PPh}_4\text{MnCr(ox)}_3 \) structural model was unsuccessful.

![Neutron diffraction profile of \( \text{PPh}_4(-d_{20})\text{FeFe(ox)}_3 \) (D2B; 50K) fitted with pattern matching to a \( R3c \) cell.](image)

Figure 4.25: Neutron diffraction profile of \( \text{PPh}_4(-d_{20})\text{FeFe(ox)}_3 \) (D2B; 50K) fitted with pattern matching to a \( R3c \) cell.

The 1.5K profile of \( \text{PPh}_4(-d_{20})\text{FeFe(ox)}_3 \) showed no significant change in lattice parameters from the 50K profile. A weak shoulder to the nuclear [202] reflection appears in the 1.5K profile centred around 17.2 degrees (\( d = 7.9\text{Å} \)). This is illustrated
in close-up (Figure 4.26) for both temperatures. The shoulder, assigned to magnetic intensity, was indexed as \([201]\).

The background intensity of the \(\text{PPh}_4(-d_{30})\text{FeFe(ox)}_3\) D2B profiles was similar to that in the \(\text{PPh}_4(-d_{30})\text{MnFe(ox)}_3\) D1A profiles varying between 25-40\% of the most intense Bragg reflection. The background was temperature independent \(1.5\text{K}<T<50\text{K}\) and was estimated by interpolation for the fitting.

![Low angle part of neutron diffraction profile of \(\text{PPh}_4\text{FeFe(ox)}_3\) (D2B; 50K).](image)

Figure 4.26(b): Low angle part of neutron diffraction profile of \(\text{PPh}_4\text{FeFe(ox)}_3\) (D2B; 1.5K) with the [201] magnetic reflection marked.
The intensity difference plot \([I(1.7K) - I(50K)]\) recorded on DIB is plotted in Figure 4.27. The plot reveals extremely weak asymmetric magnetic scattering intensities. The high angle tail to the [201] magnetic reflection extends beyond [202] and from the difference plot it is not clear whether some of the magnetic intensity is attributable to [202] or even other reflections. The temperature dependence of the magnetic intensity between 17.0 and 18.4 degrees, attributed to [201], was manually integrated from all the difference plots \([I(T) - I(50K)]\) and its temperature dependence is plotted in Figure 4.28 (errors were calculated as in the MnFe case). The [201] magnetic intensity is lost at \(T = 38K\) compared to the magnetic ordering temperature of the compound \(T_c = 34K\), obtained from susceptibility measurements (§5.2).

![Figure 4.27](image)

Figure 4.27: The DIB difference plot \([I(1.7K) - I(30K)]\) for \(\text{PPh}_4(-d_{20})\text{FeFe(ox)}_3\) with the [201] magnetic reflection marked.

The successful indexing of the magnetic intensity in \(\text{PPh}_4(-d_{20})\text{FeFe(ox)}_3\) as [201] strongly indicates an antiferromagnetic type magnetic order of the \(\text{Fe}^{2+}\) and \(\text{Fe}^{3+}\) moments with spin alignment parallel to the \(c\)-axis (susceptibility measurements (§5.2) also indicate antiferromagnetic alignment of spins with a ferrimagnetic ground state at low temperature). The weak asymmetric nature of the magnetic scattering in the compound prevents further interpretations similar to those carried out for \(\text{PPh}_4(-d_{20})\text{MnFe(ox)}_3\). The comparison in magnetic intensities with \(\text{PPh}_4(-d_{20})\text{MnFe(ox)}_3\) is quite suprising as the profiles obtained for both compounds were of similar quality and, to a first approximation, have similar moments. This discussion will be returned to in Chapter 7.
Figure 4.28: Integrated intensity of the [201] magnetic reflection of PPh$_4$(-$d_{20}$)FeFe(ox)$_3$ (D1B) versus temperature.
CHAPTER 5
Magnetic characterisation of (cation)M$^{II}$Fe$^{III}$(ox)$_3$ compounds by AC and DC SQUID Magnetometry

5.1 Overview

This chapter contains details of magnetic susceptibility measurements made on powder samples of (cation)M$^{II}$Fe$^{III}$(ox)$_3$ compounds whose synthesis and structural properties have been described in Chapter 4. The measurements on the two sets of compounds (cation)Fe$^{II}$Fe$^{III}$(ox)$_3$ and (cation)Mn$^{II}$Fe$^{III}$(ox)$_3$ are presented separately in §5.2 and §5.3. It should be noted that there are some discrepancies between the data and fitted parameters presented here and the preliminary reports on the compounds$^{31,71}$. The measurements reported in this chapter were made on samples synthesised as described in Chapter 4. Sample mounting is described in §3.2. Particular attention has been given to remanent field effects as discussed in §3.2.1. The discussion of the results is deferred to Chapter 7.

5.2 Fe$^{II}$Fe$^{III}$ oxalate salts

5.2.1 General behaviour

The basic magnetic characterisation of the series of (cation)Fe$^{II}$Fe$^{III}$(ox)$_3$ compounds was carried out by cooling samples of each compound in 100G field (100G FC) to low temperature (2K or 5K) and measuring the magnetisation while warming to 300K. The susceptibilities of the FeFe 100G FC data were fitted to the Curie-Weiss law (§2.5) from 150K to 300K, after making a numerical correction for sample diamagnetism. The validity of the fitting range was checked by fitting the data over different temperature regions. Fitting from 200K yielded similar results to from 150K, though with larger errors, whilst fitting below 150K gave a poor fit. Figure 5.1 shows the fit for compounds AsPh$_4$FeFe(ox)$_3$, NBu$_4$FeFe(ox)$_3$ and Npent$_4$FeFe(ox)$_3$. The fits for the other FeFe compounds are plotted in Appendix 4. It is evident from Figure 5.1 that the Curie-Weiss law is well obeyed above 150K, which corresponds to $T_{\text{min fit}}>3T_C$. The fit parameters are recorded in Table 5.1.
Figure 5.1: Inverse susceptibility (1/\chi) Curie-Weiss fits for (cation)Fe"Fe"*(ox)3.

The molar magnetisations versus temperature are plotted for each FeFe compound in the temperature range from 0 to 50K in Figure 5.2. The characteristics of each magnetisation curve are recorded in Table 5.1. From the Figure 5.2, it becomes clear that there are two general forms of magnetisation curve for the compounds; those which do and those which do not exhibit negative magnetisation at low temperatures.

The magnetisation of the compounds (cation)Fe"Fe"*(ox)3 (cation = PPh^ and AsPh^) increases abruptly below about 35K and rapidly rises toward lower temperature. The magnetisation continues to increase monotonically and tends to saturation with \partial M/\partial T \rightarrow 0 at the lowest measured temperature.

In striking contrast compounds (cation)Fe"Fe"*(ox)3 with cation = NPr^, NBu^, Npent^, PBu^ and PPN have an altogether different magnetic behaviour after 100G FC with a critical temperature in the region T_c \sim 45K below which the magnetisation increases abruptly. In these compounds the magnetisation reaches a rounded maximum at T_{\text{max}} \approx 40K (\partial^2 M/\partial T^2 is negative in the region 35K < T < 42K) and then falls rapidly and monotonically on further cooling. At around 30K there is a temperature of compensation T_{\text{comp}} (\S 2.4.2) at which the observed magnetisation falls to zero and below which the magnetisation becomes negative with respect to the applied field. At lower temperatures (T \leq 20K) the magnetisation becomes large and negative, tending to saturation at the lowest measured temperature with \partial M/\partial T \rightarrow 0.
Figure 5.2: The temperature dependence of the magnetisation of (cation)Fe\textsuperscript{II}Fe\textsuperscript{III}(ox)\textsubscript{3} after 100G field cooling.
Table 5.1: Magnetic characteristics of (cation)Fe$^{II}$Fe$^{III}$(ox)$_3$ (100G FC).

<table>
<thead>
<tr>
<th>(cation)Fe$^{II}$Fe$^{III}$(ox)$_3$</th>
<th>Tc (K)</th>
<th>T$_{comp}$ (K)</th>
<th>C (cm$^3$mol$^{-1}$K) (150-300K)</th>
<th>$\theta$ (K) (150-300K)</th>
<th>$\mu_{eff}$ (\mu\beta) (at 300K)</th>
<th>$M_{sat}$ (at T$_{min}$) (cm$^3$Gmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPr$_4$FeFe(ox)$_3$</td>
<td>44.5</td>
<td>34</td>
<td>7.79(13)</td>
<td>-92.2(5.0)</td>
<td>6.88</td>
<td>-385 (2K)</td>
</tr>
<tr>
<td>NBu$_4$FeFe(ox)$_3$</td>
<td>45</td>
<td>31.5</td>
<td>7.88(1)</td>
<td>-90.24(30)</td>
<td>6.87</td>
<td>-404 (5K)</td>
</tr>
<tr>
<td>Npent$_4$FeFe(ox)$_3$</td>
<td>46</td>
<td>29.5</td>
<td>9.05(1)</td>
<td>-86.92(6)</td>
<td>7.45</td>
<td>-850 (5K)</td>
</tr>
<tr>
<td>PPh$_4$FeFe(ox)$_3$</td>
<td>34</td>
<td>-</td>
<td>6.71(12)</td>
<td>-88.4(2)</td>
<td>6.43</td>
<td>243 (2K)</td>
</tr>
<tr>
<td>AsPh$_4$FeFe(ox)$_3$</td>
<td>36</td>
<td>-</td>
<td>6.41(10)</td>
<td>-88.5(5.8)</td>
<td>6.27</td>
<td>290 (2K)</td>
</tr>
<tr>
<td>PBu$_4$FeFe(ox)$_3$</td>
<td>44.5</td>
<td>33.5</td>
<td>7.76(1)</td>
<td>-89.9(2)</td>
<td>6.93</td>
<td>-392 (5K)</td>
</tr>
<tr>
<td>PPNFeFe(ox)$_3$</td>
<td>43</td>
<td>30.5</td>
<td>7.758(10)</td>
<td>-88.4(2)</td>
<td>6.92</td>
<td>-235.5 (5K)</td>
</tr>
</tbody>
</table>

(N.B. Tc arbitrarily chosen as the temperature of the abrupt increase in 100G FC magnetisation.)

To elucidate the magnetic behaviour of the (cation)Fe$^{II}$Fe$^{III}$(ox)$_3$ compounds, further experiments were made on examples which exhibit a negative magnetisation (§5.2.1) and those having a positive magnetisation (§5.2.2) at low temperatures, with respect to applied field. One compound of each type has been principally investigated; NBu$_4$FeFe(ox)$_3$ as the negative case and PPh$_4$FeFe(ox)$_3$ as the positive case. Where possible, further experiments on the other members in each series were also carried out.

5.2.2 Compounds with negative low temperature magnetisation

(i) Low field studies

The magnetisation of NBu$_4$FeFe(ox)$_3$ was investigated in very low field by first cooling the sample in a zero applied field (+/-0.05G) using the procedure outlined in §3.2.1. The magnetisation was then measured on warming from 5 to 50K in an applied field of 100G. The sample was then cooled in progressively larger fields (0 < H < 100G) and the magnetisation again measured on warming in a field of 100G. Figure 5.3 shows the magnetisation of NBu$_4$FeFe(ox)$_3$ after; (i) ZFC, (ii) 0.3G FC, (iii) 0.7G
FC, (iv) 2G FC compared to (v) the 100G FC magnetisation. Zero field cooling experiments were also carried out on the compounds PPNFeFe(ox)$_3$ and PBu$_4$FeFe(ox)$_3$. The ZFC magnetisations of these compounds are plotted in Figure 5.4 compared to that of NBu$_4$FeFe(ox)$_3$.

![Figure 5.3: The temperature dependence of the magnetisation of NBu$_4$FeFe(ox)$_3$ after zero and low field cooling (0G < H < 100G).](image)

The ZFC magnetisation of NBu$_4$FeFe(ox)$_3$ initially increased at $T_c = 45K$ in the same way as the 100G FC case. However, at 43.5K the two magnetisation curves diverged, indicating the onset of hysteresis. The ZFC magnetisation reached a maximum at 42K and then fell, with a pronounced shoulder being observed at 40K. The ZFC magnetisation reached a minimum around 35K and then rose slowly towards
lower temperatures. The ZFC magnetisation curves for PPNFeFe(ox)₃ and PBu₄FeFe(ox)₃ had similar forms to that of NBu₄FeFe(ox)₃. The small magnetisation of 6-8cm³Gmol⁻¹ at 5K is indicative that the compounds had been cooled in a demagnetised state. Cooling in very small fields (H < 1G) resulted in the appearance of negative magnetisation. For example, an applied field of only 2G during cooling gave the same saturation magnetisation as the 100G FC measurement (see Figure 5.3).

![Figure 5.4: The temperature dependence of the ZFC magnetisation of (cation)FeFe(ox)₃ (cation = NBu₄, PPN and PBu₄).](image)

The shoulder at 40K in the ZFC magnetisation was also evident as a slight discontinuity in 100G FC magnetisations of all FeFe compounds that exhibited low temperature negative magnetisation. To further investigate this effect a slow cooling experiment was carried out on NBu₄FeFe(ox)₃.

The NBu₄FeFe(ox)₃ sample was initially cooled from the paramagnetic regime to 45K in 100G applied field. The temperature was then allowed to equilibrate for 60
seconds and the magnetisation measured. The sample was then cooled, equilibrated and measured in progressively smaller temperature steps approaching 40K and larger steps below 40K, down to 35K. The resulting magnetisation curve (Figure 5.5(a)) showed a pronounced discontinuity at exactly 40.0K where the magnetisation fell by \(-2\text{cm}^3\text{Gmol}^{-1}\). The sample was then slowly warmed and cooled over the temperature region between 39.8K and 40.2K, measuring at intervals of 0.01K after a temperature equilibration time of 120 seconds. The results are plotted in Figure 5.5(b). (N.B. The errors in the measured magnetisation in Figures 5.5(a) and (b) are smaller than the markers and not shown).

![Figure 5.5: The magnetisation of NBu_4FeFe(ox)_3 in 100G applied field during (a) slow cooling and (b) slow warming/cooling between 39.8 and 40.2K (repeated in close-up O/L).](image)

The magnetisation discontinuity temperature, \(T_1\), did not show a significant temperature hysteresis between cooling and warming measurements. A similar
experiment, slow cooling and warming in 100G field, was carried out on Npent₄FeFe(ox)₃ and a similar discontinuity was also observed at exactly 40.0K (plotted in Appendix 4); however, in the Npent₄FeFe(ox)₃ case the magnetisation increased by 4cm³Gmol⁻¹ during cooling.

The sensitivity of the low temperature magnetisation behaviour of 100G FC NBu₄FeFe(ox)₃ to the temperature at which the cooling field was applied was investigated. The sample was initially zero field cooled to different temperatures: i) 45K (T > T_c), ii) 43K (T_t < T < T_c) and iii) 40K (T = T_t). After temperature equilibration (=60secs) a 100G field was applied and the sample was further field cooled to low temperature (5K). The magnetisation was then measured on warming in the field. The magnetisation behaviour arising from these experiments is plotted in Figure 5.6, with the ZFC data for comparison. The application of the fields from 45K (T > T_c) and 43K (T_t < T < T_c) resulted in a magnetisation behaviour almost identical to the 100G FC magnetisation study, with similar saturation at 5K. Field cooling from 40K (T = T_t) gave a magnetisation curve intermediate between the FC and ZFC behaviour indicating that the sample had been cooled partially in both a magnetised and a demagnetised state.

Figure 5.5(b): Close-up of the magnetisation in NBu₄FeFe(ox)₃ during slow cooling/warming in 100G field, showing the magnetisation discontinuity at T = 40.0K.
(ii) High field studies

In this section we investigate the stability of the negative low temperature magnetisation of NBu₄FeFe(ox)₃ to both high field cooling and hysteresis measurements.

An initial experiment on a sample after 100G field cooling to 5K revealed that the magnetisation became positive in a measuring field greater than 10,000G. Reducing the field to 100G resulted in the magnetisation again returning, apparently reversibly, to its initial negative value. The stability of the negative magnetisation state was
investigated by field cooling in progressively higher fields from 100G to 70,000G, measuring the magnetisation during warming from 5K to 50K in an applied field of 100G. In this way the magnetisation behaviour as a result of the field cooling history was examined, in the weakly perturbing but constant measurement field. The change in the remanent field of the magnet, as a result of the high cooling field was characterised in the paramagnetic temperature regime of the sample (§3.2.1), or simply by comparing the magnetisation in this region with the previously calibrated 100G FC data. The magnetisation behaviour for this experiment is plotted in Figure 5.7.

Cooling in fields from 100G to 2,000G increased the negative saturation at 5K; however, higher cooling fields resulted in a gradual reversal of the magnetisation direction to that of the 100G measuring field (magnetisation became more positive). The form of the curves remained similar to the 100G FC experiment for cooling fields from 100G to 10,000G; i.e. typically the magnetisation reached a maximum at 38K, exhibited a $T_{comp}$ at ~32K, with negative magnetisation at lower temperatures, monotonically approaching saturation at 5K. Field cooling in 20,000G resulted in a $T_{comp}$ at 28.5K followed by a broad minimum, a second $T_{comp}$ at 18.5K and the magnetisation reaching a positive value ~90cm$^3$Gmol$^{-1}$ at 5K.

Cooling fields of 60,000G and 70,000G gave magnetisation curves almost the inverse of the 100G FC case. The magnetisation had a large positive saturation at 5K of a greater magnitude than the low field negative saturations. A compensation temperature at 32K was exhibited in the reverse sense, magnetisation becoming positive on decreasing temperature. Above 37K the magnetisation started to return to the direction of the field with a second $T_{comp} = 39.5K$. All cooling fields gave identical magnetisations above 43.5K.

Table 5.2: Magnetisation saturation values at 5K in NBu$_4$FeFe(ox)$_3$ after cooling in different fields between 100G and 70,000G, measuring in 100G.

<table>
<thead>
<tr>
<th>Cooling field (x10$^6$ G)</th>
<th>0.01</th>
<th>0.2</th>
<th>0.3</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_{sat}$ (cm$^3$Gmol$^{-1}$) at 5K in 100G</td>
<td>-436</td>
<td>-526</td>
<td>-486</td>
<td>-404</td>
<td>-228</td>
<td>91</td>
<td>371</td>
<td>576</td>
<td>773</td>
<td>841</td>
</tr>
</tbody>
</table>

113
Figure 5.7: Temperature dependence of the magnetisation of NBu₄FeFe(ox)$_3$ after cooling in fields between 100G and 70,000G, measuring upon warming in 100G.
Magnetic hysteresis loops (+/-70,000G) were recorded on NBu$_4$FeFe(ox)$_3$ at 5K after (a) 100G FC, (b) 70,000G FC and (c) ZFC. The SQUID magnet was set in its no-overshoot mode for all hysteresis measurements, as described in §3.2.2. This induces a possible error in the actual field within the magnetometer of +/-20G, as no estimation of the remanent field can be made throughout the hysteresis measurement.

The hysteresis curve after 100G FC, plotted in Figure 5.8(a), was displaced negatively with respect to the magnetisation axis. This indicates that the sample has retained a memory of its field cooling history, despite field cycling between +/-70,000G. The hysteresis loop opened over the field cycle indicating that irreversible magnetisation processes had occurred within the compound; however, the loop did not show a characteristic coercive field ($H_c$). The remanent magnetisations of the sample $R_M = M(H\rightarrow 0)$ for decreasing ($H\rightarrow 0+ve$) and increasing fields ($H\rightarrow 0-ve$) are recorded in Table 5.3. A second hysteresis loop at 5K was found to exactly trace the first loop.

The 70,000G FC hysteresis curve at 5K (Figure 5.8(b)) was asymmetrically displaced to a positive magnetisation value, displaying a memory effect in the opposite direction, with respect to cooling field, to the 100G FC loop. The form of the loop is almost identical to that after 100G field cooling, with an asymmetry of similar magnitude. This indicates that the magnetic ground state reached after 70,000G field cooling is similar to that after 100G field cooling, however, with a reversal of the remanent magnetisation direction. Given a possible field error of +/-20G the two hysteresis loops 100G FC and 70,000G appear to be non-penetrating.

The ZFC hysteresis loop at 5K was similar in form to the field cooled loops again not exhibiting a characteristic coercive field between +/-70,000G. The hysteresis curve was symmetrical with respect to the magnetisation axis. All three plots show an opening in the hysteresis curve of between 650 and 702 cm$^3$Gmol$^{-1}$.

Table 5.3: Magnetic remanence of NBu$_4$FeFe(ox)$_3$ at 5K from hysteresis loops recorded between +/-70,000G.

| Cooling field (Gauss) | $R_M(H\rightarrow 0+ve)$ (cm$^3$Gmol$^{-1}$) | $R_M(H\rightarrow 0-ve)$ (cm$^3$Gmol$^{-1}$) | $|\Delta R_M|$ (cm$^3$Gmol$^{-1}$) |
|-----------------------|---------------------------------------------|---------------------------------------------|----------------------------------|
| 100                   | 58                                          | -585                                        | 643                              |
| 70,000                | 744                                         | 42                                          | 702                              |
| 0                     | 330                                         | -330                                        | 660                              |
Figure 5.8: Hysteresis loops of NBu₄FeFe(ox)₃ at 5K after; (a) 100G FC, (b) 70,000G FC and (c) ZFC.
The temperature evolution of the hysteresis in NBu₄FeFe(ox)₃ was investigated by recording +/-10,000G magnetisation loops at temperatures between 29 and 47K along the 100G FC magnetisation curve. The hysteresis loops are plotted in Figure 5.9 (a,b,c); the magnetic characteristics of the hysteresis loops (coercivity and remanance) are recorded in Table 5.4.

In the temperature region between 42K and 38K NBu₄FeFe(ox)₃ exhibited a conventional S-shaped hysteresis loop, symmetric with respect to the magnetisation axis, and a characteristic coercive field (Hₑ) where the magnetisation changed rapidly with the field. The hysteresis loop opened out as the temperature was lowered from 42K to 38K. The development in hysteresis can be expected from the growth of magnetic domains and magnetisation in the direction of the applied field in NBu₄FeFe(ox)₃ within this temperature range. Below 38K, at the next measured temperature of 36K the hysteresis characteristics had changed, with no observed coercivity +/-10,000G. The hysteresis loop at 36K was asymmetrically displaced towards a positive magnetisation value. Further cooling (from 36K to 32K) resulted in the hysteresis curve contracting and reducing its asymmetric shift, until at 32K the hysteresis disappeared completely. This is expected as 32K is the compensation temperature of the compound, where there is no spontaneous magnetisation. Hysteresis loops recorded between 32K and 29K shifted asymmetrically to a negative magnetisation offset and opened out as the temperature was lowered. The hysteresis at 29K resembles that recorded at 5K (Figure 5.8.(a)).

Table 5.4: The temperature dependence of the magnetic coercivity and remanance of NBu₄FeFe(ox)₃ (100G FC) from hysteresis loops recorded between +/-10,000G.

| Temperature (K) | Hₑ (G) | Rₑ(H→0+ve) (cm²Gmol⁻¹) | Rₑ(H→0-ve) (cm²Gmol⁻¹) | |ΔRₑ| (cm²Gmol⁻¹) |
|-----------------|--------|-------------------------|-------------------------|-----------------|-----------------|
| 42              | 188    | 18                      | -22                     | 40              |
| 40              | 400    | 60                      | -58                     | 118             |
| 38              | 581    | 75                      | -75                     | 150             |
| 36              | -      | 69                      | -39                     | 108             |
| 33              | -      | 22                      | 14                      | 8               |
| 31              | -      | 5                       | -13                     | 18              |
| 29              | -      | -20                     | -64                     | 44              |
Figure 5.9(a,b): The development of hysteresis of NBu$_4$FeFe(ox)$_3$ (100G FC) with temperature.
Figure 5.9(c): The development of hysteresis of NBu$_4$FeFe(ox)$_3$ (100G FC) with temperature.

(iii) AC susceptibility measurements

AC susceptibility measurements were performed at the Institute of Molecular Sciences, Okazaki Japan using the low field MPMS2 SQUID magnetometer fitted with the AC measurement insert (see §3.2.3). Measurements were performed on samples of NBu$_4$FeFe(ox)$_3$, and NPent$_4$FeFe(ox)$_3$. [N.B. The AC studies were carried out in the period July/August 1995. The samples' DC susceptibility behaviour was checked prior to measurement with brief DC SQUID FC scans. The DC susceptibility data presented throughout this chapter was performed on samples prepared in July 1996. It is therefore possible that some differences between the AC and DC data may be a result of sample effects.]

In Figure 5.10(a) the dispersion ($\chi'$) and the absorption ($\chi''$) of NBu$_4$FeFe(ox)$_3$ recorded at a frequency of 0.1Hz are plotted as a molar susceptibilities, with the measured 100G FC and ZFC $\chi_{dc}$ molar susceptibilities plotted for comparison.
Above $T_c$, at 50K, $\chi'$ matches the DC susceptibility and $\chi'' = 0$. This is consistent with the measured quantity ($\chi'$) at high temperature being the isothermal susceptibility $\chi' = \chi_{t} = \chi_{dc}$ with the magnetisation following the oscillating field precisely ($\omega \tau << 1$). $\chi'$ begins to rise at 47K and reaches a maximum at ~44K, coinciding with the onset of hysteresis between the DC FC and ZFC susceptibilities. The low temperature tail in $\chi'$ falls asymmetrically with a broad but weak shoulder at around 40K, reminiscent of that seen in the DC ZFC measurement. At temperatures lower than 35K $\chi'$ matches the ZFC $\chi_{dc}$ data, consistent with the measured quantity now being the adiabatic susceptibility $\chi' = \chi_5$ and ($\omega \tau >> 1$).

The absorption $\chi''$ rises from zero at 46K to a maximum at ~44K before falling to zero around 40K (Unfortunately the number of points collected in the $T_c$ region $\Delta T_{consecutive \ points} = 1K$ is not sufficient to be more specific with regards to exact temperatures in describing this data). The non zero $\chi''$ between 40K and 46K indicates that relaxational processes are active within this temperature range ($\omega \tau ~1$) and confirms that a magnetic transition with a spontaneous magnetisation is occurring.

The sharp peak in $\chi'$ for NBu$_4$FeFe(ox)$_3$ indicates that $T_c$ is ~44K ($T_c$ was arbitrarily defined in Table 5.1 from DC FC measurements (§5.2)). The estimated $T_c$'s for NBu$_4$FeFe(ox)$_3$ and Npent$_4$FeFe(ox)$_3$ by interpolating the AC $\chi'$ data are recorded in Table 5.5 (see Appendix 4 for the AC/DC plot of Npent$_4$FeFe(ox)$_3$).

Table 5.5: Critical temperatures in (cation)FeFe(ox)$_3$ from AC measurements.

<table>
<thead>
<tr>
<th>Compound</th>
<th>NBu$_4$FeFe(ox)$_3$</th>
<th>Npent$_4$FeFe(ox)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$ est. from $\chi'$ peak (K)</td>
<td>43.5</td>
<td>45.4</td>
</tr>
</tbody>
</table>

The frequency dependence of the AC susceptibility in NBu$_4$FeFe(ox)$_3$ was investigated over the frequency range 0.1Hz to 1500Hz, throughout the magnetic ordering region. $\chi''$ versus temperature plots over the $\chi'' \neq 0$ temperature region are plotted in Figure 5.10(b). The $\chi''$ susceptibility maximum at ~44K reduces in magnitude and rounds on increasing the measurement frequency. The temperature of the peak maximum $\chi''_{max}$ did not appear to change within the measured frequency range, however, the limiting number of temperature points precludes the total annihilation of this possibility.
Figure 5.10(a): AC and DC susceptibility behaviour of NBu$_4$FeFe(ox)$_3$.

Figure 5.10(b): $\chi''$ frequency dependence in NBu$_4$FeFe(ox)$_3$ over 0.1-1500Hz.
5.2.3 *Compounds with positive low temperature magnetisation*

(i) *Low field studies*

The magnetisation behaviour in \( \text{PPh}_4\text{FeFe(ox)}_3 \) was investigated by performing magnetisation experiments after cooling in zero or low fields (0G < \( H < 500 \text{G} \)); measuring the magnetisation on warming in a 100G field. The results are plotted in Figure 5.11.

![Figure 5.11: Temperature dependence of the magnetisation of PPh\(_4\)FeFe(ox)\(_3\) after zero and low field cooling.](image)

The ZFC magnetisation in PPh\(_4\)FeFe(ox)\(_3\) rises with the FC at the apparent critical temperature \( T_c \sim 34 \text{K} \). Branching between the ZFC and 100G FC magnetisation
curves occurs at 28K. The ZFC magnetisation reaches a broad maximum at around 25K and falls gradually towards lower temperatures reaching 6cm$^3$Gmol$^{-1}$ at 5K. Clearly, the compound has been cooled in a demagnetised state. Field cooling in 1G gave little magnetisation difference from ZFC. After field cooling in 10G the rounded maximum 25K was just evident, as a slight dip in the curve, and at 5K a magnetisation of 45cm$^3$Gmol$^{-1}$ was retained. Magnetisation curves after cooling in fields higher than 10G did not exhibit maxima at 25K. The saturation magnetisation at 5K varied smoothly with the cooling field, with $\partial M/\partial T \to 0$ towards lower temperature.

A ZFC experiment was also carried out on AsPh$_4$FeFe(ox)$_3$ and the ZFC magnetisation behaviour of the two compounds are compared in Figure 5.12. In AsPh$_4$FeFe(ox)$_3$ the initial rise at 37K is sharper than that in PPh$_4$FeFe(ox)$_3$ and exhibits a high temperature shoulder and rounded maximum at 25K. The shoulder was not visible in the FC magnetisation. In fact, a 100G FC experiment for these compounds with slow cooling and warming gave only smooth variations in magnetisation with temperature.

![Figure 5.12: Comparison of ZFC magnetisation behaviour of (a) PPh$_4$FeFe(ox)$_3$ and (b) AsPh$_4$FeFe(ox)$_3$.](image)
(ii) **High field studies**

The high field magnetisation behaviour of PPh₄FeFe(ox)₃ was investigated by performing a +/-70,000G hysteresis loop after cooling the compound to 5K in a field of 100G, using the measurement protocol described in §3.2.2. The hysteresis loop is plotted in Figure 5.13. A second hysteresis loop was also performed at this temperature and was found to exactly trace the first. The temperature evolution of hysteresis was then investigated by recording smaller loops cycling the field between +/-10,000G at 15K, 20K and 25K after 100G FC to each temperature (plotted in Figure 5.14).

The hysteresis loop at 5K has a conventional S-shape form and is symmetric about both the magnetisation axis (indicating no field cooling memory) and the field axis. The curve exhibits a characteristic coercive field of $H_c = 11500$G.

The evolution of hysteresis with temperature is unusual. At 25K, corresponding to roughly the magnetisation maximum in the ZFC data (Figure 5.11), there is apparently no measurable opening of the hysteresis loop (N.B. 25K is 9K below the estimated $T_c$ of the compound). At lower temperatures (20K and 15K) the hysteresis curve opens out, resembling the 5K curve.

The magnetic coercivity and remanence constants derived from the hysteresis loops at each temperature are recorded in Table 5.6.

---

Table 5.6: The temperature dependence of the magnetic coercivity and remanance of PPh₄FeFe(ox)₃ (100G FC) from hysteresis measurements.

| Temperature (K) | $H_c$ (G) | $R_M(H\rightarrow0^{+ve})$ (cm²Gmol⁻¹) | $R_M(H\rightarrow0^{-ve})$ (cm²Gmol⁻¹) | $|\Delta R_M|$ (cm²Gmol⁻¹) |
|----------------|-----------|-------------------------------------|-------------------------------------|--------------------------|
| 25             | 0         | 0                                   | 0                                   | 0                        |
| 20             | 541       | 140                                 | -130                                | 270                      |
| 15             | 1200      | 280                                 | -280                                | 580                      |
| 5              | 11500     | 890                                 | -890                                | 1780                     |
Figure 5.13: Hysteresis of PPh₄FeFe(ox)₃ at 5K after 100G FC.

Figure 5.14: The development of hysteresis of PPh₄FeFe(ox)₃ (100G FC) with temperature.
(iii) **AC susceptibility measurements**

AC susceptibility measurements were performed on PPh$_4$FeFe(ox)$_3$ using a MPMS2 SQUID magnetometer with an AC measurement insert, with the measurement protocol of §3.2.3 [see also [N.B...] in §5.2.1(c)]. The frequency dependence of the AC susceptibility was investigated in the frequency range from 0.05Hz to 1500Hz. In Figure 5.15 the dispersion ($\chi'$) and absorption ($\chi''$) of PPh$_4$FeFe(ox)$_3$ at 0.1Hz are plotted as molar susceptibilities over the ordering temperature region, with the DC ZFC and 100G FC molar susceptibilities plotted for comparison.

At 50K the dispersion is equal to the DC susceptibility $\chi' = \chi_{dc} = \chi_T$ and the absorption $\chi'' = 0$, this is consistent with ($\omega \tau << 1$). Upon lowering the temperature, $\chi'$ rises to a very small maximum at 40K and falls; $\chi'$ begins to rise gradually again at 35K, with a shoulder around 30K and a maximum ~18K. At 5K $\chi'$ reduces to the ZFC magnetisation. Over the peak region $\chi'$ is considerably smaller than ZFC $\chi_{dc}$. The absence of a sharp ordering peak in $\chi'$ precludes an assignment of $T_c$ in PPh$_4$FeFe(ox)$_3$ from AC measurements.

![Figure 5.15(a): AC and DC susceptibility behaviour of PPh$_4$FeFe(ox)$_3$.](image)

126
The absorption, $\chi''$, shows the same temperature dependent features as the dispersion, however, with much smaller susceptibility values ($\chi''_{\text{max}}(18K) \approx 0.006 \text{ cm}^{-3} \text{mol}^{-1}$). The AC susceptibility behaviour for both $\chi'$ and $\chi''$ are extremely unusual for regular magnets and a non zero $\chi''$ between 5K and 40K is indicative that at least some relaxation processes are active ($\alpha r^{-1}$) down to low temperature in the compound.

Figure 5.15(b) plots the AC frequency dependence of $\chi''$ in PPh₄FeFe(ox)₃. The frequency dependence is complex with considerable frequency dependence. The maximum at ~18K becomes weaker and shifts to higher temperatures with increasing measurement frequency. The high temperature shoulder is only visible for frequencies lower than 1Hz. The number of temperature points is limiting in assigning the precise $\chi''$ maximum temperature. The temperature of the peak maximum was estimated by interpolation; the estimated $T_{\text{max}}$ are recorded in Table 5.7.

Argand diagrams of $\chi'$ versus $\chi''$ were plotted at a variety of temperatures for the AC susceptibility data. However, the diagrams were inconclusive in that they did not exhibit a coherent shape (e.g. a curve) that would be indicative of the magnitude and spread of relaxation times in the sample.

![Figure 5.15(b): $\chi''$ frequency dependence in PPh₄FeFe(ox)₃ over 0.1-1500Hz.](image)
Table 5.7: The frequency dependence of the $\chi''$ maximum in PPh$_4$FeFe(ox)$_3$

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>0.05</th>
<th>0.1</th>
<th>1</th>
<th>250</th>
<th>500</th>
<th>1000</th>
<th>1500</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{max}}$ in $\chi$ (K)</td>
<td>17.8</td>
<td>17.8</td>
<td>18.5</td>
<td>19.8</td>
<td>20</td>
<td>20.5</td>
<td>21</td>
</tr>
</tbody>
</table>

If we assume a single relaxation time constant $\tau$ in the compound, the maximum in $\chi''$ corresponds to a freezing temperature ($T_f$) when the magnetisation cannot follow the oscillating field; i.e. $\tau = 1/\omega$. A test for Arrhenius magneto-dynamics (Equation 5.1) was made by plotting $\ln(\tau)$ versus $1/T_f$ for the data (Figure 15.5(c)). The plot indicates that the magneto-dynamics of the sample are more complicated than an Arrhenius dependence. This will be returned to in Chapter 7.

$$\tau = \tau_0 \exp(E_a/kT) \quad (5.1)$$

Figure 5.15(c): Test for Arrhenius magneto-dynamics in PPh$_4$FeFe(ox)$_3$ from AC susceptibility measurements.
5.3 \( \text{Mn}^{\text{II}}\text{Fe}^{\text{III}} \) oxalate salts

The series of (cation)\( \text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{ox})_3 \) compounds were characterised by performing 100G FC magnetisation experiments on samples of each compound, measuring the magnetisation during warming from 2K or 5K to 300K.

The molar susceptibilities (after adjustment for sample diamagnetism) were fitted to the Curie-Weiss law in the high temperature region from 150K to 300K. The fits for \( \text{NPr}_4\text{MnFe}(\text{ox})_3 \), \( \text{NBu}_4\text{MnFe}(\text{ox})_3 \) and \( \text{Npent}_4\text{MnFe}(\text{ox})_3 \) compounds are plotted in Figure 5.16. The fits for the other \( \text{MnFe} \) compounds are plotted in Appendix 4. The fitted Curie-Weiss parameters are recorded in Table 5.8.

Clearly, from Figure 5.16, the compounds closely follow the Curie law in the fitting region. The large negative \( \theta \) values are indicative of strong antiferromagnetic exchange interactions in the compounds.

![Inverse susceptibility (1/\( \chi \)) Curie-Weiss fits for (cation)\( \text{MnFe}(\text{ox})_3 \)](image)

Figure 5.16: Inverse susceptibility (1/\( \chi \)) Curie-Weiss fits for (cation)\( \text{MnFe}(\text{ox})_3 \)

Typically, towards lower temperatures, the 100G FC (cation)\( \text{MnFe}(\text{ox})_3 \) magnetisation curve rose gradually and passed through a broad maximum at around 50-55K, characteristic of a low dimensional antiferromagnet. Further cooling gave a
monotonical decrease in the magnetisation until at between 24 and 30K where there was a sharp increase in the magnetisation which tended to monotonical saturation \((\partial M/\partial T \to 0)\) at the lowest measured temperature. Figure 5.17 illustrates the 100G FC magnetisation curve for \(\text{Npent}_4\text{MnFe(ox)}_3\). The abrupt change in the magnetisation is indicative of a transition to long range magnetic order and the estimated critical temperatures \((T_c)\) of each compound are recorded in Table 5.8.

The low temperature saturation magnetisation, after 100G field cooling, was found to be cation dependent and is recorded for each compound in Table 5.8. Figure 5.18 plots the comparative 100G FC data for \(\text{PPN MnFe(ox)}_3\), \(\text{PPh}_4\text{MnFe(ox)}_3\), \(\text{AsPh}_4\text{MnFe(ox)}_3\) and \(\text{PBu}_4\text{MnFe(ox)}_3\) in the low temperature region.

![Figure 5.17: Temperature dependence of the ZFC and 100G FC magnetisations in \(\text{Npent}_4\text{MnFe(ox)}_3\)](image)

The evolution of magnetisation at low temperature as a function of the cooling field was investigated in a number of MnFe compounds. Samples were cooled in a set field \((0G < H < 500G)\) and the magnetisation measured during warming in 100G applied field from 5K to 35K.
Table 5.8: Magnetic characteristics of (cation)MnFe(ox)$_3$ (100G FC).

<table>
<thead>
<tr>
<th>(cation)Mn$^{III}$Fe$^{III}$(ox)$_3$</th>
<th>$T_c$ (K)</th>
<th>$C$ (cm$^3$mol$^{-1}$*K$^{-1}$)</th>
<th>$\Theta$ (K) (150-300K)</th>
<th>$\mu_{\text{eff}}$(µB)</th>
<th>$M_{\text{sat}}$(cm$^3$Gmol$^{-1}$) (at $T_{\text{min}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPr$_4$MnFe(ox)$_3$</td>
<td>27</td>
<td>8.41(12)</td>
<td>-113.0(5)</td>
<td>6.99</td>
<td>16.6 (2K)</td>
</tr>
<tr>
<td>NBu$_4$MnFe(ox)$_3$</td>
<td>26</td>
<td>10.5(5)</td>
<td>-100.8(3.8)</td>
<td>7.98</td>
<td>36.0 (5K)</td>
</tr>
<tr>
<td>NPent$_4$MnFe(ox)$_3$</td>
<td>29</td>
<td>8.69(16)</td>
<td>-103.0(5.5)</td>
<td>7.20</td>
<td>15.8 (5K)</td>
</tr>
<tr>
<td>PPh$_4$MnFe(ox)$_3$</td>
<td>23.5</td>
<td>7.27(30)</td>
<td>-111(12)</td>
<td>6.56</td>
<td>18.3 (2K)</td>
</tr>
<tr>
<td>AsPh$_4$MnFe(ox)$_3$</td>
<td>24.5</td>
<td>7.81(16)</td>
<td>-106(6)</td>
<td>6.80</td>
<td>71.8 (2K)</td>
</tr>
<tr>
<td>PBu$_4$MnFe(ox)$_3$</td>
<td>26</td>
<td>8.84(14)</td>
<td>-102.0(4.8)</td>
<td>7.27</td>
<td>22.5 2K)</td>
</tr>
<tr>
<td>PPNMnFe(ox)$_3$</td>
<td>25</td>
<td>7.97(21)</td>
<td>103.16(8)</td>
<td>6.87</td>
<td>108.1 (5K)</td>
</tr>
</tbody>
</table>

(* data recorded in temperature region 2-235K)

The ZFC magnetisation of Npent$_4$MnFe(ox)$_3$ (Figure 5.17) followed the 100G FC data down to the estimated $T_c$ at 29K. At $T_c$ there was an abrupt increase in the ZFC magnetisation analogous to the FC behaviour. Towards lower temperature the ZFC and FC magnetisation curves diverged with the onset of hysteresis. The ZFC magnetisation promptly reached a sharp maximum and fell rapidly to a small value (~5cm$^3$Gmol$^{-1}$) which was maintained down to low temperatures. This behaviour is further evidence of a transition to long range magnetic order at $T_c$ with the compound being cooled in a demagnetised state.

The ZFC magnetisation behaviour in NPr$_4$MnFe(ox)$_3$ and NBu$_4$MnFe(ox)$_3$ were qualitatively similar to that in Npent$_4$MnFe(ox)$_3$, exhibiting a peak below $T_c$ and small magnetisation values (3-6cm$^3$Gmol$^{-1}$) at the lowest measured temperature (see Figures 1.19 and 1.20); however, in these compounds the ZFC peak was broadened over a greater temperature range and generally of more complex character in comparison to Npent$_4$MnFe(ox)$_3$.

Field cooling curves recorded on NBu$_4$MnFe(ox)$_3$ and NPr$_4$MnFe(ox)$_3$ (0 < H < 500G) exhibited a gradual change in magnetisation behaviour from ZFC to FC with increasing cooling field (see Figure 5.19 and 5.20). The magnetisation reached at 5K as
a function of cooling field for the two compounds is plotted in Figure 5.21. Clearly, although both the number and range of measured fields is limiting, the low temperature magnetisation appears to be approaching a saturation value.

Attempts to obtain hysteresis curves on the MnFe series at 5K were inconclusive with the compounds apparently exhibiting a barely opened hysteresis curve after field cycling between +/-70,000G, +/-5000G and +/-100G.

The interpretation of the presented MnFe magnetisation data is discussed in Chapter 7.

![Figure 5.18: Temperature dependence of the magnetisation in (cation)MnFe(ox)_3 (100G FC) (cation = PPN, PPh₄, AsPh₄ and PBu₄).](image)
Figure 5.19: Zero field and field cooling magnetisation behaviour in NBu₄MnPe(ox)₃

Figure 5.20: Zero field and field cooling magnetisation behaviour in NPr₄MnFe(ox)₃
Figure 5.21: The magnetisation in NBu_4MnFe(ox)_3 and NPr_4MnFe(ox)_3 at 5K as a function of the cooling field (100G measuring field).
CHAPTER 6

Investigation of (cation)Fe^{II}Fe^{III}(ox)_{3} compounds with local magnetic probes

In the investigation of magnetically ordered materials local magnetic probes provide information complementary to that from bulk techniques. Mössbauer spectroscopy, MuSR spectroscopy and Nuclear Magnetic Resonance (N.M.R.) experiments can all, in principle, provide information on both the size and the distribution of static fields in a magnetically ordered compound and also on the magneto-dynamics involved in the transition to magnetic order.

In this chapter the magnetic order exhibited in the system (cation)Fe^{II}Fe^{III}(ox)_{3} has been examined with MuSR spectroscopy (measurements made on the EMU instrument at ISIS Rutherford Appleton Laboratories UK) and Fe^{57} Mössbauer spectroscopy (experiments performed by Dr. Jürgen Ensling at the University of Mainz, Germany). Experiments have been performed on representative compounds of both types of magnetic order: NBu_{4}FeFe(ox)_{3} in the case of negative magnetisation at low temperature and PPh_{4}FeFe(ox)_{3} in the case of a positive magnetisation at low temperature.

The discussion of the results, with reference to the results obtained by bulk susceptibility (Chapter 5) and neutron diffraction (Chapter 4), is deferred to Chapter 7.

6.1 MuSR spectroscopy

ZF-MuSR experiments were performed on the EMU instrument at ISIS set in longitudinal geometry (with forward and backward detectors (§3.3)) and in single pulse mode (UPPSET device on (§3.3)). All fitting procedures were carried out within the local standard mUon Data Analysis (UDA) program. Freshly prepared and characterised samples of NBu_{4}FeFe(ox)_{3} and PPh_{4}FeFe(ox)_{3} were loaded into the silver sheeted aluminium EMU sample holder (sample quantity ~0.3gcm^{-2}). The loaded sample holder was then masked with a thin mylar film and mounted in the EMU cryostat. Calibration of the forward and backward detector histograms for differences in geometry and efficiency were carried out by recording 20G transverse field (20G TF) histograms for each sample at 100K. The extracted α values were then fine-tuned by accurately fitting the oscillating decay signal of the calibration run to a single precession frequency with Lorentzian damping and allowing the balance (bal) option to
vary. The obtained calibration fit was satisfactory with \( \chi^2 < 1.05 \). The final calibration factors; \( \alpha = 0.96 \) (bal = 0.69) for NBu\(_4\)FeFe(ox)\(_3\) and \( \alpha = 1.04 \) (bal = -0.61) for PPh\(_4\)FeFe(ox)\(_3\), were assumed to be temperature independent for all measurements and therefore fixed in all subsequent fitting.

The zero field (ZF) depolarisation of NBu\(_4\)FeFe(ox)\(_3\) was first measured as a function of temperature from 4.5K to 100K. At each temperature 50,000 frames were collected summed and combined, giving a collection time for each measurement of around 45mins. Typical zero field histograms for NBu\(_4\)FeFe(ox)\(_3\) are plotted in Figure 6.1.

The first observation we can make from the NBu\(_4\)FeFe(ox)\(_3\) histogram recorded at 100K is that the initial asymmetry (a\(_0\)) of approximately 23% is lower than the 33% expected from 100% polarised muons. At 100K this loss is assigned to a non-magnetic missing fraction in the asymmetry from the sample (see §3.3). The time dependent depolarisation showed little change between the temperatures of 100K and 45K (Figure 6.1(a)), with an observed small decrease in initial asymmetry at 45K (a\(_0\)(45K) = 21%). The depolarisation curves at 100K and 45K appeared to be of Gaussian \( \{ \exp(-\sigma t)^2 \} \) form for the early part of the histograms \( (0 < t < 5\mu\text{secs}) \). At lower temperatures, and particularly through the magnetic ordering temperature \( T_c = 43.5K \), the measured a\(_0\) decreased, reaching approximately 10.5% at 4.5K. The depolarisation histogram at 4.5K was weakly decaying and featureless (Figure 6.1(c)). There was no evidence in the histograms of a coherent precession of the muon polarisation in ZF down to 4.5K, indicative of static fields.

Attempting to fit the ZF NBu\(_4\)FeFe(ox)\(_3\) histograms with simple Lorentzian \( \{ \exp(-\lambda t) \} \) or Gaussian decay functions gave fits of variable quality \( (\chi^2 = 1.1-1.5) \). At low temperatures \( (4.5K < T < 30K) \) the Lorentzian fit adequately explained the slow fall off in polarisation with time. Figure 6.1(c) shows the 4.5K histogram fitted to a Lorentzian decay \( (\chi^2 = 1.13) \). At higher temperatures \( T > 35K \) the error in a Lorentzian fit was quite significant \( (\chi^2 = 1.5) \). A better fit was obtained at higher temperatures by using a two component model including a fast Gaussian \( (\sigma = 0.35\mu\text{secs}^{-1}) \) decay term and a slow Lorentzian \( (\lambda \approx 0.06\mu\text{secs}^{-1}) \) decay term. The two component fit is shown in Figure 6.1(a) for the 100K \( (\chi^2 = 1.133) \) and 45K \( (\chi^2 = 1.046) \) histograms. The same two component model yielded reasonable fits \( (\chi^2 = 1.00-1.18) \) throughout the studied temperature range, however, the largest errors in the fits occurred between temperatures 42K and 44K where the initial asymmetry was significantly underestimated. The 43K histogram plotted in Figure 6.1(b) exemplifies this error which occurs at \( t < 0.3\mu\text{secs} \). The inclusion of a further very fast Lorentzian decay term into the model in order to account for the apparent very rapid decay of polarisation in this temperature range did not give convergence.
Figure 6.1: ZF-MuSR of NBu₄FeFe(ox)₃ at (a) 100 and 45K, (b) 42K and (c) 4.5K.
Figure 6.2: ZF-MuSR of PPh₄FeFe(ox)₃ at (a) 80K, (b) 33K and (c) 4.5K.
The temperature dependent ZF-MuSR depolarisation in PPh₄FeFe(ox)₃ was investigated in the temperature range from 4.5K to 80K, collecting histograms at each temperature for 50,000 frames. Typical histograms of the ZF depolarisation are plotted in Figure 6.2. The 80K initial asymmetry (a₀) in PPh₄FeFe(ox)₃ is approximately 18% (c.f. a₀(100K) = 23% for NBu₄FeFe(ox)₃) indicating that PPh₄FeFe(ox)₃ had a unusually large missing fraction at high temperatures.

The depolarisation curve in PPh₄FeFe(ox)₃ showed little change in form or in initial asymmetry values between T = 80K-41K. The initial asymmetry decreased below 40K and continued to drop through the magnetic ordering temperature (Tc = 34K), reaching a minimum at 20K (a₀(20K) = 11.9(5)). The overall change in the shape of the depolarisation histogram with temperature was less pronounced than in NBu₄FeFe(ox)₃, indeed, at 4.5K a curve in the decay was still evident (see Figure 6.2(c) and c.f. 4.5K ZF NBu₄FeFe(ox)₃, Figure 6.1(c)).

The ZF PPh₄FeFe(ox)₃ histograms were best fitted with a fast Gaussian decay (σ = 0.3μsecs⁻¹) and a slow decaying Lorentzian function (λ = 0.03μsecs⁻¹) which gave a reasonable fit throughout the whole temperature range (χ² = 1.04-1.14).

Figure 6.3 plots the temperature dependence of the total fitted ZF initial asymmetries (a₀) for NBu₄FeFe(ox)₃ and PPh₄FeFe(ox)₃. The observed drop in a₀ with decreasing temperature can be correlated with the magnetic ordering transition in the compounds The most rapid fall off in a₀ occurred at around 43K for NBu₄FeFe(ox)₃ and 37K for PPh₄FeFe(ox)₃, compared with Tc = 43.5K and 34K, observed in susceptibility measurements. The fall off of a₀ in NBu₄FeFe(ox)₃ is clearly sharper than in PPh₄FeFe(ox)₃. A loss in a₀ with decreasing temperature indicates that muon relaxation or resonance processes are faster than the EMU spectrometer can measure. In the case of resonance the muon pulse width at EMU of approximately 80nsecs limits measurable precession frequencies to a maximum of ~ 100MHz⁶⁴ (see §3.3) which, in turn, corresponds to a field of only ~0.1T at the muon site. In the case of very fast relaxation processes (λ > 5μsecs⁻¹) significant depolarisation will occur within the muon pulse width and will not be measured. The loss in a₀ is therefore indicative that these processes are occurring in parallel with the magnetic ordering. Evidence of very fast relaxation has been noted in the ZF NBu₄FeFe(ox)₃ depolarisation histogram between 42K and 44K. To extract physical meaning from the fitting models and values is, hence, complicated because the measured depolarisation corresponds to the tail-end of very fast processes and histograms consequently will suffer a loss of statistics. The apparent Gaussian-like ZF depolarisation at high temperatures appearing early in the depolarisation histogram is unusual because we expect the depolarisation to have a Lorentzian decay form in the limit of fast fluctuations (τcσₓ <<1).
The fitted relaxation rates of the fast Gaussian component for NBu$_4$FeFe(ox)$_3$ and PPh$_4$FeFe(ox)$_3$ are plotted in Figures 6.4 and 6.5.

In NBu$_4$FeFe(ox)$_3$ the relaxation rate shows an apparently divergent character near T$_c$; however, the 38K histogram exhibits an anomalously high relaxation rate. Divergence in the relaxation rate is expected in a magnetic ordering transition as the result of critical fluctuations near T$_c$. The plot is not extended to low temperatures, below 15K, where the depolarisation histogram became monotonic and large correlations occurred in the two-component fit parameters.

In PPh$_4$FeFe(ox)$_3$ the Gaussian relaxation rate did not exhibit a divergence, however, a general increase in the relaxation rate was observed. The larger errors at low temperatures results from the loss of asymmetry; however, a two component fit was still valid down to 4.5K.

The fitted slow Lorentzian component exhibited only small, apparently random, changes in relaxation rate with temperature remaining at $\lambda \approx 0.06\mu$secs$^{-1}$ for NBu$_4$FeFe(ox)$_3$ and $\lambda \approx 0.03\mu$secs$^{-1}$ for PPh$_4$FeFe(ox)$_3$ for all two component fits.
Figure 6.4: Temperature dependence of the fitted fast relaxation rate of NBu₄FeFe(ox)₃ ZF-MuSR.

Figure 6.5: Temperature dependence of the fitted fast relaxation rate of PPh₄FeFe(ox)₃ ZF-MuSR.
A loss in muon asymmetry concurrent with the onset of magnetic order is typical of high moment insulating magnets. The proportion of the lost initial asymmetry may be taken as an indication of the extent of magnetic order in the sample. In a fully ordered magnet we expect approximately one third of static moments in the powder sample to be aligned parallel to the initial muon polarisation. The muons that experience static fields parallel to their spin direction will retain their polarisation and contribute a non-oscillating component, hence, a fall in $a_0$ to 33% of the full high temperature asymmetry is expected with the transition to long range magnetic order. In $\text{NBu}_4\text{FeFe(ox)}_3$ the asymmetry fall \([a_0(4.5K)/a_0(100K)]\) is approximately 46%, whilst in $\text{PPh}_4\text{FeFe(ox)}_3$ \([a_0(4.5K)/a_0(80K)]\) is around 70%. The contrast can be interpreted as an indication that the transition to long-range order is more complete, throughout the sample, in $\text{NBu}_4\text{FeFe(ox)}_3$ than in $\text{PPh}_4\text{FeFe(ox)}_3$. The larger high temperature missing fraction in $\text{PPh}_4\text{FeFe(ox)}_3$ is assumed to be temperature independent and of non-magnetic origin\(^\#\).

At 4.5K the zero field cooled $\text{NBu}_4\text{FeFe(ox)}_3$ sample was further investigated by a longitudinal field repolarisation experiment. The depolarisation in progressively increasing longitudinal fields from 0 to 4000G was measured. The purpose of the repolarisation experiment is to recover the observed loss in initial asymmetry at 4.5K, resulting from the magnetic order. An applied longitudinal field will fully recover the lost initial asymmetry when it has fully oriented the magnetic moments in the sample in the field direction. Hence, in a magnetically ordered compound a repolarisation curve provides information of the anisotropy of the magnetic system analogous to a hysteresis curve. Figure 6.6 plots the repolarisation curve at 4.5K for $\text{NBu}_4\text{FeFe(ox)}_3$. The plot reveals a gradual recovery in $a_0$ with applied field, which at the highest measured field of 4000G is asymptotically reaching the high temperature value $a_0(100K) \approx 23\%$. Removal of the longitudinal field resulted in the depolarisation histogram returning to its initial ZF form, indicating that there have been no magnetic phase transition in $\text{NBu}_4\text{FeFe(ox)}_3$ from cycling the field 0-4000G at 4.5K (this has been verified with high field hysteresis measurements, cycling the field between +/-70,000G (§5.2.2)).

Fitting the slow depolarisation at 4.5K to a simple Lorentzian decay function gave a relaxation rate of $\lambda = 0.046(5)\text{sec}^{-1}$ in zero field. Application of a longitudinal field of 100G reduced the relaxation to $\lambda = 0.004(2)\text{sec}$ and this was roughly constant throughout the field variation from 100G to 4000G. Upon removal of the field the relaxation rate returned to its initial zero field value.

\(^\#\) The missing fraction in $\text{PPh}_4\text{FeFe(ox)}_3$ may be chemical in origin: The formation of muonium radicals in phenyl compounds is a well documented subject

142
In summary, the ZF-MuSR spectra of both NBu$_4$FeFe(ox)$_3$ and PPh$_4$FeFe(ox)$_3$ are best described by a two component model including a fast Gaussian and a slow Lorentzian decay function. This model was successful in fitting the PPh$_4$FeFe(ox)$_3$ ZF-MuSR histograms throughout the measured temperature range (4.5-80K). However, for NBu$_4$FeFe(ox)$_3$ the two component fit was invalid below ~30K, where the depolarisation is weak and monotonic. The physical origin of the depolarisation's two component nature has not been identified and may have arisen from a number of effects e.g. several muon sites in the compounds or even background effects. A loss in total asymmetry in the ZF-MuSR spectra has been correlated with the transition to magnetic order in the compounds. The transition to magnetic order in NBu$_4$FeFe(ox)$_3$ is apparently sharper than in PPh$_4$FeFe(ox)$_3$; evidenced by both the relatively rapid fall off in $a_0$ and in the apparent divergence of the fast Gaussian relaxation rate in NBu$_4$FeFe(ox)$_3$. There is also evidence that at low temperature the magnetic order in PPh$_4$FeFe(ox)$_3$ is less developed than in NBu$_4$FeFe(ox)$_3$. It is clear from the histograms that the static and dynamic fields involved directly with the magnetic ordering transitions in the compounds are above the resolution of the EMU instrument and, hence, can not be estimated.
6.2 Mössbauer spectroscopy

Temperature dependent $^{57}$Fe Mössbauer spectra were collected on samples of NBu$_4$FeFe(ox)$_3$ and PPh$_4$FeFe(ox)$_3$ by Dr Jürgen Ensling at the University of Mainz, Germany. The spectra obtained for each compound are pictured in Figure 6.8 for NBu$_4$FeFe(ox)$_3$, between 1.9K and 46K, and in Figure 6.9 for PPh$_4$FeFe(ox)$_3$, between 1.9K and 60K, in relative transmission form. The data interpretations of Dr Jürgen Ensling are now given.

At high temperature (293K), in the paramagnetic state, the spectra show two quadrupolar doublets from the Fe$^{II}$ and Fe$^{III}$ ions. The fitted parameters of the two doublets are given in Table 6.1. The isomer shifts ($\delta$) of the doublets at 293K are typical of high spin octrahedrally coordinated Fe$^{III}$ ($\delta = 0.3-0.5$ mms$^{-1}$) and Fe$^{II}$ ($\delta = 1.1-1.4$ mms$^{-1}$) ions. The observation of two distinct quadrupolar doublets indicates that there is a valence localisation in the compounds on the Mössbauer time scale (~$10^{-7}$ secs). Between 293K and 45K the two component doublet structure of the spectra is maintained for both compounds. The relative areas of the high temperature quadrupolar doublets gives an accurate estimation of the relative amount of Fe$^{III}$ and Fe$^{II}$ ions in the compounds. In NBu$_4$FeFe(ox)$_3$ the ratio {Fe$^{III}$:Fe$^{II}$} was {53:47} compared to {60:40} in PPh$_4$FeFe(ox)$_3$.

In NBu$_4$FeFe(ox)$_3$ a broadening of the quadrupolar doublets becomes apparent at 40K and at 39K nuclear hyperfine splitting is evident as wings in the spectra. Hyperfine splitting is the result of slow spin fluctuations compared to the nuclear Larmour precession frequency. Upon lowering the temperature further the hyperfine splitting can be discerned as a well resolved sextet from the Fe$^{III}$ ion, which is sharp at 1.9K. The hyperfine splitting from Fe$^{II}$, an octet, is not well defined and contains an unresolved broad feature down to 1.9K. This was attributed to a distribution of hyperfine fields caused by slightly varying environments of the Fe$^{II}$ ions.

In PPh$_4$FeFe(ox)$_3$ hyperfine splitting effects characteristic of Fe$^{III}$ become visible at 25K. At 1.9K the Fe$^{III}$ sextet still exhibits a broadened and asymmetric line shape. This could be the result of a varying Fe$^{III}$ ion environment or relaxation broadening. The Fe$^{II}$ octet showed similar effects to that in NBu$_4$FeFe(ox)$_3$.

The hyperfine field at the Fe$^{III}$ site has been extracted as a function of temperature for both compounds and is plotted in Figure 6.7. The complicated octet splitting from the Fe$^{II}$ ion prevented extraction of the temperature dependent hyperfine field at the Fe$^{II}$ site. Generally, at intermediate temperatures the broad hyperfine splitting was attributed to relaxation effects in the compounds.
The fit parameters from just above the observed transition, at 42K for NBu$_4$FeFe(ox)$_3$ and 30K for PPh$_4$FeFe(ox)$_3$, and at the lowest temperature, 1.9K, are also listed in Table 6.1. The isomer shifts are again consistent with high spin Fe$^{III}$ and Fe$^{II}$ ions; however, the quadrupolar splitting parameters ($\Delta E_Q$) change considerably with temperature. The value of $\Delta E_Q$ is determined by the local structure at each ion site. Hence, there appear to be large changes in local structure above and below the magnetic ordering temperature.

Between the onset of hyperfine splitting and the base temperature there appears to be a large change in $\Delta E_Q$ at the Fe$^{III}$ ion sites in both NBu$_4$FeFe(ox)$_3$ and PPh$_4$FeFe(ox)$_3$. A change in local structure at these temperatures is unusual as thermal effects are minimal. Unfortunately, the broadened hyperfine splitting of the spectra precluded the accurate determination of the temperature dependence of these parameters. In NBu$_4$FeFe(ox)$_3$ the change in $\Delta E_Q$ at the Fe$^{III}$ site (+/-0.678 $\rightarrow$ -0.307 mms$^{-1}$) was estimated (manual fitting) to occur between 42 and 38K, indicating that a drastic local structure change occurred within the magnetic transition.

Table 6.1: Mössbauer fitted parameters for NBu$_4$FeFe(ox)$_3$ and PPh$_4$FeFe(ox)$_3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp (K)</th>
<th>$\delta$ (mms$^{-1}$)</th>
<th>$\Delta E_Q$ (mms$^{-1}$)</th>
<th>$H_{int}$ (T)</th>
<th>Rel. area (fraction)</th>
<th>Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBu$_4$FeFe(ox)$_3$</td>
<td>293</td>
<td>0.34</td>
<td>+/-0.54</td>
<td>-</td>
<td>0.53</td>
<td>Fe$^{III}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.24</td>
<td>+/-0.47</td>
<td>-</td>
<td>0.47</td>
<td>Fe$^{II}$</td>
</tr>
<tr>
<td></td>
<td>42</td>
<td>0.49</td>
<td>+/-0.678</td>
<td>-</td>
<td>-</td>
<td>Fe$^{III}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.31</td>
<td>+/-1.980</td>
<td>-</td>
<td>-</td>
<td>Fe$^{II}$</td>
</tr>
<tr>
<td></td>
<td>1.9</td>
<td>0.51</td>
<td>-0.3</td>
<td>54.6</td>
<td>= 0.6</td>
<td>Fe$^{III}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.41</td>
<td>-2.0</td>
<td>= 5</td>
<td>= 0.4</td>
<td>Fe$^{II}$</td>
</tr>
<tr>
<td>PPh$_4$FeFe(ox)$_3$</td>
<td>293</td>
<td>0.35</td>
<td>+/-0.52</td>
<td>-</td>
<td>0.61</td>
<td>Fe$^{III}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.28</td>
<td>+/-1.07</td>
<td>-</td>
<td>0.39</td>
<td>Fe$^{II}$</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.50</td>
<td>+/-0.72</td>
<td>-</td>
<td>-</td>
<td>Fe$^{III}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.32</td>
<td>+/-1.99</td>
<td>-</td>
<td>-</td>
<td>Fe$^{II}$</td>
</tr>
<tr>
<td></td>
<td>1.9</td>
<td>0.51</td>
<td>-0.3</td>
<td>54.6</td>
<td>= 0.6</td>
<td>Fe$^{III}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.40</td>
<td>-2.0</td>
<td>= 5</td>
<td>= 0.4</td>
<td>Fe$^{II}$</td>
</tr>
</tbody>
</table>

(# $\delta$ relative to $\alpha$Fe)
Figure 6.7: Temperature dependence of the fitted internal field at the Fe$^{\text{III}}$ site in (cation)Fe$^{\text{II}}$Fe$^{\text{III}}$(ox)$_3$. 

![Graph showing temperature dependence of fitted internal field](image)
Figure 6.8: Mössbauer spectra of NBu₄FeFe(ox)₃ between 1.9K and 45K.
Figure 6.9: Mössbauer spectra of PPh₄FeFe(ox)₃ between 1.9K and 60K.
CHAPTER 7

Discussion

The preceding chapters have described the synthesis, structural and magnetic characterisation of the two dimensional honeycomb oxalate compounds (cation)\(M^{III}Fe^{III}(ox)_3\), with \(M^{II} = \text{Fe and Mn}\). For each system the extent to which the templating cation determines both the crystal chemistry and the magnetic properties has been investigated by varying the cation. The magnetic characterisation of the compounds has been the focus of the work and a number of complementary magnetic measurements have been made on powder samples of the compounds. In this chapter we shall discuss the information gained on the magnetic ordering from each technique. This is particularly necessary for the (cation)\(FeFe(ox)_3\) system where the remarkable change in magnetic behaviour with cation deserves special discussion. In this respect possible mechanisms of magnetic ordering in (cation)\(FeFe(ox)_3\) will be described.

The object of this chapter is to provide a summary of the crystal chemistry discerned from the diffraction measurements reported in Chapter 4 (§7.1) and then to discuss the implications for the magnetic behaviour of the measurements made in Chapters 5 and 6 (§7.2).

7.1 Structural considerations

Considering the connectivity and topology of the metal \(tris\)-oxalate (\(D_3\)) unit two possible connecting modes can be envisaged to give infinite extended lattices of stoichiometry (cation)[\(M'M(ox)_3\)]. Firstly a three-dimensional lattice is built by connecting \(D_3\) \(M(ox)_3\) units of a single configuration and secondly a two-dimensional honeycomb layer lattice is propagated by enforcing an alternation of configurations. Previously, both structural types have been realised by altering the shape and charge of the templating cation\(^{28,29,26,68,25}\). The three dimensional lattice is realised with cations such as \(Fe(bipy)_3^{2+}\) whilst the honeycomb layer lattice has been found to be stable with mono positive quaternary cations.

In this study the templating cation has been restricted to quaternary Group V cations of both alkyl and phenyl type. Powder X-ray diffraction verified that the
resulting (cation)M^{II}\text{Fe(ox)}_3 | complications all crystallise in the honeycomb lattice type.
The cation variation has therefore probed the stability of formation of the honeycomb
lattice with respect to the templating cation. For example, crystallisation was only
successful with an alkyl chain length, n, between n = 3 and n = 5.

The room temperature X-ray data reveals that the cation plays a dominant role in
determining the unit cell parameters. The patterns were indexed on a reduced symmetry
P6(5) cell and the refined cell parameters indicated that the inter-layer separation varied
between 8Å and 14.5Å, depending on the cation. A linear correlation (Figure 4.5(a)) is
found between inter-planar separations for analogous MnFe and FeFe compounds.

The change in the intra-planar cell a parameter with cation gives an indication of
the flexibility of the oxalate lattice; in the present series a variation in a at room
temperature of between 9.32Å and 9.71Å occurred and a linear correlation in a
between analogous MnFe and FeFe compounds (see Figure 4.5(b)) was observed. The
average increase in a of 0.077Å between similar MnFe and FeFe compounds can be
explained by the different ionic radii in Mn^{2+} and Fe^{2+} ions (respectively 0.82Å and
0.77Å). The apparent in-plane flexibility of the honeycomb lattice may be due to the
ease of trigonal distortions in metal tris(bidentate) complexes\textsuperscript{69}.

Compounds (cation)M'M(ox)_3 | with the honeycomb lattice have been found to
crystallise in a number of different structures. By compariing their powder X-ray
profiles with these structural models it has proved possible to determine which
compounds adopt which structure. For example, the profiles of Npent\textsubscript{4}M^{II}\text{Fe(ox)}_3 \{M^{II}
= Mn, Fe\} showed that bulk polycrystalline samples of both compounds adopt the
orthorhombic C222(1) cell with crystal structures very similar to that identified by a
120K single crystal structure determination of Npent\textsubscript{4}MnFe(ox)_3\textsuperscript{32}.

Using the Npent\textsubscript{4}MnFe(ox)_3 structural solution as model for Rietveld
refinement highlights the limitations of the powder patterns for structural interpretation.
In particular, the highly anisotropic peak shape at low two-theta angles and the inability
of standard Rietveld packages to provide accurate descriptions of the dependence of
peak shape on angle, precludes detailed structural refinement. Further complications
arise from the possibility of preferred orientation in the samples.

Nevertheless, the X-ray data provided information that the inorganic array in
Npent\textsubscript{4}M^{II}\text{Fe(ox)}_3 crystallises with a two layer repeat of type [a-b']\textsuperscript{#} with eclipsed
honeycomb layer vacancies and also that the orthorhombic distortion to the hexagonal
oxalate array is still apparent at room temperature with b/a \neq \sqrt{3} in both the MnFe and
FeFe compounds.

\textsuperscript{#} (where \textsuperscript{*} represents a change in relative configuration of M(ox)_3)
Structural effects have complicated the situation further in compounds with cations NPr$_4$, NBu$_4$ and PBu$_4$. There are two published hexagonal structures for this set of compounds: the $R3c$ NBu$_4$MnCr(ox)$_3$ structure$^{27}$ and the $P6(3)$ NBu$_4$MnFe(ox)$_3$ structure$^{33}$. These two closely related structures differ in the relative stacking of the [M'M(ox)$_3$] anionic layers. In the $R3c$ structure the 6-layer stacking sequence can be described as [a-b'-c-a'-b-c'] whilst in $P6(3)$ we have the two layer repeat sequence [a-b]. Comparison of the measured X-ray profiles with those calculated for the two structures (with the slight adjustments detailed in §4.3.3) reveal that the powder samples contain both phases in varying amounts. It has not proved possible to prepare single phase samples of the compounds; however, it was noted that increasing the formation rate favours the $P6(3)$ phase. It is likely that both phases are of very similar stability and, furthermore, the competing by-product phase $\text{M}^{\text{II}}(\text{ox}).2\text{H}_2\text{O}$ is found in the limit of long precipitation times (§4.1). Refining the unit cell, assuming a single phase of reduced symmetry is therefore not strictly correct; however, its success in refining all indexed peaks indicates that the phases must have very similar unit cells, i.e. $a(R3c) = a(P6(3))$ and $c(R3c) = 3c(P6(3))$.

The possibility of stacking faults in the mixed phase compounds was investigated using the DIFFaX program, allowing the stacking sequence of [M$^{\text{II}}$Fe(ox)$_3$] layers to vary between those which generate the $R3c$ and $P6(3)$ structures. Simulated profiles for NPr$_4$MnFe(ox)$_3$ with a relatively high faulting probability of between 20% to 30% exhibited peak broadening similar to that observed in the experimental X-ray profile, providing strong indication that stacking faults do occur in these compounds.

X-ray powder diffraction profiles of the compounds formed with PPh$_4$ and AsPh$_4$ cations were compared to the structural model of the $R3c$ PPh$_4$MnCr(ox)$_3$ (with suitable adaptations §4.3.4). This 6-layered structure provided quite a good representation of the powder diffraction profiles, although interpretations are again limited by data quality. In the PPh$_4$MnFe(ox)$_3$ profile there was some indication of a $P6(3)$ phase. Greater evidence of a $P6(3)$ phase was apparent in AsPh$_4$ compounds.

The $R3c$ PPh$_4$MnCr(ox)$_3$ structure is distinct from the $R3c$ NBu$_4$MnCr(ox)$_3$ structure as the unit cell is doubled in the basal plane. This is caused by a slight distortion from an ideal hexagonal array in the [M$^{\text{II}}$Cr(ox)$_3$] anionic layer (§1.3). In the PPh$_4$FeFe(ox)$_3$ profile (the best one obtained in this series of compounds) there are, in fact, no satellite reflections attributable to the doubled cell. This is not surprising as the maximum intensity expected from a satellite reflection is only 0.5% of the most intense reflection. The same argument applies to the neutron data obtained from PPh$_4$(-d$_{20}$) compounds and therefore there is no proof that PPh$_4$M$^{\text{II}}$Fe(ox)$_3$ or AsPh$_4$M$^{\text{II}}$Fe(ox)$_3$ compounds exhibit a similar structural distortion to PPh$_4$MnCr(ox)$_3$. However, we can
be certain that the structures are similar in both the stacking of \([\text{M}^{II}\text{Cr(ox)}_3]\) layers and in the \(\text{PPh}_4^+\) positioning, with one phenyl group penetrating the honeycomb layer vacancy.

The powder X-ray diffraction profiles of \((\text{PPN})\text{MHpe(ox)}_3\) compounds have been indexed on a hexagonal \(P6(5)\) cell as described, however, no suitable model for these compounds is available or could be generated. Indeed the PPN cation \([\text{P}(\text{C}_6\text{H}_5)^3=\text{N}=\text{P}(\text{C}_6\text{H}_5)]^+\) has only pseudo-\(C_2\) symmetry, so a hexagonal cell is only compatible with considerable disorder of the cation. There may also be different stacking sequences. Considering the inter-layer separation of 14.5\(\text{Å}\) extracted from the data and the approximate dimensions of PPN (9.5\(\text{Å}\) along the P-N-P plane compared with 7.5\(\text{Å}\) across the PPh\(_3\) base) it seems likely that PPN is in a standing orientation with P-N-P plane aligned near to the \(c\)-axis, perpendicular to the layer.

### 7.2 Interpretation of the magnetic behaviour

#### 7.2.1 \((\text{cation})\text{Fe}^{II}\text{Fe}^{III}(\text{ox})_3\)

(i) **High temperature magnetic behaviour**

The susceptibilities of FeFe compounds, in 100G applied field, obey the Curie-Weiss law closely in the temperature range from 150 to 300\(K\). The mean fitted Curie constant \((C)\) of \(C = 7.662\text{cm}^3\text{mol}^{-1}\text{K}\) for the FeFe compounds is consistent with the presence of high spin Fe\(^{III}\) and Fe\(^{II}\) ions in the lattice: assuming spin-only moments \(S(\text{Fe}^{III}) = 5/2\) and \(S(\text{Fe}^{II}) = 2\) and an isotropic Landé splitting factor, \(g = 2\), for both ions, the calculated \(C = 7.375\text{cm}^3\text{mol}^{-1}\text{K}\).

The Curie constants for the compounds can be correlated with the variation in their Fe analyses (Table 4.1(a)). Where we have an Fe analysis within 2% of the calculated value (i.e. at the limit of analytical accuracy) the fitted Curie constant is above the spin-only value. However, for the FeFe compounds with PPh\(_4\) (\(C = 6.7(1)\text{cm}^3\text{mol}^{-1}\text{K}\)) and AsPh\(_4\) (\(C = 6.4(1)\text{cm}^3\text{mol}^{-1}\text{K}\)) cations the Fe content was deficient, at 92% and 82% of the calculated values. Charge neutralisation in the Fe deficient lattice could occur by a partial oxidation of ions \(\text{Fe}^{II}\rightarrow\text{Fe}^{III}\). In the case of the PPh\(_4\) compound this would correspond to a nominal stoichiometry of \(\text{PPh}_4\{[(\text{Fe}^{III})_{1.2}\text{(Fe}^{II})_{0.8}]_{0.93}(\text{ox})_3\}\) giving a spin-only Curie constant of \(C = 7.08\text{cm}^3\text{mol}^{-1}\text{K}\). The high temperature Mössbauer spectra of PPh\(_4\)FeFe(ox)_3 confirm the postulated Fe oxidation state ratio in
the compound. The fitted area of the quadrupolar doublets attributed to each ion yielded a \( \{\text{Fe}^{\text{III}}:\text{Fe}^{\text{II}}\} \) ratio of \( \{60:40\} \). In \( \text{NBu}_4\text{FeFe(ox)}_3 \) the Mössbauer data are consistent with an almost equal proportion, \( \{53:47\} \), of \( \text{Fe}^{\text{II}} \) and \( \text{Fe}^{\text{III}} \) ions whilst the analysis and Curie constant are consistent without a \( \text{Fe} \) deficiency.

The assumption of spin-only moments in the above interpretation, whilst a good approximation to the \( ^5\text{A}_1 \) ground state of the \( \text{Fe}^{\text{III}} \) ion, is a poor approximation for \( \text{Fe}^{\text{II}} \) ions. The \( ^5\text{D} \) (\( L = 2 \)) free-ion state of \( \text{Fe}^{\text{II}}(d^6) \) ions has orbital degeneracy and in a cubic ligand field the \( ^5\text{T}_{2g} \) ground term still manifests an orbital contribution to the total moment (\( L = 1 \)). With the introduction of a trigonal distortion the ground state is split both by the distortion and spin-orbit coupling. The resulting ground state may either be a singlet (\( M_J = 0 \)) or doublet (\( M_J = \pm 1 \))\(^70\). The energy separation between the spin-orbit components in \( \text{Fe}^{\text{II}} \) is the order of 200 cm\(^{-1}\) so an orbital contribution to the \( \text{Fe}^{\text{II}} \) moment is expected. The \( \text{Fe}^{\text{II}} \) ground state can be investigated with Electron Paramagnetic Resonance or inelastic neutron diffraction experiments; however, this thesis does not present such data. The slightly high value of the Curie constants in the non-Fe deficient compounds could, therefore, be the result of a non-zero orbital moment on the \( \text{Fe}^{\text{II}} \) ion. The Curie constants of \( \text{NPr}_4 \) (7.79(13)), \( \text{NBu}_4 \) (7.88(1)) and \( \text{PBU}_4 \) (7.758(10)) \( \text{FeFe} \) compounds are all in excess of the spin-only value by approximately 0.43 cm\(^2\)Gmol\(^{-1}\); however, for the \( \text{Npent}_4\text{FeFe(ox)}_3 \) we have \( C = 9.05 \text{ cm}^2\text{Gmol}^{-1} \) corresponding to an excess of approximately 1.6 cm\(^2\)Gmol\(^{-1}\). This might be the result of a differing crystallographic symmetry environment of the \( \text{Fe}^{\text{II}} \) sites; for \( \text{NPr}_4 \), \( \text{NBu}_4 \) and \( \text{PBU}_4 \) the powder patterns were modelled by hexagonal cells with \( C_3 \) site symmetry of the \( \text{Fe}^{\text{II}}(\text{ox})_3 \) unit, while for \( \text{Npent}_4 \) the model structure has a \( C_2 \) site symmetry of \( \text{Fe}^{\text{II}}(\text{ox})_3 \). This can only be conjectured as we do not have detailed structural refinements.

The Curie-Weiss \( \theta \) values are large and negative for all \( \text{FeFe} \) compounds, indicating a mean antiferromagnetic interaction between \( \text{Fe} \) moments in the compounds. The dominant magnetic interaction in the honeycomb lattice is expected to be between nearest neighbours, separated by a single oxalate group (separation \( = 5.5\AA \)). Assuming that \( \theta \) is proportional to the nearest neighbour exchange constant (\( J_1 \)) the small spread in \( \theta \) values of between \(-86.9\)K and \(-92.2\)K (mean \( \theta(\text{FeFe}) = 89\)K) indicates that the magnetic exchange is of similar strength for all \( \text{FeFe} \) compounds.

The ratio \( |T_c/\theta| \) (using the apparent \( T_c \) from DC low field measurements \( \S 4.1 \)) makes an interesting comparison; the \( \text{NPr}_4 \), \( \text{NBu}_4 \), \( \text{Npent}_4 \), \( \text{PBU}_4 \) and \( \text{PPN} \) \( \text{FeFe} \) compounds have \( |T_c/\theta| = 0.5 \) whilst for \( \text{PPh}_4 \) and \( \text{AsPh}_4 \) \( |T_c/\theta| = 0.4 \). Molecular field theory predicts \( |T_c/\theta| = 1 \), however, large deviations from molecular field theory are expected in low dimensional magnets because of the build up in short range correlations above \( T_c \) (\( \S 2.4.3 \)). Indeed \( |T_c/\theta| \) has been calculated for a ferromagnetic two-
dimensional Ising honeycomb lattice as $|T_c/\theta| = 0.506^{38}$. The reduction in $|T_c/\theta|$ in PPh$_4$ and AsPh$_4$ compounds, with apparently similar $J_1$ exchange, must therefore result from a reduction of the average number of magnetic nearest neighbours, $z$. Molecular field theory yields $T_c \propto zJ$ (§2.4.2), thus, the average reduction in $|T_c/\theta|$ in PPh$_4$ and AsPh$_4$ compounds resulting from the Fe deficiency is expected to be $|T_c/\theta| \approx 0.5 \times (0.873) \approx 0.44$.

In the previously reported study$^{71}$ of (cation)Fe$^{II}$Fe$^{III}$(ox)$_3$ compounds all compounds exhibited analyses with Fe deficiencies of between 8-20%. The improved synthesis detailed in Chapter 4 has clarified the analytical results so that the above correlations between the observed Fe deficiencies and the magnetic data are possible. Also the fitting of the paramagnetic susceptibilities has improved in accuracy because: (i) measurements were completed after remanent field calibration +/-0.05G and (ii) the sample holder (§3.2) did not contribute to the measured susceptibility. These factors are responsible for the differences between the measurements reported in this thesis and those reported previously.

(ii) Low temperature magnetic behaviour

Below 100K the magnetisation behaviours of the FeFe series below 100K differ profoundly depending on the cation. When measuring the magnetisation after cooling in a 100G field a magnetic compensation point ($T_{comp}$) and low temperature negative magnetisation, with respect to the field, is observed in the NPr$_4$, NBu$_4$, Npent$_4$, PBu$_4$ and PPN compounds whilst for PPh$_4$ and AsPh$_4$ compounds a positive magnetisation is found at low temperature. Since the compounds can be described as nominally ferrimagnetic with Fe$^{III}$ and Fe$^{II}$ ions propagating an antiferromagnetic exchange (negative $\theta$) throughout the lattice, it is useful to compare the magnetisation curves with those predicted classically, by Néel (§2.4.2). By inspection, the 'normal' positive magnetisation curves of PPh$_4$ and AsPh$_4$ compounds resemble a Néel type Q ferrimagnetic order whilst the negative magnetisation curves apparently exhibit a variant of Néel type N order.

The Néel ground state of a ferrimagnet is determined by both the saturation magnetisations ($M_s(T = 0K)$) and the relative ordering rates, with temperature, of each magnetic sublattice (as described in §2.4.2). A compensation temperature ($T_{comp}$) in the magnetisation is expected if the sublattice with the smaller saturation magnetisation orders initially at a higher rate, with temperature, than the sublattice with the larger
saturation magnetisation. If we return to the honeycomb oxalate lattice in (cation)Fe\textsuperscript{II}Fe\textsuperscript{III}(ox)\textsubscript{3} with alternating Fe\textsuperscript{II} and Fe\textsuperscript{III} ions and consider spin-only moments, this situation corresponds to an initially faster ordering rate in the Fe\textsuperscript{II} ion sublattice to achieve a compensation point. This is drawn schematically in Figure 7.1.

![Diagram of magnetic sublattice ordering](image)

**Figure 7.1:** The relative magnetic sublattice ordering in the ferrimagnet (cation)Fe\textsuperscript{II}Fe\textsuperscript{III}(ox)\textsubscript{3} required for a compensation point (type N Néel order).

Evidence concerning the sublattice ordering rates in the FeFe compounds comes from the Mössbauer data collected on NBu\textsubscript{4} and PPh\textsubscript{4} compounds (§6.2), where the hyperfine field at the Fe\textsuperscript{III} nucleus as a function of temperature was successfully extracted for both compounds (see Figures 6.8 and 6.9). Continuing within the molecular field approximation, the molecular field experienced at the Fe\textsuperscript{III} nucleus is the sum of exchange fields acting on the Fe\textsuperscript{III} ion. To a first approximation this is only from the neighbouring Fe\textsuperscript{II} sublattice. Hence, the development of hyperfine field at Fe\textsuperscript{III} nucleus provides a measure of the magnetisation of the Fe\textsuperscript{II} sublattice and vice versa. Thus the Mössbauer data indicate that there is an onset and sharp increase in the Fe\textsuperscript{II} sublattice magnetisation in the NBu\textsubscript{4} compound below 40K. Unfortunately, the
temperature dependence of the Fe$^{II}$ hyperfine field could not be extracted from the data; however, there was some indication that it was not fully developed ($H_{\text{int}} \approx 5T$ at 1.9K). Clearly, therefore, we have some evidence that the Fe$^{II}$ sublattice does order at a faster rate than Fe$^{III}$ in NBu$_4$FeFe(ox)$_3$. The situation in PPh$_4$ is more complex, with the occurrence of a hyperfine splitting at the Fe$^{III}$ nucleus occurring only below 25K. Similarly in PPh$_4$, the Fe$^{II}$ hyperfine splitting is not clearly resolved as a function of temperature.

The molecular field argument predicts that the magnetic saturation at 0K for a two-sublattice ferrimagnet is simply the difference between the saturation magnetisations on each sublattice which in the magnetic order types N and Q are both fully saturated (§2.4.2). Therefore, in the hypothetical spin-only Fe$^{II}$Fe$^{III}$ case the saturation moment at 0K would be $M_s(0K) = +/\mp g\mu_B(S(Fe^{III}) - S(Fe^{II})) = +/\mp 1\mu_B$ (i.e. 1-spin per Fe$^{II}$Fe$^{III}$ unit) for repsectively type Q and type N ferrimagnetic order. In the 100G FC magnetisation curves of the FeFe series $\partial M/\partial T \rightarrow 0$ at the lowest measured temperature so we can make the approximation that $M_s(2K$ or 5K $) = M_s(0K)$. The negative magnetisation compounds exhibited a variation in saturation at 5K (after 100G FC) of between -$235 cm^3 G mol^{-1}$ (PPN) and -$850 cm^3 G mol^{-1}$ (NPent$_4$) which corresponds to moments of between 0.0422$\mu_B$ and 0.1522$\mu_B$. In the compounds with positive magnetisation the (100G FC) saturation moment was 0.0435$\mu_B$ and 0.052$\mu_B$ for PPh$_4$ and AsPh$_4$ respectively. Thus the observed uncompensated moment throughout the FeFe series is an order of magnitude weaker than that predicted by molecular field theory. However, in real powder samples the actual measured saturation is affected by crystallite orientations, non-crystallinity and/or domain effects which all contribute to a reduction in the measured saturation. However, we note that in NBu$_4$FeFe(ox)$_3$ a saturation $\sim 0.07 \mu_B$ at 5K was reached after cooling in fields between 2G and 5000G.

A quantitative treatment of the molecular field approach, to extract molecular field parameters and construct a Néel plot similar to Figure 2.2, is not appropriate in the (cation)Fe$^{II}$Fe$^{III}$(ox)$_3$ series for a variety of reasons: (i) the honeycomb lattice is approximately a two-dimensional magnetic system which deviates considerably from the molecular field approximation; $|\theta|/\theta < 0.5$; (ii) the Fe$^{II}$ ion exhibits an orbital moment and hence it is likely that its magnetisation curve does not follow a Brillouin function, and also (iii) it is likely that the spin-orbit coupling in Fe$^{II}$ introduces considerable anisotropy into the system that is not accounted for by the molecular field model.

Figure 7.1 illustrates two possible forms for the temperature evolution of magnetisation in Néel type N ferrimagnets. In case (i) the magnetisation curve bounces, with magnetic pole reversal {Fe$^{II}(\uparrow)$Fe$^{III}(\downarrow) \rightarrow Fe^{II}(\downarrow)Fe^{III}(\uparrow)$} at $T_{\text{comp}}$ resulting in
positive magnetisation at low temperature whilst in case (ii) the initial magnetic pole direction is maintained and the magnetisation becomes negative below $T_{\text{comp}}$. In $(\text{cation})\text{Fe}^{II}\text{Fe}^{III}(\text{ox})_3$ we have already identified the case (ii) variant. It is interesting to consider the stability of both possible magnetisation curves. Thermodynamically, a low temperature positive magnetisation is favoured over the development of negative magnetisation. In the molecular field approximation with fully isotropic exchange fields there is no energy barrier to magnetic pole reversal and magnetisation behaviour similar to case (i) results. In $(\text{cation})\text{Fe}^{II}\text{Fe}^{III}(\text{ox})_3$, the fact that the magnetisation curve is similar to case (ii) indicates that a barrier, sufficient to hinder pole reversal, exists at the compensation temperature. This can be characterised as an anisotropy in the magnetisation.

The magnetic hysteresis loops recorded on $\text{NBu}_4\text{FeFe(ox)}_3$ provide information on the anisotropy behaviour and stability of the negative magnetisation in this compound. Typically, at low temperature we might expect that negative magnetisation will be unstable to alignment with field above a characteristic anisotropy field $H_a$. However, in $\text{NBu}_4\text{FeFe(ox)}_3$ the hysteresis curve at 5K did not exhibit a magnetic transition or coercive field ($H_c$) during field cycling between +/-70,000G but rather remained centred about the negative remanance, exhibiting a magnetic memory effect. The type of hysteresis curve and absence of a coercive field $\leq$70,000G indicates that there is a giant anisotropy in the magnetisation in $\text{NBu}_4\text{FeFe(ox)}_3$ at 5K (discussed in §5.2.1(b)). The memory effect was confirmed locally and dynamically in the MuSR repolarisation experiment cycling the field between +/-4000G (described in §6.1).

The temperature dependent investigation of the hysteresis behaviour in $\text{NBu}_4\text{FeFe(ox)}_3$ revealed that the onset of giant anisotropy ($H_c > 10,000$G) and the magnetic memory effect were coincident, occurring between 36K and 38K. The temperature dependent properties of the hysteresis in $\text{NBu}_4\text{FeFe(ox)}_3$ are plotted in Figure 7.2. The divergence in coercivity is clearly correlated with a magnetostriction (narrowing) of the hysteresis curve. The hysteresis in $\text{NBu}_4\text{FeFe(ox)}_3$ has been extrapolated to its apparent onset at 43.5K, confirmed by the branching of ZFC and FC magnetisation curves at this temperature. The sharp peak in the AC susceptibility also observed at 43.5K indicates that this is a better estimate of $T_c$ than that identified in the DC measurements.

In a ferrimagnet a divergence in the coercivity and an associated striction of the hysteresis curve are expected when approaching a compensation temperature in both cooling and warming regimes. This can be seen simply by considering that $M_s(T = T_{\text{comp}}) = 0$. Whilst a closure of the hysteresis loop in $\text{NBu}_4\text{FeFe(ox)}_3$ is observed at $T_{\text{comp}}$ (see Figure 5.9(b)), the pronounced change in magnetic characteristics occurring...
between 36K and 38K indicates that some form of magnetostriction transition is occurring at a temperature below $T_c$ and yet above $T_{comp}$.

![Diagram showing hysteresis properties](image)

**Figure 7.2:** The temperature dependent hysteresis properties of NBu$_4$FeFe(ox)$_3$.

Evidence of a magnetic transition in NBu$_4$FeFe(ox)$_3$ occurring between $T_c$ and $T_{comp}$ was found in the more careful low field measurements. The secondary shoulder at 40K observed in the ZF cooled magnetisation in NBu$_4$FeFe(ox)$_3$ was revealed to be an apparent 1st order discontinuity at $T = 40.0$K in the 100G FC magnetisation. Similar discontinuities in the FC magnetisation were observed in all FeFe compounds that exhibited low temperature negative magnetisations. The field cooling history through $T_I$ and not $T_c$ was found to be critical in determining the low temperature negative magnetisation in NBu$_4$FeFe(ox)$_3$ (see Figure 5.6).

Reversal of the low temperature negative magnetisation in NBu$_4$FeFe(ox)$_3$ was achieved only after cooling the compound through $T_c$ and $T_I$ in large applied fields ($\geq 60,000$G). The properties of the resulting low temperature positive magnetisation were confirmed to be identical to that after 100G FC by: (i) a temperature evolution of magnetisation almost the inverse to that of the 100G FC curve below $T_I$ and (ii) a
hysteresis loop at 5K similar in form to the 100G FC loop, asymmetrically displaced to positive magnetisation.

The first order jump in the magnetisation at $T_t$ is clearly critical in determining the low temperature magnetisation properties of (cation)Fe$^{II}$Fe$^{III}$(ox)$_3$ compounds with negative magnetisation. However, the physical origin of the transition has not been identified. One possibility is that at $T_t$ there is a locking in of Fe$^{II}$ ion moments in the compound or an orbital ordering. If we have such a case, then cooling through $T_t$ in small applied fields would provide the Fe$^{II}$ moments with a preferred ordering direction. Provided the ferrimagnet has a sublattice ordering similar to the Néel type N order the magnetisation will become negative at low temperatures. The anisotropy below a magneto-strictive orbital ordering of Fe$^{II}$ moments at $T_t$ would be expected to be giant as is observed in NBu$_4$FeFe(ox)$_3$. A structural phase transition at $T_t$ would also occur as the Fe$^{II}$ moments couple to the lattice; however, in this thesis we do not present low temperature structure studies on (cation)Fe$^{II}$Fe$^{III}$(ox)$_3$ compounds with low temperature negative magnetisation. The 1st order jump in the magnetisation is only an indication that a phase transition is occurring. Similarly, the change in the Mössbauer quadrupolar splitting of the Fe$^{III}$ nucleus below 40K is also indicative that a structural transition occurs.

Orbital ordering transitions ($T_t < T_c$) occur when unquenched orbital moments align co-operatively below a magnetic ordering transition as a consequence of the spin-orbit coupling interaction. The theory has been developed by Goodenough$^{73}$ and has been used to explain the negative magnetisation and anisotropy behaviour in the ferrimagnetic spinel Co[CoV]O$_4$$^{74}$ and in the antiferromagnet LaVO$_3$$^{75,76}$.

Returning to the magnetisation behaviour in PPh$_4$ and AsPh$_4$ compounds which were assigned to Néel type Q ferrimagnetic order, the question remaining is why there is such a large change between the low temperature magnetic behaviour in these compounds and those with low temperature negative magnetisation. We now examine more closely the magnetic information collected on the PPh$_4$ compound and contrast it with the negative NBu$_4$ case.

The transition temperature to long-range magnetic order in PPh$_4$ is less distinct than in NBu$_4$. The increase in DC magnetisation in PPh$_4$ occurs at 34K, which we nominally assigned as the critical temperature $T_c$. However, in the AC measurements there was no sharp ordering peak in either the dispersion or absorption down to low temperature. Moreover, a complex AC susceptibility curve was observed with considerable frequency dependence of the broad maximum at ~22-18K. The ZF-MuSR measurements in the PPh$_4$ compound did not show a divergence in relaxation rates down to low temperature and the high temperature form of the depolarisation was maintained down to 4.5K. Similarly hysteresis and Mössbauer hyperfine splitting were
observed in the PPh₄ compound only below 25 K, approximately the ZFC DC peak temperature. This behaviour contrasts with NBu₄ where AC susceptibility, ZF-MuSR, Mössbauer, and hysteresis measurements all gave evidence of a sharp magnetic transition within the temperature region between 43.5 and 40 K. The temperature dependent hysteresis characteristics of PPh₄FeFe(ox)₃ are shown in Figure 7.3. They should be contrasted with those of NBu₄FeFe(ox)₃ in Figure 7.2.

![Figure 7.3: The temperature dependent hysteresis properties of PPh₄FeFe(ox)₃.](image)

The neutron diffraction study of PPh₄(-d₂₀)FeFe(ox)₃ (§4.4.2) revealed weak asymmetric magnetic scattering intensity below 38 K at the [201] reciprocal lattice point which was attributed to moments ordering parallel to the c-axis. Although coherent magnetic scattering is evidence of long-range magnetic order the weak scattering in PPh₄(-d₂₀)FeFe(ox)₃, in comparison to PPh₄(-d₂₀)MnFe(ox)₃ (the integrated magnetic intensity [201]M for the FeFe compound scaled to the largest nuclear reflection is ~7% compared to ~25% in the MnFe compound), is an indication that the magnetic order is not fully developed in the former, even at 5 K. This can be the result of either a finite
spin correlation length or that only parts of the sample undergo a transition to long-range magnetic order.

A further clue to the extent of magnetic order at low temperatures in the FeFe series can be gained by the temperature dependence of the initial asymmetries of the ZF-MuSR spectra. In PPh₄FeFe(ox)₃ the low temperature asymmetry is 70% of the high temperature value whilst in NBu₄FeFe(ox)₃ only 46% is retained. Theoretically we reason that a drop to 33% is expected with the transition to long-range magnetic order throughout the sample. Therefore there is some evidence that PPh₄FeFe(ox)₃ is not fully ordered down to low temperatures.

Considering these comparisons, one possible view of the magnetic order in PPh₄FeFe(ox)₃ is that only a glassy type magnetic order develops. Below 34K correlated ferrimagnetic regions of the sample begin to develop with random anisotropy. At around 22-25K the correlated regions become blocked by one another and hysteresis develops. Below the blocking temperature the bulk of the moments are fixed by anisotropy pinning; however, a percentage remain mobile down to 5K.

The reasons for such glassy type magnetic ordering in PPh₄FeFe(ox)₃ could lie in the Fe deficiency and the postulated charge compensating oxidation process FeⅡ→FeⅢ which introduces a considerable amount of disorder in the magnetic sublattices. Such disorder may produce random anisotropies in the FeⅡ moments. Hence, ferrimagnetically correlated regions of random anisotropy will develop, pinned to the FeⅡ moments. When the correlated regions of different anistropy, interact magnetic frustration and consequent glassy ordering would occur.

7.2.2 (cation)MnⅡFeⅢ(ox)₃

(i) High temperature magnetic behaviour

The high temperature susceptibility behaviour of MnFe compounds (100G FC) obey the Curie-Weiss law closely between 150 and 300K. The mean fitted Curie constant (C) for the MnFe compounds of C = 8.50 cm³ mol⁻¹ K⁻¹ is consistent with the presence of high spin FeⅢ and MnⅡ ions in the lattice; assuming spin-only moments S(FeⅢ) = 5/2 and S(MnⅡ) = 5/2, and an isotropic Landé splitting factor, g = 2, for both ions, yields C = 8.75 cm³ mol⁻¹ K⁻¹. In a cubic field the approximation of spin-only moments is valid for both FeⅢ and MnⅡ ions as both have an 6A₁g ground state.

The variation of the fitted Curie constants for the MnFe series can be correlated with the Mn and Fe analyses of the compounds. The correlation is less exact than in the
FeFe compounds; however, similarly to the FeFe series, the PPh₄ and AsPh₄ compounds have significantly greater metal deficiencies and lower Curie constants than the rest. For example, in PPh₄MnFe(ox)₃ the average metal deficiency of 85% would cause a reduction in the spin-only Curie constant \( C = (0.85) \times (8.750) = 7.438 \text{cm}^3\text{Gmol}^{-1} \) which compares favourably with the fitted Curie constant of \( C = 7.27 \text{cm}^3\text{Gmol}^{-1} \).

The fitted Curie-Weiss \( \theta \) values for all MnFe compounds are large and negative indicating a mean antiferromagnetic interaction between Fe³⁺ and Mn²⁺ moments. The small spread in \( \theta \) values between -111(12)K and -103(5)K (mean \( \theta(\text{MnFe}) = -105.6 \text{K} \)) indicates that the nearest neighbour exchange \( (J_1) \) is of similar magnitude for all compounds. The mean \( \theta \) for the MnFe series is larger than in the FeFe series by a factor \( [\theta(\text{MnFe})/\theta(\text{FeFe})] = 1.2 \). For classical spins interacting via Heisenberg exchange the magnitude of the interaction scales with \( JS(\text{Mn}^{III})S(\text{Mn}^{II}) \) which, if we assume proportionality with \( \theta \), gives an expected ratio of \( [\theta(\text{MnFe})/\theta(\text{FeFe})] = 1.4 \).

The average \( |\Delta T/\theta| \) for the MnFe series is 0.24 which contrasts with \(-0.5\) for the FeFe series. The reduction arises from the fact that both Mn²⁺ and Fe³⁺ moments are approximately isotropic and hence the system approximates a two-dimensional Heisenberg antiferromagnet²⁸,⁷⁷ (c.f. in the FeFe series Fe²⁺ is highly anisotropic). The small variation in \( |\Delta T/\theta| \) within the MnFe series of between 0.21 and 0.28 correlates with the experimental metal deficiency in each compound and hence relates to changes in the average number of magnetic neighbours \( (z) \) in each compound.

(ii) Low temperature magnetic behaviour

The magnetisation behaviour below 100K in the MnFe series is characteristic of two-dimensional antiferromagnets. In each compound the 100G FC magnetisation rises into a broad maximum at around 50-55K and then falls monotonically towards lower temperatures. At between 24 and 27K the magnetisation rises sharply, indicating a magnetic ordering transition, and tends towards saturation at the lowest measured temperature. The ZFC magnetisation behaviour, examined in Npent₄MnFe(ox)₃, NBu₄MnFe(ox)₃ and NPr₄MnFe(ox)₃, branched sharply with the 100G FC magnetisation below \( T_c \), with the onset of hysteresis; forming a peak and reaching small magnetisation values at the lowest measured temperature.

A transition to long-range magnetic order was confirmed in the powder neutron diffraction experiments performed on PPh₄(-d₂₀)MnFe(ox)₃ which exhibited magnetic diffraction intensity below 26K. The magnetic order in PPh₄(-d₂₀)MnFe(ox)₃ was
verified to be antiferromagnetic: moments align parallel to the c-axis with Shubnikov magnetic group symmetry $R3c$ (§4.4.1).

The increase in 100G FC magnetisation below $T_c$ in the MnFe series is intriguing with a variation $M_s(T = 5K)$ of between $16cm^3Gmol^{-1}$ ($NPr_4$) and $108cm^3Gmol^{-1}$ (PPN). The low temperature magnetisation is not a Curie-tail as often seen in powder antiferromagnetic samples; confirmed by both the temperature dependence of the magnetisation, apparently approaching a saturation at low temperature, and also by the hysteresis between ZFC and FC magnetisation behaviour. Small ferromagnetic moments may arise in the predominantly antiferromagnetic MnFe compounds from either slightly uncompensating antiferromagnetic sublattices (i.e. the compounds approximate weak ferrimagnets), a slightly non-collinear antiparallel alignment of spins (resulting from single ion anisotropy effects), or from a spin-canting interaction (§2.3.3). The differentiation of these mechanisms is often a difficult process and requires sophisticated techniques e.g. single crystal magnetisation experiments and or high field Mössbauer studies\textsuperscript{78}. Considering the disorder effects identified in the powder samples (both structural and the inherent magnetic disorder from the metal deficiencies) it seems inappropriate to try; however, it should be noted that by far the largest moment is observed in the PPN compound which is also the least structurally characterised compound.

Previously\textsuperscript{32}, a single crystal study of $Npent_4MnFe(ox)_3$ (100G FC) concluded that an uncompensated moment of $8.78\times 10^{-5}{\mu_Bspin}^{-1}$ (correcting for an estimated susceptibility) was aligned parallel to the c-axis of the crystal at 5K. In the powder study of $Npent_4MnFe(ox)_3$ presented here the moment of $16cm^3Gmol^{-1}$ corresponds to $1.43\times 10^{-3}{\mu_Bspin}^{-1}$. The similarity of the magnetic constants ($T_c$, $\theta$ and the ratio $|T_c/\theta|$) throughout the MnFe series indicates that the magnetic order is similar throughout the series, i.e. the antiferromagnetic alignment is perpendicular to the honeycomb layer as in $PPh_4(-d_20)MnFe(ox)_3$. In this case an uncompensated moment parallel to the c-axis in $Npent_4MnFe(ox)_3$ must arise from uncompensated antiparallel sublattices. This would appear to explain that the larger the moment in the powder sample of $Npent_4MnFe(ox)_3$ results from a greater disorder over that in the single crystal.

7.3 Conclusions

The two-dimensional ferrimagnets $\text{(cation)}M^{II}Fe^{III}(ox)_3$ ($M^{II} = Mn$, Fe) have been examined over a wide variation of the templating cation. In all, 14 compounds have been examined structurally and magnetically. The compounds have been found to
crystallise in a number of different structures depending on the cation. A number of compounds were found to be bi-phasic in their bulk polycrystalline form. In these compounds stacking faulting between the two phases was evident. Structural correlations throughout the series were possible by a comparison of the compounds' unit cell.

In the Fe$^{II}$Fe$^{III}$ series some of the compounds exhibit a compensation temperature and a low temperature negative magnetisation. The magnetic order is qualitatively explained by Néel's theory of two-sublattice ferrimagnets. The negative magnetisation is stabilised by a magneto-strictive transition at $T_t = 40.0K$ ($T_{comp} < T_t < T_c$) below which the magnetisation displays a giant anisotropy and a memory effect. This type of behaviour is similar to that observed in the ferrimagnetic spinel Co[CoV]O$_4$ and is probably related to an orbital ordering transition of the orbitally unquenched Fe$^{II}$ moments. In PPh$_4$FeFe(ox)$_3$ and AsPh$_4$FeFe(ox)$_3$ an unusual weak ferrimagnetism is observed at low temperature with considerable glassy-properties; correlating with the Fe deficiency and consequent loss of Fe$^{II}$ in the compounds.

In the Mn$^{II}$Fe$^{III}$ series the magnetic ordering approximates a two-dimensional antiferromagnet. The moments align antiparallel to one another perpendicular to the honeycomb plane. At low temperature the compounds exhibit a small ferromagnetic moment that is cation dependent and appears to be a consequence of non-compensating magnetic sublattices.

The present work reveals and characterises a wide range of magnetic phenonema in the series of compounds (cation)M$^{II}$Fe(ox)$_3$ \{M$^{II}$ = Mn, Fe\}. The apparently cation dependent magnetic properties of each series cannot be unravelled from the disorder evident in each compound. It is clear that in order to achieve this a greater synthetic control of both the structural and magnetic disorder has to be gained. One method would be the production of single crystals of the compounds (which to date has been unsuccessful). Similarly, the production of bulk powder samples without (or with minimal) disorder is essential and remains elusive.
References

18. Figgis, B. N.; Lewis, J. *Progress in Inorganic Chemistry* 1964, 6, 188.


54. Berar; Baldinoozzi *Journal of Applied Crystallography* 1993, 26, 128.
65. Michealis; Soden, V. *Annales* 1885, 229, 298.
66. Dodanov; Medox *Ber.* 1928, 61, 907.


APPENDIX 1

Factors in Rietveld refinements:

\[ R_f = \frac{\sum \sqrt{|I_{hkl}(\text{obs})|} - \sqrt{|I_{hkl}(\text{calc})|}}{\sum \sqrt{|I_{hkl}(\text{obs})|}} \]  
(Structural Factor)

\[ R_B = \frac{\sum |I_{hkl}(\text{obs}) - I_{hkl}(\text{calc})|}{\sum I_{hkl}(\text{obs})} \]  
(Bragg Factor)

The pattern and weighted pattern R-factors are related to the intensity of each step, i, rather than the overall calculated intensity for the Bragg reflections.

\[ R_p = \frac{\sum |y_i(\text{obs}) - y_i(\text{calc})|}{\sum y_i(\text{obs})} \]  
(Pattern Factor)

\[ R_{wp} = \sqrt{\frac{\sum w_i(y_i(\text{obs}) - y_i(\text{calc}))^2}{\sum w_i(y_i(\text{obs}))^2}} \]  
(Weighted Pattern Factor)

A 'goodness of fit' factor, \( \chi \), is defined as,

\[ \chi^2 = \left[ \frac{R_{wp}}{R_e} \right]^2 \]

where \( R_e \) is the expected R-factor,

\[ R_e = \sqrt{\frac{N - P + C}{\sum_i w_i y_i^2(\text{obs})}} \]

\( N \) is the number of data points, \( P \) is the number of refined parameters, \( C \) is the number of constraints giving a value for \( N - P + C \), which defines the number of degrees of freedom.
Figure A2.1: Two phase fits for PBu₄MIIFeIII(ox)₃ powder X-ray profiles; fitting to R3c and P6(3) structural models for (a) PBu₄FeFe(ox)₃ and (b) PBu₄MnFe(ox)₃.
Figure A2.2: Two phase fits for As\textsubscript{4}M\textsuperscript{II}Fe\textsuperscript{III}(ox\textsubscript{3} powder X-ray profiles; fitting to $R3c$ and $P6(3)$ structural models for (a) As\textsubscript{4}FeFe(ox)\textsubscript{3} and (b) As\textsubscript{4}MnFe(ox)\textsubscript{3}. 
APPENDIX 3
Example DIFFaX input file
(with edited structural information)

Instrumental
X-RAY

1.5418 \{input wavelength Å\}

PSEUDO-VOIGT 0.400 -0.109 0.026 0.78
\{peak shape parameters for pseudo-Voigt function u, v, w and \( \eta \)\}

STRUCTURAL
9.416 9.416 8.186 120 \{unit cell size of all layers \( a, b, c \) and \( \beta \)\}

UNKNOWN \{unknown overall symmetry\}

8 \{total number of layers\}

LAYER 1 \{first layer of \( R3c \) structure\}
NONE \{no symmetry given for layer 1 atomic coordinates in \( P1 \)\}
Fe 1 0.33330 0.66670 0.0000 1.0 1.0
Mn 1 0.66670 0.33330 0.0000 1.0 1.0 \{atom, No., x,y,z, occ., therm.\}
(cut)...........

Layer 2
NONE
Mn 1 0.0000 0.0000 0.0000 1.0 1.0
Fe 1 0.6667 0.3333 0.0000 1.0 1.0
(cut)...........

LAYER 3 = 1 \{layer 3 is equivalent to layer 1\}
LAYER 4 = 2
LAYER 5 = 1
LAYER 6 = 2 \{layer 6 of \( R3c \) structure\}
Layer 7

{first layer of P6(3) structure}

NONE

Fe 1 0.66670 0.33330 0.00000 1.0 1.0
Mn 1 0.00000 0.00000 0.00000 1.0 1.0

(cut)...........

{atomic coordinates of layer 1 of P6(3) structure in P1}.....................

Layer 8

{second layer of P6(3) structure}

NONE

Fe 1 0.33330 0.66670 0.0000 1.0 1.0
Mn 1 0.00000 0.00000 0.0000 1.0 1.0

(cut)...........

{atomic coordinates of layer 2 of P6(3) structure in P1}.....................

STACKING

recursive

{layer stacking is recursive}

infinite

(infinite layer arrays)

TRANSITIONS

{transition vectors (R_ij) and probabilities follows (alpha_ij)}

{1}

{layer 1 vectors (R_ij) and probabilities (alpha_ij)}

0.000 0 0 1  {alpha_11 = 0 (format is alpha_ij then R_ij with unit cell scaling)}
0.800 0 0 1  {alpha_12 = 0.80 transition to second layer in R3c}

0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.200 0 0 1  {alpha_17 = 0.20 (faulting transition to 1st layer in P6(3))}
0.000 0 0 1

{2}

0.000 0 0 1
0.000 0 0 1
1.000 0.66667 0.33333 1  {alpha_23 = 1 transition from layer 2 to layer 3 layer in R3c}
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1

{3}
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
1.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1

{4}
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
1.000 -0.33333 0.33333 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1

{5}
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
1.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1

{6}
1.000 -0.33333 -0.66667 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1

{7}
0.000 0 0 1
0.000 0 0 1
0.200 0.66667 0.33333 1 \{ \alpha_{73} = 0.20 \text{ (faulting } P6(3) \rightarrow R3c) \}
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.800 0 0 1 \{ \alpha_{78} = 0.80 \text{ (transition generating } P6(3) \text{ structure)} \}

{8}
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
0.000 0 0 1
1.000 0 0 1 \{ \alpha_{87} = \text{ (transition generating } P6(3) \text{ structure)} \}
0.000 0 0 1

{ END OF FILE}
APPENDIX 4

Figure A4.1: Inverse susceptibility $(1/\chi)$ Curie-Weiss fits for (cation)FeFe(ox)$_3$
Figure A4.2: Inverse susceptibility ($1/\chi$) Curie-Weiss fits for (cation)MnFe(ox)$_3$
Figure A4.3: The magnetisation of Npent₄FeFe(ox)₃ in 100G applied field during (a) slow cooling and (b) slow warming/cooling between 39.8K and 40.2K.
A4.4: AC and DC susceptibility behaviour of $\text{Np}_{\text{pent}}\text{FeFe(ox)}_3$. 