Synthesis and Characterisation of Layered Magnetic Oxalato-Salts

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Abstract

This thesis describes the synthesis and characterisation of magnetic oxalato-salts of general formula $AM^{II}M^{III}(C_2O_4)_3$, where A is a monovalent organic cation and $M^{II}$ and $M^{III}$ are transition metals. Compounds of this type crystallise as honeycomb layers of metal-oxalate sheets interleaved by layers of the cation and may be considered quasi two-dimensional molecular-based magnets. The compounds considered are derived from $Fe^{II}Fe^{III}$ and $Mn^{II}Fe^{III}$ with the cations tetraphenylphosphonium, tetrabutylammonium and alkyltriphenylphosphonium, where the alkyl chain ranges from propyl to heptyl inclusive.

Structural characterisation by powder X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) is presented; lattice parameters at room temperature have been determined from XRD and the temperature-dependence of the local structure around the metal ions has been investigated by EXAFS on $(n$-$C_4H_9)_4NFeFe(C_2O_4)_3$, $(n$-$C_4H_9)_4NMnFe(C_2O_4)_3$, $PPh_4FeFe(C_2O_4)_3$ and $PPh_4MnFe(C_2O_4)_3$ ($PPh_4 =$ tetraphenylphosphonium).

Bulk magnetic behaviour has been studied by DC magnetometry. Magnetic data in the paramagnetic regime have been fitted to the Curie-Weiss law enabling Curie and Weiss constants to be determined. Variation of the magnetic behaviour by changing the organic cation and by dilution of the magnetic centers with the diamagnetic ions $Zn^{II}$ and $Ga^{III}$ has been investigated. The local magnetic properties of $(n$-$C_4H_9)_4NFeFe(C_2O_4)_3$ and $PPh_4MnFe(C_2O_4)_3$ have been probed by muon spin relaxation.

The magnetic structure of deuterated examples of $PPh_4MnFe(C_2O_4)_3$ and $PPh_4FeFe(C_2O_4)_3$ has been studied by polarised neutron diffraction. The temperature-dependence of the two-dimensional magnetic correlation length has been determined by fitting these data to a Warren peak shape function.
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Contents

Title page ................................................................................................................... 1

Abstract ............................................................................................................................ 2

Acknowledgements ...................................................................................................... 3

Contents ............................................................................................................................ 4

List of Tables ................................................................................................................. 8

List of Figures ............................................................................................................. 10

Chapter 1 - Introduction ......................................................................................... 22
  1.1 Overview ................................................................................................. 22
  1.2 Molecular and Molecular-based Magnets .......................................... 22
  1.3 Molecular-based Magnets Containing the Oxalate Ligand ............... 26
  1.4 Scope of the Research ........................................................................... 33
  1.5 References .............................................................................................. 35

Chapter 2 - Theory .................................................................................................... 38
  2.1 Diffraction .............................................................................................. 38
    2.1.1 Powder X-ray Diffraction ..................................................... 42
    2.1.2 Neutron Diffraction ............................................................. 43
    2.1.3 Polarised Neutron Diffraction ........................................... 44
    2.1.4 The Warren Peak Shape Function ................................. 45
Chapter 3 Experimental

3.1 Synthesis ................................................................. 74
3.1.1 (cation)MFe(C_2O_4)_3 ........................................... 74
3.1.2 (n=C_4H_9)_4Nzn_xFe_(1-x)Fe(C_2O_4)_3 ..................... 76
3.1.3 (cation)FeGa_xFe_(1-x)(C_2O_4)_3 (cation = (n=C_4H_9)_4N,PPh_4) ........................................ 77
3.1.4 PPh_4(d=20)MnFe(C_2O_4)_3 and PPh_4(d=20)FeFe(C_2O_4)_3 ........................................... 77
3.1.5 Elemental Analysis ................................................. 79
3.2 Powder X-ray Diffraction ............................................ 80
3.3 High Resolution Powder X-ray Diffraction ..................... 80
3.4 Extended X-ray Absorption Fine Structure (EXAFS) .......... 81
3.5 Polarised Neutron Diffraction .............................................................. 82
3.6 Muon Spin Relaxation (μSR) ................................................................. 84
  3.6.1 Rutherford–Appleton Laboratory ......................................... 84
  3.6.2 Paul Scherrer Institut ............................................................... 86
3.7 Magnetometry ......................................................................................... 88
3.8 References ............................................................................................... 89

Chapter 4 - Chemical and Structural Characterisation ................................................ 90

4.1 General ...................................................................................................... 90
4.2 Elemental Analysis .................................................................................. 90
  4.2.1 \( C_{n}H_{(2n+1)}PPh_{3}MFe(C_{2}O_{4})_{3} \) (n = 3 - 7) ........................................ 90
  4.2.2 \( (n-C_{4}H_{9})_{4}N\text{Zn}_{x}\text{Fe}_{(1-x)}\text{Fe(C}_{2}\text{O}_{4})_{3} \) ........................................ 92
  4.2.3 \( (n-C_{4}H_{9})_{4}N\text{FeGa}_{x}\text{Fe}_{(1-x)}\text{(C}_{2}\text{O}_{4})_{3} \) ........................................ 94
  4.2.4 PPh\(_{4}\text{FeGa}_{x}\text{Fe}_{(1-x)}\text{(C}_{2}\text{O}_{4})_{3} \) ..................................................... 95
4.3 Crystal Structure .................................................................................... 96
  4.3.1 Lattice Parameters of \( C_{n}H_{(2n+1)}PPh_{3}MFe(C_{2}O_{4})_{3} \) (n = 3 to 7) ........................................ 96
  4.3.2 Lattice Parameters of Doped Compounds .................................... 105
  4.3.3 \( (n-C_{4}H_{9})_{4}N\text{Zn}_{x}\text{Fe}_{(1-x)}\text{Fe(C}_{2}\text{O}_{4})_{3} \) ........................................ 105
  4.3.4 \( (n-C_{4}H_{9})_{4}N\text{FeGa}_{x}\text{Fe}_{(1-x)}\text{(C}_{2}\text{O}_{4})_{3} \) ........................................ 108
  4.3.5 PPh\(_{4}\text{FeGa}_{x}\text{Fe}_{(1-x)}\text{(C}_{2}\text{O}_{4})_{3} \) ..................................................... 111
4.4 EXAFS ...................................................................................................... 113
  4.4.1 \( (n-C_{4}H_{9})_{4}N\text{FeFe(C}_{2}\text{O}_{4})_{3} \) and PPh\(_{4}\text{FeFe(C}_{2}\text{O}_{4})_{3} \) .......... 114
  4.4.2 \( (n-C_{4}H_{9})_{4}N\text{MnFe(C}_{2}\text{O}_{4})_{3} \) and PPh\(_{4}\text{MnFe(C}_{2}\text{O}_{4})_{3} \) .......... 119
4.5 High Resolution Powder X-ray Diffraction ......................................... 123
4.6 References ............................................................................................... 126
Chapter 5 - Magnetic Characterisation .................................................. 128

5.1 General ........................................................................................................ 128

5.2 Magnetometry .............................................................................................. 128

5.2.1 (Cation)MnFe(C₂O₄)₃ ................................................................. 128

5.2.2 (Cation)FeFe(C₂O₄)₃ ................................................................. 132

5.2.3 (n-C₄H₉)₄NZnₓFe₁₋ₓFe(C₂O₄)₃ .................................................. 146

5.2.4 (n-C₄H₉)₄NFeGaₓFe₁₋ₓ(C₂O₄)₃ .............................................. 150

5.2.5 PPh₄FeₓGaₓFe₁₋ₓ(C₂O₄)₃ ...................................................... 152

5.3 Muon Spin Relaxation ............................................................................... 154

5.3.1 Rutherford-Appleton Laboratory .............................................. 154

5.3.2 Paul Scherrer Institut ......................................................................... 163

5.4 Polarised Neutron Diffraction ................................................................. 165

5.4.1 PPh₄(d-20)MnFe(C₂O₄)₃ ......................................................... 165

5.4.2 PPh₄(d-20)FeFe(C₂O₄)₃ .......................................................... 172

5.5 References ................................................................................................. 180

Chapter 6 Discussion ......................................................................................... 181

6.1 Structure ..................................................................................................... 181

6.1.1 (cation)M⁺²M⁺³(C₂O₄)₃ ........................................................... 181

6.1.2 (n-C₄H₉)₄ZnₓFe₁₋ₓFe(C₂O₄)₃ .................................................. 188

6.1.3 (n-C₄H₉)₄FeGaₓFe₁₋ₓ(C₂O₄)₃ .................................................. 188

6.1.4 PPh₄FeGaₓFe₁₋ₓ(C₂O₄)₃ ........................................................ 189

6.2 Magnetic Properties .................................................................................. 189

6.2.1 (cation)MnFe(C₂O₄)₃ ................................................................. 189

6.2.2 (cation)FeFe(C₂O₄)₃ ................................................................. 192

6.3 References .................................................................................................. 199
List of Tables

Table 2.3.1 - Effects of spin and lattice dimensionalities on the magnetic ordering ................................................. 55

Table 2.3.2 - Critical site and bond probabilities pc(s) and pc(b) for some common lattices .................................. 64

Table 4.2.1 - Elemental analysis of C_nH_{2n+1}PPh_3FeFe(C_2O_4)_3 (n = 3 to 7) .... 91

Table 4.2.2 - Elemental analysis of C_nH_{2n+1}PPh_3MnFe(C_2O_4)_3 (n = 3 to 7) ... 92

Table 4.2.3 - Elemental analysis for representative (n-C_4H_9)_4NZn_xFe_{(1-x)}Fe(C_2O_4)_3 compounds synthesised by the 'block' method ............................................................... 93

Table 4.2.4 - Elemental analysis for representative (n-C_4H_9)_4NZn_xFe_{(1-x)}Fe(C_2O_4)_3 compounds synthesised by the 'ionic' method ............................................................... 94

Table 4.2.5 - Elemental analysis for representative (n-C_4H_9)_4NFeGa_xFe_{(1-x)}(C_2O_4)_3 compounds ................................. 95

Table 4.2.6 - Elemental analysis for representative PPh_4FeGa_xFe_{(1-x)}(C_2O_4)_3 compounds ................................. 96

Table 4.3.1 - Lattice parameters for (cation)MFe(C_2O_4)_3 compounds ......................... 101
Table 5.2.1 - Magnetic parameters for (cation)MnFe(C\(_2\)O\(_4\))\(_3\)  

Table 5.2.2 - Magnetic parameters for (cation)FeFe(C\(_2\)O\(_4\))\(_3\)  

Table 5.2.3 - Elemental analysis of C\(_3\)H\(_7\)PPh\(_3\)FeFe(C\(_2\)O\(_4\))\(_3\)  

Table 5.2.4 - Magnetic parameters for (n-C\(_4\)H\(_9\))\(_4\)N\(\text{Zn}_{x}\)Fe\(_{(1-x)}\)Fe(C\(_2\)O\(_4\))\(_3\)  

Table 5.2.5 - Magnetic parameters for (n-C\(_4\)H\(_9\))\(_4\)N\(\text{FeGa}_{x}\)Fe\(_{(1-x)}\)(C\(_2\)O\(_4\))\(_3\)  

Table 5.2.6 - Magnetic parameters for PPh\(_4\)FeGa\(_x\)Fe\(_{(1-x)}\)(C\(_2\)O\(_4\))\(_3\)  

Table 6.1.1 - Comparison of calculated and experimental values for increase in interlayer separation of the alkyltriphenylphosphonium series of compounds.
List of Figures

Figure 1.2.1 - Structure of the molecular magnet Fe(Me$_5$C$_5$)$_2$TCNE .............. 23

Figure 1.2.2 - One-dimensional chain structure of Mn(hfa)$_2$NITPrn ............... 24

Figure 1.2.3 - Fully interlocked three-dimensional structure of
(rad)$_2$Mn$_2$(Cu(opba))$_3$(DMSO)$_2$.2H$_2$O ........................................... 25

Figure 1.2.4 - View of one Mn$^{II}$Cu$^{II}$ hexagonal layer of
(rad)$_2$Mn$_2$(Cu(opba))$_3$(DMSO)$_2$.2H$_2$O ........................................... 25

Figure 1.3.1 - The metal-trisoxalate unit (A isomer shown) .......................... 26

Figure 1.3.2 - Helical chain structure formed by metal-trisoxalate units with the
same chirality (only one chain is shown for clarity) ..................................... 27

Figure 1.3.3 - Honeycomb layer assembly of metal-trisoxalate units with
alternating chiralities .......................................................... 27

Figure 1.3.4 - Metal-oxalate backbone of [Fe(bipy)$_3$][Fe$_2$(C$_2$O$_4$)$_3$] ........... 28

Figure 1.3.5 - Layered structure of (n-C$_5$H$_{11}$)$_4$NMnFe(C$_2$O$_4$)$_3$ viewed
perpendicular to the c axis .................................................. 29

Figure 1.3.6 - Metal-oxalate layer of (n-C$_5$H$_{11}$)$_4$NMnFe(C$_2$O$_4$)$_3$ viewed along
the c axis .......................................................... 30
Figure 1.3.7 - Honeycomb layer stacking sequence in
\((n-C_5H_{11})_4NMnFe(C_2O_4)_3\) .................................................. 31

Figure 1.3.8 - Honeycomb layer stacking sequences in (a) R3c and (b) P6(3) ..... 32

Figure 2.1.1 - Ewald sphere construction .................................................. 40

Figure 2.2.1 - Schematic diagram of the radial portion of the photoelectron wave
being backscattered by the neighbouring atoms ...................................... 46

Figure 2.2.2 - Schematic of the conditions for multiple scattering .............. 48

Figure 2.3.1 - Illustration of the mixing of orbital states in the superexchange
mechanism for a dimer ................................................................. 52

Figure 2.3.2 - Two-dimensional representations of (a) ferromagnetism, (b)
antiferromagnetism, (c) ferrimagnetism and (d) spin canting ............... 54

Figure 2.3.3 - Illustration of Néel ferrimagnetic order types .................... 60

Figure 2.3.4 - Representation of (a) site percolation and (b) bond percolation for
a two dimensional lattice ............................................................... 63

Figure 2.4.1 - Decay of pion ................................................................. 65

Figure 2.4.2 - Decay of muon ............................................................... 65
Figure 2.4.3 - Angular distribution $P(q) = 1 + \cos q$ of the positron intensity for the positrons of the highest energy (asymmetry parameter $a = 1$), and averaged over all positron energies ($a = 1/3$) .................................. 66

Figure 2.4.4 - Illustration of (a) implantation, (b) precession and (c) decay in the $\mu$SR experiment .......................................................... 67

Figure 3.1.1 - Arrangement for synthesis of $(n-C_4H_9)_4NMnFe(C_2O_4)_3$ ............ 76

Figure 3.3.1 - Schematic of the BM16 instrument at the ESRF in Grenoble ....... 81

Figure 3.4.1 - Typical arrangement for transmission mode EXAFS experiment ... 82

Figure 3.5.1 - Schematic of the D7 instrument at the ILL in Grenoble .................. 83

Figure 3.6.1 - Layout of the MuSR instrument at the Rutherford-Appleton Laboratory in Oxfordshire ..................................................... 85

Figure 3.6.2 - Plan section of the Dolly instrument at the PSI in Switzerland .... 87

Figure 4.3.1(a) - Powder XRDs of $C_5H_{13}PPh_3MnFe(C_2O_4)_3$ (solid line) and $(n-C_5H_{11})_4NMnFe(C_2O_4)_3$ (dotted line) ........................................... 97

Figure 4.3.1(b) - Powder XRDs of $C_5H_{11}PPh_3FeFe(C_2O_4)_3$ (solid line) and $(n-C_5H_{11})_4NMnFe(C_2O_4)_3$ (dotted line) ........................................... 97

Figure 4.3.2 - Relationship between the crystallographic axes of $C222_1$ and $P6(5)$ ................................................................. 99
Figure 4.3.3 - LeBail extraction for C₃H₇PPh₃MnFe(C₂O₄)₃ in the P6(5) space group ................................................................. 100

Figure 4.3.4(a) - Lowest angle 00l peak for CₙH(2n+1)PPh₃MnFe(C₂O₄)₃
(n = 3 to 7) ........................................................................................................... 102

Figure 4.3.4(b) - Lowest angle 00l peak for CₙH(2n+1)PPh₃FeFe(C₂O₄)₃
(n = 3 to 7) ........................................................................................................... 102

Figure 4.3.5 - C axis vs alkyl chain length for CₙH(2n+1)PPh₃MnFe(C₂O₄)₃
(dotted line) and CₙH(2n+1)PPh₃FeFe(C₂O₄)₃ (solid line) (n = 3 to 7) .... 103

Figure 4.3.6 - Powder X-ray diffraction profiles for C₄H₅PPh₃MnFe(C₂O₄)₃
(solid line) and C₄H₅PPh₃FeFe(C₂O₄)₃ (dotted line) ................................. 104

Figure 4.3.7(a) - Powder X-ray diffraction profile of
(n–C₄H₉)₄NZn₀.₁Fe₀.₉Fe(C₂O₄)₃ ................................................................. 106

Figure 4.3.7(b) - Powder X-ray diffraction profile of
(n–C₄H₉)₄NZn₀.₇Fe₀.₃Fe(C₂O₄)₃ ................................................................. 106

Figure 4.3.8(a) - Variation in a axis with concentration of zinc ................. 107

Figure 4.3.8(b) - Variation in c axis with concentration of zinc ................. 107

Figure 4.3.9(a) - Powder X-ray diffraction profile of
(n–C₄H₉)₄NFeGa₀.₂Fe₀.₈(C₂O₄)₃ ................................................................. 108

Figure 4.3.9(b) - Powder X-ray diffraction profile of (n–C₄H₉)₄NFeGa(C₂O₄)₃ .. 109
Figure 4.3.10(a) - Variation in a and b axes for \((n-C_4H_9)_4NFeGa_xFe_{(1-x)}(C_2O_4)_3\) with concentration of gallium ........................................... 110

Figure 4.3.10(b) - Variation in c axis for \((n-C_4H_9)_4NFeGa_xFe_{(1-x)}(C_2O_4)_3\) with concentration of gallium ........................................... 110

Figure 4.3.11(a) - Powder X-ray diffraction profile of \(PPh_4FeGa_{0.2}Fe_{0.8}(C_2O_4)_3\). .................................................. 111

Figure 4.3.11(b) - Powder X-ray diffraction profile of \(PPh_4FeGa(C_2O_4)_3\) .................................................. 112

Figure 4.3.12(a) - Variation in a axis with concentration of gallium .......................... 113

Figure 4.3.12(b) - Variation in c axis with concentration of gallium .......................... 113

Figure 4.4.1(a) - Fitted room temperature Fe-K edge EXAFS spectrum for \((n-C_4H_9)_4NFeFe(C_2O_4)_3\) ........................................... 114

Figure 4.4.1(b) - Fitted room temperature Fe-K edge EXAFS spectrum for \(PPh_4FeFe(C_2O_4)_3\) ........................................... 115

Figure 4.4.2(a) - Fourier transform of fitted room temperature Fe-K edge EXAFS spectrum for \((n-C_4H_9)_4NFeFe(C_2O_4)_3\) ........................................... 115

Figure 4.4.2(b) - Fourier transform of fitted room temperature Fe-K edge EXAFS spectrum for \(PPh_4FeFe(C_2O_4)_3\) ........................................... 116
Figure 4.4.3 - Fe-Fe distances determined from EXAFS for

\((n\text{-}C_4H_9)_4\text{NFeFe(C}_2\text{O}_4)_3\) (diamonds) and \(\text{PPh}_4\text{FeFe(C}_2\text{O}_4)_3\) (squares) . . 117

Figure 4.4.4 - Variation of Debye-Waller factors for \((n\text{-}C_4H_9)_4\text{NFeFe(C}_2\text{O}_4)_3\)

(diamonds) and \(\text{PPh}_4\text{FeFe(C}_2\text{O}_4)_3\) (squares) ......................... 118

Figure 4.4.5(a) - Fitted room temperature Fe K-edge EXAFS spectra for

\((n\text{-}C_4H_9)_4\text{NMnFe(C}_2\text{O}_4)_3\) ...................................................... 119

Figure 4.4.5(b) - Fitted room temperature Fe K-edge EXAFS spectra for

\(\text{PPh}_4\text{MnFe(C}_2\text{O}_4)_3\) ................................................................. 119

Figure 4.4.6(a) - Fourier transforms of fitted room temperature Fe K-edge EXAFS spectra for \((n\text{-}C_4H_9)_4\text{NMnFe(C}_2\text{O}_4)_3\) ............................................ 120

Figure 4.4.6(b) - Fourier transforms of fitted room temperature Fe K-edge EXAFS spectra for \(\text{PPh}_4\text{MnFe(C}_2\text{O}_4)_3\) ......................................................... 120

Figure 4.4.7(a) - Fitted room temperature Mn K-edge EXAFS spectra for

\((n\text{-}C_4H_9)_4\text{NMnFe(C}_2\text{O}_4)_3\) .............................................................. 121

Figure 4.4.7(b) - Fitted room temperature Mn K-edge EXAFS spectra for

\(\text{PPh}_4\text{MnFe(C}_2\text{O}_4)_3\) ................................................................. 121

Figure 4.4.8(a) - Fourier transforms of fitted room temperature Mn K-edge EXAFS spectra for \((n\text{-}C_4H_9)_4\text{NMnFe(C}_2\text{O}_4)_3\) .............................. 122

Figure 4.4.8(b) - Fourier transforms of fitted room temperature Mn K-edge EXAFS spectra for \(\text{PPh}_4\text{MnFe(C}_2\text{O}_4)_3\) .............................. 122
Figure 4.5.1 - High resolution powder X-ray diffraction profiles for

\[(n-\text{C}_4\text{H}_9)\text{NFeFe(C}_2\text{O}_4)\text{)}\] ......................................................... 124

Figure 4.5.2 - Temperature dependence of peak positions for

\[(n-\text{C}_4\text{H}_9)\text{NFeFe(C}_2\text{O}_4)\text{)}\] ......................................................... 125

Figure 5.2.1(a) - Temperature-dependent field-cooled magnetisation of

\[\text{C}_n\text{H}(2n+1)\text{PPh}_3\text{MnFe(C}_2\text{O}_4)\text{)} (n = 3 to 7) \] ........................................... 129

Figure 5.2.1(b) - Broad maxima characteristic of 2-D antiferromagnetism in the magnetisation of \[\text{C}_n\text{H}(2n+1)\text{PPh}_3\text{MnFe(C}_2\text{O}_4)\text{)} (n = 3 to 7) \] ............... 130

Figure 5.2.2 - Temperature-dependent field-cooled and zero-field-cooled magnetisation of \[\text{C}_4\text{H}_9\text{PPh}_3\text{MnFe(C}_2\text{O}_4)\text{)} \] ................................................ 131

Figure 5.2.3 - Inverse susceptibility of \[\text{C}_n\text{H}(2n+1)\text{PPh}_3\text{MnFe(C}_2\text{O}_4)\text{)} (n = 3 to 7) \] ......................................................... 131

Figure 5.2.4 - Temperature-dependent field-cooled magnetisation of

\[\text{C}_n\text{H}(2n+1)\text{PPh}_3\text{FeFe(C}_2\text{O}_4)\text{)} (n = 3 to 7) \] ......................................................... 133

Figure 5.2.5 - Neél model for Type N ferrimagnetism ........................................ 134

Figure 5.2.6 - Temperature-dependent field-cooled and zero-field-cooled magnetisation of \[\text{C}_4\text{H}_9\text{PPh}_3\text{FeFe(C}_2\text{O}_4)\text{)} \] ......................................................... 135

Figure 5.2.7 - Inverse susceptibility of \[\text{C}_n\text{H}(2n+1)\text{PPh}_3\text{FeFe(C}_2\text{O}_4)\text{)} (n = 3 to 7) \] ................................................................. 135
Figure 5.2.8 - Temperature-dependent field-cooled magnetisation of
  PPh₄FeFe(C₂O₄)₃ ......................................................... 137

Figure 5.2.9 - Discontinuity in the magnetisation of (n-C₄H₉)₄NFeFe(C₂O₄)₃ ... 137

Figure 5.2.10(a) - Discontinuity in the magnetisation of
  C₄H₉PPh₃FeFe(C₂O₄)₃ ......................................................... 138

Figure 5.2.10(b) - Discontinuity in the magnetisation of
  C₇H₁₅PPh₃FeFe(C₂O₄)₃ ......................................................... 138

Figure 5.2.11 - Discontinuity in the magnetisation of PPh₄FeFe(C₂O₄)₃ .......... 139

Figure 5.2.12 - Temperature-dependent field-cooled magnetisation of three
  samples of C₄H₉PPh₃FeFe(C₂O₄)₃ ......................................................... 140

Figure 5.2.13 - Temperature-dependent field-cooled magnetisation of
  C₃H₇PPh₃FeFe(C₂O₄)₃ compounds synthesised at different temperatures 142

Figure 5.2.14 - Temperature-dependent field-cooled magnetisation of
  C₃H₇PPh₃FeFe(C₂O₄)₃ compounds synthesised at different pH ...... 143

Figure 5.2.15 - Temperature-dependent field-cooled magnetisation of
  C₃H₇PPh₃FeFe(C₂O₄)₃ compounds precipitated from varying
  amounts of solvent ......................................................... 144

Figure 5.2.16 - Temperature-dependent field-cooled magnetisation of
  C₃H₇PPh₃FeFe(C₂O₄)₃ compounds synthesised using varying cation
  solution molarities ......................................................... 145
Figure 5.2.17 - Temperature-dependent field-cooled magnetisation of 

\[(n-C_4H_9)_4NZn_xFe_{(1-x)}Fe(C_2O_4)_3\] ........................................ 147

Figure 5.2.18 - Temperature-dependent field-cooled magnetisation of 

\[(n-C_4H_9)_4NZn_xFe_{(1-x)}Fe(C_2O_4)_3 \ (x = 0.3-0.6)\] ............... 148

Figure 5.2.19 - Inverse susceptibility of \[(n-C_4H_9)_4NZnFe(C_2O_4)_3\] ............... 149

Figure 5.2.20 - Temperature dependence of the magnetisation for 

\[(n-C_4H_9)_4NFeGa_xFe_{(1-x)}(C_2O_4)_3\] ........................................ 150

Figure 5.2.21 - Temperature dependence of the magnetisation for 

\[PPh_4FeGa_xFe_{(1-x)}(C_2O_4)_3\] ........................................ 152

Figure 5.3.1 - Fitted \(\mu\)SR spectra for \[PPh_4MnFe(C_2O_4)_3\] .................. 155

Figure 5.3.2 - Temperature dependence of the zero-field initial asymmetry of 

\[PPh_4MnFe(C_2O_4)_3\] ........................................ 156

Figure 5.3.3 - Temperature dependence of the zero-field relaxation rate of 

\[PPh_4MnFe(C_2O_4)_3\] ........................................ 157

Figure 5.3.4 - Temperature dependence of the zero-field initial asymmetry of 

\[(n-C_4H_9)_4NFeFe(C_2O_4)_3\] ........................................ 158

Figure 5.3.5 - Temperature dependence of the zero-field relaxation rate of 

\[(n-C_4H_9)_4NFeFe(C_2O_4)_3\] ........................................ 159

Figure 5.3.6 - Field dependence of the initial asymmetry of 

\[(n-C_4H_9)_4NFeFe(C_2O_4)_3 \ at \ 8.2 \ K\] ........................................ 160
Figure 5.3.7 - Field dependence of the initial asymmetry of
$(n-C_4H_9)_4NFeFe(C_2O_4)_3$ at 38 K .......................... 161

Figure 5.3.8 - Field dependence of the initial asymmetry of
$(n-C_4H_9)_4NFeFe(C_2O_4)_3$ at 54 K ......................... 162

Figure 5.3.9 - Temperature dependence of the zero-field initial asymmetry of
$(n-C_4H_9)_4NFeFe(C_2O_4)_3$ ................................. 164

Figure 5.3.10 - Temperature dependence of the relaxation rate of
$(n-C_4H_9)_4NFeFe(C_2O_4)_3$ ................................. 165

Figure 5.4.1 - Total neutron diffraction pattern for PPh$_4$(d–20)MnFe(C$_2$O$_4$)$_3$
at 5 K ......................................................... 166

Figure 5.4.2 - Partitions of the diffraction pattern for PPh$_4$(d–20)MnFe(C$_2$O$_4$)$_3$
at 5 K; (a) Nuclear coherent component; (b) Spin incoherent component;
(c) Magnetic coherent component ............................... 166

Figure 5.4.3 - Temperature dependence of the magnetic coherent component of
the diffraction pattern for PPh$_4$(d–20)MnFe(C$_2$O$_4$)$_3$ ............... 167

Figure 5.4.4 - Simulated diffraction pattern of the R3c Shubnikov group magnetic
structure ................................................................. 168

Figure 5.4.5 - [110] projection of the six layers of the R3c magnetic structure of
PPh$_4$(d–20)MnFe(C$_2$O$_4$)$_3$ ........................................ 168
Figure 5.4.6 - Magnetic profiles for PPh₄(d-20)MnFe(C₂O₄)₃ at 5 K
(fitted to Warren and Gaussian peak shape functions) and 50 K
(fitted to Warren peak shape function) ................................. 170

Figure 5.4.7 - Temperature-dependence of the two-dimensional magnetic
  correlation length for PPh₄(d-20)MnFe(C₂O₄)₃ ................................. 171

Figure 5.4.8 - Total neutron diffraction pattern for PPh₄(d-20)FeFe(C₂O₄)₃ at
  5 K (4.9 g sample) ........................................................................ 172

Figure 5.4.9 - Partitions of the diffraction pattern for PPh₄(d-20)FeFe(C₂O₄)₃
  at 5 K (4.9 g sample); (a) Nuclear coherent component;
  (b) Spin incoherent component; (c) Magnetic coherent component .... 173

Figure 5.4.10 - Total neutron diffraction pattern for PPh₄(d-20)FeFe(C₂O₄)₃ at
  2 K (7.3 g sample) ........................................................................ 174

Figure 5.4.11 - Partitions of the diffraction pattern for PPh₄(d-20)FeFe(C₂O₄)₃
  at 2 K (7.3 g sample); (a) Nuclear coherent component;
  (b) Spin incoherent component; (c) Magnetic coherent component .... 175

Figure 5.4.12 - Magnetic profiles for PPh₄(d-20)FeFe(C₂O₄)₃ at 2 K and 50 K
  fitted to the Warren peak shape function ...................................... 177

Figure 5.4.13 - Temperature-dependence of the two-dimensional magnetic
  correlation length for PPh₄(d-20)FeFe(C₂O₄)₃ ................................. 178

Figure 6.1.1 - Cation orientations in (a) PPh₄MnCr(C₂O₄)₃ and
  (b) (n-C₅H₁₁)₄NMnFe(C₂O₄)₃ ...................................................... 183
Figure 6.1.2 - View along the c axis showing the honeycomb layer and orientation of the penetrating phenyl group in PPh₄MnCr(C₂O₄)₃ ....... 184

Figure 6.1.3 - Predicted increase in interlayer separation consequent on extending the alkyl chain in the FeFe series ................................................................. 185

Figure 6.1.4 - Possible cation orientations for CₙH₂ₙ₊₁PPh₃MFe(C₂O₄)₃
(n = 4 - 7, M = Mn, Fe) ................................................................. 186

Figure 6.2.1 - Triangular sublattice formed by Fe²⁺ (or Fe³⁺) ions in a hexagonal lattice ................................................................. 194

Figure 6.2.2 - 100 G field-cooled magnetisation of C₃H₇PPh₃FeFe(C₂O₄)₃ compounds synthesised using varying cation solution molarities ........... 196
Chapter 1 - Introduction

1.1 Overview

Synthesis of solid state materials from molecular precursors has attracted considerable
interest in recent years. Reasons for this interest include the large degree of
flexibility inherent in this type of synthesis and the generally mild preparative
conditions required. The identity and nature of the molecular 'building blocks' has a
direct influence on the structural and physical properties of the resultant material and
simple variation of the precursors may have a dramatic effect on these properties. As
well as the opportunity to test and refine physical theories by constructing new and
unusual structures, the prospect of synthesising practically useful materials without the
need for the often extreme processing techniques of metallurgy is an attractive goal.
Molecular-based synthesis has yielded a wide range of one, two and three-dimensional
materials with a variety of physical properties; electrical conductivity and
superconductivity, optical effects and magnetism. The work presented in this thesis is concerned with quasi two-dimensional molecular-based
magnets.

1.2 Molecular and Molecular-based Magnets

In 1967, the square-pyramidal complex Fe[S2CN(C2H5)2]2Cl was reported to order
ferromagnetically. The compound consists of discrete molecules in which each
FeIII is coordinated to two dithiocarbamato anions and one chloride anion. Compounds
such as Fe[S2CN(C2H5)2]2Cl may be considered as molecular magnets in that they
comprise isolated magnetic species in the solid state. Later examples include the
ferromagnetic electron-transfer salt FeCp2TCNE (Cp = cyclopentadienyl, TCNE =
tetracyanoethylene). The structure of the related compound, Fe(Me5C5)2TCNE, is
shown in Figure 1.2.1.
Figure 1.2.1 - Structure of the molecular magnet Fe(Me₅C₅)₂TCNE

This compound, synthesised by Miller et al in 1987, comprises discrete molecules of decamethylferrocinium and tetracyanoethylene. A disadvantage of this type of compound from the point of view of controlling magnetic interactions is that the magnetic centres are isolated and often spatially remote, leading to little structural control and generally low magnetic ordering temperatures. The example shown in Figure 1.2.1 is ferromagnetic, with an ordering temperature of 4.8 K.

By contrast, molecular-based magnets are also synthesised from molecular precursors and contain recognisable molecular species but these species are chemically linked and the magnetic exchange is propagated via the efficient super-exchange mechanism (Section 2.3.3) through ligands connecting the magnetic centres. Early examples of this type of compound include the two-dimensional (RNH₃)₂MCl₄ salts where R = alkyl group and M = Mn, Fe, Cu, Cr. The Mn and Fe derivatives have antiferromagnetic near-neighbour exchange while the Cu and Cr ones are ferromagnetic. Syntheses of this type allow a far greater degree of structural control and include examples of one, two, and three-dimensional structures. The molecular-based magnets V(TCNE)x.yCH₂Cl₂ and
V[Cr(CN)_6]_{0.86}^{24} were the first examples of materials synthesised from molecular precursors to have higher than ambient magnetic ordering temperatures.

Figure 1.2.2 shows the crystal structure of a one-dimensional molecular-based magnet formed by manganese(II) and a nitronyl nitroxide radical, of formula Mn(hfa)_2NITPrn, where hfa = hexafluoroacetylacetonate and NITPrn = 2-isopropyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxyl-3-oxide. Intra-chain magnetic exchange is propagated between the metal ions via the bridging organic radical ligands. The compound, reported by Caneschi et al in 1988 \(^{25}\), undergoes a ferrimagnetic transition at 7.6 K.

A structurally more complex example of a molecular-based magnet is provided by \((\text{rad})_2\text{Mn}_2[\text{Cu(opba)}]_3(\text{DMSO})_2\cdot2\text{H}_2\text{O}\), where rad is 2-(4-N-methylpyridinium)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide, opba is orthophenylenediamine (oxamato), and DMSO is dimethyl sulfoxide \(^{26}\). As represented in Figure 1.2.3, it consists of two nearly perpendicular graphite-like networks of edge-sharing Mn\(^{II}\)\_6Cu\(^{II}\)\_6 hexagons. The two networks are fully interlocked giving rise to a three-dimensional structure. A view of one of the layers is given in Figure 1.2.4.
Magnetic exchange is ferrimagnetic between the Mn and Cu ions in the layers but ferromagnetic through the rad$^+$ cations which connect the layers. The compound orders magnetically at 22.5 K.
1.3 Molecular-based Magnets Containing the Oxalate Ligand

One of the most commonly used ligands for bridging the magnetic centres in molecular-based magnets is the oxalate dianion $\text{C}_2\text{O}_4^{2-}$. This ligand is attractive for a number of reasons. Firstly, water-soluble salts of many tris-oxalate transition metals are readily available or easily synthesised, thus simplifying at least one step of the overall synthesis. Secondly, the ligand provides an efficient route for superexchange between magnetic centres. Thirdly, the bis-bidentate nature of the ligand and the inherent chirality of the metal-trisoxalate unit enables construction of extended lattices in two and three-dimensions.

The structure of the metal-trisoxalate unit has the same form as a three-bladed propellor and is represented schematically in Figure 1.3.1. The metal ion is a chiral centre, with trigonally distorted $D_3$ symmetry, the distortion arising from the metal ion radii and the bite angle of the ligand.

![Figure 1.3.1 - The metal-trisoxalate unit (A isomer shown)](image)

Consideration of the chirality and connectivity of the metal-trisoxalate units leads to two possible structures. In the first case, if all the metal-trisoxalate units have the same chirality, a three-dimensional network of orthogonal helical chains, illustrated in Figure 1.3.2, is formed.
Figure 1.3.2 - Helical chain structure formed by metal-trisoxalate units with the same chirality (only one chain is shown for clarity)

On the other hand, assembly of metal-trisoxalate units with alternating chiralities results in a layered honeycomb structure, as illustrated in Figure 1.3.3.

Figure 1.3.3 - Honeycomb layer assembly of metal-trisoxalate units with alternating chiralities
Both topologies illustrated above have been realised in real compounds and Figure 1.3.4 shows an example of the three-dimensional structure. This compound was reported by Decurtins et al in 1993 and is antiferromagnetic with an ordering temperature of 15 K.

Figure 1.3.4 - Metal-oxalate backbone of [Fe(bipy)$_3$][Fe$_2$(C$_2$O$_4$)$_3$] (Fe(bipy)$_3$ cations not shown for clarity)

Charge balance is achieved by a guest cation, in this case iron-trisbipyridine (not shown in the figure). In addition, the cation acts as a template, both in its space filling role, but also, since it is itself chiral, in influencing the chirality of the host framework. Thus a $\Lambda$-$\Delta$ or $\Delta$-$\Lambda$ pairing is observed between the host and guest.

Compounds containing the other structure type described above, that of a honeycomb layer, are the subject of this thesis. All these compounds are of general formula $\text{AM}^{II}\text{M}^{III}(\text{C}_2\text{O}_4)_3$ where $\text{A}$ is an organic or organo-metallic cation and $\text{M}^{II}$ and $\text{M}^{III}$ are transition metals. Since they were first reported by Tamaki et al in 1992, an extensive series has been synthesised, incorporating a variety of metals and cations. In common with the three-dimensional oxalate compounds described above, the cation has
the dual role of providing charge balance and acting as a structural template. Although in this case there is no chiral influence, the cation largely determines the separation of the metal-oxalate layers, the currently reported limits of which are 49.207 Å and 87.1 Å for \((n\text{-C}_3\text{H}_9)\text{}_4\text{NMnCr(C}_2\text{O}_4\text{)}\text{)}_3\) 29 and \((\text{C}_6\text{H}_5\text{)}\text{}_3\text{PNP(C}_6\text{H}_5\text{)}\text{)}_3\text{MnFe(C}_2\text{O}_4\text{)}\text{)}_3\) 30 respectively.

The crystallinity of \((\text{cation})\text{M}^{\text{III}}\text{M}^{\text{III}}(\text{C}_2\text{O}_4\text{)}\text{)}_3\) compounds is often very poor and hence crystal structures determined from single crystal X-ray data have been published for only seven members of the series 31,32,33,29,34,35. In spite of this, powder X-ray diffraction indicates all these compounds have a similar structure, comprising metal-oxalate honeycomb layers interleaved by layers of a monopositive cation. An example is shown in Figure 1.3.5.

Figure 1.3.5 - Layered structure of \((n\text{-C}_5\text{H}_{11})\text{}_4\text{NMnFe(C}_2\text{O}_4\text{)}\text{)}_3\) viewed perpendicular to the \(c\) axis
As mentioned previously, the metal-trisoxalate units have alternating chiralities and this can be clearly seen in a view of one of the metal-oxalate layers along the c axis, shown in Figure 1.3.6.

The chirality of the metal ions in \((n\text{-C}_5\text{H}_{11})_4\text{MnFe(C}_2\text{O}_4)_3\) also alternates between the layers i.e. Mn(\(\Lambda\)) and Fe(\(\Delta\)) in one layer and Mn(\(\Delta\)) and Fe(\(\Lambda\)) in the next. The same effect has been found in other compounds for which structures have been determined, for example \(\text{PPh}_4\text{MnCr(C}_2\text{O}_4)_3\) \(^{32}\). However, the compound illustrated in Figures 1.3.5 and 1.3.6 crystallises in the orthorhombic space group \(\text{C}_2\text{C}_2\text{C}_1\), in contrast with other published structures which have all been solved in hexagonal space groups, either R3c or P6(3).

One effect of crystallisation of \((n\text{-C}_5\text{H}_{11})_4\text{MnFe(C}_2\text{O}_4)_3\) in the orthorhombic space group is to alter the metal ion site symmetry to \(\text{C}_2\), instead of \(\text{D}_3\). The stacking sequence of the honeycomb layers also influences the space group. Thus, \((n\text{-C}_5\text{H}_{11})_4\text{MnFe(C}_2\text{O}_4)_3\) has an ABAB... stacking sequence such that the
honeycomb 'pores' of each layer are aligned along the c axis. The metal ions are thus also aligned but alternate between Mn and Fe in adjacent layers. See Figure 1.3.7.

By contrast, the compounds crystallising in the hexagonal space groups, R3c and P6(3), have the honeycomb pores staggered between the layers. This again results in an ABAB... stacking sequence for P6(3) but ABCA'B'C'ABC... for R3c where A' indicates a change of chirality at the metal site. These stacking sequences are illustrated in Figure 1.3.8.
Figure 1.3.8 - Honeycomb layer stacking sequences in (a) R3c and (b) P6(3)

A consequence of the generally poor crystallinity already mentioned is that many of the (cation)\(\text{II}\text{III}(\text{C}_2\text{O}_4)_3\) compounds suffer from stacking faults between the layers. The consequence of faulting for the X-ray diffraction profiles has been modelled by
Nuttall et al.\textsuperscript{36} and it has been shown that many (cation)\textsuperscript{II}M\textsuperscript{III}(C\textsubscript{2}O\textsubscript{4})\textsubscript{3} samples are biphasic, containing contributions from both R3c and P\textsuperscript{6}(3) phases.

The magnetic properties of the (cation)\textsuperscript{II}M\textsuperscript{III}(C\textsubscript{2}O\textsubscript{4})\textsubscript{3} series are mainly influenced by the identity of the metal ions. Thus, all MnCr and MnFe derived compounds reported are ferromagnetic and antiferromagnetic respectively.\textsuperscript{33,32,31,34} The mixed valence Fe\textsuperscript{II}Fe\textsuperscript{III} compounds however, while all being ferrimagnetic, exhibit either a compensation point and transition to negative magnetisation or apparently normal ferrimagnetism, depending on the identity of the cation.\textsuperscript{37,38,39}

The majority of cations employed in the synthesis of the (cation)\textsuperscript{II}M\textsuperscript{III}(C\textsubscript{2}O\textsubscript{4})\textsubscript{3} series have been both symmetrical and unsymmetrical tetra-substituted ammonium, phosphonium or arsonium.\textsuperscript{30,40} However, the use of metallocinium cations such as decamethylferrocenium has also been reported.\textsuperscript{41,42}

### 1.4 Scope of the Research

The work described in this thesis concerns the compounds (cation)MnFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3} and (cation)FeFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}. Both these series have been extended by synthesis of examples derived from unsymmetrical alkyltriphenylphosphonium cations, where the alkyl chain ranges from propyl to heptyl inclusive. Structural and magnetic characterisation has been undertaken by powder X-ray diffraction and DC SQUID magnetometry respectively. Variation of synthetic conditions and the consequent effect on the magnetisation of the resultant samples is described.

As mentioned above, the magnetisation of Fe\textsuperscript{II}Fe\textsuperscript{III} derived compounds exhibits a remarkable cation dependence. For this reason, and following on from previous work,\textsuperscript{43} further investigation into PPh\textsubscript{4}FeFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3} and (n-C\textsubscript{4}H\textsubscript{9})\textsubscript{4}NFeFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}, which exhibit normal and compensated ferrimagnetism respectively, has been undertaken. The local structures have been investigated by EXAFS experiments and the local magnetic environment probed with \(\mu\)SR. The magnetic properties of deuterated forms of
PPh₄MnFe(C₂O₄)₃ and PPh₄FeFe(C₂O₄)₃ have been studied with polarised neutron diffraction and the structural temperature-dependence of (n-C₄H₉)₄NFeFe(C₂O₄)₃ investigated with high-resolution powder X-ray diffraction. The modification of the magnetisation of (n-C₄H₉)₄NFeFe(C₂O₄)₃ and PPh₄FeFe(C₂O₄)₃ by dilution with diamagnetic ions is also presented.

Chapter 2 is an introduction to magnetism and also describes the theory underlying the physical techniques used to characterise the compounds described in this thesis. In Chapter 3, the synthesis, and practical aspects of physical techniques are described. Structural details are contained in Chapter 4, while Chapter 5 details the results of magnetic measurements. Chapter 6 summarises the structural and magnetic data.
1.5 References


2) Noid, D. W.; Sumpter, B. G.; Tuzun, R. E. Abstracts of Papers of the American Chemical Society 1997, **213**, 370-COMP.


Chapter 2 - Theory

2.1 Diffraction$^{1,2,3}$

A crystal is a three-dimensional array of atoms which repeats at regular intervals in space. It is therefore convenient to represent the crystal as a regularly repeating array of points i.e. a lattice. Each lattice point has an identical grouping of atoms (or just a single atom) associated with it. This group of atoms is referred to as the basis. The lattice may be defined as the set of points at the ends of the vectors

\[ \mathbf{t} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \]  

where \( n_1, n_2 \) and \( n_3 \) can take all integral values, positive, negative or zero, and \( \mathbf{a}_1, \mathbf{a}_2 \) and \( \mathbf{a}_3 \) are fixed, non-coplanar vectors, known as the base vectors of the lattice. Equation 2.1.1 defines the set of translations defining points in the lattice with identical atomic environments.

The vector definition of a lattice leads to the concept of a unit cell. The unit cell is a parallelepiped whose edges are the vectors \( \mathbf{a}_1, \mathbf{a}_2 \) and \( \mathbf{a}_3 \). The lattice can be considered as an assembly of unit cells, packed together corner to corner to fill all space, with a lattice point at each corner. Such a cell is referred to as a primitive unit cell. It may be that the primitive unit cell is not the most symmetrical that can be defined for the lattice and hence the lattice may be considered as an assembly of larger unit cells but now there will also be lattice points at positions other than the corners of the unit cells.

Lattices generally possess certain elements of symmetry but the symmetry of a crystal structure is not necessarily the same as the symmetry of the lattice on which it is based. Whether it is or not will depend on the arrangement of atoms around each lattice point. In a crystal it may be possible to identify complex symmetry operations, involving translations as well as rotations or reflections which leads to a much greater variety of
possible combinations of symmetry elements, or space groups, for a crystal structure than for a lattice.

Crystals (and lattices) are divided into seven crystal systems, according to the symmetry of the most symmetrical unit cell it is possible to find in the structure. As mentioned previously, it may be possible to find in a lattice a non-primitive unit cell with greater symmetry than the most symmetrical primitive unit cell and consequently the seven crystal sytems are subdivided into fourteen Bravais lattices.

The reciprocal lattice is a useful concept in diffraction theory. Consider a lattice defined by the vectors \( \mathbf{a}, \mathbf{b} \) and \( \mathbf{c} \). The lattice defined by the vectors \( \mathbf{a}^*, \mathbf{b}^* \) and \( \mathbf{c}^* \) is the reciprocal of the first lattice if \( \mathbf{a}^*.\mathbf{a} = \mathbf{b}^*.\mathbf{b} = \mathbf{c}^*.\mathbf{c} = 1 \) and \( \mathbf{a}^*.\mathbf{b} = \mathbf{a}^*.\mathbf{c} = \mathbf{b}^*.\mathbf{a} = \mathbf{b}^*.\mathbf{c} \) etc = 0. Thus the reciprocal lattice can be constructed from the real-space lattice by the relations

\[
\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}, \quad \mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{b} \cdot \mathbf{c} \times \mathbf{a}}, \quad \mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{c} \cdot \mathbf{a} \times \mathbf{b}}
\]

2.1.2

It follows that a reciprocal lattice translation \( \mathbf{d'}_{hkl} \) defined by

\[
\mathbf{d'}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*
\]

2.1.3

is perpendicular to the \((hkl)\) plane of the real-space lattice and has magnitude

\[
||\mathbf{d'}_{hkl}|| = \frac{1}{\mathbf{d}_{hkl}}
\]

2.1.4

Thus a point in the reciprocal lattice represents a set of planes with the Miller indices \((hkl)\) in the real-space lattice.

Elastic scattering of X-rays or neutrons in crystals results from constructive interference or Bragg reflection from the set of lattice planes \((hkl)\) in a direction where there is zero
phase change between beams reflected from adjacent planes. The angle $\theta$ for which reflection occurs is determined by Bragg's law

$$n\lambda = 2dsin\theta$$

2.1.5

where $\lambda$ is the wavelength of the incident radiation, $d$ is the spacing of the lattice planes and $n$ is an integer.

This condition for constructive interference can also be represented geometrically by the Ewald construction. A vector $-k$ is drawn from a point on the reciprocal lattice, $O$, to a point $O'$, and a sphere of radius $|k|$ constructed with $O'$ at its centre. If the sphere passes through another reciprocal lattice point, $G$, then there will be an intense diffracted beam with wavevector $k' = O'G$. This is represented schematically by Figure 2.1.1.

![Ewald sphere construction](image)
The vector \( \mathbf{g} \) from the origin to the reciprocal lattice point \( \mathbf{G} \) is normal to the set of lattice planes with Miller indices \((hkl)\) and is of length \( |\mathbf{g}| = 1/d\_{hkl} \), where \( d\_{hkl} \) is the spacing of the crystal lattice planes. Hence the incident and diffracted beams make equal angles \( \theta \) with the crystal lattice planes and

\[
|\mathbf{g}| = 2 |\mathbf{k}| \sin \theta
\]

i.e.

\[
\lambda = 2d\_{hkl}\sin \theta
\]

The lattice determines the possibility and positions of Bragg reflections. Diffraction experiments measure the positions and intensities of the reflections. Reflection intensities \( I\_{hkl} \) 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 \( I_{hkl} = |F_{hkl}|^2 \). The structure factor \( F_{hkl} \), summing over all \( i \) atoms within the unit cell, is

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

where \( f_i \) is the scattering amplitude in X-ray diffraction and the scattering length in neutron diffraction (more commonly referred to as \( b_j \)). \( x_i, y_i \) and \( z_i \) are the partial coordinates of the atoms within the unit cell and \( W_i \) are the Debye-Waller isotropic temperature factors which result in a reduction in scattered intensity from thermal motions.

In some cases, systematic absences occur \((F_{hkl} = 0)\) as a result of lattice planes in the crystal being arranged such that there is total destructive interference of the diffracted beam.
2.1.1 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 addition, thermal vibrations of the atoms lead to a progressive decrease of intensity with increasing angle of diffraction.

In a single crystal, reflections can be assigned to distinct sets of lattice planes because the crystal will reflect from different sets of planes depending on its orientation. With a powder sample, the individual crystallites adopt all possible orientations, resulting in some peaks in the diffraction pattern being overlaid on others. However, providing the sample is of sufficient crystallinity, the structure can be solved by the method developed by Rietveld\(^4\). In the Rietveld method, an X-ray pattern simulation of a model structure is compared with the observed pattern and the model refined by least-squares methods until the best fit is obtained. The quantity minimised in the least-squares refinement is the residual \( S_y \)

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

where \( w_i = 1/y_i^{\text{obs}} \) and \( y_i \) is the intensity at the \( i \)th step.

Unfortunately, many powder samples have poor crystallinity and a small particle size, which causes broad, poorly defined peaks in the X-ray profile and Rietveld analysis is not possible. These problems are certainly prevalent in the AM\(^{11}\)Fe(C\(_2\)O\(_4\))\(_3\) compounds described in Section 4.3 as they generally precipitate very rapidly from solution. Further problems are associated with the layered nature of these compounds. Firstly, when the powder is mounted in the X-ray sample holder in Bragg-Brentano geometry\(^5\), the individual crystallites tend to adopt a preferred orientation with their c axes aligned parallel to the plate. As a result, reflections from the 0 0 1 set of lattice
planes are more intense than from any other set of planes. In addition, grinding the sample prior to mounting in the holder (which is desirable to ensure homogeneity of the sample) tends to reduce the particle size even further due to the facile cleavage between the layers.

Although the compounds studied in Section 4.3 are not sufficiently crystalline to support full Rietveld analysis, lattice parameters have been determined by the use of LeBail extractions. In this technique, only the profile parameters such as lattice parameters and peak shape and machine variables such as wavelength and zero error are refined by the Rietveld least-squares method. The intensities of the individual peaks are extracted from the data and not modelled. Thus, LeBail extractions may be used for confirmation of the space group and accurate determination of lattice parameters.

2.1.2 Neutron Diffraction

Neutrons are scattered as a result of the interactions with nuclei. Hence there are a number of differences between coherent elastic diffraction of neutrons and that of X-rays. In particular, although the coherent scattering lengths, $b_i$, tend to increase slowly with atomic number, there are large, irregular variations superimposed, so neighbouring elements in the periodic table sometimes have very different scattering lengths. There are also often large differences between isotopes. In addition, the nucleus effectively behaves as a point scatterer to the incident neutrons and hence there is no form factor effect, although, in common with X-rays, there is a progressive decrease of intensity with increasing angle of diffraction due to thermal vibrations of the atoms.

Neutrons are spin 1/2 particles and hence there are also interactions between the neutron's magnetic moment and any electrons with unpaired magnetic moments, resulting in elastic magnetic scattering. Coherent magnetic diffraction (magnetic Bragg diffraction) will occur if there is long-range magnetic order between scattering spins.
With unpolarised neutrons, the nuclear and magnetic scatterings are incoherent, and so the intensities of the nuclear and magnetic diffraction peaks are additive and simplify to the sum of the squared moduli of two terms

$$I_{hkl} = |F_{hkl}|^2 = |F_{N\text{ar}}|^2 + |F_{M\text{at}}|^2$$  \hspace{1cm} \text{(2.1.9)}

where $|F_{N\text{ar}}|^2$ is defined in Equation 2.1.7 above and

$$|F_{M\text{at}}|^2 = \sum q_{j} p_{i} \exp(-2\pi i (h x_{j} + k y_{j} + l z_{j}) \exp(-W_{j}))$$  \hspace{1cm} \text{(2.1.10)}

where $p_{i}$ is the magnetic counterpart to the nuclear scattering length and is 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.

### 2.1.3 Polarised Neutron Diffraction

With polarised neutrons, the nuclear and magnetic scatterings are coherent; their relative phases depend on the orientation of the neutron spins and so the resultant amplitude of a diffraction peak may be the sum or difference of the nuclear and magnetic scattering amplitudes (or something intermediate). In a polarised neutron diffraction experiment, measurements are made in spin-flip (i.e. the reverse of the initial polarisation) or non spin-flip modes. The individual components of the scattering process respond differently to a polarised neutron beam. The coherent and isotope incoherent scattering contribute only to non spin-flip scattering while the nuclear spin incoherent scattering is seen in both the spin-flip and non spin-flip cross-sections. The magnetic part of the scattering will show contributions from neutrons spin-flipped by the magnetic moments of the sample.
Experiments with polarised neutrons, and especially with polarisation analysis, always suffer from intensity problems. The application of multidetectors similar to experiments without polarisation analysis can help to alleviate such problems. Unfortunately, the original method of polarisation analysis (the so-called $//-\perp$ difference method) requires that the polarisation be rotated into a direction parallel to the scattering vector which thus prevents its use with a multidetector. Hence, modern multidetector instruments use three dimensional analysis, or the $xyz$-difference method. In this approach, six measurements are made; spin-flip and non spin-flip in each of three polarisation directions produced by a set of orthogonal Helmholtz coils (hence $xyz$). Combination of these spectra then allows separation of the total scattering into its component parts. A detailed explanation of the $xyz$-difference method may be found in e.g. Schärf.

2.1.4 The Warren Peak Shape Function

Warren showed that the scattering power of a two-dimensional lattice X-ray reflection is given by

$$P_{2\theta} = K m \frac{F^2(1 + \cos^2 2\theta)}{2(sin\theta)^{3/2}} \left[ \frac{L}{\sqrt{\pi \lambda}} \right]^{1/2} F(a) \quad 2.1.11$$

where $K$ is a constant, $m$ is the multiplicity, $F$ is the structure factor, $L$ is the two-dimensional correlation length, $\lambda$ is the wavelength, $a = (2\sqrt{\pi L/\lambda})(\sin\theta - \sin\theta_0)$ and $\theta_0$ is the peak position. $F(a)$ is an integral over the range of interest;

$$F(a) = \int_{-\infty}^{\infty} \exp\left[-(x^2 - a)^2\right] dx \quad 2.1.12$$

In the case of diffraction profiles arising from neutron scattering by two-dimensional magnetic structures, the Warren function may be used to determine the magnetic correlation length within the layers. Section 5.4 describes polarised neutron diffraction
experiments to determine the two-dimensional magnetic correlation lengths of deuterated samples of \( \text{PPh}_4\text{MnFe(C}_2\text{O}_4)_3 \) and \( \text{PPh}_4\text{FeFe(C}_2\text{O}_4)_3 \).

2.2 Extended X-ray Absorption Fine Structure (EXAFS)\(^{10}\)

Extended X-ray Absorption Fine Structure (EXAFS) is a probe of the local structure in solids. The X-rays are tuned to an absorption edge of a particular element in the sample and cause the ejection of a core photoelectron from the atoms of that element. The loss of intensity on transmission of X-rays through a sample of thickness \( x \) is given by

\[
I = I_0 \exp(-\mu x)
\]

where \( \mu \) is the X-ray absorption coefficient. At an absorption edge, \( \mu \) suddenly increases as the X-rays have sufficient energy to overcome the binding energy of the core electron. The ejected photoelectron is backscattered by the neighbouring atoms in the sample. This is shown schematically in Figure 2.2.1.

![Schematic diagram of the radial portion of the photoelectron wave (solid lines) being backscattered by the neighbouring atoms (broken lines)](image)

Figure 2.2.1 - Schematic diagram of the radial portion of the photoelectron wave (solid lines) being backscattered by the neighbouring atoms (broken lines)
The EXAFS spectrum consists of the oscillations of $\mu$ on the high-energy side of the edge caused by the constructive or destructive interference of the outgoing and backscattered waves. Obviously, for an isolated atom, there will be no backscattering and no variation in $\mu$. Analysis of the oscillations yields information on the local structure around the absorbing atom.

The photoabsorption cross section, representing the probability that a photon will be absorbed, is given by

$$\mu(E) = \mu_0(E)[1 + \chi(E)]$$  \hspace{1cm} 2.2.2

where $\mu_0(E)$ is the background absorption from the isolated atom and $\chi(E)$ is the EXAFS modulation of interest. Normalising $\chi(E)$ for background absorption gives

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\text{step height}}$$  \hspace{1cm} 2.2.3

where step height refers to the magnitude of the sharp increase of absorption at the edge. Converting $E$ to $k$ (photoelectron wavevector space) gives $\chi(k)$, which is related to $N_j$, the number of neighbours of type $j$ surrounding the absorbing atom, $r_j$, their distance and $\sigma_j$, their Debye-Waller factors by

$$\chi(k) = \sum_j N_j S_j(k) F_j(k) \left[ \frac{\sin(2kr_j + \phi_0(k))}{kr_j^2} \right] \exp(-2\sigma_j^2k^2)\exp(-2r_j/\lambda,(k))$$  \hspace{1cm} 2.2.4

where $F_j$ is the backscattering amplitude of each neighbouring atom of type $j$ at a distance $r$ from the absorbing atom. $S_j(k)$ is the amplitude reduction factor, incorporated to account for other processes which reduce the EXAFS amplitude such as shake up (excitation of other electrons along with the photoelectron) or shake off...
(ionisation of weakly bound electrons by the photoelectron). $\phi_{ij}(k)$ is the total phase shift experienced by the photoelectron and depends on the photoelectron wavelength, $\lambda_{ij}(k)$, and on the type of scatterers. The EXAFS may be Fourier-transformed into real space and the result is a radial distribution function of neighbouring atoms.

The squares of the Debye-Waller factors $\sigma_j^2$, are the mean square displacements of atoms about their mean positions. Nearest-neighbour distances are dominated by chemical forces and are usually extremely precise and hence $\sigma_j^2$ is small, while correlations with more distant neighbours are progressively less well defined with increasingly large $\sigma_j^2$ generally increases with temperature due to thermal vibrations of the lattice.

In some cases, the single scattering of a photoelectron by its neighbours considered so far is not sufficient to describe the EXAFS spectrum, and multiple scattering effects must be included. Multiple scattering effects become important when the absorbing atom-neighbour-next nearest neighbour angle is around 180°. As Figure 2.2.2 shows, the photoelectron is forward-scattered from the neighbour and next-nearest neighbour unit, before being backscattered and this can have a marked effect on the modulation of the EXAFS.

![Figure 2.2.2 - Schematic of the conditions for multiple scattering.](image)

It should be noted that the discussion of EXAFS presented above is based on the planewave approximation. At low values of k the plane wave approximation is no
longer valid and hence modern EXAFS analysis programs use *curved-wave theory* which is a better representation of the photoelectron wave\textsuperscript{11}. Section 4.4 describes the results of EXAFS experiments on \( \text{(cation)MFe(C}_2\text{O}_4)_3 \) where cation = PPh\(_4\), \((n-C_4H_9)_4N\) and \( M = \text{Mn, Fe}. \)

### 2.3 Magnetism\textsuperscript{3,12,13,14}

Electronic energies of all compounds are perturbed by a magnetic field and acquire a magnetisation. The response to the field is characterised by the magnetic susceptibility \( \chi \).

\[
\chi = \frac{\partial M}{\partial H} \tag{2.3.1}
\]

where \( M \) is the magnetisation and \( H \) is the magnetic field strength.

#### 2.3.1 Diamagnetism

If a sample is placed in a magnetic field \( H \), the field within the material will generally differ from the free space value. The body has therefore become magnetised and, if the density of the magnetic lines of force within the sample is reduced, the substance is said to be diamagnetic. Since this is equivalent to the substance producing a flux opposed to the field causing it, it follows that the substance will tend to move to regions of lower field strength, or out of the field.

Diamagnetism is a property of all matter and arises from the interaction of paired electrons with the magnetic field. Thus all materials have a diamagnetic contribution to their susceptibilities.

The susceptibility of a diamagnetic material is negative, does not depend on field strength and is independent of temperature. Typical values of diamagnetic
susceptibilities are $10^{-6}$ to $10^{-7}$ ergOe$^{-1}$g$^{-1}$. Data from magnetic measurements are usually corrected for diamagnetic susceptibility by subtraction of its value estimated from Pascal’s constants$^{12,15,16}$.

2.3.2 Paramagnetism

A paramagnet concentrates the lines of force from an applied magnetic field and thereby moves into regions of higher field strength. Paramagnetism is a property exhibited by substances containing unpaired electron spins and is generated by the Zeeman perturbation tending to orient magnetic angular momenta in a magnetic field. At room temperature, paramagnetism is usually 1 to 3 orders of magnitude larger than diamagnetism and results in a positive contribution to the magnetic susceptibility, $\chi$.

The magnetisation of a paramagnetic sample containing non-interacting spins follows a Brillouin function$^{12}$ which, in low fields, yields a magnetic susceptibility that is inversely proportional to the temperature in accordance with the Curie Law

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

where $C$ is the Curie constant. It can be calculated that the Curie constant for an orbitally quenched ion is dependent on the number of unpaired electrons and the Landé constant, $g$, for the ion. The curie constant for the spin-only magnetic susceptibility is

$$C = \frac{Ng^2\mu_B^2S(S + 1)}{3k}$$

where $N$ is Avogadro's number, $\mu_B$ is the Bohr magneton, $S$ is the total spin and $k$ is Boltzmann's constant.

The Curie law breaks down either when the spins are not isolated, there is mixing of the
ground-state wavefunction into thermally non-populated excited states or spin-orbit coupling is present. In these cases, if all the energy levels are known, the Van Vleck\textsuperscript{17,12} equation may be used to calculate the susceptibility.

2.3.3 Magnetic Interactions

Two modifications to purely paramagnetic behaviour arise from the parallel (ferromagnetic) or antiparallel (antiferromagnetic) alignment of neighbouring spins through magnetic exchange. Magnetic exchange occurs when magnetic orbitals are close enough to interact.

a) Direct Exchange

Direct exchange is the mechanism responsible for the magnetic interactions in the 3d transition metals. It arises from intra-atomic Coulombic interactions. For example, in Ti (d\textsuperscript{2}), the magnetic orbitals adopt a ferromagnetic alignment in order that the conduction electrons may move through the lattice by occupying empty orbitals in accordance with Hund's rule. By contrast, in Mn (d\textsuperscript{5}), the magnetic orbitals adopt an antiferromagnetic alignment in order that the conduction electrons may move through the lattice in accordance with the Pauli exclusion principle.

b) Indirect Exchange

Indirect exchange is mainly observed in 4f elements. A spin localised on atom \textit{i} interacts with conduction electrons and leads to spin-polarisation. The itinerant, spin-polarised electrons then interact with a spin on atom \textit{j} and create an indirect interaction between spins \textit{i} and \textit{j}. This is the so-called RKKY model\textsuperscript{14}.

c) Super-exchange

Localised spins in insulating magnets, the subject of this thesis, interact through an
intervening ligand via the superexchange mechanism. The simplest view of this interaction is to consider the effect of mixing small amounts of excited states into the orbital ground state of a dimer, represented in Figure 2.3.1 for the ligand 2p orbitals and the metal d orbitals. The ground state is a singlet if the metal ion spins are antiparallel and a triplet if they are parallel (cases a and b in the diagram). If there is partial transfer of some of the ligand electron spin density into a half-filled metal orbital, the resulting excited state is an orbital singlet in case c and a triplet in case d. The remaining ligand electron can now couple with a lone electron on the other adjoining metal ion, resulting in an antiferromagnetic exchange for the singlet case and ferromagnetic for the triplet case.

![Figure 2.3.1 - Illustration of the mixing of orbital states in the superexchange mechanism for a dimer. + and - denote spins up and down respectively.](image)

Qualitative prediction of the nature of superexchange interactions is provided by the Goodenough-Kanamori rules which are based on consideration of alignment and overlap of magnetic orbitals:
Magnetic orbitals with a large overlap result in antiferromagnetic exchange.

Magnetic orbitals which are orthogonal result in ferromagnetic exchange.

Magnetic orbitals which overlap with empty orbitals result in ferromagnetic exchange.

The superexchange interaction between neighbouring magnetic ions in insulators with spins $S_i$ and $S_j$ can be represented by the Hamiltonian

$$H = -2\sum_{i<j}JS_iS_j$$

This is called an isotropic or Heisenberg (see later) Hamiltonian is defined such that negative $J$ refers to antiferromagnetic interactions and positive $J$ to ferromagnetic.

2.3.4 Long-range Magnetic Order

Magnetic superexchange interactions between spins in an extended lattice may result in a transition to long-range order at a critical temperature $T_c$. Various physical techniques may be used to monitor this transition including specific heat, susceptibility, $\mu$SR and neutron diffraction experiments. Measurements from the latter three are presented later in this thesis (Chapter 5).

Ferromagnetic transitions are characterised by parallel alignment of local moments in the lattice. Antiferromagnetic transitions occur as a result of antiparallel alignment. If the moments involved in an antiferromagnetic transition are equal in magnitude, the resultant magnetisation will be zero. If the moments are not equal, due for example to different numbers of unpaired electrons on the magnetic ions, a ferrimagnetic state results, with a remaining uncompensated moment. Weak ferromagnetism, or spin-canting, arises from antiferromagnetic moments that are not aligned exactly antiparallel, but at a small angle.
to each other, again resulting in an uncompensated moment. These four arrangements of spins are represented schematically in Figure 2.3.2.

![Diagram of four arrangements of spins](image)

Figure 2.3.2 - Two-dimensional representations of (a) ferromagnetism, (b) antiferromagnetism, (c) ferrimagnetism and (d) spin canting

A system of interacting spins can be described by the magnetic model Hamiltonian

\[ H = -2 \sum_{i,j} (J_x S_i \cdot S_j + J_y S_i \cdot S_j + J_z S_i \cdot S_j) \] 2.3.5

where the summation is made over neighbouring pairs of spins \( i, j \). If only one spin component takes part in the interaction, the spin dimensionality (or order parameter), \( n \), is one. Similarly, if two or three spin components take part in the interaction, the spin dimensionality is two and three respectively. The case where \( J_x = J_y = J_z \) and \( n = 3 \) is known as the Heisenberg model and is isotropic. \( J_x = J_y \neq 0, J_z = 0 \) characterises the
planar model for \( n = 2 \) and the XY model for \( n = 3 \). \( J_x = J_y = 0, J_z \neq 0 \) and \( n = 1 \) corresponds to the Ising model.

Superexchange interactions in transition metal compounds are usually isotropic but significant anisotropy may be exhibited by certain ions as a result of spin-orbit coupling and crystal field effects. For example, high-spin \( \text{Fe}^{II} \) ions typically show Ising behaviour. The anisotropy of the system may be described by a second term in the model Hamiltonian

\[
H = -2 \sum_{i<j} (J_x S_x^i S_x^j + J_y S_y^i S_y^j + J_z S_z^i S_z^j) - D \sum_i S_z^i \tag{2.3.6}
\]

where \( D \) describes the anisotropy in a uniaxial system. For \( D \to +\infty \) and \( D \to -\infty \), the moments are forced to lie along and perpendicular to the \( z \) axis, respectively.

Spin (\( n \)) and lattice (\( d \)) dimensionalities strongly affect the thermodynamic properties of magnetic systems, as summarised in Table 2.3.1. Thus, no long-range magnetic order can be expected for pure 1D lattices, only the Ising model can undergo magnetic ordering in a 2D lattice and 3D lattices will always order irrespective of spin-dimensionality.

Table 2.3.1 - Effects of spin and lattice dimensionalities on the magnetic ordering

<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></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XY</td>
<td><strong>No long-range order</strong></td>
<td>( \xi \to \infty )</td>
<td></td>
</tr>
<tr>
<td>Heisenberg</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The 2D XY model exhibits a special transition described by Kosterlitz and Thouless \(^{20}\) in which there is a divergence of the correlation length, \( \xi \), at finite temperature in the absence of long-range ordering.
Real layer lattice magnets are best described as quasi two-dimensional spin systems because weak inter-layer exchange interactions, $J'$, act to couple the layers ($J' \ll J$). A transition to long-range 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 approximately described by the model magnetic Hamiltonian presented above. For example, finite positive or negative $D$ values in Equation 2.3.6 describe 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\textsuperscript{13}.

Exact solutions to the Hamiltonian are limited to the two-dimensional Ising model. Interpretations of many real magnetic systems are accomplished by an approximation to magnetic theory known as molecular field (or mean field) theory first postulated by Weiss\textsuperscript{21}.

2.3.5 Molecular Field Theory

The basis of molecular field theory is that the sum of the exchange terms acting on a single spin may be approximated to a mean exchange field which serves to orient the spins while thermal agitation opposes this effect. Below the critical temperature, $T_c$, thermal energy is insufficient to overcome the influence of the internal field, resulting in long-range magnetic order.
Weiss introduced the MFT concept by assuming the existence of an internal field, $H_m$, in a ferromagnet which is proportional to the magnetisation

$$H_m = \lambda M$$  \hspace{1cm} 2.3.7

where $\lambda$ is the Weiss molecular field constant. Assuming the system obeys the Curie law at temperatures above $T_c$, the total magnetic field $H_T$ is the sum of $H_m$ and the external field, $H_{\text{ext}}$

$$H_T = H_{\text{ext}} + H_m$$  \hspace{1cm} 2.3.8

and hence

$$M/H_T = M/(H_{\text{ext}} + \lambda M) = C/T$$  \hspace{1cm} 2.3.9

which gives

$$M[1 - (\lambda C/T)] = C H_{\text{ext}}/T$$  \hspace{1cm} 2.3.10

or

$$\chi = M/H_{\text{ext}} = C/(T - \lambda C)$$  \hspace{1cm} 2.3.11

When $H_{\text{ext}} = 0$, $M$ is not zero at $T_c$ (because of $H_m$) and so Equation 2.3.10 yields $T_c = \lambda C$ and

$$\chi = C/(T - T_c)$$  \hspace{1cm} 2.3.12

or

$$\chi = C/(T - \theta)$$  \hspace{1cm} 2.3.13

which is the Curie-Weiss law.
In the case of antiferromagnets, the molecular field theory approach is similar but the system is considered to consist of two interpenetrating sublattices. Each sublattice is uniformly magnetised with spins aligned parallel, but the spins on one sublattice are antiparallel to those on the other. It is assumed that spins on one sublattice (A) interact only with spins on the B sublattice, and vice versa and hence the field \( H_A \) acting on the A sublattice is

\[
H_A = H_{\text{ext}} + H_{\text{int}B} = H_{\text{ext}} - \lambda M_B
\]

while similarly,

\[
H_B = H_{\text{ext}} - \lambda M_A
\]

where the negative signs indicate the antiferromagnetic exchange.

Again assuming the system obeys the Curie law above the critical temperature \( T_c \), the magnetisations of the sublattices are given by

\[
M_A = \frac{[C(H_{\text{ext}} - \lambda M_B)/T]/2}{2.3.16}
\]

\[
M_B = \frac{[C(H_{\text{ext}} - \lambda M_A)/T]/2}{2.3.16}
\]

and the total magnetisation \( M = M_A + M_B \). Following procedures similar to the ferromagnetic case again results in a modified Curie or Curie-Weiss law

\[
\chi = C/(T + \theta')
\]

where, in this case, \( \theta' = \lambda C/2 \).

Inspecting Equations 2.3.13 and 2.3.17 it can be seen that molecular field theory predicts \( T_c/\theta = 1 \) for ferromagnets and \( T_c/\theta' = -1 \) for antiferromagnets, neither of which are generally found experimentally.
The common empirical usage of the Curie-Weiss law writes it as

\[ \chi = C/(T - \theta) \]  \hspace{1cm} 2.3.18

and a plot of \( \chi^{-1} \) against \( T \) at temperatures above \( T_c \) yields a straight line from whose slope and intercept on the x-axis \( C \) and \( \theta \) may be determined. Positive values of \( \theta \) indicate dominant ferromagnetic interactions while negative \( \theta \) indicates antiferromagnetic interactions.

Néel extended the two sublattice model of molecular field theory to the case where the spins on the sublattices are uncompensating to predict ferrimagnetism. Néel's model was the general spinel \( \text{AB}_2\text{O}_4 \) lattice containing one magnetic ion distributed between the two sublattices. In zero external field, the internal fields are

\[ H_A = n(\alpha \lambda M_A + \epsilon \mu M_B) \]  \hspace{1cm} 2.3.19

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

where \( \lambda \) and \( \mu \) are the fractional occupancies of the magnetic ion in the A and B sites respectively, \( \alpha \) and \( \beta \) are 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 A and B sublattice magnetisations and \( \epsilon = \pm 1 \) (= -1 for antiferromagnetism or ferrimagnetism). The molecular field energy is given by

\[ W = -(\lambda M_A H_A)/2 - (\mu M_B H_B)/2 \]  \hspace{1cm} 2.3.20

and solving this equation for a minimum at absolute zero gives four possible solutions for the saturated spontaneous magnetisation, \( M_s \). Consideration of the variation in magnetisation near \( T_c \) 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 for the six types are shown in Figure 2.3.3.
Figure 2.3.3 - Illustration of Néel ferrimagnetic order types
The magnetisation of types M, R and V has a finite slope at absolute zero \( \frac{\partial M}{\partial T} \neq 0 \) which violates the third law of thermodynamics and hence these types are not found in real systems. Many of the (cation)Fe\(^{II}\)Fe\(^{III}\)(C\(_2\)O\(_4\))\(_3\) compounds described in this thesis conform to the Néel type N model (Section 5.2.2).

It is important to note that molecular field theory, although providing a good description of the basic features of ferro-, ferri- and antiferromagnets, ignores short-range interactions and fails to give a good description of a magnetic system in the region of \( T_c \). In addition while the theory provides a reasonable description of 3-dimensional systems, it fails completely for systems of lower dimension.

2.3.6 Weak Ferromagnetism

Weak ferromagnetism (or spin-canting) arises as a result of antiferromagnetically coupled spins not aligning exactly antiparallel but with a small tilting of the moments towards each other. In a two-sublattice antiferromagnet below \( T_c \), canting results in a small ferromagnetic moment in the direction of the canting. By considering a general expression for the free energy in terms of the sublattice magnetisations, Dzyaloshinskii\(^{23}\) has shown that the term

\[
d \cdot [S_i \times S_j]
\]

where \( d \) is a constant vector, is allowed under certain symmetry conditions. In fact, spin canting is only possible if the lack of collinearity of the spins does not change the magnetic symmetry of the crystal.

Two mechanisms of spin canting have been found. The first requires the presence in the crystal of two non-equivalent sites for the magnetic ions. The combined action of the different crystal field acting at each site, together with the spin orbit coupling, results in non-parallel directions of the magnetic anisotropy for the non-equivalent sites. The second mechanism takes into account the effects of spin orbit coupling and the
superexchange interaction. It can be shown that, under certain symmetry constraints, a term with the antisymmetric form of Equation 2.3.21 can arise.

2.3.7 Spin Glasses

Another magnetic state that has been the subject of considerable study in recent years is that of the spin glass. A spin glass may be defined as a random, mixed interacting (i.e. ferromagnetic and antiferromagnetic) magnetic system characterised by a random, yet cooperative, freezing of spin orientations at a well-defined temperature $T_f$. Below $T_f$, there is a metastable state with no long-range magnetic order. One consequence of the lack of long-range order is an absence of Bragg peaks in neutron diffraction patterns of spin glasses.

2.3.8 Percolation

Percolation is relevant to a number of problems in condensed matter physics. A few examples are:

- The flow of a fluid through a porous material (e.g. rock) is dependent on the number and length of open channels within the material. If there are a few short channels distributed at random, the fluid cannot pass through. At some point, there will be enough connected channels to allow the fluid to flow. This point is called the percolation threshold.

- In a mixture of conducting and insulating material, the question arises as to how conductivity varies with the concentration of the conducting component. At the percolation threshold, there are sufficient connections between the conducting elements to allow conduction through the material.
A magnetic material diluted with a non-magnetic component will, at the percolation threshold, cease to exhibit long-range order due to the non-magnetic component 'blocking' the formation of such order. Sections 5.2.3 - 5.2.5 describe the dilution of the Fe\(^{II}\) and Fe\(^{III}\) sites in (cation)Fe\(^{II}\)Fe\(^{III}\)(C\(_2\)O\(_4\))\(_3\) with diamagnetic Zn\(^{II}\) and Ga\(^{III}\) respectively.

In a lattice, percolation can occur at lattice sites or at bonds between the sites. The percolation threshold (or critical concentration \(p_c\)) for lattice sites is the point where there are enough immediate neighbours in contact to allow uninterrupted passage through the lattice by moving from one site to the next. In the case of bond percolation, the threshold is the point where there is a path through the lattice by following bonds. These two cases, for two-dimensional lattices, are shown schematically in Figure 2.3.4.

Figure 2.3.4 - Representation of (a) site percolation and (b) bond percolation for a two-dimensional lattice.

For magnetic lattices, the critical concentration depends on the lattice dimensionality, \(d\), the magnetic coordination number, \(z\), and, for two-dimensional lattices, also on the spin dimensionality. Critical concentrations have been calculated for lattices of various topography. These are presented below as Table 2.3.2.
Table 2.3.2 - Critical site and bond probabilities $p_c(s)$ and $p_c(b)$ for some common lattices

<table>
<thead>
<tr>
<th>Lattice</th>
<th>$z$</th>
<th>$p_c(s)$</th>
<th>$p_c(b)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Honeycomb</td>
<td>3</td>
<td>0.700</td>
<td>0.653</td>
</tr>
<tr>
<td>Square</td>
<td>4</td>
<td>0.590</td>
<td>0.500</td>
</tr>
<tr>
<td>Triangular</td>
<td>6</td>
<td>0.500</td>
<td>0.347</td>
</tr>
<tr>
<td>Diamond</td>
<td>4</td>
<td>0.425</td>
<td>0.388</td>
</tr>
<tr>
<td>Simple cubic</td>
<td>6</td>
<td>0.307</td>
<td>0.247</td>
</tr>
</tbody>
</table>

2.4 The $\mu$SR Technique$^{25}$

$\mu$SR stands for muon spin rotation, relaxation or resonance or just muon spin research and involves implanting muons into a sample and observing the effects of the local environment on the muon behaviour. Sections 5.3.1 and 5.3.2 describe $\mu$SR experiments on $(n-C_4H_9)_4NFeFe(C_2O_4)_3$ and $PPh_4MnFe(C_2O_4)_3$.

Essentially, a muon acts as a sensitive magnetometer. Once inside a material, it responds to the effects of local magnetic and hyperfine fields, and its resonance and precession signals allow these fields to be measured.

Muons are a decay product from pions according to the scheme

$$\pi^+ \rightarrow \mu^+ + \nu_\mu$$  \hspace{1cm} 2.4.1

Conservation of angular momentum ensures that all the muons can be produced with their spins polarised longitudinally along the beam (Figure 2.4.1).
Muons are unstable particles with a half-life of 2.2 μs. They decay according to the scheme

\[ \mu^+ \rightarrow e^+ + \nu_e + v_\mu \]  

2.4.2

It is the positron produced in this process which is detected in the μSR experiment as it is preferentially emitted in the polarisation direction of the muon at the moment of its decay (Figure 2.4.2)

The polarisation of the muon tends to be preserved during the whole process of thermalisation (dissipation of the beam energy by collisions etc.) and implantation (eventual trapping in the material either by chemical combination or trapping in a lattice). However, a fraction of muons may experience prompt depolarisation during thermalisation, from spin-flip collisions with radiolysis products or by the formation of muonium, \( \mu^+e^- \). These processes give rise to the so-called missing fraction of the initial asymmetry. The formation of muon radicals in phenyl compounds is well documented and may also add to the missing fraction.
In the three-body decay of Figure 2.4.2 the positron has maximum energy when it is ejected in line with the two neutrinos, and therefore in line with the instantaneous spin orientation of the parent muon. The highest energy positrons exhibit an anisotropy of close to 100%. The angular distribution of the positron intensity is given by

\[ P(\theta) = 1 + \cos \theta \]  

where \( a = 1 \) for positrons of the highest energy and \( a = 1/3 \) averaged over all positron energies. See Figure 2.4.3.

**Figure 2.4.3** - Angular distribution \( P(\theta) = 1 + \cos \theta \) of the positron intensity for the positrons of the highest energy (asymmetry parameter \( a = 1 \)), and averaged over all positron energies (\( a = 1/3 \)).

### 2.4.1 Muon Spin Rotation

Muon spin *rotation* is depicted in cartoon form in Figure 2.4.4. A bunch of muons (or a single muon) is implanted in the sample at time zero and with an initial polarisation close to 100% (Figure 2.4.4(a)).
If the muons experience a magnetic field that is not parallel with their initial polarisation, they will begin to precess around it at the corresponding Larmor frequency, given by the muon magnetogyric ratio

\[ \gamma_\mu/2\pi = 136 \text{ kHzmT}^{-1} \]

as illustrated in Figure 2.4.4(b). This description is valid whether the field is externally applied or generated internally within the sample. If the muons adopt equivalent sites within the sample, and experience identical fields, they will precess in phase and the magnitude of their initial polarisation will be preserved. On the other hand, any variation of the local field between occupied sites will cause out of phase precession and hence a gradual loss of muon polarisation and, after muon decay, a corresponding loss in asymmetry of the emitted positrons. This time-dependence of the positron asymmetry can be described by a transverse relaxation function \( G(t) \).

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Figure 2.4.4 - Illustration of (a) implantation, (b) precession and (c) decay in the \( \mu \)SR experiment
In *longitudinal geometry*, detectors placed forward and backward of the sample will detect positrons at the following rates

\[ N(t)_F = N_0 \exp(-t/\tau_\mu)(1 + a_0 G_x(t)\cos\omega t) \quad 2.4.5 \]

\[ \alpha N(t)_B = N_0 \exp(-t/\tau_\mu)(1 - a_0 G_x(t)\cos\omega t) \quad 2.4.6 \]

where \( \alpha \) is a measure of the differences in efficiency and solid angle coverage of the detectors. Hence the time-dependence of the muon polarisation is extracted as

\[ a_0 G_x(t)\cos\omega t = \frac{N_F - \alpha N_B}{N_F + \alpha N_B} \quad 2.4.7 \]

\( G_x(t) \) is determined by the magnetic field distribution and dynamics at the muon site. In the static limit, depolarisation is assumed to result from a continuous and isotropic Gaussian distribution of static fields

\[ P(B_x) = \frac{\gamma \mu}{\sqrt{2\pi} \sigma_x} \exp\left[-\frac{\gamma^2 B_x^2}{2\sigma_x^2}\right] \quad 2.4.8 \]

giving a Gaussian form for \( G_x(t) \)

\[ G_x(t) = \exp\left(-\frac{1}{2} \sigma_x^2 t^2\right) \quad 2.4.9 \]

where \( \sigma_x^2 = \gamma^2 \left\langle B_\mu^2 \right\rangle \).
Should the random fields fluctuate (either because the muon is hopping or due to fluctuation of the local moments) with a correlation time $\tau_c$ such that $\tau_c \sigma_x \ll 1$, $G_x(t)$ has the Lorentzian form

$$G_x(t) = \exp(-\lambda t)$$

where $\lambda = \sigma_x^2 \tau_c$.

### 2.4.2 Muon Spin Relaxation

In muon spin relaxation, $G_x(t)$ is the longitudinal relaxation function in zero or longitudinal applied fields. A muon implanted in a sample in zero field will not precess in the absence of an internal local field. Any coherent precession in the muon polarisation indicates the presence of a coherent internal field i.e. long-range order. Any decay in the initial asymmetry indicates components of field perpendicular to the initial muon polarisation. The time evolution of the longitudinal component of the muon polarisation is

$$P_x(t) = \cos^2 \delta_i + \sin^2 \delta_i \cos \omega t$$

In a polycrystalline sample, only 2/3 of muons will contribute to the precession as 1/3 will have their polarisation parallel to the internal field. A characteristic of static moments (and muons) is the recovery of the asymmetry to 1/3 of its initial value as $t \to \infty$. Averaging over all field directions, the distribution becomes

$$\langle P_x(t) \rangle = \frac{1}{3} + \frac{2}{3} \langle \cos \omega t \rangle$$

giving the Kubo-Toyabe form of the relaxation function.
\[ G_z(t) = \frac{1}{3} + \frac{2}{3} (1 - \sigma_z^2 t^2) \exp(-\frac{1}{2} \sigma_z^2 t^2) \] 2.4.13

where \( \sigma_z^2 = \gamma_\mu^2 \langle B_x^2 \rangle = \gamma_\mu^2 \langle B_y^2 \rangle = \gamma_\mu^2 \langle B_z^2 \rangle \). Again, fluctuations in the random fields (either because the muon is hopping or due to fluctuations of the local moments), with a correlation time \( \tau_c \) such that \( \tau_c \sigma_x << 1 \), result in the Lorentzian form

\[ G_z(t) = \exp(-\lambda t) \] 2.4.14

where \( \lambda = \sigma_z^2 \tau_c \). Fluctuations in the local fields also result in exponential decay of the \( 1/3 \) tail in the asymmetry.

2.4.3 Repolarisation

Applying longitudinal fields of increasing strength to the sample in a \( \mu \)SR experiment may recover some or all of the lost initial asymmetry by forcing more local fields to align with the original muon polarisation. This process is known as repolarisation. Repolarisation curves may be used to determine the proportion of muons that adopt a stationary spin state as, in the limit of fast fluctuations, no recovery of initial asymmetry will be observed. In some cases information may also be deduced about the nature of the missing fraction. For example the presence of muonium may be detected when the applied field is large enough to decouple the electron and muon spins.

2.4.4 Continuous and Pulsed \( \mu \)SR

There are some differences between \textit{pulsed} \( \mu \)SR and \textit{continuous} \( \mu \)SR. In the pulsed technique, a bunch of muons is implanted in the sample over a short period of time (~ 80 ns). Time zero is then taken as the centre of the pulse. In the limit of high precession frequencies, there will be appreciable phase difference between precessing muons from the start and end of the pulse and a corresponding loss of asymmetry in the
polarisation of the detected positrons. This places an upper limit on the measurable frequencies approximately the inverse of the pulse width. Similarly, fast relaxation processes that decay quickly with respect to the pulse width cannot be measured accurately.

In the continuous technique, muons are implanted singly in the sample and hence time zero is known accurately for each muon. Therefore, higher rates of precession or relaxation can be measured but the requirement that only one muon be present in the sample at a time, in order to achieve unambiguous detection of positrons, necessarily means that data acquisition rates are slower than in the pulsed technique.
2.5 References

Chapter 3 Experimental

3.1 Synthesis

All chemicals used in the syntheses were purchased from Aldrich and used as supplied. Water was distilled in the laboratory.

3.1.1 (cation)MFe(C₂O₄)₃

In general, (cation)MFe(C₂O₄)₃ samples presented in this thesis were synthesised by a modified version of the 'ionic' procedure reported by Nuttall¹. 1.5 mmol of the bromide salt of the cation was dissolved in 5 ml methanol or water (depending on the solubility of the salt). The resulting solution was mixed with 5 ml of an 0.2 M solution of Fe(NO₃)₃·9H₂O in water. If necessary, the mixed solutions were allowed to cool to room temperature to dissipate the heat produced by mixing methanol and water. 1 mmol of solid FeSO₄·7H₂O or MnCl₂·4H₂O, as appropriate, was added to the solution and agitated until dissolved. Typically six drops of 1 M HCl solution was added to suppress the formation of oxalate complexes of the divalent metal. Finally, 5 ml of a 0.6 M solution of oxalic acid was added, resulting in the formation of green (Fe²⁺Fe³⁺ compounds) or yellow (Mn²⁺Fe³⁺ compounds) microcrystals over a timescale ranging from a few seconds to several hours. The product was collected by suction filtration and washed twice with 20 ml of water and twice with 20 ml of methanol. The product was dried in vacuo over blue silica gel and stored in the dark.

As already mentioned, oxalate complexes of the divalent metal were competing by-products in these reactions, identified by extra peaks in the powder X-ray diffraction patterns. Acidifying the solution helped to suppress the formation of these impurities but, the longer the precipitation time, the more likely was their presence. Addition of more acid, in an attempt to further inhibit formation of the impurity, also resulted in complete suppression of formation of the desired product. Consequently,
samples of the binary metal oxalates were prepared by mixing solutions of
MnCl₂·4H₂O or FeSO₄·7H₂O and oxalic acid and the X-ray diffraction profiles of all
samples of (cation)MFe(C₂O₄)₃ were checked against these to ensure absence of the
impurities.

It should be noted that there was considerable variation in the ease of synthesis,
particularly for the CₙHₙ(2n+1)₄N₃MFe(C₂O₄)₃ (n = 3 - 7) series. Those compounds
containing the smaller cations (n = 3 to 5) formed readily, the n = 5 derivatives
apparently being the most crystalline, with the largest crystallite size. By contrast,
many preparations based on the n = 6,7 cations yielded largely amorphous products.
Obviously, an upper size limit on the cation able to be accommodated between the
metal-trisoxalate layers decribed in Chapter 1 is to be expected; in the
(cation)MFe(C₂O₄)₃ series formed from tetra-alkylammonium substituted cations, only
the compounds derived from (CₙHₙ(2n+1))₄N (n = 3 - 5) have been synthesised,
preparations of (C₆H₁₃)₄NMFe(C₂O₄)₃ being unsuccessful. Among the compounds
derived from alkyltriphenylphosphonium salts C₇H₁₁PPh₃MnFe(C₂O₄)₃ was the most
synthetically challenging, an additional problem being that the cation tended to react
with MnCl₂·4H₂O. In this case, therefore, the divalent metal salt was added last to the
reaction vessel.

Although, as stated in the previous paragraph, synthesis of CₙHₙ(2n+1)₄PPh₃MFe(C₂O₄)₃
(n = 3 - 5) was relatively facile, it was found that variation of the synthetic conditions
could have a dramatic effect on the magnetic behaviour of the resultant compounds.
Therefore, exact details of syntheses, where they vary from the foregoing, are presented
with the discussion of magnetometry in Section 5.2.2.

In part due to the problem of divalent metal oxalate formation, attempts to slow down
the precipitation rate in order to produce single crystals were unsuccessful. Samples of
improved crystallinity were synthesised but these were always heavily contaminated
with divalent metal oxalate except in the case of (n-C₄H₉)₄NFeFe(C₂O₄)₃. A sample of
this compound was synthesised by allowing a methanol solution of FeSO₄·7H₂O to
diffuse slowly into an aqueous solution of K$_3$Fe(C$_2$O$_4$)$_3$·5H$_2$O, and (C$_4$H$_9$)$_4$NBr to which eight drops of 1M HCl solution had been added. The arrangement, shown in Figure 3.1.1, was kept in the dark for two months while the precipitate formed. In this case alone, the required product formed on the walls of the outer tube while the ferrous oxalate formed on the inner tube and frit. The product was collected, washed, dried and stored as previously described.

![Figure 3.1.1 - Arrangement for synthesis of (n-C$_4$H$_9$)$_4$NFeFe(C$_2$O$_4$)$_3$](image)

3.1.2 (n-C$_4$H$_9$)$_4$Nzn$_x$Fe$_{(1-x)}$Fe(C$_2$O$_4$)$_3$

This series of compounds were synthesised by the 'block' method described by Nuttall$^1$. Standard aqueous solutions of K$_3$Fe(C$_2$O$_4$)$_3$·5H$_2$O, FeSO$_4$·7H$_2$O, ZnCl$_2$ and (n-C$_4$H$_9$)$_4$NBr were made and used immediately. The ZnCl$_2$ solution, in a 10 ml volumetric flask, had 10 drops 1 M HCl added to dissolve the zinc chloride. 5 ml of a 0.2 M solution of K$_3$Fe(C$_2$O$_4$)$_3$·5H$_2$O was mixed with the required proportions of 0.2 M solutions of FeSO$_4$·7H$_2$O and ZnCl$_2$. The solutions were filtered after 30 minutes to remove any precipitated ferrous oxalate and 5 ml of a 0.3 M solution of (n-C$_4$H$_9$)$_4$NBr was added to the filtrate. The precipitated (n-C$_4$H$_9$)$_4$Nzn$_x$Fe$_{(1-x)}$Fe(C$_2$O$_4$)$_3$ was collected by suction filtration after about 60 minutes, washed with water and methanol and stored in the dark, in vacuo, over blue
silica gel. The compounds ranged in colour from dark green for 
\((n-C_4H_9)_4NFeFe(C_2O_4)_3\) to yellow for \((n-C_4H_9)_4NZnFe(C_2O_4)_3\). Although it has 
been found that the 'ionic' method\(^1\) was the superior synthetic technique for undoped 
(cation)\(M^{II}M^{III}(C_2O_4)_3\) compounds, in the case of Zn doped samples, elemental 
analysis proves this method results in more zinc in the compound than intended (see 
Section 4.2.2).

3.1.3 (cation)\(FeGa_xFe(1-x)(C_2O_4)_3\) (cation = \((n-C_4H_9)_4N, PPh_4\))

In the case of the (cation)\(FeGa_xFe(1-x)(C_2O_4)_3\) series, the best synthetic technique was 
found to be the 'ionic' method. The 'block' technique resulted in very little modification 
of magnetic behaviour and no discernible colour change in the range of compounds. It is 
supposed this is due to the gallium trisoxalate unit being unable to form unless there is 
an excess of free oxalate in the solution. Standard solutions of the starting materials 
were made and used immediately; aqueous for \(Fe(NO_3)_3\cdot9H_2O, FeSO_4\cdot7H_2O, \) 
\(Ga(NO_3)_3\) and \((n-C_4H_9)_4NBr\) and 50:50 water:methanol for \(PPh_4Br\). 5 ml of a 0.2 M 
solution of \(Fe(NO_3)_3\cdot9H_2O\) was mixed with the required proportions of 0.2 M 
solutions of \(FeSO_4\cdot7H_2O\) and \(Ga(NO_3)_3\) and 5 ml of a 0.3 M solution of the cation. 6 
drops of 1 M HCl were added to suppress the formation of ferrous oxalate. 5 ml of a 
0.6 M solution of \(C_2H_2O_4\cdot2H_2O\) was added to the mixed solutions. The precipitated 
(cation)\(FeGa_xFe(1-x)(C_2O_4)_3\) was collected by suction filtration after about 60 minutes, 
washed with water and methanol and stored in the dark, \(in vacuo\), over blue silica gel. The 
compounds ranged in colour from dark green for (cation)\(FeFe(C_2O_4)_3\) to yellow for 
(cation)\(FeGa(C_2O_4)_3\).

3.1.4 \(PPh_4(d-20)MnFe(C_2O_4)_3\) and \(PPh_4(d-20)FeFe(C_2O_4)_3\)

The samples of \(PPh_4(d-20)MnFe(C_2O_4)_3\) and \(PPh_4(d-20)FeFe(C_2O_4)_3\) used for the 
first polarised neutron diffraction experiments (Section 5.4) were synthesised by 
C J Nuttall. The larger sample of \(PPh_4(d-20)FeFe(C_2O_4)_3\) used for the second 
experiment was synthesised by the same method\(^3\), as follows.
Preparation of the PPh$_4$(d-20) cation as its bromide salt was by a modification of the method of Michaelis$^4$ and Dodanov$^5,6$. 3.7 g (0.15 mol) of Mg turnings were placed in a 250 ml three-neck round-bottom flask with a magnetic stirrer bar. The flask and its contents, together with all other glassware required for the preparation, were dried in a drying cabinet overnight at ~ 85$^\circ$ C. The following day, the flask was fitted with a equal pressure dropping funnel and an ether condenser and the assembly clamped on a magnetic stirrer. While the glassware was still warm, the flask was flushed with a flow of nitrogen dried by passing it through a column of anhydrous CaCl$_2$. When the flask had cooled, the nitrogen flow was reduced and a small crystal of iodine and 50 ml of dried ether (KOH) were added. 24.9 g (0.15 mol) of deuterated bromobenzene were dissolved in 50 ml of ether and added to the dropping funnel. The magnetic stirrer was started and a few drops of the bromobenzene solution were added to the round-bottom flask. After about 5 minutes, the Grignard reaction started, indicated by the loss of colour in the reaction mixture. The remaining bromobenzene solution was added dropwise to the round-bottom flask over about 90 minutes. Stirring was continued for another 30 minutes after all the solution had been added.

The solution was cooled in an ice bath and 10 g (0.036 mol) of deuterated triphenylphosphine was dissolved in 100 ml ether and added to the round-bottom flask via the dropping funnel. The nitrogen flow was discontinued and oxygen was bubbled through the reaction mixture while stirring continued. After approximately 5 minutes, a gluey brown residue congealed. Magnetic stirring became impossible and agitation of the residue was continued with a glass rod. The oxygen flow was maintained during this procedure and the ice-bath maintained at 0$^\circ$ C. 20 ml aliquots of ether were added periodically to replace that lost by evaporation. The brown residue gradually became dough-like and started to break up and form a white powder of PPh$_4$(d20)OH. Mechanical stirring was resumed and conversion to the hydroxide was complete in approximately 2 hours. The oxygen flow was discontinued and a solution of 23.75 ml HBr (48%) in 51.25 ml H$_2$O was added dropwise to the vessel, resulting in vigorous
quenching of the remaining Grignard reagent and production of white crystals of PPh$_4$(d20)Br.

The reaction mixture was again cooled in an ice-bath and the ether layer decanted and discarded. The aqueous layer was washed with 50 ml aliquots of ether until the decanted ether layer was colourless. The remaining mixture was stored overnight in a refrigerator, filtered and washed with ether. The crude product was recrystallised from 100 ml boiling D$_2$O (yield 48%).

3.1.4.2 PPh$_4$(d-20)FeFe(C$_2$O$_4$)$_3$

7.474 g of Fe(NO$_3$)$_3$.9H$_2$O and 5.143 g of FeSO$_4$.7H$_2$O were each dissolved in 20 ml H$_2$O and the resulting solutions mixed. A solution of 8.131 g of PPh$_4$(d20)Br in 20 ml methanol was added to the iron solutions and the resulting solution was allowed to cool to dissipate the heat produced by mixing methanol and water. 6.997 g of C$_2$O$_4$H$_2$.2H$_2$O was dissolved in 60 ml H$_2$O and this solution added to the iron/cation solution. Precipitation of PPh$_4$(d-20)FeFe(C$_2$O$_4$)$_3$ was very slow and the product was collected after 2 days. The yield was 7.32 g (53.8%). A powder X-ray diffraction profile of the compound confirmed it was free of ferrous oxalate.

3.1.5 Elemental Analysis

Metal analysis was carried out at the Microanalytical Department, University of Manchester and C,H,N,P analysis at the Chemistry Department, University College London.
3.2  Powder X-ray Diffraction

Powder X-ray diffraction profiles were collected at room temperature on a Siemens D500 X-ray diffractometer set in Bragg-Brentano reflection geometry. The diffractometer was fitted with a primary monochromator providing Cu Kα1 radiation (λ = 1.5406 Å). Samples were mounted on a flat ceramic plate. Soller slits of 0.3°, 0.3°, 0.3° and 0.15° were used in positions I, II, III and IV respectively; positions I and II being between the X-ray source and the sample and positions III and IV between the sample and the detector. Initial characterisation scans were carried out over the two-theta range 5° to 45° with a step size of 0.04° and a count time of 2 s per step. Profiles used for determination of lattice parameters were recorded using the same range and step size but a count time of 50 s per step.

3.3  High Resolution Powder X-ray Diffraction

High resolution powder X-ray diffraction profiles of (n-C₄H₉)₄NFeFe(C₂O₄)₃ were recorded at various temperatures between 5 K and 60 K on instrument BM16 at the ESRF in Grenoble. The sample was sealed in a glass capillary of 1 mm internal diameter and the capillary mounted in the instrument's cryostat and aligned with the X-ray beam. The capillary was rotated to reduce the effects of preferred orientation. As shown in Figure 3.3.1, the X-ray beam was monochromated by a double crystal sagitally focussing monochromator. The wavelength was 0.800615 Å, calibrated with NBS silicon. The analyser comprises nine Ge(1 1 1) crystals separated by ~ 2° intervals and data were recorded in continuous scanning mode.
Following data collection, the counts from the nine detectors were rebinned and normalised using local software to give the equivalent step scan between $1^\circ$ - $21^\circ$ two-theta, with a step size of 0.003°.

3.4 Extended X-ray Absorption Fine Structure (EXAFS)

Temperature dependent K–edge EXAFS spectra were recorded on Station 8.1 at the SRS in Daresbury. The instrument was used in transmission mode which relies on the measurement of photons using ion chambers to measure the incident ($I_0$) and transmitted ($I_1$) beam intensities, where the absorption coefficient (Section 2.2), $\mu(E) = \ln(I_0/I_1)$. A double Si crystal monochromator is employed to step scan the desired energy range as well as to allow the second crystal to be slightly detuned from the first, to suppress any higher harmonics in the X-ray beam. A typical experimental arrangement is illustrated in Figure 3.4.1.
The ion chambers are filled to a pressure of 1000 mbar with mixtures of Ar and Ne relevant to the edge being excited, the first chamber, \( I_0 \), being filled with a mixture of gas to absorb 20% of the incident flux and the second chamber 80%. Calibration is carried out with a thin foil of the element of interest.

The sample was mixed with the zeolite MCM41 in an approximately 50:50 ratio to prevent excessive X-ray absorption, and the mixture formed into a 20 mm diameter disc in a pellet press at a pressure of 0.5 tonne for 30 s. The prepared disc was mounted inside the instrument refrigerator and aligned in the X-ray beam. Data were collected up to the monochromator angular range corresponding to approximately 15 Å\(^{-1}\). Total counting times for each temperature were around 45 min. The data were normalised, background-subtracted and converted into wavevector vs absorption coefficient using the local programs ECALIB\(^9\) and EXBROOK\(^10\).

3.5 Polarised Neutron Diffraction\(^11\)

Polarised neutron diffraction experiments were carried out on fully deuterated samples of \( \text{PPh}_4(\text{d}-20)\text{FeFe}(\text{C}_2\text{O}_4)_3 \) and \( \text{PPh}_4(\text{d}-20)\text{MnFe}(\text{C}_2\text{O}_4)_3 \) on the D7 instrument at the ILL in Grenoble. A schematic of the instrument is shown in figure 3.5.1.
As the figure shows, the white, unpolarised neutron beam is monochromated and polarised before passing through a spin flipper which allows the initial polarisation direction to be defined. The beam then passes through a chopper (used in time-of-flight experiments) and through the sample. A set of three Helmholtz coils (not shown) around the sample position produce magnetic fields in orthogonal directions. This allows the incident neutron spin direction to be defined. Six measurements are made; spin-flip and non spin-flip for each of the three magnetic field directions generated by the Helmholtz coils. Analysis of the neutrons subsequently flipped by the sample
allows separation of the total diffraction pattern into its nuclear coherent, spin incoherent and magnetic coherent contributions.

Powder samples were accurately weighed into a cylindrical vanadium can and this was mounted inside the instrument's cryostat and aligned in the neutron beam. The same sample can was used for all samples. Data were collected over the range $0.15 \leq Q \leq 2.51$ Å$^{-1}$. Full xyz polarisation analysis was carried out with a total count time at each temperature of 12 hours for the PPh$_4$(d–20)MnFe(C$_2$O$_4$)$_3$ sample (4.9 g) and 24 hours for the PPh$_4$(d–20)FeFe(C$_2$O$_4$)$_3$ sample (3.58 g). In order to improve the statistics and reduce the count time, a larger sample of PPh$_4$(d–20)FeFe(C$_2$O$_4$)$_3$ (7.3 g) was synthesised (Section 3.1.4) and data recorded at more temperatures. It was found that statistics comparable to the smaller sample could be obtained in 16 hours but it was concluded that further improvement would not be possible as the limiting factor was now the instrument rather than the sample. The data were corrected for background and non-sample scattering and normalised using a calibration with a known amount of vanadium.

### 3.6 Muon Spin Relaxation (μSR)

#### 3.6.1 Rutherford–Appleton Laboratory

Temperature-dependent muon spin relaxation data were collected on the MuSR instrument on the pulsed muon source at the Rutherford-Appleton Laboratory in Oxfordshire for the compounds $(n$-$C_4H_9)_4$NFeFe(C$_2$O$_4$)$_3$, PPh$_4$FeFe(C$_2$O$_4$)$_3$ and PPh$_4$MnFe(C$_2$O$_4$)$_3$. The layout of the instrument is shown in Figure 3.6.1.
The polarised muon beam is directed into the sample which is mounted (in a cryostat, if required) in the centre of two banks of positron detectors. Helmholtz coils (not shown in the figure) allow the application of magnetic fields either longitudinal or transverse to the muon beam polarisation.

Samples were formed into 16 mm diameter discs in a pellet press at a pressure of 2 t for 60 s. The discs were held in place on a silver plate by a covering sheet of Mylar and the assembly mounted in the MuSR cryostat. The forward and backward detectors of the instrument were calibrated for differences in geometry and efficiency by recording spectra in a 20 G transverse field at temperatures around 100 K i.e. well above the magnetic ordering temperatures.
The form of this calibration is

\[ a_0 = \frac{F - \alpha B}{F + \alpha B} \]

where \(a_0\) is the initial muon polarisation asymmetry and \(F, B\) are the signals from the forward and backward detectors respectively. \(\alpha\) is the calibration variable. The local software UDA\textsuperscript{12} allows fine-tuning of \(\alpha\) by a further variable, 'balance'.

Due to temperature control and other instrument problems, only zero-field depolarisation measurements were made on \(\text{PPh}_4\text{MnFe(C}_2\text{O}_4)_3\). However, measurements were made on \((\text{nC}_4\text{H}_9)_4\text{NFeFe(C}_2\text{O}_4)_3\) at various temperatures in longitudinal fields between 100 G and 2 kG. A total of approximately 6 million events was collected at each temperature (an event being the detection of a muon-decay positron).

3.6.2 Paul Scherrer Institut\textsuperscript{13}

Temperature dependent muon spin relaxation data were collected on the Dolly instrument on the continuous muon source at the Paul Scherrer Institut in Switzerland for the compound \((\text{nC}_4\text{H}_9)_4\text{NFeFe(C}_2\text{O}_4)_3\). The layout of the instrument is shown in Figure 3.6.2. The sample is aligned in the polarised muon beam (in a cryostat, if required) and the muons and their decay positrons are monitored by a system of eight detectors.
As shown in the figure, the detection system comprises a muon detector M, five positron detectors (forward F, backward B, up U, down D and right R) and two veto detectors (B_{veto} and F_{veto}). The backward veto detector consists of a hollow scintillator pyramid with a 7 mm x 7 mm hole facing the muon counter M. B_{veto} collimates the muon beam and rejects muons (and decay positrons) missing the aperture. The forward veto detector rejects muons (and decay positrons) which have not stopped in the sample. Magnetic fields can be applied either longitudinal or transverse to the muon beam polarisation and three pairs of orthogonal Helmholtz coils provide correction for the Earth's magnetic field.

A 16 mm diameter disc of the sample was formed in a pellet press at a pressure of 2 t for 60 s. The disc was mounted on a silver mounting plate and held in place by non-magnetic adhesive tape. This assembly was mounted inside the Dolly cryostat. Measurements were made at various temperatures in zero applied field. Scan times were around 45 minutes, giving approximately 5.5 million events. No calibration runs were performed as the local data analysis software Minfit\textsuperscript{14} takes account of differences in the efficiency and geometry of the detectors.
3.7 Magnetometry

Temperature and magnetic field dependence of all compounds studied in this work were measured with a Quantum Design MPMS7 SQUID magnetometer. 10 - 20 mg of the sample was mounted in a gel cap which was held inside a plastic drinking straw. Three empty gel caps were inserted into the straw above and below the sample to provide a constant background in the range of the measurement coils. The straw was attached to the instrument's sample stick by adhesive Kapton tape. The measurement protocol was the same for all samples; the remanent field at the instrument setting of 0 G was determined at 100 K by applying small fields and measuring the SQUID response until a figure of $< 10^{-6}$ emu was achieved. This field was then taken as zero. The sample was cooled in zero field and the magnetisation measured while warming in 100 G (allowing for the zero field correction) to 60 K. The sample was then cooled in the 100 G field and the magnetisation measured while warming to 300 K. The data were corrected for sample diamagnetism by use of Pascal's constants\textsuperscript{15,16,17}. 

88
3.8 References


4) Michaelis, D.; Soden, V. *Annales* 1885, **229**, 298.


9) Dent, A. J.; Mosселmans, J. F. W. *An Introduction to EXAFS Data Analysis*; CCLRC: Daresbury Laboratory.


Chapter 4 - Chemical and Structural Characterisation

4.1 General

This chapter presents chemical and structural characterisation of a range of \((\text{cation})\text{M}^{II}\text{F}^{III}(\text{C}_2\text{O}_4)_3\) compounds. Ten new compounds in this series have been synthesised derived from alkyltriphenylphosphonium cations, where the alkyl chain extends from propyl to heptyl inclusive, and the divalent metal ions \(\text{M}^{II}\) and \(\text{Fe}^{II}\). In addition, three series of compounds doped with diamagnetic ions have been synthesised, namely \((n-C_4\text{H}_9)_4\text{NZn}_x\text{Fe}_{(1-x)}\text{Fe}(\text{C}_2\text{O}_4)_3\), \((n-C_4\text{H}_9)_4\text{NFeGa}_x\text{Fe}_{(1-x)}(\text{C}_2\text{O}_4)_3\) and \(\text{PPh}_4\text{FeGa}_x\text{Fe}_{(1-x)}(\text{C}_2\text{O}_4)_3\). All compounds synthesised have been structurally characterised by powder X-ray diffraction. The temperature dependence of the local structure of \((n-C_4\text{H}_9)_4\text{NFeFe}(\text{C}_2\text{O}_4)_3\), \(\text{PPh}_4\text{FeFe}(\text{C}_2\text{O}_4)_3\), \((n-C_4\text{H}_9)_4\text{NMnFe}(\text{C}_2\text{O}_4)_3\) and \(\text{PPh}_4\text{MnFe}(\text{C}_2\text{O}_4)_3\) has been studied by EXAFS and the temperature dependence of the bulk structure of \((n-C_4\text{H}_9)_4\text{NFeFe}(\text{C}_2\text{O}_4)_3\) by high resolution powder X-ray diffraction.

4.2 Elemental Analysis

4.2.1 \(C_n\text{H}_{(2n+1)}\text{PPh}_3\text{MFe}(\text{C}_2\text{O}_4)_3\) \((n = 3 - 7)\)

Found and calculated values of elemental analysis are presented in Tables 4.2.1 and 4.2.2. It can be seen from Table 4.2.1 that all the \(\text{Fe}^{II}\text{Fe}^{III}\) compounds are deficient in iron. It is common for the \((\text{cation})\text{M}^{II}\text{M}^{III}(\text{C}_2\text{O}_4)_3\) compounds to be deficient in the divalent metal and also show a variation in the trivalent metal content\(^1,2,3\). Mössbauer spectroscopy on \((n-C_4\text{H}_9)_4\text{NFeFe}(\text{C}_2\text{O}_4)_3\) and \(\text{PPh}_4\text{FeFe}(\text{C}_2\text{O}_4)_3\) has indicated the \(\text{Fe}^{II}/\text{Fe}^{III}\) ratio to be 47:53 and 40:60 respectively for these two compounds\(^4\). Four of the \(\text{Mn}^{II}\text{Fe}^{III}\) compounds shown in Table 4.2.2 also exhibit these characteristics; there is
a deficiency in Mn\textsuperscript{II} and variation in the Fe\textsuperscript{III} content. In the case of C\textsubscript{7}H\textsubscript{11}PPh\textsubscript{3}MnFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3} however, the value for Mn\textsuperscript{II} content is higher than expected.
As explained in Section 3.1.1, the cation reacted with MnCl\textsubscript{2}·4H\textsubscript{2}O during the synthesis and the high Mn content is probably due to a small amount of the product of this reaction remaining trapped in the lattice. In spite of this, the structural and magnetic properties of C\textsubscript{7}H\textsubscript{11}PPh\textsubscript{3}MnFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3} are similar to the other compounds in the series.

Table 4.2.1 - Elemental analysis of C\textsubscript{n}H\textsubscript{(2n+1)}PPh\textsubscript{3}FeFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3} (n = 3 to 7)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percentage by Weight</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>C\textsubscript{3}H\textsubscript{7}PPh\textsubscript{3}FeFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}</td>
<td>Calculated</td>
<td>47.61</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>48.37</td>
</tr>
<tr>
<td>C\textsubscript{4}H\textsubscript{9}PPh\textsubscript{3}FeFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}</td>
<td>Calculated</td>
<td>48.38</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>49.51</td>
</tr>
<tr>
<td>C\textsubscript{5}H\textsubscript{11}PPh\textsubscript{3}FeFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}</td>
<td>Calculated</td>
<td>49.12</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>50.25</td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{13}PPh\textsubscript{3}FeFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}</td>
<td>Calculated</td>
<td>49.82</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>50.73</td>
</tr>
<tr>
<td>C\textsubscript{7}H\textsubscript{15}PPh\textsubscript{3}FeFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}</td>
<td>Calculated</td>
<td>50.50</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>51.77</td>
</tr>
</tbody>
</table>
Table 4.2.2 - Elemental analysis of C\textsubscript{n}H\textsubscript{(2n+1)}PPh\textsubscript{3}MnFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3} (n = 3 to 7)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percentage by Weight</th>
<th>Element</th>
<th>C</th>
<th>H</th>
<th>P</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{3}H\textsubscript{7}PPh\textsubscript{3}MnFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}</td>
<td>Calculated</td>
<td>47.68</td>
<td>3.26</td>
<td>4.55</td>
<td>8.08</td>
<td>8.21</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>48.34</td>
<td>3.17</td>
<td>4.69</td>
<td>6.44</td>
<td>8.49</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{4}H\textsubscript{9}PPh\textsubscript{3}MnFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}</td>
<td>Calculated</td>
<td>48.44</td>
<td>3.48</td>
<td>4.46</td>
<td>7.91</td>
<td>8.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>49.53</td>
<td>3.57</td>
<td>4.70</td>
<td>6.51</td>
<td>7.82</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{5}H\textsubscript{11}PPh\textsubscript{3}MnFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}</td>
<td>Calculated</td>
<td>49.18</td>
<td>3.70</td>
<td>4.37</td>
<td>7.76</td>
<td>7.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>49.93</td>
<td>3.95</td>
<td>4.53</td>
<td>6.18</td>
<td>8.22</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{13}PPh\textsubscript{3}MnFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}</td>
<td>Calculated</td>
<td>49.89</td>
<td>3.91</td>
<td>4.29</td>
<td>7.61</td>
<td>7.73</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>50.30</td>
<td>4.00</td>
<td>4.52</td>
<td>6.67</td>
<td>7.99</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{7}H\textsubscript{15}PPh\textsubscript{3}MnFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}</td>
<td>Calculated</td>
<td>50.57</td>
<td>4.11</td>
<td>4.21</td>
<td>7.46</td>
<td>7.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>49.37</td>
<td>4.09</td>
<td>4.09</td>
<td>7.81</td>
<td>7.30</td>
<td></td>
</tr>
</tbody>
</table>

4.2.2 \((n-C_4H_9)_4NZn_xFe_{(1-x)}Fe(C_2O_4)_3\)

As mentioned in Chapter 3, the 'block' synthetic technique was found to be the best for the \((n-C_4H_9)_4NZn_xFe_{(1-x)}Fe(C_2O_4)_3\) compounds. Table 4.2.3 shows reasonable agreement between calculated and found values although, in common with the undoped (cation)FeFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3} compounds, the Fe content is low in each case. In addition, there is some variation in the Zn content.
Table 4.2.3 - Elemental analysis for representative \( (n-C_4H_9)_4NZn_xFe(1-x)Fe(C_2O_4)_3 \) compounds synthesised by the 'block' method

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percentage by Weight</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>( (n-C_4H_9)<em>4NZn</em>{0.1}Fe_{0.9}Fe(C_2O_4)_3 )</td>
<td>Calculated</td>
<td>42.68</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>42.79</td>
</tr>
<tr>
<td>( (n-C_4H_9)<em>4NZn</em>{0.2}Fe_{0.8}Fe(C_2O_4)_3 )</td>
<td>Calculated</td>
<td>42.61</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>42.50</td>
</tr>
<tr>
<td>( (n-C_4H_9)<em>4NZn</em>{0.3}Fe_{0.7}Fe(C_2O_4)_3 )</td>
<td>Calculated</td>
<td>42.55</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>42.62</td>
</tr>
<tr>
<td>( (n-C_4H_9)<em>4NZn</em>{0.4}Fe_{0.6}Fe(C_2O_4)_3 )</td>
<td>Calculated</td>
<td>42.48</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>42.40</td>
</tr>
<tr>
<td>( (n-C_4H_9)<em>4NZn</em>{0.5}Fe_{0.5}Fe(C_2O_4)_3 )</td>
<td>Calculated</td>
<td>42.35</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>42.82</td>
</tr>
<tr>
<td>( (n-C_4H_9)_4NZnFe(C_2O_4)_3 )</td>
<td>Calculated</td>
<td>42.09</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>42.58</td>
</tr>
</tbody>
</table>

For comparison, Table 4.2.4 shows the metal content of two samples synthesised by the 'ionic' method. In this case, the Zn content is much higher than expected and the deficiency in the Fe content is greater than in the compounds synthesised by the 'block' method. This has a dramatic effect on the magnetic behaviour of these compounds which is discussed further in Section 5.2.2.
Table 4.2.4 - Elemental analysis for representative $(n{-}C_4H_9)_4NZN_xFe_{(1{-}x)}Fe(C_2O_4)_3$

compounds synthesised by the 'ionic' method

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percentage by Weight</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(n{-}C_4H_9)<em>4NZN</em>{0.2}Fe_{0.8}Fe(C_2O_4)_3$</td>
<td>Calculated</td>
<td>Fe 16.21 Zn 2.11</td>
</tr>
<tr>
<td>Found</td>
<td>14.31 3.66</td>
<td></td>
</tr>
<tr>
<td>$(n{-}C_4H_9)<em>4NZN</em>{0.4}Fe_{0.6}Fe(C_2O_4)_3$</td>
<td>Calculated</td>
<td>Fe 14.37 Zn 4.2</td>
</tr>
<tr>
<td>Found</td>
<td>12.01 6.55</td>
<td></td>
</tr>
</tbody>
</table>

4.2.3 $(n{-}C_4H_9)_4NFexFe_{(1{-}x)}(C_2O_4)_3$

Elemental analysis for the $(n{-}C_4H_9)_4NFexFe_{(1{-}x)}(C_2O_4)_3$ series (Table 4.2.5) shows a consistently low Ga content and high Fe content. As explained in Chapter 3, it was only the 'ionic' synthetic technique that resulted in any discernible modification of the parent compound (colour or magnetic behaviour) and it is concluded that the Ga deficiency is due to a similar barrier to the formation of gallium trisoxalate.
Table 4.2.5 - Elemental analysis for representative \((n-C_4H_9)_4NFega_{x}Fe_{(1-x)}(C_2O_4)_3\) compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percentage by Weight</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>((n-C_4H_9)<em>4NFega</em>{0.2}Fe_{0.8}(C_2O_4)_3)</td>
<td>Calculated</td>
<td>C 42.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H 5.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N 2.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe 16.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ga 2.25</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>C 43.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H 5.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N 2.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe 16.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ga 1.05</td>
</tr>
<tr>
<td>((n-C_4H_9)<em>4NFega</em>{0.6}Fe_{0.4}(C_2O_4)_3)</td>
<td>Calculated</td>
<td>C 42.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H 5.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N 2.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe 12.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ga 6.68</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>C 40.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H 5.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N 2.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe 14.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ga 4.11</td>
</tr>
<tr>
<td>((n-C_4H_9)_4NFega(C_2O_4)_3)</td>
<td>Calculated</td>
<td>C 41.8</td>
</tr>
<tr>
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<td></td>
<td>H 5.74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N 2.22</td>
</tr>
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<td></td>
<td></td>
<td>Fe 8.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ga 11.03</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>C 41.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H 5.69</td>
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<tr>
<td></td>
<td></td>
<td>N 2.15</td>
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<tr>
<td></td>
<td></td>
<td>Fe 10.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ga 9.45</td>
</tr>
</tbody>
</table>

4.2.4 PPh\(_4\)FeGa\(_x\)Fe\(_{(1-x)}\)(C\(_2\)O\(_4\))\(_3\)

The PPh\(_4\)FeGa\(_x\)Fe\(_{(1-x)}\)(C\(_2\)O\(_4\))\(_3\) series show a similar trend to the other Ga-doped compounds in that the Ga content is lower than expected in all cases. The Fe content, however, does not show a consistent trend across the series, being low for the \(x = 0.2, 0.4\) and 0.6 compounds and high for the \(x = 0.8\) and 1.0 compounds (Table 4.2.6).
Table 4.2.6 - Elemental analysis for representative PPh₄FeGaₓFe₁₋ₓ(C₂O₄)₃ compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percentage by Weight</th>
<th>Element by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>PPh₄FeGa₀.₂Fe₀.₈(C₂O₄)₃</td>
<td>Calculated</td>
<td>50.19</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>51.97</td>
</tr>
<tr>
<td>PPh₄FeGa₀.₄Fe₀.₆(C₂O₄)₃</td>
<td>Calculated</td>
<td>50.00</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>51.89</td>
</tr>
<tr>
<td>PPh₄FeGa₀.₆Fe₀.₄(C₂O₄)₃</td>
<td>Calculated</td>
<td>49.81</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>51.54</td>
</tr>
<tr>
<td>PPh₄FeGa₀.₈Fe₀.₂(C₂O₄)₃</td>
<td>Calculated</td>
<td>49.62</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>50.28</td>
</tr>
<tr>
<td>PPh₄FeGa(C₂O₄)₃</td>
<td>Calculated</td>
<td>49.43</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>48.93</td>
</tr>
</tbody>
</table>

4.3 Crystal Structure

4.3.1 Lattice Parameters of CₙH(2n+1)PPh₃MFe(C₂O₄)₃ (n = 3 to 7)

As mentioned in Chapter 1, crystal structures have been determined for seven (cation)M⁺⁺M⁺⁺⁺(C₂O₄)₃ compounds from single crystal X-ray data and three of these are (cation)MnFe(C₂O₄)₃ compounds; (n-C₄H₉)$_n$NMnFe(C₂O₄)₃, (n-C₅H₁₁)$_n$NMnFe(C₂O₄)₃ and PPh₄MnFe(C₂O₄)₃. By contrast, no crystal structures based on single crystal X-ray data have yet been published for any (cation)Fe⁺⁺Fe⁺⁺⁺(C₂O₄)₃ compounds. However, powder X-ray diffraction indicates that all the (cation)M⁺⁺M⁺⁺⁺(C₂O₄)₃ compounds have a similar layered structure. A
comparison of part of the powder X-ray diffraction pattern of two of the new compounds synthesised in this work, namely C_{6}H_{13}PPh_{3}PMnFe(C_{2}O_{4})_{3} and C_{5}H_{11}PPh_{3}FeFe(C_{2}O_{4})_{3}, and that of a powder sample of (n-C_{5}H_{11})_{4}NMnFe(C_{2}O_{4})_{3} is shown in figure 4.3.1.

Figure 4.3.1(a) - Powder XRDs of C_{6}H_{13}PPh_{3}PMnFe(C_{2}O_{4})_{3} (solid line) and (n-C_{5}H_{11})_{4}NMnFe(C_{2}O_{4})_{3} (dotted line). The arrows indicate the 00/ peaks.

Figure 4.3.1(b) - Powder XRDs of C_{5}H_{11}PPh_{3}FeFe(C_{2}O_{4})_{3} (solid line) and (n-C_{5}H_{11})_{4}NMnFe(C_{2}O_{4})_{3} (dotted line). The arrows indicate the 00/ peaks.
Figure 4.3.1 illustrates the problem of preferred orientation when diffraction data are collected in flat plate geometry, particularly for the alkyltriphenylphosphonium derived compounds. The layered nature of the compounds results in reflections from the indicated $0 0 l$ set of lattice planes being much more intense than those from all other sets of planes. It is also clear from Figure 4.3.1 that the crystallinity of all three compounds is rather poor. The reflections are broad, their shapes have unusual hkl dependencies and they exhibit considerable asymmetry at low angle. These effects are indicative of layer-disorder in the compounds as demonstrated by Nuttall\textsuperscript{8}. The progressive fall-off in peak intensity with two-theta also indicates that the compounds are not fully crystalline. It is generally true that compounds containing the unsymmetrical cations $C_nH_{(2n+1)}PPH_3$ ($n = 3$ to $7$) are less crystalline than those formed from symmetrical cations such as $(n-C_4H_9)_4N$ and PPh$_4$. As a consequence of the poor crystallinity, determination of lattice parameters by the usual method of finding the peak positions and refining the unit cell was not possible. Various peak-fitting programs were tried, including WinFit\textsuperscript{9}, ABFfit\textsuperscript{10} and MacDiff\textsuperscript{11}, but none was able to reliably deconvolute sufficient peaks into their constituent reflections to enable unit cell refinement. For this reason, the $c$ axes were determined by finding the positions of the strong $0 0 l$ peaks using the program MacDiff and calculation from the Bragg equation (Section 2.1). The $a$ and $b$ axes were then determined by carrying out LeBail extractions (Section 2.1.1) using the program GSAS\textsuperscript{12}, by fixing the previously calculated value of $c$ and allowing $a$ and $b$ to vary.

As explained in Chapter 1, the fact that compounds of this type suffer from stacking faults generally results in contributions to the diffraction pattern from two phases, in the space groups R3c and P6(3). LeBail extractions were attempted using both these space groups together but it was found that $a$ of the two phases differed considerably, whereas previous work has shown that $a(R3c) = a(P6(3)) \pm 0.01 \text{ Å}^8$. Attempts to constrain $a$ to the same value for both phases were unsuccessful and it should be noted that the relationship between the two space groups was determined for systems containing symmetrical cations and a greater variation in lattice parameters between the two phases might be expected for unsymmetrical cations due to the possibility of
differences in the packing arrangement of the cations between the two stacking sequences ABAB... and ABCABC... However, it is also likely that the fitting program varied the lattice parameters between the two phases in attempting to fit the asymmetric peak shapes. Thus the space group P6(5), which includes all the reflections from R3c and P6(3), was used for the extraction in all cases except those of C$_7$H$_{15}$PPh$_3$MnFe(C$_2$O$_4$)$_3$ and C$_7$H$_{15}$PPh$_3$FeFe(C$_2$O$_4$)$_3$. The best extractions achieved for these latter compounds were in the orthorhombic space group C$_{2}2_{1}$2. Other (cation)M$_{III}$M$^{III}$(C$_2$O$_4$)$_3$ compounds have been found to crystallise in this space group, notably (n-C$_5$H$_{11}$)$_4$NFeFe(C$_2$O$_4$)$_3$$^4$ and (n-C$_5$H$_{11}$)$_4$NMnFe(C$_2$O$_4$)$_3$.$^6$ The effect of crystallisation in C$_{2}2_{1}$2 is that the metal-trisoxalate site symmetry is changed from C$_3$ (for P6(5)) to C$_2$. The relationship of the crystallographic axes of the two space groups to the hexagons of the honeycomb layer is illustrated in Figure 4.3.2.

![Figure 4.3.2 - Relationship between the crystallographic axes of C$_{2}2_{1}$2 and P6(5)](image)

An example LeBail extraction, for C$_3$H$_7$PPh$_3$MnFe(C$_2$O$_4$)$_3$, is shown in Figure 4.3.3.
Figure 4.3.3 - Le Bail extraction for $C_3H_7PPh_3MnFe(C_2O_4)_3$ in the P6(5) space group. The tie marks indicate positions of the expected Bragg reflections.

The refined unit cell parameters for the series $C_nH_{(2n+1)}PPh_3MnFe(C_2O_4)_3$ and $C_nH_{(2n+1)}PPh_3FeFe(C_2O_4)_3$ (n = 3 to 7) are presented in Table 4.3.1. The parameters for $(n-C_4H_9)_4NMnFe(C_2O_4)_3$, $PPh_4FeFe(C_2O_4)_3$ and $PPh_4FeFe(C_2O_4)_3$, determined by Nuttall, and for $(n-C_4H_9)_4NFeFe(C_2O_4)_3$, grown by slow diffusion (Section 3.1.1), are also included. It has been reported before that cation disorder in the (cation)$M^{II}M^{III}(C_2O_4)_3$ series results in a doubling of the a and b axes, particularly in the case of compounds containing $PPh_4$, and this is also true of compounds containing the alkyltriphenylphosphonium cations.
Table 4.3.1 - Lattice parameters for (cation)MFe(C2O4)3 compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space Group</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3H7PPh3FeFe(C2O4)3</td>
<td>P6(5)</td>
<td>18.64(5)</td>
<td>56.92(3)</td>
<td></td>
</tr>
<tr>
<td>C4H9PPh3FeFe(C2O4)3</td>
<td>P6(5)</td>
<td>18.62(3)</td>
<td>57.76(2)</td>
<td></td>
</tr>
<tr>
<td>C5H11PPh3FeFe(C2O4)3</td>
<td>P6(5)</td>
<td>18.49(9)</td>
<td>60.9(5)</td>
<td></td>
</tr>
<tr>
<td>C6H13PPh3FeFe(C2O4)3</td>
<td>P6(5)</td>
<td>18.81(5)</td>
<td>62.9(5)</td>
<td></td>
</tr>
<tr>
<td>C7H15PPh3FeFe(C2O4)3</td>
<td>C2221</td>
<td>16.82(3)</td>
<td>31.32(2)</td>
<td>22.1(1)</td>
</tr>
<tr>
<td>(n-C4H9)4NFeFe(C2O4)3</td>
<td>R3c</td>
<td>9.39(1)</td>
<td>53.75(5)</td>
<td></td>
</tr>
<tr>
<td>PPh4FeFe(C2O4)3</td>
<td>P6(5)</td>
<td>18.76(2)</td>
<td>57.1(1)</td>
<td></td>
</tr>
<tr>
<td>C3H7PPh3MnFe(C2O4)3</td>
<td>P6(5)</td>
<td>18.96(2)</td>
<td>56.22(5)</td>
<td></td>
</tr>
<tr>
<td>C4H9PPh3MnFe(C2O4)3</td>
<td>P6(5)</td>
<td>18.81(1)</td>
<td>57.24(5)</td>
<td></td>
</tr>
<tr>
<td>C5H11PPh3MnFe(C2O4)3</td>
<td>P6(5)</td>
<td>18.76(1)</td>
<td>59.3(3)</td>
<td></td>
</tr>
<tr>
<td>C6H13PPh3MnFe(C2O4)3</td>
<td>P6(5)</td>
<td>18.90(3)</td>
<td>60.8(2)</td>
<td></td>
</tr>
<tr>
<td>C7H15PPh3MnFe(C2O4)3</td>
<td>C2221</td>
<td>16.1(5)</td>
<td>30.4(8)</td>
<td>21.63(2)</td>
</tr>
<tr>
<td>(n-C4H9)4NMnFe(C2O4)3</td>
<td>P6(5)</td>
<td>9.47(1)</td>
<td>53.5(1)</td>
<td></td>
</tr>
<tr>
<td>PPh4MnFe(C2O4)3</td>
<td>P6(5)</td>
<td>18.87(2)</td>
<td>56.84(5)</td>
<td></td>
</tr>
</tbody>
</table>

The 00l peaks in the powder X-ray diffraction patterns for the compounds CnH(2n+1)PPh3MFe(C2O4)3 (n = 3 to 7) shift to lower angle with increasing size of the cation, as expected, corresponding to an increase in the c axis and greater interlayer separation. Figure 4.3.4 illustrates this effect for the lowest angle 00l reflection (006 for P6(5) and 002 for C2221) at approximately 9° 20.
Figure 4.3.4(a) - Lowest angle 00/ peak for $C_nH_{(2n+1)}PPh_3MnFe(C_2O_4)_3$ ($n = 3$ to 7)

Figure 4.3.4(b) - Lowest angle 00/ peak for $C_nH_{(2n+1)}PPh_3FeFe(C_2O_4)_3$ ($n = 3$ to 7)
The intensity variation in the reflections shown in Figure 4.3.4 is ascribed to differences in the amount of preferred orientation caused by varying crystallite size between the samples; larger plate-like crystallites would be more prone to adopt a preferred orientation than smaller particles and result in enhanced intensity from the 00/ set of planes. This is consistent with the apparent level of crystallinity noted in the syntheses described in Section 3.1.1. The variation of intensities follows the same trend with respect to the alkyl chain length of the cation in both series; the intensity decreases from C₃ to C₄, increases to C₅ and then decreases again through C₆ and C₇.

Comparison of the increase in interlayer separation, calculated from c/6 for P6(5) compounds and c/2 for c22/₁ compounds, for the two series highlights a similar dependence on the alkyl chain length of the cation. In both series, the increase in alkyl chain length gives rise to the well-known alternation effect whereby increasing the number of carbons in the alkyl chain from even to odd has a greater effect on the interlayer separation than from odd to even. See Figure 4.3.5.

![Graph](image_url)

**Figure 4.3.5** - C axis vs alkyl chain length for CₙH₂₃₋₁PPh₃MnFe(C₂O₄)₃ (dotted line) and CₙH₂₃₋₁PPh₃FeFe(C₂O₄)₃ (solid line) (n = 3 to 7)
Figure 4.3.5 also illustrates that the interlayer separation in the MnFe series is consistently smaller than the analogous compounds in the FeFe series. This effect has been reported previously for compounds derived from the same metal ions but different cations\textsuperscript{14}. The difference is explained by consideration of the ionic radii of Mn\textsuperscript{II} and Fe\textsuperscript{II}. As the radius of Mn\textsuperscript{II} is larger than that of Fe\textsuperscript{II}, the honeycomb 'pore' size in the MnFe series is slightly larger than the FeFe series. Consequently the cation is able to penetrate further into the metal-trisoxalate layer and hence the interlayer separation decreases. The similarity of the variation in interlayer separation between the two series indicates that the templating effect (and hence the orientation) of each cation is the same for both compounds derived from it. This is also illustrated by comparison of the powder X-ray diffraction profiles for each pair of compounds. For example, Figure 4.3.6 shows a section of the profiles of $\text{C}_4\text{H}_9\text{PPh}_3\text{MnFe(C}_2\text{O}_4\text{)}_3$ and $\text{C}_4\text{H}_9\text{PPh}_3\text{FeFe(C}_2\text{O}_4\text{)}_3$. It is clear the profiles are very similar, again indicating the cation is adopting the same orientation in both compounds.

![Figure 4.3.6 - Powder X-ray diffraction profiles for $\text{C}_4\text{H}_9\text{PPh}_3\text{MnFe(C}_2\text{O}_4\text{)}_3$ (solid line) and $\text{C}_4\text{H}_9\text{PPh}_3\text{FeFe(C}_2\text{O}_4\text{)}_3$ (dotted line)](image)

Figure 4.3.6 also provides further evidence for the generally poor crystallinity of the
alkytriphenylphosphonium derived compounds; the high background indicates a large amorphous component.

Table 4.3.1 shows the a and b axes also exhibit a dependence on the alkyl chain length of the cation. The a axis decreases for the first three members of each series and increases for the fourth member. There is a dramatic decrease for the fifth member but, in this case, the honeycomb layer is distorted by crystallisation in the $C222_1$ space group. Again this indicates that the pair of compounds derived from each cation are structurally very similar.

4.3.2 Lattice Parameters of Doped Compounds

As mentioned previously, compounds containing symmetrical cations such as $(n-C_4H_9)_4N$ and $PPh_4$ tend to be more crystalline than those containing the unsymmetrical alkyltriphenyl cations. Thus determination of lattice parameters for these compounds was achieved by determining peak positions using the program MacDiff$^{11}$ and refining the unit cell with Refcel$^{15}$. In common with the alkyltriphenylphosphonium-containing compounds described in Section 4.3.1, the fact that there are stacking faults between the layers of compounds of this type results in contributions to the X-ray diffraction profiles from reflections in the space groups $R3c$ and $P6(3)$. Thus, the space group $P6(5)$, which includes all the reflections from $R3c$ and $P6(3)$ was used for the refinements.

4.3.3 $(n-C_4H_9)_4NZn_xFe_{(1-x)}Fe(C_2O_4)_3$

Figure 4.3.7 shows the powder X-ray diffraction profiles of $(n-C_4H_9)_4NZn_{0.2}Fe_{0.8}Fe(C_2O_4)_3$ and $(n-C_4H_9)_4NZn_{0.8}Fe_{0.2}Fe(C_2O_4)_3$. It is clear that the contribution from the $P6(3)$ space group becomes more intense with the increasing zinc dilution and this is ascribed to the differing solubilities of iron and zinc.
Figure 4.3.7(a) - Powder X-ray diffraction profile of \((n-C_4H_9)_4NZn_{0.1}Fe_{0.9}Fe(C_2O_4)_3\).

Figure 4.3.7(b) - Powder X-ray diffraction profile of \((n-C_4H_9)_4NZn_{0.7}Fe_{0.3}Fe(C_2O_4)_3\).

The arrows indicate peaks belonging to the P6(3) phase.
The variation of the lattice parameters with concentration of zinc is plotted in figure 4.3.8. While there is a large degree of scatter in these plots, caused by the generally poor crystallinity of the compounds, the trend for the a axis to shorten and the c axis to lengthen with increasing zinc dilution can be clearly seen.

![Figure 4.3.8(a) - Variation in a axis with concentration of zinc. The dotted line is a least-squares fit to the data.](image)

![Figure 4.3.8(b) - Variation in c axis with concentration of zinc. The dotted line is a least-squares fit to the data.](image)
The contraction in the a axis can be explained by the smaller ionic radius of Zn$^{II}$ compared to Fe$^{II}$. As mentioned in the comparison of MnFe and FeFe compounds in Section 4.3.1, the identity of the metal ions influences c by changing the honeycomb pore size and hence altering the cation's penetration of the layer.

4.3.4 $(n\text{-C}_4\text{H}_9)_4\text{NFeGa}_x\text{Fe}_{(1-x)}(\text{C}_2\text{O}_4)_3$

In common with the $(n\text{-C}_4\text{H}_9)_4\text{NZn}_x\text{Fe}_{(1-x)}\text{Fe}(\text{C}_2\text{O}_4)_3$ series, the $(n\text{-C}_4\text{H}_9)_4\text{NFeGa}_x\text{Fe}_{(1-x)}(\text{C}_2\text{O}_4)_3$ compounds also exhibit an increasing contribution from the P6(3) phase with the extent of doping. The effect is again ascribed to differing solubilities of the ions in solution, in this case Ga$^{III}$ and Fe$^{III}$, and is shown for $(n\text{-C}_4\text{H}_9)_4\text{NFeGa}_{0.2}\text{Fe}_{0.8}(\text{C}_2\text{O}_4)_3$ and $(n\text{-C}_4\text{H}_9)_4\text{NFeGa}(\text{C}_2\text{O}_4)_3$ in Figure 4.3.9.

![Figure 4.3.9(a) - Powder X-ray diffraction profile of $(n\text{-C}_4\text{H}_9)_4\text{NFeGa}_{0.2}\text{Fe}_{0.8}(\text{C}_2\text{O}_4)_3$](image-url)
Figure 4.3.9(b) - Powder X-ray diffraction profile of $(n\text{--}C_4H_9)_4N\text{FeGa(C}_2\text{O}_4)_3$. The arrows indicate peaks belonging to the P6(3) phase.

The variation of the lattice parameters with concentration of gallium is plotted in figure 4.3.10. In common with the $(n\text{--}C_4H_9)_4NZn_{1\alpha}\text{Fe(C}_2\text{O}_4)_3$ compounds, the trend for the a axis to shorten and the c axis to lengthen with increasing dilution can again be clearly seen.
Figure 4.3.10(a) - Variation in a and b axes for $(n\text{-C}_4\text{H}_9)_4\text{NFeGa}_x\text{Fe}_{(1-x)}(\text{C}_2\text{O}_4)_3$ with concentration of gallium. The dotted line is a least-squares fit to the data.

Figure 4.3.10(b) - Variation in c axis for $(n\text{-C}_4\text{H}_9)_4\text{NFeGa}_x\text{Fe}_{(1-x)}(\text{C}_2\text{O}_4)_3$ with concentration of gallium. The dotted line is a least-squares fit to the data.
The variation in the lattice parameters is again explained by comparison of the ionic radii. In this case, the smaller ionic radius of Ga\textsuperscript{III} compared to Fe\textsuperscript{III} results in shortening of the a axis and lengthening of the c axis by reduction of the honeycomb 'pore' size.

4.3.5 PPh\textsubscript{4}FeGa\textsubscript{x}Fe\textsubscript{1-x}(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}

The trend seen in Sections 4.3.3 and 4.3.4 for powder X-ray diffraction patterns of doped compounds to exhibit an increasing contribution from the P6(3) phase with the extent of doping can also be seen in the PPh\textsubscript{4}FeGa\textsubscript{x}Fe\textsubscript{1-x}(C\textsubscript{2}O\textsubscript{4})\textsubscript{3} series. The effect is illustrated in Figure 4.3.11 for the compounds PPh\textsubscript{4}FeGa\textsubscript{x}\textsubscript{0.2}Fe\textsubscript{0.8}(C\textsubscript{2}O\textsubscript{4})\textsubscript{3} and PPh\textsubscript{4}FeGa(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}.

![Figure 4.3.11(a) - Powder X-ray diffraction profile of PPh\textsubscript{4}FeGa\textsubscript{x}\textsubscript{0.2}Fe\textsubscript{0.8}(C\textsubscript{2}O\textsubscript{4})\textsubscript{3.}](image)
Figure 4.3.11(b) - Powder X-ray diffraction profile of PPh₄FeGa(C₂O₄)₃. The arrows indicate peaks belonging to the P6(3) phase.

The variation of the lattice parameters with concentration of gallium is plotted in figure 4.3.12. In common with other compounds derived from cations containing phenyl groups ¹³, it was necessary to double the a axis to cater for disorder of the cation. Again, the effect of increasing dilution is a shortening of the a axis. However, in contrast to the other doped compounds, there is a slight increase in the c axis at a doping level of 10% but the value then remains constant until 80% at which point the c axis starts to increase again. The c axis appears to decrease again at 100% doping but the error bar on this last point is very large so the apparent decrease may not be genuine.
Figure 4.3.12(a) - Variation in a axis with concentration of gallium. The dotted line is a least-squares fit to the data.

Figure 4.3.12(b) - Variation in c axis with concentration of gallium. The dotted line is a least-squares fit to the data.

4.4 EXAFS

All the EXAFS data recorded in the experiments described in Section 3.4 were fitted to the same model, comprising six oxygens in the first shell, six carbons in the second shell, six oxygens in the third shell and three metal atoms in the fourth shell, using the program Excurv98\textsuperscript{16}. Multiple scattering was enabled for all fits and the C–C and C–O
bond lengths constrained to the values determined from single crystal X-ray diffraction data on \((n\text{-C}_5\text{H}_{11})_4\text{NMnFe(C}_2\text{O}_4)_3\)\(^6\). Refinements were attempted with three arrangements of constraints on the metal-oxygen bondlengths for the shells of oxygens; all six bondlengths equal, three short and three long bondlengths and four short and two long bondlengths. Three short and three long bondlengths may be expected (particularly for Fe\(^{II}\)Fe\(^{III}\) compounds) as the higher positive charge on Fe\(^{III}\) would tend to shorten the Fe-O bond. Four short and two long bondlengths have been observed in single crystal X-ray diffraction data for \((n\text{-C}_3\text{H}_{11})_4\text{NMnFe(C}_2\text{O}_4)_3\)\(^6\). In this compound, the Mn-O bondlengths are approximately 2.08 and 2.11 Å and those for Fe-O are 2.10 and 2.13 Å at 120 K. However, there was no discernible difference between the quality of fits from these three arrangements and it should be noted that the limit of resolution of the EXAFS technique is 0.03 Å, i.e. the same as the bondlength differences given above. The fitted spectra below have therefore been refined with all metal-oxygen bondlengths equal.

4.4.1 \((n\text{-C}_4\text{H}_9)_4\text{NFeFe(C}_2\text{O}_4)_3\) and \(\text{PPh}_4\text{FeFe(C}_2\text{O}_4)_3\)

Figure 4.4.1 shows the fitted room temperature Fe-K edge EXAFS spectra for \((n\text{-C}_4\text{H}_9)_4\text{NFeFe(C}_2\text{O}_4)_3\) and \(\text{PPh}_4\text{FeFe(C}_2\text{O}_4)_3\).

![Figure 4.4.1(a) - Fitted room temperature Fe-K edge EXAFS spectrum for \((n\text{-C}_4\text{H}_9)_4\text{NFeFe(C}_2\text{O}_4)_3\)](image)
Figure 4.4.1(b) - Fitted room temperature Fe-K edge EXAFS spectrum for PPh$_3$FeFe(C$_2$O$_4$)$_3$

Figure 4.4.2 shows the Fourier transforms of the EXAFS spectra of figure 4.4.1. Four peaks can clearly be seen in the Fourier transforms, corresponding to the four shells of atoms around the excited Fe atom.

Figure 4.4.2(a) - Fourier transform of fitted room temperature Fe-K edge EXAFS spectrum for ($n$-C$_4$H$_9$)$_4$NFeFe(C$_2$O$_4$)$_3$
Bond lengths and metal-metal distances were determined for both compounds at various temperatures although many more spectra were recorded for $(n\text{-}C_4H_9)_4$NFeFe(C$_2$O$_4$)$_3$ than for PPh$_4$FeFe(C$_2$O$_4$)$_3$. A plot of metal-metal distance against temperature (Figure 4.4.3) shows this quantity increasing with temperature, as would be expected due to thermal expansion of the crystal lattice. There appears to be a steeper increase in the metal-metal distance for $(n\text{-}C_4H_9)_4$NFeFe(C$_2$O$_4$)$_3$ up to approximately $T_N$ (= 45 K) but this result should be treated with caution as the total change in M-M distance is only 0.03 Å which, as mentioned previously, is the limit of resolution of the EXAFS technique.
Figure 4.4.3 - Fe-Fe distances determined from EXAFS for \((n-C_4H_9)_4NF\)FeFe(C_2O_4)_3 (diamonds) and PPh_4FeFe(C_2O_4)_3 (squares).

Figure 4.4.4 shows the variation of Debye-Waller factors (Section 2.2) with temperature. For \((n-C_4H_9)_4NF\)FeFe(C_2O_4)_3, the values exhibit a steady decrease with increasing temperature until at 40 K there is a sharp increase. The values then decrease again until 100 K when they start to increase with temperature as would be expected. Although again this result must be treated with caution, due to the large errors on the data, it is interesting to note that at 40 K \((n-C_4H_9)_4NF\)FeFe(C_2O_4)_3 also displays a discontinuity in its temperature dependent magnetisation curve which is discussed in Chapter 5.

In the case of PPh_4FeFe(C_2O_4)_3, there also appears to be an initial decrease with increasing temperature, with a minimum at approximately \(T_N (= 34 \text{ K})\), but the small number of data points does not allow further interpretation.
Metal-metal distances and metal-oxygen bondlengths derived from the EXAFS experiments compare favourably with those determined from single crystal X-ray diffraction for the analogous \((n-C_5H_{11})_4NMnFe(C_2O_4)_3\) compound, allowing for the constraints imposed by the resolution of the technique and the smaller ionic radius of Fe\(^{II}\) compared to Mn\(^{II}\); Fe - O (EXAFS) = 2.06(3) Å, Fe - O (XRD) = ~2.10 Å, Fe - Fe (EXAFS) = 5.42(3) Å, Mn - Fe (XRD) = 5.51 Å (EXAFS values determined at 100 K, XRD values determined at 120 K).
4.4.2 \((n-C_4H_9)_4NMnFe(C_2O_4)_3\) and PPh\(_4\)MnFe(C\(_2\)O\(_4\))\(_3\)

Figure 4.4.5 shows the fitted room temperature Fe K-edge EXAFS spectra for \((n-C_4H_9)_4NMnFe(C_2O_4)_3\) and PPh\(_4\)MnFe(C\(_2\)O\(_4\))\(_3\).
Figure 4.4.6 shows the Fourier transforms of the EXAFS spectra of figure 4.4.1. In common with the FeFe compounds, four peaks can be seen in the Fourier transforms, corresponding to the four shells of atoms around the central Fe atom.

Figure 4.4.6(a) - Fourier transforms of fitted room temperature Fe K-edge EXAFS spectra for \((n-C_4H_9)_4NMnFe(C_2O_4)_3\)

Figure 4.4.6(b) - Fourier transforms of fitted room temperature Fe K-edge EXAFS spectra for \(\text{PPh}_4\text{MnFe(C}_2\text{O}_4)_3\)
For comparison, Figures 4.4.7 and 4.4.8 show the room temperature Mn K-edge spectra and Fourier transforms for the same compounds. The model used for these fits was the same as for the Fe K-edge patterns, with the exception that manganese was substituted for iron as the central atom.

Figure 4.4.7(a) - Fitted room temperature Mn K-edge EXAFS spectra for $(n-C_{4}H_{9})_{4}NMnFe(C_{2}O_4)_3$

Figure 4.4.7(b) - Fitted room temperature Mn K-edge EXAFS spectra for $PPh_4MnFe(C_2O_4)_3$
Figure 4.4.8(a) - Fourier transforms of fitted room temperature Mn K-edge EXAFS spectra for \((n-C_4H_9)_4NMnFe(C_2O_4)_3\)

Although the quality of fits for the MnFe compounds is lower than those for the FeFe.
compounds (particularly for the Mn edge data), Mn-Fe distances and metal-oxygen bond lengths derived from the EXAFS experiments are similar to those determined from single crystal X-ray diffraction for the analogous \((n-C_3H_11)_4NMnFe(C_2O_4)_3\) compound; Mn - O (EXAFS) = 2.19(3) Å, Mn - O (XRD) = 2.10 Å, Mn - Fe (EXAFS) = 5.49(3) Å, Mn - Fe (XRD) = 5.51 Å (EXAFS values determined at 50 K, XRD values determined at 120 K).

As already stated, all the EXAFS spectra for both the MnFe and FeFe compounds were fitted to the same model (substituting Mn for Fe as necessary) indicating that the local structure around the metal atoms is very similar irrespective of the identity of the cation. This lends further weight to the idea that, as far as the arrangement of atoms in the metal-oxalate layers is concerned, all these compounds are isostructural. In addition, the quality of the EXAFS data collected from relatively short scans indicates that, although these compounds suffer from stacking faults and cation disorder resulting in generally poor X-ray diffraction profiles, the local order around the metal centres is very well defined.

### 4.5 High Resolution Powder X-ray Diffraction

Figure 4.5.1 shows the high resolution powder X-ray diffraction profiles recorded between 5 and 60 K for a sample of \((n-C_4H_9)_4NFeFe(C_2O_4)_3\) grown by slow diffusion (Section 3.1.1). The patterns are clearly very similar but there is evidence of thermal expansion of the crystal lattice in the shift of peaks towards lower two-theta values as the temperature is raised.
Although the room temperature data collected on the D500 laboratory diffractometer could be convincingly fitted by a LeBail extraction in the R3c space group, attempts to determine a space group applicable to the low temperature BM16 data were unsuccessful. Single crystal X-ray diffraction data on the analogous \((n\text{-C}_4\text{H}_9)_4\text{NMnFe(C}_2\text{O}_4)_3\) compound has shown evidence of a phase transition between 160 K and room temperature so it is likely that a similar effect would be exhibited by \((n\text{-C}_4\text{H}_9)_4\text{NFeFe(C}_2\text{O}_4)_3\). In addition, Bhattarcharjee et al have reported a heat capacity anomaly for \((n\text{-C}_4\text{H}_9)_4\text{NFeFe(C}_2\text{O}_4)_3\) at 217 K, assigned to an order-disorder phase transition due to increasing conformational change of the organic cation. Unfortunately however, there was insufficient beam time to record profiles at higher temperatures.

The positions of the peak at approximately 5.24° two-theta in Figure 4.5.1 were determined using the program MacDiff and the results are plotted in Figure 4.5.2.
As mentioned above, the peak is displaced to higher angle as the temperature is reduced, corresponding to the thermal contraction of the lattice. However, two abrupt changes in this otherwise smooth trend are evident at approximately 30 K and 40 K. 30 K is the compensation temperature at which the magnetisation of this compound changes from positive to negative. As already mentioned in Section 4.4.1 above, at 40 K there is a discontinuity in the magnetisation. Thus \((n\text{C}_4\text{H}_9)_4\text{NFeFe(C}_2\text{O}_4)_3\) appears to undergo at least three structural phase transitions; one above 160 K and two more below the magnetic ordering temperature.
4.6 References


17) Bradley, J. M. *Unpublished result*. 

126
Chapter 5 - Magnetic Characterisation

5.1 General

This chapter presents magnetic characterisation of the compounds derived from alkyltriphenylphosphonium cations and those diluted with diamagnetic ions described in Chapter 4. In addition, the local magnetic properties of \((n-C_4H_9)_4\)NFeFe(C_2O_4)_3 and PPh_4MnFe(C_2O_4)_3 have been investigated by Muon Spin Relaxation and the magnetic structures of deuterated forms of PPh_4MnFe(C_2O_4)_3 and PPh_4FeFe(C_2O_4)_3 studied by polarised neutron diffraction.

5.2 Magnetometry

5.2.1 (cation)MnFe(C_2O_4)_3

Figure 5.2.1 shows the temperature-dependent magnetisation of the \(C_n\text{H}_{(2n+1)}\)PPh_3MnFe(C_2O_4)_3 \((n = 3 \text{ to } 7)\) compounds recorded on warming after cooling in a 100 G magnetic field. It is clear the behaviour of all the compounds is similar in that they all feature a broad maximum at approximately 50 K and a rapid increase in magnetisation at lower temperature. The data above 40 K have been expanded to illustrate the magnitude of the maxima. This type of behaviour has been found in all (cation)MnFe(C_2O_4)_3 compounds reported to date\(^1\)\(^2\) and the broad maxima (expanded in Figure 5.2.1(b)) are characteristic of Heisenberg two-dimensional antiferromagnetism\(^3\). The quantity \(\chi_{\text{max}}T(\chi_{\text{max}})/C\), where \(\chi_{\text{max}}\) = the susceptibility of the maximum, \(T(\chi_{\text{max}})\) = the temperature of the maximum and \(C\) = Curie constant, has been calculated for ideal two-dimensional antiferromagnets for various lattice topologies and spin values from high-temperature series expansions\(^3\)\(^4\). The value for a honeycomb lattice of \(S = 5/2\) spins is 0.330, assuming an isotropic Landé g factor of 2. The values for the compounds illustrated in Figure 5.2.1 range from 0.232 - 0.284, suggesting a deviation from ideal two-dimensional behaviour.
The increase in magnetisation at lower temperature indicates a remaining uncompensated momenta and this has recently be shown to be due to spin-canting by Mössbauer studies on the related compound \((n-C_5H_{11})_4NMnFe(C_2O_4)_3\). It should be noted that the form of the increase in magnetisation for \(C_7H_{15}PPh_3MnFe(C_2O_4)_3\) is different from the other members of the series and this is presumably a consequence of the excess manganese in this compound shown in the results of elemental analysis presented in Section 4.2.1. However, it is believed the major contribution to the magnetic behaviour arises from the honeycomb metal-trisoxalate layers described in Chapter 1 and this is borne out by the similarity of the maxima in Figure 5.2.1(b).

![Graph](image)

**Figure 5.2.1(a) - Temperature-dependent field-cooled magnetisation of \(C_nH_{(2n+1)}PPh_3MnFe(C_2O_4)_3\) (n = 3 to 7)**
The ordering temperature of these compounds was taken to be the temperature at which the field-cooled curve in the magnetisation plots diverged from the zero-field-cooled curve as shown in Figure 5.2.2 for \( \text{C}_4\text{H}_9\text{PPh}_3\text{MnFe(C}_2\text{O}_4)_3 \). Curie and Weiss constants were calculated from fits of inverse susceptibility against temperature in the paramagnetic region as shown in Figure 5.2.3. Magnetic parameters are presented in Table 5.2.1. The values for \((n-\text{C}_4\text{H}_9)_4\text{NMnFe(C}_2\text{O}_4)_3\) and \(\text{PPh}_4\text{MnFe(C}_2\text{O}_4)_3\) are also included in the table for comparison\(^1\). The large negative Weiss constants confirm the strongly antiferromagnetic nature of the magnetic exchange.
Figure 5.2.2 - Temperature-dependent field-cooled and zero-field-cooled magnetisation of $C_4H_9PPh_3MnFe(C_2O_4)_3$

Figure 5.2.3 - Inverse susceptibility of $C_nH_{(2n+1)}PPh_3MnFe(C_2O_4)_3$ ($n = 3$ to $7$)
Table 5.2.1 - Magnetic parameters for (Cation)MnFe(C\(_2\)O\(_4\))\(_3\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(T_c / K)</th>
<th>(C / \text{erg Oe}^{-2}\text{mol}^{-1}\text{K})</th>
<th>(\Theta / K)</th>
<th>(\mu_{\text{eff}} / \mu_B (2\ K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_3H_7PPh_3)MnFe(C(_2)O(_4))(_3)</td>
<td>32.5(2)</td>
<td>9.03(7)</td>
<td>-101(2)</td>
<td>0.0447</td>
</tr>
<tr>
<td>(C_4H_9PPh_3)MnFe(C(_2)O(_4))(_3)</td>
<td>30.0(2)</td>
<td>8.8(2)</td>
<td>-97.4(6)</td>
<td>0.0132</td>
</tr>
<tr>
<td>(C_5H_{11}PPh_3)MnFe(C(_2)O(_4))(_3)</td>
<td>33.2(2)</td>
<td>10.1(2)</td>
<td>-83(7)</td>
<td>0.0185</td>
</tr>
<tr>
<td>(C_6H_{13}PPh_3)MnFe(C(_2)O(_4))(_3)</td>
<td>33.0(2)</td>
<td>11.7(4)</td>
<td>-113(12)</td>
<td>0.0175</td>
</tr>
<tr>
<td>(C_7H_{15}PPh_3)MnFe(C(_2)O(_4))(_3)</td>
<td>32.9(2)</td>
<td>10.7(1)</td>
<td>-99(4)</td>
<td>0.0022</td>
</tr>
<tr>
<td>((n-C_4H_9))NMnFe(C(_2)O(_4))(_3)</td>
<td>26.0(2)</td>
<td>10.5(5)</td>
<td>-101(4)</td>
<td>0.0065</td>
</tr>
<tr>
<td>(PPh_4)MnFe(C(_2)O(_4))(_3)</td>
<td>23.5(2)</td>
<td>7.3(3)</td>
<td>-111(12)</td>
<td>0.0033</td>
</tr>
</tbody>
</table>

It is clear from the table that the Curie and Weiss constants vary between compounds but it is believed that this behaviour is largely the result of small differences in the \(\text{Mn}^{II}/\text{Fe}^{III}\) ratio arising from the variations of metal content already mentioned. However, there is no correlation between the Mn/Fe ratio and any of the magnetic parameters in the table which suggests that this is not the only factor affecting the magnetic behaviour. The crystallinity of the compounds and the relative contributions from the R3c and P6(3) phases (see Chapter 4) would also be expected to have an effect. In addition, the possibility of the presence of a small magnetic impurity cannot be discounted. This point is considered further in Chapter 6.

5.2.2 (Cation)FeFe(C\(_2\)O\(_4\))\(_3\)

Figure 5.2.4 shows the temperature-dependent magnetisation of the \(C_n\)\((2n+1)\)PPh\(_3\)FeFe(C\(_2\)O\(_4\))\(_3\) \((n = 3 \text{ to } 7)\) compounds, recorded on warming after cooling in a 100 G magnetic field. Again, the behaviour of all the compounds is similar in that the magnetisation at the ordering temperature is initially positive but, after reaching a maximum, decreases with decreasing temperature through a compensation point where there is zero net magnetisation, to negative magnetisation at low temperature.
This type of magnetic behaviour in (Cation)Fe$^{II}$Fe$^{III}$(C$_2$O$_4$)$_3$ compounds was first reported by Mathoniere et al. and was explained by attributing the net magnetisation to the sum of the magnetisations of two sublattices with different temperature dependencies. This idea, first proposed by Neél and labelled by him Type N ferrimagnetism (see Chapter 2), is represented schematically in Figure 5.2.5.
As shown in Figure 5.2.5, both sublattices start to order at the same temperature, $T_c$, but one sublattice, in this case the Fe$^{II}$ sublattice, initially has the larger $dM/dT$ due to the strongly anisotropic nature of the Fe$^{II}$ moment. Thus it is this sublattice that aligns with the applied field and the resultant magnetisation is positive. As the temperature is decreased, the Fe$^{III}$ sublattice becomes more strongly ordered causing a reduction in the net magnetisation until a compensation temperature, $T_{comp}$, at which the moments from the two sublattices are equal and opposite, resulting in zero net magnetisation. As the temperature is reduced further, the moment arising from the Fe$^{III}$ sublattice becomes larger than that from the Fe$^{II}$ sublattice, resulting in net negative magnetisation.

The ordering temperature of these compounds was estimated from the divergence of field-cooled and zero field-cooled data as shown for $C_4H_9PPh_3FeFe(C_2O_4)_3$ in Figure 5.2.6.
Curie and Weiss constants were calculated from fits of inverse susceptibility against temperature in the paramagnetic region as shown in Figure 5.2.7. Magnetic parameters are presented in Table 5.2.2. The values for \((n-C_4H_9)_{2n}NFeFe(C_2O_4)_3\) and \(PPh_4FeFe(C_2O_4)_3\) are also included for comparison. The large negative Weiss constants indicate the magnetic exchange is strongly antiferromagnetic.

Figure 5.2.6 - Temperature-dependent field-cooled and zero-field-cooled magnetisation of \(C_4H_9PPh_3FeFe(C_2O_4)_3\)

Figure 5.2.7 - Inverse susceptibility of \(C_nH_{(2n+1)}PPh_3FeFe(C_2O_4)_3\) \((n = 3 \text{ to } 7)\)
Table 5.2.2 - Magnetic parameters for (Cation)FeFe(C_2O_4)_3

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tc / K</th>
<th>C / erg G^-2 mol^-1 K</th>
<th>θ / K</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_7H_15PPh_3FeFe(C_2O_4)_3</td>
<td>45</td>
<td>7.88(1)</td>
<td>-90.2(3)</td>
</tr>
<tr>
<td>(n-C_4H_9)_4NFeFe(C_2O_4)_3</td>
<td>34</td>
<td>6.7(1)</td>
<td>-88.4(2)</td>
</tr>
<tr>
<td>PPh_4FeFe(C_2O_4)_3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It can be seen from the table that the magnetic parameters vary between compounds, as was the case for the (Cation)MnFe(C_2O_4)_3 compounds discussed in Section 5.2.1. As in the MnFe series, it is believed that this variation is largely due to small differences in the divalent/trivalent metal ratio, although varying crystallinity among the compounds and the contributions from the R3c and P6(3) phases would also be expected to have an effect.

Negative magnetisation has also been reported for other (Cation)Fe^{II}Fe^{III}(C_2O_4)_3 compounds\(^1\), and it is now known that the only compounds reported so far never to display negative magnetisation are those derived from the cations PPh_4 and AsPh_4 (negative magnetisation was not originally reported for (n-C_3H_7)_4NFeFe(C_2O_4)_3 but improved synthesis in subsequent work has shown that it too displays this behaviour\(^7\)). Figure 5.2.8 shows the field-cooled magnetisation of PPh_4FeFe(C_2O_4)_3.
As the figure shows, PPh₄FeFe(C₂O₄)₃ exhibits apparently 'normal' ferrimagnetic behaviour, labelled Type Q under the Neél classification (see Chapter 2).

A feature common to the magnetisation curves of all (cation)FeFe(C₂O₄)₃ compounds displaying negative magnetisation is a discontinuity in the magnetisation at 40 K. This has been described before for (n-C₄H₉)₄NFeFe(C₂O₄)₃ and is shown in Figure 5.2.9 for this compound and in Figure 5.2.10 for C₄H₉PPh₃FeFe(C₂O₄)₃ and C₇H₁₅PPh₃FeFe(C₂O₄)₃.
Figure 5.2.10(a) - Discontinuity in the magnetisation of $\text{C}_4\text{H}_3\text{PPh}_3\text{FeFe(C}_2\text{O}_4)_3$

Figure 5.2.10(b) - Discontinuity in the magnetisation of $\text{C}_7\text{H}_{15}\text{PPh}_3\text{FeFe(C}_2\text{O}_4)_3$
This discontinuity can also been found in samples of compounds displaying positive low temperature magnetisation. For example, Figure 5.2.11 shows the effect for PPh₄FeFe(C₂O₄)₃.

Comparison of the figures highlights a difference in the magnetic behaviour at the discontinuity. On raising the temperature, the magnetisation at the discontinuity of C₇H₁₅PPh₃FeFe(C₂O₄)₃ decreases whereas it increases for the other compounds shown. Similar behaviour to C₇H₁₅PPh₃FeFe(C₂O₄)₃ has been found before in the compound (n-C₅H₁₁)₄NFeFe(C₂O₄)₃ and was ascribed to a difference in the symmetry at the Fe²⁺ site. The lattice parameters of this compound were refined in the orthorhombic C222₁ space group, in common with C₇H₁₅PPh₃FeFe(C₂O₄)₃, and hence the Fe²⁺ site symmetry is C₂, whereas the other compounds shown all crystallise in the hexagonal space groups R3c or P6(5) resulting in C₃ symmetry at the Fe²⁺ site.

Although the absolute value of magnetisation at the lowest temperature has been found
to be sample-dependent, the overall magnetic behaviour of samples of \((n\text{-C}_4\text{H}_9)_4\text{NFeFe(C}_2\text{O}_4)_3\) and \(\text{PPh}_4\text{FeFe(C}_2\text{O}_4)_3\) is very consistent, always exhibiting negative and positive low-temperature magnetisation respectively. As mentioned above, both types of behaviour have been found for samples of \((n\text{-C}_3\text{H}_7)_4\text{NFeFe(C}_2\text{O}_4)_3\), depending on the synthetic conditions. An even more sensitive dependence on the exact details of the synthesis has been found in this study for certain alkyltriphenyl-phosphonium cations, notably \(\text{C}_3\text{H}_7\text{PPh}_3\) and \(\text{C}_4\text{H}_9\text{PPh}_3\). For example, Figure 5.2.12 shows the field-cooled magnetisation of three samples of \(\text{C}_4\text{H}_9\text{PPh}_3\text{FeFe(C}_2\text{O}_4)_3\).

![Temperature-dependent field-cooled magnetisation of three samples of \(\text{C}_4\text{H}_9\text{PPh}_3\text{FeFe(C}_2\text{O}_4)_3\)](image-url)

Figure 5.2.12 - Temperature-dependent field-cooled magnetisation of three samples of \(\text{C}_4\text{H}_9\text{PPh}_3\text{FeFe(C}_2\text{O}_4)_3\)
The two samples displaying positive magnetisation at low temperature were both synthesised by mixing ethanolic solutions of the cation with aqueous solutions of Fe(NO$_3$)$_3$.9H$_2$O, FeSO$_4$.7H$_2$O and oxalic acid. The sample displaying negative magnetisation was synthesised in the same way except that the cation was dissolved in methanol. 6 drops of 1 M HCl were added to the solutions in each case. Positive low temperature magnetisation was also found for samples which had been synthesised from methanolic solutions of all the components, samples synthesised under cooler or more acidic conditions and samples precipitated from excess quantities of solvent. Consequently synthesis was carried out under a variety of reaction conditions. The cation used for these studies was C$_3$H$_7$PPh$_3^+$ as its bromide salt is soluble in water and thus any effects due to the mixing of methanol and water were avoided.

5.2.2.1 Effect of Temperature

Figure 5.2.13 shows the magnetisation of compounds synthesised at varying temperatures. In each case, 1.5 mmol of the cation was dissolved in 5 ml H$_2$O. The resulting solution was mixed with 5 ml of an 0.2 M solution of Fe(NO$_3$)$_3$.9H$_2$O in H$_2$O. 1 mmol of solid FeSO$_4$.7H$_2$O was added to the solution and agitated until dissolved. Six drops of 1 M HCl solution was added to suppress the formation of ferrous oxalate. The resulting solution was equilibrated at the chosen temperature along with 5 ml of an 0.6 M solution of oxalic acid. The two solutions were mixed after 1 hour. The samples were collected, washed, dried and stored as described in Section 3.1.1.
The magnetisation curves of the compounds synthesised at 19° C and 25° C are almost identical but the curve at 4° C has very much reduced negative magnetisation at the lowest temperature. Unfortunately, it was not possible to reduce the temperature further with the facilities available without freezing the solutions.

5.2.2.2 Effect of pH

Figure 5.2.14 shows the magnetisation of compounds synthesised at varying pH. In this case, the same concentrations of aqueous solutions was used but in two cases the pH was adjusted from the usual value of 1 by addition of small quantities of 1 M solutions of HCl or NaOH, as appropriate. Although previous work in this thesis and elsewhere\(^7\) had suggested that raising the pH of the solution was likely to result in formation of ferrous oxalate as an impurity, this did not occur for the sample precipitated from the pH = 0.5 solution presented in figure 5.2.14.
Figure 5.2.14 - Temperature-dependent field-cooled magnetisation of $\text{C}_3\text{H}_7\text{PPh}_3\text{FeFe(C}_2\text{O}_4)_3$ compounds synthesised at different pH

5.2.2.3 Effect of Solvent Concentration

Figure 5.2.14 shows that raising or lowering the pH resulted in positive low temperature magnetisation and thus it was reasoned that the positive magnetisation may have resulted from increasing the amount of solvent consequent on adjusting the pH, rather than the pH variation itself. Hence, compounds precipitated from varying amounts of solvents were synthesised. Their temperature-dependent magnetisation is shown in figure 5.2.15. Again, aqueous solutions of all the components were mixed together, but extra water was added as indicated in the key to the diagram.
In this case, all the compounds have negative low temperature magnetisation and the variable in the synthesis correlates with the magnetisation at the lowest temperature; the largest volume of solvent results in the greatest negative magnetisation. This, however, contradicts the idea above that increasing the amount of solvent, consequent on adjusting the pH, was responsible for the positive low-temperature magnetisation shown in Figure 5.2.14.

5.2.2.3 Effect of Cation Concentration

It was found that the only way to produce a wide variation, both positive and negative, in the magnetic behaviour of these compounds by adjusting a single variable in the synthesis was to vary the molarity of the cation solution. Figure 5.2.16 shows the magnetisation of the compounds synthesised in this way. In this case, the molarity of the aqueous solution of the cation was as indicated in the figure.
As shown in the figure, the largest negative magnetisation is exhibited by the compound synthesised from the 0.2 M cation solution. The magnetisation then becomes less negative with increasing molarity until 0.6 M, for which sample the low temperature magnetisation is positive. Further increases in molarity result in reduction of the positive magnetisation at 0.7 M and a return to negative magnetisation at 0.8 M.

Figures 5.2.12 to 5.2.16 show that the magnetic behaviour of the RPh3FeFe(C2O4)3 compounds is very sensitive to reaction conditions; every change of synthetic variable resulted in modification of the low temperature magnetisation. Short 'fingerprint' X-ray powder diffraction profiles were obtained for all the samples to ensure the magnetic variations were not due to major structural changes but elemental analysis of three of the compounds in Figure 5.2.16 shows a correlation between the magnetic behaviour and the Fe deficiency discussed in Chapter 3. The sample with the greatest negative
magnetisation has the smallest Fe deficiency while the sample with positive magnetisation has the greatest deficiency. The data are presented in Table 5.2.3.

Table 5.2.3 - Elemental analysis of C₃H₇PPh₃FeFe(C₂O₄)₃

<table>
<thead>
<tr>
<th>Molarity of cation solution</th>
<th>Percentage by Weight</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>0.2 M</td>
<td>Calculated</td>
<td>47.61</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>49.08</td>
</tr>
<tr>
<td>0.6 M</td>
<td>Calculated</td>
<td>47.61</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>49.94</td>
</tr>
<tr>
<td>0.8 M</td>
<td>Calculated</td>
<td>47.61</td>
</tr>
<tr>
<td></td>
<td>Found</td>
<td>49.29</td>
</tr>
</tbody>
</table>

5.2.3 (n-C₄H₉)₄NZnₓFe(1₋ₓ)Fe(C₂O₄)₃

Figure 5.2.17 shows the temperature dependent magnetisation of the (n-C₄H₉)₄NZnₓFe(1₋ₓ)Fe(C₂O₄)₃ compounds, recorded on warming after cooling in a 100 G magnetic field. The effect of the zinc doping is to reduce the magnitude of the low-temperature magnetisation until, at a nominal doping level of >30%, positive low-temperature magnetisation is observed. Further doping results in increasingly positive magnetisation until ~65%, after which the magnetisation again reduces until almost perfectly paramagnetic behaviour is observed for (n-C₄H₉)₄NZnFe(C₂O₄)₃.
Figure 5.2.17 - Temperature-dependent field-cooled magnetisation of 
\((n-C_4H_9)_nNZn_3Fe_{(1-x)}Fe(C_2O_4)_3\). The nominal zinc percentages are indicated.

The field-cooled magnetisation curves of dilution levels of between 30 and 60 % are plotted in Figure 5.2.18. It is clear the levels of low-temperature magnetisation do not follow the expected trend with the extent of dilution. In particular, the curve for 50 % dilution exhibits a return to negative magnetisation while that for 55 % shows a greater positive magnetisation at the lowest temperature than the 60 % dilution curve. This point will be discussed further in Chapter 6.
Curie and Weiss constants for the compounds shown in Figures 5.2.17 and 5.2.18 were calculated from fits of inverse susceptibility against temperature in the paramagnetic region. Figure 5.2.19 shows the fit for \((n-C_4H_9)_4N\text{Zn}_x\text{Fe}_{(1-x)}\text{Fe(C}_2\text{O}_4)_3 \) which is paramagnetic over the whole temperature range. Ordering temperatures were estimated from the point at which field-cooled and zero field-cooled data diverged but no figures are presented for Zn doping levels of 80% and above as there was no discernible difference between the curves down to the lowest temperature. Magnetic parameters are presented in Table 5.2.4.
Figure 5.2.19 - Inverse susceptibility of \((n-C_4H_9)_4NZnFe(C_2O_4)_3\). The straight line is a Curie-Weiss fit to the data.

Table 5.2.4 - Magnetic parameters for \((n-C_4H_9)_4NZn_{1-x}Fe(C_2O_4)_3\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tc / K</th>
<th>C / ergG⁻²mol⁻¹K</th>
<th>θ / K</th>
</tr>
</thead>
<tbody>
<tr>
<td>((n-C_4H_9)_4NFeFe(C_2O_4)_3)</td>
<td>45.5(5)</td>
<td>7.88(1)</td>
<td>-90.2(3)</td>
</tr>
<tr>
<td>((n-C_4H_9)<em>4NZn</em>{0.1}Fe_{0.9}Fe(C_2O_4)_3)</td>
<td>45.5(5)</td>
<td>7.06(1)</td>
<td>-78.8(6)</td>
</tr>
<tr>
<td>((n-C_4H_9)<em>4NZn</em>{0.3}Fe_{0.7}Fe(C_2O_4)_3)</td>
<td>45.5(5)</td>
<td>6.79(1)</td>
<td>-64.9(6)</td>
</tr>
<tr>
<td>((n-C_4H_9)<em>4NZn</em>{0.4}Fe_{0.6}Fe(C_2O_4)_3)</td>
<td>45.0(5)</td>
<td>5.61(2)</td>
<td>-47.1(9)</td>
</tr>
<tr>
<td>((n-C_4H_9)<em>4NZn</em>{0.5}Fe_{0.5}Fe(C_2O_4)_3)</td>
<td>44.0(5)</td>
<td>4.877(5)</td>
<td>-42.4(3)</td>
</tr>
<tr>
<td>((n-C_4H_9)<em>4NZn</em>{0.55}Fe_{0.45}Fe(C_2O_4)_3)</td>
<td>38.0(5)</td>
<td>5.08(2)</td>
<td>-34.9(8)</td>
</tr>
<tr>
<td>((n-C_4H_9)<em>4NZn</em>{0.6}Fe_{0.4}Fe(C_2O_4)_3)</td>
<td>38.0(5)</td>
<td>5.52(2)</td>
<td>-30.9(8)</td>
</tr>
<tr>
<td>((n-C_4H_9)<em>4NZn</em>{0.65}Fe_{0.35}Fe(C_2O_4)_3)</td>
<td>38.0(5)</td>
<td>5.08(2)</td>
<td>-22.5(9)</td>
</tr>
<tr>
<td>((n-C_4H_9)<em>4NZn</em>{0.7}Fe_{0.3}Fe(C_2O_4)_3)</td>
<td>35.0(5)</td>
<td>4.208(6)</td>
<td>-15.3(2)</td>
</tr>
<tr>
<td>((n-C_4H_9)<em>4NZn</em>{0.8}Fe_{0.2}Fe(C_2O_4)_3)</td>
<td>-</td>
<td>3.13(2)</td>
<td>-12(2)</td>
</tr>
<tr>
<td>((n-C_4H_9)<em>4NZn</em>{0.9}Fe_{0.1}Fe(C_2O_4)_3)</td>
<td>-</td>
<td>3.87(2)</td>
<td>-6.6(9)</td>
</tr>
<tr>
<td>((n-C_4H_9)_4NZnFe(C_2O_4)_3)</td>
<td>-</td>
<td>3.971(3)</td>
<td>-0.5(1)</td>
</tr>
</tbody>
</table>
The ordering temperatures, Curie and Weiss constants all reduce with the extent of dilution except for low values of Curie constants for the 50 and 55% compounds, i.e. the compounds that exhibit apparently anomalous low temperature magnetisation in Figure 5.2.18.

5.2.4 \((n-C_4H_9)_4NFeGa_xFe_{(1-x)}(C_2O_4)_3\)

Figure 5.2.20 shows the temperature dependent magnetisation of the \((n-C_4H_9)_4NFeGa_xFe_{(1-x)}(C_2O_4)_3\) compounds, recorded on warming after cooling in a 100 G magnetic field. As the gallium content is increased, the extent of negative magnetisation is reduced until a doping level of \(-20\%\) when the magnetisation remains positive down to the lowest temperature measured. Further doping increases the positive magnetisation until \(-60\%\), after which the magnetisation again reduces and tends towards paramagnetic behaviour. The positive magnetisation at \(-40\) K, which was earlier ascribed to the initially stronger ordering of the Fe\textsuperscript{II} sublattice (Section 5.2.2), also increases with the extent of dilution until \(-60\%\). It also appears that the initial ordering temperature decreases with the extent of dilution and this is confirmed by the divergence of the field-cooled and zero field-cooled data.

Figure 5.2.20 - Temperature dependence of the magnetisation for 
\((n-C_4H_9)_4NFeGa_xFe_{(1-x)}(C_2O_4)_3\). The nominal gallium percentages are indicated.
Curie and Weiss constants were calculated from fits of inverse susceptibility against temperature in the paramagnetic region. As already indicated, ordering temperatures were estimated from the point at which field-cooled and zero field-cooled data diverged. Magnetic parameters are presented in Table 5.2.5.

Table 5.2.5 - Magnetic parameters for \((n-C_4H_9)_4NFeGa_{x}Fe_{(1-x)}(C_2O_4)_3\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(T_c / K)</th>
<th>(C / \text{ergG}^{-2}\text{mol}^{-1}\text{K})</th>
<th>(\theta / K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((n-C_4H_9)_4NFeFe(C_2O_4)_3)</td>
<td>45.5(5)</td>
<td>7.88(1)</td>
<td>-90.2(3)</td>
</tr>
<tr>
<td>((n-C_4H_9)<em>4NFeGa</em>{0.05}Fe_{0.95}(C_2O_4)_3)</td>
<td>45.5(5)</td>
<td>8.06(7)</td>
<td>-89(3)</td>
</tr>
<tr>
<td>((n-C_4H_9)<em>4NFeGa</em>{0.1}Fe_{0.9}(C_2O_4)_3)</td>
<td>44.5(5)</td>
<td>8.15(6)</td>
<td>-92(2)</td>
</tr>
<tr>
<td>((n-C_4H_9)<em>4NFeGa</em>{0.15}Fe_{0.85}(C_2O_4)_3)</td>
<td>44.0(5)</td>
<td>7.92(9)</td>
<td>-89(3)</td>
</tr>
<tr>
<td>((n-C_4H_9)<em>4NFeGa</em>{0.2}Fe_{0.8}(C_2O_4)_3)</td>
<td>43.0(5)</td>
<td>7.75(4)</td>
<td>-84(1)</td>
</tr>
<tr>
<td>((n-C_4H_9)<em>4NFeGa</em>{0.3}Fe_{0.7}(C_2O_4)_3)</td>
<td>42.0(5)</td>
<td>7.2(1)</td>
<td>-72(60)</td>
</tr>
<tr>
<td>((n-C_4H_9)<em>4NFeGa</em>{0.4}Fe_{0.6}(C_2O_4)_3)</td>
<td>36.0(5)</td>
<td>7.33(3)</td>
<td>-68.5(8)</td>
</tr>
<tr>
<td>((n-C_4H_9)<em>4NFeGa</em>{0.5}Fe_{0.5}(C_2O_4)_3)</td>
<td>24.0(5)</td>
<td>6.52(4)</td>
<td>-52(1)</td>
</tr>
<tr>
<td>((n-C_4H_9)<em>4NFeGa</em>{0.6}Fe_{0.4}(C_2O_4)_3)</td>
<td>12.0(5)</td>
<td>5.29(6)</td>
<td>-19(3)</td>
</tr>
<tr>
<td>((n-C_4H_9)_4NFeGa(C_2O_4)_3)</td>
<td>7.0(5)</td>
<td>4.97(1)</td>
<td>-10.6(6)</td>
</tr>
</tbody>
</table>

Elemental analysis presented in Chapter 4 shows that this series of compounds tend to have lower gallium content than expected from the proportions of reactants in the synthesis. Hence \((n-C_4H_9)_4NFeGa(C_2O_4)_3\), which would ideally be paramagnetic, has a magnetic ordering temperature. Apart from this, the table repeats the trends found in the Zn-diluted compounds i.e. the ordering temperature, Curie and Weiss constants all reduce with the extent of dilution.
5.2.5 PPh$_4$FeGa$_x$Fe$_{(1-x)}$(C$_2$O$_4$)$_3$

Figure 5.2.21 shows the temperature dependent magnetisation of the PPh$_4$FeGa$_x$Fe$_{(1-x)}$(C$_2$O$_4$)$_3$ compounds, recorded on warming after cooling in a 100 G magnetic field. In this series, as the gallium content is increased, the initially positive magnetisation is reduced until a nominal doping level of $\sim$20% when negative magnetisation is observed. Further doping results in a return to positive magnetisation with the maximum corresponding to $\sim$50%, after which the magnetisation again reduces and tends towards paramagnetic behaviour. The initial positive magnetisation, described for the (n-C$_4$H$_9$)$_4$NFeGa$_x$Fe$_{(1-x)}$(C$_2$O$_4$)$_3$ series is evident in the 20, 30 and 40% doped compounds and again the highest ordering temperature is found in the compound with the greatest negative magnetisation.

Figure 5.2.21 - Temperature dependence of the magnetisation for PPh$_4$FeGa$_x$Fe$_{(1-x)}$(C$_2$O$_4$)$_3$. The nominal gallium percentages are indicated.
Curie and Weiss constants were calculated from fits of inverse susceptibility against temperature in the paramagnetic region. As already indicated, ordering temperatures were estimated from the point at which field-cooled and zero field-cooled data diverged. Magnetic parameters are presented in Table 5.2.6.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tc / K</th>
<th>C / ergG⁻²mol⁻¹K</th>
<th>θ / K</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPh₄FeFe(C₂O₄)₃</td>
<td>34.0(5)</td>
<td>7.49(8)</td>
<td>-88.4(2)</td>
</tr>
<tr>
<td>PPh₄FeCo₉.₀Fe(C₂O₄)₃</td>
<td>31.0(5)</td>
<td>7.85(3)</td>
<td>-86(1)</td>
</tr>
<tr>
<td>PPh₄FeCo₈.₂Fe(C₂O₄)₃</td>
<td>39(1)</td>
<td>7.66(4)</td>
<td>-83(1)</td>
</tr>
<tr>
<td>PPh₄FeCo₇.₇Fe(C₂O₄)₃</td>
<td>37.0(5)</td>
<td>7.45(3)</td>
<td>-76(1)</td>
</tr>
<tr>
<td>PPh₄FeCo₆.₆Fe(C₂O₄)₃</td>
<td>30.5(5)</td>
<td>7.11(3)</td>
<td>-75(1)</td>
</tr>
<tr>
<td>PPh₄FeCo₅.₅Fe(C₂O₄)₃</td>
<td>26.5(5)</td>
<td>7.10(2)</td>
<td>-68.3(7)</td>
</tr>
<tr>
<td>PPh₄FeCo₄.₄Fe(C₂O₄)₃</td>
<td>23(5)</td>
<td>6.15(2)</td>
<td>-53.8(7)</td>
</tr>
<tr>
<td>PPh₄FeCo₃.₃Fe(C₂O₄)₃</td>
<td>18.5(5)</td>
<td>5.95(1)</td>
<td>-45.6(3)</td>
</tr>
<tr>
<td>PPh₄FeCo₂.₈Fe(C₂O₄)₃</td>
<td>-</td>
<td>5.28(3)</td>
<td>-35(1)</td>
</tr>
<tr>
<td>PPh₄FeCo₁.₉Fe(C₂O₄)₃</td>
<td>-</td>
<td>5.08(4)</td>
<td>-23(2)</td>
</tr>
<tr>
<td>PPh₄FeGa(C₂O₄)₃</td>
<td>-</td>
<td>4.51(2)</td>
<td>-8.6(9)</td>
</tr>
</tbody>
</table>

In common with the other diluted compounds the Curie and Weiss constants both reduce with the extent of dilution. In this case, however, the ordering temperatures initially increase with dilution until 20% at which point they decrease again, following the change in magnetic behaviour from wholly positive to compensated and back to positive.
5.3 Muon Spin Relaxation

Muon spin relaxation measurements on the compounds \((n-C_4H_9)_4NFeFe(C_2O_4)_3\) and \(\text{PPh}_4\text{MnFe(C}_2\text{O}_4)_3\) were made on the MuSR instrument at the Rutherford Appleton Laboratory in Oxfordshire. These measurements and previous work\(^9\) had indicated that the relaxation or resonance processes in these compounds were faster than the timescale of the experiment on the instruments at the pulsed muon source at RAL and hence further measurements were made on \((n-C_4H_9)_4NFeFe(C_2O_4)_3\) using the Dolly instrument on the continuous muon source at the Paul Scherrer Institut in Switzerland.

5.3.1 Rutherford-Appleton Laboratory

Manipulation and analysis of the data was carried out using the local program UDA\(^{10}\). The \(\alpha\) value was extracted from the calibration runs (Section 3.6) for each sample by using the 'guess' routine of the program. Calibration run data were then fitted to a Lorentzian decay function superimposed with a precession frequency and the balance variable refined by adjusting \(\alpha\) until balance was as close as possible to zero. The refined \(\alpha\) and balance values were fixed during subsequent fitting of the data.

5.3.1.1 \(\text{PPh}_4\text{MnFe(C}_2\text{O}_4)_3\)

The \(\alpha\) and balance values were refined from the calibration run as 1.18 and -0.02 respectively and the zero-field depolarisation of \(\text{PPh}_4\text{MnFe(C}_2\text{O}_4)_3\) was measured as a function of temperature between 10 and 50 K. The best fits to the data were obtained by using a two-component model, in common with \(\mu\)SR data from RAL on similar compounds\(^9\). However, in this case, the model used comprised a Lorentzian term with a Gaussian background term \((\sigma = 0)\) at low temperatures and a Gaussian term with the same Gaussian background term at temperatures above \(T_N\) \((\approx 23.5\, \text{K})\). It should be noted that \(\sigma\) for the background term was allowed to vary in the refinement but remained zero in all cases. This contrasts with \(\mu\)SR data on \(\text{PPh}_4\text{FeFe(C}_2\text{O}_4)_3\) for...
which a model comprising slow Lorentzian ($\lambda = 0.03 \, \mu s^{-1}$) and fast Gaussian ($\sigma = 0.3 \, \mu s^{-1}$) terms was found to be valid throughout the whole temperature range$^9$. Examples of the fitted spectra are given in Figure 5.3.1.

Figure 5.3.1 - Fitted $\mu$SR spectra for PPh$_4$MnFe(C$_2$O$_4$)$_3$
Static fields in the sample give rise to oscillations in the depolarisation spectra, due to coherent precession of the muons, but it is clear there is no evidence of this in the spectra of Figure 5.3.1. This may be due to the relaxation processes occurring too fast for the timescale of the MuSR instrument and further evidence for this is provided by the loss of initial asymmetry with decreasing temperature, plotted in Figure 5.3.2.

![Figure 5.3.2](image.png)

Figure 5.3.2 - Temperature dependence of the zero-field initial asymmetry of PPh₄MnFe(C₂O₄)₃

As the figure shows, the initial asymmetry starts to decrease at approximately Tₙ and continues to decrease with temperature down to the lowest temperature measured. Thus the magnetic order of the sample is reducing the polarisation of the muons. This, coupled with the lack of coherent precession observed in the depolarisation spectra, suggests that either the internal field is too large to be measured within the muon pulse width or the muons are experiencing significant depolarisation before decay, possibly by hopping from site to site within the sample. The same conclusion was reached in earlier work on PPh₄Fe^{II}Fe^{III}(C₂O₄)₃ and (n-C₄H₉)₄NFe^{II}Fe^{III}(C₂O₄)₃ by Nuttall et al.¹⁵⁶
It is clear that the initial asymmetry at temperatures above $T_N$ is considerably lower than the 33% expected from 100% polarised muons. This effect is ascribed to a non-magnetic *missing fraction* of the sample (see Chapter 2) and was also found in the studies of $\text{PPh}_4\text{Fe}^{II}\text{Fe}^{III}(\text{C}_2\text{O}_4)_3$ and $(n-\text{C}_4\text{H}_9)_4\text{NFe}^{II}\text{Fe}^{III}(\text{C}_2\text{O}_4)_3$ by Nuttall *et al*. In the case of $\text{PPh}_4$ containing compounds, the missing fraction has been found to be larger than for compounds containing $(n-\text{C}_4\text{H}_9)_4\text{N}$ and this is attributed to the presence of the phenyl rings causing formation of muon radicals (Chapter 2). The initial asymmetry, of about 17%, at temperatures above $T_N$ in Figure 5.3.2 is very similar to that reported for $\text{PPh}_4\text{Fe}^{II}\text{Fe}^{III}(\text{C}_2\text{O}_4)_3$, suggesting that the same processes are occurring in both compounds.

The temperature dependence of the zero-field relaxation rate of $\text{PPh}_4\text{MnFe}(\text{C}_2\text{O}_4)_3$ is plotted in Figure 5.3.3. Divergence in the relaxation rate is expected at the magnetic ordering temperature due to critical fluctuations and this occurs in the data presented in Figure 5.3.3 at approximately $T_N$ determined by susceptibility and neutron diffraction experiments ($\approx 23.5$ K).
The $\alpha$ and balance values were refined from the calibration run as 1.20 and -0.03 respectively and the repolarisation of $(n$-$C_4H_9)_4$NFeFe(C$_2$O$_4$)$_3$ was measured at 8.2, 38 and 54 K. In addition, the zero-field depolarisation was measured as a function of temperature between 8.2 and 90 K. The zero-field depolarisation data were fitted to models comprising a single Lorentzian function at low temperature and fast Gaussian and slow Lorentzian functions at temperatures above $T_N$. These models are in agreement with those used in previous studies on this compound by Nuttall et al. However, in contrast to the earlier work, it was found that at temperatures around $T_N$, the best fit to the data was achieved by two Lorentzian terms, with relaxation rates comparable to the fast Gaussian and slow Lorentzian functions used at higher temperatures. The temperature dependence of the initial asymmetry and of the fast relaxation rate are plotted in Figures 5.3.4 and 5.3.5 respectively.

![Graph](image.png)

**Figure 5.3.4 - Temperature dependence of the zero-field initial asymmetry of $(n$-$C_4H_9)_4$NFeFe(C$_2$O$_4$)$_3$**
Figure 5.3.5 - Temperature dependence of the zero-field relaxation rate of $(n$-$C_4H_9)_4$NF$eFe(C_2O_4)_3$

The data presented in Figures 5.3.4 and 5.3.5 compare very well with those reported for the same compound from the EMU instrument at ISIS\textsuperscript{9}, suggesting that sample dependence effects were negligible.

All the depolarisation spectra from the repolarisation experiment on $(n$-$C_4H_9)_4$NF$eFe(C_2O_4)_3$ at 8.2 K were fitted to a single Lorentzian decay function. The field dependence of the initial asymmetry is plotted in Figure 5.3.6.
As the figure shows, the effect of the increasing longitudinal field is to cause a recovery in the lost initial asymmetry up to the highest field available on the MuSR instrument. These data again compare very well with those recorded at 4.5 K on the EMU instrument although, in that case, the maximum field available was 4000 G and the initial asymmetry could be seen to be asymptotically approaching its high-temperature value. The relaxation rates extracted from the fitted Lorentzian functions reduced from 0.034(3) µs⁻¹ in zero field to between 0.003(2) and 0.010(2) µs⁻¹ in fields of 200 G and above.

At 38 K, it was necessary to use a two-component model to fit the repolarisation data comprising two Lorentzian terms, one with a fast (≈ 1 µs⁻¹) and the other with a slow (≈ 0.03 µs⁻¹) relaxation rate. The field dependence of the initial asymmetry is plotted in Figure 5.3.7.
Although the errors in fitting the repolarisation curves are larger than those for the data at 8.2 K, caused by fluctuations of the moments near the magnetic ordering temperature of the compound, the recovery of the initial asymmetry with increasing longitudinal field can be clearly seen. Again, the largest field available on the MuSR instrument was insufficient to recover the initial asymmetry to its high temperature value (≈ 24%).

The zero-field data at 54 K were fitted to a two-component model comprising fast Gaussian and slow Lorentzian terms, in common with the other high temperature zero-field runs shown in Figure 5.3.4. Application of a longitudinal field caused the Gaussian term to disappear and the remaining spectra were fitted to a single Lorentzian with an almost constant relaxation rate (\( \lambda = 0.030 \ \mu s^{-1} \)). The field dependence of the initial asymmetry is plotted in Figure 5.3.8.
In this case, there is no further recovery of initial asymmetry with increasing longitudinal field indicating that the missing fraction is non-magnetic in origin. At fields above 500 G, there is a slight reduction in initial asymmetry. The reason for this is not clear but it may be due to the competition between the applied field and the randomising effects of thermal fluctuations. At zero or low fields, thermal effects ensure that the local field arising from the moments of the sample is completely random and hence the muons experience a net zero field and their polarisation is preserved. At higher fields, the local moments will tend to align but there will be components of the local field perpendicular to the muon polarisation, causing a loss in initial asymmetry. As the field is increased further, thermal effects are less able to cause random fluctuations and hence the contribution from the perpendicular field components will increase, leading to a further reduction in initial asymmetry. By this reasoning, it would be expected that
fields large enough to completely align the moments in the sample would result in a recovery of initial asymmetry to its zero-field value.

5.3.2 Paul Scherrer Institut

Manipulation and analysis of the data was carried out using the program Minfit\textsuperscript{11}. Minfit differs from the RAL program UDA in that it fits the spectra from the forward and backward detectors of the instrument simultaneously, rather than combining the two sets of data before fitting. There is therefore no need for a calibration run to determine constants to account for differences in detector efficiency or geometry.

The zero-field depolarisation of $(n$-C$_4$H$_9$)$_4$NFeFe(C$_2$O$_4$)$_3$ was measured as a function of temperature between 30 and 100 K. It was found that the depolarisation curves at all temperatures could be fitted to Gaussian decay functions. Attempts to fit to Lorentzian decay functions gave poorer fits with large errors. A combination function, comprising both fast Gaussian and slow Lorentzian decay terms, as used for data from MuSR experiments on the same compound (Section 5.3.1), was also less successful than the pure Gaussian function; the Lorentzian term tended to disappear in the refinement. In common with the data collected on the MuSR instrument, there is no evidence of muon precession in the depolarisation curves, suggesting that the relaxation processes are occurring too fast for even the instruments on the continuous muon source at PSI to measure. The temperature dependence of the initial asymmetry is plotted in Figure 5.3.9.
In common with other \(\mu\)SR data on these compounds, the initial asymmetry at temperatures above the magnetic ordering temperature is considerably lower than the 33\% expected from 100\% polarised muons. Again this is ascribed to a *missing fraction* in the sample (Chapter 2). However, in this case, the missing fraction is greater than that found in the data on this compound from the instruments at RAL. This may be due to sample dependence effects but it is also likely that the continuous muon source employed at PSI may give different results to the pulsed muon source used at RAL. As the recorded spectra correspond to the tail-end of very fast processes in the samples, direct comparison of the two methods is not possible. In common with the RAL data, the sharp drop in asymmetry correlates with the magnetic ordering temperature determined by susceptibility measurements (\(\approx 43.5\) K).

The temperature dependence of the fitted Gaussian relaxation rate is plotted in figure 5.3.10.
Again in common with the data from RAL, the relaxation rate exhibits apparent divergence at the magnetic ordering temperature.

5.4 Polarised Neutron Diffraction

5.4.1 PPh₄(d-20)MnFe(C₂O₄)₃

Figure 5.4.1 shows the total diffraction pattern recorded at 5 K and Figure 5.4.2 shows the result of the polarisation analysis of the same data whereby the total pattern has been separated into its nuclear coherent, spin incoherent and magnetic coherent contributions.
Figure 5.4.1 - Total neutron diffraction pattern for PPh₄(d–20)MnFe(C₂O₄)₃ at 5 K

Figure 5.4.2 - Partitions of the diffraction pattern for PPh₄(d–20)MnFe(C₂O₄)₃ at 5 K;
(a) Nuclear coherent component; (b) Spin incoherent component; (c) Magnetic coherent component
Figure 5.4.3 shows the temperature dependence of the magnetic component. It is clear that magnetic Bragg reflections, indicating a transition to long-range magnetic order, start to appear in the patterns at approximately the reported magnetic ordering temperature of this compound (23.5(2) K), as would be expected. In particular, the two clearly identifiable reflections in the range $0.75 \leq Q \leq 1.00$ Å$^{-1}$ in the 5 K data were identified by Nuttall et al as 201 and 205 in the Shubnikov R3c space group (Figure 5.4.4) from temperature-difference profiles of unpolarised neutron diffraction data on the same sample$^{12}$.  

Figure 5.4.3 - Temperature dependence of the magnetic coherent component of the diffraction pattern for $\text{PPh}_4(\text{d-20})\text{MnFe(C}_2\text{O}_4)_3$
The magnetic structure corresponding to the diffraction data is presented in Figure 5.4.5. In this structure, the \( \text{Mn}^{\text{II}} - \text{Fe}^{\text{III}} \) exchange is antiferromagnetic in the honeycomb layer but ferromagnetic between layers.

Figure 5.4.5 - [110] projection of the six layers of the R3c magnetic structure of \( \text{PPh}_4(d-20)\text{MnFe(C}_2\text{O}_4)_3 \) (open circles \( \text{Fe}^{\text{III}} \), filled circles \( \text{Mn}^{\text{II}} \))\(^{12} \)
Two very weak reflections are also visible in the 5 K data set of Figure 5.4.3, in the range $1.0 \leq Q \leq 1.1 \, \text{Å}^{-1}$. These were identified as 206 and 207 in the previous work and are not predicted by the model of Figure 5.4.5. The authors considered the effects of stacking faults or non-collinearity of the Mn and Fe spins with the c-axis (i.e. spin-canting) to account for these extra reflections but simulated diffraction patterns based on these two proposals did not reproduce the observed pattern. However, as mentioned in Section 5.2.1, recent Mössbauer studies on the related $(n-C_5H_{11})_4NMnFe(C_2O_4)_3$ have revealed evidence of spin canting.

Underlying the Bragg reflection at $Q \approx 0.8 \, \text{Å}^{-1}$ there is a broad, asymmetric feature which persists at the highest temperature for which data were recorded. Structures such as this have been observed before in neutron powder diffraction profiles of quasi two-dimensional magnets and have been ascribed to magnetic correlations within the layers. The shape of these features is similar to the so-called Warren peak shape which was originally invoked in order to determine particle size from X-ray diffraction data on layered materials such as graphite and clays. In the case of magnetic data, the Warren function can be used to determine magnetic correlation lengths. The broad feature in the magnetic component of the diffraction data for $\text{PPh}_4(d-20)\text{MnFe(C}_2\text{O}_4)_3$ has therefore been fitted to the Warren function using the program Profit, written by S G Carling. The program was specifically written for the data presented in Figure 5.4.3 and thus it also fits the two strongest magnetic Bragg reflections to Gaussian peak shape functions. Examples of fitted magnetic neutron scattering profiles, at 5 K and 50 K, are presented in Figure 5.4.6. Attempts to include the two weaker reflections in the fits were unsuccessful.
Figure 5.4.6 - Magnetic profiles for PPh₄(d-20)MnFe(C₂O₄)₃ at 5 K (fitted to Warren and Gaussian peak shape functions) and 50 K (fitted to Warren peak shape function)

The variation of the two-dimensional magnetic correlation length with temperature is
plotted in Figure 5.4.7. It is clear that the onset of magnetic correlations occurs well above \( T_N \) and increases as the temperature is lowered to a maximum at approximately \( T_N \). Below \( T_N \), the correlation length decreases again rather than diverging to infinity as may be expected. This effect has been found before in, for example, Rb\(_2\)CrCl\(_4\)\(^{15}\) and is ascribed to the predominantly two-dimensional nature of the magnetic interactions. In reciprocal space, two and three-dimensional magnetic ordering gives rise to lines and peaks respectively. Thus, in two-dimensional systems, Bragg ridges will be observed in the diffraction profile. As the temperature is lowered, Bragg peaks will appear on top of the Bragg ridges and the intensity gained by the peaks will be that lost by the ridges. At this point the two-dimensional correlations become of such long-range that the anisotropy causes a long-range order within the layers and, once long-range order is established in two dimensions, it will occur in the third since the interlayer interaction is then multiplied by the number of spins within a layer\(^3\).

![Figure 5.4.7 - Temperature-dependence of the two-dimensional magnetic correlation length for \( \text{PPh}_4(\text{d}-20)\text{MnFe(C}_2\text{O}_4)_3 \)](image)

Integration of intensity over the range \( 0.25 < Q < 2.5 \text{ Å}^{-1} \) at 5 K gives the value of the
total magnetic cross-section \( \sigma_{\text{mag}} = 3.5(8) \text{ barn sr}^{-1} \text{ fmu}^{-1} \). This compares very well with the value expected from two \( S = 5/2 \) spins per formula unit \( (3.38 \text{ barn sr}^{-1} \text{ fmu}^{-1}) \) and hence it is concluded that the material is fully ordered and that most of the magnetic scattering is present in the Q-range covered by the experiment.

5.4.2 \( \text{PPh}_4(\text{d-20})\text{FeFe(C}_2\text{O}_4)_3 \)

As explained in Section 3.5, polarised neutron diffraction experiments were carried out on two different samples of \( \text{PPh}_4(\text{d-20})\text{FeFe(C}_2\text{O}_4)_3 \). Figure 5.4.8 shows the total diffraction pattern at 5 K and Figure 5.4.9 shows the nuclear coherent, spin incoherent and magnetic coherent contributions for the first sample. Figures 5.4.10 and 5.4.11 show the analogous data at 2 K for the second sample.

![Figure 5.4.8 - Total neutron diffraction pattern for PPh₄(d-20)FeFe(C₂O₄)₃ at 5 K (4.9 g sample)](image-url)
Figure 5.4.9 - Partitions of the diffraction pattern for PPh₄(d-20)FeFe(C₂O₄)₃ at 5 K (4.9 g sample); (a) Nuclear coherent component; (b) Spin incoherent component; (c) Magnetic coherent component
Figure 5.4.10 - Total neutron diffraction pattern for PPh₄(d–20)FeFe(C₂O₄)₃ at 2 K
(7.3 g sample)
Figure 5.4.11 - Partitions of the diffraction pattern for PPh₄(d-20)FeFe(C₂O₄)₃ at 2 K (7.3 g sample); (a) Nuclear coherent component; (b) Spin incoherent component; (c) Magnetic coherent component
The profiles presented in Figures 5.4.8 - 5.4.11 are similar although there is evidence of some sample dependence. As discussed in Section 5.2.2, the magnetic and structural properties of compounds of this type are very sensitive to the reaction conditions and variation between samples is common. In the case of deuterated samples, the requirement to synthesise the cation (Section 3.1.4) adds another possible source of variation.

By contrast with the profiles presented for PPh$_4$(d-20)MnFe(C$_2$O$_4$)$_3$, there is no evidence of Bragg reflections down to the lowest temperature for which data were recorded and consequently it is concluded that PPh$_4$(d-20)FeFe(C$_2$O$_4$)$_3$ does not undergo a transition to long range 3D magnetic order. The same conclusion was reached in previous work from μSR, unpolarised neutron scattering and Mössbauer spectroscopy experiments$^{9,9,7}$. However, in common with the magnetic neutron scattering profiles of PPh$_4$(d-20)MnFe(C$_2$O$_4$)$_3$, there is a broad, asymmetric feature at $Q \sim 0.8$ Å$^{-1}$ which persists at the highest temperature for which data were recorded. Two-dimensional magnetic correlation lengths were again determined by fitting the asymmetric feature to the Warren peak shape function using the program Profit. Examples of fitted profiles, at 2 K and 50 K, are presented in Figure 5.4.12.
The variation of the two-dimensional magnetic correlation length with temperature is
plotted in figure 5.4.13. It is clear that the onset of magnetic correlations occurs well above the apparent $T_N$ determined by bulk susceptibility measurements ($\sim$34 K) and increases as the temperature is lowered, as expected. However, the maximum in correlation length occurs well below $T_N$ and, although the position of the maximum appears to be sample-dependent, the behaviour of both samples is similar. Below the maximum, the correlation length decreases again, similarly to $\text{PPh}_4(d-20)\text{MnFe(C}_2\text{O}_4)_3$.

![Graph](image)

**Figure 5.4.13 - Temperature-dependence of the two-dimensional magnetic correlation length for $\text{PPh}_4(d-20)\text{FeFe(C}_2\text{O}_4)_3$**

The correlation length at 2 K is approximately $50(5) \, \text{Å}$, corresponding to about three nuclear/magnetic unit cells in the honeycomb layer compared with the long-range order observed in $\text{PPh}_4(d-20)\text{MnFe(C}_2\text{O}_4)_3$. Integrating the intensity over the range $0.25 < Q < 2.5 \, \text{Å}^{-1}$ gives a magnetic cross-section of $2.7(3) \, \text{barns sr}^{-1} \, \text{fmu}^{-1}$ compared with the calculated value of $2.85 \, \text{barns sr}^{-1} \, \text{fmu}^{-1}$ expected from one $S = 2$ and one $S = 5/2$ moments per formula unit. Hence, within the error bar and Q-range of the experiment, $\text{PPh}_4(d-20)\text{FeFe(C}_2\text{O}_4)_3$ displays its full magnetic moment.
The lack of long-range order in PPh₄(d-20)FeFe(C₂O₄)₃ may be due to a dynamic glassy behaviour, which has been suggested by hysteresis and frequency-dependent AC susceptibility measurements on the analogous hydrogenous compound, PPh₄FeFe(C₂O₄)₃.⁸. Muon spin relaxation measurements on the same compound⁹ indicate a very fast spin relaxation which supports the picture of a dynamic spin glass down to low temperature.
5.5 References


Chapter 6 Discussion

6.1 Structure

6.1.1 \( \text{(cation)M}^{II}\text{M}^{III}(\text{C}_2\text{O}_4)_3 \)

Although the production of single crystals of compounds of this type is rare and the crystallinity of powder samples is too poor to support Rietveld refinement, much structural data has been gleaned from powder XRD and EXAFS. As explained in Chapter 1, consideration of the chirality of the metal-trisoxalate unit yields two possible topologies. In the first case, all the metal-trisoxalate units have the same chirality and form a three-dimensional structure. On the other hand, if the metal-trisoxalate units have alternating chiralities, two-dimensional honeycomb sheets result. All the compounds considered in this thesis have the latter structure, as do all compounds with the above general formula, when based on monopositive cations.

Powder X-ray diffraction profiles of samples derived from unsymmetrical alkytriphenylphosphonium cations show that these compounds are much less crystalline than those derived from symmetrical cations such as \( \text{PPh}_4 \) or \( (n-\text{C}_4\text{H}_9)_4\text{N} \). In addition, these compounds are more prone to stacking faults between the layers. In spite of this, lattice parameters have been determined by means of LeBail extractions (Section 4.3) and the space groups used for the extractions are similar to other compounds of this type. Structures determined from single crystal diffraction data have been assigned to the orthorhombic \( \text{C222}_1 \) or hexagonal \( \text{R3c} \) or \( \text{P6}(3) \) space groups \(^{1,2,3,4,5,6} \) whereas the Lebail extractions in this thesis were achieved in \( \text{C222}_1 \) or \( \text{P6}(5) \), the lower symmetry \( \text{P6}(5) \) being necessary to account for the biphasic nature of many of the compounds which include contributions from \( \text{R3c} \) and \( \text{P6}(3) \) due to stacking faults. There is a high probability, therefore, that all the compounds considered have a similar layered structure. In fact, it should be noted that over many preparations, with large variations in the crystallinity, the 00\( l \) peaks could always be identified in the X-ray
diffraction profiles, suggesting that however much disorder of the cation and stacking faults of the layers, the basic layered nature was preserved.

Lattice parameters for the compounds derived from alkyltriphenylphosphonium cations are comparable to other compounds of this type. The a axis varies between 18.49 Å and 18.96 Å while the c axis ranges from 56.22 Å for $C_3H_7PPh_3MnFe(C_2O_4)_3$ to 66.20 Å for $C_7H_{13}PPh_3FeFe(C_2O_4)_3$ (converting from the C2221 space group for the latter compound for ease of comparison). The smallest and largest c axes reported are 49.207 Å and 87.1 Å for $(n-C_3H_9)_4NMnCr(C_2O_4)_3$ and PPNMnFe(C2O4)3 respectively. As the alkyltriphenylphosphonium series fall in the middle of this range, it would be interesting to determine the upper limit for the length of the alkyl chain. Preparations derived from $C_nH_{(2n+1)}PPh_3$ where $n = 8$ to 11 were not attempted in this study due to the difficulty in obtaining the cations. Attempts to synthesise compounds from $C_{12}H_{25}PPh_3^+$, which is readily available, were unsuccessful. However, as mentioned in Chapter 3, compounds containing symmetrical tetra-alkyl substituted cations are restricted to those derived from $(C_nH_{(2n+1)})_4N$ ($n = 3 - 5$), which suggests that the limiting factor is not the c axis, or more importantly, the interlayer separation, but the size of the cation that can be accommodated before it interferes with its neighbour. In view of the difficulty of synthesis of the $C_6H_{13}PPh_3$ and $C_7H_{15}PPh_3$ derivatives described in Section 3.1, the upper limit for the alkyltriphenylphosphonium cations may already have been reached.

The templating effect of the cation has been demonstrated in compounds derived from alkyltriphenylphosphonium salts. In the two series containing $C_nH_{(2n+1)}PPh_3$ ($n = 3$ to 7) and the metal ions $Mn^{II}Fe^{III}$ and $Fe^{II}Fe^{III}$, powder X-ray diffraction profiles are very similar for each pair of compounds derived from the same cation. In addition, the interlayer separation demonstrates the alternation effect in a similar fashion for both series.
It is interesting to speculate on the orientation of the unsymmetrical cations. Single crystal diffraction data on \( \text{PPh}_4\text{MnCr(C}_2\text{O}_4\text{)}_3 \) and \( \text{(n-C}_5\text{H}_{11}\text{)}_4\text{NMnFe(C}_2\text{O}_4\text{)}_3 \) indicates the orientations of the cations in these two cases are as shown in Figure 6.1.1. In the \( \text{PPh}_4 \) case, one of the phenyl rings penetrates the honeycomb layer, while the other three are positioned between the layers. By contrast, \( \text{(n-C}_5\text{H}_{11}\text{)}_4\text{N} \) adopts a conformation whereby two of the alkyl chains are in the \( ab \) plane while the other two are in a plane perpendicular to this. Thus only the final methyl groups of two of the chains penetrate the layers, one above and one below the cation.

Figure 6.1.1 - Cation orientations in (a) \( \text{PPh}_4\text{MnCr(C}_2\text{O}_4\text{)}_3 \) and (b) \( \text{(n-C}_5\text{H}_{11}\text{)}_4\text{NMnFe(C}_2\text{O}_4\text{)}_3 \)
The a axis of PPh₄MnCr(C₂O₄)₃ is doubled because the honeycomb layer is distorted away from an ideal hexagonal arrangement by the axial three-fold symmetry of the R3c space group. Thus three of the hexagons in the unit cell are elongated by the orientations of the penetrating phenyl rings while the fourth is occupied by a disordered ligand and is not distorted. The honeycomb layer and orientations of the cations are shown in Figure 6.1.2.

![Figure 6.1.2 - View along the c axis showing the honeycomb layer and orientation of the penetrating phenyl group in PPh₄MnCr(C₂O₄)₃](image)

Doubling of the a axis has also been found to be necessary in the compounds derived from the unsymmetrical alkyltriphenylphosphonium cations, which may suggest that one of the phenyl rings penetrates the layer in these compounds also. It could be visualised that the cation adopts the same orientation in each compound, keeping the alkyl chain at the same angle, and the increase in interlayer separation would then equate to extending the chain by one carbon. Thus a calculation of the angle of the alkyl chain should enable prediction of the increase in interlayer separation caused by the addition of one more carbon. This is represented in Figure 6.1.3.
Figure 6.1.3 - Predicted increase in interlayer separation consequent on extending the alkyl chain in the FeFe series (angles are not drawn accurately).

However, as shown in the figure, the predicted increase in interlayer separation on extending the alkyl chain from butyl to pentyl in the FeFe series is 1.49 Å, whereas the actual figure is 0.52 Å. Comparisons for all the alkyl chain lengths for both series of compounds are presented in Table 6.1.1.

Table 6.1.1 - Comparison of calculated and experimental values for increase in interlayer separation of the alkyltriphenylphosphonium series of compounds.

<table>
<thead>
<tr>
<th>Alkyl chain length / Å</th>
<th>Increase in interlayer separation / Å</th>
<th>Predicted increase in interlayer separation / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FeFe</td>
<td>MnFe</td>
</tr>
<tr>
<td>3</td>
<td>0.14</td>
<td>0.17</td>
</tr>
<tr>
<td>4</td>
<td>0.52</td>
<td>0.34</td>
</tr>
<tr>
<td>5</td>
<td>0.33</td>
<td>0.25</td>
</tr>
<tr>
<td>6</td>
<td>0.55</td>
<td>0.68</td>
</tr>
</tbody>
</table>
It can be seen from the data in the table that the predicted increase in interlayer separation is always approximately the length of one C-C bond whereas the actual figure is at most around 1/3 of that value. This suggests that the actual configuration adopted is always such that the terminal C-C bond is twisted away from the prediction of near parallelism with the c axis, to instead make a small angle with the a axis and thus limit the increase in interlayer separation. This can be achieved by slight variations of the cation orientation combined with changes of the conformation of the alkyl chain as shown in Figure 6.1.4 for the butyl to heptyl compounds.

Another possibility is that the alkyl chains are not all trans-configuration but contain one, or more, gauche bonds; the terminal bond of the pentyl chains of (C_{5}H_{11})_{4}NMnFe(C_{2}O_{4})_{3} has been shown to be gauche\(^3\).

Consideration of the variation in the a axis suggests that the cation's penetration of the
layer reduces for the first three members of the series, increases for the fourth member and reduces again for the final member. While it is difficult to explain this in terms of the variation in the c axis, it is worth noting that the same trend is observed in both series of compounds.

Of course, the variation in lattice parameters discussed above may be due to a large degree of disorder in the cation and the derived lattice parameters may be an average resulting from multiple orientations of the cation. However, the similarity of powder X-ray diffraction profiles for each pair of compounds derived from the same cation suggest that each cation is oriented (or disordered) in a similar fashion.

The background in the powder X-ray diffraction profiles of all the compounds derived from alkyltriphenylphosphonium cations is very high, typically accounting for 20 - 40% of the intensity of the largest reflection in the profile. This diffuse scattering suggests a large amorphous component and is further evidence for disorder of the cation, as the presence of the intense 00l reflections in all the profiles indicate that the metal-trisoxalate layers are well defined.

Further evidence for the well-defined nature of the metal-trisoxalate layers in compounds derived from symmetrical cations has been provided by EXAFS studies on \((n\text{-C}_4\text{H}_9)_4\text{MFe}(\text{C}_2\text{O}_4)_3\) and \(\text{PPh}_4\text{MFe}(\text{C}_2\text{O}_4)_3\) \((\text{M} = \text{Mn, Fe})\) (Section 4.4). All the data were fitted to the same model comprising three oxalate ligands around the excited atom and metal-oxygen bond lengths and metal-metal distances compare very well with those determined from single crystal diffraction data on analogous compounds.

Metal-metal distances and Debye-Waller factors derived from EXAFS data on \((n\text{-C}_4\text{H}_9)_4\text{FeFe}(\text{C}_2\text{O}_4)_3\) suggest a structural phase transition at 40 K, the temperature at which this compound exhibits a discontinuity in its temperature-dependent magnetisation. Although the change in metal-metal distance derived from EXAFS is at the limit of the resolution of the technique, high-resolution X-ray powder diffraction studies on the same compound indicate a structural phase transition at the same
temperature. In fact, the high-resolution studies suggest at least three structural phase transitions; one above the magnetic ordering temperature and two more below it. As already mentioned, an apparent transition at 40 K correlates with a discontinuity in the magnetisation and a further transition at approximately 30 K correlates with the compensation temperature at which the magnetisation changes from positive to negative as the temperature is decreased. The third transition, above $T_N$, is implied by the fact that room temperature powder X-ray diffraction data could be convincingly extracted in the R3c space group whereas it was not possible to determine a space group suitable for the lower temperature data (Section 4.5). In addition, heat capacity measurements suggest a phase transition at 217 K and single crystal X-ray diffraction data for the analogous $(n$-$C_5H_{11})_4NMnFe(C_2O_4)_3$ indicates a structural phase transition above 160 K.

6.1.2 $(n$-$C_4H_9)_4Zn_xFe_{(1-x)}Fe(C_2O_4)_3$

The a axis in this series has been found to decrease with the extent of zinc dilution (Section 4.3.3), corresponding to a reduction in the honeycomb 'pore' size consequent on the smaller ionic radius of Zn$^{II}$ compared to Fe$^{II}$. The c axis increases with the extent of dilution and this is ascribed to the reduction in the pore size causing reduced penetration of the metal-trisoxalate layer. Another effect of increasing dilution has been found to be an increased contribution in the powder X-ray diffraction profiles from the P6(3) phase, indicating that the smaller pore size and reduced penetration of the layers by the cation favours crystallisation with an ABAB... stacking sequence.

6.1.3 $(n$-$C_4H_9)_4FeGa_xFe_{(1-x)}(C_2O_4)_3$

Structural properties of these compounds (Section 4.3.4) were found to be similar to the Zn-doped series. They also display a decrease in a axis and increase in c axis with the extent of dilution and this is ascribed to the same reason i.e. the smaller ionic radius of the dopant atom causing a reduction in the honeycomb pore size and hence reduced
penetration by the cation. The increased contribution to the X-ray diffraction profiles from the P6(3) phase with the extent of dilution is also evident in this series.

6.1.4 PPh₄FeGaₓFeₓ⁻¹(C₂O₄)₃

In the case of the PPh₄FeGaₓFeₓ⁻¹(C₂O₄)₃ series (Section 4.3.5), while there is a reduction in the a axis with the extent of dilution, the c axis does not increase regularly as found for the other doped compounds, but only increases slightly at the smallest and largest levels of dilution. This suggests that the contraction in the pore size is not forcing the cation out of the layer and this may be due to the fact that a distortion of the pores to accommodate the phenyl group is already present in these compounds. As mentioned in Section 6.1.1 above, this effect is evident in the structure of PPh₄MnCr(C₂O₄)₃ solved from single crystal X-ray diffraction data² and necessitates a doubling of the a axis to cater for the distortion. A doubled a axis was also found to be necessary for the lattice parameter refinements of the PPh₄FeGaₓFeₓ⁻¹(C₂O₄)₃ series and so it is likely that a similar distortion is present. In common with the other diluted series there is an increased contribution to the X-ray diffraction profiles from the P6(3) phase with the extent of dilution.

6.2 Magnetic Properties

6.2.1 (cation)MnFe(C₂O₄)₃

All compounds of this type presented in this thesis (and all those reported so far ⁵,³,⁷) derived from the metal ions Mn²⁺ and Fe³⁺ are quasi two-dimensional antiferromagnets. Susceptibility data (Section 5.2.1) exhibit a broad maximum characteristic of two-dimensional antiferromagnetism, and the Weiss constants are large and negative (-83 to -113 K). Curie constants, determined from inverse susceptibility data in the paramagnetic regime, range between 7.3(3) and 11.7(4) ergOe⁻²·mol⁻¹. Assuming high spin Mn²⁺ and Fe³⁺ ions with spin-only moments S = 5/2 and a Landé constant of 2 yields a Curie constant of 8.75 ergOe⁻²·mol⁻¹. Experimental values of C smaller than the
expected value can be explained by a small metal deficiency in the compounds as indicated by elemental analysis but, obviously, the same reasoning cannot be used to rationalise the behaviour of those compounds with Curie constants higher than the calculated values. Contributions from spin-orbit coupling and magnetic anisotropy leading to deviations away from 2 in the Landé constant may be considered but it is difficult to explain why these effects should be present in some members of the series and not others. For this to be the case, some correlation between cation size and the magnetic parameters would be expected. It is therefore concluded that the magnetisation of these compounds is influenced by a variety of factors including distortions in the metal-trisoxalate layers, variations in the inter-layer registry (stacking faults) and variations in the content of one (or both) of the magnetic ions. This is further supported by the poor reproducibility of magnetic behaviour between different samples of the same compound, in particular the increase in magnetism at low temperature discussed in the next paragraph.

All members of the series display a sharp increase in magnetisation at a temperature, $T_c$, of between 23.5 and 33.2 K (Section 5.2.1). Polarised neutron diffraction on a deuterated sample of $\text{PPh}_4\text{MnFe(C}_2\text{O}_4)_3$ (Section 5.4.1) indicates that this increase correlates with the transition to long-range three-dimensional magnetic order and the same conclusion was reached from unpolarised neutron diffraction measurements on the same sample in earlier work$^{10}$. The transition suggests a remaining uncompensated moment and it has been postulated that this could be due either to spin canting or inequivalence of the two magnetic sublattices caused by deficiency of Mn$^{\text{II}}$. Although the unpolarised neutron diffraction study just mentioned could find no evidence of spin canting, recent Mössbauer studies on $(\text{n-C}_3\text{H}_{11})_4\text{NMnFe(C}_2\text{O}_4)_3$ suggest this is the reason for the uncompensated moment$^6$. As for Mn$^{\text{II}}$ deficiency, while four of the compounds synthesised in this work are deficient, there is no correlation with the magnitude of the uncompensated moment.

For compounds derived from the symmetrical tetra-substituted ammonium, phosphonium or arsonium cations, the range of $T_c$ is 23.5 to 29 K$^7$, whereas
compounds derived from unsymmetrical alkyltriphenylphosphonium cations have $T_c$ in the range 30 to 33.2 K (Section 5.2.1). The most obvious difference between these two series is the level of crystallinity. The compounds based on unsymmetrical cations are much less crystalline than those containing symmetrical cations and it would be expected that lower, rather than higher $T_c$s, would result. Indeed, the compound with the highest $T_c$ among those containing symmetrical cations, $(n$-$C_5H_{11})_4NMnFe(C_2O_4)_3$, is also the most crystalline. However, this compound, uniquely among the symmetrical cation compounds, crystallises in the orthorhombic space group $\text{C}2\text{2}2_1$ rather than the hexagonal P6(5) $\text{C}$. The difference in interlayer registry between $\text{C}2\text{2}2_1$ and P6(5) is that each Mn ion in the former space group is directly in line with Fe ions in the adjacent layers and vice-versa, whereas the ions are displaced in the latter space group (see Chapter 1). Thus interlayer exchange would be expected to be stronger in the orthorhombic space group. The stacking faults evident in compounds derived from unsymmetrical cations will also have an effect on inter-layer exchange and it may be that there is also a contribution from the orthorhombic space group; the best LeBail extraction for $C_7H_{15}PPh_3MnFe(C_2O_4)_3$ was in $\text{C}2\text{2}2_1$. Attempts to improve other LeBail extractions by inclusion of an orthorhombic phase were, however, unsuccessful and hence the reason for the higher $T_c$s of the unsymmetrical cation derived compounds remains unknown.

As already mentioned, polarised neutron diffraction on a deuterated sample of $\text{PPh}_4\text{MnFe(C}_2\text{O}_4\text{)}_3$ indicates a transition to three-dimensional magnetic order at $T_c$ (Section 5.4.1). At temperatures well above $T_c$, however, the data show evidence of short-range two-dimensional magnetic correlations, ascribed to intra-layer magnetic exchange. Correlation lengths have been determined by fitting the data to the Warren peak shape function$^{11}$. Muon spin relaxation studies on $\text{PPh}_4\text{MnFe(C}_2\text{O}_4\text{)}_3$ (Section 5.3.1) indicate a loss of initial muon asymmetry and a divergence in the zero-field relaxation rate at approximately $T_c$. There is also strong evidence of muon attack of the phenyl rings, indicated by the large 'missing fraction' (see Chapter 2) of the initial asymmetry. In
common with measurements made on other members of the (cation)\(\text{M}^{II}\text{Fe}^{III}(C_2O_4)_3\) series\(^{12}\), no coherent precession was found in the muon depolarisation spectra, indicating that the muon processes are occurring too fast for the timescale of the experiment.

6.2.2 (cation)\(\text{FeFe}(C_2O_4)_3\)

All (cation)\(\text{FeFe}(C_2O_4)_3\) compounds reported to date are ferrimagnetic\(^{13,14,15}\). Within this broad classification however, two subdivisions are presented, characterised by the low-temperature magnetisation of the compounds in small applied fields. In one case, compounds derived from the majority of cations exhibit a compensation point and transition to negative low temperature magnetisation and may be considered as Type N under the Neél classification (Section 2.3.5). On the other hand, the magnetisation of compounds derived from \(\text{PPh}_4\) or \(\text{AsPh}_4\) remains positive down to the lowest measured temperatures and appears to be of Neél Type Q. In Section 5.2.2, it was demonstrated that compounds derived from some alkyltriphenylphosphonium cations can exhibit either type of magnetic behaviour, depending on the synthetic conditions.

The Weiss constants of all (cation)\(\text{FeFe}(C_2O_4)_3\) compounds considered in this thesis are large and negative (-85 to -101 K), confirming the antiferromagnetic nature of the magnetic exchange. Curie constants, with the exception of those reported for \(\text{PPh}_4\text{FeFe}(C_2O_4)_3\) and \(\text{AsPh}_4\text{FeFe}(C_2O_4)_3\) by Nuttall\(^{16}\), are higher than the calculated values, assuming spin-only moments of 5/2 for \(\text{Fe}^{III}\) and 2 for \(\text{Fe}^{II}\) and a Landé constant of 2. That the experimental should be higher than the calculated values is not surprising given that the moment of \(\text{Fe}^{II}\) is highly anisotropic and is expected to have a significant orbital contribution.

Among the compounds studied by Nuttall, the one with the smallest Curie constant, \(\text{AsPh}_4\text{FeFe}(C_2O_4)_3\), also had the greatest Fe deficiency and the greatest positive low temperature magnetisation. The compound with the smallest Fe deficiency, \((n-C_5H_{11})_4\text{NFeFe}(C_2O_4)_3\), had the largest Curie constant and the largest negative low temperature magnetisation\(^{16}\). The compounds derived from the unsymmetrical
alkyltriphenylphosphonium cations (Section 5.2.2) fall between these two extremes; the Fe deficiencies, extent of low temperature magnetisation and Curie constants all lie between the values reported for the two symmetrical cation compounds just mentioned. Thus it would appear that, from a molecular field point of view, the Fe deficiency has the effect of weakening the Fe$^{II}$ sublattice such that it is less strongly 'pinned' to the applied field, resulting in partial field alignment of the Fe$^{III}$ sublattice leading to a reduction in the negative magnetisation and a corresponding decrease in the Curie constant, the ultimate effect being that the Fe$^{II}$ sublattice is so weakened that negative magnetisation is not observed at all. This correlation is not strictly observed for all compounds. For example, while the low temperature magnetisation of three samples of $C_3H_7PPh_3FeFe(C_2O_4)_3$ does correlate with the Fe deficiency (Section 5.2.2), the Curie constants do not, suggesting that other factors are also having an effect; poor crystallinity, sample dependence, stacking faults, and the uncertainty of space group have already been mentioned. However, it is believed that the major factor affecting the low temperature magnetisation is the Fe$^{II}$/Fe$^{III}$ ratio arising from metal deficiency.

Further evidence for the effect of metal deficiency is provided by dilution of the magnetic centers with diamagnetic ions (Sections 5.2.3 to 5.2.5). In the case of Zn dilution of $(n$-$C_4H_9)_4NFeFe(C_2O_4)_3$, the Fe$^{II}$ sublattice is progressively weakened until positive low temperature magnetisation results. The Curie and Weiss constants also reduce as would be expected. For Ga dilution of PPh$_4$FeFe(C$_2$O$_4$)$_3$, the Fe$^{III}$ sublattice is being weakened and negative low-temperature magnetisation is observed. It should also be noted that it has not been possible, either previously or in the present work, to synthesise undoped samples of PPh$_4$FeFe(C$_2$O$_4$)$_3$ or $(n$-$C_4H_9)_4NFeFe(C_2O_4)_3$ with respectively negative and positive low-temperature magnetisation.

It has not been possible to equate the level of Zn dilution required to produce the maximum positive magnetisation in $(n$-$C_4H_9)_4NFeFe(C_2O_4)_3$ with the Fe$^{II}$/Fe$^{III}$ ratio determined by Mössbauer experiments on PPh$_4$FeFe(C$_2$O$_4$)$_3$. The Mössbauer measurements indicate a ratio of 3:2 in favour of Fe$^{III}$ whereas the Zn dilution experiments indicate the maximum positive magnetisation arises at a dilution level of
~ 65%, or an Fe^{III}/Fe^{II} ratio of approximately 3:1. The dilution level corresponding to the ratio determined by the Mössbauer experiments is 33%, but the magnetisation curves of compounds at around this level of doping do not have the same form as that for PPh_{4}FeFe(C_{2}O_{4})_{3}. In particular, the hump at around 40 K is still evident in the diluted samples. Of course, the two systems are not exactly equivalent; in the doped compounds, Zn^{II} can replace Fe^{II} with no effect other than a slight structural distortion caused by differing ionic sizes. On the other hand, introducing a vacancy in the Fe^{II} sublattice requires further changes to maintain charge balance. The most likely possibility is the oxidation of another Fe^{II} to Fe^{III} and the occupation of the vacant site by, for example, H_{3}O^{+}. In addition, the compounds are not strictly isostructural as they are derived from different cations. Thus, direct comparison of doped with undoped samples is not possible.

The Fe^{II} (or Fe^{III}) sites in the (cation)Fe^{II}Fe^{III}(C_{2}O_{4})_{3} compounds form a triangular sublattice of next-nearest neighbours as shown in Figure 6.2.1.

![Figure 6.2.1 - Triangular sublattice formed by Fe^{II} (or Fe^{III}) ions in a hexagonal lattice](image)

Thus the experiments described in Chapter 5 may be considered as dilution of a triangular lattice. The percolation limit for site dilution of a triangular lattice is 50% (see Section 2.3.8) and hence, at this level of dilution, an absence of long-range two-dimensional magnetic correlations would be expected. In the case of the
(\(n\cdot C_4 H_9\))\(_4\)NZn\(_x\)Fe\(_{(1-x)}\)Fe(C\(_2\)O\(_4\))\(_3\) series, the maximum positive low-temperature magnetisation occurs at dilution levels of between 40 and 70 %. Unfortunately, a more accurate estimate is not possible due to the uncertainty of the exact doping levels and variations in crystallinity and stacking faults between samples. It is believed this is the reason for the apparently anomalous behaviour of the 50 and 55 % diluted compounds described in Section 5.2.3. However, the form of the magnetisation curves for those compounds with nominal dilution levels of 55 to 70 % is very similar to that for PPh\(_4\)FeFe(C\(_2\)O\(_4\))\(_3\) which does not exhibit a transition to long-range magnetic order, as shown by polarised neutron diffraction (Section 5.4.2).

For the (\(n\cdot C_4 H_9\))\(_4\)NFeGa\(_x\)Fe\(_{(1-x)}\)(C\(_2\)O\(_4\))\(_3\) series, the maximum positive magnetisation at low temperature is found in the 40 and 60 % compounds and that for PPh\(_4\)FeGa\(_x\)Fe\(_{(1-x)}\)(C\(_2\)O\(_4\))\(_3\) in the 50 % compound, although it should be noted that these figures are not an accurate indication of the Fe\(^{II}\)/Fe\(^{III}\) ratio due to the large discrepancies between found and calculated values of elemental analysis presented in Sections 4.2.3 and 4.2.4. In addition, the values for PPh\(_4\)FeGa\(_x\)Fe\(_{(1-x)}\)(C\(_2\)O\(_4\))\(_3\) will be affected by the increased Fe\(^{II}\) deficiency in these compounds. Thus dilution of one sublattice is effectively already present (due to Fe\(^{II}\) deficiency) and hence complete destruction of long range magnetic correlations requires a lower dilution of the other sublattice.

For certain alkyltriphenylphosphonium cations, modifying the synthetic conditions had a dramatic effect on the magnetic behaviour of the resultant compounds. Variations of solvent, pH, temperature, amount of solvent and concentration of the cation solution all affected the low-temperature magnetisation (Section 5.2.2). The widest variation in a single compound, both positive and negative at low temperature, was found to arise from different molarities of the cation solution in preparations of C\(_3\)H\(_7\)PPh\(_3\)FeFe(C\(_2\)O\(_4\))\(_3\). Why this should be so is not understood but it is worth noting that the variation in magnetic behaviour resulting from so many factors in the synthesis suggests that the energetics of producing a compound with positive or negative low temperature magnetisation are similar. This is further supported by the fact that these compounds appear to display a continuum of magnetic behaviour, rather
than two distinct types i.e. positive or negative at low temperature. The magnetisation
data for the cation molarity experiment of Chapter 5 are reproduced here as Figure 6.2.2
and evidence for the continuum can be seen in the small hump in the magnetisation
curves at around 40 K.

![Figure 6.2.2 - 100 G field-cooled magnetisation of C₃H₇PPh₃FeFe(C₂O₄)₃ compounds
synthesised using varying cation solution molarities](image)

This feature was earlier ascribed (Section 5.2.2) to the larger dM/dT of the Fe⁺⁺ sublattice in the Neél Type N model of ferrimagnetism. Figure 6.2.2 shows the feature reduces in size with the reduction of the magnitude of negative magnetisation and is still evident even in samples with positive low temperature magnetisation. It can be envisaged that a continuation of this trend would result in a fully positive magnetisation curve with no hump at 40 K, shown for PPh₄FeFe(C₂O₄)₃ in Section 5.2.2. The maximum positive or negative magnetisations shown in Figure 6.2.2 are at least an order of magnitude lower than those found in the compounds for which these values are the largest, i.e. PPh₄FeFe(C₂O₄)₃ and (n-C₅H₁₁)₄NFeFe(C₂O₄)₃ respectively. In addition, the hump is an order of magnitude smaller than for (n-C₅H₁₁)₄NFeFe(C₂O₄)₃. Thus it
appears that the reduction of the hump implies a weaker field alignment of the Fe\textsuperscript{II} sublattice, allowing the ultimately larger moment of the Fe\textsuperscript{III} sublattice to itself align with the field. The most likely cause for this effect would seem to be Fe\textsuperscript{II} deficiency.

As noted in Section 6.1.1, there is a discontinuity in the magnetisation curve at 40 K which has been ascribed to a structural phase change due to the 'locking' of the Fe\textsuperscript{II} sublattice with the applied field\textsuperscript{7}. As mentioned in Section 6.1.1, a structural phase change at this temperature is indicated by EXAFS and high-resolution powder X-ray diffraction experiments on \((n-C_4H_9)_4NF\textsubscript{e}Fe(C_2O_4)_3\). It was shown in Section 5.2.2 that the discontinuity is also present in samples exhibiting positive low-temperature magnetisation, albeit to a much reduced extent. This again gives weight to the idea that the magnetisation of these compounds is part of a continuum of behaviour. It is also consistent with the two-sublattice model of these compounds and the effect of Fe deficiency on the magnetisation; if the discontinuity is evidence of the Fe\textsuperscript{II} sublattice 'locking in' with the applied field such that the Fe\textsuperscript{III} sublattice is forced to order against the field, any weakening of the former sublattice (by Fe\textsuperscript{II} deficiency) would be expected to reduce the magnitude of the discontinuity and this is observed experimentally.

Evidence for the influence of structure on the magnetic behaviour is provided by the fact that the discontinuity in samples crystallising in the C\textsubscript{2}2\textsubscript{1} space group is reversed from that of samples crystallising in the hexagonal space groups, i.e. the magnetisation exhibits a sharp increase, rather than a decrease, as the temperature is reduced. This effect had been seen before in the magnetisation of \((n-C_5H_11)_4NF\textsubscript{e}Fe(C_2O_4)_3\textsuperscript{16} but this work has shown it is also present in C\textsubscript{7}H\textsubscript{15}PPh\textsubscript{3}FeFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3}. As indicated in Section 5.2.2, the explanation appears to be related to the site symmetry of the Fe\textsuperscript{II} ion; C\textsubscript{2} in the orthorhombic space group and C\textsubscript{3} in the hexagonal.

Polarised neutron diffraction experiments on deuterated samples of PPh\textsubscript{4}FeFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3} (Section 5.4.2) indicate an absence of magnetic Bragg scattering and hence no transition to long-range three-dimensional magnetic order, in contrast with PPh\textsubscript{4}MnFe(C\textsubscript{2}O\textsubscript{4})\textsubscript{3} (Section 6.2.1). As mentioned in Section 5.4.2, it has been suggested before that
PPh$_4$FeFe(C$_2$O$_4$)$_3$ exhibits a glassy magnetic ordering and this is probably due to random anisotropy of the moments caused by the Fe$^{II}$ deficiency. In common with PPh$_4$MnFe(C$_2$O$_4$)$_3$, short-range two-dimensional magnetic correlations have been determined by fitting the polarised neutron diffraction data to the Warren peak shape function.

Field-dependent muon repolarisation experiments on (n-C$_4$H$_9$)$_4$NFeFe(C$_2$O$_4$)$_3$ (Section 5.3) indicate a recovery of lost initial muon asymmetry with increasing field. The data collected above $T_c$ show no further recovery in the asymmetry, suggesting that the missing fraction (Section 2.4) is non-magnetic in origin. Zero field muon spin relaxation experiments indicate a divergence in the muon relaxation rate and a decrease in initial muon asymmetry which correlate with the magnetic ordering temperature. In common with the data for PPh$_4$MnFe(C$_2$O$_4$)$_3$, the lack of coherent muon precession indicates the relaxation processes are occurring too fast for the timescale of the experiment.
6.3 References


9) Bradley, J. M. *Unpublished result*.


