Muon spin relaxation studies of magnetic ordering in the molecular-based ferrimagnets $PPh_4Mn^{II}Fe^{III}(C_2O_4)_3$ and $(n\text{-}C_4H_9)_4NFe^{II}Fe^{III}(C_2O_4)_3$

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Abstract

Muon spin relaxation measurements are reported on two molecular-based ferrimagnets, $PPh_4Mn^{II}Fe^{III}(C_2O_4)_3$ and $(n\text{-}C_4H_9)_4NFe^{II}Fe^{III}(C_2O_4)_3$, at temperatures from 8 to 100 K and applied fields up to 2.5 T using pulsed (ISIS) and continuous (PSI) muon sources. In zero field, the initial asymmetry in the muon depolarization falls sharply, and the muon relaxation rate diverges, in the vicinity of the transition to long-range order (T_c) measured by bulk susceptibility. The onset of both effects takes place significantly about T_c, indicating low-dimensional short-range fluctuations in these larger materials. No coherent muon precession is observed in either compound, with pulsed or continuous muons.

1. Introduction

Muon spin rotation and relaxation (μSR) have proved useful tools for studying the magnetisation of a wide range of magnetic materials (Schenk 1985, Cox 1987). Implanted into the lattice of a magnetic material, the muon acts as a probe of its magnetic environment by reason of its own magnetic moment, which processes round any magnetic field, whether generated internally by aligned atomic moments (as in a ferri- or ferromagnetic below its ordering temperature) or externally by an applied field. The muon's subsequent decay into a positron and a neutrino is recorded by forward and back scattering detectors, asymmetry between them being ascribed to precession and relaxation. In favourable cases, oscillations in the time evolution of the asymmetry yield direct estimates of the internal field and its variation with temperature. The latter effect has been exploited most effectively in studies of the important new class of purely organic molecular-based magnets, the nitronylnitroxides (Le *et al* 1993, Pratt *et al* 1993). However, little has been done to investigate the applicability of μSR to the wider class of molecular-based magnets in which the moments originate from a d- or f-block metal ion, mediated via organic ligands. Recently we made preliminary measurements

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on some ferromagnetic tris-oxalatometallate (II, III) salts using the pulsed muon source at ISIS, but found no oscillating behaviour in the zero-field decay asymmetry (Nuttall *et al* 1999). Believing that the precession frequency could be too high to be compatible with the true structure of the pulsed source, we have now augmented these measurements with ones on the continuous muon source at Paul Scherrer Institute (PSI), Villigen, Switzerland. In parallel, we measured temperature dependence of the initial asymmetry and relaxation time through the ordering transitions on both sources, together with the field dependence of initial asymmetry at temperatures in the paramagnetic and ordered regions. Whilst no oscillations are seen in the zero-field μSR for the continuous source, the initial asymmetry and relaxation correlate clearly with the transition to long-range order.

2. Experiment

Temperature-dependent muon spin relaxation data were collected on molecular-based ferrimagnets $(n\text{-}C_4H_9)_4NFe^{II}Fe^{III}(C_2O_4)_3$, $PPh_4Fe^{II}Fe^{III}(C_2O_4)_3$ and $PPh_4Mn^{II}Fe^{III}(C_2O_4)_3$ (Mathionière *et al* 1996, Nuttall and Day 1998a) using the MuSR instrument at the pulsed muon source at the Rutherford Appleton Laboratory, Oxfordshire. The polarized muon beam is directed into the sample, which is mounted in the centre of two banks of positron detectors. Helmholtz coils allow the application of magnetic fields either longitudinal or transverse to the muon beam polarization. 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 polarization asymmetry and F, B are the signals from the forward and backward detectors respectively. α is the calibration variable. The local software UDA (King *et al* 1999) allows fine-tuning of α by a further variable, balance.

Only zero-field depolarization measurements were made on $PPh_4Mn^{II}Fe^{III}(C_2O_4)_3$, but measurements were made on $(n\text{-}C_4H_9)_4NFe^{II}Fe^{III}(C_2O_4)_3$ at various temperatures in longitudinal fields between 100 G and 2 kG. A total of approximately 6 million muon decay events were collected at each temperature. Manipulation and analysis of the data was carried out using the local program UDA (King *et al* 1999). The α value was extracted from the calibration runs 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 α until balance was as close as possible to zero. The refined α and balance values were fixed during subsequent fitting of the data.

Temperature dependent muon spin relaxation data were also collected for $(n\text{-}C_4H_9)_4NFe^{II}Fe^{III}(C_2O_4)_3$ using the Dolly instrument on the continuous muon source at the PSI. The sample is aligned in the polarized muon beam and the muons and their decay positrons are monitored by a system of eight detectors. Magnetic fields can be applied either longitudinal or transverse to the muon beam polarization 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 plate and held in place by non-magnetic adhesive tape 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 muon decay events. No calibration runs were performed as the local data analysis software takes account of differences in the efficiency and geometry of the detectors.

Manipulation and analysis of the data was carried out using the program Minfit (Reid 1998), that 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.

3. Results and discussion

The muon spin relaxation measurements on $(n\text{-}C_4H_9)_4NFe^{II}Fe^{III}(C_2O_4)_3$ and $PPh_4Mn^{II}Fe^{III}(C_2O_4)_3$ made on the MuSR instrument at the Rutherford Appleton Laboratory, and previous work on related compounds (Nuttall *et al* 1999) indicates that the relaxation or resonance processes in these compounds are faster than the timescale accessible at the pulsed muon source. Further measurements on $(n\text{-}C_4H_9)_4NFe^{II}Fe^{III}(C_2O_4)_3$ were therefore carried out on the continuous muon source at PSI.

3.1. $PPh_4Mn^{II}Fe^{III}(C_2O_4)_3$

In the case of $PPh_4MnFe(C_2O_4)_3$, the α and balance values were refined from the calibration run and the zero-field depolarization was measured on the pulsed source 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 μSR data from RAL on similar compounds (Nuttall *et al* 1999). However, in the present case, the model 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 K). It should be noted that σ for the background term was allowed to vary in the refinement but remained zero in all cases. This contrasts with μSR data on $PPh_4Fe^{II}Fe^{III}(C_2O_4)_3$ (Nuttall *et al* 1999), for which a model comprising slow Lorentzian ($\lambda \approx 0.03\ s^{-1}$) and fast Gaussian ($\sigma \approx 0.3\ \mu s^{-1}$) terms was found to be valid throughout the whole temperature range. Examples of the fitted spectra are given in figure 1.

Static fields within the sample would give rise to oscillations in the depolarization spectra, due to coherent precession of the muons, but no such oscillations are evident in figure 1. Most probably this is because the rotation frequency is too fast for the timescale of the μSR instrument. Evidence that this is so is provided by the loss of initial asymmetry with decreasing temperature (figure 2). It can be seen that the initial asymmetry starts to decrease at approximately T_N and continues to decrease monotonically down to the lowest temperature measured. Thus, the magnetic order of the sample is reducing the polarization of the muons. This, coupled with the lack of coherent precession observed in the depolarization spectra, suggests that either the internal field is too large to be measured within the muon pulse width or the muons are experiencing significant depolarization before decay, possible by hopping from site to site within the sample.

Figure 2 shows that the initial asymmetry at temperatures above T_N is considerably lower than the 33% expected from 100% polarized muons. This effect, ascribed to a non-magnetic *missing fraction* of the sample, was also found in earlier studies of this type of compound (Nuttall *et al* 1999). The missing fraction is larger in PPh_4 compounds than in ones containing $(n\text{-}C_4H_9)_4$, most likely because the phenyl rings in the former cause formation of muon radicals (Cox 1987). The initial asymmetry, of about 17%, at temperatures above T_N (figure 2) is

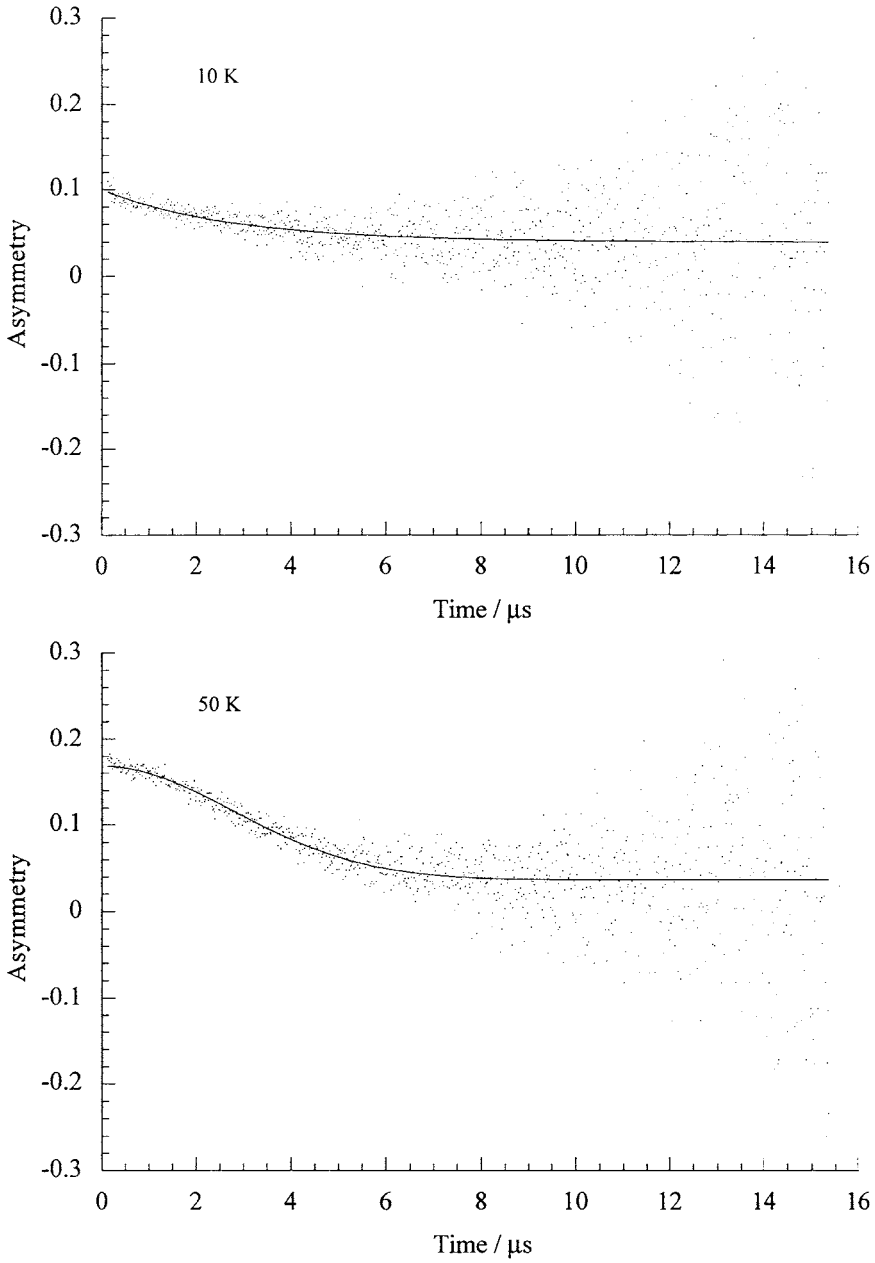

Figure 1. Fitted μSR spectra for $PPh_4Mn^{II}Fe^{III}(C_2O_4)_3$.

very similar to that reported for $PPh_4Fe^{II}Fe^{III}(C_2O_4)_3$, suggesting that the same processes are occurring in both compounds.

The temperature dependence of the zero-field relaxation rate of $PPh_4MnFe(C_2O_4)_3$ is plotted in figure 3. Divergence in the relaxation rate is expected at the magnetic ordering temperature due to critical fluctuations, an effect that is clearly observed in figure 3 close to T_N determined by susceptibility and neutron diffraction experiments (≈23.5 K) (Mathionière *et al* 1996).

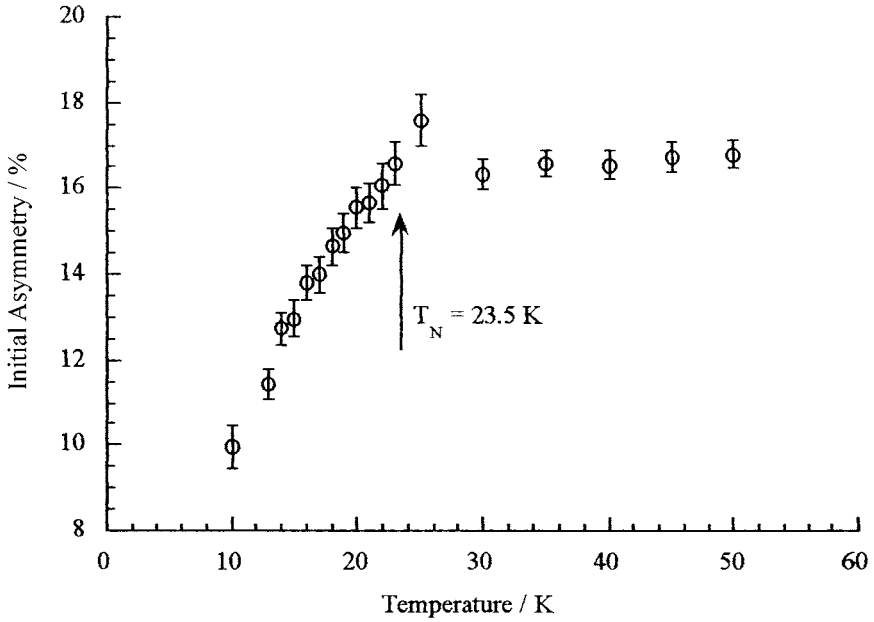

Figure 2. Temperature dependence of the zero-field initial asymmetry of $PPh_4Mn^{II}Fe^{III}(C_2O_4)_3$.

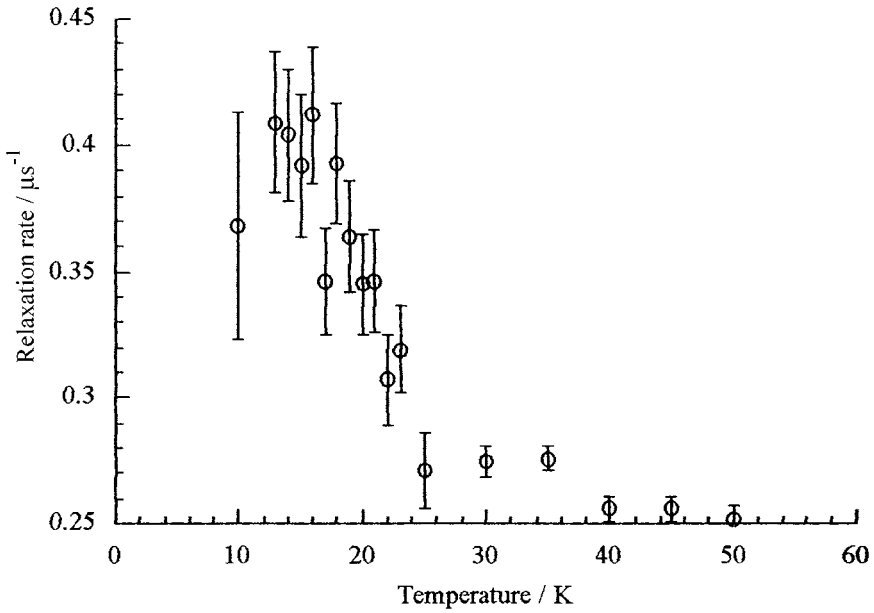

Figure 3. Temperature dependence of the zero-field relaxation rate of $PPh_4Mn^{II}Fe^{III}(C_2O_4)_3$.

3.2. $(n\text{-}C_4H_9)_4NFe^{II}Fe^{III}(C_2O_4)_3$

The zero-field muon depolarization of $(n\text{-}C_4H_9)_4NFe^{II}Fe^{III}(C_2O_4)_3$ was measured as a function of temperature between 8.2 and 90 K at the ISIS pulsed source and between 30 and 100 K at the PSI continuous source. The ISIS depolarization data were fitted to models comprising a

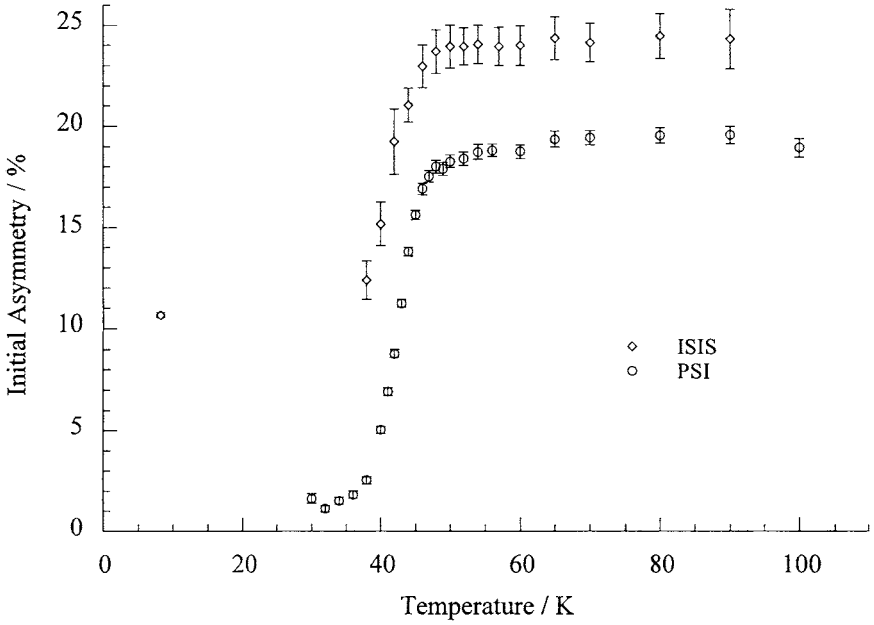

Figure 4. Temperature dependence of the zero-field initial asymmetry of $(n\text{-}C_4H_9)_4NFe^{II}Fe^{III}(C_2O_4)_3$: (a) measured at ISIS; (b) measured at PSI.

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. 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.

In contrast, the depolarization curves measured at the continuous source could be fitted to Gaussian decay functions at all temperatures. Indeed, attempts to fit to Lorentzian decay functions gave poorer fits with large errors. A combination of fast Gaussian and slow Lorentzian decay terms, as used for data from ISIS, was also less successful than the pure Gaussian function, the Lorentzian term tending to zero in the refinement. In common with the data collected on the pulsed source there is no evidence of muon precession in the depolarization curves, suggesting that the relaxation processes are too fast for even the instruments on the continuous muon source at PSI to measure. The temperature dependence of the initial asymmetry measured on both sources is shown in figure 4.

In common with $PPh_4Mn^{II}Fe^{III}(C_2O_4)_3$, the initial asymmetry at temperatures above the magnetic ordering temperature is considerably lower than the 33% expected from 100% polarized muons. However, in this case, the missing fraction is greater in the continuous source than the pulsed source data. Whilst this may be due to differences between the two samples, it is more likely that the two sources are yielding different results. 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.

Nevertheless, the two sets of data (figure 4) agree closely in respect of the temperature dependence of the initial asymmetry, in particular the sharp drop correlating with the onset of long-range magnetic order, measured as 43.5 K by bulk susceptibility (Nuttall and Day 1998a). It is also noteworthy that the initial asymmetry begins to fall at temperatures well in excess of 43.5 K, indicating the importance of the build-up of short-range two-dimensional correlations

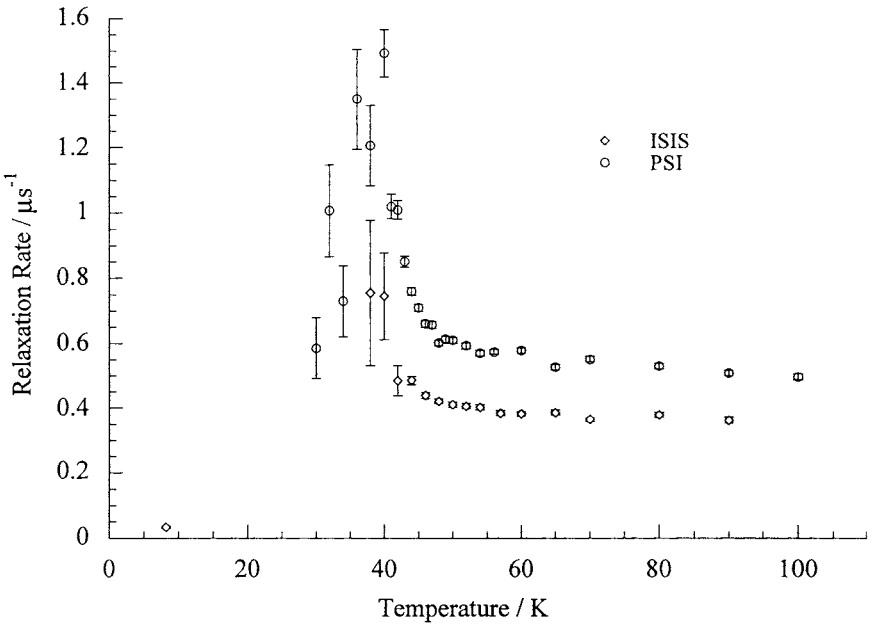

Figure 5. Temperature dependence of the zero-field relaxation rate of $(n\text{-}C_4H_9)_4NFe^{II}Fe^{III}(C_2O_4)_3$: (a) measured at ISIS; (b) measured at PSI.

in these layer materials. A corresponding effect is seen in the temperature dependence of the relaxation rate which, although it diverges in the vicinity of T_c in the data measured at both sources (figure 5), begins to rise at temperatures well in excess of this.

The final experiment showing the effect of the long-range magnetic ordering in $(n\text{-}C_4H_9)_4NFe^{II}Fe^{III}(C_2O_4)_3$ measures the recovery of initial asymmetry brought about by applying longitudinal fields at temperatures up to and above T_c. The measurements, which were carried out at ISIS, are displayed in figure 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 accessible. 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 model to fit the repolarization data comprising two Lorentzian terms, one with a fast ($\approx$1 μs^{-1}) and the other with a slow ($\approx$0.03 μs^{-1}) relaxation rate, yielding the field dependence in figure 6(b). Although the error in fitting the repolarization curves are larger than those for the 8.2 K data because of fluctuations of the moments near T_c, the recovery of the initial asymmetry with increasing longitudinal field can be clearly seen.

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 (figure 4(a)). 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 ($\lambda \approx 0.030$ μs^{-1}). In this case (figure 6(c)) the initial asymmetry is essentially independent of longitudinal field confirming that the missing fraction is non-magnetic in origin. At fields above 500 G, the initial asymmetry falls slightly, due to the competition between the applied field and the randomizing 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

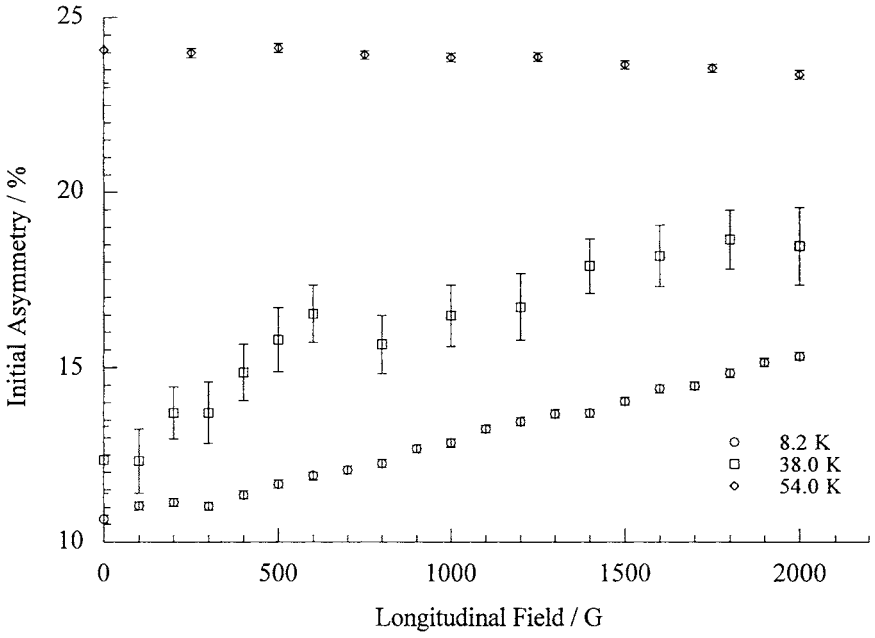

Figure 6. Field dependence of the initial asymmetry of $(n\text{-}C_4H_9)_4NFe^{II}Fe^{III}(C_2O_4)_3$ at 8.2 K (bottom); 38 K (middle); 54 K (top).

hence the muons experience a net zero field and their polarization 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 polarization, 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.

4. Conclusions

Muon spin relaxation has been used to study the magnetic ordering processes in two metal–organic molecular-based ferrimagnets. Data recorded at pulsed (ISIS) and continuous muon sources (PSI) are in good agreement. In $PPh_4Mn^{II}Fe^{III}(C_2O_4)_3$ and $(n\text{-}C_4H_9)_4NFe^{II}Fe^{III}(C_2O_4)_3$ we found a loss of initial muon asymmetry and a divergence in the zero-field relaxation rate in the neighbourhood of the transition to long-range order, T_c. In both compounds the effects become evident significantly above T_c showing the importance of low-dimensional short-range order in these layer materials. There is also strong evidence of muon attack of the phenyl rings in the PPh_4 compound, indicated by a large 'missing fraction' of the initial asymmetry.

Field-dependent muon repolarization experiments on $(n\text{-}C_4H_9)_4NFeFe(C_2O_4)_3$ demonstrate that the lost initial muon asymmetry below T_c is recovered with increasing field. Above T_c applied fields do not bring about recovery in the asymmetry, suggesting that the missing fraction is non-magnetic in origin. The lack of coherent muon precession in both compounds indicates that the relaxation processes occur too fast for the timescale of the experiment, at the continuous and pulsed sources.

Acknowledgments

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