Studies of critical phenomena in molecular magnets by $\mu$SR spectroscopy

T Wasiutyński$^1$, M Balanda$^1$, M Czapla$^1$, R Pelka$^1$, P M Zielński$^1$, F L Pratt$^2$, T Korzeniak$^3$, R Podgajny$^3$, D Pinkowicz$^3$ and B Sieklucka$^3$

$^1$Institute of Nuclear Physics PAN, Radzikowskiego 152, 31-342 Kraków, Poland
$^2$ISIS Facility, Rutherford Appleton Laboratory, Chilton, Oxfordshire OX11 0QX, UK
$^3$Faculty of Chemistry, Jagiellonian University, Kraków, Poland

Abstract. The rapidly developing field of molecular magnetism supplies a multitude of novel compounds of unprecedented properties and structure. Molecular magnets predominantly belong to the class of compounds involving well localized magnetic moments. This feature together with the fact that the nature and symmetry of magnetic interactions is encrypted in the critical behaviour makes them a perfect testing ground of the existing theoretical spin models. It is demonstrated that the experimental technique of the $\mu$SR spectroscopy is perfectly suited to study magnetic fluctuations and spin dynamics in the neighbourhood of a phase transition. This unique method can even dispense with the complementary measurements of the AC susceptibility or heat capacity to supply a complete set of the static and dynamic critical exponents. It can thus be used to pinpoint the universality class of the material of interest.

1. Introduction

Novel magnetic materials based on molecular building blocks offer unprecedented properties which are due to the interplay of unique architectures of molecular networks and magnetic anisotropy induced by different coordination patterns. Magnetic interactions mediated by molecular bridges may be of different nature and symmetry, which is inscribed in the critical behaviour near the transition point to the ordered state. Due to the fact that molecular magnets display low density of magnetic moments and weak couplings between them even a low magnetic field may destroy the ground state. The experimental technique of $\mu$SR (muon spin rotation/relaxation) [1] represents a unique method for studying magnetic properties of materials in zero applied magnetic field. The present paper reports the results of a study of the critical behaviour in the family of octacyanometallates $\text{M(CN)}_8$ [2] which is of special interest in the field of molecular magnetism.

2. Experimental

2.1. Muon implantation

Our experiments were performed on the positive muon beam at ISIS facility with the spectrometers MuSR and Argus. Pions produced in the collisions of sufficiently high-energy protons with a graphite or other light element target decay quickly to muons and neutrinos ($\tau_\pi = 26$ ns). Muons are then implanted in a sample. The key point of the method is that muons are 100 % spin polarized: $\mu^+$ has spin 1/2 aligned antiparallel to its momentum. This high level of polarization is preserved during the beam transport and, as the spin state is insensitive to electrostatic interactions, also during the thermalization process in a sample. The muon itself is an unstable particle with the lifetime of $\tau_\mu \approx 2.2 \mu$s and decays to positrons.
\( \mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu \) emitted preferentially in the spin direction of the parent muon with the probability distribution \( p(\theta) = 1 + a \cos \theta \), where \( \theta \) is the angle between the instantaneous muon spin orientation and the positron momentum, and \( a \approx 0.3 \). The asymmetry function

\[
A(t) = \frac{N_B(t) - N_F(t)}{N_B(t) + N_F(t)},
\]

where \( N_B(t) \) and \( N_F(t) \) denote the numbers of decay positrons detected by the backward and forward counters, respectively, gives us information about the time evolution of the muon spin. It is governed by the interaction of the muon magnetic moment with the dipolar magnetic field due to electrons and nuclei of the species of interest. This provides a unique opportunity to study the distribution of the local magnetic field static on the microsecond scale at the stopping sites of the muons without the need to apply external magnetic field. Moreover, the in-field experiments provide further insights into spin correlations and spin dynamics in the system. Applying magnetic field so that it is parallel to the initial muon spin polarization (longitudinal mode) does not affect the spin of the muon but modifies the local field in the sample. Contrary to that, a small field applied perpendicular to the initial muon spin polarization (transverse mode) does not affect spins in the sample but may affect the muon spins which precess in it in phase. If the field varies from site to site, the individual precessions dephase and the initial precession signal is damped. In addition, there is always relaxation of the muon spin due to the hyperfine interactions with the nuclear spins of a sample.

2.2. Relaxation functions
The muon asymmetry function (1) is proportional to the average muon-spin polarization \( G_z(t) \). The muon-spin precesses around the local magnetic field \( \vec{B} \) with angular frequency \( \gamma_\mu |\vec{B}| \), where \( \gamma_\mu = 2\pi \times 135.5 \text{ MHz T}^{-1} \) is the muon gyromagnetic ratio. If the local magnetic field at the muon site is at an angle \( \theta \) to the initial muon-spin-direction, the muon-spin will precess around the end of a cone of semi-angle \( \theta \) about the magnetic field. The normalized decay positron asymmetry is then given by \( G_z(t) = \cos^2 \theta + \sin^2 \theta \cos(\gamma_\mu |\vec{B}| t) \). If the direction of the local magnetic field is entirely random, as for polycrystalline samples, the averaging over all possible directions of field \( \vec{B} \) yields \( G_z(t) = \frac{1}{3} + \frac{2}{3} \cos(\gamma_\mu |\vec{B}| t) \). Next, if the strength of the local field \( |\vec{B}| \) is itself a random variable distributed around zero according to the Gaussian distribution of width \( \Delta \gamma_\mu \), the corresponding averaging gives \( G_z(t) = \frac{1}{3} + \frac{2}{3} (1 - \Delta^2 t^2) \exp(-\frac{1}{2} \Delta^2 t^2) \), a result first obtained by Kubo and Toyabe and known as the Kubo-Toyabe function \( f_{\text{KT}}(t) \). In the studies reported in this paper the experimental asymmetry function (1) was fitted to the following formula

\[
G_z(t) = A_0 [\frac{2}{3} e^{-\lambda_1 t} \cos(\gamma_\mu B t + \phi) + \frac{1}{3} \exp(-\lambda_2 t)] + A_1 f_{\text{KT}}(t)
\] (2)

where \( A_0, A_1, \lambda_1, \lambda_2, B, \phi \) are to be determined, and the last contribution is taken into account only in the paramagnetic regime above the transition temperature. The output data of our \( \mu \)SR experiments were analysed with the WIMDA software [3].

2.3. Critical behaviour
The phase transition to a magnetically ordered state is clearly signalled by the onset of spontaneous oscillations in the time dependence of the asymmetry function as exemplified by figure 1. This fact enables us to study the critical behaviour. Different spatial dimensions of a spin network as well as different dimensions of the spin space (due to exchange anisotropy) lead to a variety of critical patterns displayed by molecular magnets. By selecting appropriately the experimental set-up one can uncover diverse aspects of the critical behaviour:
3. Results

3.1. Mn$_2$Nb(CN)$_8$

[Mn$^{III}$(H$_2$O)$_2$(pydz)][Mn$^{III}$(H$_2$O)$_2$][Nb$^{IV}$(CN)$_8$]$\cdot$2H$_2$O (pydz=pyridazine) crystallizes in the monoclinic system with space group P2$_1$/c, and with unit cell parameters $a = 10.605$ Å, $b = 15.575$ Å, $c = 14.386$ Å, and $\beta = 108.3^\circ$. The compound represents a three dimensional (3D) network of cyanidobridged framework composed of corrugated square-grid motifs parallel to the bc crystallographic plane cross-linked at the Nb centers by the ladder motifs running along the a crystallographic axis. Figure 3 shows the projection of the crystal structure onto the ac crystallographic plane. Each Nb ion is coordinated by eight cyanide ligands, of which seven link it to the Mn ions. The eighth terminal NC$^-$ group together with pyridazine ligand and crystallization water is involved in the network of hydrogen bonds ensuring the stabilization of the crystal structure. There are two distinct Mn sites; sites of the first type build the ladder motifs and are bridged to three Nb ions, whereas those of the second type are coordinated to four Nb ions and are incorporated in the square-grid motifs. The Mn$^{II}$ ions carry spin $5/2$, whereas the Nb$^{IV}$ ions carry spin 1/2. The temperature dependence of the AC susceptibility, see figure 4, shows an unusually sharp anomaly at $T_c \approx 42$ K revealing the transition to an ordered phase. Large values of the AC signal persisting below the transition temperature indicate that the compound can be classified as a soft magnet. The analysis of the DC susceptibility (not shown) in the paramagnetic regime implies antiferromagnetic coupling between the Nb ions and the Mn ions. This is consistent with the saturation value of the isothermal magnetization amounting to 9.5 $\mu_B$, which is slightly higher than the value expected for a perfect antiparallel alignment of the magnetic moments suggesting the presence of weak non-collinearity. The scaling analysis of $\chi_{ac}$ performed using the classical scaling relation $\chi = c(T/T_c - 1)^{-\gamma}$ yielded $\gamma = 1.18$, the value placed between that for the mean-field model (1.0) and the 3D Ising model ($\approx 1.24$). The $\mu$SR experiment performed in zero magnetic field reveal the onset of spontaneous oscillation of the asymmetry function below the transition temperature, see figure 5. A single precession frequency was observed in the measured asymmetry spectra pointing to a
magnetically unique stopping site in this material. Most probably it is located near the terminal CN\(^{-}\) ligands which due to their uncompensated negative charge are good candidates to capture the incident muons. The temperature dependence of the local field inferred from the µSR experiment was fitted to the phenomenological form \( B(T) = B(0)[1 - T/T_c]^\beta \) yielding \( \beta = 0.53(2) \), see figure 6. This finding corroborates the mean-field character of the transition. The transverse field mode of the µSR experiment in the field of 50 G permitted the estimation of the \( \gamma \) critical exponent. The value of \( \gamma = 1.1(1) \) agrees with that found from the ac susceptibility analysis. The temperature dependence of the muon longitudinal relaxation rate \( \lambda_L \), originating from the muon-lattice interaction, revealed a sharp peak (not shown) at \( \sim 42 \) K. In the fast fluctuation limit it is directly proportional to the diverging spin-spin correlation time \( \tau \propto |T - T_c|^{-\omega} \) corresponding to the slowing down of critical fluctuations. The scaling analysis of \( \lambda_L \) gave the critical exponent \( \omega = 0.12(1) \). The exponent \( \omega \) is related to the dynamic exponent \( z \) and two static exponents by \( z = d(2\beta + \omega)/(2\beta + \gamma) \), where \( d = 3 \) is the dimension of the spin network. Using this relation and the values of the exponents \( \beta, \gamma \) and \( \omega \) one obtains \( z = 1.6(4) \). This estimate is close to the value of \( d/2 = 1.5 \) expected for dynamical model G of isotropic antiferromagnet [4]. In conclusion, it was found that the Mn\(_2\)Nb(CN)\(_8\) compound is a soft ferrimagnet displaying the critical features of the mean-field model.

3.2. Cu\(_4\)W(CN)\(_8\)I\(_4\)

The crystal structure of the compound (tetrenH\(_5\))\(_{0.8}\)Cu\(_{4}\)II[W\(_V\)(CN)\(_8\)]\(_4\) \cdot 7.2H\(_2\)O was solved by the single-crystal x-ray diffraction and is depicted in figure 7 (left). It crystallizes in the orthorhombic system (space group Cmc\(_2\)_1) with unit cell parameters \( a=7.3707 \) Å, \( b=31.725 \) Å, \( c=7.017 \) Å. It consists of anionic double layers formed by copper and tungsten ions distributed in an alternating fashion and linked through the cyanide bridges. Within the double-layer each Cu ion is surrounded by five NC bridges connecting it to the neighbouring W ions. The coordination sphere of each W ion comprises eight cyanido ligands. Five of them mediate the linkage to the neighbouring Cu ions, and the three remaining ones stand out of the double-layers and are presumably involved in the hydrogen-bond network. The space between the double-layers is filled with water molecules and the tetrenH\(_5\) molecules to maintain the electrostatic charge balance. Due to the the sizeable interbilayer distance of 10 Å the magnetic interaction between the double-layers is significantly smaller than the intrabilayer coupling. The real component of the AC susceptibility shows a sharp peak at \( T_c \approx 33 \) K marking the transition to an ordered state, see figure 8. The single crystal study of Cu\(_4\)W(CN)\(_8\)I\(_4\) [5] revealed a strong easy-plane anisotropy and a weak metamagnetism with spin-flop field on the order of 50 Oe. The classical scaling analysis of the AC signal

### Figure 3
Projection of the crystal structure of Mn\(_2\)Nb(CN)\(_8\) onto the ac crystallographic plane.

### Figure 4
AC susceptibility of Mn\(_2\)Nb(CN)\(_8\) for four different frequencies.
yielded a large value of the critical exponent $\gamma = 1.63(1)$. It is higher than the values expected for the standard universality classes ($\gamma \sim 1.24$ for the 3D Ising model, 1.32 for the 3D XY model, and 1.38 for the 3D Heisenberg model). However, it is placed consistently between $\gamma_\perp (\approx 0.67)$ and $\gamma_\parallel (\approx 2.2)$ found in the single crystal study for the direction perpendicular and parallel to the double-layers, respectively. That coincides with the Monte Carlo results for systems with a strong easy-plane anisotropy, thus with a reduced dimensionality of the spin space [5]. The onset of an ordered state is also apparent in the temperature dependence of the transverse relaxation rate $\lambda_1$ inferred from the $\mu$SR experiment. It can be seen from figure 9 that $\lambda_1$ diverges at the transition point. The time evolution of the muon asymmetry function in the vicinity of the phase transition is shown in figure 10. The measured signals in the whole temperature range below the transition were satisfactorily reproduced if two oscillating amplitudes in Eq. (2) were introduced, which indicates that there are two distinct muon stopping sites. The temperature dependence of the two local fields corresponding to those stopping sites are shown in figure 11. The scaling analysis indicated that both of them have the same temperature dependence yielding a single value of the critical exponent $\beta = 0.23(2)$. The zero-field $\mu$SR experiment carried out for the analog of $\text{Cu}_4[W(\text{CN})_8]_4$, where the W atoms were replaced by the Mo atoms, revealed a similar value of
the exponent $\beta = 0.27$. These values imply that the compounds can be classified to the group of 2D systems with XY exchange anisotropy. The anomalous part of the specific heat shown in figure 12 has a symmetric shape, which is typical for the transition involving reduced dimensionality of the spin network. The scaling analysis can be further extended by combining the results of the $\mu$SR spectroscopy with those obtained by a complementary calorimetric measurement. It was demonstrated [6] that the excess entropy and the square of the order parameter satisfy a combined scaling law involving the critical exponents $\kappa$ and $\kappa'$. Their values determined for Cu$_4$[W(CN)$_8$]$_4$ pointed consistently to the XY anisotropy of the exchange interaction. The compound can thus be classified as a quasi-2D magnet with the XY exchange anisotropy. To our knowledge it is the first example of a molecular magnet displaying the signatures of the Berezinskii-Kosterlitz-Thouless topological transition [5].

3.3. Cu$_6$[W(CN)$_8$]$_4$

The molecular magnet Cu$_6$[W$_4$V(CN)$_8$]-4H$_2$O was obtained by withdrawing the tetren molecule from the synthesis path of the previous compound Cu$_4$[W(CN)$_8$]$_4$ with the view to enhance the magnetic coupling between the structural double-layers [6]. In consequence additional Cu ions were located in the interbilayer spaces and the magnetic transition temperature was raised up to 40 K. The compound...
crystallizes in the tetragonal system with space group I4/mmm and unit cell parameters $a = b = 7.2678$ Å, $c = 28.2373$ Å. Figure 7 (right) shows the projection of the crystal structure onto the bc crystallographic plane. Each W ion is coordinated by eight CN ligands providing a linkage to the Cu ions. Four Cu ions of the formula unit are involved with the W ions in the formation of the double-layers. The remaining two Cu ions are located between the double layers providing direct exchange pathways between the double-layers. Both ions $W^{V}$ and $Cu^{II}$ carry spin 1/2.

Temperature dependence of the AC susceptibility shows a rather sharp peak at $T_c \approx 40$ K, see figure 8, revealing the transition to an ordered phase. There is an apparent difference in the high-temperature slope of the AC signal between this compound and $Cu_4[W(CN)_8]_4$, which suggests distinct critical behaviour related to the change in the dimensionality of the spin network. Classical scaling analysis of the AC signal yielded the critical exponent $\gamma = 1.05(2)$. It is close to the value predicted in the mean-field model and consistent with the value of 1.063(8) found from the transverse field scan obtained in the $\mu$SR experiment, see figure 2. On the other hand, the zero-field asymmetry spectra, see figure 1, processed for the temperature dependence of the local field (figure 13) yielded $\beta = 0.373(8)$ which agrees with the value expected for the 3D Heisenberg model.

4. Conclusions

It was demonstrated that the $\mu$SR spectroscopy represents a unique experimental technique perfectly suited to the investigations of the critical behaviour of molecule based magnets. What is most important in this technique is that one can dispense with subjecting a sample to external magnetic field to get a signal. If only the critical region is sufficiently broad, $\mu$SR provides a matchless means to extract a complete set of static and dynamic critical exponents. Firstly, implanted muons in magnetically ordered phase precess in the local magnetic field with frequency proportional to the magnitude of that field, which permits the determination of the critical exponent $\beta$. Secondly, the frequency shift in a small transverse field detected in the paramagnetic regime yields the exponent $\gamma$. Finally, the longitudinal muon spin relaxation is a probe sensitive to the spin correlation time giving the dynamical exponent $w$. The remaining static and dynamic exponents can be deduced from the scaling or hyperscaling relations, such as $\alpha + 2/\beta + \gamma = 2$ (the Rushbrook equality), $\nu = (2\beta + \gamma)/d$, $\eta = 2 - \gamma/\nu$, and $w = \nu(z + 2 - d - \eta)$, where $d$ is the dimension of the spin network. Table 1 summarizes the critical exponents determined experimentally for four representatives of molecular magnets mentioned in this work. For comparison, the static and dynamic exponents for five model systems have also been quoted. It can be seen that $Mn_2Nb$ can be classified as the mean-field magnet, and $Cu_4W_4$ and $Cu_4Mo_4$ are consistent with the 2D XY model. For $Cu_6W_4$ a discrepancy is observed, as according to the $\beta$ exponent this material corresponds to the 3D Heisenberg model, while the $\gamma$ exponent is close to the mean-field
value. Interestingly, for both molecular magnets with the 3D spin network reduced values of the $\gamma$ exponent were observed. Further studies of molecule based magnets are bound to shed some light on this conjecture.

Table 1. Experimental critical exponents compared to different models. The values of the dynamical exponent $w$ for the model systems are quoted from [1].

| model       | $\beta$ | $w$      | $\gamma$  |
|-------------|---------|----------|------------|
| Ising d=2   | 1/8     | 3/2      | 7/4        |
| XY d=2      | (0.24)  | 0.309    | 1.80 (2.17 for XXY) |
| Ising d=3   | 0.326   | 0.717(FM)| 1.239      |
|             |         | 0.596(AF)|            |
| Heisenberg d=3 | 0.369 | 1.026(FM)| 1.36        |
|             |         | 0.328(AF)|            |
| mean field  | 0.5     | 0        | 1          |
| Mn$_2$Nb    | 0.53(2) | 0.12(1)  | 1.15(5)    |
| Cu$_6$W$_4$ | 0.373(8)|         | 1.05(2)    |
| Cu$_4$W$_4$ | 0.23(2) | 1.35(5)  | 1.63(1)    |
| Cu$_4$Mo$_4$| 0.27(2) | 0.18(2)  | 1.495(2)   |

Acknowledgments
This work has been partially supported by the Polish Ministry of Science and Higher Education within Research Projects 0087/B/H03/2008/34 and 1535/B/H03/2009/36.

References
[1] Pratt F L, Lancaster T, Baker P, Blundell S, Kaneko W, Ohba M, Kitagawa S, Ohira-Kawamura S and Takagi S 2009 Physica B 404 585–589
[2] Przychodzen P, Korzeniak T, Podgajny R and Sieklucka B 2006 Coord. Chem. Rev. 250 2234–2260
[3] Pratt F L 2000 Physica B 289-290 710–714
[4] Hohenberg P C and Halperin B I 1977 Rev. Mod. Phys. 49 435
[5] Bałanda M, Pelka R, Wasiułski T, Rams M, Nakazawa Y, Miyazaki Y, Soraï M, Podgajny R, Korzeniak T and Sieklucka B 2008 Phys. Rev. B 78 174409
[6] Czapla M et al 2010 Phys. Rev. B 82 094446