



# Experimental observation of quantum coherence in molecular magnetic clusters with half-integer spin

F.L. Mettes <sup>a</sup>, G. Aromí <sup>b</sup>, F. Luis <sup>c</sup>, M. Evangelisti <sup>a</sup>, G. Christou <sup>d</sup>, D. Hendrickson <sup>e</sup>,  
L.J. de Jongh <sup>a,\*</sup>

<sup>a</sup> Kamerlingh Onnes Laboratory, Leiden University, PO Box 9506, 2300 RA, Leiden, The Netherlands

<sup>b</sup> Leiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA, Leiden, The Netherlands

<sup>c</sup> Instituto de Ciencia de Materiales de Aragón, Univ. de Zaragoza, Facultad de Ciencias, 50009 Zaragoza, Spain

<sup>d</sup> Department of Chemistry, Indiana University, Bloomington, IN 47405-4001, USA

<sup>e</sup> Department of Chemistry, University of California at San Diego, La Jolla, CA 92093, USA

Received 17 September 2000; accepted 15 December 2000

## Abstract

From field-dependent specific heat studies we conclude that magnetic relaxation becomes temperature independent for two  $Mn_4$  compounds, below some temperature  $T_Q$ . At low temperatures, the specific heat gives evidence for the presence of a tunnel splitting  $\Delta_t$  of the ground state  $S_z = \pm 9/2$  for both compounds. The predicted quenching of  $\Delta_t$  for clusters with half-integer spin apparently does not occur, probably due to the joint action of dipolar and hyperfine fields, in combination with the applied perpendicular field of sufficient strength. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Magnetic relaxation; Manganese; Molecular magnetic clusters; Specific heat

## 1. Introduction

We present specific heat data on magnetic clusters of  $Mn_4O_3X(OAc)_3(dbm)_3$ , with  $X = Cl$  and  $OAc$ , in the

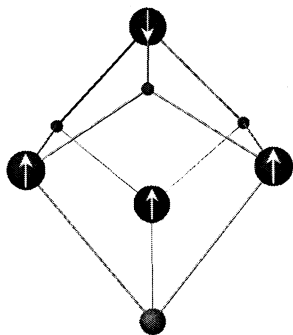


Fig. 1. Representation of the  $Mn_4O_3X$  cluster core.

temperature range  $T = 0.2$ – $6$  K and in magnetic fields up to 6 T. At high temperatures ( $T > 1$  K) we find that our data can be represented by a total spin  $S = 9/2$  per cluster, which is zero-field split by a uniaxial anisotropy. For  $T < 1$  K, the specific heat shows an up-turn for both compounds, which can be explained by introducing dipolar interactions between the clusters and hyperfine interactions within each cluster. The hyperfine contribution from the Mn nuclei can be calculated exactly [1,2] and, consequently, the average strength of the dipolar fields can be estimated.

The field dependence of the specific heat at low temperatures ( $T < 1$  K) reveals fascinating magnetic quantum behavior for the total spin of the clusters. At low temperatures the magnetic relaxation time of the clusters can become much longer than the characteristic time in the experiment, resulting in a freezing or blocking of the magnetic moment. We have studied the magnetic relaxation as a function of temperature and observed that it becomes temperature independent below some temperature, denoted  $T_Q$ . Clearly,  $T_Q$  will depend on the strength of the anisotropy. Below  $T_Q$ , magnetic relaxation can occur through the (tunnel-split)

\* Corresponding author. Present address: Faculty of Mathematics and Natural Sciences, Leiden University, PO Box 9506, 2300 RA, Leiden, The Netherlands. Tel.: +31-71-5275625; fax: +31-71-5275404.

E-mail address: dejongh@phys.leidenuniv.nl (L.J. de Jongh).

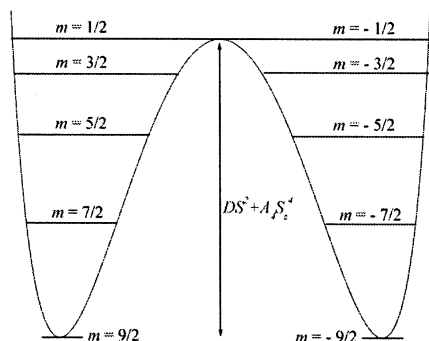


Fig. 2. Schematic drawing of the energy levels according to the diagonal terms in Eq. (1).

ground state. Indeed, at these temperatures the field dependence of the specific heat evidences the presence of a tunnel splitting  $\Delta_t$  of the two lowest energy levels  $S_z = \pm 9/2$ .

## 2. Experimental

Analytically pure samples of the compounds  $\text{Mn}_4\text{O}_3\text{X}(\text{OAc})_3(\text{dbm})_3$ ,  $\text{X} = \text{Cl}, \text{OAc}$ , were prepared at the University of Leiden [3]. All compounds were characterized by elemental analysis. From X-ray powder diffraction analysis on previous samples of the series [4] it was concluded that the  $\text{X} = \text{OAc}$  compound is single phase, whereas the  $\text{X} = \text{Cl}$  compound contains an impurity phase of about 5–10%. In this work, the  $\text{X} = \text{OAc}$  compound is prepared in the same way as in Ref. [4], whereas the  $\text{X} = \text{Cl}$  sample is obtained by a slightly different method [3].

The series ( $\text{X} = \text{Cl}, \text{OAc}$ ) molecules possess a distorted cubane core ( $\text{Mn}_4\text{O}_3\text{X}$ ) of one  $\text{Mn}^{4+}$  ion (spin  $S = 3/2$ ) and three  $\text{Mn}^{3+}$  ions ( $S = 2$ ), super-exchange coupled by three oxygen ions, see Fig. 1. The exchange couplings between the four Mn ions have been studied by magnetic susceptibility measurements [5,6]. The coupling between the  $\text{Mn}^{3+}$  ions was found to be ferromagnetic ( $J \approx 12$  K and 8 K respectively for  $\text{X} = \text{Cl}$  and  $\text{OAc}$ ), whereas the  $\text{Mn}^{4+}$  ion couples anti-ferromagnetically to the  $\text{Mn}^{3+}$  ions ( $J \approx 41$  K and 48 K respectively for  $\text{X} = \text{Cl}$  and  $\text{OAc}$ ). At low temperatures, the four Mn spins order in a total spin  $S = 9/2$ , which is subject to a uniaxial crystal field [5,7], the symmetry axis of which runs through the  $\text{Mn}^{4+}$  ion and the X ligand. The X ligand acts as a bridge between the three  $\text{Mn}^{3+}$  ions and by changing X the magnitude of the uniaxial anisotropy along the  $\text{Mn}^{4+} - \text{X}$  ligand symmetry axis is affected [5,6].

All low-temperature specific heat measurements were performed as described in Refs. [8,9]. In the experiments described in this paper, the samples we measured consisted of 2–3 mg of polycrystalline sample, which was mixed with 4–5 mg of Apiezon-N grease.

## 3. Theoretical

The spin Hamiltonian describing the  $\text{Mn}_4\text{O}_3\text{X}$  ( $\text{X} = \text{Cl}, \text{OAc}$ ) magnets in an applied field  $\mathbf{B}$  has the following form

$$H = -DS_z^2 - g\mu_B B_{\parallel} S_z - g\mu_B B_{\perp} [\cos(\phi)S_x + \sin(\phi)S_y] - E(S_x^2 - S_y^2) - A_4 S_z^4 + C(S_+^4 + S_-^4) + H_{\text{dip}} + H_{\text{hf}} \quad (1)$$

Here,  $S_z$  is the component of the total spin of the clusters along the anisotropy axis  $z$ . All crystal field parameters have been determined previously by EPR [10] and inelastic neutron scattering (INS) [4] techniques. We adopt the values  $D = 0.59$  K,  $E = -2.43 \times 10^{-2}$  K,  $A_4 = 3.96 \times 10^{-3}$  K and  $C = -1.21 \times 10^{-4}$  K for  $\text{X} = \text{OAc}$  and  $D = 0.69$  K,  $E = -3.15 \times 10^{-2}$  K,  $A_4 = 3.25 \times 10^{-3}$  K and  $C = -9.95 \times 10^{-5}$  K for  $\text{X} = \text{Cl}$ . In the above expression,  $B_{\parallel}$  and  $B_{\perp}$  are, respectively, the components of the applied field parallel and perpendicular to the anisotropy axis and  $\phi$  is defined as the angle between the field  $B_{\perp}$  and the hard axis  $x$ .

If only diagonal terms in Eq. (1) are considered, the zero-field energy– $S_z$  diagram has the well-known double-well potential shape, as depicted schematically in Fig. 2, for a total spin  $S = 9/2$ .

The terms  $H_{\text{dip}}$  and  $H_{\text{hf}}$  in Eq. (1) include dipolar and hyperfine interactions, which are always present even in zero applied field. The hyperfine contribution originates mainly from interactions between the four Mn nuclei ( $I = 5/2$ ) (and to a much lesser extent from interactions between the surrounding protons) and the total electronic spin  $S = 9/2$ . Its magnitude can be estimated, since the hyperfine interaction constants for  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  are known. The dipole–dipole contributions arise from interactions between electronic spins of neighboring molecules and between the electronic spin and its surrounding nuclear spins, which are the Mn nuclei and the protons in the ligands. They are approximated by a time-independent bias field with Gaussian distribution, the width of which is taken as an adjustable parameter.

Off-diagonal perturbation terms in Eq. (1) (e.g. a magnetic field perpendicular to the anisotropy axis) can induce quantum tunneling between those states that are degenerate, thereby lifting the degeneracy. The splitting of two initially degenerate energy levels caused by off-diagonal elements only is defined as the tunnel splitting, here denoted as  $\Delta_t$ . Diagonal terms, arising from hyperfine and dipolar interactions will introduce an additional splitting of the energy levels, which we denote by  $\delta$ . In Fig. 3 we show the tunnel splitting of the two lowest energy levels  $S_z = \pm 9/2$ , as calculated by diagonalization of Eq. (1), as a function of the applied field perpendicular to the anisotropy axis of the cluster ( $B_{\perp}$ ). For small fields ( $B_{\perp} < 1.5$  T),  $\Delta_t \ll \delta$ , so

that tunneling is clearly blocked. However, for sufficiently large fields ( $B_{\perp} \approx 2.5$  T),  $\Delta_i$  can be made larger than all diagonal splittings and can therefore be detected, e.g. by specific heat measurements.

The specific heat is calculated using the model proposed in Ref. [11]. The model takes into account excited levels to calculate the total relaxation rate  $\Gamma$  for

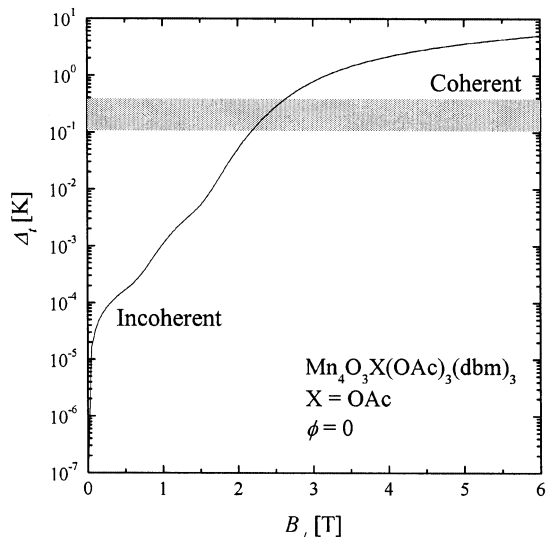


Fig. 3. Calculated tunnel splitting of the two lowest energy levels,  $S_z = \pm 9/2$ , as a function of applied field perpendicular to the anisotropy axis  $B_{\perp}$ . The gray area represents the energy scale for (Zeeman) splittings caused by diagonal terms in Eq. (1).

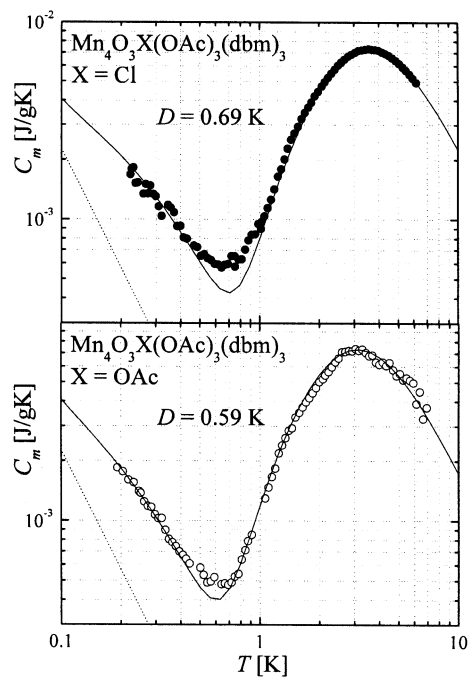


Fig. 4. Temperature dependence of the specific heat for  $X = \text{Cl}$  and  $X = \text{OAc}$  in zero applied field. The full lines denote the calculated specific heat; the dotted lines represent the calculated nuclear contribution due to the hyperfine interaction.

spin–flip processes. For every individual level the rate is calculated, making use of Fermi’s ‘Golden rule’. An important implication of the model is that tunneling processes are naturally included by taking into account eigenstates of the full Hamiltonian, Eq. (1).

## 4. Experimental results

### 4.1. Specific heat in zero applied field

Fig. 4 shows the equilibrium specific heat of both magnetic clusters in zero applied field. The data above 1 K are well reproduced by a spin 9/2 multiplet, whereas the low- $T$  increase is ascribed to the combination of intracluster hyperfine interactions and intercluster dipolar couplings. The full lines shown in the figures are the calculations as described in Section 3. The calculations were found to fit the data best when taking for the width 0.025 T for  $X = \text{Cl}$  and 0.020 T for  $X = \text{OAc}$ . We can compare these values to 0.02 T, which is estimated on the basis of the available quantitative information on hyperfine interactions and dipolar fields in the  $\text{Mn}_{12}$ -acetate molecule [2,12,13]. It should be noted that the  $\text{Mn}_{12}$  core carries a much bigger net moment of  $S = 10$ . However, we have to pay some caution to the values obtained for the dipolar fields. At least for the  $X = \text{Cl}$  sample, there could be an extra contribution due to an impurity phase, even in zero field.

### 4.2. Magnetic relaxation through lower-lying states

The field dependence of the specific heat at low temperatures ( $T < 1$  K) shows a kink-type anomaly for fields  $B < 1.5$  T, as can be seen in Fig. 5. This anomaly is associated with the transition from non-equilibrium to equilibrium specific heat [8,9,14]. The field value for which it occurs is denoted the crossover field  $B_c$ . Previously, we have observed in similar experiments performed on  $\text{Fe}_8$  molecules that  $B_c$  depends on the experimental time  $\tau_c$  [8,9,14]. In fact,  $B_c$  decreased when  $\tau_c$  was increased. The explanation of this effect was as follows. At fixed  $T$  and  $\tau_c$ , the transition appears when the spin–lattice relaxation time becomes fast enough through the action of the applied field, such that the condition  $\Gamma\tau_c \approx 1$  is fulfilled. Here,  $\Gamma$  is the magnetic relaxation time of the clusters. The measurement of the temperature dependence of  $B_c$  is therefore useful in order to determine the dominant relaxation process. In Fig. 6 we show the crossover field, measured at different temperatures. The figure implies that, below some temperature denoted  $T_Q$ ,  $B_c$  saturates at values  $B_c \approx 1.45$  T and 0.9 T for  $X = \text{Cl}$  and  $\text{OAc}$ , from which we may conclude that magnetic relaxation becomes temperature independent below  $T_Q = 0.3$  K for  $X = \text{Cl}$  and

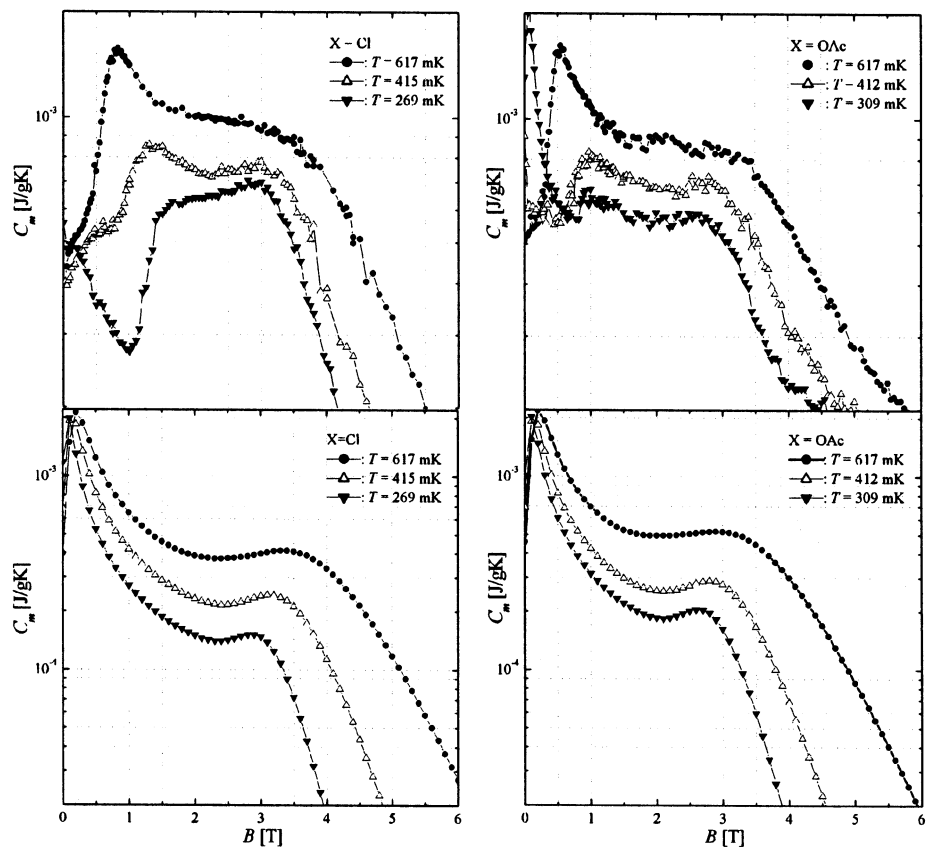


Fig. 5. The upper part shows the field dependence of the specific heat of both clusters at low temperatures. In the lower part the equilibrium specific heat calculated for a random distribution of easy axes and averaging over  $\phi$  is shown.

$T_Q = 0.4$  K for  $X = \text{OAc}$ . Apparently, below these temperatures relaxation can occur through the  $S_z = \pm 9/2$  ground state. In Fig. 5, the measurements taken at the lowest temperatures for both compounds correspond to slightly longer experimental times than for higher temperatures. We see that these data follow more closely the calculated equilibrium curves (bottom of the figure) even at low fields. This is an additional indication of the weak temperature dependence of the relaxation time, in sharp contrast with the exponential decay predicted for thermally activated relaxation. The crossover temperature for the  $X = \text{Cl}$  compound can be compared with  $T_Q = 0.6$  K, as obtained with a different method by Aubin et al. [10]. They found that the magnetic decay curves (as a function of time) in zero field (after initially saturating the sample in a field of 2 T), merge when the temperature of the sample is reduced below  $T_Q$ . The rate is then found to be  $3.2 \times 10^{-2} \text{ s}^{-1}$ . We find, at the onset of the saturation in  $B_c$ , similar values for the experimental time  $\tau_e$ .

#### 4.3. Quantum coherence in large (perpendicular) fields

As already pointed out in Section 3, a magnetic field of sufficient strength applied perpendicular to the an-

isotropy axis can increase the tunnel splitting of the two lowest energy levels to values large enough that  $\Delta_t \gg \delta$ . Furthermore, we have seen above that magnetic relaxation can occur through the  $S_z = \pm 9/2$  ground state when the temperature is sufficiently reduced and the field is sufficiently large. In Fig. 5 the field dependence of the specific heat measured at low temperatures is

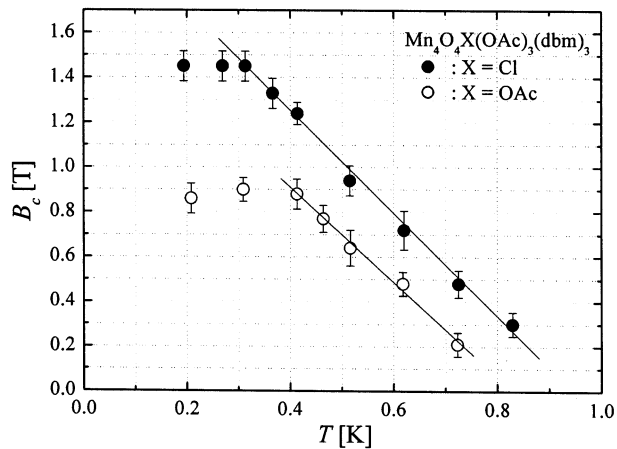


Fig. 6. Temperature dependence of the crossover field  $B_c$ , as obtained from the small-field part of the field scans of the specific heat, for both compounds.

depicted. The upper part of Fig. 5 shows the measured data, whereas the calculations, following the model proposed in Ref. [11], are given in the lower part. Upon increasing the field, the specific heat first reaches equilibrium at some field  $B_c$  (as described above) and then shows a maximum around 2.5–3.5 T, after which it decreases rapidly. The maxima are seen to shift to lower fields when the temperature is decreased. Exactly the same behavior is found in the calculations. Furthermore, the field values at which the maxima appear coincide nicely with those in the experiment. These features are in full agreement with the presence of a tunnel splitting of magnitude  $\Delta_t \approx k_B T$ . All measurements are performed on non-oriented (powder) samples, which implies that under the (extreme) conditions of low  $T$  and large  $B$ , only those clusters contribute to  $C_m$  that have their easy axes aligned sufficiently perpendicular to the field [8,9,14].

As seen in Fig. 5, the ‘plateaus’ in the experimental data are considerably higher than those in the calculated curves. This difference most probably originates from impurity phases, which are liable to occur in the  $X = \text{Cl}$  sample [3,4], but apparently are also present in our  $X = \text{OAc}$  sample. Measurements on sufficiently purified samples might facilitate a more quantitative comparison with the calculations.

## 5. Conclusions

We have measured the electronic and nuclear contributions to the specific heat of both compounds in applied fields ranging from 0–6 T. Recently obtained crystal field parameters are successfully used to account for the observed multiplet anomaly at high temperatures. The data at low temperatures have enabled us to estimate the magnitude of dipole–dipole fields between neighboring molecules.

From our field-dependent specific heat studies we conclude the following. Magnetic relaxation is seen to become temperature independent for both compounds, below some temperature  $T_Q$ . At low temperatures, the specific heat gives evidence for the presence of a tunnel splitting  $\Delta_t$  of the ground state  $S_z = \pm 9/2$  for both compounds. The predicted quenching of  $\Delta_t$  for clusters

with half-integer spin [15] apparently does not occur, probably due to the joint action of dipolar and hyperfine fields, in combination with the applied perpendicular field of sufficient strength.

## Acknowledgements

This work was part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). F.L. acknowledges a grant funded by the European Union in the frame of its TMR Marie Curie Program.

## References

- [1] A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford, 1970.
- [2] W. Wernsdorfer, R. Sessoli, D. Gatteschi, *Europhys. Lett.* 47 (1999) 254.
- [3] G. Aromí, S. Bhaduri, P. Artús, K. Folting, J.C. Huffman, G. Christou, *Inorg. Chem.*, submitted for publication.
- [4] H. Andres, R. Basler, H.-U. Güdel, G. Aromí, G. Christou, H. Büttner, B. Rufflé, *J. Am. Chem. Soc.* 50 (2000) 12469.
- [5] S. Wang, H.-L. Tsai, E. Libby, K. Folting, W.E. Streib, D.N. Hendrickson, G. Christou, *Inorg. Chem.* 35 (1996) 7578.
- [6] M.W. Wemple, D.M. Adams, K. Folting, D.N. Hendrickson, G. Christou, *J. Am. Chem. Soc.* 117 (1995) 7275.
- [7] S.M.J. Aubin, M.W. Wemple, D.M. Adams, H.-L. Tsai, G. Christou, D.N. Hendrickson, *J. Am. Chem. Soc.* 118 (1996) 7746.
- [8] F. Luis, F.L. Mettes, J. Tejada, D. Gatteschi, L.J. de Jongh, *Polyhedron* (2001) this issue.
- [9] F.L. Mettes, F. Luis, L.J. de Jongh, *Phys. Rev. D.*, submitted for publication.
- [10] S.M.J. Aubin, N.R. Dilley, L. Pardi, J. Krzystek, M.W. Wemple, L.-C. Brunel, M.B. Maple, G. Christou, D.N. Hendrickson, *J. Am. Chem. Soc.* 120 (1998) 4991.
- [11] F. Luis, J. Bartolomé, J.F. Fernández, *Phys. Rev. B* 57 (1998) 505.
- [12] F. Hartmann-Boutron, P. Politi, J. Villain, *Int. J. Mod. Phys. B* 10 (1996) 2577.
- [13] W. Wernsdorfer, T. Ohm, C. Sangregorio, R. Sessoli, D. Mailly, C. Paulsen, *Phys. Rev. Lett.* 82 (1999) 3903.
- [14] F. Luis, F.L. Mettes, J. Tejada, D. Gatteschi, L.J. de Jongh, *Phys. Rev. Lett.* 85 (2000) 4377.
- [15] N.V. Prokofev, P.C.E. Stamp, *J. Phys.: Condens. Matter* 5 (1993) L663.