Magnetization Density in an Iron(III) Magnetic Cluster. A Polarized Neutron Investigation

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Received January 29, 1999
Revised Manuscript Received April 22, 1999

Magnetic molecular clusters, formed by a large number of strongly interacting metal ions, have been extensively investigated during recent years,[1] as models of nanometer-sized single-domain magnetic particles. Particular attention[2] has been devoted to clusters with high spins in the ground state and Ising-type anisotropy showing slow relaxation of the magnetization at low temperature, which eventually relaxes with a tunneling mechanism. Slow relaxation and the even more interesting phenomenon of pure quantum tunneling of the magnetization have been recently reported[3a] for an octanuclear iron(III) cluster, $\{[Fe_8O_2(OH)_{12}(tacn)_6]Br_7 \cdot H_2O\}^+[Br \cdot 8H_2O]^-$, Fe_8, where tacn = 1,4,7-triazacyclononane. It is characterized by a ground $S = 10$ state originated by the presence of competing antiferromagnetic interactions between the $S = {}^5/_2$ spins[3b−c] of the iron atoms and by very weak dipolar intercluster interactions. A model for the coupling scheme, presented in Figure 1, has been proposed,[3c] but given the complexity of the system and the large number of independent exchange pathways, the exact nature of the ground state cannot be unambiguously described by fitting thermodynamic properties such as magnetic susceptibility. On the other hand, the spin structure and the dipolar magnetic fields inside the sample seem to play an important role in the tunneling mechanism,[3d] requiring a detailed knowledge of the global spin density.

Therefore, to obtain a better description of the ground state it is necessary to use experimental techniques, which give access to the unpaired magnetization density of the cluster, like EPR, NMR, and neutron diffraction. In the latter case, two types of techniques were used: polarized and unpolarized neutron diffraction. However, the latter, which has been applied on a Mn_{12} cluster,[4] seems to provide results which are not very accurate.

Polarized neutron diffraction, PND, applies to single crystals of paramagnetic species in which the magnetization density is aligned by an external magnetic field. The incident neutron beam is polarized either parallel (↑) or antiparallel (↓) to the applied magnetic field, and the so-called flipping ratios R between the intensities $I^{\uparrow}$ and $I^{\downarrow}$ respectively at the Bragg positions (*hkl*) are measured

$$R(hkl) = \frac{I^{\uparrow}}{I^{\downarrow}} = \frac{F_N^* F_N + \sin^2\alpha(F_N^* F_M + F_M^* F_N) + \sin^2\alpha(F_M^* F_M)}{F_N^* F_N - \sin^2\alpha(F_N^* F_M + F_M^* F_N) + \sin^2\alpha(F_M^* F_M)} \quad (1)$$

where F_N and F_M are the nuclear and magnetic structure factors, respectively, and α is the angle between the spin (magnetic moment) direction and the scattering vector $\vec{K}$ of the Bragg reflection (*hkl*). Although PND is a powerful technique for mapping the unpaired electron, thus far it has been little applied to magnetic clusters, with the exception of preliminary report on a Mn_{11} cluster.[5]

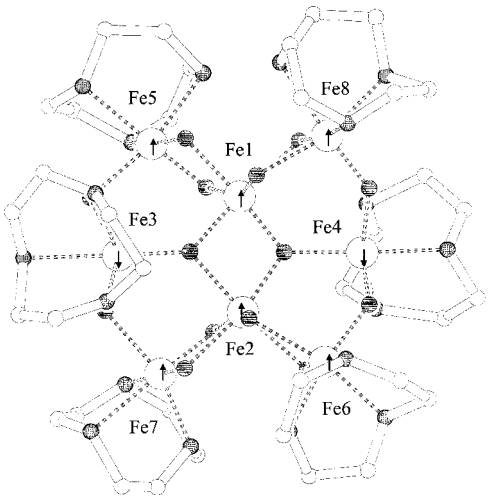

Figure 1. View of the structure of the Fe_8 cluster. The large open empty circles represent iron atoms; full, hatched and empty small ones stand, respectively, for oxygen, nitrogen, and carbon atoms. The proposed spin structure of the $S = 10$ ground state is schematized by the arrows.

In this paper we wish to report the preliminary results concerning PND of the Fe_8 cluster, and we suggest that it can be used as a case study for the large possibilities of PND in providing information on the magnetic coupling schemes which are operative in the cluster.

The experiment was performed on the polarized neutron diffractometer D3 of the Institut Laue Langevin (Grenoble, France) at a wavelength $\lambda = 0.843$ Å. This instrument is a lifting counter diffractometer, with a cryomagnet which holds the sample and provides a vertical magnetic field. A crystal of size 1.3 × 3.0 × 1.08 mm was mounted with the *a* crystal axis (easy axis) parallel to the 4.6 T applied magnetic field. One hundred and ninety-eight independent flipping ratios were measured at $T = 2$ K.

Since Fe8 crystallizes in an acentric space group,[6] both F_N and F_M are complex quantities ($F_{N,M} = F'_{N,M} + i\,F''_{N,M}$), and the magnetic structure factors cannot be directly obtained from the flipping ratio measurements. The magnetization density, MD, reconstruction is then directly performed from the flipping ratios. The data were treated in two ways.[7]

First, we used the 3D maximum entropy (MaxEnt) method[8] which was recently extended to the treatment of acentric structures.[9] In this case, the MD is obtained without imposing

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10.1021/ja9903126 CCC: $18.00
Published on Web 05/25/1999

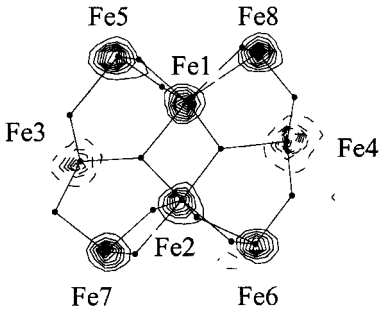

Figure 2. MaxEnt reconstructed magnetization density projected onto the *bc* crystallographic plane of the Fe_8 cluster (negative contours are dashed, step 0.7 $\mu_B/Å^2$).

Table 1. Refined Magnetic Moments of the Iron Ions of the Fe_8 Cluster

atoms	moments (μ_B)	atoms	moments (μ_B)
Fe1	4.79 (22)	Fe5	3.77 (22)
Fe2	2.34 (26)	Fe6	4.01 (20)
Fe3	−1.94 (31)	Fe7	4.31 (27)
Fe4	−4.91 (32)	Fe8	3.35 (34)

any predefined model.[10] The MaxEnt reconstructed density projected onto the *bc* crystallographic plane is presented in Figure 2.

Second, we used a method based on the modeling of the density; namely the multipolar expansion[11] approach. With this approach,[12] we have refined the moments on all of the iron ions and on neighboring O and N atoms.

Contrary to what was reported for Mn_{12},[4] but as previously observed for Mn_{11},[5] the density is essentially located on the metallic sites: the measured magnetization on the organic part remains of the order of the experimental uncertainty (the refined values of the iron atoms are reported in Table 1, the corresponding refined Slater radial exponent is 3.725 (4)). The eight iron ions can be grouped in two sets, one comprising the 4 and 3 ions, whose moments are opposed to the applied field, and the other, comprising the ions 1,2,5,6,7,8 whose moments are parallel to the field. In qualitative terms these results are in agreement with the coupling scheme previously proposed on the basis of the comparison of the exchange pathways with those of simple dinuclear iron(III) compounds.[13] The simple scheme of Figure 1 would suggest a moment of 5 μ_B ($2S_i\mu_B$) for the up spin and −5 μ_B for the down spin. Clearly the ground-state cannot be described by a single configuration. The ground-state eigenvector will be a contribution of several different configurations.

To develop a suitable model it is useful to look at the cluster as formed by a central "butterfly" core,[3c,14] defined by the 1,2,3, and 4 ions, with 1 and 2 on the body and the other on the wings. Assuming that the coupling mechanisms are dominated by the μ-oxo bridges connecting the butterfly ions, then the observed pattern of MD is reproduced, assuming that the coupling constant connecting the body ions 1 and 2, which corresponds to a double bridge with Fe−O−Fe angles of 96.8° on the average, is much smaller than those defining the wings, in which the single μ-oxo bridges form in average an Fe−O−Fe angle of 128.8°. Such a trend in the strength of the interaction is in agreement with the angular dependence of the coupling constants in iron(III) pairs, recently well-established,[13] both experimentally and theoretically. Moreover the average $Fe-O_{bridge}$ distance is significantly shorter for the wing-core pairs. The MD map shows also that the spins of the four peripheral iron atoms are aligned parallel to Fe1 and Fe2 suggesting that the antiferromagnetic interactions with Fe1 and Fe2 are weaker than those with Fe3 and Fe4. In this case the $Fe-O_{bridge}$ distances are similar, but the Fe−O−Fe angles are significantly smaller for the first type of bridge. The temperature dependence of χT has been successfully reproduced, assuming D_2 symmetry for the cluster in order to reduce the matrices to a tractable size, using $J_{27} = 15-18$ cm^{-1}, $J_{37} = 35-40$ cm^{-1}, $J_{12} = 20-25$ cm^{-1}, and $J_{24} = 130-140$ cm^{-1} (with a Hamiltonian of the type $H = \Sigma J_{ij}S_iS_j$), whose relative order of magnitude is in agreement with the present results. With these values the first $S = 9$ state is calculated to lie about 30 K above the $S = 10$ ground state, in agreement with neutron spectroscopy results[15] where no contributions of $S = 9$ excited states are visible at 10 K. However, due to the strong correlation between the J parameters,[16] these values should be considered as indicative.[17]

Looking in more detail at the experimental MD we see that it substantially deviates from the assumed D_2 symmetry, and in fact there are marked asymmetries in the moment on the 1 and 2 and on the 3 and 4 pairs, respectively. The asymmetry is much less marked on the 5,6,7,8 ions. From the point of view of the crystal symmetry this is not surprising because the cluster lacks a center of symmetry, but no large differences are observed in the exchange pathways. It is possible that, given the presence of eight triangles, spin frustration effects finely determine the MD. Unfortunately it is not possible to calculate the spin levels without using symmetry because the matrices become too large. Further, allowing 13 coupling constants to vary independently would probably be not meaningful at any rate.

In conclusion PND has provided a strong confirmation to the description of the nature of the ground state in Fe8, and shows how the technique can provide unique information for the understanding of the magnetic properties of large clusters.

Acknowledgment. The financial support of MURST and TMR grant 3MD (No. ERB 4061 PL 97-0197) is gratefully acknowledged.

JA9903126

(7) The structure, at the temperature where the PND experiment is performed, is required (see refs 8, 9, and 11). This experiment was performed on the unpolarized lifting counter diffractometer D15 at the ILL's reactor (single crystal of size 2.9 × 1.8 × 1.0 mm, *b*-axis vertical, $T = 5$ K). The position and the isotropic thermal factors were refined using the SHELX93 program down to an agreement factor R1 = 9.6% (1455 reflections with $I > 4\sigma I$) and R1 = 12.7% (all the 1959 independent reflections). The corresponding cell parameters are: $a = 10.470$ Å (11), $b = 14.036$ Å (22), $c = 14.987$ Å (18), $\alpha = 89.645°$ (67), $\beta = 109.948°$ (42), $\gamma = 109.595°$ (67). Precise nuclear structure factors were calculated from this refined low-temperature crystal structure.

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(10) The MaxEnt method, based on a Bayensian approach, evaluates, for each possible reconstructed map, the probability of this map. Such a conditional probability, or "posterior probability", is the product of two probabilities: the "likelihood" and the "prior". The " likelihood" represents the probability for the set of experimental data to be observed if the map were the real map and can be expressed by $\exp(-\chi^2/2)$ where χ^2 is the agreement between calculated and observed data. The "prior" probability represents the intrinsic probability of the map, prior to the experiment, and can be expressed in term of the entropy of the map. The map is then chosen with the best map as being that which maximizes the entropy and keeps a good agreement with the experimental data.

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(12) In this case, the spin density is expanded around the nuclei into a multipolar series. The spin density is treated as a sum of real harmonic functions centered at each atomic site included in the refinement:

$$S(r) = \sum_{\text{atoms}} \sum_{k=0}^{\infty} R_k(r) \sum_{m=-l}^{l} P_l^m y_l^m(\hat{r})$$

where P_l^m and $R_k(r)$ are the population coefficients and Slater type radial functions, respectively. The population coefficients as well as the Slater radial exponents are the parameters of the model.

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