Neutron Spectroscopy for the Magnetic Anisotropy of Molecular Clusters

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Neutron spectroscopy has been used to observe transitions between the energy levels for the 21 different orientations of the $S = 10$ spin ground state of an octanuclear iron molecular cluster (Fe_8) exhibiting quantum tunneling of the magnetization. The results obtained on nondeuterated samples provide the first direct measurement of the zero-field splitting in a large cluster nanomagnet. A reliable and accurate determination of the composition of the cluster's spin wave functions and the spin-Hamiltonian parameters are deduced from the experimental observations, giving crucial information for the study of the macroscopic quantum tunneling process. [S0031-9007(98)07673-X]

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Molecular clusters composed by a large number of strongly interacting metal ions have been of growing scientific interest as models of nanometer-sized single-domain magnetic particles with high spin ground state [1]. Compared to conventional nanomagnets obtained by sputtering, wet precipitation synthesis, or ball milling of bulk magnetic materials, the molecular systems offer the advantage of being formed by identical particles, whose structure can be precisely determined by diffraction measurements. Moreover, diluted systems characterized by a very weak cluster-cluster interaction (typically of the order of a few μeV) can be easily prepared [2]. Ensembles of weakly interacting magnetic clusters with large Ising-type anisotropy appeared to be very promising for the observation of mesoscopic quantum coherence. It has recently been realized that the cluster magnetization can tunnel coherently between the two opposite directions corresponding to the pair of degenerate potential wells created by the anisotropy barrier [3,4]. Such a phenomenon provides the signature of quantum behavior in mesoscopic systems and is of great relevance not only from a fundamental point of view, but also because it may prove to have important technical applications [5,6].

Knowledge of the magnetic anisotropy of the clusters is central to our understanding of the conditions under which the quantum tunneling of the magnetization (QTM) can occur. In the presence of uniaxial anisotropy, the spectral energy of a cluster depends on the orientation of the spin S relative to its symmetry axis, z. In the simplest case, with zero external magnetic field, the spin Hamiltonian is defined by a single anisotropy parameter D and depends on the spin projection along z, $H = DS_z^2$. However, for QTM to be allowed, the rotational symmetry about the z axis must be broken by fourth-order spin terms, which do not commute with S_z [7–9]. In general, theories of QTM depend critically on the knowledge of the anisotropy parameters, whose precise determination requires a suitable experimental technique.

Recently, high-frequency electron paramagnetic resonance (EPR) was used to determine the spin Hamiltonian for Mn12ac [10], a molecular cluster for which resonant QTM was observed below 2 K [3,4]. The analysis of EPR spectra taken in magnetic fields up to 25 T proved the presence of fourth-order spin terms, which in Mn12ac are responsible for the transverse magnetic anisotropy and the occurrence of QTM. In EPR measurements, however, the zero-field-splitting terms in the Hamiltonian are deduced from their effect on the level scheme in the presence of a strong magnetic field, and the data interpretation requires complementary assumptions on the parameters defining the Zeeman term. Inelastic neutron scattering (INS) is particularly appealing under this respect, because it can in principle give a detailed picture of the low lying energy levels from a straightforward analysis of spectra taken with zero magnetic field.

In this Letter we report the results of high resolution INS experiments which give directly the anisotropy splitting of the $S = 10$ spin ground state in an octanuclear iron

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molecular cluster (Fe_8) where the existence of QTM has been clearly established [11]. The system investigated is $[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$, where tacn is the organic ligand triazacyclononane [1]. The cluster of 8 Fe(III) ions has the two-dimensional structure shown in Fig. 1 and is characterized by an overall symmetry D_2. The four ions in the middle of the molecule are in the so-called butterfly arrangement, which can be considered as the first step toward the formation of a triangular planar lattice. Hydroxo bridges connect the central motif to the four peripheral Fe(III) ions, while the organic ligands prevent the growth of the iron hydroxide.

The inelastic neutron scattering experiments were performed with the high energy resolution multichopper time-of-flight spectrometer IN5, at the Institute Laue Langevin, in Grenoble, France. Because of the large scattering cross section of hydrogen and the associated unwanted incoherent scattering and multiple scattering, it is often found to be convenient for experimental reasons to replace hydrogen by deuterium, which has a much lower cross section. We have, instead, used a thin sample consisting of two grams of a nondeuterated powder which was encapsulated in an aluminum can and put into a standard liquid He cryostat. Because of the enormous amount of hydrogen present in the investigated system, the quality of the magnetic spectra provided by the experiment is quite astonishing.

Data were collected at temperatures between 1 and 10 K, using an incident neutron energy of 1.01 meV, corresponding to a resolution of 19 μeV at zero energy transfer (1 eV $= 1.6 \times 10^{-19}$ J). The scattered neutrons are counted by an array of 1068 ^{3}He detectors spanning the scattering angle range between 11° and 128.7°. The signals from the individual detectors are sorted according to time of flight and added up. The maximum value for the scattering vector was $Q_{max} = 1.28$ Å^{-1}, and the neutron flux at the sample was about 2×10^5 s^{-1}.

Magnetization, susceptibility, and high frequency EPR measurements show that the spin ground state of the Fe_8 cluster is $S = 10$, arising from competing antiferromagnetic interactions between the $S_{Fe} = 5/2$ spins of the Fe(III) centers [12]. The EPR spectra have been interpreted by a zero-field spin Hamiltonian $H = DS_z^2 + E(S_x^2 - S_y^2)$, with an axial term $D = -23.7$ μeV and a rhombic parameter $E = -4$ μeV [12]. With this Hamiltonian, the components of the ground manifold at the bottom of the anisotropy potential wells would mainly be $M = \pm 10$ states, followed by the $M = \pm 9$ levels at about 443 μeV. On approaching the top of the anisotropy barrier, the mixing of states with different M becomes more and more effective due to the nondiagonal terms in the Hamiltonian.

The neutron experiments confirm that the above picture is essentially correct, except for several modifications as discussed below. As shown in Fig. 2, the scattering cross section measured for the sample at 1.3 K exhibits a single excitation at 465 μeV. At such a low temperature the excited states are not populated, and the only allowed dipolar transition (with selection rule $\Delta M = 0$ or ± 1) is that between the $|S = 10; M = \pm 10\rangle$ and the $|S = 10; M = \pm 9\rangle$ levels. However, on increasing the temperature the excited levels become populated progressively and transitions between them can be observed, offering the possibility of studying the details of the spin Hamiltonian. The results are shown in Fig. 3 where the intensity distribution measured at 4.8 and 9.6 K is reported. Peaks on the positive energy-transfer side are due to transitions from lower to higher energy states; the corresponding deexcitation peaks appear on the negative energy-transfer side of the spectrum. We find that the simple Hamiltonian used for the interpretation of the EPR response [12]

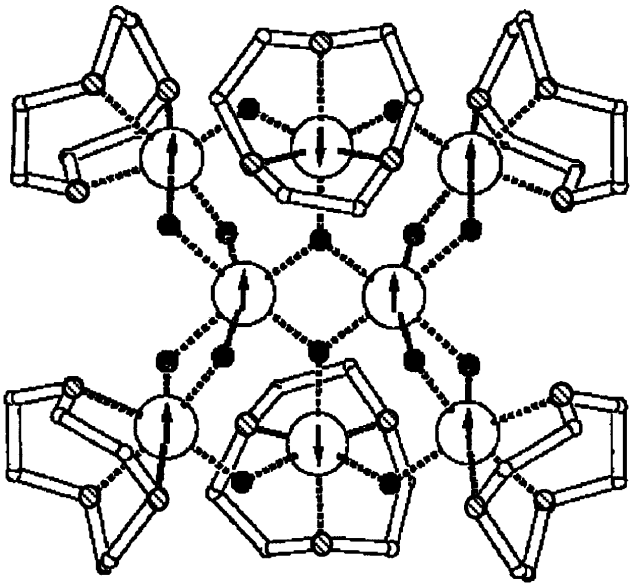

FIG. 1. The structure of $[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$. The large empty circles represent iron atoms, full circles are oxygen atoms, hatched circles are nitrogen, and small empty circles are carbon atoms. The spin structure of the $S = 10$ ground state is illustrated by the arrows.

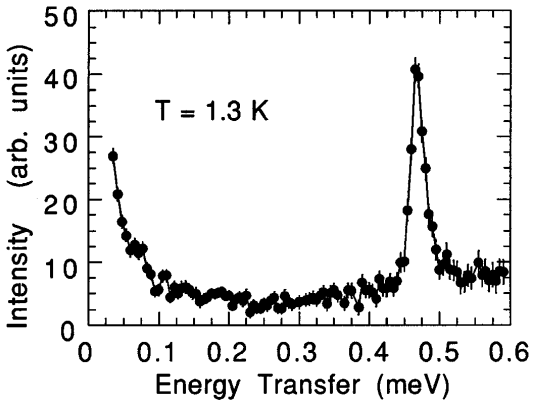

FIG. 2. Inelastic neutron scattering spectrum measured at $T = 1.3$ K, with an incident energy of 1.01 meV. The energy transfer resolution is 19 μeV at the elastic line.

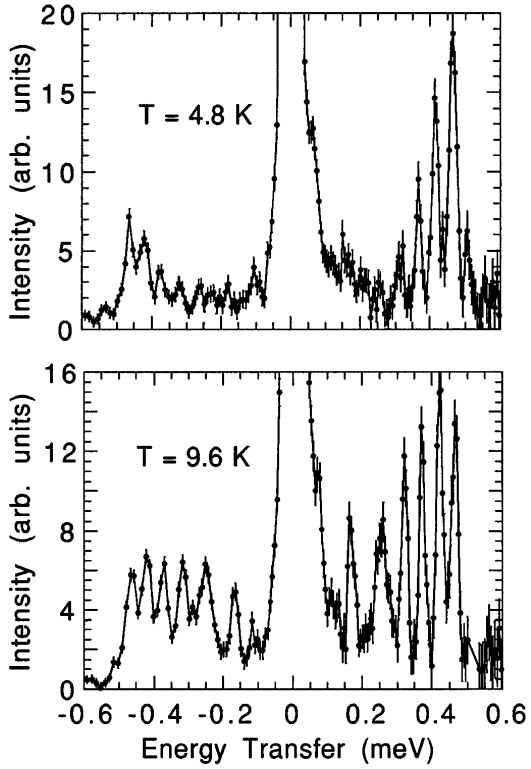

FIG. 3. Inelastic neutron scattering spectrum measured at $T = 4.8$ K and $T = 9.6$ K. The empty can signal has been subtracted.

does not give a sufficiently accurate reproduction of the observed spectrum and further symmetry-allowed terms must be added. The width of the observed excitations is resolution limited, and no information on the relaxation rate is obtained from the present experiment.

In the dipole approximation, the magnetic scattering function $S(Q, \hbar\omega)$ for unpolarized neutrons can be written as [13]

$$S(Q,\hbar\omega) = \frac{N}{4}(g_N r_e)^2 f^2(Q) g_J^2 \times \sum_{i,f} p_i |\langle f|S_\perp|i\rangle|^2 P(\hbar\omega - \Delta_{fi}, \Gamma_{fi}), \quad (1)$$

where $(g_N r_e)^2 = 0.29$ barn/sr, $\hbar\omega$ is the neutron energy transfer, $|\mathrm{n}\rangle$ are spin eigenstates with energies E_n and thermal occupation probabilities $p_n = \exp(-E_n/k_\mathrm{B}T)/\sum_n \exp(-E_n/k_\mathrm{B}T)$, $\Delta_{fi} = E_f - E_i$, $S_\perp$ is the spin component perpendicular to the neutron scattering vector $\mathbf{Q}$, and $P(\hbar\omega - \Delta_{fi}, \Gamma_{fi})$ is the line shape for a peak of full width at half maximum Γ_{fi} and energy transfer centered at Δ_{fi}. For a polycrystalline sample, it is

$$|\langle f|S_\perp|i\rangle|^2 = \frac{1}{3}(2|\langle f|S_z|i\rangle|^2 + |\langle f|S_+|i\rangle|^2 + |\langle f|S_-|i\rangle|^2). \quad (2)$$

The matrix elements and the energies can be obtained by diagonalization of the spin Hamiltonian [14]

$$H_S = D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2) + D'\hat{O}_4^0(S) + E'\hat{O}_4^2(S) + C\hat{O}_4^4(S), \quad (3)$$

where the fourth-order spin operators are defined as

$$\hat{O}_4^0(S) = 35S_z^4 - [30S(S+1) - 25]S_z^2 - 6S(S+1) + 3S^2(S+1)^2,$$

$$\hat{O}_4^2(S) = \frac{1}{4}\{[7S_z^2 - S(S+1) - 5](S_+^2 + S_-^2) + (S_+^2 + S_-^2)[7S_z^2 - S(S+1) - 5]\}, \quad (4)$$

$$\hat{O}_4^4(S) = \frac{1}{2}(S_+^4 + S_-^4).$$

The position of the peaks in the INS cross section gives a direct measurement of the eigenvalues of the spin Hamiltonian, and their intensities provide information about the wave functions through the matrix elements of $S_\perp$. In principle, the parameters of the Hamiltonian can be determined from the experimental data by a least-squares fit procedure.

In the first step of this procedure only the second-order terms were considered. We found that the best fit value of the axial parameter $D = -25.2(2)$ μeV is 6% larger than the EPR value quoted in [12], while the rhombic parameter $E = -4.02(3)$ μeV remains unchanged. With these parameters, however, it was impossible to account at the same time for the exact position of the high energy sharp peaks and the low energy part of the experimental spectrum, which is characterized by broad unresolved peaks. By allowing for a simultaneous variation of all the parameters in (3), we found that the best-fit values of D and E did not change within the errors, while for the fourth-order parameters we obtained $D' = 0.87(6) \times 10^{-4}$ μeV, $E' = 0.1(1) \times 10^{-4}$ μeV, and $C = 7.4(6) \times 10^{-4}$ μeV. With these parameters, the height of the barrier for the reorientation of the magnetization is $A/k = 32.8(1)$ K, to be compared with the value of 24.5 K obtained from magnetic ac susceptibility measurements [11].

Figure 4 shows that the agreement between calculation and experiment is very good, both for the position and the intensity of the peaks. In the excitation part, the calculated intensity of the peak at 0.17 meV is lower than the experimental one, whereas the agreement is good for the corresponding peak at negative energy transfer. This is almost certainly due to a spurious signal originated by the detector electronics. Also, the excitation at 0.074 meV appears to be more intense than calculated, probably because of the overlap with the tail of the very strong elastic peak, as confirmed by a preliminary scan with even higher energy resolution.

The spectral energy region below about 0.3 meV (and in particular the interval 0.2–0.3 meV) presents more complex features than the higher energy one. This is

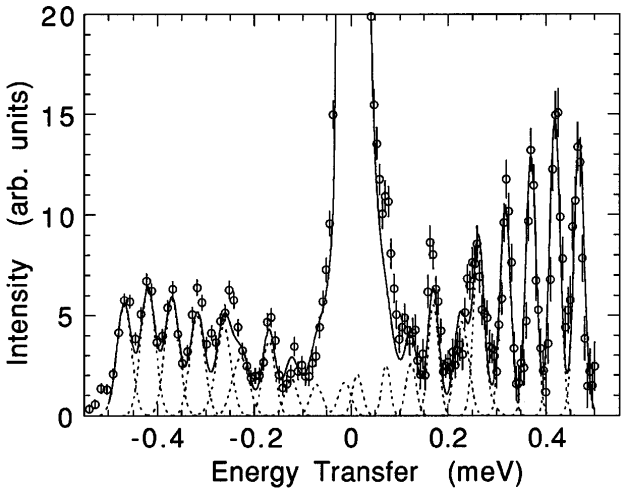

FIG. 4. Inelastic neutron scattering spectrum measured at 9.6 K. The smooth line is the theoretical spectrum for the Hamiltonian given by Eq. (3), with the parameters quoted in the text. The individual excitations are represented by Gaussian line shapes.

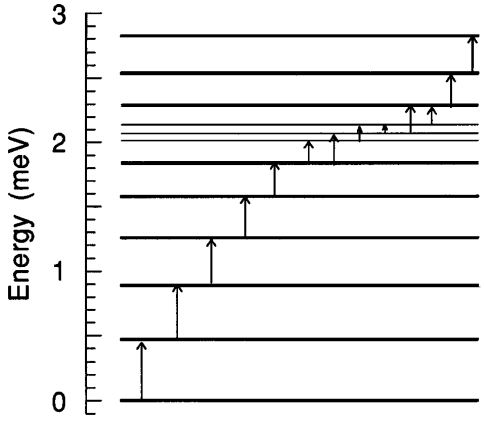

FIG. 5. Zero-field splitting of the $S = 10$ ground state multiplet of Fe_8. Thicker lines correspond to doubly degenerate states (within 0.01 meV); the main transitions allowed in the dipole approximation are indicated by arrows.

due to the mixing of the $|SM\rangle$ states by the nondiagonal terms in the spin Hamiltonian, which is very effective for $|M| \leq 6$. As appears from Fig. 5, the scattered intensity in this energy range is due to the superposition of several very close transitions between the mixed wave functions, having nonzero matrix elements of comparable magnitude. As a consequence, the shape of the peaks is very sensitive to small variations of the spin Hamiltonian coefficients.

In conclusion, the high resolution INS spectrum of the nondeuterated Fe_8 nanomagnet shows how accurate this technique can be for the determination of the zero-field splitting and the magnetic anisotropy of molecular clusters. The results obtained open exciting perspectives for the investigation of this class of materials and offer the possibility of a very precise determination of the spin Hamiltonian parameters, which critically influences the composition of the wave functions taking part in the macroscopic tunneling process. Important information has been obtained to develop a quantitative understanding of the mechanism of QTM in Fe_8. In particular, the height of the barrier for the reorientation of the magnetization has been determined to be $A/k = 32.8(1)$ K. This value is significantly higher than the 24.5 K deduced from measurements of the relaxation time [11]. A similar situation has been observed for Mn12ac, where the spin Hamiltonian provided by EPR gives a barrier height of 67.1 K, whereas a fitting of the relaxation data leads to $A/k = 61$ K [10]. A relaxation barrier lower than the energy difference between the lowest $M = \pm 10$ and the highest $M = 0$ level could be an indication of QTM acting between excited M levels and speeding up the relaxation of the magnetization also in the thermally activated regime. A high resolution neutron scattering experiment in Mn12ac would be interesting to verify the actual strength of the zero-field splitting potential and confirm if the above difference is a characteristic of systems exhibiting QTM. Moreover, it has been shown that the INS spectrum is sensitive to the higher order parameters, which in this way can be accurately determined in zero field. This is particularly important for systems with axial anisotropy, where the off-diagonal fourth-order spin operator $(S_+^4 + S_-^4)$ is essential to induce tunneling, being the only term in the spin Hamiltonian which contributes to the in-plane magnetic anisotropy.

[1] D. Gatteschi, A. Caneschi, L. Pardi, and R. Sessoli, Science **265**, 1054 (1994).
[2] H. J. Eppley, H.-L. Tsai, N. de Vries, K. Folting, G. Christou, and D. N. Hendrickson, J. Am. Chem. Soc. **117**, 301 (1995).
[3] J. R. Friedman, M. P. Sarachick, J. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996).
[4] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, Nature (London) **383**, 145 (1996).
[5] D. D. Awschalom and D. P. Di Vincenzo, Phys. Today **48**, No. 4, 43 (1995).
[6] *Quantum Tunnelling of the Magnetization*, edited by L. Gunther and B. Barbara, NATO ASI Series E, Vol. 301 (Kluwer, Dordrecht, 1995).
[7] A. Fort, A. Rettori, J. Villain, D. Gatteschi, and R. Sessoli, Phys. Rev. Lett. **80**, 612 (1998).
[8] A. L. Burin, N. V. Prokof'ev, and P. C. E. Stamp, Phys. Rev. Lett. **76**, 3040 (1996).
[9] P. C. E. Stamp, Nature (London) **383**, 125 (1996).
[10] A.-L. Barra, D. Gatteschi, and R. Sessoli, Phys. Rev. B **56**, 8192 (1997).
[11] C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, and D. Gatteschi, Phys. Rev. Lett. **78**, 4645 (1997).
[12] A.-L. Barra, P. Debrunner, D. Gatteschi, Ch. E. Schulz, and R. Sessoli, Europhys. Lett. **35**, 133 (1996).
[13] R. J. Birgenau, J. Phys. Chem. Solids **33**, 59 (1972).
[14] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Dover, New York, 1986).