Effects of Nuclear Spins on the Quantum Relaxation of the Magnetization for the Molecular Nanomagnet Fe_8

W. Wernsdorfer,[1] A. Caneschi,[2] R. Sessoli,[2] D. Gatteschi,[2] A. Cornia,[3] V. Villar,[4] and C. Paulsen[4]

[1]*Laboratoire L. Néel, associé à l'UJF, CNRS, BP 166, 38042 Grenoble Cedex 9, France*
[2]*Department of Chemistry, University of Firenze, via Maragliano 77, 50144 Florence, Italy*
[3]*Department of Chemistry, University of Modena, 41100 Modena, Italy*
[4]*CRTBT, associé à l'UJF, CNRS, BP 166, 38042 Grenoble Cedex 9, France*

(Received 4 November 1999)

The strong influence of nuclear spins on resonant quantum tunneling in the molecular cluster Fe_8 is demonstrated for the first time by comparing the relaxation rate of the standard Fe_8 sample with two isotopic modified samples: (i) ^{56}Fe is replaced by ^{57}Fe, and (ii) a fraction of ^1H is replaced by ^2H. By using a recently developed "hole digging" method, we measured an intrinsic broadening which is driven by the hyperfine fields. Our measurements are in good agreement with numerical hyperfine calculations. For $T > 1.5$ K, the influence of nuclear spins on the relaxation rate is less important, suggesting that spin-phonon coupling dominates the relaxation rate.

PACS numbers: 75.45.+j, 75.60.Ej

Mesoscopic quantum phenomena are actively investigated both for fundamental science and for future applications, for instance in quantum computing. Magnetic molecular clusters are among the most promising candidates to observe mesoscopic quantum phenomena [1,2]. One of the most prominent examples is an octanuclear iron(III) cluster, called Fe_8 (Fig. 1), with a spin ground state of $S = 10$ [3]. Below 360 mK, the magnetization relaxes through a pure tunneling process giving rise to a stepped hysteresis cycle [4]. Furthermore, the tunnel splitting Δ of Fe_8 shows periodic oscillations when a transverse magnetic field is applied along the hard axis [5], a long searched phenomenon in magnetism associated with the Berry phase [6], and predicted several years before [7]. Since Δ is extremely small for the ground state tunneling, ca. 10^{-7} K at $H = 0$, the tunneling process should occur only in an extremely narrow magnetic field range, ca. 10^{-8} T, and should be practically unobservable. However, a recent theory proposes that the tunneling is mediated by fluctuating hyperfine fields generated by magnetic nuclei [8], but direct experimental evidence is so far lacking.

In order to study the influence of nuclear spins, we increased the hyperfine coupling by the substitution of ^{56}Fe with ^{57}Fe, and decreased it by the substitution of ^1H with ^2H. We found that the relaxation rate of magnetization in the tunneling regime shows a clear isotope effect which we attribute to the changed hyperfine coupling.

The crystals of the standard Fe8 cluster, $^{st}Fe_8$ or Fe_8, $[Fe_8(tacn)_6O_2(OH)_{12}]Br_8.9H_2O$ where tacn = 1, 4, 7-triazacyclononane, were prepared as reported by Wieghardt *et al.* [9]. For the synthesis of the ^{57}Fe-enriched sample, $^{57}Fe_8$, a 13 mg foil of 95% enriched ^{57}Fe was dissolved in a few drops of HCl/HNO_3 (3:1) and the resulting solution was used as the iron source in the standard procedure. The ^2H-enriched Fe_8 sample, $^DFe_8$, was crystallized from pyridine-d_5 and D_2O (99%) under an inert atmosphere at 5 °C by using a nondeuterated $Fe(tacn)Cl_3$ precursor. The amount of isotope exchange was not quantitatively evaluated, but it can be reasonably assumed that the H atoms of H_2O and of the bridging OH groups, as well as a part of those of the NH groups of the tacn ligands, are replaced by deuterium while the aliphatic hydrogens are essentially not affected. The crystalline materials were carefully checked by elemental analysis and single-crystal x-ray diffraction.

The magnetic measurements were made on single-crystal samples by using an array of micro-SQUIDs [10], which measure the magnetic field induced by the magnetization of the crystal. The advantage of this magnetometer lies mainly in its high sensitivity and fast response, allowing short-time measurements down to 1 ms. Furthermore the magnetic field can be changed rapidly and along any direction.

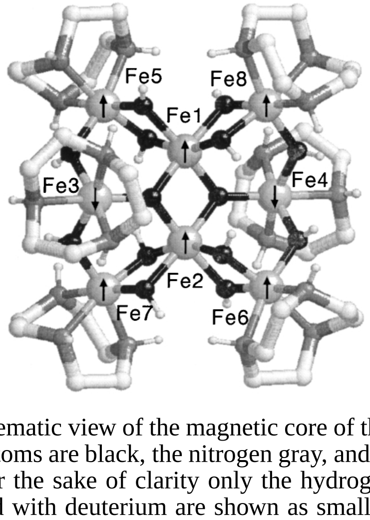

FIG. 1. Schematic view of the magnetic core of the Fe_8 cluster. The oxygen atoms are black, the nitrogen gray, and carbon atoms are white. For the sake of clarity only the hydrogen atoms that are exchanged with deuterium are shown as small spheres. The arrows represent the spin structure of the ground state $S = 10$ as experimentally determined through polarized neutron diffraction experiments [17].

In order to avoid the influence of the crystal shape [11] the relaxation was measured starting at an initial magnetization $M_{\rm init} = 0$ where intermolecular dipolar interactions lead to a field distribution with a width of about 50 mT [10]. A small field H_z was then applied and the relaxation of magnetization was measured (inset of Fig. 2). For all three samples the relaxation was clearly nonexponential and could be adjusted to a $\sqrt{\Gamma_{\rm sqrt} t}$ law for the short time regime ($t < 100$ s) for $T < 0.4$ K. Figure 3 displays the field dependance of $\Gamma_{\rm sqrt}(H_z)$. The relaxations of the three samples at 40 mK are strikingly different from each other. The ^{57}Fe$_8$ sample is the fastest relaxing one, whereas the $^{\rm D}$Fe$_8$ shows the slowest relaxation rate. As a complete theory of the relaxation behavior of crystals of molecular clusters is still missing [12], we plot in Fig. 2 the time needed to relax 1% of the saturation magnetization $M_{\rm s}$ as a function of the inverse temperature $1/T$. Relaxation and ac susceptibility measurements at $T > 1.5$ K showed no clear difference between the three samples, suggesting that above this temperature the relaxation is predominately due to spin-phonon coupling [13,14]. Although the increased mass of the isotopes changes the spin-phonon coupling, we believe that this effect is small.

In principle, the change of mass does not change the crystalline field of the Fe ions, i.e., the anisotropy constants. Experimentally, this is confirmed with measurements below $T < 0.35$ K, where spin-phonon coupling is negligible, by two observations: (i) relative positions of the resonances as a function of the longitudinal field H_z are unchanged [15], and (ii) all three samples showed the same period of oscillation of Δ as a function of the transverse field H_x [5], a period which is very sensitive to any change of the anisotropy constants. Finally, we point out that the mass is increased in *both* isotopically modified samples whereas the effect on the relaxation rate is opposite.

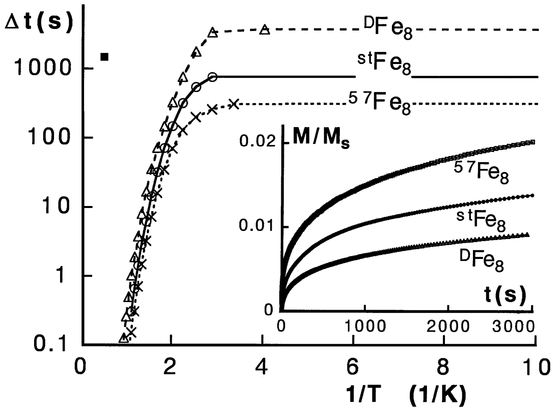

FIG. 2. Comparison of the relaxation rates of three different Fe$_8$ samples. The time Δt needed to relax 1% of the saturation magnetization $M_{\rm s}$ is plotted versus inverse temperature $1/T$. The initial magnetization $M_{\rm init}$ was reached by a fast cooling in zero applied field. The relaxation was measured in a field of $\mu_0 H_z = 42$ mT. In the inset typical relaxation curves (M versus time) recorded for the three samples at $T = 40$ mK are shown.

A deeper insight into the relaxation mechanism can be achieved by using our recently developed hole digging method which allows us to estimate the hyperfine level broadening [10]. Starting from the well-defined magnetization state $M_{\rm init} = 0$, and after applying a small field $H_{\rm dig}$, the sample is allowed to relax for a time $t_{\rm dig}$, called digging field and digging time, respectively. During the digging time, a small fraction $\Delta M_{\rm dig}$ of the molecular spins tunnel and reverse the direction of their magnetization. Finally, a field H is applied to measure the short time square root relaxation rate $\Gamma_{\rm sqrt}$ [10,11]. The entire procedure is then repeated to probe the distribution at other fields yielding the field dependence of the relaxation rate $\Gamma_{\rm sqrt}(H, H_{\rm dig}, t_{\rm dig})$ which is more or less proportional to the number of spins which are still free for tunneling. The result of this procedure is that a very sharp "hole" is dug into the rather broad distribution of $\Gamma_{\rm sqrt}$ [10]. A typical example is shown in the inset of Fig. 3.

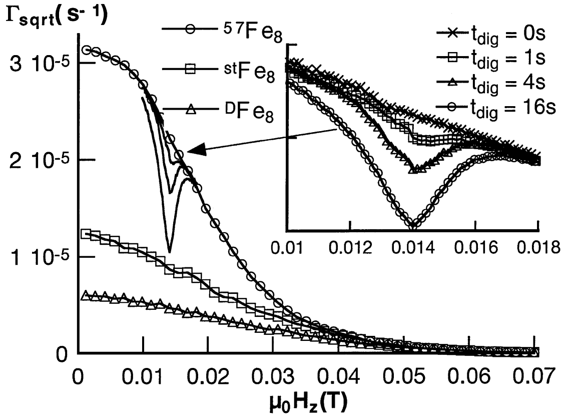

FIG. 3. Comparison of the short time relaxation rates of three different Fe$_8$ samples at $T = 40$ mK with $H_{\rm trans} = 0$ and $M_{\rm init} = 0$. The inset displays a typical example of a hole which was dug into the distribution by allowing the sample to relax for the time $t_{\rm dig}$ at $\mu_0 H_{\rm dig} = 14$ mT.

In the limit of very short digging times, the difference between the relaxation rate in the absence and in the presence of digging, $\Gamma_{\rm hole} = \Gamma_{\rm sqrt}(H, H_{\rm dig}, t_{\rm dig} = 0) - \Gamma_{\rm sqrt}(H, H_{\rm dig}, t_{\rm dig})$, is approximately proportional to the number of molecules which reversed their magnetization during the time $t_{\rm dig}$. $\Gamma_{\rm hole}$ is characterized by a width that we call the hole line width σ. In order to find a hole line width that is close to the hyperfine level broadening, all the effects that can broaden the measured hole width must be reduced. The experimental condition giving the smallest line width was found for hole digging in the tails of the dipolar distribution and for small initial magnetization. Under these conditions the spins that tunnel are statistically far from each other, allowing us to measure tunneling in the diluted limit. In addition, we applied a transverse field of $\mu_0 H_{\rm trans} = 200$ mT parallel to the hard axis which reduces the tunnel rate allowing us to dig very tiny holes. Figure 4 displays the hole line width σ as a function of the reversed fraction $\Delta M_{\mathrm{dig}}/2M_{\mathrm{s}}$ of molecular spins. A linear extrapolation of σ to $\Delta M_{\mathrm{dig}}/2M_{\mathrm{s}} = 0$ gives σ_0 which is directly associated to the hyperfine level broadening [8]. Experimentally, we found σ_0 to be 0.6 ± 0.1, 0.8 ± 0.1, and 1.2 ± 0.1 mT, for $^{\mathrm{D}}\mathrm{Fe}_8$, $^{\mathrm{st}}\mathrm{Fe}_8$, and $^{57}\mathrm{Fe}_8$, respectively.

The isotope effect, observed here for the first time in magnetic nanostructures, clearly points out the role of the magnetic nuclei in the relaxation of the magnetization. An evaluation of the hyperfine fields in the three different samples is therefore necessary. The hyperfine interaction between the total spin S of the cluster and the magnetic nuclei can be decomposed into the sum of terms related to the interactions between the magnetic moment I_i of the ith nucleus and the individual spin S_j, assumed to be localized on the jth iron center [16]:

$$H_{\mathrm{hf}} = \sum_i \mathbf{S}\mathbf{A}_i\mathbf{I}_i = \mathbf{S}\sum_i\left(\sum_j c_j\mathbf{A}_{ij}\right)\mathbf{I}_i\,. \tag{1}$$

The projection coefficients c_j in Eq. (1) depend on the wave function of the ground state $S = 10$, which can be calculated by diagonalizing the $S = 10$ block (6328 × 6328) of the exchange spin-Hamiltonian matrix of $H = \sum_{j\neq k}\mathbf{S}_j\mathbf{S}_k$.

With the exchange-coupling parameters that best reproduce the temperature dependence of the magnetic susceptibility [17], the spin configuration depicted in Fig. 1 provides a large contribution (of ca. 70%) of the ground state $S = 10$. According to this picture, which has been recently confirmed by polarized neutron diffraction data [17], the projection coefficients are $c_3 = c_4 = -5/22$ for the spins pointing down and $c_1 = c_2 = c_5 = \cdots = c_8 = 8/33$ for the remaining iron spins.

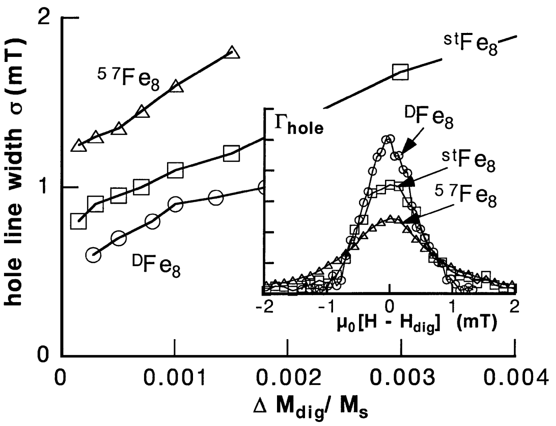

FIG. 4. Hole line width σ as a function of reversed fraction ΔM_{dig} to dig the hole. The initial thermal distribution of diploar fields was reached by a fast cooling in zero applied field. In order to reduce the line width the hole was dug at a longitudinal field of $\mu_0 H_z = 42$ mT, and in the presence of a transverse field of $\mu_0 H_{\mathrm{trans}} = 200$ mT applied along the hard axis. The inset shows typical hole shapes observed at $\Delta M_{\mathrm{dig}} = 0.001\ M_{\mathrm{s}}$.

The hyperfine interaction described by the $\mathbf{A}_{ij}$ tensors is both through space (dipolar) and through bond (contact) in nature. The dipolar components can be easily calculated with the point dipolar approximation. The most important coupling with the ^{1}H nuclei are those of the bridging OH groups having $\mathbf{A}_{ij}$ constants as large as 0.045 mT, while the hyperfine coupling with N and Br nuclei does not exceed 0.005 and 0.003 mT, respectively. An order of magnitude for the contact terms was estimated using a Density-Functional Theory calculation [18] at the B3LYP level [19] on a model symmetric dimer $[(\mathrm{NH}_3)_4\mathrm{Fe(OH)}_2\mathrm{Fe(NH}_3)_4]^{4+}$.

The hyperfine interaction generates a field which splits the $m_S = \pm 10$ states. Since each nuclear spin I splits each state into $2I + 1$ sublevels, the number of sublevels generated by the coupling of 18 ^{14}N atoms ($I = 1$), 8 ^{79,81}Br atoms ($I = 3/2$), and 120 ^{1}H atoms ($I = 1/2$) present in $^{\mathrm{st}}\mathrm{Fe}_8$ is prohibitively large, being $3^{18} \times 4^8 \times 2^{120}$. We therefore made an approximation taking into account only the most significant terms. In fact, the total line width goes as the geometric sum of the individual contributions and therefore the largest contributions dominate over the smaller ones. We evaluated the Gaussian broadening determined by the 12 ^{1}H nuclei of the OH groups, assuming them equivalent with a contact hyperfine coupling constant $A_{\mathrm{cont}} = 0.05$ mT, of the 18 ^{1}H nuclei of the NH groups assuming $A_{\mathrm{cont}} = 0.025$ mT, and of the 14 N nuclei with $A_{\mathrm{cont}} = 0.2$ mT. These values introduced in Eq. (1) gave Gaussian lines with widths at half-height of 0.2, 0.15, and 0.4 mT, respectively. By combining these we estimate a resulting Gaussian distribution with a line width of 0.5 mT, in acceptable agreement with the experimental value of 0.8 mT.

The effect of the ^{57}Fe nuclear spins in the enriched samples was estimated by assuming that each nucleus feels only its own electron spin. Therefore Eq. (1) is simplified as only the terms with $i = j$ are different from zero. Using $A(^{57}\mathrm{Fe}) = 1.0$ mT, in agreement with reported data [20], we calculate the stick diagram reported in Fig. 5 which arises from the coupling of six equivalent ^{57}Fe $I = 1/2$ with $A = 8/33 \times 1.0$ mT and two other nuclear spins $I = 1/2$ with coupling $A = -5/22 \times 1.0$ mT. The related histogram can be fitted with a Gaussian whose line width is ca 0.8 mT. If we consider the experimental line width of the resonance, ca. 0.8 mT, of $^{\mathrm{st}}\mathrm{Fe}_8$ and we add the contribution of the ^{57}Fe nuclei we obtain $\Delta H \approx 1.1$ mT, in close agreement with the experimentally observed value of 1.2 mT.

The partial substitution for the ^{1}H nuclei of the OH and NH groups with the less magnetic ^{2}H isotopes leads to a reduction of the line width which in our calculations is estimated to be ca. 0.1 mT, which should be compared with the experimental narrowing of ca. 0.25 mT. The difference between the calculated and observed reduction of the line width is similar to the smaller calculated line width compared to the observed one of the $^{\mathrm{st}}\mathrm{Fe}_8$ sample. This

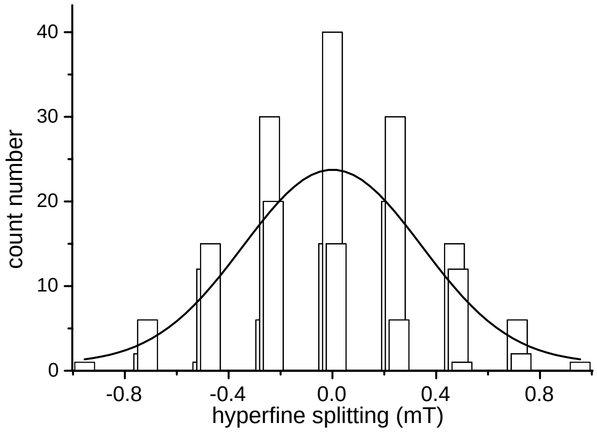

FIG. 5. Calculated histogram of level splitting due to the coupling with ^{57}Fe $I = 1/2$ nuclear spins in the Fe_8 clusters. In Eq. (1), the $\mathbf{A}_{ij}$ constant has been assumed to be 1.0 mT for $i = j$ and zero for $i \neq j$. The solid line represents the best fit using a Gaussian line.

may come from an underestimation of the interactions with the ^{1}H nuclei.

The present data show the fundamental role of the nuclear spins in the relaxation of the magnetization of Fe_8 in the quantum regime. Indeed, this is in contrast to the familiar role of isotope substitution which is generally associated with phonon coupling and thus proportional to the mass of the nuclei. Here we show that it is the magnetic moment of the nuclei which is important at temperatures well above those at which nuclear spin polarization is observed.

We are indebted to A. Bencini for his help in DFT calculations, and to P. C. E. Stamp, I. Tupitsyn, N. V. Prokof'ev, and J. Villain for many fruitful and motivating discussions. The financial contributions of Italian MURST, CNR, PFM-STAII, and the French DRET are acknowledged.

Note added.—Our numerical simulations are in good agreement with the calculation of the altered hyperfine coupling in Ref. [21]. Also, we recently confirmed the influence of nuclear spins via measurements based on a Landau Zener method showing a clear influence on the level lifetimes of the $S = 10$ system [22]. Our measurements demonstrate again that molecular magnets offer a unique opportunity to explore the quantum dynamics of a large but finite spin. We believe that more sophisticated theories are needed describing the dephasing effects of the environment.

[1] A. Thiaville and J. Miltat, Science **284**, 1939 (1999).
[2] A. Caneschi *et al.*, J. Magn. Magn. Mater. **200**, 182 (1999).
[3] A.-L. Barra, P. Debrunner, D. Gatteschi, Ch. E. Schulz, and R. Sessoli, Europhys. Lett. **35**, 133 (1996).
[4] C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, and D. Gatteschi, Phys. Rev. Lett. **78**, 4645 (1997).
[5] W. Wernsdorfer and R. Sessoli, Science **284**, 133 (1999).
[6] M. V. Berry, Proc. R. Soc. London A **392**, 45 (1984); D. Loss, D. P. DiVincenzo, and G. Grinstein, Phys. Rev. Lett. **69**, 3232 (1992); J. von Delft and C. L. Hendey, Phys. Rev. Lett. **69**, 3236 (1992).
[7] A. Garg, Europhys. Lett. **22**, 205 (1993); S. Weigert, Europhys. Lett. **26**, 561 (1994).
[8] N. V. Prokof'ev and P. C. E. Stamp, Phys. Rev. Lett. **80**, 5794 (1998); N. V. Prokof'ev and P. C. E. Stamp, J. Low Temp. Phys. **104**, 143 (1996); N. V. Prokof'ev and P. C. E. Stamp, J. Phys. Condens. Matter **5**, L663 (1993); A. Cuccoli, A. Fort, A. Rettori, E. Adam, and J. Villain, Eur. Phys. J. B **12**, 39 (1999).
[9] K. Wieghardt, K. Pohl, I. Jibril, and G. Huttner, Angew. Chem., Int. Ed. Engl. **23**, 77 (1984).
[10] W. Wernsdorfer, T. Ohm, C. Sangregorio, R. Sessoli, D. Mailly, and C. Paulsen, Phys. Rev. Lett. **82**, 3903 (1999); W. Wernsdorfer, R. Sessoli, and D. Gatteschi, Europhys. Lett. **47**, 254 (1999).
[11] T. Ohm, C. Sangregorio, and C. Paulsen, Euro. Phys. J. B **6**, 195 (1998); T. Ohm, C. Sangregorio, and C. Paulsen, J. Low Temp. Phys. **113**, 1141 (1998).
[12] The Prokof'ev Stamp theory is valid only in the pure quantum regime [8], i.e., below 360 mK for Fe_8 [4].
[13] A. Fort, A. Rettori, J. Villain, D. Gatteschi, and R. Sessoli, Phys. Rev. Lett. **80**, 612 (1998).
[14] M. N. Leuenberger and D. Loss, Europhys. Lett. **46**, 692 (1999).
[15] We observed a small shift of the resonances of the order of magnitude of 1 mT, positive for $^{57}Fe_8$ and negative for $^{D}Fe_8$ ($M_{\mathrm{init}} = -M_s$). This can also be attributed to the modified hyperfine fields. However, a quantitative measurement is complicated by the fact that it is impossible to have two crystals with exactly the same shape, i.e., the same internal fields.
[16] A. Bencini and D. Gatteschi, *EPR of Exchange Coupled Systems* (Springer-Verlag, Berlin, 1990).
[17] Y. Pontillon, A. Caneschi, D. Gatteschi, R. Sessoli, E. Ressouche, J. Schweizer, and E. Lelievre-Berna, J. Am. Chem. Soc. **121**, 5342 (1999).
[18] M. J. Frisch *et al.*, *Gaussian 98* (Gaussian, Inc., Pittsburgh, Pennsylvania, 1998), Rev. A.5.
[19] A. D. J. Becke, J. Chem. Phys. **98**, 5648 (1993).
[20] B. R. McGarvey, Electron. Reson. Transit.-Met. Complexes Transit. Met. Chem. **3**, 89 (1966).
[21] G. Rose, P. C. E. Stamp, and I. S. Tupitsyn, report, 1999 (to be published).
[22] W. Wernsdorfer, R. Sessoli, A. Caneschi, D. Gatteschi, and A. Cornia, http://xxx.lanl.gov/cond-mat/0001346