Proton spin-lattice relaxation induced by quantum tunneling of the magnetization in the molecular nanomagnet Fe_8

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We report the observation of the effect of the quantum tunneling of the magnetization in the molecular nanomagnet $[Fe_8(N_3C_6H_{15})_6O_2(OH)_{12}]\cdot[Br_8\cdot 9H_2O]$ (in short, Fe_8) on the proton spin-lattice relaxation rates (T_1^{-1}) measured in single crystal Fe_8 at 1.5 K. When the external field is applied parallel to the magnetic easy axis of the molecular nanomagnet, T_1^{-1} decreases monotonically, a behavior well explained in terms of the magnetization fluctuations due to spin-phonon interaction. On the other hand, a peak of T_1^{-1} is observed as a function of transverse field for a value of H in the range 2.5–3.5 T. The position and shape of the peak depend upon the orientation of the field in the hard plane and the peak disappears as soon as a small out-of-plane magnetic-field component is introduced by misaligning the crystal. The experimental observations can be explained by considering the effect of the transverse field on the tunneling splitting whereby the peak of T_1^{-1} is a direct consequence of the matching condition of the incoherent tunneling probability with the proton Larmor frequency.

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I. INTRODUCTION

The study of quantum tunneling of the magnetization (QTM) has received a new impulse following the discovery of this phenomenon in single molecule magnets (SMM).[1] The two systems which have been most widely investigated are $[Fe_8(N_3C_6H_{15})_6O_2(OH)_{12}]\cdot[Br_8\cdot 9H_2O]$ which is the target of the present investigation and will be referred to hereafter as Fe_8,[2–4] and the similar cluster Mn_{12}.[2,5,6] QTM in Fe_8 is associated with the existence in the high-spin ground state ($S=10$) of pairwise degenerate $\pm m$ magnetic levels separated by an energy barrier (about 24 K) due to easy axis crystal-field anisotropy in the z direction.[3]

The occurrence of QTM in zero external magnetic field is related to the splitting of the magnetic levels by an amount Δ_T which is due to off diagonal terms in the magnetic Hamiltonian arising from anisotropy in the xy plane, intermolecular dipolar interactions, and hyperfine interactions. Normally the tunnel splitting Δ_T in the above clusters is much smaller than the level broadening so that measurements of Δ_T is difficult. However, by applying a magnetic field perpendicular to the easy axis (transverse field), one can increase Δ_T of all levels while leaving the symmetry of the double well potential intact. Figure 1 shows the calculated transverse field dependence of the tunnel splitting Δ_T for the ground-state sublevels $m=\pm 10$ for the two orientations of the transverse field in the xy hard plane (y-medium and x-hard axis). The results were obtained from the diagonalization of the model spin Hamiltonian,

$$H=DS_z^2+E(S_x^2-S_y^2)+g\mu_B\mathbf{S}\cdot\mathbf{H}, \qquad (1)$$

where, for Fe_8, the axial anisotropy D and the in-plane anisotropy E constants are known to be $D\sim -0.292$ K and $E\sim 0.047$ K, respectively, from electron paramagnetic resonance (EPR),[7,8] neutron spectroscopy,[9] optical spectroscopy,[10] and magnetization measurements.[11] The tunneling splitting for pairwise degenerate levels with lower m is much bigger. Their calculated value is not shown in Fig. 1 for the sake of simplicity and since they do not play a relevant role in our low-temperature experiments. Somewhat different results are obtained by including higher-order terms and/or by changing the D and E parameters in Eq. (1). However, these details are not relevant to our experiment as will be perceived in the following. The important fact is that, as can be seen in Fig. 1, Δ_T for both directions increases by about ten orders of magnitude with increasing transverse field thus making Δ_T big enough to be measured, e.g., by ac susceptibility,[12] high-frequency resonant experiments,[13] and specific-heat measurements.[14–16] For $H>1$ T, the relaxation (fluctuation) of the magnetization driven by tunneling (coherent and/or incoherent) becomes so fast that it falls into the characteristic frequency domain (MHz) of nuclear magnetic resonance experiment.

Motivated by this idea we set up to measure the proton NMR and relaxation in a single crystal of Fe_8 as a function of external magnetic field and crystal orientation at 1.5 K. We find that when the magnetic field is applied perpendicular to the main easy axis z (transverse field) a pronounced peak in the proton spin-lattice relaxation rate $1/T_1$ occurs at some field value which depends on the orientation of the transverse field in the hard xy plane. The effect is well explained by

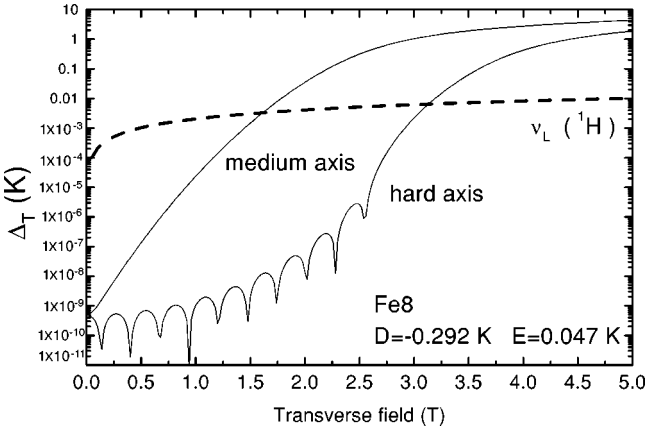

FIG. 1. Calculated transverse field dependence of the tunnel splitting Δ_T for two directions (y-medium and x-hard axes). The broken line shows the field dependence of the proton NMR Zeeman splitting. The dips in the curve for the hard axis correspond to the quenching of the tunneling splitting due to the Berry phase effect.

considering that by increasing the transverse field the incoherent tunneling probability becomes sufficiently high as to match the proton Larmor frequency. In fact, the proton spin-lattice relaxation measures the spectral density at the Larmor frequency of the fluctuations of the hyperfine field associated with the change in orientation of the molecular magnetization. When the applied field goes through this condition the fluctuation rate of the magnetization is most effective in driving the nuclear relaxation and a maximum appears in $1/T_1$.

II. EXPERIMENTAL DETAILS

The single crystal Fe_8 [$\sim 3\times 2\times 1$ (mm^3)] used in this study is synthesized following the method reported previously.[17] The proton NMR in oriented powders and oriented small single crystals of Fe_8 has been reported previously[18] and we refer to that paper for details about the experimental setup. We summarize here the main findings. Upon decreasing the temperature the NMR spectrum becomes broad and with a structure which reflects the different local fields at the different proton sites in the molecule. Below 4.2 K the separation of the peaks in the structure becomes field independent indicating spin freezing in the time window of the NMR experiment. By measuring $1/T_1$ at any position in the spectrum, one obtains information about the fluctuations of the magnetization of the molecule. $1/T_1$ was measured at a slightly shifted position in the ^1H-NMR spectrum (0.25 kOe from the proton Larmor field) to exclude possible effects due to impurities which would be most relevant at the Lamor field. The recovery of the nuclear magnetization $M(t)$ following a saturation sequence of radio frequency pulses was found to be nonexponential, as typically shown in Fig. 2. $1/T_1$ was extracted from the slope of the initial part of the recovery curve representing the weighted average of the relaxation rates of the different nonequivalent protons in the SMM.[19]

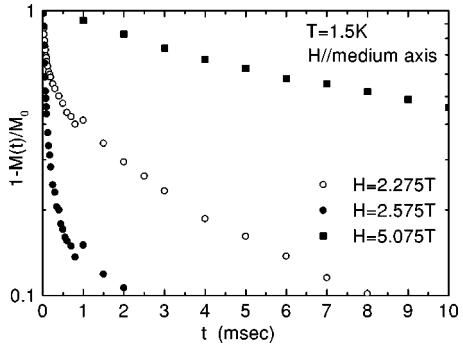

FIG. 2. Typical experimental recovery curves of ^1H magnetization measured at $H=2.275$ T (open circles), $H=2.575$ T (closed circles), and $H=5.075$ T (closed squares) where external magnetic field is applied parallel to the medium axis.

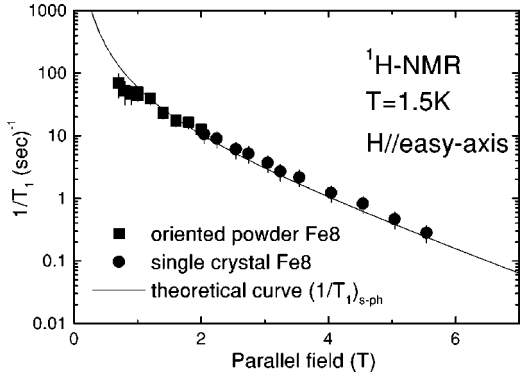

FIG. 3. Parallel field dependence of $1/T_1$ in single-crystal Fe_8 (closed circles) and oriented powder sample (closed squares) measured at $T=1.5$ K. The data for powder sample (Ref. 18) were rescaled for the different hyperfine coupling constant. The solid line is a calculated result based on the model in terms of spin-phonon interaction [Eq. (2)].

III. RESULTS AND DISCUSSION

For the sake of comparison we show first in Fig. 3 the results of the proton relaxation rate in Fe_8 single crystal when the magnetic field is applied parallel to the easy axis. Some measurements obtained previously[18] in the oriented powder sample are also shown in the figure. Under parallel field the tunneling rate is negligibly small and it does not influence $1/T_1$ as can also be evidenced by the absence of anomalies at the critical fields $H_C \sim 0.22\times n$ T ($n=1,2,3\ldots$) corresponding to level crossings (see low-field results in Ref. 18). It was shown[18] that for an external field along the easy axis z, the results can be explained in terms of a simple model[19] which describes the fluctuations of magnetization among the different quantum number m substates of the $S=10$ ground state in terms of spin-phonon interaction. The monotonic decrease of $1/T_1$ at 1.5 K, shown in Fig. 3, can be fitted very well with the expression for $1/T_1$ in Ref. 18,

$$\left(\frac{1}{T_1}\right)_{s\text{-}ph} = \frac{A}{Z}\sum_{m=+10}^{-10} \frac{(\tau_m)_{s\text{-}ph}\exp\left(-\frac{E_m}{k_B T}\right)}{1+\omega_L^2(\tau_m)_{s\text{-}ph}^2}, \qquad (2)$$

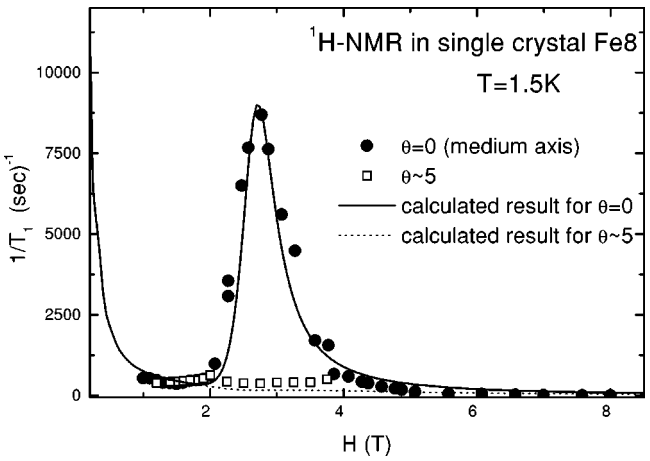

FIG. 4. Transverse field dependence of $1/T_1$ measured at $T=1.5$ K in single-crystal Fe_8 as a function of the field along the *y*-medium axis (closed circles). Open squares are the results obtained when the single crystal is tilted so that the applied field is 5° off the *xy* plane. Solid and broken lines are calculated curves according to Eqs. (3)–(5) with the set of parameters discussed in the text.

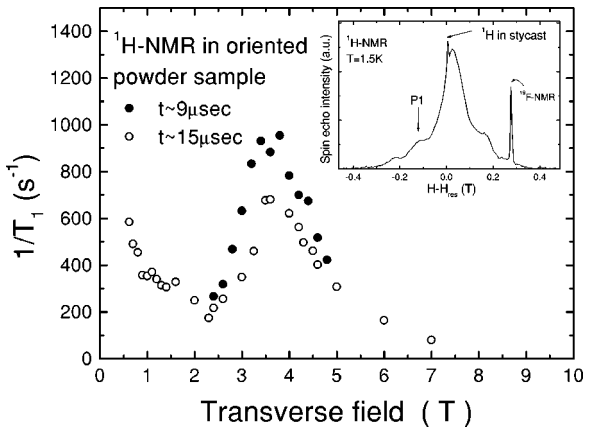

FIG. 5. Transverse field dependence of $1/T_1$ at $T=1.5$ K in oriented powder Fe_8 sample measured at P1 position present in NMR spectrum. The two set of data refer to measurements done on different delay time *t* between two radio frequency pulses (open circles were reported previously in Ref. 20).

where *A* is the square average fluctuating hyperfine field, *Z* is the partition function, and $(\tau_m)_{s\text{-}ph}$ is the lifetime of the *m*th sublevels due to the spin-phonon interaction. The solid line is a calculated result with the same spin-phonon coupling constant reported in Ref. 18 and almost the same the hyperfine coupling constant $A=0.7\times10^{12}$ (rad Hz)^2. Thus we may conclude that for $H//z$ no effects of quantum tunneling can be observed on $1/T_1$ as expected since the tunneling dynamics is too slow for longitudinal applied fields and most of clusters occupies the ground-state sublevel which does not cross the other magnetic sublevels.

On the other hand, a dramatic enhancement of T_1^{-1} is observed centered around $H=2.6$ T when the magnetic field is applied in the hard *xy* plane along the medium axis $y(H//y)$ as shown in Fig. 4. The peak disappears when a parallel field component is introduced in addition the transverse field, by tilting the single crystal about 5° in the *yz* plane (see Fig. 4). Since the parallel field component removes the degeneracy of the $\pm m$ magnetic states and consequently the possibility of tunneling it is clear that the peak of $1/T_1$ must be related to a contribution to the nuclear relaxation rate from the tunneling dynamics.

First we discuss the possibility that the peak of T_1^{-1} is due to a cross relaxation between the nuclear Zeeman reservoir and the tunneling reservoir. For cross relaxation to occur the Zeeman splitting of the nuclear states must be equal to the tunneling splitting of the Fe_8 magnetic ground state $m=\pm10$. This is indeed the interpretation that we gave to the preliminary data obtained in oriented powder where a peak of $1/T_1$ is observed around 3.5 T as shown in Fig. 5.[20] However, in the present single-crystal data (Fig. 4) the peak occurs at $H\sim2.6$ T while the matching condition, $\nu=\Delta_T$, in Fig. 1 takes place at $H\sim1.6$ T. The discrepancy is too large to be ascribed to the uncertainty in the parameters *D* and *E* or to the neglect of higher-order terms in Hamiltonian Eq. (1).

The discrepancy between the oriented powder data and the single-crystal data is most likely due to the distribution of field orientation in the hard *xy* plane present in the oriented powder in transverse field. In fact in the previous interpretation[20] we assumed that the measured $1/T_1$ was indeed a weighted average of relaxation rates for the different crystal grains. However, from additional measurements we discovered that the measured $1/T_1$ depends on the distance between the two radio frequency pulses used to read the echo intensity after the saturation pulse, as shown in Fig. 5. This indicates that the measured $1/T_1$ in oriented powder may not be attributed to a weighted average from the all the clusters distributed in the hard *xy* plane, since one can miss the contribution from grains for which the relaxation rate is very short. Having argued that the much more reliable data are the present ones in single crystal which is actually one of the reasons why we have carried out the experiments in the single crystal, we can conclude that the peak in Fig. 4 cannot be due to a simple cross-relaxation effect. Careful measurements were performed around the field $H=1.6$ T to make sure that another peak is not present at the matching condition in Fig. 4 and none was found as seen in Fig. 4.

An alternative explanation can be envisaged to interpret the peak of $1/T_1$ observed in Fig. 4. In fact, the large tunneling splitting in transverse field can generate fluctuations of the magnetization at frequencies close to the proton Larmor frequency that can induce enhanced spin-lattice relaxation. We assume that, besides the contribution from thermal fluctuations due to spin-phonon interactions discussed above, i.e., $(T_1^{-1})_{\text{s-ph}}$, there exists a second contribution to nuclear relaxation, $(T_1^{-1})_T$, arising from the fluctuations of the hyperfine field resulting from the tunneling transitions between $m=\pm10$ and between smaller *m* states higher in energy,

$$\left(\frac{1}{T_1}\right)=\left(\frac{1}{T_1}\right)_{\text{s-ph}}+\left(\frac{1}{T_1}\right)_{\text{T}}. \tag{3}$$

We further assume for the tunneling contribution an expression similar to Eq. (2) whereby the random change of hyper-

fine field results now from the total reversal of the magnetization between $\pm m$ states:

$$\left(\frac{1}{T_1}\right)_{\mathrm{T}} = \frac{B}{Z}\sum_{m=+10}^{-10}\frac{(\tau_m)_{\mathrm{T}}\exp\left(-\frac{E_m}{k_{\mathrm{B}}T}\right)}{1+\omega_L^2(\tau_m)_{\mathrm{T}}^2}, \tag{4}$$

where B is the square average fluctuating hyperfine field originated from the tunneling transition. For the tunneling rate $[(\tau_m)_T^{-1}]$ between $\pm m$ levels we assume the expression[21]

$$\left(\frac{1}{\tau_m}\right)_{\mathrm{T}} = \frac{(\Delta_{\mathrm{T}})_m^2\Gamma_m}{\Gamma_m^2+[(E_m-E_{-m})/\hbar]^2}, \tag{5}$$

where Γ_m is a level broadening parameter and (E_m-E_{-m}) is the energy-level mismatch due to any longitudinal component of the bias field.

The theoretical curve obtained from Eqs. (3)–(5) and by using the tunneling splitting values calculated in Fig. 1 is shown in Fig. 4. The experimental data are fitted reasonably well by setting $B=1.3\times10^{13}$ (Hz rad)^2, $\Gamma_{10}=2\times10^8$ (Hz rad), and $(E_m-E_{-m})/\hbar=4.2\times10^{10}$ (Hz rad). For a negligible single-crystal misalignment the above mismatch (E_m-E_{-m}) must correspond to a longitudinal local-field component of the bias field independent from the applied field arising from intermolecular dipolar interactions and/or hyperfine interactions.[2] The value of the bias field is roughly estimated to be $H_z\sim120$ Oe with a simple assumption of $m=10$. It is noted that this estimate must be regarded just as an order of magnitude since quantum number $m=10$ for the ground-state magnetic sublevel is not a good quantum number under application of the strong transverse field.[22]

Furthermore, as seen in Fig. 4, the disappearance of the peak due to a misalignment of 5° between the applied field and the *xy* plane is also well reproduced by the theoretical model [Eqs. (3)–(5)], by taking into consideration the effect of the additional longitudinal field component as $(E_m-E_{-m})/\hbar=g\mu_{\mathrm{B}}[m-(-m)][H_z+H\sin(5)]$.

It is noted that at the temperature of our measurements ($T=1.5$ K), the dominant contribution in Eq. (4) comes from the ground-state term $m=10$ although all levels have been included in the theoretical fit. We are aware that in Ref. 2, the expression for the tunneling probability is different from the one adopted here [Eq. (5)], since the former includes a term $(\Delta_T)_m^2$ in the denominator. Although the more general expression should be used to describe thermally activated tunneling near the top of the barrier, it yields the wrong fit in our case particularly at high fields. We argue that, when the tunneling splitting is made large by the transverse field and the dominant contribution in Eq. (4) comes from the ground-state term $m=10$ at the temperature of our measurements ($T=1.5$ K) one should use Eq. (5) from Ref. 21 to describe the tunneling probability.

Finally, we report in Fig. 6 the transverse field dependence of $1/T_1$ for different orientations of the field in hard *xy* plane. With increasing the angle ϕ between the medium *y* axis and the external field in the *xy* plane, the peak position shifts to higher field, as expected from the behavior of the tunneling splitting and thus of the tunneling probability (see Fig. 1). The solid lines in the figure are calculated results utilizing Eqs. (3)–(5) with the same value of the bias field $(E_m-E_{-m})/\hbar=4.2\times10^{10}$ (Hz rad). For the case of $\phi\sim20°$, the experimental results are well fitted with the parameters $B=1.3\times10^{13}$ (Hz rad)^2 and $\Gamma_{10}=2\times10^8$ (Hz rad) which are identical as for $\phi=0°$. On the other hand, for the case of $\phi\sim90°$ (H//hard axis), the peak is smaller and broader and the fit is not good even with a different choice of parameters: $B=1.3\times10^{12}$ (Hz rad)^2 and $\Gamma_{10}=5\times10^9$ (Hz rad).

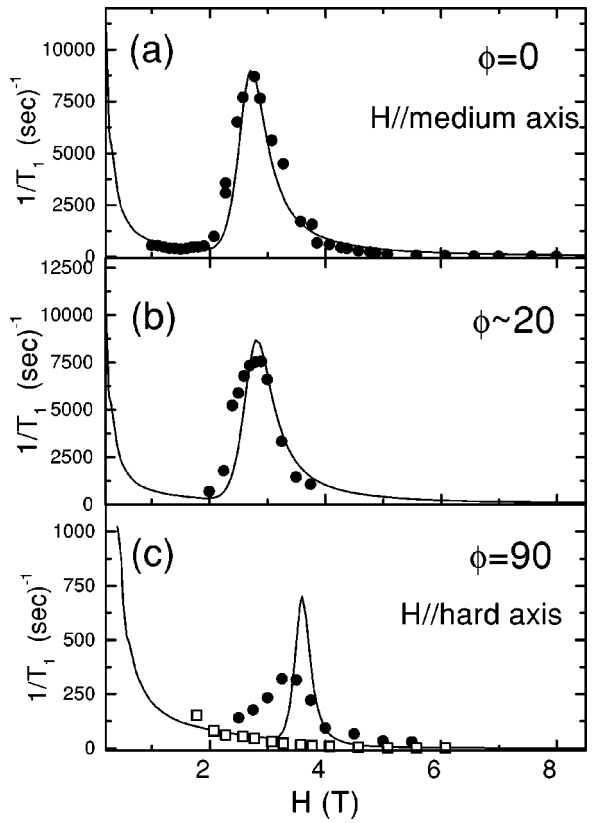

FIG. 6. Transverse field dependence of $1/T_1$ measured at $T=1.5$ K in single-crystal Fe_8 with different orientations of the magnetic field with respect to the *y* axis in the *xy* plane: (a) $\phi=0°$ (*y*-medium axis), (b) $\phi\sim20°$, (c) $\phi\sim90°$ (*x*-hard axis). Open squares in (c) are the results obtained when the single crystal is tilted by 5° off the *xy* plane. Solid lines are calculated curves according to Eqs. (3)–(5) with the set of parameters discussed in the text.

In order to check whether the peak for the case of $H//x$ still comes from the effects of tunneling dynamics, we introduced a longitudinal field component by tilting the crystal in the *xz* plane about 5° as in the case of the *y*-medium axis. The fact that the peak of $1/T_1$ does disappear seems to indicate that the same is still originating from the tunneling dynamics. It is noted that the transverse field at which the peak of $1/T_1$ occurs in Fig. 6 is smaller than the anisotropy field at which the classical energy barrier vanishes (estimated at $H\sim3.3$ T and $H\sim4.7$ T for $\phi\sim0°$ and $\phi\sim90°$,

respectively[12]). The experimental peak positions are $H \sim 2.6$ T and $H \sim 3.5$ T for $\phi \sim 0°$ and $\phi \sim 90°$, respectively, where the barriers' height is still about 3 K and first excited sublevels are close to the top of the barrier for each case. Although most of molecules (about 90%) occupy the ground-state sublevel at the temperature of 1.5 K for both cases, it is conceivable that the lack of quantitative agreement for the $\phi \sim 90°$ case in Fig. 6 is due to the breakdown of the simple model based on the incoherent tunneling of the ground state $m = \pm 10$.

IV. SUMMARY AND CONCLUSIONS

We have shown that the proton $1/T_1$ in single-crystal Fe_8 is strongly affected by the tunneling dynamics when the magnetic field is applied perpendicular to the easy z axis. The peak that one would have expected in the field dependence of $1/T_1$ due to cross relaxation at the matching conditions $\nu_L = \Delta_T$ was not observed. This could be due to the excessive broadening of the magnetic levels. It would be interesting to search for the cross-relaxation effects at a temperature much lower than 1.5 K. On the other hand a big peak was detected at a higher field corresponding to the condition that the Larmor frequency ν_L equals the incoherent tunneling transition probability in agreement with a simple phenomenological model of nuclear relaxation due to quantum fluctuations of the magnetization. A good fit of the data was obtained in all cases except when the direction of the transverse field was along the hard x axis. The interest of the present results resides in the fact that it was shown that in particular circumstances the nuclear Zeeman reservoir and the tunneling reservoir are strongly coupled. It is thus natural to think about double resonance experiments to further explore the issue.

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[1] For an exhaustive review of SMM, see, for example, G. Christou, D. Gatteschi, D.N. Hendrickson, and R. Sessoli, MRS Bull. **25**, 66 (2000).

[2] A review of the literature on quantum tunneling in Mn_{12} and Fe_8 can be found in I. Tupitsyn and B. Barbara, in *Magnetism: Molecules to Materials III*, edited by J. S. Miller and M. Drillon (Wiley-VHC, Verlag GmbH, Weinheim, 2002), p. 106.

[3] C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, and D. Gatteschi, Phys. Rev. Lett. **78**, 4645 (1997).

[4] W. Wernsdorfer and R. Sessoli, Science **284**, 133 (1999).

[5] J.R. Friedman, M.P. Sarachik, J. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996).

[6] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, Nature (London) **383**, 145 (1996).

[7] A.L. Barra, P. Debrunner, D. Gatteschi, Ch.E. Shulz, and R. Sessoli, Europhys. Lett. **35**, 133 (1996).

[8] A.L. Barra, D. Gatteschi, and R. Sessoli, Chem.-Eur. J. **6**, 1608 (2000).

[9] R. Caciuffo, G. Amoretti, A. Murani, R. Sessoli, A. Caneschi, and D. Gatteschi, Phys. Rev. Lett. **81**, 4744 (1998).

[10] A. Mukhin, B. Gorshunov, M. Dressel, C. Sangregorio, and D. Gatteschi, Phys. Rev. B **63**, 214411 (2001).

[11] M. Ueda, S. Maegawa, H. Miyasaka, and S. Kitagawa, J. Phys. Soc. Jpn. **70**, 3084 (2001).

[12] E. Del Barco, N. Vernier, J.M. Hernandez, J. Tejada, E.M. Chudnovsky, E. Molins, and G. Bellessa, Europhys. Lett. **47**, 722 (1999).

[13] E. del Barco, J.M. Hernandez, J. Tejada, N. Biskup, R. Achey, I. Rutel, N. Dalal, and J. Brooks, Phys. Rev. B **62**, 3018 (2000).

[14] F. Luis, F.L. Mettes, J. Tejada, D. Gatteschi, and L.J. de Jongh, Phys. Rev. Lett. **85**, 4377 (2000);

[15] F.L. Mettes, F. Luis, and L.J. de Jongh, Phys. Rev. B **64**, 174411 (2001).

[16] F. M. Luis, F. L. Mettes, and L. J. de Jongh, in *Magnetism: Molecules to Materials III* (Ref. 2), p. 169.

[17] K. Wieghardt, K. Pohl, H. Jibril, and G. Huttner, Angew. Chem., Int. Ed. Engl. **23**, 77 (1984).

[18] Y. Furukawa, K. Kumagai, A. Lascialfari, S. Aldrovandi, F. Borsa, R. Sessoli, and D. Gatteschi, Phys. Rev. B **64**, 094439 (2001).

[19] A. Lascialfari, Z.H. Jang, F. Borsa, P. Carretta, and D. Gatteschi, Phys. Rev. Lett. **81**, 3773 (1998).

[20] Y. Furukawa, K. Aizawa, K. Kumagai, R. Ullu, A. Lascialfari, and F. Borsa, J. Appl. Phys. **93**, 7813 (2003).

[21] A. Fort, A. Rettori, J. Villain, D. Gatteschi, and R. Sessoli, Phys. Rev. Lett. **80**, 612 (1998).

[22] In Ref. 16, an average moment of the ground state is reported to be $\pm 6\mu_B$ along the z axis under application of transverse field of 2.5 T so that the bias field H_z is estimated to be 200 Oe. This value is close to our approximate estimate $H_z = 120$ Oe obtained by assuming $m = \pm 10$ to be the correct quantum number.