Effects of the environment on nonadiabatic magnetization process in uniaxial molecular magnets at very low temperatures

Keiji Saito and Seiji Miyashita
Department of Applied Physics, Graduate School of Engineering, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

Hans De Raedt
Institute for Theoretical Physics and Materials Science Centre, University of Groningen, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands

(Received 16 August 1999)

We discuss the effect of the thermal environment on the low-temperature response of the magnetization of uniaxial magnets to a time-dependent applied magnetic field. At very low temperatures the stepwise magnetization curves observed in molecular magnets such as Mn_{12} and Fe_8 display little temperature dependence where the apparent thermal assisted process are suppressed. We show that the changes of the magnetization at each step cannot be analyzed directly in terms of a quantum-mechanical nonadiabatic transition. In order to explain this nonadiabatic behavior, we study the quantum dynamics of the system weakly coupled to a thermal environment and propose a relation between the observed magnetization steps and the quantum-mechanical transition probability due to the nonadiabatic transition. [S0163-1829(99)04045-X]

Magnetization processes of nanoscale molecules such as Mn_{12} and Fe_8 have attracted much interest. For such small systems the discreteness of energy level plays an important role and staircase structures of the response of the magnetization to a sweeping magnetic field have been observed.[1–6] The staircase is explained as a quantum-mechanical transition at the avoided level crossing points, where levels of the Hamiltonian become almost degenerate, and form repulsive structures as shown in Fig. 1, which has been called resonant tunneling. This quantum-mechanical transition has been studied from the point of view of the nonadiabatic transition.[7–10] There are two characteristic features of each nonadiabatic transition.[9] One is the localization of the transition because it occurs only around avoided level crossing points. The other is the dependence of the transition probability on sweeping rate of the magnetic field, the energy gap, and the gradients of the levels. Since at each avoided level crossing point only two levels play an important role, the transition probability can be described by the well-known Landau-Zener-Stückelberg (LZS) mechanism.[11–13]

However, the behavior of these magnetic systems can easily be affected by thermal fluctuations even at low temperatures, because the energy scales involved are rather small. At relatively high temperatures ($T\sim 1$ K) the temperature dependence of the magnetization process is very significant, where excitations to higher levels provide other channels of resonance tunneling, which is called thermally assisted resonant tunneling.[14–16] The external noise may affect the LZS mechanism itself which has been also studied.[17–19]

On the other hand, at very low temperatures ($T\sim 60$ mK), the magnetization curve shows very little change with temperatures and only quantum-mechanical phenomena seem to be dominant.[6] However, as we will show below, even at such low temperatures, thermal fluctuations cause inevitable effects, which prevent a direct application of mechanism of the nonadiabatic transition.

In this paper, we investigate the effect of the thermal environment at very low temperatures on nonadiabatic transitions and find a relation between the observed data and the true quantum-mechanical transition probability, from which the energy gap at the avoided level crossing point via the LZS formula can be deduced.

Let us consider the change of magnetization when the external field is swept from a negative value to a positive value. Initially the system is assumed to be in the ground state with the magnetization $m_0 \simeq -S$ (approximately). As the field increases, the state with m_0 crosses states with the magnetization S, $S-1, \ldots,$ and 0. At each avoided level crossing point a nonadiabatic transition occurs (Fig. 1). We assign numbers i ($i=1,2,\ldots$) for the avoided level crossing point where the state of m_0 crosses a state with $m_i \simeq S-i+1$ ($=S, S-1, \ldots,$ respectively). Let p_i denote the probability staying the same level at the ith avoided level crossing point. In the pure quantum dynamical case, we have the following relation between the change of the observed magnetization at the crossing point $i, \Delta M_i \equiv M_i - M_{i-1}$ and the transition probabilities $\{p_i\}$:

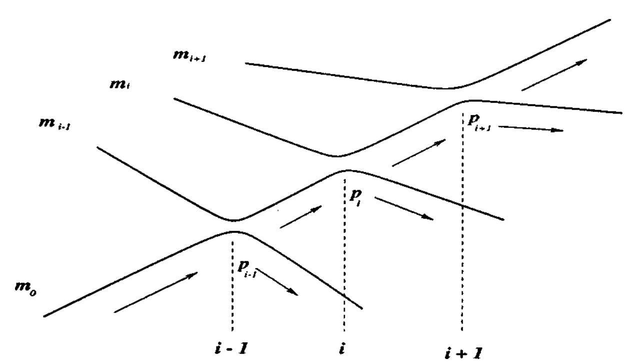

FIG. 1. Schematic energy level diagram and the nonadiabatic transitions. p_i denotes the probability that the system remains in the same eigenstate.

0163-1829/99/60(21)/14553(4)/$15.00

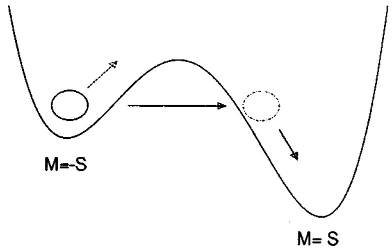

FIG. 2. Potential picture of the metastability.

$$\Delta M_i = \prod_{n=1}^{i-1} (1-p_n)\{[m_0(1-p_i)+m_i p_i]-m_0\}, \quad (1)$$

where M_i is the observed magnetization between avoided level crossing point i and $i+1$. By this relation (1), all the transition probabilities $\{p_i\}$ are obtained from the magnetizations in pure quantum cases.

In the experiment of Perenboom *et al.* for $Mn_{12}(S=10)$ ($T=59$ mK),[6] shape of the magnetization process seems to saturate with the lowering of the temperature. When we analyze the data using the relation (1), we cannot find any consistent set of the transition probabilities $\{p_i\}$. In the experiment, the stepwise changes of the magnetization occur at the avoided level crossing points where the state with $m_0 \simeq -10$ crosses with states with $m_i \simeq 3$, 2, 1, and 0 ($i = 7,8,9$, and 10, respectively). The changes of the magnetization at the points are 0.62, 3.54, 8.00, and 6.77, respectively. The relation (1) yields $p_7 = 0.0480$, $p_8 = 0.315$, $p_9 = 1.13$, and $p_{10} = -7.976$, in contradiction to the trivial condition $0 \leqslant p_i \leqslant 1$. Therefore a naive application of nonadiabatic transition theory fails to explain the saturated magnetization curve in the very low temperature.

We attribute this failure to the effect of thermal environment even at such a low temperature. In terms of the potential picture (Fig. 2), the states with $M>0$ belong to the right valley and we expect that these states easily relax to the bottom of the valley, i.e., to the state with $M=S$. Thus, once a quantum-mechanical transition from the metastable state of $M=-S$ to a state of $M>0$ takes place, the state is expected to relax easily to the lowest level due to some dissipation mechanism in the absence of an energy barrier. In the case of a pure quantum transition, such a relaxation to the state of $M=S$ is prohibited because of the large separation between the levels. If the time scale of dissipation is much shorter than that of the system and the scale on which the magnetic field changes, the transfer to the lowest state takes a short time. As a result the magnetization curve will show a staircase as in the case of pure quantum dynamics, but the change of magnetization at each step is different because of the relaxation transition $M \rightarrow S$ instead of $S-i+1$. This additional process causes changes of the steps.

In this scenario, we assume the following three properties: (i) First, a quantum-mechanical transition for $m_0(\simeq -S) \rightarrow m_i$ occurs with the probability of the pure nonadiabatic (LZS) transition $\{p_i^{\mathrm{LZS}}\}$, and then (ii) the relaxation from $m_i \rightarrow m_1(\simeq S)$ occurs by some dissipation mechanism. (iii) There is no direct relaxation from m_0 by the dissipation mechanism and therefore the amount of magnetization change depends only on $\{p_i^{\mathrm{LZS}}\}$ and does not depend on the temperature. Replacing m_i by m_1 in the relation (1), the change of the magnetization in this case is given by

$$\Delta M_i = \prod_{n=1}^{i-1} (1-\tilde{p}_n)\{[m_0(1-\tilde{p}_i)+m_1 \tilde{p}_i]-m_0\}. \quad (2)$$

Using the data of Perenboom *et al.*[6] now yields a reasonable solution for the $\{\tilde{p}_i\}$'s: $\tilde{p}_7 = 0.0313$, $\tilde{p}_8 = 0.185$, $\tilde{p}_9 = 0.515$, and $\tilde{p}_{10} = 0.898$.

In order to demonstrate that the above three properties are really possible at very low temperatures, we simulate a relaxation phenomena of a magnetic system, which very weakly couples to the external bath. Here we use a quantum master equation,[20]

$$\frac{\partial \rho(t)}{\partial t} = -i[\mathcal{H},\rho(t)] - \lambda([X,R\rho(t)]+[X,R\rho(t)]^{\dagger}), \quad (3)$$

where

$$\langle k|R|m\rangle = \zeta\left(\frac{E_k - E_m}{\hbar}\right) n_\beta(E_k - E_m)\langle k|X|m\rangle,$$

$$\zeta(\omega) = I(\omega) - I(-\omega), \quad \text{and} \quad n_\beta(\omega) = \frac{1}{e^{\beta\omega}-1}.$$

Here, β is an inverse temperature of the reservoir $1/T$, and we set $\hbar=1$. $|k\rangle$ and $|m\rangle$ are the eigenstates of $\mathcal{H}$ with the eigenenergies E_k and E_m, respectively. $I(\omega)$ is the spectral density of the boson bath. We take here an infinite number of phonons with the Ohmic dissipation $I(\omega) = I_0\omega$.[21] As a more realistic bath for the experimental situation at very low temperature, we may take the dipole-field from the nuclear spins[22] or other types of spectrum such as super-Ohmic type. X is an operator of the magnetic system that interacts linearly with the bosons of the reservoir. The relaxation process can be affected by the form of interaction of the system with the thermal bath, i.e., by the choice of X. Here, we take $X = \frac{1}{2}(S_x + S_z)$. Generally $X = S_x$ is more efficient than $X = S_z$ for the relaxation. A detailed comparison with other choices will be presented elsewhere. Different choices of the concrete form of the thermal bath, however, do not cause any significant qualitative change because the couplings to the bath is very weak.

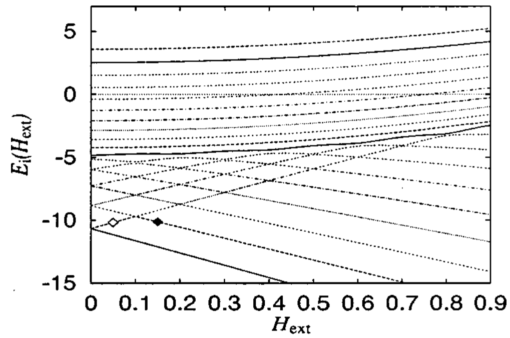

FIG. 3. Energy level diagram of the model (4) as a function of H_{ext}. The white and black diamonds correspond to the case (1) and the case (2), respectively.

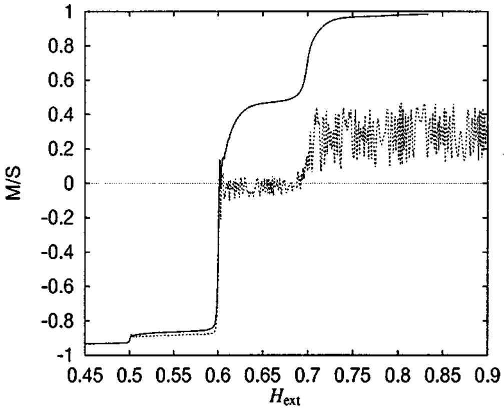

FIG. 4. Magnetization as a function of $H_{\rm ext}$. The dashed line denotes the pure quantum dynamics $[P]$, and the solid line denotes the dissipative quantum dynamics $[D]$.

For Mn_{12}, a detailed form of the Hamiltonian has been proposed.[23] However, the energy gap of the Mn_{12} is too small to observe the phenomena within the available computation time. Thus, here, we demonstrate the qualitative features of the dynamics, i.e., the three properties (i), (ii), and (iii). We believe that the key ingredients of the general qualitative feature are the existence of the avoided level crossing points and weak coupling to the external bath. For the realistic model with a much smaller energy gap, the features observed here should be realized on a much longer time scale. Thus, we adopt a minimal model of a uniaxial $S=10$ spin system with the two ingredients:

$$\mathcal{H}=-DS_z^2+\Gamma S_x-H_{\rm ext}(t)S_z, \tag{4}$$

with a linearly increasing external field, $H_{\rm ext}=ct-H_0$ where c is the sweeping velocity. The transverse field Γ represents the terms causing quantum fluctuations. We choose $D=0.1,\Gamma=0.5$ in what follows.

In order to see the difference of relaxations between the case with and without the potential barrier, we compare two typical cases: (1) $H_{\rm ext}=0.05$ and (2) $H_{\rm ext}=0.15$ and set the sweep velocity $c=0$. As the initial state we take the second level, as indicated in Fig. 3. The second level has $M\simeq-10$ in the case (1) and $M\simeq 9$ in the case 2. In the both cases, the ground state has $M\simeq 10$. The parameters are set to $T=0.1$, $I_0=1.0$, and $\lambda=1.0\times10^{-4}$. We study the relaxation for both cases by solving Eq. (3). These probabilities are given by a diagonal element of $\rho(t)$, i.e., $\langle 1|\rho(t)|1\rangle$ and $\langle 2|\rho(t)|2\rangle$, respectively. We observe almost no damping in the case (1), whereas a rather fast relaxation occurs in the case (2). Thus, at a fairly low temperature, the thermal environment causes significant difference in the relaxation process depending on the presence of a potential barrier. The difference between the cases (1) and (2) can be understood by analyzing the matrix elements of Eq. (3).

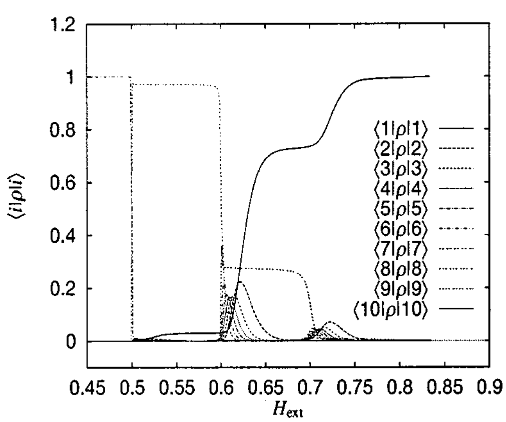

FIG. 5. The time evolution of the probability of individual levels.

TABLE I. The changes of magnetization. $\Delta M_{[\rm P]}$ and $\Delta M_{[\rm P]}$ are the changes for the case $[P]$ and $[D]$, respectively.

Cross point (m_0,m_i)	$\Delta M_{[\rm P]}$	$\Delta M_{[\rm D]}$
$(-10,5)$	0.511	0.693
$(-10,4)$	8.32	13.3
$(-10,3)$	3.50	5.03

We now investigate the time evolution of the system for a sweeping field $c=1.0\times10^{-5}$ starting at $H_0=-0.05$. We study the case of pure quantum dynamics $(\lambda=0)$ $[P]$ and the case with a weak dissipation $(\lambda=1.0\times10^{-4})$ $[D]$. These magnetization curves are shown in Fig. 4. We show data for $H_{\rm ext}\geqslant 0.45$ because almost no change is observed for $H_{\rm ext}<0.5$. For the case $[P]$, we observe oscillating behavior due to spin precession, whereas in the case $[D]$ this detailed structure is smoothed out by the dissipation. We find stepswise magnetization curves in both cases. The changes of the magnetization are listed in Table I.

From these data we estimate the transition probabilities by the relations (1) and (2) which are listed in Table II. First we obtain the transition probabilities from the data in Table I setting $m_0=-S$ and $m_i=S-i+1$. From the data $\Delta M_{[D]}$, unacceptable values $\{p_{[\rm D],i}\}$ are obtained from the relation (1), while acceptable ones $\{\tilde{p}_{[\rm D],i}\}$ are obtained by the relation (2). $\{\tilde{p}_{[\rm D],i}\}$ agree with $\{p_{[\rm P],i}\}$ obtained by the relation (1) from the data $\Delta M_{[P]}$. This agreement shows that the three properties (i), (ii), and (iii) are really realized in the present model and therefore we can estimate the quantum-mechanical nonadiabatic transition by the relation (2). Although the magnetization m_i is almost constant: $m_0\simeq -S,m_i\simeq S-i+1\,(i\geqslant 1)$, they show a little dependence on the magnetic field $H_{\rm ext}$. Taking the $H_{\rm ext}$ dependence of m_i into consideration, we also calculated the transition probabilities in the case $[D]$ with Eq. (2). They are shown as $\{\overline{p}_{[\rm D],i}\}$. We confirmed that $\{\overline{p}_{[\rm D],i}\}$ agree with the probabilities $\{p_{[\rm R],i}\}$ directly obtained from the diagonal elements of the density matrix. The difference between $\tilde{p}_{[\rm D],i}$ and $\overline{p}_{[\rm D],i}$ simply comes from the large value of Γ taken for conve-

TABLE II. The transition probabilities obtained in various ways, see the text.

i	(m_0,m_i)	$p_{[\rm R],i}$	$p_{[\rm P],i}$	$p_{[\rm D],i}$	$\tilde{p}_{[\rm D],i}$	$\overline{p}_{[\rm D],i}$
6	$(-10,5)$	0.0280	0.0341	0.0460	0.0346	0.0291
7	$(-10,4)$	0.730	0.616	0.995	0.688	0.716
8	$(-10,3)$	1.000	0.726	78.0	0.835	0.970

nience of simulation. If Γ is very small as in the case of the experiment, m_i is very close to $S-i+1$ and it is expected that $\tilde{p}_{[D],i}$ and $\overline{p_{[D],i}}$ are very close. We present the time evolution of $\langle i|\rho|i\rangle$ in Fig. 5. This figure explicitly shows the three properties (i), (ii), and (iii).

We estimate the energy gap from the transition probabilities with the extended LZS formula p_i^{LZS}

$$p_i^{\mathrm{LZS}}=1-\exp\left[-\frac{\pi(\Delta E_i)^2}{2(m_i-m_0)c}\right], \qquad (5)$$

where c is the changing rate of the Zeeman energy. Using $\{\tilde{p}_{[D],i}\}$, we obtain the energy gaps for the avoided level crossings as $\Delta E_6=1.83\times10^{-3}, \Delta E_7=10.1\times10^{-3}$. These estimates agree with the correct value $\Delta E_6=1.54\times10^{-3}$ and $\Delta E_7=10.0\times10^{-3}$ directly obtained from the energy levels.[24] If we use $\overline{p_{[D],i}}$, we have, of course, almost the exact values, $\Delta E_6=1.57\times10^{-3}, \Delta E_7=9.9\times10^{-3}$. Thus, we conclude that we can estimate the energy gap from the deceptive apparent magnetization by the relation (2).

In summary, we have considered a mechanism for nonadiabatic magnetization process at very low temperatures where apparently no temperature dependence is observed. We proposed the general relation (2) between the steps in the magnetization and the energy-level splittings at very low temperatures. Using relation (2) we have estimated the quantum transition rate $\{p_i\}$ at the low temperatures for which the experiments[6] have been performed. We demonstrated an example of apparent nonadiabatic magnetization process in a minimal model with the avoided level crossing points and weak coupling to the external bath. Elsewhere we will report on our investigation of the energy gaps $\{\Delta E_i\}$ of Mn_{12} and Fe_8 based on the detailed information of the values of jumps and the scanning speed c.

The present study is partially supported by the Grant-in Aid for Research from the Ministry of Education, Science and Culture.

[1] J. R. Friedman M. P. Sarachik, T. Tejada, and R. Ziolo, Phys. Rev. Lett. **76**, 3830 (1996).
[2] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, Nature (London) **383**, 145 (1996).
[3] J. M. Hernandez, X. X. Zhang, F. Luis, T. Tejada, J. R. Friedman, M. P. Sarachik, and R. Ziolo, Phys. Rev. B **55**, 5858 (1997).
[4] F. Lionti, L. Thomas, R. Ballou, B. Barbara, A. Sulpice, R. Sessoli, and D. Gatteschi, J. Appl. Phys. **81**, 4608 (1997).
[5] C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, and D. Gatteschi, Phys. Rev. Lett. **78**, 4645 (1997).
[6] J. A. A. J. Perenboom, J. S. Brooks, S. Hill, T. Hathaway, and N. S. Dalal, Phys. Rev. B **58**, 330 (1998).
[7] S. Miyashita, J. Phys. Soc. Jpn. **64**, 3207 (1995).
[8] S. Miyashita, J. Phys. Soc. Jpn. **65**, 2734 (1996).
[9] H. De Raedt, S. Miyashita, K. Saito, D. García-Pablos, and N. García, Phys. Rev. B **56**, 11 761 (1997).
[10] S. Miyashita, K. Saito, and H. De Raedt, Phys. Rev. Lett. **80**, 1525 (1998).
[11] L. Landau, Phys. Z. Sowjetunion **2**, 46 (1932).
[12] C. Zener, Proc. R. Soc. London, Ser. A **137**, 696 (1932).
[13] E. C. G. Stückelberg, Helv. Phys. Acta **5**, 369 (1932).
[14] D. A. Granin and E. M. Chudnovsky, Phys. Rev. B **56**, 11 102 (1997).
[15] A. Fort, A. Rettori, J. Villain, D. Gatteschi, and R. Sessoli, Phys. Rev. Lett. **80**, 612 (1998).
[16] F. Luis, J. Bartolomé, and F. Fernández, Phys. Rev. B **57**, 505 (1998).
[17] Y. Kayanuma and H. Nakayama, Phys. Rev. B **57**, 13 099 (1998).
[18] V. V. Dobrovitski and A. K. Zvezdin, Europhys. Lett. **38**, 377 (1997).
[19] L. Gunther, Europhys. Lett. **39**, 1 (1997).
[20] K. Saito, S. Takesue, and S. Miyashita, cond-mat/9810069 (unpublished).
[21] H. Grabert, P. Schramn, and G. Ingold, Phys. Rep. **3**, 115 (1988).
[22] N. V. Prokof'ev and P. C. E. Stamp, J. Low Temp. Phys. **104**, 143 (1996).
[23] M. I. Katsnelson, V. V. Dobrovitski, and B. N. Harmon, J. Appl. Phys. **85**, 4533 (1999).
[24] Due to the large value of Γ and thus, $p_8\sim1$, it is difficult to estimate precisely the concrete value of ΔE_8.