PHYSICAL REVIEW B **70**, 220401(R) (2004)

Pulsed-field studies of the magnetization reversal in molecular nanomagnets

J. Vanacken, S. Stroobants, M. Malfait, and V. V. Moshchalkov
Pulsed Field Group, Laboratory of Solid-State Physics and Magnetism, K.U.Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium

M. Jordi, J. Tejada, and R. Amigo
Department de Física Fonamental, Universitat de Barcelona, Diagonal 647, 08024 Barcelona, Spain

E. M. Chudnovsky
Department of Physics, Lehman College, CUNY, Bronx, New York 10468-1589, USA

D. A. Garanin
Institut für Physik, Johannes-Gutenberg-Universität, D-55099 Mainz, Germany

(Received 12 July 2004; published 3 December 2004)

We report experimental studies of crystals of Mn_{12} molecular magnetic clusters in pulsed magnetic fields with sweep rates up to 4×10^3 T/s. The steps in the magnetization curve are observed at fields that are shifted with respect to the resonant field values. The shift systematically increases as the rate of the field sweep goes up. These data are consistent with the theory of the collective dipolar relaxation in molecular magnets.

DOI: 10.1103/PhysRevB.70.220401 PACS number(s): 75.50.Xx, 42.50.Fx, 75.60.Ej

I. INTRODUCTION

High-spin molecular nanomagnets, like Mn_{12} acetate, have unusual magnetic properties related to their high magnetic anisotropy and to the quantization of the magnetic moment **M**. For certain values of the magnetic field, quantum states characterized by different projections of **M** onto the anisotropy axis come to resonance. At these fields the magnetization curve of the crystal exhibits distinct steps due to quantum transitions between the resonant energy levels.[1] The steps, for a field-sweep experiment, have been successfully described in terms of single-molecule Landau-Zener (LZ) transitions.[2–7] To date the information about spin Hamiltonians, extracted from the magnetization measurements,[1,8–11] has been compared with the EPR data,[12–17] and a good agreement has been achieved.

Among interesting effects observed in crystals of molecular magnets are magnetic avalanches.[18–21] At low temperature, sufficiently large crystals exhibit abrupt magnetization reversal that may take less than 1 ms. Initially, it was suggested[18–20] that the avalanche is some kind of a thermal chain reaction. In large samples at low temperature, the heat released by molecular moments relaxing towards the direction of the field does not have sufficient time to flow out of the sample. Instead, it is absorbed by other moments, causing them to relax and generate more heat. Recently this picture has been challenged by the observation that the magnetization reversal during avalanche occurs much faster than the temperature rise.[22] The electromagnetic effects associated with avalanches have been explored.[21] At this point, the nature of the avalanche and the connection between the magnetization reversal, thermal effects, and electromagnetic radiation remain unclear.

In this paper we report low temperature magnetization studies of Mn_{12} single crystals at a field sweep rate $\mu_0\, dH/dt$ up to 4 kT/s. We find, unexpectedly, that at such high sweep rates avalanches take place at lower fields as compared to the case of low sweep rate. The field at which the magnetization reversal occurs is shifted by ΔH from the resonance field. The shift increases as the sweep rate goes up. We have been able to scale the relaxation curves obtained at different sweep rates onto one curve. One possible explanation of this scaling can be given along the lines of the model of collective magnetic relaxation suggested in Ref. 23. In this model the magnetic moments of the molecules rotate in unison due to electromagnetic interactions. We also consider an alternative explanation based upon the existence of fast-relaxing second species in Mn_{12} acetate.[24]

II. EXPERIMENT

Mn_{12} single crystals of high purity were used in the experiments. The conventional composition and the structure of the crystals were established by chemical, infrared and X ray diffraction methods. In addition, dc and ac magnetometry of the crystals was carried out in order to verify their conventional behaviour at low sweep rates. We have checked that the values of the blocking temperatures and resonant fields of the crystals coincide with previously published values.

Measurements of the magnetization using fast magnetic field pulses up to 4 kT/s and at a temperature $T=0.6$ K were performed at the K.U. Leuven. The pulsed magnetic fields were generated by a modular capacitor bank whose capacitance was systematically tuned from $C=4$ mF to $C=28$ mF while the voltage was adapted from $V=5000$ V to $V=600$ V in such a way that the capacitor energy, $\frac{1}{2}CV^2$, remained constant. A homemade coil with an inductance of 650 μH was used to produce the magnetic field pulse. A crow bar diode of resistance $R=0.08\ \Omega$ provided a critical damping of the magnetic pulse which has a duration of $\sim$20 ms. The magnetization measurements were performed with the use of an inductive magnetization sensor designed to measure samples of volume up to 1 mm^3. The sensor coil had 640 turns in one direction and 345 turns in the opposite direction. Its sensitivity reaches 10^{-4} emu in the fields up to 10 T. During the measurements, the sample and the detec-

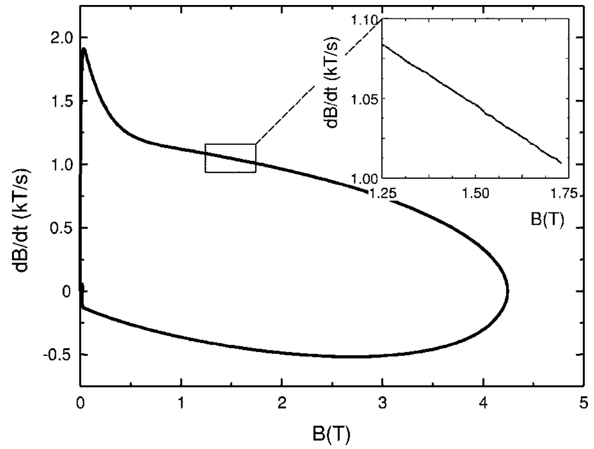

FIG. 1. Field dependence of the sweep rate.

tion coils were submerged in liquid ^{3}He. The ^{3}He temperature probe was made entirely of nonmetallic materials; we have verified that during a 50 T field pulse the temperature change, measured by a calibrated RuO sensor, did not exceed 100 mK. The sweep rate versus magnetic field of a typical magnetic field pulse is shown in Fig. 1.

The typical field dependence of the differential susceptibility, dM/dH, of a single crystal of Mn_{12} acetate, taken at various sweep rates and $T=670$ mK, is shown in Fig. 2. The magnetization reversal occurs at a field that is close to the third resonant field, $\mu_0 H \sim 1.3$ T.[1] The most surprising feature of the data is the dependence of the position and the height of the peaks on the field sweep rate. According to the conventional theory of resonant spin tunneling,[1] confirmed by all previous experimental studies, the positions of the peaks are determined entirely by the Hamiltonian of the nanomagnet and should not depend on the sweep rate. Note that some dependence of the peaks on the rate may occur in the case of thermal avalanches.[18–21]

In this case, however, the magnetization reversal is always accompanied by a measurable increase of the temperature of the sample. In our experiments no significant change in the temperature has been detected, making avalanches an improbable explanation. Figure 3 shows additional experimental data, in which the sweep rate was kept constant $(dB/dt = 1.1\ \mathrm{kT/s})$, but the measuring temperature changed. The peak position of dM/dH at $T=0.723$ K is $B=1.502$ T, and at $T=1.074$ K is $B=1.510$ T (Gaussian fits); a difference in peak position less than $\Delta B=0.01$ T, i.e., within our experimental error bar. The sweep rate dependence is thus much more significant, and for comparable effects, temperature changes much larger than $\Delta T=0.3$ K would be needed; such temperature raises were not experimentally observed.

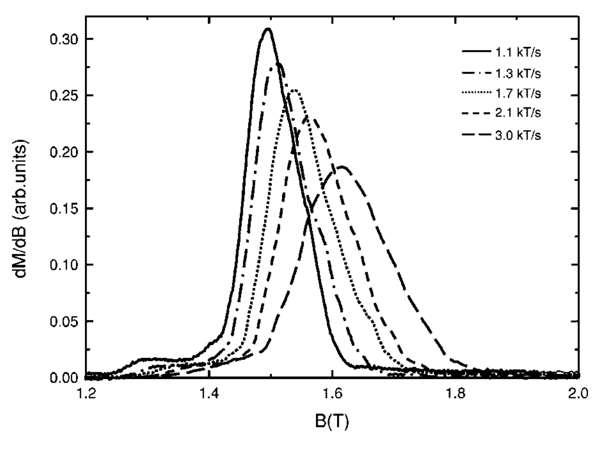

FIG. 2. Field dependence of dM/dB for different sweep rates at $B=1.3$ T.

III. THEORY

One *possible* explanation to the above findings can be obtained along the lines of the collective magnetization reversal expected at a very high sweep rate. According to Ref. 23, for such a sweep the relaxation of the magnetization at the level crossing occurs in two stages.

The first stage is the Landau-Zener process that leaves the fraction of magnetic molecules P in the excited states (the upper energy branch ε^+ in Fig. 4). This fraction is given by the Landau-Zener formula: $P_{LZ}=\exp(-\varepsilon)$, where $\varepsilon = \pi\Delta^2/2\hbar\nu$, Δ is the tunnel splitting and ν is the energy sweep rate $W=\nu t = g|\Delta m|\mu_B(H(t)-H_R)=\varepsilon_m-\varepsilon_{m'}$. During the second stage, these excited states decay due to the Dicke superradiance onto the lower branch ε^- (Fig. 4). In the limit of a very small sweep rate, $\varepsilon \gg 1$, almost all molecules follow the lower energy branch, so that the evolution of the system is entirely determined by the Landau-Zener effect and the superradiance is irrelevant.

At a high sweep rate, $\varepsilon \ll 1$, the majority of the molecules initially cross to the upper branch and then decay to the lower branch due to the superradiance. At this stage $S_z = M_z/M$ (**M** being the magnetic moment of the system) satisfies the following equation:[23]

$$\frac{d}{dt}s_z(t) = \frac{\alpha}{\hbar}[1 - S_z^2(t)]W(t), \qquad (1)$$

where

$$\alpha = \frac{1}{6}N\langle S_z\rangle^2 g^2\left(\frac{e^2}{\hbar c}\right)\left(\frac{\Delta}{m_e c^2}\right)^2, \qquad (2)$$

N is the total number of Mn_{12} molecules in the crystal, $S=10$ is the spin of the molecule, g is the gyromagnetic ratio, e and m_e are the electron charge and mass, c is the speed of light, and $\langle S_z\rangle = (m'-m)/2$. In the last expression, $m=-10$ and $m'=7$ are the magnetic quantum numbers or the resonant levels at the third resonant field, $\mu_0 H \sim 1.3$ T.

The exact solution of Eq. (1) depends strongly on the initial condition for the superradiance stage. The latter is difficult to predict because of the contribution of both coherent and incoherent processes to the initial Landau-Zener stage.[23,25] However, one observation immediately follows from Eq. (1). Consider crossing of the third resonance, where $H=H_R$, by a linear field sweep, $\delta H = H(t)-H_R = rt$. The relation between the energy sweep rate, ν, introduced earlier, and the field sweep rate, r, is $\nu = 2g\mu_B\langle S_z\rangle r$. Equation (1) can then be rewritten as

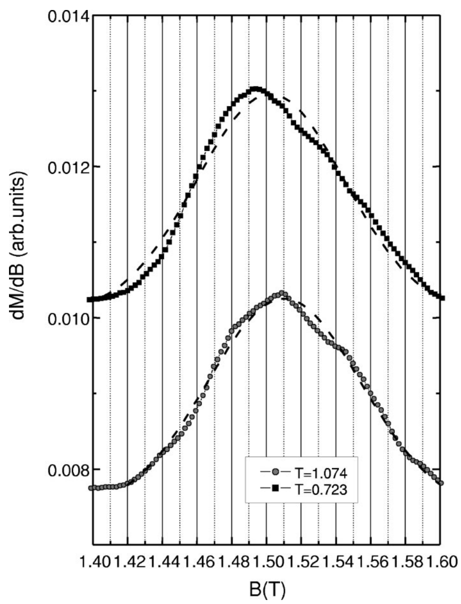

FIG. 3. Field dependence of the third resonance peak for a fixed sweep rate $(dB/dt=1.1\ \mathrm{kT/s})$ and for different temperatures $T=0.723$ K and $T=1.074$ K.

$$\frac{dS_z}{dt}=\frac{\alpha}{\hbar}(1-S_z^2)\nu t=\frac{\alpha}{\hbar}g|\Delta m|\mu_B(1-S_z^2)rt=C(1-S_z^2)rt,$$

where $C=(\alpha/\hbar)g|\Delta m|\mu_B$, leading to the scaling relation:

$$\frac{dS_z}{d\sqrt{rt}}=C(1-S_z^2)\sqrt{rt},$$

$$\frac{dS_z}{dH}\sqrt{r}=C(1-S_z^2)\frac{H}{\sqrt{r}}.$$

One observation immediately follows from these equations. Since $S_z\sim M_z$, the dependence of $\sqrt{r}(dM_z/d\delta H)$ on $\delta H/\sqrt{r}$ must be independent of r if the initial condition for S_z at the beginning of the superradiant relaxation is independent of r.[26]

IV. COMPARISON WITH EXPERIMENT

It has been observed in the past that as the temperature goes down or the field sweep rate goes up, avalanches typically shift towards higher fields. At 0.6 K and low sweep rate one would typically observe an avalanche above 3 T. The fact that at a very high sweep rate the magnetization reversal takes place at a significantly lower field is, therefore, surprising and invites explanation outside the conventional framework of thermal runaway. The above theoretical model presents one such possibility. As can be seen from the inset of Fig. 1, the field sweep in the field range shown in Fig. 2 is, with good accuracy, linear on time. The scaling of the experimental data along the lines of the theoretical model considered above is shown in Fig. 5. Given the approximations involved, the scaling appears to be rather good.

It allows one to estimate the constant α in Eq. (1), $\alpha\sim10^{-8}$. For $N\sim10^{18}$ this requires $\Delta\sim10^{-3}$ K, which seems

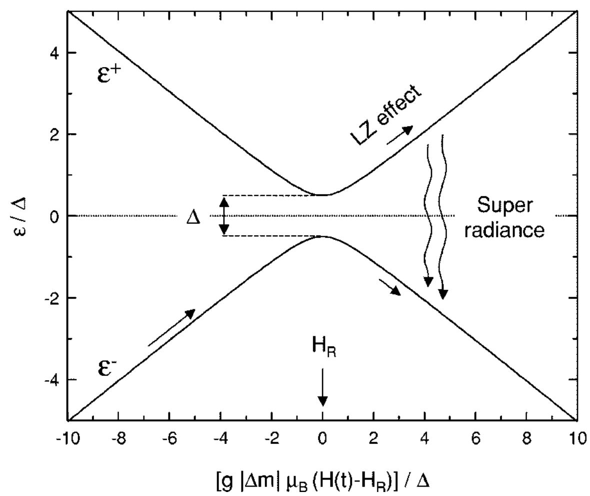

FIG. 4. A pair of tunnel-split levels $\varepsilon^+/\varepsilon^-$ versus the energy bias $W=\varepsilon_m-\varepsilon_{m'}=g|m-m'|\mu_B(H(t)-H_R)$. H_R denotes the (third) resonance field. The total magnetization reversal occurs after crossing the resonance $H(t)>H_R$ via superradiant magnetic dipolar transitions between the levels m and m', with unperturbed energies ε_m and $\varepsilon_{m'}$, respectively.

to be three to four orders of magnitude higher than expected at the third resonance. When taking this value for Δ, the LZ probability $P_{LZ}(\varepsilon)$ becomes reasonable, since $\varepsilon=\pi\Delta^2/2\hbar\nu\sim1$. One should note, however, that the tunnel splitting depends exponentially on the magnetic anisotropy that, in turn, depends strongly on the elastic stress. A small change in the magnetic anisotropy can have a dramatic influence on the tunnelling probability.[25] It is not inconceivable, therefore, that at very high magnetic field sweep rates the magnetostriction effects are responsible for the high value of the tunnel splitting at the third resonance.

It has been suggested in Ref. 24 that the shift of the avalanches to lower fields at a very high sweep rate, as well as the sweep-rate dependence of the field at which the magnetization reversal occurs, can be due to a faster relaxing species of Mn_{12}. While this might be worthy of testing in experiment, our setup does not permit the experimental

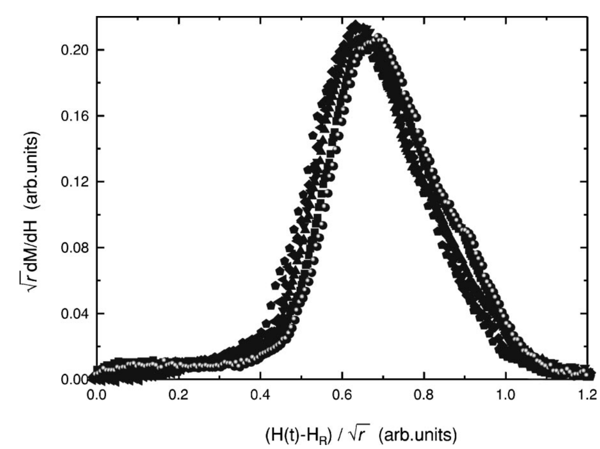

FIG. 5. Plot of $\sqrt{r}(dM_z/d\delta H)$ versus $\delta H/\sqrt{r}$ with $\delta H=H(t)-H_R$ at $\mu_0H_R=1.34$ T for all curves at different sweep rates from 1 to 3 kT/s.

protocol suggested in Ref. 24. At this point the relevance of the second species to our findings is a higher speculative suggestion which has not been investigated theoretically nor experimentally. The existence of the second species itself is an idea periodically brought up to explain the mirror image of the staircase hysteresis loop at low fields, as well as other unexplained phenomena in Mn_{12}. The percentage of the second species, if any, has to be small. If not, the initial fast relaxation due to that species would significantly affect the main part of the magnetization curve. The second species cannot simply include all defective molecules because, then, quantum steps in the magnetization curve would be smeared out. A second species of Mn_{12} with a known molecular structure has never been identified. Even if one assumes the existence of such a species, it is not clear why it should trigger a low-field avalanche at a high sweep rate but not at a low sweep rate. Independent evidence that the effect observed by us is not due to any defective molecules comes from the field-pulse measurements of molecular magnets that are not known to have any second species. Our recent measurements of Fe_8 crystals[27] have revealed exactly the same features that we observed in Mn_{12}. This suggests that the observed effects have universal nature and are not due to the presence of impurities.

The authors of Ref. 24 also stated that they did not dismiss the possibility of collective effects based upon spin-spin interactions, referring to their earlier paper.[28] The exchange interaction between Mn_{12} molecules is considered in Ref. 28 in the framework of an analysis which is based upon an incorrect model that reduces a spin chain to a hydrogen molecule. On the contrary, our model employs conventional electromagnetic interaction between magnetic dipoles. It is based upon the assumption that the inhomogeneous broadening of the Landau-Zener parameter ε is small. This translates into a requirement of a narrow distribution of the tunnel splitting and narrow distribution of the magnetic field felt by the spins. Both conditions must be satisfied in Fe^8. In Mn_{12} the situation is less clear due to solvent disorder, large hyperfine interactions, dislocations, etc., which result in a distribution of the tunnel splitting.[7,11,17,29] If that distribution consists of a finite number of narrow lines due to, e.g., finite number of nuclear spin states, finite number of isomers in the structure of the Mn_{12} molecule,[29] etc., the collective effects may still be possible. As for the narrow distribution of the magnetic field, it should be achieved automatically when the spins of the initially saturated sample rotate coherently due to collective electromagnetic relaxation. We emphasize that the latter is only a conjecture until one measures electromagnetic radiation that accompanies relaxation.

V. CONCLUSIONS

We have found a new spin relaxation effect in a single crystal of Mn_{12} molecular magnets at a high field-sweep rate. The magnetization reversal occurs at a significantly lower field as compared to experiments with low sweep rate. This field shifts away from the tunnelling resonance with increasing the sweep rate. The observed dependence of the differential susceptibility on the magnetic field correlates with the theory of collective electromagnetic relaxation.

ACKNOWLEDGMENTS

The Belgian IUAP, the Flemish GOA/2004/02 and FWO have supported this work. J.V. acknowledges financial support from the FWO—Vlaanderen. The work of the group of Barcelona has been supported by the EC through Contract No. IST-2001-33186 and by the Spanish Government through Contract No. MAT-2002-03144. The work of E.M.C. has been supported by the NSF Grant No. EIA-0310517.

[1] J. R. Friedman *et al.*, Phys. Rev. Lett. **76**, 3830 (1996).
[2] L. D. Landau, Phys. Z. Sowjetunion **2**, 46 (1932); C. Zener, Proc. R. Soc. London, Ser. A **137**, 696 (1932).
[3] V. V. Dobrovitsky and A. K. Zvezdin, Europhys. Lett. **38**, 377 (1997); L. Gunther, *ibid.* **39**, 1 (1997).
[4] M. N. Leuenberger and D. Loss, Phys. Rev. B **61**, 12 200 (2000).
[5] E. M. Chudnovsky and D. A. Garanin, Phys. Rev. Lett. **87**, 187203 (2001); D. A. Garanin and E. M. Chudnovsky, Phys. Rev. B **65**, 094423 (2002).
[6] W. Wernsdorfer and R. Sessoli, Science **284**, 133 (1999).
[7] K. M. Mertes *et al.*, Phys. Rev. Lett. **87**, 227205 (2001).
[8] J. M. Hernandez *et al.*, Europhys. Lett. **35**, 301 (1996).
[9] L. Thomas *et al.*, Nature (London) **383**, 145 (1996).
[10] C. Sangregorio *et al.*, Phys. Rev. Lett. **78**, 4645 (1997).
[11] E. del Barco *et al.*, Phys. Rev. Lett. **91**, 047203 (2003).
[12] A. L. Barra *et al.*, Phys. Rev. B **56**, 8192 (1997).
[13] S. Hill *et al.*, Phys. Rev. Lett. **80**, 2453 (1998).
[14] J. M. Hernandez *et al.*, Europhys. Lett. **47**, 722 (1999).
[15] E. del Barco *et al.*, Phys. Rev. B **62**, 3018 (2000).
[16] B. Parks *et al.*, Phys. Rev. B **64**, 184426 (2001).
[17] S. Hill *et al.*, Phys. Rev. Lett. **90**, 217204 (2003).
[18] C. Paulsen and J.-G. Park, in *Quantum Tunneling of Magnetization—QTM'94*, edited by L. Gunther and B. Barbara (Kluwer, Dordrecht, 1995) pp. 189–207.
[19] F. Fominaya *et al.*, Phys. Rev. Lett. **79**, 1126 (1997).
[20] E. del Barco *et al.*, Phys. Rev. B **60**, 11 898 (1999).
[21] J. Tejada *et al.*, Appl. Phys. Lett. **84**, 2373 (2004).
[22] J. Tejada *et al.*, cond-mat/0406389 (unpublished).
[23] E. M. Chudnovsky and D. A. Garanin, Phys. Rev. Lett. **89**, 157201 (2002).
[24] W. Wernsdorfer *et al.*, cond-mat/0405014 (unpublished).
[25] D. A. Garanin and E. M. Chudnovsky, Phys. Rev. B **65**, 094423 (2002).
[26] Notice that after the coherent Landau-Zener stage, $s_z = 1-2P_{LZ} = -1+2\varepsilon$, the initial condition for Eq. (1) does depend on r. However, the solution of Eq. (1) with this initial condition gives $S_z(t) = \tanh[(\alpha g \mu_B \langle S_z \rangle)/\hbar(\delta H/\sqrt{r})^2 - 1/2 \ln 1/\varepsilon]$which has only a logarithmic deviation on r from the proposed scaling.
[27] M. Jordi *et al.*, Europhys. Lett. (to be published).
[28] W. Wernsdorfer *et al.*, Phys. Rev. Lett. **89**, 197201 (2002).
[29] A. Cornia *et al.*, Phys. Rev. Lett. **89**, 257201 (2002).