

Large Quantum Nonlinear Dynamic Susceptibility of Single-Molecule Magnets

F. Luis, V. González, A. Millán, and J. L. García-Palacios

Instituto de Ciencia de Materiales de Aragón, C.S.I.C.–Universidad de Zaragoza, 50009 Zaragoza, Spain

(Received 3 November 2003; published 10 March 2004)

The nonlinear dynamical response of Mn_{12} single-molecule magnets is experimentally found to be very large, quite insensitive to the spin-lattice coupling constant, and displaying peaks reversed with respect to classical superparamagnets. It is shown that these features are caused by the strong field dependence of the relaxation rate due to the detuning of energy levels between which tunneling takes place. The nonlinear susceptibility technique, previously overlooked, is thus proposed as a privileged probe to ascertain the occurrence of quantum effects in mesoscopic magnetic systems.

DOI: 10.1103/PhysRevLett.92.107201

PACS numbers: 75.50.Xx, 75.40.Gb, 75.45.+j, 75.50.Tt

The possibility to observe quantum phenomena, such as tunneling or even quantum coherence, occurring in mesoscopic magnetic or superconducting materials is a subject of considerable interest [1]. These systems are also important for the study of the fuzzy border between the classical and quantum worlds [2]. As the size increases, tunneling probabilities decrease exponentially and the system becomes more entangled with its environment (phonons, electromagnetic fields, nuclear spins, electrons, etc.). This interaction plays a crucial role as it enables the system to approach equilibrium [3] but also causes decoherence of its quantum dynamics [4]. Besides its fundamental interest, decoherence sets the limits for application of the quantum behavior of mesoscopic systems to, e.g., quantum computing.

Molecular crystals are ideal for these studies [5]. They are ordered lattices of identical molecules, each containing a magnetic cluster that is isolated from its neighbors by a shell of organic ligands. Because of strong intramolecular superexchange interactions, each cluster behaves at low temperatures as a superparamagnet with a large spin S that flips as a whole. The best studied of these is the Mn_{12} acetate, for which $S = 10$. Its strong magnetic anisotropy produces magnetic relaxation and hysteresis at low temperatures [6], which make it a potential candidate for information storage at the molecular level. The spin reversal takes place via quantum tunneling through the anisotropy energy barrier whenever the magnetic field brings into resonance magnetic states located at both sides of the anisotropy barrier [7].

For classical superparamagnets, García-Palacios and Svedlindh [8] predicted that the nonlinear dynamic susceptibility can be very large and, in contrast to the linear susceptibility, quite sensitive to the spin-bath coupling strength (damping parameter). In this work we apply this technique, unexploited in this field, to investigate environmental effects in molecular clusters. We have studied two compounds, both having the same Mn_{12} magnetic core but different ligand molecules. This enables us to investigate how the spin dynamics is affected by different couplings to the phonon bath.

Our results show that the nonlinear response of these single-molecule magnets is dominated by a very large contribution, hitherto unforeseen, whose sign is opposite to the classical one. This contribution is interpreted in terms of the extreme sensitivity of quantum tunneling probabilities to the detuning of the magnetic levels by the external field. Therefore, the dynamical nonlinear susceptibility permits one to ascertain unambiguously if tunneling plays a role in the relaxation of magnetic molecular clusters and nanoparticles. In addition to its fundamental interest, this phenomenon might be relevant in situations where nonlinear effects become important (e.g., magneto-optical applications of these systems).

The preparation of the Mn_{12} acetate $[\text{Mn}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4\text{O}_{12}]\cdot 2\text{CH}_3\text{COOH}\cdot 4\text{H}_2\text{O}$ was based on the original method of Lis [9]. The Mn_{12} 2-Cl benzoate $[\text{Mn}_{12}(\text{2ClPhCOO})_{16}(\text{H}_2\text{O})_4\text{O}_{12}]\cdot \text{CH}_2\text{Cl}_2\cdot 5\text{H}_2\text{O}$, hereafter abbreviated to Mn_{12}Cl , was prepared following the method described in Ref. [10]. X-ray diffraction patterns of powders of both materials show peaks corresponding to the crystal structures described in the literature [9,10]. In order to avoid uncertainties concerning the orientation of the crystals, we measured powdered samples embedded in a two-component glue.

The nonlinear susceptibility is usually obtained (see, e.g., Ref. [11]) from the third harmonic of the response to an ac magnetic field $\sim \Delta h e^{i\omega t}$. Alternatively [12], one can consider the first-harmonic response $\chi(\omega)$ but in the presence of weak superimposed dc fields H , from which one can get a quantity that possesses similar dependences on the relevant parameters (frequency, damping, etc.). Specifically, the (first) nonlinear susceptibility χ_3 was obtained by fitting the real and imaginary components of the field-dependent ac susceptibility to a polynomial [13]

$$\chi(\omega, H) = \chi_1(\omega) + 3\chi_3(\omega)H^2 + 5\chi_5(\omega)H^4 + \dots, \quad (1)$$

where χ_1 is the custom linear susceptibility. The “expansion coefficients” χ_1, χ_3, \dots are H independent and the factors 1, 3, 5, ... arise when raising to n in $\chi_n(H + \Delta h)^n$ and retaining terms linear in Δh . Below, we will show

that the classical χ_3 obtained in the above way is equivalent to the third-harmonic susceptibility.

All magnetic measurements were performed using a commercial SQUID magnetometer. Measurements were performed in a broad range of temperatures $1.8 < T < 60$ K and frequencies $0.025 \text{ Hz} < \omega/2\pi < 1.5 \text{ kHz}$. We took special care to ensure that the amplitude of the ac field ($\Delta h = 4.5$ Oe) was sufficiently small not to induce any additional nonlinearity (i.e., χ_1, χ_3, \dots are independent of Δh). Previous results on $\chi(\omega, H)$ [14] contain the dependences of the linear and nonlinear susceptibilities mixed, whereas the above method enables one to separate and analyze the genuine nonlinear contributions. An example of its application is shown in Fig. 1.

Linear ac susceptibility data measured as a function of ω at zero field are shown in Fig. 2. The results are well described by a Debye law

$$\chi = \chi_s + \frac{\chi_T - \chi_s}{1 + i\omega\tau}, \quad (2)$$

where χ_T and χ_s are the isothermal (equilibrium) and adiabatic limits of χ_1 . The samples have therefore well-defined relaxation times τ , which follow an Arrhenius law $\tau = \tau_0 \exp(U/k_B T)$. The activation energy U is the same for both compounds (same slopes in the inset in Fig. 2); i.e., tunneling takes place via the same excited levels, corresponding approximately to the tunnel-split $m = \pm 4$ states. In contrast, the preexponential factor τ_0 of Mn_{12}Cl is a factor of 2 shorter than τ_0 of Mn_{12} acetate. τ_0 is related to the lifetime of excited states, which decay by emitting phonons to the lattice. Therefore, the spin-

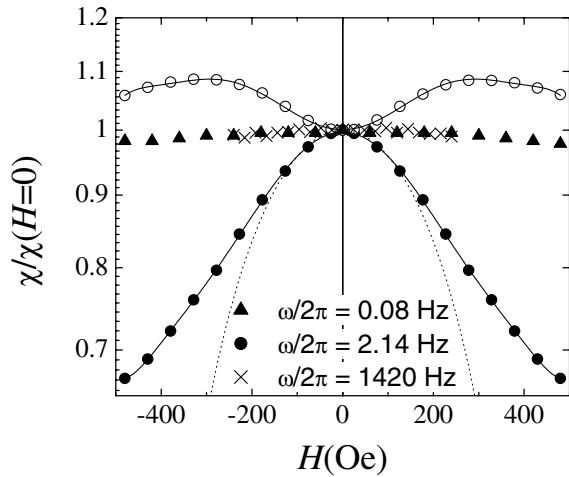


FIG. 1. Dynamical susceptibility of Mn_{12}Cl , normalized by its zero-field value, measured at $T = 4.5$ K as a function of the dc magnetic field. Solid symbols, real part; open symbols, imaginary part. The frequencies used correspond to $\omega\tau = 0.015, 0.4$, and 265 . The solid lines represent polynomial fits (of order 8) from which the nonlinear susceptibility is obtained [see Eq. (1)]. The dotted line is the parabolic term $\chi_1 + 3\chi_3 H^2$ that dominates the low-field behavior.

lattice interaction, or damping, appears to be stronger for Mn_{12}Cl , in agreement with previous results [15]. This shows that these two materials are suited to study how a magnetic cluster behaves in different environments.

Before presenting the results for the nonlinear susceptibility for these systems, let us consider the theoretical behavior of this quantity in the classical limit. We have calculated χ_3 from the exact (continued-fraction) solution of the corresponding Fokker–Planck equation [8,16]. To mimic the experiments: (i) the calculation is done for spins with randomly distributed anisotropy axes, and (ii) the first harmonic of the response is computed in weak dc fields, and the quadratic coefficient extracted [see Eq. (1)]. The results are displayed in Fig. 3 for various values of the Landau–Lifshitz damping parameter λ . It is seen that the ω dependence of the so-obtained χ_3 , as well as its damping sensitivity, are qualitatively similar to those of the third-harmonic χ_3 studied in Ref. [8]. In the classical case λ determines the time available for the spin to precess around the anisotropy axis before decaying to the bottom of the potential wells.

The experimental χ_3 data of both compounds are also shown in Fig. 3 (lower panel). They agree, when $\omega\tau \ll 1$ (sufficiently high temperatures or low frequencies), with the expected equilibrium behavior $\chi_{3T} \propto 1/T^3$. When $\omega\tau \approx 1$, χ_3 becomes strongly dependent on ω . It exhibits a large maximum $\chi'_3 \approx 60\chi_{3T}$ near $\omega\tau = 1$, which depends weakly on the damping (i.e., on τ_0). However, even more striking is the fact that the experimental and classically calculated peaks of $\chi_3(\omega)$ have opposite signs.

We next try to explain the origin of this large and (classically) unexpected nonlinear response. We observe that Eq. (2) also describes the susceptibility of Mn_{12} in moderate fields. Therefore, χ_3 can be estimated by

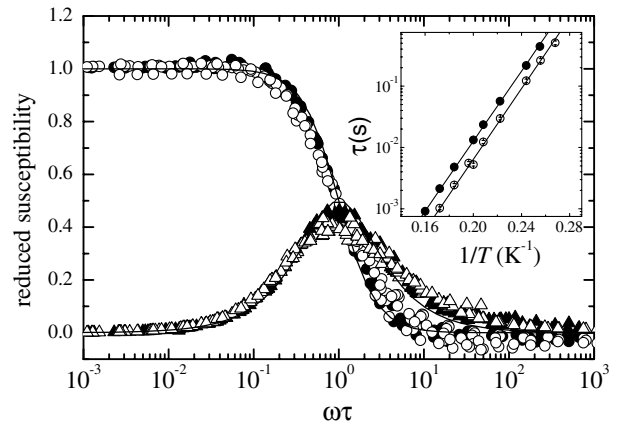


FIG. 2. Real (circles) and imaginary (triangles) parts of the reduced linear susceptibility $(\chi_1 - \chi_s)/(\chi_T - \chi_s)$, measured between $T = 3.7$ and 6.6 K in the frequency range $2.5 \times 10^{-2} < \omega/2\pi < 1.5 \times 10^3$ Hz. The lines are calculated using Debye law [Eq. (2)]. The inset shows the temperature dependence of the relaxation time τ . Solid and open symbols correspond to Mn_{12} acetate and Mn_{12}Cl , respectively.

differentiating Debye's expression with respect to H , getting

$$\chi_3 \sim \frac{\chi_{3T}}{1 + i\omega\tau} - \frac{i\omega\chi_T}{6(1 + i\omega\tau)^2} \frac{\partial^2 \tau}{\partial H^2} \bigg|_0, \quad (3)$$

where the subscript indicates evaluation at $H = 0$. The second, dominant, term is directly related to the field derivative of the relaxation time. For a classical spin, the main contribution comes from the derivative with respect to the component of the field that is perpendicular to the anisotropy axis [8]. The effect of the longitudinal field H_z is expected to be small. The reason is that, classically, the energy scale over which τ changes is determined by the very large anisotropy field $H_K \approx 10^5$ Oe. Note also that, classically, $\partial^2 \tau / \partial H^2|_0 < 0$ (see the inset in Fig. 3).

For a molecular cluster, however, the magnetization reversal takes place by quantum tunneling. As in a two-

level problem, the probability of tunneling is determined by the ratio between the tunnel splitting Δ and the bias ξ generated by H_z . For states with $m = \pm 4$ of Mn_{12} we have $\Delta \sim 10^{-1}$ K. As a result, τ increases sharply between $H_z = 0$ and a few hundred oersteds ($\ll H_K$), as the inset in Fig. 3 shows [7]. The large "positive" contribution to χ_3 that we observe near $\omega\tau = 1$ can therefore be associated to the strong dependence of the tunneling probability on H_z , which renders $\partial^2 \tau / \partial H^2|_0 > 0$.

In Fig. 3, the experimental data are also compared with theoretical calculations that take into account the quantum nature of the molecular spins [17,18]. The relaxation time and susceptibility are calculated by solving a standard Pauli master equation, which includes transition rates between energy eigenstates induced by the interaction with the phonon bath. Emulating the experimental conditions, we have computed χ' and χ'' for different applied fields $|H| > 50$ Oe and fitted them to Eq. (1). Despite the fact that the calculation does not take into account the precession of the spins, which produces the main classical contribution, it accounts remarkably well for the experimental results, including the change of sign with respect to the classical prediction.

Before concluding, let us briefly consider the limit of large dc fields. Then the relaxation time approaches its classical limit, because the field blocks tunneling via all levels lying in energy below the classical anisotropy barrier. In order to check how this change of the relaxation process modifies the nonlinear response, we have extracted, using the same method described above, χ_3 from experimental data measured at $|H| > 1.5 \times 10^3$ Oe. The results, plotted in Fig. 4, resemble indeed the predictions for classical spins. In particular, the inequality $|\chi'_3| \leq |\chi_{3T}|$ is fulfilled in the whole frequency range.

Interestingly, these high-field results agree well with calculations for overdamped classical spins ($\lambda \gtrsim 1$ in the upper panel in Fig. 3). This is at first surprising, since

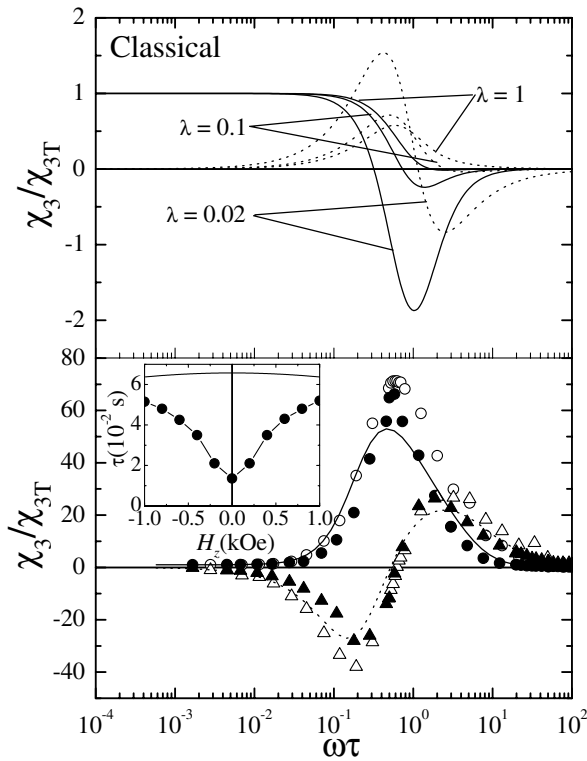


FIG. 3. Upper panel: nonlinear susceptibility of classical spins, calculated by the method of Ref. [8], at $k_B T/U = 5/70$ for three damping coefficients λ . Solid lines, real part; dotted lines, imaginary part. Lower panel: nonlinear susceptibility of Mn_{12} acetate (solid symbols) and Mn_{12}Cl (open symbols) measured at $T = 5$ K. Dots and triangles represent the real and imaginary parts. We have multiplied ω by the zero field $\tau = 1.31 \times 10^{-2}$ s and 5.55×10^{-3} s, for Mn_{12} acetate and Mn_{12}Cl , respectively. The lines are quantum calculations performed as in Ref. [17]: solid line, real part; dotted line, imaginary part. The inset shows the relaxation time of a single crystal of Mn_{12} acetate measured with the field applied along the anisotropy axis (●) and the classical result (solid line).

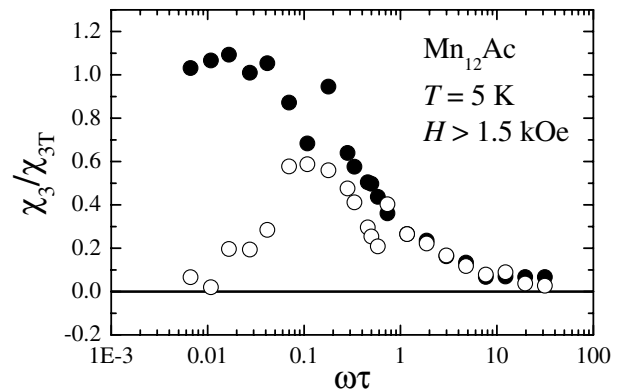


FIG. 4. Real (●) and imaginary (○) nonlinear susceptibilities of Mn_{12} acetate obtained as described in the text [see Eq. (1)], from susceptibility data measured for $|H| \geq 1.5 \times 10^3$ Oe.

classically $\lambda \approx 2\pi/\omega_L\tau_0$, where $\omega_L = g\mu_B H_K/\hbar$ is the Larmor frequency. For Mn_{12} clusters, $2\pi/\omega_L \sim 4 \times 10^{-12}$ s while $\tau_0 \approx 1.3 \times 10^{-8}$ s and 2.7×10^{-8} s for Mn_{12}Cl and Mn_{12} acetate, respectively. This gives $\lambda \sim 10^{-4}$. For such a low damping the classical contribution is expected to dominate over the quantum one, whereas clearly the opposite is observed.

We argue, however, that the situation might become different if the spins relax via quantum tunneling. Their precession around the anisotropy axis, as well as any other coherent dynamics, are then limited not by the decay towards lower lying energy states but rather by the tunneling time $\tau_{\text{tun}} = \hbar/\Delta$ [17]. For times longer than τ_{tun} the system evolves towards an incoherent mixture of delocalized (i.e., with $\langle S_z \rangle \sim 0$) energy eigenstates. Near the top of the energy barrier (i.e., $|m| \leq 4$), we have $\tau_{\text{tun}} \leq 5 \times 10^{-11}$ s. Replacing τ_{tun} for τ_0 in the above λ gives $\lambda \sim 0.1$, approximately equal for both compounds. Under these conditions, χ_3 is expected to depend weakly on the spin-lattice interaction, which agrees with the observed features. In addition, our results show that coherence is lost for times much shorter than τ_0 .

In summary, we have investigated experimentally the nonlinear dynamical susceptibility of molecular nanomagnets and performed theoretical calculations at both the classical and quantum levels of description. We have found that Mn_{12} single-molecule magnets show a large quantum nonlinear magnetic response, which can be directly linked to the tunneling mechanism by which their spins flip and whose sign is opposite to the classical predictions. This phenomenon should not be restricted to Mn_{12} , but it could be observable as well for other mesoscopic magnetic systems (e.g., other magnetic clusters and nanoparticles). The nonlinear magnetic susceptibility therefore offers a privileged probe to ascertain if tunneling plays a role in these mesoscopic materials, for which standard (in particular, linear) relaxation experiments do not always provide a definite answer [20].

The authors benefited from enlightening discussions with J. F. Fernández and P. Svedlindh. This work has been funded by Grants No. MAT02-0166 and No. BFM2002-00113 from the Spanish Ministerio de Ciencia y Tecnología. V.G. acknowledges a grant from Consejo Superior de Investigaciones Científicas.

-
- [1] A. J. Leggett, *J. Phys. Condens. Matter* **14**, R415 (2002).
[2] W. H. Zurek, *Phys. Today* **44**, No. 10, 36 (1991).

- [3] N. V. Prokof'ev and P. C. E. Stamp, *J. Low Temp. Phys.* **104**, 143 (1996).
[4] A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fisher, A. Garg, and W. Zwerger, *Rev. Mod. Phys.* **59**, 1 (1987).
[5] D. Gatteschi, A. Caneschi, L. Pardi, and R. Sessoli, *Science* **265**, 1054 (1994).
[6] R. Sessoli, D. Gatteschi, A. Caneschi, and M. A. Novak, *Nature (London)* **365**, 141 (1993).
[7] J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, *Phys. Rev. Lett.* **76**, 3830 (1996); J. M. Hernández, X. X. Zhang, F. Luis, J. Bartolomé, J. Tejada, and R. Ziolo, *Europhys. Lett.* **35**, 301 (1996); L. Thomas, F. Lioni, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, *Nature (London)* **383**, 145 (1996).
[8] J. L. García-Palacios and P. Svedlindh, *Phys. Rev. Lett.* **85**, 3724 (2000); J. L. García-Palacios and D. A. Garanin, *Phys. Rev. B* (unpublished).
[9] T. Lis, *Acta Crystallogr. Sect. B* **36**, 2042 (1980).
[10] D. Ruiz, Z. M. Sun, B. Albela, K. Folting, J. Ribas, G. Christou, and D. N. Hendrickson, *Angew. Chem., Int. Ed. Engl.* **37**, 300 (1998).
[11] T. Bitoh, K. Ohba, M. Takamatsu, T. Shirane, and S. Chikazawa, *J. Phys. Soc. Jpn.* **62**, 2583 (1993).
[12] See, e.g., W. Wu, D. Bitko, T. F. Rosenbaum, and G. Aeppli, *Phys. Rev. Lett.* **71**, 1919 (1993); P. Schiffer *et al.*, *ibid.* **74**, 2379 (1995); T. Jonsson, P. Svedlindh, and M. F. Hansen, *ibid.* **81**, 3976 (1998).
[13] The fit was done using polynomials of increasing order until convergence of χ_3 was observed. The results agree with those obtained by fitting only the susceptibility in the low field region (parabolic dependence; see Fig. 1).
[14] See, e.g., Hernández *et al.* (Ref. [7]).
[15] F. Luis, J. M. Hernández, J. Bartolomé, and J. Tejada, *Nanotechnology* **10**, 86 (1999).
[16] Yu. P. Kalmykov and W. T. Coffey, *Phys. Rev. B* **56**, 3325 (1997).
[17] F. Luis, J. Bartolomé, and J. F. Fernández, *Phys. Rev. B* **57**, 505 (1998); F. Luis, F. Mettes, and L. J. de Jongh, in *Magnetoscience—From Molecules to Materials*, edited by J. S. Miller and M. Drillon (Wiley-VCH, Weinheim, 2002), Vol. III, p. 169.
[18] The field-dependent ac susceptibility was calculated as described in Ref. [17] averaging over a random orientation of easy axes and over a Gaussian distribution of bias dipolar fields. Its width $\sigma = 190$ Oe was estimated from $2g\mu_B S\sigma = k_B T_c$, where $T_c \sim 0.5$ K is the ordering temperature extracted from Monte Carlo simulations [19].
[19] J. F. Fernández and J. J. Alonso, *Phys. Rev. B* **62**, 53 (2000).
[20] See, e.g., H. Mamiya, I. Nakatani, and T. Furubayashi, *Phys. Rev. Lett.* **88**, 067202 (2002), and references therein.