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Classical and quantum magnetisation reversal studied in single nanometer-sized particles and clusters using micro-SQUIDs

W. Wernsdorfer[a,*], E. Bonet Orozco[a], B. Barbara[a], A. Benoit[b], D. Mailly[c]

[a]Lab. L. Néel-CNRS, BP166, 38042 Grenoble, France
[b]CRTBT-CNRS, BP166, 38042 Grenoble, France
[c]LMM-CNRS, 196 av. H. Ravera, 92220 Bagneux, France

Abstract

Recent progress in experiment on quantum tunnelling of the magnetic moment in mesoscopic systems will be reviewed. The emphasis will be made on measurements of individual nanoparticles. These nanomagnets allow one to test the border between classical and quantum behaviour. Using the micro-SQUID magnetometer, waiting time, switching field and telegraph noise measurements show unambiguously that the magnetisation reversal of small enough single-crystalline nanoparticles is described by a model of thermal activation over a single-energy barrier. Results on insulating BaFeO nanoparticles show strong deviations from this model below 0.4 K which agree with the theory of macroscopic quantum tunnelling in the low dissipation regime. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Macroscopic quantum tunnelling (MQT) represents one of the most fascinating phenomena in condensed matter physics. MQT means the tunnelling of a macroscopic variable through a barrier characterized by an effective potential of a macroscopic system. Today, macroscopic systems showing amazing agreements with theoretical predictions are Josephson–Junctions and SQUIDs. Here, quantum tunnelling between two macroscopically distinct current states has been observed. After a slow evolution during the last ten years, MQT in magnetism now constitutes a new and very interesting field of research. It has been predicted that MQT can be observed in magnetic systems with low dissipation. In this case, it is the tunnelling of the magnetisation vector of a single-domain particle through its anisotropy energy barrier or the tunnelling of a domain wall through its pinning energy. These phenomena have been studied theoretically and experimentally [1].

This brief review focuses on MQT studied in individual nanoparticles or nanowires where the complications due to distributions of particle size, shape, etc. are avoided. The experimental evidence of MQT in a single-domain particle or in assemblies of particles is still a controversial subject. Therefore, we pay most attention to the necessary experimental conditions for MQT and review some experimental results. We start by reviewing some important predictions concerning MQT in a single-domain particle.

2. Magnetisation reversal by quantum tunnelling

On the theoretical side, it was shown that in small magnetic particles, a macroscopically large number of spins coupled by strong exchange interaction, can tunnel through the energy barrier created by magnetic anisotropy. It has been proposed that there is a characteristic

* Correspondence address. LLN-CNRS, BP166, 38042 Grenoble, France. Fax: + 33-476-88-11-91.

E-mail address: wernsdor@labs.polycnrs-gre.fr (W. Wernsdorfer)

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crossover temperature T_c below which the escape of the magnetisation from a metastable state is dominated by quantum barrier transitions, rather than by thermal over barrier activation. Above T_c the escape rate is given by thermal over barrier activation.

In order to compare experiments with theories, predictions of the crossover temperature T_c and the escape rate Γ_{QT} in the quantum regime are relevant. Both variables should be expressed as a function of parameters which can be changed experimentally. Typical parameters are the number of spins S, effective anisotropy constants, applied field strength and direction, etc. Many theoretical papers have been published during the last few years [1]. We discuss here a result specially adapted for single-particle measurements which concerns the field dependence of the crossover temperature T_c.

The crossover temperature T_c can be defined as the temperature where the quantum switching rate equals the thermal one. The case of a magnetic particle, as a function of the applied field direction, was considered by several authors [2–4]. We have chosen the result for a particle with biaxial anisotropy as the effective anisotropy of most particles can be approximately described by a strong uniaxial and a weak transverse anisotropy. The result of Kim can be written in the following form [4]:

$$T_c(\theta) \sim \mu_0 H_{\|}\varepsilon^{1/4}|\cos\theta|^{1/6}(1+|\cos\theta|^{2/3})^{-1} \times\sqrt{1+a(1+|\cos\theta|^{2/3})}, \quad (1)$$

where $\mu_0 H_{\|}$ and $\mu_0 H_{\perp}$ are the parallel and transverse anisotropy field given in Tesla, θ is the angle between the easy axis of magnetisation and the direction of the applied field, and $\varepsilon = (1 - H/H^0_{sw})$. H^0_{sw} is the classical switching field at zero temperature [5]. Eq. (1) is valid for any ratio $a = H_{\perp}/H_{\|}$. The proportionality coefficient of Eq. (1) is of the order of unity (T_c is in units of Kelvin) and depends on the approach of the calculation [4]. Eq. (1) is plotted in Fig. 1 for several values of the ratio a. It is valid in the range $\sqrt{\varepsilon} < \theta < \pi/2 - \sqrt{\varepsilon}$.

The most interesting feature which may be drawn from Eq. (1) is that the crossover temperature is tuneable using the external field strength and direction (Fig. 1) because the tunnelling probability is increased by the transverse component of the applied field. At high transverse fields, T_c decreases again, though, due to a broadening of the anisotropy barrier. Therefore, quantum tunnelling experiments should always include studies of angular dependencies. When the effective magnetic anisotropy of the particle is known, MQT theories give clear predictions with no fitting parameters.

MQT should also be studied as a function of the effective magnetic anisotropy. In practice, it is well known for single-particle measurements that each particle is in reality somewhat different. Therefore, the effective magnetic anisotropy has to be determined for each individual particle.

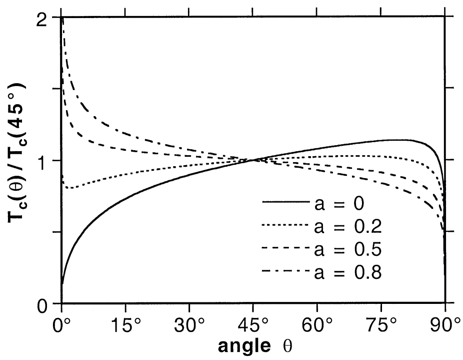

Fig. 1. Normalised crossover temperature T_c as given by Eq. (1), and for several values of the ratio $a = H_{\perp}/H_{\|}$.

In general, T_c does not depend directly on the particle volume because T_c is proportional to the barrier and inversely proportional to the total spin of the particle. However, there is a slight volume dependence arising from the ε-dependence. As experiments are always limited by a certain time window and as the tunnelling rate is exponentially dependent on the particle volume, higher applied field values are required for larger particles to see the tunnelling in the given experimental time window, i.e. ε is small for larger particles. Moreover, the magnetisation reversal of larger particles becomes slightly incoherent, destroying MQT effects. Therefore, the volume dependence (i.e. ε-dependence) of MQT should be studied in the particle size range where magnetisation reversal by uniform rotation exists.

Finally, it is important to note that most of the MQT theories neglect damping mechanisms. We discussed the case of ohmic damping in Ref. [6] which is the simplest form of damping. More complicated damping mechanisms are not excluded and might play an important role. We expect more theoretical work on this in the future.

3. Brief review of magnetisation measurements of individual single-domain nanoparticles and wires at very low temperatures

In order to avoid the complications due to distributions of particle size, shape, etc., some groups tried to study the thermal and field dependence of magnetisation reversal of individual magnetic particles or wires. Most of the recent studies were done by using Magnetic Force Microscopy at room temperature. Low-temperature investigations were mainly performed via resistance measurements.

The first magnetisation measurements of individual single-domain nanoparticles at low temperature (0.1–6 K) were presented by Wernsdorfer et al. [7–9]. The detector (a Nb micro-bridge-DC-SQUID) and the particles studied (ellipses with axes between 50 and 1000 nm and thickness between 5 and 50 nm) were fabricated using electron beam lithography. Electrodeposited wires (with diameters ranging from 40 to 100 nm and lengths up to 5000 nm) were also studied [10,11]. Waiting time and switching field measurements showed that the magnetisation reversal of these particles and wires results from a single thermally activated domain wall nucleation, followed by a fast wall propagation reversing the particle's magnetisation. For nanocrystalline Co particles of about 50 nm and below 1 K, a flattening of the temperature dependence of the mean switching field was observed which could not be explained by thermal activation. These results were discussed in the context of MQT of magnetisation. However, the width of the switching field distribution and the probability of switching are in disagreement with such a model because nucleation is very sensitive to factors such as surface defects, surface oxidation and perhaps nuclear spins. The fine structure of pre-reversal magnetisation states is then governed by a multivalley energy landscape (in a few cases distinct magnetisation reversal paths were effectively observed [7–9] and the dynamics of reversal occurs via a complex path in configuration space.

Coppinger et al. [12] used telegraph noise spectroscopy to investigate the two-level fluctuations (TLF) observed in the conductance of a sample containing self-organising ErAs quantum wires and dots in a semi-insulating GaAs matrix. They showed that the TLF could be related to two possible magnetic states of a ErAs cluster and that the energy difference between the two states was a linear function of the magnetic field. They deduced that the ErAs cluster should contain a few tens of Er atoms. At temperatures between 0.35 K and 1 K, the associated switching rate of the TLF were thermally activated, however below 350 mK the switching rate became temperature independent. Tunnelling of the magnetisation was proposed in order to explain the observed behaviour.

Some open questions remain: What is the object which is really probed by TLF? If this is a single ErAs particle, as assumed by the authors, the switching probability should be an exponential function of time. The pre-exponential factor τ_0^{-1} (sometimes called attempt frequency) was found to lie between 10^3 and 10^6 s^{-1} whereas expected values are between 10^9 and 10^{12} s^{-1}. Why must one apply fields of about 2 T in order to measure two-level fluctuations which should be expected near zero field? What is the influence of the measurement technique on the sample?

By measuring the electrical resistance of isolated Ni wires with diameters between 20 and 40 nm, Hong and Giordano studied the motion of magnetic domain walls [13,14]. Because of surface roughness and oxidation, the domain walls of a single wire are trapped at pinning centres. The pinning barrier decreases with an increase in the magnetic field. When the barrier is sufficiently small, thermally activated escape of the wall occurs. This is a stochastic process which can be characterised by a switching (depinning) field distribution. A flattening of the temperature dependence of the mean switching field and a saturation of the width of the switching field distribution (rms deviation σ) were observed below about 5 K. The authors proposed that a domain wall escapes from its pinning sites by thermal activation at high temperatures and by quantum tunnelling below $T_c \sim 5$ K.

These measurements pose several questions: What is the origin of the pinning center which may be related to surface roughness, impurities, oxidation, etc.? The sweeping rate dependence of the depinning field, as well as the depinning probability, could not be measured even in the thermally activated regime. Therefore, it was not possible to check the validity of the Neél–Brown model [15,16] or to compare measured and predicted rms deviations σ. Finally, a crossover temperature T_c of about 5 K is three orders of magnitude higher than T_c predicted by current theories.

Later, Wernsdorfer et al. published results obtained on nanoparticles synthesised by arc discharge, with dimensions between 10 and 30 nm [17]. These particles were single crystalline, and the surface roughness was about two atomic layers. Their measurements showed for the first time that the magnetisation reversal of a ferromagnetic nanoparticle of good quality can be described by thermal activation over a single-energy barrier as proposed by Neél and Brown [15,16]. The activation volume, which is the volume of magnetisation overcoming the barrier, was very close to the particle volume, predicted for magnetisation reversal by uniform rotation. No quantum effects were found down to 0.2 K. This was not surprising because the predicted crossove r temperature is $T_c \sim 20$ mK. The results of Wernsdorfer et al. constitute the preconditions for the experimental observation of MQT of magnetisation on a single particle.

Just as the results obtained with Co nanoparticles [17], a quantitative agreement with the Neél–Brown model of magnetisation reversal was found on BaFeO nanoparticles [18]. However, strong deviations from this model were evidenced for the smallest particles containing about $10^5\mu_B$ and for temperatures below 0.4 K. These deviations are in good agreement with the theory of macroscopic quantum tunnelling of magnetisation. The main results are reviewed in the following section.

Other low temperature techniques which are adapted to single-particle measurements are Hall probe magnetometry [19], magnetometry based on the giant magnetoresistance or spin-dependent tunnelling with Coulomb blockade [20].

4. Example: magnetisation reversal by thermal activation and quantum tunnelling in BaFeCoTiO nanoparticles

This section presents a brief discussion of individual particle measurements suggesting quantum effects at low temperature. In order to confirm the single-domain character of the particles, the magnetisation reversal as a function of the applied field direction were studied for each particle. For Co and BaFeCoTiO nanoparticles with diameters between 10 and 30 nm, it was found that the angular dependence of the switching field H^0_{sw} agrees well with the model of Stoner and Wohlfarth [5] taking into account mainly second and small fourth-order anisotropy terms. The effective magnetocrystalline anisotropy field (the main second-order anisotropy term), found by these measurements for particles with a $Co_{0.8}Ti_{0.8}$ substitution, is about 0.4 T. A detailed discussion of the angular dependence of H^0_{sw} is presented in Refs. [21,22].

The influence of temperature and time on the statistics of the magnetisation reversal was studied by waiting time and switching field experiments. Both types of measurements were studied as a function of the applied field direction. Except in some special cases at very low temperatures, these measurements were in complete agreement with the Neél–Brown theory [15,16]: (i) exponential probabilities of not-switching with mean waiting times following an Arrhenius law; (ii) mean switching fields and widths of the switching field distribution following the model of Kurkijärvi [23,24], which is based on the Néel–Brown theory.

This agreement could be confirmed by studying the angular dependence of the anisotropy barrier $E_0(\theta)$ following roughly the prediction of the Stoner and Wohlfarth [5]. The number of spins S in the nanoparticle can be estimated by $S \sim E_0/(2\mu_B\mu_0 H^0_{sw})$. We found values of $S \sim 10^6$ to 10^5 depending on the particles size. Finally, the angular dependence of τ_0 followed well the prediction of Coffey et al. [25–27]. The phenomenological damping constant α from Gilbert's equation could be found: $\alpha \sim 10^{-1}$ in the case of Co and $\alpha \sim 10^{-2}$ in the case of BaFeCoTiO [6]. Such values are expected for metallic and insulating particles, respectively.

Below 0.4 K, several of the smallest particles showed strong deviations from the Neél–Brown model. These deviations were a saturation of the thermal dependence of H_{sw} and σ, and a faster field sweeping rate dependence of H_{sw} than given by the Neél–Brown model. In order to investigate the possibility that these low-temperature deviations are due to an escape from the metastable potential by MQT, a common method is to replace the real temperature T by an effective temperature $T^*(T)$ in order to restore the scaling plot. In the case of MQT, $T^*(T)$ should saturate at low temperatures. Indeed, the ansatz of $T^*(T)$, can restore unequivocally the scaling plot demonstrated by a straight master curve. The flattening of T^* corresponds to a saturation of the escape rate Γ which is a necessary signature of MQT. As measurements at zero temperature are impossible, the effective temperature at the lowest measuring temperature can be investigated and one can define the crossover temperature between thermally activated and the quantum regime by $T_c = T^*$ at lowest measuring temperature.

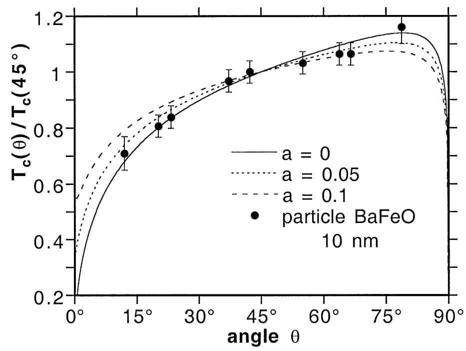

Fig. 2. Angular dependence of the crossover temperature T_c for BaFeCoTiO particle. The lines are given by Eq. (1) for different values of the ratio $a = H_\perp/H_{||}$. The experimental data are normalised by $T_c(45°) = 0.31$ K.

The measured angular dependence of $T_c(\theta)$ is in excellent agreement with the prediction given by Eq. (1) (Fig. 2). The normalisation value $T_c(45°) = 0.31$ K compares well with the theoretical value of about 0.2 K. This quantitative agreement of the crossover temperature versus an external parameter suggest MQT in these BaFeCoTiO particles.

Measurements on other particles with anisotropies between $H_a = 0.3$ and 1 T showed that $T_c(\theta)$ is about proportional to H_a. Furthermore, for a given anisotropy field H_a, $T_c(\theta)$ decreased for bigger particles which is also in agreement with Eq. (1) as $T_c(\theta)$ is in proportion to $\varepsilon^{1/4}$ (for a larger particle, ε must be smaller in order to measure a magnetisation switching in the same time window, which is fixed by the field sweeping rate). Finally, the width of the switching field distribution should be constant in the quantum regime which was also verified.

The test of the validity for $\theta \to 0°$ and $\theta \to 90°$ would be interesting. However, the limit $\theta \to 90°$ is experimentally very difficult as the measurable signal at the magnetisation reversal becomes smaller and smaller for $\theta \to 90°$. Furthermore, by using the micro-SQUID technique, one can only sweep the applied magnetic field in the plane of the SQUID, i.e. in order to measure in the limit of $\theta \to 0°$, the easy axis of magnetisation needs to be in the plane of the SQUID which has not yet been achieved for a small particle.

In the case of 20 nm Co particles, no clear quantum effects were found down to 0.2 K. This was not surprising for two reasons: (i) the calculated crossover temperature for such a particle is smaller than 0.2 K and (ii) the dissipation effects due to conduction electrons may strongly reduce quantum effects which should not be the case in insulating BaFeCoTiO particles having a very small damping factor [6].

Although the above measurements are in good agreement with MQT theory, we should not forget that the MQT is based on several strong assumptions. Among them, there is the assumption of a giant spin, i.e. all magnetic moments in the particle are rigidly coupled together by strong exchange interaction. This approximation might be good in the temperature range where thermal activation is dominant but is it not yet clear if this approximation can be made for very low-energy barriers. Future measurements will tell us the answer.

The proof for MQT in a magnetic nanoparticle could be the observation of level quantisation of its collective spin state which was recently evidenced in molecular Mn_{12} and Fe_8 clusters having a collective spin state $S = 10$. Also the quantum spin phase or Berry phase associated with the magnetic spin $S = 10$ of a Fe_8 molecular cluster was evidenced [28,29]. In the case of BaFeCoTiO particles with $S = 10^5$, the field separation associated with the level quantisation is rather small: $\Delta H = H_a/2S \sim 0.002$ mT. Future measurements should focus on the level quantisation of collective spin states of $S = 10^2$–10^4 and their quantum spin phases.

References

[1] L. Gunther, B. Barbara (Eds.), Quantum Tunneling of Magnetization – QTM'94, NATO ASI, Serie E: Applied Sciences, Vol. 301, 1995.
[2] O.B. Zaslavskii, Phys. Rev. B 42 (1990) 992.
[3] M.C. Miguel, E.M. Chudnovsky, Phys. Rev. B 54 (1996) 388.
[4] Gwang-Hee Kim, Dae Sung Hwang, Phys. Rev. B 55 (1997) 8918.
[5] E.C. Stoner, E.P. Wohlfarth, Philos. Trans. London Ser. A 240 (1958) 599. Reprinted in IEEE Trans. Magn. MAG-27 (1991) 3475.
[6] W.T. Coffey et al., Phys. Rev. Lett. 80 (1998) 5655.
[7] W. Wernsdorfer et al., J. Magn. Magn. Matter. 145 (1995) 33.
[8] W. Wernsdorfer et al., J. Magn. Magn. Matter. 151 (1995) 38.
[9] W. Wernsdorfer et al., Phys. Rev. B 53 (1996) 3341.
[10] W. Wernsdorfer et al., Phys. Rev. Lett. 77 (1996) 1873.
[11] W. Wernsdorfer et al., Phys. Rev. B 55 (1997) 11 552.
[12] F. Coppinger et al., Phys. Rev. Lett. 75 (1995) 3513.
[13] K. Hong, N. Giordano, J. Mag. Mag. Matter. 151 (1995) 396.
[14] K. Hong, Europhys. Lett. 36 (1996) 147.
[15] L. Néel, Ann. Geophys. 5 (1949) 99.
[16] L. Néel, C.R. Acad, Sci. Paris 228 (1949) 664.
[17] W. Wernsdorfer et al., Phys. Rev. Lett. 78 (1997) 1791.
[18] W. Wernsdorfer et al., Phys. Rev. Lett. 79 (1997) 4014.
[19] J.G.S. Lok et al., Phys. Rev. B 58 (1998) 12 201.
[20] S. Guéron, M.M. Deshmukh, E.B. Myers, D.C. Ralph, Phys. Rev. Lett. 83 (1999) 4148.
[21] E. Bonet Orozco et al., Phys. Rev. Lett. 83 (1999) 4188.
[22] E. Bonet Orozco, Ph.D. Thesis, Joseph Fourier University, Grenoble, 1999.
[23] J. Kurkijärvi, Phys. Rev. B 6 (1972) 832.
[24] A. Garg, Phys. Rev. B 51 (1995) 15 592.
[25] W.T. Coffey et al., Phys. Rev. B 52 (1995) 15 951.
[26] L.J. Geoghegan, W.T. Coffey, B. Mulligan, Adv. Chem. Phys. 100 (1997) 475.
[27] W.T. Coffey, Adv. Chem. Phys. 103 (1998) 259.
[28] W. Wernsdorfer, R. Sessoli, Science 284 (1999) 133.
[29] W. Wernsdorfer et al., in these proceedings (LT-22), Physica B (2000).