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THERMAL RELAXATION AND QUANTUM TUNNELLING OF THE MAGNETIZATION IN Mn_{12}-ACETATE

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Dedicated to Professor Boran Leontić on the occasion of his 70$^{\mathbf{th}}$ birthday

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The dependence of the magnetic moment m on the temperature T and the magnetic field H in a synthesized molecular magnet Mn_{12}-acetate has been measured using a SQUID magnetometer. The splitting of zero-field cooled (ZFC) and field-cooled (FC) $m(T)$ curves below the so-called blocking temperature $T_{\rm B}$ (≈ 3.6 K at $H = 0$) was observed. By measuring the time relaxation of m, it was found that it tended to the same value with the same relaxation time (≈ 560 s at 3 K) for both ZFC and FC processes. This indicates spin freezing below $T_{\rm B}$ and the single molecule process in the explored temperature range (2 K $< T <$ 4 K). The dependence of $T_{\rm B}$ on applied H was also investigated. The decreasing of $T_{\rm B}$ with increasing H can be explained in the frame of barrier reduction in the applied field.

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1. Introduction

By decreasing the size of particles, one hopes to test the basic laws of quantum physics, especially in magnetism. The problem with the small signal coming from the single tiny particle, scarcely measurable using standard techniques, forces us

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to use many particles to amplify the signal by the common behaviour in all of them [1]. However, it is very hard to produce a large number of precisely equal particles. Instead, there is a distribution, so the different contributions to the total magnetization of the sample from different particles result in an average over sizes and shapes [2]. Therefore, the quantum effects are obscured by the averaging, so that the system of many particles is not very convenient for investigation of the typical quantum processes.

On the other hand, there are systems composed of regularly arranged identical units. A molecular magnet was synthesized in 1980 [3] having the chemical formula $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$, known as Mn_{12}-ac (acetate), with a tetragonal crystal structure. In this system the Mn_{12}-ac units of ground-state spin $S = 10$ all point in the same direction. This leads to a fairly high anisotropy [4] and magnetic bistability [5]. The spin 10 is not too large, making the quantization of its projection observable on macroscopic level. Nevertheless, spin 10 is high enough to get into the mesoscopic physics and bulk magnetism [4]. Hence, the Mn_{12}-ac is suitable for the investigation of quantum processes on a macroscopic scale. It may also be useful for observing how the classical physics emerges from the quantum physics [6,7]. Magnetic bistability and high anisotropy may be useful, not only for cognitive purposes, but also for applying the Mn_{12}-ac molecular magnets in tiny systems, such as memory units and magneto-optical microelements.

Quantum tunnelling is one of peculiar processes in quantum physics. The direct proof of quantum tunnelling of magnetization was the discovery of the steps on the magnetic hysteresis curve in Mn_{12}-ac [8,9]. In general, spin changes its projection by two processes evoking magnetic relaxation: thermal transition over the barrier and quantum tunneling through it. If the thermal transition is suppressed, the resonant tunneling can be observed [10,11]. At lower temperatures thermal relaxation becomes slow on the experimental time scale. Then the presence of tunnelling manifests itself in faster relaxation.

In this paper we present the results of magnetic relaxation in synthesized Mn_{12}-ac and show the influence of the magnetic field on the relaxation. The results are fitted by the model of slow relaxation on experimental time scale and quantum tunnelling effect.

2. *The sample and experimental procedure*

The compound was prepared using a slightly modified procedure published earlier [3]. Manganese carbonate was used as the starting material. The solution of manganese(II) acetate was prepared by dissolving the carbonate in 60 vol. % acetic acid. An aqueous solution of potassium permanganate was added dropwise to the solution of manganese(II) acetate. The reaction mixture was cooled in an ice bath and vigorously stirred. The compound was isolated as a black powder. A vibrational spectrum of the product was recorded on NICOLET Magna IR 760 spectrometer from a KBr pelleted sample. IR (KBr) $\nu_{\max}$ / cm^{-1}: 3436s, 2930s, 2861m, 1723w, 1590vs, 1578vs, 1533vs, 1453vs, 1390vs, 1335m, 1255m and 613m.

The agreement between the measured X-ray powder pattern and the one calculated from the published single-crystal data confirmed the identity of the compound. The X-ray powder pattern was obtained on a PHILIPS 1738 automatic diffractometer (CuK$\alpha = 0.154056$ nm, $2\theta = 10 - 100°$, counter step 0.02 s^{-1}). The thermal measurements were performed on a METTLER DSC30 calorimeter and a METTLER TG 50 thermobalance using a heating rate of 1 Kmin^{-1}. Pure dry argon was passed through the system at 200 cm^{3}min^{-1}. The temperature range was 298 – 573 K. Finely powdered sample was placed in 40 μL aluminium crucible with a perforated seal. The DSC signal was integrated using a linear extrapolation of the base line. The beginning of the thermal events is identified as the onset temperature.

The endothermic decomposition of the product (the splitting off of the acetic acid and water molecules of crystallization) started at 329 K and continued up to 393 K. The enthalpy change during this process amounts to 109.7 Jg^{-1}. A rapid two-step decomposition of the residue began at 461 K. The DSC curve showed that three sharp exothermal events took place with corresponding peaks in the DTG curve. An investigation of these events is in progress.

The powder obtained consists of needlelike particles as a consequence of a high anisotropy on the molecular level. In order to explore the same properties in every molecule, it is neccessarry to orient all of the needles in the same direction. This was done by freezing the magnetized needles in toluene.

All magnetic measurements were performed on Quantum Design MPMS magnetometer equipped with a SQUID. The applied magnetic field in the vertical direction was generated by a superconducting magnet and varied from –5.5 T to 5.5 T. The temperature of the sample ranged from 1.8 K up to 400 K. Using the extraction method, the dipole magnetic moment m of the sample was measured as a function of the applied stable magnetic field H and the stable surrounding temperature T.

3. Results

In order to confirm whether the newly synthesized sample possesses the specific properties of blocking and bistability, the measurements of the dependence of the magnetic moment m on the temperature T have been performed. This was done in two ways: after cooling down the sample in the zero field from 35 K to 1.8 K (so called ZFC curve), and after cooling down from 35 K to 1.8 K in a chosen magnetic field H in the z direction in which the measurement took place (so called FC curve), both of them for the increasing temperature. The bifurcation of the ZFC and FC curves is shown in the inset of Fig. 1, as is the case in Ref. [5] . This branching off appears at the temperature defined as the blocking temperature T_{B}. The way we obtained T_{B} is just that: we looked at this branching off. Some authors use the maximum of the ZFC curve to read off T_{B}. It is important to point out that these two values are different, as can be clearly seen in the inset of Fig. 1. Ordinarily, the splitting is characteristic of the systems in which the freezing below a specific temperature appears and, as is known, it appears in anisotropic molecular magnets, too [5,12]. Here the value of m changes for more than a factor of two if the temperature is increased from 1.8 K to T_B for ZFC process, so that the splitting effect is well noticeable.

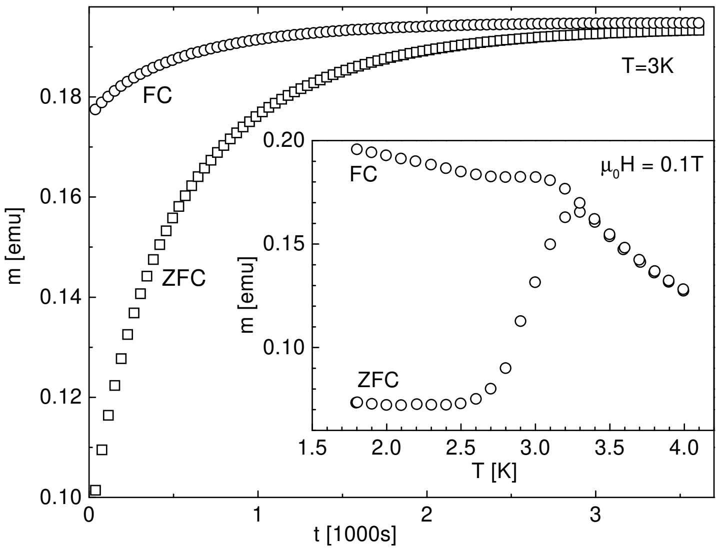

Fig. 1. Dependence of magnetic moment m of the sample on time t for ZFC and FC sample at 3 K. *Inset: dependence of m on temperature T in 0.1* T.

The difference between ZFC and FC curves suggested a study of the relaxation process below T_B for both cooling processes. The dependence of m on time t in the magnetic field of 0.1 T at 3 K after ZFC and FC preparation is shown in Fig. 1. After one hour, the total magnetic moments for both FC and ZFC separately reach almost the same value of m. This signals the tendency of the system to reach the same macroscopic equilibrium state. The measured relaxation data are fitted very well by the simple exponential function

$$m = m_0(1 - \mathrm{e}^{-(t-t_0)/\tau}), \tag{1}$$

where m_0 is the equilibrium value of the magnetic dipole moment for given H and T, t_0 determines the initial conditions connected mainly with the measurement starting time, and τ is the characteristic relaxation time. The values obtained by fitting are 0.1924 emu for m_0, –406 s for t_0, 555 s for τ corresponding to the ZFC process, and 0.1947 emu for m_0, –1395 s for t_0, 581 s for τ corresponding to the FC process.

The ZFC and FC curves were measured for different values of the applied magnetic field. As expected, m attains a higher value if the applied H increases. At the same time the curves shift toward the lower temperatures, lowering the bifurcation temperature. However, an irregularity was observed in the field of 0.45 T, as reported also in Ref. [8]. The dependence of T_B on imposed H is shown in Fig. 2.

Generally, $T_{\rm B}$ decreases if the field is increased, but there is a local minimum around $\mu_0 H \approx 0.45$ T. This value corresponds to one of the steps of every hysteresis curve.

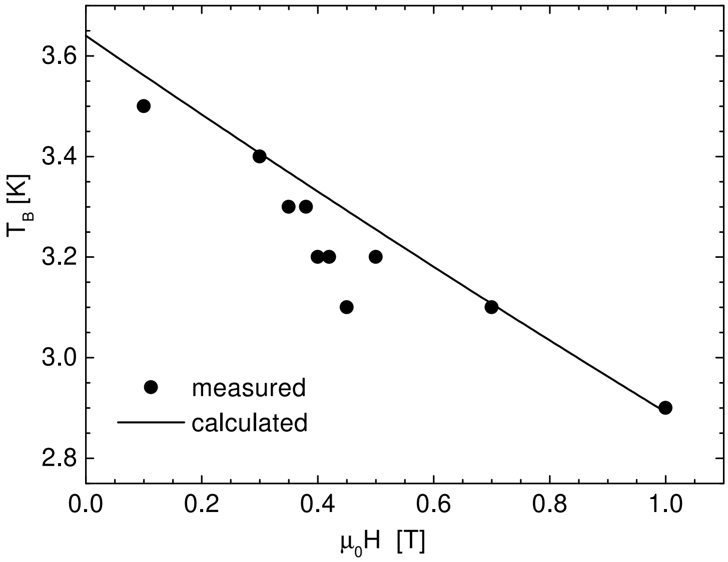

Fig. 2. Measured and calculated dependence of blocking temperature $T_{\rm B}$ on applied magnetic field H.

Magnetic-hysteresis curves were also measured at different temperatures. Below approximately 3 K, these loops are wide and each of them has equidistant steps placed at integer multiples of 0.46 T, as previously reported in Refs. [8] and [9].

4. Discussion

Wide magnetic hysteresis loops point to a high magnetic anisotropy [4,5,8] which originates from the structural anisotropy on the molecular level. It means that the spin tends to occupy two preferred directions separated by an energy barrier. Wide hysteresis loops below $T_{\rm B}$, measured in our experiments too, came from slow relaxation of spins over the barrier.

The results of more detailed investigation of the ZFC and FC curves can be explained using aforementioned slow relaxation. The magnetic moment of the sample increases in the ZFC process when the temperature rises. This is because more and more spins alter their direction to the preferred one. Further increase of temperature increases the number of thermal transitions backwards and the magnetic moment falls off. Above $T_{\rm B}$, the thermal fluctuations become rapid. Then, the bulk of the unblocked spins behave in a paramagnetic manner manifested as a decrease of m with further increase in T, like in Curie's law. For the FC process, the spins stay blocked mainly in the direction of the applied magnetic field. The states of higher energy, hence of a smaller S_z, become more populated if temperature is increased, so the magnetic moment of the sample slightly decreases. Above $T_{\rm B}$, the blocking in one direction takes a short time, compared with the experimental time, and the dependence merges with the ZFC curve. Hence, the maximum in the ZFC curve and the splitting of the ZFC and FC curves are not linked with a magnetic phase transition, but with the slow relaxation on the experimental time scale. This is clearly confirmed by measuring the dependence $m(t)$ at $H = 0.1$ T and $T = 3$ K, as shown in Fig. 1.

Experimentally, $T_{\rm B}$ is defined very sharply, in the sense that below this temperature the freezing effect is observable and above it there is a paramagnetic-like behaviour, as can be seen in the inset of Fig. 1. In fact, the analysis of our experimental results promotes the assertion that the slow relaxation is a matter of the freezing effect. The explanation is the following. Because of a high magnetic anisotropy, the reorientation of individual spins takes a long time. Hence the ZFC and FC curves differ below $T_{\rm B}$. Their branching off moves to a lower temperature if the time of measurement increases, as confirmed by attaining almost the same value of m (approximately 0.193 emu, shown in Fig. 1) during one hour of waiting at 3 K in 0.1 T for ZFC- and FC-prepared sample. Moreover, the characteristic relaxation time τ is also the same for the FC and ZFC processes, within fitting errors, attaining approximately 560 s at 3 K in 0.1 T. The relaxation for zero-field initial condition in non-zero field is tied up only with m at a given time, but not with the history. The different initial time parameter t_0, while m_0 and τ stay almost the same, suggests that the same process is captured at a different time of evolution towards equilibrium. It is important to remember that these arguments are correct in the region where the simple exponential relaxation is present, that is out of resonance for our temperature interval. The scaling properties of relaxation data investigated in Ref. [13] also confirm the individuality of processes and freezing of single molecular spin projection on the specific side of the barrier. Of course, we may compare it only in the temperature interval pertaining to our measurements.

It has been found [5] that the relaxation time τ at the temperature T is determined by Arrhenius law $\tau = \tau_0 {\rm e}^{S^2 D/T}$, where $S^2 D = 62$ K is the barrier height, and $\tau_0 = 2.1 \cdot 10^{-7}$ s is the parameter determined from measurements. Using for $T_{\rm B}$ the temperature at which the relaxation time equals the experimental time (in our experiment about 10 s), we obtain for $T_{\rm B}$ the value of 3.5 K. This is in good agreement with our estimation of $T_{\rm B}$ from the measurements of the ZFC and FC curves, plotted in the inset of Fig. 1.

In general, one can see that $T_{\rm B}$ decreases if H is increased (Fig. 2). Actually, faster relaxation can be imagined as a consequence of the reduction of the barrier. It means the blocking temperature is lower, too. Aforementioned dependence of $T_{\rm B}$ on H comes from the influence of the applied field on the real barrier shape. Using the simple model Hamiltonian $\mathcal{H} = -DS_z^2 - g\mu_B H S_z$, where S_z represents projection of S, g the g-factor, μ_B Bohr magneton and D the anisotropy constant, the height of the barrier in zero field is determined by the difference of energies between the highest state ($S_z = 0$) and the lowest one ($S_z = \pm 10$), and is equal to $S^2 D = 62$ K. If the magnetic field in the positive z-direction is applied, the maximum of the Hamilton function appears at $S_z = -g\mu_B H/2D$, neglecting the quantization. It is natural to look for the relaxation from the upper minimum over the maximum to the lower minimum, giving the new barrier height

$$S^2 D_H = S^2 D \left(1 - \frac{H}{20H_1}\right)^2 \tag{2}$$

as the difference of the energies of the new maximum and $S_z = -10$ state, where $H_1 = 0.46$ T is the field of the first resonance, and $20H_1$ corresponds to the total destruction of the barrier. Inverting the Arrhenius law and taking into account the distorted barrier height (Eq. 2), the $T_{\rm B}$ is given by

$$T_{\rm B-theor} = \frac{S^2 D}{\ln(\tau_E/\tau_0)} \left(1 - \frac{H}{20H_1}\right)^2 . \tag{3}$$

So, we included the applied magnetic field H in the equation for $T_{\rm B}$. Taking $\tau_E =$ 10 s, we obtained the dependence of the blocking temperature on the applied field shown by the solid line in Fig. 2. The result (Eq. 3) agrees quite well with our measured data and predicts the classical decrease of $T_{\rm B}$ in applied magnetic field. Equation 3 gives $T_{\rm B}(H = 0) \approx 3.6$ K. A similar expression has been derived [10] for the influence of transversal magnetic field, but there is H_x instead of H, and H_1 is different.

The apparent local minimum of $T_{\rm B}(H)$ can be attributed to resonant tunnelling that makes the relaxation faster, resulting in an increase of $T_{\rm B}$. It is the same reason why the steps on hysteresis loops appear at the specific values of magnetic fields, as explained in Refs. [7,11,14]. We determined the local minimum on $T_{\rm B}(H)$ curve experimentally. The local minimum should appear on $\tau(H)$ curve at the same magnetic field, too, but the relaxation near the resonance is not a simple exponential in any case, and τ does not have the defined meaning.

5. *Conclusion*

The analysis of the magnetic relaxation process in the synthesized Mn_{12}-ac below the blocking temperature $T_{\rm B}$ (≈ 3.6 K for $H = 0$) and above 2 K shows a single particle spin freezing on the two sides of the anisotropy barrier. Below $T_{\rm B}$, the relaxation is slow on the time scale of the experiment, resulting in the splitting of the ZFC and FC curves. The splitting would be less if the measurement took longer time. In that case $T_{\rm B}$ would be lower, too.

In an applied magnetic field, $T_{\rm B}$ decreases again. Now, it is based on the lowering of the barrier. The $T_{\rm B}(H)$ dependence is predicted very well and calculated using a classical reduction of barrier in applied H. The local minimum of $T_{\rm B}$ around $\mu_0 H = 0.45$ T is explained by quantum tunnelling which is also responsible for the steps on the measured hysteresis curves.

The blocking of spins is a matter of high anisotropy. During the measurement, the system tends to an equilibrium state, uniquely determined for given H and T, as confirmed in the relaxation measurements. The slow relaxation is responsible for all changes in the system investigated. It appears because of spin ordering similar to freezing (below characteristic temperature T_B) which takes some time. Therefore, the experimental time scale plays an important role in investigation of magnetic properties of Mn_{12}-ac that are determined mostly by barrier height and energy levels.

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TERMIČKA RELAKSACIJA I KVANTNO TUNELIRANJE MAGNETIZACIJE U Mn_{12}-ACETATU

Mjerili smo ovisnost magnetskog momenta m sintetiziranog molekulskog magneta Mn_{12}-acetat o temperaturi T i magnetskom polju H pomoću SQUID magnetometra. Ispod tzv. temperature kočenja T_B (≈ 3.6 K pri $H = 0$) primijetili smo razdvajanje krivulja $m(T)$ za uzorak hlađen bez polja (ZFC) i hlađen u polju (FC). Mjerenja vremenske relaksacije m pokazuju da m teži istim vrijednostima s jednakim relaksacijskim vremenima (≈ 560 s na 3 K) za oba procesa, ZFC i FC. Narečeno ukazuje na zamrzavanje spinova ispod temperature kočenja T_B (≈ 3.5 K) i jednočestičnu prirodu procesa u istraživanom temperaturnom području (2 K $< T <$ 4 K). Istraživali smo i ovisnost T_B o primijenjenom polju H. Pad T_B s povećanjem H objašnjavamo sniženjem bedema u primijenjenom polju.