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Thermally-assisted tunnelling of magnetization in $(Mn_{0.96}Cr_{0.04})12$-ac

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The thermally assisted resonant tunnelling in a single crystal $(Mn_{0.96}Cr_{0.04})12$-ac is studied in this paper. The obtained hysteresis loops at seven different temperatures between 1.8 and 3K show obvious dependence on temperature. The magnetization steps occur at specific field values of nH_R with $H_R \approx 0.46$T, which are approximately independent of the temperature. As the temperature decreases, the area enclosed in the hysteresis loops and the actual number n of the resonances increase, which provides clear evidence of thermally assisted resonant tunnelling in $(Mn_{0.96}Cr_{0.04})12$-ac.

Keywords: quantum tunnelling, thermally assisted resonant tunnelling
PACC: 7550S, 7560E, 7980

1. Introduction

The study of quantum tunnelling in magnetism has been a fruitful field of theoretical and experimental research because it can provide a signature of quantum mechanical behaviour in macroscopic systems. The magnetic molecule magnet $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4] \cdot 2CH_3COOH \cdot 4H_2O$, abbreviated Mn12-ac, is up to now the best studied for these investigations. It helps us to determine the size limit for information storage[1] and has also been proposed as a potential candidate for a quantum-computing element.[2] This compound can be considered as monodisperse ensembles of weakly interacting nanomagnets with a net spin S=10 and a strong uniaxial anisotropy (∼60K) along the longitudinal axis which splits the $2S+1$ degeneracy of the magnetic levels in zero field, creating a double well configuration.

Mn12-ac, first synthesized by Lis[3] in 1980, contains 8 ferromagnetically coupled Mn^{3+} (S=2) and 4 ferromagnetically coupled Mn^{4+} (S=3/2) ions. The Mn ions are coupled by superexchange through oxygen bridges; the measurements of high-field magnetization and ac susceptibility indicate at an S=10 ground state,[4,5,6] suggesting a simple picture of the magnetic order with the magnetic moments of the 8 Mn^{3+} ions antiparallel to those of the 4 Mn^{4+} ions, as shown in Fig.1.

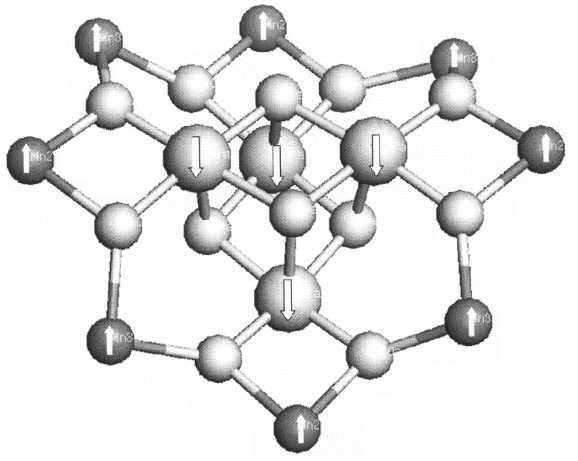


Fig.1. Sketch of the structure of the magnetic core of the cluster. Only the Mn^{4+} (large light-grey balls), Mn^{3+} (small dark-grey balls), and oxygen (small light-grey balls) ions are shown. The arrows show the spin structure of the ground S=10 state.

Mn12-ac exhibits anomalous hysteresis loops with steps at certain critical fields of integer multiples of 0.46T, providing clear evidence of a quantum tunnelling of the magnetization (MQT).[7] Recent studies show that the quantum tunnelling of the magnetization involves both phonon-assisted tunnelling and pure quantum tunnelling at lower temperature.[8] Fort

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et al[9] and Bokacheva *et al*[10] have made theoretical and experimental studies of the crossover at ~1K between the thermally assisted and the pure quantum tunnelling for Mn12. Above 1K, the tunnelling becomes thermally assisted. Spin-phonon coupling plays an important role, that is, the resonant tunnelling effect is governed not only by the tunnelling rate of the dominant spin level(s) but also by the thermal population of each spin level.

In this paper we make a similar study about thermally assisted resonant tunnelling, in a single crystal of Cr-doped Mn12-ac, we have succeeded in growing a single crystal $(Mn_{0.96}Cr_{0.04})$12-ac of large size, and observed a significant modulation of the probability of the MQT by little Cr substitution for Mn.

2. Experimental

Single crystals of $(Mn_{0.96}Cr_{0.04})$12-ac were grown following a modification of the procedure of Lis.[3] The resulting mixture was left uncapped and undisturbed for two months. The crystallites of $(Mn_{0.96}Cr_{0.04})$12-ac grew up to a dimension of about $7.0\times2.0\times2.0mm^3$, at least four times larger than that of its parent compound Mn12-ac, with the long axis parallel to the c direction. Cr doping into Mn12-ac was achieved by substituting K_2CrO_4 for $KMnO_4$. The Cr content was determined by an inductively coupled plasma-atomic emission spectrometry (model Tarrel–Ash AtomComp 96-786) and S-4200 scanning electron microscope. A good agreement of the two measurements was obtained with 4% Cr doped, and confirmed a homogeneous composition in the single crystal of $(Mn_{0.96}Cr_{0.04})$12-ac. The crystallites, as checked by four-circle single crystal x-ray diffractometer, crystallize in tetragonal system (space group: I-4) with a=1.7319(2)nm and c=1.2401(3)nm. The dc magnetization was measured in a Quantum Design physical property measurement system (PPMS). All measurements were made on samples mounted with their c axis along the field direction. The angle between the c axes and the field direction was estimate to be less than 5°.

3. Results and discussion

Figure 2 shows several staircase-like hysteresis loops in a longitudinal field up to 3T at seven different temperatures between 1.8 and 3K. The rate of sweep of the external field was 10^{-3}T/s. Similar to the crystal of Mn12-ac,[9] a succession of steps and flat terraces in the hysteresis loops was observed with increasing field below the blocking temperature. The obtained hysteresis loops show obvious dependence on temperature. As the temperature decreases, the area enclosed in the hysteresis loops and the number of steps increase. At higher temperature, steps are seen to occur at lower-indexed resonance, while at the lowest temperature of 1.8K resonance at indices n=0, 1, 2, 3, 4, 5 and 6 can be observed.

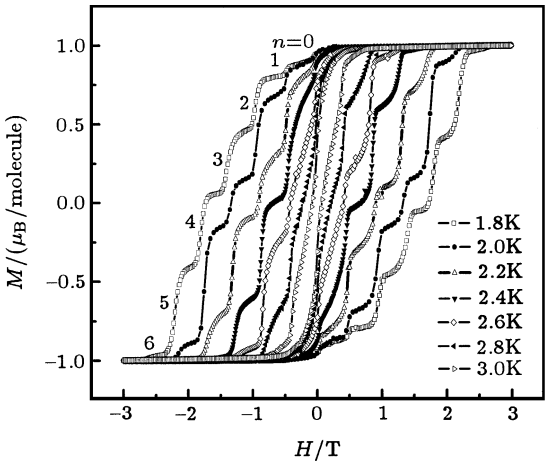


Fig.2. Magnetization hysteresis loops of $(Mn_{0.96}Cr_{0.04})$12-ac measured at seven different temperatures.

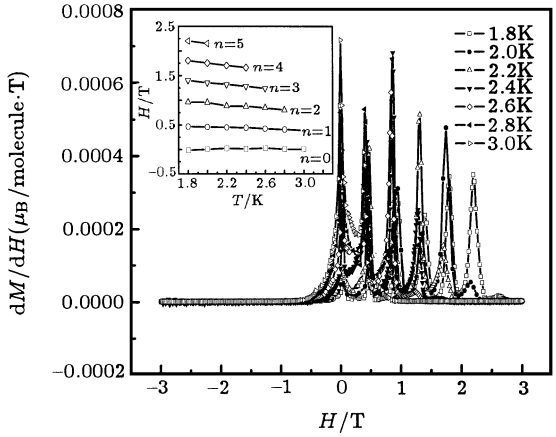


Fig.3. The derivative dM/dH as a function of the external magnetic field H. The inset shows the external magnetic field at which maxima occur, plotted as a function of temperature.

The steps occur at well defined field values that are approximately independent of the temperature. Figure 3, where the derivative dM/dH was plotted as a function of field H, shows this characteristic clearly. We have observed seven peaks and the intervals of field ΔH is about 0.46T. But there are obvious differences between the heights of the peaks at these different temperatures. As the temperature is lowered, more and more new peaks arise. In addition, the inset of Fig.3 shows that the external field nH_R for each

step decreases slightly with temperature, confirming the existence of a relatively high crossover temperature T_c, which is quite similar to those observed for Mn12-ac.[11,12]

This temperature dependence of the resonance tunnelling implies the contribution of the thermal activation at the temperature range of 1.8–3K. The similar phenomenon, observed in Mn12-ac, is also attributed to magnetic resonant tunnelling between energy levels in opposite well of the double-well potential. No change of S=10 was found out from the saturation magnetization measurement due to the small Cr content. Therefore, we apply the model as shown in Fig.4, proposed by del Barco *et al.* In zero field, the two levels of the minimal energy (S=±10) belong to the two opposite orientations of the spin along the anisotropy axis. As illustrated in Fig.4, the system is initially thermally activated in all metastable $m = 0, 1, \ldots, 9$ ground states in the left-hand well, with the population of each level proportional to the Arrhénius factor $\exp(-E_m/T)$. At $H = nH_R$ each m-level in the left-hand well matches the $(n$-$m)$-level in the right-hand well, and resonant tunnelling takes place. In this process, spins are first thermally activated to a fast-tunnelling level near the top of the barrier, then tunnel to the opposite side of the double well and spontaneously decays into the ground state.

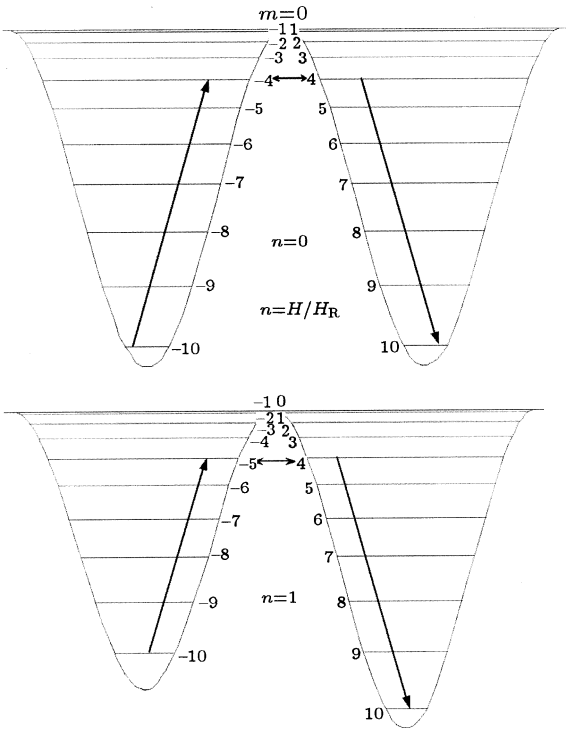


Fig.4. Schematic diagram illustrating thermally assisted resonant spin tunnelling process, consisting of a thermal activation from the ground state (m=–10) to activated state (m=–4 or –5) and pure quantum tunnelling from left level (m=–4 or –5) to right level (m=4). The index n shows the external field $H = nH_R$ ($H_R \approx$0.46T).

4. Conclusions

The thermally assisted resonant tunnelling in a single crystal $(Mn_{0.96}Cr_{0.04})$12-ac has been studied. A small amount of doped Cr doesn't change Mn12-ac crystal structure and the basic magnetization state. Though the discrete fields nH_R ($H_R \sim$0.46T) are approximately independent of the temperature, the hysteresis loops show obvious dependence on temperature. As the temperature decreases, the area enclosed in the hysteresis loops and the number of steps increase. At the highest temperature of 3.0K, quite near the blocking temperature, only two steps with lower-indexed resonance (n=0,1) are observed, while at the lowest temperature of 1.8K the seven resonances with indices n=0, 1, 2, 3, 4, 5 and 6 can be observed. These can be attributed to thermally assisted resonant tunnelling in $(Mn_{0.96}Cr_{0.04})$12-ac.

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