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Resonant tunnelling of the magnetization in molecular crystal of $[(Mn_{1-x}Cr_x)_{12}O_{12}\ (CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$ (x=0,0.03,0.04,0.05)*

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The quantum tunnelling of magnetization (QTM) in single crystals of the single molecule magnet $(Mn_{1-x}Cr_x)$12-Ac (x=0, 0.03, 0.04, 0.05) has been investigated. In comparison with its parent Mn12-Ac, a greater rate of magnetization relaxation and a lower effective potential-energy barrier have been observed in Cr-doping samples. This modulation of QTM due to the Cr-doping could be attributed to the small change of S_z due to the smaller spin of Cr itself and additional intrinsic but distributed transverse and longitudinal anisotropy raised by a subtle change of the local environment in the magnetic Mn12 core.

Keywords: quantum tunnelling of magnetization, magnetization relaxation, single molecule magnet
PACC: 7550S, 7560E, 7980

1. Introduction

Magnetic quantum tunnelling in single molecule magnets (SMMs), such as Mn12-Ac, is one of a few macroscopic quantum phenomena (MQP).[1−3] How one may apply the MQP of SMM to the practical application is the recent research goal. SMM has been proposed as a candidate of high density storage and quantum computation.[4,5] How one can control the manufacture of the single crystal and make the quantum tunnelling of magnetization(QTM) undergo significant change is very interesting for the fundamental research as well as the study of the proposed quantum device, which is a key step for future applications.

$[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$ (hereafter Mn12) is built of discrete dodecanuclear Mn12 molecules, water of crystallization and disordered acetic acid molecules. The antiferromagnetic coupling of the Mn^{3+} and Mn^{4+} ions results in the ground state with a net spin $S = 10$.[6−8] A strong magnetocrystalline anisotropy splits the magnetic degeneracy into the $2S+1$ sublevels with $-10 \ll M \ll 10$ levels separated by the anisotropic potential-energy barrier.

Much effort has been devoted to design Mn12 molecular magnet to control or modulate the QTM, for which there are mainly two methods.[9−15] One popular way is to use other solvent molecules to replace the acetic acid or water molecules, leading to a local broken symmetry around the Mn_{12} core. The other is to modulate the ground state spin S and the relaxation property by doping other transition-metal ions at the Mn sites, the kernel of the QTM in Mn12-Ac. In our previous work,[12−15] we have studied the QTM in the single crystals of Mn12-Ac lightly doped with Cr. In this paper, we extend our study to the system of a series of single crystals of Cr-doped $(Mn_{1-x}Cr_x)$12-Ac (x=0, 0.03, 0.04, 0.05), to investigate the variation of QTM with the increase of the Cr doping content.

2. Experiment

Single crystals of $(Mn_{1-x}Cr_x)$12-Ac (x=0, 0.03, 0.04, 0.05) was synthesized following a modification of the procedure of Lis.[16] The Cr atoms were doped into Mn12-Ac by substituting K_2CrO_4 for $KMnO_4$ at different temperatures from 55 to 70 °C. The doping concentration was determined using an inductively cou-

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pled plasma-atomic emission spectrometer (ICP-AES, Thermo Jarrell Ash Co. IRIS Advantage) and S-4200 scanning electron microscope (SEM). Both measurements confirmed a homogeneous composition within the single crystals. The dc magnetization was measured in a quantum design physical property measurement system (PPMS-14 T). This system has the highest dc magnetic field of 14 T and the operating temperature ranges from 1.8 to 400 K for magnetic measurements. Measurements were made on the samples mounted with their tetragonal c axis along the magnetic field direction with a deviation less than 5°.

3. Results and discussion

Figure 1 shows the temperature dependence of the zero-field-cooled (ZFC) and the field-cooled (FC) magnetizations for the single crystals of $(Mn_{1-x}Cr_x)$12-Ac (x=0, 0.03, 0.04, 0.05).

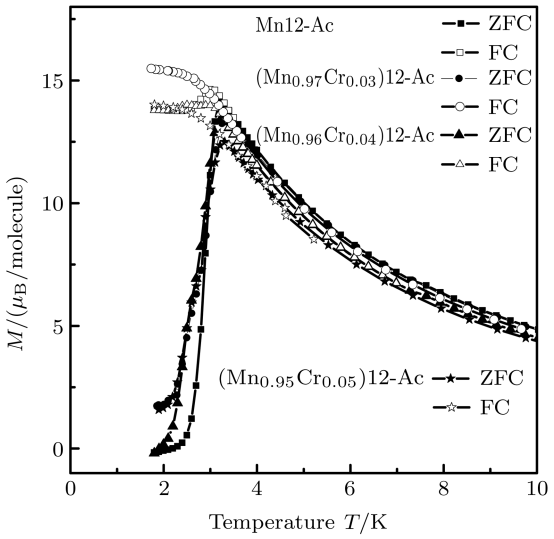


Fig.1. The temperature dependence of the ZFC and FC magnetizations for the single crystals of $(Mn_{1-x}Cr_x)$12-Ac (x = 0, 0.03, 0.04, 0.05) in a field of 0.2 T.

For all the samples, we can observe apparently a sharp cusp at about 3.2 K in the zero-field-cooled (ZFC) curves while their sharpness is lost in the field-cooled (FC) ones. With decreasing temperature, the FC data coincide with the ZFC ones before reaching the cusp, but deviate from them after the cusp, and the deviation increases gradually. It is a typical blocking behaviour of the magnetic clusters. The large difference between the ZFC and the FC curves results from the slow relaxation of the magnetization.[17]

In order to investigate the change of the magnetic relaxation at low temperatures with the increase of Cr doping content, dc measurements have been performed. In Fig.2(a) we show the magnetization hysteresis loops of $(Mn_{1-x}Cr_x)$12-Ac (x=0, 0.03, 0.04, 0.05) monocrystals taken with the magnetic field applied along the c axis at 2 K. The rate of sweep of the external field is 10^{-3} T/s. Similar to the crystal of Mn12-Ac,[1,2] a succession of steps and flat regions in the hysteresis loops is observed with increasing Cr content. This behaviour is a characteristic of QTM. Figure 2(a) shows the interesting changes that occur with variation of Cr content: as the Cr content increases, the area enclosed within the hysteresis loops decreases and the steps at low field become clear. The saturated magnetic moment for the whole molecule of $(Mn_{1-x}Cr_x)$12-Ac (x=0, 0.03, 0.04, 0.05) decreases slowly with the increase of Cr doping content. For example, the saturated magnetic moment for the whole molecule of $(Mn_{0.95}Cr_{0.05})$12-Ac has dropped to 19 μ_B, while the ideal value is 20 for S = 10 in Mn12-Ac. Considering the smaller spin of Cr, we can understand this decrease of saturated magnetic moment.

The steps occur at well defined field values that are approximately independent of the Cr doping content. Figure 2(b), where the derivative dM/dH is plotted as a function of field H, shows this characteristic clearly. For all samples with the field sweeping from −3T to +3T, six peaks are marked at zero field, 0.46, 0.92, 1.32, 1.74 , 2.16T, and thus the intervals of field ΔH ∼0.46 T. But the peaks' heights in the correspondent fields are quite different with the increase of Cr doping content. The first and second peaks that are very weak for Mn12-Ac become pronounced for the Cr-doped samples. These behaviours imply that the doping of Cr into Mn12-Ac will induce a greater relaxation rate of magnetization in the low magnetic field.

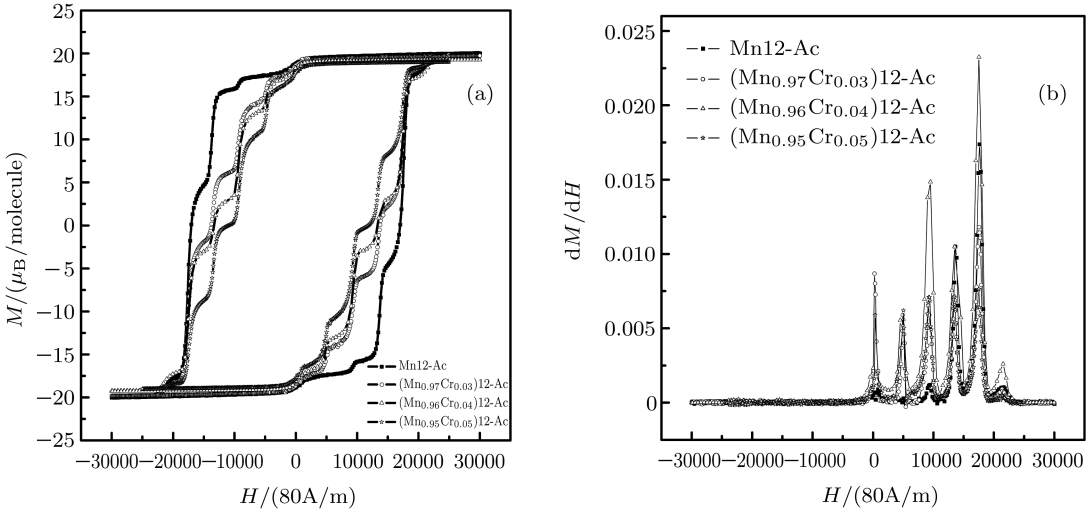


Fig.2. (a) Magnetization hysteresis loops of $(Mn_{1-x}Cr_x)$12-Ac (x = 0, 0.03, 0.04, 0.05) measured at 2 K and (b) their derivative dM/dH as a function of the external magnetic field H.

From the peaks in the χ'' versus temperature measurement, the values of the magnetization relaxation time are determined at each temperature. The data are least-squares fit to the Arrhenius law to give the value of $U_{\rm eff}$ for the single crystals of $(Mn_{1-x}Cr_x)$12-Ac (x=0, 0.03, 0.04, 0.05). Figure 3 shows the effective potential-energy barriers decrease with the increase of Cr doping content.

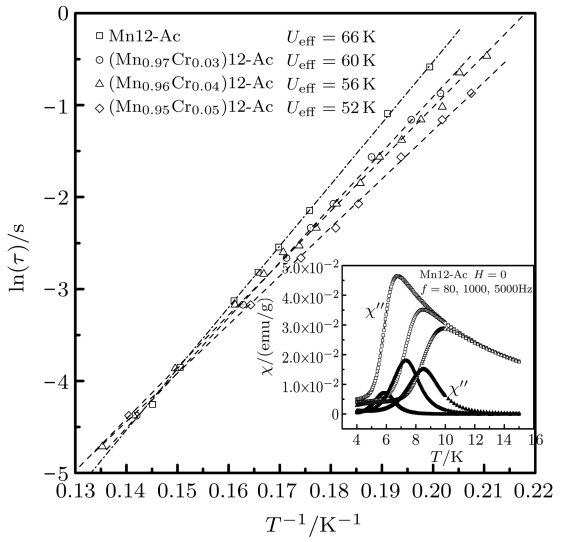


Fig.3. Arrhenius plots for the relaxation time τ obtained from the frequency dependence of the ac susceptibility. The fit gives $U_{\rm eff}$ for $(Mn_{1-x}Cr_x)$12-Ac (x = 0, 0.03, 0.04, 0.05). The inset shows a typical ac susceptibility for Mn12-Ac.

We have known that the effective potential-energy barrier between the two opposite orientations of S_Z with respect to the anisotropy axis is $U_{\rm eff} = DS_Z^2$. Consequently, this variation of $U_{\rm eff}$ should result from the change of S_z due to the substituting Cr for Mn since the anisotropy constants D are similar for all samples, as indicated by the intervals of field $\Delta H(\sim 0.46\,{\rm T})$ between two steps in the hysteresis loops (Fig.2). In fact, our saturation magnetization MS of Cr-doped samples is smaller than that of Mn12-Ac. Furthermore, we have calculated the values of $DM_{\rm S}^2$ for the Cr-doped samples, which are larger than their corresponding $U_{\rm eff}$ in the undoped ones. This implies that substituting Cr for Mn can make the easy-axis direction deviate from the crystallographic c axis.

It is surprising that such a little chemical doping of 3%–5% Cr could result in obvious changes of magnetization relaxation rate without any structural difference in XRD pattern. It is worth pointing out that $Mn^{+3,+4}$ and $Cr^{+3,+4}$ ions have similar sizes, and thus the doped Cr ion is possibly substituted for Mn^{+3} or Mn^{+4}. Substituting Cr for Mn can produce a small change of fine structure and exchange interactions within the local molecular environment that results in broken symmetry as well as the tilt of easy-axis from the crystallographic c axis. Such a tilt of the magnetic easy axis brings about a distribution of transverse and longitudinal anisotropies and thus leads to a greater magnetization relaxation rate in Cr-doped samples.[9,10]

3.1. Conclusions

The QTM in single crystals of $(Mn_{1-x}Cr_x)$12-Ac (x=0, 0.03, 0.04, 0.05) have been investigated. Although the single crystals of $(Mn_{1-x}Cr_x)$12-Ac

(x=0.03, 0.04, 0.05) also have a regular series of steps and plateaus in the magnetic hysteresis loop at well defined field intervals (ΔH ∼0.46 T) as its parent compound Mn12-Ac, an obviously different magnetization relaxation has been observed. The substitution of small amount Cr for Mn depresses the height of effective potential-energy barrier and modulates significantly the probability of the QTM, which are clearly shown by the narrow hysteresis loop and a greater rate of magnetization relaxation at low fields in Cr-doped samples. All these results can be interpreted by the small change of S_z due to the smaller spin of Cr itself and the additional intrinsic but dispersed transverse and longitudinal anisotropies caused by a subtle change of the Mn12 magnetic core arising from the Cr doping. Our study illustrates how subtle changes in molecule environment can modulate the internal transverse interaction and thus the QTM. This sensitivity to local chemical environment is very interesting for future applications, which makes it possible to modulate QTM by controlling the manufacture of SMM.

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