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Structure and magnetic properties of a new single-molecule magnet $[Mn_{11}Fe_1O_{12}\ (CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$*

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A new single-molecule magnet $[Mn_{11}Fe_1O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$ ($Mn_{11}Fe_1$) has been synthesized. The structure has been studied by the single crystal x-ray diffraction. The difference of Jahn–Teller distortion between Fe^{3+} and Mn^{3+} ion reveals that Fe^{3+} ion substitutes for Mn^{3+} ion on the Mn(3) sites in the Mn_{12} skeleton. The temperature dependence of the magnetization gives a blocking temperature T_B=1.9K for $Mn_{11}Fe_1$. Based on the magnetization process analysis of the crystal at T=2K, we suggest that $Mn_{11}Fe_1$ has the ground state with a total spin S= 11/2.

Keywords: quantum tunnelling, Jahn–Teller distortion, blocking temperature
PACC: 7550S, 7560E, 7980

1. Introduction

The structure of $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$, denoted by Mn_{12},has been studied in detail by Lis in 1980.[1] However, the magnetization quantum tunnelling (MQT) on Mn_{12} was found in the experiments[2−4] until 1996. Thereafter widely theoretical and experimental investigations were performed[5−15] on Mn_{12}. Mn_{12} consists of an outer ring of 8 Mn^{3+} ions each with spin S=2 and an inner tetrahedron formed by 4 Mn^{4+} ions each with spin S=3/2. The antiferromagnetic coupling of the Mn^{3+} and Mn^{4+} ions results in the ground state with a total spin S=10.[7,16,17] The strong uniaxial magnetic anisotropy leads to an effective potential barrier (∼66K) between the up and down spin states.[3,7,11,12,14] The MQT was observed from magnetization hysteresis loops of Mn_{12}[2−4] below a blocking temperature about 3K. At temperatures higher than 3K, Mn_{12} exhibits superparamagnetism.

Synthesis of Mn_{12} derivatives provides an opportunity to extensively study the MQT. One popular way is to replace the acetic acid or water molecules with other solvent molecules, which induces the variation of the MQT properties due to the breaking of the local symmetry around the Mn_{12} core. Takeda *et al*[18] found two kinds of molecules with different relaxation rates in $[Mn_{12}O_{12}(C_6H_5COO)_{16}(H_2O)_4]\cdot 2C_6H_5COOH$: the fast relaxation molecule has an unusual Jahn–Teller distortion at a certain Mn^{3+} ion. Aubin *et al*[19] studied several single molecule magnets (SMMs) with the composition $[Mn_{12}O_{12}\ (O_2CR)_{16}(H_2O)_x]$($x$=3 or 4) and found that different solvent microenvironment results in different Jahn–Teller distortion at Mn^{3+} ion, reflecting different local symmetries and MQT properties. However, few reports, except for recent Mn_{12} with Cr-substitution,[20,21] have been published on ionic substitution at the Mn sites, the kernel of the MQT in Mn_{12}. In fact, these substitutions will lead to the local symmetry breaking and the change of exchange interactions within local molecular environment that significantly influences the MQT.

In this paper we study the $Mn_{11}Fe_1$, a new object for research of the MQT, through Fe-substitution for Mn in Mn_{12}.

2. Experiment

The $Mn_{11}Fe_1/Mn_{12}$ mixed crystal (later discussion will prove this description) with the average size

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of $4.0\times0.7\times0.7\text{mm}^3$ was synthesized through the reaction of $Fe(CH_3COOH)_2$ and $KMnO_4$ at T=60°C, following a modification of the procedure of Lis.[1] The image of scanning electronic microscopy (SEM) of the crystal is shown in Fig.1.

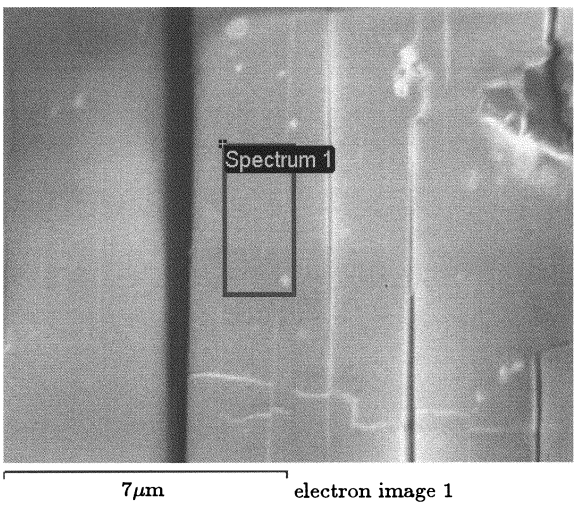


Fig.1. SEM image of $Mn_{11}Fe_1/Mn_{12}$ mixed crystal.

The Fe content was determined by the inductively coupled plasma–atomic emission spectrometry (ICP-AES, Thermo Jarrell Ash Co. IRIS Advantage) and S-4200 SEM, indicating that Fe ions occupy 6.00% of the metal ions in the mixed crystal.

A crystal with a size of $0.60\times0.60\times0.40\text{mm}^3$ was selected for lattice parameters and intensity measurements by a four-circle x-ray diffractometer (Rigaku RAXIS RAPID IP, Rigaku Co.) with graphite monochromator and Mo Kα radiation (λ=0.071073nm). The crystal data was measured at room temperature. The crystal parameters are as follows: The crystal system is tetragonal with space group $I\overline{4}$, unit cell dimensions a=1.7308(2)nm, c=1.2415(3)nm, Z=2, calculated density 2.064Mg/m^3. Within the θ range between 3.10° and 25.01°, 1732 reflections were collected, of which 1493 with $I > 2\sigma(I)$ were used. Scattering factors of the atoms were taken from International Tables Vol C Tables 4.2.6.8 and 6.1.1.4. The structure was resolved by direct methods using SHELXL98 from University of Gottingen, Germany.

The dc magnetization was measured in a physical property measurement system (PPMS) from Quantum Design. The sample was measured under an applied magnetic field along the c axis of the crystal. The angle between the easy axis and the field direction was estimated to be less than 5°.

3. Results and discussion

The single-crystal x-ray diffraction (XRD) did not reveal a second phase in the $Mn_{11}Fe_1/Mn_{12}$ mixed crystal, and the structure parameters are the same as those of Mn_{12}. Its structure is shown schematically in Fig.2. Table 1 lists the M–O (M represents Mn or Fe ion) bond lengths in $Mn_{11}Fe_1/Mn_{12}$ and Mn_{12} obtained from our single crystal x-ray diffraction and those from Ref.[1]. There are three different crystallographic sites of Mn ions in Mn_{12}. The Jahn–Teller distortion only occurs for the Mn^{3+} ions, which differentiates Mn^{3+} ions from Mn^{4+} ions.[1] The Mn^{4+} ions occupy the M(1) sites. The Mn^{3+} ions on M(2) have two types of M–O bond lengths, four short (0.1878–0.1939nm) and two long (0.2187 and 0.2248nm), which corresponds to a tetragonal-elongated Jahn–Teller distortion. For $Mn_{11}Fe_1/Mn_{12}$, the M(2)–O bond lengths have no obvious difference compared with Mn_{12}, that is, the Jahn–Teller distortion has not changed. So this means that the Fe ions do not substitute for the Mn ions on M(2) sites. For Mn_{12}, Mn^{3+} ions on M(3) sites have three types of M–O bond lengths, two short (0.1892 and 0.1902nm), two intermediate (0.1978 and 0.2011nm), and two long (0.2178 and 0.2132nm), which is classified as orthorhombic Jahn–Teller distortion. The M(3)–O bond lengths in $Mn_{11}Fe_1/Mn_{12}$ have a considerable change, and there are two types of bond lengths, two short

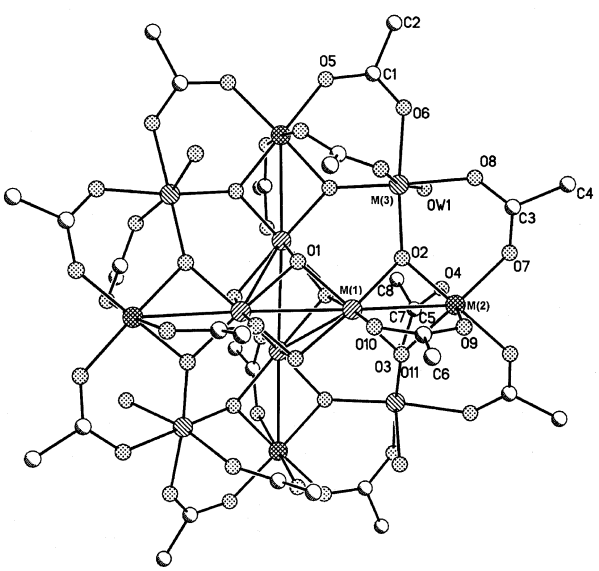


Fig.2. Schematic of the structure of the mixed crystal. The metal ions are labelled by M. Mn^{4+} ions occupy the M(1) sites with spin-down, Mn^{3+} ions occupy the M(2) and M(3) sites with spin-up and Fe^{3+} ion occupies the M(3) sites with spin-down in stead of a certain Mn^{3+} ion with spin-up.

(0.1911 and 0.1931nm) and four long (0.2015–0.2088nm). The length of M(3)–O bonds (along the c axis) decreases (by 0.01nm), and the lengths of the intermediate and short M–O bonds (perpendicular to the c axis) increase (by 0.001–0.004nm), so the Jahn–Teller distortion has a quite big reduction in the mixed crystal. We conclude that the reduction should be attributed to the substitution of non Jahn–Teller Fe^{3+} ions for Mn^{3+} ions.

Table 1. Bond lengths of M–O $Mn_{11}Fe_1/Mn_{12}$ and Mn_{12}.

Bond/10^{-1}nm	$Mn_{11}Fe_1/Mn_{12}$	Mn_{12} * (Lis)	Difference
M(1)–O(2)	1.858(4)	1.854(7)	0.004
M(1)–O(1)#2	1.922(4)	1.916(7)	0.006
M(1)–O(3)	1.881(4)	1.883(7)	–0.002
M(1)–O(1)	1.931(4)	1.908(8)	0.023
M(1)–O(1)#1	1.892(5)	1.901(8)	–0.009
M(1)–O(10)	1.929(5)	1.912(8)	0.017
M(2)–O(2)	1.887(4)	1.878(7)	0.009
M(2)–O(5)#1	1.942(5)	1.939(8)	0.003
M(2)–O(3)	1.892(4)	1.894(7)	–0.002
M(2)–O(7)	1.941(5)	1.928(8)	0.013
M(2)–O(4)	2.220(6)	2.187(10)	0.033
M(2)–O(9)	2.212(5)	2.248(8)	–0.036
M(3)–O(2)	1.911(4)	1.902(8)	0.009
M(3)–O(6)	2.028(5)	2.011(8)	0.017
M(3)–O(3)#3	1.931(4)	1.892(7)	0.039
M(3)–O(8)	2.015(5)	1.978(8)	0.037
M(3)–O(11)#3	2.027(6)	2.132(8)	–0.105
M(3)–OW1	2.088(6)	2.178(9)	–0.090

The ICP–AES and SEM consistently give the Fe-substitute fraction 6.00%. But this value is lower than the lowest atom-substitution ratio 8.33% corresponding to $Mn_{11}Fe_1$. Thus, we think we obtained a $Mn_{11}Fe_1/Mn_{12}$ mixed crystal with the mol ratio 2.58: 1, which agrees with the magnetic measurement results.

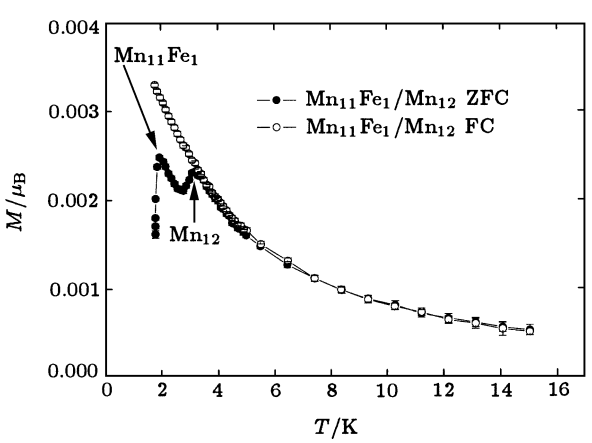


Fig.3. Magnetization of the mixed crystal as a function of temperature. Closed and open circles represent the zero-field-cooled (ZFC) curves and the field-cooled (FC) curves at applied magnetic field H=0.2T, respectively.

The temperature dependence of the magnetization is displayed in Fig.3. At an applied magnetic field H=0.2T, the zero-field-cooled (ZFC) curves shows two peaks at temperature T=3.1 and 1.9K, which corresponds to the blocking of Mn_{12} and $Mn_{11}Fe_1$, respectively.

The magnetic measurements on PPMS indicate that the mixed crystal has the saturation magnetization M_s=13.5μ_B per molecule. Mn_{12} in the mixed crystal with a content 28% contributes 5.6 μ_B (Mn_{12} has an M_s=20μ_B per molecule) to the total M_s. So $Mn_{11}Fe_1$ with a content 72% will contribute the difference of 7.9 μ_B, which means that $Mn_{11}Fe_1$ should have a saturation magnetization M_s=11μ_B per molecule (S=11/2). This implies that Fe-substitution induces a reverse of the spin. $Mn_{11}Fe_1$ contains four Mn^{4+} (S=3/2) ions at the centre of tetrahedron surrounded by seven Mn^{3+} (S=2) ions and one Fe^{3+} (S=5/2) ion. The spin of Fe^{3+} ion has an antiferromagnetic coupling with the spins of the neighbouring Mn^{3+} ions and a ferromagnetic coupling with the spins of the neighbouring Mn^{4+} ions. Thus $Mn_{11}Fe_1$ has a ground state with a total spin S=11/2.

Since the blocking temperature of $Mn_{11}Fe_1$ is T_B=1.9K, the normalized magnetization curve of the mixed crystal ($Mn_{11}Fe_1/Mn_{12}$Exp. in Fig.4) at T=2K should consist of a superparamagnetic magnetization curve of $Mn_{11}Fe_1$ and a hysteresis loop of Mn_{12}. The magnetization of superparamagnetic $Mn_{11}Fe_1$ should be zero at applied magnetic field H=0T; in other words, the non-zero magnetization of the mixed crystal originates from Mn_{12}. From the discussions above, it follows that the magnetization curve of the mixed crystal contains 41.3% normalized magnetization curve of Mn_{12}, which is plotted in Fig.4 (Mn_{12}Exp.). Consequently, we can obtain the magnetization curve of $Mn_{11}Fe_1$ with the ratio of 58.7% ($Mn_{11}Fe_1$ fit in Fig.4) by subtracting the decreased field magnetization curve (the part without quantum steps except for that at H=0T) of Mn_{12} from the corresponding part of the crystal. Considering the saturation magnetization, we can calculate the mol ratio 2.58: 1 for $Mn_{11}Fe_1$ to Mn_{12} in the crystal, which coincides with the results from the ICP–AES and SEM. We can have a good fit ($Mn_{11}Fe_1/Mn_{12}$ fit in Fig.4) of the experimental result by the magnetization curve of $Mn_{11}Fe_1$ plus that of Mn_{12}, seeing Fig.4.

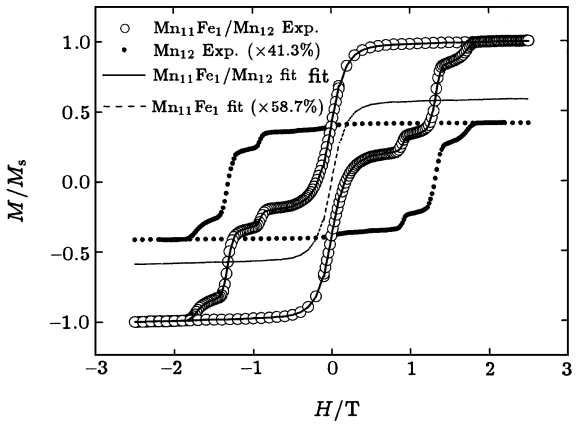


Fig.4. Normalized magnetization curves of $Mn_{11}Fe_1/Mn_{12}$ mixed crystal and Mn_{12}. The open and closed circles denote the experimental curves of the mixed crystal and Mn_{12} (41.3% of the normalized curve), respectively. Solid and dashed lines indicate fitted curves for $Mn_{11}Fe_1/Mn_{12}$ mixed crystal and $Mn_{11}Fe_1$ (58.7% of the normalized curve), respectively.

4. Conclusion

The structure and some magnetic properties of the SMM $Mn_{11}Fe_1$ in $Mn_{11}Fe_1/Mn_{12}$ mixed crystal have been studied. The reduction of Jahn–Teller distortion on M(3) sites proves that Fe^{3+} ions substitute for Mn^{3+} ions on M(3) sites in Mn_{12}. The new magnet $Mn_{11}Fe_1$ has a blocking temperature T_B=1.9K and a saturation magnetization $M_s=11\mu_B$ per molecule. In our model, the $Mn_{11}Fe_1$ consists of an outer ring of seven Mn^{3+} (S=2) ions and one Fe^{3+} (S=5/2) ion and an inner tetrahedron formed by four Mn^{4+} (S=3/2) ions. The up spins of Mn^{3+} ions and the down spins of Fe^{3+} ions and Mn^{4+} ions result in the ground state with a total spin S=11/2.

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