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Determination of the sites of Fe atoms in Fe-substituted Mn_{12}*

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In this paper neutron diffraction experiments were performed for Fe-substituted Mn_{12} in order to determine the sites of Fe atoms. The results of structure refinements for the sample with our accessed highest Fe content showed that all Fe atoms occupied Mn(3) sites in the Mn_{12} skeleton. The x-ray absorption fine structure experiments as well as multiple scattering simulations gave the same result. Thus we concluded that Fe atoms only occupied Mn(3) sites. This conclusion also means that Fe-substituted Mn_{12} series only includes the four single-molecule magnets of $[Mn_{12-x}Fe_xO_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$ ($x = 1, 2, 3$, and 4), denoted by $Mn_{11}Fe_1$, $Mn_{10}Fe_2$, Mn_9Fe_3, and Mn_8Fe_4, respectively.

Keywords: single-molecule magnets, neutron diffraction, x-ray absorption fine structure
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1. Introduction

Mn_{12} is the single-molecule magnet with high spin ($S = 10$) and strong uniaxial anisotropy (~ 60 K). It is attractive as one of the potential molecular-based magnetic materials. Specially, since macroscopic quantum tunnelling of magnetization in Mn_{12} was found in 1996,[1−3] more attentions have been paid to the Mn_{12}. Since Mn_{12} has been familiar to us, ion substitution will be effective methods for further study.[4−6]

In our works, Mn atoms in Mn_{12} were partly substituted by Fe atoms. The magnetic and quantum properties of the Fe-substituted Mn_{12} have been reported in our previous works.[7,8] However, we could not distinguish the identities of metal atoms with similar atomic numbers by x-ray diffraction (XRD). In addition, we could not grow the Fe-substituted Mn_{12} with higher Fe atoms content than 33.3%.

So the neutron diffraction and x-ray absorption fine structure (XAFS) experiments as well as multiple scattering simulation based on FEFF8.2 code[9] were performed to determine the occupancy sites of Fe atoms in the Mn_{12} skeleton.

2. Experiment

The Fe-substituted Mn_{12} was synthesized through the reaction of $Fe(CH_3COOH)_2$, $Mn(CH_3COOH)_2$ and $KMnO_4$ at the temperature $T = 60\,^{\circ}$C, which follows a modification of the procedure provided by Lis.[10]

The powdered sample with the Fe atom content 33.3 ± 0.1 % among all metal atoms, denoted by Mn_8Fe_4, was selected for the neutron diffraction experiments and extended XAFS (EXAFS) measurements.

The neutron diffraction experiments were performed at HRPT of Swiss Spallation Neutron Source. The measurements utilized an incident neutron whose wavelength $\lambda = 1.88570$ Å. The powdered sample were put in a cylindrical container with a volume $V = 8\ \text{mm}^2 \times 50$ mm. We collected the data at the temperature of 1.6 K in the angular range $5^{\circ} < 2\theta < 165^{\circ}$.

Both Fe and Mn K-edge absorption spectra were measured at the XAFS station of 4W1B beamline of Beijing Synchrotron Radiation Facility. The electron beam energy was 2.2 GeV and the maximum stored current was about 80 mA. The fixed-exit Si(111) flat double crystals were used as monochromator. The x-

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ray harmonics were minimized by detuning the two flat Si(111) crystals to about 60% of the maximum incident light intensity. Data for Mn and Fe K-edge were collected in a transmission mode by using ion chambers with mixed Ar/N_2 fill gas at room temperature.

3. Results and discussion

The neutron diffraction spectrum of the Mn_8Fe_4 was showed in Fig.1. The fitting and refinement of the diffraction spectrum were performed by using the FULLPROF program based on the Rietveld method.[11] The scattering lengths used in the refinement were taken from the internal table of the FULLPROF program.

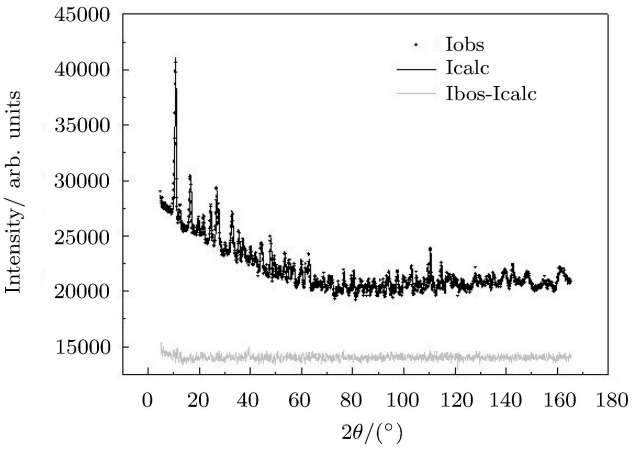


Fig.1. Neutron diffraction spectra of $[(Mn_8Fe_4)O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$ at $T = 1.6$ K measured on HRPT ($\lambda = 1.88570$ Å).

Because the effective diffractive peaks were not enough to determine all parameters, the refinements were based on the structure obtained by the single crystal x-ray diffraction.[7] Firstly we fixed the parameters related to the positions of Mn, C, and O and refined the parameters which could not be exactly determined by x-ray, such as the occupancies of Fe/Mn atoms and the positions of hydrogen atoms. Then we refined the parameters of carbon and oxygen atoms. Finally the parameters of Mn atoms were refined. In the whole procedure, the occupancies of Fe/Mn atoms were relaxed. The calculated spectrum and its difference from experimental spectrum are showed in Fig.1. The fitting factor R_p and R_{wp} are both 15.7 and the χ^2 factor is 2.25. Figure 2 gives the molecular structure of Mn_8Fe_4. The parameters of the atoms are listed in Table 1. We can see that all Fe atoms should occupy Mn(3) sites.

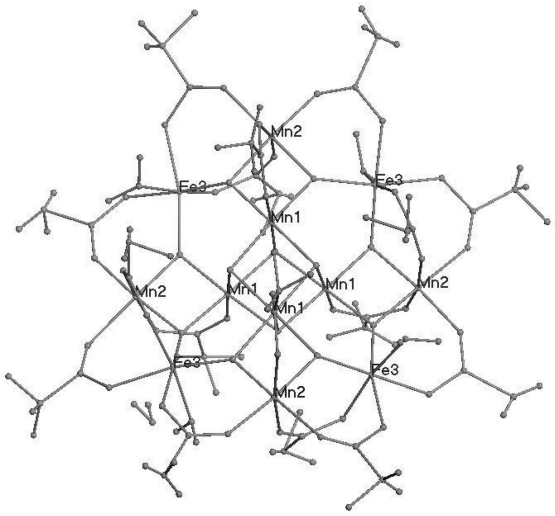


Fig.2. The molecular structure of Mn_8Fe_4.

Table 1. The metallic atom parameters of Mn_8Fe_4.

Atom	x	y	z	Occupation
Mn(1)	0.017(2)	0.083(2)	0.076(2)	1.000(12)
Fe(1)	0.017(2)	0.083(2)	0.076(2)	−0.002(12)
Mn(2)	0.048(2)	0.240(2)	0.086(3)	0.982(17)
Fe(2)	0.048(2)	0.240(2)	0.086(3)	−0.004(17)
Mn(3)	−0.1410(9)	0.1955(9)	0.0229(12)	−0.02(3)
Fe(3)	−0.1410(9)	0.1955(9)	0.0229(12)	1.00(3)

The Fe and Mn K-edge EXAFS functions $k^3\chi(k)$ and their Fourier transformations (FT) of Mn_8Fe_4 sample are shown in Figs.3(a) and 3(b) respectively. The FT is performed by using the k-region from 2.3 to 11.4 Å^{-1} and a Hanning window. It can be observed that the oscillations of Fe K-EXAFS function as shown in Fig.3(a) are weaker than that of Mn K-EXAFS function in high-k region extended to 12 Å^{-1}. There are three stronger peaks located at about 1.5, 2.3 and 3.1 Å in the FT curve in Fig.3(b). The first peak is attributed to the nearest six oxygen atoms. The second and third peaks are mainly associated with Fe–Mn/ Mn–Mn coordination shell in the higher shells.

Both Fe and Mn K-edge EXAFS simulations are performed by using FEFF8.2 code. The molecular structure parameters used in the calculations are determined by our XRD results. As shown in Fig.3, the calculations of Fe and Mn K-edge EXAFS functions and their FT are carried out for Fe occupied in Mn(1)

(dotted curve), Mn(2) (dashed curve) and Mn(3) sites (solid curve) respectively. It can be clearly seen that the main features of the calculated curves of Mn(3) site for both Fe K-edge EXAFS function $k^3\chi(k)$ and its FT are in good agreement with those of the experimental curves. It suggests that the coordination environment of Fe atoms in our Mn_8Fe_4 sample is identical with that of Mn atoms occupied at Mn(3) sites in the Mn_{12}. Therefore the XAFS results reveal unambiguously that the Fe atoms in our Mn_8Fe_4 sample are inclined to occupy the Mn(3) sites in the Mn_{12} skeleton.

The results that Fe atoms all occupy Mn(3) sites in Mn_{12} skeleton support our previous works.[7,8] At the same time, it explained why the content of about 33% is the upper limit of Fe atom content in our crystals synthesized by our growth methods similar to Lis.[10]

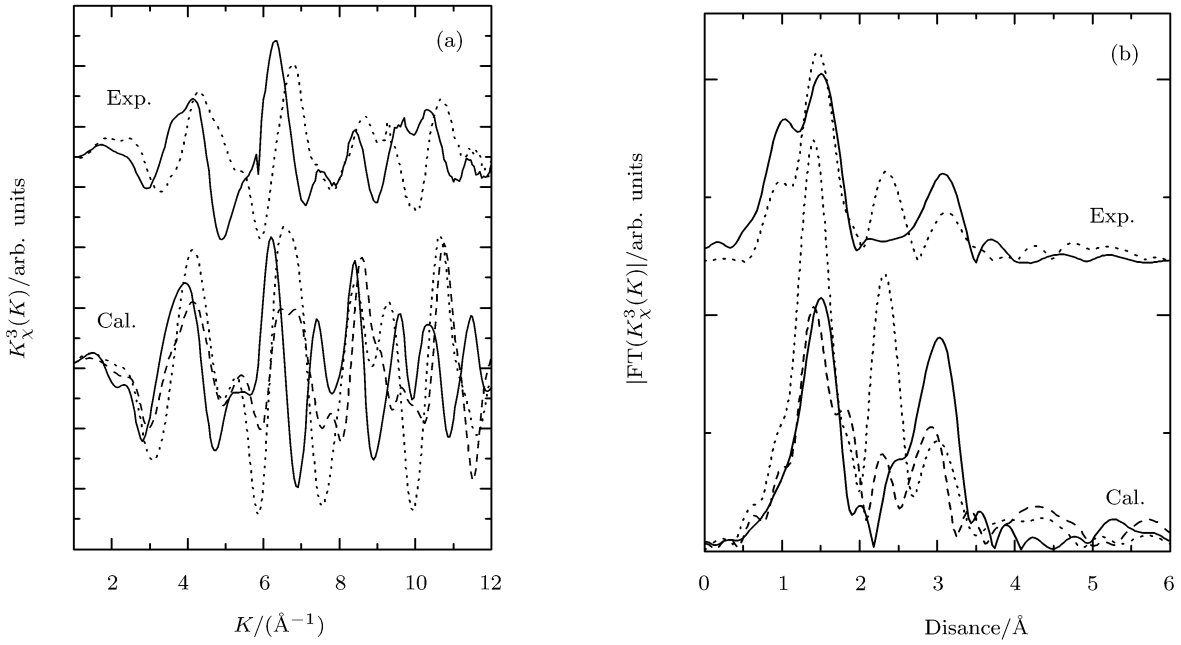


Fig.3. (a) The Fe (solid curve) and Mn (dotted curve) K-EXAFS experimental and calculated function $k^3\chi(k)$ of Mn_8Fe_4 sample are displayed in top and bottom respectively. The calculated $k^3\chi(k)$ functions correspond to Fe atom occupied on Mn(1)(dotted curve), Mn(2)(dashed curve) and Mn(3) (solid curve) sites respectively. (b) The Fe (solid curve) and Mn (dotted curve) experimental and calculated FT curves of Mn_8Fe_4 sample are displayed in top and bottom respectively. The calculated FT curves correspond to Fe atom occupied on Mn(1) (dotted curve), Mn(2) (dashed curve) and Mn(3) (solid curve) sites respectively.

4. Conclusion

The neutron diffraction, EXAF experiments as well as multiple scattering simulation presented that Fe atom substitutes Mn atoms in Mn(3) sites of the Mn_{12} skeleton. It means that the substitution occurs at the Mn(3) sites much more easily than the Mn(1) and Mn(2) sites, which is the reason that we could not obtain the Fe-substituted Mn_{12} sample with higher Fe atoms content than 33.3%. That is to say, Fe-substituted Mn_{12} series only includes the four single-molecule magnets of $Mn_{11}Fe_1$, $Mn_{10}Fe_2$, Mn_9Fe_3, and Mn_8Fe_4.

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