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Molecular structure of single-molecule magnet $Mn_{10}Fe_2$ and $Mn_{11}Cr^-$

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Introduction

Single-molecular magnet of $[Mn_{12}(AcO)_{16}(H_2O)_4]$ ($Ac=CH_3COO$) has extensively been investigated because of its interesting properties such as stepwise magnetization due to the quantum tunneling effect. Previously, we have investigated structural and magnetic properties of $Mn_{11}Cr$ (one Mn is substituted by one Cr) by means of several kinds of physical techniques including XAFS [1]. In this work, we will report further progress concerning $Mn_{10}Fe_2$ ($[Mn_{10}Fe_2O_{12}(AcO)16(H_2O)_4]$) and $Mn_{11}Cr^-$ ($[(Ph)_4P][Mn_{11}CrO_{12}(PhCOO)_{16}(H_2O)_4]$), which were successfully synthesized very recently. The single crystal x-ray diffraction analysis could not determine the positions of Fe or Cr because of the crystalline disorder. In such a case, EXAFS is the most suitable technique to determine the molecular structure since Fe or Cr may locate at one of the three inequivalent sites of Mn.

Experimental

Cr, Mn and Fe *K*-edge x-ray absorption spectra of Mn10Fe2/Mn12 (mixed crystal) and $Mn11Cr^-$ were recorded at BL9A with a conventional transmission mode at room temperature.

Results and discussion

Figure 1 depicts the Fourier transforms of the Fe and Mn *K*-edge EXAFS functions $k^3\chi(k)$ functions. The employed k range is around 2.5-10.3 $Å^{-1}$. The Fourier transform of Fe (red curve) gives two distinct peaks at 1.5 and 3.1 Å, while the Mn one (green) shows three prominent peaks at 1.3, 2.4, and 3.2 Å. The shortest distance (1.3-1.5 Å) is assignable to the O shells around Fe or Mn, and the other two shells at 2.4-3.2 Å are ascribed to those of Fe-Mn or Mn-Mn.

In order to determine the Fe site, we have performed theoretical simulations by using FEFF8 assuming the molecular structure determined in the single-crystal x-ray diffraction analysis. The x-ray molecular structure gives the average structure where Fe is not distinguished from Mn and is almost identical with the Mn_{12} one. In one molecule, there exist three types of Fe/Mn sites: sites **a**, **b** and **c**, as shown in the inset in Fig. 1. Site **a** is occupied by Mn^{4+}, which gives the simulation results of the blue curve in Fig. 1. Sites **b** and **c** are for Mn^{3+} in Mn_{12}, which show the results of the lighjt-blue and pink curves in Fig. 1, respectively. The experimental Fourier transform of Mn (green) can be well understood as a superposition of the three theoretical curves. This is consistent with the fact that the Mn ions occupy the three sites, and in other words, this finding justifies the present analysis procedure. In contrast, the Fourier transform of Fe is similar to the simulated one of site **c**. It is thus concluded that, in $Mn_{10}Fe_2$, Fe^{3+} exclusively occupies site **c**, the tilted site for Mn^{3+} in the Mn_{12} skeleton. This result is essentially the same as in $Mn_{11}Cr$ previously investigated [1].

The magnitude of the Fourier transform of the experimental Fe-O shell (R=2.08±0.01 Å) is much stronger than that of the theoretical one of site **c**. This is however easily understandable. The Mn^{3+} ion in site **c** exhibits significantly distorted octahedron due to the Jahn-Teller effect, resulting in the suppression of the Mn-O contribution in the simulation. On the contrary, the Fe^{3+} ion shows no Jahn-Teller distortion, yielding more intense Fe-O contribution in the Fourier transform.

The molecular structure of $Mn_{11}Cr^-$ has been determined in a similar manner. The specimen shows more complicated structure because of the presence of one Mn(II) ion, and strictly speaking, all the metal ions should be crystallographically inequivalent to each other. However, the EXAFS results show similar features to those of $Mn_{10}Fe_2$ and $Mn_{11}Cr$, and one can conclude that Cr(III) locates exclusively at site **c**. The obtained Cr-O interatomic distance is 1.86±0.01 Å.

In conclusion, the Fe and Cr substituted sites in $Mn_{10}Fe_2$ and $Mn_{11}Cr^-$ were determined as site **c** in Fig. 1, this consequence being identical with the $Mn_{11}Cr$ one.

References

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