# Molecular structure of single-molecule magnet Mn11Cr

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## Introduction

Single-molecular magnet of $[Mn_{12}(AcO)_{16}(H_2O)_4]\cdot 4H_2O$ (Ac=$CH_3CO_2$) has extensively been investigated because of its interesting properties such as stepwise magnetization due to the quantum tunneling effect. One of the outstanding features of molecular magnets is the ease of chemical modification. In this work, we have synthesized a Mn11Cr cluster with a half-integer spin of $S$=19/2. Although the single crystal x-ray diffraction analysis has been performed, the location of Cr cannot be determined because of the crystalline disorder of the Cr position. In such a case, EXAFS is the most suitable technique to determine the molecular structure since in one molecule Cr may locate at one of the three inequivalent sites of Mn.

## Experimental

Cr and Mn K-edge x-ray absorption spectra of a Mn11Cr/Mn12 mixed crystal were recorded at BL9A with a conventional transmission mode at room temperature. The ratio of Mn11Cr and Mn12 was found to be almost 1:1. A Si(111) double crystal monochromator was employed and detuned by 40% to suppress higher-order harmonics. Both the incident and transmitted X-ray intensities were measured by ionization chambers filled with pure $N_2$.

## Results and discussion

The EXAFS functions of $k^3\chi(k)$ were obtained by the standard procedures. Figure 1 depicts the Fourier transforms of the Cr and Mn K-edge $k^3\chi(k)$ functions. The employed $k$ range is around 2.5-11.0 Å$^{-1}$. The Fourier transform of Cr gives two distinct peaks at 1.3 and 3.0 Å, while the Mn one shows three prominent peaks at 1.3, 2.4, and 3.0 Å. The shortest distance (1.3 Å) is assignable to the O shells around Cr or Mn, and the other two shells at 2.4 and 3.0 Å are ascribed to those of Cr-Mn or Mn-Mn.

In order to determine the Cr 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 Cr is not distinguished from Mn and is almost identical with the Mn12 one. In one molecule, there exist three types of Cr/Mn sites: Sites **1**, **2**, and **3**, as shown in Fig. 2. Site **1** is occupied by Mn$^{4+}$, which gives the simulation results of the dotted line in Fig. 1. Sites **2** and **3** are for Mn$^{3+}$ in Mn12, which show the results of the dot-dashed and dashed lines in Fig. 1, respectively. The experimental Fourier transform of Mn (dot-dot-dashed line) 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 Cr (solid line) is similar to the simulated one of Site **3**. It is thus concluded that, in Mn11Cr, Cr$^{3+}$ exclusively occupies Site **3**, the tilted site for Mn$^{3+}$ in the Mn12 skeleton.

The magnitude of the Fourier transform of the experimental Cr-O shell is much stronger than that of the theoretical one of Site **3**. This is however easily understandable. The Mn$^{3+}$ ion in Site **3** 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 Cr$^{3+}$ ion shows no Jahn-Teller distortion, yielding more intense Cr-O contribution in the Fourier transform.

In conclusion, the Cr ion locates exclusively at Site (3) with normal valency of Cr(III).
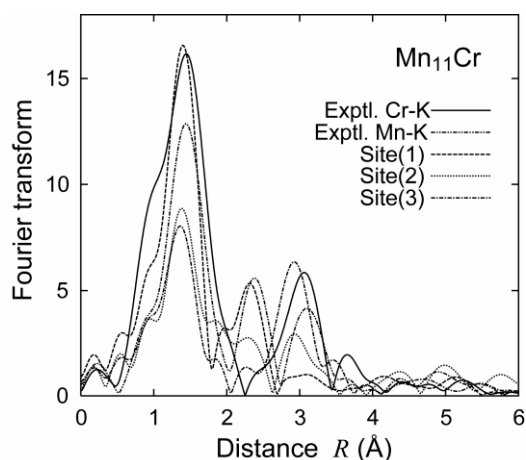


Fig. 1: Fourier transforms of the Cr (solid line) and Mn (dot-dot-dashed) K-edge $k^3\chi(k)$ functions, together with the FEFF simulation results for sites (1) (dotted), (2) (dot-dashed) and (3) (dashed).
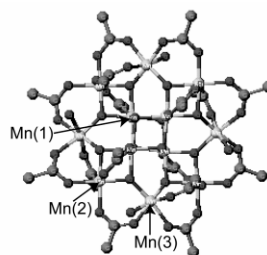


Fig. 2: Molecular structure of Mn12. Mn atoms locate three inequivalent sites (1), (2) and (3).

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