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PES and XAS studies of Mn12-Ac molecular magnet

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Abstract

The electronic structure of Mn12-Ac has been investigated using photoemission spectroscopy (PES) and X-ray absorption spectroscopy (XAS). The PES spectrum indicates that Mn 3d states are located near the top of the valence band, and the Mn 2p XAS spectrum provides clear evidence for the Mn^{3+}–Mn^{4+} mixed-valent states.

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$[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$, generally referred to as Mn12 acetate (Mn12-Ac), has been investigated extensively due to the possibility of studying magnetism on a molecular scale [1–3]. The steps observed in the magnetization hysteresis curves at low temperature (T) have been interpreted as due to quantum tunneling. According to a polarized neutron diffraction experiment [4], the inner tetrahedron of four Mn^{4+} ions ($S=\frac{3}{2}$) is polarized antiparallel to the outer ring of eight Mn^{3+} ions ($S=2$), resulting in the high-spin $S=10$ ground state, which, together with its large easy-axis anisotropy, is then considered to give rise to the superparamagnetic behavior at low T [5].

In order to understand the unusual magnetic behavior of molecular magnets, it is important to investigate the electronic structures of these systems. Photoemission spectroscopy (PES) is one of the powerful experimental methods for providing direct information on the electronic structures of solids. In this paper, we report the PES and soft X-ray absorption spectroscopy (XAS) study of Mn12-Ac using synchrotron radiation. PES and XAS experiment was performed on Mn12-Ac single crystals [6]. PES and XAS spectra were obtained at the 2B1 beamline of the PAL at room temperature with the FWHM of about 0.1–0.6 eV between $h\nu\sim 30$ eV and $h\nu\sim 600$ eV. XAS spectra were obtained by employing the total electron yield method.

Fig. 1 shows the valence-band spectra of Mn12-Ac for 25 eV$\leqslant h\nu\leqslant$1486.6 eV, scaled at the peak maxima. The valence-band spectra for Mn12-Ac shows the negligible spectral weight near E_F, consistent with the insulating nature of Mn12-Ac.[1] As shown in the inset, the valence-band spectrum of Mn12-Ac at a low $h\nu$ ($\approx$30 eV) is dominated by the O 2p electron emission. Therefore, compared to the negligible spectral weight near E_F for $h\nu\leqslant 50$ eV, an enhanced emission near the top of the valence band at $h\nu=500$ and 1486.6 eV indicates that the Mn 3d states are located near the top of the valence band, in agreement with the DVM calculation for Mn12-Ac [7].

Fig. 2 shows the Mn 2p XAS spectrum of Mn12-Ac, in comparison with those of reference materials having the formal Mn valences of 2+, 3+, and 4+. The data for MnO (Mn^{2+}), Mn_2O_3(Mn^{3+}), and MnO_2(Mn^{4+}) were reproduced from Ref. [8], Ref. [9], and Ref. [8], respectively, and shifted by −0.9, 0.7 and −1.8 eV, respectively. The Mn $2p_{3/2}$ XAS spectrum of Mn12-Ac shows three sharp structures (labeled as A, B, C). This comparison indicates that these three structures in

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[1] Since Mn12-Ac is insulating, there is ambiguity in E_F by about ~1 eV.

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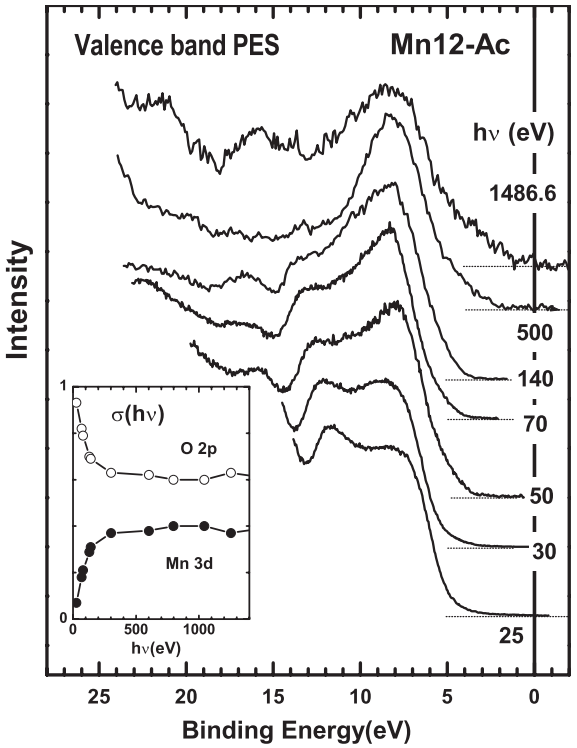

Fig. 1. Valence-band spectra of Mn12-Ac for 25 eV $\leqslant h\nu \leqslant$ 1486.6 eV. Inset: the atomic photoionization cross-sections $\sigma_1(h\nu)$ of O 2p and Mn 3d electrons in Mn12-Ac.

Mn12-Ac originate from the mixture of the different valence states, such as Mn^{2+} (A), Mn^{3+} (B), and Mn^{4+} (C) ions. The origin of the Mn^{2+} valence state in Mn12-Ac is not clear at the moment. On the other hand, the sharp shoulder below the main peak in MnO ($\sim$640 eV) is not observed in Mn12-Ac, probably because the amount of Mn^{2+} ions is rather small and/or the local symmetry around Mn ions in Mn12-Ac is different from that in MnO. In any case, the Mn 2p XAS spectrum provides clear evidence that Mn ions in Mn12-Ac are in the mixed-valence states, mainly in Mn^{3+}–Mn^{4+} states.

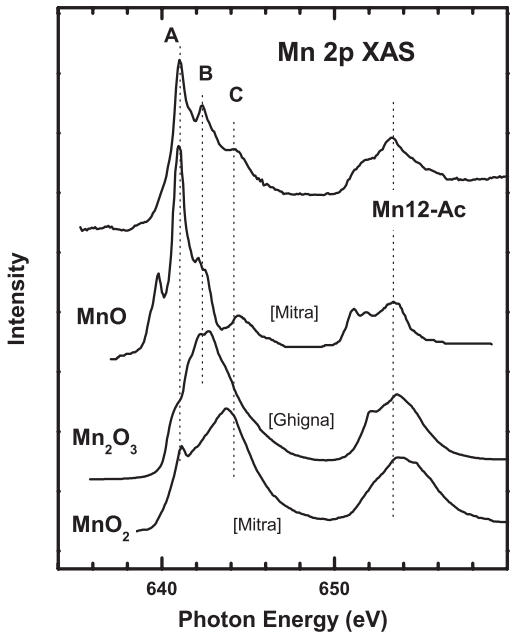

Fig. 2. Comparison of the Mn 2p XAS spectra of Mn12-Ac, MnO (Ref. [8]), Mn_2O_3 (Ref. [9]), and MnO_2 (Ref. [8]).

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