

Investigation of the Electronic Structure of Mn12 Molecular Magnet Using Synchrotron Radiation

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(Received 2 December 2003)

The electronic structure of Mn12-Ac molecular magnet has been investigated using synchrotron radiation. The valence-band photoemission spectroscopy (PES) measurement reveals that Mn 3d states are located near the top of the valence band. The trend in the measured valence-band PES spectra is found to be consistent with that in the calculated local density of states. The Mn 2p x-ray absorption spectroscopy (XAS) measurement provides evidence for the Mn³⁺-Mn⁴⁺ mixed-valent states.

Key words : molecular magnet, Mn12-Ac, photoemission spectroscopy, x-ray absorption spectroscopy

1. Introduction

[Mn₁₂O₁₂(CH₃COO)₁₆(H₂O)₄] · 2CH₃COOH · 4H₂O, generally referred to as Mn12 acetate (Mn12-Ac), has been investigated intensively because of the possibility of studying magnetism on a molecular scale [1-4]. The steps observed in the magnetization hysteresis curves at low temperature (T) have been interpreted as due to quantum tunneling [2-4]. According to a polarized neutron diffraction experiment [5], the inner tetrahedron of Mn⁴⁺ ions ($S = 3/2$) is polarized antiparallel to the outer ring of Mn³⁺ 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 [6].

In order to understand the unusual magnetic behavior of molecular magnets, it is important to investigate the electronic structures of these systems [7, 8]. Photoemission spectroscopy (PES) and x-ray absorption spectroscopy (XAS) are the powerful experimental methods for providing direct information on the electronic structures and the valence states of solids. In this paper, we report the

valence-band PES and the Mn 2p XAS study of Mn12-Ac using synchrotron radiation. We also compare the measured valence-band PES spectra to the calculated local density of states (LDOS).

2. Experimental Details

Black parallelepiped Mn12-Ac single crystals (average dimensions of 0.3 × 0.3 × 2.0 mm) were prepared using the procedure reported by Lis [1, 9]. Chemical analysis and magnetic measurements confirmed the purity of the prepared Mn12-Ac samples. PES and XAS measurements were performed at the 2B1 beamline of the Pohang Accelerator Laboratory (PAL), equipped with a SCIENTA SES100 analyzer. PES and XAS spectra were obtained at room temperature with the pressure better than 2 × 10⁻⁹ Torr. The Fermi level E_F and the overall instrumental resolution (FWHM) of the system were determined from the valence-band spectrum of a sputtered Au foil in electrical contact with a sample [10]. The FWHM was about 100 meV for a photon energy $h\nu \sim 30$ eV and about 600 meV for $h\nu \geq 600$ eV. XAS spectra were obtained by employing the total electron yield method.

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3. Results and Discussion

Fig. 1 shows the valence-band spectra of Mn12-Ac for $25 \text{ eV} \leq h\nu \leq 1486.6 \text{ eV}$, scaled at the peak maxima. The valence-band spectra for Mn12-Ac shows the negligible spectral weight near E_F , which is consistent with the insulating nature of Mn12-Ac. In general, the different line shapes for different $h\nu$ -values reflect the matrix element effect, namely, the different relative strengths in the photoionization cross sections. The inset shows the relative strengths of the photoionization cross sections $\sigma_i(h\nu)$ of the Mn 3d and O 2p electrons per formula unit (f.u.) of Mn12-Ac. Here we have counted 56 O atoms and 12 Mn atoms per f.u., and assumed a mixed valence of ~ 3.33 for the Mn ions, consisting of 4 Mn^{4+} ($3d^3$) ions and 8 Mn^{3+} ($3d^4$) ions, and the filled O 2p bands ($2p^6$). The contributions from C atoms (36) is ignored because the C 2p electron emission is negligible ($\leq 3\%$) with respect to other electron emissions for $h\nu \geq 100 \text{ eV}$ [11] and C atoms are not involved in bonding with Mn ions directly.

The inset clearly shows that, as $h\nu$ increases, the cross section of the O 2p electrons decreases with respect to that of the Mn 3d electrons. Consequently the valence-

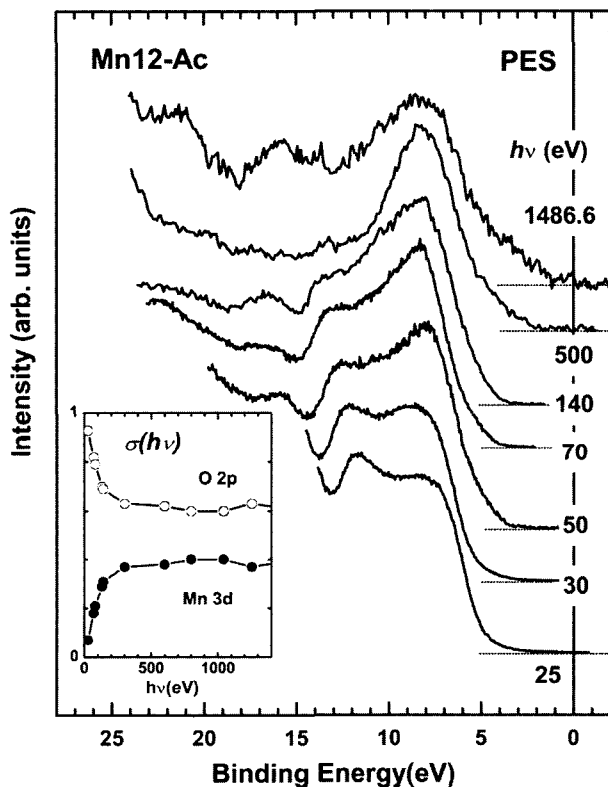


Fig. 1. Valence-band PES spectra of Mn12-Ac for $25 \text{ eV} \leq h\nu \leq 1486.6 \text{ eV}$. Inset: The atomic photoionization cross sections $\sigma_i(h\nu)$ of O 2p and Mn 3d electrons in Mn12-Ac.

band spectrum of Mn12-Ac at a low $h\nu$ ($\approx 30 \text{ eV}$) can be considered to represent the measured O 2p partial spectral weight (PSW) distribution. Then the difference between the valence-band spectrum at a low $h\nu$ ($\sim 30 \text{ eV}$) and that at a high $h\nu$ ($< 500 \text{ eV}$) reflects the contribution from the increasing Mn 3d electron emission. Therefore an enhanced emission near the top of the valence-band at $h\nu = 1486.6 \text{ eV}$, compared to the negligible spectral weight near E_F for $h\nu \leq 50 \text{ eV}$, indicates that the Mn 3d states in Mn12-Ac are located near the top of the valence band. This identification of the electronic states in the valence-band spectra is supported by the comparison made in Fig. 2. The similar line shapes of the valence-band spectrum of Mn12-Ac for different $h\nu$ -values reflect the large hybridization between Mn 3d and O 2p states (see Fig. 2).

The top panel of Fig. 2 shows the calculated local density of states (LDOS) of the Mn atom and the O atom of Mn12-Ac, respectively. We have determined the average LDOSs of Mn and O atoms by taking an weighted average of the calculated spin-polarized LDOSs

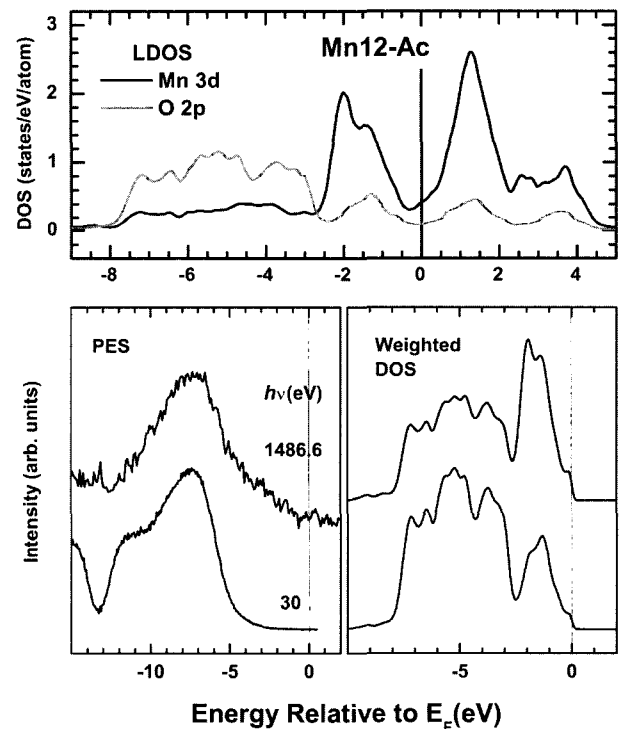


Fig. 2. Top: The local density of states (LDOS) of Mn 3d and O 2p electrons per atom. These LDOSs are constructed by using the calculated spin-polarized LDOSs in Ref. [7]. Bottom: Comparison of the measured valence-band PES spectra (left) at $h\nu = 30 \text{ eV}$ and $h\nu = 1486.6 \text{ eV}$ with the corresponding LDOSs (right) of the Mn 3d and the O 2p states. The LDOSs were determined using the calculated results of Ref. [7]. See the text for details.

of different atomic types in Ref. [7]. These spin-polarized LDOSs were calculated using the discrete variational method (DVM) in the local density-functional approximation (LDA) [7]. The left low panel of Fig. 2 show the valence-band PES spectra, obtained at $h\nu=30$ eV and $h\nu=1486.6$ eV. The right low panel of Fig. 2 show the weighted sum of spin-averaged Mn 3d and O 2p LDOSs, corresponding to $h\nu=30$ eV and $h\nu=1486.6$ eV, respectively. The comparison made in the low panel reveals that the major trend observed in the measured valence-band spectra (left) is consistent with that in the calculated LDOS (right). That is, the DOS near E_F increases with increasing $h\nu$. This trend arises from the increased contribution from the Mn LDOS with increasing $h\nu$ (see the top of Fig. 2), which has been explained in the description of the inset of Fig. 1. This finding supports the above assignment of the Mn e_g states to that near E_F (see Fig. 1).

Despite the finding that the trend in the experimental PES spectra of Mn12-Ac is consistent with that in the calculated LDOS, some discrepancies are also observed between theory and experiment. First, the calculated

energies of the Mn 3d and O 2p states are quite different from the measured values. Second, the metallic DOS in the calculated LDOS does not agree with the nearly zero spectral weight near E_F in the measured PES spectra. The most likely factor causing such discrepancies might be the strong on-site Coulomb interaction U between Mn 3d electrons that was not included in the DVM calculations. It is generally known that the LDA approach does not describe well the electronic structures of strongly correlated electron systems and insulators and the LDA was employed in calculating the spin-polarized LDOSs of Mn12-Ac [7]. Indeed, the metallic ground state for Mn12-Ac, predicted from the DVM calculations, is contradictory to the insulating nature of Mn12-Ac. Therefore, a more realistic theoretical model including the effect of U is required to describe the electronic structure of Mn12-Ac more precisely. More precise experiment will also help to resolve these discrepancies.

Fig. 3 shows the $2p_{3/2}$ part of the Mn 2p XAS spectrum of Mn12-Ac. It is well known that the peak positions and the line shape of the transition-metal (TM) 2p XAS spectrum depend on the local electronic structure of the TM ion, and so the TM 2p XAS spectrum provides the information about the valence state and the ground state symmetry of the TM ion [12, 13]. In order to estimate the valence state of Mn ions in the ground states, we have analyzed the Mn 2p XAS spectrum of Mn12-Ac within the configuration interaction (CI) cluster model where the effects of the multiplet interaction, the crystal field, and the hybridization with the O p ligands are included [13]. In this analysis, we have considered two configurations, d^n and $d^{n+1}\underline{L}^1$ (\underline{L} : a ligand hole), under the octahedral (O_h) symmetry. Note that the local environment of the Mn ions in Mn12-Ac has a distorted O_h symmetry. In the calculation of the Mn^{3+} ($n=4$) and Mn^{4+} ($n=3$) XAS spectra, we have used the same parameters as used for Mn^{3+} and Mn^{4+} in Ref. [12]. We have checked that small changes in the parameters do not affect the overall spectral shape including the prominent peak positions.

The calculated XAS spectrum is shown at the bottom of Fig. 3. We have found that including two configurations, corresponding to Mn^{3+} (d^4) and Mn^{4+} (d^3), and the O_h crystal field energy of $10Dq=1.0$ eV yields a good fit for the measured 2p XAS spectrum [14]. Therefore the calculated Mn 2p XAS spectrum reveals that the ground states of Mn ions in Mn12-Ac are strongly mixed-valent with the Mn^{3+} and Mn^{4+} configurations. This finding is consistent with the local symmetry of Mn ions in Mn12-Ac. Since the Mn ions in Mn12-Ac have the O_h coordinations, four Mn^{4+} ions and eight Mn^{3+} ions are expected to have the $t_{2g}^3 e_g^1$ and $t_{2g}^3 e_g^0$ configurations,

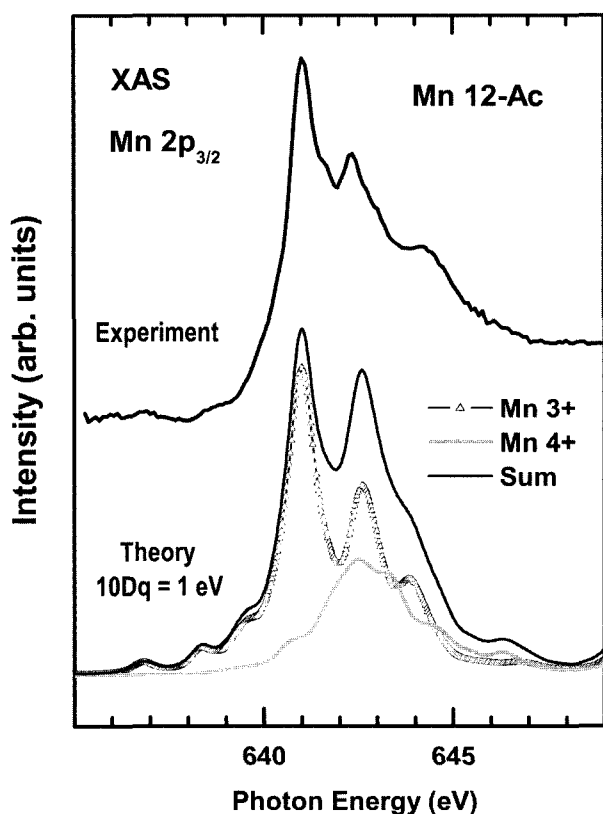


Fig. 3. Comparison of the measured Mn 2p XAS spectrum (top) with the fitting results (bottom). In the calculated XAS spectrum, the triangles, grey lines, and solid lines denote the Mn^{3+} and Mn^{4+} components, and their sum, respectively.

respectively, resulting in an inhomogeneous mixed-valence of about ~ 3.33 .

4. Conclusion

We have investigated the electronic structure of Mn12-Ac by using synchrotron radiation. It is found that the Mn $3d$ states in Mn12-Ac are located near the top of the valence band. The trend in the measured valence-band spectra for Mn12-Ac is consistent with that in the calculated LDOS, supporting the finding that the Mn e_g states are located near E_F . The Mn $2p$ XAS spectrum provides evidence for the Mn³⁺-Mn⁴⁺ mixed-valent states.

Acknowledgements

This work was supported by the KRF (KRF-2002-070-C00038) and in part by the 2003 Research Fund of the Catholic University of Korea. The PAL is supported by the MOST and POSCO in Korea.

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