Magnetic Frustration in a Mn Honeycomb Lattice Induced by Mn-O-O-Mn Pathways

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We investigated the electronic structure of layered Mn oxide Bi3Mn14O12(NO3) with a Mn honeycomb lattice by x-ray absorption spectroscopy. The valence of Mn was determined to be 4+ with a small charge-transfer energy. We estimated the values of superexchange interactions up to the fourth nearest neighbors (J1, J2, J3, and J4) by unrestricted Hartree-Fock calculations and a perturbation method. We found that the absolute values of J1 through J4 are similar with positive (antiferromagnetic) J1 and J4, and negative (ferromagnetic) J2 and J3, due to Mn-O-O-Mn pathways activated by the smallness of charge-transfer energy. The negative J3 provides magnetic frustration in the honeycomb lattice to prevent long-range ordering.

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Since the resonating valence bond state in geometrically frustrated magnets has been proposed by Anderson [1], spin-disordered ground states in Mott insulators on frustrated lattices have been attracting great interest in condensed-matter physics. The exchange interaction J in a Mott insulator is roughly given by −2t2/Eg, where t is the transfer integral between the two localized orbitals and Eg is the excitation energy across the Mott gap. In Mott insulators on frustrated lattices, spin-disordered systems including organic and inorganic materials [2–6] all have relatively small Eg, suggesting that the smallness of Eg or the closeness to the Mott transition would be important to realize the spin-disordered ground states.

Various insulating transition-metal oxides are known as Mott insulators and can be classified into (i) the Mott-Hubbard type insulators where the Mott gap Eg is mainly determined by the Coulomb interaction U between the transition-metal d electrons and (ii) the charge-transfer type insulators where Eg is determined by the charge-transfer energy Δ from the oxygen p state to the transition-metal d state [7]. Therefore, the smallness of Eg can be obtained in transition-metal oxides with small U or small Δ. In the small U case, theoretical studies on triangular-lattice Hubbard models proved that a spin-disordered phase is realized near the Mott transition [8–11], which could be related to the higher order exchange terms. As for the small Δ case, in addition to the higher order terms, the exchange pathways through the oxygen p state may give unexpectedly long ranged exchange terms and may affect the spin disordering.

Very recently, a spin-disordered ground state is reported in a layered Mn oxide Bi3Mn14O12(NO3) with a Mn honeycomb lattice in which the exchange interaction between second neighbor Mn sites introduces a kind of frustration in the honeycomb lattice [12]. In this material, there is a network of MnO6 octahedrons and Fig. 1 shows the definitions of interactions in the nearest-neighbor J1, the second nearest-neighbor J2, the third nearest-neighbor J3, and the fourth nearest neighbor J4.

FIG. 1: (Color online): Network of MnO6 octahedrons in the honeycomb lattice with the definitions of interactions in the nearest-neighbor J1, the second nearest-neighbor J2, the third nearest-neighbor J3, and the fourth nearest neighbor J4.
third nearest-neighbor $J_3$, and the fourth nearest neighbor $J_4$. The exchange interaction $J_2$ between second neighbor sites could be derived from the Mn-O-O-Mn exchange pathways which becomes important in small $\Delta$ systems. The values of these interactions were studied both theoretically \cite{footnote12} and experimentally by inelastic neutron scattering \cite{footnote13}. In these studies, only $J_1$ and $J_2$ are considered by assuming that the values of $J_3$ and $J_4$ are small enough to be neglected. However, since the exchange interaction $J_3$ between the third neighbor sites is also derived from the Mn-O-O-Mn exchange pathways, it is not a trivial question whether $J_3$ is negligible compared to $J_2$ or not. In this context, it is very interesting and important to study the electronic structure of the Mn oxide, especially the values of interactions $J_1$ - $J_4$, using spectroscopic methods and to reveal the origin of the spin-disordered state from the electronic structural viewpoint. In this paper, we investigated the electronic structure of this material by x-ray absorption spectroscopy (XAS), and also estimated the values of magnetic interactions. Unrestricted Hartree-Fock calculations and a perturbation method revealed that the nearest neighbor and fourth nearest neighbor $J_1$ and $J_4$ are positive (antiferromagnetic), and the next nearest neighbor and third nearest neighbor $J_2$ and $J_3$ are negative (ferromagnetic). In the present analysis, the ferromagnetic $J_2$ does not introduce magnetic frustration in the honeycomb lattice. We conclude that the ferromagnetic $J_3$ is the origin of magnetic frustration and the absence of long-range ordering in this material.

The synthesis of Bi$_3$Mn$_4$O$_{12}$(NO$_3$) polycrystalline powder is described in Ref. \cite{footnote12}. X-ray absorption experiments were performed at 11ID-1 (SGM) of the Canadian Light Source. The spectra were measured in the total-electron-yield (TEY) mode. The total energy resolution was set to 100 meV. All the spectra were measured at room temperature. The obtained spectrum is analyzed by standard cluster-model calculations \cite{footnote13} to obtain electronic parameters. The parameters in this model are 3d - 3d and 3d - 2p Coulomb interactions ($U_{dd}$ and $U_{dc}$, respectively), charge-transfer energy from O 2p to Mn 3d states $\Delta$, hopping integrals between Mn 3d and O 2p molecular states $[V(t_{2g})$ and $V(\epsilon_g)]$, and crystal field parameter 10$Dq$. The superexchange interactions are evaluated using unrestricted Hartree-Fock calculation with a multi-band $d$ – $p$ Hamiltonian with Mn 3d and O 2p states \cite{footnote16}. The Hamiltonian is given by

$$H = H_p + H_d + H_{pd},$$

$$H_p = \sum_{k,l,\sigma} \epsilon_{k,l,\sigma} n_{k,l,\sigma} + \sum_{k,l \neq k',l'} V_{k,l,\sigma}^{p,p'} n_{k,l,\sigma} n_{k',l',\sigma} + H.c.,$$

$$H_d = \sum_{k,m,\sigma} \epsilon_{d,k,m,\sigma} n_{d,k,m,\sigma} + \sum_{k,m > m',\sigma} V_{d,k,m,m',\sigma} n_{d,k,m,\sigma} n_{d,m,m',\sigma} + H.c.$$

$$+ \sum_{i,m} d_{i,m,\uparrow}^{\dagger} n_{i,m,\uparrow} + d_{i,m,\downarrow}^{\dagger} n_{i,m,\downarrow} + \sum_{i,m \neq m'} d_{i,m,\uparrow}^{\dagger} n_{i,m,\uparrow} + d_{i,m',\downarrow}^{\dagger} n_{i,m',\downarrow} + (u' - j') \sum_{i,m > m',\sigma} d_{i,m,\sigma}^{\dagger} n_{i,m,\sigma} d_{i,m',\sigma}^{\dagger} n_{i,m',\sigma} + j' \sum_{i,m \neq m'} d_{i,m,\sigma}^{\dagger} n_{i,m,\sigma} d_{i,m',\sigma}^{\dagger} n_{i,m',\sigma} + H_p.$$

Here, $d_{i,m,\sigma}^{\dagger}$ are creation operators for the Mn 3d electrons at site $i$. $d_{i,m,\sigma}$ and $p_{k,l,\sigma}^{\dagger}$ are creation operators for Bloch electrons with momentum $k$ which are constructed from the $m$-th component of the Mn 3d orbitals and from the $l$-th component of the O 2p orbitals, respectively. The intra-atomic Coulomb interaction between the Mn 3d electrons is expressed using Kanamori parameters, $u$, $u'$, $j$ and $j'$ satisfying the relations $u = u' + j + j'$ and $j = j'$. The transfer integrals between the Mn 3d and O 2p orbitals $V_{k,lm}$ are given in terms of Slater-Koster parameters $(pd\sigma)$ and $(pd\tau)$. The parameters determined by the cluster-model calculation are used as input of the unrestricted Hartree-Fock analysis.

Figure 2 shows the Mn 2p XAS spectrum of Bi$_3$Mn$_4$O$_{12}$(NO$_3$). There are two structures, Mn 2p$_3/2 \rightarrow 3d$ absorption at 640 - 650 eV and Mn 2p$_1/2 \rightarrow 3d$ absorption at 650 - 660 eV. The experimental spectrum has a sharp peak at $\sim 641.5$ eV characteristic of Mn$^{4+}$, concluded by comparing with the reference data of Mn$^{2+}$ (MnO), Mn$^{3+}$ (LaMnO$_3$) and Mn$^{4+}$ (EuCoO$_5$,MnO$_3$ and SrMnO$_3$) from Ref. \cite{footnote17}. This indicates that the valence of Mn is 4+ in Bi$_3$Mn$_4$O$_{12}$(NO$_3$), consistent with the valence state of Bi$_3^{4+}$Mn$_4^{4+}$O$_{12}^-(NO_3)^-$ obtained in Ref. \cite{footnote12}. We performed configuration-interaction (CI) cluster-model calculations \cite{footnote13} to obtain electronic parameters. Here we fixed the following values $U_{dd} = 6.0$ eV, $U_{dc} = 7.5$ eV, $V(\epsilon_g) = 3.0$ eV, and $10Dq = 1.3$ eV and changed the value of $\Delta$ from 0.0 eV to 4.0 eV, as shown in Fig. 2 (a). The calculated spectra do not depend on the value of $\Delta$ so much, but the small $\Delta$ values of $1.0 \pm 1.0$ eV reproduce the experiment most successfully from a peak at $\sim 641.5$ eV and Mn 2p$_1/2$ structures.
Bi octahedron. Here $\Delta$ denotes the charge-transfer energy $6_t$ively, for the honeycomb lattice with the regular MnO $t$ spin analysis. The ratio $(1−d_{2g})/d_{2g}$ is fixed at $0.3, 0.15, −0.3, and 0.15$ eV, respectively, for the honeycomb lattice with the regular MnO$_6$ octahedron. Here $\Delta$ denotes the charge-transfer energy specifically $\Delta = \epsilon_d − \epsilon_p + 3U$.

With this parameter set, the lowest energy state is found to be the conventional antiferromagnetic state where the first neighboring sites are antiferromagnetically coupled. In the antiferromagnetic ground state, the second, third, and forth neighboring sites are ferromagnetically, antiferromagnetically, and antiferromagnetically coupled, respectively. We have calculated energies of ferromagnetic state as well as modified antiferromagnetic states which are obtained by exchanging spins of some neighboring sites in the ground state. As expected, the ferromagnetic state is very much higher in energy than the antiferromagnetic ground state. However, some of the modified antiferromagnetic states were found to have energies very close to that of the ground state. By mapping the Hartree-Fock energies to the Heisenberg model with $J_1, J_2, J_3$, and $J_4$, the obtained values are:

$$
\begin{align*}
J_1 & = 9.15 \text{ meV} \\
J_2 & = −5.32 \text{ meV} \\
J_3 & = −4.80 \text{ meV} \\
J_4 & = 5.77 \text{ meV}
\end{align*}
$$

While the antiferromagnetic $J_1$ and ferromagnetic $J_2$, and antiferromagnetic $J_4$ are consistent with the antiferromagnetic ground state, the ferromagnetic $J_3$ can introduce frustration effect on it. Since the magnitude of the ferromagnetic $J_3$ is comparable to those of the antiferromagnetic $J_1$ and ferromagnetic $J_2$, the ferromagnetic $J_3$ by the Mn-O-O-Mn superexchange pathways is responsible for the absence of long-range ordering in the present honeycomb system.

Let us also examine the sign of $J_3$ by considering superexchange pathways in Bi$_3$Mn$_2$O$_{12}$(NO$_3$) using a perturbation method based on the electronic structure parameters obtained from the analysis of the Mn 2p XAS spectrum. Here, we will use Slater-Koster parameters, $(pp\sigma), (pd\sigma), (dd\sigma)$, and so on [18].
\[
J_3 \text{ is given as }
\]
\[
J_3 = \frac{(pd\sigma)^4}{\Delta + (pp\sigma)/2 + (pp\pi)/2^2} + \frac{(pd\pi)^4}{\Delta + (pp\sigma)/2 - (pp\pi)/2^2} \left( \frac{1}{\Delta + u_p} + \frac{1}{u} \right)
\]
\[
+ \frac{[\Delta - (pp\sigma)/2 + (pp\pi)/2^2]}{2(pd\pi)^2} \left( \frac{1}{\Delta + u_p} + \frac{1}{u - \Delta + u_p - j_p} \right)
\]
\[
- \frac{[\Delta - (pp\sigma)/2 - (pp\pi)/2^2]}{2(pd\pi)^2} \left( \frac{1}{\Delta + u_p} + \frac{1}{u - 3j - \Delta + u_p - j_p} \right)
\]
\[
\times \frac{2(pd\pi)^2}{4(pd\pi)^4} \left( 1 - \frac{[pp\pi/2 - (pp\pi)/2]^2}{\Delta^2} \right) \frac{1}{\Delta + u_p} \frac{1}{u - (\Delta + u_p)^2} + \frac{1}{u - (\Delta + u_p)^2}
\]
\[
\times \frac{2(pd\pi)^2}{4(pd\pi)^2} \left( 1 - \frac{[pp\pi/2 + (pp\pi)/2]^2}{\Delta^2} \right) \frac{1}{\Delta + u_p} \frac{1}{u - (\Delta + u_p)^2}
\]
\[
\times \frac{j}{u^2 - (\Delta + u_p)^2}
\]
\[
(2)
\]
Here we considered the molecular orbitals made from two oxygen sites. The first and second terms proportional to \((pd\pi)^4\) are given by the pathway from the Mn \(t_{2g}\) states to the O \(2p\) molecular orbitals to the Mn \(t_{2g}\) states. The third and fourth terms proportional to \((pd\pi)^2(pd\sigma)^2\) are given by the pathway from the Mn \(e_g\) states to the O \(2p\) molecular orbitals to the Mn \(t_{2g}\) states. 

\(J_3\) is dominated by the negative third term and causes ferromagnetic interactions, which is consistent with the result of the unrestricted Hartree Fock calculations.

From the neutron measurements, it was found that the values of interlayer interactions \((J_c)\) are also comparable to \(J_1\) [14]. This is consistent with our result because \(J_c\) is also determined by Mn-O-O-Mn pathways.

We investigated the electronic structure of \(\text{Bi}_2\text{Mn}_4\text{O}_{12}(\text{NO}_3)\) by XAS. The valence of Mn was determined to be \(4+\), and from CI theory we found that a charge-transfer energy is small in this material. Then we estimated the values of \(J_{1,2,3,4}\) by unrestricted Hartree-Fock calculations and a perturbation method. We found antiferromagnetic \(J_1\) and ferromagnetic \(J_2\) and \(J_3\), leading to the existence of magnetic frustration and the absence of long-range ordering, as experimentally confirmed.

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