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Photoemission spectroscopy and x-ray absorption spectroscopy studies of double perovskite oxides: $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$

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Abstract

Electronic structures of La-doped $\text{Ba}_2\text{FeMoO}_6$ double perovskite oxides have been investigated using photoemission spectroscopy and soft x-ray absorption spectroscopy. The ground states of $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ are found to be in the $\text{Fe}^{2+}\text{--Fe}^{3+}$ mixed-valent states and the Fe valence state increases toward 3+ with increasing x . The states close to E_F consist of the degenerate Mo–Fe $t_{2g}\downarrow$ states. The LSDA + U calculations for $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ ($x = 0, 1$) show a larger occupied bandwidth of the Mo $t_{2g}\downarrow$ states for $x = 1$ than for $x = 0$, which is consistent with the higher T_C value predicted in a type of the double exchange mechanism.

Large magnetoresistance (MR) has been observed in the ordered double-perovskite oxides of A_2FeMoO_6 ($A = \text{Sr}, \text{Ba}$) with the very high magnetic transition temperature T_C ($\approx 330\text{--}450$ K) [1]. A metal–insulator transition occurs simultaneously with the ferromagnetic transition in A_2FeMoO_6 . Magnetization data for $\text{Sr}_2\text{FeMoO}_6$ indicated the ferrimagnetic coupling between Fe^{3+} and Mo^{5+} ions, and large MR was interpreted as being due to intergrain tunnelling with the half-metallic electronic structure. When La^{3+} ions were substituted for Ba^{2+} ions in $\text{Ba}_2\text{FeMoO}_6$, T_C was enhanced significantly [2]. The substitution of La^{3+} in $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ has two effects: (i) the reduction of the average ionic radius without distorting the cubic symmetry, and (ii) the change of the valence states and magnetic moments of Fe/Mo ions via electron doping. The exact mechanism of the enhanced T_C with increasing x in $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ has not been clarified yet.

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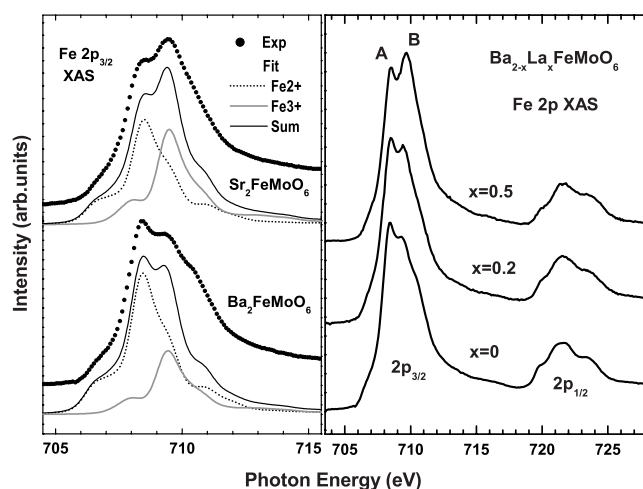


Figure 1. Left: the measured Fe $2p_{3/2}$ XAS spectra (dots) of $\text{Sr}_2\text{FeMoO}_6$ (shifted by -0.35 eV) and $\text{Ba}_2\text{FeMoO}_6$, and the fitting results (solid curves). Right: comparison of the Fe 2p XAS spectra of $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ ($x = 0, 0.2, 0.5$).

In order to understand the origin of the enhanced T_C in $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$, it is essential to investigate the valence and spin states of the constituent elements. Photoemission spectroscopy (PES) and x-ray absorption spectroscopy (XAS) are the powerful methods that provide information on the electronic structures and the valence states. In this work we have investigated the electronic structures of A_2FeMoO_6 ($\text{A} = \text{Sr}, \text{Ba}$) and $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ using PES and XAS.

Polycrystalline $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ ($x = 0, 0.2, 0.5$) samples were prepared by the standard solid-state reaction method [2]. The measured XRD patterns showed single-phase perovskite structure without traces of impurity phases. T_C was enhanced from 316 K for $x = 0$ to 336 K for $x = 0.5$. The magnitude of M_s decreased systematically with increasing x . High-resolution PES and XAS experiments were performed at the twin-helical undulator beam line BL25SU of SPring-8 [3]. Samples were fractured and measured in vacuum better than 3×10^{-10} Torr at $T \leq 20$ K, and the overall energy resolution of the system was about 130 meV at a photon energy ($h\nu$) ~ 700 eV for PES data and better than 100 meV for XAS data.

The left of figure 1 presents the measured Fe 2p XAS spectra of $\text{Sr}_2\text{FeMoO}_6$ and $\text{Ba}_2\text{FeMoO}_6$ along with the calculated spectra. The calculated XAS spectra were obtained by employing the configuration interaction (CI) cluster model [4]. In this analysis, we have considered two configurations, d^n and $d^{n+1}\underline{L}^1$ (\underline{L} : a ligand hole). The $2p_{3/2}$ XAS spectra of both $\text{Sr}_2\text{FeMoO}_6$ and $\text{Ba}_2\text{FeMoO}_6$ exhibit two-peak structures. It is known that the $2p_{3/2}$ absorption edge of Fe^{2+} ions in the octahedral (O_h) symmetry exhibits a main peak at a lower $h\nu$ than that of Fe^{3+} ions [5]. We have used the same parameters as used for FeO and $\alpha\text{-Fe}_2\text{O}_3$ for the Fe^{2+} (d^6) and Fe^{3+} (d^5) components, respectively [5]. The calculated XAS spectra (solid curves) reveal that the ground states of both $\text{Sr}_2\text{FeMoO}_6$ and $\text{Ba}_2\text{FeMoO}_6$ are strongly mixed-valent with the Fe^{2+} and Fe^{3+} configurations. The estimated Fe valences are about 2.5 for $\text{Sr}_2\text{FeMoO}_6$ and 2.3 for $\text{Ba}_2\text{FeMoO}_6$.

The right of figure 1 compares the Fe 2p XAS spectra of $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ ($x = 0, 0.2, 0.5$). As x increases, the peak at a higher $h\nu$ (B: ~ 710 eV) increases, compared to that at a lower $h\nu$ (A: $h\nu \sim 708$ eV). The trend in the measured Fe 2p XAS spectra of $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ indicates that Fe ions are in the $\text{Fe}^{2+}\text{-Fe}^{3+}$ mixed-valent states, and that their valences increase toward 3+ with increasing x .

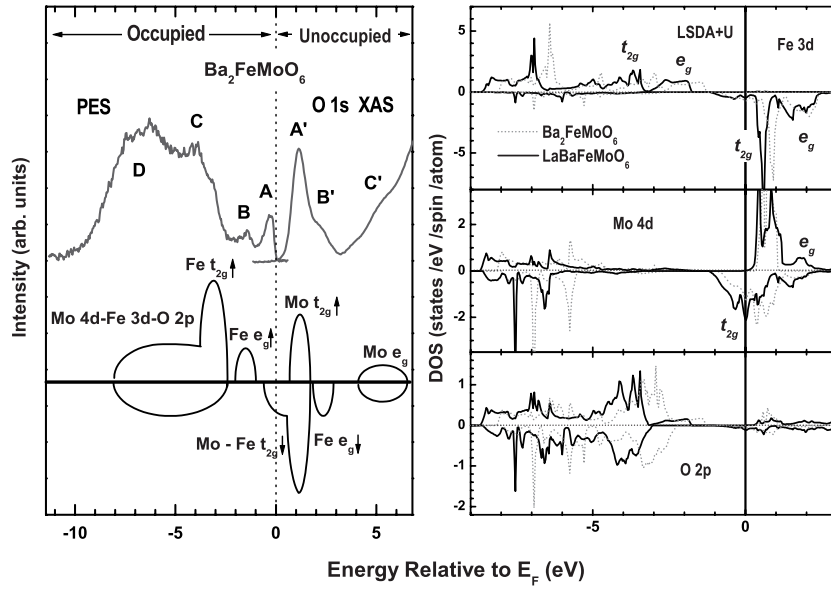


Figure 2. Left, top: the valence-band PES spectrum, combined with the O 1s XAS spectrum of $\text{Ba}_2\text{FeMoO}_6$ (shifted by -528.4 eV); bottom: schematic diagram for the PDOS (partial density of states) of $\text{Ba}_2\text{FeMoO}_6$. Right: comparison of the calculated PDOS of $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ ($x = 0, 1$) obtained by using the LSDA + U method.

The left of figure 2 shows the combined valence-band PES and O 1s XAS spectra of $\text{Ba}_2\text{FeMoO}_6$. The O 1s XAS spectrum provides a reasonable approximation for the unoccupied conduction bands via hybridization to the other electronic states. A metallic Fermi edge is observed in the valence-band PES spectrum, consistent with its metallic behaviour at low T . Based on a comparison of the measured PES/XAS spectra to the LSDA + U calculation, we provide a schematic diagram for the partial density of states (PDOS) at the bottom. Fe $t_{2g}\downarrow$ and Mo $t_{2g}\downarrow$ bands are almost degenerate and t_{2g} electrons are itinerant in $\text{Ba}_2\text{FeMoO}_6$. Consequently, Fe and Mo ions do not have definite valence states. This suggests that two valence states of $\text{Fe}^{3+}\text{-Mo}^{5+}$ and $\text{Fe}^{2+}\text{-Mo}^{6+}$ are degenerate in $\text{Ba}_2\text{FeMoO}_6$, which would then produce a type of double-exchange (DE) interaction [6].

The right of figure 2 shows the calculated PDOS of $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ ($x = 0, 1$) obtained from the LSDA + U calculations. The parameters used in this calculation are $U = 3.0$ eV and the exchange $J = 0.97$ eV for Fe 3d electrons. Both of the calculated electronic structures for $x = 0$ and 1 seem to show the half-metallic nature. But LaBaFeMoO_6 is not a complete half-metal, since a very small majority-spin DOS exists at E_F , which is mostly from the La 5d PDOS. Spins of the Fe and Mo ions are polarized antiferromagnetically. The calculated magnetic moments for Fe and Mo are $4.03 \mu_B$ and $-0.46 \mu_B$ for $x = 0$ and $4.09 \mu_B$ and $-1.11 \mu_B$ for $x = 1$, so that the total magnetic moments of $4.00 \mu_B$ ($x = 0$) and $-3.01 \mu_B$ ($x = 1$) per formula unit are obtained.

La-doping has the effect of electron doping. This would cause the rigid-band shift of E_F upward, corresponding to the downward shift of PDOS. The largest effect of La-doping is the larger occupied bandwidth of the Mo $t_{2g}\downarrow$ states. Note that, in the simplest DE Hamiltonian, T_C is proportional to the kinetic energy of the itinerant carriers [7]. Accordingly, T_C would be proportional to the occupied bandwidth for the low carrier concentration. Therefore the increased occupied bandwidth of the Mo $t_{2g}\downarrow$ states with La-doping is consistent with the DE mechanism. On the other hand, according to the LSDA + U calculation, the Fe valence states in

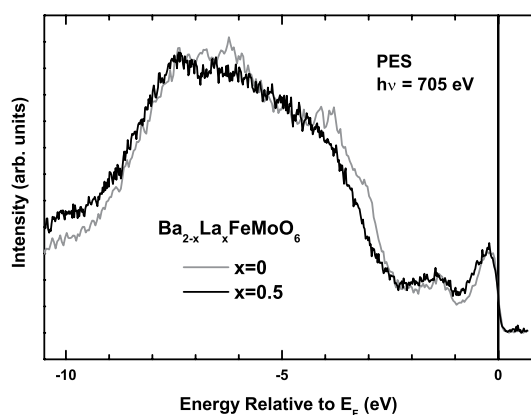


Figure 3. Comparison of the valence-band PES spectra of $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ ($x = 0, 0.5$) for $h\nu \approx 705$ eV.

$\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ do not change much, contradictory to the experimental finding in figure 1. This problem needs to be resolved both theoretically and experimentally. Finally La-doping will increase the DOS at E_F [$N(E_F)$] since the Mo $t_{2g}\downarrow$ states have the largest contribution to $N(E_F)$ in $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$.

Figure 3 compares the valence-band PES spectra of $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ ($x = 0, 0.5$) near the off-resonance energy ($h\nu \approx 705$ eV) in Fe $2p \rightarrow 3d$ resonant PES. At this $h\nu$, the Mo d emission is relatively large [3]. This comparison shows that the trend in the measured PES spectra is consistent with that in the calculated PDOSs. That is, the occupied bandwidth near E_F , i.e. that of the Mo–Fe $t_{2g}\downarrow$ states, becomes slightly wider for $x = 0.5$ than for $x = 0$. However, to confirm the predicted larger occupied bandwidth of the Mo $t_{2g}\downarrow$ states, a more systematic high-resolution PES study for $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ with different x values will be necessary.

In conclusion, electronic structures of $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ have been investigated by using PES and XAS. The Fe $2p$ XAS spectra show that the ground states of $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ are in the $\text{Fe}^{2+}\text{--}\text{Fe}^{3+}$ mixed-valent states, and that the Fe valence increases toward $3+$ with increasing x . Valence-band PES spectra reveal that the states close to E_F have the Mo–Fe $t_{2g}\downarrow$ character, and that the degenerate Mo–Fe $t_{2g}\downarrow$ states are itinerant. The LSDA + U calculations for $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ ($x = 0, 1$) show the higher occupied bandwidth of the Mo $t_{2g}\downarrow$ states for $x = 1$ than for $x = 0$, which is consistent with the measured PES data for $x = 0$ and 0.5 . These findings suggest that a type of DE interaction is operative in $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ to enhance T_C with increasing x .

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