Strong electron correlation of Re 5d electrons in Ca$_2$FeReO$_6$

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Abstract

We have investigated the electronic structure of a double perovskite Ca$_2$FeReO$_6$ using photoemission spectroscopy and LDA + U band-structure calculations. Small spectral weight at the Fermi level observed above the metal–insulator transition temperature, gradually disappears with decreasing $T$, forming a small ($\leq 50$ meV) energy gap. To reproduce this small energy gap, we require a very large effective $U$ ($4$ eV) for Re in addition to $U_{eff}$ of $4$ eV for Fe. From simple calculations in terms of the ionic radii, we demonstrate that the Fe–Re bandwidth is smaller than that of Fe–Mo in Ca$_2$FeMoO$_6$, which should yield a strong electron correlation in the Re 5d bands.

Keywords: Ca$_2$FeReO$_6$, Photoemission, Band-structure calculation

1. Introduction

The discovery of the large room temperature tunneling magnetoresistance in a ferrimagnetic double perovskite Sr$_2$FeMoO$_6$ has triggered renewed interest in the family of double perovskites in view of the possibility of industrial applications for spintronics [1]. Band-structure calculations have revealed that metallic double perovskites are generally half-metallic [1–5] which has been confirmed by optical and electron-spectroscopic studies [4–6]. Ferrimagnetism accompanied by metallic conductivity and the half-metallic density of states (DOS) naturally remind us of the colossal magnetoresistive manganites and the double exchange (DE) mechanism. However, Ca$_2$FeReO$_6$ exhibits a metal–insulator transition (MIT) at $T_{MI}$ of $\sim 150$ K and more interestingly its ferrimagnetic $T_c$ ($\sim 540$ K) is the highest among the Fe–Mo and Fe–Re based double perovskites [7]. Those two facts are apparently incompatible with the simple DE scenario because it predicts the proportional change of $T_c$ to the bandwidth. To get insight into those problems, we have performed a set of photoemission and LDA + U band-structure calculations study.

2. Experiment and calculation

Polycrystalline samples of Ca$_2$FeReO$_6$ were prepared by solid-state reaction [7]. Experiments have been performed at BL-11D of the Photon Factory using a Scienta SES-200 electron analyzer. Samples were either scraped or fractured in situ at 200 K and measured at about $2 \times 10^{-10}$ Torr at several temperatures. The total energy resolution was about 70–80 meV. Band-structure calculations have been performed with full potential linearized augmented GLAUX3 code.

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plane-wave (FLAPW) method within the LDA + U scheme.

3. Results

Fig. 1 shows LDA + U band-structure calculations. In spite of the fact that we used the lattice parameters of the low-\(T\) insulating phase [8], we required a large \(U_{\text{eff}}(=U-J)\) value of 4.0 eV for both Fe 3d and Re 5d to reproduce a finite but small (\(\sim 30\) meV) energy gap. The down-spin band just below \(E_F\) is dominated by the Re 5d \(t^{2g}\) and the O 2p states with a tiny contribution of the Fe 3d \(t^{2g}\) states. On the other hand, the first up-spin band below \(E_F\) is mostly due to the Fe 3d \(e_{g}\) and the O 2p states without any appreciable Re 5d contribution.

Fig. 2 shows a comparison of the valence-band spectra at 20 K with the band theory. The relative intensity of the three partial DOS was fixed to that of the calculated photoionization cross-sections of each orbital [9]. The theoretical curve was obtained by broadening the cross-section-corrected total DOS with a Gaussian due to the experimental resolution as well as with an energy-dependent Lorentzian due to the lifetime effect [5,10]. The experimental background was subtracted.

One can assign the structures a–g in the theoretical curve to A–G in experiment. The characteristic double-peak structure A–B is essentially reproduced in theory as a–b although the agreement is not good. The two structures c and d are due to the Fe \(t^{2g}\) and the O 2p states. e consists mainly of the O 2p nonbonding states. It is obvious that the agreement between theory and experiment is not satisfactory. The main part of the valence band seems to be shifted towards \(E_F\) by \(\sim 1\) eV [5].

Fig. 3 shows near-\(E_F\) spectra of Ca\(_2\)FeReO\(_6\) from scraped surfaces. A small but finite Fermi cut-off observed at 200 K gradually fades away with decrease in \(T\) and completely disappears below 100 K. The observed energy gap in the low-temperature insulating phase is vanishingly small even at the lowest \(T\). We estimate the energy gap (below \(E_F\)) is about or even less than 50 meV.

4. Discussion

Since the only difference between Sr\(_2\)FeReO\(_6\) and Ca\(_2\)FeReO\(_6\) is the bond angle of Fe–O–Re, the simplest reason for the MIT would be the bond-angle distortion due to Ca substitution. However, this is not the only reason because Ca\(_2\)FeMoO\(_6\), with almost the same bond-angle and the crystal structure as Ca\(_2\)FeReO\(_6\), does not show any MIT [11].

Here, we focus on the Re and Mo ionic radius. Assuming \(\sim 2.5+\) for Fe [12], we adopt the average valence of 5.5+ for those ions. The average ionic radius can be estimated to be 0.565 and 0.600 Å for Re\(^{5.5+}\) and Mo\(^{5.5+}\), respectively [13].
Hence, Re$^{5.5+}$ is actually even smaller than Mo$^{5.5+}$. The Harrison’s formula confirms that the bandwidth of the hybridized Re–O and Mo–O states are approximately the same [14].

In this situation, another important factor is that Ca$_2$FeReO$_6$ has two Re 5d electrons while Ca$_2$FeMoO$_6$ has only one Mo 4d electron per one Re/Mo atom. This gives rise to a substantially larger electron-electron interaction on Re sites than on Mo sites, which justifies a large $U_{eff}$ for Re in our LDA + $U$ calculation. The actual MIT is probably driven by this strong electron correlation coupled with the Jahn–Teller distortion due to the 5d$^2$ configuration [8].

5. Conclusion

We have investigated the electronic structure of Ca$_2$FeReO$_6$ by photoemission spectroscopy and LDA + $U$ band-structure calculations. The observed small $E_F$ spectral weight above $T_{MI}$ completely disappeared below 100 K, forming a tiny energy gap. Employing large $U_{eff}$’s for both Fe and Re, we have reproduced the energy gap. The overall agreement between the theory and the valence-band spectra was not satisfactory. Based on the ionic radii and the lattice parameters, we have revealed that the effective Fe–Re bandwidth is actually smaller than the Fe–Mo one in Ca$_2$FeMoO$_6$. This should yield a substantially large electron correlation on Re site, which would be the major driving force of the MIT in this compound.

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References

[11] The Gaussian FWHM was 80 meV and the energy-dependent term of the Lorentzian was 0.1.