

Strong electron correlation of Re 5d electrons in $\text{Ca}_2\text{FeReO}_6$

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Abstract

We have investigated the electronic structure of a double perovskite $\text{Ca}_2\text{FeReO}_6$ 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 (≤ 50 meV) energy gap. To reproduce this small energy gap, we require a very large effective U (U_{eff}) for Re (4 eV) 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 $\text{Ca}_2\text{FeMoO}_6$, which should yield a strong electron correlation in the Re 5d bands.

Keywords: $\text{Ca}_2\text{FeReO}_6$; Photoemission; Band-structure calculation

1. Introduction

The discovery of the large room temperature tunneling magneto-resistance in a ferrimagnetic double perovskite $\text{Sr}_2\text{FeMoO}_6$ 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, $\text{Ca}_2\text{FeReO}_6$ exhibits a metal–insulator transition (MIT) at T_{MI} of ~ 150 K and more interestingly its

ferrimagnetic T_c (~ 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 $\text{Ca}_2\text{FeReO}_6$ 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 2×10^{-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

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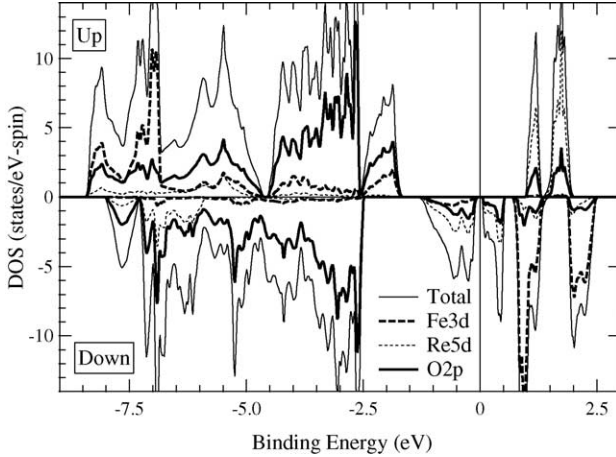


Fig. 1. Total and partial DOS of insulating $\text{Ca}_2\text{FeReO}_6$ calculated with LDA + U method. U_{eff} is 4.0 eV for both Fe 3d and Re 5d.

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_{eff} ($=U - J$) value of 4.0 eV for both Fe and Re to reproduce a finite but small (~ 30 meV) energy gap. The down-spin band just below E_F is dominated by the Re 5d $t_{2g\downarrow}$ and the O 2p states with a tiny contribution of the Fe 3d $t_{2g\downarrow}$ states. On the other hand, the first up-spin band below E_F is mostly due to the Fe 3d $e_{g\uparrow}$ 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 photoioniza-

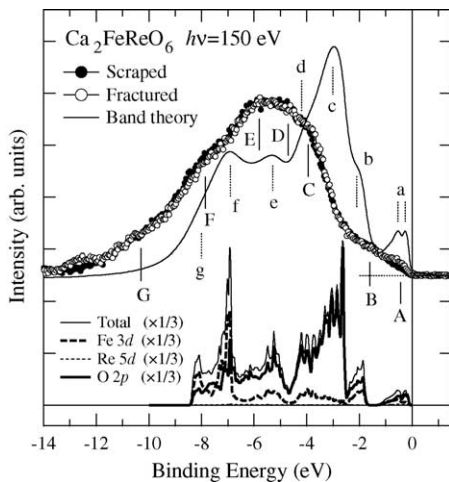


Fig. 2. 150 eV valence-band spectra of $\text{Ca}_2\text{FeReO}_6$ at 20 K (circles) compared with the theoretical curve (solid curve).

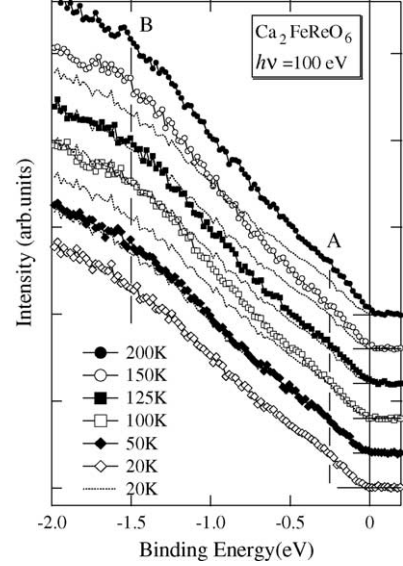


Fig. 3. Photoemission spectra of $\text{Ca}_2\text{FeReO}_6$ from scraped surface in a very near- E_F region.

tion 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 $t_{2g\uparrow}$ and the O 2p nonbonding 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 ~ 1 eV [5].

Fig. 3 shows near- E_F spectra of $\text{Ca}_2\text{FeReO}_6$ 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 $\text{Sr}_2\text{FeReO}_6$ and $\text{Ca}_2\text{FeReO}_6$ 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 $\text{Ca}_2\text{FeMoO}_6$, with almost the same bond-angle and the crystal structure as $\text{Ca}_2\text{FeReO}_6$, 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 $\text{Re}^{5.5+}$ and $\text{Mo}^{5.5+}$, respectively [13].

Hence, $\text{Re}^{5.5+}$ is actually even smaller than $\text{Mo}^{5.5+}$. 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 $\text{Ca}_2\text{FeReO}_6$ has *two* Re 5d electrons while $\text{Ca}_2\text{FeMoO}_6$ 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 $\text{Ca}_2\text{FeReO}_6$ 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 $\text{Ca}_2\text{FeReO}_6$. 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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