

Angle- Resolved Photoemission Study of Verwey Transition of Fe₃O₄(001) Films

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Introduction

Magnetite (Fe₃O₄) has gained much interest due to its predicted spin polarization of -100% at Fermi level (E_F) [1] and its well known Verwey transition. Magnetite crystallizes in the face-centered-cubic (fcc) inverse spinel structure ($Fd\bar{3}m$). On cooling through $\sim 122\text{K}$ (T_V), magnetite undergoes a metal-insulator transition, which is characterized by an abrupt decrease in the electrical conductivity by two orders of magnitude [2] and accompanied by a structure distortion from cubic to monoclinic.[3] By supposing that the high RT conductivity of magnetite is attributed to electron hopping between the Fe²⁺ and Fe³⁺ in sites that octahedrally coordinated to oxygen, Verwey interpreted the transition as a charge ordering (CO) of Fe³⁺ and Fe²⁺ ions (CO model).[4] However, the CO model was not well proved by experiments later. Although intensive investigations for over 70 years, fundamental questions about the Verwey transition, such as the existence and origin of the CO, the nature of the electronic structure, are still under highly debate.[5] In this work, effect of Verwey transition on the electronic structure of Fe₃O₄(001) film was investigated by measuring the band dispersion at RT and 100 K using angle-resolved photoemission spectroscopy (ARPES). In addition, effect of Co doping on the Verwey transition of Fe₃O₄(001) is discussed.

Experimental

The experiment was carried out at the Photon Factory beamline 18A. High quality 200 Å Fe₃O₄ (100) films and Co-doped Fe₃O₄ (100) films were deposited on MgO(100) substrates using molecular beam epitaxy method in a preparation chamber (base pressure, $< 2 \times 10^{-10}$ mbar). The O₂ pressure was 2×10^{-6} mbar, and the substrate temperature was about 250 °C.

After preparation, the films were *in situ* transferred into an analysis chamber (base pressure, $< 8 \times 10^{-11}$ mbar). Then, the structural properties were investigated by low-energy electron diffraction (LEED). Using a photon energy of 48 eV, ARPES spectra were measured at RT and 100 K to investigate the valence band structure of the prepared films.

Results and discussion

Figure 1 shows LEED pattern of Fe₃O₄(001) film. Clear $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction (white solid square) and (1×1) unit cell (black solid square) are visible, indicating clean and well-ordered surface. Brillouin zone and $\bar{\Gamma}$ - \bar{M} direction of Fe₃O₄(001) surface are schematically represented (white dashed line). A lattice constant of 8.28 ± 0.68 Å is obtained from the LEED pattern, this value is very close to bulk value of 8.396 Å. LEED investigations on Co-doped films suggest that the Co doping blocks the reconstruction. X-ray photoelectron spectroscopy analyses reveals that the Co²⁺ ions substitute the Fe²⁺ ions of Fe₃O₄. Magnetic measurement shows that pure film exhibits Verwey transition in the range of 100-120 K, however Co doping quenches Verwey transition.[6]

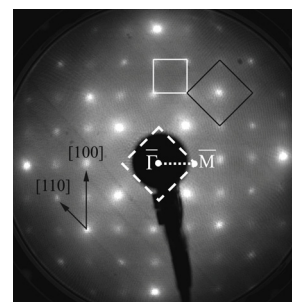


Fig. 1 LEED pattern of Fe₃O₄(001) film with an electron energy of 93.5 eV.

Figure 2 shows ARPES spectra of $\text{Fe}_3\text{O}_4(001)$ film and Co-doped $\text{Fe}_3\text{O}_4(001)$ films measured at RT and 100 K. As can be seen from fig. 2(a), the spectral feature crosses the E_F at RT, indicating metallic feature of the film. On cooling to 100 K, the photoelectron intensity

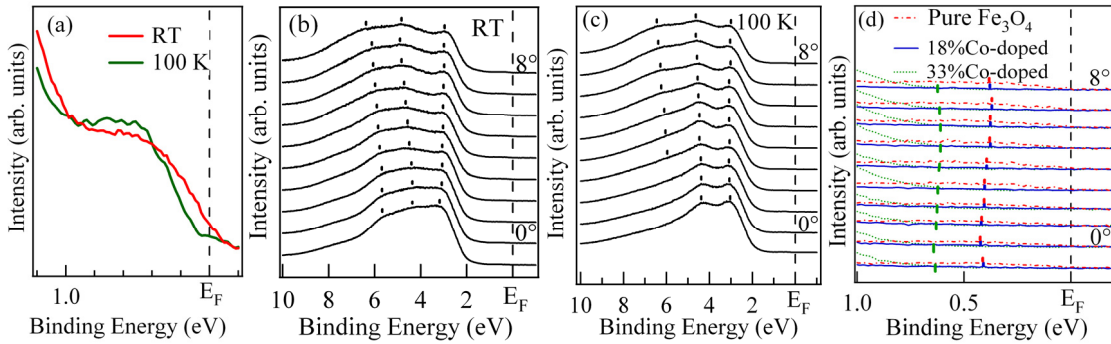


Figure 2 (a) Normal emission ARPES spectra of $\text{Fe}_3\text{O}_4(001)$ film measured at RT and 100 K; (b) and (c) ARPES spectra of $\text{Fe}_3\text{O}_4(001)$ film measured at RT 100 K; (d) Near E_F ARPES spectra of Co-doped $\text{Fe}_3\text{O}_4(001)$ films.

near E_F is reduced dramatically. A bandgap of about 70 meV below E_F can be observed at 100 K, suggesting a metal-insulator transition. Figure 2(b) and (c) show the ARPES spectra of $\text{Fe}_3\text{O}_4(001)$ films measured at RT and 100 K. There are three obvious features, which locate near 5.9 eV, 4.6 eV and 3 eV, respectively, are recognizable in the RT spectra. These features are mainly O $2p$ -derived emissions. With temperature reduces from RT to 100 K, the feature at about 3 eV is nearly not changed. The feature at about 4.6 eV shifts about 0.15 eV to E_F side near 7° . Feature at about 5.5 eV disappears near 0° ($\bar{\Gamma}$). Turning points can be observed at 0° and 7° at RT spectra, indicating the $\bar{\Gamma}$ point and \bar{M} point, respectively. However, no obvious turning point can be observed for the 100 K spectra except at 0° . Investigation of the near E_F ARPES spectra indicates that the valence band maximum of $\text{Fe}_3\text{O}_4(001)$ films at 100 K is about 0.1 eV deeper than that at RT. The differences between the features in RT and 100 K ARPES spectra might attribute to the fact that Verwey transition is accompanied by a structure distortion from cubic to monoclinic, which might change band dispersion of Fe_3O_4 , and influence Brillouin zone as well. Co is employed to substitute Fe^{2+} ions in Fe_3O_4 so as to investigate magnetite and its Verwey transition. Near E_F ARPES spectra of Co-doped $\text{Fe}_3\text{O}_4(001)$ films are shown in fig. 2(d). It is found that the photoelectron intensity is reduced with Co doping, and become nearly 0 for Fe_3O_4 film doped with about 33% Co. Especially, density of states (DOS) at E_F is found to be 0 for Co doped films, suggesting a metal-insulator transition induced by Co doping. These might responsible for the disappearance of Verwey transition in Co-doped Fe_3O_4 films.

References

- [1] G. Hu, and Y. Suzuki, Phys. Rev. Lett. **89**, 276601 (2002).
- [2] B. A. Calhoun, Phys. Rev. **94**, 1577 (1954).
- [3] J. Yoshida, and S. Iida, J. Phys. Soc. Jpn. **42**, 236 (1977).
- [4] Y. Fujii, G. Shirane, and Y. Yamada, Phys. Rev. B **11**, 2036 (1975).
- [5] J. Garcíá, G. Subiás, M. G. Proietti, J. Blasco, H. Renevier, J. L. Hodeau, and Y. Joly, Phys. Rev. B **63**, 054110 (2001).
- [6] F. Y. Ran, Y. Tsunemaru, T. Hasegawa, Y. Takeichi, A. Harasawa, K. Yaji, S. Kim, and A. Kakizaki, J. Appl. Phys. **109**, 123919 (2011).