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# Valence Band Structure of $Fe_3O_4$(100) Film Across Verwey Transition

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## 1 Introduction

Magnetite undergoes Verwey transition on cooling through ~122 K (*T*v), which is characterized by an abrupt decrease in the electrical conductivity by two orders of magnitude and accompanied by a structure distortion from cubic to monoclinic [1]. It is found that low temperature phase exhibits a monoclinic superstructure with *Cc* space group symmetry [2]. However, the origin of Verwey transition is still under highly debate. Verwey interpreted the transition as an electron delocalization-localization transition accompanied by a long-range charge ordering (CO) of $Fe^{3+}$ and $Fe^{2+}$ ions (CO model) [3]. Recently, a $t_{2g}$ orbital ordering (OO) on the $Fe^{2+}$ sublattice is also revealed [4]. To clearly understand the Verwey transition, systematic work on the electronic band structures of $Fe_3O_4$ below and above *T*v is required.

## 2 Experiment

The experiments were carried out at the Photon Factory beamline 18A. $Fe_3O_4$ (001) films were deposited on MgO(001) surface in a preparation chamber with a base pressure of < $2\times10^{-10}$ mbar. During the growth, the $O_2$ pressure was maintained at $2\times10^{-6}$ mbar, and a substrate temperature of about 250 °C was used. After preparation, the films were *in situ* transferred into an analysis chamber (base pressure, < $8\times10^{-11}$ mbar). Then, the structural properties and chemical composition were investigated by low-energy electron diffraction (LEED) and x-ray photoelectron spectroscopy (XPS), respectively. Using a photon energy of *h*v=48 eV, valence band structure along $\bar{\Gamma}$-$\bar{M}$ direction in the surface Brillouin zone of $Fe_3O_4$ films were measured at RT and 90 K using angle-resolved photoemission spectroscopy (ARPES).

## 3 Results and Discussion

Figure 1(a) shows LEED pattern of surface of pure $Fe_3O_4$ films. Clear $(\sqrt{2}\times\sqrt{2})R45^o$ reconstruction (white solid square) and (1×1) unit cell (white dashed square) are visible, indicating well-ordered surface. The Brillouin zone and $\bar{\Gamma}$-$\bar{M}$ direction of $Fe_3O_4$(100) surface are schematically represented in Fig. 1(a) (black solid line). Zero field cooled curve suggests that the Verwey transition occurs at about 115 K for the $Fe_3O_4$ (001) film.

Figure 1(b) exhibits normal emission measured at RT and 90 K. The spectral feature crosses the $E_F$ at RT, indicating metallic feature of the film. On cooling to 90 K, a band gap of about 70 meV below $E_F$ can be observed. ARPES spectra along the $\bar{\Gamma}$-$\bar{M}$ direction in the surface Brillouin zone measured at RT and 90 K are indicated in

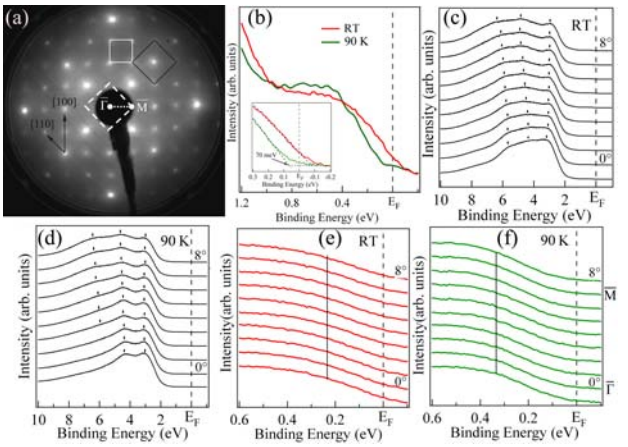


Fig. 1: (a) LEED pattern of $Fe_3O_4$ (001) film; (b)-(f) ARPES spectra of $Fe_3O_4$ (001) film measured at RT and 90 K.

Fig. 1(c)-(f). The major dispersions are marked in the figures. In Fig. 1(c), there are three O 2*p*-derived features, which locate near 5.9 eV, 4.6 eV and 3 eV of the binding energy can be observed. With temperature reduces from RT to 90 K (Fig. 1(d)), the feature at about 3 eV is nearly not changed through $0^o$ - $8^o$, while the other two features are varied a lot. The feature at about 4.6 eV shifts about 0.15 eV to $E_F$ side near $7^o$, however no obvious change can be observed for the feature around $0^o$ ($\bar{\Gamma}$). Feature at about 5.5 eV disappears near $0^o$ ($\bar{\Gamma}$), whereas it is almost the same to that of RT spectra in the range of $5^o$ - $8^o$. ARPES spectra near $E_F$ (< 0.6 eV) at RT and 90 K are shown in Fig. 1(e)-(f). No regular band dispersion can be observed, suggesting that the Fe *d* states are non-dispersive or the dispersions are hard to track due to the broad Fe *d* states. It can be seen that the feature near $E_F$ of $Fe_3O_4$(001) films at 90 K locates at about 0.34±0.05 eV, about 0.1 eV deeper than that at RT. These results are reasonably in agreement with recent band calculations.

## References

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