

Valence Band Structure of Co-Doped Fe₃O₄(100) Films

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Introduction

Magnetite (Fe₃O₄) has been widely studied due to its predicted spin polarization of -100%[1]. On cooling through ~122K (T_v), it undergoes a first-order phase transition, named Verwey transition[2]. Co-doped Fe₃O₄ has attracted particular attention because of its enhanced structural anisotropy and magnetic anisotropy. The magnetocrystalline anisotropy constant of Fe₂CoO₄ is about 1.8×10^5 J/m³[3]. It is reported that Co ions mainly substitutes the Fe²⁺ ions in magnetite[4]. Co doping changes magnetic properties, destroys Verwey transition and reduces megnetoresistance[5]. So far, there is still lack of evidence on the valence band structure of Co- doped Fe₃O₄, which is significant to understand its physical and chemical properties.

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

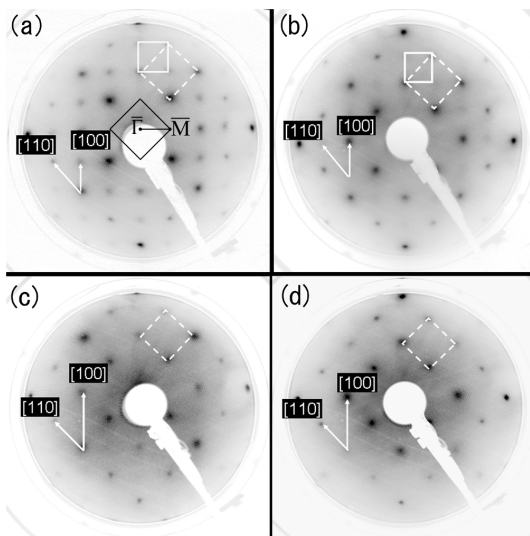


Figure 1 LEED patterns of (a) pure Fe₃O₄ film, 95 eV; (b) 8%Co-doped Fe₃O₄ film, 96.2eV; (c) 18%Co-doped Fe₃O₄ film, 100.8eV; (d) 33%Co-doped Fe₃O₄ film, 102eV.

Figure 1 shows typical LEED patterns of the surface of pure and Co-doped Fe₃O₄ films grown on MgO(100) substrate. A clear $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction (white solid square) with respect to the (100) –unreconstructed Fe₃O₄ surface (1×1) unit cell (white dashed square) is visible for pure film (Fig. 1(a)). The reconstruction spots are weak, which is typical reconstruction for MBE grown films. However, the reconstruction spots become weaker for Fe₃O₄ film doped with 8% Co (Fig. 1(b)) and disappear for the Fe₃O₄ films doped with about 18% (Fig.1 (c)) and 33% Co (Fig.1 (d)), suggesting that the Co doping blocks the reconstruction. Clear (1×1) unit cell spots of Fe₃O₄ indicate clean and well-ordered surfaces. No spot of secondary phase can be observed in all the patterns. The Brillouin zone and $\bar{\Gamma}-\bar{M}$ direction of Fe₃O₄(100) surface are schematically

represented in Fig. 1(a) (black solid line).

ARPES was measured to investigate the valence band structure of Co-doped Fe_3O_4 films at RT. A photon energy of $h\nu=48$ eV was used in all photoemission experiments. ARPES spectra obtained in normal emission mode correspond to the $\bar{\Gamma}$ point of surface Brillouin zone of Fe_3O_4 . Spectral features corresponding to the energy dispersion of the valence band along $\bar{\Gamma}-\bar{M}$ direction in the surface Brillouin zone are shown in Fig. 2(a)-(d). The major dispersions are marked in the figures. For pure Fe_3O_4 film (Fig. 2(a)), the spectral feature below 0.5 eV originates from 3d bands of Fe in B sites with Fe^{2+} character. These feature cross the Fermi level (E_F) at RT, indicating metallic feature of the film. The spectral profiles in the range of about 0.5-2.5 eV are attributed to 3d bands of the other Fe ions in A sites and B sites. O 2p-derived emissions are observed at the binding energies larger than 2.5 eV[6]. As can be seen in Fig. 2(a)-(c), there are three features, which locate near 5.9 eV, 4.6 eV and 3 eV, are recognizable above 2.5 eV. Dispersions of these features are nearly not changed by Co doping. The spectral intensity at 0.5-3 eV is enhanced by Co doping, which are assigned to the d states originated from doped Co ions. Figure 2(d) shows the ARPES spectra near E_F . A feature located at about 0.46 eV at $\bar{\Gamma}$ point can be observed. This feature shifts to E_F side along $\bar{\Gamma}-\bar{M}$ direction and reaches about 0.4 eV at $\bar{M}$ point. The photoelectron intensity of this band is reduced with Co doping, and become nearly 0 for Fe_3O_4 film doped with about

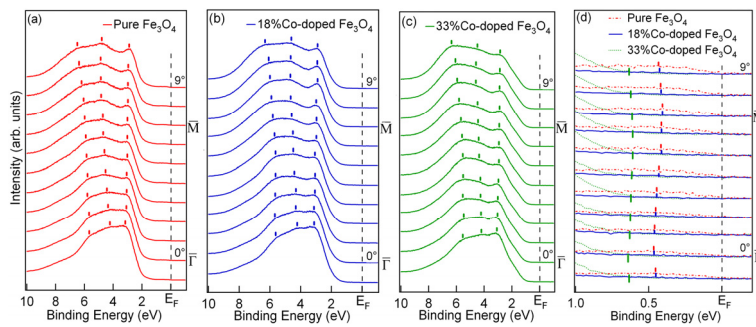


Figure 2 ARPES spectra measured at RT with a excitation energy of 48 eV and emission angle from 0° to 9° , which corresponding to the $\bar{\Gamma}-\bar{M}$ direction in the surface Brillouin zone: (a) ARPES spectra of pure Fe_3O_4 films; (b) ARPES spectra of Fe_3O_4 films doped with 18% Co; (c) ARPES spectra of Fe_3O_4 films doped with 33% Co; (d) ARPES spectra near E_F of Fe_3O_4 films doped with various amount of Co.

33% Co. Especially, density of states (DOS) at E_F was found to be 0 for Co doped films, suggesting a metal-insulator transition induced by Co doping.

It is known that hopping process between Fe^{2+} and Fe^{3+} at B site is the conduction route in magnetite. As we have analyzed, Co^{2+} ions substitute the Fe^{2+} at B site of Fe_3O_4 . The reduction in Fe^{2+} would decrease the probability of the hopping process; otherwise, the formation of interacting Co ion pairs would also block the hoping process. These would dramatically reduce the DOS at and near E_F , which result in an increase in resistance as well as disappearance of Verwey transition. Fe_3O_4 is predicted to be a half-metallic material with a spin up band gap and a partially filled metallic spin down t_{2g} conduction band at E_F (However, experimental work has failed to observe -100% polarization in Fe_3O_4 so far). DOS at E_F is from the spin down t_{2g} band. The reduction of DOS at E_F will result in an decrease of polarization, which might contribute to reduction in magnetoresistance of Co-doped Fe_3O_4 [7].

References

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