Electronic structure of the $\text{Fe}_3\text{O}_4(111)$ surface

Yu. S. Dedkov,^{1,*} M. Fonin,^{1,†} D. V. Vyalikh,² J. O. Hauch,¹ S. L. Molodtsov,² U. Rüdiger,³ and G. Güntherodt¹

¹*II. Physikalisches Institut, Rheinisch-Westfälische Technische Hochschule Aachen, D-52056 Aachen, Germany*

²*Institut für Festkörperphysik, Technische Universität Dresden, D-01062 Dresden, Germany*

³*Fachbereich Physik, Universität Konstanz, D-78457 Konstanz, Germany*

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The surface electronic band structure of thin, well-ordered epitaxial $\text{Fe}_3\text{O}_4(111)$ films has been investigated at room temperature by means of angle-resolved photoelectron spectroscopy using synchrotron radiation. In the $\bar{\Gamma}-\bar{M}$ direction of the $\text{Fe}_3\text{O}_4(111)$ surface Brillouin zone (SBZ), two types of dispersion states originating from a periodic multilayered structure of iron and oxygen ions, in which Fe^{2+} and Fe^{3+} cations are incorporated into the close-packed fcc oxygen sublattice, were identified. Oxygen $2p$ -derived states at binding energies between 2.5 and 8 eV follow a strong, monotonic dispersion extending from $\bar{\Gamma}$ to $\bar{M}$ of the oxygen-sublattice originating SBZ. On the other hand, the iron $3d$ -derived states near the Fermi energy show a weak dispersion with a period half of the $\bar{\Gamma}-\bar{M}$ distance of the latter. The surface electronic band structure of the $\text{Fe}_3\text{O}_4(111)$ film measured with photoemission is described as composed from matrix-element governed contributions of the oxygen and the iron sublattices which are related to the different symmetries of their SBZs.

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Oxides with strong electronic correlations exhibit various interesting physical phenomena such as metal-insulator phase transitions,^{1,2} superconductivity,³ and colossal magnetoresistance.^{4–6} The nature of the electronic states and their influence on the physical properties are of detrimental importance. Magnetite (Fe_3O_4) is an intensively studied, strongly correlated transition metal oxide, which is ferrimagnetically ordered below a relatively high transition temperature ($T_C=851$ K).⁷ This material has recently received renewed attention because of its potential application in spintronics related to its high spin polarization due to the half-metallic ferromagnetic electronic structure.^{8–10}

The electronic band structure of Fe_3O_4 films has been extensively investigated by means of x-ray magnetic circular dichroism,^{11,12} ultraviolet photoelectron spectroscopy,^{13,14} as well as spin- and angle-resolved photoelectron spectroscopy.^{14–16} However, the interpretation of the valence-band photoemission spectra of Fe_3O_4 has been a matter of debate since decades.^{13,15–17} Previous photoemission studies were mostly interpreted on the basis of the ligand-field theory, in which the localized $3d$ cation levels, split further by the oxygen ligand field, were found responsible for the spectral features rather than the recently observed dispersing, band-like $3d$ states.^{13,16} Further theoretical studies at the time found that it was necessary to include configuration interactions within the $3d$ multiplet as well as charge transfer between the $3d$ and the ligand orbitals to improve the agreement with experiment and to account for the satellite features observed in photoemission.^{17–19} The recent investigations,^{13,16} however, showed that theoretically calculated band dispersions^{8–10} should be taken into account for the interpretation of photoelectron spectra of Fe_3O_4 .

Up to now the surface electronic structure of magnetite was investigated only in normal emission photoelectron spectroscopy. This particular method does not reflect the symmetry properties of the surface electronic states of magnetite. In this paper we report on investigations of the surface

electronic band structure of *in situ* prepared epitaxial, well-characterized $\text{Fe}_3\text{O}_4(111)$ thin films by means of angle-resolved photoelectron spectroscopy (ARPES). The dispersions of the O $2p$ and Fe $3d$ electronic states were measured along the $\bar{\Gamma}-\bar{M}$ direction of the $\text{Fe}_3\text{O}_4(111)$ surface Brillouin zone (SBZ). The experimentally observed band dispersions are interpreted in a model which considers magnetite $\text{Fe}_3\text{O}_4(111)$ thin films as a stacked layered system, in which Fe^{2+} and Fe^{3+} cations are incorporated into the tetrahedral and octahedral interstitial sites of a close-packed fcc oxygen sublattice.²⁰ The Fe cations form the (2×2) superstructure at the surface. The surface crystallographic structure of the (111) plane can thus be represented as two sublattices which have different symmetries: the iron and oxygen ones. While the photoemission dispersion of the O $2p$ -derived states is determined by the SBZ of the oxygen sublattice, the Fe $3d$ -derived states near the Fermi energy (E_F) have a weak, periodic dispersion across the SBZ determined by the sublattice of the Fe_{tet} cations. The invisibility of the O $2p$ -derived states folded accordingly to the symmetry of the Fe sublattice is explained by matrix elements that decrease for decreasing strength of interaction of the involved electronic states with the superstructure crystal potential.

The experiments were carried out in two separate experimental stations. The first is located at the Russian-German Laboratory at the BESSY II storage ring. The dipole beamline DIP-16-1A provides a tuneable source of photons over a 30–1500 eV energy range. The ultrahigh vacuum (UHV) system for ARPES and x-ray absorption spectroscopy (XAS) at room temperature consists of a UHV chamber equipped with low energy electron diffraction (LEED) optics, a gas inlet, electron-beam evaporation cells, and a 127° CLAM4 analyzer for ARPES measurements. The total energy resolution in the ARPES measurements was set to 100 meV and the angle resolution was 1° . XAS spectra have been collected in the total electron yield mode and normalized to the maximum intensity. The base pressure in the vacuum chamber

FIG. 1. (Color online) Fe $L_{2,3}$ -edge XAS spectra of (a) the epitaxial $\text{Fe}_3\text{O}_4(111)$ films and (b) the epitaxial Fe(110) films. Insets show corresponding LEED patterns. (c) STM image of a defect-free surface of the epitaxial $\text{Fe}_3\text{O}_4(111)$ film and (d) the corresponding height profile taken along the line “A” marked in the STM image (c).

was 1×10^{-10} mbar. The second station is an Omicron Surface Science UHV system with a base pressure of 8×10^{-11} mbar equipped with an electron-beam evaporator for thin film deposition. *In situ* surface characterization was performed by low energy electron diffraction and scanning tunneling microscopy (STM). All STM measurements were carried out at room temperature using electrochemically etched polycrystalline tungsten tips cleaned in UHV by Ar^+ sputtering.

Clean 100-Å thick Fe(110) films were prepared *in situ* by electron-beam deposition on a W(110) substrate, while the thickness was simultaneously monitored by a quartz microbalance. The Fe(110) thin films were successfully oxidized to $\text{Fe}_3\text{O}_4(111)$ films by exposure to high-purity oxygen gas at a pressure of 5×10^{-6} mbar for 15 min and subsequent annealing at 300°C for 5 min. The same preparation procedure of high-quality ferromagnetic $\text{Fe}_3\text{O}_4(111)$ thin films was used successfully in earlier works.^{16,21} The high degree of crystalline order of the epitaxial $\text{Fe}_3\text{O}_4(111)$ films obtained in our experiments has been checked by LEED and STM. The surface cleanliness has been monitored by valence-band as well as core-level photoemission and STM.

Figure 1 shows the characterization of *in situ* prepared $\text{Fe}_3\text{O}_4(111)$ films performed by means of XAS, LEED, and STM. The left panel presents the Fe $L_{2,3}$ -edge XAS spectrum of the epitaxial $\text{Fe}_3\text{O}_4(111)$ thin film [Fig. 1(a)] in comparison with that of the epitaxial Fe(110) thin film [Fig. 1(b)]. As insets the corresponding LEED patterns of $\text{Fe}_3\text{O}_4(111)$ and Fe(110) surfaces are shown. The right panel of Fig. 1 presents the STM characterization of the $\text{Fe}_3\text{O}_4(111)$ surface: (c) topographical image and (d) corresponding line scan along trace A in (c). The important results are (i) the characteristic multiplet structure of the XAS spectrum at the Fe $L_{2,3}$ - and the O K -edges (not shown here) of Fe_3O_4 agree

FIG. 2. ARPES spectra of a $\text{Fe}_3\text{O}_4(111)$ thin film surface at 293 K recorded at $h\nu=58$ eV for emission polar angles of 0–25° (relative to the surface normal) along the $\bar{\Gamma}-\bar{M}$ direction of the $\text{Fe}_3\text{O}_4(111)$ surface Brillouin zone. Dashed lines 1–5 mark the major O $2p$ electronic states dispersions. The upper panel shows a LEED image ($E=121$ eV) of the prepared $\text{Fe}_3\text{O}_4(111)$ surface and the schematic representation of the oxygen-derived (dashed lines) and the Fe-derived surface Brillouin zones (solid lines).

with earlier experiments,^{11,12,22} (ii) the hexagonal (2×2) LEED patterns indicate the formation of a $\text{Fe}_3\text{O}_4(111)$ surface,^{12,14,16,21,23} and (iii) the defect free STM images of the $\text{Fe}_3\text{O}_4(111)$ films exhibit a hexagonal structure with (6.0 ± 0.1) Å periodicity. These data confirm the high bulk and surface quality of the investigated $\text{Fe}_3\text{O}_4(111)$ films.

The bottom panel of Fig. 2 shows representative valence band spectra of an epitaxial $\text{Fe}_3\text{O}_4(111)$ thin film as a function of the emission polar angle $\Theta(0-25^\circ)$ along the $\bar{\Gamma}-\bar{M}$ direction of the SBZ. All spectra are normalized to the maximum intensity for each spectrum. A photon energy of $h\nu = 58$ eV, which corresponds to the Fe $3p$ - $3d$ resonance,^{13,24} was used in all photoemission experiments yielding an increased photoemission intensity from Fe $3d$ states near E_F . As reported before, no significant difference in the band structure derived from experiment was found for the photon energy in the off- and on-resonance measurement regimes.^{25,26} The ARPES spectra in Fig. 2 show the Fe $3d$ -derived emission extended over 2 eV below E_F and the O $2p$ -derived emission between 2.5 and 8 eV of binding energy. The major dispersions of the O $2p$ states in the $\text{Fe}_3\text{O}_4(111)$ valence band are marked by dashed lines (1–5).

The borders of the SBZs were calculated separately for the oxygen sublattice and the iron sublattice SBZs (upper panel in Fig. 2). Following the $\text{Fe}_3\text{O}_4(111)$ surface structure the oxygen sublattice SBZ was taken into account by the $\bar{M}_{0\frac{1}{2}}^{\text{O}}$ point at $1.22 \text{ \AA}^{-1}$ giving the emission angle values of $\Theta=19.04^\circ$ and $\Theta=22.32^\circ$ for photoelectrons with the binding energies equal to 0 and 14 eV, respectively. The line

FIG. 3. (Color online) Contour plots of the ARPES intensity of a $\text{Fe}_3\text{O}_4(111)$ film at 293 K along the $\bar{\Gamma}-\bar{M}$ direction: (a) for the emission between E_F and 14 eV binding energy; and (b) expanded over 1.5 eV below the Fermi level.

between these two points represents the photoemission SBZ border of the oxygen sublattice in the present experiment (line B in Fig. 3). The iron sublattice was considered in a similar way with the $\bar{M}_{0/2}^{\text{Fe}}$ point at $0.61 \text{ \AA}^{-1}$ giving the corresponding angle values of $\Theta=9.39^\circ$ and $\Theta=10.95^\circ$. The line between these two points represents the SBZ border of the iron sublattice (line A in Fig. 3).

The obtained spectra for different emission angles (Fig. 2) were used to plot colored intensity maps of the $\text{Fe}_3\text{O}_4(111)$ thin film valence band as shown in Fig. 3: (a) over a range of 14 eV below E_F and (b) over a range of 1.5 eV below E_F .

The O $2p$ electronic states show a pronounced almost monotonic experimental dispersion from about 8 eV down to 2.5 eV of binding energy within polar angle changes from 0 to about 20° ($\bar{M}_{0/2}^{\text{O}}$) [lines 1–5 in Fig. 3(a)]. At the same time the Fe $3d$ electronic states reveal an obviously nonmonotonic dispersion with a period of 19° starting at the $\bar{\Gamma}_{00}$ point and ranging up to the $\bar{M}_{0/2}^{\text{O}}$ point (marked also as $\bar{\Gamma}_{01}^{\text{Fe}}$) [see Fig. 3(b)]. This evidences that the dispersion of the Fe $3d$ -derived states follows the symmetry of the iron sublattice. However, the dispersion symmetry of the O $2p$ electronic states measured with photoemission cannot be described in terms of the $\text{Fe}_3\text{O}_4(111)$ SBZ as a whole as it follows the symmetry of the oxygen sublattice. This means that the correct description

of the surface electronic band structure of the $\text{Fe}_3\text{O}_4(111)$ film obtained in the photoemission experiment is only possible when two different representations of the surface Brillouin zones are considered. The first one is the oxygen derived SBZ $\bar{\Gamma}_{00}-\bar{M}_{0/2}^{\text{O}}$ corresponding to the emission angles $0-20^\circ$ [line B in Figs. 3(a) and 3(b)] and the second one is the iron-derived SBZ $\bar{\Gamma}_{00}-\bar{M}_{0/2}^{\text{Fe}}$ corresponding to the emission angles $0-9^\circ$ [line A in Figs. 3(a) and 3(b)]. Different representations of the surface Brillouin zones have recently been used for the interpretation of photoemission spectra in a quasi-two-dimensional La-graphite intercalation compound (La-GIC).²⁷ In such intercalation systems guest La-metal atoms are periodically placed between the carbon planes and the electronic structure of the whole system can primarily be described on the basis of the charge transfer from the metal d -orbitals to graphite π^* -orbitals. It was shown that the suppression of the photoemission from folded bands in this layered compound is caused by vanishing of the corresponding matrix elements due to weak interaction between graphene and La sublattices. Based on the considered example of La-GIC a general conclusion that appearance of folded bands in photoemission spectra depends crucially on the matrix elements reflecting strength of interaction of the involved electronic states with the crystal potential is derived. Although unlike La-GIC, Fe_3O_4 is not considered to be an almost ideal quasi-two-dimensional electronic system, the weak dispersion of some O $2p$ and Fe $3d$ states in the valence-band structure of $\text{Fe}_3\text{O}_4(111)$ observed along the $\bar{\Gamma}-L$ direction^{13,24} indicates their two-dimensional properties.

FIG. 4. (Color online) Cross section (a) and top (b) view of the $\text{Fe}_3\text{O}_4(111)$ surface crystallographic structure. In (a) the (111) layer sequence of tetrahedrally and octahedrally coordinated Fe cations in between the close-packed ABC-stacked oxygen layers is shown. In (b) the top view of the $\text{Fe}_3\text{O}_4(111)$ surface unit cell with a lattice constant of $5.96 \text{ \AA}$ (white hexagon) and of the oxygen-sublattice surface unit cell with a lattice constant of $2.98 \text{ \AA}$ (black-hexagon) are represented.

The possibility to represent measured surface electronic structure of these bands as decoupled Fe- and O-derived electronic subsystems is closely related to the crystallographic structure of the $\text{Fe}_3\text{O}_4(111)$ surface. This surface can be described as a multilayered system consisting of hexagonal close-packed oxygen (111) layers with a cubic $ABCABC\dots$ stacking sequence along the $[111]$ direction [Fig. 4(a)] with the A - A periodicity of $7.30 \text{ \AA}$ and a separation of $2.43 \text{ \AA}$ between the close-packed oxygen layers. In between the oxygen (111) planes tetrahedrally and octahedrally coordinated Fe anions are located. The regular $\text{Fe}_3\text{O}_4(111)$ surface forms an unreconstructed bulk termination that exposes $1/4 \text{ ML}$ of Fe_{tet} atoms above the close-packed oxygen layer [Fig. 4(b)]. The $\text{Fe}_3\text{O}_4(111)$ surface can be described as a layered structure where Fe^{2+} and Fe^{3+} cations are incorporated, into the tetrahedral and octahedral interstitial sites of the close-packed fcc oxygen sublattice.²⁰ The Fe-derived electronic states near E_F are essentially localized,^{9,10} forming to some extent hybrids with $2p$ states of adjacent oxygen layers. Oxygen states (with binding energy of about 7 eV at the $\bar{\Gamma}_{00}$ point) which are not strongly hybridized with Fe $3d$ states, experience only a weak perturbation from the crystal potential of the Fe atoms due to the higher binding energy of oxygen states. As a result, due to

the matrix element effects²⁷ oxygen-originated $2p$ -bands folded according to the Fe sublattice symmetry are not visible in the ARPES spectra and mostly oxygen sublattice derived $2p$ -bands can be observed.

In conclusion, we present an angle-resolved photoelectron spectroscopy study of the surface electronic band structure of thin epitaxial $\text{Fe}_3\text{O}_4(111)$ films at 293 K along the $\bar{\Gamma}-\bar{M}$ direction of the $\text{Fe}_3\text{O}_4(111)$ SBZ. Oxygen $2p$ -derived states show a strong dispersion between 8 and 2.5 eV binding energies, whereas the iron $3d$ -derived states reveal only a weak, but periodic dispersion near E_F . The latter periodicity is half that of the oxygen $2p$ -derived states. Apart from Fe_3O_4 being a complex three-dimensional crystal, the surface electronic band structure of the epitaxial $\text{Fe}_3\text{O}_4(111)$ films measured with photoemission can be understood by considering the layered periodic multilayered structure of iron and oxygen, where Fe^{2+} and Fe^{3+} cations are incorporated into the close-packed fcc oxygen sublattice layers.

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*Present address: Institut für Festkörperphysik, Technische Universität Dresden, D-01062 Dresden, Germany.

†Present address: Fachbereich Physik, Universität Konstanz, D-78457 Konstanz, Germany.

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