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Identification of Fe 3d empty states from the total current spectra of an α -Fe₂O₃(0001) surface

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Abstract. An intensive triplet line is revealed in the total current spectrum (TCS) of a reconstructed α -Fe₂O₃(0001) surface. The nature of the observed structure in the TCS is discussed in comparison with previously reported data from photoemission, inverse photoemission and theoretical investigations. It is found to be a consequence of the electron transitions into an Fe 3d band of empty states. Energy locations of Fe 3d-band extrema (0.8 ± 0.05 and 1.8 ± 0.05 eV above the bottom of the conduction band) and its splitting (1 ± 0.05 eV) are estimated from the proposed schemes of electron transitions.

1. Introduction

The iron oxide band structures in the vicinity of the Fermi level (valence and conduction bands) have been the subject of experimental and theoretical investigations during the last decade [1–7]. The main efforts were focused on elucidating the nature of the valence and conduction band electronic states and on obtaining data on the locations of the density-of-states maxima and on the energy widths of the gaps. It was found that the iron oxides are characterized by an insulating gap of a width of about 2–3 eV and that the upper part of the valence band originates from O 2p states and the lower part of the conduction band originates from Fe 3d states. Experimental information on the valence band structure was obtained by using photoelectron spectroscopy [5] and on the conduction band structure (empty electronic states) by extraction from inverse photoemission [3, 6] and from x-ray absorption [7].

In the present investigation we have applied low-energy total current spectroscopy (TCS) to study the structure of empty electronic states localized below the vacuum level of the α -Fe₂O₃(0001) surface. TCS is a surface-sensitive technique useful for materials characterization in which band-structure effects play an important role [8–10]. In particular, a most pronounced fine structure in a TC spectrum originates when a sample under investigation is characterized by well defined narrow maxima of empty states. Such a property is fortunately exhibited by α -Fe₂O₃ samples. Additionally, TCS has several advantages such as low electron energies, low beam current and high surface sensitivity.

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2. Experimental procedure

All of the measurements were performed in an ultrahigh-vacuum system (base pressure 10^{-8} Pa) that combines different surface analytical techniques. Surface characterization by Auger electronic spectroscopy (AES) was performed by using a (Perkin–Elmer) double-pass cylindrical mirror analyser. A four-grid LEED system can be switched between the diffraction mode and an operational mode in which the TC spectra are measured. The experimental set-up has previously been described in more detail [11]. In the TCS experiment a well collocated beam of slow electrons is directed at normal incidence onto the surface under investigation, and the total current $I(E_1)$ passing in the sample circuit is monitored as a function of the incident-electron energy E_1 in the range $0 \leq E_1 \leq 15$ eV. In order to reveal the fine structure present in the total current, the first derivative of the current, $S(E_1) = dI(E_1)/dE_1$, is measured using a lock-in amplification technique. $S(E_1)$ is referred to as the TCS signal [8–10]. In our equipment the half-width of the incident-electron beam was about 0.6 eV (this magnitude defines the energy resolution), the incident-electron energy being modulated at 800 Hz, 0.1 eV peak-to-peak. The incident-electron current was normally equal to 10 nA, independent of the energy, and was focused onto a surface spot 0.5 mm in diameter.

The sample under study was a synthetically grown crystal of α -Fe₂O₃(0001) (haematite), with a 3×5 mm² surface area (Atomergic Chemetals, USA). The surface of interest was prepared by cleaving just before installation into high-vacuum conditions. The sample was mounted on a manipulator with auxiliary facilities for heating, temperature measurement, rotation and motion.

3. Results

A sharp LEED pattern from the surface under investigation was obtained after brief annealing at about 850 K. The surface cleanliness was checked by AES. The spectrum exhibited very distinct peaks of iron and oxygen and a small surface impurity of carbon (the intensity from carbon was less than 3% of that from oxygen). LEED patterns were observed over a wide range of incident-electron energies E_1 . First-order diffraction spots appeared at $E_1 \simeq 7$ eV. LEED patterns obtained at different E_1 are presented in figure 1 (frames (a), (b) and (c) were obtained at electron energies of 14.5, 21.5 and 38.5 eV, respectively). The diffraction pictures observed at different E_1 exhibit a composite of two hexagonal structures characterized by different lattice parameters, and rotated by 30° with respect to each other. The scattering angle θ of the diffraction beam varies in accordance with the common model of surface diffraction, and the $E_1 = f(1/\sin^2 \theta)$ dependence shows a linear behaviour. An inner potential $V_0 = 3.5 \pm 0.5$ eV and lattice parameters $a_1 = 0.59 \pm 0.05$ nm and $a_2 = 0.50 \pm 0.05$ nm were calculated from the cut-off at $1/\sin^2 \theta \rightarrow 0$ and from the slope of the straight-line fit of the experimental dependencies for (01) beams. The parameters obtained correspond well to the surface unit-cell constants for α -Fe₂O₃(0001) (0.503 nm) and for Fe₃O₄(111) (0.593 nm). The α -Fe₂O₃(0001) surface unit cell is rotated by 30° with respect to that of Fe₃O₄(111) [12, 13], suggesting that the surface under investigation is a clean α -Fe₂O₃(0001) surface containing reconstructed Fe₃O₄(111) patches. This conclusion is in agreement with recently published results [14, 15].

Investigations of the low-energy TCS were performed *in situ* on this well defined surface of α -Fe₂O₃(0001) with reconstructed Fe₃O₄(111) patches. Experimental spectra were measured at normal incidence of the electron beam and spectra variations were traced under variation of the incidence angle. Angle-dependent TCS measurements allow one to

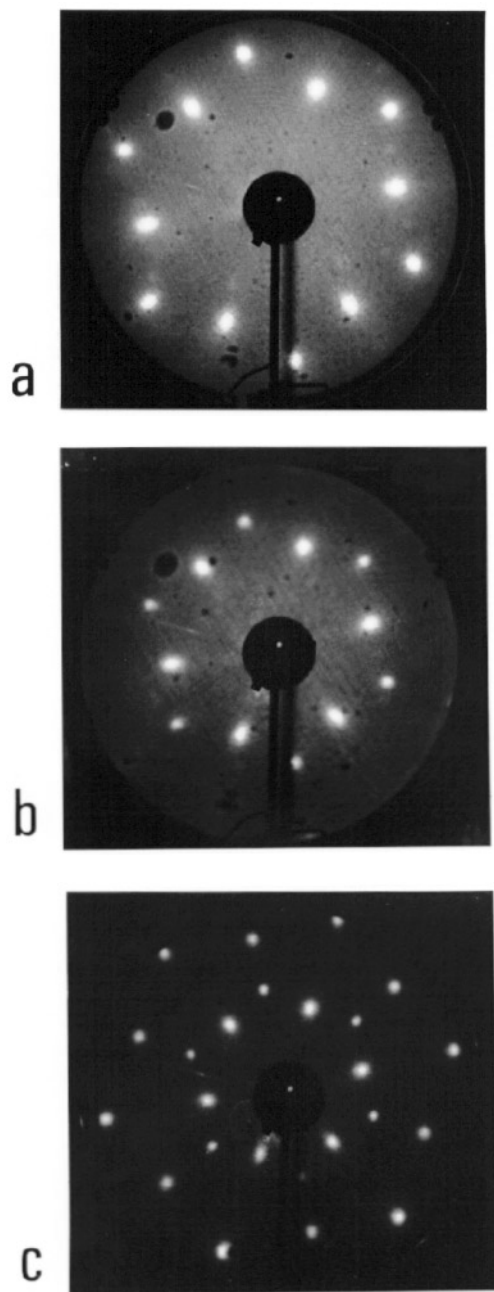


Figure 1. LEED patterns from an $\alpha\text{-Fe}_2\text{O}_3(0001)$ surface at different primary-electron energies: (a) 14.5 eV, (b) 21.5 eV, (c) 38.5 eV.

distinguish the different mechanisms of the TCS signal formation [10]. One of these is based on an inelastic scattering model (or interband transition model) in which a peak in the TC spectrum appears at the electron energy corresponding to the threshold of discrete interband transition excitation between maxima of the density of states. The energy locations of these

features in TCS are not dependent on the incidence angle of the exciting beam [8–10]. A second mechanism is based on an elastic scattering model (or electron diffraction model) in which the energy dependence of the electron elastic scattering reflectivity coefficient is determined by the band dispersion of empty electronic states located above the vacuum level [10, 16, 17]. Corresponding features in TCS are characterized by a strong angular dependence in accordance with the band dispersion along the Brillouin zone line coinciding with the direction of the incident-electron wave vector [18, 19].

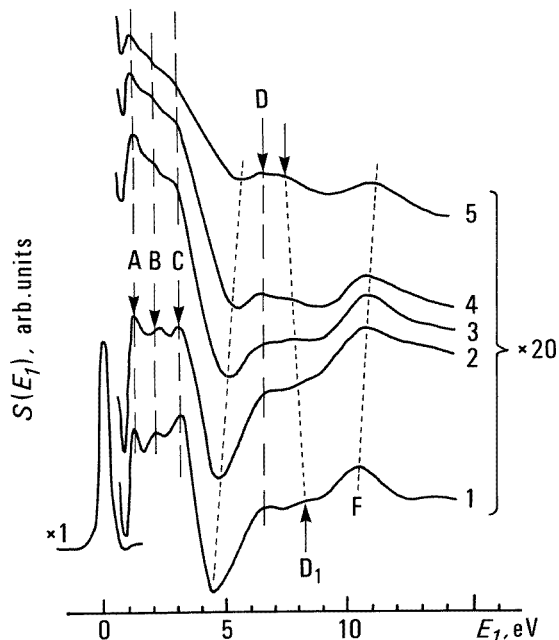


Figure 2. TC spectra of the α -Fe₂O₃(0001) surface measured at normal (1) and inclined (2–5) incidence. The corresponding values of k_{\parallel} are (1) 0, (2) 0.73, (3) 1.26, (4) 1.92 and (5) 2.52 nm⁻¹.

The TC spectra obtained are presented in figure 2. The primary-electron energy E_1 is measured with respect to the vacuum level which coincides with the position of the primary peak in the TC spectrum at normal incidence (this primary peak is shown only for curve 1, measured at normal incidence). The incidence angle was varied by rotating the sample. Normal incidence corresponds to a zero value of the incidence angle. With incidence-angle increase, the primary peak shifts upwards by the energy ΔE associated with the primary-electron velocity component parallel to the surface. The parallel component of the incident-electron wave vector may be found as $k_{\parallel} = (2 \Delta E m / \hbar)^{1/2}$, where m is the electron mass and \hbar is Planck's constant [10, 19]. Estimations yield $k_{\parallel} = 0.73, 1.26, 1.92$ and 2.52 nm^{-1} for curves 2, 3, 4 and 5, respectively. The corresponding values of the sample rotation with respect to the surface normal in the $[11\bar{2}0]$ direction were $2^\circ, 4^\circ, 6^\circ$ and 8° , respectively.

In the TC spectra, the most pronounced fine structure is associated with a very intensive triple set of lines consisting of maxima A (1.2 eV), B (2.2 eV) and C (3.2 eV). There are two less intensive and wider maxima at D (6.4 eV), D₁ (8.2 eV) and F (10.4 eV), respectively. The nondispersive character of the maxima A, B and C configures their inelastic threshold

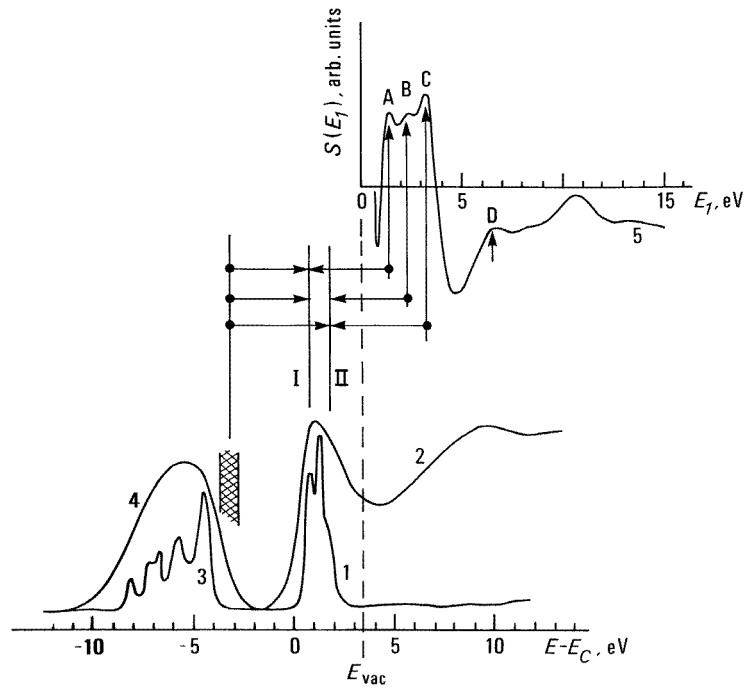


Figure 3. The energy diagram for Fe₂O₃: (1), (3) calculated DOS [3], (2) an inverse photoemission spectrum [6], (4) a photoemission spectrum [5], and (5) a TC spectrum (this work). The horizontal pairs of arrows indicate electron transitions responsible for the TCS triplet-structure (A, B, C) formation.

nature associated with electron transitions between maxima of the density of states. A distortion of the triplet shape with the incidence-angle increase is due to a primary-peak shift (for curve 5, ΔE is about 0.3 eV) resulting in a strong change of the background in the region of the triplet location. The structure of the TC spectrum at energies $E_1 > 4$ eV is characterized by an angle-dispersive behaviour (excluding maximum D). A trough at 4.5 eV and the maxima D₁ and F change their energy location with incidence-angle variation (in figure 2, the movements of these features are indicated by dotted lines). Identification of angle-dispersive features for energies $E_1 > 5$ eV seems in our case to be very complicated. In this energy region, emergence of the first-order diffracted beams takes place, and as a consequence the energy dependence of the total current is caused by added effects of the 00-beam and 01-beam intensity variations [20].

4. Discussion

In this section we will focus our consideration on the origin of the triple-line structure in the TC spectrum. According to theoretical results [8–10], pronounced fine structures in TC spectra are predicted for materials in which narrow maxima of empty densities of states (DOS) are localized between the Fermi and vacuum levels. Similar conclusions were made on the basis of experimental investigations on samples of cadmium sulphide and vanadium [8, 10, 21]. The condition for a TCS peak appearing is a coupling transition of both

valence and primary electrons to the maxima of the empty DOS, resulting in a threshold increase of the inelastic scattering probability. The latter process is accompanied by the threshold decrease of an elastic reflection component, i.e. one deals with the influence of the inelastic channel on the elastic one. In the approximation considered [8–10], the shape of the TCS signal is defined by the gradient of the valence DOS. In figure 3 an energy diagram explaining the triplet-structure formation in the TC spectrum of an Fe₂O₃ surface is shown. Curves 1 and 3 present the results of theoretical calculations of the iron oxide DOS [3]. The valence band DOS (curve 3) is mainly determined by the O 2p contribution, and the empty DOS (curve 1) is mainly determined by an Fe 3d contribution. Curves 2 and 4 present the results of experimental studies of the empty states (inverse photoemission [6]) and the valence states (photoemission [5]) in Fe₂O₃, respectively. One can see that photoemission and inverse photoemission data correspond well to the theoretical DOS. The TCS spectrum obtained in this study for the Fe₂O₃(0001) surface is shown by curve 5. The fitting of the energy scales is based upon the value of the inner potential $V_0 = 3.5$ eV (estimated from LEED pattern behaviour) which corresponds to the magnitude of the electron affinity in the case of wide-gap materials. The range of the energy location of the maximum of the gradient of the valence DOS is indicated on the diagram by a hatched vertical band. As mentioned above, the appearance of the maximum in the TC spectrum corresponds to the following scheme of electron transitions: the initial state is the maximum of the gradient of the valence DOS, the final state is the maximum of the empty DOS, and the coupling transitions of both valence and primary electrons take place to the maximum of the empty DOS. In terms of such electron transitions the triplet structure in the TC spectrum (maxima A, B and C) may be understood in terms of the proposition of the doublet structure of an Fe 3d-derived empty-states band. The locations of these two empty-state peaks that satisfy the above-discussed electron transition diagrams are marked by the vertical lines I and II, and the corresponding electron transitions are shown by three pairs of horizontal arrows in figure 3. From the above-discussed schemes of electron transitions, the energies of both maxima of the Fe 3d empty states were estimated to lie 0.8 ± 0.05 and 1.8 ± 0.05 eV above the bottom of the conduction band, respectively. The Fe 3d-band splitting $\Delta E = 1 \pm 0.05$ eV is in accordance with the data reported earlier [7], in which the Fe 3d-band splittings for Fe₂O₃ ($\Delta E = 1.3$ eV) and for Fe₃O₄ ($\Delta E = 0.9$ eV) were observed by x-ray absorption spectroscopy. These Fe 3d-band splittings ΔE are average values. Therefore, it is not possible for us, with our TCS resolution, to distinguish between the two surfaces, even though their LEED patterns (figure 1) are different.

As for the nondispersive low-intensity peak D we can propose a relation to the age of the high-lying band of empty states which was traced as the second maximum (at $E - E_c = 9.5$ eV) in an inverse photoemission spectrum (curve 2 in figure 3) [6].

5. Conclusions

In this communication we have presented data from TCS studies of a reconstructed α -Fe₂O₃(0001) surface. An intensive triplet line was observed in the TC spectrum. A comprehensive analysis of the results obtained in comparison with the previously reported data from photoemission, inverse photoemission and theoretical investigations [3, 5, 6] resulted in the identification of the observed structure in the TC spectrum as related to the electronic transitions into the Fe 3d band of empty states. The energy location of the Fe 3d-band extrema (0.8 ± 0.05 and 1.8 ± 0.05 eV above the bottom of the conduction band, respectively) and its splitting (1 ± 0.05 eV) were estimated on the basis of schemes of electron transitions.

Acknowledgments

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