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Role of final states in photoemission from Al(1 1 1)

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Abstract

Enhancement of surface state peaks in angle resolved ultraviolet photoelectron spectra (ARUPS) from the Al(1 1 1) surface is studied experimentally and theoretically within the one-step model of photoemission. The resonant enhancement of the surface state emission is explained by the crucial role of elastic scattering of the outgoing electron. Dipole transitions to evanescent states in the final bands of the crystal are shown to determine photoemission at the resonant photon energy. The band structure based explanation is confirmed by the measurements of electron reflectivity and of the fine structure of valence band spectra. The surface sensitivity of ARUPS is shown to depend strongly on the complex band structure of the crystal and to be finely tunable by the choice of photoemitted electron energy.

Keywords: Synchrotron radiation photoelectron spectroscopy; One-step model of photoemission; Complex electron band structure; Ab initio theory; Surface states; Al(1 1 1); Augmented plane waves

1. Introduction

Energy dependence of the electron mean free path and surface sensitivity of photoemission and LEED experiments is traditionally interpreted with the universal U-shaped curve [1]. Deviations from this simple dependence have recently become a subject of study: in [2] the strong, periodic in photon energy, enhancements of the surface state emission from Al(1 0 0) relative to bulk emission were observed in the energy range 125–760 eV. The unexpected result was explained by the effect of atomic vibrations, which influence bulk and surface state excitations differently. Surface state emission has recently been studied within an ab initio one-step theory [3], and the important role of the photoemission final states was revealed. The shape of the surface state emission spectrum (constant initial state – CIS) was found to depend on details of the complex band structure of the semi-infinite crystal [4]. In [3] the enhancement of the normal emission from the surface state at the Al(1 1 1) surface was theoretically predicted to be accompanied by a decrease of the electron transmission at the final state energy, and the width of the CIS spectrum was found to be determined by the elastic scattering, i.e., by band structure effects rather than by the inelastic scattering of the photoelectron. Here, ARUPS spectra at lower excitation energies, where phonon contributions to the photoemission line shape are small [5], are presented for Al(1 1 1): a combined experimental and theoretical study of the normal emission provides an experimental confirmation of the theoretical predictions and explains both the surface state and the bulk emission within the same ab initio theory.

The surface state at the center of the (1 1 1) Brillouin zone was first observed by Kevan et al. [6] within a narrow interval of photon energies around 53 eV. An attempt to explain the width of this interval in terms of direct transitions within a nearly-free-electron (NFE) model has, however, lead to a strongly overestimated inelastic scattering of the photoelectron: the experimentally determined mean free path of 7 Å was associated with an inverse lifetime of 4.5 eV [6]. We shall show that for Al(1 1 1) inelastic

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scattering is much weaker, and that the mean free path around 53 eV is determined by elastic scattering. Regarding the bulk emission from Al(1 1 1), a transfer of intensity with increasing photon energy from the lower to the upper valence band was observed in [6] and qualitatively explained within the NFE model. In this paper we present the fine structure of the spectra and its explanation in terms of band structure.

2. Experiment

The ARUPS measurements were performed at the Elettra synchrotron light source in Trieste at the Material Science Beamline. The photon energy was changed from 44 eV to 164 eV. The UHV experimental chamber with a base pressure in the 10^{-10} mbar range is equipped with a 150 mm mean radius electron energy analyzer Phoibos 150. The electron energy analyzer worked in the constant pass energy mode (5 eV). An energy resolution for monochromator and electron energy analyzer was 150 meV. The angular resolution was $\pm$ 2.0°. The valence band spectra were collected in normal emission and the synchrotron radiation was directed at 45° with respect to the surface normal. The background of the EDCs was subtracted by the Shirley procedure. All photoemission spectra were measured at room temperature.

The aluminum crystal was cut and polished normal to the (1 1 1) axes to within 0.5°. The cleaning was made by several ion-bombardment-annealing cycles (1000 eV Ar^+ ions, ~15 μA, ~30 min sputtering; 450 °C flash for 10 s). This produced atomically clean surface as determined by XPS with good surface crystallinity checked by LEED. The LEED intensity of the specular beam was measured in the ADES 400 photoelectron spectrometer equipped with rear view LEED. To visualize the beam the Al(1 1 1) crystal was slightly deflected (~5°) from the normal direction. The electron diffraction was measured from 25 eV to 60 eV with 2 eV step. The intensity was normalized to the incident beam current.

3. Computations

The ab initio ARUPS calculations are performed within the one-step photoemission theory [7] using the band structure approach both to final and to initial states [3]. A detailed description of the methodology for an all-electron potential of general shape within the augmented plane wave formalism has been presented in [8]. The LEED wave function is a scattering solution for a plane wave incident from vacuum. In the bulk the wave function is damped owing to the presence of an imaginary part of the crystal potential (optical potential) taken to be $V_i = 2$ eV. For the initial states the potential is assumed real; the finite hole lifetime is included by a Lorentzian broadening of the spectral function, with the FWHM growing linearly from 0.25 eV at the Fermi level to 0.75 eV at the bottom of the valence band.

4. Results and discussion

The unoccupied conducting complex band structure of Al(1 1 1) in the presence of absorbing potential $V_i = 2.0$ eV is shown in Fig. 1b, and the resulting spectrum of the specularly reflected electron beam intensity I_0 in Fig. 1c. Below 45 eV a single CBS branch strongly dominates, as one

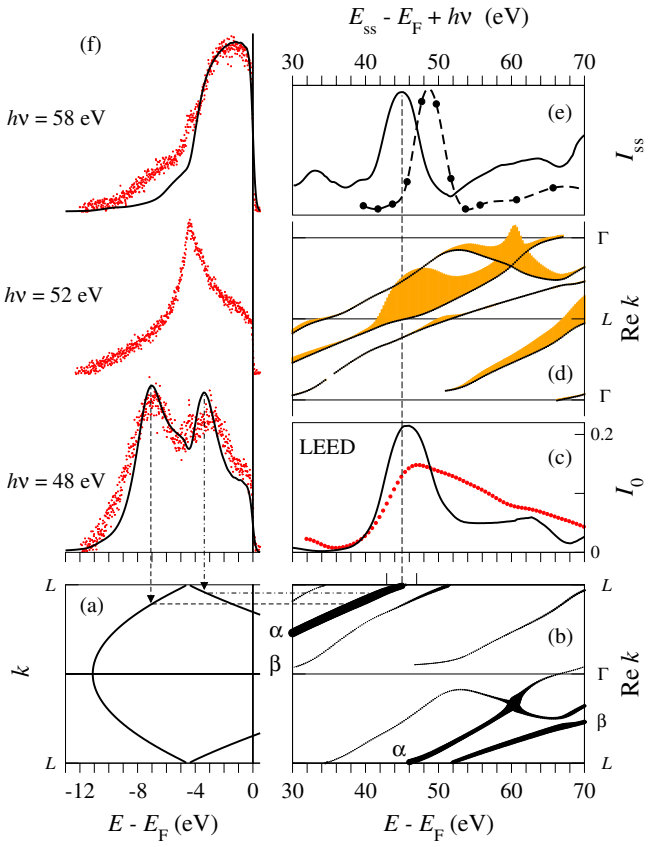

Fig. 1. Interpretation of the valence band normal emission from Al(1 1 1) in terms of ab initio complex band structure. (a) Ab initio band structure of initial states along the LΓL interval. (b) Ab initio complex band structure (CBS) of final states obtained with the optical potential $V_i = 2$ eV; shown is the real part of the complex Bloch vector as a function of energy. Only the branches of the CBS strongly contributing to the LEED states are shown. The thicknesses of the lines are proportional to their contribution. The letters α and β label two branches of the CBS responsible for the electron transmission in the LEED experiment. (c) LEED: experimental (dots) and theoretical (line) intensities of the specularly reflected beam. The same LEED states are used to obtain the photoelectron EDCs in graph (f). I_0 is the ratio of the current carried by the normally reflected beam to the incident current. Experimental spectrum is scaled. (d) Partial wave decomposition of the transition probability from the surface state. Vertical extent of the shaded area is proportional to the squared modulus of the momentum matrix element between the surface state and the Bloch wave. (e) Photon energy dependence of the surface state emission. Theoretical line and experimental circles show the ratio of the surface state emission intensity to the integral intensity from the bulk valence states. (f) Experimental (dots) and theoretical (line) EDCs at $h\nu = 48$, 52 and 58 eV. A uniform shift by 2.5 eV is assumed for theoretical final states. The dashed and dot-dashed lines show the direct transitions from the initial states at binding energies 7.0 and 3.3 eV, respectively.