

Application of (e,2e) spectroscopy for studying surface states of W(001)

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Abstract

We applied the experimental technique of low energy (e,2e) spectroscopy in back-reflection geometry to measure the two-dimensional energy distributions of correlated electron pairs excited by 20 eV primary electrons from a clean and oxygen covered W(001) surface. For the first time the contribution of correlated electron pairs originating from two different W(001) surface states S_1 and S_2 was identified in the (e,2e) spectra, thus demonstrating the high surface sensitivity of low energy (e,2e) spectroscopy. It was found that the generation of electron pairs from W(001) surface states is considerably suppressed by the adsorption of 0.1 L of oxygen. The binding energies and the k_{\parallel} -distributions of these states as determined in our measurements are in a reasonable agreement with the photoemission data. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The measurement of energies and momenta of two electrons originating from a collision between an incident electron and a target is usually known as '(e,2e) technique'. This technique was successfully applied to measure momentum density distribution (i.e. the square of the wavefunction in momentum representation) of electrons in free atoms and molecules [1] which is often referred to as 'wavefunction mapping'. Over the last 20 years the (e,2e) spectroscopy was developed as a tool for studying the electron momentum density distribution in solid free standing films [2, 3]. In this case high energy incident electrons ($E_p \approx 20$ keV) penetrate through a thin solid film

(thickness ≈ 100 – 200 Å) where they can scatter off target electrons such that two electrons leave the film in a forward direction. By measuring the energies and momenta of both outgoing electrons the initial energy and momentum of the target electron can be determined. In this geometry the fast electron–electron collision can be described in the Born approximation where the incident and scattered electrons are represented by plane waves. Within this approach the differential cross section for the scattering process is proportional to the momentum distribution of the target electrons [1, 3].

In order to increase the surface sensitivity of the (e,2e) technique and to study the electronic structure of solid surfaces and surface phenomena, experimental arrangements for investigating (e,2e) reactions in back-reflection geometry with low energy incident electrons ($E_p = 10$ – 80 eV) [4, 5] and medium primary

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energy (300 eV) [6] have been designed. In this geometry the incident electron with well defined energy and momentum impinges on the surface of a solid sample, while the two outgoing electrons are detected coincidentally in the back hemisphere, i.e. the half sphere above the sample's surface. In order to understand the underlying scattering process, further momentum exchange between electrons and lattice has to be considered in addition to the electron–electron collision. For a single crystal sample it was found [6–8] that the experimental data are in good agreement with a two-step model, assuming an elastic diffraction process leading to the back reflection of the primary electron as a first step, followed by an electron–electron collision in the second step. In the frame of this picture one can consider the incident electron first being elastically backscattered at the lattice and then generating correlated electron pairs, which leave the sample in a backward direction. On the basis of this kinematical model, energy and momentum of the incident (diffracted) electron just before the electron–electron collision is known, such that the measurement of energy and momenta of the two coincident final electrons allows to analyze the scattering dynamics of the process.

For low energy primary electrons, the theoretical treatment of this process requires the initial and final state wave functions to be described by LEED states [9], which leads to a more complicated relation between the differential (e,2e) cross section and the momentum density distribution of the valence electrons than in the case of transmission geometry.

In the present paper we report on the first experimental results obtained from applying low energy back-reflection (e,2e) spectroscopy for investigating surface phenomena on W(001). We have chosen W(001) as a sample since its electronic properties have been widely studied by different techniques (field emission spectroscopy [10, 11], photoemission spectroscopy [12–17]).

An important issue of this work is the evaluation of the contribution of emitted electron pairs originating from the surface states to the total emission of correlated pairs. We can extract k_{\parallel} -distribution functions for W(001) surface states from our data if we assume the (e,2e) cross section to be proportional to the target electron momentum distribution. By comparing our k_{\parallel} -distributions with those obtained

from photoemission measurements, we gain an 'order of magnitude' estimate on the deviation of the assumed proportionality between (e,2e) cross section and initial momentum distribution for the case of our geometry and energy range.

2. Experiment

Our experimental setup consists of two 75 mm MCP-based position sensitive electron detectors oriented in a plane that contains both detector axes and the surface normal of the sample. Each detector is 140 mm from the sample, resulting in an angular acceptance in the scattering plane of $\pm 15^{\circ}$. The two detector axes are at an angle of 80° to each other. A parallel electron beam of about 1 mm diameter impinges on the sample surface such that it includes an angle of 2.2° with the surface and an angle of 95° with the bisector between both detectors, the electron gun being in the plane of the detectors. A sketch of the setup is shown in Fig. 1. The electron beam intensity has a bunched time structure, i.e., the intensity is concentrated in regular bunches of 1 ns width and 300 ns time distance. Pairs of electrons generated in the sample by the primary electron beam that leave the sample in a backward direction are detected coincidentally by the two MCP-detectors. The time structure of the incident electron beam allows to measure the flight time of outgoing electrons between sample and detector and consequently to determine their kinetic energy. In the range of electron energies investigated here, we achieve an energy resolution of $\Delta E_{\text{kin}} = 0.4\text{--}0.7$ eV. The advantage of this spectroscopic technique

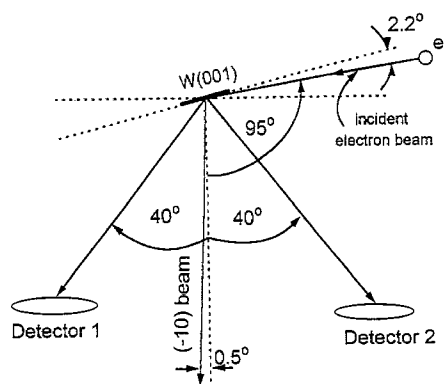


Fig. 1. Sketch of the experimental setup.

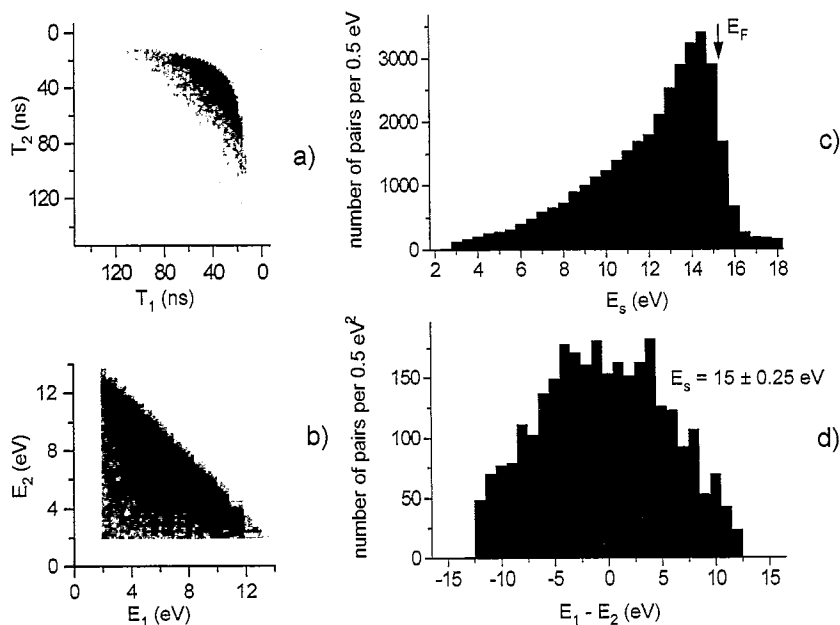


Fig. 2. Different representations of correlated electron pairs from a clean W(001) crystal: (a) two-dimensional time-of-flight distribution; (b) two-dimensional energy distribution; (c) distribution of the sum energy of electron pairs; (d) distribution of energy sharing between the electrons of a pair within a sum energy range of $E = 15 \pm 0.25$ eV.

with respect to conventional electron spectroscopy techniques is a large detection efficiency.

Clean surface conditions of the W(001) sample during the measurement are provided by standard cleaning and analysis procedures. Orientation of the sample is achieved by a rotatable holder where each particular setting is controlled by observing the LEED-patterns of elastically diffracted primary electrons in the position sensitive electron detectors. The base pressure in the scattering chamber during the measurement was in the 10^{-11} mbar range.

All experimental data presented in this paper have been measured with a primary electron energy of $E_p = 20$ eV.

3. Experimental results and discussion

Fig. 2(a) shows a density plot of the two-dimensional time-of-flight distribution of electron pairs from a clean W(001) surface. The coordinate axes in this plot represent the flight times of electron 1 and 2, respectively, in reversed direction such that the velocity of electron pairs increases from the lower left to

upper right. The intensity distribution in the plot shows a ridge-like maximum and a pronounced cutoff along a curved line. When transforming the electron's flight time into kinetic energy (Fig. 2(b)), the curved intensity cutoff is converted into a straight diagonal line representing a constant sum energy of electron pairs of $E_s = E_1 + E_2 = 15$ eV, while the maximum of intensity can be found in a diagonal band of about 1 eV width below the cutoff line. The integrated numbers of counts within bands of 0.5 eV width for different E_s represent the distribution of correlated electron pairs as a function of the sum energy. This distribution, which is shown in Fig. 2(c), again reflects a maximum in the vicinity of $E_s \cong 14.5$ eV. Considering the primary electron energy of $E_p = 20$ eV and the work function of W(001) equal to 4.6 eV, we interpret the electron pairs with maximum sum energies to be generated from the vicinity of the Fermi level.

Further analysis of the two dimensional energy distribution of correlated electron pairs is done by plotting the intensity distribution of the energy difference ($E_1 - E_2$) between two electrons of a pair within a band of constant sum energy. As an example, this

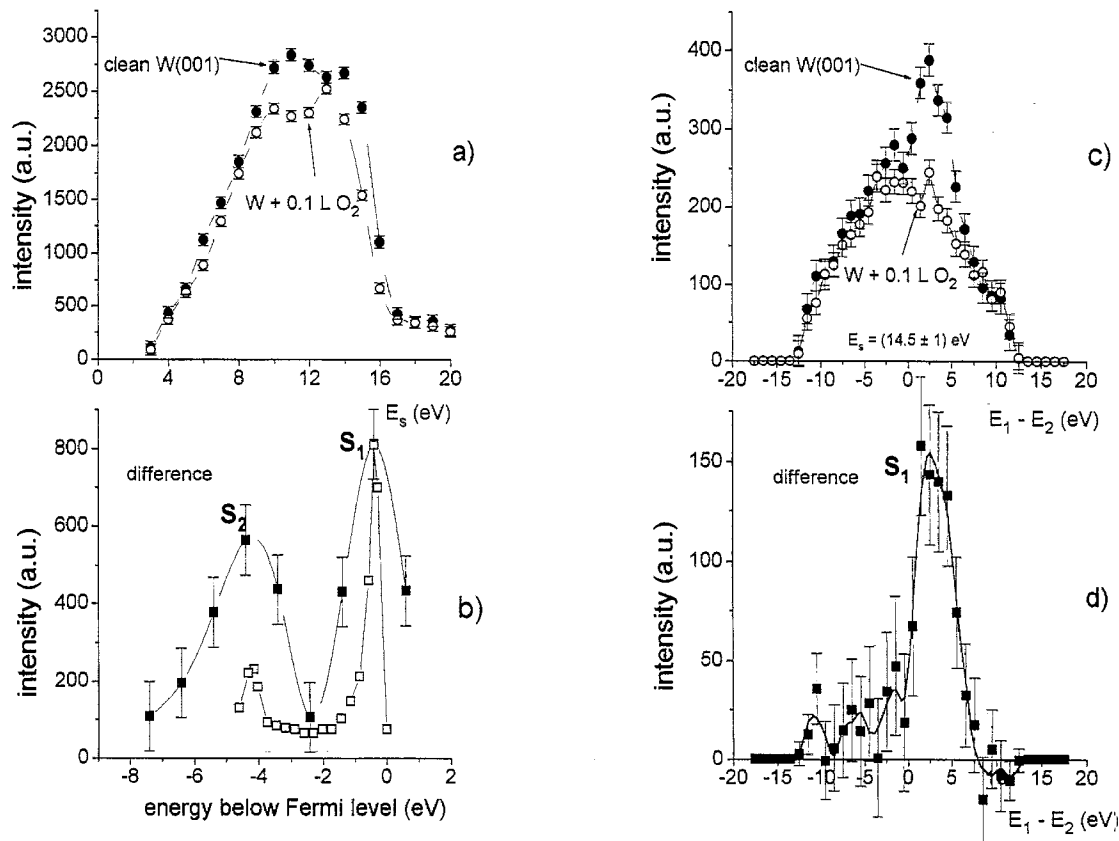


Fig. 3. Effect of the oxygen adsorption on the energy distribution of correlated electron pairs. (a) Sum energy distribution of electron pairs from the clean (full circles) and oxygen covered (open circles) W(001) surface. (b) Difference between the energy sum distribution shown in (a) (full squares) in comparison with the energy distribution of two W(001) surface states (S_1, S_2) measured by photoemission [14]. The abscissa represents the binding energy with respect to the Fermi level. (c) Energy sharing distribution of electron pairs related to the surface state S_1 from the clean (full circles) and oxygen covered (open circles) W(001) surface. (d) Difference between the two distributions shown in (c).

so-called energy sharing distribution for electrons originating from the vicinity of the Fermi level ($E_s \pm 0.25$ eV) is shown in Fig. 2(d).

In the present work we focus our attention on the manifestation of W(001) surface states in the ($e, 2e$) spectra. Therefore, we studied the effect of oxygen adsorption on the ($e, 2e$) spectra, since it was found in photoemission spectroscopy [12, 13] that the adsorption of O_2 suppresses the observation of W(001) surface states. In Fig. 3(a) we present the sum energy distribution of electron pairs measured from a clean W(001) surface (solid circles) in comparison with the corresponding distribution obtained from the oxygen covered surface (open circles). The spectra are normalized to equal acquisition time,

while the incident electron current was kept constant for both measurements. The difference between the two spectra is presented by solid squares in Fig. 3(b), where the sum energy of correlated electron pairs is converted into binding energy of the initial valence state with respect to the Fermi level considering the primary electron energy and the W(001) work function. The difference spectrum shows two pronounced maxima at the binding energies (E_1) _{$e, 2e$} = -0.4 eV and (E_2) _{$e, 2e$} = -4.4 eV. These energies coincide fairly well with the energies of two surface states S_1 : (E_1)_{PE} = -0.3 eV and S_2 : (E_2)_{PE} = -4.2 eV found in the photoemission spectrum of W(001) [16] that is presented by open squares in Fig. 3(b). Although the relative intensities between the two

maxima are different for the photoemission and (e,2e) spectrum, we take the coinciding energy peak positions as identifying signatures for the W(001) surface states, contributing to the (e,2e) cross section. We note that the maxima in the (e,2e) difference of Fig. 3(b) are considerably broader than those in the photoemission spectrum, which we attribute to a higher energy and angular resolution in the photoemission measurement than in ours. The difference between the sum-energy spectra for the clean and oxygen covered W(001) surface indicates that the oxygen layer on the W(001) surface strongly suppresses the generation of correlated electron pairs from surface states. In general, we point out that these results demonstrate the high surface sensitivity of low energy back-reflection (e,2e) spectroscopy.

In Fig. 3(c) the energy sharing distribution of electron pairs with sum energies $E_s = 14.5 \pm 1$ eV, corresponding to the initial valence state energy related to the surface state S_1 , is presented. The figure shows the distributions obtained from the clean W(001) surface (full circles) and from the 0.1 L O_2 -covered surface (open circles). The spectrum measured with the clean surface shows a pronounced peak at $E_1 - E_2 = 3$ eV on top of a nearly symmetric distribution, while this peak is almost invisible in the distribution from the oxygen covered surface. As shown in Fig. 3(d), the difference between both spectra illustrates the additional contribution of the clean surface distribution. In accordance with the analysis done for the sum energy distributions (Fig. 3(a/b)), we identify the electron pairs represented by the distribution in Fig. 3(d) as the contribution of W(001) surface states to the measured (e,2e) cross section from the clean surface. Fig. 3(d) shows that electron pairs originating from S_1 -states share their sum energy of $E_s = 14.5 \pm 1$ eV most likely in fractions of $E_1 = 9 \pm 0.5$ eV and $E_2 = 5.5 \pm 0.5$ eV. According to our two-step model for the low energy back-reflection (e,2e) process, we consider the correlated electron pairs to be generated by primary electrons that have been elastically diffracted at the lattice in the first step. In the present case, the diffraction of 20 eV primary electrons at the lattice structure of the W(001) crystal leads to an elastic diffraction maximum ('(-10) diffracted electron beam') in a position close to the bisector between both detectors (see Fig. 1). By turning the W-sample towards detector 1 or detector 2, respectively, we can observe this diffraction

maximum as a small spot in the particular detector, thus enabling us to verify the (-10)-beam position for the particular sample setting and primary energy during the measurement as shown in Fig. 1. According to former results [8], we consider the major contribution of correlated electron pairs observed in our geometry to be generated by the (-10) diffracted electron beam. Based on this assumption the initial momentum q of the valence electron inside the solid is given by the momentum conservation law:

$$q = k_1 + k_2 - k_0 \quad (1)$$

where k_1 and k_2 are the momenta of the two scattered electrons and k_0 is the momentum of the elastically diffracted electron inside the solid. During penetration into and exit out of the solid the electrons have to pass through the surface potential barrier which modifies their momenta components perpendicular to the surface (refraction), but does not affect the parallel components. Therefore, we can apply relation (1) only to the parallel components of the measured and primary electrons for calculating the parallel momentum components of the initial valence electrons in the direction defined by the plane of detection. This direction is equivalent to the [10] direction of the surface Brillouin zone of W(001). We note that we did not resolve the electrons' emission angles within the solid angles of our detectors in order to increase the statistical accuracy of our data. Thus, determination of the final electronic momenta is based on the assumption of point-like detectors including the integration of scattering angles over the experimental angular acceptance. Fig. 4(a) shows the distribution of $(q_{\parallel})_{e,2e}$ for S_1 as obtained from the measured energy sharing distributions by applying relation (1). The equivalent curve for the surface state S_2 is presented in Fig. 4(b). The dashed curves in both figures represent the $(q_{\parallel})_{PE}$ -distributions for both surface states measured with angle-resolved photoemission spectroscopy (ARPES) [16]. When neglecting the k -dependence of the dipole transition matrix elements, we can assume to a good approximation [17] the $(q_{\parallel})_{PE}$ -distributions as measured by ARPES to be proportional to the parallel momentum distribution of the two surface states S_1 and S_2 . In both figures, especially in Fig. 4(b), we find a reasonable agreement in the relative

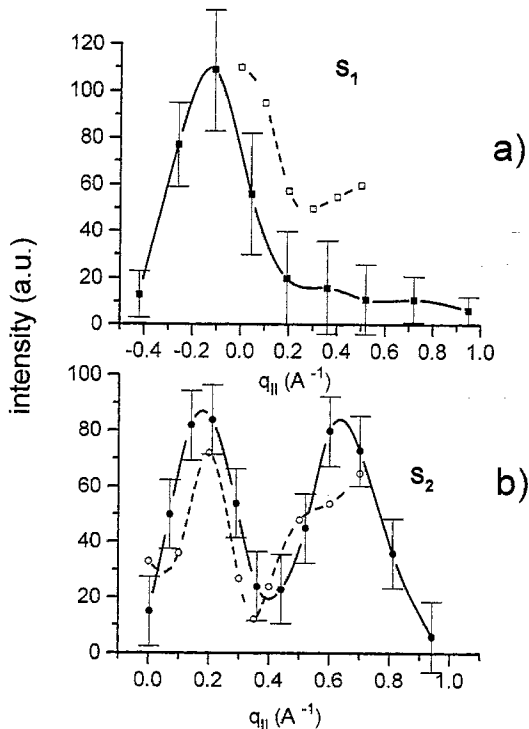


Fig. 4. $q_{||}$ -distribution of the surface states S_1 (a) and S_2 (b) deduced from our measurement (full squares/full circles) in comparison with those obtained from photoemission measurements (open squares/open circles).

shapes between the $(q_{||})_{e2e}$ and $(q_{||})_{PE}$ distributions, while in Fig. 4(a) the $(e,2e)$ distribution is shifted by about 0.2 \AA^{-1} towards lower parallel momenta and in Fig. 4(b) the half-width of the peak at $(q_{||}) = 0.2 \text{ \AA}^{-1}$ is about twice as large in the $(e,2e)$ curve ($\Delta q_{||} \approx 0.25 \text{ \AA}^{-1}$) as in the distribution obtained from ARPES. We assume these differences to be partly due to the fairly low momentum resolution in the $(q_{||})_{e2e}$ distributions. Considering the acceptance angle of the electron detectors and the experimental energy resolution, we estimate the resulting momentum uncertainty in the calculated $(q_{||})_{e2e}$ distributions to be approximately 0.25 \AA^{-1} .

In spite of the described discrepancies, we find a general similarity of the parallel momentum distribution of W(001) surface states obtained from ARPES measurements with the $(q_{||})_{e2e}$ distributions of these states extracted from low energy back-reflection

$(e,2e)$ data. We take this finding as a suggestion that the momentum distribution of the initial valence electrons determines the main features of the differential cross section for low energy back-reflection $(e,2e)$ processes.

4. Conclusions

The experimental results presented in this paper demonstrate a high surface sensitivity of low energy back-reflection $(e,2e)$ spectroscopy. For the first time we applied this technique to investigate the surface states on W(001). A considerable contribution of electron pairs generated from surface states was observed. We extracted the binding energies and $k_{||}$ distributions of two W(001) surface states from our data and found a fair agreement with the corresponding distributions from ARPES measurements.

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