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Observation and angular behavior of Rydberg surface resonances on W(110)

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The observation of surface resonances in the (00) beam *I-V* curves from a W(110) surface in the [01] azimuth is reported. High-resolution low-energy electron diffraction experiments show that they form a Rydberg series converging to the $(0\bar{4})$ beam threshold. From measurements at various angles of incidence, a part of the dispersion curves of the surface resonance fringes is also obtained.

Electronic surface resonances are encountered in low-energy electron diffraction on well-characterized crystal surfaces. They are evidenced by narrow fluctuations in the intensity profile of the specular beam caused by the interference between direct reflection and an indirect process involving quasistationary states above vacuum level trapped between the surface barrier and the substrate.[1] This phenomenon occurs just below the energy threshold of a grazing diffracted beam when it lies in a forbidden gap of the bulk surface projection band structure. Surface resonances form a Rydberg series converging to this threshold.[2,3] A survey of theoretical and experimental aspects of the subject can be found in a recent review article by McRae.[4] The study of surface-resonance line shape is a good way to test surface-barrier models.[5] This technique has been used extensively for fixing parameters of the modified image barrier model[6] on several metal surfaces like Cu(001) (Ref. 7), Ni(001) (Ref. 8), and W(001) (Ref. 9). Studies with high energy and angular resolution are particularly relevant for the determination of the effective potential far from the surface.[1,3,5,10] Measurements at various angles of incidence are also desirable. They permit us to establish the surface-resonance band structure which is of great interest for surface characterization.[4] In this paper, surface-resonance observation in high-resolution low-energy electron diffraction (LEED) experiments on W(110) are presented. To our knowledge, it is the first time that Rydberg surface resonances are detected on a metal single-crystal face other than the (001) face and with such a high resolution (up to five fringes are resolved). Measurements at many angles of incidence are also reported giving the angular behavior of the Rydberg resonance fringes.

The experiment is carried out with a tandem 127° electrostatic electron spectrometer, the same as previously used for the study of W(001) surface-resonance fine structure.[11] Design details of the spectrometer are presented elsewhere.[12] Modification of the sample holder now permits the study of the (00) beam intensity profile for angles of incidence in the range 42°–90° with $\pm\frac{1}{2}°$ accuracy. The W(110) face is oriented within $\pm\frac{1}{2}°$ and the plane of incidence contains the [01] direction (azimuthal angle of $90° \pm \frac{1}{2}°$). The energy resolution is about 12 meV (full width at half maximum) while angular resolution is estimated better than 0.5°. This improvement is obtained by reducing the width of the entrance slit of the analyzer lens by about a factor of 2. Most of the measurements have been performed at a base pressure of $(2-4)\times 10^{-10}$ Torr. Identical results are obtained at $(2-4)\times 10^{-11}$ Torr. During experiments, the crystal is repeatedly flashed at 2400 K. The sample having been submitted to intensive high-temperature oxygen treatment for carbon removing in another UHV system, no other cleaning procedure was performed for the present experiment.

In Fig. 1, curve (a) illustrates a typical *I-V* profile of the (00) beam obtained at an angle of incidence $\theta = 75°$ on a clean surface. It reveals a series of narrow resonances similar to those observed on W(001).[11] Measured from the slope discontinuity labeled *D*, successive peaks of the profile fit the Rydberg series:

$$e'_n = -13.6[16(n+a_n)^2]^{-1} \qquad (1)$$

expressed in units of eV with numbers $(n+a_n)$ indicated. This result is in agreement with the current theory of surface resonances.[2,3] Note that e'_n refers to the position of the fringes relative to the threshold (point *D*) at fixed angle. It is not to be confused with e_n, the binding energy at fixed parallel momentum $\vec{K}_{\parallel}$ (mod $\vec{g}$). We note also the absence of any ringing above point *D*. This ringing does appear in Jennings' calculation of intensity profile for a W(001) surface. However, in recent theoretical studies[13] it is not found. Exposure to residual gases gradually reduces the amplitude of the resonance fringes. Curve (c) of Fig. 1 shows an *I-V* curve taken 48 h after curve (a).

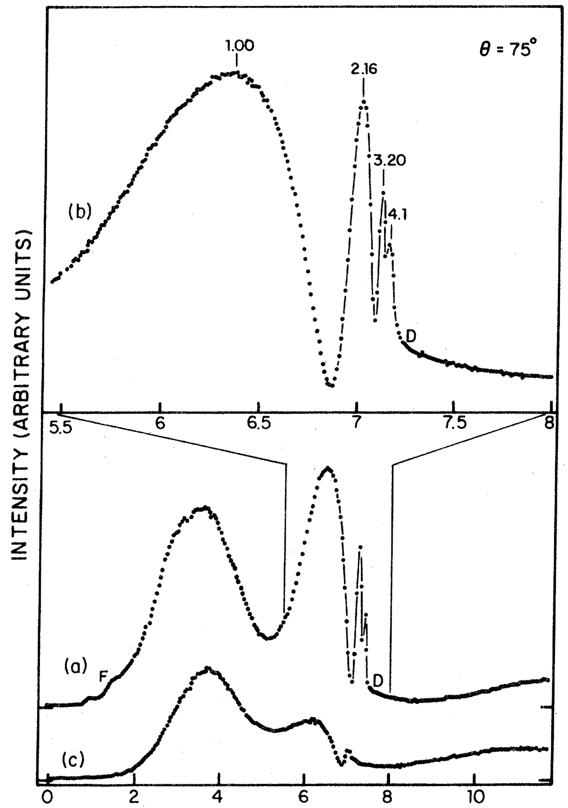

FIG. 1. *I-V* curves of the (00) beam taken at $\theta = 75°$. Curve (a) and its enlargement (b) were obtained on a clean surface, curve (c) after 48-h exposure to the residual gases. A dash on each side of the figure indicates the origin of each curve.

Change in contact potential causes a shift of about 200 mV of the entire profile. A similar weakening, though more accentuated, has been observed on W(001).[14] The energy scale given in Fig. 1 corresponds to the measured accelerating potential rather than the absolute electron energy, a quantity impossible to measure accurately in the present experimental setup. The correlation between the position of point *D* and a beam emergence energy is established by systematic angular measurements. Recording (00) beam *I-V* curves at various angles of incidence one finds that the resonances could be assigned to the $(0\bar{4})$ beam emergence [associated with the $(0, -8^{1/2}\pi/a)$ reciprocal lattice rod] since it is always located about 0.7 eV above the measured slope discontinuity at *D*. The small feature labeled *F* in Fig. 1 is interpreted as a resonance associated with the emergence of the diffracted $(0\bar{2})$ beam.

Comparison of the peak separation within a Rydberg series as a function of the angle of incidence is considered to be an efficient way to check the accuracy of surface-barrier models.[9] Figure 2 shows the surface-resonance fine-structure profile for different angles of incidence plotted against $e' = E - E_T$, E_T being the position of the slope discontinuity taken to be the $(0\bar{4})$ beam threshold. It is apparent from Fig. 2 that higher-order resonance fringes are more easily resolved at a large angle of incidence; in these conditions five fringes are clearly detectable. This result is to be expected[3] on the basis of beam spread and chromatic aberration considerations which show that resonance observation is favored at a large angle of incidence and low beam-energy threshold. In fact, these experimental results can be used to obtain a better estimate of the angular resolution of our instrument.[13] Calculation shows that 0.2° is a more accurate value of its angular acceptance. A regular shift of the higher-resonance fringes toward E_T for increasing angles is observed, causing the quantum defect a_n to vary with the angle as indicated in Fig. 2. Despite its large width, no significant energy shift of the first resonance peak near $e_1' = -0.85$ eV is observed. The angle depen-

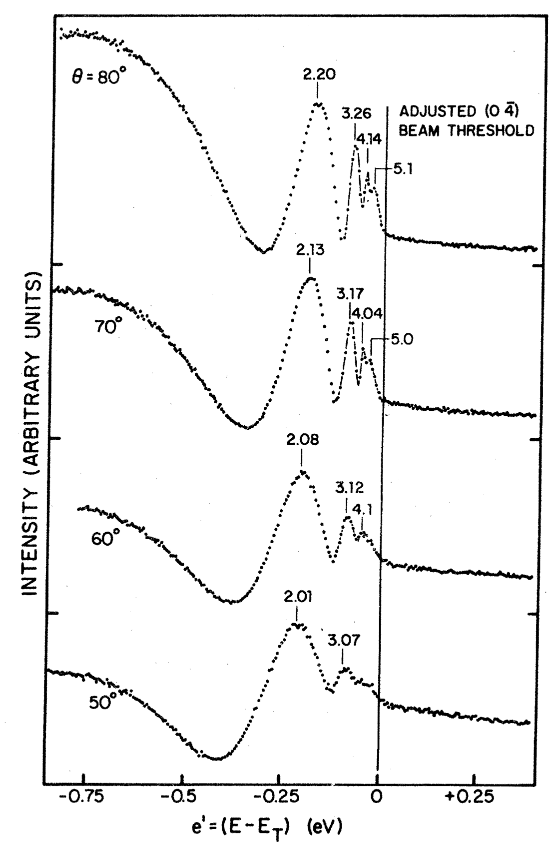

FIG. 2. Angular behavior of surface resonance fine structure.

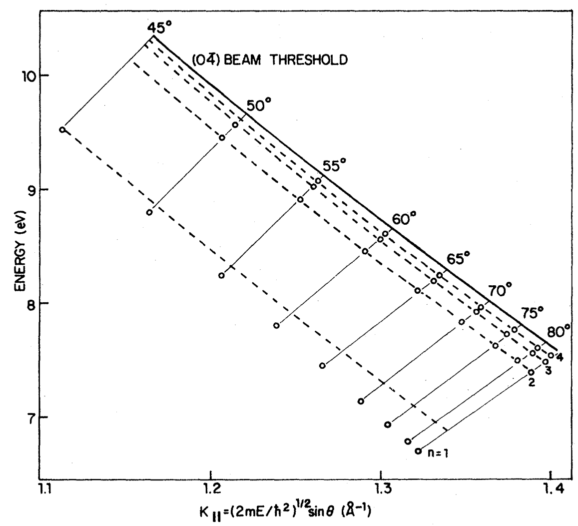

FIG. 3. Dispersion of the Rydberg resonances. The open circles represent the energy of the maximum of each resonance fringe for various constant incidence angles, plotted against their respective parallel momentum $K_{\parallel}$. The broad full line is the (0$\bar{4}$) beam threshold and the dashed curves are reproductions of the latter vertically shifted in order to be located around each $n=1,2,3,4$ energy level. The light full lines are joining data taken at constant incidence angle.

dence of the quantum defect a_n in Fig. 2 could be due to the variation of $K_{\parallel}$ with E at fixed θ. To clarify this point we have plotted in Fig. 3 the dispersion $E(K_{\parallel})$ of the maximum of the surface resonance fringes. The higher fringes can be fitted by the 2D free-electron dispersion relation $E(K_{\parallel}) = E_T(K_{\parallel}) + e_n$ with $e_2 = -0.31$ eV, $e_3 = -0.11$ eV, and $e_4 \simeq -0.05$ eV, following a Rydberg sequence. However, for the first fringe the apparent binding energy increases slowly with $K_{\parallel}$, the variation being about 0.3 eV from $K_{\parallel} = 1.12$ to 1.32 Å^{-1}, as shown in Fig. 3. A similar shift, but in opposite direction, has been reported in low resolution angular study of the W(001) surface resonance[14] and interpreted as a consequence of changes in the bulk reflectivity across a band gap.[4] Also, in a recent observation of Rydberg resonance fringes on Cu(001),[15] it is noted that the line shape is independent of the threshold energy up to the second fringe, in agreement with observations reported here.

The existence of Rydberg surface resonances on W(110) has been demonstrated. The high-resolution characteristics of the apparatus have made possible the study of the angular behavior of the resonance fringes. The higher fringes follow a 2D free-electron dispersion relation as is to be expected for states very loosely bound to the surface. Small angular dependence of the first-order fringe is observed. This feature, being associated with a more tightly bound quasistationary surface state, departs from the classical image potential, and absorption close to the surface could explain this different behavior. Dynamical effects,[16] so far neglected in surface-barrier models, may play a role in the explanation of the observed incidence angle dependence. These novel data about resonance phenomena in LEED are thought to be very useful and stimulating for further theoretical as well as experimental studies of surface resonances and barriers.

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