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STRUCTURE OF THE CLEAN Ta(100) SURFACE

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The clean Ta(100) surface and some aspects of hydrogen adsorption have been studied by LEED and AES. The thorough examination of LEED patterns did not provide any evidence for an atomic reconstruction of the clean surface over the entire temperature range investigated, 150–600 K. The *r*-factor analysis used for comparison between measured and calculated $I-V$ spectra yields a contraction of the topmost layer spacing of about 11% and an expansion of the second layer spacing of about 1% compared to the bulk value. The hydrogen adsorption does not induce any superstructures, but small hydrogen exposures lass then 1 L influence $I-V$ spectra substantially.

Although a number of adsorption studies on Ta surfaces have been published [1–4], a structure of its clean surface was not yet determined. On the matter of the surface structure of the group Vb metals there is only one detailed work on the structure of the clean V(100) surface [6]. In contrast to the elements of group VIb, Cr, Mo and W, also having bcc structure, no reconstruction on the clean (100) surfaces of group Vb metals was observed. A previously reported reconstruction on V(100) [7] is probably induced by oxygen [8], on Nb(100) no reconstruction was found down to a temperature of 15 K [9], and there are no works concerning the matter of reconstruction on clean Ta surfaces. This article aims to present refined structural data for the clean Ta(100) surface, briefly reported previously [5], as well as the results of experimental studies of hydrogen adsorption.

Experiments were carried out in a stainless steel UHV chamber with a base pressure of 2×10^{-11} Torr and a working pressure below 8×10^{-11} Torr during $I-V$ measurements without cooling, and 4×10^{-11} Torr with cooling, respectively. Data collection and rotations of the Faraday cup about two axes during $I-V$ measurements were computer controlled. The specimen holder was developed to enable rotations about two mutually perpendicular axes, as well as resistive heating of the sample up to its melting point. Crystal cooling was also possible down to 150 K by heat conduction through copper braids in contact with a liquid nitrogen reservoir. The crystal was cut by spark erosion and mechanically and electrochemically polished in a standard manner. The prepared sample, 6 × 2.35 × 0.12 mm, had a surface oriented to a (100) plane within 1°. It was spot welded to tantalum strips and mounted to the specimen holder in a way, that any tensions during heating and cooling were avoided. The crystal temperature during cooling was monitored by a chromel–constantan thermocouple attached to the tantalum strips and during heating up to 2500 K by an optical pyrometer. Above this point the temperature–current curve was extrapolated to the melting point. The temperatures measured by the pyrometer were corrected for true crystal temperature.

The presence of any likely impurities except hydrogen on the crystal surface was checked by AES. With an AES signal from the tantalum (181 eV) peak as a basis, the relative noise/signal was 0.02. The usual crystal cleaning procedure was flash heating to 2800 K for 30–60 s to remove oxygen, the main contaminant. Flash duration depended upon the amount of oxygen on the surface. Other contaminants, H, S, C, N and P, desorbed at substantially lower temperatures. After cooling down to room temperature no contaminants were found in the AES spectra, and the LEED pattern of the (1 × 1) structure was observed, see fig. 1.

No indications of surface reconstruction were found by examination of the LEED patterns over the entire temperature range investigated, 150–600 K. Since various contaminants can stabilize a bulk structure on the surface, the crystal was rapidly cooled to keep it free of any impurities. The cooling time to 170 K after flashing to 2800 K took about 2 min, in this way the exposure to hydrogen, the dominant constituent of residual gas, was kept below 0.01 L. Such a low coverage is unlikely to cause a stabilization of the bulk structure, so we conclude that if any atomic reconstruction might take place, it would occur

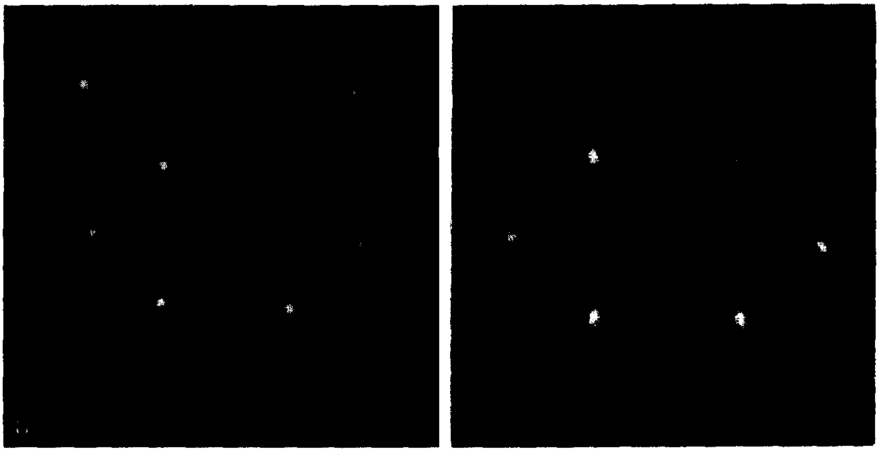

Fig. 1. LEED patterns of the clean Ta(100) surface: (a) at 310 K, 103 eV; (b) at 160 K, 77 eV.

either at lower temperatures or would need longer time than some minutes to build up.

Once the Ta crystal was cleaned from oxygen, it appeared that the main disturbing factor for taking *I–V* spectra was adsorption of hydrogen from residual gas. Hydrogen adsorption causes an increase of diffuse background in the LEED patterns but no extra spots or superstructures. As shown below, its influence upon *I–V* spectra is significant. Due to this fact the intensity measurements were carried out on surfaces exposed to hydrogen for less than 0.15 L. The desorption temperature of hydrogen was determined from thermal desorption measurements carried out by means of a quadrupole mass spectrometer, $T_{\mathrm{DES}} = 1430$ K. The thermal desorption curves are shown in fig. 2.

The *I–V* curves at normal incidence were obtained by averaging the intensities $I(hk)$ and $I(\overline{h}\overline{k})$, since the limited mobility of the Faraday cup did not allow to measure all degenerate beams. The fact that the regular flashings to 1500 K were necessary to desorb hydrogen has resulted in a rather broad temperature range during measurements, 230 to 290 K, with a variation during a single measurement less than 10 K. The intensities of five beams at normal incidence and of the specular beam at $\vartheta = 9°$ were measured and compared with calculated curves. The comparison is shown in fig. 3.

The phase shifts used in the calculation were obtained from a crystal

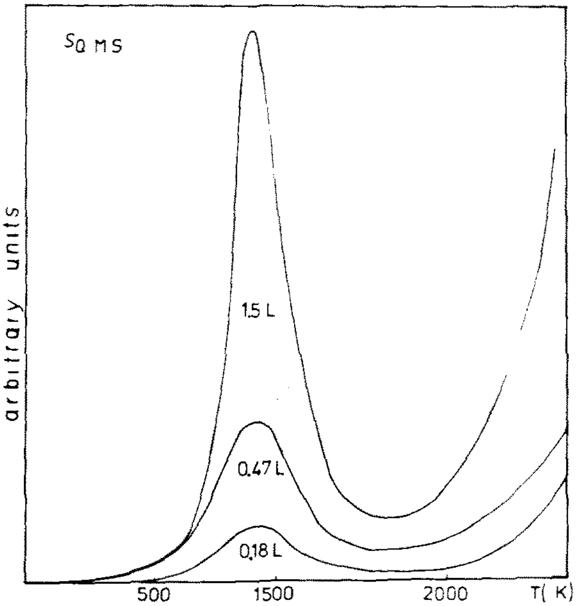

Fig. 2. Experimental TDS curves as H_2 signal from quadrupole mass spectrometer (S_{QMS}) via temperature, heating rate 70 K/s, H_2 initial exposures in L.

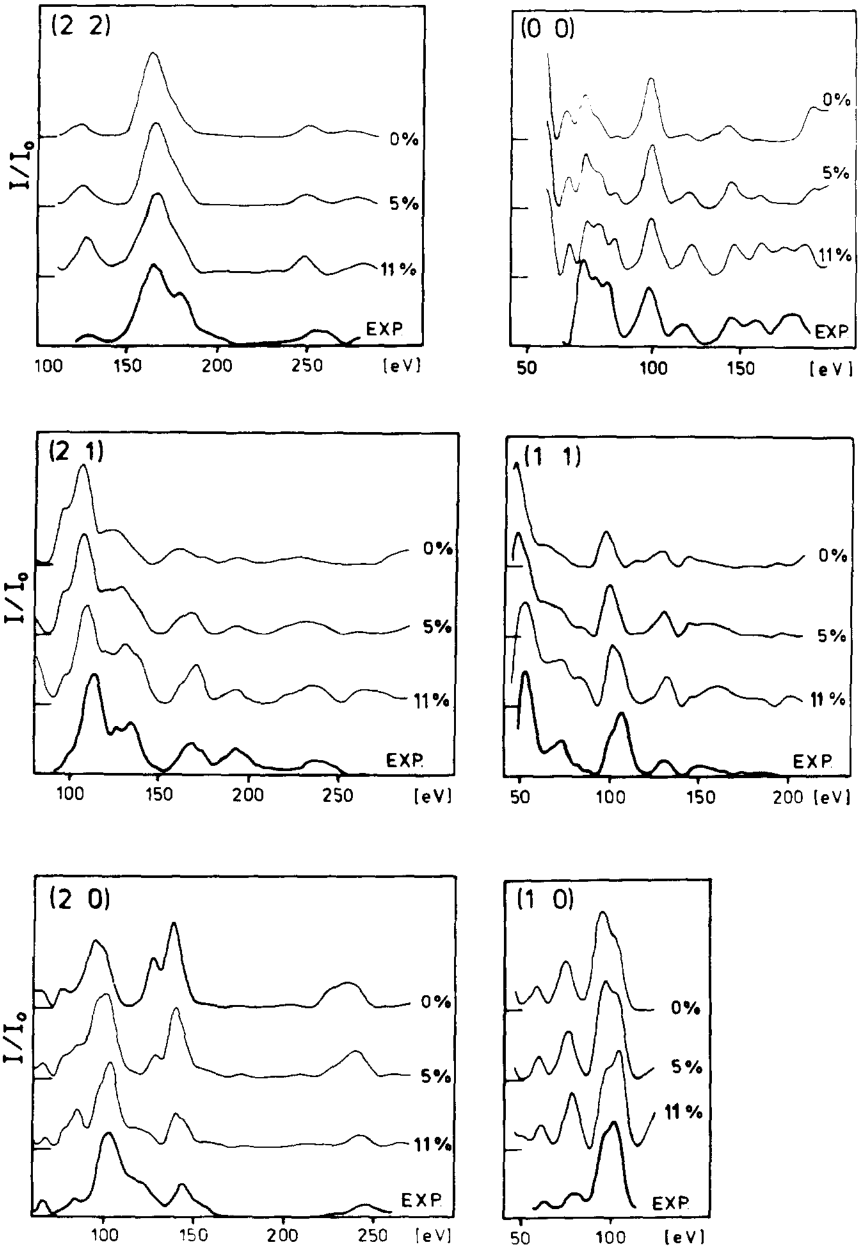

Fig. 3. Comparison between experimental and theoretical $I-V$ spectra. The contraction of the first layer spacing is indicated in the figure. The second interlayer spacing is $d_2 = 1.67$ Å. The specular beam at $\vartheta = 9°$, $\varphi = 45°$. All other curves at normal incidence.

potential constructed by overlap from free atom potentials and using a modified Slater exchange term with an optimised α-parameter [10]. Potential and phase shifts were calculated relativistically. Up to twelve spin averaged phase shifts were used in the multiple scattering program, which is more than sufficient up to 250 eV. The layer doubling method was chosen for interlayer scattering [11] with a maximum of 25 nondegenerate beams at normal incidence and 60 beams at oblique incidence, respectively. The bulk Debye temperature was $\theta_D^b = 240$ K [12] and the surface Debye temperature for the top layer was varied between 240 and 160 K, the imaginary part of the inner potential was set to $V_i = 0.85 \times E^{1/3}$ [eV]. The first two layer spacings were varied in steps of 0.02 Å.

The quantitative comparison using an r-factor method, defined by Zanazzi and Jona [13] gives a minimum r-factor, $\bar{r} = 0.21$, and leads to a topmost layer spacing $d_1 = 1.47 \pm 0.03$ Å corresponding to 11% contraction of the bulk spacing $d = 1.65$ Å and a very small expansion of the second interlayer spacing of about 1%, see fig. 4. In this analysis the real part of the inner potential was set independent of energy and the average value is $V_0 = -9.0$ eV. The minimum r-factors for single beams together with the values for the inner potential are shown in fig. 5. The variation of the surface Debye temperature led to a faint minimum in the mean r-factor curve at $\theta_D^s = 200$ K. However, the results did not allow us to draw quantitative conclusions about mean square

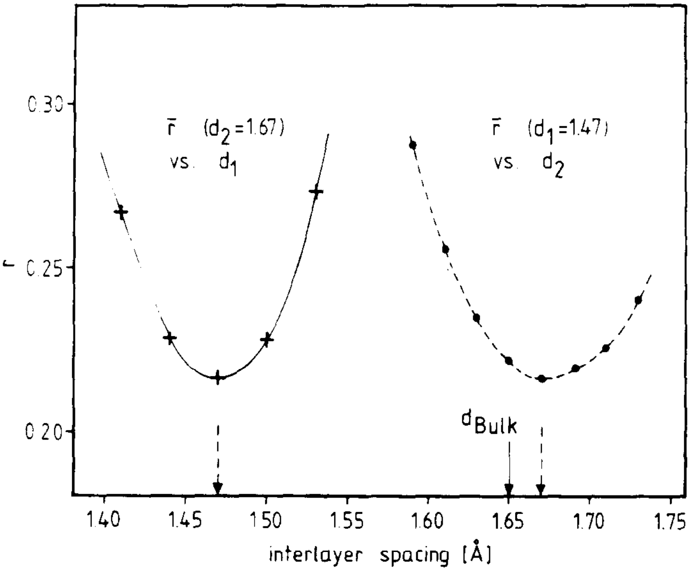

Fig. 4. Averaged r-factor of six beams as a function of the first interlayer spacing at the fixed optimum second interlayer spacing (left curve) and vice versa (right curve).

vibrational amplitudes in the surface layer. The experimental value of the surface Debye temperature obtained from intensity measurements between 160 and 600 K is $\theta_D^s = 160$ K.

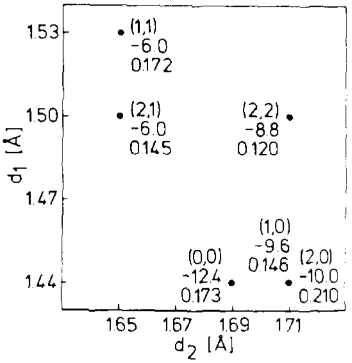

Fig. 5. Minima of the single beam r-factors as a function of the first and second interlayer spacing. The optimum value of the inner potential for each beam is given in the figure.

Although the minimum r-factor, $\bar{r} = 0.21$, is relatively high for a simple structure, the main features of the experimental curves and relative peak heights are well reproduced by the calculations. One of the reasons for the remaining discrepancies may be found in nonstructural parameters in the calculation. The model for the crystal potential has certainly some more or less significant insufficiencies, for example, another potential than the one for the bulk atoms should be given to the top layer atoms, since the electron density of surface atoms is certainly changed due to relatively large contraction of the first layer spacing. To a lesser extent, experimental errors may play a role due to small deviations from normal incidence, since the experimental set up did not allow us to measure all degenerate beams simultaneously. Only a small contribution to the deviation between experiment and theory could result from the fact that curves for different beams were measured at somewhat different temperatures, as described above.

The influence of small hydrogen exposures less than 1 L on the $I-V$ spectra is shown in fig. 6. As can be seen, the $I-V$ curves are negligibly changed up to hydrogen exposures of 0.15 L, therefore measurements used for comparison with calculations were taken at exposures below this value. To get an estimate of its influence in terms of the quantitative r-factor analysis the r-factors between the curve with the lowest hydrogen exposure, less than 0.01 L, and the other curves are also given in fig. 6.

As a result we conclude that on the clean Ta(100) surface no reconstruction takes place above 150 K and that the first interlayer spacing is contracted by

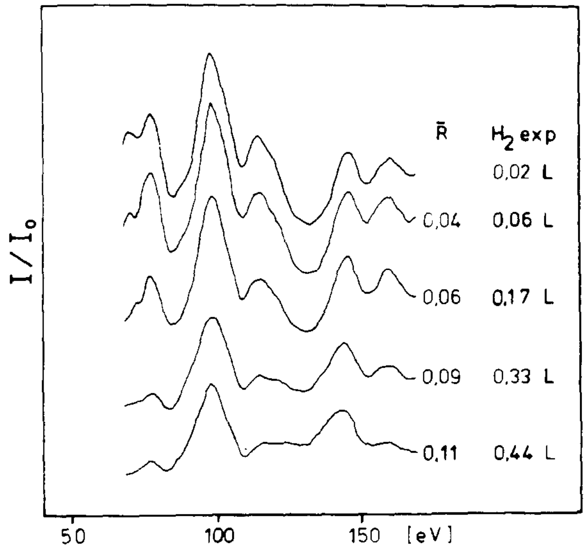

Fig. 6. Influence of hydrogen adsorption on the intensity spectra of the (00) beam. The hydrogen exposure and the *r*-factors between the upper curve and the lower curves are given in the figure.

11% with respect to the bulk value, while the second interlayer spacing is slightly expanded by about 1%. A similar result, namely alternation of contraction and expansion of topmost interlayer spacings relative to the bulk equilibrium spacing was also reported for the V(100) surface [6], but not found by Clarke for another bcc metal, Mo [14], whose results speak for uniformly inward directed relaxation of the Mo(100) surface. The direction and magnitude of the surface relaxation as a function of various models for the interatomic potential was calculated by Ma et al. [15] for Fe(100) and Cu(100) surfaces. In view of the qualitative agreement achieved between their results and the structural data determined by LEED it would be interesting to apply their approach to (100) faces of other metals, Ta, V and Mo, with known structure parameters, which generally show large relaxations of the first interlayer spacing.

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