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Evidence for a Clean $(\sqrt{2}\times\sqrt{2})R45°$ Surface Structure on Cr(100)

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Low-energy electron diffraction observations of carefully cleaned and annealed Cr(100) surfaces show a sharp and intense $(\sqrt{2}\times\sqrt{2})R45°$ structure. Auger-electron spectroscopy measurements indicate that this "anomalous" structure is actually a clean-surface effect. A strong contamination-sensitive feature is revealed by angle-resolved photoemission and it is suggested that reconstruction results from an instability connected with a peak near E_F in the surface density of states of the Cr(100) (1×1) surface.

The simplest model of reconstruction considered for low-index faces of metals with respect to the bulk is just a relaxation in the direction normal to the surface. However, it was soon recognized that certain crystallographic orientations of Pt[1] and Au[2] show a more complicated surface reconstruction. More recently the existence of a surface phase transition near room temperature has been conclusively demonstrated for W(100) and Mo(100) surfaces.[3-5] Chromium has a body-centered-cubic lattice and 5*d* electrons and thus it is, in many respects, similar to Mo and W. Most likely interesting facts should be learned from investigations of chromium surfaces.

In this Letter we report on the successful preparation of the clean Cr(100) surface which we studied using Auger electron spectrometry (AES), low-energy electron diffraction (LEED), and photoemission. We find that this surface is not stable in the (1×1) configuration and that reconstruction into a $(\sqrt{2}\times\sqrt{2})R45°$ structure occurs. Basically, as to the corresponding electronic structure, it is found by ultraviolet photoemission (UPS) that a sharp feature in the energy distribution curves (EDC's) at ~1 eV below the Fermi level (E_F) is associated with the reconstructed surface and it is suggested that the reconstruction of the Cr(100) surface is an electronically driven lattice distortion due to a peak near E_F in the surface density of states of the undistorted (1×1) surface.[6,7]

Measurements were carried out in an ultrahigh-vacuum electron spectrometer equipped with a windowless discharge lamp for UPS and a rotatable hemispherical energy analyzer collecting electrons ejected within a cone of 2° semiangle. An electron gun for AES and four-grid LEED optics were also available. After mechanical and electropolishing, the well-oriented single crystal was cleaned *in situ* by Ar-ion bombardment and annealing at various temperatures below 900 °C. Annealing above 600 °C led to impurity segregation of carbon and sulfur but cleaned the surface with respect to oxygen. Generally a $c(2\times2)$-S structure was then observed. We note here that this structure is very different from the $c(2\times2)$ structure of clean Cr(100) described below since no sulfur at all was detected for the latter and even a qualitative inspection of the LEED spectra showed a striking difference in the beam intensity versus energy curves. Actually in the final stage of the cleaning procedure the annealing temperature was kept below 500 °C. Only carbon and oxygen were then still detected by AES and a sharp and intense $(\sqrt{2}\times\sqrt{2})R45°$ LEED pattern was observed. We have carefully estimated the residual amounts of carbon and oxygen using AES. The results are summarized in Table I for four typical

TABLE I. Residual amount of impurities as monitored by AES for various preparations of the surface. (a) Clean surface after annealing 5 min at 400°C. (b) Surface (a) exposed to 0.8 L of oxygen. (c) Surface (a) exposed to 1.3 L of oxygen. (d) Carbon-contaminated surface observed during the cleaning procedure. In the calculations we assume that the impurities are located in or on the top layer.

Surface preparation	(a)	(b)	(c)	(d)
C (monolayer)	0.05	0.05	0.05	0.3
O (monolayer)	0.01	0.2	0.4	0.05
LEED pattern	$(\sqrt{2}\times\sqrt{2})R45°$	$(\sqrt{2}\times\sqrt{2})R45°$ (fading)	(1×1)	Quartet of spots around (1/2, 1/2) positions

preparations of the Cr(100) surface. The case (a) corresponds to the clean surface for which the residual amount of C and O is far below a coverage of 0.5 expected for an intense $c(2\times2)$ impurity structure. The relevant LEED pattern is shown in Fig. 1(a).

We conclude that the observed surface structure is not due to any impurities detectable by AES. The exception is hydrogen but we were not able to observe any characteristic feature due to this adsorbate by UPS. In contrast, the presence of C and O even below 0.1 monolayer is reflected in the EDC at normal photoemission by features at 3.2 and 6.5 eV below E_F, respectively. Actually, there is likely no fast chemisorption of H_2 on Cr(100) surfaces since neither LEED nor UPS reveal any change after a deliberate exposure as high as 1000 L (1 L = 1 μTorr sec). At any rate, it is found that after ion bombardment (500 eV, 200 μA sec) an anneal at 200°C is sufficient to obtain the intense $(\sqrt{2}\times\sqrt{2})R45°$ pattern. This rules out adsorption from residual atmosphere (H_2 partial pressure $\sim 5\times10^{-11}$ Torr) in nonnegligible amounts. Moreover, hydrogen diffusion from the bulk in significant and reproducible amounts in the above annealing conditions seems quite improbable. Most likely we are dealing with a clean-surface effect.

Actually various observations strongly support this statement. The preparations (b) and (c) (Table I of the Cr(100) surface are obtained when the clean surface [Table I(a)] is exposed to 0.8 and 1.3 L of oxygen, respectively. The relevant LEED patterns are shown in Figs. 1(b) and 1(c). It is apparent that increasing the oxygen content of the surface destroys the "anomalous" structure.

From a general point of view, the annealing temperature necessary to produce the $(\sqrt{2}\times\sqrt{2})R45°$ structure is lower the cleaner the surface appeared by AES.[8] If the carbon concentration is significant the half-order spots are broader and streaky. Moreover, at a carbon content of, say, 0.3 monolayer the $(\sqrt{2}\times\sqrt{2})R45°$ structure is no longer obtained; instead we have a new pattern [Fig. 1(d)] which is characterized by a quartet of spots around the $(\frac{1}{2},\frac{1}{2})$ positions and similar to that observed on Mo(100).[3] The interesting point is that this pattern appears only if the sample is cooled at temperatures below about 250°C, suggesting a surface phase transition into a (1×1) pattern above this temperature. In contrast, in the range 300–800 K we could not detect any change in the diffraction pattern of the clean surface [Fig. 1(a)] which might not be attributed to a Debye-Waller effect. Indeed, from an energetics point of view one might argue that the presence of carbon stabilizes the (1×1) configuration and hence that the surface energy difference between the reconstructed and nonreconstructed surfaces is significantly greater for the clean surface. Though we cannot eliminate the possibility that only carbon rearranges below 250°C on contaminated Cr(100), it is clear that at least the $(\sqrt{2}\times\sqrt{2})R45°$ structure of clean Cr(100) results from a periodic displacement of the chromium atoms.

In fact, the maximum intensities of both half- and integral-order spots are approximately the same and the pattern persists at high electron energy. This implies that the present structure is not only due to a magnetic superstructure.[9] The atomic displacements might be described by a displacement wave similar to that proposed by

Felter, Barker, and Estrup[3] for W(100). Using their notations the relevant Δ values are ~ 0 and $\sim \frac{1}{6}$ for the clean [Fig. 1(a)] and carbon contaminated [Fig. 1(d)] structures, respectively.[10] Yet the displacements are, most likely, parallel to the surface,[4,11] but at present little may be said as to the actual surface crystallography.

One of the strongest facts against any impurity, whatever its origin, is that a strong contamination-sensitive peak is observed by UPS on the reconstructed $(\sqrt{2}\times\sqrt{2})R45°$ surface. Figure 2 displays three typical angle-resolved EDC's obtained with photons of 16.8 eV at a polar photoemission angle of $\theta = 55°$ along an azimuth corresponding to the $\overline{\Sigma}$ symmetry line of the surface Brillouin zone of the reconstructed Cr(100) surface. The interesting feature, in the EDC of the clean reconstructed surface, is the dominant peak at ~ 1 eV below E_{F} [Fig. 2(b)]. This peak, which is prominent along the $\overline{\Sigma}$ symmetry line and shows a dispersive character, is essentially excited by the normal component of the polarization vector $\vec{A}$. This is apparent from Fig. 2(a) where the polar incidence angle is 0° as opposed to 45° for Fig. 2(b). Furthermore, we note that the usual experimental criteria for an assignment to a surface state (resonance) are fulfilled. Indeed, a drastic reduction of peak A is observed when the surface is exposed to 1.3 L of oxygen [Fig. 2(c)]. On the other hand, on extending the measurements to other photon energies (21.2 and 26.9 eV) it appea that the energy position of peak A is independent of photon energy. Basically, this peak should be the result of a surface umklapp process[12] involving a surface reciprocal-lattice vector with $K_{\parallel} = 2.18\ \text{Å}^{-1}$.

Surface projections of the bulk band structure suggest that surface states (resonances) might exist on the Cr(100) (1×1) surface[13] but no detailed calculations are available. Yet it has been shown that there is a peak near E_{F} in the surface density of states of the Cr(100) (1×1) surface.[6,7]

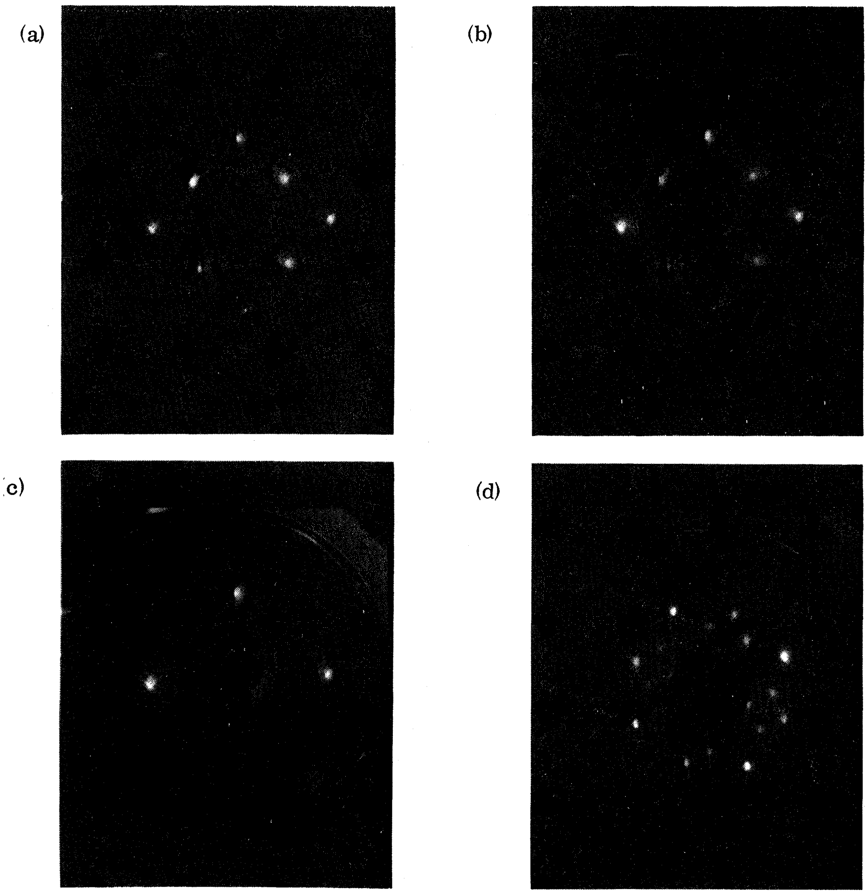

FIG. 1. LEED patterns relevant to the surface preparations (a), (b), (c), and (d) characterized in Table I. The beam voltage is 46 V. The pattern (c) contains only the expected "normal" diffraction spots.

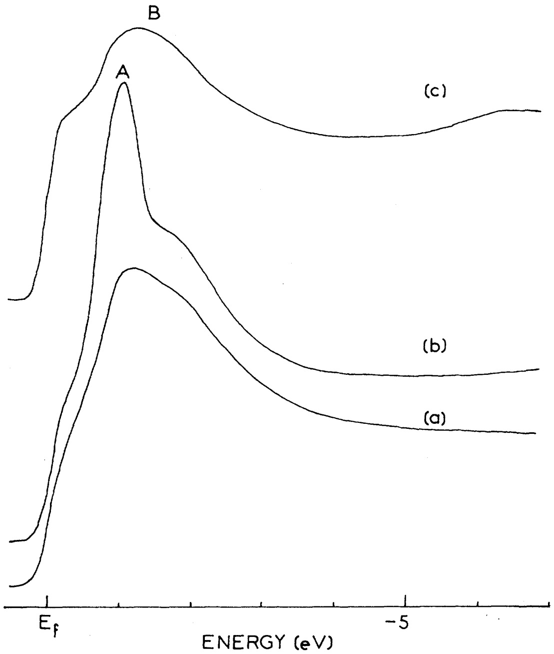

FIG. 2. EDC's for electrons emerging at a polar angle of 55° along an azimuth corresponding to a ΓNH plane of the bulk Brillouin zone. The photon energy is 16.8 eV. With this collection geometry the ratio of surface to bulk features is greatly enhanced. Curve a, clean $(\sqrt{2}\times\sqrt{2})R45°$ surface. The polar angle of incidence is 0° as opposed to 45° for both curves b and c. Curve b, clean $(\sqrt{2}\times\sqrt{2})R45°$ surface. The peak A is assigned to a surface resonance. Curve c, reconstructed surface subsequently exposed to 1.3 L of oxygen. The peak B is most likely due to emission from bulk electron states.

We looked for such dominant electron states over $\frac{1}{8}$ of the surface Brillouin zone but found only features of small intensity. We propose that the latter result and the presence of a strong peak A at lower energies indicate that the surface is reconstructed. This peak is probably to be assigned to $3d$ electrons whose energy has been lowered by a rearrangement of the surface atoms. Seemingly, this peak is basically a $3d$ virtual bound state,[14] i.e., surface resonance overlapping the bulk feature B [Fig. 2(c)].

Tosatti[15] proposed to describe the reconstruction of Mo(100) and W(100) by means of an interaction between a soft surface phonon and a charge density wave. In particular a noticeable depletion in the surface density of states near E_F should be observed on the reconstructed surface. Yet our results suggest that in the case of Cr(100) the energy extension of the depletion region is very large suggesting a situation which is better described within the usual chemical-bond scheme. The great stability of the Cr(100)-$(\sqrt{2}\times\sqrt{2})R45°$ structure prevents the observation of the nonreconstructed Cr(100) (1×1) surface at temperatures (< 500°C) where outward diffusion of impurities is negligible.

In the case of carbon-contaminated surfaces, the charge-density-wave picture is perhaps more appropriate since the corresponding structure [Fig. 1(d)] is much less stable (transition temperature ~ 250°C) and there is at present no reason to believe that the displacement wave is commensurate with the lattice parameter.[10]

Finally, the stability of the reconstructed Cr(100) surface might explain the anomalous trend of the Cr(110) surface to reconstruct into (100) facets[16] since the surface energy of reconstructed Cr(100) may be lower than that of the densely packed Cr(110) face.

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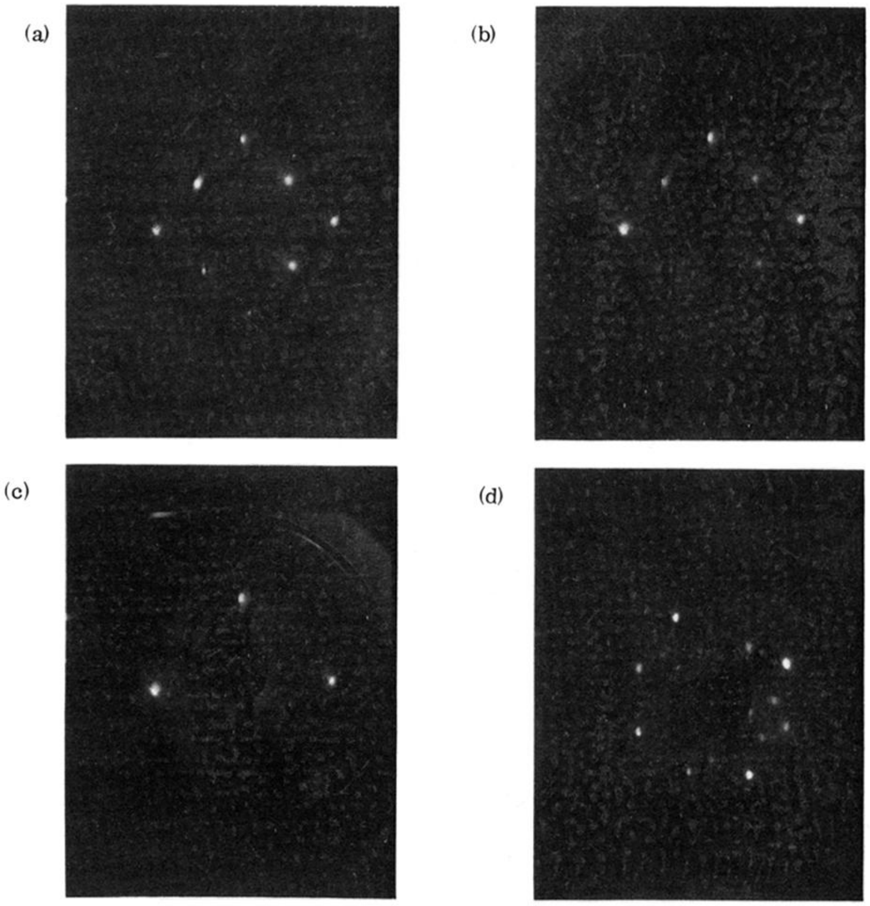

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