

## Dispersion of Surface States on W(100) and the Surface Reconstruction

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The dispersion and symmetry of the surface states along the  $\bar{\Gamma}$ - $\bar{M}$  symmetry line of the W(100) surface Brillouin zone have been determined with use of high-resolution angle-resolved photoemission. Comparison with available calculations shows poor agreement, throwing serious doubts on the role played by the surface states in the W(100) reconstruction.

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It has recently been shown that the superstructures observed by low-energy electron diffraction (LEED) on W(100) (Ref. 1) and Mo(100) below room temperature (RT) are properties of the clean surface.<sup>2,3</sup> Further, it has been argued that these observations provide evidence for a reversible phase transition from a  $(1 \times 1)$  phase existing at and above RT to reconstructed phases.<sup>2,3</sup> The driving force behind the proposed transition is at present not understood, and several different mechanisms have been suggested.<sup>4-8</sup>

It is well known that the (100) faces of W and Mo possess an unusually rich collection of surface electronic states close to the Fermi level.<sup>9</sup> It was therefore proposed that these states could drive the instability in a Peierls type of mechanism (charge-density wave).<sup>2-5,8</sup> Inglesfield<sup>6</sup> and, later, Posternak *et al.*<sup>10</sup> calculated in detail the surface electronic structure and from that the surface response function,<sup>6,8</sup> however, with contradictory results as far as the mechanism for the reconstruction was concerned. Inglesfield concluded that the surface-state-induced (electronic) instability was too weak to be the major effect whereas Krakauer, Posternak, and Freeman, in their self-consistent calculation, came to the opposite conclusion.<sup>8</sup> The surface susceptibility is presumably a sensitive function of the dispersion and energy of the surface electronic states. It therefore appeared important to us to ascertain, using angle-resolved photoemission, to what extent the existing calculations gave a correct description of the surface electronic structure of W(100), as it exists at or slightly above room temperature. A comparison is particularly easy with the work of Posternak, Krakauer, and co-workers,<sup>8,10</sup> who present detailed calculations of the energy ( $E$ ) versus wave vector parallel to the surface ( $k_{\parallel}$ ) for surface states. As the energy difference between the two proposed phases is so small, the experiments require good

angular and energy resolution. Also, the instrument response function has to be taken into account. We believe that these factors are of a critical importance and we will therefore describe our data evaluation procedure in detail.

Debe and King have shown that the (uniaxial) displacements at low temperatures are in a  $(11)$  direction in the surface Brillouin zone (SBZ).<sup>11</sup> The important surface states are consequently those along a  $(11)$  direction ( $\bar{\Sigma}$ ) in reciprocal space.<sup>8,10</sup>

Synchrotron radiation from the storage ring at the University of Wisconsin was dispersed with a toroidal grating monochromator. The photoelectrons were energy analyzed with an analyzer, rotatable around two orthogonal axes. The angular resolution is  $\pm 2.5^{\circ}$ .<sup>12</sup> The total energy resolution ( $\Delta E$ ) was 0.2 eV. The effects of contamination were monitored by observing the prominent surface state at  $-0.3$  eV at  $k_{\parallel} = 0$ .

The crystal was positioned with a  $(11)$  direction in the SBZ in the plane of incidence, which also contained the polarization vector. A mirror plane of the crystal is then in the plane of incidence with another mirror plane perpendicular to it. Using well established selection rules,<sup>13</sup> one can now determine the symmetry of the electronic states involved: By collecting electrons in the plane of polarization (perpendicular to it) only states of even (odd) symmetry are detected. An angle of incidence of  $45^{\circ}$  was used when moving the analyzer in the plane of incidence (mainly even states). Perpendicular to this plane (odd states) the analyzer blocked the light beam for angles of collection of  $15^{\circ}$  or less for normally incident light. The angular uncertainty in the plane of incidence (even states) can, as discussed below, be determined to less than  $\pm 1^{\circ}$ . The uncertainty perpendicular to this plane (odd states) is, because of the above-mentioned difficulties, larger.

The criteria we used to distinguish between surface and bulk states were those used by Weng, Plummer, and Gustafsson.<sup>9,14</sup> In Fig. 1 we show some typical energy distribution curves for different polar angles of collection from the normal,  $\theta$ . We locate the Fermi level ( $E_F$ ) at the halfway point of the high-energy cutoff. The resulting energy dispersions for the surface states are shown in Fig. 2. It is well established that a finite resolution  $\Delta E$  makes all states within  $\Delta E$  of  $E_F$  appear to be located too far away from the Fermi level.<sup>15</sup> The position of these data points was smoothly adjusted towards the Fermi level. This procedure was adopted as it tends to, if anything, make the electronic mechanism<sup>4,5,8,10</sup> more plausible.

State SH ("Swanson hump") is last observed at  $k_{\parallel} = 0.69 \text{ \AA}^{-1}$ . Taking into account the general upward trend in the dispersion, as well as the finite angular acceptance of the analyzer and the error in angular setting, this provides a *strict* upper limit on the  $E_F$  crossing of state SH, independent of the above-mentioned adjustment for finite  $\Delta E$ .

The data in Fig. 2 are shown for  $k_{\parallel}$  up to  $1.9 \text{ \AA}^{-1}$ , i.e., well into the second SBZ. The data show mirror symmetry around the zone boundary. From the data for the even state we can determine

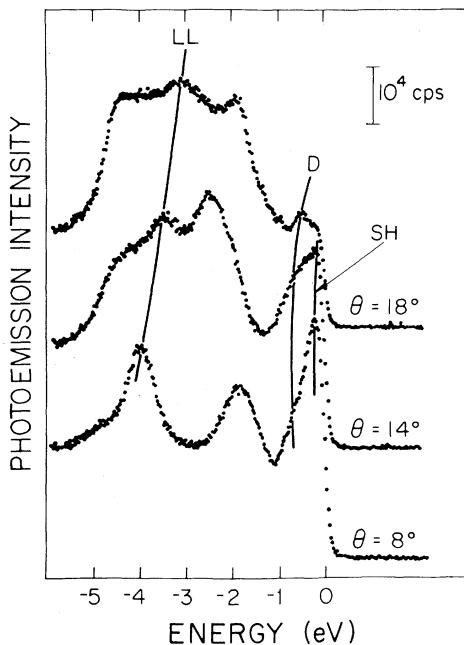


FIG. 1. Photoelectron energy distributions for W(100) for various angles of collection from the normal,  $\theta$ . The plane of incidence coincides with the plane of collection and is a (011) plane.  $\hbar\omega = 22 \text{ eV}$ .

the error in  $k_{\parallel}$  to be  $0.025 \text{ \AA}^{-1}$ , which (at  $\hbar\omega = 22 \text{ eV}$ ) corresponds to a misalignment of less than  $1^\circ$ , introduced by errors in the cutting and polishing of the sample. The odd states show a larger angular error, as expected. Following Weng, Plummer, and Gustafsson<sup>9</sup> we identify three different bands of surface states:

(1) A low-lying (LL) state of even symmetry. This state is located at  $-4.3 \text{ eV}$  at  $\bar{\Gamma}$  and shows significant dispersion along  $\bar{\Sigma}$ . This is different from the behavior along (10) ( $\bar{\Delta}$ ), where no dispersion is observed.<sup>9</sup> The dispersion is accurately given by the calculation,<sup>8,10</sup> whereas the absolute energy is off by approximately  $0.6 \text{ eV}$ .

(2) A doublet (D) surface state, absent at  $\bar{\Gamma}$  and crossing the Fermi level at  $\sim 1.2 \text{ \AA}^{-1}$ . The symmetry selection rules establish that this state has *both* an even and an odd component. The calculation by Posternak *et al.*<sup>10</sup> gives, as do most other

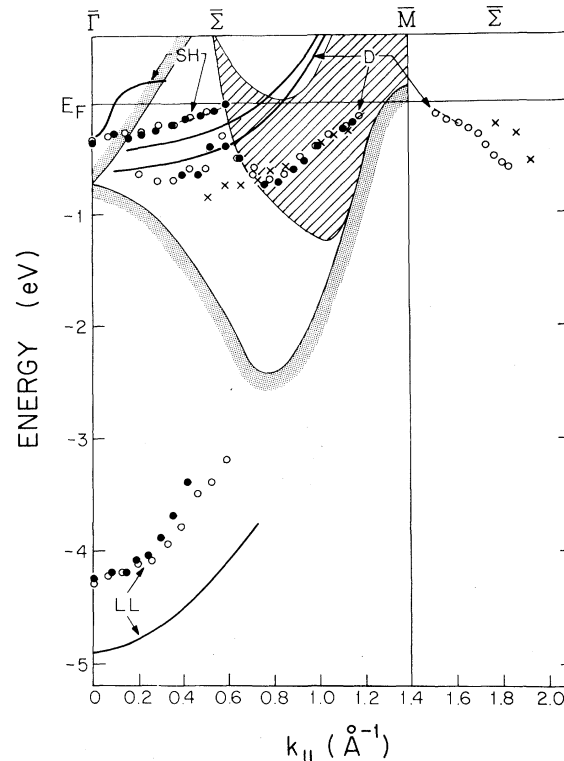


FIG. 2. Dispersion of surface states on W(100) along  $\bar{\Sigma}$ . Circles are even states, crosses odd states. Filled circles are for  $\hbar\omega = 18 \text{ eV}$ , open for  $\hbar\omega = 22 \text{ eV}$ . Theoretical results (Refs. 8 and 10) are shown with full drawn curves. Also shown is the absolute band gap (cross-hatched) and the much larger odd band gap, from Grise *et al.* (Ref. 16), which is (with spin-orbit parameters set equal to 0) fitted to the relativistic band structure of Christensen and Feuerbacher (Ref. 17).

calculations,<sup>9</sup> the existence and dispersion of this doublet correctly, while the splitting may be overestimated. More importantly, the energy position and hence the Fermi-level crossing is incorrect. The even state crosses the even-band-gap boundary at  $k_{\parallel} \sim 0.7 \text{ \AA}^{-1}$ , evidently leading to a perturbation in the dispersion. The odd component exists entirely within an odd band gap.

(3) An even surface state (SH) located 0.3 eV below  $E_F$  (at  $\bar{\Gamma}$ ) and crossing the Fermi level at  $0.6 \text{ \AA}^{-1}$ . This is the well-known "Swanson hump."<sup>18</sup> The calculation<sup>10</sup> predicts a Fermi-level crossing at  $k_{\parallel} = 0.1 \text{ \AA}^{-1}$ , in poor agreement with experiment.

Our data for states SH and *D* are when overlapping in excellent agreement ( $\leq 0.1$  eV) with Weng, Plummer, and Gustafsson.<sup>9</sup>

It has, over the years, been difficult to obtain a theoretical description of state SH.<sup>9</sup> The calculation by Posternak *et al.* is the first to yield an occupied state SH on W(100).<sup>10</sup> However, as the dispersion is poorly given even by this calculation we conclude that a complete understanding of state SH is still lacking. This may be due to an incomplete understanding of the structure of the  $(1 \times 1)$  phase. Stensgaard, Feldman, and Silverman<sup>19</sup> have shown that the outermost layer of atoms on W(100) is, even above RT, displaced from the positions expected from a straightforward continuation of the bulk, a conclusion supported by recent LEED work.<sup>20</sup> A lateral displacement<sup>20</sup> may not affect state *D* very much, as in-plane interactions are mainly responsible for this state.<sup>10</sup> However, the effects on state SH could be quite large as this state is affected by normal-to-the-plane interactions.<sup>10</sup>

Our data do not support the electronic mechanism for the reconstruction as it has been proposed by Krakauer, Posternak, and Freeman.<sup>8</sup> The fact that state *D* crosses the Fermi level very close to the halfway point to the SBZ boundary is the driving force behind the reordering in their model. They misplace, however, the Fermi-level crossing of state *D* by a very significant amount (Fig. 2). The crossing point of state SH is closer to the halfway point and this state would be a less unlikely candidate for a role in the reconstruction.

Hence, the calculated surface susceptibility<sup>8</sup> is incorrect and it appears that *surface states play a much smaller role for an understanding of the low-temperature structure of W(100)* than proposed.<sup>8</sup> Our data do, on the other hand, suggest a reevaluation of the idea put forward by Inglesfield<sup>6</sup> and Terakura, Terakura, and Toraoka<sup>7</sup> that

the reconstruction is the result of the surface atoms being unstable to arbitrary atomic displacements.

The ordering in the low-temperature phase is in this model provided by the surface states marginally favoring the displacement which couples them together.<sup>6</sup>

Recently, Campuzano *et al.* have performed angle-resolved temperature-dependent photoemission measurements on W(100) using unpolarized radiation.<sup>21</sup> Their data for the dispersion of surface states at RT agree poorly with ours, considering the subtlety of the effects involved. They show a state of mixed (odd and even) symmetry crossing the Fermi level halfway to the SBZ boundary,<sup>21</sup> in sharp contradiction with the present results. The origin of these differences is unclear. The fact that they observe temperature-induced effects might simply be an indirect manifestation of the superstructure below RT.<sup>6,7</sup>

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*Note added.*—In very recent work by Campuzano *et al.*,<sup>22</sup> conclusions in essential agreement with ours are reached. Differences between their data and our data are attributed to their use of considerably worse energy resolution.

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## Easily Implementable Nonlocal Exchange-Correlation Energy Functional

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An exchange-correlation functional for nonuniform electronic systems is developed which provides an easily implementable correction to the local density approximation. It is applied to metallic surface energies, as well as to self-consistent atomic calculations which include the ground-state energies of a number of atoms, plus the removal energies for  $1s$ ,  $2s$ ,  $3s$ ,  $4s$ ,  $2p$ ,  $3p$ , and  $3d$  electrons. In all cases tried a substantial improvement was found.

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For a number of years our group has studied the corrections<sup>1,2</sup> to the local density approximation<sup>3</sup> (LDA) for the exchange-correlation energy for nonuniform electronic systems. The ideas which evolved led to a nonlocal functional<sup>2</sup> which worked well when tested on planar metallic surfaces. Here we apply the same ideas to develop a functional which is easily implementable for any electronic system for which the LDA provides a reasonable starting point. We apply the new functional not only to planar surfaces, but also to the ground-state energy of a number of atoms, as well as the removal energies for a variety of atomic states. We find a systematic improvement over the LDA, and in fact, the improvement was substantial for all atoms tested.

To motivate what follows we begin with a qualitative discussion of length scales. Instead of using electron density  $n$  as the basic variable, it is more appropriate for our purposes to use inverse particle spacing or local Fermi wave vector  $k_F \equiv (3\pi^2 n)^{1/3}$ . This makes the coefficient  $Z_{\text{grad}}$  in the expansion for the energy functional,

$$E^{\text{xc}} = E_{\text{LDA}}^{\text{xc}} + \gamma \int Z_{\text{grad}}(k_F) (\nabla k_F)^2 d^3r + \dots, \quad (1)$$

a slowly varying function<sup>2,4</sup> of  $k_F$ . The constant

$\gamma = e^2/16\pi^3$  makes  $Z$  agree with the notation used in Ref. 2 and by Rasolt and Geldart.<sup>4</sup> Of prime importance is a length (call it  $\xi$ ) which characterizes the scale over which the density varies. This is the surface healing length, the size of the orbital one is in, or whatever. For concreteness imagine a surface whose local  $k_F$  varies linearly with distance from its value  $k_{FB}$  in the bulk to zero. Then the width of the surface layer is  $k_{FB}/|\nabla k_F| = 2k_F/|\nabla k_F|$ , where we eliminate  $k_{FB}$  in favor of the typical local value in the middle of the layer. We will use this as a definition of  $\xi$  (for an arbitrary density variation), that is  $\xi^{-1} \equiv \frac{1}{2}|\nabla k_F/k_F|$ , where  $k_F \equiv k_F(\vec{r})$  and  $\nabla k_F$  is its gradient. We thus assume that there is only one important length scale for a given region of space.

For the LDA to be valid [for the first term of (1) to be a good approximation to the whole series], inequalities like

$$k_F \xi \gg 1, \quad k_{FT} \xi \gg 1 \quad (2)$$

presumably must hold, where  $k_{FT}$  is the local Fermi-Thomas wave vector. For materials of interest  $k_F$  and  $k_{FT}$  are roughly the same, and the numbers are such that (2) is neither obviously satisfied nor obviously violated. For example,