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W{100} clean surface phase transition studied by core-level-shift spectroscopy: Order-order or order-disorder transition

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W$4f_{7/2}$ core-level spectra are recorded from the high- and low-temperature phases on a "flat" W(100) crystal. In the high-temperature phase, the core-level binding energy associated with surface atoms is 370±10 meV lower than that from the bulk atoms. This binding energy is found to be shifted by 15±5 meV in the low-temperature phase. The magnitude of this shift and an excess broadening observed in the surface peak from the high-temperature phase give evidence for disorder in this phase, in which the surface atoms have similar local coordination to those of the low-temperature phase. The surface core-level shift of the low-temperature phase agrees well with the structural model proposed for this phase by Debe and King, in contrast with a previous conclusion. Assuming that defects can induce long-range order in the high-temperature phase which differs in nature from that in the low-temperature phase, one can explain the disagreement in the literature concerning the value of the binding energy associated with the W(100) surface atoms in the high-temperature phase, as well as the discrepancies over the observed shifts of this binding energy upon the low-temperature phase transition.

I. INTRODUCTION

The thermally induced clean-surface phase transition on the W(100) face is probably the most studied clean surface phenomenon in the field of surface science. But despite the great effort applied to the study of this surface, utilizing a wide range of experimental and theoretical techniques, only the structure of the low-temperature phase has been determined with any great certainty. The nature of the phase transition, its driving force and the structure of the higher-temperature phase remain to be determined unambiguously.

Yonehara and Schmidt[1] were the first to observe that on cooling below room temperature, the low-energy electron diffraction (LEED) pattern exhibited by a clean W(100) surface changed from (1×1) to a $c(2\times2)$, subsequently shown by Debe and King[2–4] to be a clean-surface phase transition, between high-temperature (HT) and low-temperature (LT) phases. At temperatures below 200 K the half-order features appear sharp and intense. It is now generally agreed[5] that this change in surface periodicity arises from a lateral displacement of the top-layer tungsten atoms in the $\langle 11 \rangle$ directions, forming "zig-zag" rows (the Debe-King model[2,3]), the surface atoms being displaced by ≈0.2 Å.[6]

Two other models for the low-temperature (LT) phase have been suggested, both of which involve vertical displacements of the top-layer atoms. Melmed and coworkers[7] proposed a model involving alternate vertical displacements of tungsten atoms on the basis of field-ion microscopy (FIM) observations. Another model involving both lateral and vertical displacements was proposed by Legrand and co-workers[8] and has claimed support from surface core-level spectroscopy data.[9] However, both of these models fail to generate the observed $p2mg$ symmetry, which also requires the top-layer atoms to be coplanar to less than 0.01 Å.[10] Frozen-phonon total-energy calculations[11,12] have confirmed that the Debe-King (DK) model is most energetically favorable.

In many previous studies the high-temperature phase has been implicitly assumed to have a truncated bulk structure, the top-layer atoms being located in the bulk lattice sites and the whole top layer being uniformly relaxed inwards. Several LEED calculations[13] have been performed assuming this structure, leading to a wide range of surface-to-bulk interlayer spacings, from 4.5% to 11% relaxation. However, MeV ion-scattering results have shown that at room temperature the top-layer atoms are displaced from the bulk positions by ≈0.2 Å.[14] A nontruncated bulk structure has also been supported by several recent theoretical models, based on both lattice-dynamical and all-electron calculations.[12,15,16] Further experimental data from electron-energy-loss spectroscopy (EELS) (Ref. 17) have suggested that the HT phase is disordered. Recent thermal-atom-scattering data[18,19] have been interpreted to favor both a disordered[18] and an ordered[19] high-temperature phases. As can be seen from the above outline, there is a general agreement on the structure of the LT phase; however there is little consensus on the structure of the HT phase and consequently, the nature of the phase transition.

Previous studies using surface core-level spectroscopy[20–23] have shown it to be an extremely sensitive probe of the selvedge. The technique is especially suited to the study of clean surfaces since it is uniquely sensitive to changes in charge density in the vicinity of the surface atoms. Changes in coordination at the surface result in changes in the shape and position of the surface-atom local density of states. This directly affects the charge on the surface atoms, shifting their core-level binding energy with respect to the bulk. Hence surface core-level spectroscopy is sensitive to changes in the local geometry of the atoms in the surface layer typically within the next-nearest-neighbor shell. This sensitivity to changes in coordination at the surface makes surface core-level spectroscopy a useful technique for investigating reconstructions at metal surfaces.

The surface core-level binding energies (SCL) of the HT phase has been measured previously.[24–27] The data of van der Veen *et al.*[24] have been reexamined[28] and a slightly different set of fitting parameters obtained. Experimental spectra could be fitted with three peaks, assigned to the bulk, the underlayer, and the surface atoms. SCL from the LT phase have previously been reported[9] by only one group. They found that on cooling the W(100) crystal to 160 K the surface peak shifted 50 meV towards the bulk and increased in intensity. The magnitude of this shift was smaller than their calculated value for either of the two models (the lateral or vertical shift) they considered. They interpreted the results as agreeing more closely with the value calculated for a model involving both lateral and vertical displacements of the surface tungsten atoms, concluding that their results were not consistent with any of the suggested models of the LT phase.

In this paper we wish to report the results of a surface core-level shift study of the clean high- and low-temperature phases on a "flat" W(100) crystal surface. The core level chosen is the $4f_{7/2}$, lying at about 31.4 eV below the Fermi level.[24,26,28] This core level has been found to be well suited for SCL studies:[29] on tungsten surfaces, the line is fairly narrow with respect to the observed shifts[28] and highly surface sensitive if excited with photons at energies ranging from 50 to 100 eV.[29] In previous SCL studies of W(100) the crystals used were cut to within 0.5° of the (100) plane; the resulting terrace widths are in the range 100–300 Å. Wendelken and Wang have shown that terrace widths of this size can smear out the temperature range of the phase transition[30] leading to a situation where a substantial amount of the surface is in the LT phase at room temperature and above. In this paper we present results obtained using a crystal cut to within 0.1° of the (100) face. Such a crystal exhibits a sharp phase transition at around 210 K, with the surface being fully in the LT phase below 180 K and nearly completely composed of the HT phase at room temperature and above.[30] This means that we have unambiguously measured the binding energies for the HT and LT phases, each in the absence of the other phase.

II. EXPERIMENT

Data for both the HT and LT phases were obtained in the Daresbury SRS ADES 2 system attached to a grazing-incidence monochromator, providing monochromatic VUV radiation, at a photon energy of 75 eV with a resolution of 0.16 eV. A double-pass cylindrical mirror analyzer was used to analyze the emitted photoelectrons. The overall resolution of the system was calculated to be 0.22 eV, based on experimentally determined values for the monochromator and analyzer resolutions. The value estimated for the system resolution agrees with that obtained from the spectra of the Fermi level. For both HT and LT phases the data were collected with the light incident at 70° to the surface normal. The base pressure of the system was better than 4×10^{-11} torr, with a working pressure of less than 7×10^{-11} torr. The primary contaminant in the residual gas in the chamber was hydrogen. With the crystal at room temperature it was noted that if the crystal was exposed to the residual gases in the chamber for more than 10 min a very faint $c(2\times2)$ pattern could be observed. This was attributed to uptake of hydrogen from the background gas and the onset of the symmetry switch due to the hydrogen-induced reconstruction.[31]

The crystal, oriented to within 0.1° of the (100) face, was attached using 0.5-mm-tungsten wire to the copper base of a hollow stainless-steel probe filled with liquid nitrogen. This arrangement enabled cooling of the crystal to a minimum temperature of $\approx$120 K. Electron bombardment from a filament located behind the crystal heated the crystal to 2500 K. A thermocouple (WRe3%–WRe25%) was tied through a hole drilled in the crystal. LEED measurements were performed using a Varian four-grid LEED optics.

The crystal was initially cleaned by repeated heating to 1800 K in 10^{-6} torr oxygen and flashing in vacuum to 2400 K. Once the carbon had been removed from the bulk, cleaning was performed by flashing to between 2300–2500 K. Several criteria were used to determine the cleanliness of the crystal. Using the CMA, the Auger signals of the primary contaminants, oxygen and carbon, were reduced to below the noise level of the Auger system, corresponding to less than 0.2% monolayer on the surface. The thermally induced reconstruction could be obtained and maintained for more than 10 min while observing the $c(2\times2)$ LEED pattern after a flash to 2500 K. It was observed that the thermally induced phase transition was sharp and reversible, the appearance of weak half-order beams starting at 250 K. The half-order beams reached a maximum intensity at temperatures below 180 K.

The count rate was $10\,000\ \mathrm{s}^{-1}$ as an average. It enabled us to take our spectra as single scans of 200 sec duration. The crystal was flashed to 2500 K and cooling to 200 K required approximately 200 sec. Spectra from the HT phase were systematically recorded either before or after the spectrum from the LT phase was collected. The data collection was thus entirely done well before the hydrogen-induced reconstruction due to residual adsorption was detected by LEED observation.

III. RESULTS

Figure 1 shows the data from the HT (solid line) and LT (dashed line) phases. These data have had a linear background subtracted and the intensity of each peak has been normalized, so that both peaks have the same area. The HT phase spectrum was taken at 500 K to minimize the adsorption of hydrogen from the residual gas background in the chamber. The lower line is the difference between the two spectra, which shows a small shift in in-

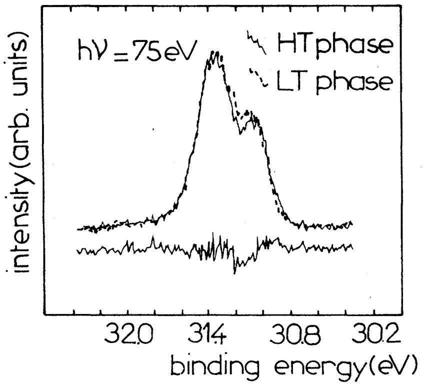

FIG. 1. W(100) $4f_{7/2}$ core-level spectra from the high-500 K solid line and low- (< 150 K, dashed lined) temperature phases. These data are background subtracted using a linear background and both peaks have been normalized to the same area. The effect observed on cooling is clearly visible. The surface peak shifts slightly towards the bulk peaks (higher binding energy) and increases in amplitude. The difference between the two spectra is shown by the jagged line beneath the spectra.

tensity from the low-binding-energy side of the surface peak towards the bulk peak. It should be noted that the difference spectrum is asymmetric, indicating a small shift in the position of the surface peak. A symmetric difference spectrum would be expected from a temperature-induced change in broadening of the surface peak with no shift in peak position. The shift may be estimated roughly by subtracting the bulk and underlayer peaks, which are presumed not to be affected by the reconstruction, leaving the surface peak. This was done by fixing the shift of the underlayer peak to a known value and altering the bulk position until the surface peak looks symmetric. This is shown in Fig. 2. The LT surface peak is shifted by ≤15 meV to higher binding energy compared to its position in the HT spectrum. When examined in the LEED optics at 500 K only a $p(1\times1)$ LEED pattern from the clean HT phase could be seen, free from any trace of the $c(2\times2)$. Below 200 K a sharp $c(2\times2)$ pattern characteristic of the LT phase was observed. This $c(2\times2)$ pattern was demonstrated to be re-

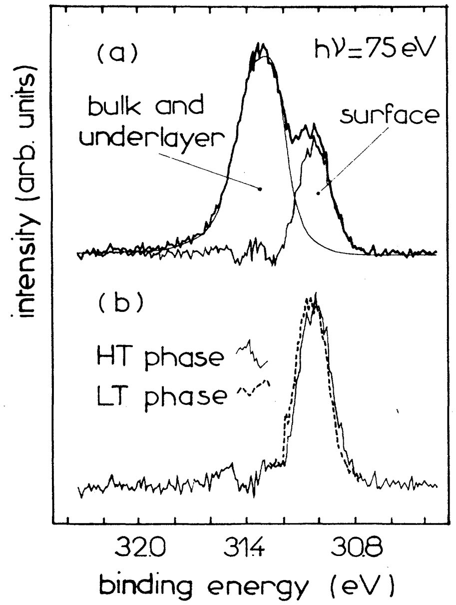

FIG. 2. An attempt to determine the shift of the W$4f_{7/2}$ surface core level by subtracting the peak and underlayer components. (a) The surface component extracted from the spectrum. (b) A binding-energy shift of < 15 meV is seen in the surface peak between the high- and low-temperature phases.

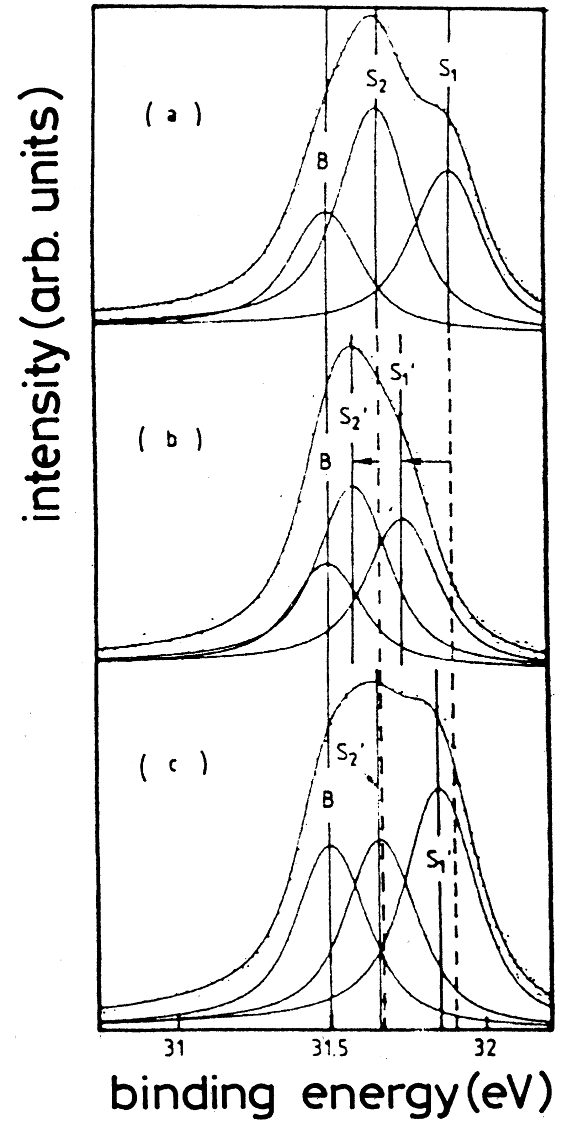

FIG. 3. W(100) $4f_{7/2}$ core-level spectra from Guillot *et al.* (Ref. 9) (with permission). (a) Clean surface at room temperature. (b) Hydrogen reconstructed surface. (c) Clean reconstructed surface at 160 K; the surface peak S_1 is shifted by 50 meV. We note that the reconstructed surface peak increases in intensity in a very similar manner to our results (see Fig. 1).

versible by heating the crystal while observing the LEED pattern. The $c(2\times2)$ structure rapidly disappeared at temperatures above 220 K. This temperature is below the onset of the thermal desorption of hydrogen, which precludes any role for hydrogen adsorption on the observed $c(2\times2)$ structure. These results are in good agreement with previous work on a similar flat crystal.[30] Consequently, we believe the SCL we have measured are from the HT and LT phases for this surface, even though the results differ substantially from those obtained previously for the LT phase.[9]

Comparing these results with the previous measurement for the LT phase (see Fig. 3, taken from Guillot *et al.*[9]) one can see immediately that there is a qualitative difference. The size of the shift is much smaller in our data, the difference between HT and LT spectra being much less marked. It could be argued that this discrepancy arises from hydrogen adsorption (and a possibility of reconstruction), since even small exposures of hydrogen can have a profound effect on the core-level spectra.[20,25,28,32] There is a strong argument against this. Both our results and those obtained by Guillot *et al.*[9] have one unusual feature in common; the surface peak appears to increase in amplitude upon reconstruction. We have *never* seen a similar effect with any other system. In those systems in which the shift is induced by chemisorption there is always a decrease in amplitude of the surface peak as the coverage of the adsorbate increases.

To produce direct evidence that the observed shift in our data did not arise from hydrogen chemisorption we took spectra in the following way. After first cooling the crystal to 120 K, the crystal was flashed to 2500 K to remove contaminants before the start of the cycle. It was then allowed to cool to 150 K, when a second scan was started to record the core-level spectrum for the low-temperature phase. At the end of this scan the crystal was heated radiatively to 300 K, below the temperature of desorption of any possible contaminent, including hydrogen,[33] and a second spectrum was taken. This is shown in Fig. 4.

The magnitude of the shifts has been put on a more quantitative basis by least-squares fitting the spectra to estimate the positions of their components. In our fitting procedure each peak is associated with two parameters, its amplitude and its energy position, and a line shape. We have approximated the line shape of the tungsten $4f_{7/2}$ core levels with a Doniach-Šunjić line shape,[34] which has two parameters, a Lorentzian width and an asymmetry parameter α, and which has previously been shown to be a good representation of the experimental core-level line shape.[35] The line-shape parameters of the $4f_{7/2}$ core level was derived from the values obtained by Wertheim and co-workers:[28] a Lorentzian width 0.05 eV and an asymmetry parameter 0.06. All of the core levels were assumed to have the same core-hole lifetime and asymmetry parameter. Additionally, two parameters were used to adjust a linear background and the whole spectrum was convolved with a Gaussian, to represent both the instrument response and inhomogeneous and phonon broadening. This was set to 0.22 eV. For those fits in which the Gaussian width was left unconstrained a value very close to 0.22 eV was obtained. The Gaussian instrumental response function was fixed, and the energy and amplitudes of each of the peaks together with the slope and intercept of the background were allowed to vary. The spectra from both phases could be best fitted with three peaks, using the parameters specified above. These peaks are assigned in a similar manner to previous work to one peak from bulk atoms and to two shifted core levels from underlayer and surface atoms.[25,27] The best-fit values are shown for both phases in Table I.

The second spectrum in Fig. 4 shows a shift of the surface core level of 15±5 meV, in agreement with the estimate obtained from Fig. 2. Though this spectrum has been recorded at an even higher level of contamination than the first spectrum in Fig. 4, it exhibits a shift of the surface core level towards higher binding energy that is of an opposite sign from a shift due to any contamination. These data give definite evidence for that shift to originate from the low-temperature to higher-temperature phase transition.

However, the final spectrum probably shows the presence of a small quantity of a contaminant on the surface. Assuming that the system pressure of 4×10^{-11} torr is mostly hydrogen, one can estimate the amount of hydrogen to which the surface is exposed during both the cooling from the onset of hydrogen adsorption ($\approx$700 K) to

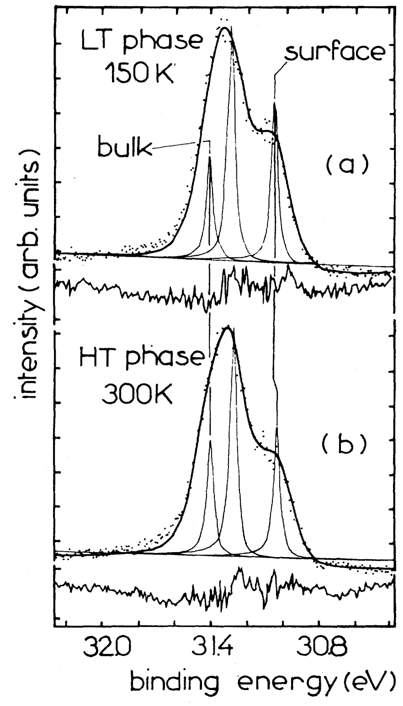

FIG. 4. W(100) $4f_{7/2}$ core-level spectra decomposed into their components assuming all have the same line shape. (a) Low-temperature phase below 150 K. (b) High-temperature phase, after heating the low-temperature phase [shown in (a)] to room temperature; we note that the figure shows a shift towards lower binding energy of the surface core level from (a) to (b) (−15 meV), despite the increasing level of contamination.

TABLE I. Surface and underlayer W $4f_{7/2}$ core-level binding energies of the HT and LT phases of the W(100) surface and shift experienced upon the low-temperature phase transition (Δ underlayer and Δ surface). The binding energies are recorded with respect to the binding energy of the bulk peak [31.41±0.05 eV (Ref. 26)]. All the given values are in eV. In our work the measurement is more accurate for Δ surface than for surface core-level shifts: This results in a slight misfit between the value given to Δ surface (15 meV) and the magnitude of the difference over the surface core-level shifts (20 meV).

	Underlayer HT	Δ underlayer	Surface HT	Surface LT	Δ surface
Guillot *et al.*[a]	−0.16	<0.02	−0.40	−0.35	0.050
This work	−0.14		−0.37	−0.35	0.015
	±0.01		±0.01	±0.01	±0.005

[a] Reference 9.

the first scan (50 sec) and the scan itself (200 sec) as ≈0.01 Langmuir (1 Langmuir: 10^{-6} torr sec), resulting in a coverage of about 2×10^{13} hydrogen atoms cm^{-2} [the initial sticking probability of hydrogen on the W(100) surface is 0.6 (Ref. 33)], i.e., 0.02 monolayers [the W(100) surface contains 1×10^{15} atoms cm^{-2}]. Although an adsorbed hydrogen atom can influence not only the tungsten atoms to which it is bonded, but also the surrounding surface tungsten atoms (Refs. 36 and 37 and results to be published), the above coverage is well below that required to begin switching the surface symmetry from *p2mg* to *c2mm*,[31] characteristic of the hydrogen-induced $c(2\times2)$ phase.

We conclude for the data presented above, which is only a small sample of a large set of spectra, that the clean phase transition at 210 K on this W(100) surface induces a shift of 15±5 meV in the core-level energy. Surprisingly enough, that is smaller than on a less flat surface,[9] though the reverse was expected, as in the present work a completely reconstructed surface is compared with a completely "unreconstructed" one.

IV. DISCUSSION

There are a number of possible explanations for the small size of the shift upon cooling. The most obvious is that the reconstruction was not obtained during the course of the experiments. This is evidently untrue as a $c(2\times2)$ LEED pattern, which could be reversible converted to the (1×1) by changing the crystal temperature alone, was observed at several points during the collection of the photoelectron spectra. For some spectra a thermally reversible $c(2\times2)$ LEED pattern was observed after the spectrum had been collected. Given that the data presented here are from the reconstructed LT phase, we are faced with explaining (i) why the phase transition has such a small effect on the SCL, and (ii) why the results differ from those already obtained by another group. In the following we consider both of these questions.

A. Theoretical estimates of the shift associated with clean reconstruction

Estimates of the magnitude of the shift on reconstruction have been made by two groups using two different techniques. Tománek and co-workers[38] have used their bond-breaking model to estimate the value of the core-level shift for a wide range of systems. For the clean-surface phase transition on W(100), they estimate a shift of 20 meV to higher binding energy for the surface peak on changing the structure of the surface from the unreconstructed (truncated bulk) surface to the Debe and King displacively reconstructed surface in which the top-layer atoms are displaced by 0.2 Å in the ⟨11⟩ direction. They also found that the underlayer atoms should experience a 30-meV shift to lower binding energy upon reconstruction.

The effect of the reconstruction upon the SCL has also been estimated with a tight-binding model which appeared with the experimental results of Guillot *et al.*[9] The same values were obtained for the change in the surface core-level shift upon reconstruction for two different models, involving displacements in the surface plane in the ⟨11⟩ and ⟨10⟩ directions: a shift to higher binding energy of 130 meV for the surface atoms and 70 meV for the underlayer atoms. They also presented results for a model involving alternate vertical displacements of the top-layer atoms, resulting in two different shifts upon reconstruction of 70 and 30 meV for the top-layer atoms and 20 meV for the underlayer atoms. It was this latter model which best agreed with the experimental results they had obtained, a shift of 50 meV of the surface peak and no observable additional shift for the underlayer peak. However, since this model involves vertical displacements of the surface atoms, it contradicts the symmetry shown by the LEED results.[10]

The accuracy of the models used to estimate SCL should also be examined. Neither of the above models is parameter free and both involve assumptions which may not be valid. The accuracy of these calculations may be best assessed by comparing the values they produce with those that can be measured unambiguously. The microscopic model of Spanjaard and Desjonquères[9] gives estimates for the SCL of the W(100) and W(111) surfaces which are in good agreement (within ≈20 meV) with the experimentally deduced values, but the results for the clean W(100) surface are very different from those obtained by experiment. For the top-layer atoms on the unreconstructed surface a shift of −0.55 eV is calculated, whereas the experimental results for the HT phase of W(100) give values of −0.40,[25] −0.36,[28] −0.39,[26] and −0.37 eV.[27] This could partly explain the discrepancy between calculated and experimental values for the LT (reconstructed) surface phase.

Based on the Johansson and Mårtensson thermodynamic cycle,[39] the bond-breaking model[38] assumes that both the equivalent core and excited atom approximations are valid. It thus includes a final-state contribution (complete screening). It approximates the SCL as the difference in surface energies of the Z and $(Z+1)$th elements, ignoring the solution energy of $Z+1$ host in the Z element. These surface energies are estimated by differences in cohesive energies modified by an effective coordination number. Despite these approximations the values calculated for several low-index surfaces are in good agreement with experimental results. But, for the unreconstructed W(100) surface the value for the SCL associated with top-layer atoms is underestimated (-0.30 eV) and the underlayer atoms are calculated to have a core-level shift which is only half of the value observed. Doubt is also cast upon the accuracy of the results for the reconstruction by considering the lack of sophistication used in determining the effect of distance to the nearest neighbor. This becomes even more apparent when a symmetry of the system is broken, such as following a surface reconstruction, when obtaining the right bonding versus distance function becomes critical. To summarize, the bond-breaking model is not sufficiently precise to accurately determine the changes in SCL on reconstruction. A more advanced version of the bond-breaking model, such as that introduced by Rosengren,[35] could possibly give more accurate results for a reconstructed surface, but to date no such calculations have been published. The above calculations consider that the HT surface is bulk terminated which is another possible explanation for the discrepancies with experimental data. This will be discussed below.

Another route may be used to estimate the core-level shift upon reconstruction. Egelhoff[23] has pointed out that the core-level binding energy is the difference in total energy between the initial and final states in the photoemission process. The surface core-level shift is the difference between the core-level binding energy in the bulk and at the surface and hence is a second difference in total energies involving both initial-state (ground-state) and final-state contributions. Although the latter is out of grasp, the former is generally the main component of the observed SCL:[21] Therefore, surface core-level spectroscopy can be used to estimate the difference in ground-state energies between two different states of the same surface. We can apply this idea to the HT and LT phases on W(100). Several calculations of the change in ground-state energy upon reconstruction exist in the literature: 27 (Ref. 40), 20 (Ref. 8), 10 (Ref. 11), 100 (Ref. 12), 35 to 75 (model dependent),[41] and 30 meV.[42] The first four of these calculations are the energy differences between the LT reconstructed phase and the ideal bulk truncated surface. The last two results are from effective Hamiltonian calculations and represent the energy difference between the Debe and King LT model and a disordered HT phase. The scatter in these energies is large, but this is understandable as the reconstruction energy is a very small difference between two large total energies.

Fasolino and Tosatti[42] calculated the distortion energy as a function of displacement along both the $\langle 10 \rangle$ and $\langle 11 \rangle$ directions at $T=0$, finding the $\langle 11 \rangle$ displacement preferred with a well minimum of 30 meV. However, care should be taken when comparing this $T=0$ value with experimental results at $T>0$, as Roelofs[41] has pointed out that the variation in energy between $T=0$ and T_c is almost the same as that between T_c and room temperature.

The estimate of the reconstruction energy derived from our SCL measurements is simply the difference between the surface-atom SCL of the HT phase and the LT phase, $15+5$ meV. This is less than almost all the values quoted above and considerably less than the estimate of Singh *et al.*[12] If the accuracy of the latter calculation is believed, then these experimental measurements support the idea that in the HT phase the surface does not correspond to the bulk terminated lattice.

B. The structure of the HT phase

Three different groups of structures have been proposed to describe the HT phase. (i) A bulk terminated structure with the top-layer atoms in the bulk lattice sites. It is this model that is classically assumed to be the structure of the HT phase. This model appears inconsistent with our SCL data. (ii) A disordered surface, in which the top-layer atoms are randomly displaced in the $\langle 11 \rangle$ directions with respect to the bulk lattice sites.[12,41–45] (iii) A laterally displaced surface layer, in which the surface layer is displaced either rigidly or gradually[4,6] with respect to the bulk. Singh *et al.*[12] have used this third model in their calculation and have found that, assuming a rigid subsurface layer, the ideal W(100) surface is stable against this distortion.

1. *Is the HT phase ordered or disordered?*

The suggestion of a disordered HT phase is not new, but increasing amounts of data have been collected to support its consideration as the structure of the HT phase. Initially, high-energy ion-scattering data indicated that half of the surface atoms were displaced from bulk sites at room temperature[14] but this result was treated as anomalous for some time as it agreed with no other results. Debe and King[2,3] originally proposed that the transition was order-order, citing evidence from Debye-Waller plots of the LEED beam intensities of the (00) and (01) beams, but this has been criticized by Roelofs,[41] who pointed out that a change in slope of the specular beam intensity against temperature would be expected for both order-order and order-disorder transitions. Barker and Estrup[43] also favor a disordered high-temperature phase, with the size of the surface-atom displacements being related to the order. In a similar way, Wood and Erskine have interpreted their high-resolution electron-energy-loss spectroscopy (HREELS) data in terms of HT disordered phase.[46] More recently, thermal-atom-scattering data[18] have also been interpreted as demonstrating that the surface disorders with increasing temperature, although a second study by this technique[19] has been used to justify the displacive model of the phase transition (which implies an order-order transition) with identical data. A disordered HT phase can also explain the value obtained for the first interlayer spacing, determined by LEED; this value is similar for both the HT and LT phases.[47] This does not result from the particular data-analysis procedure used, but from the observation that the Bragg peak energies in the integral order LEED $I(V)$ spectra do not move upon reconstruction. However, total-energy calculations of the surface geometry have found that the unreconstructed surface should be relaxed outward by $\approx 5\%$, whereas the reconstructed surface should be relaxed by $\approx 1\%$.[11,12] This would support the contention that there is only a very small change in the surface geometry through the phase transition.

Support for a disordered surface also comes from theoretical models based on local interactions. Effective Hamiltonian models, such as those used by Fasolino and Tosatti,[42] Roelofs,[41,44,45] and Yoshimori[46] lead to surface structures which are more ordered at low temperature but which become increasingly disordered as the temperature increases. Fasolino and Tosatti's models indicate that the surface-atom displacement remains constant through the phase transition with the other component of the order parameter (the phase) changing the surface from ordered to disordered. Yoshimori's results show that even at 100 K there is still a significant amount of disorder with the surface fully ordered only below 20 K. From the higher magnitude of the total-energy difference they have found between the bulk-truncated end of the reconstructed surface, Singh *et al.*[12] inferred that the HT phase was unlikely to be the ideal $p(1\times1)$ structure. They suggested that the surface could be disordered with random parallel shifts. As a matter of fact, all the calculations[41,42,44,45,46] assuming an order-disorder transition give a lower energy difference than that found by Singh *et al.*:[12] for all the cases including a disordered HT phase, although the phase of the order parameters changes rapidly through the phase transition, there is little change in the local geometry around a surface-tungsten atom on a surface without steps or defects. The shift we have found through the reconstruction—15±5 meV—is even smaller than all the above calculated values. If we assume that the SCL shift is a correct estimate of the total-energy difference (see above), our experimental findings obtained from a very flat, defect-free surface, thus support two conclusions. First, the HT phase is disordered in nature. Second, the magnitude of the SCL shift induced by the low-temperature phase transition is consistent with the Debe and King model, provided the phase transition is indeed order-disorder.

2. *The broadening of the surface peaks*

One measurable property of the core-level data which should be sensitive to the amount of local-scale disorder in the top-most layers is the apparent width of the core level. If the atoms at the surface experience slightly different effective coordination numbers by being closer to or further away from their immediate neighbors due to static disorder, for example, then there should be a spread in the energy position of the core level corresponding to this range of coordination numbers. Combining information from the changes in width with changes in energy position of the surface peak through the transition one should be able to distinguish whether the phase transition is order-disorder or displacive in nature. Unfortunately, in our data the effective changes in width of the surface peak are very small compared to the width of the instrument response function. Using the calculated value of Sebilleau *et al.*[48] for the phonon broadening, and assuming an instrument response of 0.22 eV, the underlayer and bulk (surface) peaks should have a Gaussian width of 0.228 (0.245) eV. Changes of this order are very difficult to measure accurately, but we can use results in the literature to estimate this effect.

Wertheim *et al.*[28] found the core-level spectra from W(100) at room temperature could be best fitted using three Doniach-Šunjić peaks all with the same width convolved with a Gaussian width of 0.15 eV for the bulk and underlayer peaks, and 0.20 eV for the surface peak. They account for this excess width in terms of crystal-field splitting of the surface peak. The Gaussian width accounts for the instrument response, phonon broadening of the line at the surface, and other inhomogeneous contributions to the linewidth. It may be decomposed into its components if these results are used in conjunction with the theoretical calculations of the phonon-broadening contribution to the Gaussian width of the tungsten $4f_{7/2}$ core levels, i.e., 0.06 eV for the bulk and underlayer peaks and 0.11 eV for the surface peaks.[48] We have already shown[49] that for the close-packed tungsten surface W(110), the values extracted for the phonon broadening are in good agreement with those calculated.[48] Using these values for the phonon contribution and assuming no other inhomogeneous contribution to the bulk peak, the Gaussian width of the instrument response function is found to be 0.137 eV. Summing the surface phonon broadening and the width of the instrument response in quadrature, we obtain an expected value for the Gaussian width for the surface peak of 0.175 eV. This is less than the observed value of 0.20 eV. To match the experimentally determined broadening we need an extra Gaussian broadening of 0.11 eV. This additional broadening could result from crystal-field splitting,[28] but we suggest an alternative origin. We attribute this excess width as arising from the variations in the displacement of the surface atoms in the disordered HT phase. In the case of the W$4f_{7/2}$ core level, the Doniach-Šunjić line shape is very narrow with respect to the Gaussian line, which can thus approximate the overall line shape. In the HT phase, a displacement of $\pm 0.012_5$ eV around a midpoint of a 0.175-eV-wide Gaussian line would produce the expected 0.200-eV-wide surface line shape. This would lead to a possible 12.4-meV shift upon the LT phase transition, a value which is very consistent with the above experimentally desired result (15 meV). Again, this consistently supports the idea of a disordered HT phase.

The change in the width of the surface peak also gives an explanation for the change in the amplitude in the surface-peak region upon reconstruction. The surface peak has a given intensity (area) which is dependent upon the number of surface atoms, but the amplitude of the peak is inversely related to the width. As ordering of surface atoms occur during a reduction in temperature, the width of the surface peak decreases and its amplitude increases to maintain the same area. This increase in amplitude of the surface peak upon reconstruction is seen in both our data and the data of Guillot *et al.*[9]

3. *Step ordering of the HT phase*

From the above brief review, it can be seen that recent theoretical results favor a disordered HT phase, while the analysis of experimental data is more divided on the issue. On the crystal used in the present study, the $(\sqrt{2}\times\sqrt{2})\rightarrow(1\times1)$ transition involves the whole surface, and a larger shift was expected in the core-level binding energy than previously observed. As discussed above, the LT phase is somewhat unambiguously defined, and there is perfect agreement concerning the core-level shift associated with the reconstructed surface, i.e., 0.35 eV towards lower binding energy as shown in Table I. However, different sets of data for the room-temperature surface give values ranging from -0.36 eV to -0.40 eV (Refs. 25–28) for the top-layer shift. This scatter is outside the experimental error estimated for each result. This could indicate a real effect dependent on the quality of the surface used or it could be a result of systematic errors which have not been fully considered. The former is likely to have a more profound effect on the SCL as steps on the surface can promote the growth of reconstructed domains well above T_c. It has been shown that steps orientated along the $\langle 100 \rangle$ direction only limit the size of a reconstructed domain, and so increase the transition width (a finite-size effect). In contrast, steps in the $\langle 11 \rangle$ direction select one of the two degenerate domains in the reconstruction.[45] The same mechanism serves to induce order well above the defect-free surface-transition temperature. However, this mechanism would not change the local geometry and does not explain the scatter in experimental SCL.

We have thus to suppose that steps can induce an ordering of the surface and produce a different ordered phase than the low-temperature phase transition. On the basis of the formation of a mirror plane in the HT $p(1\times1)$ phase, King and co-workers[4,6] suggested that the steps could induce a shift along the $\langle 100 \rangle$ direction of the top layer as a whole. Although Singh and co-workers[12] have estimated that the W(100) surface is stable against this distortion, the effect of steps was obviously not accounted for in their calculation. The SCL data are consistent with such an ordering, as any other which would be induced by steps and would correspond to change in local geometry compared to the LT and HT ideal surfaces. The kind of step-induced ordering of the HT phase which explains the discrepancies over the measurements of the shift associated with the clean phase transition, would also explain the scattering over the published values of the W(100) surface core-level shift.

V. SUMMARY

In this paper we have presented surface core-level spectra from the high- and low-temperature phases of a flat W(100) crystal. The core-level binding energy associated with the surface atoms has been found to be shifted by 15 ± 5 meV to higher binding energy below T_c (210 K). The magnitude of this shift has been shown to be consistent with a disordered high-temperature phase, in which the surface atoms have a similar (although not identical) coordination to those of the LT phase. It is suggested that the phase transition is order-disorder in nature. Unlike previous SCL results for this system, we find the SCL of the LT phase agree with the model of the low-temperature phase proposed by Debe and King.

We have proposed that the surface core-level shift can be used as an estimate of the total energy difference between two states of the same surface and have compared our results with those found through calculations. This comparison supports our assignment of a disordered surface to the HT phase. We have also considered the effect of inhomogeneous broadening, such as might arise from static disorder in the displacement of the surface atoms. Using the theoretical results of Sebilleau[48] for phonon broadening, we have reexamined the SCL results of Wertheim *et al.*[28] from a room-temperature W(100) surface. We find an excess (inhomogeneous) broadening of 0.11 eV, previously attributed to unresolved crystal-field splitting, which we assign to the effects of disorder (such as varying displacements of surface atoms) in the HT phase. The difference in shift between our results and those of Guillot *et al.*[29] may arise from differences in degrees of perfection of the crystals used for each experiment; we believe their crystal was slightly stepped and that steps induce an ordering at higher temperatures, with a change of local geometry compared to ideal LT and HT phases. This could also partly explain the disagreement in the literature concerning the structure of the HT phase.

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