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Evidence for a temperature-induced order-disorder phase transition on W(100)

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High-energy ion scattering measurements on a flat W(100) surface have been carried out in the temperature range 80–600 K. The results indicate conclusively that the surface atoms are displaced laterally at all temperatures. The lateral displacement is estimated as ≈ 0.14 Å. The low-temperature $(\sqrt{2}\times\sqrt{2})R45°$ to high-temperature (1×1) phase transition is therefore an order-disorder transition.

INTRODUCTION

The phase transition observed at the clean W(100) surface below room temperature has been the object of several studies since it was discovered by Debe and King[1] and by Felter, Barker, and Estrup[2] in 1977. On cooling below room temperature the (1×1) phase observed with low-energy electron diffraction (LEED) at high temperatures (HT) transforms into a $(\sqrt{2}\times\sqrt{2})R45°$ low-temperature (LT) phase. Based on a detailed symmetry analysis of LEED *I-V* spectra it was concluded[3] that the surface is reconstructed in the LT phase with the top-layer atoms shifted along the diagonals to form zigzag rows along the ⟨11⟩ surface direction. This model is now generally accepted to be correct.

The HT phase has been assumed in most studies to be a simple termination of the bulk with no lateral displacements and the whole surface layer relaxed inward. Several LEED investigations[4–10] and a single high-energy ion scattering (HEIS) study[11] carried out to determine the surface contraction are based on this assumption. Core-level shift studies for the W 4*f* level[12] led to the conclusion that the HT (1×1) phase is unreconstructed.

There are, however, a large number of indications in the literature that this conclusion is incorrect. An early ion scattering study[13] gave clear evidence that the clean surface is reconstructed at room temperature although at that time the result was conveniently ascribed to poor surface cleanliness (hydrogen contamination).[14] Electron-energy-loss spectroscopic (EELS) experiments[15] detected no phonon modes at the clean surface at room temperature. This could be attributed to the loss of long-range order at the surface. Evidence for atomic-scale disorder in the HT phase was also found from He scattering work,[16] where only specular intensity was observable and with low intensity. In the course of the present work a tensor LEED study[17] was published, in which the agreement between measured and calculated *I-V* curves was improved by assuming disorder in the top layer caused by statistical in-plane displacements. The present work was initiated following recent surface core-level shift studies of the clean W(100) surface through the phase transition[18] which indicated that the observed core-level shift of the surface atoms was consistent with a disordered HT phase. Finally, some very recent grazing incidence x-ray diffraction measurements of integrated intensities have not revealed any discontinuity at the transition temperature.[19]

Furthermore, various theoretical studies of the energetics of the W(100) reconstruction[20–22] have indicated that it is highly unlikely that the room-temperature phase is an ideal $p(1\times1)$ phase.

It has been shown[23] that steps on the W(100) surface will smear out the phase transition and result in a situation where parts of the surface at room temperature and above are still in the LT phase. Therefore, it appeared highly desirable to carry out a new analysis of the surface structure at different temperatures on a "flat" surface (terrace-width larger than 1000 Å).

HEIS is one of the most direct ways to probe surface geometries.[13,24] For ion-beam incidence along a major axis the surface peak in the energy spectrum of backscattered ions can be converted into a number of "visible" surface atoms.[25] Therefore, lateral shifts of the surface atoms are readily detectable at normal incidence.

In the following we report results from such a study with particular emphasis on demonstrating whether or not the HT (1×1) phase is a truncated bulk surface.

EXPERIMENT

The experiments were carried out in an ultrahigh vacuum (UHV) system equipped with facilities for LEED, Auger electron spectroscopy (AES), HEIS, sputtering, and residual gas analysis (RGA). The system is coupled to a 2 MV van de Graaff accelerator via differential pumping. The pressure in the system during measurements was in the 10^{-11} mbar range.

The W crystal, cut and polished to within 0.1° of the (100) face, was mounted in a three-axis goniometer. The temperature of the crystal could be measured with a W-(5 at.% Re)-W-(26 at.% Re) thermocouple. The crystal was heated by electron bombardment from the back and could be cooled efficiently by thermal conduction to a liquid-nitrogen (LN) reservoir.

Standard procedures, i.e., repeated cycles of heating in oxygen to 1800 K and flashing in vacuum to 2400 K, were used for initial cleaning. With most of the carbon contamination removed, flashes to 2500 K were sufficient to restore a clean surface.

It is well known[26] that very small amounts of surface impurities may inhibit the formation of the clean surface phase. The cleanliness of the surface was assured by noting that the excellent LT $(\sqrt{2}\times\sqrt{2})R45°$ LEED pattern (which could be observed without any visible degradation for at least 15 min after a flash) transformed reversibly into the HT (1×1) pattern at ≈ 210 K. Therefore, the pattern was indicative of the temperature-induced phase and not the hydrogen adsorption induced $c(2\times2)$ phase.[27]

The ion scattering spectra were collected during cool down after a flash (the cooling time after a high-temperature flash from ≈ 700 to ≈ 80 K was 4 min). Therefore, the temperatures indicated below are average temperatures during each data accumulation. Surface-peak (SP) yields have been converted into absolute units by comparison with backscattering yields from a standard with a known concentration of implanted Bi.

For practical reasons deuterium instead of hydrogen was used for adsorption. This has no influence on the present results.

RESULTS AND DISCUSSION

Ion scattering data were collected from the clean and from the hydrogen-exposed W(100) surface in the temperature interval ≈ 80 to ≈ 600 K for incident ^{4}He energies of 0.5, 1, and 2 MeV. The results for normal incidence are shown in Fig. 1 in units of atoms/row, i.e., the effective number of atoms per row of incidence which contribute to the surface peak. (For normal incidence, where two layers are fully visible, 0.5 atoms/row is equivalent to a monolayer.)

Several qualitative effects may be noted. There is a general increase in SP yield with temperature. To first order this simply reflects the increase in vibrational amplitude giving rise to reduced shadowing of the atoms along the row. It is also seen that hydrogen adsorption on the surface [which under the present conditions takes place when the temperature drops below ≈ 350 K (Ref. 28)] caused a clear reduction in the SP yield. We note, in particular, that the data for the clean surface show no indication of any discontinuity around the transition temperature T_c, which for this flat crystal is ≈ 210 K.[23]

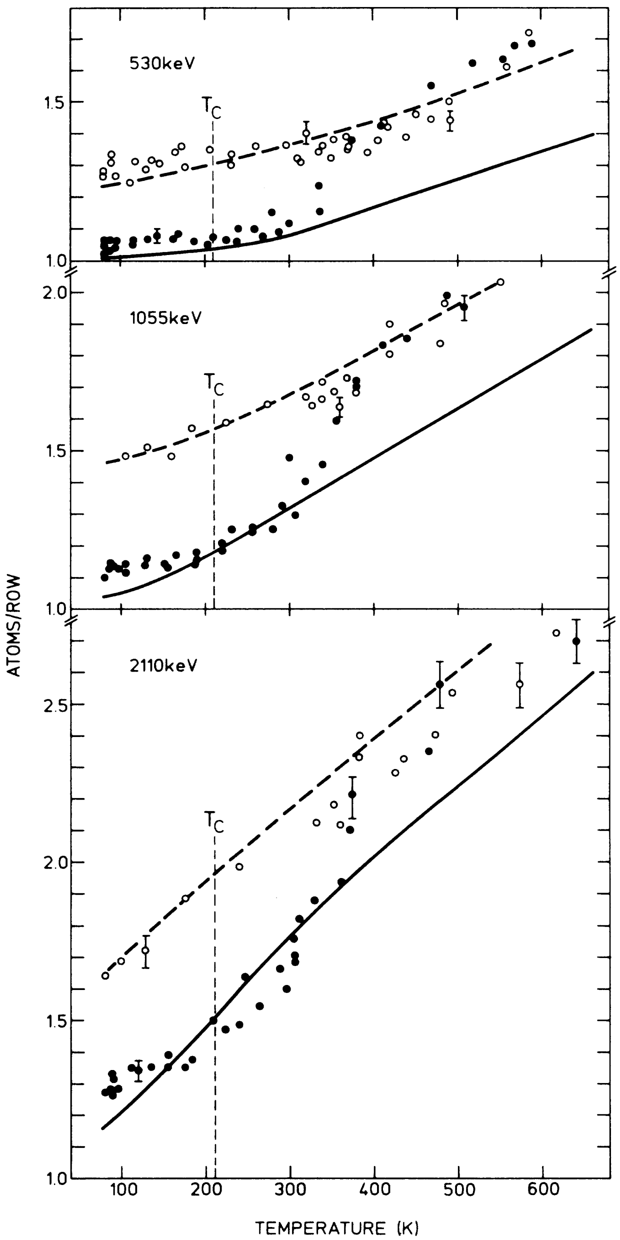

FIG. 1. Measured surface-peak yields for normal incidence of ^{4}He on W(100) at three different energies. Open circles are for the clean surface and filled circles for the surface cooled in a D_2 ambient of $\approx 3\times10^{-8}$ mbar. The solid lines show calculated yields for a bulklike surface structure while the dashed lines correspond to a surface where all atoms have been shifted laterally by 0.14 Å. The critical temperature T_c for the phase transition is indicated.

Also shown in Fig. 1 (solid line) are calculated surface-peak yields for a truncated bulk surface structure, i.e., with no static lateral displacement. A detailed description of the calculations involved is found in Ref. 25. The surface and bulk atoms are assumed to have a Gaussian displacement distribution corresponding to a Debye temperature of 310 K. The present data confirm the conclusion drawn in the first HEIS study[13] that the surface structure is bulklike when saturated with hydrogen. [The small deviations observed could be due to a small error in normalization (estimated uncertainty 5%) and/or deviations from bulklike dynamics in the surface, even in the hydrogen saturated state.]

The SP yields for the clean surface are clearly much higher than for the bulklike surface over the whole temperature range. This can only be explained by the presence of lateral displacements in the surface at all temperatures. An estimate of the displacement distances involved can be obtained by noting that the shadow-cone radius[25] varies from ≈ 0.18 Å at 530 keV to ≈ 0.10 Å at 2110 keV. (The shadow-cone radius can be taken as an approximate value for the minimum lateral displacement needed of the surface atoms to expose an extra monolayer.) The decrease in SP yield by hydrogen adsorption is smaller at 0.5 MeV than at the higher energies. If all surface atoms were displaced laterally to the same extent, this would indicate that the static lateral displacement lies between 0.10 and 0.18 Å.

A more detailed *ab initio* analysis of the surface geometry is difficult to undertake on the basis of the present data. Models with only a fraction of the surface atoms displaced as well as models with a distribution of displacement distances should be considered. However, if the analysis is made on the basis of the accepted LT phase model the displacement distances can be estimated by computer simulations for different displacements along the surface diagonals. A reasonable fit (dashed line in Fig. 1) in the low-temperature regime has been obtained for a displacement value of 0.14 Å, with an enhancement of the surface vibrations chosen somewhat arbitrarily to correspond to a surface Debye temperature of 220 K. (For such large displacements the SP yields are not very sensitive to the value of the surface vibrational amplitude.) For the low-temperature ordered phase an earlier LEED analysis concluded with a static lateral displacement of 0.16 Å.[29]

The fit is less satisfactory in the high-temperature region where the detailed surface structure is unknown. However, the present data suggest that the displacements are of the same order of magnitude in the HT as in the LT phase.

The sensitivity of the SP yield to the magnitude of the displacements can be judged from the fact that a 0.03 Å change in displacement causes a change in SP yield of ≈ 0.1 atom/row.

The present model for the clean surface is at variance with the one proposed on the basis of earlier HEIS measurements,[13] which were carried out at room temperature on a crystal of unknown step density. In that case the data were fitted by displacing only half the surface atoms by ≈ 0.23 Å.[30] Such a model would fit the present 530 keV data as well, but results in large deviations for the two higher energies. The detailed reason for this discrepancy is at present unknown but it is likely that crystal quality (especially the step density) has been different in the original measurements.

If the LT to HT phase transition around T_c corresponded to a transformation from a surface with displaced surface atoms at low temperatures to one without at high temperature, the clean surface data would follow the higher theoretical curves in Fig. 1 below T_c and drop to the lower curve above T_c. The present data do not show such a drop. Therefore, the $(\sqrt{2}\times\sqrt{2})R45°$ LT to (1×1) HT phase transition must be an order-disorder rather than an order-order transition.[31]

In conclusion, the present HEIS data support a model where the hydrogen-saturated surface of W(100) is bulklike with no static lateral displacements. The data for the clean surface are consistent with a structure having all surface atoms displaced laterally by ≈ 0.14 Å in the LT phase and involving similar displacement values in the HT phase. The LT to HT phase transition is shown to be an order-disorder transition.

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[1] M. K. Debe and D. A. King, J. Phys. C 10, L303 (1977).

[2] T. A. Felter, R. A. Barker, and P. J. Estrup, Phys. Rev. Lett. **38**, 1138 (1977).

[3] M. K. Debe and D. A. King, Phys. Rev. Lett. **39**, 708 (1977).

[4] M. A. Van Hove and S. Y. Tong, Surf. Sci. **54**, 91 (1975).

[5] M. K. Debe, D. A. King, and F. S. Marsh, Surf. Sci. **68**, 437 (1977).

[6] B. W. Lee, A. Ignatiev, S. Y. Tong, and M. A. Van Hove, J. Vac. Sci. Technol. **14**, 291 (1977).

[7] J. Kirschner and R. Feder, Surf. Sci. **79**, 176 (1979).

[8] M. N. Read and G. F. Russell, Surf. Sci. **88**, 95 (1979).

[9] P. Heilman, K. Heinz, and K. Müller, Surf. Sci. **89**, 84 (1979).

[10] F. S. Marsh, M. K. Debe, and D. A. King, J. Phys. C **13**, 2799 (1979).

[11] L. C. Feldman, R. L. Kauffman, P. J. Silverman, R. A. Zuhr, and J. H. Barrett, Phys. Rev. Lett. **39**, 38 (1977).

[12] C. Guillot, C. Thuault, Y. Jugnet, D. Chauveau, R. Hoogewijs, J. Lecante, Tran Min Duc, G. Treglia, M. C. Desjonqueres, and D. Spanjaard, J. Phys. C **15**, 4023 (1982).

[13] I. Stensgaard, L. C. Feldman, and P. J. Silverman, Phys. Rev. Lett. **42**, 247 (1979).

[14] D. A. King and G. Thomas, Surf. Sci. **92**, 201 (1980).

[15] J. P. Woods and J. L. Erskine, J. Vac. Sci. Technol. A **4**, 1414 (1986).

[16] B. Salonen and J. Lapujoulade, Surf. Sci. **173**, L613 (1986).

[17] J. B. Pendry, K. Heinz, W. Oed, H. Landskron, K. Müller, and G. Schmidtlein, Surf. Sci. **193**, L1 (1988).

[18] K. G. Purcell, J. Jupille, and D. A. King, (unpublished); J. Jupille, K. G. Purcell, G. Derby, J. Wendelken, and D. A. King, in *The Structure of Surfaces II,* edited by J. F. van der Veen and M. A. Van Hove (Springer-Verlag, Berlin 1987).

[19] I. K. Robinson (private communication).

[20] D. Singh, S-H. Wei, and H. Krakauer, Phys. Rev. Lett. **57**, 3292 (1986).

[21] L. D. Roelofs and J. F. Wendelken, Phys. Rev. B **34**, 3319 (1986).

[22] T. Sugibayashi, M. Hara, and A. Yoshimori, J. Vac. Sci. Technol. A **5**, 771 (1987).

[23] J. F. Wendelken and G. -C. Wang, Phys. Rev. B **32**, 7542 (1985).

[24] W. N. Unertl, Appl. Surf. Sci. **11/12**, 64 (1982).

[25] I. Stensgaard, L. C. Feldman, and P. J. Silverman, Surf. Sci. **77**, 513 (1978).

[26] K. Griffiths and D. A. King, J. Phys. C **12**, L755 (1979).

[27] P. J. Estrup and J. Anderson, J. Chem. Phys. **45**, 2254 (1966).

[28] Hydrogen adsorption to $\Theta = 0.25$ ML causes no change in the ion scattering yield (Ref. 13) and may already have occurred at 350 K.

[29] J. A. Walker, M. K. Debe, and D. A. King, Surf. Sci. **104**, 405 (1981).

[30] L. C. Feldman, P. J. Silverman, and I. Stensgaard, Surf. Sci. **87**, 410 (1979).

[31] The lateral registry reconstruction model, an ordered surface with unidirectional lateral displacements, has been considered for the HT phase in connection with steps [see, for example, D. A. King, Phys. Scr. **T4**, 34 (1983)]. This model, however, is not relevant for flat, almost step-free surfaces.