Novel Phonon Anomaly and Reconstruction in Hydrogen-Covered W(110)*

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Further hydrogen adsorption onto the hydrogen-covered W(110)-(1×1) phase results in the reconstruction of the surface hydrogen layer with a sizable corrugation in one direction. The wave vector for the superstructure is found to be very close to the nesting vector of the Fermi surface. Upon the rearrangement, the characteristic surface phonon anomaly becomes much more pronounced. The further pronounced anomaly can be explained by the modification of the electronic band around the Fermi level, concerted with the imposed superperiodicity. [DOI: 10.1380/ejssnt.2006.548]

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I. INTRODUCTION

Electron-phonon coupling at a surface is one of the central subjects in current surface science [1, 2]. It causes a drastic alteration of the surface electronic property, because it modulates the electronic band just around the Fermi level (E_F), or even opens a band gap. The effect of the electron-phonon coupling is usually pronounced when the dimension of the system is reduced, via a singularity in the electronic screening response. This in turn brings about a significant softening of the corresponding phonon (giant Kohn anomaly), and sometimes triggers a metal-insulator transition accompanied with the lattice reconstruction (Peierls instability, or the charge density wave (CDW) ground state formation) [1-4].

Hydrogen-covered W(110), namely the (1×1)-H phase, has been one of the most well-known model system of the giant Kohn anomaly at the surface [2-13]. Hydrogen-derived surface state exhibits a Fermi surface that shows parallel segments, or a “nesting” of the Fermi surface, with a “nesting vector (Q_N)” of 0.9 Å⁻¹ in the [001] direction [5, 6]. This quasi one-dimensional Fermi surface causes the electronic instability against an external perturbation, e.g., a surface phonon, with the wave vector of Q_N. Indeed, in the surface phonon dispersion along the [001] direction, a very pronounced dip has been found just at the Q_N [6-10]. On the other hand, in spite of the significant electronic instability, no surface reconstruction has been found so far in this system. Thus the CDW picture has been abandoned [13].

In this paper we present an evidence of the reconstruction of the surface hydrogen layer, when the hydrogen coverage is further increased by means of atomic hydrogen deposition onto the (1×1)-H phase. Measurements are done by means of elastic and inelastic helium atom scattering (HAS), which has higher sensitivity to hydrogen. The wave vector corresponding to the superperiodicity of the reconstruction is found to be very close to the Q_N. At the same time, the characteristic phonon anomaly becomes much more pronounced. Then an interesting question would be whether this reconstruction is due to the Peierls instability or not. It is argued that the further pronounced anomaly is closely linked to a modification of the electronic band around the Fermi level, concerted with the imposed superstructure.

II. EXPERIMENTAL

The measurements were carried out with a conventional HAS machine described in detail elsewhere [14], with the base pressure in the sample chamber of about 5×10⁻¹¹ mbar (without He beam). The W(110) surface was cleaned by annealing in an oxygen environment and subsequent flashing up to 2300 K. The surface cleanliness was confirmed directly by the helium diffraction, which is quite sensitive to surface disorders [15]. Atomic hydrogen was generated by means of thermal cracking of H₂ by a hot tungsten filament. All the diffraction and phonon measurements were carried out with surface temperature of about 180 K.

III. RESULTS AND DISCUSSION

The change in the He-diffraction spectra in the [001] direction upon a further atomic hydrogen deposition onto the H/W(110)-(1×1) phase ((1×1)-H phase) is shown in Fig.1-(A). The (1×1)-H phase is prepared by exposure of the clean surface kept at 180K to 15 Langmuirs of H₂. This phase is characterized by the additional small elastic peaks at an incommensurate wave vector of ±0.9 Å⁻¹ in the [001] direction, identical to the nesting vector of the Fermi surface, Q_N [7, 8]. These peaks could be due to the diffraction from weak CDW [13], although the origin of them has not been well clarified. It is noted here that, in any case, these are related closely to the Fermi surface instability and the phonon anomaly. Upon further adsorption of atomic hydrogen, it is found that the anomaly-related elastic peak originally at 0.9 Å⁻¹ increases in intensity significantly and shifts gradually toward a commensurate position of 1.0 Å⁻¹. The surface ends up with a formation of a superstructure, showing a 4x periodicity in the [001] direction with clear higher order diffraction

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FIG. 1: (A) He diffraction spectra in the [001] direction obtained from (a) (1 × 1)-H phase, (b) intermediate coverage, (c) reconstructed phase. Arrows indicate the anomaly-related elastic peaks in the (1 × 1)-H phase. (B) Development of the peak around 0.9 Å⁻¹ upon the reconstruction.

Peaks. It is noted that the low energy electron diffraction (LEED) on this phase does not produce any extra spots. Thus the superstructure seen by HAS can be attributed to the reconstruction of the surface hydrogen layer, not the substrate reconstruction, because He atoms have a larger cross section to hydrogen than electrons. The surface corrugation is pronounced only in the [001] direction, determined from the intensity of the diffraction peaks in the helium diffraction measurements along several azimuthal directions (not shown). This might support the idea of the one-dimensional ordering of the hydrogen along the [1–10] direction proposed in the previous investigations [11].

Details of the development of the peak around 0.9 Å⁻¹ upon the reconstruction are shown in Fig.1-(B). In the initial stage, the peak grows in intensity without a sizeable shift in the peak position, and then starts to shift rather quickly. This behavior suggests that the mechanism underlying the reconstruction is not so simple. The enlargement of the intensity in the anomaly-related peak component at 0.9 Å⁻¹ implies that there exists a significant modification in the electronic structure which enhances the phonon anomaly.

Such an electronic modification should also show up in the surface phonon dispersion. The surface phonon spectra for three different coverages, namely, (a) the (1 × 1)-H phase, (b) intermediate coverage, and (c) the reconstructed phase, are compared in Fig. 2-(A). Corresponding time-of-flight (TOF) spectra measured along the scan curves indicated in the dispersions are shown in Fig. 2-(B). The surface phonon dispersion of the (1 × 1)-H phase reveals the well-known sharp anomaly at 0.9 Å⁻¹, the wave vector identical to the $Q_X$ [7]. In this article, this branch will be called as "anomalous branch", because it is not really due to the soft phonon but the low energy electronic excitation [6, 9]. This implies that this branch is sensitive to the topology of the Fermi surface. In the intermediate coverage, although the shape of the dispersion remains almost unchanged, the intensity of the anomalous branch is increased significantly. This is clearly seen in the TOF spectra, as an enhanced intensity of the energy loss peak due to the anomalous branch labeled as "A". This is consistent with the initial growth of the anomaly-related elastic peak found in the diffraction spectra, supporting the idea of the electronic modification. In the reconstructed phase, in addition to the further pronounced anomalous branch, a backfolded Rayleigh branch can be seen due to the new periodicity. (The 4× periodicity produces the new zone boundary at 0.5, and 1.5 Å⁻¹ in the [001] direction.) The features at 2.0 Å⁻¹ are also considered to be due to the backfolding. The intensities for the backfolded features are found to be rather strong, suggesting a significant corrugation amplitude in the [001] direction of the superstructure.

To summarize the results so far, the anomalous features in the elastic and inelastic HAS in the (1 × 1)-H phase, the additional elastic peak and the deep dip in the surface phonon dispersion at 0.9 Å⁻¹ in the [001] direction, become much more pronounced by further adsorption of atomic hydrogen. And the hydrogen overlayer forms a superstructure corrugated strongly in the [001] direction with a wave vector very close to the $Q_X$. These observations are considered to be closely linked to the instability of the Fermi surface and its further modification by additional hydrogen, as discussed below.

First, we should check the possibility of the CDW formation. These observations remind us intuitively of the formation of a CDW ground state, i.e., the atomic rearrangement with the wave vector identical to the $Q_X$. If the $Q_X$ is slightly incommensurate to the lattice, an incommensurate CDW can even drive a commensurate reconstruction. Such an example has been reported in the thermal-induced phase transition in W(100), by means of a detailed HAS investigation [16]. There, it is found that a small quasi-elastic peak originally at an incommensurate position, which is attributed to the scattering from the incommensurate CDW, grows and shifts continuously towards a commensurate position upon the transition. This
FIG. 2: (A) Surface phonon dispersion in the [001] direction obtained from (a) (1 × 1)-H phase, (b) intermediate coverage, (c) reconstructed phase. The gray lines in the figure show the part of the scan curves for several selected angles of incidence. (B) TOF spectra measured along the scan curves shown in the dispersion; (a) (1 × 1)-H phase, (b) intermediate coverage, (c) reconstructed phase. The quasi-elastic peak is labeled as "e", at zero energy exchange. Energy loss peaks due to the anomalous branch, the backfolded Rayleigh branch, and the normal Rayleigh branch, are indicated as "A", "R_B", and "R", respectively.

has been explained by a mechanism of the incommensurate CDW "locking" into a commensurate structural modulation [16]. Although the present observations in H/W(110) are quite similar to this type, it is noted that the present case does not involve a substrate reconstruction, but the rearrangement of the hydrogen overlayer. Even in such a case, we can speculate that this rearrangement of the overlayer is triggered by the electronic instability. Although the exact origin and mechanism of the superstructure formation is still unclear at the moment, it is very likely that the observed superstructure is related with the Fermi surface nesting because of the similarity in the wave vector and of their quasi 1-D nature.

On the other hand, even without knowing the origin of the superstructure, a close relation between superstructure formation of the hydrogen layer and observed enhancement of the anomalous features can be understood. No matter what the origin is, it is obvious that a structural modulation with a wave vector nearly $Q_N$ exists. This structural modulation can affect the electronic band structure just around the Fermi level, because it results in a Brillouin zone boundary at around the Fermi surface. This can qualitatively explain the observation of the pronounced anomaly in HAS. The new periodicity of $1.0 \, \text{Å}^{-1}$ would produce a band gap at an energy slightly higher than E_F, flattening the band just at E_F, as schematically shown in Fig. 3. The flat band in turn increases the density of states at E_F. The resulting increased electronic instability causes the further pronounced apparent phonon anomaly seen by HAS.

This resembles what the CDW transition does. Here, the important question would be, whether there really ex-
FIG. 3: Schematic drawing of the quasi one dimensional electronic surface state band of the H/W(110) in the [001] direction, with the nesting vector of 0.9 Å⁻¹ (blue arrow). When the structural periodicity of 1.0 Å⁻¹ (red arrow) is imposed, the gap will open just above the E_F. This flattens the band around the E_F, increasing the density of states at the E_F.

ist the states just at E_F or not in the superstructure phase. If not, the situation would be identical to the CDW formation. There are some difficulties to settle this matter only from the HAS observation. In the TOF spectra, the backfolded Rayleigh branch (labeled "R₂" in Fig.2-(B)) at the new zone center (1.0 Å⁻¹) overlaps with the anomalous branch, especially at the low energy region, making it difficult to determine whether the anomalous branch still exists or not. However, at a rather higher energy (in TOF spectra in 33, 34 deg), the energy loss peak due to the anomalous branch and the backfolded one can be clearly separated. Thus we conclude that the anomalous branch, and thus the nesting in the Fermi surface, still exists. The reason why this system prefers the commensurate periodicity over the incommensurate modulation that could eliminate the Fermi surface depends on a structural energy cost in the hydrogen overlayer.

Modification of the electronic band around the E_F, especially in the quasi one-dimensional system, is important because it changes the electronic property drastically. Thus the new findings presented here call for further investigations on this already well-studied system. Fermi surface measurements by means of the angle-resolved photoemission would be highly important to clarify the modification of the Fermi surface discussed in the above scenario, and are currently underway. And at the same time, surface phonon measurement by means of HREELS would be also of great interest because it provides the "true" surface phonon spectra, while HAS can also interact with the electrons at E_F [6].

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