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Hydrogen-Induced Phonon Anomaly on the W(110) Surface

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Collective vibrations of the clean and hydrogen-saturated W(110) surface have been investigated with high-resolution inelastic helium-atom scattering. In contrast to the clean W(110) surface which exhibits "normal" surface phonon dispersion, the hydrogen-saturated surface shows a pronounced surface phonon anomaly in terms of a sharply defined dip in the surface phonon dispersion at $Q=0.9$ Å^{-1} along the $\bar{\Gamma}\bar{H}$ ([001]) direction. The anomalous behavior extends into the neighborhood of this high-symmetry direction.

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Hydrogen adsorption on metal surfaces leads to a great variety of surface structures and adsorbate-induced reconstructions [1], and powerful theoretical techniques have been developed to study the dynamics of these hydrogen phases [2]. As a common rule, chemisorbed hydrogen renders densely packed metal surfaces chemically inert and dynamically stable at saturation coverage. Such a behavior indicates that all broken bonds become saturated upon hydrogen adsorption. In this Letter we report on a spectacular exception to this rule: For the first time a strong surface phonon anomaly has been detected which is brought about by saturating a metal surface with chemisorbed hydrogen. The anomaly consists of a sharply defined soft elementary excitation at an incommensurate wave vector.

Extensive studies of clean and hydrogen-covered W(110) surfaces have previously been undertaken [3-6]. In particular, the phase diagram with respect to H adsorption is well known [7]. From electron-energy-loss spectroscopy measurements [8] it was concluded that the hydrogen atom is bonded in the long bridge site above the hourglass-shaped hole between the tungsten atoms in the surface layer. In recent LEED studies [9] a loss of symmetry in the diffraction pattern was observed for hydrogen coverages exceeding half a monolayer. This asymmetry has been interpreted by Chung, Ying, and Estrup [9] as being due to an adsorbate-induced shift of all tungsten atoms in the topmost layer along the ⟨001⟩ direction. Even though such a reconstruction leads to a (1×1) superstructure it changes the environment of the tungsten atoms in the surface and should bear on the surface lattice dynamics.

The present measurements were performed in a helium scattering apparatus [10] suited for elastic and inelastic (time-of-flight) measurements. The $5\times10\times1$-mm^3 tungsten crystal specimen was prepared using standard techniques [11], kept in ultrahigh vacuum, and characterized with LEED and Auger electron spectroscopy (AES). After cleaning, the carbon AES signal was below the detection limit of the analyzer.

Elastic helium scattering from the clean W(110) surface along the [001], the [1$\bar{1}$0], and the [1$\bar{1}$1] directions in the surface yields sharp reflections with weak diffracted intensities typical for weakly corrugated and well-ordered, closely packed metal surfaces [12]. An analysis of the inelastic He scattering data reveals the existence of two phonon branches in each one of the high-symmetry directions, [001], [1$\bar{1}$0], and [1$\bar{1}$1], as shown in Fig. 1. Comparing the slopes of measured surface phonon dispersion curves with those of the appropriate bulk phonon dispersion curves [13] close to $\bar{\Gamma}$ allows the determination of the basic polarizations of these surface modes. Thus we can identify the mode at lower energies as the transversally polarized Rayleigh mode and the other mode as a longitudinally polarized surface resonance. Because of the small surface corrugation along $\bar{\Gamma}\bar{H}$ the phonon inelastic signal decreases dramatically towards the surface Brillouin-zone boundary [14]. Therefore the dispersion curves in the [110] direction could only be detected in the first $\frac{2}{3}$ of the surface Brillouin zone.

The dispersion curves (Fig. 1) show an almost regular behavior of the surface lattice dynamics, similar to that observed on many clean metal surfaces [15]. Aside from small kinks in the high-energy branch, in need of experimental verification, no anomalies or pronounced temperature dependence in the range between 200 and 1000 K could be detected. Photoemission data for the clean W(110) surface reveal that the two-dimensional Fermi surface exhibits parallel sections separated by $Q_c=0.3$ Å^{-1} in the [110] direction [16]. This "nesting" can give rise to an enhanced electron-phonon coupling. The resulting Kohn anomaly manifests itself in a lowering of the phonon frequency at the wave vector $\mathbf{Q}_c$. Even though such an effect appears to be favored by the kinematics, the measured phonon dispersion curves for the clean W(110) surface do not show any related signatures.

With hydrogen exposure at low surface temperatures (200 K) the hydrogen superstructures, known from earlier LEED investigations [7], are reproduced in the helium diffraction patterns. Prolonged hydrogen exposure leads to a decrease of the superstructure peak intensities and at an exposure of 10 L H_2 [1 L (langmuir)$=10^{-6}$ Torrs] the (1×1) periodicity of the clean surface is restored. At this stage saturation coverage is reached and, according to Ref. [9], the surface is reconstructed. The influence of H saturation on the surface phonon dispersion curves is shown in Fig. 2. For the sake of comparison the clean-surface data are included and sketched as

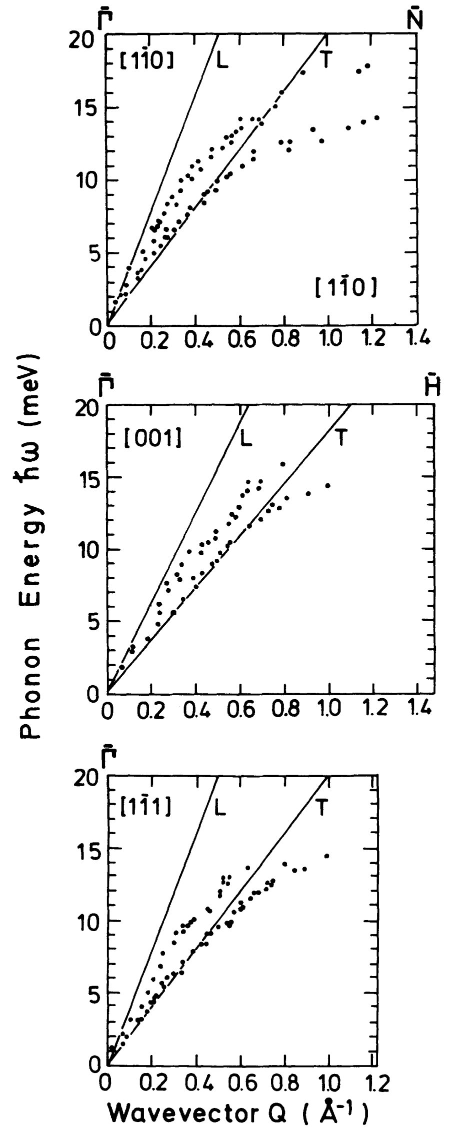

FIG. 1. Surface phonon dispersion curves of the clean W(110) surface along the three high-symmetry directions indicated in each panel. The solid lines represent the slope of the lower edges of the surface-projected longitudinal (L) and transverse (T) bulk phonon bands at Γ̄.

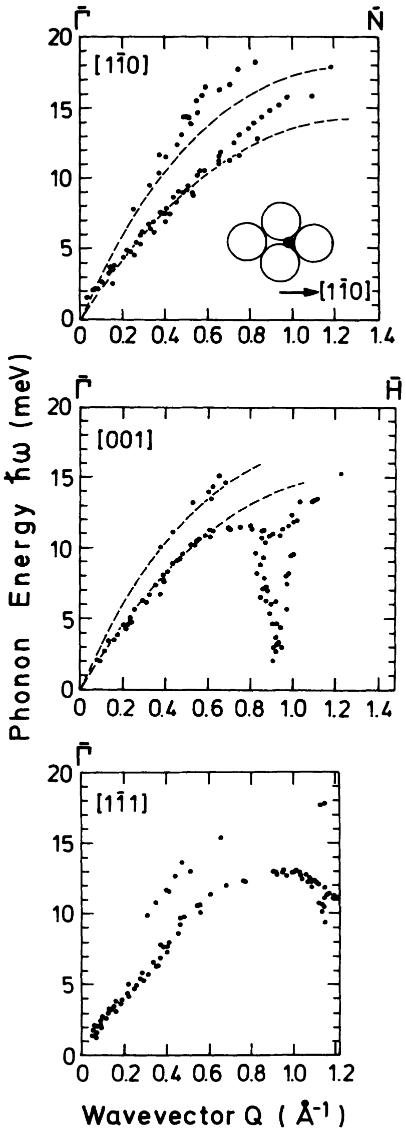

FIG. 2. Surface phonon dispersion of the hydrogen-saturated W(110)(1×1)H surface along the three high-symmetry directions indicated in each panel. The top panel also contains a sketch of the H adsorption site after the hydrogen-induced reconstruction, as suggested by Chung, Ying, and Estrup [9]. Dashed lines indicate phonon dispersion curves of the clean surface.

dashed lines. Along the [1$\bar{1}$0] direction, in which the shift of the top-layer tungsten atoms is supposed to occur, merely a "hardening" of both surface phonon modes is observed. Such an increase in phonon frequencies on H adsorption is well known from other metal surfaces, e.g., W(001) [17]. In the latter case it is due to the fact that on the time scale of the surface vibrations the bridge-bonded hydrogen atoms, because of their comparatively small mass, follow the motion of the substrate atoms adiabatically and merely contribute additional interatomic forces in the first layer. The result is a "stiffening" of the force constants within the surface layer.

A dramatic change in the surface phonon dispersion curves takes place in the [001] direction which is perpendicular to the proposed top-layer shift. In contrast to W(100) where the phonon hardening is isotropic on the surface, the frequencies of both phonon branches for $Q \leq 0.6$ Å^{-1} seem to be unchanged by the presence of adatoms along [001]. However, for larger wave vectors dramatic deviations from the clean-surface results are observed and the phonon frequency of the low-energy branch is drastically lowered at a wave vector $Q=0.9$

Å^{-1}, as shown in Fig. 2. At surface temperatures below 250 K the phonon energy is reduced to less than 1 meV. The sharp dip in the phonon dispersion curve remains when the crystal is rotated about its surface normal and is observed for azimuthal orientations between [001] and [1$\bar{1}$1] as shown in Fig. 3. The phonon energy at the center of this dip increases continuously with increasing deviation from the $\bar{\Gamma}\bar{H}$ direction. The half-width of the dip in the $\omega(\mathbf{Q})$ surface perpendicular to the [001] direction amounts to about 0.5 Å^{-1}, which is twice the width found along [001]. An interesting feature of the anomaly is that on rotating the sample out of the [001] azimuth, the wave vector at which the anomaly occurs shifts towards higher values, but the component of the anomalous phonon wave vector parallel to [001] remains constant (cf. Fig. 3).

The anomaly discussed here is a feature specific to the hydrogen-saturated phase: Surface phonons on the tungsten substrate for the $p(2\times1)$ and the $p(2\times2)$ hydrogen phases display smooth dispersion curves and backfolding due to the reduced sizes of the superstructure Brillouin zones [12]. The unexpected discovery of this pronounced phonon anomaly on (1×1)H/W(110) renders a number of puzzling problems.

Anomalies of such a sharpness have been observed in the bulk phonon dispersion of certain quasi-one-dimensional conductors (e.g., KCP [18]) which are prone to a strong coupling between the quasi-one-dimensional electron gas and the vibrational lattice excitations giving rise to so-called giant Kohn anomalies. The observation of soft phonon wave vectors $\mathbf{Q}_c$ in the surface plane which are characterized by a constant component in one direction gives a clue to the presence of quasi-one-dimensional effects. One could thus conclude that the observed anomaly on H/W(110) is of the above type.

Not perfectly in agreement with this interpretation is the fact that the anomaly seems to affect the Rayleigh wave which is a predominantly transverse mode, polarized perpendicular to the surface. Usually the above electron-phonon interaction has its strongest influence on the longitudinal modes, as observed in the systems W(001) and Mo(001) [19,20]. This difficulty would be solved if a second mode, at higher energies, and displaying the symmetry of the Rayleigh wave, were softened and would hybridize with the latter one. Such an assumption is compatible with the experimental observation of a weak second mode in the $\mathbf{Q}$ range of the anomaly (cf. Fig. 2).

An even more interesting interpretation of our phonon data is based on the fact that electron-phonon coupling leads to a situation in which, for $\mathbf{Q}$ within the interaction region, electron-hole pair excitations and phonons become mixed in character. The observed inelastic features in the He scattering can therefore be partly due to electron-hole pair excitations in addition to the phonon inelastic interaction. Note that the weak upper "phonon" branch can be only measured in the $\mathbf{Q}$ range of the anomaly which is consistent with this interpretation.

A very interesting topic is the question of whether such a pronounced phonon anomaly leads to an instability of the lattice. At temperatures of about 120 K we have observed weak and broad additional elastic peaks in the helium-atom diffraction pattern along the [100] direction that appear for parallel momentum transfers of about 0.88 Å^{-1} (Fig. 4). This value is in good agreement with the $\mathbf{Q}$ value at the minimum in the phonon dispersion curve along this azimuth. The appearance of the broad spots can therefore be interpreted as the onset of critical scattering. In the range of surface temperatures obtainable in the present experimental setup, i.e., for $T\geq120$ K, no sharp superstructure diffraction spots have been detected that would indicate the condensation of a soft phonon. If the phonon frequency at $\mathbf{Q}_c$ would vanish at all it must therefore occur at temperatures below 120 K.

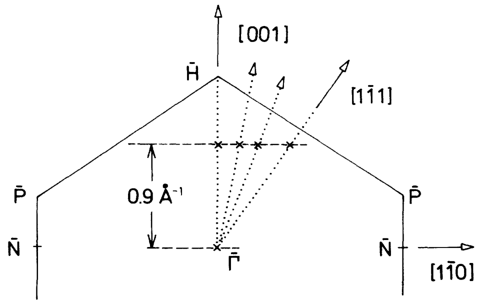

FIG. 3. Upper half of the surface Brillouin zone for W(110) which is symmetrical with respect to the line connecting the $\bar{N}$ points. The crosses mark the position of the anomaly-related energy minimum in phonon dispersion curves which have been measured along directions indicated by arrows and the dotted lines.

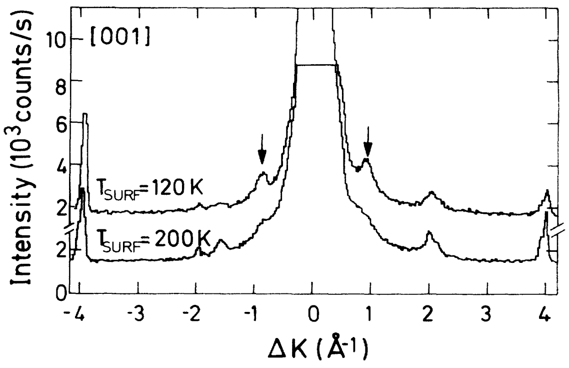

FIG. 4. Helium-atom diffraction pattern of the H-saturated W(110) surface along [001] at temperatures below 200 K. The peaks at 0.88 Å^{-1}, marked by the arrows, indicate the onset of critical scattering due to the soft phonon. The features at ±4.0 and ±2.0 Å^{-1} represent integer-order diffraction spots; those at −1.5 Å^{-1} contain inelastic intensity enhanced by kinematic focusing.

The most serious difficulty with labeling the observed behavior a giant Kohn anomaly arises from recent photoemission data for the hydrogen-saturated W(110) surface [16]. The measured two-dimensional Fermi surface provides a number of parallel sections but none that can be connected by the appropriate $\mathbf{Q}_c$. The photoemission experiments have been performed at room temperature and it is very possible that saturation coverage had not been achieved. For the time being this discrepancy is not yet resolved and might even imply the existence of a novel type of phonon anomaly [21]. Hence theoretical work is highly desirable in order to explain the connection between the symmetry loss of the surface on hydrogen adsorption observed in the LEED pattern and the appearance of the pronounced phonon anomaly discovered in this work.

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[21] G. Benedek suggests the following interesting explanation: The collective motion of H atoms connected with the Rayleigh wave along $\overline{\Gamma H}$ is such as to increase and reduce the in-plane separation of nearest-neighbor H atoms located above an "open" region of the surface. In the course of a vibrational period the electronic charge is redistributed and temporarily forms H-H bonds resulting in a weakening of the W-W bonding and thus in a softening of surface force constants.