

Anomalous dispersion of adsorbate phonons of Mo(110)-H

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(Received 8 November 2001; published 21 August 2002)

The dispersion curve of the longitudinal-optical adsorbate phonon on hydrogen-saturated Mo(110) along [001] is found to exhibit an anomalous indentation. The maximum indentation is observed at a wave vector, which coincides within the experimental angular resolution with the wave vector, at which the known giant Kohn anomaly for the transverse- and longitudinal-acoustic substrate surface phonons along [001] occurs.

DOI: 10.1103/PhysRevB.66.073414

PACS number(s): 68.35.Ja, 63.20.Kr, 68.43.Pq, 73.20.At

It is of fundamental importance in surface science to understand the interaction between electronic and vibronic excitations of an adsorbate system. The results of electron-phonon coupling investigations can provide insight into, e.g., the energy transfer within the adsorbate-substrate complex,^{1,2} the reactivity of molecules,³ the impact of the electronic system on the substrate lattice,^{2,4-6} and the mechanism of high-temperature superconductivity.⁷

The study of electron-phonon coupling can be divided into two major fields. One of them deals with the interaction between the electronic system of a substrate and its lattice. The consequences of this kind of coupling range from a dynamic softening of substrate surface phonons to the static rearrangement of the substrate lattice. Experimental evidence for the former consequence is provided by the adsorbate systems W(110)-H and Mo(110)-H where substrate surface phonons couple nonadiabatically to adsorbate-induced electronic surface states, i.e., the surface phonons are damped by an energy transfer to electron-hole pair excitations, and thus lead to pronounced and sharp indentations in the dispersion curves of the surface phonons at several wave vectors.^{2,4-6} It was demonstrated theoretically⁸ and experimentally^{9,10} that the surface phonon anomalies are of the giant Kohn type due to a hydrogen-induced electronic instability, which is generally referred to as quasi-one-dimensional Fermi-surface nesting. The other field concerning the investigation of electron-phonon coupling is dedicated to the interaction between the electronic system and adsorbate phonons. It could be shown that a nonadiabatic interaction between electronic and adsorbate vibrational excitations can lead to Fano-type asymmetric line shapes of vibrational loss peaks. These asymmetric line shapes were revealed for Mo(100)-H using surface infrared reflectance spectroscopy,¹ Mo(110)-H (Ref. 2) and Mo(110)-Li (Ref. 11) using electron energy-loss spectroscopy. Fano line shapes of vibrational loss peaks are the consequence of an interaction between a discrete excitation, which here is the vibronic excitation, and a continuum of excitations, which is provided in this case by thermally excited electron-hole pairs. Electron-phonon interaction can likewise affect the electronic states involved in the coupling as demonstrated clearly in a recent angle-resolved photoelectron spectroscopy study of W(110)-H.¹² This analysis reports the strong energy dissipation of a hydrogen adsorbate pho-

non by exciting electrons of the substrate giving rise to a splitting of the corresponding electronic band for binding energies in the vicinity of the vibrational energy of the adsorbate phonon.

To our knowledge, no attention has been paid to the dispersion of adsorbate phonons in the case of electron-phonon coupling so far. We report on electron energy-loss spectroscopy measurements for hydrogen adsorbed onto the molybdenum (110) surface where a nonadiabatic interaction between substrate surface phonons and electronic surface states is already present.^{2,5} The main result of this paper is to demonstrate that also adsorbate phonons can exhibit a similar anomalous dispersion curve as observed for the substrate surface phonons, i.e., the dispersion curve of an adsorbate phonon reveals a pronounced indentation. Interestingly, the wave vector at which the maximum softening occurs equals the wave vector at which the substrate surface phonon anomaly of the adsorbate system is observed.

The sample was cleaned by repeated oxygen heating cycles (≈ 1200 K) with intermediate electron bombardments of the backside of the crystal (≈ 2000 K). Crystalline order was checked by low-energy electron diffraction and cleanliness was monitored using Auger-electron spectroscopy and specular electron energy-loss spectra (angle of incident electron beam equals angle of scattered electron beam). Adsorption of 1 monolayer (ML) of atomic hydrogen onto the liquid-nitrogen-cooled surface (110 K) was accomplished by backfilling the ultrahigh vacuum recipient (base pressure 2×10^{-9} Pa) to 5×10^{-6} Pa with hydrogen gas of 99.995% purity for about 1200 s. The well-ordered (1×1) hydrogen superstructure was checked by low-energy electron diffraction and specular electron energy-loss spectra. The employed homemade spectrometer is of the Ulti 100 type¹³ with a routinely achievable energy resolution of 1.5 meV full width at half maximum and an angular resolution of 1° full width at half maximum for all primary electron energies employed for this analysis. Thus a wave vector is known within an accuracy of $\pm 0.03 \text{ \AA}^{-1}$. In order to trace the dispersion curves of surface phonons, the analyzer of the instrument is rotated in the sagittal plane ($1\bar{1}0$) (the sagittal plane is spanned by the surface normal and the direction of the incident electron beam). The resulting off-specular scattering geometry allows us for detecting electrons, which transferred

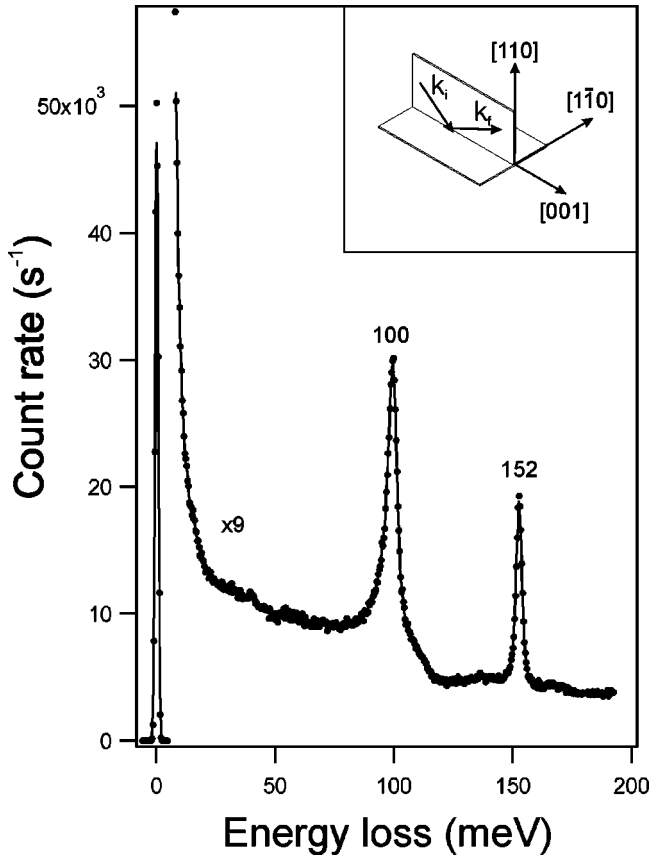


FIG. 1. Specular electron energy-loss spectrum of Mo(110)-(1 \times 1)H at 110 K [primary energy of impinging electrons is $E_0 = 5$ eV and the angle of the incident electron beam is 71° with respect to the surface normal, the sagittal plane is $(1\bar{1}0)$, confer the inset for a definition of the scattering geometry]. The spectrum shows two dipole active vibrational loss peaks: the peak at ≈ 100 meV corresponds to the longitudinal-optical adsorbate phonon whereas the peak at ≈ 152 meV represents the excitation of a transverse-optical adsorbate phonon.

momentum to the investigated surface phonon.

It is known that hydrogen atoms occupy a threefold coordinated adsorbate site on 1 ML hydrogen-covered Mo(110) that exhibits C_s symmetry² and thus gives rise to two vibrational loss peaks in electron energy-loss spectra with a specular scattering geometry. A specular electron energy-loss spectrum of this surface is shown in Fig. 1. Elastically scattered electrons contribute to the zero-energy peak, the vibrational loss peak at ≈ 100 meV is due to the excitation of the longitudinal-optical adsorbate phonon (this phonon corresponds to a hydrogen vibrational mode that is polarized mainly parallel to the surface along [001]) whereas the loss peak at ≈ 152 meV corresponds to a transverse-optical adsorbate phonon (polarization mainly perpendicular to the surface). Note that the loss peak at ≈ 100 meV exhibits an asymmetric line shape, which remains after subtraction of a background matching the tail of the elastic peak and which disappears for off-specular scattering conditions. The line shape of the specular loss peak was demonstrated to be of the Fano type.² The loss peak of the perpendicular vibration mode, however, is a (symmetric) Lorentzian. The purpose of

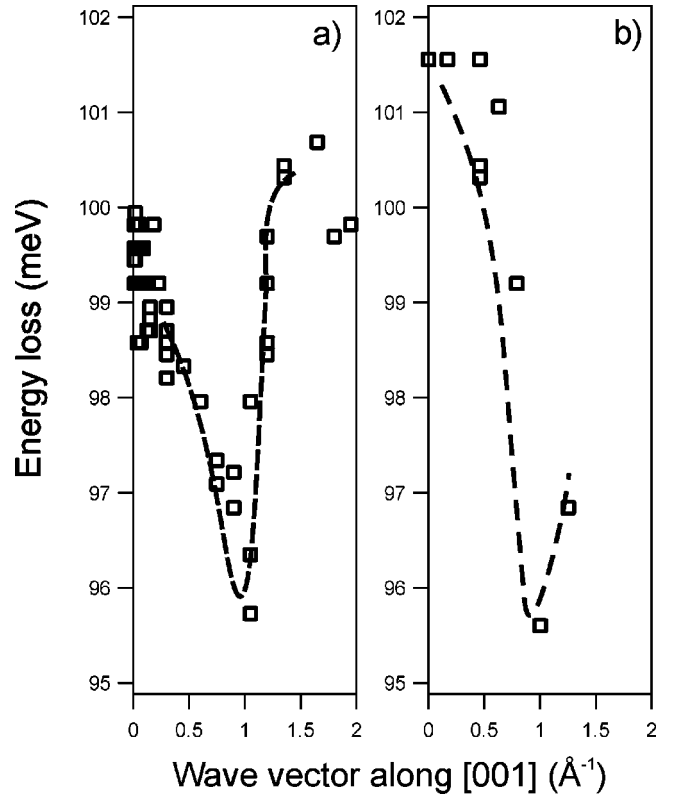


FIG. 2. (a) Dispersion of the longitudinal-optical adsorbate phonon of Mo(110)-H. The boundary of the surface Brillouin zone is located at 1.5 \AA^{-1} . (b) Dispersion of the longitudinal-optical adsorbate phonon of W(110)-H (data taken from Ref. 6, the boundary of the surface Brillouin zone along [001] are reached at 1.5 \AA^{-1}). Both surfaces are covered by 1 ML of hydrogen. The maximum indentation in the dispersion curves is located at $\approx 0.95 \text{ \AA}^{-1}$ (the dashed lines are a guide to the eye).

Fig. 1 is to introduce the adsorbate phonon in question. In the following, we focus our interest onto the dispersion of the longitudinal-optical adsorbate phonon.

Figure 2 presents the main results of this paper. In Fig. 2(a) we plotted the wave-vector dependence of the energy of the longitudinal-optical adsorbate phonon along the [001] direction. Whereas the transverse-optical adsorbate phonon reveals only a weak dispersion (not shown), the longitudinal-optical adsorbate phonon exhibits an anomalous dispersion curve: the energy of this adsorbate phonon decreases with increasing wave vector, reaches its maximum indentation, and increases again as the wave vector approaches the boundary of the surface Brillouin zone, which is located at 1.5 \AA^{-1} . We assert that this anomalous behavior of the dispersion relation is due to a Kohn effect, i.e., like the acoustic substrate surface phonons, the longitudinal-optical adsorbate phonon also suffers a severe energy softening due to a non-adiabatic coupling to electronic surface states. This behavior is surprising since for Mo(110)-Li where similar substrate surface phonon anomalies occur¹¹ and nested Fermi-surface contours are present,¹⁴ the adsorbate phonons do not reveal any anomalous dispersion. In the subsequent paragraphs we present the reasons for our assertion. First, the maximum indentation is located at a wave vector of $0.95 \pm 0.03 \text{ \AA}^{-1}$,

which within the experimental angular resolution is identical with the wave vector of the substrate surface phonon anomaly^{2,5} and with the spanning vector of nested Fermi-surface contours as discovered theoretically⁸ and experimentally.¹⁰ Second, with respect to the energy at zero wave vector (≈ 100 meV) the energy of the adsorbate phonon at the maximum indentation is lowered by ≈ 4 meV and is thus of similar magnitude as observed for the substrate surface phonons. Third, we revisit the adsorbate system W(110)-H whose vibrational properties were investigated using inelastic helium atom scattering⁴ and electron energy-loss spectroscopy.⁶ The 1-ML hydrogen-covered surface likewise exhibits substrate surface phonon anomalies of the giant Kohn type. Here we concentrate on the dispersion curve of the longitudinal-optical adsorbate phonon, which we display in Fig. 2(b) on a smaller energy scale than in the original paper.⁶ Also in this case an anomalous softening at $\approx 0.95 \text{ \AA}^{-1}$ is observed and has previously been ignored. This is the same wave vector along [001] where the substrate surface phonon anomaly of this adsorbate system occurs. Unfortunately, only poor scattering cross sections were found for this vibrational mode for wave vectors greater than $\approx 1.3 \text{ \AA}^{-1}$ and consequently the dispersion curve could not be traced to the boundary of the surface Brillouin zone. Another test for the correctness of our hypothesis would be to monitor the dispersion of the longitudinal-optical adsorbate phonon along $[1\bar{1}2]$, where for Mo(110)-H at $\approx 1.2 \text{ \AA}^{-1}$ the second giant Kohn anomaly is present for the acoustic substrate surface phonons. Unfortunately, none of the various scattering conditions we tried allowed us to push the signal of the sought-after adsorbate phonon above the detection limit of the instrument for wave vectors greater than $\approx 0.2 \text{ \AA}^{-1}$. We notice that for hydrogen on Mo(110) we observed the above-mentioned anomalous dispersion exclusively at a complete monolayer coverage and only for the longitudinal-optical adsorbate phonon. For all remaining adsorbate phonons and hydrogen coverages up to 1 ML, we found weak dispersion indicating a negligible vibrational coupling between the hydrogen adatoms. This fact is another hint that the anomalous dispersion relation does not result from a direct interaction between the hydrogen atoms but from a coupling to the substrate's electronic system, which leads to the severe energy damping.

As a result of our findings and interpretation, the concept of the Kohn anomaly¹⁵ has to be extended from the substrate lattice regime to adsorbate phonons. To our knowledge, this is the first time that such an anomalous behavior of adsorbate phonons is investigated in the literature.

In order to complete our discussion of the observed adsorbate phonon anomalies we note, first, that the anomalous indentation in the dispersion curves of the longitudinal-optical adsorbate phonon both for Mo(110)-H and W(110)-H is rather broad ($\approx 0.6 \text{ \AA}^{-1}$ in both cases) compared to the sharp dips in the dispersion curves of the substrate surface phonons ($\approx 0.1 \text{ \AA}^{-1}$ and $\approx 0.2 \text{ \AA}^{-1}$ for the transverse- and the longitudinal-acoustic modes, respectively).² It is known from molecular-dynamics simulations that due to a flat potential well of the hydrogen adsorption site on both surfaces the adsorbate exhibits an enhanced mobility parallel to the

TABLE I. The table compares the adsorbate systems Mo(110)-H and W(110)-H with respect to the observed surface phonon anomalies. The first row characterizes the anomaly of the longitudinal-optical adsorbate phonons (LO) dealt with in the paper whereas the second and the third rows are dedicated to the anomaly of the transverse- and longitudinal-acoustic substrate surface phonons (TA and LA, respectively). Both the wave vector q along [001] and the lowering of the energy, ΔE , are presented. For the adsorbate phonons, ΔE is measured with respect to the energy at zero wave vector whereas for the substrate surface phonons this quantity is given with respect to the phonon energies of the clean surface (data concerning the tungsten surface are taken from Ref. 6, substrate surface phonon data of molybdenum are taken from Ref. 2).

	Mo(110)-(1 \times 1)H		W(110)-(1 \times 1)H	
	q (\AA^{-1})	ΔE (meV)	q (\AA^{-1})	ΔE (meV)
LO (H)	0.95 ± 0.03	4.1	0.95 ± 0.03	5.9
TA (Mo)	0.90 ± 0.03	3.5	0.93 ± 0.03	4.2
LA (Mo)	0.90 ± 0.03	3.2	0.93 ± 0.03	2.1

surface.¹⁶ This mobility is a possible factor for broadening the observed indentations in the dispersion curves. Second, it is remarkable that exclusively the longitudinal-optical adsorbate phonon suffers a softening. To date, no definite answer has been given to this observation. One may speculate that certain symmetry selection rules govern the coupling of adsorbate vibrational modes and electronic states. We hope to stimulate theoretical work that might enlighten this topic. Finally, we exclude the observed adsorbate phonon anomaly to be simply a concomitant effect of the substrate surface phonon anomaly since both vibrational excitations are decoupled due to their largely differing energies (the energy of, e.g., the longitudinal-acoustic substrate surface phonon of 1-ML hydrogen-covered Mo(110) is ≈ 25 meV at the boundary of the surface Brillouin zone).² In Table I we summarize some aspects of the encountered surface phonon anomalies of the adsorbate systems Mo(110)-H and W(110)-H: the wave vectors (q) where the anomalies are observed as well as the magnitude of the energy decrease (ΔE) are listed. It is remarkable that both the substrate surface phonons and the longitudinal-optical adsorbate phonon suffer a softening of comparable magnitude and at the same wave vector. The data of this table may serve as a summarizing argument that the adsorbate phonon anomaly is probably driven by the Kohn effect as observed for the substrate surface phonons.

An intriguing consequence, which could result from an enhanced electron-phonon coupling, is two-dimensional superconductivity. The corresponding attraction between electrons of a Cooper pair, which would be restricted to the surface, would be mediated by adsorbate phonons. Since we do not know the actual electron-phonon coupling parameter we are not able to estimate the critical temperature T_c .¹⁷ Rotenberg *et al.*,¹² analyzed the coupling between adsorbate vibrations and electronic surface states for the adsorbate system W(110)-H and extracted the electron-phonon coupling parameter, which led to a $T_c \approx 50$ K. It would be very nice to see whether the electronic surface-state band of Mo(110)-H

is similarly affected by adsorbate phonons as it is for W(110)-H.

To summarize, we reported on the anomalous dispersion curve of the longitudinal-optical adsorbate phonon of Mo(110)-(1×1)H, which consists of a pronounced indentation at $\approx 0.95 \text{ \AA}^{-1}$ along [001]. A similar softening has been reported so far only for the substrate surface phonons of this adsorbate system. Since the wave vectors at which the maximum softening of the surface phonons occurs coincide and since the energy lowering in both the substrate and the adsorbate case is comparable, we suggest that

the same mechanism, which is responsible for the substrate surface phonon anomaly, also drives the softening of the adsorbate phonon, namely, the Kohn effect. This hypothesis is corroborated by the adsorbate system W(110)-(1×1)H, where similar substrate surface phonon anomalies are reported and an adsorbate phonon has been ignored in the past.

One of us (J. K.) gratefully acknowledges discussions with K.-P. Bohnen and thanks G. Hoffmann, L. Limot, and T. Maroutian for critically reading the manuscript.

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