

Quantum delocalization of H on Pd(110): A vibrational study

N. Takagi, Y. Yasui, T. Takaoka,* M. Sawada,† H. Yanagita, T. Aruga, and M. Nishijima
Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606, Japan

(Received 10 August 1995; revised manuscript received 6 November 1995)

The vibrational spectra of H on Pd(110) at 90 K have been measured in the low-H-coverage region, by using high-resolution electron-energy-loss spectroscopy. Three dipole-active loss peaks associated with H adatoms were observed at 87–89, 96–100, and 121–122 meV. A model calculation based on the delocalization of H was made, which gives the energy positions and relative intensity variation of the two loss peaks in the range of 87–100 meV for different H coverages. There is a reasonable agreement between the calculated and experimental results. It is concluded that vibrationally excited H atoms on Pd(110) are described by the delocalized model.

I. INTRODUCTION

The transition-metal/H system is of great interest, not only from the scientific viewpoint, but also from the technological applications in connection with heterogeneous catalysis. Christmann *et al.*¹ suggested the H-band model, in which H is delocalized on the transition-metal surface [Ni(111)] and is described in terms of the two-dimensional atomic energy bands. Puska and co-workers^{2,3} have calculated the energy-band structures of H(D) chemisorbed on Ni(100), (111), and (110) surfaces by using the effective-medium theory. This theoretical calculation showed that H is delocalized in both ground and excited states, especially on Ni(111) and Ni(110), the bandwidth of the ground state being a few meV and those of the excited states of the order of several tens of meV.

Experimental studies have been made that support the calculation of Puska and co-workers^{2,3} by the use of high-resolution electron-energy-loss spectroscopy (EELS). For H on Rh(111), Mate and Somorjai⁴ have reported that broadened energy-loss peaks are observed, due to the delocalized nature of hydrogen, and that the loss energies are in reasonable agreement with the calculation of Puska *et al.* For H on Cu(110), Astaldi *et al.*⁵ have shown that the measured H-coverage-dependent EELS spectra are explained by a simple one-dimensional model based on the delocalization of H.

We have made a detailed study of H on Pd(110) in the low-coverage region, using EELS. The results are compared with the model calculation based on the delocalization of H.

II. EXPERIMENT

The experiments were carried out using an ultrahigh-vacuum chamber, which housed a high-resolution electron spectrometer for EELS, a four-grid retarding-field analyzer with a normal-incidence electron gun for low-energy electron diffraction (LEED), a cylindrical mirror analyzer for Auger electron spectroscopy (AES), and a quadrupole mass spectrometer for thermal-desorption spectroscopy (TDS). The base pressure of the vacuum system was 4×10^{-11} Torr.

The high-resolution electron-energy-loss spectrometer used for the present study is a double-pass spectrometer with

127° cylindrical deflectors each for the monochromator and analyzer.⁶ For EELS measurements, a primary energy E_p of 4 eV, an energy resolution of 4.5 meV (full width at half maximum, FWHM), and an incidence angle of 60°, with respect to the surface normal, were used. The electron beam was scattered along the $[1\bar{1}0]$ azimuth. The acceptance angle of the analyzer was 1.5°. The off-specular measurements were made by rotating the analyzer around the axis, which is perpendicular to the incidence plane of the electron beam. The EELS measurements were made at 90 K.

The Pd(110) clean surface was carefully prepared by Ar⁺-ion bombardment (650 eV, 4 $\mu\text{A}/\text{cm}^2$, 30 min), oxidation, and annealing (20 min) cycles. Cleanness of the Pd(110) clean surface was carefully checked by EELS, TDS, and AES. No peaks associated with, e.g., Pd-C, CO, etc., were observed in the EELS spectrum. Small amounts of CO and CO₂ desorption corresponding to the coverage θ_C (number of C adatoms per surface Pd atom) below 0.01 were observed in the TDS measurements after the sample oxidation. These originate from “bulk” C, and not from the surface C, because no loss peaks related to Pd-C were detected. EELS measurements were made for samples with different amounts of the residual bulk C, and it was confirmed that the experimental results discussed below are not influenced by the residual bulk C.

Research-grade H₂ and D₂ (99.5-mol % purity) were used. Hydrogen gases were introduced into the vacuum chamber through a gas doser, which produced a flux at the sample surface about 100 times the background hydrogen flux. The fractional H coverage θ_H was determined by comparing the area intensity of the corresponding H₂ thermal-desorption peak with that of the Pd(110)(2×1)-H surface in which $\theta_H = 1$.^{7–11}

III. RESULTS

Figure 1 shows EELS spectra in the specular mode of H on Pd(110) for various θ_H . The loss-peak intensities were normalized by the elastic peak intensities. Loss peaks are observed at 87–89, 96–100, and 121–122 meV. The 87–89-meV peak is observed in the H-coverage region, where θ_H is below 0.3. The 96–100-meV peak is observed at 100 meV for $\theta_H = 0.04$. The 100-meV peak monotonically shifts to

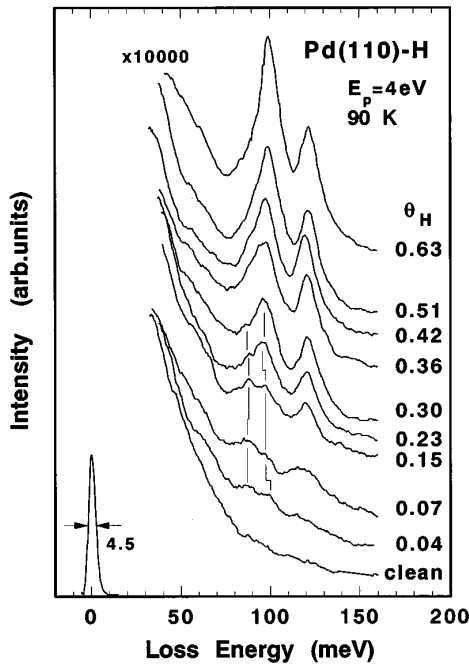


FIG. 1. EELS spectra in the specular mode of H on Pd(110) at 90 K in the low-coverage region. Primary electron energy $E_p=4$ eV.

wards lower energy with increasing coverage, and is observed at 96 meV for $\theta_H=0.23$. The 96-meV peak shifts towards higher energy for higher H coverages. For $\theta_H=0.63$, the peak is observed at 100 meV. In the low-coverage region ($\theta_H=0.04$ – 0.07), the 121-meV peak may consist of two subpeaks. For $\theta_H=1$, loss peaks are observed at 100 and 122 meV, in good agreement with the previous results.^{9–11} The intensities of the 87- and 100-meV loss peaks are almost the same for $\theta_H=0.04$. It is emphasized that very careful and detailed measurements were made, and hence the losses are not associated with the impurities, for example, CO, H₂O, etc. Angle-dependent measurements have shown that intensities of all the observed loss peaks are decreased in intensity, as the off-specular angle is increased similarly to the elastic peak intensity. This indicates that all the observed loss peaks are excited mainly by the dipole mechanism.^{3,12}

EELS measurements for D on Pd(110) were also performed. The spectra are shown in Fig. 2. Only two peaks are observed at 66 and 88 meV, for θ_D below 0.34. For higher coverages, the loss at 66 meV shifts gradually towards higher energy and is observed at 74 meV for $\theta_D=0.8$. The loss at around 120 meV is related to the residual H₂.

IV. DISCUSSION

A. Delocalized model

Puska and co-workers^{2,3} calculated the energy-band structure of H on Ni surfaces. According to their results on Ni(110), H is delocalized especially along the close-packed Ni-atom rows in the $[1\bar{1}0]$ azimuth, and the energy bandwidth of the ground state is a few meV, and those of the excited states of the order of several tens of meV. By the use of EELS, the energy losses of electrons scattered by the excitations of H atoms from the ground state to the excited

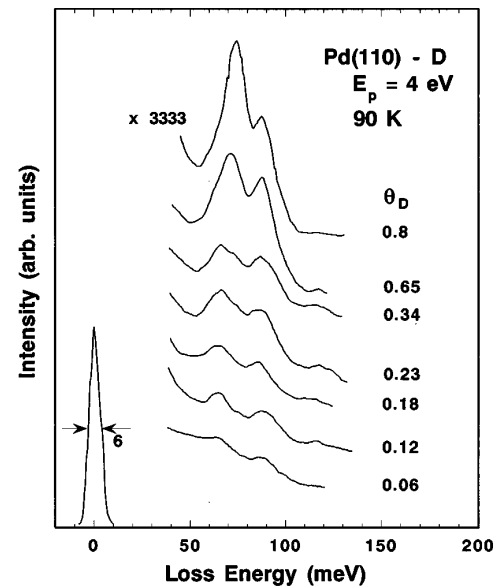


FIG. 2. EELS spectra in the specular mode of D on Pd(110) at 90 K in the low-coverage region. Primary electron energy $E_p=4$ eV.

states can be measured. The direct transitions ($\Delta\mathbf{q}=0$, \mathbf{q} : wave vector parallel to the surface) at any \mathbf{q} within the surface Brillouin zone are predominantly observable in the specular mode.³ Thus, for H on Pd(110) at 90 K in which all states within the ground-state band are considered to be populated, the loss intensity measured in the specular mode is proportional to the density of states (DOS) of H in the excited-state energy bands on the basis of the assumption that the energy band of the ground state is nearly flat and the excitation cross section is independent of \mathbf{q} . It is noted that the assumption of the flat band for the ground state is correct for H on Ni surfaces.^{2,3} The bandwidth of the ground state for H on Ni(100) is experimentally estimated to be about $0.8 \mu\text{eV}$.¹³ Moreover, as H on Pd(110) is a quasi-one-dimensional system, (apparently) two peaks are expected to be observed, which are associated with the excitation from the ground state to an excited-state band, because the density of states are generally large near the band edges.¹⁴ For high-H coverages, Puska and co-workers^{2,3} have reported that the H-H interaction leads to H blocking at the adsorption sites already occupied by other H atoms and that the bandwidth is decreased.

From the above discussion, the θ_H -dependent variation of the shape of the peaks observed in the 87–100-meV range (Fig. 1) can be interpreted as follows: for high coverages, H in both the ground and excited states is localized in a well-defined adsorption site, i.e., the quasi-three-coordinated site, due to the H blocking, and a sharp loss peak is observed at 100 meV (Sec. IV C). With decreasing H coverage, the H blocking due to the H-H interaction decreases, and the bandwidth increases. A broadened bandwidth of the excited state results in two loss peaks at 87–89 and 96–100 meV corresponding to the band edges for low coverages. The separation of the two peaks reaches 13 meV for $\theta_H=0.04$. We do not understand why the broadening of the 121–122-meV peaks is very small.

For the 66-meV peak of D on Pd(110), we have not observed two peaks which are associated with the band edges

of the excited-state band. This is understood as follows: as the mass of D is twice that of H, the bands are shifted towards lower energies for D on Pd(110), and thus the bandwidth for D is smaller than that for H.^{2,3} The bandwidth in the tight-binding approximation is determined by the quantum hopping energy (as discussed in Sec. IV B), which is related to the tunneling current between nearest-neighbor sites.¹⁵ It can be shown that, similarly to the tunneling current across a one-dimensional rectangular barrier, the bandwidth is proportional to $\exp(-am^{1/2})$ (m : particle mass).

All the observed loss peaks are excited mainly by the dipole mechanism. Thus, considering the surface-normal dipole selection rule,^{3,12} the losses correspond to the excitations from the ground-state band A_1^0 , which is a totally symmetric A_1 band, to the excited-state A_1 bands. According to the calculation of Puska and Nieminen³ for H on Ni(110), the excited-state A_1 bands are in the ranges between 15 and 30 meV (A_1^1 band), between 45 and 90 meV (A_1^2), and between 75 and 140 meV (A_1^3). It is considered that the losses in the 87–100-meV range correspond to the $A_1^0 \rightarrow A_1^2$ band excitations and the 120–121-meV peak to the $A_1^0 \rightarrow A_1^3$ band excitation. The $A_1^0 \rightarrow A_1^1$ band excitation may be hidden in the tail of the elastic peak.

In the past, two EELS experiments, which support the delocalized H model, have been carried out: one by Mate and Somorjai⁴ for H on Rh(111) and the other by Astaldi *et al.*⁵ for H on Cu(110). In the former experiment, the evidence for the model is the absence of an isotope shift for the lowest-energy-band excitation, broadened energy-loss peaks, and reasonable agreement of the loss energies with the calculation of Puska and co-workers.^{2,3} In addition, they reported a remarkable dependence of the width of the EELS peaks on the electron energy (0.5–8 eV). We measured the width of loss peaks for various electron energies (2–4 eV). But we did not observe the electron energy dependence of the width. In the latter experiment, the evidence is the broadened energy-loss peaks and coverage-dependent shift of the loss energies; the coverage dependence was analyzed by a one-dimensional model. Qualitatively speaking, the present results for H on Pd(110) are similar to those for H on Cu(110).

B. Model calculation

As mentioned above, EELS spectra, in particular, the energy positions and the relative intensities of the $A_1^0 \rightarrow A_1^2$ band excitations in the range of 87–100 meV show the dependence on θ_H . We made a model calculation for the excited H atom on the Pd(110) surface, in order to discuss these results quantitatively. This is based on one-dimensional Hubbard-like Hamiltonian used to explain the delocalized nature of the excited H atom adsorbed on the Cu(110) surface.⁵ The Hamiltonian, H , is written as

$$H = E \sum_i n_i^1 + T \sum_{ij} c_j^\dagger c_i^1 + U \sum_i n_i^1 n_i^0 + V \sum_{ij} n_i^1 n_j^0,$$

where E corresponds to the band center of the A_1^2 band, T is the quantum hopping (not thermal overbarrier hopping) energy for the excited H atom between the nearest-neighbor (N-N) sites, U is the repulsive energy when the excited H

atom shares a site with another H atom in the ground state, and V is the repulsive energy between the excited H atom and the ground-state H atom in the N-N sites. The indexes 1, 0, i , and j denote the excited state, the ground state, a site in the linear chain, and the nearest neighbor of the site i , respectively. c_i^\dagger (c_i) is the creation (annihilation) operator for the site i and $n_i = c_i^\dagger c_i$ is the occupation number of the site i . The details of this model and the physical meaning of the parameters (E , T , U , and V) are discussed in Ref. 5.

The energy eigenvalues of this Hamiltonian for the linear chain composed of 20 sites were numerically calculated by diagonalizing the 20×20 matrix, the matrix elements of which are

$$H_{i,i} = E + U n_i^0 + V(n_{i+1}^0 + n_{i-1}^0),$$

$$H_{i,i+1} = H_{i,i-1} = T,$$

with the others equal to zero. Applying the periodic-boundary condition, $i+1=1$ if $i=20$ and $i-1=20$ if $i=1$. The density of states (DOS) curves are averaged over the various spatial distributions of H atoms in the ground state as the diagonal terms depend on the distributions, and are convoluted with a Gaussian (FWHM, $\Gamma = 10$ meV) to fit them to the EELS spectra.

It is well established that the adsorption of H on the Pd(110) surface induces the formation of the (2×1) -H phase for $\theta_H \leq 1$. According to the LEED measurements of Cattania *et al.*,⁷ the LEED spots corresponding to the (2×1) -H phase are observed for $\theta_H \sim 0.3$. This suggests that H atoms in the ground state are located in the quasi-three-coordinated sites to form zigzag chains along the closed-packed $[1\bar{1}0]$ rows, even for low θ_H by the H-H attractive interaction; H atoms in one side of the row are located with the periodicity twice that of the substrate. Thus, the DOS curves for $\theta_H \geq 0.2$ were evaluated for this distribution. For example, the DOS curve for $\theta_H = 0.3$ is calculated for the distribution of $ABABABABABAAAAAAAAAAA$, where A and B denote empty and occupied sites of the H atoms in the ground state, respectively. On the other hand, the DOS curves for $\theta_H < 0.2$ are averaged over the distributions, where the H atoms in the ground state are randomly located.

Figure 3(a) shows the DOS curves calculated for $\theta_H = 0.05 - 0.4$, with $E = 94$, $T = 5$, $U = 80$, and $V = 1$ meV. The calculated peak energies corresponding to the two excitations from the ground state to the excited state A_1^2 band are plotted as a function of θ_H in Fig. 3(b), together with the experimental results. There is a reasonable agreement between the model calculation and the experimental results. When the DOS curves were averaged over the random distribution for $\theta_H \geq 0.2$, the agreement between the calculation and the experimental results was not good. In the calculation of Astaldi *et al.*⁵ for the excited H atom on Cu(110), $E = 74$, $T = 9$, $U > 70$, and $V = 2.75$ meV were used. The quantum hopping energy for H on Pd(110) is about a half of that for H on Cu(110). This is consistent with the difference of the lattice constants; the lattice constant of Pd(110) (0.389 nm) is larger than that of Cu(110) (0.361 nm).

It is interesting to compare the bandwidth for the excited state of H on Pd(110) with those on (100) and (111). In the vibrational study for H on Pd(100),¹⁶ only a single loss peak

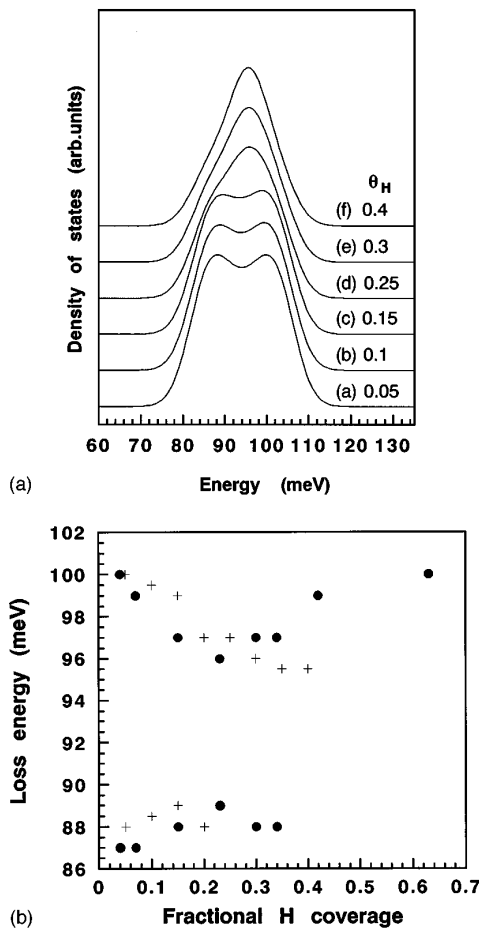


FIG. 3. (a) Calculated density of states of the A_1^2 band for various θ_H (fractional H coverage). (b) The θ_H dependence of the energy positions of the loss peaks. The experimental and calculated results are shown by filled circles and crosses, respectively. The parameters used are $E=94$, $T=5$, $U=80$, $V=1$, and $\Gamma=10$ meV (see text for more explanation).

is observed at 60 meV, with the FWHM almost the same as that of the elastic peak (4 meV). Thus, the bandwidth for (100) is considered to be narrow. The same experimental result is also obtained in our laboratory. According to the calculation of Rick and Doll¹⁷ for H on Pd(111), the bandwidth corresponding to, e.g., the A_1^1 band, is estimated to be 2.17 meV. The bandwidths for (100) and (111) are much narrower than the bandwidth for (110), which is roughly estimated to be ~ 20 meV ($4T$). The distances between the N-N sites on (100), (110), and (111) are 0.275, 0.275, and 0.159 nm, respectively. [The fourfold hollow, quasi-three-coordinated, and threefold hollow sites are assumed for the N-N sites of the (100), (110), and (111) surfaces, respectively.] Thus, there is no simple correlation between the bandwidths and the N-N site distances. Therefore, it is interpreted that the difference of the bandwidth reflects the difference of the shape of the adiabatic potential-energy surface for H. More detailed theoretical and experimental analyses are needed in order to understand the delocalized nature of H on various single-crystalline Pd surfaces systematically. The measurements of the surface diffusion barrier are especially needed, because it is closely related to the adiabatic potential-energy surface.

C. Localized model

The results obtained in this work might be interpreted by the localized model. The 97–100- and 122-meV peaks observed for $\theta_H=0.30$ –1 are ascribed to the localized vibrations of H atoms located in the quasi-three-coordinated sites of the (111) facets of the unreconstructed Pd(110) surface, as supported by experiments^{7–11} and theories.^{18,19} Applying the surface-normal-dipole selection rule,¹² the 97–100-meV peak is ascribed to the hindered translation parallel to the (111) facet and along the [100] azimuth; the 122-meV peak is attributed to the hindered translation of H atoms perpendicular to the (111) facets.^{9,11} It is noted that the energy ratios ν_H/ν_D of the 100-(74-) and 122-(88-) meV peaks are 1.35 and 1.39, respectively, which are smaller than the mass dependence for a harmonic oscillator, respectively. The 3-meV increase in energy of the hindered translation parallel to the (111) facets from $\theta_H=0.30$ –1 may be associated with the through-Pd-substrate H-H interaction.²⁰

For $\theta_H \leq 0.3$, the loss peaks are observed at 87–89, 96–100, and 121 meV. Similar to the identifications for $\theta_H > 0.3$, the 96–100- and 121-meV peaks may be attributed to H atoms in the (111) facets. The 87–89-meV peak is observed only for low H coverages. Thus, it may be associated with the defects on the Pd(110) clean surface. According to the high-resolution LEED measurements of Hörnis *et al.*,²¹ clean Pd(110) consists of semioordered (110) islands (terraces) separated by steps. The steps have (111) facets, and thus, the 87–89-meV peak may be ascribed to the hindered translation of H atoms parallel to the (111) facets of the steps. The corresponding peak associated with the hindered translation perpendicular to the (111) facets of the steps is not resolved. It may be embedded in the 121-meV peak.

However, the number of step sites is much smaller than that of the terrace sites. The ratio of the number of step sites to the number of the terrace sites is of the order of 1%. Thus, it is difficult to explain the (relatively) strong intensity of the 87–89-meV peak by the localized model.

It is well known that the subsurface sites are occupied by H on the Pd(110) surface.^{7–11} Therefore, the subsurface H might have some contribution to the losses in the range of 87–100 meV observed for the low θ_H region (Fig. 1). This possibility can be ruled out for the following two reasons: (1) According to the neutron-scattering measurements for Pd powders, vibrational modes of the bulk hydrides are observed at 59 and 69 meV,²² and the vibrational mode of H occupying subsurface sites is observed at 58 meV.²³ These energy values are far from the energy region of 87–100 meV. Thus, it is considered that the subsurface H does not exist in the low θ_H region. (2) The EELS spectra for Pd(110) (1 \times 2)-H with the subsurface H were compared to those without the subsurface H.^{9,11} No significant difference was found between the two cases. This indicates that EELS is not sensitive to the subsurface H for Pd(110) even if it exists, and that of the existence of the subsurface H has no significant effect on the adsorbed state of the surface H.

V. CONCLUSION

In conclusion, we have measured EELS spectra for H(D) on Pd(110) in the low-coverage region. Both the delo-

calized and localized models of H adatoms were examined. The experimental results were compared with the model calculation based on the delocalized nature of H. It is concluded that the vibrationally excited H atoms on Pd(110) are described by the delocalized model.

ACKNOWLEDGMENTS

This work was supported in part by Grants-in-Aid from the Ministry of Education, Science and Culture (Japan) and from the Jeol Ltd.

*Present address: Research Institute for Scientific Measurements, Tohoku University, Sendai 980, Japan.

†Present address: Hitachi, Ltd. Semiconductor and Integrated Circuits Division, 190 Kashiwagi, Komoro-shi, Nagano 384, Japan.

¹K. Christmann *et al.*, *J. Chem. Phys.* **70**, 4168 (1979).

²M. J. Puska *et al.*, *Phys. Rev. Lett.* **51**, 1081 (1983).

³M. J. Puska and R. M. Nieminen, *Surf. Sci.* **157**, 413 (1985).

⁴C. M. Mate and G. A. Somorjai, *Phys. Rev. B* **34**, 7417 (1986).

⁵C. Astaldi *et al.*, *Phys. Rev. Lett.* **68**, 90 (1992).

⁶M. Nishijima *et al.*, *Rev. Sci. Instrum.* **58**, 307 (1987).

⁷M. G. Cattania *et al.*, *Surf. Sci.* **126**, 361 (1983).

⁸R. J. Behm *et al.*, *J. Chem. Phys.* **78**, 7486 (1983).

⁹M. Jo *et al.*, *Solid State Commun.* **55**, 639 (1985).

¹⁰M. Skottke *et al.*, *J. Chem. Phys.* **87**, 6191 (1987).

¹¹T. H. Ellis and M. Morin, *Surf. Sci.* **216**, L351 (1989).

¹²H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and*

Surface Vibrations (Academic, New York, 1982).

¹³X. D. Zhu *et al.*, *Phys. Rev. Lett.* **68**, 1862 (1992).

¹⁴N. W. Ashcroft and N. D. Mermin, *Solid State Physics: Advances in Research and Applications* (Holt, Rinehart, and Winston, New York, 1976).

¹⁵E. G. Goldberg *et al.*, *Phys. Rev. B* **39**, 5684 (1989).

¹⁶C. Nyberg and C. G. Tengstål, *Solid State Commun.* **44**, 251 (1982).

¹⁷S. W. Rick and J. D. Doll, *Surf. Sci.* **302**, L305 (1994).

¹⁸P. Nordlander *et al.*, *Surf. Sci.* **136**, 59 (1984).

¹⁹J. P. Muscat, *Phys. Rev. B* **34**, 8863 (1986).

²⁰C. Nyberg and C. G. Tengstål, *Phys. Rev. Lett.* **50**, 1680 (1983).

²¹H. Hörnis *et al.*, *Phys. Rev. B* **48**, 14 577 (1993).

²²J. J. Rush *et al.*, *Z. Phys. B* **55**, 283 (1984).

²³J. M. Nicol *et al.*, *Phys. Rev. B* **36**, 9315 (1987).