

Adsorbed states of H on Ni(111) at 100 K: A vibrational study

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The adsorbed states of H on the Ni(111) surface have been investigated at 100 K as a function of H coverage, θ_H , mainly by using high-resolution electron-energy-loss-spectroscopy. Losses are observed at 90 and 130 meV for $\theta_H \leq 0.5$. For $\theta_H = 1$, two losses are observed at 115 and 140 meV. In the region where $0.5 < \theta_H < 1$, vibrational spectra are the weighted superpositions of those for $\theta_H = 0.5$ and 1. We correlate losses for $\theta_H \leq 0.5$ and 1 with the (2×2) -2H and (1×1) -H structures, respectively. No evidence of the quantum delocalization of H is obtained, which is attributed to the island formation of the (2×2) -2H structure even for the low θ_H . [S0163-1829(97)04548-7]

I. INTRODUCTION

The interaction of hydrogen with transition-metal surfaces, e.g., Ni(111), has been investigated extensively by both experimental and theoretical methods, because it is important to applications such as catalytic reaction and H storage, and because it has given fundamentally interesting topics full of variety such as the H-induced surface reconstruction, the two-dimensional phase transition, the indirect interaction between adsorbed H atoms, and the quantum delocalization.¹⁻¹³

In this Brief Report, we investigate the adsorbed states of H on Ni(111) at 100 K as a function of the fractional H coverage, θ_H [the number of H atoms per Ni atom of the bulklike Ni(111)], mainly by using high-resolution electron-energy-loss spectroscopy (EELS). The adsorbed states are correlated with the ordered structures formed by the H adatoms. The quantum delocalization of H on Ni(111) is also discussed.

II. EXPERIMENT

The experiments were carried out by using an ultrahigh-vacuum chamber equipped with EELS, low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and thermal-desorption spectroscopy (TDS). Details of the apparatus and the experimental techniques were described in our previous paper.¹⁴

The clean Ni(111) surface was carefully prepared by repeated cycles of Ar^+ -ion bombardment ($10 \mu\text{A}/\text{cm}^2$, 650 eV, 30 min) followed by annealing at about 1200 K. The cleanness of the Ni(111) surface was checked by AES, TDS, and EELS. No peaks associated with, e.g., C, O, etc., were observed in the EELS spectrum. The defect density is estimated to be < 0.01 from the H_2 -TDS spectrum of the H-saturated surface. It is noted that the H_2 -TDS is sensitive to the existence of defects.¹⁵ The sample was dosed with H_2 at about 200 K in order to avoid the adsorption of water when dosed at 100 K.

The fractional H coverage, θ_H , was determined by comparing the area intensity of the corresponding H_2 thermal-desorption peak with that of the H-saturated surface in which $\theta_H = 1$.^{1,8}

III. RESULTS

Figure 1 shows EELS spectra in the off-specular mode of H on Ni(111) as a function of θ_H ($\theta_H = 0.05-1$). The primary

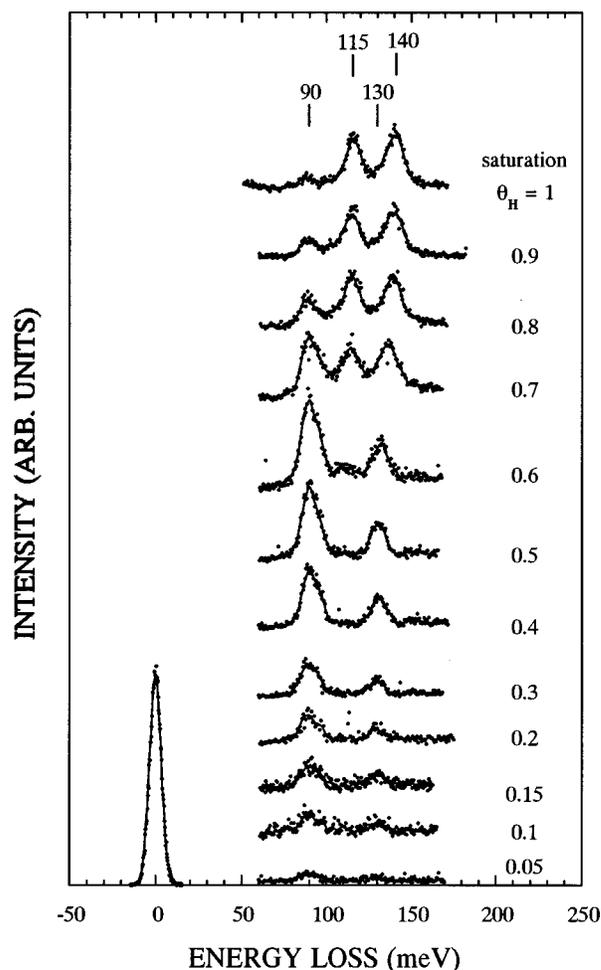


FIG. 1. EELS spectra of H on Ni(111) at 100 K as a function of coverage θ_H . $\theta_i = 60^\circ$, $\theta_e = 50^\circ$, and $E_p = 5.0$ eV. All the loss spectra are normalized to the background (Ref. 16). The elastic peak for $\theta_H = 0.05$ is shown as a reference. Data were obtained every 0.6-meV loss energy, and for a single data point, electron pulses were counted for 30 s.

energy of $E_p = 5$ eV was used. The angle between the specular and off-specular directions used is 10° (incidence angle $\theta_i, 60^\circ$, emission angle $\theta_e, 50^\circ$). Losses are observed at 90 and 130 meV for $\theta_H = 0.05$. These losses grow in intensity with increasing θ_H from 0.05 to 0.5. The 90- and 130-meV losses are correlated with the (2×2) -2H structure, since (1) a sharp (2×2) LEED pattern was observed for $\theta_H = 0.5$, and (2) the loss spectral shape remains the same below $\theta_H = 0.5$. For $\theta_H = 0.6$, a loss appears at about 115 meV. For $\theta_H = 0.7$, the intensity of the 115-meV loss is increased, but that of the 90-meV loss is decreased. For $\theta_H = 1$, two losses are clearly observed at 115 and 140 meV, and the intensity of the 90-meV loss (nearly) vanishes. The 115- and 140-meV losses are correlated with the (1×1) -H structure, since a (1×1) LEED pattern is observed for $\theta_H = 1$.

Apparently, the 130-meV loss is shifted to 140 meV in the coverage range of $\theta_H = 0.5$ –1, but this can be explained by the superposition of the independent 130- and 140-meV losses. The angle-dependent measurements indicate that all the losses are excited via impact scattering,¹⁶ which is in agreement with the results of Ref. 3. No dispersions were observed as far as we investigated. For D on Ni(111), ($\theta_D = 0.5$), losses are observed at 69 and 98 meV. This is explained by the mass ratio of H and D ($\nu_H/\nu_D \sim 1.3$).

The temperature dependence of the EELS spectra of H on Ni(111) for $\theta_H = 0.5$ was also measured in the range of 100–320 K. The measurements were made by cooling (heating) the sample from 320 (100) to 100 (320) K. The changes of the spectra obtained in both cooling and heating processes were reversible. Figure 2 shows a series of the EELS spectra during the cooling process ($E_p = 6$ eV, $\theta_i = 60^\circ$, and $\theta_e = 70^\circ$). Each spectrum is acquired during cooling, and hence, the sample temperature is gradually decreased. The temperatures except for 100 and 320 K shown in Fig. 2 are average values from the beginning to the end of an acquisition period (30 min per spectrum). Losses are observed at 88 and 130 meV at 100 K. The vibrational energy of the former loss is slightly different from that of the corresponding peak in Fig. 1. This is probably because the energy accuracy and signal-to-noise ratio were sacrificed in order to reduce the acquisition time. Relative intensity of the 88- and 130-meV losses is somewhat different from that in Fig. 1. This may originate from the differences of E_p and θ_e chosen. A broad loss is observed at around 85 meV at 320 K. As the sample temperature is lowered, the loss at around 85 meV grows in intensity, and is gradually sharpened. Changes in the peak intensity and width seem to be continuous. This is in good agreement with previous reports which indicate that the disorder-order transition occurs at 270 K for $\theta_H = 0.5$, and that the phase transition is continuous.^{1,13} The inset of Fig. 2 shows the phase diagram of H on Ni(111).¹ The spectral changes in the energy range corresponding to the 130-meV loss are not clearly observed. This is probably because the excitation cross section of the 130-meV loss is so small that enough signal-to-noise ratio was not obtained in the present experimental conditions.

IV. DISCUSSION

From the coverage-dependent measurements, it is found that the 90- and 130-, and 115- and 140-meV losses are

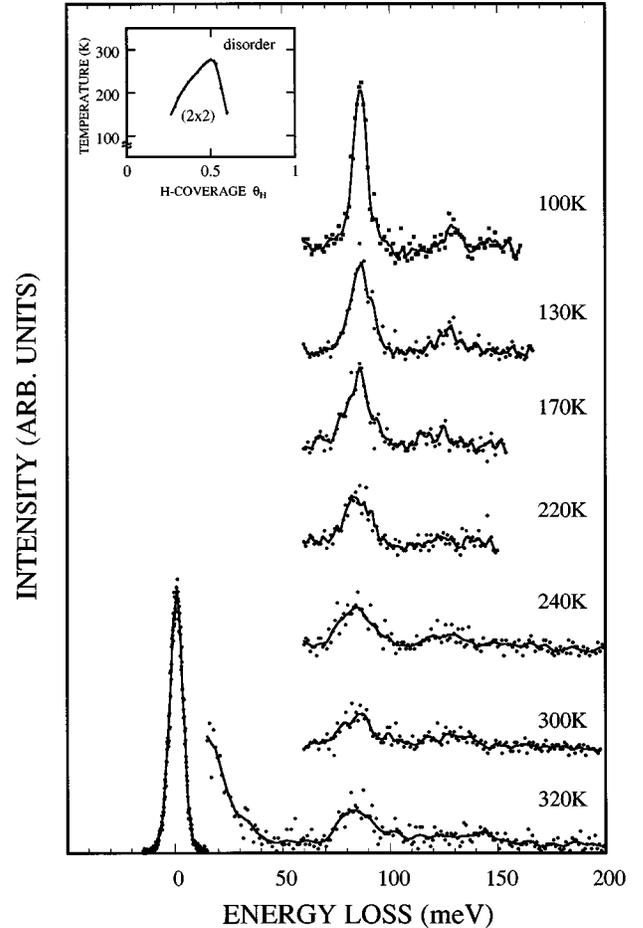


FIG. 2. The temperature dependence of the EELS spectra of H on Ni(111) for $\theta_H = 0.5$. $\theta_i = 60^\circ$, $\theta_e = 70^\circ$, and $E_p = 6.0$ eV. All the loss spectra are normalized to the background (Ref. 16). The elastic peak at 320 K is shown as a reference. Data were obtained every 1.1-meV loss energy, and for a single data point, electron pulses were counted for 15 s. The inset shows the phase diagram for H on Ni(111) (Ref. 1).

paired, and that the EELS spectra can be classified into three coverage regions. Losses are observed at 90 and 130 meV for $\theta_H \leq 0.5$ (I); at 90, 115, and 130–140 meV for the region where $0.5 < \theta_H < 1$ (II), and at 115 and 140 meV for $\theta_H = 1$ (III).

Since H generally “prefers” the high-coordination site, these losses are related to H in the threefold hollow sites. A symmetric (ν_s) and two degenerate asymmetric (ν_{as}) stretching modes can be observable for H in the threefold hollow site. The dipole selection rule cannot be applied in the present case, because the losses are dominantly excited via the impact-scattering mechanism.¹⁶ The nearest-neighbor force-constant model is useful to interpret the EELS spectra, and has been successfully applied. However, Richter and Ho¹⁷ reported that the value of ν_{as} is overestimated in this model for H in the threefold hollow sites on the fcc(111) and hcp(0001) surfaces, and that there is the general tendency of $\nu_{as} < \nu_s$ for H on these closed-packed surfaces. Based on this relation, the 90 (115)- and 130 (140)-meV losses are attributed to ν_{as} and ν_s of H in the threefold hollow site, respectively.

According to the transmission-channeling experiment,⁸ al-

most all (90%) H atoms occupy the fcc sites on the H-saturated Ni(111) surface ($\theta_H=1$). Therefore, the 115- and 140-meV losses for $\theta_H=1$ are attributed to ν_{as} and ν_s of H in the fcc site, respectively.

The assignments of the 90- and 130-meV losses correlated with the (2×2) -2H structure are complicated. It is found that H atoms occupy both fcc and hcp sites to form the honeycomb lattice of the (2×2) -2H structure.¹ Considering the assignments of the 115- and 140-meV losses, the 90- and 130-meV losses are associated with the ν_{as} and ν_s of H in the fcc (or hcp) site, respectively. The values of the vibrational energies of H in both sites are so close that they are not resolved. The difference in the vibrational energy of the ν_{as} and ν_s between the fcc and the hcp sites is, if at all, less than 5 meV. Recent theoretical work shows that the calculated values of ν_s are 129 and 146 meV for H in the fcc and the hcp sites, respectively.¹⁸ (This work also reports that the bond lengths and binding energies of H in both sites are almost the same, which suggests that the relation of the vibrational energy of H with the bond length and binding energy is not straightforward.)

The spectral shape remains the same in region (I). The 90- and 130-meV losses show no coverage-dependent peak shift and broadening. Thus we predict that the (2×2) -2H islands are formed by the attractive interaction between H adatoms.¹⁹ The EELS spectra for region (II) can be qualitatively explained by the weighted superposition of those for $\theta_H=0.5$ and 1. Thus, the (2×2) -2H and (1×1) -H structures coexist in the intermediate region (II).

The vibrational energies of H in the (2×2) -2H phase are significantly different from those in the (1×1) -H phase. In particular, as the 90-meV loss is associated with ν_{as} of H in the (2×2) -2H phase, the difference in ν_{as} is 25 meV. Theoretical calculation suggests that the indirect H-H interaction induces the blueshift in the vibrational energy of H adatoms on Ni(100) and Pd(100).²⁰ The indirect interaction consists of the static and dynamic contributions. The former originates from the change in the strength of the H-substrate bond induced by the presence of other H adatoms, while the latter originates from the dynamic coupling when the neighboring H adatoms are vibrating. This has been experimentally confirmed by the EELS measurements for H on Ni(100),²¹ Pd(100),²² Rh(100),²³ and Pt(111).¹⁷ However, the amounts of the shifts for these systems lie in the range of 7–15 meV. The large value of 25 meV cannot be rationally explained by considering only the indirect interaction.

Detailed studies of the (2×2) -2H structure for $\theta_H=0.5$ by using LEED (Ref. 12) and He diffraction¹⁰ showed that the substrate reconstruction is induced by the adsorption of H. (The structural model proposed by LEED is slightly different from that proposed by He diffraction. The Ni atoms bonded with H are shifted outward relative to those not bonded with H for the former, but Ni atoms which are not bonded with H show the outward relaxation for the latter.) For the (1×1) -H phase, no significant substrate relaxation is observed, and all Ni atoms are equivalent, so the substrate must be flat.⁸ Therefore, the structure change of (2×2) -2H $\rightarrow(1\times 1)$ -H is accompanied by the substrate reconstruction. This reconstruction seems to contribute to the observed large shift in the vibrational energy of H. It is noted that the vibrational energy shift of ~ 10 meV, accompanied

by the structural change of the substrate, is observed for H on Mo(110).²⁴

Christmann *et al.*¹ proposed the formation process of the (2×2) -2H structure as follows: The $p(2\times 2)$ -H phase (in which θ_H is 0.25) is formed for $\theta_H<0.25$, and afterwards the (2×2) -2H structure, is formed with increasing θ_H from 0.25 to 0.5. They proposed that the interaction between the third-nearest-neighbor H atoms (i.e., the interaction between nearest H atoms of the honeycomb lattice) is essentially repulsive, and hence, the (2×2) -2H island is not formed for low θ_H . Furthermore, they suggested that the steeper phase boundary in the higher θ_H region (the inset of Fig. 2) can be explained as follows: Since the (2×2) -2H structure is formed by the repulsive interaction (just like the Wigner crystal of electrons²⁵), it is easily destroyed by the additional H.

We have concluded that the (2×2) -2H islands are formed by the attractive interaction between H adatoms for $\theta_H\leq 0.5$. This is in disagreement with the above model. It might be considered that the H-H interaction is so weak that the coverage-dependent peak shift is not observed for $\theta_H\leq 0.5$. If so, the (2×2) -2H structure cannot be discerned from the $p(2\times 2)$ -H by EELS. This may be ruled out by considering the origin of the broad loss spectrum at 320 K which corresponds to the disordered phase: H atoms are randomly distributed in the disordered phase, and thus, the regions with the local θ_H smaller or larger than that of the (2×2) -2H phase are mixed. The broadening reflects the existence of H in these various local configurations. Since the indirect H-H interaction induces a blueshift in the vibrational energy of H adatoms, it is considered that the lower- and higher-energy components of the broadening correspond to H in the lower and higher local-coverage configurations, respectively.

Although the third-nearest-neighbor interaction is considered to be attractive, the steep phase boundary may be explained by considering that the first-nearest-neighbor, second-nearest-neighbor interactions, etc., are repulsive. Roelofs *et al.*⁶ calculated the phase diagram, by using the parameter set obtained by Muscat,⁵ in which the third-nearest-neighbor interaction is attractive. They found very broad coexistence regions, which is in agreement with the present result. However, in the parameter set of Muscat, the sixth-nearest-neighbor interaction is abnormally attractive, and, hence, it has been suspected.⁶ On the other hand, according to Nagai, Ohno, and Nakamura,⁴ the following parameter set rationally produces the phase diagram and the results of the isosteric heat of adsorption measurements:¹ first- to fifth-nearest-neighbor interactions are repulsive, and the sixth-nearest neighbor interaction is slightly attractive. In addition, they reported that the attractive sixth-nearest-neighbor interaction favors the formation of the $p(2\times 2)$ -H structure for $\theta_H<0.25$. More theoretical efforts will be needed. Finally, it is emphasized that the phase diagram reported by Christmann *et al.*¹ has been measured in the temperature region above 150 K. Measurements below 150 K are greatly expected to be performed.

It is interesting to discuss the quantum delocalization of H on the Ni(111) surface. Christmann *et al.*¹ suggested the atomic-band model for H on Ni(111), where H is delocalized and thus the vibrational levels form energy bands just like an

electron in a periodic potential well. Puska and Nieminen²⁶ calculated the band structures of H on Ni(100), (110), and (111) surfaces by using effective-medium theory. In particular, the bandwidth of the ground state and those of the excited states are calculated to be a few and several tens of meV for H on Ni(111), respectively. Experimentally, the EELS spectra resulting from the delocalized nature of H at low H coverage are reported for H/Rh(111),²⁷ H/Cu(110),²⁸ and H/Pd(110).¹⁴

The widths of the losses for $\theta_H=0.05$ are narrow and are comparable to that of the elastic peak. The EELS spectra for the low θ_H region show no peak broadening. This is closely connected with the formation of the (2×2) -2H islands. The attractive interaction makes H localized even for $\theta_H=0.05$. It is noted that the theoretical calculations are made for single H on the unreconstructed Ni(111) surface, and that H-H interaction is not included.

V. CONCLUSION

The adsorbed states of H on the Ni(111) surface have been studied at 100 K as a function of H coverage, θ_H , mainly by using high-resolution EELS. Losses are observed at 90 and 130 meV for $\theta_H\leq 0.5$. For $\theta_H=1$, two losses are

observed at 115 and 140 meV. In the region where $0.5<\theta_H<1$, vibrational spectra are the weighted superposition of those for $\theta_H=0.5$ and 1. Thus we propose that the structure change of H on Ni(111) with θ_H occurs as follows: For low θ_H , the (2×2) -2H islands are formed, the domain size becomes larger with increasing θ_H , and the surface is fully covered with the (2×2) -2H structure at $\theta_H=0.5$. The (2×2) -2H and (1×1) -H structures coexist in the intermediate region where $0.5<\theta_H<1$. The surface is covered with the (1×1) -H structure at $\theta_H=1$.

The vibrational energies of H in the (2×2) -2H phase are significantly different from those in the (1×1) -H phase, in particular, the difference in ν_{as} is 25 meV. The large difference indicates that the structure change of (2×2) -2H \rightarrow (1×1) -H is accompanied by the substrate reconstruction. No evidence of the quantum delocalization of H is obtained, which is attributed to the island formation of the (2×2) -2H structure even for the low θ_H .

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¹⁹One might argue that the vibrational shift between a single H atom adsorbed in a threefold site and H atoms in the same sites of the (2×2) -2H islands is very small and that the (2×2) -2H phase has a continuous phase transition to disorder in the low-coverage region. In order to clarify this, detailed measurements of the intensities and sizes of the LEED spots at 100 K are desirable.

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