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# Observation of a transition from over-barrier hopping to activated tunneling diffusion: H and D on Ni(100)

A. Lee, X. D. Zhu, and L. Deng*
*Department of Physics, University of California, Davis, California 95616-8677*

U. Linke
*Institut für Grenzflächenforschung und Vakuumphysik, Forschungszentrum Jülich, D-5170 Jülich, Federal Republic of Germany*

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Using a linear optical diffraction technique, we measured the surface diffusion coefficients for hydrogen (H) and deuterium (D) on Ni(100) at coverage $\theta=0.7$. From 200 K down to 120 K, the diffusion for both H and D evolves from a high-temperature activated behavior to a low-temperature activated behavior. For hydrogen, $D_0=1.1\times10^{-6}$ cm$^2$/sec, $E_{\text{diff}}=3.5$ kcal/mol from 200 to 160 K and $D_0=1.5\times10^{-9}$ cm$^2$/sec, $E_{\text{diff}}=1.2$ kcal/mol from 160 to 120 K. For deuterium, $D_0=5\times10^{-5}$ cm$^2$/sec, $E_{\text{diff}}=5.0$ kcal/mol from 200 to 170 K and $D_0=9\times10^{-10}$ cm$^2$/sec, $E_{\text{diff}}=1.05$ kcal/mol from 170 to 120 K. Our preliminary analysis based upon small-polaron theories and available surface-phonon data suggests that the observed transition is most likely to be from an over-barrier hopping to an activated tunneling diffusion.

Quantum tunneling transport of particles in or on surfaces of condensed media is one of the most fascinating topics in the field of condensed matter research.[1–17] The richness and complexity of the topics arise from the explicit involvements of dissipative forces due to phonons and other forms of excitations, defects, and necessarily the particle-particle interaction at finite concentrations and hence the many-body effect. The investigation in both theory and experiment has significantly contributed to the understanding of the intricate interplay of various interactions as functions of time, temperature, the length scale of the system, and densities of the moving particles.

As the energy scale of a quantum tunneling processes is determined by the tunneling matrix element $J$, which is roughly $10^{-6}$ eV or less even for hydrogen atoms, such a quantum behavior appears only at temperatures below 100 K.[1,2,8–11] The hydrogen isotope family, including a positive muon, deuterium, and tritium, are ideal candidates to exhibit quantum tunneling behavior in solids at reasonably high temperature due to their small masses. Besides the large range of isotope mass ratio, early temperature onsets of quantum tunneling over the over-barrier hopping at 120–130 K give experimenters a large temperature range from 120 to 15 K for in-depth temperature dependence studies.[8,12,13] Such a temperature range can be easily achieved by using conventional cooling techniques in an ultrahigh-vacuum chamber equipped with a variety of conventional sample preparation and characterization instrumentation.[11]

Experimentally, most measurement techniques are limited to probe rather rapid diffusion rates, $\geq 10^{-8}$ cm$^2$/sec, and consequently can investigate only high-temperature behaviors of diffusion.[8,14] In the temperature range which has been explored by many researchers, diffusions of hydrogen and deuterium are mostly characterized by a simple over-barrier diffusion with a single activation energy. The experimental finding of the diffusion coefficient of a muon in Cu by Gebennik *et al.* suggests that the above experimental limit of $10^{-8}$ cm$^2$/sec is at least 1–2 orders of magnitude above the point below which quantum tunneling motion becomes dominant.[9,10]

Recently, using a field emission microscope and monitoring the density fluctuation of adsorbates, Gomer and co-workers were able to measure diffusion coefficients as low as $10^{-13}$ cm$^2$/sec.[12,13] In the temperature range from 130 to 30 K, they indeed observed the evidence of quantum tunneling diffusion of hydrogen and deuterium on both W and Ni surfaces. Even more interesting is that in all cases, they found that the diffusion coefficients leveled off with temperature almost abruptly from a high-temperature activated region and stayed flat over a temperature range from 100 K to as low as 30 K.[12,13]

The observations by Gomer and co-workers have stimulated strong and renewed theoretical as well as experimental efforts into quantum tunneling transport phenomena as their experimental results of the temperature and isotope dependence do not simply reconcile with the existing polaron theories involving linear coupling of the particle motion to the dissipative substrate phonons.[7,11,12,15–17]

Very recently, we demonstrated an optical diffraction technique which is also capable of probing diffusion coefficients over a range from $10^{-7}$ to $10^{-16}$ cm$^2$/sec.[11,18,19] This technique offers an alternative method which is readily applied to hydrogen atoms on a large variety of substrates. In an earlier paper, we reported the first confirmation of the prevalence of quantum tunneling diffusion for hydrogen on Ni(100) using this technique.[11] In this paper, we present the detailed result of the temperature dependence of the diffusion coefficients for both hydrogen and deuterium on Ni(100). The measurement was performed at a well-defined coverage $\theta=0.7$ over the temperature range from 120 to 200 K. The refined measurement shows that for both H and D, the diffusion is characterized by two clearly activated processes. The results are at variance with the previous measurements.[13] Our analysis based upon small-polaron theories and the available surface-phonon data suggest that the low-temperature region is most likely to be an activated tunneling diffusion with the activation energy mostly associated with the local lattice relaxation energy.

We carried out the measurement with a Ni sample disk placed in an ultrahigh-vacuum chamber. The disk exposes the (100) face to within 0.1°. The surface of Ni(100) was cleaned with cycles of Ne-ion sputtering, oxidation, and finally annealing at 1000 K for a few seconds. The cleaned surface showed no traces of sulfur and carbon by a retarding-field Auger electron spectrometer. The sample temperature was varied from 120 to 200 K with an accuracy of $\pm 3$ K. It was monitored with a Chromel-Alumel thermocouple which is spot welded to the side of the sample disk. The thermocouple was referenced to the air-conditioned ambient air whose temperature was 298 K (i.e., 25 °C) with a fluctuation of $\pm 2$ K. The cooling was achieved through a copper braid to a liquid-nitrogen cold finger. The coverages of atomic hydrogen and deuterium on Ni(100) were controlled at $\theta=0.7$, by carefully controlling the dosage. The relation between the dosage and the coverage was calibrated in detail with thermal desorption mass spectrometry. The operating pressure was kept at $1\times10^{-10}$ torr. During a 20–30 min measurement period, the coverage change was less than 5% of one monolayer and was negligible for our purpose. For the coverage grating spacing, we used both 16.6 and 8.3 $\mu$m to check the consistency of the measurement and to maintain the observation time within 30 min. The initial grating modulation was maintained at less than 10% of 1 monolayer. The details of the coverage grating preparation and the detection by optical diffractions can be found elsewhere.[11,18,19] We monitored the change of a first-order diffraction of a He-Ne probe beam from the coverage grating over a 20–30 min time period. The data allowed us to directly extract the macroscopic diffusion coefficient $D(T)$.

In Figs. 1 and 2, we depict the Arrhenius plots of the measured diffusion coefficients $D(T)$ from 120 to 200 K for hydrogen and deuterium, respectively. The data do not fall on a single straight line as would be the case for a simple activated diffusion. We notice a kink in the data at around 160 K in both cases. Furthermore, from 160 to 120 K, the diffusion coefficients continue to decrease instead of leveling off.[12,13] We were not able to extend the measurement to temperatures below 120 K with our current cooling setup, although we are in the process of setting up a different cooling system capable of achieving sample temperature as low as 20 K. Therefore, it is possible that at lower temperatures the diffusion coefficients may level off as observed by Gomer and co-workers.[12,13] In the temperature range of our present measurement, however, it seems appropriate to characterize the diffusion of hydrogen and deuterium as governed by two thermally activated processes. If we fit the data in both temperature regions with Arrhenius forms $D(T)=D_0\exp(-E_{\mathrm{diff}}/RT)$ as also shown in Fig. 1 and 2, we obtain the diffusivities $D_0$ and the activation energies $E_{\mathrm{diff}}$ as listed in Table I.

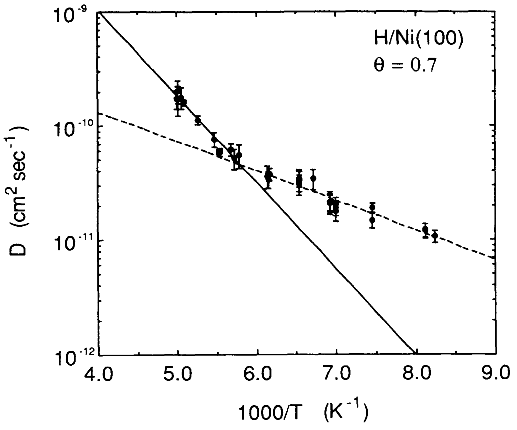

FIG. 1. Arrhenius plot of the diffusion coefficient $D(T)$ for hydrogen atoms on Ni(100) with a coverage $\theta=0.7$. The temperature range is from 120 to 200 K. The kink in the data occurs at $T=160$ K. Solid line: an Arrhenius fit to the high-temperature behavior. Dashed line: an Arrhenius fit to the low-temperature behavior. The fitting parameters are listed in Table I.

We now discuss the experimental results. The high-temperature behavior has previously been observed by other groups for H and D on Ni(100).[13,20,21] It is attributed to an over-barrier diffusion. The diffusivities and the activation energies in the high-temperature region reproduce the findings previously reported by the groups of George, White, and Gomer using different techniques. We should add here that the coverage dependence of the diffusion coefficients for both H and D in the coverage range from $\theta=0.3$ to 0.8 was found as rather weak. This

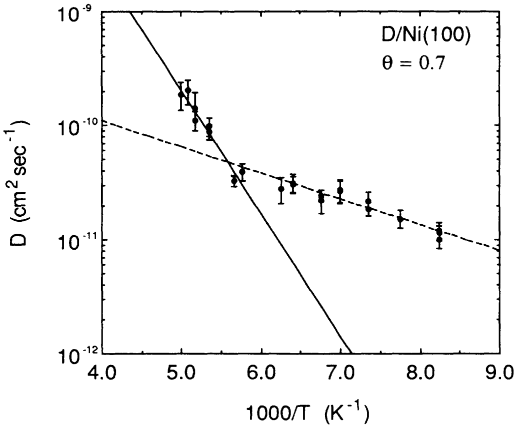

FIG. 2. Arrhenius plot of the diffusion coefficient $D(T)$ for deuterium atoms on Ni(100) with a coverage $\theta=0.7$. The temperature range is from 120 to 200 K. The kink in the data occurs at $T=170$ K. Solid line: an Arrhenius fit to the high-temperature behavior. Dashed line: an Arrhenius fit to the low-temperature behavior. The fitting parameters are listed in Table I.

TABLE I. The measured diffusivities and the activation energies of diffusion for hydrogen and deuterium on Ni(100) from $T = 120$ to 200 K.

| | High-temperature region (200–170 K) | | Low-temperature region (170–120 K) | |
|---|---|---|---|---|
| | $D_0$ (cm$^2$/sec) | $E_{\text{diff}}$ (kcal/mol) | $D_0$ (cm$^2$/sec) | $E_{\text{diff}}$ (kcal/mol) |
| Hydrogen on Ni(100) | $1.1\times10^{-6}$ | 3.5 | $1.5\times10^{-9}$ | 1.2 |
| Deuterium on Ni(100) | $5\times10^{-5}$ | 5 | $9\times10^{-10}$ | 1.05 |

is consistent with the previous report by Lin and Gomer.[13] We thus believe that the role of adsorbate-adsorbate interaction is likely to be small in determining the temperature behavior of diffusion.

To understand the data in the low-temperature region, we need to examine possible causes for the second activated process. We first consider impurity-limited diffusions such as by steps or point defects. It is known that if an adsorbate can be trapped at a point defect site or must cross a line defect such as a step with different activation energies from that on an otherwise flat surface, a diffusion crossing from a high-temperature activated to a low-activated region is expected. However, in order to observe the effect due to point defects, the coverage of the adsorbate has to be comparable to the defect density. This is not the case in our experiment. The defect density is expected to be at least 2–3 orders of magnitude lower than the coverages of hydrogen and deuterium. The low-temperature behavior cannot be caused by the diffusion across the steps either. We notice that for a 0.1° miscut angle, the averaged step spacing is 1000 Å or 400 surface lattice spacings (one surface lattice spacing $a_0$ is 2.5 Å). If the low-temperature region were caused by crossing steps with a lower activation energy, we would require the diffusivity at the steps to be $D_0$ (at steps) $=D_0$ (at low temperature)/$(400)^2 \sim 10^{-15}$ or $10^{-16}$ cm$^2$/sec. This means that the trial frequency for hopping at steps is at most $10^{-7}$–$10^{-8}$/sec. This is not possible.[14] In fact, a diffusivity of $10^{-9}$ cm$^2$/sec is also too small for a second over-barrier channel in the low-temperature region.

We thus suggest that the observed low-temperature behavior is governed by an activated tunneling diffusion and therefore the transition at around 160 K is from an over-barrier hopping to a small-polaron-type activated tunneling.[1,2,8–10] The qualitative features of the results are consistent with such a picture. First, the decreasing diffusivity can be understood as caused by the small WKB overlap integral or the small tunneling matrix element $J$.[1,2,8–10] Second, the activation energies are much smaller than those in the high-temperature region. Such a behavior has been predicted by small-polaron theories and elegantly observed for positive muons in copper by Grebinnik *et al.*[9] They found that evolving from a high-temperature region to a low-temperature region around 250 K, the diffusive motion of a muon in Cu maintains activated but with the activation energy changing from 10 kcal/mol to 1.1 kcal/mol, and the diffusivity changing from $10^{-2}$ cm$^2$/sec to $4\times10^{-9}$ cm$^2$/sec. The low-temperature behavior was analyzed by Teichler and attributed to an activated tunneling diffusion.[10]

To further examine the suggestion of an activated tunneling diffusion, we compare the activation energy with the relaxation energy as a result of hydrogen adsorption. The latter can be estimated based upon the available surface-phonon data and small-polaron theories.[1,2] As the Born-Oppenheimer approximation of separating the fast hydrogen motion from the slow motion of the Ni substrate atoms can still apply, a small-polaron analysis based upon the linear coupling model due to Holstein, Flynn, and Stoneham is a good start.[1,2,10,12] We point out that the temperature region for an activated tunneling diffusion is about one-half to one-third of the bulk Debye temperature $\theta_D = 450$ K, which is the case in the present experiment.[1,10]

The surface vibrational spectra in the presence of adsorbates have become increasingly available in recent years following the significant advancement in He scattering spectroscopy and electron-energy-loss spectroscopy.[22–28] This information can now be used directly or indirectly for analyzing other surface dynamical processes involving coupling between the adsorbate motion and the substrate motion such as tunneling diffusion. However, most attention has been focused upon the surface-phonon spectra of clean surfaces and adsorbate-covered surfaces with well-defined superlattice structures.[22] The coupling of the hydrogen motion to the substrate motion has been discussed only in terms of force constants rather than the local relaxation of the substrate atoms. Understandably, the former is directly observable from the changes in surface-phonon frequencies.[22–28] The relaxation of the substrate atoms due to adsorption of a single adsorbate is not directly deduced in surface-phonon spectra. Furthermore, at coverages when adsorbates form well-defined superlattices, the induced relaxation can be restored and the resultant hydrogen-substrate coupling exhibits itself only in the form of either lateral stresses or strain.[22,24–28] These have been observed in many surface-phonon spectra with ordered adsorbate overlayers, and for some systems, *ab initio* calculations have confirmed such a scenario.[24–28] However, the theory does not exclude the possibility that at coverages less than what it takes to form an ordered superlattice, the local relaxation of substrate atoms is energetically favored. Because the linear coupling model of Holstein, Flynn, and Stoneham does not lead to changes in phonon spectra of host lattices, we can only indirectly deduce the relaxation energy due to adsorption of a single hydrogen atom.[1,2] The following deduction is based on assumptions which need to be verified experimentally or by appropriate *ab initio* calculation.

We consider changes of the Ni(100) substrate atomic motion as a result of adsorption. A number of atomic species, C, N, O, S, and H, on Ni(100) have been extensively investigated by a variety of surface analysis techniques. For C, N, O, and S, there are also extensive surface-phonon data mostly obtained by Ibach and coworkers.[22,24–28] To our knowledge, there is not yet a complete set of surface-phonon data for hydrogen on

Ni(100). Our analysis will thus be based upon the information contained in the surface-phonon dynamics of C, N, O, S on Ni(100) and hydrogen on Ni(110).[24–28] Unlike O and S, it is observed that C and N induce a reconstruction on a Ni(100) surface at high coverages. The adsorption of these two species tends to maximize the bonding coordination number. The same behavior has also been found for hydrogen on Ni(110).[28] It seems reasonable to assume that the effect of adsorbed hydrogen on Ni(100) should be much more similar to those of C and N. Because the smaller electron affinity of hydrogen compared with those of carbon and nitrogen atoms, it is also reasonable to expect the substrate relaxation due to hydrogen adsorption, if it occurs, to be accordingly smaller. If we assume that a substantial part of the reconstruction at high coverages is caused by the local relaxation around an adsorbed carbon or nitrogen in addition to the phonon softening effect, we can then estimate the relaxation energy associated with the surface reconstruction. The most prominent change of the substrate atomic position due to adsorbed atoms (C, N, and possibly H) occurs in association with the $A_2$ Rayleigh mode. At the $X$ point of the first Brillouin zone, the displacements of the substrate atoms in the $A_2$ mode are such that the top-layer atoms rotate around an adsorbed atom. When the reconstruction sets in, the centers of the substrate atoms shift along the directions of the displacements by about $\delta q = 0.5$ Å for C on Ni(100). If we assume that a relaxation of the same magnitude also occurs at a local level at low coverages, we can use the above displacement to calculate the local relaxation energy $E_{\rm relax}$. Using the bulk force constant for Ni(100), $\Phi_{11} = 3.8\times 10^4$ dyn/cm (as C, N, and H tend to restore the force constant from the surface value to the bulk value), the relaxation energy is estimated to be $E_{\rm relax} = (\Phi_{11}/2)(\delta q)^2 \sim 4.8\times 10^{13}$ erg$=0.3$ eV$=6.8$ kcal/mol for C on Ni(100).[24–28] The tunneling activation energy is usually one-half of the relaxation energy.[1,2] If we assume that the relaxation of Ni atoms due to the adsorption of hydrogen is one-half of that caused by carbon, we arrive at an estimate of the tunneling activation for adsorbed hydrogen atoms, $E_a = 0.9$ kcal/mol. Despite of the gross approximation and simplification, the estimate is instructively close to the experimental values, $E_{\rm diff} = 1.1$ kcal/mol for hydrogen, and 1.05 kcal/mol for deuterium. It is safe to conclude that the result of the present analysis is consistent with the tunneling diffusion picture.

Within the tunneling diffusion picture, we can deduce a few other useful results from the data. From the small-polaron theories, the diffusivity of an activated tunneling diffusion is given by[1,2,8]

$$D_0 = \frac{a_0^2 J^2}{\hbar}\left[\frac{\pi}{4k_B T E_{\rm diff}}\right]^{1/2} . \qquad (1)$$

Here $a_0 = 2.49$ Å is the surface lattice constant, $J$ is the bare tunneling matrix element. $E_{\rm diff}$ is the activation energy which is presently determined by the experiment. From the measured diffusivities for both hydrogen and deuterium, $D_0 \approx 10^{-9}$ cm$^2$/sec, we calculated the bare matrix element, $J \approx 5\times 10^{-6}$ eV. This means that the ground-state hydrogen bandwidth should be of the order of 0.01 meV. Recently, Puska and co-workers have calculated the energy bandwidths of vibrational excitations of hydrogen atoms on Ni(100) using the effective-medium method.[29,30] They found from the calculation that the low-lying vibrational energy states are better described in terms of energy bands for hydrogen atoms. The bandwidths for excited states are as large as over a few meV. Due to the limitation of the calculation, they placed the upper limit of the ground-state bandwidth at 1 meV. Their results are consistent with our experimental finding.

We notice that the dependence of the activation energy and the deduced tunneling matrix element on isotope masses are rather weak. This has also been observed by Lin and Gomer.[13] This is surprising for an activated tunneling diffusion. It is possible that the coupling constants of the hydrogen motion to the phonon coordinates are independent of the adsorbate mass, e.g., the coupling to acoustic phonons.[31] This may lead to a relaxation energy independent of isotope masses. It is, however, difficult to imagine the absence of a strong isotope dependence in the tunneling matrix element.[1,2,12] This difficulty seems irreconcilable with the conventional small-polaron theories as the tunneling matrix element usually involves the overlap of two vibrational ground-state wave functions of hydrogen localized at a pair of neighboring sites. The latter is expected to be strongly mass dependent. At this point, we do not have an explanation.

It is clearly necessary that the measurement is extended further down to lower temperatures. Such an effort is under the way. The low-temperature data should help further to elucidate the mechanisms behind the diffusion of hydrogen on Ni(100).

In conclusion, we have observed two activated regions for the diffusion of hydrogen and deuterium on Ni(100) over the temperature range from 120 to 200 K. The low-temperature region is attributed to an activated tunneling diffusion. The analysis is in part based on the available surface-phonon data of Ni(100) with atomic adsorbates and small-polaron theories. The lack of a strong isotope dependence in the deduced tunneling matrix element $J$ remains an open question as it is not consistent with the conventional wisdom of a quantum tunneling process.

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[*] Permanent address: Department of Physics, Georgia Southern University, Statesboro, GA 30460.

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