Diffusion of Hydrogen on Ni(111) over a Wide Range of Temperature: Exploring Quantum Diffusion on Metals

G. X. Cao, E. Nabighian, and X. D. Zhu*

Department of Physics, University of California, Davis, California 95616

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We measured the temperature and azimuthal dependence of the diffusion rates of hydrogen (^{1}H) and deuterium (^{2}H) on Ni(111) from 65 to 240 K where the diffusion rates vary by 8 orders of magnitude. The diffusion of hydrogen crosses over from an activated behavior above 110 K to another activated behavior below 110 K with a smaller activation energy. By ruling out the possibility of a step effect, we suggest that the crossover is from a classical overbarrier hopping to a quantum mechanical underbarrier tunneling. [S0031-9007(97)04429-3]

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Unlike other adsorbate-substrate systems, hydrogen and its isotopes on metals form a uniquely interesting system whose transport along a surface may take the form of both classical overbarrier hopping and quantum mechanical underbarrier tunneling in a temperature range achievable in a conventional surface science chamber [1–3]. This is because of the small mass of hydrogen and presumably small variation of the surface potential for hydrogen on metals [4]. Quantum tunneling diffusion of positive muon and hydrogen in a solid under the dissipative influence of phonons, conduction electrons near Fermi surface, or other forms of low energy excitations has been a rich topic of experimental and theoretical research over the past few decades [5–18]. In contrast, there have been few reports of quantum tunneling diffusion *on* metals that resemble the behaviors of muon and hydrogen in metals [1–3]. Gomer and co-workers were the first to report the evidence of quantum tunneling diffusion on metals in a series of field emission current fluctuation studies of hydrogen isotopes on W surfaces [1]. Of the most intriguing observations by these authors are (i) the near temperature-independence of the tunneling diffusion rates over a wide temperature range, and (ii) very small isotope dependence of the tunneling diffusion rates, only a factor of 4 variation from ^{1}H to ^{3}H on W(110). Since these observations are not mirrored by known cases of diffusion of hydrogen isotopes in metals, they have stimulated a great deal of research interest [19]. As the experimental data are still very limited, it is early to draw general conclusions as to what one should expect of the quantum diffusion on metal surfaces.

In this Letter, we report the results of an extensive measurement of the temperature and azimuthal dependence of the diffusion rates of hydrogen and deuterium on Ni(111) using a combination of laser-induced desorption and optical diffraction techniques [20]. By being able to vary the periodicity of the hydrogen density grating from 0.4 to 60 μm, we were able to use the optical technique to measure diffusion rates from 10^{-7} to 10^{-15} cm^2/s. From these new results, we will show the strong evidence of quantum diffusion of hydrogen on Ni(111) that in fact resembles the behaviors of hydrogen in metals [5].

The experiment is conducted in a conventional ultrahigh vacuum chamber at an operating pressure less than 5×10^{-12} torr. A Ni(111) disk of 1 cm in diameter with a miscut less than 0.1° is used as the substrate. It is oriented such that one of its [110] axes within the surface plane is along the horizontal direction. The details of the sample preparation and the optical setup have been described elsewhere [20,21]. To form adsorbate density gratings with laser-induced desorption, we use 10 ns optical pulses from a Nd:YAG laser either at the fundamental wavelength of $\lambda_\omega = 1.064$ μm or at the second harmonic wavelength of $\lambda_{2\omega} = 0.532$ μm. As described in Ref. [20], at an incidence angle Φ_{exc}, the grating period is given by $2a = \lambda_{\mathrm{exc}}/2\sin\Phi_{\mathrm{exc}}$. For the diffusion measurement, we detect the first-order diffraction of a He-Ne probe laser at $\lambda_p = 0.633$ μm from the adsorbate density grating. The optical signal $S(t)$ is proportional to the square of the first spatial Fourier component of the adsorbate density grating and thus decays as $S(t) = S(0)\exp(-2\pi^2 Dt/a^2)$ [20]. We extract the diffusion rate constant D from the decay exponent $2\pi^2 D/a^2$. In contrast to our earlier studies, we use four different excitation-detection arrangements in order to change the grating period from 61 to 0.38 μm [21]. The ability to successively change the grating period enables the detection of diffusion rates from 2×10^{-7} to 2×10^{-15} cm^2/s (the largest range ever reported *for surface diffusion*). The decay rate at a given temperature is found to vary as $1/a^2$, a signature of surface diffusion. Our earlier observation of an onset of a weakly temperature dependent diffusion at around 120 K was incorrect due to the presence of a weak system transient response and that we failed to vary grating periods at temperatures below 120 K to detect this error [21]. For azimuthal dependence measurement, we incorporated into our excitation-detection system the capability to rotate continuously the hydrogen density grating about the surface normal.

Hydrogen molecules adsorb on Ni(111) dissociatively. Up to an atomic coverage of 50% or $\theta = 0.5$, hydrogen atoms occupy both fcc and hcp threefold hollow sites indistinguishably [22]. Theoretical studies of hydrogen binding on Ni(111) all indicate that an adsorbed hydrogen moves from a threefold hollow site to a neighboring one by hopping over a twofold bridge site as the least energetic saddle point [4,23–25]. In Fig. 1, we display the Arrhenius plots of the diffusion rates for hydrogen and deuterium obtained at $\theta \approx 0.3$. The orientation of the density grating is perpendicular to the horizontal direction so that the diffusion is along the [110] direction as indicated in the inset. The diffusion rates in the investigated temperature range vary from 2×10^{-15} to 2×10^{-7} cm^2/s. It is clear that the diffusion of hydrogen from 220 down to 65 K is characterized by a crossover from a thermally activated behavior at above 110 K with an activation energy of 18.9 kJ/mol to another thermally activated behavior at below 110 K with a smaller activation energy of 10.1 kJ/mol. For deuterium, the diffusion is characterized by a similar and yet incomplete crossover. For hydrogen, we also measured the temperature dependence of the diffusion rates at $\theta \approx 0.06$ from 80 to 110 K and the coverage dependence at 100 K. At $\theta \approx 0.06$, the temperature dependence is essentially the same as at high coverage ($\theta \approx 0.3$) except that the activation energy is slightly higher by 0.71 kJ/mol. At 100 K, the rate increases monotonically from 3×10^{-13} cm^2/s at $\theta \approx 0.02$ to 1.3×10^{-12} cm^2/s at $\theta \approx 0.5$, indicative of a small repulsive hydrogen-hydrogen interaction on Ni(111) with a magnitude of no more than 0.84 kJ/mol. The repulsive nature of the hydrogen-hydrogen interaction is also consistent with the small increase in the activation energy at low coverage. The facts that the hydrogen-hydrogen interaction energy is much smaller than the observed activation energies and that the overall coverage dependence is weak even at 100 K indicate that the temperature characteristic is dominated by that of the tracer diffusion of hydrogen. The latter is directly related to the microscopic mechanisms that govern the site-site hopping.

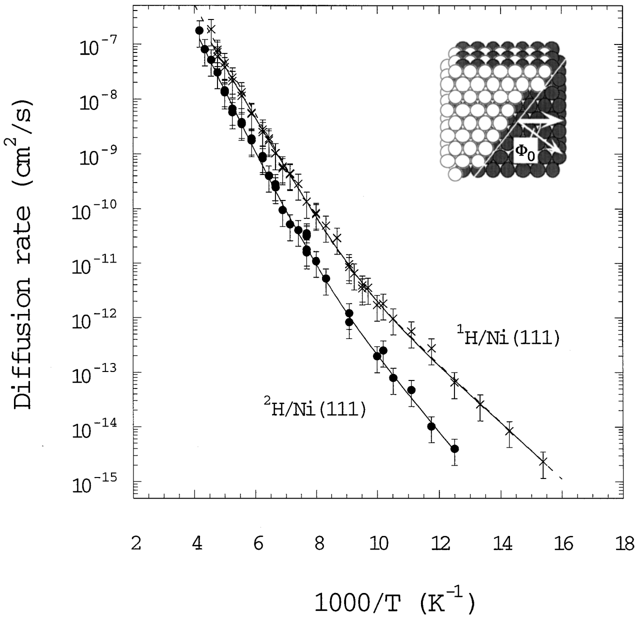

FIG. 1. Arrhenius plots of the diffusion rates for hydrogen (crosses) and deuterium (solid circles) at a mean coverage is $\theta = 0.3$. The solid lines are fit to a model described by Eq. (2). The dashed line in the case of hydrogen is a fit to a model described by Eq. (1). The inset shows the orientation of the sample and the arrow points along the direction along which the diffusion rates are measured.

To understand the temperature dependence, it is important to note that the rates measured with the optical diffraction technique are averaged over a distance of the grating period. The miscut angle of our Ni(111) sample is less than 0.1° so that the averaged terrace width is expected to be 1000 Å, a factor of 4 smaller than the smallest grating period (3800 Å). We do not know, however, *a priori* the orientation of the steps relative to that of the adsorbates density grating. Hydrogen atoms are thus expected to encounter step edges as they traverse along the direction normal to the density grating. We note that at a low step density as is the case here, step edges change the diffusion kinetics only if the energy barrier for crossing a step edge is significantly larger than that on a flat terrace. Therefore the diffusion at temperatures below 110 K must be predominantly over flat terraces. It is possible that the kinetics of crossing step edges dominates in the high temperature region if the orientation of the steps happens to be *almost* parallel to the hydrogen density grating. In this case the results shown in Fig. 1 may be a crossover from a step-edge-crossing limited diffusion at high temperatures to a diffusion over terraces only at low temperatures. Let Φ_0 be the angle between the orientation of the steps and that of the adsorbate density grating; it is easily shown that the effective tracer diffusion rate is given by

$$D(\Phi_0, T) = D_{\text{terrace}}(T) \sin^2 \Phi_0 + \frac{\cos^2 \Phi_0}{\alpha / D_{\text{step}}(T) + (1 - \alpha)/D_{\text{terrace}}(T)} . \quad (1)$$

Here $D_{\text{terrace}}(T) = D_{\text{terrace},0} \exp(-E_{\text{terrace}}/RT)$ is the diffusion rate on a terrace. $D_{\text{step}}(T) = D_{\text{step},0} \exp(-E_{\text{step}}/RT)$ is the rate on a surface with the potential energy surface periodically replaced by that at a step edge. α is the linear fractional density of steps along the direction normal to the step orientation. Assuming that the step density is limited by the miscut-cut angle, we expect $\alpha \sim 2 \times 10^{-3}$. Using the activation energies, the diffusivities, and the azimuthal angle Φ_0 as the parameters, we find that the model can fit the data for hydrogen very well as shown in the dashed line in Fig. 1. The fitting parameters are as follows: $\Phi_0 = 2.9°$, $D_{\text{step},0}(^1\text{H})/\alpha = 5 \times 10^{-3}$ cm^2/s, $E_{\text{step}}(^1\text{H}) = 19.3$ kJ/mol, $D_{\text{terrace},0}(^1\text{H}) = 5 \times 10^{-5}$ cm^2/s, and $E_{\text{terrace}}(^1\text{H}) = 10.1$ kJ/mol. From the estimate of the step density of $\alpha \sim 2 \times 10^{-3}$, we find that $D_{\text{step},0}(^1\text{H}) \sim 1 \times 10^{-5}$ cm^2/s. Both $D_{\text{step},0}(^1\text{H})$ and $D_{\text{terrace},0}(^1\text{H})$ are smaller by 2 orders of magnitude than an estimate of 10^{-3} cm^2/s from the transition-state theory. This observation alone is not sufficient to dismiss the model. However, the proposal of a predominantly step-crossing limited diffusion between 110 and 200 K with a small angle $\Phi_0 = 2.9°$ between the orientations of the step and the hydrogen density grating implies that at $T = 140$ K the diffusion rates should have a large azimuthal dependence. The calculated azimuthal dependence from the fitting parameters is shown as the dashed line in Fig. 2. Also shown in Fig. 2 is the experimentally measured azimuthal dependence. To display the results at the same scale, the data are multiplied by a factor of 10 in this figure. The data show far less azimuthal dependence than what the model predicts. In fact, the direction along which the diffusion rate takes the minimum value is 37° from the horizontal direction. This large discrepancy rules out the step effect as one of the plausible explanations of the temperature dependence.

Since the horizontal direction ($\Phi = 0$) is at 37° from the step orientation, it is likely that the diffusion over terraces dominates at high temperatures as well provided the activation barrier crossing a step edge is not much larger than that on a terrace. From the theoretical calculation of hydrogen binding energy on Ni surfaces by Nordlander and co-workers, it seems that this is the case for hydrogen on Ni(111) [4]. At $\Phi_0 = 37°$ from the [110] axis, the step edges consist of segments of close-packed rows of 7 Ni atoms long. The segments are connected by a kink. Our miscut Ni(111) surface is thus conceptually represented by the inset in Fig. 1. Near a step edge, it resembles a Ni(110) surface. Since hydrogen atoms reside at the threefold hollow sites on both Ni(111) and Ni(110) [4,22,23,26], crossing a step edge on the miscut Ni(111) is equivalent to crossing close-packed rows on Ni(110), and is between a threefold hollow site on an upper terrace and a threefold corner site on the lower terrace over a twofold short-bridge site. In an effective-medium calculation of hydrogen binding energies on Ni(111) and Ni(110), Nordlander and co-workers showed that the energy barrier for crossing a close-packed row on Ni(110) is almost the same as that between two threefold hollow sites on an open (111) terrace [4]. This is quite reasonable as the coordination number of a hydrogen atom as it traverses over a twofold short-bridge site is the same (=2) in both cases. We therefore propose that the observed temperature dependence is characteristic of that over flat terraces in the entire temperature range and the crossover is from a classical overbarrier hopping to an underbarrier quantum tunneling diffusion [5,12–16]. If we assume that the rates of a classical overbarrier hopping and a quantum underbarrier tunneling are additive, the total tracer diffusion rate is given by

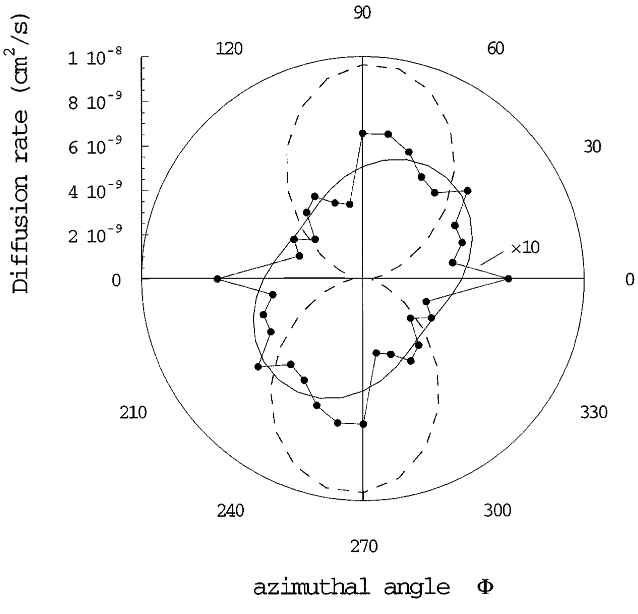

FIG. 2. Azimuthal dependence of the diffusion rates for hydrogen at $T = 140$ K. $\Phi = 0$ corresponds to the horizontal direction and is along one of the [110] axes on Ni(111). Dashed line: calculated diffusion rates using the parameters from the fit to Eq. (1). Solid circles: measured diffusion rates versus Φ. Solid line: a fit to the measured rates (scaled) using $D_{\text{terrace}} \sin^2(\Phi + \Phi_0) + \cos^2(\Phi + \Phi_0)/[\alpha/D_{\text{step}} + (1 - \alpha)/D_{\text{terrace}}]$. The minimum is at $\Phi_0 = 37°$.

$$D(T) = D_0^{\text{cl}} \exp\left(-\frac{E_{\text{cl}}}{RT}\right) + D_0^{\text{quant}} \exp\left(-\frac{E_{\text{quant}}}{RT}\right). \quad (2)$$

With the diffusivities and the activation energy barriers as adjustable parameters, Eq. (2) describes very well the experimental results as shown in the solid line in Fig. 1. For hydrogen the best fit is obtained with $D_0^{\text{cl}}(^1\text{H}) = 2.8 \times 10^{-3}$ cm^2/s, $E_{\text{cl}}(^1\text{H}) = 18.9$ kJ/mol, $D_0^{\text{quant}}(^1\text{H}) = 2.4 \times 10^{-7}$ cm^2/s, and $E_{\text{quant}}(^1\text{H}) = 10.1$ kJ/mol. For deuterium, the crossover is incomplete. If we assume that the diffusion for deuterium at low temperatures is characterized by the same activation energy as for hydrogen (consistent with the small-polaron theory of quantum diffusion) [13], the rates can be fit also very well with $D_0^{\text{cl}}(^2\text{H}) = 3.4 \times 10^{-3}$ cm^2/s, $E_{\text{cl}}(^2\text{H}) = 21.0$ kJ/mol, $D_0^{\text{quant}}(^2\text{H}) = 1.6 \times 10^{-8}$ cm^2/s, and $E_{\text{quant}}(^2\text{H}) = E_{\text{quant}}(^1\text{H}) = 10.1$ kJ/mol. By allowing for the activation energy E_{step} for crossing step edges to vary from 4.5 kcal/mol to as much as 9 kcal/mol, we find that the step effect is not observable in the temperature dependence while it is sufficient to cause the observed azimuthal dependence as displayed in Fig. 2.

We now discuss the implication of the present results. In the classical overbarrier hopping region, the diffusivities for both isotopes are of 10^{-3} cm^2/s, in excellent agreement with the estimates from the transition-state theory. The energy barrier for deuterium is larger by 2.1 kJ/mol. This "anomalous" isotope effect is ubiquitous for hydrogen isotopes in metals as well as on metals at high temperatures [1,2,5]. In metals, the difference in activation energy barrier in the classical region varies between 0.84 kJ/mol (H in Ni) and 2.7 kJ/mol (H in vanadium). Our result is in this range. It is noteworthy though that such an activation energy difference is not satisfactorily accounted for by the current theoretical calculation of the difference in zero-point energy of the vibrational ground states at the saddle point (twofold bridge site) and at a hollow site [4,25,27]. A possible explanation of this isotope effect was given by Affleck and by Emin, Baskes, and Wilson

(EBW) [13]. They argued that as an adatom with mass m crosses over a potential barrier, the transmission coefficient was not unity but that of a plane wave passing through a parabolic potential barrier, $V(x) = V_b - \frac{1}{2}k(x - x_b)^2$. The probability of crossing the barrier at an energy E above the barrier top is given by $P(E,T,m) = \exp(-E/k_BT)/\{1 + \exp[-2\pi(E - V_b)/\hbar\sqrt{k/m}\,]\}$ after being weighted by the Boltzmann factor. The optimal energy at which $P(E,T,m)$ maximizes increases with the mass of the atom. It is conceivable that this effect is at work in the case of hydrogen on Ni(111).

In the quantum tunneling region, the activated behavior is characteristic of a phonon-assisted small-polaron diffusion with a rate given by [11,12]

$$D(T) \approx \frac{a_0^2}{4}\,\frac{\Delta_0^2}{\hbar}\sqrt{\frac{\pi}{4k_BTE_a}}\,\exp\left(-\frac{E_a}{k_BT}\right). \qquad (3)$$

From the activation energy and diffusivity for hydrogen, $E_{\text{quant}}(^1\text{H}) = 10.1$ kJ/mol and $D_0^{\text{quant}}(^1\text{H}) = 2.4 \times 10^{-7}$ cm^2/s, respectively, and the distance between two neighboring threefold hollow sites $a_0 = 1.49$ Å, we calculated the tunneling matrix element to be $\Delta_0 = 4.6 \times 10^{-4}$ eV. This value is between the estimate of 4.0×10^{-3} eV from the effective medium theory calculation by Puska and Nieminen and an estimate of 7×10^{-5} eV from a one-dimensional sinusoidal potential with a peak-to-peak magnitude of 2.4 kcal/mol and a periodicity of 1.49 Å [24]. The diffusion rates of deuterium increasingly deviate from those of hydrogen in the low temperature region and the crossover is not complete with the diffusion rate being as small as 2×10^{-15} cm^2/s at $T = 80$ K. This isotope effect is similar to what was observed of hydrogen in Nb and vanadium and is consistent with the quantum tunneling diffusion picture [5]. The relatively large activation energy in the phonon-assisted small-polaron tunneling region (10.1 kJ/mol) renders the onset of a conduction electron limited tunneling diffusion in the range of 3×10^{-17} cm^2/s $\sim 5.6 \times 10^{-16}$ cm^2/s. It is at least a factor of 4 smaller than the smallest diffusion rate 2×10^{-15} cm^2/s that we are currently able to measure.

We should point out that our results at temperatures below 110 K differ from the earlier observation made by Lin and Gomer using a field emission current fluctuation method [2]. From 130 to 110 K Lin and Gomer observed the similar temperature dependence for both isotopes. However, from 110 to 70 K, these authors found the diffusion rates to become almost temperature independent while in our case the rates continue to decrease with the decreasing temperature. Knowing this discrepancy, we have taken extra care to make sure that the decay of the optical diffraction signals in our measurement is indeed the result of surface diffusion and the decay rate constants indeed decrease from 110 to 65 K by using three grating periods (4.2, 0.76, and 0.38 μm) in this temperature range. We can rule out the effect of steps in this temperature range as we would observe a larger activation energy. At this moment, we do not have a satisfactory explanation for this discrepancy.

In conclusion, we have measured the diffusion rates of hydrogen and deuterium on Ni(111) from 65 to 240 K with the rates varying over 8 orders of magnitude. The temperature dependence is characterized by a crossover from one thermally activated process to another activated process at low temperatures with a smaller activation energy. Combined with the experimental evidence of the azimuthal and coverage dependence of the diffusion rates, we can conclude that the observed crossover is from a classical overbarrier hopping to a quantum underbarrier tunneling.

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*To whom all correspondence should be addressed. Electronic address: xdzhu@ucdphy.ucdavis.edu

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