Surface Diffusion of Hydrogen on Ni(100): An Experimental Observation of Quantum Tunneling Diffusion

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We studied the surface diffusion of hydrogen on Ni(100) by linearly diffracting a probe laser beam from a monolayer grating of adsorbed hydrogen. In the temperature range from 110 to 161 K, the Arrhenius plot shows a significant level off of the diffusion coefficient $D(T)$ at around 144 K. Such a deviation from the behavior of a thermally activated diffusion suggests the onset of quantum tunneling diffusion.

One of the most interesting aspects of the transport of massive particles in condensed media is quantum tunneling motion. The process is most sensitive to various interactions and their interplay. The motion of the hydrogen atom and its isotopes in solids has attracted considerable attention in the past two decades [1,2]. Because the characteristic vibrational energies of hydrogen atoms in or on a solid are much closer to the substrate phonon energies, the screening effect is expected to be much stronger. The isotope dependence of the quantum motion of hydrogen should be the strongest of all stable elements because of the large mass ratios. As chargeless particles, hydrogen atoms may be one of the best systems for investigation of transport phenomena in the strong scattering limit, which will complement the investigation on electrons and electromagnetic radiation [3-6]. Theoretical studies and indirect experimental evidences indicate that the wave functions of hydrogen atoms on metals have sufficiently large spreads that the transport and vibrational properties may behave more like band electrons [7]. Experimentally, hydrogen atoms are relatively easily dissolved into many metals [1]. They also readily adbsorb onto the surfaces of many materials [8].

However, direct experimental observation of the quantum motion of hydrogen atoms is rather scarce. The mobilities of hydrogen atoms in bulk solids have not been found other than those characteristics of thermally activated diffusions. The theories of quantum transports of hydrogen atoms such as the "small-polaron" theories and narrow-band particle models, all predicting power-law behaviors for diffusion coefficients at low temperatures, have yet to be tested against experimental observation [1,9,10].

Recently, Gomer and co-workers measured the surface diffusion coefficients $D(T)$ of hydrogen and its isotopes on W and Ni single crystals using a field-emission microscope (FEM) [11,12]. They found that the Arrhenius plots of $D(T)$ level off at temperatures as high as 130 K and that $D(T)$ exhibits large and yet reduced (from a rigid lattice model) isotope dependence, indicating the

onset of quantum tunneling motion and a large mass renormalization effect. Even more interesting is that in a large temperature range from roughly 100 down to 30 K $D(T)$ shows little temperature dependence. These results present a new case which is not yet explained satisfactorily by the existing theories [13]. On the experimental side, Gomer's reports stand alone and the progress with the field-emission microscopy has been slow. This is mainly due to the difficulties of working on materials other than refractory metals with the FEM technique which requires extremely high and often destructive electric fields.

In this Letter, we report a linear optical diffraction technique which (1) is nonevasive, (2) has the capability of measuring diffusion coefficients as small as 10^{-14} to 10^{-15} cm^{2}sec^{-1}, and (3) is versatile enough so that one can choose substrate materials based upon the virtues of their properties suitable for elucidating the physical natures of quantum tunneling instead of the applicability of the technique itself. We applied this technique to measure surface diffusion of hydrogen atoms on Ni(100). In the temperature range from 161 to 110 K, we also observed a significant level off of the Arrhenius plot of $D(T)$. This is the first independent confirmation of the results of Gomer and co-workers using a different technique.

The principles of this technique involve two experimental steps [14-16]. The first is to prepare a monolayer or submonolayer coverage grating of hydrogen on a substrate by laser-induced desorption with a pair of interfering optical pulses. The second is to probe the evolution of the grating by measuring linear optical diffractions of a weak laser beam which in our case is a 2-mW He-Ne laser. A schematic of the setup is shown in Fig. 1. The merits of the technique are ideal for the study of the surface diffusion of atoms. The preparation of monolayer gratings of adsorbates by laser-induced desorption can be applied to substrates of practically any material. Depending upon the wavelength of the excitation laser beam, the spacing $2a$ of an adsorbate coverage grating
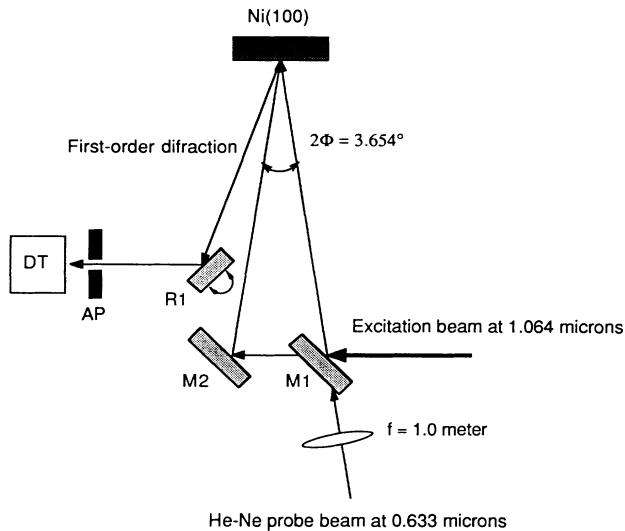
FIG. 1. Schematic of the experimental setup. M1 is a dielectric beam splitter for the excitation laser beam at 1.064 μm. The He-Ne laser beam passes through M1 with negligible reflection loss. M2 is a reflector. AP is an aperture of 0.5 mm diam. DT is a photodetector. The Ni(100) sample is situated in an ultrahigh vacuum chamber (not shown).
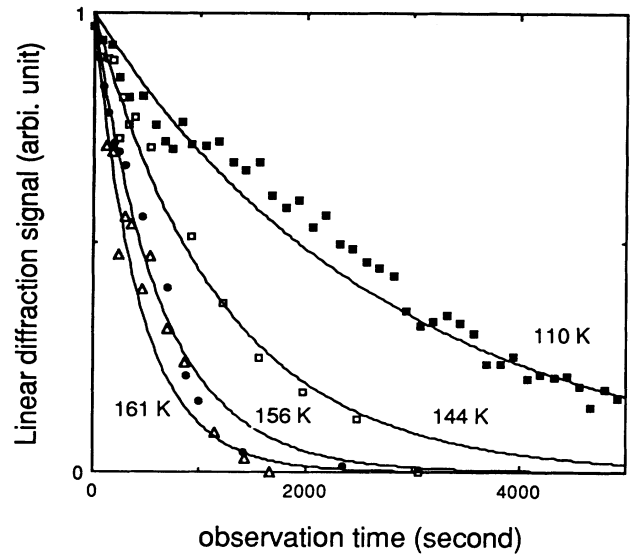

FIG. 2. Plots of linear diffraction signals $S_1(t)$ from monolayer gratings of hydrogen on Ni(100) measured at different temperatures. The solid lines are fits by single exponential functions $\exp[-\alpha(T)t]$.

can be made as small as a fraction of 1 μm, i.e., $a \sim 10^{-5}$ cm. As diffraction signals vary as $\exp[-2n^2\pi^2D(T)t/a^2]$ [15,17], with n being the diffraction order for a maximum detection time $t \sim 10^4$ sec, the minimum detectable diffusion coefficient $D(T)$ is 5×10^{-16} cm^{2}sec^{-1} if the first-order diffraction is measured, and drops down to 2×10^{-17} cm^{2}sec^{-1} if the fifth-order diffraction is measured. This covers well the range where one expects to observe the quantum tunneling diffusion. The main problem with the detection of a linearly diffracted light from an adsorbate grating is the diffusely scattered lights [16]. The latter, coming from the residual roughness of a nominally flat surface, may easily overwhelm the diffraction signals. This was first recognized and avoided by Zhu et al. who instead detected the optical and second-harmonic diffraction from the monolayer gratings of CO on Ni surfaces (the nonlinear optical diffraction, though suffering from much weaker signal strength, is almost free of diffuse scattering for centrosymmetric substrate materials) [14,15].

We recently succeeded in suppressing the linear diffuse scattering background by 4 orders of magnitude [16], so that we can detect the first-order diffracted signal with an extremely high (10^3-10^4) signal-to-background ratio. With the high signal-to-background ratio, we are able to work with much smaller coverage modulation. This is crucial for the investigation of the coverage dependence of the diffusion. Finally, the temperature rise caused by a 1-mW continuous-wave probe beam is much less than a degree. Consequently, its effect on diffusion measurements can be neglected even at liquid-helium temperatures. The low-temperature limit will be the most in-

teresting region for new physics to be discovered regarding massive neutral-particle tunneling motion.

We now present the experimental results of the diffusion of hydrogen on Ni(100). The Ni(100) single-crystal disk is polished and oriented to the (100) plane within 0.1°. The measurement is carried out under ultrahigh vacuum conditions with an operating pressure of 2×10^{-10} torr. The sample is held at a constant temperature within ± 3 K during the laser-induced desorption as well as the diffusion measurement. With the excitation wavelength $\lambda_{exc} = 1.064$ μm and the angle of incidence $\Phi = 1.827°$, the grating spacings $2a = \lambda_{exc}/(2\sin\Phi)$ are 16.6 μm. They are oriented parallel to one of the crystallographic axes in the surface. The linear diffraction measurements start within 1 min after the desorption. The average coverage of the hydrogen atom is $\theta = 0.9$. The modulation of the initial grating is $\Delta\theta \sim 0.1$. The latter was deduced from both the laser-induced desorption mass yields and the magnitudes of the diffraction signals. The first-order linear diffraction signal $S_1(t=0)$ normalized to the incident beam intensity S_i is $\sim 4 \times 10^{-8}$ from such a 10% modulated coverage grating. As a comparison, the diffuse scattering is $(4-8) \times 10^{-6}$ if no suppression schemes are used [16].

The first-order linear diffraction signals $S_1(t)$ are plotted in Fig. 2. The temperature is varied from 110 to 161 K. The fluctuation in the data is caused by the drifts in our electronic system and the mechanical system. Over the measurement time, $S_1(t)$ decay exponentially. The solid lines are fits by single exponential functions $\exp[-\alpha(T)t]$. To relate $\alpha(T)$ to the diffusion coefficient $D(T)$, we adopt the same analysis given by Zhu et al.

[15,17]. With the small initial coverage modulation $\Delta\theta \sim 0.1$, it is reasonable to assume that the optical susceptibility $\chi^{(1)}(\theta)$ varies linearly with the coverage θ, and the variation of the diffusion coefficient $D(T)$ with θ is small. In this case,

$$S_1(t) = S_1(0)\exp[-2\pi^2 D(T)t/a^2]. \qquad (1)$$

In Fig. 3, we depict the Arrhenius plot of the diffusion coefficient $D(T)$ obtained from $a(T)$. $D(T)$ shows a clear sign of leveling off at temperatures below 144 K, instead of falling on a straight line as would be the case for thermally activated diffusion [1]. The temperature range appears to cover the transition region from a thermally activated diffusion to seemingly quantum tunneling diffusion [11,12]. If we plot a straight line through the first two points measured at 161 and 156 K (see Fig. 3), the slope would yield an activation energy of $E_{\text{diff}} = 3.5$ kcal/mol, which agrees well with the measurements by Gomer, George, White, and co-workers at elevated temperatures [12,18,19]. The intercept of the line would give the thermal diffusivity $D_0 \sim 8 \times 10^{-6}$ cm^{2}sec^{-1}, which also agrees quite well with the results obtained by the above three groups. Below 144 K, $D(T)$ starts to deviate from the straight line and begins to level off to 1×10^{-11} cm^{2}sec^{-1}. This observation for the first time qualitatively confirms the measurement by Gomer and co-workers and is attributed to the prevalence of quantum tunneling diffusion [11,12]. We are in the process of extending our measured temperature down to 20 to 15 K to further determine the behavior of $D(T)$ at low temperatures. Within the errors of our measurements, the transition from the thermally activated diffusion to the plateau region appears to be not as sharp as observed by Lin and
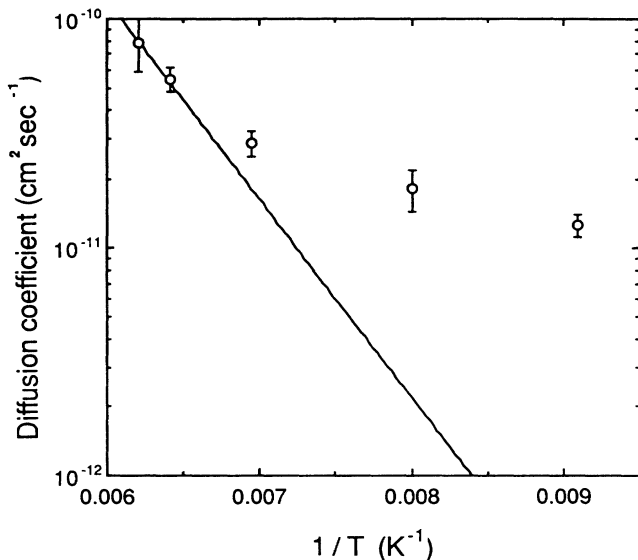

FIG. 3. Arrhenius plot of the diffusion coefficient $D(T)$ $= a(T)a^2/2\pi^2$. The solid line passes the first two data points. The slope yields an activation energy $E_{\text{diff}} = 3.5$ kcal/mol.

Gomer [12]. Furthermore, the transition begins at around 140 instead of 110 K. We note that these differences might be due to the fact that the present diffusion coefficient was measured at higher coverages, $\theta \sim 0.9$, than those in Ref. [12].

We now discuss the possible significance of the present measurement and the results of Lin and Gomer with regard to the theoretical understanding of the tunneling diffusion. Specifically, we wish to make a tentative estimate of the ground-state energy bandwidth of adsorbed hydrogen [7,9,20]. We assume that the tunneling diffusion coefficient D_{tunnel} is roughly 1×10^{-11} cm^{2}sec^{-1}. Since the average coverage is high, $\theta \sim 0.9$, a tunneling hydrogen atom travels along a potential surface which is locally periodic over no more than a few lattice spacings a_L. If we neglect the possible collective tunneling involving more than one hydrogen atom, *the diffusion is expected to be incoherent due to static disorders caused by coadsorbed hydrogen atoms* [9,20]. Within this picture, we may estimate the ground-state energy bandwidth Δ_g. The latter is roughly equal to the product of the overlap integral η over both the hydrogen tunneling coordinate and the phonon coordinates, and the potential-energy variation along the tunneling coordinate for an adsorbed hydrogen atom. For an estimate of the potential-energy variation, we use the vibrational excitation energy $\hbar\omega_H$. If the scattering rate is Γ, we expect [9,20]

$$D_{\text{tunnel}} \sim (\text{tunneling velocity})^2/\Gamma = (\omega_H a_L \eta)^2/\Gamma.$$

If Γ is mainly determined by the presence of coadsorbed hydrogen atoms, we expect $\Gamma \sim \omega_H a_L (N_s \theta)^{1/2}$. According to Auerbach, Freed, and Gomer [11], we have here assumed that the disorder energy caused by the coadsorbates varies with the hydrogen coverage as $\hbar\omega_H a_L (N_s \theta)^{1/2}$. $N_s = 1.5 \times 10^{15}$ cm^{-2} is the density of hollow sites on Ni(100). With $a_L = 3.5 \times 10^{-8}$ cm and $\omega_H \sim 10^{14}$ sec^{-1}, the bandwidth of the ground state is calculated as $\Delta_g = (\hbar/a_L)(\Gamma D_{\text{tunnel}})^{1/2} \sim 0.8$ μeV. (This result does not change significantly if we use the result of Lin and Gomer [12].) The estimated bandwidth is to be compared with the conclusion arrived at by Puska *et al.* [7]. Using the effective medium theory, they found that the energy levels of a hydrogen atom on Ni(100) are broadened to less than 1 meV for the ground state and to a few meV for the excited states. The significant broadening of the vibrational energy levels as predicted by Puska *et al.* suggests a sizable quantum-mechanical effect upon the vibrational properties. Such an effect should also affect the transport properties. We particularly note that it will be an important theoretical task to calculate the ground-state bandwidth down to μeV or even neV range. This will make a comparison with the experimental measurements much more informative. As to whether the scattering rate is truly only caused by adsorbate-adsorbate interaction, we have to await the experimental determination of the roles of surface phonons

through the isotope effect and details of the coverage dependence of D_{tunnel}. We are currently measuring the diffusion coefficient $D(T)$ for deuterium on Ni(100). By extending the measurement temperature range down to 20 to 15 K, we will be able to study the effects of surface phonons in detail.

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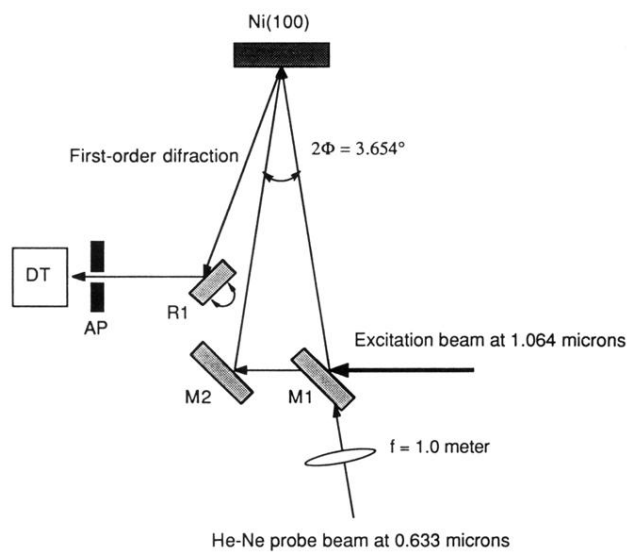[20] K. B. Whaley, A. Nitzan, and R. B. Gerber, J. Chem. Phys. **84**, 5181 (1986).

Ni(100)

First-order difraction

$2\Phi = 3.654°$

DT

AP

R1

M2   M1

Excitation beam at 1.064 microns

f = 1.0 meter

He-Ne probe beam at 0.633 microns

FIG. 1. Schematic of the experimental setup. M1 is a dielectric beam splitter for the excitation laser beam at 1.064 μm. The He-Ne laser beam passes through M1 with negligible reflection loss. M2 is a reflector. AP is an aperture of 0.5 mm diam. DT is a photodetector. The Ni(100) sample is situated in an ultrahigh vacuum chamber (not shown).