Tunneling of Hydrogen in Surface Diffusion on the Tungsten (110) Plane

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The diffusion coefficients of ^{1}H and ^{2}H on the (110) plane of W have been measured by the field-emission fluctuation method. Below 140 K ^{1}H diffusion corresponds to pure tunneling. The barrier is shown to be 0.21 eV high and ~ 0.5 Å wide, and probably corresponds to passage over the saddle formed by two nearest-neighbor W atoms. Evidence for a phase transition at 89 K (at $\theta = 0.6$) is also presented.

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Tunneling of atoms or molecules through potential barriers is often discussed but definitive experimental proof seems to be quite scarce. We present here results for the diffusion of hydrogen and deuterium on the (110) plane of tungsten which can only be interpreted in terms of H atom tunneling at $T < 140$ K. These experiments also provide an estimate of the width of the potential barrier, a quantity not obtainable from measurements of thermally activated diffusion. Finally, they explain the observation of Polizotti and Ehrlich[1] that H diffuses into the (110) plane at 78 K, while extrapolation of the thermally activated diffusion results of Gomer, Wortman, and Lundy[2] suggest that diffusion should be negligible at this temperature.

Measurements were carried out by means of the field-emission current-fluctuation method described previously in some detail.[3] It consists of measuring the time autocorrelation function of current fluctuations from a small region ($r_0 \sim 100$ Å) in the center of the (110) plane when the emitter is covered with adsorbate under conditions where the latter is mobile. Over the small probed region, appreciable adsorbate density fluctuations occur and generate corresponding current fluctuations. The mean relaxation time for buildup or decay of fluctuations is $\tau_0 = r_0^2/4D$, D being the adsorbate surface diffusion coefficient. A comparison of theoretical and experimental correlation functions allows determination of τ_0 and thus of D.

The apparatus used in the present experiments consisted of a glass field-emission tube, attached to a stainless-steel ultrahigh-vacuum system pumped by ion and Ti sublimation pumps to a base pressure of 2×10^{-11} Torr. Detection of the probehole current was accomplished by postaccelerating the electrons passing through the probehole to 10 kV, allowing them to impinge on a P-47 phosphor screen and amplifying the light signal with a phototube. The photocurrent was amplified with a wide-band amplifier. The signal was then passed through a Rockland 452 filter and fed into a Honeywell Model SAI-43A correlator.

Figure 1 shows a plot of D vs $1/T$ for ^{1}H at a coverage of $0.6\theta_{\max}$. This coverage was determined from the work-function decrement. For $200 \geq T \geq 143$ K, ln$D$ decreases linearly with $1/T$ as expected for activated diffusion. In this regime $E_{\rm dif} = 4.80 \pm 0.3$ kcal/mole (0.21 eV) and $D_0 = 5 \times 10^{-5}$ cm^2/sec. $E_{\rm dif}$ is in good agreement with the value found in this laboratory in 1957 by a

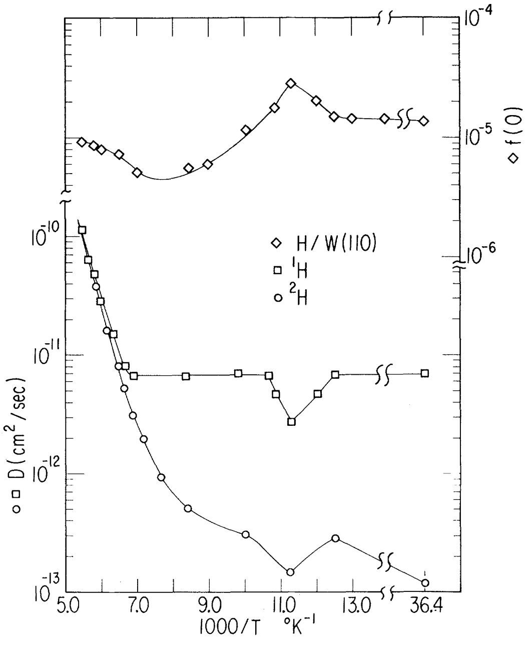

FIG. 1. Plots of ln$D$ vs $1/T$ for ^{1}H and ^{2}H diffusion on the W(110) plane. Also shown is $f(0)$, the correlation function at $t = 0$.

different method,[2] 6 ± 1 kcal at $\theta = 1$. Below 140 K, D is constant to 28 K, except for a dip near 90 K. In this regime the fit of the experimental to the theoretical correlation functions is still excellent (Fig. 2), indicating that diffusion is occurring. As already mentioned, additional evidence for diffusion at low temperature also comes from the work of Polizotti and Ehrlich.[1] These authors found that H does not chemisorb dissociatively on a perfect (110) plane of a tungsten field emitter but reaches it by diffusion from its vicinals where H_2 adsorbs dissociatively. We have confirmed their observation by dosing the emitter at 78 K and noting a current change on the (110) plane with time, resulting from H diffusion into the plane.

If diffusion observed below 140 K is in fact the result of H tunneling, there should be a very strong isotope effect, since the tunneling probability P is of the general form

$$P \propto \exp[-2(2m/\hbar^2)^{1/2} \int_{x_1}^{x_2} (V - E\,dx)^{1/2}]. \qquad (1)$$

The results for ^{2}H diffusion shown in Fig. 1 bear this out. Activated diffusion occurs to lower temperatures than for ^{1}H, and the limiting value of D for pure tunneling is ~ 1/57 of that for ^{1}H. These results and Eq. (1) allow a determination of P and D_0 in the tunneling regime and yield $P = 8.69\times 10^{-5}$ and $D_0 = 7.83\times 10^{-8}$ cm^2/sec for ^{1}H. Presumably the value of D_0 for tunneling is much less than for thermally activated diffusion because the barrier penetration probability is a sensitive function of the adatom's position and momentum components transverse to the tunneling direction. If the barrier height is taken as 0.21 eV from the thermal part of the diffusion regime, the barrier width l_0 can be estimated from P and Eq. (1). For a triangular barrier $l_0 = 0.70$ Å while for a rectangular barrier $l_0 = 0.47$ Å. It will be shown in a subsequent publication that the rather sharp transition from thermal activation to tunneling for ^{1}H and the less sharp one for ^{2}H can most easily be explained by assuming a rectangular shape. Thus the present results provide information not only on the height but also on the width of the potential seen by an H atom. The small value of l_0 suggests that the rate-limiting step in diffusion corresponds to passage from a_1 via C to a_2 in Fig. 3, by barrier climbing or by tunneling, with H atoms moving freely in the region a_1-b-a_3. The latter assumption is also in accord with the positive dipole moment of H on W(110).

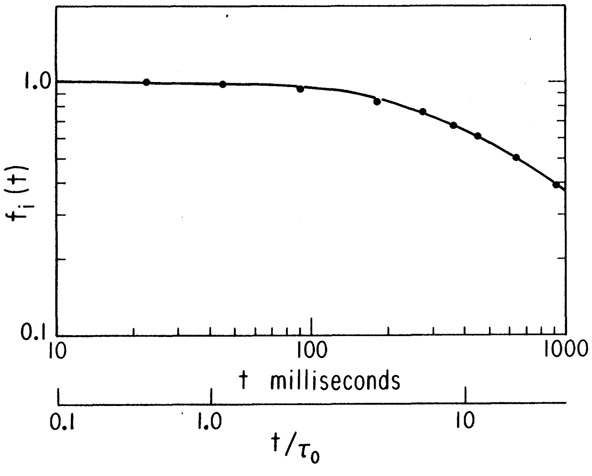

FIG. 2. Comparison of theoretical (solid line) and experimental (solid data points) correlation functions for ^{1}H diffusion on the W(110) plane at 27.5 K. The theoretical curve was determined from Eq. (20) of Ref. 3 with the appropriate field-emission parameters for hydrogen.

The activation energy for ^{2}H diffusion is 4.85 ± 0.15 kcal, i.e., essentially indistinguishable from that of ^{1}H within the precision of our results. Since $\Delta E_{\text{dif}} = \frac{1}{2}h\nu(1 - 1/\sqrt{2})$ we can conclude that $\nu \leqslant 3\times 10^{13}$ sec^{-1} for ^{1}H diffusion. Improved precision of these results should allow putting narrower limits on ν.

Figure 1 also shows the mean square fluctuation, $f(0)$, which is a measure of the two-dimensional compressibility of the adsorbed phase.[3] $f(0)$ shows a strong oscillation near 90 K both for ^{1}H and ^{2}H. We believe this to be eivdence for a phase transition, possibly order-disorder. The dips in D near this temperature probably correspond to critical slowing.

The present experiments also have bearing on the behavior of adsorbed hydrogen on interstellar particles, since they demonstrate diffusion even at very low temperatures and provide a mechanism for it.

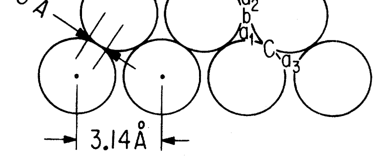

FIG. 3. Diagram of the W(110) plane, with some positions and spacings designated.

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[1] R. S. Polizzotti and Gert Ehrlich, J. Chem. Phys. 71, 259 (1979).

[2] R. Gomer, R. Wortman, and R. Lundy, J. Chem. Phys. 26, 1147 (1957).

[3] J.-R. Chen and R. Gomer, Surf. Sci. 79, 413 (1979).