Observation of Jump Diffusion of Isolated Sodium Atoms on a Cu(001) Surface by Helium Atom Scattering

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The diffusion of sodium adatoms on a Cu(001) surface has been studied with quasielastic helium atom scattering. A jump mechanism was found with activation energy 51 meV, jump length 2.56 Å, and jump attempt frequency v_0 0.53 THz. The adatom vibrational frequency parallel to the surface is measured to be 1.23 THz. The data are interpreted with the aid of a realistic molecular-dynamics simulation which reveals that v_0 is governed by the rate of energy exchange between the adatoms and the substrate, and not, as transition state theory would predict, by the vibrational frequencies of the adatom.

The two-dimensional diffusion of atoms on surfaces is an important elementary process in surface chemistry and provides an ideal model system for studying activated processes [1]. In the experiments to be reported here we have used helium atom scattering to identify a single-jump diffusion mechanism, measure the activation energy, and even determine the related vibrational frequencies of adatoms diffusing on a well defined single-crystal surface. The present detailed results make it possible to carry out a direct comparison with a realistic molecular-dynamics simulation of the diffusing adatoms' motion which confirms the interpretation of the data and provides information on the role of energy dissipation and multiple jumps.

The technique used here relies on the fact that helium atoms have large diffuse scattering cross sections from defects on a crystal surface [2]. It has been shown both theoretically [3,4] and experimentally [5] that the diffuse "elastic" scattering from mobile defects has an energy broadening due to the finite residence time of the defect at a particular surface site. From the dependence of this broadening on the scattering wave vector it is possible to determine the microscopic surface diffusion mechanism. The first such experiments were performed on a premelting lead surface [5] just below the melting point where neither the concentration of the diffusing atoms nor the surface structure are well defined [6]. In this new experiment a known small concentration of sodium adatoms ($\theta = 0.1$) was evaporated onto a clean Cu(001) surface and the angular distributions of elastically scattered helium atoms were used to show that the sodium adatoms are widely separated and interact only weakly with each other by long-range dipole-dipole repulsive forces [7] of the type predicted by Kohn and Lau [8]. The diffusion measurements were made over a range of temperatures far below the bulk copper melting point, where only relatively small substrate vibrations are expected.

The theory of the quasielastic scattering phenomena is described elsewhere [3–5,9,10]. If diffusion proceeds by single jumps with jump vectors $\{j\}$ and mean jump frequencies $\{v_j\}$, then the quasielastic peak shape is a Lorentzian with an energy FWHM

$$\Delta E (\Delta \mathbf{K}) = 2\hbar \sum_j v_j [1 - \cos(\Delta \mathbf{K} \cdot \mathbf{j})], \tag{1}$$

where $\Delta \mathbf{K}$ is the component of the scattering wave vector parallel to the surface [10]. The periodic behavior of ΔE with $\Delta \mathbf{K}$ arises because if, for a particular jump, $\Delta \mathbf{K} \cdot \mathbf{j}$ is an even multiple of π then the adatoms scatter with an effectively identical phase before and after a jump and the helium atoms are "unaware" that jumps are occurring and consequently there is no quasielastic broadening contribution. Between these equal-phase conditions on $\Delta \mathbf{K}$, there is always a change of the scattering phase after a jump of the adatom, and the elastic peak is correspondingly lifetime broadened.

The interpretation relies on Vineyard's convolution approximation, which models the behavior of the total system in terms of that of an individual atom, and so is only valid if the adatoms move independently of each other. To test the Vineyard assumption the Kohn-Lau potential [7,8] is used to model the effect of removing one of six symmetrically placed nearest neighbors. The activation energy for jumps towards the removed adatom is reduced by only 1.0 meV, which is small in comparison with the activation energy and increases the jump probability by only 4% in that direction. Thus at these relatively large adatom separations the coupling of adatom motions is indeed weak and the Vineyard approximation should apply.

The 90° fixed angle helium atom scattering apparatus and Cu(001) cleaning procedure are described elsewhere [7]. The specularly scattered helium intensity was used to measure the sodium coverage θ, which is expressed as a fraction of that of the one monolayer, $c(2\times2)$, structure [7]. The quasielastic peak shape was measured by performing time-of-flight measurements at an incident beam energy $E_i = 15.15$ meV with an instrumental resolution of 0.55 meV (FWHM). As can be seen from Fig. 1(b), at low surface temperatures (T_s) the shape of the diffuse elastic peak is dominated by the experimental resolution, but as T_s is raised, the quasielastic peak is
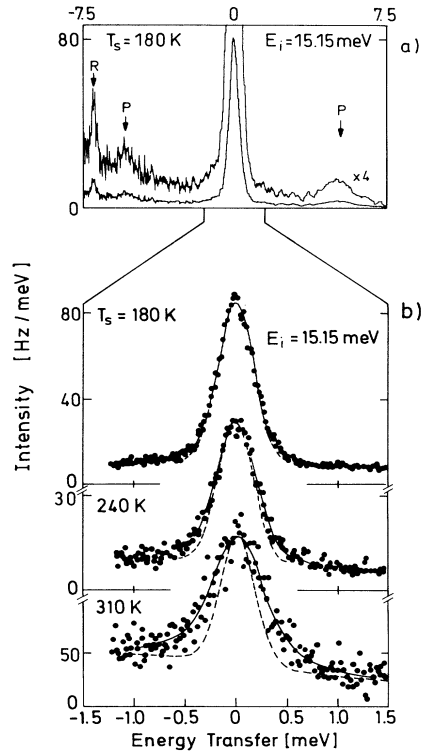
FIG. 1. Time-of-flight distributions (converted to an energy scale) of helium atoms scattered along the [100] azimuth from a Cu(001) surface with a low coverage of sodium atoms ($\theta=0.1$). E_i is 15.15 meV and ΔK is 1.74 Å^{-1}. (a) Wide energy range showing peaks due to energy exchange with the surface Rayleigh phonon (R), and the surface parallel sodium atom vibration mode (P). (b) Restricted energy range showing the T_s dependence of the quasielastic peak shape. Dashed curves: instrument function. Solid curves: peak shape fit obtained by convoluting the instrument function with a Lorentzian broadening.

clearly broadened. In order to extract the diffusion induced broadening a least-squares fit was performed with a Lorentzian [5,10] of variable width convoluted with the instrument function and superimposed on a cubic background to account for multiphonon processes.

The dependence of ΔE on ΔK in the [100] direction was obtained from time-of-flight (TOF) measurements for various incident angles at $T_s = 200$ K and $T_s = 300$ K. As can be seen from Fig. 2, the data are characterized by a broadening which is zero at $\Delta K = 0$, rises to a maximum at around $\Delta K = 1.7$ Å^{-1}, and then remains approximately constant for $T_s = 200$ K and for $T_s = 300$ K drops slightly. This behavior contrasts with that expected for continuous diffusion, namely, $\Delta E \propto (\Delta K)^2$, and points to a jump diffusion mechanism [5,10]. The position of the maximum is consistent with jumps of length $a = 2.56$ Å between fourfold hollow sites on the surface which would have jump vectors of $(a/\sqrt{2})[1,1,0]$ and $(a/\sqrt{2})[-1,1,0]$ (Fig. 2, inset). In Fig. 2 dashed and solid lines show the
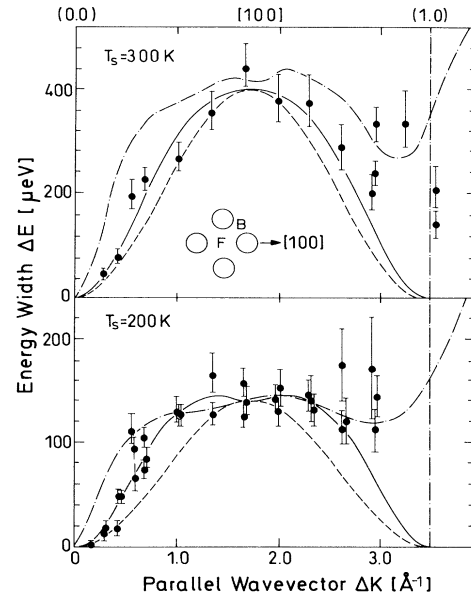

FIG. 2. Wave vector dependence of the quasielastic peak energy broadening in the [100] direction for helium atoms, $E_i = 15.15$ meV, scattered from sodium adatoms ($\theta=0.1$) on a Cu(001) surface. Dashed curve: fit for single jumps between fourfold sites. Solid curve: single jumps with an additional fraction of double jumps of 0.16 at 300 K and 0.32 at 200 K. Dash-dotted line: broadening predicted by molecular-dynamics simulation. Inset: Location of fourfold (F) adsorption site and twofold transition state bridge site (B) with respect to the first copper surface layer.

$\Delta E(\Delta K)$ given by Eq. (1) for single and single plus a fraction x of double jumps, respectively, where x is 0.32 for $T_s = 200$ K and 0.16 for $T_s = 300$ K. The addition of double jumps improves the fit in the region $0 < \Delta K < 1.74$ Å^{-1}. However, the zero broadening predicted at $\Delta K = 3.48$ Å^{-1} is not observed. The molecular dynamics model described below shows that this can be explained by the motion of the adatoms about their mean positions which blurs the definition of a "jump length."

Figure 3 shows an Arrhenius plot of the maximum energy broadening (at $\Delta K = 1.74$ Å^{-1}) against the reciprocal of the surface temperature. The straight line shows that the diffusion is an activated process with a mean single jump frequency in one of the two possible directions given by

$$\nu_j = \nu_0 \exp(-E_d/kT_s), \qquad (2)$$

where ν_0 and E_d have best fit values of 0.53 ± 0.2 THz and 51 ± 6 meV, respectively. The measured value of E_d is unusually low for surface diffusion, values of 0.12 to 1.0 eV being more typical [1], and explains why diffusion is fast enough to be seen with helium scattering at these relatively low temperatures. Small activation energies have also been found in recent *ab initio* calculations for the diffusion of Na on the Al(111) surface, which showed
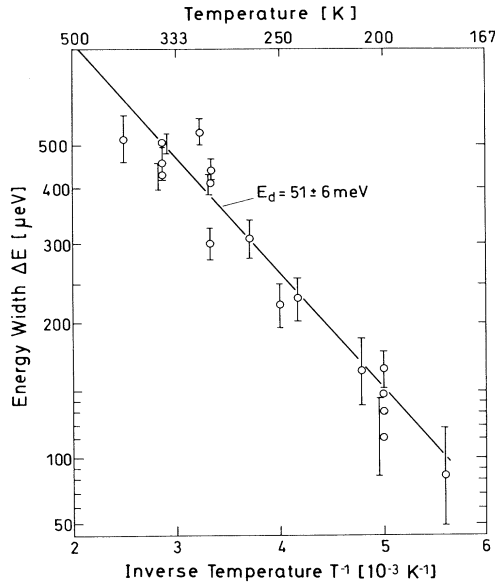
FIG. 3. Arrhenius plot of the measured energy width at $\Delta K = 1.74$ Å^{-1} for the quasielastic peak in TOF spectrum of helium atoms, $E_i = 15.15$ meV, scattered from sodium adatoms ($\theta = 0.1$) on a Cu(001) surface in the [100] direction.

that the activation energy should be less than 30 meV [11].

We have also performed a molecular-dynamics simulation of an adatom's motion. The substrate was represented by four layers of 8×8 freely moving copper atoms on a fixed fifth layer with cyclic lateral boundary conditions. The lattice was assumed to be harmonic with a single nearest-neighbor force constant of 28 N/m obtained from a fit to the bulk phonon dispersion curves [12]. The interaction of the sodium with the copper was modeled with a pairwise Morse potential, $V(r) = V_0\{1 - \exp[-\beta(r - r_0)]\}^2$, summed over Cu atoms until convergence at a distance of 4 times the Cu-Cu separation. The values of V_0, β, and r_0 were determined to be 0.135 eV, 0.875 Å^{-1}, and 3.30 Å by fitting the estimated values of the binding energy, 2.5 eV [13] (fitted value 2.35 eV), the height of the sodium adatom above the first copper layer, 2.2 Å [13] (fitted value 1.8 Å), the measured frequency of sodium adatom vibration perpendicular to the surface, 4.5 THz [14] (fitted value 3.8 THz), the activation energy as given above, 51 meV (fitted value 49 meV), and the frequency of the parallel adatom vibration v_x, 1.23 THz (fitted value 1.34 THz), which we have measured for the first time [15] [Fig. 1(a)]. Despite the fact that the Morse potential is overdetermined (three variables, as opposed to five data points), the rms deviation from the five experimental measurements is only 13%, suggesting a reasonable fit to the true potential. The simulation is started by giving each atom a random kinetic energy from a Boltzmann distribution in each of the coordinate directions, and 500 ps runs performed for temperatures

between 200 and 300 K. The form of the simulated quasielastic peak is obtained by convoluting the instrument function with the structure factor, which is obtained as the average over a number of runs of the square of the Fourier transform with respect to space and time of the atom's position [9]. The peak shape is then analyzed in the same way as the experimental data in order to give a direct comparison between the molecular dynamics simulation and the quasielastic scattering measurements. The resulting dependence of the energy broadening on ΔK is shown as a dash-dotted line in Fig. 2, from which it can be seen that good agreement is obtained with the experimental results, not only in functional form, but in absolute magnitude. The only failure of the model is that it predicts a small fraction of jumps over three or more lattice spacings, which produces a more rapid initial rise of ΔE with ΔK than is experimentally observed. These multiple jumps probably arise because no account has been made of the damping effects caused by the electron-hole pair creation induced by the moving, partially charged sodium adatoms. The value of v_0 obtained from an Arrhenius plot of the simulated jump rate is 0.56 THz, in excellent agreement with the experimental value of 0.53 ± 0.2 THz. The agreement of the model with the data is surprisingly good and confirms the interpretation that the sodium diffuses along the surface predominately by single jumps from site to site.

It is now interesting to compare the experimental jump rate with that predicted by transition state theory, which is widely used in theoretical estimates of diffusion rates [16]. In essence the theory predicts that the preexponential factor for jumps in a particular direction is given by

$$v_0^{\text{TST}} = \frac{2kT_s}{h} \frac{Q^*}{Q^0}, \tag{3}$$

where Q^0 and Q^* are the partition functions in the ground and transition states. (The factor 2 arises because positive and negative jumps in a particular direction are included in v_0.) In the harmonic approximation, and for temperatures $T_s \gg hv_x/k$ the partition functions are determined by the vibrational frequencies of the adatom. If these are assumed comparable in the ground and transition states then v_0^{TST} should be approximately equal to $2v_x$ [16], i.e., 2.46 THz, a value 4.6 times greater than observed here. As a crude approximation the agreement might be regarded as satisfactory, although the discrepancy is more than is expected to arise from experimental errors and approximations in the theory. As first noted by Kramers [17], deviations from transition state theory are expected if the rate of energy exchange between substrate and adatom is so slow that an equilibrium population of the transition state cannot be maintained. Under these conditions the effective attempt frequency is governed by the rate of energy exchange with the substrate rather than the adatom vibrational frequency. A consideration of the adatom energy autocorrelation func-

tion, $\langle E(t)E(t-t_0)-\langle E(t)\rangle^2\rangle$, predicted by the simulation indicates that the characteristic time for energy exchange between the adatom and the substrate at 300 K is 1.25 ps [18]. This is 50% longer than the vibrational period (0.81 ps) and suggests that a low rate of energy exchange with the surface may indeed be the cause of the deviation from the transition state theory prediction.

Summarizing, we have used quasielastic helium atom scattering to show that sodium adatoms diffuse on the Cu(001) surface by a jump mechanism with predominantly single steps of 2.56 Å, which corresponds to the separation of the fourfold hollow sites, an activation energy of 51 meV, and an effective jump attempt frequency $v_0 = 0.53$ THz. The sodium atoms are shown to be far enough apart for it to be unlikely that correlations of the atomic motions have an appreciable effect. v_0 is significantly lower than predicted by transition state theory, the drop being due to a low rate of energy transfer between the substrate and the sodium atom.

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