Nothing Moves a Surface: Vacancy Mediated Surface Diffusion

R. van Gastel,[1] E. Somfai,[2] S. B. van Albada,[1] W. van Saarloos,[2] and J. W. M. Frenken[1]

[1]*Kamerlingh Onnes Laboratory, Universiteit Leiden, P.O. Box 9504, 2300 RA Leiden, The Netherlands*
[2]*Instituut-Lorentz, Universiteit Leiden, P.O. Box 9506, 2300 RA Leiden, The Netherlands*
(Received 8 September 2000)

We report scanning tunneling microscopy observations, which imply that *all* atoms in a Cu(001) surface move frequently, even at room temperature. Using a low density of embedded indium "tracer" atoms, we visualize the diffusive motion of surface atoms. Surprisingly, the indium atoms seem to make concerted, long jumps. Responsible for this motion is an ultralow density of surface vacancies, diffusing rapidly within the surface. This interpretation is supported by a detailed analysis of the displacement distribution of the indium atoms, which reveals a shape characteristic for the vacancy mediated diffusion mechanism that we propose.

Atomic rearrangements on low-index surfaces are often thought to predominantly take place at steps, which serve as sources and sinks for adatoms. The diffusion of adatoms along or between steps leads to characteristic step fluctuations. Also adatom and vacancy islands are known to move via rearrangements at their perimeter. Many STM studies have been devoted to the mobility of surfaces. Most of these have focused on the motion of steps [1–3], islands [4], or adsorbates [5]. Recently it has been proposed that surface vacancies are responsible for mass transport between adatom islands on Cu(001) [6]. Unfortunately, there are no experimental techniques available with both the spatial and the temporal resolution necessary to follow the diffusion of naturally occurring vacancies in a low-index metal surface.

Indium which is deposited on Cu(001) has been found to modify the epitaxial growth of copper on this surface. Its presence results in layer-by-layer growth instead of rough three-dimensional growth [7]. After deposition, the indium atoms proceed to steps on the copper surface [8,9]. At temperatures just below room temperature they are incorporated in the outermost layer on substitutional terrace sites. In this study we have used indium atoms that are embedded within the first layer of a Cu(001) surface to monitor the diffusion of surface atoms [10]. Our observations lead us to conclude that surface vacancies are responsible for the mobility of the indium and that this low-index metal surface is far from static, even at room temperature.

The experiments were performed with a variable temperature scanning tunneling microscope (STM) [11] in ultrahigh vacuum (UHV). A Cu single crystal of 99.999% purity was mechanically polished parallel to the (001) plane [12]. Prior to mounting the crystal in the UHV system we heated it in an Ar/H_2 atmosphere to remove sulfur impurities. The sample surface was further cleaned in UHV by several tens of cycles of sputtering with 600 eV Ar ions and annealing to 675 K. After approximately every fifth cycle the surface was exposed to a few Langmuir of O_2 to remove carbon from the surface. STM images showed a well-ordered surface with terrace widths up to 8000 Å. Small quantities of indium were deposited on the surface from a Knudsen cell.

The starting point of the observations is shown in Fig. 1. At room temperature we have deposited 3% of a monolayer of indium on the Cu(001) surface. The STM image shows a region around an atomic step, separating two flat terraces of the copper surface. The image was taken 42 min after deposition and shows that most indium atoms are within 150 Å from the step. From the apparent height of 0.4 Å of the indium atoms, we infer that they are embedded within the first copper layer. What we know from lower-temperature STM experiments is that a newly deposited indium atom first "hops" over the surface until it encounters a step. At the step it enters the outermost copper layer (either on the upper or on the lower side of the step), after which it diffuses away from the step, while remaining embedded within the copper surface layer.
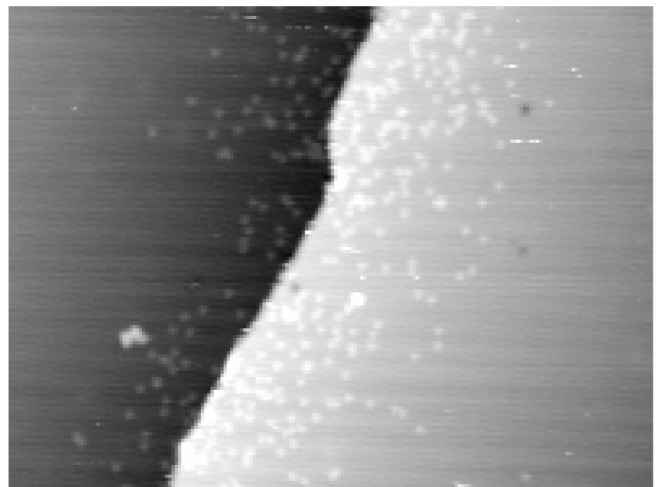

FIG. 1. A 548×409 Å^2 STM image of a step on a Cu(001) surface, taken 42 min after deposition of 0.03 ML of indium at room temperature. Embedded indium atoms show up as bright dots. The image shows a high density of embedded indium atoms near the step ($I_t = 0.1$ nA, $V_t = -0.70$ V).

We follow the diffusion of the embedded indium atoms in the copper terrace by making a series of images of the same area on the copper surface to form an STM movie of the motion [13]. To our initial surprise, we found that the indium atoms move via long jumps of more than a single lattice spacing, separated by long time intervals [14]. In addition, the movies show that there is a strong tendency for nearby indium atoms to jump at the same time. Figure 2 illustrates this peculiar motion with a set of three images taken from a movie measured at 320 K. From the STM movies we have measured the distribution of jump lengths of the embedded indium atoms, which has been plotted in Fig. 3. Note that there is a significant probability for the indium atoms to make jumps as far as five lattice spacings.

The long jumps and the high probability of nearby indium atoms to jump simultaneously suggest strongly that diffusion of the indium is mediated by another particle, which diffuses so rapidly that it remains invisible to the STM. The scenario that we propose is that the indium moves over several lattice spacings during a multiple encounter with a single assisting particle by changing places several times with that particle. The two obvious candidates for this particle are adatoms (copper atoms on top of the surface layer) and vacancies (missing atoms in the outermost copper layer). We can rule out the first possibility on the basis of Fig. 1. If an indium atom were to change places with an adatom, it would thereby become an adatom itself. We know from Fig. 1 and from other observations that indium adatoms rapidly hop over the outermost copper layer to the steps, without entering the copper surface directly. This means that if an embedded indium atom would trade places with a copper adatom, it would immediately disappear from the STM image and reappear somewhere at the step, which is definitely not what we observe.

Figure 4 illustrates how a single surface vacancy can displace an atom in the outermost copper layer, either an indium or a copper atom, over several lattice spacings. In this mechanism, the length of the long jumps of the indium atoms depends on the average number of times that a single
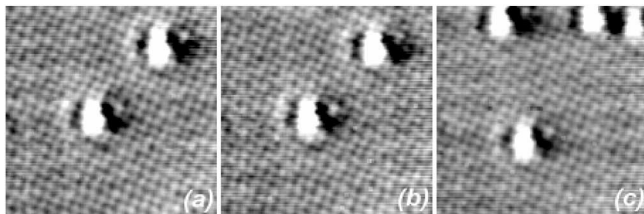
vacancy changes places with an indium atom, and we associate the frequency of the (long) indium jumps with the frequency with which the indium is encountered by new vacancies. We have measured the distribution of time intervals between consecutive jumps (see Fig. 5). The waiting time distribution is purely exponential, from which we infer that individual long jumps are uncorrelated in time and are therefore caused by different vacancies, independently formed at random times. The fact that a single vacancy will usually encounter various In atoms, naturally explains the tendency for nearby indium atoms to jump at the same time.

The fact that we never see individual vacancies in the STM images and the fact that the STM movies do not resolve the elementary steps in a multi-lattice-spacing jump need not surprise us. Using the embedded atom model (EAM), we estimate that the formation energy of a vacancy in the Cu(001) surface is 0.51 eV and that the activation energy for a surface atom to exchange with the empty site, and thereby move the vacancy, amounts to 0.29 eV [15]. Based on these estimates, we expect that at room temperature only one surface atom out of roughly 6×10^9 is missing, and that each empty site changes position with a high frequency, on the order of 10^8 Hz. These numbers are typical for low-index metal surfaces and illustrate why it is so difficult to see the vacancy diffusion at all. At low temperatures, where vacancy motion would be slow enough to be followed by an inherently slow instrument such as the STM, the probability of finding a vacancy is hopelessly close to zero. At temperatures high enough for the surface to contain a sufficiently high density of vacancies, the vacancies move much too fast to be imaged at all.

In order to obtain a quantitative understanding of the jump vector distribution of the embedded indium atoms, we performed a numerical calculation as well as a continuum approximation, according to the following model:

FIG. 2.   Three 50×50 Å^2 STM images selected from a movie measured at RT illustrating the unusual diffusion of embedded indium atoms. In the time interval of 160 s between images (a) and (b), no diffusion of the embedded indium atoms has taken place. In image (c), taken 20 s later, a diffusion event has taken place. Both indium atoms present in images (a) and (b) have moved over several lattice spacings and two more indium atoms have jumped into the imaged region ($I_t = 0.9$ nA, $V_t = -0.58$ V).
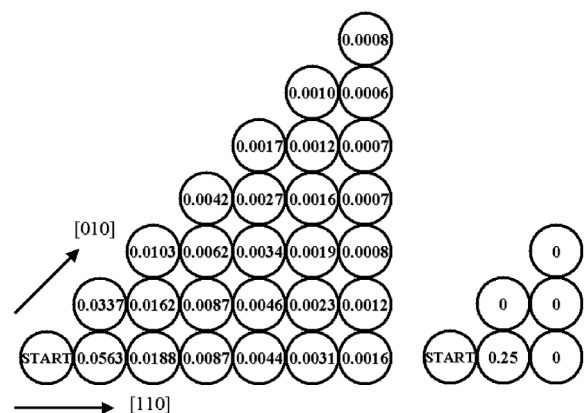

FIG. 3.   The distribution of jump vectors measured from STM movies at 320 K. Plotted is the probability for jumps of an indium atom from its starting position to each of the shown nonequivalent lattice sites. To illustrate the unusual diffusion behavior, the expected jump vector distribution for the case of simple hopping is plotted to the right.
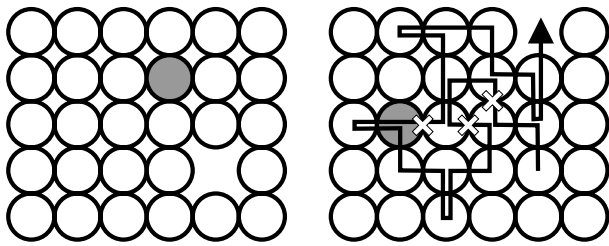
FIG. 4.   An example diffusion event which leads to a multi-lattice spacing displacement of the indium atom. The indium-vacancy exchanges are marked in the figure with crosses to show the pathway of the indium between its beginning and end points.

The Cu(001) surface is a finite $l \times l$ square lattice, with copper atoms at the lattice sites; the boundary of the lattice corresponds to the steps. One copper atom at the center of the lattice is replaced by indium, and a vacancy is released one atomic site next to it. The vacancy performs a biased random walk, its hopping probabilities to the four different directions from each site are set from the diffusion barriers calculated using the EAM potentials [15].

The vacancy displaces the atoms in its path, including the indium atom. When the vacancy arrives at the boundary of the lattice, it is annihilated (it recombines at the steps). At this moment the displacement of the indium atom is evaluated, and the whole process is repeated for the next vacancy to acquire the distribution of the In jump vectors.

For the case of equal diffusion barriers and infinite lattices, this problem has been solved analytically [16]. Although the results in some limits are quite similar to our continuum solution (see below), the equal-barrier results are not directly applicable to the case of indium in copper. Instead of moving isotropically, the vacancy neighboring the indium atom has a much stronger preference to jump towards the indium than to other directions. On the basis
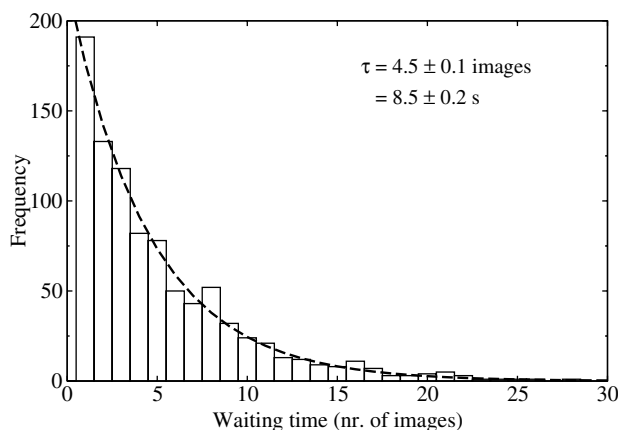

FIG. 5.   Time-interval statistics for subsequent jumps of individual indium atoms, measured from STM movies at 320 K with a time per image of 1.88 s. The dotted curve is an exponential fit with a time constant $\tau = 8.5$ s.

of the values of the barriers, as calculated with the EAM, we estimate the direct return jump to be a factor of 10^6 more probable than a jump in any of the other three directions. This difference has a significant impact on the indium jump distribution: the mean square displacement is about $2.2\times$ larger than in the equal-barrier case, while the overall shape of the distribution is about the same [15].

It is computationally beneficial to separate the motion of the vacancy from that of the indium atom. For the indium atom, only the *direction* of the next return of the vacancy is of importance, rather than the vacancy path which leads to it. Therefore it is enough to calculate the probabilities of first return of the vacancy to the indium atom from the four different directions after it left the indium in one direction, as well as the probability of the vacancy's recombination before return. The In atom performs a random walk, where the direction of each step with respect to the previous one is chosen according to these return probabilities, and after each step the walk terminates with the vacancy's recombination probability. This procedure yields the proper final jump distribution, while giving up the time information, which is experimentally irrelevant anyway. (This approach is valid under the assumption that the environment of the indium does not change with the steps it takes, i.e., it is still close to the middle of the lattice.)

In practice, instead of using Monte Carlo–type methods, we enumerate the possible trajectories to obtain the return probabilities and the indium jump vectors; this provides superior convergence. The following numerical values were calculated for $T = 320$ K (EAM barriers) and for a lattice size $l = 401$, which corresponds to the typical experimental terrace width of 1000 Å. After leaving the indium atom to the right, the vacancy's return probabilities from the four directions are the following: $p_{\text{right}} = 1 - 2.4 \times 10^{-7}$, $p_{\text{up}} = p_{\text{down}} = 1.1 \times 10^{-7}$, $p_{\text{left}} = 4.2 \times 10^{-9}$, and the vacancy recombines with probability $p_{\text{rec}} = 1.1 \times 10^{-8}$. These values depend very weakly on the lattice size l. The fact that two dimensions is the marginal dimension for the return problem of a random walker implies a logarithmic l dependence of p_{rec}. The root mean square jump length of the In atoms is 3.5 nearest neighbor spacings. The full distribution of the In jump lengths is plotted in Fig. 6 together with the experimental values. The quantitative agreement supports our interpretation of the mechanism of the indium diffusion.

We now show that a simple continuum approach to this problem gives a quite good approximation to the jump statistics. Let us denote the probability of "mobile indium" at position $\mathbf{r}$ with $\varrho(\mathbf{r}, n)$, where the counter n measures the number of times the vacancy returns to the In atom. The indium is considered "mobile" while the vacancy is still around, and "immobile" after the vacancy has recombined. The effective diffusion equation for $\varrho(\mathbf{r}, n)$ is

$$\frac{\partial \varrho(\mathbf{r}, n)}{\partial n} = D_{\text{eff}} \nabla^2 \varrho - \epsilon \varrho. \tag{1}$$
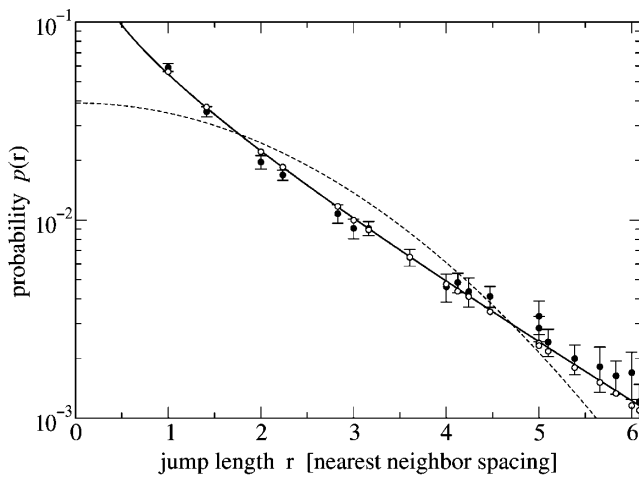
FIG. 6. The distribution of the jump lengths of the indium atoms at 320 K. Filled circles correspond to the experimental values, open circles are from the numerical calculation, and the solid curve is the isotropic continuum (Bessel) approximation. For comparison, the dashed curve shows the best-fit Gaussian distribution.

The first term corresponds to the vacancy mediated diffusion of the mobile indium (isotropic, in this continuum approach), and the second term to the recombination of the vacancy, which makes the indium immobile. The solution in the case of Dirac-delta initial conditions at the origin is

$$\varrho(\mathbf{r}, n) = \frac{1}{4\pi D_{\text{eff}} n} e^{-(r^2/4D_{\text{eff}} n) - \epsilon n}. \tag{2}$$

We are interested in the final, immobile distribution of In:

$$p(\mathbf{r}) = \int_0^\infty \epsilon \varrho(\mathbf{r}, n)\, dn = \frac{1}{2\pi} \frac{\epsilon}{D_{\text{eff}}} \text{K}_0\!\left(\frac{r}{\sqrt{D_{\text{eff}}/\epsilon}}\right), \tag{3}$$

where K_0 is the modified Bessel function of order 0. The parameters can all be calculated: ϵ is the recombination probability p_{rec} of the vacancy, and the effective diffusion coefficient D_{eff} can be calculated from the return probabilities, as will be discussed in detail elsewhere [15]. Equation (3) gives a good approximation of the jump length distribution (Fig. 6), without any fitting parameter.

Finally, we evaluate the resulting diffusion coefficient D for copper terrace atoms. Using numerical calculations, we calculate that the multiple encounter of a single vacancy with a copper atom in a clean copper surface results in a root mean square displacement of the atom of 1.6 nearest

neighbor spacings. Multiplying this number with the observed average jump rate of the embedded indium atoms (Fig. 5), we obtain $D = 0.42$ Å$^2 \cdot$ s^{-1}.

In conclusion, the diffusive motion of the indium atoms can be explained by the presence of a low density of extremely mobile vacancies in the first layer of the surface. This interpretation is supported by the shape of the distribution of measured jump lengths. The root mean square jump length can be reproduced accurately in calculations if we take into account the chemical difference between the indium and copper atoms. We conclude that terraces of low-index metal surfaces, such as Cu(001), cannot be considered as static, even at room temperature. The naturally occurring vacancies lead to a continuous reshuffling of the surface, as if it were an atomic realization of a slide puzzle.

[1] H.-C. Jeong and E. D. Williams, Surf. Sci. Rep. **34**, 171 (1999).
[2] Z. Zhang and M. G. Lagally, Science **276**, 377 (1997).
[3] L. Kuipers, M. S. Hoogeman, and J. W. M. Frenken, Phys. Rev. Lett. **71**, 3517 (1993).
[4] K. Morgenstern, G. Rosenfeld, B. Poelsema, and G. Comsa, Phys. Rev. Lett. **74**, 2058 (1995).
[5] F. Besenbacher, Rep. Prog. Phys. **59**, 1737 (1996).
[6] J. B. Hannon et al., Phys. Rev. Lett. **79**, 2506 (1997).
[7] H. A. van der Vegt et al., Phys. Rev. B **51**, 14 806 (1995).
[8] M. Breeman and D. O. Boerma, Phys. Rev. B **46**, 1703 (1992).
[9] M. Breeman and D. O. Boerma, Surf. Sci. **287/288**, 881 (1993).
[10] R. van Gastel, E. Somfai, W. van Saarloos, and J. W. M. Frenken, Nature (London) **408**, 665 (2000).
[11] M. S. Hoogeman et al., Rev. Sci. Instrum. **69**, 2072 (1998).
[12] R. J. I. M. Koper, Surface Preparation Laboratory, http://www.surface-prep-lab.com
[13] For the full movie please visit http://www-lion.leidenuniv.nl/groups/ip
[14] STM observations show qualitatively similar motion of Pd atoms in the Cu(001) surface, B. S. Swartzentruber (private communication).
[15] R. van Gastel et al. (to be published).
[16] M. J. A. M. Brummelhuis and H. J. Hilhorst, J. Stat. Phys. **53**, 249 (1988).