Atomic slide puzzle: Self-diffusion of an impure atom

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In a series of recent papers [Phys. Rev. Lett. **86**, 1562 (2001); Nature (London) **408**, 665 (2000)] van Gastel and co-workers have presented what may be the first experimental evidence, based on a series of scanning tunnel microscope images, that impure, Indium atoms, embedded into the first, close-packed layer of a Cu(001) surface, are not localized but make concerted, long excursions. Such excursions occur due to continuous reshuffling of the surface following the position exchanges of both impure and host Cu atoms with the naturally occurring surface vacancies. van Gastel and co-workers have also formulated an original lattice-gas type model with asymmetric exchange probabilities, whose numerical solution is in a good agreement with the experimental data. In this paper we propose an exact lattice solution of several versions of this model.

Surface mobility is usually believed to be localized in the vicinity of the terrace steps and kinks of crystal surfaces. These sites form the natural locations for atoms to attach to or to detach from the terraces; the diffusion of adatoms along or between the steps is known to induce their roughening and is responsible for the two-dimensional diffusive motion of adatom and vacancy islands [1–4]. By contrast, the atoms within the close-packed terraces that are not in the immediate vicinity of steps have often been considered as immobile since they are tightly packed by their neighbors. Although some suggestions have been made that the surface vacancies may diffusive themselves within the surface layers (see, e.g., Ref. [5]), up to a very recent time there were no experimental techniques allowing for the direct observation of the diffusion of vacancies or atoms within the close-packed surfaces.

In a recent Letter and two accompanying papers, van Gastel and co-workers [6–8] presented an indirect experimental evidence that, remarkably, the atoms of the close-packed surfaces do undergo themselves continuous random motion. In a set of ingenious scanning tunnel microscope (STM) experiments, van Gastel and co-workers [6–8] have managed to introduce impure (Indium) atoms within the first layer of a Cu(001) surface and were able to follow their positions by analyzing the series of consecutive STM images. They found that the embedded In atoms make concerted, long excursions within the first surface layer, which motion can be only explained (see Refs. [6–8] for more details) by continuous reshuffling of the surface in a way which resembles a slide puzzle due to position exchanges of both the Cu and In atoms with the naturally occurring surface vacancies [9].

van Gastel and co-workers [6,7] also proposed a simple model describing the In atom dynamics. In this model, the authors considered a terrace on a stepped Cu surface as a finite square lattice all $L \times L$ sites of which except two are filled with Cu atoms; the In atom is initially placed at the lattice origin and the vacancy, at one of the adjacent sites. Both In and Cu atoms move randomly along the lattice by exchanging their positions with the vacancy, whose random walk terminates (and may reappear again) as soon as it reaches the lattice boundary.

A salient feature of the physical situation is that, due to the difference of the Cu-Cu and the Cu-In interactions, the vacancy being at the adjacent to the In atom site has a preference to exchange its position with the In atom, compared to three adjacent Cu atoms. The chemical specificity of atoms is then taken into account by introducing unequal hopping probabilities; that is, in case when one of atoms adjacent to the vacancy is the In atom, the vacancy exchanges its position with the latter or with one of three Cu atoms with the probabilities

$$p_{In} = \frac{1}{4}(1+\epsilon), \quad p_{Cu} = \frac{1}{4}\left(1 - \frac{\epsilon}{3}\right), \qquad (1)$$

respectively. For the chemical species under study and at the room temperature the asymmetry parameter ϵ assumes the value $\epsilon^* = 3 - 10^{-6}$, according to the embedded atom model calculations [6]. In case when all four adjacent to the vacancy atoms are the Cu atoms, the vacancy exchanges its position with any of them with the probability $= 1/4$. As a matter of fact, numerical simulations [6] show that the difference in the exchange probabilities has a significant impact on the In atom displacements: the average length of excursions is 2.2 times larger than in the $\epsilon = 0$ case. Monte Carlo simulations of this model produce the results which are in a good agreement with the experimentally obtained jump length distribution [7] and, hence, confirm the vacancy-assisted mechanism of the In atom dynamics proposed in Ref. [6].

Exact solution of this model is known only in the limit $\epsilon = 0$ [10] (see also Ref. [11] for the analysis in case of arbitrary vacancy concentrations ρ). van Gastel and co-workers [6,7] have, however, furnished an approximate, continuous-space solution for the jump length distribution function supposing that the boundary conditions associated with the vacancy creation-annihilation appearing at the terrace edges can be modeled by introducing some, *a priori* given vacancy lifetime. Despite the fact that it is possible to find such values of this heuristic parameter at which the obtained results for the jump length probability distribution

agree quite well with the experimental ones, it is, however, difficult to claim that such a comparison can provide meaningful values of other physical parameters. Clearly, an assumption that the vacancy can spontaneously disappear at any lattice point, not necessarily at the terrace edges, might be a useful simplification but is not controllable. On the other hand, it is well-known that in two-dimensions the continuous-space description may incur significant errors in the numerical factors, which will result in modified values of the physical parameters. Last, the continuous-space approach is hardly appropriate for studying the probability distributions on scales of order of several lattice spacings only. Consequently, for meaningful interpretation of the experimental data an exact lattice solution of the model is highly desirable.

In this Rapid Communication we present an exact lattice solution of several versions of the model introduced by van Gastel and co-workers [6–8] for arbitrary values of the parameter ϵ, $-1 \leq \epsilon < 3$, where positive (negative) values of ϵ correspond to the physical situation in which the In atom has a preference (reduced probability) for the position exchanges with the vacancy. More specifically, we consider a situation with a single vacancy performing the just described random walk on a finite lattice with periodic boundary conditions, which mimic annihilation-creation of the vacancy at the terrace boundaries and also solve the case with a single vacancy and $L = \infty$, which is appropriate for evaluation of the transient dynamics. We note that in view of a very low concentration ρ of the vacancies [9], this transient regime may be very important and may persist over a wide time range. In both situations we determine exactly the leading long-time asymptotical behavior of the mean-square displacement (MSD) and the diffusivity of a single In atom, as well as of the probability that the In atom appears at position $\mathbf{X}$ at time moment t. All our results will be presented in dimensionless form as functions of the discrete time n and for the lattice spacing set equal to unity. Dimension-dependent forms can be obtained by rescaling $n \to t/\Delta t$ and $\mathbf{X} \to \mathbf{X}/\sigma$, where Δt ($\approx 10^{-8}$ s) is the typical time interval between successive jumps and σ (≈ 2.5 Å) is the intersite distance [6].

We begin with more precise definition of the model. Consider a two-dimensional periodic in both the x_1 and x_2 directions, square lattice of unit spacing all $L \times L$ sites of which except two (a vacancy and an In) are filled by Cu atoms (see Fig. 1). The In atom is placed initially at the origin, while the vacancy is at position with the vector $\mathbf{Y} = \mathbf{e}_{-1}$. Here, $\mathbf{e}_\nu$, $\nu \in \{\pm 1, \pm 2\}$, denotes unit lattice vectors; $\mathbf{e}_1$ ($\mathbf{e}_{-1}$) is the unit vector in the positive (negative) x_1 direction, while $\mathbf{e}_2$ ($\mathbf{e}_{-2}$) is the unit vector in the positive (negative) x_2 direction.

Next, at each tick of the clock, $n = 1,2,3,\dots$, a vacancy exchanges its position with one of four neighboring atoms according to the probabilities defined in Eqs. (1). That is, it has a preference (or, on contrary, a reduced probability for $\epsilon < 0$) to exchange its position with the In atom, when this one is at the neighboring site, and no preference for exchange with any of atoms when all four adjacent to the vacancy sites are occupied by the Cu atoms. Hence, the vacancy moves randomly displacing the atoms in its path,
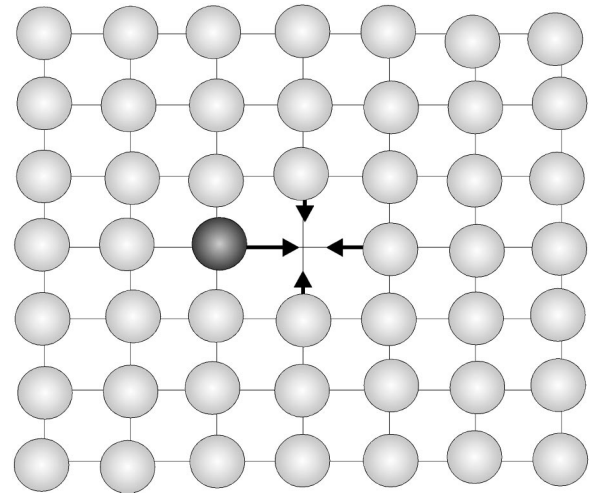

FIG. 1. An illustration of the vacancy-assisted diffusion mechanism of the In atom (black sphere) on a lattice filled with the Cu atoms (grey spheres). The arrows depict the asymmetric hopping probabilities of the In and Cu atoms.

including the In atom; apart from four "defective" sites adjacent to the In atom, it performs conventional symmetric random walk.

Let $P_n(\mathbf{X})$ be the probability that the In atom, which starts its random walk at the origin, appears at the site $\mathbf{X}$ at time moment n, given that the vacancy is initially at the site $\mathbf{e}_{-1}$. Then, following the approach of Ref. [10], we write down the equation obeyed by $P_n(\mathbf{X})$ as:

$$
\begin{aligned}
P_n(\mathbf{X}) = &\sum_{p=1}^{+\infty} \sum_{m_1=1}^{+\infty} \cdots \sum_{m_p=1}^{+\infty} \sum_{m_{p+1}=0}^{+\infty} \sum_{\nu_1} \cdots \sum_{\nu_p} \\
&\times \left(1 - \sum_{j=0}^{m_{p+1}} F_j(\mathbf{0}| - \mathbf{e}_{\nu_{\mathbf{p}}}) \right) F_{m_1}(\mathbf{0}|\mathbf{e}_{\nu_1}|\mathbf{e}_{-1}) \\
&\times \left(\prod_{i=2}^{p} F_{m_i}(\mathbf{0}|\mathbf{e}_{\nu_{\mathbf{i}}}| - \mathbf{e}_{\nu_{\mathbf{i}}-1}) \right) \delta_{m_1 + \dots + m_{p+1}, n} \\
&\times \delta_{\mathbf{e}_{\nu_1} + \dots + \mathbf{e}_{\nu_p}, \mathbf{X}} + \delta_{\mathbf{X},\mathbf{0}} \left(1 - \sum_{j=0}^{n} F_j(\mathbf{0}|\mathbf{e}_{-1}) \right),
\end{aligned}
$$

(2)

where $F_n(\mathbf{0}|\mathbf{e}_\mu)$ is the probability that the vacancy, which starts its random walk at the site $\mathbf{e}_\mu$, arrives at the origin $\mathbf{0}$ for the first time at the nth step, while $F_n(\mathbf{0}|\mathbf{e}_\nu|\mathbf{e}_\mu)$ stands for the *conditional* probability that the vacancy, which starts its random walk at the site $\mathbf{e}_\mu$, appears at the origin for the first time at the nth step, being at the $(n-1)$th step at the site $\mathbf{e}_\nu$.

General solution of Eq. (2) can be written down in form of the following contour integral (see Refs. [10] and [12]):

$$
P_n(\mathbf{X}) = \frac{-i}{(2\pi)^3} \oint_C \frac{d\xi}{\xi^{n+1}} \int d\mathbf{k}\, e^{i(\mathbf{k}\cdot\mathbf{X})} P_{\xi}(\mathbf{k}),
$$

(3)

where the contour of integration C encircles the origin counterclockwise, $(\mathbf{k}\cdot\mathbf{X})$ denotes the scalar product, and

$$P_\xi(\mathbf{k}) = \frac{1}{1-\xi}\left[1 + \mathcal{D}_\xi^{-1}(\mathbf{k})\sum_\mu U_\xi^{(\mu)}(\mathbf{k})F_\xi(\mathbf{0}|\mathbf{e}_\mu|\mathbf{e}_{-1})\right] \tag{4}$$

In Eq. (4) $\mathcal{D}_\xi(\mathbf{k})$ denotes the following determinant:

$$\mathcal{D}_\xi(\mathbf{k}) \equiv \det[\mathbf{I} - T_\xi(\mathbf{k})], \tag{5}$$

the elements $(\mathbf{T}_\xi(\mathbf{k}))_{\nu,\mu}$ of the 4×4 matrix $\mathbf{T}_\xi(\mathbf{k})$ obey

$$(\mathbf{T}_\xi(\mathbf{k}))_{\nu,\mu} \equiv \exp[i(\mathbf{k}\cdot\mathbf{e}_\nu)]F_\xi(\mathbf{0}|\mathbf{e}_\nu|\mathbf{e}_{-\mu}), \tag{6}$$

the indices ν and μ assume successively the values 1, $-1, 2, -2$; $F_\xi(\mathbf{0}|\mathbf{e}_\nu|\mathbf{e}_{-\mu})$ is the generating function of the conditional first-visit probability $F_n(\mathbf{0}|\mathbf{e}_\nu|\mathbf{e}_{-\mu})$, i.e.,

$$F_\xi(\mathbf{0}|\mathbf{e}_\nu|\mathbf{e}_{-\mu}) \equiv \sum_{n=0}^\infty F_n(\mathbf{0}|\mathbf{e}_\nu|\mathbf{e}_{-\mu})\xi^n, \tag{7}$$

and the matrix $U_\xi^{(\mu)}(\mathbf{k})$ is given by

$$\frac{U_\xi^{(\mu)}(\mathbf{k})}{\mathcal{D}_\xi(\mathbf{k})} \equiv e^{i(\mathbf{k}\cdot\mathbf{e}_\mu)}\sum_\nu (1 - e^{-i(\mathbf{k}\cdot\mathbf{e}_\nu)})[\mathbf{I} - \mathbf{T}_\xi(\mathbf{k})]_{\nu,\mu}^{-1}. \tag{8}$$

In turn, the MSD of the In atom is defined as

$$\overline{\mathbf{X}^2} \equiv 4D_n(\epsilon)n \equiv \frac{i}{2\pi}\oint_\mathcal{C}\frac{d\xi}{\xi^{n+1}}\frac{d^2P_\xi(\mathbf{k})}{d\mathbf{k}^2}\Big|_{|\mathbf{k}|=0}, \tag{9}$$

where $P_\xi(\mathbf{k})$ is determined by Eq. (4).

We note now that as far as we are interested only in the leading large-n behavior of $P_n(\mathbf{X})$ and of the MSD, we may constrain ourselves to the study of the asymptotic behavior of the generating function $\tilde{P}^{(tr)}(\mathbf{k};\xi)$ in the vicinity of its singular point nearest to $\xi=0$. Omitting the details of straightforward, but rather tedious calculations, we find that the leading, in the combined $\mathbf{k}\to0$ and $\xi\to1^-$ limit, behavior of $\mathcal{D}_\xi(\mathbf{k})$ follows

$$\mathcal{D}_\xi(\mathbf{k}) = \mathcal{F}_1(\epsilon)\mathbf{k}^2 + \mathcal{F}_2(\epsilon)(1-\xi) + \cdots, \tag{10}$$

where

$$\mathcal{F}_1(\epsilon) = -\frac{(\pi-2)(\pi+2L^2)(\epsilon-3)^2}{2(5\pi\epsilon-16\epsilon-3\pi)}$$
$$\times\frac{(-14\epsilon L^2+6\pi\epsilon L^2-7\pi\epsilon+6\pi L^2-6L^2-3\pi)}{((8\epsilon-3\pi\epsilon-3\pi)L^2+4\pi\epsilon)^2} \tag{11}$$

and

$$\mathcal{F}_2(\epsilon) = \frac{2(\pi-2)(3-\epsilon)((3-\epsilon)L^2+5\epsilon-3)}{3(1+\epsilon)(16\epsilon-5\pi\epsilon+3\pi)}$$
$$\times\frac{[(14\epsilon-6\pi\epsilon-6\pi+6)L^2+7\pi\epsilon+3\pi]^2}{((8\epsilon-3\pi\epsilon-3\pi)L^2+4\pi\epsilon)^2}. \tag{12}$$
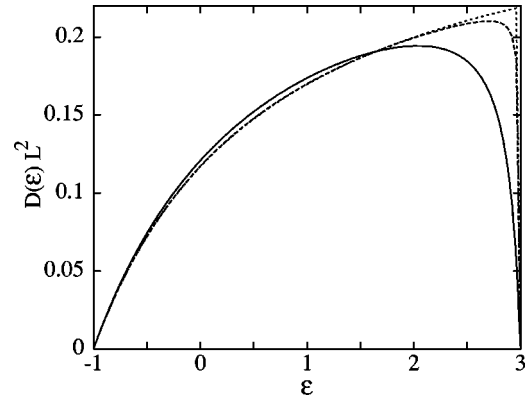

FIG. 2. Plot of $D(\epsilon)$, Eq. (14), vs the parameter ϵ for different values of the terrace width. The solid line corresponds to $L=15$, the dashed line to $L=40$, and the dotted line to $L=600$, respectively. For notational convenience $D(\epsilon)$ is multiplied by the terrace area L^2.

Then, substituting these expressions into Eqs. (4) and (9), and noticing that

$$\sum_\mu U_\xi^{(\mu)}(\mathbf{k})F_\xi(\mathbf{0}|\mathbf{e}_\mu|\mathbf{e}_{-1}) = \mathcal{F}_1(\epsilon)\mathbf{k}^2 + \cdots, \tag{13}$$

we find that as $n\to\infty$, the diffusivity $D_n(\epsilon)$ of the In atom, Eq. (9), tends to a constant value

$$D(\epsilon) = \frac{3(1+\epsilon)(3-\epsilon)}{4((3-\epsilon)L^2+5\epsilon-3)}$$
$$\times\frac{(\pi+2L^2)}{[(6\pi\epsilon-14\epsilon+6\pi-6)L^2-7\pi\epsilon-3\pi]}. \tag{14}$$

Note that $D(\epsilon)$ appears to be a non-trivial, non-monotonous function of the parameter ϵ (see Fig. 2); $D(\epsilon)$ attains a maximal value when $\epsilon=\epsilon_c\approx3-12\sqrt{\pi-2}/L$, and is exactly equal to zero for $\epsilon=-1$ and $\epsilon=3$. In the case $\epsilon=-1$, the In atom does not move at all, since it is not allowed to change its position with the vacancy, while in the $\epsilon=3$ case it gets localized because at each time step it is forced to exchange its position with the single available vacancy. Note that such a "localization effect" for $\epsilon=3$ is, of course, specific to the situation with a single available vacancy; as a matter of fact, the indium atom can get delocalized already if a second vacancy is present. Consequently, the result in Eq. (14) concerns only the leading at $\rho=0$ behavior. For finite but small ρ, there should be a correction term to Eq. (14) proportional to ρ^2. On the other hand, in view of a very small concentration of the naturally occurring vacancies [9], observation of such correction terms [nonzero values of $D(\epsilon=3)$] would require very large observation times. Note also that the ratio $D(\epsilon=\epsilon^*)/D(\epsilon=0)$ is approximately equal to 1.8 for terrace width $L=400$, which shows that, indeed, asymmetric exchange probabilities have also a strong effect on the In atom diffusivity, not only on the average excursion length [6].

Last, following Ref. [10], we get from Eqs. (3) and (4), and the asymptotical expansions in Eqs. (10) to (13), that for sufficiently large n, such that $L^2 \ln(L) \ll n \ll L^4$, the scaling variables $\xi_1 = x_1 / D(\epsilon) n$ and $\xi_2 = x_2 / D(\epsilon) n$ are distributed according to a Gaussian law:

$$P(\xi_1, \xi_2) = (2\pi)^{-1} \exp[-(\xi_1^2 + \xi_2^2)/2]. \quad (15)$$

We turn now to the case $L = \infty$, which will allow us to obtain a meaningful transient behavior. Again, omitting the details of calculations, we find that the leading, in the combined $\mathbf{k} \to 0$ and $\xi \to 1^-$ limit, behavior of $\mathcal{D}_\xi(\mathbf{k})$ obeys:

$$\mathcal{D}_\xi(\mathbf{k}) = \tilde{\mathcal{F}}_1(\epsilon)\mathbf{k}^2 - \tilde{\mathcal{F}}_2(\epsilon)[\ln(1-\xi)]^{-1} + \cdots, \quad (16)$$

where

$$\tilde{\mathcal{F}}_1(\epsilon) = -2 \frac{(\pi-2)(\epsilon-3)^2(3\pi\epsilon-7\epsilon+3\pi-3)}{(5\pi\epsilon-16\epsilon-3\pi)(3\pi\epsilon-8\epsilon+3\pi)^2}, \quad (17)$$

and

$$\tilde{\mathcal{F}}_2(\epsilon) = -\frac{8\pi(\pi-2)(\epsilon-3)^2(3\pi\epsilon-7\epsilon+3\pi-3)^2}{3(1+\epsilon)(5\pi\epsilon-16\epsilon-3\pi)(3\pi\epsilon-8\epsilon+3\pi)^2}, \quad (18)$$

while the sum $\Sigma_\mu U_\xi^{(\mu)}(\mathbf{k})F_\xi(\mathbf{0}|\mathbf{e}_\mu|\mathbf{e}_{-1})$ still obeys Eq. (13) with $\mathcal{F}_1(\epsilon)$ replaced by $\tilde{\mathcal{F}}_1(\epsilon)$. Consequently, we find that in the leading in n order the diffusivity of the indium atom obeys, for $\epsilon < 3$,

$$D_n(\epsilon) \sim \frac{3(1+\epsilon)}{\pi(3\pi\epsilon-7\epsilon+3\pi-3)} \frac{\ln(n)}{n}, \quad (19)$$

and $D_n(\epsilon=3)=0$. Hence, $D_n(\epsilon)$ is a monotonically growing function of ϵ for $\epsilon < 3$, and is discontinuous at $\epsilon = 3$. The ratio $D_n(\epsilon = \epsilon^*)/D_n(\epsilon = 0)$ is now of order of 1.9, which shows that also for infinite lattices asymmetric exchange probabilities enhance the In diffusivity.

Finally, similarly to the approach of Ref. [10], we derive from Eqs. (3) and (4), and the asymptotical expansions in Eqs. (16) to (18), the asymptotic form of the probability distribution $P_n(\mathbf{X})$. We find that as $n \to \infty$, the distribution function of two scaling variables

$$\eta_{1,2} = \left(\frac{4\pi[(3\pi-7)\epsilon+3(\pi-1)]}{3(1+\epsilon)} \ln(n) \right)^{1/2} x_{1,2}, \quad (20)$$

converges to a limiting, non-Gaussian form,

$$P(\eta_1, \eta_2) = \frac{1}{2\pi} K_0(\sqrt{\eta_1^2 + \eta_2^2}), \quad (21)$$

where K_0 is the modified Bessel function of the zeroth order. Note that for $\epsilon = 0$, the results in Eqs. (15), (20), and (21), as well as $D_n(\epsilon)$ in Eqs. (14) and (19), coincide with the ones obtained in Ref. [10].

In conclusion, we have presented here an exact lattice solution of several versions of the model originally devised by van Gastel and co-workers [6–8] to describe dynamics of an impure Indium atom within the first layer of a Cu(001) surface. We have evaluated, for arbitrary values of the asymmetry parameter ϵ, the long-time asymptotical behavior of the impure atom MSD, as well as the limiting scaling forms of the probability distribution. Our analytical results can be useful for further interpretation of the experimental data on dynamics of impure atoms in close-packed surface layers.

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