PRL **95,** 226102 (2005) PHYSICAL REVIEW LETTERS week ending 25 NOVEMBER 2005

Excitation of Frustrated Translation and Nonadiabatic Adatom Hopping Induced by Inelastic Tunneling

Kai Liu[1] and Shiwu Gao[1,2]
[1]*Institute of Physics, Chinese Academy of Sciences, 100080 Beijing, China*
[2]*Department of Physics, Göteborg University, SE-41296, Göteborg, Sweden*

(Received 31 August 2005; published 21 November 2005)

The dynamics of lateral manipulation for cobalt/Cu(111) has been investigated combining the model of vibrational heating and first-principles density functional calculations. The frustrated translational mode responsible for lateral excitation is identified as a vibrational resonance involving a concerted motion between the adatom and surface phonons. The calculated frequency shows good agreement with the onset energy for adatom hopping induced by inelastic tunneling. Simulation of the power law, compared with experiment, suggests that the atom hopping overcomes a nonadiabatic barrier due to the nonequilibrium local heating of the translational mode.

DOI: 10.1103/PhysRevLett.95.226102 PACS numbers: 68.35.Ja, 68.35.Fx, 73.20.Hb, 73.40.Gk

Manipulation of single adatoms with a scanning tunneling microscope has made it possible to create artificial nanostructures with desired size, shape, and functional properties. Already in the early experiments, atoms were manipulated both laterally [1–3] and vertically [4,5] at surfaces. Vertical manipulation was found to be governed by a vibrational heating mechanism [6–9] via direct excitation of the atom-surface bond. In contrast, the mechanism for lateral excitation is less understood. In molecular manipulation, rotational and translational motions of admolecules have been observed for a number of systems [10–15]. The lateral motion was found to be triggered by indirect excitation of the high-frequency stretch mode followed by energy transfer to the translational mode (T mode) via anharmonic coupling [12,13]. In order to control the dynamics of lateral motion of a single adatom, Stroscio and Celotta have recently made quantitative measurement of the hopping rate for cobalt adatoms on a Cu(111) surface [16]. The nonlinear hopping rate between the fcc and hcp site and its polarity independence are characteristics for the vibrational heating mechanism, as found in vertical and molecular manipulation. However, it is unclear whether the hopping is triggered by direct T mode excitation or indirectly via the vertical mode followed by mode-mode energy transfer, as found on molecular systems. This uncertainty partially results from the fact that little is known about the vibrational and diffusion properties in the lateral motion [17].

During the past decade, vibrational excitation and relaxation of the T mode of adatoms [18–20], an elementary surface process responsible for adsorbate diffusion, sliding, lubrication, and friction [21], has been studied intensively. It was generally established that, in the high temperature [50–200 K] regime, relaxation of the T mode is dominated by phonon excitation in the substrate via resonance broadening [20] and anharmonic coupling. While at low temperatures (<50 K), relaxation via nonadiabatic electron-hole pair excitation becomes dominant. Such vibrational studies were mainly concentrated on the first excited state of the T mode.

This Letter reports a comprehensive theoretical study of lateral atomic manipulation for Co/Cu(111) combining quantum kinetic modeling and first-principles density-functional-theory (DFT) calculations. First, the energetics of adatom diffusion and vibrational spectra of the adsorbate and surface phonons were determined. Both the vertical mode and the T mode show strong hybridization with the surface phonons. We demonstrate that multiple excitation of the T mode, which is a concerted motion between the adsorbate and surface phonons, is responsible for lateral manipulation. The calculated frequency of this mode is in close agreement with the onset energy for atom hopping in the inelastic regime. Within the vibrational heating model, the hopping rate has been simulated as a function of bias. The calculated power law with partial adiabadicity in the substrate is comparable with experiment. Our finding suggests that barrier crossing at low temperatures (2.3 K in this case) is nonadiabatic, when a system is locally driven out of equilibrium. It has general implications for atomic diffusion, friction, and dissipation at nanoscale.

To base our analysis on reliable data, we first calculated the energetics and vibrational spectrum of Co/Cu(111) from first-principles calculations using the Vienna *ab initio* simulation package (VASP) [22]. This approach has been used successfully before as a theoretical tool for vibrational recognition of adatoms and admolecules at surfaces, giving highly credible results for both the high-frequency stretch modes, like the OH stretch (~450 meV) and the low-frequency translational mode (5 meV in the water bilayer) [23,24]. We used a 7-layer slab with one adatom in a 3×3 two-dimensional supercell, which was separated vertically by a 13.7 Å vacuum space. The k points were sampled on a $4 \times 4 \times 1$ grid. Extensive convergence tests have been done over the k points, the thickness of the slab, and with a larger ($4 \times 4 \times 7$) unit cell. Other details of the calculations are the same as those in previous publications

[23,24]. Both the velocity correlation function method and the dynamical matrix method have been used for vibrational calculations. For Co/Cu(111), spin polarization of the Co atom leads to a magnetic moment around 2 Bohr magneton, very localized on the adatom at all adsorption sites. The total energies of the magnetic states are usually lower than those of the nonmagnetic ones and thus give more reliable energetics.

Figure 1 shows the calculated vibrational spectra using the dynamical matrix method. The derivatives were extracted from the finite difference of atomic forces at given atom displacements. Both the adsorbate and the top three layers of the slab were allowed to move symmetrically by 0.03 Å off their equilibrium positions in all directions (x, y, and z), leading to an 84×84 matrix. Diagonalizing the matrix gives the eigenfrequencies $\{\nu_j\}$ and the polarization vectors $\{u_{jk}\}$. The local vibrational densities were obtained by projecting these eigenmodes to local atoms in a given direction. The two upper panels show the parallel ($x + y$) and vertical (z) vibrational densities of the adatom adsorbed at an fcc site, while the lower two panels are the total densities ($x + y + z$) for one of the neighboring Cu atoms and a bulklike atom away from the adsorbate (bulk). The parallel density of the Co atom shows a double degenerate peak at 5.4 meV, which is the frustrated translation along the surface. This mode hybridizes with the surface Cu atoms, as can be seen from the density distribution in panel (c) in the same energy range, suggesting that the T modes are strongly coupled to the atomic motion of the substrate. In contrast, it shows negligible coupling to the vibration of the bulk atoms [Fig. 1(d)]. The vertical mode of the Co atom also shows strong mixing with surface phonons. The principal peak, 33 meV, is located, however, above the bulk phonon bands. The strong coupling between the adsorbate and surface phonons is reasonable due to the comparable mass between Co and Cu atoms. Although there is no experimental data available for adsorbate vibration in the literature for Co/Cu(111), good agreement can be seen for the bulk phonon bands, in comparison with previous calculations and experiments: e.g., the optical (27 meV) and acoustic mode (13 meV) at the Γ point [25,26]. In addition, the vibrational energy of the T mode falls in the narrow range of a variety of adsorbates: Na/Cu(001), 6 meV; CO/Pt(111), 5.94 meV [18]; CO/Cu(001), 4.1 meV [27]; and water/Pt(111), 5 meV [23,24].

The coupling between the T mode and the surface phonons can be seen more clearly from its polarization vector. Figure 2 shows the polarization distribution of the T mode. The adsorbate is polarized to the bridge site, where the barrier for diffusion is located. It engages simultaneous motions of the surrounding atoms, especially those four Cu atoms in its nearest neighborhood. Quantitative analysis shows that the T mode has about 57% of weight on the adatom and 25% on the four neighboring Cu atoms, yielding a partial sum of 82% of weight in the local region. Moreover, the four Cu atoms in the surface participate in different ways in the parallel and perpendicular motions. The two atoms beside the bridge site move away from the bridge position, while the other two (before and behind the Co) move along with the adatom, forming a coherent

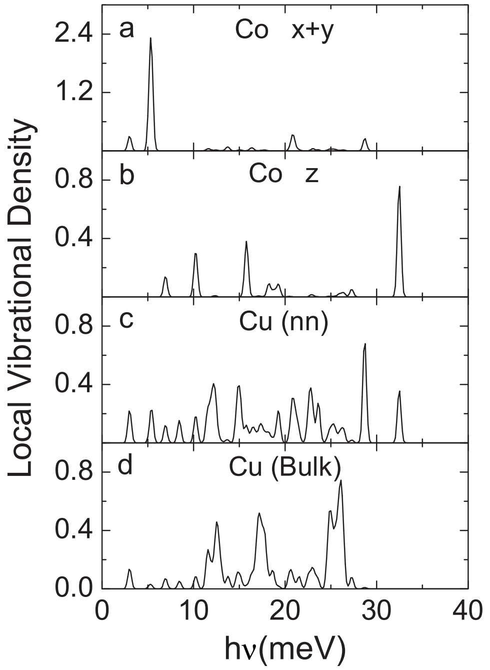

FIG. 1. The local vibrational densities for the parallel (a) and the vertical (b) components of the adsorbate vibrations. The two lower panels show the local vibrational densities for a neighboring Cu atom (c) in the surface layer and a bulk atom (d). The calculation was done in a $3 \times 3 \times 7$ supercell.

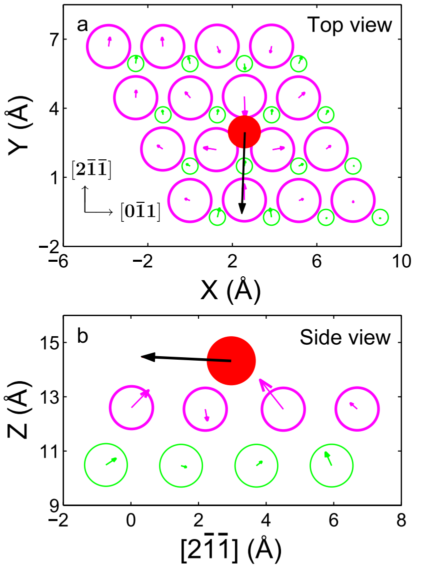

FIG. 2 (color online). The polarization distribution for the frustrated translation mode, $\hbar\Omega = 5.4$ meV. The length and the direction of the arrows on each atom represent the amplitude and direction of the atomic displacement projected parallel (top view) and perpendicular to the surface (side view). The $[2\bar{1}\,\bar{1}]$ axis is the direction of adsorbate hopping from fcc to hcp site.

motion with the adatom. The concerted motion of the substrate atoms seems to facilitate the adatom hopping. As we see below, excitation of this mode is responsible for adatom hopping, while the vertical mode (33 meV) can be excluded because it could not be excited in the applied bias range (0–15 mV) [16].

The energy barriers and transition states corresponding to different rigidity of substrate are determined using the nudged elastic band method (Fig. 3). The fully relaxed barrier (the lower dashed curve), 32 meV, was obtained by relaxing all three-layer Cu atoms along with the hopping path. This barrier is fully adiabatic, where all surface atoms are assumed to follow the adsorbate motion instantly during barrier crossing. It is comparable to the diffusion barriers available in the literature, 37 ± 5 meV for Co/Cu(111) [17], and 41 meV for Cu/Cu(111) [28]. This barrier will be referred to as the adiabatic barrier hereon. We also calculated several nonadiabatic potential barriers by relaxing fewer numbers of atoms in the substrate, while keeping the rest atoms at their equilibrium configuration at the fcc site. For example, relaxing the 4 active Cu atoms in the T mode gives a barrier of 79 meV. While relaxing the surface layer (9 atoms), the barrier is reduced to 49 meV. For comparison, the barrier obtained with the completely rigid lattice is 169 meV. In this case no atom would ever follow the hopping motion of the adatom. Such nonadiabatic calculations were motivated by two reasons: (1) vibrational relaxation of the T mode is known to be suppressed at low temperatures (2.3 K); (2) heating of the T mode by tunneling electrons only enhances the local temperature around the adsorbate, and leaves the rest of the substrate at essentially the experimental temperature (2.3 K). Surface atoms, which are driven out of thermal equilibrium by the current, do not assure the same adiabaticity homogeneously in the whole substrate.

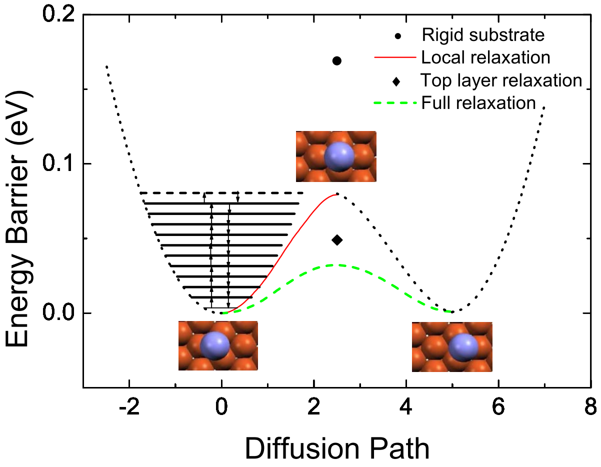

FIG. 3 (color online). The paths and energy barriers for lateral atom hopping between the fcc and hcp site for Co on Cu(111) calculated using the nudged elastic band method. The lower (dashed line) curve was obtained by relaxing all atoms in the three surface layers of the substrate, while the upper curve assumes relaxation of those excited atoms in the T mode. The dots mark the barriers obtained with a completely rigid substrate and with a relaxed first layer.

Now we turn to analyze the mechanism and dynamics of adatom hopping in the Stroscio experiment. Before any numerical simulation, qualitative understanding on the hopping rate can be gained in the model of vibrational heating, as discussed extensively in the original article. First, the measured nonlinear hopping rate $I^{12\pm1.5}$ and its polarity independence are strong evidences for the vibrational heating mechanism. The vibrational frequency of the T mode, 5.4 meV, immediately explains the abrupt transition from the atomic tunneling regime ($|V| < 5$ mV) to the vibrationally activated regime ($|V| > 5$ mV). Comparing Fig. 1 with the experimental data [Fig. 4 of Ref. [16]], we can conclude that the manipulated mode is the frustrated translational mode. The potential barrier involved in adatom hopping can also be inferred from the measured power law, because the power directly reflects the number of electronic transitions involved in ladder climbing. The measured power law, $I^{12\pm1.5}$, at the onset of inelastic tunneling, $V = 7$–9 mV, implies an initial potential barrier $E_B \simeq 12 \times 5.4 = 65$ meV in the truncated harmonic oscillator approximation. Such a relationship has been universally justified by many STM experiments and femtosecond laser induced processes.

With these analyses, we have simulated the adatom hopping from fcc to hcp site as a function of bias voltage. The hopping rate was obtained by solving the Pauli master equation for the truncated harmonic oscillator, where the key input parameters are the rates for vibrational damping $\Gamma_\downarrow$ and excitation $\Gamma_\uparrow$. Within the resonance model for electron-vibrational coupling, these rates read [6,7],

$$\Gamma_\downarrow = \gamma_{\mathrm{eh}} + \gamma_{\mathrm{ph}} + \gamma_{\mathrm{iet}}, \qquad \Gamma_\uparrow = \gamma_{\mathrm{iet}},$$

$$\gamma_{\mathrm{iet}} = \frac{|eV|}{\hbar\Omega}\frac{\Delta^t}{\Delta^s}\gamma_{\mathrm{eh}}\theta(|eV| - \hbar\Omega).$$

Here γ_{eh} and γ_{ph} are the damping rate due to electron-hole pairs and the substrate phonons, and γ_{iet} is the inelastic rate induced by the tunneling current. Thermal excitation of the T mode is negligible at 2.3 K and is not taken into account. The resonance parameter, Δ_t/Δ_s, determines the fraction of inelastic current crossing the adsorbate compared to the total one. Here we used $\gamma_{\mathrm{eh}} = \gamma_{\mathrm{ph}} = 10^{10}/s$, estimated from the typical rate of the T mode $\gamma \sim 0.01$–$0.1\ \Omega$ [18], and $\frac{\Delta^t}{\Delta^s} = 0.2$. Assuming 11 bound states in the potential well (Fig. 3), a nonlinear hopping rate close to the experimental data is reproduced (see Fig. 4). This power-law dependence has been analyzed to be $R_{\mathrm{hopping}} = N\Gamma_\uparrow(\Gamma_\uparrow/\Gamma_\downarrow)^{N-1} \sim V^N$ [6], where N is the number of vibrational levels in the potential well. It gives a potential barrier of $E_B = (N + 1/2)\hbar\Omega = 62$ meV. We would like to mention that although the magnitude of the hopping rate depends on these parameters, the power law is rather insensitive to the specific values in a wide range of parameter space.

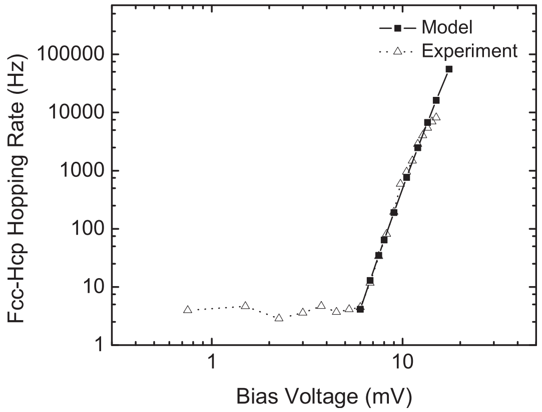

FIG. 4. The simulated adatom hopping rate as a function of bias. Here 11 vibrational bound states are used in the simulation.

The diffusion barrier obtained from the power law, 62 meV, is much higher than the adiabatic one, 32 meV, but falls in the range of nonadiabatic barriers, 79 meV and 49 meV. It suggests that some substrate atoms may not follow instantly the hopping motion of the adatom during barrier crossing. Whether this is true depends on the time scale for barrier crossing, $\sim\Gamma_{\uparrow}^{-1}$, in comparison to the time for barrier relaxation at the transition state, the bridge site. The latter is unknown and remains a subject for future studies. However, it should be infinitely long at zero temperature where the anharmonic coupling is suppressed. This indicates that nonadiabatic hopping at 2.3 K is very possible. Recently, nonadiabatic hopping of CO has been observed in hot electron activated diffusion under femtosecond irradiation [29]. The local heating of the Co/Cu(111) by the tunneling current resembles the nonequilibrium heating induced by hot electrons. Here the local T mode is heated up to about 40 K at $V = 10$ mV, while the rest of the phonon bath remains essentially at 2.3 K. Along this line, the reduction of the power law at larger bias, I^{11-12} at 7–9 mV to I^{6-8} at 10–15 mV, is a direct indication of the gradual reduction of potential barrier due to increased adiabadicity at larger bias. It is our prediction that a lower power law, which corresponds to more adiabatic barriers, is measurable if the same experiment is done at elevated temperatures.

Summarizing, we presented a combined first principles calculation and theoretical modeling of the atomic hopping induced by inelastic tunneling. Our calculation identified the frustrated translational mode. Localized heating of this mode by tunneling electrons leads to nonadiabatic lateral hopping in the low temperature regime. Similar nonadiabatic processes can occur when a system is locally driven out of equilibrium, which can be expected in, for example, the transport processes under current and ultrafast processes driven by hot electrons.

This work has been supported by the 100-Talent Program (Bairen Jihua) of Chinese Academy of Sciences and the material consortium-ATOMICS, funded by the Foundation for Strategic Research (SSF) of Sweden. We thank Dr. J. A. Stroscio for sending us his experimental data. Discussions with D. S. Wang, M. Persson, and G. Wahnström and a critical reading of the manuscript by M. Persson are gratefully acknowledged.

---

[1] D. M. Eigler and E. K. Schweizer, Nature (London) **344**, 524 (1990).

[2] J. A. Stroscio and D. M. Eigler, Science **254**, 1319 (1991).

[3] L. Bartels, G. Meyer, and K.-H. Rieder, Phys. Rev. Lett. **79**, 697 (1997).

[4] D. M. Eigler, C. P. Lutz, and W. E. Rudge, Nature (London) **352**, 600 (1991).

[5] T.-C. Shen *et al.*, Science **268**, 1590 (1995).

[6] S. W. Gao, M. Persson, and B. I. Lundqvist, Solid State Commun. **84**, 271 (1992); Phys. Rev. B **55**, 4825 (1997).

[7] R. E. Walkup, D. M. Newns, and Ph. Avouris, Phys. Rev. B **48**, 1858 (1993).

[8] G. P. Salam, M. Persson, and R. E. Palmer, Phys. Rev. B **49**, 10 655 (1994).

[9] N. Lorente and M. Persson, Faraday Discuss. **117**, 277 (2000).

[10] B. C. Stipe, M. A. Rezaei, and W. Ho, Science **279**, 1907 (1998).

[11] B. C. Stipe, M. A. Rezaei, and W. Ho, Phys. Rev. Lett. **81**, 1263 (1998).

[12] T. Komeda, Y. Kim, M. Kawai, B. N. J. Persson, and H. Ueba, Science **295**, 2055 (2002).

[13] B. N. J. Persson and H. Ueba, Surf. Sci. **502-503**, 18 (2002).

[14] J. I. Pascual, N. Lorente, Z. Song, H. Conrad, and H.-P. Rust, Nature (London) **423**, 525 (2003).

[15] H. Ueba and B. N. J. Persson, Surf. Sci. **566-568**, 1 (2004).

[16] J. A. Stroscio and R. J. Celotta, Science **306**, 242 (2004).

[17] D. V. Tsivlin, V. S. Stepanyuk, W. Hergert, and J. Kirshner, Phys. Rev. B **68**, 205411 (2003).

[18] J. L. Vega, R. Guantes, S. Miret-Artés, and D. A. Micha, J. Chem. Phys. **121**, 8580 (2004).

[19] B. N. J. Persson, Phys. Rev. B **44**, 3277 (1991).

[20] S. P. Lewis and A. M. Rappe, Phys. Rev. Lett. **77**, 5241 (1996).

[21] B. N. J. Persson, *Sliding Friction* (Springer, New York, 2000), 2nd ed., and references therein.

[22] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); **49**, 14 251 (1994); G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996); Phys. Rev. B **54**, 11 169 (1996).

[23] S. Meng, L. F. Xu, E. G. Wang, and S. W. Gao, Phys. Rev. Lett. **89**, 176104 (2002).

[24] S. Meng, E. G. Wang, and S. W. Gao, Phys. Rev. B **69**, 195404 (2004).

[25] M. H. Mohamed, L. L. Kesmodel, B. M. Hall, and D. L. Mills, Phys. Rev. B **37**, R2763 (1988).

[26] J. S. Nelson, M. S. Daw, and E. C. Sowa, Phys. Rev. B **40**, 1465 (1989).

[27] M. Bertino, J. Ellis, F. Hofmann, J. P. Toennies, and J. R. Manson, Phys. Rev. Lett. **73**, 605 (1994).

[28] M.-C. Marinica, C. Barreteau, M.-C. Desjonquères, and D. Spanjaard, Phys. Rev. B **70**, 075415 (2004).

[29] L. Bartels, F. Wang, D. Möller, E. Knoesel, and T. F. Heinz, Science **305**, 648 (2004).