

**Fig. 3.** Magnetic field ( $H$ ) dependence of the square root of MSHG intensity, representing the interface magnetism ( $M_{\text{int}}$ ), measured at 50 K.  $M_{\text{int}}$  (**bottom**) and normalized  $M_{\text{int}}$  [ $M_{\text{int}}(H)/M_{\text{int}}(7\text{ T})$ ] (**top**). STO/LSMO, LAO/LSMO, STO/LMO/LSMO interfaces are displayed with red, blue, and green symbols, respectively. The solid lines are the fit, assuming spontaneous magnetization (intersection to the vertical axis) and  $H$  linear increase in  $M_{\text{int}}$  from the canted states by an external field. A black line in the top panel shows the  $H$  dependence of  $M_{\text{film}}$  at 5 K.

To enhance the interface magnetization without sacrificing the ferromagnetic and metallic characters in the film, we propose the compositionally graded LSMO interfaces, where the bulk LSMO electrode has the optimal doping level of  $x = 0.4$ , and  $x$  decreases gradually to 0 toward the insulating layer. This idea bears some analogy to the procedure to improve the superconductivity grain boundary junction (17), in which partial Ca substitution on Y sites in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  enhances the critical supercurrent density ( $J_c$ ), but at the same time suppresses  $T_c$ . In our study, the doping profile was controlled on an atomic scale. The 2-u.c. layer of  $\text{LaMnO}_3$  (LMO) was inserted as a locally underdoped layer between STO (5 u.c.) and LSMO ( $x = 0.4$ ; 300 u.c.) layers (Fig. 1A, right). We anticipated that the LMO layer, which is originally an antiferromagnet with  $T_N = 140\text{ K}$ , should be hole-donated by LSMO(0.4) and STO layers and hence can compensate for the interface effects. This compositionally modulated interface shows large MSHG and NOMOKE, which exceed by far the STO/LSMO direct interface and are comparable to those of the LAO/LSMO interface (Fig. 2B). In accord with this observation, the spin-tunnel junction equipped with such an atomically engineered interface, [LSMO(0.4)/LMO (2 u.c.)]/STO (2 nm)/[LMO (2 u.c.)/LSMO(0.4)], shows an improved (comparable)

device performance as compared with the direct-interface junction, LSMO/STO/LSMO (LSMO/LAO/LSMO) (13). As shown in Fig. 3,  $M_{\text{int}}$  for this STO/LMO/LSMO interface is almost  $H$ -independent above 0.1 T, thus confirming that the nearly bulk-like ferromagnetism is maintained even in the vicinity of STO. The normalized  $M_{\text{int}}(T)$  value of STO/LMO/LSMO reaches 0.5 at 250 K, which is close to a value (0.7) for normalized magnetization of bulk film at the same temperature and is much larger than the value ( $<0.2$ ) for the direct interface of STO/LSMO ( $x = 0.4$ ).

**References and Notes**

1. A. Ohtomo, D. A. Muller, J. L. Grazul, H. Y. Hwang, *Nature* **419**, 378 (2002).
2. K. Ueda, H. Tabata, T. Kawai, *Science* **280**, 1064 (1998).
3. J. Z. Sun *et al.*, *Appl. Phys. Lett.* **69**, 3266 (1996).
4. M. Bowen *et al.*, *Appl. Phys. Lett.* **82**, 233 (2003).
5. Y. Ogimoto *et al.*, *Jpn. J. Appl. Phys.* **42**, L369 (2003).
6. M. Izumi *et al.*, *Phys. Rev.* **B64**, 064429 (2001).

7. M. Izumi, Y. Ogimoto, T. Manako, M. Kawasaki, Y. Tokura, *J. Phys. Soc. Jpn.* **71**, 2621 (2002).
8. J. Reif, J. C. Zink, C.-M. Schneider, J. Kirschner, *Phys. Rev. Lett.* **67**, 2878 (1991).
9. G. Spierings *et al.*, *J. Magn. Magn. Mater.* **121**, 109 (1993).
10. H. Yamada, M. Kawasaki, Y. Ogawa, Y. Tokura, *Appl. Phys. Lett.* **81**, 4793 (2002).
11. Y. Ogawa *et al.*, *Phys. Rev. Lett.* **90**, 217403 (2003).
12. K. Kimoto *et al.*, *Appl. Phys. Lett.* **84**, 5374 (2004).
13. Materials and methods are available on Science Online.
14. A. Urushibara *et al.*, *Phys. Rev.* **B51**, 14103 (1995).
15. Y. Konishi *et al.*, *J. Phys. Soc. Jpn.* **68**, 3790 (1999).
16. F. Pailloux *et al.*, *Phys. Rev.* **B66**, 014417 (2002).
17. G. Hammerl *et al.*, *Nature* **407**, 162 (2000).
18. M. Izumi *et al.*, *Appl. Phys. Lett.* **73**, 2497 (1998).
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**Supporting Online Material**

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 Materials and Methods  
 Fig. S1  
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# Real-Space Observation of Molecular Motion Induced by Femtosecond Laser Pulses

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Femtosecond laser irradiation is used to excite adsorbed CO molecules on a Cu(110) surface; the ensuing motion of individual molecules across the surface is characterized on a site-to-site basis by in situ scanning tunneling microscopy. Adsorbate motion both along and perpendicular to the rows of the Cu(110) surface occurs readily, in marked contrast to the behavior seen for equilibrium diffusion processes. The experimental findings for the probability and direction of the molecular motion can be understood as a manifestation of strong coupling between the adsorbates' lateral degrees of freedom and the substrate electronic excitation produced by the femtosecond laser radiation.

Scanning tunneling microscopy (STM), through its direct imaging on the atomic length scale, has dramatically advanced our ability to probe the geometric and electronic structure of surfaces. The introduction of variable temperature STM has further enabled researchers to follow atomic motion on surfaces in real time. Although this capability permits the examination of processes on the millisecond time scale, the inherent characteristics of STM imply that new approaches are required to reach the intrinsic time scale of atomic motion, which is in the pico- to femtosecond range.

Several researchers have explored gating and correlation techniques to improve the time resolution of STM measurements (1–3), but their focus has been on electron dynamics rather than on the nuclear motion that corresponds to chemical processes. In a separate line of research, the utility of femtosecond laser radiation to induce surface chemical reactions and to clarify rates of energy transfer and nuclear motion has been demonstrated (4–14). Although they access the ultrafast dynamics of surface reactions, these methods do not provide the direct real-space imaging of STM.

We describe here the successful combination of the atomic-scale spatial resolution provided by STM with ultrafast surface dynamics driven by femtosecond laser excitation. In this fashion, we are able to determine the initial and final configurations of individual molecules undergoing nonequilibrium surface diffusion induced by electronic exci-

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tation. Given the critical role that surface diffusion plays in phenomena as varied as crystal growth and catalytic activity of surfaces, many techniques have been applied to probe the diffusion of adsorbed atoms and molecules under equilibrium conditions (15, 16). By exciting the molecules electronically rather than thermally, we can now examine surface diffusion processes occurring under nonequilibrium conditions on the ultrafast time scale. The measurements, carried out on the CO/Cu(110) system, reveal adsorbate motion with different propensities for displacement along and perpendicular to the atomic rows of the surface compared with those previously observed under conditions of thermal equilibrium. The experimental results demonstrate the importance of the electronic adsorbate-substrate coupling for surface migration, as well as the existence of distinctive new surface phenomena on the ultrafast time scale.

We chose the CO/Cu(110) system for study because its equilibrium and dynamical properties have been well characterized. CO adsorbs in a molecular state at on-top sites of the Cu(110) surface and is stable against thermal desorption up to a temperature of  $\sim 190$  K (17). With the use of STM imaging, Briner *et al.* (18) found that thermally induced diffusion starts at temperatures around 40 K and proceeds exclusively along the close-packed  $\langle 1\bar{1}0 \rangle$  rows of the substrate. Researchers have also recently investigated STM-induced lateral motion of adsorbed CO (19–23). These measurements in the spatial domain have been complemented by experimental investigations of femtosecond laser-induced processes, including research on desorption (5, 7) and adsorbate-substrate vibrational coupling (24–27), as well as several related theoretical studies (28–31). These experimental and theoretical investigations have revealed the importance of nonadiabatic coupling of the adsorbate to the high electronic temperature of the substrate produced by femtosecond laser excitation.

During the experiment (32), the Cu(110) sample was held at a temperature of 22 K, well below the threshold for thermally driven surface diffusion of CO. The CO coverage of  $\sim 0.01$  monolayer permitted isolated molecules to be studied. STM images were taken at tunneling currents of  $\sim 100$  pA with a bias of a few hundred millivolts. Under these conditions, no STM-induced changes of the CO-covered surface were observed. Laser radiation was provided by a regeneratively amplified mode-locked Ti:sapphire laser. We used the second harmonic of this source (405 nm) to irradiate the sample with 200-fs laser pulses at a repetition rate of  $\sim 1$  kHz.

We recorded the positions of CO molecules on the Cu(110) surface by STM before and after irradiation by the laser and thereby traced the motion of individual adsorbed molecules. Although conceptually simple, this procedure requires careful consideration from the experimental standpoint. The principal complication is that the surface cannot be irradiated with the STM tip in its tunneling position because of thermal expansion.

The experimental approach adopted to circumvent this problem is sketched in Fig. 1. After acquisition of an initial STM image, the tip is quickly withdrawn from the substrate by  $\sim 1$   $\mu\text{m}$  with the vertical piezoelectric drive. With the tip retracted, the surface is exposed to the fs-pulse laser radiation. The STM tip is then allowed to reapproach the surface. To use the STM to follow atomic-scale motion, we must be able to image precisely the same region of the surface. Control experiments, as indicated in Fig. 2, A and B, confirm this capability and verify that the molecules retain exactly the same positions. In contrast, Fig. 2, B and C, show STM images of adsorbed CO molecules before and after exposure to fs-pulse laser radiation. Because the probability of laser-induced events is low for a single pulse, we typically applied 1000 or more pulses between successive images. In our measurements, a total of  $\sim 3000$  isolated molecules were

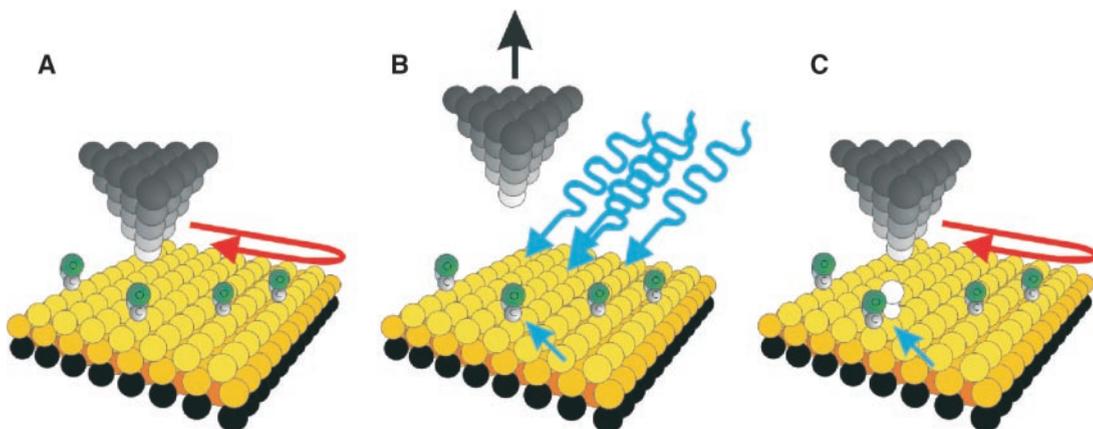
analyzed, half of them subject to laser irradiation and half in control experiments.

Under irradiation by the femtosecond laser pulses, we observed surface diffusion as summarized in Fig. 3. In contrast to the thermal behavior, adsorbate migration occurs across the close-packed rows of the substrate (in the  $\langle 001 \rangle$  direction) as well as along them (in the  $\langle 1\bar{1}0 \rangle$  direction). Also in marked distinction to conventional thermal behavior, desorption occurs at a rate similar to surface diffusion.

An important experimental issue concerns the determination of the absorbed laser fluence, which has been shown to be a critical experimental parameter (4–13). The geometry of the present experiment makes a direct determination of the absorbed fluence difficult: Even with the STM tip retracted, we expect that its presence will alter the strength of the laser field at the surface. We can, however, apply an internal calibration scheme on the basis of the presence of laser-induced CO desorption. To convert the observed desorption rates into an absorbed fluence, we apply the phenomenological model developed by Struck *et al.* (7) for Cu(001), with an adjustment to reflect the empirical Arrhenius rate law for CO desorption from Cu(110). Given the sharp dependence of the desorption rate on the absorbed laser fluence, we believe that this procedure yields a relatively precise local value of this parameter of  $30 \pm 3$  J/m<sup>2</sup>.

We now discuss the mechanism for femtosecond laser-induced diffusion and the origin of the anomalous branching ratio for motion in the  $\langle 1\bar{1}0 \rangle$  and  $\langle 001 \rangle$  directions. The absorbed laser radiation produces electron-hole pairs that thermalize rapidly to a Fermi-Dirac distribution. However, this electronic temperature can far exceed that of the phonons (25). To model this transient substrate excitation, we have solved coupled diffusion equations for the substrate electronic and lattice temperatures at the surface (Fig. 4). A transient electronic temperature approaching

**Fig. 1.** Overview of experimental procedure. (A) Initially, a molecularly resolved STM image of the surface is acquired. (B) The tip is retracted to the limit of the feedback loop, the vertical piezo is switched to a high-voltage supply, and the tip is retracted more than 1  $\mu\text{m}$  from the sample. Laser radiation is then applied. (C) The tip is brought back toward the surface, and the feedback loop becomes operational. After creep compensation, the surface is reapproached and stable tunneling is achieved. Finally, we restart the STM imaging. In the following control cycle, the entire procedure is repeated without laser irradiation.



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3000 K is achieved for a time of  $\sim 1$  ps; heating of the lattice also occurs, but the lattice only reaches a temperature of 140 K in a trans-

ient of a few tens of picoseconds in duration.

With this description of the substrate excitation, we first consider whether the ob-

served diffusion arises from a transient thermal process associated with the (relatively) slow equilibrium heating in the metal. With the use of data from Briner *et al.* (18), we find that the expected number of hops along the atomic rows falls short by more than an order of magnitude. Also, CO hopping across the rows is negligible under conventional thermal conditions and should, contrary to our experimental findings, still be relatively minor for transient thermal excitation. Further, a purely thermal mechanism could not explain the concurrent CO desorption process observed under laser excitation.

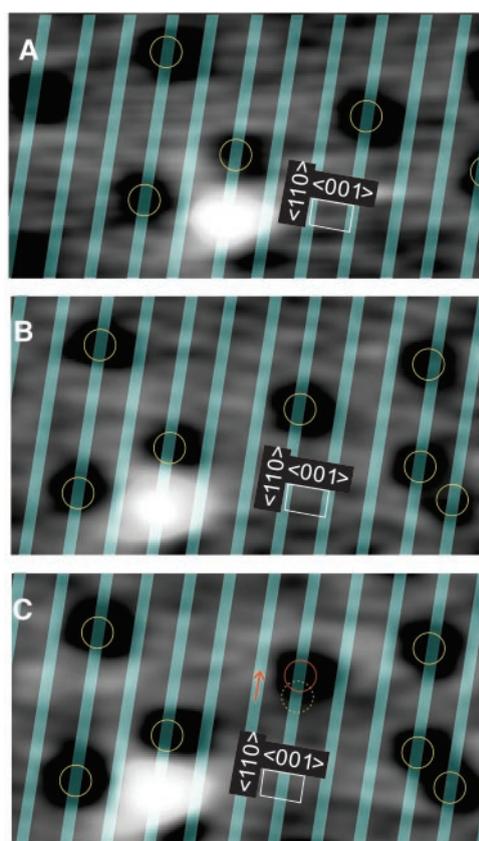
These considerations strongly suggest that an electronically driven process is responsible for the observed surface diffusion. Although theoretical attention has focused largely on the role of electronic temperature in driving desorption processes, the notion of electronic coupling to coordinates relevant for lateral adsorbate motion is also inherently reasonable, because strong adsorbate-substrate charge transfer is expected as the adsorbate moves from one surface binding site to the next. Indeed, in the calculations of Kindt *et al.* (30), it was explicitly noted that electronic coupling to modes other than the molecule-surface vibration for CO/Cu(100) should play an important role.

Here, we introduce a simple phenomenological model of such an electronically driven diffusion process. With the use of only parameters from the literature, we can roughly reproduce the experimental rate for diffusion along the atomic rows of the Cu(110) surface and account for the anomalous behavior for diffusion across these rows. Our starting point is the experimental Arrhenius rate law reported by Briner *et al.* (18) for CO diffusion along the  $\langle 1\bar{1}0 \rangle$  direction. We now, however, consider energy transfer separately from the electronic and lattice degrees of freedom of the substrate, following a model previously introduced to examine coupling between the substrate and adsorbate vibrations:

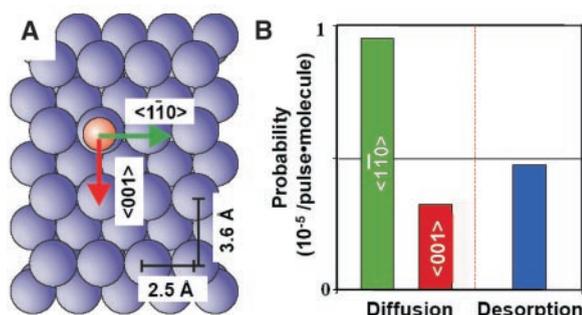
$$dU_{ad}/dt = (U_{el} - U_{ad})/\tau_{el} + (U_{ph} - U_{ad})/\tau_{ph} \quad (1)$$

where  $U_x = hv/\exp(hv/kT_x - 1)$  denotes the energy content of a harmonic oscillator corresponding to the frustrated translational mode ( $\nu = 1.1 \times 10^{12} \text{ s}^{-1}$ ) at the specified temperature  $T_x$  (where ad, el, and ph indicate the adsorbate, electronic, and phonon degrees of freedom, respectively) and  $h$  and  $k$  are the usual Planck and Boltzmann constants. The coupling parameters ( $\tau_{el} = 5.1 \text{ ps}$  and  $\tau_{ph} = 4.2 \text{ ps}$ ) for frustrated translational motion, which is assumed to be the reaction coordinate for surface diffusion, were obtained experimentally by Germer *et al.* for the CO/Cu(001) system (24, 25). Although we have included for

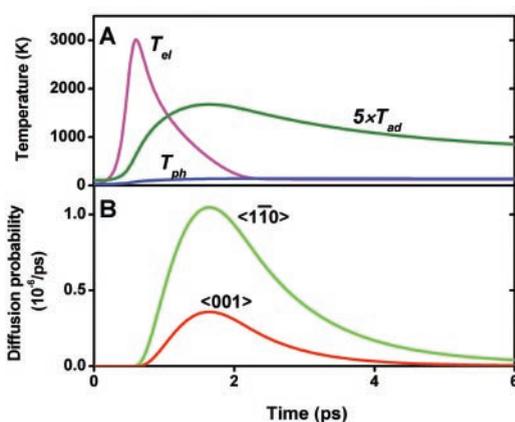
**Fig. 2.** Portion of STM images (1.00 V, 200 pA, and  $50 \text{ \AA}$  by  $25 \text{ \AA}$ ) of CO molecules (dark regions indicated by circles) on the Cu(110) surface taken at high scan speed. The rows of surface atoms along the  $\langle 110 \rangle$  direction are highlighted on the basis of separate slow scans. The tip was removed and reapprached without optical excitation between images (A) and (B). Although a slight drift is seen, precisely the same region of the surface has been found. Between images (B) and (C), fs-pulse laser excitation was applied. One adsorbed CO molecule (with an initial position indicated by the dashed yellow circle) moved to a new position (red circle) one site along the  $\langle 110 \rangle$  direction. The bright spot in the bottom of the images is a metal cluster that was deposited by controlled tip-sample contact for tip preparation and as a registry marker. Analysis of hundreds of such images led to the data set presented in this work.



**Fig. 3.** (A) Schematic representation of Cu(110) indicating the crystallographic axis and interatomic distances. (B) Summary of experimental results of fs laser-induced diffusion and desorption for CO-Cu(110) measured with a total of  $\sim 3000$  adsorbed molecules. The ratio of hopping across the close-packed rows ( $\langle 001 \rangle$ ) to hopping along the rows ( $\langle 110 \rangle$ ) is 0.34.



**Fig. 4.** (A) Calculated temperature profiles for the substrate electrons ( $T_{el}$ ) and phonons ( $T_{ph}$ ), and the adsorbate frustrated translational mode ( $T_{ad}$ ) under laser irradiation of the Cu(110) sample. A peak electronic temperature  $T_{el,max} = 3000 \text{ K}$  is reached, in contrast to a peak phonon temperature  $T_{ph,max} = 140 \text{ K}$ . (B) The CO diffusion probability across the close-packed rows ( $\langle 001 \rangle$ ) and along the rows ( $\langle 110 \rangle$ ) from the calculated increase in the adsorbate temperature.



completeness both electronic and phononic couplings, the observed surface hopping is driven by the high electronic temperature.

The predicted temperature of the translational degree of freedom of the adsorbed CO molecules is shown in Fig. 4. We calculate a hopping probability per laser pulse of  $2 \times 10^{-6}$ . Given the severe approximations in this treatment, the agreement with the experimental result of  $9 \times 10^{-6}$  is satisfactory.

Can this analysis also explain the anomalous behavior with respect to adsorbate motion perpendicular to the atomic rows? Here, we cannot rely on an established Arrhenius rate law; all we know is that measurable hopping perpendicular to the atomic rows has not been observed under conventional thermal conditions. For purposes of a semiquantitative discussion, we assume that the lack of thermal diffusion in the perpendicular direction is attributable primarily to a larger energy barrier associated with the increased hopping distance to the next atom. Taking the lack of thermal diffusion across the rows in the measurements of Briner *et al.* (18) to mean that it is at least three orders of magnitude less probable than diffusion along the rows, we then deduced a minimum barrier height of 128 meV for diffusion across the rows, compared to a barrier of 97 meV for motion along the rows. With this parameter, our analysis of an electronically driven process yields a branching ratio for diffusion across the rows of 0.25. This value is comparable to our experimental finding of 0.34 but stands in sharp contrast to the equilibrium behavior. The observed branching ratio reflects the relative insensitivity to barrier heights of the electronically driven process.

These experiments show the possibility of combining direct imaging of molecules by STM with access to the ultrafast time scale by femtosecond laser excitation. The extension of these measurements to multiple-pulse laser excitation should retain the atomic-scale spatial resolution while providing further insight into the temporal evolution of ultrafast dynamical processes.

#### References and Notes

- R. J. Hamers, D. G. Cahill, *Appl. Phys. Lett.* **57**, 2031 (1990).
- S. Weiss, D. F. Ogletree, D. Botkin, M. Salmeron, D. S. Chemla, *Appl. Phys. Lett.* **63**, 2567 (1993).
- V. Gerstner, A. Knoll, W. Pfeiffer, A. Thon, G. Gerber, *J. Appl. Phys.* **88**, 4851 (2000).
- J. A. Prybyla, T. F. Heinz, J. A. Misewich, M. M. T. Loy, J. H. Glowina, *Phys. Rev. Lett.* **64**, 1537 (1990).
- J. A. Prybyla, H. W. K. Tom, G. D. Aumiller, *Phys. Rev. Lett.* **68**, 503 (1992).
- D. G. Busch, S. W. Gao, R. A. Pelak, M. F. Booth, W. Ho, *Phys. Rev. Lett.* **75**, 673 (1995).
- L. M. Struck, L. J. Richter, S. A. Buntin, R. R. Cavanagh, J. C. Stephenson, *Phys. Rev. Lett.* **77**, 4576 (1996).
- J. A. Misewich, S. Nakabayashi, P. Weigand, M. Wolf, T. F. Heinz, *Surf. Sci.* **363**, 204 (1996).
- R. J. Finlay, T. H. Her, C. Wu, E. Mazur, *Chem. Phys. Lett.* **274**, 499 (1997).
- G. Eichhorn, M. Richter, K. Al-Shamery, H. Zacharias, *Chem. Phys. Lett.* **289**, 367 (1998).
- M. Bonn *et al.*, *Science* **285**, 1042 (1999).
- D. N. Denzler, C. Frischkorn, C. Hess, M. Wolf, G. Ertl, *Phys. Rev. Lett.* **91**, 226102 (2003).
- K. Watanabe, N. Takagi, Y. Matsumoto, *Phys. Rev. Lett.* **92**, 057401 (2004).
- H. Petek, M. J. Weida, H. Nagano, S. Ogawa, *Science* **288**, 1402 (2000).
- R. Gomer, *Rep. Prog. Phys.* **53**, 917 (1990).
- T. T. Tsong, *Prog. Surf. Sci.* **67**, 235 (2001).
- J. Ahner, J. T. Yates, *J. Chem. Phys.* **105**, 6553 (1996).
- B. G. Briner, M. Doering, H.-P. Rust, A. M. Bradshaw, *Science* **278**, 257 (1997).
- L. Bartels, M. Wolf, G. Meyer, K. H. Rieder, *Chem. Phys. Lett.* **291**, 573 (1998).
- H. J. Lee, W. Ho, *Science* **286**, 1719 (1999).
- A. J. Heinrich, C. P. Lutz, J. A. Gupta, D. M. Eigler, *Science* **298**, 1381 (2002); published online 24 October 2002; 10.1126/science.1076768.
- T. Komeda, Y. Kim, M. Kawai, B. N. J. Persson, H. Ueba, *Science* **295**, 2055 (2002).
- J. I. Pascual, N. Lorente, Z. Song, H. Conrad, H. P. Rust, *Nature* **423**, 525 (2003).
- T. A. Germer, J. C. Stephenson, E. J. Heilweil, R. R. Cavanagh, *Phys. Rev. Lett.* **71**, 3327 (1993).
- T. A. Germer, J. C. Stephenson, E. J. Heilweil, R. R. Cavanagh, *J. Chem. Phys.* **101**, 1704 (1994).
- J. P. Culver, M. Li, Z. J. Sun, R. M. Hochstrasser, A. G. Yodh, *Chem. Phys.* **205**, 159 (1996).
- J. P. Culver, M. Li, R. M. Hochstrasser, A. G. Yodh, *Surf. Sci.* **368**, 9 (1996).
- M. Head-Gordon, J. C. Tully, *Phys. Rev. B* **46**, 1853 (1992).
- C. Springer, M. Head-Gordon, *Chem. Phys.* **205**, 73 (1996).
- J. T. Kindt, J. C. Tully, M. Head-Gordon, M. A. Gomez, *J. Chem. Phys.* **109**, 3629 (1998).
- D. A. Micha, Z. G. Yi, *Chem. Phys. Lett.* **298**, 250 (1998).
- Our experiments were performed with a variable-temperature STM, which was operated at a base pressure of  $8 \times 10^{-11}$  mbar. The Cu(110) sample was prepared by multiple cycles of sputtering (Ne<sup>+</sup> at 1 keV) and annealing (300 s at 900 K).
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## Nanoparticles: Strained and Stiff

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Nanoparticles may contain unusual forms of structural disorder that can substantially modify materials properties and thus cannot solely be considered as small pieces of bulk material. We have developed a method to quantify intermediate-range order in 3.4-nanometer-diameter zinc sulfide nanoparticles and show that structural coherence is lost over distances beyond 2 nanometers. The zinc-sulfur Einstein vibration frequency in the nanoparticles is substantially higher than that in the bulk zinc sulfide, implying structural stiffening. This cannot be explained by the observed 1% radial compression and must be primarily due to inhomogeneous internal strain caused by competing relaxations from an irregular surface. The methods developed here are generally applicable to the characterization of nanoscale solids, many of which may exhibit complex disorder and strain.

The electronic properties of nanoparticles can differ from those of their corresponding bulk form due to confinement effects caused only by their finite size, and because they are structurally distinct. Quantum confinement is the dominant size effect, and has been well studied (1–6). Structural deviations in nanoparticles relative to bulk material are not well understood because they are hard to resolve experimentally (7). Consequently, theoretical models of nanoparticles generally assume they have bulklike interior structure (8). Tight-binding calculations that optimized

nanoparticle structure, and assumed full theoretical passivation of surface anions, suggested that surfaces of nanoparticles relax in a manner comparable to that of bulk surfaces (9). However, classical and quantum molecular dynamics simulations have indicated that disorder may pervade throughout nanoparticles (10, 11). We previously showed that nanoparticles can undergo substantial transformation in structure at low temperature, driven by surface interactions, indicating that internal strain depends upon the nature of the surroundings as well as size (12). However, a detailed description of the strain within nanoparticles has not been experimentally obtained. We combine pair distribution function and extended x-ray absorption fine structure (EXAFS) analyses to quantify the structural distortion within mercaptoethanol-coated zinc sulfide (ZnS) nanoparticles and the consequent changes in lattice dynamics.

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