

achieved IR mode-selective chemistry. The atomic-level mechanism underlying this process is far from clear, however.

The authors observe a quadratic dependence of desorption yield on laser intensity. It is tempting to implicate two neighboring H-Si units, each vibrationally excited by a single IR photon. Liu *et al.* correctly caution, however, that a quadratic dependence on intensity does not necessarily imply a two-photon process. The measured activation energy for thermal desorption of H<sub>2</sub> from H-Si(111) is 2.4 eV (6)—far more than two 0.26-eV IR photons. The measured activation energy of a chemical reaction does not necessarily equal the height of an actual energy barrier. Nevertheless, it is difficult to see how only two photons can produce desorption. Any atomic trajectory that might be launched by IR laser excitation of two neighboring-singly excited H-Si bonds can also be produced by heating—there cannot be any secret passages that are accessed only by IR laser excitation. Therefore, if only two photons worth of energy can produce desorption in the laser experiment, then the same amount of energy can produce desorption thermally. But if so, the activation energy would be far lower than 2.4 eV.

It thus appears necessary to invoke many IR photons. Perhaps there is some contribution

from vibrational energy pooling. Chang and Ewing have observed this effect in physisorbed layers of CO on NaCl (7), where dipole-dipole coupling induces many molecules excited by a single photon to pool their energy into a few highly vibrationally excited molecules (8). For the H-Si(111) system, however, this effect is expected to be much less important; the dipole-dipole coupling is weaker than for CO, and the vibrational lifetime is much shorter.

It appears more likely that the high intensities achievable with the free-electron laser produce multiple (sequential) photon absorption by individual H-Si bonds. Much of this energy must remain localized long enough for two H atoms to combine and surmount the 2.4-eV barrier. Scanning tunneling microscopy studies of the H-Si(100) surface have shown that energetic electrons are far more likely to induce the breaking of an Si-H bond than the breaking of an Si-D bond (9). This difference is believed to be the reason for the increased lifetime of semiconductor devices upon deuterium substitution (10). Van de Walle and Jackson (11) have proposed that energetic electrons excite both Si-H and Si-D vibrations. However, the Si-D vibrational frequencies more closely match those of the silicon substrate, and energy dissipation should thus

occur more rapidly for Si-D, leading to preferential breaking of Si-H bonds.

The experiments of Liu *et al.* may exhibit similar behavior, where energy transferred to Si-D units quickly dissipates, leaving only the Si-H units energized. But whatever the mechanism, Liu *et al.* have successfully accomplished a long-standing goal: IR mode-selective chemistry in a many-atom system.

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10.1126/science.1126341

## APPLIED PHYSICS

# Assembly and Probing of Spin Chains of Finite Size

Harald Brune

The creation, investigation, and manipulation of low-dimensional model systems is of fundamental importance in condensed-matter physics. Moreover, an understanding of the wide variety of electronic and magnetic properties of these models—and their associated phase transitions—may lead to applications in spintronics and other areas of device physics. To an increasing degree, such model systems have been created by researchers in surface science. A well-known example was achieved in 1993 by Eigler and co-workers at IBM Almaden, who used a low-temperature scanning tunneling microscope (STM) to arrange adsorbed atoms into a corral that imposed a circular boundary on the surface-state electrons of the underlying single crystal (1). The resulting quantum interference patterns exactly displayed the solution of the Schrödinger equation, which

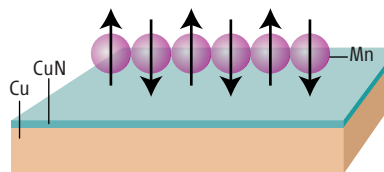
for that geometry can be given in analytical form. A second but no less exciting example is now reported from the same lab on page 1021 of this issue by Hirjibehedin *et al.*, who have carried out low-temperature STM measurements of manganese atom chains (of up to 10 atoms), assembled by atomic manipulation on copper nitride islands that provide an insulating monolayer between the chains and a copper substrate (2). These chains are model systems representing one-dimensional (1D) Heisenberg antiferromagnets of finite size.

A Heisenberg chain is a linear arrangement of spins  $S$  mutually coupled by an exchange interaction with energy  $J$ . Several order-disorder transitions are predicted for such chains. In the absence of magnetic anisotropy, for example, long-range order is predicted to be lost at any finite tem-

Understanding magnetic ordering at the atomic scale is essential for spintronic technology. A linear chain of manganese atoms has been created for studying one-dimensional systems.

perature (3, 4). A model system for a ferromagnetic Heisenberg chain (where all the spins are aligned parallel to each other) has been realized in the form of atomic cobalt chains created by step decoration of vicinal platinum single-crystal surfaces. In this case, anisotropy was found to stabilize small ferromagnetic spin blocks (5). 1D ferrimagnets (where neighboring spins are antiparallel but do not cancel, leaving a net moment) have been realized with molecular magnets (6) and have been found to display the predicted slow magnetization relaxation (7). However, a chain with antiferromagnetic coupling (where neighboring spins are antiparallel)

is of fundamental importance in many-body physics, as it is one of the few systems where a nontrivial many-particle ground state is known exactly (8). The quantum mechanical nature of the spins gives rise to the collapse of the Néel state (the arrangement of antiparallel spins) into a single



**Model magnet.** Schematic representation of an antiferromagnetic chain of six manganese atoms residing on a monolayer of insulating copper nitride grown on a Cu(100) substrate.

The author is at the Institut de Physique des Nanostructures, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland. E-mail: harald.brune@epfl.ch

wave function of the entire chain, which is subject to quantum fluctuations and displays quantum phase transitions in high magnetic fields (9).

Until now, model systems of 1D Heisenberg antiferromagnets have been bulk crystals with electronically coupled quasi-1D chains, such as  $\text{CuGeO}_3$ , copper tetraminsulfate,  $\text{CsNiCl}_3$ , or copper benzoate  $\text{Cu}(\text{C}_6\text{D}_5\text{COO})_2 \cdot 3\text{D}_2\text{O}$  (10), which have been investigated by electron spin resonance, nuclear magnetic resonance, magnetic susceptibility, and inelastic neutron scattering. Similar to the quasi-1D bulk samples, the manganese atom chains are strongly coupled along the chain yet weakly coupled to the environment. In contrast to the bulk samples, the chains have finite length, but structures with arbitrary geometries can be assembled, and the nearest neighbor distance as well as the adsorption site can be freely chosen. The STM allows direct measurement of the chain properties for each configuration—for instance, by inducing spin-flips and total spin changes that appear as steps in differential conductance curves ( $dI/dV$ , where  $I$  is current and  $V$  is voltage).

Odd chains have a zero-bias dip in  $dI/dV$  caused by spin-flip excitation (change in magnetic quantum number  $m$ ); all chains have conductance steps arising from the total spin change. The size of the conductance steps in the even chains can reach up to one order of magni-

tude. The absence of spin-flip excitations for even chains shows that the total spin in the ground state is  $S_{\text{tot}} = 0$ , and the presence of such excitations in odd chains implies their ground state to have  $S_{\text{tot}} \neq 0$ ; therefore, the chains are ordered antiferromagnetically. The interatomic coupling strength  $J$  of the chains is measured by means of the energy difference between ground and first excited state of a dimer at zero field. The influence of the chemical environment on  $J$  is clearly evident, as Hirjibehedin *et al.* find  $J = 6.2$  meV in chains placed on Cu atoms of the insulating CuN layer, but  $J = 3.0$  meV for a chain placed on nitrogen atoms. In the presence of a magnetic field, the total spin transition of a dimer splits up into three energies, corresponding to a transition from  $S_{\text{tot}} = 0$  to  $S_{\text{tot}} = 1$  with quantum numbers  $m = 0, \pm 1$ . From the energy of the total spin change of a linear trimer, the authors deduce  $S_{\text{tot}} = S = \frac{1}{2}$ . Because  $J$  and  $S$  are known, the energies for the total spin transitions for all chain lengths  $n$  can be predicted with a Heisenberg open-chain model. The peak positions up to  $n = 6$  of this model are in excellent agreement with experiment. Moreover, the authors find inelastic electron tunneling spectroscopy (IETS) selection rules for spin transitions in the chains:  $\Delta S_{\text{tot}} = 0, \pm 1$ , and  $\Delta m = 0, \pm 1$ , but not  $\pm 2$ .

These results represent an important step in the creation, understanding, and manipulation of

low-dimensional spin systems. Understanding the selection rules is a theoretical challenge, and the role of magnetic anisotropy needs to be highlighted. Further experimental progress should be possible with spin-polarized STM, which might reveal whether internal order is indeed absent or may allow direct excitation of magnetic transitions with the injection of spin-polarized currents. The most exciting part of this report is that one can now create and explore any arrangement of spins, in particular those less likely to be found in nature's crystals.

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10.1126/science.1127387

## BEHAVIOR

# Foresight and Evolution of the Human Mind

Thomas Suddendorf

What is in your pockets? Chances are you carry keys, money, cosmetics, a Swiss Army knife, or other tools—because they may be useful at some future point. Humans have the ubiquitous capacity to imagine, plan for, and shape the future (even if we do frequently get it wrong). This capacity must have long been of major importance to our survival (see the figure) and may have been a prime mover in human cognitive evolution (1). Stone toolkits and spears from archaeological finds suggest that the ancestors of modern humans already prepared for the future hundreds of thousands of years ago. On page 1038 of this issue, Mulcahy and Call (2) show that the roots of these abilities

may go much deeper still. Though great apes have not invented containers to carry tools, the experiments demonstrate that they can save tools for future use.

Of course, other animals also act in ways that increase their chances of future survival. Many species have evolved preparatory instincts that lead them, for example, to build nests or hoard food. Associative learning mechanisms further allow individuals, rather than entire species, to predict recurrences on the basis of cues (for example, a smell signaling food). But animals are not mere associative automatons. Recent evidence shows that some can make causal inferences (3, 4). Great apes even seem capable of imagining situations they cannot directly perceive (5). They can also make simple tools to solve nearby problems, such as fashioning an appropriate stick to obtain food that would otherwise be out of reach (6). Yet there seems little evidence that animals ponder the more distant future. Wolfgang Köhler, who

Planning for the future is a fundamental human survival strategy. New results suggest that great apes can anticipate future needs and that this ability has roots more ancient than previously thought.

first documented “insightful” problem-solving in chimpanzees nearly 90 years ago, concluded that “The time in which the chimpanzee lives is limited in past and future” (6). Recent reviews concur that animal foresight more generally may be profoundly restricted (7, 8), even though innovative work on scrub-jays suggests that these birds have some surprising competence in the specific context of food caching (9). In this week's *Science Express*, Dally *et al.* (10), for example, report that scrub-jays adjust their caching behavior in ways that effectively decrease the chances that the food will be stolen by others. They appear to keep track of what caching was observed by which other jay and move food to new locations accordingly. However, the caching behaviors may be driven by a combination of predispositions and specific learning algorithms rather than by reasoning about past and future (10, 11). It remains unclear what exactly the limits are for animal foresight.

Enhanced online at  
www.sciencemag.org/cgi/  
content/full/312/5776/1006

The author is in the School of Psychology, Early Cognitive Development Unit, University of Queensland, Brisbane, QLD, 4072 Australia. E-mail: t.suddendorf@psy.uq.edu.au