ATOMIC SPINS on surfaces

Andreas Heinrich

Atomic and solid-state physics have mostly led separate lives. Atomic physics was born in the 1920s out of a desire to understand the optical and magnetic properties of atoms in the gas phase; it was in that playground that quantum mechanics emerged. In contrast, solid-state physics matured through the purification of materials; that purification was, among other aspects, crucial to understanding the influence of chemical doping on conductivity in semiconductors and led to the plethora of electronic devices we enjoy today. Not surprisingly, the experimental and theoretical concepts used in the two fields are often quite different. For example, the magnetic properties of isolated gas atoms are described by quantum spin states, whereas the magnetic properties of solids are obscured by the formation of a band structure.

Half of all atoms in the periodic table are magnetic in the gas phase by virtue of their odd number of electrons, but magnetic solids are much rarer. To find them, one usually turns to transition metals and rare-earth solids, whose atomic spin properties are preserved in their partially filled *d* and *f* electron shells. To explore magnetism in more exotic materials, researchers in the 1950s and 1960s intensively studied the electron spin resonance of nonmagnetic insulators after doping them with transition-metal and rare-earth atoms.[1] The dopant atoms, though embedded in the solid, retain their quantum spin states, as if still in the gas phase. Spin resonance has undergone a major revival in recent years through investigations of individual defects in insulators. Perhaps the most prominent subject is the so-called nitrogen–vacancy defect in diamond, thanks to its potential applications in quantum computing and sensing (see the article by Lilian Childress, Ronald Walsworth, and Mikhail Lukin, PHYSICS TODAY, October 2014, page 38).

Atom-like magnetic defects in solids interact with conduction electrons and thus influence the behavior of electronic devices. Putting magnetic atoms in the gap between the two electrodes of a micron-scale planar tunnel junction offered a conceptually easy way to probe those interactions as current passed through the atoms. The electrical transport properties observed at low voltages deviated wildly from the naively expected linear Ohm's law behavior—a deviation often called the "zero-bias anomaly."[2] In retrospect, it's clear that understanding the transport anomaly was all but impossible. The uncontrolled placement of the magnetic atoms in tunnel junctions and the atoms' strongly varying interactions with their local environments presented too complicated a system.

In this article I describe experiments developed over the past decade that overcome the random placement and probe junctions one spin at a time.

Looking for single spins

The most important ingredient for researching individual magnetic atoms in tunnel junctions is a scanning tunneling microscope (STM), which can localize an electric current through a single atom. It was invented in 1981 by Gerd Binnig and Heinrich Rohrer (figure 1a), who received the 1986 Nobel Prize in Physics for the achievement. In an STM, an atomically sharp tip is brought to within a few atomic diameters of a clean surface, and a bias voltage is applied between them to establish a tunneling current.

In one mode of operation, the bias voltage is fixed and the tip height is adjusted to keep the current constant while the tip scans across the surface; the height modulation maps the topography. Shortly after the STM's invention, Binnig and Rohrer used that technique to settle a long-standing debate about the atomic structure of a particular for-

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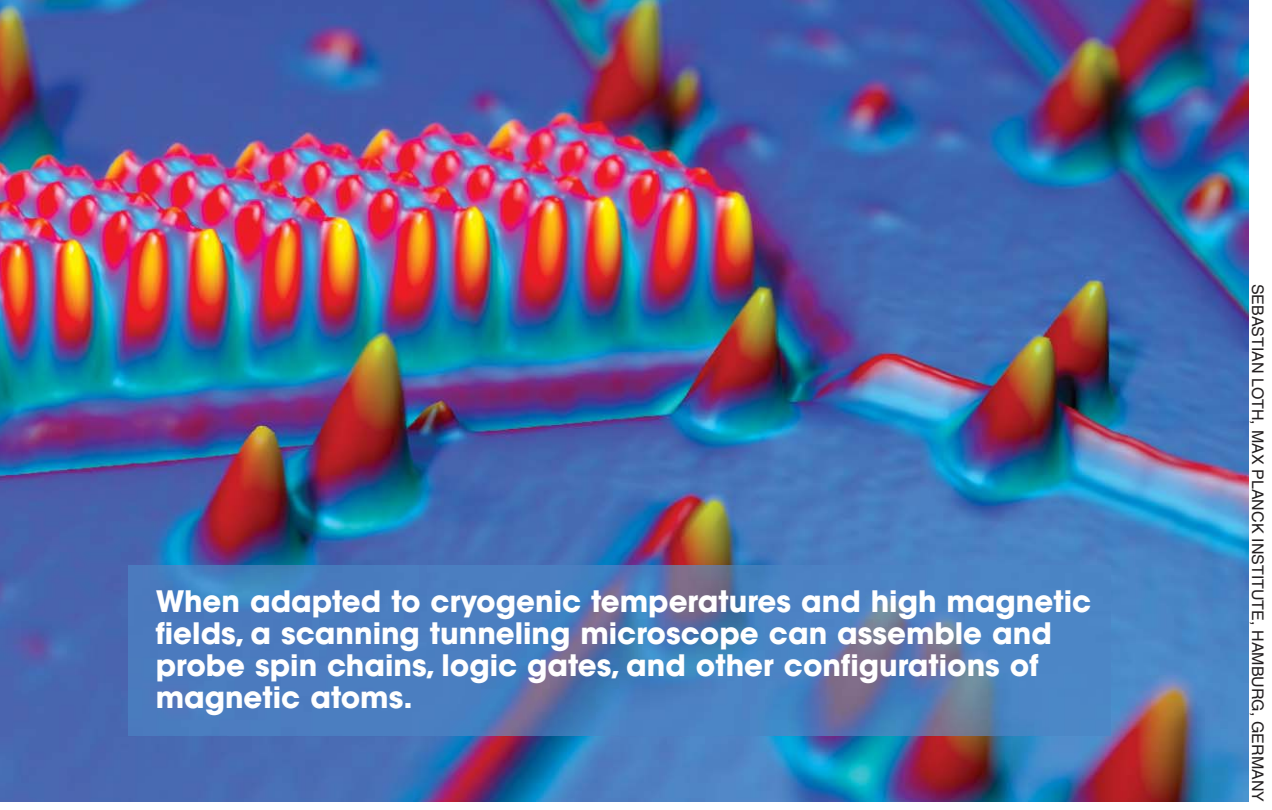

When adapted to cryogenic temperatures and high magnetic fields, a scanning tunneling microscope can assemble and probe spin chains, logic gates, and other configurations of magnetic atoms.

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mation on the surface of silicon, a significant feat for the new tool.

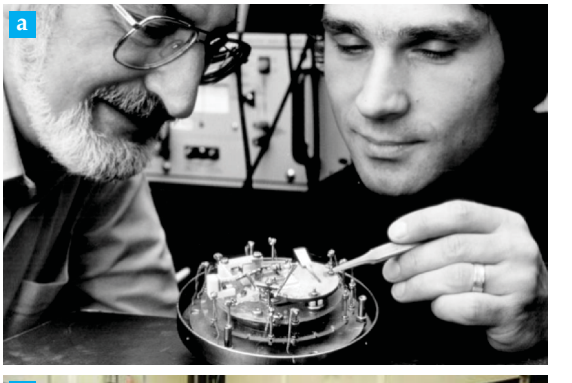
Half a decade after the STM's discovery, Donald Eigler, shown in figure 1b, successfully wed the experimental techniques of low-temperature physics to the ultrahigh-vacuum environment common in surface-science experiments and created the first STM that could be brought to bear on surfaces at liquid-helium temperature. Low-temperature systems invariably cause vibrations—for example, from the bubbling of cryogenic liquids or the mechanically driven circulation of helium gas. Engineering a platform that would isolate the STM tip, which must be held stable to within one hundredth of an atomic diameter, from such vibrations was impressive.

Eigler's achievement enabled two great breakthroughs: first, and most famous, the ability to move atoms one at a time to build structures with atomic-scale precision; second, and possibly as important, the ability to measure the conductance through individual atoms with the high energy resolution afforded by the low temperature. (See PHYSICS TODAY, November 1993, page 17.)

Most of the magnetic field of an ordinary permanent magnet comes directly from the unpaired electron spins it contains. The energy of a quantum spin, such as the electron spin of a gas atom, is degenerate in the absence of a magnetic field. But when a field is applied, the spin splits into differing energy states. For atoms in free space, that Zeeman splitting is governed by the interplay of orbital and spin magnetic moments. When the atoms are embedded in a solid or collectively form a molecule, however, the splitting is altered by the local environment in ways that reveal valuable information about that environment.[1]

Magnetic measurements

Can an STM measure the Zeeman splitting one atom at a time? A back-of-the-envelope calculation quickly



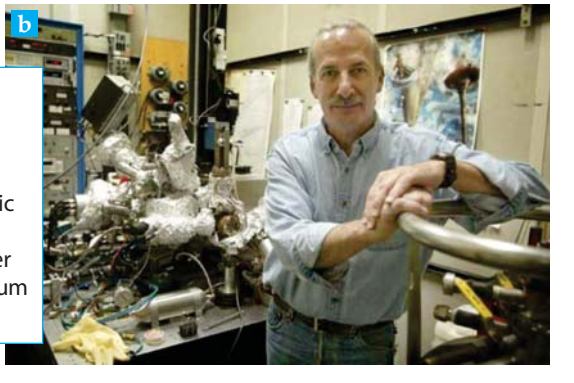
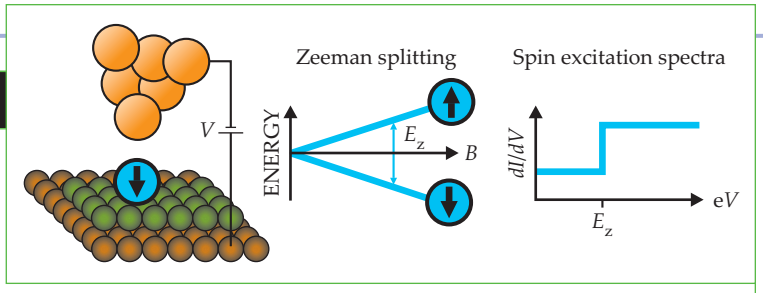


Figure 1. Pioneers of scanning tunneling microscopy. **(a)** Gerd Binnig and Heinrich Rohrer, shown here with one of their original instruments, invented the scanning tunneling microscope (STM) about 35 years ago. They overcame the conceptual and engineering challenge of placing a macroscopic object—a sharp tip—an atomic-scale distance from a surface and demonstrated atomic-resolution imaging. **(b)** Donald Eigler stands in front of the liquid-helium-temperature, ultrahigh-vacuum STM he developed at IBM. (Photographs courtesy of IBM.)

Box 1. Spin excitation spectroscopy



A quantum spin can be described with discrete spin states, the energy eigenstates that depend on the quantum state of the spin. The simplest example is a spin-½ atom in a magnetic field B. The field gives rise to the Zeeman energy E_z, which lifts the degeneracy of the two spin states, usually called up and down. To put the Zeeman energy scale into perspective, note that the energy to flip an atom's spin at a magnetic field B of 1 T is four orders of magnitude smaller than that of a typical molecular bond. But provided one has access to a stable enough scanning tunneling microscope (STM), spin excitation spectroscopy (SES) can exploit the eigenstates' discrete nature.

In SES, an STM's nonmagnetic tip is placed in tunneling range of a spin on a surface, as shown here. Often that spin is placed atop a thin insulator (green) to slightly decouple it from the underlying conduction electrons in the substrate (brown). The conductance—or more precisely, the differential conductance dI/dV, where I is the tunnel current—of the tunnel junction is then measured as a function of bias voltage V along with external parameters such as magnetic field. As the applied voltage is increased, the conductance remains constant until the tunneling electrons deliver enough energy to excite the spin from the ground to an excited state. At that voltage, a characteristic change in differential conductance occurs. Below the excitation voltage threshold, the electrons can only tunnel via an elastic channel, but above the threshold, an inelastic channel opens as well. The conductance of the tunnel junction is generally greater when both channels are open, and dI/dV increases in a stepwise fashion.

The voltage at which the step in SES occurs is a direct measure of the energy required to flip the spin or, equivalently, the strength of the Zeeman interaction. Besides the magnetic field, the local environment of the binding site also strongly modifies the magnetic behavior of atoms on surfaces. In many cases a spin prefers to point along a particular spatial direction, and the energy cost, known as magnetic anisotropy and often referred to as the zero-field splitting, can be directly measured with SES. In addition, SES can be used to measure the coupling strength between spins, as, for example, in the spin chains discussed in the main text.

suggests that in readily achievable magnetic fields of a few tesla, a temperature below 1 K is needed to reach the necessary energy resolution. But additional modifications had to be added to the low-temperature STM to maintain its stability in high magnetic fields. In November 1998, I joined Eigler's group at the IBM Almaden Research Center, where, as a postdoc, I took on that challenge. At extremely low temperatures and high fields, most materials become at least partially magnetic, so a large part of the work was to replace many of the materials that make up the STM housing and components with less magnetic versions to prevent them from coupling to the surrounding superconducting magnet.

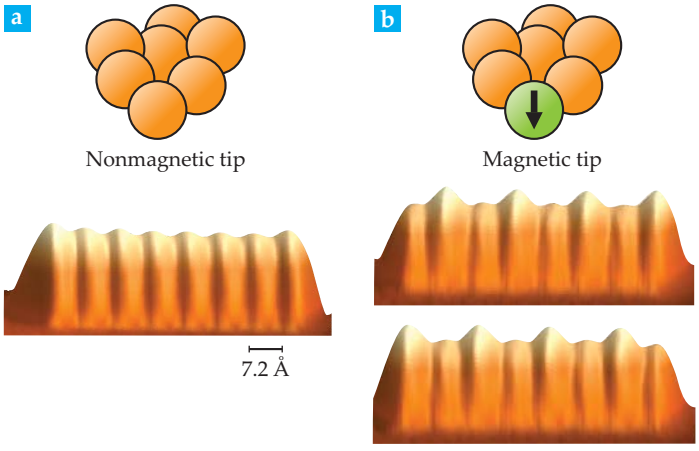
Five years later, my colleagues and I used the newly developed 0.5-K, 7-T STM to measure the Zeeman splitting of the spin states of individual magnetic atoms on a surface. In our first experiment, we placed manganese atoms on a thin, insulating film of alumina to prevent their magnetic moments from mixing with the underlying copper's large number of conduction electrons.[3] Box 1 describes the mechanism underlying the spin excitation spectroscopy (SES) used in that work. Because the entire tunnel current flowed through individual, widely spaced Mn atoms, the magnetic signal turned out to be surprisingly large, with the inelastic tunneling current—that which flips the atom's spin state—reaching about 25% of the total current.

An alternative approach to magnetic measurements using an STM is to outfit its tip with magnetic atoms and measure the differential conductance in an applied magnetic field. At the heart of that approach, known as spin-polarized scanning tunneling microscopy and described in box 2, is the fact that a tunnel junction's electrical conductance changes with the relative magnetic orientation of two magnetic materials on opposite sides of the junction—an effect called tunneling magnetoresistance. In the 1990s Roland Wiesendanger and his group at the University of Hamburg in Germany first applied that approach, studying bulk magnetic samples and thin-film magnetic materials. Later, around the same time my group introduced single-spin spin-excitation spectroscopy in 2002, researchers in Wiesendanger's lab began measuring the magnetoresistance of tunnel junctions, each consisting of an STM tip atop a single paramagnetic atom on a metal surface.[4]

What did researchers learn from those single-spin tunneling experiments? For one, we learned that no zero-bias anomaly exists in such controlled tunnel junctions, although some magnetic atoms on metal surfaces show complex conductance variations due to correlations with substrate electrons (see PHYSICS TODAY, January 1998, page 17, and May 2002, page 21). Similarly, when magnetic atoms are placed on a thin, insulating layer, strong inelastic conductance features arise from spin excitations in the atoms. In the case of spin-polarized tunneling, those spectroscopic signatures are sensitive to the degree of spin polarization of the tip and sample and may differ dramatically from spin-averaged measurements. The zero-bias anomaly in planar tunnel junctions may have stemmed from the spatial averaging over all those varying spectroscopic channels that are present in macroscopic tunnel junctions.

Second, we researchers learned that the transition from the magnetic behavior in solids, characterized by their spin-polarized band structure, to the atomic character of quantum spins can be surprisingly complex and rich. Even today, many spin properties in tunnel junctions with single or small clusters of magnetic atoms are not fully understood. Nonetheless, the simplification of tunnel junctions to well-controlled individual magnetic atoms and

Figure 2. A classical antiferromagnetic spin chain composed of eight iron atoms assembled on a copper nitride substrate appears as identical bumps **(a)** when imaged using a nonmagnetic tip of a scanning tunneling microscope (STM). But when the nonmagnetic tip is swapped out for a magnetic one **(b)**, adjacent iron atoms alternate between appearing short and appearing tall. The contrast is the result of atomic-scale magnetoresistance, an effect in which each atom's spin orientation, parallel or antiparallel to the tip's field, influences how much current flows through the STM. The spin chain appears to be in a classical magnetic state, called a Néel state, in which spins alternate between definite orientations, either up or down. Both Néel states are equally likely to occur in the antiferromagnetic chain, and the chain can be switched between them by temperature, quantum fluctuations, or controlled voltage pulses. (Adapted from ref. 6.)



nanostructures has dramatically eased the task of understanding their electron-transport properties for experimentalists and theorists alike.

Spin chains

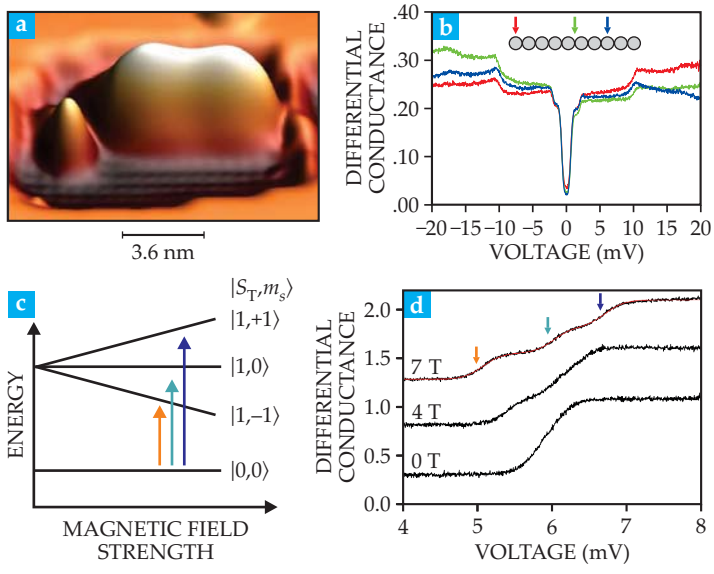
Combining single-atom STM spectroscopy with precise atom manipulation allows the study of artificial structures[5] such as one-dimensional spin chains, logic gates, and spin storage devices. Traditionally, access to spin-chain physics was achieved using bulk materials whose strongly anisotropic structure renders their magnetic properties effectively one dimensional (see the article by Yoshinori Tokura in PHYSICS TODAY, July 2003, page 50). But a spin chain consisting of atoms on a surface allows precise control: Every spin can be prepared and flipped on cue, and their exchange energy—the spins' coupling strength—can be directly measured. The STM does each of those tasks (see PHYSICS TODAY, July 2006, page 13).

Figure 2a shows an example of an STM-assembled chain of iron atoms on a thin, insulating substrate.[6] When scanned with a nonmagnetic tip, each Fe atom appears identical, as a small bump in the chain. When scanned with a spin-polarized tip, as shown in figure 2b, by contrast, four Fe atoms appear short and the other four appear tall, a manifestation of the change in tunneling current that occurs as the tip encounters opposite spin alignments in Fe as it moves along the chain.

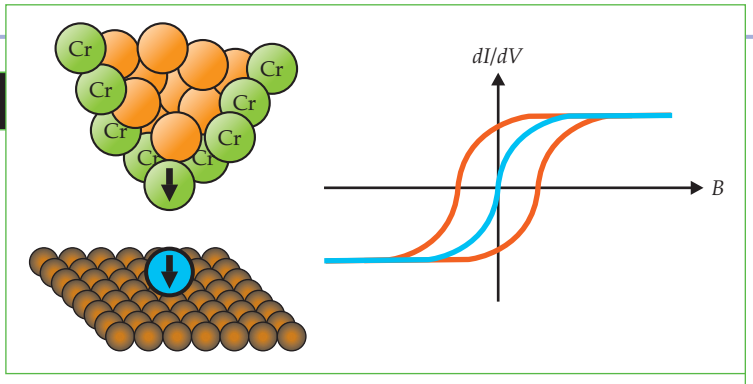
Box 2 explains the mechanism for such spin contrast. In an antiferromagnetic chain, one of the two states shown in figure 2b can emerge: In one, the leftmost atom appears in the spin-up state (tall), its neighbor appears spin down (short), and atoms in the rest of the chain follow suit with alternating spins. In the other state, the atoms have the opposite spin orientations, with the leftmost atom spin down. The two states, mirror images of each other, are often called Néel states. In the sense that each atom in the chain points either up or down, one can call the spin chain classical. At any instant, a classical chain resides in either of its two degenerate spin configurations.

In the quantum world, though, a spin can reside in two states at the same time, pointing up and down simultaneously. Figure 3 shows an example: a linear chain of 10 Mn atoms that, unlike the Fe chain,

Figure 3. A quantum antiferromagnetic spin chain composed of 10 manganese atoms (adjacent to one standing apart) on a bed of insulating copper nitride over conducting copper. **(a)** A scanning tunneling microscope assembled the chain one Mn at a time and then imaged it with a nonmagnetic tip. The indistinct structure suggests the presence of delocalized electrons shared among the atoms. **(b)** As the tip hovers above one of three different locations on the chain, an applied voltage injects current into the surface. The differential conductance spectra depend little on the tip location, and in all three cases, a large step in electrical conductance occurs around ±1 mV due to spin-flipping excitations. Further excitations, at ±2 mV and ±12 mV, take the chain into higher-energy states. **(c)** If an external magnetic field is added, the degeneracy of the excitations is broken into three distinct states $|S_T, m_s\rangle$. **(d)** In this spectra of a much shorter chain—two coupled Mn atoms—the subtle triplet excitations at 6 mV are fully discernable only when the magnetic field reaches 7 T. (Adapted from ref. 5.)



Box 2. Spin-polarized tunneling



Spintronics is an established field of solid-state electronics in which the electron's spin can be used, either with or independently of its charge, to carry information in a circuit (see the article by Gary Prinz, PHYSICS TODAY, April 1995, page 58).[8] At its core lies the fact that electrical current in magnetic materials depends on the relative alignment of the electron spin and the material's magnetization. The technology can be applied using a scanning tunneling microscope (STM) by replacing the normal tip—typically a metal such as tungsten—with a magnetic one such as chromium, as shown here. The instrument, whose tunneling current depends on the relative alignment of the tip's magnetization with the magnetization of the surface, can nowadays image magnetic materials down to the atomic scale, including single magnetic atoms on surfaces.

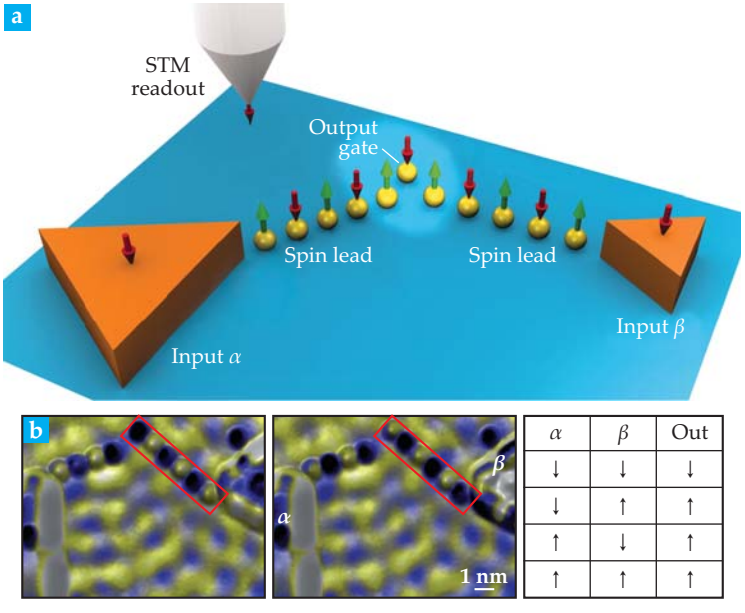
Because the tip's magnetization can be fixed, it can be used to measure the spin orientation of surface atoms. Most often, individual magnetic atoms have no fixed magnetic orientation at zero field; instead, their spins become oriented with increasing field. The blue curve in the figure here is the trace of the spin-polarized differential conductance *dI/dV*, for fixed tip height and voltage, plotted as a function of applied magnetic field *B*. At large enough positive and negative fields, the differential conductance becomes constant, which indicates that the magnetic moment of the atom on the surface has reached its peak value. The orange traces indicate the hysteretic behavior of a magnetic surface atom or nanostructure whose magnetic state is bistable.

Such single-atom magnetization curves reveal details about the interaction of the atom with its environment. Routinely used to characterize magnetic materials, the curves allow, for instance, a comparison of single-atom measurements to the ensemble averages given by bulk measurements.[9] They can also be complicated by surface step-edge effects and material inhomogeneities. Thus measurements of the simplest magnetic constituents can be revealing. Even weak interactions with other magnetic atoms or extended magnetic nanostructures such as islands can be directly observed.

resides in a quantum-coherent ground state. In that state, the total spin S_T and magnetization m_s of the chain are both zero, which implies that the chain is nonmagnetic. The spectroscopic data confirm that picture of a quantum-coherent ground state. When the chain is excited into one of its triplet states, the spins of the atoms don't quite cancel, and the chain as a whole has a net spin S_T of 1. The energy of that excitation changes as a function of chain length and splits into three distinct excitation energies at finite magnetic fields.

What distinguishes the two spin chains is that an Fe atom's spin has a strongly preferred spatial axis, a so-called easy magnetic axis, whereas Mn is nearly isotropic. The Mn chain thus closely follows the Heisenberg spin-interaction model, in which the total spin quantum number S_T characterizes the state of the chain. The Fe chain, on the other hand, follows the Ising model, in which spins always point either up or down along a certain spatial direction. Even an Fe chain shows more quantum mechanical character, however, as its length is reduced. Removing two Fe atoms from an eight-member chain[6] increases the quantum tunneling between the two Néel states by a factor of about 1000.

Theoretical modeling of such spin chains, including their interaction with the local environment, is an active field. For example, even though both Fe and Mn spin chains are usually placed on an insulating monolayer, the conduction elec-



α	β	Out
↓	↓	↓
↓	↑	↑
↑	↓	↑
↑	↑	↑

Figure 4. Magnetic logic at the atomic scale. **(a)** This device consists of two ferromagnetic islands, *α* and *β*, that serve as inputs and two spin leads made of iron atoms that serve as wires connecting them. The two spin leads meet in a central spot, where another atom (the output gate) is located, and a logical OR operation is performed. The gate's spin is then read by a scanning tunneling microscope (STM). **(b)** Externally applied magnetic fields set the islands' input states to either up or down, which appear dark blue or green in the STM images. The spin chains each reside in an antiferromagnetic Néel state, so the magnetic state of the atom closest to an island, and therefore the rest of them in the chain, are determined by the island's input state. As seen in the right STM image, the spins of a six-atom chain flip when input *β* is flipped, while a four-atom chain remains unaffected. The logic table gives the state of an output gate atom as a function of both islands' input states. (Adapted from ref. 7.)

trons in the underlying metal appear to help break the coherence; how that works in detail remains unresolved.

Devices and directions

In a beautiful piece of recent work,[7] Alexander Khajetoorians, Jens Wiebe, Bruno Chilian, and Wiesendanger demonstrated logic operations with spin chains on the atomic scale. Figure 4 illustrates the basic idea. Two magnetic islands serve as inputs; their magnetic states can be switched up or down using applied magnetic field pulses. The islands' states are then transferred to two adjacent spin chains, each residing in an antiferromagnetic Néel state. In figure 4b, the magnetic state of the right island is switched, which in turn switches the Néel state of its adjacent spin chain. Where the two chains meet, the spin state depends on the states of both chains; its output is read by a spin-polarized STM.

Classical spin chains such as the ones imaged in figure 2, and arrays such as the one on pages 42–43 and the cover of this issue, can potentially be used for magnetic data storage.[6] As discussed earlier, such chains reside in one of two ground states that are equally stable; call one of the states 0 and the other 1. Given short voltage pulses, an STM can switch the chain between those logic states to record one bit of data. In data-storage applications, such antiferromagnetic bits might actually offer some advantages over ferromagnets whose longer-range magnetic fields can inadvertently flip adjacent bits. That advantage may allow denser packing in devices. On the downside, however, the absence of long-range magnetic fields prohibits the use of read heads that sense the stray field and are now commonplace among today's computer hard drives.

Laboratory implementations of data storage and computation on the atomic scale reveal both the promise and pitfalls of miniaturizing real-world devices. Many researchers are striving to harness the emergent quantum effects for computing purposes. Much more work is needed to assess whether the various scaling approaches are feasible, but there's no doubt that controlling matter on an atomic scale will continue to provide insights into the workings of nature. And the richness of solids, such as the complex systems found in spin ices (see the article by Roderich Moessner and Art Ramirez, PHYSICS TODAY, February 2006, page 24), correlated-electron materials (see the article by Gabriel Kotliar and Dieter Vollhardt, PHYSICS TODAY, March 2004, page 53), and other systems will also, no doubt, continue to inspire novel devices.

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