Magnetism for nanoelectronics

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Magnetism for Nanoelectronics
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at Eindhoven University of Technology
Introduction

The phenomena of magnetism – compass needles, north and south poles of magnets, repulsion and attraction – are among the most familiar and appealing of pure physical behaviors to children. Magnetic materials also have a deep connection to technology, from early navigation tools to essential elements of electric motors and generators, and more recently to the storage of information. An early popular demonstration of recording information using magnetism was at the 1900 World's Fair, where a method of recording and replaying information on a magnetic wire was presented. The same basic approach has evolved, both in the media used and the sensing technology, to the magnetic-media hard disk drive, within which the information density is exceptionally high, and the storage price per bit is correspondingly low. The length scales for storing information in magnets, and for the devices used to read the magnetic information, are only a few nanometers ($10^{-9}$ meters). Thus the devices and theoretical descriptions naturally belong to the realm of “nanomagnetism”, which pertains to magnetic systems of roughly a few nanometer scale, and containing anywhere from $10^3$ to $10^9$ atoms.

Current hard disks rely on fundamental advances in nanomagnetism achieved in the late 1980’s to early 1990’s. The initial discovery in 1988 of how electrical current moves through hybrid magnetic/nonmagnetic materials that have structure on the nanometer scale (the so-called giant magnetoresistive effect) formed the basis of a new field of spin transport electronics (spintronics), and the foundational work was honored with the Nobel prize in 2007. It was noted by the Nobel committee that devices produced using this effect “can also be considered one of the first real applications of the promising field of nanotechnology”.

The commercialization of these devices, especially the hard-disk read heads, has revolutionized the nature of information storage for the world. It is perhaps educational to compare the history of two great discoveries in the 1980’s in solid state physics – high-temperature (here meaning above liquid nitrogen temperature, but not room temperature) superconductivity and spintronics. Superconducting materials carry electrical current without loss; the discoverer of superconductivity (Onnes, at Leiden) demonstrated the motion of a current in a superconducting loop without observable loss for over one year. The importance
of high-temperature superconductivity was recognized quickly by the physics community (and with a Nobel prize in 1987), but without a room-temperature superconductor commercial applications have been elusive. In contrast, the tremendous success of the practical application of magnetism to recording has led magnetic storage companies such as Seagate to close their research laboratories and high-technology companies such as IBM to move their researchers off of the topic.

So what then is the future for nanomagnetism and spintronics? You may have noticed that the speed of computers, which until the early 2000’s was rapidly increasing, has now saturated at a clock speed of a few GHz. In the meantime the price, density and access speed of storage, and the quality of the computer display and software, are the principal drivers of an improving computer experience. Semiconductor electronics based on silicon transistors on a chip, the bedrock technology of computers since the 1970’s, is slowly reaching its limits. Thus the semiconductor electronics community is now turning outward to see if other approaches may allow the improvements in information processing driven by silicon technology to continue. We may now be approaching the point where nanomagnetism and spintronics can offer opportunities for the manipulation, processing and transport of information – a realm described as nanoelectronics. Some of these opportunities rely on the understanding and control of the smallest possible unit of magnetism in the solid state – a single magnetic atom or complex within a solid. In this regime all elements of the behavior of materials come into play – electrical, magnetic, strain, optical, and thermal.
Moving single atoms around on a solid surface

In order to consider structures and devices that depend on the behavior of a single atom it is vital to be able to image and position such single atoms. The scanning tunneling microscope, invented in 1981 at IBM Zurich by Gerd Binnig and Heinrich Rohrer, allows both. The principle of operation is to use a small metal wire that ends in a very sharp tip (ideally with a single atom at the end) placed near to a conducting surface. If a sufficiently large voltage is applied the electrons in the tip become unbound and fly to the surface in a process known as “field emission”. Binnig and Rohrer recognized, however, that if the voltage was lower the electrons could also move from the tip to the surface without ever becoming unbound, through a process called “quantum tunneling”. Quantum tunneling is so sensitive to the distance from the tip to the surface that the tunneling current is almost entirely dominated by electrons moving through the very last atom at the tip of the wire. This provides unequalled spatial resolution for a low-energy, non-destructive probe. By moving this tip carefully around the surface and measuring the current through the tip (or, more commonly, fixing the current with a feedback loop and measuring the height of the tip above the surface), atom-scale features could be determined and energy spectra could be taken near individual atoms.

It is difficult to convey now to new researchers in this field how controversial the scanning tunneling microscope was during its first decade of use, even after the awarding of a Nobel prize in 1986 to Binnig and Rohrer. Tied up with complex philosophical issues from quantum mechanics, many professional physicists did not believe such measurements were “real”, and some would apply Heisenberg’s uncertainty principle incorrectly to the situation to argue that atomic-scale measurements were impossible at realistic temperatures. The turning point in overcoming such resistance appears to be the use of the scanning tunneling microscope to position individual atoms on a surface, demonstrated in 1990 by Don Eigler and Erhard Schweizer of IBM. For the first time scientists and non-scientists alike could feel they “saw” atoms as movable, controllable entities in an ordinary environment – the surface of a solid. Shortly thereafter it was demonstrated that the scattering of electron waves by individual iron atoms on a copper surface could be directly imaged with a scanning tunneling microscope –
here then was the start of researchers using single atoms as sensors or probes for the properties of an extended solid state system. The relationship between the energy and the wavelength of electrons in a surface state on that copper surface was directly mapped with the microscope with exquisite precision.
As a graduate student in 1991, looking for a new area to explore, the scattering of electron waves from individual atoms seemed an ideal direction – a paradigm shift with an extensive set of implications to unravel. The type of atom could be varied, the host material could be varied, and little was understood about how these electron waves should behave in exotic materials. Through lengthy discussions, my collaborator Jeff Byers and I formulated a picture of the scattering of electronic waves by single magnetic atoms on the surface of a superconductor, and proposed the measurement of those waves as a means of determining the nature of the superconducting state. Such effects were subsequently seen in several superconducting materials, and provided some of the strongest evidence for the origin of superconductivity in high-temperature superconductors.

Figure 1
Theoretical calculations of electron waves scattering from a single atom on the surface of a superconductor, shown with the spatial variation. The spatial units are Fermi wavelengths. The ordinary, isotropic superconductor on the left has electron waves similar to those seen at the surface of copper. The highly anisotropic superconductor on the right generates focused electron waves traveling along high-symmetry directions of the superconductor, related to the pairing potential between electrons.
In solving the above problem we needed to consider the magnetic properties of the scattering electrons themselves. Electrons are intrinsically magnetic – they behave as if they have a small magnet within them, even though they have no apparent size. To distinguish this intrinsic magnet from the magnetism caused when electrons move in a current loop, the intrinsic magnetic property is called “spin”. The electron’s spin will reorient dynamically in an applied magnetic field, and can also orient nearby electron spins. The calculations of electron wave scattering from magnetic atoms depended sensitively on the electron spin. Part of this sensitivity emerges because a superconductor is characterized by a complex paired state between two electrons of opposite spin.

The mechanism for reorienting nearby electron spins is not, however, through the magnetic field generated by the little electron magnet. That magnetic field is extremely weak, so if that were the total effect of one electron spin on another then magnetic materials would only occur at exceptionally low temperatures and all the phenomenology of magnets would be completely unknown to common experience. It’s perhaps surprising that the reason some materials are magnetic at room temperature, and others are not, is first taught (at least in the United States) in a solid state physics course to senior undergraduates. The effect itself could be explained in the first course on quantum mechanics. It is due to a peculiar feature of the quantum mechanical wave function of multiple electrons. A mathematical symmetry is always observed in these wave functions, whereby that wave function must change sign when two electrons with the same spin are exchanged. The origin of this symmetry is unknown – so much so that in Richard Feynman’s pedagogical formulation of quantum mechanics he took this symmetry principle as one of the postulates. This symmetry effect produces a new term in the (ordinarily repulsive) electron interaction energy, which has the opposite sign (due to the sign change in the wave function), and occurs between electrons of the same spin. As it has the opposite sign from a repulsive interaction, the result of this is an effective lowering of the energy for electrons with the same spin. This “exchange energy” stabilizes the magnetic state in those materials which are magnetic at room temperature.
A new type of current – spin current

The magnetic atoms we considered above do not move, but by their presence they change the propagation of electrons – producing a current of spin. Spin currents were known to flow in magnetic materials since the 1930’s, but only understood in nanoscale structures in the 1980’s. Unlike for an ordinary electrical current, there is no electric charge buildup associated with an inhomogeneous spin current; thus there is no Coulombic energy to produce capacitive energy. These charging and capacitive effects often limit the performance of semiconductor electronics. If they are eliminated or reduced, one might expect the flow of the corresponding current to be more efficient. Furthermore, all the information contained within an electrical current is contained within the spatial dependence of the current; to increase or decrease the current requires bringing charges in or out of the system. For a spin current the value of the current can be completely changed (e.g. from spin up to spin down) without adding or subtracting current carriers – just by rotating the electron spin axis using a magnetic field or other tool.

Such spin currents provide new ways to manipulate electronic properties of a device, offering the possibility of switching current on and off more rapidly and with less energy than in a traditional semiconductor transistor. To see the difference, consider the highly simplified diagram of a traditional semiconductor transistor. Shown is the lowest energy possible for an electron, as a function of the position of that electron between the entry point (the source) and the exit point (the drain) of the transistor. When the barrier in the middle is up, then no current can flow and the transistor is off. When the barrier in the middle is down, then current can flow and the transistor is on. This approach underlies semiconductor transistor behavior, no matter what material or application of the device. It also identifies some of the functional limitations of these devices. In order to effectively turn the current on and off the barrier must be high – preferably many times the thermal energy to prevent thermal activation over the barrier (i.e. about fifteen times the thermal energy). To prevent the phenomenon of quantum tunneling, so important to the functioning of the scanning tunneling microscope, the barrier must be wide. Changing the barrier by a minimum height and minimum
thickness requires a minimum energy – these considerations prevent the switching energy of a traditional semiconductor device from being reduced arbitrarily. But these constraints are different for a spin transistor.

Also shown is a diagram of just one type of semiconductor spin transistor. In this device the lowest possible energy for an electron depends on the spin of the electron – there is one energy “landscape” for a spin-up electron, and a different one for a spin-down electron. In the landscape shown above neither the spin-up nor the spin-down electrons can move through the device – they each are blocked by a barrier. The major difference in the spin transistor, however, is that spin-up electrons can be turned into spin-down electrons simply by changing the spin of the electron. So, if the rate that a spin-up electron turns into a spin-down electron can be changed, then the current through this device could be switched on and off, without raising or lowering one of the barriers.

There are several ways to cause this to happen, including creating a small magnetic field to change the spin of the electron. The method most similar to the switching method of a traditional transistor creates a small effective magnetic field using a small electric field to distort the wave functions of the solid material the electron moves through. But how can one make the distortion large? The small effective magnetic fields emerge because different electronic states of a material have different internal angular momenta – they can be thought of as containing small internal currents like those associated with an electron circling the nucleus of an atom. If the energies of the states in the solid with different angular momenta are very close together then the distortion in response to an electric field is larger. This suggests using materials with small gaps between state energies, such as is found in semiconductors. The narrower the gap the better,
pointing towards narrow-gap semiconductor materials such as indium arsenide. There is no barrier to raise or lower in the spin transistor, so the power required to switch this transistor depends on the efficiency of the conversion from a small electric field to a small magnetic field, which can be very high. Calculations for indium arsenide suggest that this means of switching would require orders of magnitude lower power than the switching of a traditional transistor.

The other key element of this type of spin transistor design is the differing landscape for spin-up and spin-down electrons. This requires magnetic materials – in order for this landscape to exist for individual electrons without much scattering, then a magnetic metal is not suitable. The material must be a magnetic semiconductor or magnetic insulator. Magnetic semiconductors built around traditional semiconductor materials such as indium arsenide and gallium arsenide were discovered in the late 1980’s and early 1990’s, and may offer the most compatible interfaces with the spin-switching material also required for the device to function. But these materials pose their own problems for theory and application.
Magnetic semiconductors are commonly constructed by alloying a magnetic material with an ordinary nonmagnetic semiconductor, such as by adding manganese to gallium arsenide. Magnetic manganese atoms replace nonmagnetic gallium atoms. Often physicists will simplify the theoretical model for such a system by ignoring most of the differences between the magnetic material and the nonmagnetic material, and assuming there is a single material with some average properties. However, a more fundamental approach is possible. The behavior of a single magnetic atom within an otherwise perfect and nonmagnetic host material can be predicted, and studied experimentally.

For the past ten years the properties of one, two, or a few magnetic atoms within such a host have been major emphases of my research. Ten years ago our theoretical calculations predicted a large anisotropy in the electronic structure around a manganese dopant in gallium arsenide. The valence of manganese differs from the atom it substitutes for in the crystal, gallium, by one, so there is one excess negative charge in the nucleus from a missing proton. Just as one would have for antihydrogen, a positively-charged carrier from the surrounding material binds to the manganese atom within the solid to make a pseudo-atomic system. The shape of the bound orbital of this pseudo-atomic system, however, depends sensitively on the properties of the host crystal, which differ profoundly from the properties of a vacuum. For example, in gallium arsenide the speed of

Figure 3
Theoretical prediction (left) and experimental measurement (right) of the orbital around manganese in gallium arsenide. The manganese atom is five layers below the surface.
a carrier of a given energy will depend on the direction it travels within the crystal. The hybridization of the orbitals of the manganese with the gallium arsenide is also highly anisotropic, with strong hybridization along the direction of tetrahedrally-coordinated chemical bonds between the manganese and the host, and weak hybridization along directions in between. This produces a highly anisotropic “bowtie” shape, which was subsequently observed in a collaborative project with TU/e.

Although sometimes it is theoretical predictions that drive experimental measurements, often it is the other way around. Our theoretical predictions suggested the shape of the manganese orbital would be mostly symmetric around the horizontal plane in the image below, but experimental measurements clearly showed a much greater degree of asymmetry. Our calculations were performed for a magnetic atom deep within the center of a crystal, but the measurements were performed by splitting the crystal and examining the effect of atoms only a few layers deep on the electronic structure at the surface. To reconcile the discrepancy between theory and experiment required a return to the theoretical toolbox, and the development of a way to include the spatial shifts of atoms that occur near the surface of gallium arsenide. Including these effects provided a consistent view of the wave function shape near the surface.

As described earlier, materials become magnetic through the interactions between electronic carriers with the same spin. Thus the simplest physical example of a magnetic interaction in these magnetic semiconductors would consider the interaction between a carrier in the bound orbital around one magnetic atom with a carrier in the bound orbital around a second, nearby magnetic atom. The interaction between such orbitals had been used as a fundamental model of magnetism in a wide variety of materials since the 1950’s, but the interaction had never been visualized for the simple case of two isolated magnetic atoms. We predicted in 2000 that this interaction should manifest itself in the magnetically modified energies of states measured with a scanning tunneling microscope around the two magnetic atoms. In 2004 we calculated the expected size of the magnetic shifts in the energies of states for manganese atoms in gallium arsenide and found it to be very large; the energy shifts for such atoms were measured experimentally in 2006. The strength of the magnetic interactions was almost completely controlled by the shape of the bound orbitals, yielding a highly anisotropic magnetic coupling. Others have argued, based on these results,
that room-temperature magnetic semiconductors should be achievable, if it were possible to completely control the position of the magnetic atoms within the nonmagnetic host.

![Diagram](image)

**Figure 4**

Theoretical prediction and experimental measurement of the energy splitting between two magnetically-modified states around two magnetic atoms. The bound orbitals associated with the two atoms are shown in (a)-(d), and the energies in (e).
Room-temperature single-spin information processing

Can magnetic systems for information processing be shrunk farther than the proposed device described as a spin transistor? What is the smallest size possible for a magnetic system, useful at room temperature for information processing? The hard disk industry has invested considerable effort and resources into determining a commercial answer to the question for magnetic storage, however their criteria differ greatly from those of the information processing community. Information stored on a hard disk must remain stable for years without outside intervention, and so magnetic regions must be resilient at room temperature to perturbations from the surroundings, requiring a cooperative magnetization involving millions of atoms, corresponding to magnetic regions approximately the size of several nanometers. For information processing, however, if the magnetic entity is protected from the effects of surrounding perturbations, and is stable on a timescale of microseconds, then that could be sufficient for this entity to be useful.

Over the past few years examples have been found of individual spin systems, associated with single atoms or small complexes embedded within semiconductors, that have this resilience. The most intensively explored of these is the nitrogen-vacancy center in diamond. This spin center is created by replacing one carbon atom within a diamond crystal with a nitrogen atom, and also removing a neighboring carbon atom. The resulting complex has a ground state spin equal to the spin of two electrons combined, and is very common; yellow diamonds, which are common colored diamonds, are typically yellow due to the nitrogen within them. The nitrogen-vacancy spin center has several remarkable features – the spin can be polarized by illumination with a simple green laser, it remains oriented for times greatly exceeding one microsecond at room temperature, and the spin polarization can also be detected in a fluorescence cycle again using a green laser. Over the past few years these unusual features have permitted the demonstration of a wide variety of single-spin manipulations at room temperature, suggesting that single spins can be used for information processing. Much of the effort on these single-spin centers has been devoted to so-called “quantum operations” where the quantum mechanical nature of the spin state is preserved, permitting possible quantum computation. However, the
measurements also demonstrate the initialization, control and detection of information stored in a solid region smaller than one cubic nanometer, which may approach the ultimate limit of solid-state computation.

The journey ahead for single-spin information processing in nanoelectronics remains lengthy and challenging for commercial applications. The cost of the diamond semiconductor used in the experiments above is not a significant part of this challenge, however, as similar effects are now being seen in more common materials such as silicon carbide. The true challenge will be to replace each portion of the control demonstrated optically with electrical means, so the large wavelength of the optical probe does not limit the density of the computation elements. This will mean methods to electrically initialized spins – perhaps by injecting them from magnetic semiconductors. Manipulation of the spin directions of these single-spin centers using electric fields and strain are in the initial stages of demonstration (with optical initialization and detection). Finally, electrical detection of the spin would complete the transformation of this from laboratory demonstration to potential commercial device. At this point perhaps the ultimate limit of computation density will have been reached – leading to the same result as greeted the success of the hard disk community, the firing of the research staff.
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