Half Metallic Magnets

Not to be confused with semiconductors, half metals belong to a new class of materials that look set to play a key role in next-generation electronic devices.

Warren E. Pickett and
Jagadeesh S. Moodera

In the early 1980s, during a computational study of magnetic compounds, the University of Nijmegen's Rob de Groot and collaborators discovered a new type of magnetic material.[1] Dubbed "half metallic" by de Groot, the new materials are unusual in that only one of the two spin directions is metallic. That is, the electrons responsible for the metallic behavior share the same spin; the electrons with the opposite spin are insulating.

Now, almost two decades later, half metallicity has been recognized in real, as opposed to virtual, compounds. Combining metallic and insulating properties in a single system and at a microscopic level within each unit cell, half metals can be thought of as a new state of matter. Applications that exploit half metallicity—for memory devices and computer processors—are already being investigated, especially in the nascent field of spintronics (see David Awschalom and James Kikkawa's article, PHYSICS TODAY, June 1999, page 33).

Magnetic materials encompass a rich variety of spin alignments: all parallel (ferromagnetism), periodic arrangements with equal and opposite spins (antiferromagnetism), several spins up and some down (ferrimagnetism), and more. However, this picture is an overly simple one even for conventional magnets, primarily because the moments in a magnet choose a direction with respect to the crystal axes through relativistic coupling of the electron spin to its orbital motion (spin–orbit coupling). Many alignment configurations are possible. For example, the moments may become noncollinear, forming spiral spin-density wave phases; or they may adopt canted antiferromagnetic arrangements. Moreover, the response of a magnetic material to an applied magnetic field depends on whether the applied field is collinear with the moments or not.

But for this introduction to half metallic magnets, these interesting complications are neglected. We consider only systems with spin up and spin down. And, even though magnetization is a vector quantity, our discussion addresses only longitudinal changes.

A tale of two spins

Before de Groot named the phenomenon, hints of half metallicity had been glimpsed by others. In 1950, G. H. Jonker and J. H. Van Santen found the saturation moment of metallic $La_{1-x}Ca_xMnO_3$ ferromagnets to be just what would result if all of the doped-in holes had their spins aligned, which is the simplest case of a half metal. A year later, L. Castelliz measured the magnetic moment of NiMnSb and found it to be close to four times the value of the electron's magnetic moment μ_B. Thanks to work done by Laurent Ranno's group at the Louis Néel Laboratory in Grenoble, France, NiMnSb is now understood to be half metallic.

But possibly the earliest suggestion of half metallic character was from a calculation of the spinel structure magnet $CuCr_2S_4$ by Jun'ichi Horikawa and coworkers at the University of Electro-Communications in Chofu, Japan, in 1982. The magnetic configuration of $CuCr_2S_4$ can be described schematically as two Cr^{3+} ions (3 electrons in the 3*d* shell with spin up) and a Cu^{2+} ion (one hole in the 3*d* shell with spin down). Each Cr^{3+} ion has a moment of $3\mu_B$, and each Cu^{2+} has a moment of $1\mu_B$ in the opposite direction. As a result, the formula unit of $CuCr_2S_4$ has a net moment of $5\mu_B$. An integer value of the spin moment is a central feature of half metallic character, as is the combination of metallic conductivity but vanishing spin susceptibility.

Energy bands in crystalline solids embody the relationship between the energies an electron is allowed to have and its momentum. In general, each spin direction has its own set of bands, but for nonmagnetic materials such as silicon, the bands are identical, and one often neglects the spin entirely. In a magnet, the spins are unbalanced, and because electrons interact differently with like-spin electrons compared with unlike-spin electrons, the spin-up and spin-down band structures differ.

This description holds for perfectly aligned atomic spins, a condition that occurs only at absolute zero. In the real world, thermal effects jiggle the spins, but for temperatures below about one third of the magnetic ordering temperature, the idealized picture remains a good description.

To be a half metalic magnet, a material must have a collinear magnetic arrangement with the following qualitatively different types of up and down band structures: One spin direction has partially occupied bands (for clarity, we choose "up" throughout this article), whereas the other (spin-down) system has a precisely filled set of bands that are separated from unoccupied bands by a bandgap. The uppermost occupied energy level of the up spins defines the system's Fermi level, which lies within the bandgap of the spin-down electrons. This situation is shown in figure 1, in which the densities of states of silicon and iron are contrasted with the density of states of a model half metallic ferromagnet.

In Si, the energy gap (identical for both spins) is responsible for the material's semiconducting behavior. In half metals, the gap in only one spin channel is just as important: It produces the blocking effect that prevents a spin flip because no states of down spin are available within the gap.

WARREN PICKETT *is a physics professor at the University of California, Davis.* **JAGADEESH MOODERA** *is a physics professor at the Massachusetts Institute of Technology's Francis Bitter Magnet Laboratory in Cambridge, Massachusetts.*

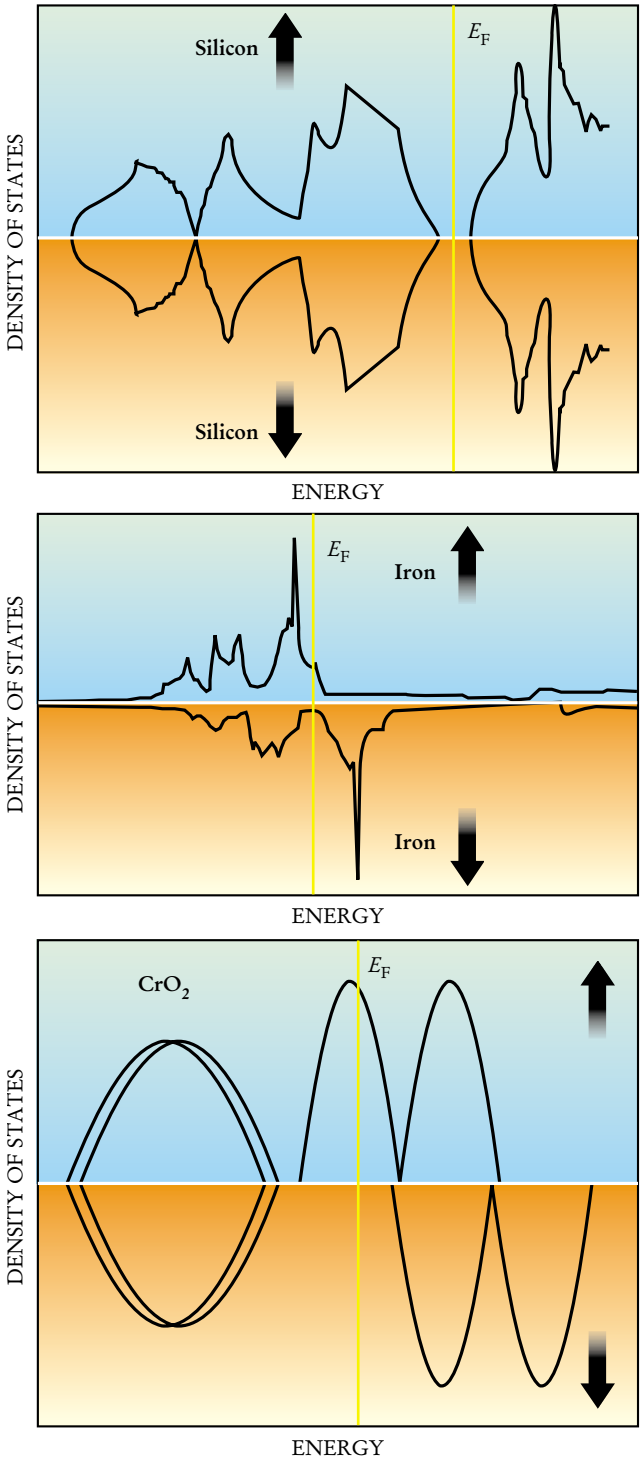

FIGURE 1. THE DENSITY OF STATES of silicon is shown in the top panel. Si has a band gap between occupied and unoccupied states, but it is nonmagnetic so the spin-up and spin-down densities of states are identical. The Fermi energy (yellow line) lies in the gap. In the middle panel, the spin-up and spin-down densities of states of ferromagnetic iron are shown. Iron has no gap, although the density of states of the spin-up states at the Fermi energy is quite low. At the bottom is a model density of states for half metallic ferromagnet CrO_2, which has an energy gap at the Fermi energy only in the spin-down states.

In stoichiometric half metallic compounds, the energy gap between spin channels leads to the intriguing "quantization" of the magnetic moment. Within the down channel exists a set of bands—$N_\downarrow$ of them, say—that are fully occupied and each of which holds one down electron per unit cell. Because an integer number $N = N_\uparrow + N_\downarrow$ of valence electrons occupy the unit cell, an integer number $N_\uparrow = N - N_\downarrow$ are left in the up bands, which are only partially filled. The spin magnetic moment M reflects the spin imbalance—that is, $M = \mu_B(N_\uparrow - N_\downarrow)$, which, as an integer number of Bohr magnetons, is therefore quantized. (This result is approximate when relativistic effects are taken into account because spin–orbit coupling induces an orbital moment. But the induced moment is small for 3*d* elements, and magnetic moments near integer values are often observed.) By contrast, both the up and down bands of normal magnetic metals are partially filled, so neither $N_\uparrow$ nor $N_\downarrow$ is an integer, nor is their difference. The moment of Fe, for example, is 2.2 μ_B per atom.

Arbitrarily small energy excitations are possible in a half metal if they involve an up spin and if the electron retains its spin direction. But no low-energy spin-flip processes occur. Energy is required to flip a spin—that is, to move an electron from an occupied spin-up state to an unoccupied spin-down state in the bottom panel of figure 1, or convert a spin-down electron below the gap to a spin-up state above the Fermi level.

The spin susceptibility is the derivative of the magnetization with respect to an applied codirectional magnetic field. A vanishing spin susceptibility means that the magnetization does not change as the field is applied. In half metals, the state of the system does not change when a codirectional magnetic field is applied, and therefore nothing whatsoever changes. Valentin Irkhin and Mikhail Katsnel'son of Russia's Institute of Metal Physics have reviewed the properties of half metals in some detail.[2]

The unusual suspects

The properties of solids strongly depend on their crystal structure and their electronic bonding. Semiconducting Si is a covalent semiconductor because the highly directional bonding in the diamond structure gives rise to occupied valence bands and empty conduction bands. By contrast, the ferromagnetic metal cobalt has a close-packed structure with weakly overlapping 3*d* atomic orbitals.

Bonding in elemental crystals generally leads to a simple electronic structure. Half metallic ferromagnets, however, require a certain amount of complexity in their electronic characteristics, which, in turn, usually requires a certain amount of structural complexity. Though more complex in these two respects than fully metallic or insulating ferromagnets, half metallic ferromagnets can be remarkably simple, as shown by the examples in figure 2.

Half metallic characteristics have been studied primarily in ternary compounds, specifically spinels (minerals with the general formula AB_2O_4, such as $Fe_3O_4 \equiv FeFe_2O_4$); Heuslers (alloys with the general formula A_2MnB, such as Co_2MnSi); and half Heuslers ($AMnB$, such as NiMnSb). The binary compound CrO_2 is also a half metal. These crystal classes contain numerous magnetic compounds. In fact, because a half metallic material must be magnetic, it must incorporate atoms, such as transition metals, that form magnetic moments. Crucially, the bonding in these spinels, Heuslers, and so on is just complex enough to encourage gaps in the density of states—another requirement for half metallicity.

In elemental metals, the spectrum of excitations (the density of states) forms one continuous band because the states of one atom line up exactly with those of the next

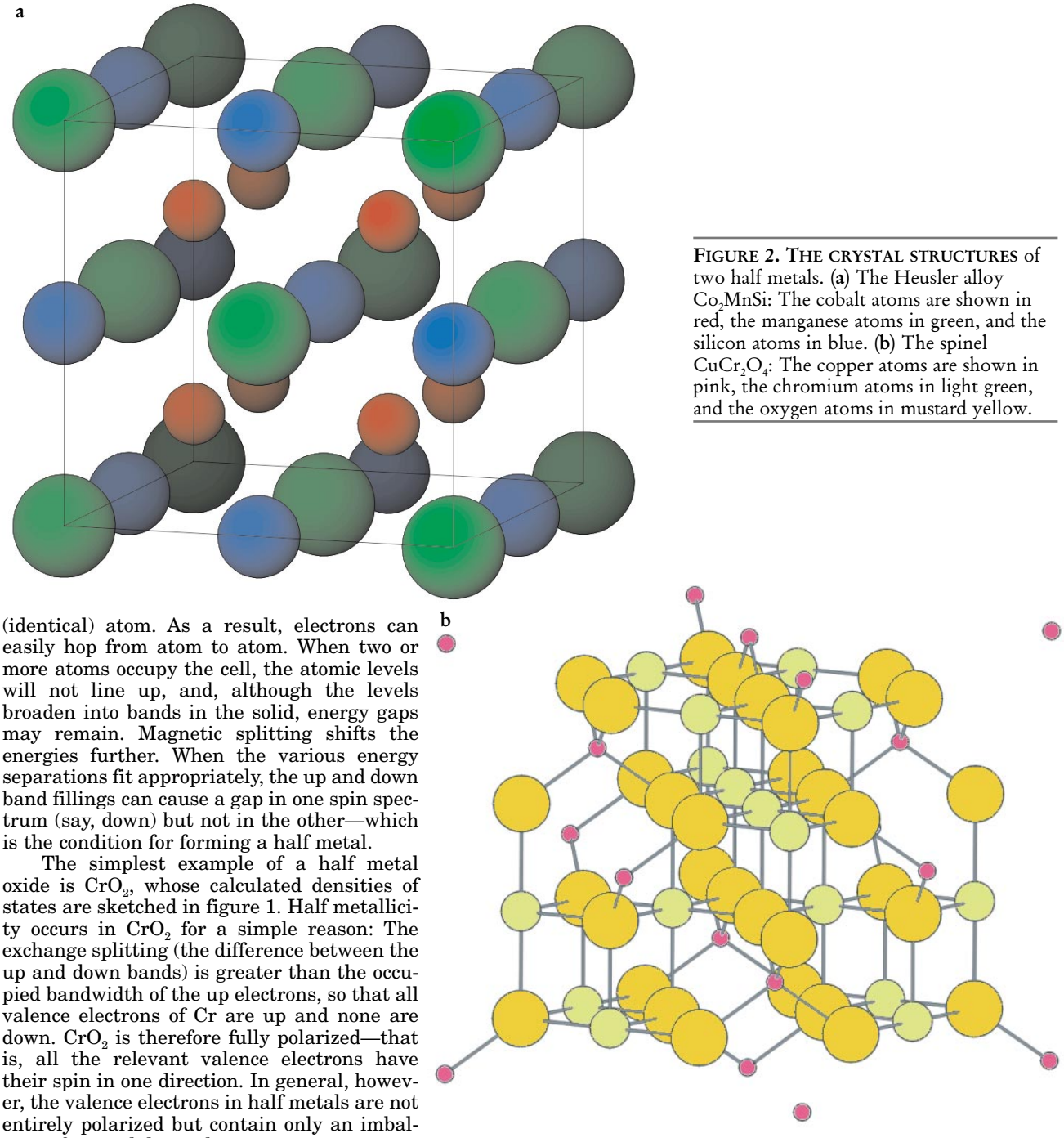

FIGURE 2. THE CRYSTAL STRUCTURES of two half metals. (**a**) The Heusler alloy Co_2MnSi: The cobalt atoms are shown in red, the manganese atoms in green, and the silicon atoms in blue. (**b**) The spinel $CuCr_2O_4$: The copper atoms are shown in pink, the chromium atoms in light green, and the oxygen atoms in mustard yellow.

(identical) atom. As a result, electrons can easily hop from atom to atom. When two or more atoms occupy the cell, the atomic levels will not line up, and, although the levels broaden into bands in the solid, energy gaps may remain. Magnetic splitting shifts the energies further. When the various energy separations fit appropriately, the up and down band fillings can cause a gap in one spin spectrum (say, down) but not in the other—which is the condition for forming a half metal.

The simplest example of a half metal oxide is CrO_2, whose calculated densities of states are sketched in figure 1. Half metallicity occurs in CrO_2 for a simple reason: The exchange splitting (the difference between the up and down bands) is greater than the occupied bandwidth of the up electrons, so that all valence electrons of Cr are up and none are down. CrO_2 is therefore fully polarized—that is, all the relevant valence electrons have their spin in one direction. In general, however, the valence electrons in half metals are not entirely polarized but contain only an imbalance of up and down electrons.

A more complicated half metal oxide is Sr_2FeMoO_6. Its half metal character was revealed by the combined work of Yoshinori Tokura's experimental group and Kiyoyuki Terakura's theoretical one, both of which are based at the Joint Research Center for Atom Technology in Tsukuba, Japan. Sr_2FeMoO_6 has the double perovskite structure, in which the unit cells of the perovskites $SrFeO_3$ and $SrMoO_3$ alternate to form an ordered crystal (perovskites have the general formula ABO_3). Both Fe and molybdenum are magnetic ions in this compound. They have different 3*d* site energies and different electronegativities. Because each electronic state consists of some Fe *d*, Mo *d*, and O *p* character, a full band structure calculation is required to reveal the electronic structure.

The result, however, is a fairly easy one to picture. The ions are Fe^{3+} (5 electrons in the 3*d* shell with spin up) and Mo^{5+} (1 electron in the 4*d* shell with spin down). The moments of these ions are antiparallel (it is a ferrimagnetic compound) and the net moment is $5\mu_B - \mu_B = 4\mu_B$. In Sr_2FeMoO_6, the metallicity comes from the spin-down electrons. The up states of the Fe ion are all filled, but the down states are available so that the Mo electrons may hop to them. Only a third of the down states of Mo are occupied, leading to metallic conduction.

Compared with the oxides, the densities of states of the intermetallic half metals (mostly Heusler and half Heusler crystal structures) are much less straightforward to approximate by a simple picture because the crystal field splittings are smaller; the interatomic couplings (hence band widths) are larger; and the distinctions caused by ferromagnetic, ferrimagnetic, or antiferromag-

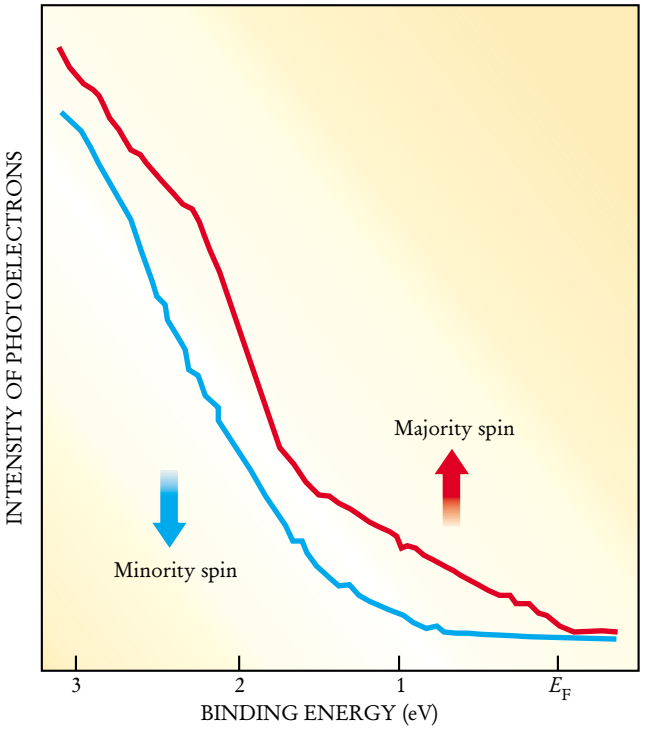

FIGURE 3. THE MEASURED PHOTOELECTRON EMISSION spectra of spin-up and spin-down electrons from the surface of a thin film of $La_{0.7}Sr_{0.3}MnO_3$. The spectra illustrate the lack of detectable spin-down photoelectrons at the Fermi level, or even a few tenths of an eV below. Such a result, which indicates metallic spin-up electrons but a gap in the spin-down spectrum, is expected for half metallic character. The result also requires that both the bulk and the surface of the system be half metallic (because both regions are probed in this photoemission experiment). (Adapted from J.-H. Park et al., *Nature*, volume 392, page 794, 1998.)

netic ordering can be very pronounced. In CrO_2 and Sr_2FeMoO_6, the ionic picture suggests they will be half metals, but it is not possible to guess which Heusler or half Heusler compounds might be half metals, although verification can be obtained from band structure calculations. For example, whereas Fe_2MnSi is calculated to be half metallic, the closely related compounds Fe_3Si and Mn_3Si (that is, Fe_2FeSi and Mn_2MnSi) are not. In fact, their densities of states are completely without gaps.

Dilute magnetic semiconductors such as (Ga,Mn)As and (Hg,Mn)Se form another class of half metal. Studied since the 1960s, these ferromagnetic semiconductors have two distinct band gaps, one for each spin direction. When a small concentration of electrons or holes is doped (or, in more recent experiments, injected) into these semiconductors, the carriers will only conduct current if their spins are completely polarized. Conceptually, the carriers in a dilute magnetic semiconductor form a gas whose constituents have their spins aligned with the internal magnetic field. As such, dilute magnetic semiconductors are the simplest of half metals and are now integrated into spin electronics devices, as described in recent overviews by Hideo Ohno and by David Awschalom and Nitin Samarth.[3]

Looking for nothing (in one spin direction)

The existence of a gap in half metals for only one spin direction is so unusual that one expects to observe its manifestation in various magnetic, electrical, and optical properties. Obtaining clear evidence has not been easy, however. In many cases, one is looking either for a vanishing signal or a 100% signal in a property whose allowed values form a continuum.

Another complication is that experiments must be done at temperatures much lower than the magnetic ordering temperature T_c, which usually means cryogenically. Imperfect crystal quality—site disorder in intermetallics, or oxygen and cation stoichiometry in oxides—can also be a problem because disorder usually destroys half metallicity. In addition, many probes of half metallic character require the transport of electrons across interfaces or surfaces whose electronic structure may differ from that of the bulk (and may not even be half metallic). Magnetic disorder in these regions may flip spins and degrade the signal, which is proportional to $N_\uparrow - N_\downarrow$. Despite all these complications that conspire to reduce observed polarizations, strong evidence of half metallicity has been accumulating, and half metallicity has become an accepted phenomenon.

Half metallicity has been probed by a variety of experimental techniques, including positron annihilation, optical spectroscopy, and normal state transport. The two most obvious approaches have been the most successful. The first one is the measurement of magnetic moment, which, as noted previously, should be an integer. Castelliz's 1951 observation of a magnetic moment near $4\mu_B$ for the half Heusler NiMnSb has already been mentioned. The magnetic moments of other suspected half metals have been measured and found to be close to the calculated integer values. Examples include the Heusler compound Mn_2VAl ($2\mu_B$), the rutile structure CrO_2 ($2\mu_B$), and the double perovskite Sr_2FeMoO_6 ($4\mu_B$).

Spin-resolved photoelectron emission spectroscopy, in which electrons are photoemitted from the surface of the half metal, offers the hope of directly observing conduction electrons of only one spin. If the sample is half metallic, emission corresponding to only one spin direction will be observed in the zero binding energy limit—that is, at the Fermi level. Unfortunately, photoemission is very sensitive to surface properties. The surface might not be representative of the bulk material, or it might not be half metallic even if it is stoichiometric, or the emission process itself might be spin-dependent. Observation of less than full polarization at threshold in suspected half metals has been common, such as in the results for NiMnSb of Gian-Luca Bona and coworkers at the Swiss Federal Institute of Technology in Zürich and for CrO_2 by Gernot Güntherodt's group at the Technical University of North Rhine–Westphalia in Aachen, Germany. These discouraging results could well be due to the various difficulties just mentioned.

But two positive results from spin-resolved spectroscopy have been reported. Taking advantage of the high-intensity synchrotron radiation available at the National Synchrotron Light Source, Jae-Hoon Park and his coworkers at Brookhaven National Laboratory and the University of Maryland, College Park, observed more than 90% polarization in the photoemission spectrum of $La_{0.7}Sr_{0.3}MnO_3$, which is shown in figure 3. For carefully monitored surfaces of NiMnSb, a joint collaboration between the Louis Néel Laboratory and the University of Nebraska–Lincoln observed close to 100% polarization of the inverse photoemission spectrum.

Tunneling of electrons between a half metal and

another electrode is another potential way to measure the polarization. Attempts in this direction using spin-polarized tunneling between a ferromagnet and a superconductor seem promising, but so far have not led to observation of 100% polarization. In this method, the superconductor's quasiparticle density of states is Zeeman split, providing a probe of spin-up and spin-down carriers. Among several samples of NiMnSb, the highest value of polarization obtained by MIT's Clifford Tanaka, Janusz Nowak, and one of us (Moodera) was 30%. Daniel Worledge and Ted Geballe of Stanford University obtained a polarization of 72% for $La_{1-x}Sr_xMnO_3$.

Recently, Robert Soulen and collaborators at the Naval Research Laboratory (NRL) in Washington, DC, have investigated half metallicity with point-contact Andreev reflection. In this technique, normal current is converted to supercurrent at the metallic interface, a process that strongly depends on the availability of spin states at the Fermi level. Polarization values for NiMnSb, $La_{1-x}Sr_xMnO_3$, and CrO_2 have been observed to be in the 60–90% range, giving encouraging evidence of half metallicity.

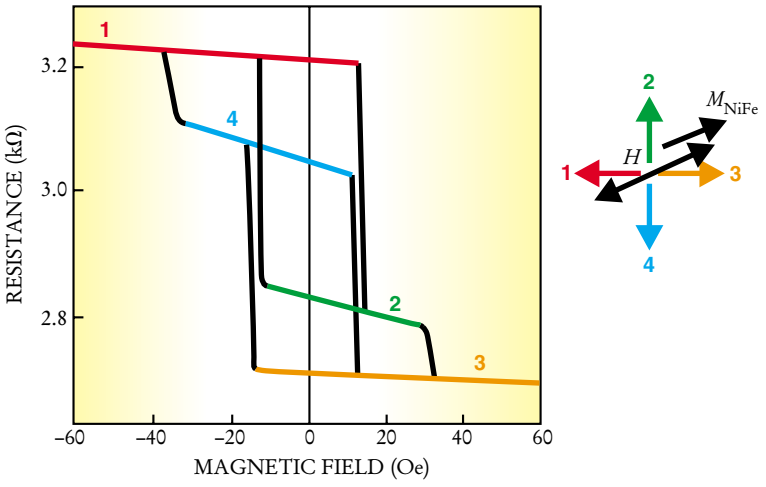

FIGURE 4. THE VARIATION OF RESISTANCE with applied magnetic field for an epitaxial $NiMnSb/Al_2O_3/Ni_{0.8}Fe_{0.2}/CoO$ tunnel junction. An ultrathin layer of CoO was used to bias the permalloy ($Ni_{0.8}Fe_{0.2}$) film at an angle of 22° from one of the [100] cubic NiMnSb axes along which its magnetic moment normally points. The labels 1 to 4 correspond to the four crystalline [100] directions in the NiMnSb film. When the magnetization of NiMnSb and permalloy are nearly parallel (*H* along direction 4) the lower resistance state is achieved. With the field reversed (*H* along direction 1), the resistance is highest. Depending on how the field is reduced, two additional, intermediate resistance levels can be reached. These resistance states, reflecting NiMnSb's cubic magnetocrystalline isotropy directions, illustrate the principle of a four-state spin tunneling nonvolatile memory element. These data were taken at 77 K. Room-temperature operation can be achieved by using an exchange biasing material such as FeMn or IrMn instead of CoO. (Adapted from C. Tanaka, J. Nowak, J. S. Moodera, *Journal of Applied Physics*, volume 86, page 6239, 1999).

Toward spin control

Discovered by Lord Kelvin in 1856, magnetoresistance (MR) is the name given to the relative change in a material's electrical resistance due to an applied magnetic field. In the best conductors, such as copper, MR is a very small effect—a tiny fraction of 1%. "Large MR," therefore, came to denote a value that is some larger fraction of 1%. When much bigger MR effects of a few percent were seen in layered sandwiches of two or more different materials, the term "giant MR" was introduced. Then, in the early 1990s, certain manganites were found to exhibit MR that could approach 100%, but usually only near the magnetic ordering temperature. The term "colossal MR" (CMR) was coined to denote the phenomenon (and accepted by journal editors after a short time).

The prediction from band calculations that these manganites are half metallic (or nearly so) at low temperature has led to the loose association of half metallicity and CMR. However, the two phenomena cannot be directly connected because the manganites (or any system) are half metallic only at temperatures very much below T_c. At or near T_c, the systems have very little magnetic order—that is, up and down spin subsystems differ very little, although application of a field increases the difference dramatically. By itself, half metallicity is not a crucial ingredient of the manganite CMR effect.

For layered devices, however, half metals may be essential for obtaining maximum CMR performance. The simplest situation—one that is attractive for applications—is the spin valve device, which can be considered as an extension of tunneling MR (TMR). In TMR devices, an insulating tunnel barrier is sandwiched between magnetic metals (see the article by Peter Grünberg on page 31). $Co/Al_2O_3/Co$ is one example. When the magnetic layers are aligned, majority spin electrons on one side can tunnel with some resistance into the same states on the other side, as can the minority electrons. If the spins in one of the Co layers are flipped by an applied field, then majority electrons must tunnel into minority states on the other side, which now have the same direction of spin. As a result of this mismatch, tunneling is inhibited and the resistance of the device increases.

This effect is used to manipulate current flow by pinning one magnetic layer and flipping the magnetization of the other layer with an applied field, or conversely, it is used to detect magnetic fields by the amount of resistance. Even if the MR is a modest 5%, the effect is useful. The magnetic read heads in information storage devices are now based on this spin valve effect of resistance change.

But with half metals on both sides and with ideal interfaces, the effect would be 100% and current across the valve would be either on or off. Even with a resistance drop of less than 100%, half metals would still provide a much greater signal-to-noise ratio than conventional metals, making it possible to build devices that run at lower voltages and higher speeds. A number of groups are pursuing spin valves based on half metals. That half metallicity is fully manifested only at low temperature does not limit its application in spin valves or in most other devices. Such devices require only spin polarization—the larger the better—and half metals will have much larger polarization at the operating temperature than normal metals.

Magnetotransport in granular systems with half metallic materials may also promote the technological application of MR. Compared with bulk half metals, the MR in granular systems seems to be less sensitive to surface character and the MR extends over a wider temperature range. Colossal intergrain MR (IMR) has been reported in several half metals: in $La_{1-x}Sr_xMnO_3$ by Harold Hwang and Sang-Wook Cheong of Bell Labs in Murray Hill, New Jersey; in CrO_2 by Michael Coey and coworkers of Dublin's Trinity College; and in Sr_2FeMoO_6 by

Tokura's group in Tsukuba. The IMR effect has been related to the large spin polarization of the conduction electrons in the grains and would be maximized by half metallic grains. Indeed, in the case of CrO_2, Coey and coworkers modeled the tunneling across a half metal/insulator/half metal sandwich and attributed the large IMR at 5 K to complete spin polarization of tunneling electrons.

Half metals could be used in components for other devices as well. A spin tunneling device with four states (as opposed to the usual two: 0 or 1) would offer a novel, and nonvolatile, memory element for computers. Demonstration of the four states in an epitaxial tunneling structure made from $NiMnSb/Al_2O_3/Ni_{0.8}Fe_{0.2}/CoO$ is displayed in figure 4. Efficient programmable logic functions may be realized with either giant magnetoresistance elements or spin-dependent tunneling magnetic devices made of half metals, in conjunction with relatively simple circuitry.[4] These functions may be designed as relatively conventional programmable logic arrays using the magnetic devices as nonvolatile programming elements, or as magnetically programmed core logic functions in arrays of universal logic gates.

Half metals of no moment

More is left to do in the field of half metals besides producing more convincing data, finding more examples of half metals, and moving the phenomenon toward applications. One unexplored area is the case in which the moment of the half metal is zero. Such magnetic materials, dubbed "half metallic antiferromagnets" (HMAFs) by Hendrikus van Leuken and de Groot, possess no macroscopic magnetization, yet their carriers are fully spin polarized. Because the system producing the polarized carriers would be relatively insensitive to applied fields, HMAFs could lead to a new subfield in spin electronics. No actual HMAFs have been found yet. Indeed, identifying, or perhaps constructing, an HMAF is one of the exciting challenges in this field, but theoretical efforts to predict specific possibilities have begun.

Half metals are likely to draw increasing attention because they provide a scientific playground in which the fermionic excitations (or quasiparticles) have no spin degree of freedom at very low temperature. Rob Rudd and one of us (Pickett, then at NRL), pointed out that HMAFs are subject to superconducting instabilities, a condition that typically requires the pairing of unlike spins.[5] The resulting superconducting states will, however, have novel properties, and because only carriers of one spin are superconducting, it is not hard to conceive of novel applications such as single-spin Josephson junctions and related offshoots.

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