CONDENSED MATTER PHYSICS

Magnetoresistance in Layered Manganite Compounds

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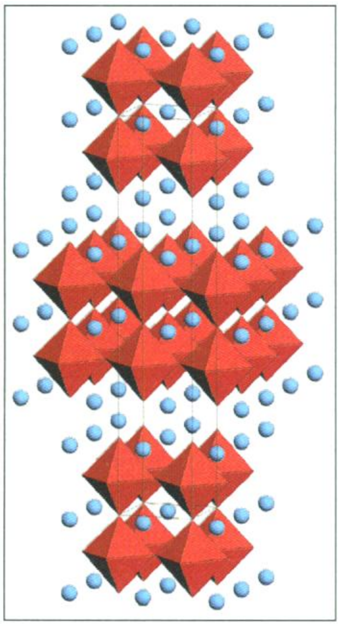
At present there is great technological interest in the phenomenon of magnetoresistance, the change in electrical resistance of a material when subject to a magnetic field. This effect is central to the operation of devices that decipher the pattern of bits in magnetic storage media and is a ubiquitous feature of a wide variety of magnetic sensors. In general, research into spin-polarized transport is more than 60 years old. It has been undergoing a rapid evolution that began almost a decade ago with the discovery by Fert and his collaborators of giant magnetoresistance (GMR) (*1*). This phenomenon was found in materials consisting of atomically engineered alternating layers of ferromagnetic and nonmagnetic metals deposited on an insulating substrate. The study of interplane tunneling magnetoresistance in layered manganite crystals reported by Kimura *et al.* on page 1698 of this issue is an important step in the continuing evolution of this field (*2*).

The key to the behavior of layered manganite compounds is the phenomenon of spin-polarized tunneling. The possibility that carriers of electric current in metallic ferromagnets could be magnetically polarized was realized very early in the development of the quantum theory of magnetism. Ferromagnetism results from electron spin and its associated magnetic moment when there is an imbalance between spin-up and spin-down electrons that can affect the polarization of the conduction electrons. A striking demonstration of this idea came from the investigation of the tunneling of electrons from a ferromagnetic metal across a nonmagnetic insulating layer into a superconductor, which served as a detector of spin polarization (*3*). A further elaboration on the use of tunneling to study spin-polarized charge carriers involved the replacement of the superconductor with a second ferromagnetic layer (*4*). This setup led to what might be termed a magnetic valve, in which the tunneling current at the same voltage is much higher if the magnetic moments of the two electrodes are aligned than if they are not. This phenomenon is analogous to the operation of optical polarizers, although in that case, light is extinguished for crossed polarizers, whereas in the magnetic case, the current is at a minimum when the magnetizations are antiparallel (rotated by 180°)(*5*).



Crystal structure of $La_{1.2}Sr_{1.8}Mn_2O_7$. The MnO_6 octahedrons are interspersed with (La,Sr) sites (spheres). [Adapted from (*8*)]

For ordinary ferromagnets, the most useful magnetoresistance phenomenon, anisotropic magnetoresistance, depends on the extent to which an applied field can rotate the direction of magnetization. For Permalloy, which is the most commonly used material, the fractional change in resistance when the current changes from being parallel to the internal magnetization to being perpendicular is only a few percent. In GMR materials, changes in resistance of 100 to 200% are possible. The GMR effect in metallic magnetic multilayers depends on electron scattering processes set by spin orientation. The first GMR experiments involved current transport parallel to the film plane. More recent studies have been in a geometry in which the current flows perpendicular to the plane, which forces all of the current to cross every interface in its traversal of the structure and thus maximizes the spin scattering.

Another important step in the evolution of magnetoresistance has been the rediscovery of a class of compounds in which electrical resistance is an intrinsic property dependent on the magnetic ordering of its spins (*6*). These compounds—which are derived from substitutions of divalent ions such as Sr^{2+}, Ca^{2+}, and Ba^{2+} into the antiferromagnetic compound $LaMnO_3$, a cubic perovskite—become ferromagnetic at a certain level of substitution. Electrical conduction in the ferromagnetically ordered phase involves a process in which electrons hop from the Mn^{3+} to the Mn^{4+} ions with an intermediate stop at an O^{2-} ion, which is allowed quantum mechanically only if the spin orientations on the Mn ions involved in the process are the same. There is a strong suppression of spin-dependent scattering upon the application of a magnetic field, which results in spin alignment. This effect has been termed colossal magnetoresistance (CMR) because it can be as large as several thousand percent. In contrast with the GMR, CMR requires very large magnetic fields to produce large changes in resistance.

The size of the CMR effect and its implication for devices have stimulated a worldwide research effort whose goal in part has been to find a way to realize the effect in low magnetic fields. A creative approach to reducing the required magnetic field has been to synthesize a variant of the cubic perovskite compound in which there are layers containing magnetic Mn ions within the unit cell. Such structures were first reported by Moritomo *et al.* (*7*). The arrangement of the atoms in a layered manganite is illustrated in the figure, which shows the crystal structure of the compound $La_{1.2}Sr_{1.8}Mn_2O_7$, produced at Argonne National Laboratory (*8*). In effect, the layered manganite crystal forms a virtually infinite array of ferromagnetic-insulator-ferromagnetic junctions. The ferromagnetic metallic sheets are separated by $(La,Sr)_2O_2$ layers, which form a nonmagnetic insulating barrier. The current along the normal to the ferromagnetic sheets is carried by nearly fully spin-polarized electrons, and in traversing the sample, it must cross every magnetic layer, which again maximizes spin scattering. Kimura *et al.* (*2*) suggest that this vertical transport involves tunneling.

The temperature dependencies of the in-plane and normal resistivities of $La_{1.4}Sr_{1.6}Mn_2O_7$ suggest that in-plane magnetic ordering sets in at a high temperature, on the order of 300 K (T^{c}_{max}), and is not complete until about 100 K (T^{ab}_{max}) (*2*). The layered manganite behaves like a two-dimensional ferromagnetic metal in the range, $T^{ab}_{max} < T < T^{c}_{max}$. The magnetoresistance of the compound is strongly anisotropic, and in the case of the out-of-plane transport, is qualitatively consistent with field-enhanced, or field-restored, tunneling of spin-polarized electrons be-

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tween ferromagnetic MnO_2 bilayers through (La,Sr) blocking layers. There is also a significant out-of-plane magnetoresistance of 200% in low fields (<1 kOe).

These layered manganites are in many ways much more complicated than metallic multilayers, and much work needs to be done to develop a complete physical picture of their behavior. A full understanding will involve consideration of interplay between complicated electronic, magnetic, and structural features. As an example, neutron scattering studies of $La_{1.2}Sr_{1.8}Mn_2O_7$ by the Argonne group have revealed structural changes associated with the onset of ferromagnetism (*8*).

Certainly there is a long way to go before oxide manganites are technologically competitive with metallic magnetic multilayers. The synthesis of single crystals of a compound with strong anisotropy in the transport properties, with the out-of-plane transport being determined by spin-dependent tunneling between magnetic metallic layers, is an important advance. Technological application will require the compound in thin-film form and certainly an increase of the temperature at which low-field magnetoresistance is found. Another aspect of this work that should be recognized is the effective use of the floating-zone method for the growth of high-quality single crystals of complex compounds. This approach to crystal growth will impact many areas of materials research.

References

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PROTEIN STRUCTURE

Nanosecond Crystallographic Snapshots of Protein Structural Changes

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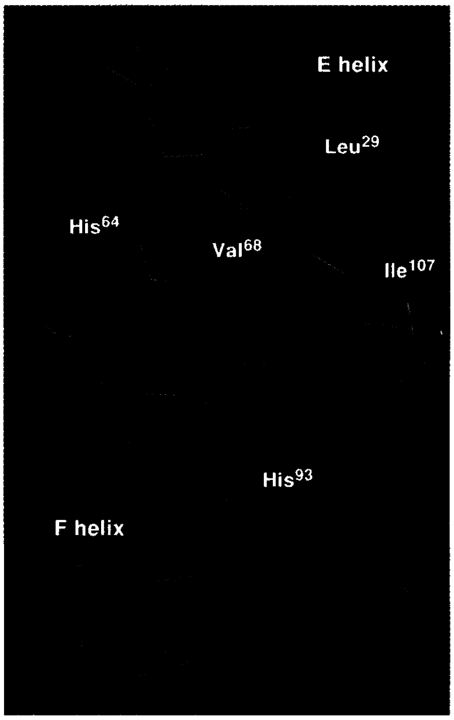
Šrajer *et al.* report in this issue on a dramatic development in protein science (*1*)—they have virtually "watched" a protein function. This group, led by K. Moffat and M. Wulff, has developed time-resolved x-ray crystallography to obtain nanosecond-long snapshots of the complete three-dimensional structure of a protein as it changes in response to ligand dissociation and rebinding. The new technology, made possible by the very intense x-ray pulses at the European Synchrotron Radiation Facility, opens the way to understanding the kinetics and dynamics of protein function in atomic detail. With this x-ray source it will be possible to determine the structure of intermediates with lifetimes as short as a few hundred picoseconds.

To take advantage of this enormous improvement in time-resolution, Šrajer *et al.* examined the photodissociation of the carbon monoxide (CO) complex of myoglobin, a protein reaction that can be rapidly triggered. Light dissociates CO from the heme of myoglobin in less than a picosecond (*2*), and the subsequent ligand rebinding and structural changes have been studied extensively by various time-resolved spectroscopies. The study of Šrajer *et al.* not only is a technological tour de force, but also addresses fundamental issues in understanding how proteins work.

All proteins undergo some structural changes while carrying out their biological function (*3*). Enzymes alter their structure as part of the catalytic mechanism. Antibodies change conformation upon binding antigen. Ligand binding to cell surface receptors induces conformational changes that transmit the signal across the membrane. Viruses use conformational changes of their coat proteins to enter cells. Measuring and understanding the kinetics of conformational changes in proteins is, however, a largely unexplored area. Hemoglobin and myoglobin have been the paradigms for such studies. To facilitate oxygen unloading in the tissues, hemoglobin undergoes conformational changes that are coupled to the rearrangement of its four myoglobin-like subunits. The structure of myoglobin also changes upon oxygen dissociation. How fast does the protein conformation respond to oxygen dissociation? What is the sequence of structural changes? These and other questions have motivated a large number of time-resolved spectroscopic investigations since the initial observations of structural changes in hemoglobin and myoglobin on the microsecond (*4*), nanosecond (*5*, *6*), and picosecond (*7*) time scales.

The basic idea of the time-resolved x-ray crystallographic and spectroscopic experiments is very similar. A laser pulse breaks the covalent bond between the heme iron and CO. (CO is used instead of oxygen because of the higher quantum yield of photodissociation.) In the spectroscopic experiment, the probe is a second laser pulse that interrogates the photolyzed portion of a myoglobin solution at a series of time delays after the photolysis pulse. Theoretical methods and empirical correlations are then used to interpret the changes in the electronic and vibrational spectra in terms of structural changes. In many instances, however, interpretation is



Partial structures of myoglobin (blue) and the myoglobin–carbon monoxide complex (MbCO) (red) (*8*). Blue spheres, the iron and dissociated CO of photolyzed MbCO at 4 ns; red spheres, the iron and CO of MbCO. The two static x-ray structures have been superimposed by minimizing the differences in positions of backbone atoms in the A, B, D, G, and H helices. Residues in green (Leu^{29}, Val^{68}, Ile^{107}) contact the dissociated CO. The displacement of the F helix is only ~0.05 nm, but its motion is detected in the electron density difference maps.

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