Giant Magnetoresistance in Transition Metal Oxides

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Magnetoresistance (MR)—the change in the electrical resistance of a material in the presence of a magnetic field—is of great importance because of its technological implications in magnetic recording, actuators, and sensors. It has been known for some time that some layered and granular intermetallic materials (*1*), as well as doped magnetic semiconductors (*2*), exhibit large MR effects known as giant magnetoresistance (GMR), but only recently has it been observed in oxides. The GMR effect is particularly strong in perovskite manganates of the type $La_{1-x}A_xMnO_3$ (where A is a divalent cation such as an alkaline earth or Pb). The phenomenon was first observed in thin films of these oxides (*3*), but it also occurs in polycrystalline (*4*, *5*) and single-crystal (*6*) materials. There has been a surge of activity in the last 3 years to explore GMR in a variety of manganates, and the results offer guidance in the search for new materials. The discovery of GMR adds another dimension to the great technological possibilities of oxide electronics, high-temperature superconductivity being the other well-known aspect.

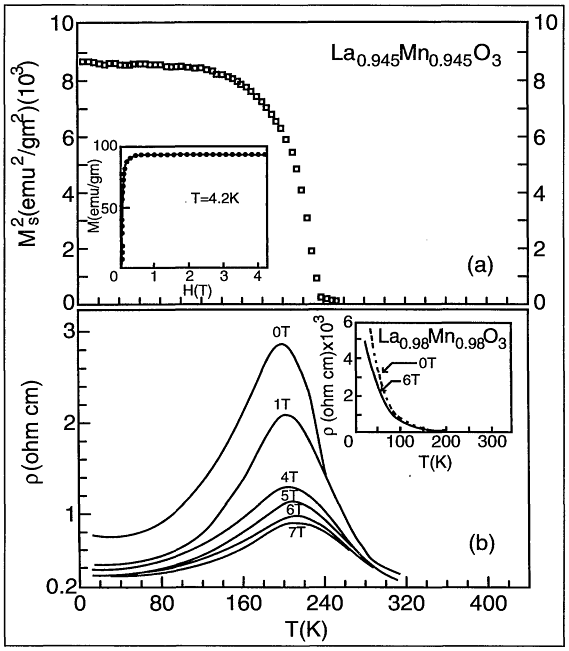

Fig. 1. Giant steps. (**Top**) Magnetization data of polycrystalline $La_{0.945}Mn_{0.945}O_3$. (**Bottom**) Temperature variation of the resistivity of $La_{0.945}Mn_{0.945}O_3$ for different values of *H* (*5*). [Modified from a figure in (*5*)]

The compound $LaMnO_3$ is an antiferromagnetic insulator. When doped with a sufficient concentration of holes (Mn^{4+} ions) by aliovalent substitution or other means (*7*), the material becomes a ferromagnetic conductor with a metal-like temperature variation of resistivity. An Mn^{4+} concentration of around 33% is optimal for obtaining good ferromagnetic characteristics. What one observes in resistivity measurements of such samples is a change from an insulating to a metallic behavior, giving rise to a peak in the resistivity at a temperature T_p close to the ferromagnetic transition temperature T_c (Fig. 1). The double-exchange mechanism of Zener and de Gennes (*8*) has been invoked to account for these properties. The application of a magnetic field in the range of 1 to 10 T causes a large decrease in the resistivity of the manganates, particularly in the region of T_c (see Fig. 1, bottom). Decrease in resistance of close to 100% (*9*) has been observed in $La_{1-x}A_xMnO_3$ and the related rare-earth derivatives $Ln_{1-x}A_xMnO_3$ (Ln = rare earth) (*10*). The variation of MR with magnetic field generally follows the magnetization behavior, with a sharp increase in MR at low fields and low temperatures (Fig. 2).

High values of GMR are generally found when T_c or T_p is low and the peak resistivity at T_p is high. Hydrostatic pressure increases T_c as a result of changes in the Mn-Mn transfer integral or the Mn-O-Mn angle (*11*). Increasing the radius of the A-site cations, $\langle r_A \rangle$, has the same effect as increasing the pressure. A plot of T_c or T_p against $\langle r_A \rangle$ affords a phase diagram (*12*) that separates the paramagnetic insulator and ferromagnetic metal regimes; at small $\langle r_A \rangle$, we have the ferromagnetic insulator regime. The magnitude of GMR and the peak resistivity decrease with an increase in $\langle r_A \rangle$.

Some of the unusual features of the manganates are noteworthy, the most striking one being the "metallic" state at $T < T_p$. The resistivity at the insulator-metal transition is very high compared with other oxide systems exhibiting such transitions (such as $La_{1-x}Sr_xCoO_3$), the resistivity being considerably higher than Mott's maximum metallic resistivity. The temperature variation of resistivity at $T < T_c$ is unusual, with the value for residual resistivities at low temperatures being high; in some instances, $r(T < T_c) > r(T > T_c)$ (*5*). Furthermore, $La_{1-x}A_xMnO_3$ has a negligible density of states at the Fermi level, and the hole states appear to be essentially localized (*13*). What, then, is this unusual metallic state (at $T < T_c$) in the manganates? In order to describe the marginal metallicity of manganates in the ferromagnetic regime, one has to include not only correlation and disorder effects but also magnetic polaron and other effects.

There is reason to believe that the manganates possess inhomogeneities (*4*, *14*). It is not entirely surprising that in a compositionally controlled magnetic system such as $La_{1-x}A_xMnO_3$ there would be ferromagnetic clusters in an antiferromagnetic matrix at large *x* (say $x \geq 0.5$). Many of the $La_{1-x}A_xMnO_3$ compositions exhibit broad magnetic or insulator-metal transitions owing to such inhomogeneities. Particle size, however, appears to have no effect on the magnitude of GMR (*15*), corroborating the view that long-range magnetic order is not a prerequisite for the phenomenon. Accordingly, $La_{0.98}Mn_{0.98}O_3$ (% Mn^{4+}~10), which is really an antiferromagnetic insulator with a few Mn^{8+}-O-Mn^{4+}–type ferromagnetic clusters, shows GMR.

Some of the $Ln_{1-x}A_xMnO_3$ compositions show hysteresis effects, the resistance becoming dependent on magnetic history (*16*). In $La_{0.83}Sr_{0.17}MnO_3$, the structure can be changed by applying a magnetic field, confirming that the local spin moments and the charge carriers are coupled to the structure (*17*). More interestingly, $Nd_{0.5}Sr_{0.5}MnO_3$ and a few other manganates exhibit charge-ordering and a first-order insulator-metal transition induced by the magnetic field (*18*).

Although GMR studies of manganates have been rewarding, it is not yet clear how these materials can be used in technology. What is required is a material with high GMR at ambient temperatures and at modest fields. Other materials must be explored. Among transition metal oxides alone, several other systems have already shown promise. Thus, $Ln_{1-x}A_xCoO_3$, which becomes ferromagnetic and metallic at $x \geq 0.3$, shows GMR (*19*), as does $Tl_2Mn_2O_7$, which is a pyrochlore rather than a perovskite (*20*). The common features of GMR in the manganates also provide certain guidelines for the discovery or design of new GMR materials. For example, because the magnitude of MR is highest around T_c

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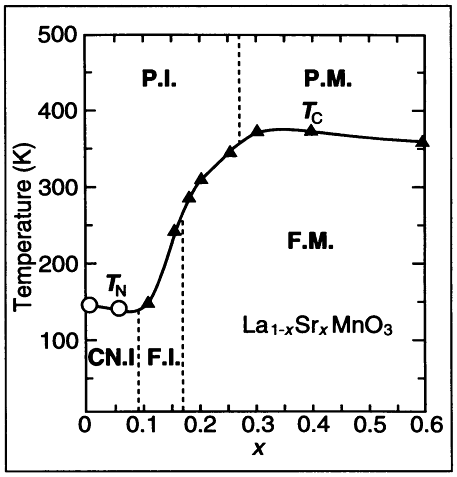

Fig. 2. Electronic phase diagram of $La_{1-x}Sr_xMnO_3$. PI, Paramagnetic insulator; PM, paramagnetic metal; CNI, spin-canted insulator; FI, ferromagnetic insulator; FM, Ferromagnetic metal [from (*6*)].

and increases with the resistivity at this temperature, it seems desirable to examine materials that are magnetic insulators (with reasonable resistivities) at room temperature in order to exploit the property for technological applications. Quaternary oxides, such as $LnMn_{1-y}Cr_yO_3$, would be good candidates for this purpose. Oxide spinels, the $A_2Mn_3O_8$ family of oxides, as well as oxides with the scheelite structure (with appropriate modifications), would be other suitable candidates. Among nonoxide materials, magnetic sulfides, rendered marginally metallic by appropriate substitution, could be examined. There is also need for good measurements on well-characterized samples of the manganates and other oxides exhibiting GMR. For example, structural studies in the presence of a magnetic field would be of considerable interest.

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Green Light for Steroid Hormones

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Since its founding in the 19th century, endocrinology has been constantly innervated by the contributions and methodologies of other fields. These innervations came first from chemists who elucidated the structures of steroid hormones, then from biochemists who purified peptide hormones and their receptors, and eventually from molecular biologists who isolated the genes encoding these molecules. These incursions have forced card-carrying endocrinologists to constantly learn new techniques, new literature, and new approaches, which in turn has allowed them to shed more light on the mechanisms by which tissues and cells communicate across vast distances.

Throughout this history, endocrinologists have assumed that at least one research field could be safely ignored: the field of botany. For although we may have learned as undergraduates that plants have hormones, so-called phytohormones—auxins, abscisic acid, and gibberellin—it was widely held in advanced training that the mechanisms green plants use to send intercellular signals are radically different from those of higher mammals, which have complex circulatory systems and rights of passage such as puberty.

The work described by Li and co-workers in this issue renders these notions antiquated (*1*). They have isolated by positional cloning an *Arabidopsis* gene (*DET2*) that markedly affects light-regulated development (*2*) (Fig. 1), and they determined the molecular basis of seven defects in this gene. Database searches reveal that the protein encoded by *DET2* is almost certainly a plant ortholog of the mammalian steroid 5α-reductases, a group of enzymes involved in male hormone (androgen) biosynthesis (*3*). This sequence identity in turn led the authors to test the hypothesis that plants lacking an active DET2 protein might be defective in the biosynthesis of a phytohormone, specifically one that possessed or was derived from a cyclopentanoperhydrophenanthrene skeleton. Proof of principle was obtained when the plant steroid brassinolide, a bizarre steroid with 28 carbon atoms, successfully reversed the growth defects associated with a genetic deficiency (null allele) in the DET2 protein. Together, the sequence identity and the rescue experiments indicate that the product of the *DET2* gene is involved in the biosynthetic pathway leading to brassinolide (Fig. 2), a member of a large class of ubiquitous plant

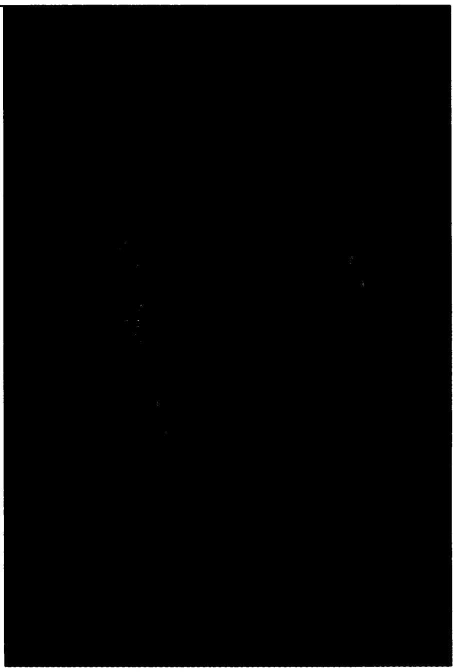

Fig. 1. Wild-type and *det2 Arabidopsis thaliana*. The wild-type plant is on the left. The *det2* plant on the right exhibits dwarfism, infertility, reduced apical dominance, and a darker green color due to delayed leaf and chloroplast senescence. *DET2* encodes a steroid 5α-reductase and its mutation eliminates the biosynthesis of brassinolide, a plant steroid hormone required for development and light-regulated gene expression. [Reprinted from (*7*) with permission]

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