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Author(s): Robert H. Heffner, Michael F. Hundley
John J. Neumeier, Joe D. Thompson,
Xin Di Wu, Jun Zhang, MST-10

Quanxi Jia, MST-STC

Alan R. Bishop, Stewart A. Trugman,
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Science and Technology of Reduced-Dimensional Magnetic Materials

Robert H. Heffner*, Alan R. Bishop, Michael F. Hundley, Quanxi Jia,
John J. Neumeier, Stewart A. Trugman, Joe D. Thompson, Xin Di Wu, and Jun Zhang

Abstract

This is the final report of a three-year, Laboratory Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). This work involved the synthesis of single crystal and thin film samples of magnetoresistive manganites (LaMnO_3 doped with Ca and Sr) and the characterization of their electronic transport properties to understand the underlying physical mechanisms responsible for the colossal magnetoresistance (CMR) of these materials. The experimental program was supplemented by a modeling effort that sought to develop microscopic mathematical models of the observed phenomena. We succeeded in finding an important relation between the magnetization and resistivity in these materials, which helps to explain the importance of lattice distortions accompanied by clusters of ferromagnetic spins (called spin-lattice polarons) in the CMR phenomena. In addition, we developed rudimentary tunnel junctions of CMR-insulator-CMR multilayers that will lead to possible applications of these materials as magnetic sensors.

Background and Research Objectives

When the perovskite-like oxide lanthanum manganite (LaMnO_3) is doped with a divalent element, the resulting compound orders ferromagnetically at a Curie temperature T_C that can range from 100 K to 400 K [1]. A metal-to-insulator transition is associated with the magnetic order and a large reduction in electrical resistivity results if a moderate magnetic field is applied to these materials. A 10 kOe (1 tesla) field will decrease the resistivity by a factor of 10 to 100. This huge magnetoresistance is quite unusual (conventional metals and ferromagnets typically exhibit a change in resistivity of only a few percent in a 10 kOe field) and the effect is therefore referred to as *colossal magnetoresistance* (CMR). Research into the magnetism of these materials in the 1950s concluded that the ferromagnetic order is driven by the double-exchange interaction between neighboring Mn ions [2]. The novel transport in the CMR compounds, however, was only discovered in the past few years. No consensus exists at this time to explain the microscopic mechanisms at work in these compounds, but it is clear that they involve an unusually large interplay between magnetism and electronic transport.

*Principal Investigator, e-mail: heffner@mst.lanl.gov

Our research objective has been to develop a clear microscopic understanding of the physical mechanisms responsible for the unusual electronic transport properties exhibited by the CMR ferromagnetic oxides. At present it appears that a complete description of these mechanisms could involve ferromagnetic double exchange in combination with spin, lattice, or Jahn-Teller interactions leading to the formation of spin-lattice polarons [3]. A polaron in this context means a small spin-aligned region of the lattice 10 to 20 Angstroms in size accompanied by a local lattice distortion. In reaching our research goals, we have substantially increased our understanding of the way in which these lattice distortions couple to charge carriers through magnetic interactions. This understanding has had an impact on other areas of materials research where magnetism and transport couple in novel ways.

Importance to LANL's Science and Technology Base and National R&D Needs

The subject of advanced materials has been identified as a Laboratory core competency. Furthermore, increasing emphasis is now placed on developing materials related to improved economic competitiveness. Work in partnership with industry is therefore an important Laboratory priority. As an example relating to this work, by determining the underlying mechanisms at work in these compounds, we may be able to help the US magnetic recording industry improve its capability for high-density storage by creating more sensitive magnetoresistive (MR) read heads. Furthermore, MR sensors can also play important roles in other commercial and scientific activities where field sensors are used. These areas include the aerospace and automobile industries, medicine, surveillance, and manufacturing control. Hence, CMR research clearly involves two key LANL endeavors: outstanding fundamental science and high-technology industrial interactions. In the early stages of our work we interacted strongly with Hewlett Packard Corporation and continued this contact throughout the project. With HP we co-sponsored a highly successful workshop held at Los Alamos in February 1995, on the basic physics and potential applications of CMR oxides. Participants from a dozen universities, ten companies involved in magnetic recording, and several national laboratories attended this workshop.

Scientific Approach and Accomplishments

To achieve our research objective we combined the three key tools of advanced materials research: materials synthesis, physical characterization, and theoretical modeling. This project was just one part of the CMR effort at LANL; hence, we leveraged our effort in this project by tapping scientific and technical resources from other efforts to achieve our goals.

Accomplishments—Crystal/Film Growth

Single crystals of a number of CMR transition-metal oxides were grown at the single-crystal facility in the Materials Science Laboratory. Large single crystals 7 mm in diameter and 1 to 2 cm long of the ferromagnet $\text{La}_{1-x}\text{M}_x\text{MnO}_3$ ($\text{M} = \text{Ca}$ and Sr) were produced. We invested most of our time growing Ca-doped $x = 0.33$ crystals, but the phase diagram for this system limited us to a large extent. These crystals tended to have a spread of Ca compositions, and thus broad transitions. We studied this problem and isolated it to a strong compositional dependence of the melting point on x . This leads to an unstable melt zone during the crystal growth because the thermal gradients in the melt tend to segregate the various compositions.

We also used the capabilities in the Superconductivity Technology Center to grow thin Ca- and Sr-doped films of the CMR manganites using the pulsed laser deposition (PLD) technique.

Accomplishments—Experimental Physics

Research involving thin-film samples centered on $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. By varying the growth conditions during the PLD process we systematically varied the ferromagnetic ordering temperatures from 150 to 295 K. We observed a clear correlation between a given sample's ordering temperature T_c and the magnitude of its magnetoresistance; samples with increasing T_c displayed smaller MR values. Furthermore, measurements on these films indicated that the interplay between magnetism and electronic transport in these compounds is such that the resistivity $\rho(H,T)$ and magnetization $M(H,T)$ are correlated, following the phenomenological expression $\rho(H,T) \propto \exp(-M(H,T)/M_0)$, where H is the applied field and T the temperature [4]. This is illustrated in Figure 1, and is a new discovery, which has important implications for the microscopic physical mechanisms at work in the CMR materials. Beyond showing the interplay between magnetism and transport in these compounds, the specific functional form of the correlation is consistent with the interpretation that polarons are present at all temperatures, with their characteristic size strongly affected by the onset of ferromagnetic order. This is an important result and will aid theorists in formulating physical models of CMR.

Central to the conventional description of transport in CMR compounds is that divalent substitution for La^{3+} results in Mn mixed valence, and that charge-carrier transport involves holes on $3d^3$ (Mn^{4+}) sites hopping to states on neighboring $3d^4$ (Mn^{3+}) sites. We employed thermoelectric power (TEP) measurements to check for the validity of this description. These measurements are a powerful way of differentiating between alternative transport models, because the carrier's contribution to the Seebeck coefficient S depends directly upon the

fractional hole concentration. In our research we measured the temperature-dependent TEP of polycrystalline $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+\delta}$ samples with $0 \leq x \leq 0.45$.

The TEP results were fully consistent with metallic-like conduction below T_C and small-polaron hopping in the paramagnetic state [5]. The magnitude of S in the small-polaron regime indicates that there are far more holes per active transport site than would be expected based on a simple nominal $\text{Mn}^{3+/4+}$ valence description. This is displayed in Figure 2, where the high-temperature carrier contribution to the TEP is plotted as a function of Ca doping. A transport model based on nominal valence arguments (open circles) cannot account for the doping-independent small magnitude of $S_{c\infty}$. Instead, the data are very well described by a transport model that includes the effects of charge segregation or disproportionation (open triangles). This may be an indication that charge disproportionation is present in this system due to the near degeneracy of Mn^{3+} - Mn^{3+} and Mn^{2+} - Mn^{4+} complexes in octahedrally coordinated systems. If charge disproportionation can be confirmed by other measurements, our result will have a significant impact on the physics community's view of the physical mechanisms involved in the novel effects exhibited by these compounds.

Another key to understanding which underlying physical mechanisms are responsible for the CMR effect is to elucidate how these materials differ from conventional ferromagnets that display neither an anomalous MR effect nor a metal-insulator transition at T_C . In order to examine the close interplay between lattice and electronic effects in the CMR compounds we carried out thermal expansion, magnetostriction, magnetic susceptibility, and magneto-resistance measurements on two manganite samples that span the phase boundary between a ferromagnetic metal and a ferromagnetic insulator. While both of the Ca-doped lanthanum manganite samples that we studied displayed identical magnetic behavior (the ferromagnetic Curie temperatures T_C differed by only 2%), the sample with a metal-insulator transition at T_C exhibited a substantially larger thermal expansion anomaly at T_C than that exhibited by the specimen with no metal-insulator transition at T_C [6]. Our work clearly shows that the lattice is affected by the metal-insulator transition to a far larger degree than that which occurs in a conventional ferromagnet.

Accomplishments—CMR Tunnel Junctions

Beyond understanding the fundamental physical mechanisms responsible for the CMR effect, we have begun to develop these materials as magnetic field sensors. MR values of nearly 100% are obtainable in thin films, but a magnetic field of roughly 10 kOe is required to achieve this. Hence, it is questionable if the doped manganites alone will ever be useful as conventional low-field (10 to 100 Oe), room-temperature MR field sensors. An alternative

approach is to make use of the extreme polarization of the parallel and anti-parallel electronic spin distribution brought about by the large intra-atomic exchange in the manganites. This means that a tunnel junction composed of two CMR films separated by an intervening insulating layer will display a resistance that is a strong function of the magnetization in the two layers. Since the spin polarization in the doped manganites is believed to be much larger than that in conventional ferromagnetic metals, these compounds have great potential in devices that employ spin-dependent transport effects. To that end, we have fabricated proof-of-principle CMR-SrTiO₃-CMR tunnel junctions, and have carried out field-dependent and temperature-dependent characterization measurements. Our first-attempt junctions display [7] very encouraging results, with a relative magnetoresistance at 100 K of -30% in modest fields (100 Oe). This result indicates that CMR tunnel junctions may provide the means to produce a technologically useful field sensor that employs CMR materials. Work is now underway to more carefully craft the tunnel junction electrodes to improve the overall magnetoresistance effect in terms of magnitude, required applied field, and temperature-dependence.

Accomplishments—Modeling

Using a combination of analytical, exact diagonalization, and series expansion techniques, together with additional physical considerations found in real materials (multi-orbital interactions, spin-disorder, and electron-lattice coupling), we examined the commonly accepted double-exchange model of CMR perovskites and found that the ground and low-energy excited magnetic states are far richer than expected from simple Heisenberg ferromagnetism [8, 9, 10]. Specifically, non-ferromagnetic many-body ground states were predicted (except at special densities of itinerant electrons), as well as unusual spin dynamics. These properties may be consistent with recent inelastic neutron scattering and muon spin relaxation studies. We also predicted novel spin textures that should induce anomalous persistent currents in applied magnetic fields [11]. We found a strong tendency for small polaron formation, which is consistent with a large body of experimental data, including local structural and magnetic probes, very large isotope shifts, and thermodynamic, transport and susceptibility measurements. Additionally, we studied the influence of spin disorder on the paramagnetic phase of the double-exchange model. We concluded that, contrary to previous assertions, the metal-insulator transition is unlikely to be due to an Anderson-type mobility edge but rather is driven by small polaron formation. Finally, we have begun modeling polaron and spin-coupling crossover effects in layered CMR perovskites and also the mechanisms for ferromagnetic coupling in the Tl₂Mn₂O₇ pyrochlores.

Summary

In this project we synthesized single-crystal and thin-film samples of doped manganites and studied their electronic transport properties as part of a broad effort at Los Alamos to understand the fundamental origins of the colossal magnetoresistance in these materials. The experimental program was significantly enhanced by a microscopic modeling effort, which examined the role of double exchange in the CMR phenomenon, for example. Experimentally we discovered a fundamental relation between the electrical resistivity and the magnetization in the ferromagnetic state of $(\text{La}, \text{Ca})\text{MnO}_3$, which indicates the significance of magnetic polarons in the conduction process. Additionally, thermoelectric power measurements indicated that the widely accepted view that Ca doping produces only Mn^{3+} and Mn^{4+} may not be correct: substantial quantities of Mn^{2+} may be present as well. If confirmed by other measurements, this will force a reevaluation of the simple double-exchange picture of polaron transport. Finally, we participated in the successful synthesis of CMR-insulator-CMR tunnel junctions that display substantial magnetoresistive switching in a magnetic field. These devices are precursors to future device applications of the CMR materials.

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Figure 1. Correlation between $\rho(H,T)$ and $M(H,T)$. The correlation encompasses a two order-of-magnitude variation in ρ .

Figure 2. High-temperature thermoelectric power data indicate that nominal valence arguments cannot describe charge transport in CMR compounds, while disproportionation-based models work very well.