Colossal Magnetoresistance in Manganite Perovskites

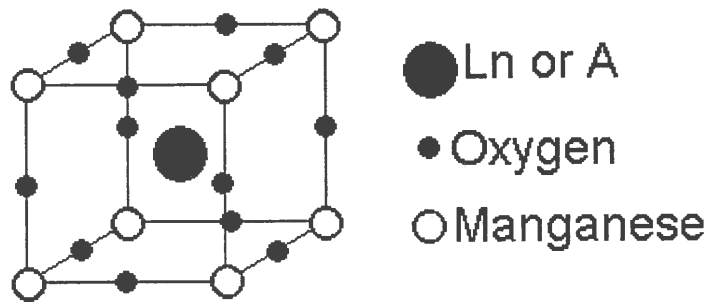
Gregory R. Potratz Literature Seminar October 6, 1999

Several classes of materials are known that exhibit an interesting phenomenon: their electrical resistivity changes when they are placed in an applied magnetic field. This phenomenon is known as magnetoresistance, and the magnitude of the effect is gauged by one (or both) of two parameters: the magnetoresistance ratio (MR) or the resistivity ratio (RR), which are defined as follows:

$$MR = (\rho_H - \rho_0)/\rho_0 \qquad RR = (\rho_H - \rho_0)/\rho_H$$

where ρ_H is the resistivity of the material in an applied field H, and ρ_0 is the zero field resistivity.[1] Many classes of materials display MR, but for most the magnitude of the effect is small. All metallic elements exhibit MR in an applied field but the effect is less than 1% at fields of 10T.[2] Some layered metallic thin films exhibit "giant" magnetoresistance, with RR values of up to 150%.[3] Giant magnetoresistance materials have been commercialized and are now used in the read heads of magnetic disk drives and in magnetic sensors.[4]

In 1993 very large or "colossal" magnetoresistance was reported in doped manganese oxide perovskites with the general formula $Ln_{1-x}A_xMnO_3$ where Ln is a lanthanide element and A is a alkaline earth element (Figure 1)[5] The value of x dramatically changes the properties of these materials by varying the Mn^{III}/Mn^{IV} ratio. The magnetoresistance effect is large for doping levels of $0.2 < x < 0.4$, with $x = 0.3$ usually providing the optimal effect. Colossal magnetoresistance materials display RR of 127,000% or greater, but these large values are seen only over a narrow temperature range near the ferromagnetic ordering temperature T_C.



Ln = Lanthanide A = Alkaline Earth

Figure 1

A common characteristic of manganites that exhibit CMR is that they display a metal insulator transition while simultaneously undergoing a ferromagnet to paramagnet transition. The basis of CMR is a temperature dependent activation barrier for electron movement. In paramagnetic materials the orientations of the electron spins are random, and owing to an interatomic analogue of Hund's rule, there is a large activation barrier for electron transfer between adjacent Mn centers. As a result, in the paramagnetic (high temperature) state the resistivity is high. In a ferromagnetic material, the spins of neighboring metal centers are cooperatively aligned and there is a low barrier for movement of an electron (with a similarly oriented spin) between adjacent Mn centers; as a consequence, in the ferromagnetic (low temperature) state the resistivity is low. Therefore, CMR materials show a dramatic change in resistivity upon passing through the phase transition to the magnetically ordered state.

Thin films of the manganese perovskites can be prepared by a variety of methods such as pulsed laser deposition,[6] molecular beam epitaxy,[7] and MOCVD. Bulk polycrystalline samples are prepared by conventional ceramic and sol gel processing routes.[8] Single crystals have been grown by the floating zone method and by fused salt electrolysis.[9] The properties of the manganese perovskites are very dependent on processing history, indicating that grain boundaries and oxygen stoichiometry play a crucial role in the properties of these materials. Therefore, it is essential to study samples prepared with strict control over the synthetic conditions.

The fundamental mechanisms of magnetotransport—which involve the impact of electronic and structural transitions on electron mobility—are still very actively being studied. The first explanation was double exchange proposed by Zener[10] In this mechanism, an electron is transferred from a Mn^{III} center to an oxygen atom and then to a Mn^{IV} center. The energy barrier for electron transfer between Mn^{III} and Mn^{IV} neighbors is dictated by the alignment of the spins on those Mn atoms. If the spins are antiparallel, the barrier to electron transfer is high and the electron is localized on the Mn^{3+} center. If the spins are parallel, the barrier is low and the electron is free to move.

Recent work has focused on the coupling of electron mobility to dynamic Jahn-Teller distortions of the lattice. Neutron diffraction experiments[11] and EXAFS studies[12] have revealed how the structure distorts under various conditions. In particular, if a variety of different lanthanide or alkaline earth cations are present, the size discrepancies cause local structural irregularities that assist in localizing the electrons, thus shifting T_c to lower temperatures.

Much work has been done to elucidate the nature of the chemical and physical properties of the manganite perovskites. However, further studies that explore the structural transitions upon passing through the Curie temperature are needed for a broad variety of compositions. Additionally, if these materials are to be utilized in practical devices, they must exhibit CMR at much lower field strengths. Finally, additional work studying the effect of substituting other metals into the manganese-containing octahedral (B) sites or substituting paramagnetic ions into the cuboctahedral (A) sites would be of great interest.

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