

Calculated Electronic Structure and Transport Properties of $\text{La}_{.67}\text{Ca}_{.33}\text{MnO}_3$

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ABSTRACT

We have calculated the electronic structure, total energy, magnetic moments and electrical resistivities of LaMnO_3 and $\text{La}_{.67}\text{Ca}_{.33}\text{MnO}_3$ using mean field band theory. The magnetic and structural properties seem to be in good agreement with experiment. The calculations predict that $\text{La}_{.67}\text{Ca}_{.33}\text{MnO}_3$ is metallic for the majority spins and semiconducting for the minority spins.

Introduction

The recent observations[1, 2, 3] of a very large negative magnetoresistance effect in perovskite compounds of composition $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ where A is an alkaline earth element have elicited considerable interest because of possible magnetic sensor applications and because of their possible similarity to materials which show giant magnetoresistance (GMR). In contrast to GMR materials which have a large magnetoresistance because of their inhomogeneous structure, the magnetoresistance of these manganite materials seems to be a property of the homogeneous, bulk material and to be associated with a ferromagnetic phase transition. The details of the transport and magnetic properties, however, vary dramatically from sample to sample and depend on the oxygen content and annealing history of the sample. Recently Hundley *et al*[3] have observed that the resistivities of their samples are a simple exponential function of the magnetization.

In this paper we present calculations of the mean field electronic structure of $\text{La}_{.67}\text{Ca}_{.33}\text{MnO}_3$ and LaMnO_3 . The calculations are performed within the local spin density approximation to density functional theory implemented using the Layer Korringa Kohn Rostoker technique[4]. The atomic potentials were assumed to be spherically symmetric about each nucleus. Space filling spheres were used with the radii chosen proportional to the ionic radii. The coherent potential approximation[5] was used to treat the disorder associated with the calcium substitution for the lanthanum. We also report on some preliminary calculations of the electrical resistivity arising from the substitutional disorder.

Electronic Structure of LaMnO_3

The calculated density of states of nonmagnetic LaMnO_3 in the cubic perovskite structure is shown in Figure 1. The primary features in the density of states are a large complex of oxygen-*p* states centered near 0.2 Hartree, and a large peak consisting of manganese-*d* states with a cusp that lies exactly at the Fermi energy. These manganese-*d* states have an admixture of oxygen-*p*. The lanthanum-*f* states lie about 2 eV above E_F .

Because of the large number of manganese-*d* states at the Fermi energy, it is not surprising that this electronic structure is unstable against spin polarization. We find that the

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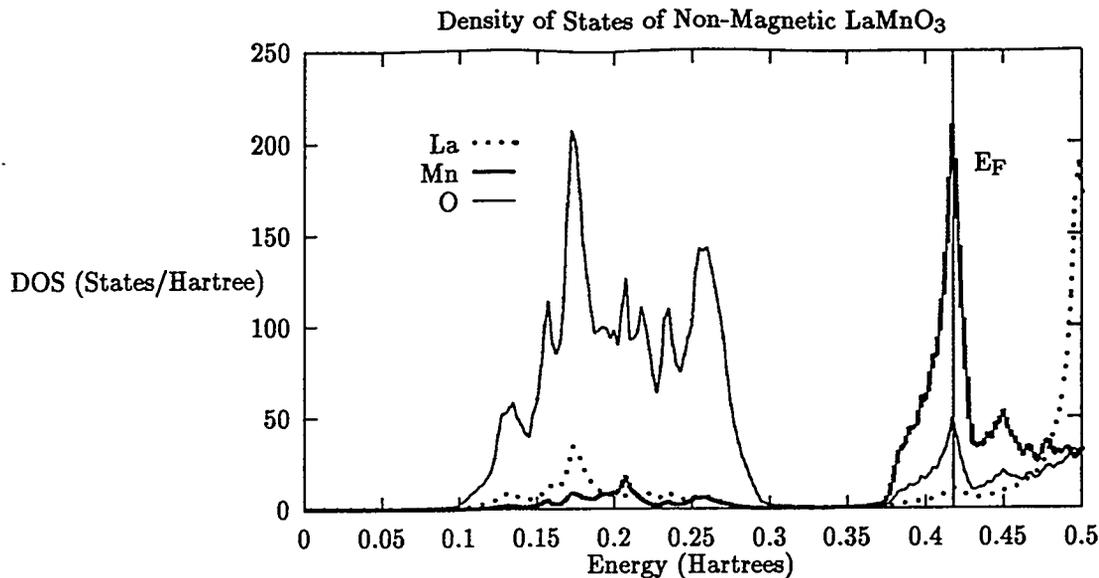


Figure 1: Calculated density of states for non-magnetic LaMnO_3 .

ferromagnetic phase and the anti-ferromagnetic (layered A-type using the nomenclature of [6]) phases are lower in energy than the non-magnetic phase by 50 and 43 mHartrees respectively. Figure 2 shows the calculated density of states for the ferromagnetic phase of the cubic perovskite structure. For clarity we have omitted the lanthanum f states which still lie 2 eV above the Fermi Energy. The interesting feature of this density of states is that the states at the Fermi energy consist entirely of hybridized manganese- d and oxygen- p of *majority spin only*. Thus ferromagnetic LaMnO_3 in the cubic perovskite phase is predicted to be a ferromagnetic “half-metal”. It is metallic for the majority spins and semi-conducting for the minority spins. The spin polarization of the hybridized manganese- d oxygen- p complex is sufficient to move the minority bands above the Fermi energy. There is a much smaller but still perceptible spin polarization of the oxygen- p complex centered near 0.2 Ha. The calculated magnetic moment is $3.9\mu_B$ per manganese atom.

It is known that the stable phase of LaMnO_3 is not the cubic one, but the Pnma structure[7] obtained by rotating and distorting the oxygen octahedra. Pickett and Singh[8] have shown that the local spin density approximation correctly yields an anti-ferromagnetic insulator as the ground state when this distortion of the structure is included.

Electronic Structure of $\text{La}_{.67}\text{Ca}_{.33}\text{MnO}_3$

Most of the recent interest in these materials has centered on the the compounds which are alloyed with alkaline earth elements. It is these that show the extraordinary magnetoresistance. In order to investigate these materials we used the coherent potential approximation to treat the disorder associated with calcium substituting for lanthanum. Figure 3 shows the calculated electronic structure of ferromagnetic $\text{La}_{.67}\text{Ca}_{.33}\text{MnO}_3$. Our calculations correctly predicted that the ferromagnetic phase is stable with respect to the anti-ferromagnetic phase. The calculated energy difference was 6 mHa per formula unit. Our calculated moment per manganese atom was $3.31\mu_B$, in good agreement with the experimental value of 3.4[6].

The major changes in the density of states from Figure 2 are that the Fermi energy has

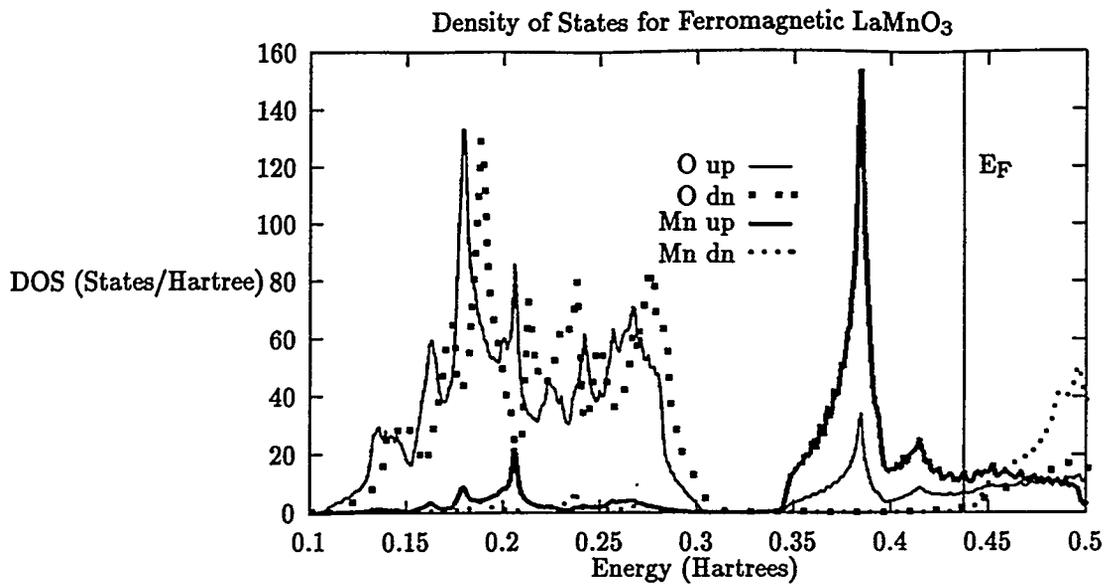


Figure 2: Calculated density of states for ferromagnetic LaMnO_3 . The lanthanum states have been omitted for clarity.

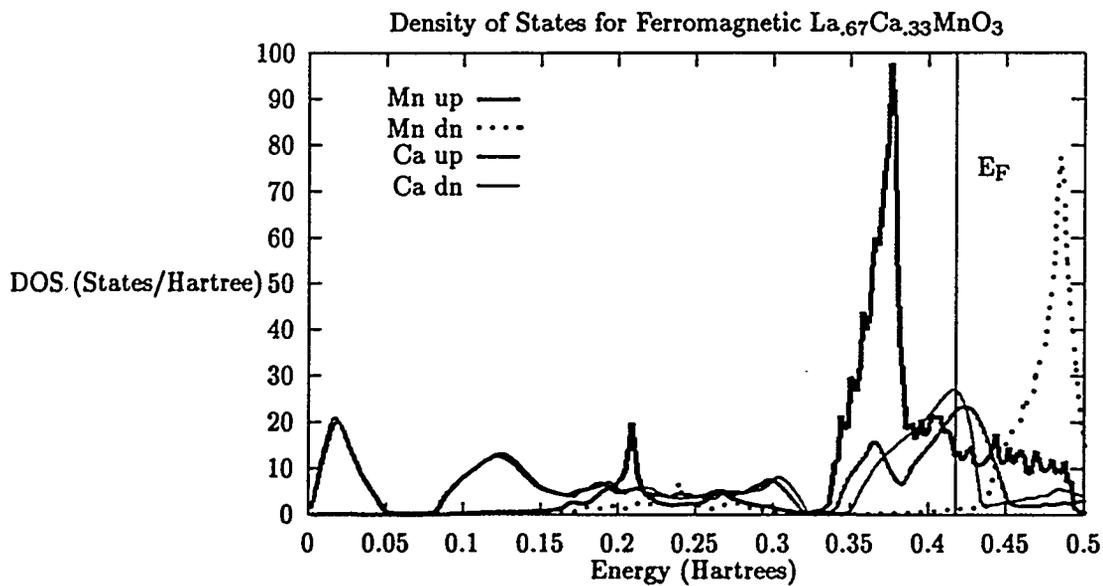


Figure 3: Calculated Density of States for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$. Oxygen and lanthanum states have been omitted for clarity.

moved lower relative to the sharp peak in the density of states associated with the majority spin manganese-*d* states and that calcium states of both minority and majority spins are found at the Fermi energy. Although the oxygen states have been omitted for clarity they still hybridize strongly with the manganese-*d* states. There is also a larger region of little or no manganese majority electron density just above E_F .

The smooth and featureless form of the calcium density of states indicates that these states are highly localized and that $\text{La}_{.67}\text{Ca}_{.33}\text{MnO}_3$ should behave as a half metal. Calculations of the electrical resistivity due to substitutional disorder at zero K yielded $6\mu\Omega\text{cm}$ for the majority spin channel and essentially an infinite resistivity for the minority spin channel. We also investigated the contributions to the conductivity through evaluation of the Kubo formula and found that the current was associated with the manganese and oxygen atoms.

Conclusions

Mean field electronic structure theory gives a surprisingly good description of the structural and magnetic properties of the $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ compounds. Their spectacular magnetotransport properties remain somewhat mysterious. We speculate, however, that they will eventually be understood in terms of the half-metallic band structure predicted by electronic structure calculations. The resistivity calculations described here only included substitutional disorder. It is likely, if indeed these systems are half-metals, that spin-disorder will give a much larger contribution to the electrical resistivity. The large variation in the transport and magnetotransport properties from sample to sample leads one to believe that these materials may not be completely homogeneous magnetically and that they may be similar to the GMR materials after all.

We speculate that the rise in electrical resistivity below the critical temperature may be explained in terms of spin disorder scattering which should be extremely large in a half-metal. The activated transport at high temperatures might arise from anti-ferromagnetic short-range order above the Curie temperature.

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