Effect of disorder on the magnetic and transport properties of

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$

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Abstract

We study a simplified model of the electronic structure of compounds of the type of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. The model represents each $\text{Mn}^{4+}$ ion by a spin $S=1/2$, on which an electron can be added to produce $\text{Mn}^{3+}$. We include two strong intratomic interactions in the Hamiltonian: exchange ($J$) and Coulomb ($U$). Finally, to represent the effect of Sr substitution by La in a simple way, we include a distribution of diagonal energies at the Mn sites. Then we use Green function techniques to calculate a mobility edge and the average density of states. We find that according to the amount of disorder and to the concentration of electrons in the system, the Fermi level can cross the mobility edge to produce a metal to insulator transition as the magnetization decreases (increase of temperature). If the disorder is large, the system remains insulating for all concentrations. Concentrations near zero or one favor the insulating state while intermediate values of concentration favor the metallic state.

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The recent discovery of extremely large magneto resistance in La$_{1-x}$A$_x$MnO$_3$ (where A stands for Ca, Sr, and Ba) and other related oxides [1] has renewed interest in these types of compounds. The magneto resistance values found at large fields seem to be connected with a metal-insulator transition found in some of the compounds at temperatures equal or lower than the ferromagnetic to paramagnetic transition. The $T$ vs. $x$ phase diagram of these compounds is quite similar to that of the high temperature superconductors at low and intermediate concentrations of A, but with the ferromagnetic phase substituting the superconducting one. At the end of the composition range both LaMnO$_3$ and CaMnO$_3$ are antiferromagnetic insulators, while in the intermediate composition range the compounds are ferromagnetic metals. Much has been learned about these compounds and alloys since the earlier studies of Jonker and Van Santen [2]. The later experimental results including single crystal measurements are listed in Ref. 3. Zener [4] advanced a mechanism to understand the properties of the different compounds. Based on the coexistence of Mn$^{3+}$ (3d$^4$) and Mn$^{4+}$ (3d$^3$) within the doped materials, he proposed that the displacement of the fourth electron between them produces the metallic conductivity and at the same time provides a mechanism for the ferromagnetic alignment of the spins. Anderson and Hasegawa [5] calculated the interaction between two magnetic ions mediated by the ”double exchange mechanism”. They point out the importance of the orbital degeneracy for this mechanism as is the case in the Mn ions. de Gennes [6] made a study of the competition between superexchange and double exchange in the dilute limit ($x << 1$) compounds and proposed the existence of canted or spiral magnetic structures. Kubo and Ohata [7] used a spin wave approach to study the temperature dependence of the resistivity well below the Curie Temperature and a mean field approach to the many body Hamiltonian to obtain the electronic and magnetic excitations in the metallic phase. Mazzaferro, Balseiro, and Alascio [8] used a strong coupling approach based on the similarity of these compounds to the intermediate valence Tm compounds. They introduced in the model the possibility of non- equivalent sites for the Mn ions. To our knowledge, this was the first time that the possibility of a metal to insulator transition was mentioned in connection with double exchange. Since magnetization and conductivity
are intimately connected it is evident that any appropriate description of the properties of these compounds must include those factors that affect the mobility of the carriers.

Furukawa used the infinite dimension Kondo lattice model with classical spins to describe several properties of the compounds. Within the model, he was able to fit the resistance versus magnetization curves of Tokura et. al. [9] showing that double exchange is essential to the theory of doped LaMnO$_3$. Millis et. al. [10] analyze a ‘ferromagnetic Kondo Hamiltonian’ using different approximate methods to conclude that double exchange alone is not sufficient to describe the properties of La$_{1-x}$Sr$_x$MnO$_3$.

In this paper we extend the study of Ref. 8 including a continuous distribution of inequivalent sites for the Mn ions. We find that as the magnetization increases from zero to saturation the system may undergo a transition from a state where the Fermi level falls below the localization edge to one where it falls above the edge thus substantially changing the transport properties.

We consider a model were one electron can hop from the 3d$^4$ configuration of Mn$^{3+}$ to the 3d$^3$ configuration of a Mn$^{4+}$ nearest neighbor. To consider the Zener double exchange mechanism, we include an exchange energy between the fourth electron and a core formed by the three localized electrons in the lower d orbitals at each site. To avoid double occupation by itinerant electrons, we take a large Coulomb interaction between them. Finally to simulate the effect of disorder produced by the substitution of La by Sr or other divalent ions and other defects, we introduce a distribution of diagonal energies for different sites. We use a very simplified model Hamiltonian that represents each Mn$^{4+}$ ion at site $i$ by a spin $S_i$, on which one electron can be added to produce Mn$^{3+}$ (for simplicity in what follows we take $S_i = \frac{1}{2}$). When an electron is added in the d-shell of site $i$, an exchange coupling $J$ is included to favor parallel alignment of the added electron to the already existing spin $\uparrow \downarrow$. Also to avoid the possibility of Mn$^{2+}$ we include a strong Coulomb repulsion $U$. The Hamiltonian reads:
\[
H = \sum_{i,\sigma} \epsilon_i c_{i\sigma}^\dagger c_{i\sigma} - t \sum_{<i,j>,\sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i c_{i\uparrow}^\dagger c_{i\uparrow} c_{i\downarrow}^\dagger c_{i\downarrow} - J \sum_i \vec{S}_i \cdot \vec{\sigma}_i ,
\]

where \( c_{i\sigma}^\dagger \) and \( c_{i\sigma} \) create and destroy an itinerant electron with spin \( \sigma \) at site \( i \), respectively. \( \vec{S}_i \) and \( \vec{\sigma}_i \) are the Pauli matrices for spin \( \frac{1}{2} \) at site \( i \) for localized and itinerant electrons respectively. \( \epsilon_i \) is the on-site energy, \( t \) the hopping parameter between nearest neighbors, \( U \) the on-site Coulomb repulsion between two itinerant electrons, and \( J \) is the ferromagnetic \( (J > 0) \) coupling between the localized and itinerant electrons. As is well known, this coupling does not give rise to divergence in the impurity scattering as in the Kondo case nor to heavy electron dynamics as in the Kondo compounds. Without losing essential physics we simplify further by taking only the \( z \) component of the exchange interaction. Thus the states of the system are characterized by itinerant electrons moving on a frozen distribution of localized up or down spins. To obtain site Green functions and thus local density of states for this problem, we start from Hamiltonian (1) for \( t = 0 \) and we calculate the local Green function. For spin up we obtain:

\[
G_{i\uparrow} = \langle \langle c_{i\uparrow}^\dagger c_{i\uparrow} \rangle \rangle = \frac{[\omega - E_{i\alpha} - U(1 - \bar{n}_{i\downarrow})]}{(\omega - E_{i\alpha})(\omega - E_{i\alpha} - U)},
\]

where \( \bar{n}_{i\downarrow} = \langle c_{i\downarrow}^\dagger c_{i\downarrow} \rangle \), \( \alpha = + (\alpha = -) \) for up (down) localized spin, and \( E_{i\alpha} = \epsilon_i - \alpha J \). In order to obtain an approximate solution to the problem for \( (t \neq 0) \) at the start we ignore the site dependence of the diagonal energies: i.e. we set \( \epsilon_i = \epsilon \) and we are left with a binary alloy problem. Using the Renormalized Perturbation Expansion (RPE) [12] and Eq. (2) for \( U \to \infty \) we obtain the corresponding local Green functions. Spin up gives

\[
G_{i\uparrow} = \frac{(1 - \bar{n}_{i\downarrow})}{[\omega - E_{i\alpha} - (1 - \bar{n}_{i\downarrow})\Delta_{i\uparrow}]},
\]

where \( \Delta_{i\uparrow} \) is the corresponding self-energy given by

\[
\Delta_{i\uparrow} = t^2 \sum_{\delta \alpha} G'_{i+\delta\uparrow \alpha},
\]

the summation over \( \delta \) runs over the nearest neighbors to site \( i \) and the \( G' \) are the local propagators avoiding \( i \). Their self-energies \( \Delta'_{i+\delta\uparrow} \) are given by
\[ \Delta^\prime_{i+\delta} = t^2 \sum_{\delta'\alpha} G''_{i+\delta+\delta'\gamma\alpha}, \]  

and so on. Thus, for a system involving an infinite number of sites the RPE iterated procedure as indicated above gives an infinite number of steps. In order to get an approximate solution we average over spin configurations the second term in Eqs. (4) and (5) which gives

\[ \Delta_t = (K + 1)t^2 \left\{ \frac{(1 - \bar{n}^+_i)\nu_+}{[\omega - E_+ - (1 - \bar{n}^+_i)\Delta^\prime_t]} + \frac{(1 - \bar{n}^-_i)\nu_-}{[\omega - E_- - (1 - \bar{n}^-_i)\Delta^\prime_t]} \right\}, \]  

where \( E_\alpha = (\epsilon - \alpha J), \bar{n}^+_i (\bar{n}^-_i) \) is the average number of itinerant electrons with spin down at localized spin up (down) sites, \( (K + 1) \) is the number of nearest neighbors (six for the simple cubic \( Mn \) lattice), \( \nu_+ (\nu_-) \) is the probability that a site has up (down) localized spin (notice that \( \nu_+ + \nu_- = 1 \)), and

\[ \Delta^\prime_t = K t^2 \left\{ \frac{(1 - \bar{n}^+_i)\nu_+}{[\omega - E_+ - (1 - \bar{n}^+_i)\Delta^\prime_t]} \right\} \]  

Notice that within this approximation the iterative procedure closes in the last Equation. This allows us to obtain average density of states for spin up and down. At \( J > \sqrt{K} t \) the density of states splits into two bands centered at \( E_\alpha \) with weights and widths that depend on the number of sites with each spin. i.e. they depend on the magnetization of the system. In Fig. 1 we show the densities of states for spin up and down for several values of the magnetization \( m \), with \( m = (\nu_+ - \nu_-) \). For \( J >> \sqrt{K} t \), the term proportional to \( \nu_- \) can be neglected in Eq.(6) and (7). Similarly for \( \Delta^\prime_- \) and \( \Delta^\prime_\uparrow \), consequently it is easy to see that \( n^\uparrow_\downarrow \rightarrow 0 \) and \( n^\downarrow_\uparrow \rightarrow 0 \). Eq.(7) reduces to

\[ \Delta^\prime_\uparrow = \frac{(\omega - E)}{2} \pm \sqrt{\frac{(\omega - E)^2}{4} - K t^2 \nu_+}, \]  

where \( E = (\epsilon - J) \) and \( \Delta_\uparrow \) results in this case

\[ \Delta_\uparrow = \frac{(K + 1)t^2\nu_+}{[\frac{(\omega - E)}{2} \pm \sqrt{\frac{(\omega - E)^2}{4} - K t^2 \nu_+}]}. \]
Finally we obtain

$$G_{\uparrow+} = \frac{(K - 1)(\omega - E) \mp (k + 1)\sqrt{(\omega - E)^2 - 4Kt^2\nu_+}}{2[(K + 1)^2t^2\nu_+ - (\omega - E)^2]}.$$  \hfill (10)

Eq. (8) allow us to obtain the density of states per site as

$$\rho_{0\uparrow+}(\omega) = \frac{(K + 1)\sqrt{4Kt^2\nu_+ - (\omega - E)^2}}{2\pi|(K + 1)^2t^2\nu_+ - (\omega - E)^2|}.$$  \hfill (11)

At this point, we introduce the site dependent diagonal energies. As is well known, since Anderson’s original paper [13], a distribution of diagonal energies produces localization of the electronic states from the edges of the bands to an energy within them which is called ”mobility edge” (ME). The precise position of the ME is difficult to calculate, different localization criteria result in different values for it [14]. Our concern here is with the changes of the ME with magnetization, which do not differ much among the different criteria. For this reason we report results using Anderson’s original criterium.

Since the resulting structure of localized and extended states in each band can only be qualitatively obtained after having tried several distribution of energies, we present the simplest mathematical model for the distributions of energies: i.e. a Lorentzian [15] distribution of width \(\Gamma\). The ensemble-averaged Green function allows us to write an approximate density of states given by

$$\rho_{\uparrow\downarrow}(\epsilon) = \int_{-\infty}^{+\infty} \rho_{0\uparrow+}(\epsilon')L(\epsilon - \epsilon')d\epsilon',$$  \hfill (12)

where \(L(x)\) is a Lorentz distribution given by

$$L(x) = \frac{\Gamma}{\pi(x^2 + \Gamma^2)}.$$  \hfill (13)

In a similar manner we obtain \(\rho_{\downarrow\downarrow}\).

In Fig. 2 we show the resulting densities of states and mobility edges for different values of the magnetization. Inspection of Fig.2 shows that the system can change from metallic at full magnetization (the Fermi level falls above the mobility edge of the majority band) to localized at the paramagnetic state (the Fermi level below the mobility edge of
the same band). Depending on the values of $\Gamma$ and $n$, situations where the system remains localized or metallic for all values of the magnetization can also be found. This possibility of the system of changing character of states at the Fermi level from extended to localized can be summarized in the phase diagram depicted in Fig. 3, where the localized or extended character of the states at the Fermi level are shown as functions of the electron concentration and magnetization for different values of $\Gamma$.

We do not derive here an expression for the Free energy of the system that would allow us to calculate different thermodynamic properties, however we can easily estimate the effect of disorder on the Curie temperatures: The energy difference between the zero-temperature, fully polarized system and the paramagnetic state can be calculated from the density of states and is a function of the disorder parameter $\Gamma$ and the bandwidth. For $\Gamma >> \sqrt{Kt}$ the total density of states (up and down bands) is weakly dependent on $m$ while in the opposite case the density of states changes substantially as $m$ decreases from saturation to zero. The entropy change between paramagnetic and ferromagnetic states, however, is practically independent of the parameters in the Hamiltonian and is dominated by the spin entropy and approximately equal to $k_B \ln(3 + n)$. In fig 4. we show the electronic energy as a function of the $n$ for two values of the disorder parameter. The Curie temperatures estimated using the above argument range from 0K to about 800K at the top of the scale. One can see that the Curie temperatures decrease with increasing $\Gamma$.

The absence of Mn$^{2+}$ and the value of the saturation magnetization indicate that our assumptions $U, J >> t, \Gamma$ are valid in most of the Mn oxides under consideration. The low energy properties then, depend only on $t, n,$ and $\Gamma$. Of these, $\Gamma$ is the most difficult parameter to estimate, as it should include all effects of disorder. Among these, substitution of La by divalent ions and O vacancies are the most evident sources of disorder, but other types of defects also contribute to $\Gamma$. Polaronic effects derived from Jahn-Teller as well as breathing phonons should be present in these materials. It is conceivable that they could also be represented within our assumptions of a distribution of diagonal energies.

We propose here a model that allows to understand the properties of the different magne-
to resistive compounds in terms of a disorder parameter $\Gamma$ and doping. For the single crystal materials, one would identify the main origin of disorder with the change of Coulomb potential at the Mn sites due to substitution of trivalent rare earths by divalent alkaline earths. This change amounts to some eV’s, so that even including a reasonable screening it remains within the order of magnitude of the bandwidth.Crudely, we can assume that the different levels of doping changes the center of the distribution of energies but do not affect $\Gamma$. In that case, samples of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ for example, differ only in the hole concentration $x$.

According to our results shown in Fig. 3, the resistive behaviour of the samples with $x = 0.15$, 0.175, 0.2, 0.3 as reported in Ref. 16 by Tokura et. al. is consistent with a value of $\Gamma$ of about 2 (in units of the hopping parameter $t \sim 0.2\text{eV}$). Cation or Oxigen vacancies should enhance the values of $\Gamma$ favoring e localization. This is found in samples of $(\text{LaMn})_{1-\gamma}\text{O}_3$ as reported in Ref. 17 and in samples of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, Ref 18. To be able to compare the temperature dependence or the resistivity with our results more precisely it is necessary to obtain the magnetization and the energy difference between the Fermi level and the mobility edge as functions of temperature. We will publish these results elsewhere.

Other experimental results as transfer of optical weight (that can be inferred from Fig. 2), or effect of pressure (increase of $t$), substitution of La by other rare earths (decrease of $t$), also find a simple and consistent explanation in terms of the model. As mentioned above, polaronic effects are expected to be present in these materials as in other perovskites in which electronic structure changes occur, but are not necessary to the understanding of the phenomena under consideration.

In summary, we present here a simple model that can describe the properties of $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ and related compounds. It allows one to describe transitions between ”metallic” and ”insulating” states by shifts of the Fermi level relative to the mobility edge of the system as the magnetization changes.
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FIGURE CAPTIONS

Figure 1. Partial densities of states for spin up and down according to Eq. (6) for $k = 5$, $E_{\pm} = \pm 6$, $\bar{n}_\sigma = 0$, $t = 1$, and different values of the magnetization.

Figure 2. Partial densities of states for spin up and down for the lower band including a Lorentzian distribution of diagonal energies of width $\Gamma = 1$, $k = 5$, $t = 1$, $n = 0.88$, and $J >> t$. Bold lines indicate the zone of energies where the states are extended. The Fermi level ($\epsilon_F$) is indicated for each value of the magnetization.

Figure 3. Electron concentration versus magnetization ”metal-insulator” phase diagram for $k = 5$, $t = 1$ and different values of $\Gamma$.

Figure 4. Energy difference between paramagnetic and ferromagnetic phases in units of...
$t$ for various values of $\Gamma$. 