Metal-insulator transition in the double perovskites

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We construct an effective Hamiltonian for the motion of electrons among the transition metal ions of ordered double perovskites like Sr$_2$FeMoO$_6$, in which strong intra-atomic Coulomb repulsion $U$ is present in only one of the inequivalent transition metal sites. Using a slave-boson formalism, we construct a phase diagram which describes a charge transfer transition between insulating and metallic behavior as the parameters of the model are changed. The parameters for Sr$_2$FeMoO$_6$ are estimated from first-principles calculations and a transition to the insulating state with negative pressure is obtained.

Two mechanisms contribute to the magnetoresistance (MR) of Mn Perovskites: one of them is an intrinsic mechanism that results from the quenching of spin scattering of the carriers by localized spins. It dominates the high field MR and is most effective at temperatures of the order of the Curie temperature $T_c$. The other mechanism which is most effective at low fields, is due to the lowering of spin scattering at interphases between two regions in the material that have different orientation of their magnetization. This mechanism is also temperature dependent and is larger at temperatures well bellow $T_c$, where the polarization of carriers is large. This explains the interest on materials where $T_c$ is appreciably larger than room temperature.

The report by Kobayashi et al. that the double perovskite Sr$_2$FeMoO$_6$ with $T_c$ of about 450 K is half metallic, with an appreciable low field magnetoresistance has renewed interest in these compounds. Furthermore, they open new questions concerning the nature of the electronic structure.

In an ionic picture, assuming that all O ions are O$^{2-}$, one can imagine the 3d transition metal ions as triply or doubly ionized, and Mo to be Mo$^{5+}(4d^1, S = 1/2)$ or Mo$^{6+}(4d^0, S = 0)$. In this picture Fe$^{3+}(3d^6, S = 5/2)$, would order antiferromagnetically with Mo to produce a magnetization saturation of $4\mu_B$ as observed or Fe$^{2+}(3d^6, S = 2)$, could order ferromagnetically to produce the same magnetization. In the extreme situation with no carriers on the Mo ion (Fe$^{2+}$ and Mo$^{6+}$), one would expect that the system is insulating, because of the strong intra-atomic Coulomb repulsion in Fe ($U \sim 7$ eV) compared with the effective Mo-Fe hopping ($V \sim 0.39$ eV from our fits explained below or $V \sim 0.25$ eV) . Actually, there is a certain degree of covalency between O and the transition metal ions. Applying perturbation theory to this insulating state, the Mo valence becomes $\nu_{Mo} = 6 - 24|t_{Mo-O}/(\epsilon_{Mo} - \epsilon_O)|^2$, where $t_{Mo-O}$ is the hopping between transition-metal $t_{2g}$ and O $p_z$ orbitals, and $\epsilon_X$ is the on-site energy for atom X. The magnetic moment of Mo $\mu_{Mo}$ remains zero in second order in $t_{Mo-O}$. This shows that $\mu_{Mo}$, rather than $\nu_{Mo}$ can indicate if the system is insulating or near a metal-insulator transition. In fact, the observed Mo-3d chemical shift is practically identical to that of MoO$_3$, but $\nu_{Mo} < 6$.

While Sr$_2$FeMoO$_6$ is in fact metallic, neutron diffraction experiments obtained magnetic moments consistent with an insulating state: $\mu_{Mo} = 0 \pm 0.1 \mu_B$ and $\mu_{Fe} = 4 \pm 0.1 \mu_B$, indicating that the system is near a metal-insulator transition. Our band structure calculations give a metallic state with $\mu_{Mo} \cong 0.2 \mu_B$, and with opposite sign as $\mu_{Fe}$. The fact that the experimental $\mu_{Mo}$ is lower, points out that the real system is nearer to the insulating state than the predictions of these calculations. Furthermore, substitution of Mo by Re seem to increase $T_c$ but renders the material insulating.

In addition, substitution of Fe by Co or Mn for example makes the compounds antiferromagnetic and insulating. Also, the physical properties (conductivity, magnetization) are very sensitive to sample preparation. Thus, it is of great interest to understand when we can expect a metallic or insulating behavior in similar systems.

In this paper, we intend to address the general question of when one should expect insulating or metallic behavior in the ordered double perovskites structures.

In order to investigate the physical properties of these materials it is necessary to gain knowledge in their intimate electronic structure, including the effects of correlations. We build a tight binding Hamiltonian to describe their electronic structure. This Hamiltonian is based on the calculated energy bands, as explained later, and is reduced to the minimum set of relevant parameters. Since the low-energy properties of the compounds are determined by the bands crossing the Fermi energy, the only interesting orbitals are the $t_{2g}$ orbitals in the interpenetrating simple cubic lattices of Fe and Mo. Itinerant electrons tunnel from the three $t_{2g}$ orbitals of Fe to the same $t_{2g}$ orbitals of nearest neighboring Mo, and between Mo and Mo with transfer energies $V$ and $V'$. In the ferromagnetic phase, which will be studied here, only spin...
down electrons can jump since the spin up orbitals at each Fe site are already filled. We consider these orbitals to be frozen. The same approach has been followed in a recent paper [6]. The resulting effective Hamiltonian, which contains strong correlations, is treated in a slave-boson approximation [4].

For our band structure calculations we use the Full-Potential Linearized Augmented Plane Wave method (FP-LAPW) [3]. In brief, this is an implementation of density functional theory using the generalized gradient approximation (GGA) of the exchange and correlation potential. [3] The Kohn-Sham equations are solved using a basis of linearized augmented plane waves. [2] Local orbital extensions to the LAPW basis [3] are used to describe the 3s and 3p orbitals of Fe, the 4s orbitals of Mo and Sr. We use a well converged basis set of around 1260 plane waves and a sampling of the Brillouin zone (BZ) of 343 points, corresponding to 20 in the irreducible wedge (IBZ). We use a muffin-tin radius of 2.2 Bohr for Fe, 2.0 Bohr for Mo, 2.3 Bohr for Sr, Mo and 1.5 Bohr for O.

To construct an effective Hamiltonian for the description of the motion of electrons among transition-metal ions, we consider a simple cubic lattice occupied by these ions, of lattice parameter a. This lattice consists of two interpenetrating f.c.c. sublattices, one occupied by the Mo ions, and the other by the Fe ions, in such a way that the nearest neighbors (NN) of each Mo ion lie in the other sublattice and vice versa. This may be extended to other transition metals. In between each two transition-metal ions lies an O ion. The O degrees of freedom can be eliminated through a low-energy reduction process (see for example, Ref. [5] and references therein). If the difference between on-site energies $\epsilon_{Mo} - \epsilon_{O}$ and $\epsilon_{Fe} - \epsilon_{O}$, is large compared with the absolute value of $t_{Mo-O}$ and $t_{Fe-O}$, this can be done by perturbation theory. The $xy$ orbitals acquire an effective hopping $V$ to the $xy$ orbitals of the four NN in the $x - y$ plane due to a process of second order in the hopping between $xy$ and $p_x$ orbitals [7]. There are two third-order processes which involve O-O hopping between two $p_x$ orbitals, which lead to a next-NN hopping $V'$ between Mo sites. The band calculations suggest that the equivalent process between Fe ions is not important and we neglect it. By symmetry, it is clear that the $xy$ orbitals cannot hop to NN or next-NN $yz$ or $zx$ orbitals. In addition (excluding direct hopping involving $d$ orbitals at distances larger than $a/2$), the $xy$ orbitals at any site cannot hop out of the plane, because its hopping to any O orbital of the sites $i \pm (a/2)\hat{z}$ is also zero by symmetry. Thus, with a high degree of accuracy, electrons occupying $xy$ orbitals move only in the $x - y$ plane. Similar considerations extend to the $yz$ and $zx$ orbitals.

This leads to the following effective Hamiltonian for the movement of electrons with spin down among $d$ orbitals:

$$H = E_{Fe} \sum_{ia} n_{ia} + E_{Mo} \sum_{ja} n_{ja} + U \sum_{i,\alpha<\beta} n_{ia} n_{i\beta} - V \sum_{ia,\alpha<\beta} (c_{i+\delta_\alpha a}^{\dagger} c_{ia} + H.c.) - V' \sum_{ja,\gamma\alpha} c_{j+\gamma\alpha a}^{\dagger} c_{ja}.$$  \hspace{1cm} (1)

Here $c_{ia}^{\dagger}$ creates an electron at the orbital $\alpha = xy, yz$ or $zx$ of site $i$ with spin down, the sum over $i$ ($j$) extends over the Fe (Mo) sites, $n_{ia} = c_{ia}^{\dagger} c_{ia}$, and $\delta_\alpha$ ($\gamma \alpha$) are vectors which connect a site with their four NN (next-NN) sites lying in the $\alpha$ plane. $U$ is the on-site Coulomb repulsion at the Fe sites. The corresponding term at the Mo sites is neglected. Eliminating the $d - p_x$ hopping through a canonical transformation, the values of the other parameters are:

$$E_{Fe} = \epsilon_{Fe} - \frac{4t_{Fe-O}^2}{\epsilon_{Fe} - \epsilon_{O}}, E_{Mo} = \epsilon_{Mo} - \frac{4t_{Mo-O}^2}{\epsilon_{Mo} - \epsilon_{O}},$$

$$V = \frac{t_{Fe-O} \epsilon_{Mo-O}}{2} \left( \frac{1}{\epsilon_{Fe} - \epsilon_{O}} + \frac{1}{\epsilon_{Mo} - \epsilon_{O}} \right),$$

$$V' = \frac{2t_{Mo-O}^2 \epsilon_{O}}{(\epsilon_{Mo} - \epsilon_{O})^2},$$  \hspace{1cm} (2)

where $t_{O-O}$ is the absolute value of the hopping between the $p_x$ orbitals of two nearest-neighbor O atoms.

In order to treat the Hamiltonian Eq. (1), we use a simple extension of the slave-boson theory of Kotliar and Ruckenstein [6], to the case in which there are two sites per elementary cell and three “colors” per Fe site (instead of two representing spin up and down). The Fock space at each Fe site $i$ is enlarged introducing boson states represented by the creation operators $e_i$ (empty), $s_{ia}$ (singly occupied at orbital $\alpha$), $d_{ia}\beta$ (doubly occupied at orbitals $\alpha$ and $\beta \neq \alpha$) and $t_i$ (triply occupied). In the combined space $H$ reads:

$$H = E_{Fe} \sum_{ia} n_{ia} + E_{Mo} \sum_{ja} n_{ja} + U \sum_{i} (\sum_{\alpha<\beta} d_{ia\beta}^{+} d_{i\alpha\beta} + 3t_i)$$

$$- V \sum_{ia,\alpha<\beta} (c_{i+\delta_\alpha a}^{\dagger} c_{ia} + H.c.) - V' \sum_{ja,\gamma\alpha} c_{j+\gamma\alpha a}^{\dagger} c_{ja}$$

$$+ \sum_{ia} \lambda_{ia} (s_{ia}^{+} s_{ia} + \sum_{\beta \neq \alpha} d_{ia\beta}^{+} d_{i\alpha\beta} + t_i d_{i\alpha\beta} - n_{ia})$$

$$+ \sum_{i} \lambda_i e_i^{+} e_i + t_i^{+} t_i + \sum_{a} s_{ia}^{+} s_{ia} + \sum_{\alpha<\beta} d_{i\alpha\beta}^{+} d_{i\alpha\beta} - 1),$$  \hspace{1cm} (3)

where $s_{ia}^{+}$ represent creation of an electron in the bosonic part of the Fock space:

$$s_{ia}^{+} = (1 - |e_i e_i - \sum_{\beta \neq \alpha} s_{i\beta}^{+} s_{i\beta} - d_{i\gamma\eta}^{+} d_{i\gamma\eta})^{-1/2}$$

$$\times (s_{ia}^{+} e_i + \sum_{\beta \neq \alpha} d_{i\alpha\beta}^{+} s_{i\beta} + t_i d_{i\gamma\eta})$$

$$\times (1 - s_{ia}^{+} s_{ia} - \sum_{\beta \neq \alpha} d_{i\alpha\beta}^{+} d_{i\alpha\beta} - t_i^{+} t_i)^{-1/2},$$  \hspace{1cm} (4)
where $\gamma$ and $\eta$ are the two orbitals different from $\alpha$, and the last two terms of Eq. (3) were introduced to satisfy the constraints of vanishing of the corresponding expressions between brackets, when the energy is minimized with respect to the Lagrange multipliers $\lambda_{\alpha}$ and $\lambda'_{\alpha}$. The roots in Eq. (3) were carefully chosen to satisfy three requirements: i) they are equal to 1 when treated exactly inside this expression, ii) they respect electron-hole symmetry, and iii) when $U = 0$, the saddle point of Eq. (3) reproduces the exact ground state energy.

In the following we consider the Hamiltonian (3) in the saddle point approximation, looking at the homogeneous symmetric solution of the minimization problem in which all values of the condensed bosons are independent of site and orbital. The problem reduces to a not interacting one with renormalized NN hopping $Vz$, where $z$ is the saddle point value of $z_{\alpha}^i$ (assumed here). We neglect the term in $V'$. Its effect near the metal-insulator transition is small and can be taken into account renormalizing $V$. Taking $V' = 0$ allows us to obtain analytical expressions for the electronic spectral densities of state $\rho_{\alpha F e}$ and $\rho_{\alpha M o}$ as a function of the saddle point values of the bosons (e, s, d, and t) and multiplier $\lambda_{\alpha} = \lambda$:

$$
\rho_{\alpha F e}(\omega) = (\omega - E_{M o})F(\omega), \quad \rho_{\alpha M o}(\omega) = (\omega - E'_{F e})F(\omega),
$$

with $E'_{F e} = E_{F e} - \lambda$, $F(\omega) = \rho_0(\omega)/r$,

$$
r = sgn(2\omega - E_{M o} - E'_{F e})\sqrt{(\omega - E_{M o})(\omega - E'_{F e})},
$$

and $\rho_0(\omega)$ is the spectral density for a square lattice with NN hopping $Vz$. For simplicity, we replace this density by a constant $\rho_0 = 1/(2W)$ extending from $-W$ to $W$ with $W = 4Vz$. This allows to perform the integral analytically and the energy per Fe site takes the form:

$$
E(s, d, t) = \frac{E_{M o} + E_{F e}}{2} - \frac{3|W^2 + (E_{M o} - E'_{F e})^2/4|1/2}{2} + 12W/9 + (E_{M o} - E'_{F e})^2/4|1/2
+ \frac{1}{4}(1 - 6m)(E_{M o} - E_{F e} - \lambda) + 3U(d^2 + t^2),
$$

where $e$ is eliminated using the constraint $1 = e^2 + t^2 + 3(s^2 + d^2)$, $m = s^2 + 2d^2 + t^2$, and $\lambda$ is eliminated from:

$$
\langle n_{\alpha} \rangle = m = \frac{1}{6} + \frac{E_{M o} - E'_{F e}}{4W} \ln \left( \frac{|W^2 + (E_{M o} - E'_{F e})^2/4|1/2 + W}{4W^2/9 + (E_{M o} - E'_{F e})^2/4|1/2 + 2W/3} \right).
$$

In Fig. 1 we show the resulting values of $z$ after minimization of $E(s, d, t)$, as a function of $U$ for several values of $\Delta = E_{M o} - E_{F e}$. For sufficiently large values of these quantities, $z = 0$. This indicates that the carriers become extremely heavy, the effective band width is zero, and the system is insulating.

FIG. 1. Reduction factor of the effective hopping as a function of $U$ for several values of $\Delta = E_{M o} - E_{F e}$.

For $z \to 0$ ($W \to 0$), the expressions (3) and (4) can be expanded and the minimization problem can be further simplified, allowing a simple analytical description of the metal-insulator boundary. Differentiating the resulting $E(s, d, t)$ leads to $t = 0$ and:

$$
\frac{3(E_{M o} - E_{F e})}{2\sqrt{38}V} = 2y + (1 + 3y^2)^{1/2} + \frac{1}{(1 + 3y^2)^{1/2}},
$$

$$
\frac{9U}{2\sqrt{38}V} = \frac{2}{y} + (1 + 3y^2)^{1/2},
$$

where $y = d/(1 - 3m)^{1/2}$. As $y$ varies from zero to $\infty$, Eqs. (5) map the metal-insulator boundary. Due to the fact that $t$ goes more rapidly to zero than $d$ and $m - 1/3$, the problem takes a similar form as the metal-insulator transition in the cuprates (7). Taking the limits of large or small $y$ in Eqs. (6), asymptotic analytical expressions for the boundary can be derived:

$$
E_{M o} - E_{F e} = \frac{152(2 + \sqrt{3})}{27}V^2, \quad U \to 0;
$$

$$
E_{M o} - E_{F e} = \frac{4\sqrt{38}}{3}V + \frac{608V^2}{27}, \quad U \to \infty
$$

One can see from here that the insulating behavior due to Coulomb repulsion at Fe sites is not possible if $E_{M o} - E_{F e} < (4\sqrt{38}/3)V \approx 8.22V$, slightly larger than the band width of $\rho_0$. This explains the different behavior of the curves in Fig. 1, depending on the value of $(E_{M o} - E_{F e})/V$. 

3
The resulting metal-insulator phase diagram and the asymptotic expressions are represented in Fig. 2. The realization of such a phase transition depends on the possibility of controlling the parameters of the Hamiltonian in these materials. As an example, we have studied the effects of pressure (positive or negative) on the parameters for Sr$_2$FeMoO$_6$. The Madelung potential at Fe sites should be very different of that at Mo sites due to the large charge difference. In consequence, one expects the application of pressure or chemical pressure should modify the energy difference between Fe and Mo ($E_{Mo} - E_{Fe}$), on one side and also the hybridization parameter $V$. These parameters were obtained from a fit of our calculated $t_{2g}$ energy bands for different values of the lattice parameter, to the bands that result from the Hamiltonian Eq. (1) with $V' = 0$, treated in the Hartree-Fock approximation. In particular the band that crosses the Fermi energy was adjusted at its bottom (point $\Gamma$), and $E_{Mo} - E_{Fe}$ was determined from a fit of the bands at the L point. The fit for the experimental lattice parameter is shown in Fig. 3. The bands at higher energies are affected by high energy states not included in Eq. (1), and a fitting of them is outside our scope. In Table I, we show the resulting parameters, and the pressure $p$ (obtained from the numerical derivative of the total energy in the band structure calculation with respect to the volume) for different lattice parameters $a$. For the experimental $a = 14.91$ Å at $p = 0$, we obtain a small but non-zero $p$ due to the errors of the method. The corresponding points in parameter space are represented by circles in Fig. 2. One can see that in fact Sr$_2$FeMoO$_6$ is not far from a metal-insulator transition and this can be achieved applying a negative pressure estimated in -8 GPa.

In summary, combining band structure calculations, with a slave boson technique (equivalent to the Gutzwiller approximation) to treat strong correlations, we have studied the possibility of a metal-insulator transition in Sr$_2$FeMoO$_6$. We expect that this approach can be used to understand the metallic or insulating behavior in other double perovskites.

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[1] K.I. Kobayashi, T. Kimura, H. Sawada, K. Terakura and Y. Tokura, Nature 395, 677 (1998).
[2] A.E. Bocquet, T. Mizokawa, T. Saitoh, H. Namatame, and A. Fujimori, Phys. Rev. B 46, 3771 (1992).
[3] A. Chattopadhyay and A. J. Millis, cond-mat/0006208.
[4] M.S. Moreno, J.E. Gayone, A. Caneiro, D. Niebieskiwiat, R.D. Sanchez, and G. Zampieri, submitted to Solid State Commun.
[5] M.E. Simon, A.A. Aligia, C.D. Batista, E. Gagliano, and F. Lema, Phys. Rev. B 54, R3780 (1996).
[6] B. García-Landa, C. Ritter, M.R. Ibarra, J. Blasco, P.A. Algarabel, R. Mahendiran, and J. García, Solid State Commun. 110, 435 (1999)
[7] J. Gopalakrishnan, A. Chattopadhyay, S.B. Ogale, T. Venkatesan, R.L. Greene, A.J. Millis, K. Ramesha, B. Hannoyer, and G. Marest, cond-mat/0004317.
[8] M. Itoh, I. Ohta, and Y. Inaguma, Mat. Science Ing. B 41, 55 (1996).
[9] G. Kotliar and A.E. Ruckenstein, Phys. Rev. Lett. 57, 1362 (1986).
[10] C.A. Balseiro, M. Avignon, A.G. Rojo, and B. Alascio, Phys. Rev. Lett. 62, 2624 (1989); 63, 696 (E) (1989).
[11] P. Blaha, K. Schwarz, and J. Luitz, WIEN97, Vienna University of Technology, 1997. (Improved and updated Unix version of the original copyrighted WIEN-code, which was published by P. Blaha, K. Schwarz, P. Soratin, and S. B. Trickey, in Comput. Phys. Commun. 59, 399 (1990)).
[12] D. Singh, Plane Waves, Pseudopotentials, and the LAPW Method (Kluwer Academic, New York, 1994).
[13] J. P. Perdew, S. Burke and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[14] D. Singh, Phys. Rev. B 43, 6388 (1991).
[15] M.E. Simon, A.A. Aligia, and E. Gagliano, Phys. Rev. B 56, 5637 (1997); references therein. H. Rosner, H. Eschrig, R. Hayn, S.-L. Drechsler, and J. Málek, ibid 56, 3402 (1997); references therein.