Electron Localization in Mixed-Valence Manganites

J. M. D. Coey, M. Viret, and L. Ranno

Physics Department, Trinity College, Dublin 2, Ireland

K. Ounadjela

Institut de Physique et de Chimie des Matériaux, 23 Rue de Loess, 67037 Strasbourg, France

Mixed-valence manganites $(A^{3+}_{0.7}B^{2+}_{0.3})MnO_3$ exhibit a resistivity peak with giant negative magnetoresistance below the Curie point. Residual resistivity ranges from 5×10^{-8} to 8×10^3 Ω m, but the electronic heat capacity when $A = Y$ or La is that of a normal d-band metal; $\gamma \approx 6$ mJ mole^{-1} K^{-2}. Spatial fluctuations in the Coulomb and spin-dependent potentials localize the $e_g \uparrow (\sigma^*)$ electrons in wave packets that are large on the scale of the Mn-Mn separation. Transport in the magnetically localized state involves zero-point-energy assisted hopping or tunneling of electrons from one weakly localized wave packet to another.

The $(La_{1-x}Ca_x)MnO_3$ manganite series was the first ferromagnetic oxide to be fully investigated in the 1950s [1]. Electron hopping with spin memory provides a ferromagnetic double exchange interaction [2], leading to canted ferromagnetic [3,4] or possibly helimagnetic [5] spin structures. Renewed interest in $(A^{3+}_{1-x}B^{2+}_x)MnO_3$ systems was stimulated by the discovery of huge negative magnetoresistance in thin films [6,7]. Structural and chemical similarities with high-temperature superconductors have led to rapid progress in film preparation and characterization. Samples with $x \approx 0.3$ exhibit a large peak in resistivity below the Curie point, which has been attributed to spin-disorder scattering of magnetic polarons [6]. Magnetoresistance effects of 99% or more [8] seen there in applied magnetic fields $B_0 > 1$ T are comparable to the largest negative magnetoresistances recorded in magnetic superconductors [9].

Ferromagnetism occurs in the composition range $0.1 < x < 0.5$, where it is associated with the simultaneous presence of Mn^{3+} and Mn^{4+} ions [10,11]. The end members, $x = 0$ and $x = 1$, are antiferromagnetic insulators, but intermediate compositions may exhibit high conductivity and magnetization approaching the spin-only value expected for a ferromagnetic mixture of $Mn^{3+} (3d^4)$ and $Mn^{4+} (3d^3)$ ions. Trivalent manganese is a strong Jahn-Teller ion in octahedral sites, and compounds such as $LaMnO_3$ crystallize in severely distorted variants of the perovskite structure. The fourth manganese d electrons, the $e_g \uparrow$ electrons, become delocalized with increasing x hopping among the Mn^{4+} ion cores. The Jahn-Teller effect is then dynamic, as evidenced by motional narrowing of the ^{55}Mn hyperfine interactions [12], and the structure becomes orthorhombic with a $(\sqrt{2}\,a_0, \sqrt{2}\,a_0, 2a_0)$ superstructure of the elementary cubic perovskite cell [13]. The electronic structure of the ferromagnetic manganites is illustrated in Fig. 1; the $e_g(\sigma^*)$ band is about 1 eV wide, and the $t_{2g} - e_g$ separation is about 1.5 eV [14]. The Fermi level is 3.0 eV above the top of the $2p(O)$ band. The carrier density in the $e_g(\sigma^*)$ band deduced from the formula is 4.5×10^{27} electrons m^{-3}.

In our investigation of the electronic properties of the mixed-valence manganites, we prepared a series of compounds with $x = 0.3$, using different pairs of cations A and B. The samples have similar lattice parameters and all of them show a peak in the resistance with large negative magnetoresistance below the Curie point. In
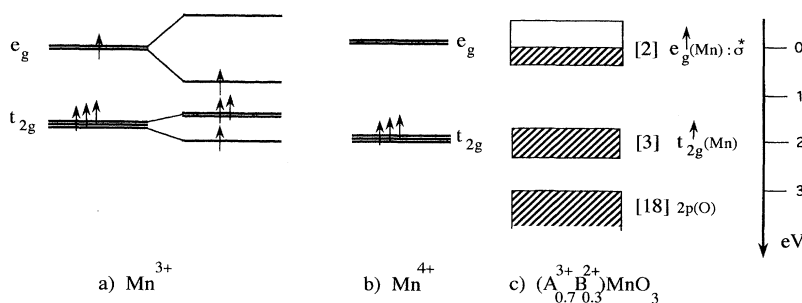

FIG. 1. Electronic structure of (a) Mn^{3+} in octahedral coordination, before and after Jahn-Teller distortion; (b) Mn^{4+} in octahedral coordination; (c) ferromagnetic manganites with $x \approx 0.3$.

each case, the resistivity approaches a temperature-independent residual value ρ_0 at low temperatures, but this value varies by *11 orders of magnitude* from the most conducting sample to the most resistive. A new type of magnetic electron localization is proposed for these ferromagnetic oxides.

Polycrystalline samples were prepared by standard ceramic methods using different trivalent (Y, La, Nd) and divalent (Ca, Sr, Ba) cations in a 7:3 atomic ratio. These were used as targets to produce thin films with a (100) orientation on MgO substrates by pulsed laser deposition [14,15]. Properties such as ρ_0 and T_c were quantitatively different for targets and films, but the qualitative behavior was always similar. The differences are ascribed to variations in oxygen stoichiometry [16]; large variations of resistivity were observed when the most conducting films were heated above 500 K in air. Lattice parameters, resistivity, and magnetoresistance were measured on both thin film and ceramic samples (four-point method); susceptibility, magnetization, and low-temperature specific heat were measured on polycrystalline ceramics only. A summary of results is provided in Table I, which includes, for two compounds, data on both thin film and polycrystalline samples.

The temperature dependence of the resistivity is illustrated in Fig. 2. A large negative magnetoresistance found below T_c [17] is similar to that described by other authors [6,7]. The value of ρ_0 varies from the respectable metallic value of 50 nΩ m (5 $\mu\Omega$ cm) for $(Y_{0.7}Sr_{0.3})MnO_3$ (the lightest cation pair, with the least mass difference) to 8 kΩ m for thin films of $(Nd_{0.7}Ba_{0.3})MnO_3$ (the pair with the greatest mass). There is no evidence of thermal activation down to 4.2 K. The carriers seem to undergo an astonishing loss of mobility, or else very few of them participate in the conduction process. Put in perspective, the resistivity of polycrystalline $(Nd_{0.7}Ba_{0.3})MnO_3$ is similar to that of silicon with 10^{20} carriers m^{-3} and the resistivity of a film is similar to that of silicon with 10^{17} carriers m^{-3}. Films of $(Nd_{0.7}Ba_{0.3})MnO_3$ were so resistive that they had to be measured with the current perpendicular to the plane. The I-V characteristics were then nonlinear, due to the interface resistance of a Schottky barrier formed
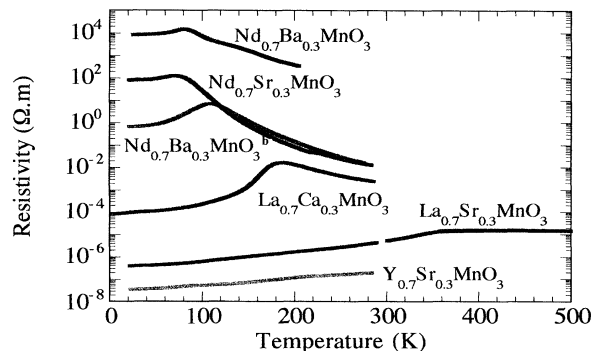

FIG. 2. Temperature dependence of the resistivity of $(A^{3+}_{1-x}B^{2+}_{x})MnO_3$ thin films ([b] denotes a polycrystalline ceramic).

with the contact. The barrier height decreases with the film's magnetization, disappearing near T_c [18].

Heat capacity was measured in the range from 1.5 to 20 K for five samples with $x = 0.3$. Except for compounds with neodymium, all show the $C = \gamma T + \beta T^3$ variation normally expected of a metal. Debye temperatures $\Theta_D = [(5 \times 1944)/\beta]^{1/3}$ and γ values deduced from C/T vs T^2 plots are listed in Table I. The measured γ values are typical of a d band of width about 1 eV. No marked enhancement of γ is associated with the high residual resistivity of $(La_{0.7}Ca_{0.3})MnO_3$, for example. The neodymium oxides exhibit a large excess heat capacity below 40 K, which is probably of crystal-field origin since $J = 9/2$ for Nd^{3+}. This Schottky anomaly makes it impossible to separate the small γT term quantitatively. The Nd orders magnetically at about 1 K [19].

When considering localization of electrons in the $e_g \uparrow$ (σ^*) band, three features of the system should be borne in mind.

(i) The random potential fluctuations experienced by the electrons in the σ^* band due to A^{3+} and B^{2+} ion cores, which if unscreened would amount to $\pm 2e/\sqrt{3}\,\pi\varepsilon_0 a_0 = \pm 1.7$ eV. Screening will reduce these potential fluctuations, but they might still be comparable to the one-electron bandwidth, leading to Anderson localization [20].

TABLE I.   Physical properties of $(A^{3+}_{0.7}B^{2+}_{0.3})MnO_3$ compounds.

System	a_0 [a] (nm)	T_c (K)	γ [b] (mJ mole^{-1} K^2)	Θ_D [b] (K)	ρ_0 (Ω m)
$(Y_{0.7}Sr_{0.3})MnO_3$	0.3858(4)	360(5)	8.1(3)	348(5)	5×10^{-8}
$(La_{0.7}Sr_{0.3})MnO_3$	0.3875	370	6.0	353	6×10^{-7}
$(La_{0.7}Ba_{0.3})MnO_3$	0.3885	330	6.1	333	1×10^{-6}
$(La_{0.7}Ca_{0.3})MnO_3$	0.3855	220			1×10^{-4}
$(La_{0.7}Ca_{0.3})MnO_3$ [b]	0.3860	260	5.2		2×10^{-4}
$(Nd_{0.7}Ba_{0.3})MnO_3$ [b]	0.3883	145			7×10^{-1}
$(Nd_{0.7}Sr_{0.3})MnO_3$	0.3872	115			8×10^{1}
$(Nd_{0.7}Ba_{0.3})MnO_3$	0.3885	110			8×10^{3}

[a]Lattice parameter of the elementary perovskite cell.
[b]Polycrystalline ceramic.

(ii) The Jahn-Teller distortion, static or dynamic, associated with the $Mn^{3+}(3d^4)$ configuration.

(iii) The spin-polarized nature of the $e_g \uparrow$ carriers and their tendency to get trapped in locally ferromagnetic regions when the overall magnetic order is less than perfectly collinear. This may be related to the steep increase in resistivity on approaching T_c from below and the negative magnetoresistance.

The first point to be make regarding the electronic state of the oxides is that the $e_g \uparrow$ electrons must always be *delocalized on the scale of the Mn-Mn distance*. Otherwise, (a) the Jahn-Teller effect would be static, leading to substantial distortion of the crystal structure, which is not the case for $x = 0.3$ [12], and (b) the materials would be antiferromagnetic. It is widely accepted that ferromagnetism in the manganites is due to double exchange mediated by the $e_g \uparrow$ electrons hopping with spin memory [4].

Although they hop and there appears to be a significant density of states at the Fermi level as evidenced by γ, the ability of electrons in the $e_g \uparrow (\sigma^*)$ band to transport charge across a specimen varies enormously. It is possible for an electron wave packet of extent ξ to be weakly localized by the variations in Coulomb potential due to A^{3+} and B^{2+} ions, as indicated in Fig. 3(a), but this does not seem to be a sufficient explanation because the potential fluctuations in all compounds should be roughly similar. No correlation is found between ρ_0 and electronegativity. The $e_g \uparrow$ electrons can be further trapped by fluctuations in the spin-dependent potential due to local deviations from ferromagnetic order. There is an indication from the values of spontaneous magnetization that there are deviations from collinear ferromagnetism (which implies a

spin-only moment of $0.7 \times 4\mu_B + 0.3 \times 3\mu_B = 3.7\mu_B$ per Mn) in all samples, which are greater in the compounds with higher resistivity and lower Curie temperature. When the electrons are already trapped, the potential well is deepened by local deviations from collinearity on the periphery of the wave packet [Fig. 3(b)] where there are fewer electrons and weaker ferromagnetic interactions. A self-consistent theory of that effect could be developed. The data suggest, however, that lattice modes play some part in triggering the magnetic localization, which is more probable when the mass of the large cations is greatest. Variations in the Mn-O-Mn bond angle from one compound to another [13] could also be significant [21].

In polaron theory [20], the temperature independence of the conductivity of a small polaron hopping at low temperatures $(T < \Theta_D/2)$ is attributed to the zero-point energy $k\Theta_D/2$. The hopping frequency is proportional to $\exp(-2W/k\Theta_D)$ where W is the energy of the intermediate state through which the polarons must pass to hop from one spot to another. The barrier height should exceed Θ_D if it is to impede transport significantly.

The wave packet in Fig. 4(b) may be regarded as a "large spin polaron" or "giant spin molecule" [22], but it is unlikely that this entity can diffuse as a whole. Instead individual electrons will hop or tunnel across the surface barriers between one wave packet and the next. The great range of ρ_0 reflects a variation in barrier height rather than a change in the number of barriers to be hopped over or tunneled through. Furthermore, the relevant scale for the energy barriers must be the Hund's-rule splitting U_H of the $e_g \uparrow$ and $e_g \downarrow$ levels (>2 eV) rather than the exchange energy (≈ 0.05 eV). The change of energy of a conduction electron diffusing out of the large magnetic polaron and finding itself in a region of reversed magnetization is U_H. Similar barriers, of order the splitting between the $\uparrow$ and $\downarrow$ d bands, are thought to control the magnetoresistance of metals such as iron [23]. The residual resistivity is then expected to vary as

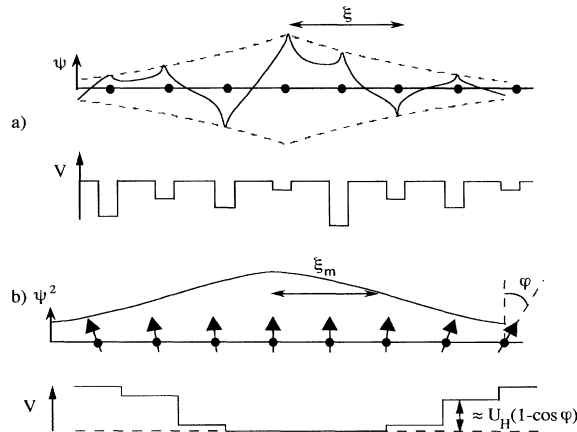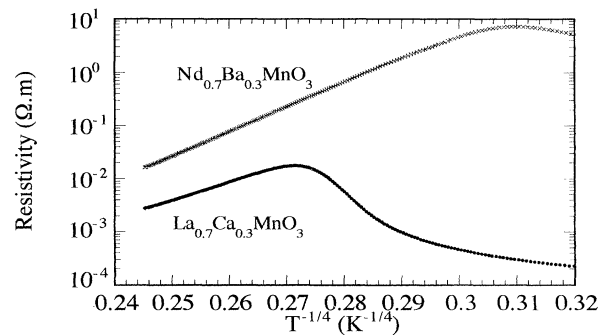$$\rho_0 \sim \rho_m \exp[2U_H(1 - \cos\varphi)/k\Theta_D],$$

FIG. 3. Illustration of (a) localization of an extended wave packet by potential fluctuations due to A^{3+} and B^{2+} ions and (b) localization of an extended wave packet by fluctuations of the spin-dependent potential. Together these fluctuations produce an immobile large magnetic polaron. Electron transport is by individual electrons tunneling or hopping from one wave packet to the next across the potential barriers at the edges.

FIG. 4. Temperature dependence of the resistivity of compounds with localized electrons above T_c.

where φ is the canting angle in the interface regions between the wave packet and ρ_m is a typical metallic resistivity. In $(La_{0.7}Ca_{0.3})MnO_3$, for example, $\ln(\rho_0/\rho_m) \approx 10$, hence $\varphi \approx 35°$ if $U_H = 2$ eV. Further experiments are necessary to determine ξ_m, the size of the large bound magnetic polaron.

Above T_c, the resistivity of the less-conducting compounds falls steadily following the law $\rho \sim \exp(T_0/T)^\nu$, with $\nu \approx 0.25$ (Fig. 4). $\nu = \frac{1}{4}$ corresponds to Mott's expression for variable-range hopping of electrons in a band of localized states in the absence of electron-electron interactions [19]. Theory gives $kT_0 = 1.5/N(E_F)\xi_p^3$, but this yields an unrealistically small value of the localization length in the paramagnetic state, $\xi_p = 0.02$ nm, when the density of states is deduced from the electronic heat capacity coefficient γ.

In conclusion, we have argued from the experimental data that the $e_g \uparrow$ electrons in ferromagnetic mixed-valence manganites are delocalized on an atomic scale, yet they may be weakly localized in large wave packets. The effect is due to fluctuations in the potential they experience which are on the scale of the $e_g \uparrow$ bandwidth, modified somehow by localized lattice modes. Negative magnetoresistance near T_c is then a consequence of a self-consistent modification of the spin-dependent part of the potential fluctuations which are a fraction of the Hund's rule energy U_H. Magnetically localized ferromagnetic metals open new perspectives in spin electronics because of the ability to tune the resistivity of the ferromagnetic metal over a wide range.

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