Pressure effects in ferromagnetic manganites and carrier scattering by disordered magnetic rare earths

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Abstract. The influence of hydrostatic pressure on the transport properties of $(La_{1-x}R_x)_{0.67}Ca_{0.33}MnO_3$ (R = Y,Tb) ferromagnetic manganites is investigated. The enhancement of the Curie temperature T_C under pressure agrees with previous data. In the paramagnetic range, the resistivity can be represented by a Mott localisation law, with a characteristic temperature T_0 decreasing with pressure. The variation of T_C with pressure is compared to the effect induced by replacing La by a magnetic rare earth in $(La_{1-x}R_x)_{0.67}$ Sr_{0.33}MnO₃ manganites (R = Pr, ..., Tm). The main effect is not related to the decrease of the mean radius of the cation, but to an additional scattering by the magnetic moment of the rare earth.

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1 Introduction

Recent studies of doped manganites with general formula $R_{1-x}M_{x}MnO_{3}$, where R = La, Pr, Nd, and M = Ca, Sr, Ba, have revealed a strong coupling between the magnetic, transport and structural properties. Doping the $LaMnO_3$ antiferromagnetic insulator either by vacancies [1] or by divalent alkaline-earth cation [2-5] leads to mixed \dot{Mn}^{3+}/Mn^{4+} valency, ferromagnetism and metallic conductivity. This was explained within the doubleexchange model [6], where the conductivity occurs by electron hopping between the neighboring Mn ions through the oxygen ions. The transfer integral is expressed as $t_{eff} = t_0 * \cos(\Theta/2)$, where Θ is the relative angle of neighbouring Mn spins. The strong local exchange interaction (Hund's-rule coupling J_H) between the localized t_{2q} spins and it inerant e_g electrons leads to a maximum hopping rate corresponding to $\Theta = 0$ or ferromagnetic ordering. A semiconductor-to-metal transition is then observed in the vicinity of the Curie temperature T_C for a doping rate close to 0.3 and the huge negative magnetoresistance observed in the vicinity of T_C can be roughly explained by the alignment of local spins by the magnetic field and the resulting reduction of e_q electrons scattering.

On the other hand, electron-phonon couplings play an important role in these materials. As the e_g state is involved in the chemical bond formation, one can expect a strong dependence of physical properties on the Mn–O–Mn bond angles and lengths, for instance with the change of the average ionic radius $\langle r_A \rangle$ of the rare earth and alcaline earth metals on the A site (chemical pressure effect). This has been observed most frequently, for instance in $(\text{La}_{1-x}Y_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ manganites [2–4]. Increasing the cell distortion lowers T_C and increases the resistivity. In addition some evidence has been brought that the local chemical disorder on the A site also leads to a decrease of the Curie temperature [7], through the standard deviation of the ionic radii around its mean value $\langle r_A \rangle$.

The application of an external pressure is the best way to modify Mn–O bond lengths and bond angles. External pressure is a simple perturbation as it does not alter the periodic nature of the lattice potential; its influence on the physical properties of doped manganites was reported in numerous recent publications [8–12]. A very strong positive shift of the Curie temperature under pressure was observed for all compounds, the value of the logarithmic derivative $d(\ln(T_C))/dP = dT_C/T_C dP$ for various samples was found to be larger for samples having lower T_C .

Combined studies of both chemical and external pressure effects can bring important information about the electronic and magnetic properties of doped manganites. In this paper we report pressure effects on the transport properties of bulk sintered manganites

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 $(\text{La}_{1-x}\text{A}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ (A = Y, Tb) with x between 0.07 and 0.15. By varying the cation concentration, the range of mean radius $\langle r_A \rangle$ from 1.176 Å to 1.204 Å was investigated. Emphasis is put also on the behaviour of the resistivity in the paramagnetic range, at variance with previous studies which were mainly focused on the variation of T_C .

A second related investigation is that of magnetic properties of $(La_{1-x}R_x)_{0.67}Sr_{0.33}MnO_3$ manganites, where La is partly replaced by a (smaller) magnetic rare earth R. It will be seen that the main effect on T_C does not arise from the decrease of the mean cation radius.

2 Experiments

Polycrystalline powders of nominal composition $(La_{0.67-x}Y_x)Ca_{0.33}MnO_3, x = 0, 0.10, 0.15, La_{0.57}$ $Tb_{0.07}Ca_{0.33}MnO_3$ and $La_{0.6}R_{0.07}Sr_{0.33}MnO_3$ (R = Pr, Nd, Eu, Gd, Tb, Dy, Er, Tm) were prepared by the co-precipitation technique [13]. In the final stage the powders were pelletized and annealed in oxygen flow for 12 hours at 1200 °C. This process previously gave us the best samples, *i.e.* a stoichiometric oxygen content, values for the magnetisation and the Curie temperature close to single crystal data. As the magnetic properties of sintered perovskites are very sensitive to preparation conditions, all the samples were prepared in the same manner in order to have comparable properties. The resistivity of samples was measured by the four-probe method using dc current, or ac current with frequencies lower than 80 Hz, within the temperature range 5–300 K. A magnetic field up to 50 kOe (5 Tesla) may be applied parallel to the current. Magnetic properties were studied in an extraction magnetometer with magnetic field values up to 80 kOe, Curie temperatures were determined from Arrott-Belov plots. Quasihydrostatic pressures up to 18 kbar (1.8 GPa) were obtained with a piston-cylinder cell.

3 Pressure dependence of the Curie temperature

Figure 1 shows the temperature dependence of resistivity $\rho(0, T)$ scaled to the room temperature value for our samples. Well defined peaks are observed at a temperature T_{MS} , which corresponds to the change of the conductivity type from metallic-like in the ferromagnetic phase to semiconductor-like in the paramagnetic phase. T_{MS} is close to the Curie temperature T_C obtained by magnetic measurements; it increases systematically with $\langle r_A \rangle$ as illustrated in Figures 1 and 2. This is in agreement with all recent publications on the subject ([2,3] for instance). In a perfect perovskite structure the Mn–O–Mn bond angle would be equal to 180°. The substitution of La for Ca or other cation with smaller ionic radius, leads to the cooperative rotation of the MnO₆ octahedra, changing the Mn– O–Mn bond angle from 180° to (180° – φ). φ decreases



La_{0.67}

La_{0.60}Tb_{0.0}

 $La_{0.57}Y_{0.10}$

 $La_{0.52}Y_{0.13}$

Fig. 1. Normalized resistivity as a function of temperature for $(La_{0.67-x}Y_x)Ca_{0.33}MnO_3$, x = 0, 0.10, 0.15, and $La_{0.60}Tb_{0.07}Ca_{0.33}MnO_3$.



Fig. 2. Variation of the semiconductor-to-metal transition temperature T_{MS} (left scale) and of the Mott localisation temperature T_0 (right scale) with the average ionic radius of A-site cation.

with $\langle r_A \rangle$. Thus, enhanced distortions of the perovskite structure, together with the reduction in the bond length equivalent to an applied chemical pressure, are lowering T_C and T_{MS} , enlarge the magnitude of the resistivity and magnetoresistance near T_{MS} .

The response of a Y-doped perovskite to the application of a magnetic field is illustrated by the upper panel of Figure 3, where the magnetic field dependence of resistivity $\rho(H, T)$ for the La_{0.52}Y_{0.15}Ca_{0.33}MnO₃ sample is presented. The temperature of metal-to-semiconductor transition is again close to the Curie temperature.



Fig. 3. Top: magnetoresistance for La_{0.52}Y_{0.15}Ca_{0.33}MnO₃ polycrystalline sample. Bottom: pressure dependence of resistivity for the same sample in zero magnetic field.

The application of a magnetic field lowers the resistivity and shifts T_{MS} to higher temperatures. As one can see from the lower panel of Figure 3, the application of hydrostatic pressure is qualitatively analogous to the action of a magnetic field as it also lowers the resistivity in the whole temperature range and increases the ferromagnetic Curie temperature. The pressure coefficient, defined as $d(\ln T_{MS})/dP$, is positive for all samples. The variation of T_C with pressure is linear except perhaps for the sample with the lowest Curie temperature at highest pressures. No hysteresis was observed for $\rho-T$ curves after repeated pressure cycles. The pressure coefficient strongly decreases with the Curie temperature, which in turn is related to the A cation mean radius (Fig. 4) and to the degree of structural distortion of the perovskite structure.

Both magnetic field and hydrostatic pressure are shifting T_{MS} to higher temperatures thus enhance the double exchange interaction. The result of the magnetic field action is to align the localized t_{2g} spins, lowering the angle Θ between Mn moments, thus increasing the effective transfer integral t_{eff} and decreasing the spin-dependent scattering of e_g electrons. The application of hydrostatic pressure leads to the reduction of the unit cell volume and modifies the Mn–O–Mn bond angle, leading to an increase in the bandwidth W and in the transfer integral. This explains the analogous influence of pressure and magnetic field, that is a weaker localisation of the carriers and an enhancement of the double exchange interactions.

In general, the response of the perovskite structure to hydrostatic or chemical pressure is difficult to predict, as it leads to a complex rotation of MnO_6 octahedra. The positive pressure coefficient, which is observed for all



Fig. 4. Variations of T_{MS} and T_0 with the average ionic radius $\langle r_A \rangle$.

samples, is thought to be mainly related to a reduction of the distortion which brings the angle of Mn-O-Mn bonds closer to 180° .

The pressure dependence of T_C , $d(\ln T_C)/dP$ (or equivalently $d(\ln T_{MS})/dP$) measured for four samples (Fig. 4) is a decreasing function of $\langle r_A \rangle$. We also plotted it as function of T_C , in order to compare with previous data. The rate of decrease of $d(\ln T_C)/dP$ with T_C is -0.65×10^{-4} kbar⁻¹ K⁻¹, close to previous results. Laukhin *et al.* [11] for instance give -1×10^{-4} kbar⁻¹ K⁻¹. The difference may arise from the different investigated systems: particularly the range of $\langle r_A \rangle$ in our case is restricted between 1.18 and 1.204 Å, whereas a larger pressure dependence has been observed for smaller $\langle r_A \rangle$ values.

We also note that one of our samples contains Tb instead of Y, and that Tb seems to have a larger effect on the depression of T_C than Y for the same concentration. This will be discussed in Section 6 concerning Sr compounds.

4 Resistivity in the paramagnetic range

A less investigated point is the quantitative influence of pressure on the resistivity in the paramagnetic range, although all authors quote the reduction in resistivity under pressure near T_C . Neumeier *et al.* [12] for instance report that the resistivity at room temperature is reduced at rate of about -50% per GPa at room temperature in La-Ca manganites.

At temperatures above T_{MS} , the resistivity of these intermediate-valent manganites is generally considered to follow a variable range hopping (VRH) model rather that an activation law. The semiconducting behaviour arises from hopping between localized states because of the chemical and magnetic disorder [14] and thus from a reduced carrier mobility, rather than from the existence of a true (or "hard") gap, analogous to $LaMnO_3$ and $CaMnO_3$ antiferromagnets. The temperature variation of the resistivity is then described, neglecting electronelectron interactions, by the Mott law:

$$\rho(0, T) = \rho_0(T)^s \exp\{T_0/T\}^{1/4}$$
(1)

with $kT_0 = 18/N(E_F)\xi^3$, where $N(E_F)$ is the density of states at the Fermi level and ξ the localization length [15].

The exponent s in the above equation was found very dependent both on investigated systems and on the detailed theoretical model, it is also difficult to extract faithful values from experimental data. Thus the equation is generally rewritten as:

$$\rho(0, T) = A \exp\{T_0/T\}^{1/4},\tag{2}$$

which will be assumed in the following.

It is difficult to distinguish between the activation or localisation law for the La compound, as our temperature range of measurements is rather narrow. But the localisation law is much better followed for the Y-substituted solid solutions. The values of T_0 at normal pressure obtained from the high-temperature parts of $\rho(H = 0, T)$ curves are presented at Figure 2 as a function of $\langle r_A \rangle$. T_0 decreases with $\langle r_A \rangle$, a similar variation was also observed in [2]. It means that the localisation becomes more important for a smaller A cation radius, which may be also interpreted as a reduction in the bandwidth. The mean hopping distance $R_{hop}(T)$ and the mean hopping energy $\Delta_{hop}(T)$ are proportional to $T_0^{1/4}$ [15], which is thus the scaling factor to be considered. This scale varies from about 102 K^{1/4} to 65 K^{1/4} as $\langle r_A \rangle$ varies from 1.18 to 1.204 Å.

We now turn to the pressure dependence of resistivity. A typical fit of $\rho(P, T)$ curves for $T > T_{MS}$ to the VRH law is presented on Figure 5 for La_{0.52}Y_{0.15}Ca_{0.33}MnO₃ sample. The Mott law is rather well followed from room temperature down to the Curie point for all pressures. The inset shows the pressure dependences for T_0 and the prefactor A. Both T_0 and A decrease with increasing pressure, with $d \ln(T_0)/dP = -2.3 \times 10^{-2}$ kbar⁻¹ and $d \ln(A)/dP =$ -6.0×10^{-3} kbar⁻¹. This indicates that the localisation energy is reduced by applying pressure. The mean hopping energy and the mean hopping distance should vary as $T_0^{1/4}$, with $d \ln(T_0^{1/4})/dP = -7.0 \times 10^{-3}$ kbar⁻¹. For this composition, $T_0^{1/4}$ varies from 102 to 89 K^{1/4} as P increases up to 18 kbar.

Comparing now different samples, the magnitude of the logarithmic derivative $d \ln(T_0)/dP$ decreases roughly lineary with $\langle r_A \rangle$ (Fig. 4), although the (La,Tb) compound deviates from the line for (La,Y) solutions. The sensitivity to pressure is smaller for samples with a higher Curie temperature, which is similar to the effect observed on the ferromagnetic Curie temperature itself.

5 Interpretation of pressure experiments

Various interpretations have been proposed in order to explain the pressure effect on the the Curie temperature,



Fig. 5. Mott plots of the paramagnetic resistivity for the $La_{0.52}Y_{0.15}Ca_{0.33}MnO_3$ sample as function of pressure. The inset displays the pressure dependences of Mott temperature T_0 and A prefactor (see text).

which should also explain the reduction of the paramagnetic resistivity under pressure. We have seen above that the influence of pressure on transport in the paramagnetic state is quite important, thus the variation of the free energy of the paramagnetic phase should be taken into account in order to describe the variation of the Curie temperature.

An attempt to analyse theoretically the pressure dependence of T_C for manganites with varying doping level and to explain the experimental data [8] was made by Furukawa [18]. In this work, the pressure dependence of T_C was attributed to the influence of the bandwidth Wonly, while the strength of the Hund's rule coupling J_H was held fixed. The bandwidth is in turn a function of the bond lengths and angles. A positive pressure dependence was deduced in agreement with experiments, but the predicted increase of T_C with increasing doping and the order of magnitude of the calculated pressure effects were much smaller than the observed experimental results.

Another interpretation is that lattice distortions and compression can enhance the $N(E_F)$ value and the localisation length. The magnetic polaron mechanism was proposed for the explanation of the transport properties above the resistivity maximum, the localisation length ξ can be considered as an estimate of the polaron size. From heat capacity measurements at low temperatures [16], $N(E_F)$ for manganites was estimated to be about 4×10^{28} m⁻³ eV⁻¹. With this value of $N(E_F)$, calculations of ξ according to the classical expression give a polaron size which is smaller than the Mn–Mn distance, which is physically unreasonable. It was proposed by Viret *et al.* [17] that an additional mechanism due to the Hund's rule coupling J_H between localized and itinerant electrons can give a significant contribution to carriers localisation (magnetic localisation model). From reference [17], the Mott temperature is given by $kT_0 = 171 * U_m v / \xi^3$, where U_m is the splitting between spin-up and spin-down e_g bands, v the lattice volume per manganese ion. The estimated ξ then exceeds the ionic radius of Mn³⁺ and the hopping distance is 3–4 times larger than the distance between Mn ions. The fact that a ferromagnetic coupling can influence the transport properties in the paramagnetic range can be expected in manganites as soon as ferromagnetic correlations exist for a range of temperatures as high as about $3T_{MS}$ [4].

Summarizing, the application of pressure increases the localization length and/or decreases the localisation energy, thus facilitates hopping. This can be interpreted as well as the increase of the polaron size and of the mobility for a less distorted structure.

The pressure dependence of the Hund's rule coupling J_H was taken into consideration to explain the systematic decrease of the pressure coefficient with increasing doping level [19]. It was proposed that, as in most magnetic insulators, $J_H(P) = J_H(0) \exp(q_J P/B)$, where B is the bulk modulus, $1/B = -d \ln V/dP$. A positive sign of q_J is required to obtain the correct doping dependence of $d\ln(T_C)/dP$. It was also assumed that the pressure increase of J_H is more rapid than that of the hopping integral. Within the double exchange model, T_C at fixed doping level increases with the e_q bandwidth W, as the intersite exchange interaction is proportional to W in the strong-coupling limit $(J \gg W)$. The exchange interaction energy can be estimated as $U_m = 3J_H/2 \sim 2$ eV. Thus according to the magnetic localisation model, the decrease of $d \ln T_C / dP$ with $\langle r_A \rangle$ can be interpreted as a weakening of Hund's rule coupling as function of lattice distortions. On the other hand, the growth of T_{MS} with the increase of $\langle rA \rangle$ and hence of W, moves the system towards the weak coupling regime, which is less sensitive to pressure.

An additional effect may be a change in the crystal field with the variation of bond lengths and angles, which changes the splitting and the mixing between e_g and t_{2g} orbitals.

6 Influence of doping by magnetic rare earths

The lowering of the Curie point by the replacement of La by another (smaller) rare earth has been so far attributed to the reduced ionic radius and also to the increased standard deviation of the cation radii on A site [20]. However, most measurements were performed on samples where La is replaced by atoms with no or weak magnetic moments (for instance Y or Pr). Only one recent experiment seems to show that the local moment of the rare earth may also have some effect on T_C [21].

In order to check these points and to investigate the magnetic coupling between rare earth and manganese moments, we have systematically studied ferromagnetic solid solutions of the type $La_{0.60}R_{0.07}Sr_{0.33}MnO_3$.



Fig. 6. Lowering of the Curie temperature for $La_{0.60}$ $R_{0.07}Sr_{0.33}MnO_3$ compounds as compared to that for the La compound (left scale) and excess magnetic moment at 5 K (right scale) as function of atomic number of magnetic rare earth.

With a concentration of 0.07, the interactions between magnetic rare earth atoms are small and rare earths should be only weakly polarised by the manganese magnetisation near the Curie point T_C . All the samples received the same treatment as told before, the spontaneous magnetisation and Curie point were obtained by Arrott-Belov analysis of magnetisation isotherms. The uncertainty on T_C is evaluated to about 4 K, that on spontaneous magnetisation is 0.05 μ_B . Experimental results concerning the Curie point and the spontaneous magnetisation at low temperature (5 K) are given in Figure 6.

A first result is that the Curie point is decreased for all (smaller) rare earths replacing La, but that the variation of T_C with the mean radius $\langle r_A \rangle$ is far from linear. Particularly, there is a much stronger decrease ΔT_C for the heavy rare earths which have a large magnetic moment: Gd, Tb, Dy. The largest depression (-37 K) is reached for Dy. For light rare earths, the depression of T_C is -13 K and -10 K for Pr and Nd respectively, and is the smallest for Sm which has a weak paramagnetic moment. Indeed, there is a strong correlation between the decrease of T_C and the value of the effective paramagnetic moment of the rare earth (Fig. 7). The value $\Delta T_C = -26$ K obtained for Eu is close to that for Gd, and may indicate a divalent state of Eu. The presence of the large divalent Sr cation on the same site may favour this divalent state of Eu. This feature should be checked by other methods, for instance X-ray absorption or Mössbauer effect. Of course T_C would be also modified in this case by the larger divalent cation concentration.

Regarding now the spontaneous magnetisation at 5 K (Fig. 6), it appears that there is an excess positive contribution ΔM for heavy rare earths compared to La compound, that is the moment of the rare earth R is parallel to that of Mn. The value $\Delta M = 0.56 \ \mu_B$ obtained for 7% Gd corresponds approximately to the full ferromagnetic polarisation of Gd (7 μ_B). For heavier rare earths, the polarisation decreases more rapidly than the free ion moment g_J of the rare earth, which probably indicates



Fig. 7. Comparison between the depression of the Curie temperature (right scale) with the paramagnetic moment of the rare earth (left scale). Eu is assumed to be divalent.

that crystal field effects lower R magnetic moments below the free ion values at low temperature. For light rare earths, the measured contribution is negligible, which may arise from the low R concentration and from a still weak paramagnetic polarisation of the rare earth at 5 K. Nevertheless, previous magnetisation experiments with a larger R concentration have shown an antiparallel coupling between Mn and light rare earths moments.

These measurements show that the cation size and distortion are not the only factors in the reduction of T_C , but that the presence of disordered magnetic moments at A site also decreases interactions between Mn atoms. This may be interpreted in the following way: there are interactions between these moments and the mobile Mn (e_g) electrons, which are revealed through the parallel coupling of the Mn and rare earth spins at low temperatures. The scattering of e_g electrons by disordered rare earth moments will modify the spin of itinerant electrons, hence lower the hopping integral and the double-exchange coupling between Mn atoms. This effect would then be analogous to the pair-breaking effect of localised magnetic moments in superconductors.

7 Conclusions

In the first part of this work, the variation of the resistivity under pressure has been studied for a few substituted manganites. The decrease of T_C with pressure was found in agreement with previous literature data. An important lowering of the resistivity was also observed in the paramagnetic range, showing that the localisation is reduced by the application of pressure. The effect is more important for compounds with higher localisation energy and lower Curie temperature.

In the second part, the partial replacement of lanthanum by a smaller rare earth showed that there is a strong correlation between the depression of the Curie temperature and the value of the paramagnetic moment of the magnetic rare earth. This was interpreted as a pairbreaking effect which reduces the double-exchange interaction between Mn atoms. These very preliminary results must be completed by a more systematic investigation, especially with different rare earth concentrations, and on other systems. The magnitude of the coupling between Mn and R spins should also be determined.

It has been previously shown that an increased atomic disorder on A site leads to a lowering of the Curie temperature [20]. Thus most probably any kind of disorder (magnetic as well as chemical disorder) on A site may affect T_C through the scattering of e_g Mn electrons, the reduction of the spin diffusion length and carrier mobility.

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