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1996 J. Phys.: Condens. Matter 8 8513

(http://iopscience.iop.org/0953-8984/8/44/006)

J. Phys.: Condens. Matter **8** (1996) 8513–8524. Printed in the UK

The effect of annealing on the magnetoresistance of polycrystalline (La–Y–Ca)MnO_3 perovskites

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Received 18 April 1996, in final form 10 July 1996

Abstract. The magnetization, resistivity and magnetoresistance of yttrium-doped polycrystalline $La_{0.6}Y_{0.7}Ca_{0.33}MnO_3$ have been studied as a function of annealing conditions. The magnetoresistance amplitude depends upon the annealing time, with an optimum corresponding to 12 h annealing at 1200 °C under oxygen. Different contributions to the magnetoresistance are separated; the first is related to the technical magnetization, the second, dominant one, to the influence of the total magnetic induction on the band splitting and the spin correlation function.

1. Introduction

The magnetoresistance (MR) in perovskite-like lanthanum manganites $La_{1-x}Me_xMnO_3$ (Me is Ca, Sr or Ba) has recently been the subject of attention due to the enormous changes of resistivity observed in these materials, compared with those occurring in metallic-based multilayers or granular structures. Both ferromagnetism and high conductivity are observed for the concentration range $0.2 < x < 0.5$, whereas undoped stoichiometric $LaMnO_3$ is antiferromagnetic and insulating. Very high magnetoresistance values have been reported for bulk polycrystalline compounds [1] and thin films [2, 3] just below the Curie temperature T_c, at which the resistivity changes from a semiconducting to a metallic regime at a temperature T_{ms} corresponding to the maximum resistivity. Mixed Mn^{3+}/Mn^{4+} valence states are created when La^{3+} is replaced by divalent metal ions. The double-exchange theory [4] explains the magnetic and transport properties of manganites to a large extent, considering the interaction between itinerant carriers and the local Mn^{3+}/Mn^{4+} ions, although Jahn–Teller distortions have a large effect on interactions. The Mn^{3+}/Mn^{4+} ratio is affected both by the concentration of the dopant ion and by the oxygen stoichiometry, thus leading to variations in MR value and magnetic transition temperature.

Jin *et al* [5] first reported that replacing La by a small amount of yttrium in polycrystalline $La_{0.67}Ca_{0.33}MnO_3$ leads to a decrease of T_{ms} from 240 to 160 K, and to an increase in MR amplitude of up to about 10 000%, a value comparable to that obtained in thin films. This was recently confirmed by subsequent studies by Hwang *et al* [6] and

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0953-8984/96/448513+12$19.50

Fontcuberta *et al* [7]. The decrease in T_c was mainly ascribed to the change in Mn–O–Mn bond angles following the replacement of La by a smaller atom. The increase in magnetoresistance follows the reduction of T_c, because the gap of the semiconducting phase does not change appreciably with this substitution [6].

In a previous paper [8], we studied the influence of annealing at 1200 °C under oxygen on the transport properties of $La_{0.67}Ca_{0.33}MnO_3$. The MR was found to be highest for an optimum annealing time of 12–18 h. The present investigation aims to extend the study to an Y-substituted manganite, in which we expect a further enhancement of the magnetoresistance. An yttrium concentration of 0.07 was retained, in order to have a small reduction of the ordering temperature and thus maintain a significant MR at room temperature.

2. Sample preparation and characterization

Bulk polycrystalline powders of nominal composition $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.6}Y_{0.07}Ca_{0.33}MnO_3$ were prepared by means of co-precipitation from the solutions, a procedure developed earlier for the synthesis of high-temperature superconducting materials [9]. At the final stage the powders were pelletized and annealed in an oxygen flow for 6, 12, 18 or 80 h at 1200 °C (the maximum temperature of the furnace). This procedure gives a better homogeneity than does the classical powder metallurgy process. It gives also a smaller grain size, which is important in order to control the oxidization process. X-ray diffractometry showed that the crystallographic unit cell of yttrium-doped samples is orthorhombically distorted, with the unit cell volume slightly increasing with annealing duration. The final oxygen content could not be determined, but the measurement of the saturation magnetization (see below) gives some idea of the Mn^{4+}/Mn^{3+} proportions.

The electrical resistance of the samples was measured by conventional four-probe DC and AC techniques (frequency < 80 Hz), in the temperature range 5–300 K. Applied magnetic fields of up to 5.5 T were obtained in a superconducting solenoid with the current parallel to the field. Magnetic properties were measured in an extraction magnetometer in the range 5–300 K under applied fields up to 10 T. The spontaneous magnetization or the initial susceptibility were determined from magnetization isotherms, using Arrott–Belov plots in the vicinity of the Curie temperature.

3. Results

Figure 1 shows the temperature-dependences of the spontaneous magnetization (M_{sp}) and inverse susceptibility (χ^{-1}) as functions of temperature for the samples studied. The data for the sample annealed for 6 h are rather different from the others. The magnitude of the spontaneous magnetization M_{sp} at 5 K ($3.35\mu_B$) is larger for this sample. It reaches a constant value of $3.1\mu_B$ for longer annealing times, which means that the oxygen concentration has reached equilibrium after 6–12 h. For an annealing time of 6 h, the temperature-dependence of the inverse susceptibility exhibits a nonlinear decrease with a positive curvature in the range 220–260 K, whereas $M_{sp}(T)$ varies more rapidly in the low-temperature range and drops less rapidly near T_c than it does for other samples which show a better defined Curie temperature. These features indicate that the sample annealed for 6 h is not homogeneous.

For longer annealing times, M_{sp} decreases with an increase of temperature slower than the Brillouin functions for $J = \frac{1}{2}$ or $\frac{3}{2}$ for $T < T_c - 30$ K and drops very quickly near T_c,

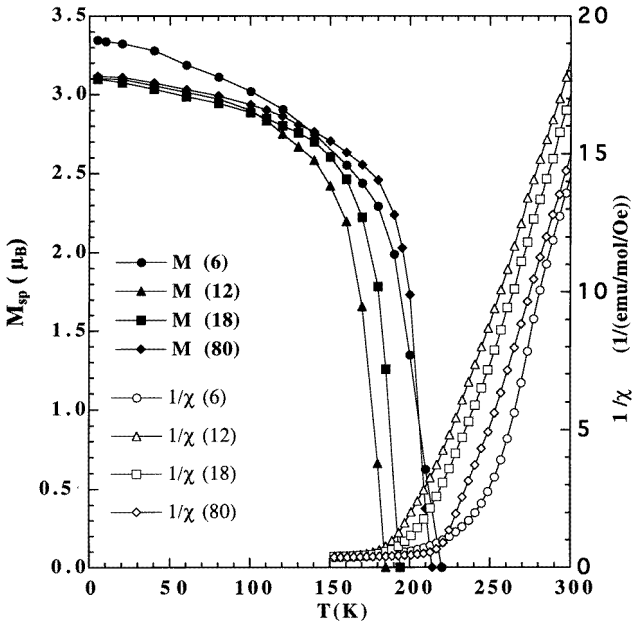

Figure 1. The temperature-dependence of the spontaneous magnetization $M_{sp}(T)$ and inverse susceptibility χ^{-1} as a function of temperature for $La_{0.6}Y_{0.07}Ca_{0.33}MnO_3$ samples annealed for 6, 12, 18 and 80 h under oxygen.

Table 1. Magnetic and transport parameters for Y-substituted manganites as functions of annealing time: spontaneous magnetization M_{sp} at 0 K, paramagnetic and ferromagnetic Curie temperatures, temperatures for the maximum resistivity T_{ms} and maximum magnetoresistance T_{MR}, the gap of the semiconducting phase and the resistivity at 300 K. Uncertainties are the same for each line, except when specified otherwise.

	Annealing time (h)			
	6	12	18	80
M_{sp} $(T = 0)$ (μ_B)	3.35 ± 0.1	3.1	3.1	3.1
Θ_p (K)	240 ± 8	200 ± 5	210 ± 5	220 ± 5
T_c (K)	220 ± 3	185	194	213
T_{ms} (K)	183 ± 5	185	192	204
T_{MR} (K)	175 ± 5	186	190	205
E_{gap} (K)	698 ± 20	656	667	598
ρ_{300} (Ω cm)	2.28 ± 0.4	0.56 ± 0.1	0.58 ± 0.1	0.63 ± 0.1

suggesting that the nature of the transition may be close to first order. Magnetic data are summarized in table 1.

Figure 2 shows the temperature-dependence of the resistivity $\rho(T, H)$ under fields in the range 0–5 T for the sample $La_{0.6}Y_{0.07}Ca_{0.33}MnO_3$ annealed for 12 h. For the zero-field resistivity, two regions can be distinguished according to the sign of its derivative $d\rho/dT$: 'semiconductor-like' and 'metal-like'. The maximum of resistivity defines a metal–semiconductor transition temperature $T_{ms} = 185$ K, which in this case nearly coincides with the Curie point T_c (table 1). Between T_{ms} and 300 K (the upper limit of measurements),

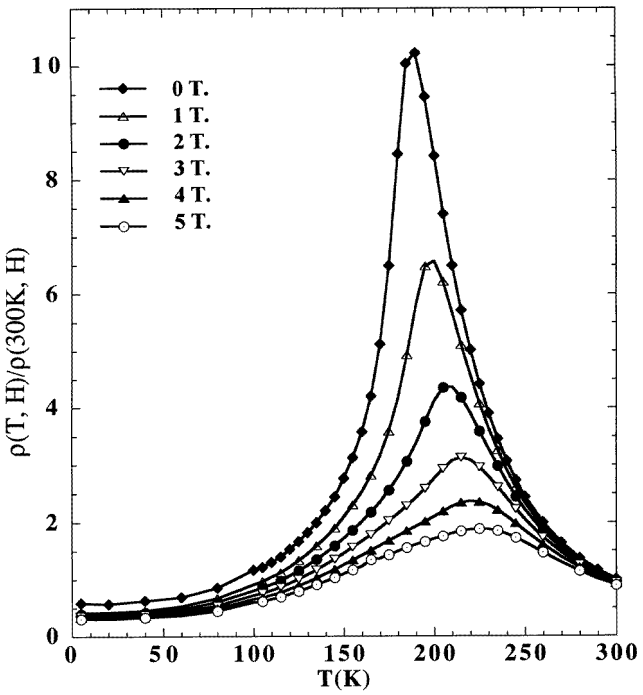

Figure 2. The temperature-dependence of the resistivity $\rho(T, H)$ under fields in the range 0–5 T for the $La_{0.6}Y_{0.07}Ca_{0.33}MnO_3$ sample annealed for 12 h.

the resistivity is governed by an activation law, from which a value of 660 ± 20 K is obtained for the semiconducting gap. This gap remains constant for annealing times in the range 12–18 h and slightly decreases to 600 K for 80 h annealing time. Meanwhile the room temperature resistivity (table 1) drops rapidly during the first 12 h of annealing, and then remains more or less constant, indicating that a stable semiconducting phase has been obtained.

As illustrated in figure 2, the effect of the magnetic field is to lower the value of resistivity and to weaken its temperature-dependence. Meanwhile the peak in resistivity becomes broader and shifts to higher temperatures.

The variations in magnetoresistance and magnetization as functions of applied field are illustrated in figure 3 for the same sample, at four different temperatures. A strong correlation between these two properties has often been observed previously. In contrast to some other publications, the magnetoresistance is defined here as $((\rho(H) - \rho(H = 0))/\rho(H = 0) \times 100$, which is more appropriate for theoretical analysis; the maximum value is obviously 100%. For temperatures higher than T_c, the initial curvature of the MR is negative. A finite slope of the MR isotherm appears below T_c and the magnetoresistance in the range 0–5 T reaches a maximum near T_c. Throughout the temperature range investigated, the magnetoresistance is not saturated in fields up to 5.5 T.

Below T_c two regions in the field-dependence of the resistivity can be distinguished, which are seen better for the 5 K isotherm: a rapid decrease in relatively low fields ($H < 0.5$ T), which coincides with the range within which the technical magnetization is not saturated, and a more gradual lowering of resistivity above. Plots of MR versus magnetization allow one to separate these two regimes. The second one is associated with

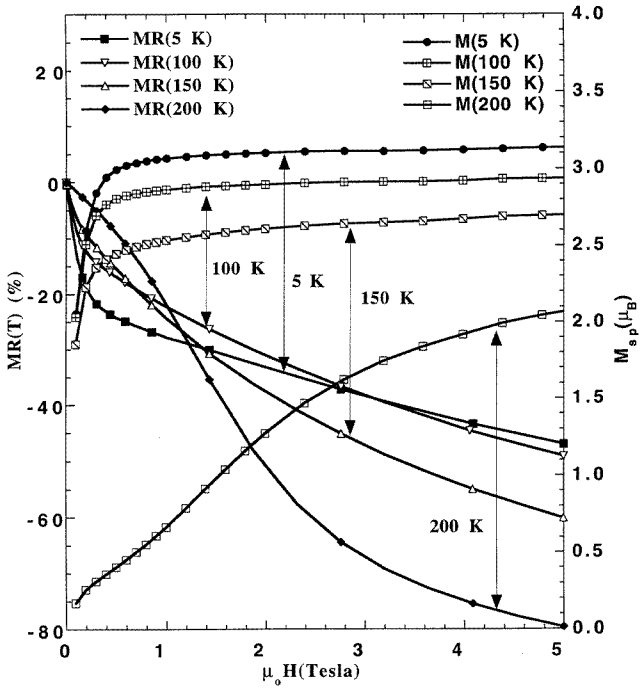

Figure 3. The field-dependences of the magnetoresistance MR(T) and magnetization $M_{sp}(T)$ for the $La_{0.6}Y_{0.07}Ca_{0.33}MnO_3$ sample annealed for 12 h.

the increase in magnetic induction, because it is present even at the lowest temperatures in well-saturated compounds and is the only regime above T_c.

Figure 4 shows the influence of annealing duration on the temperature-dependence of the zero field resistivity $\rho(H = 0)$. All samples show a similar behaviour, with a well-defined semiconductor to metal transition; however, the shape of the resistivity curves changes. Annealing for 6 h leads to $T_{ms} \approx 180$ K and approximately a factor of nine increase in resistivity from 300 to 180 K. A further increase of annealing time shifts T_{ms} as well as T_c towards higher temperatures, and at first slightly increases the $\rho(T_{ms})/\rho(300\ \mathrm{K})$ ratio. Note that $\rho(T)$ curves are sharper and narrower for annealing times of 12 and 18 h. Annealing for 80 h led to an overall increase in the absolute resistivity, as noted before, and to a relative decrease in the resistivity peak amplitude.

The temperature-dependence of the MR in a 5 T field for the same sample set is presented in figure 5. The shape of MR curves, being defined by the temperature variations both of $\rho(H = 0)$ and of $\rho(H = 5\ \mathrm{T})$ values, reveals a more complex evolution with annealing duration. The temperature T_{MR} corresponding to the maximum in MR curves remains close to T_{ms} and shifts to higher temperatures with increasing annealing time. The absolute value of the maximum magnetoresistance follows a nonlinear dependence upon annealing time. This value reaches 66% for 6 h of annealing, increases up to 84% for 12 h and decreases to 66% again for 80 h. Note the rather high values of MR at low temperatures (40–50% for all samples). From the increase in resistivity and the reductions in the amplitude of the temperature- and field-dependences in the sample annealed for 80 h, we may deduce that the 'residual value' of the resistivity, that is the value for vanishing temperature and infinite

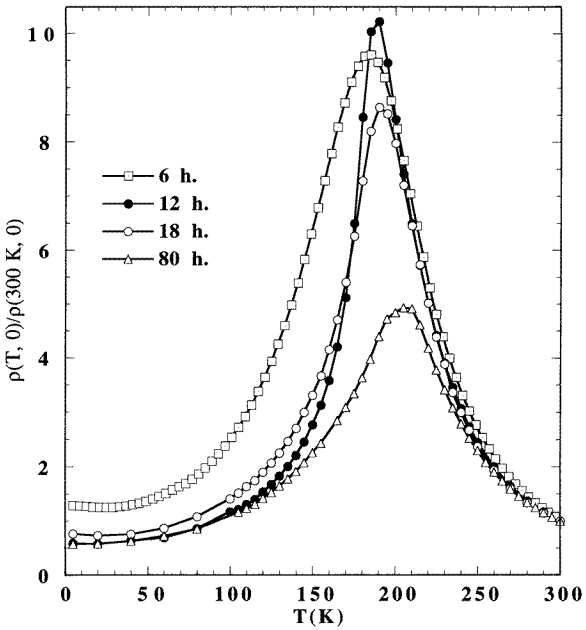

Figure 4. The influence of the annealing duration on the temperature-dependence of the zero-field resistivity $\rho(T, 0)$.

field, is increased. This may be related to the formation of insulating or semiconducting oxide barriers between metallic grains. Figure 5 demonstrates the existence of an optimum annealing with respect to the maximum MR value. A similar result was obtained for the $La_{0.67}Ca_{0.33}MnO_3$ composition, for which it was found that annealing for 12 h also leads to a maximum MR value [8].

The influence of yttrium substitution on the resistivity and magnetoresistance of (La, Ca) manganites is illustrated by the curves in figure 6: data sets both for substituted and for unsubstituted compounds correspond to 12 h of annealing, the resistivity values being normalized with respect to those corresponding to 300 K. As noted previously in more complete investigations [5–7], there is little change in the gap of the semiconducting phase. Y substitution shifts T_c and T_{ms} to lower temperatures and thus leads to an increase in the maximum resistivity value. For the La sample, the $\rho(T_{ms})/\rho(300\ \mathrm{K})$ ratio does not exceed a value of two, whereas for the La–Y sample it is close to one order of magnitude. A significant enhancement is observed for magnetoresistance also.

4. Discussion

4.1. The influence of Y substitution and annealing

The general tendencies concerning the influence of yttrium doping on the magnetotransport properties of Ca manganite presented here are consistent with previous publications [5–7]. As had already been reported and was reproduced for our samples, yttrium substitution drastically improved the magnetoresistance and lowered T_{MR}. Differences in exact T_{MR} and MR(T_{MR}) values observed in [5] and reported in the present paper can be ascribed to

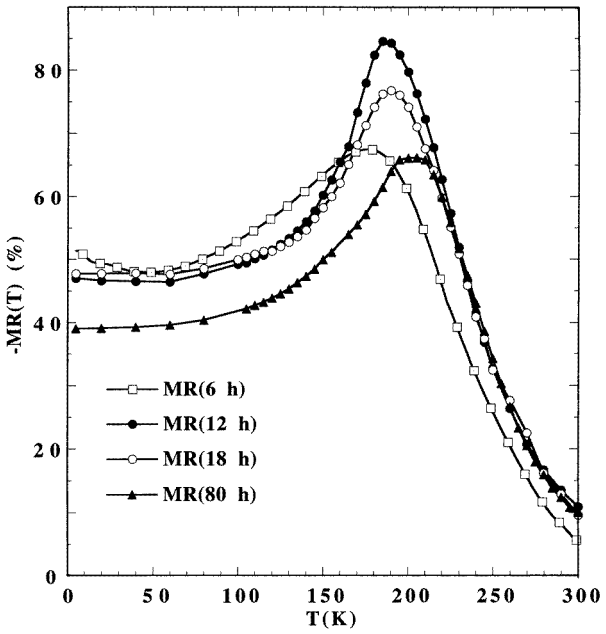

Figure 5. The influence of the annealing duration on the temperature-dependence of the magnetoresistance in a 5 T field.

several reasons. Traditional ceramic technology was used for preparations of samples in [5–7], whereas our materials were obtained by the co-precipitation technique. Annealing regimes were also different: annealing temperatures were 1200 °C and annealing durations 6–80 h in the present work compared to 1400 °C and 4 h respectively in [5]. In [5], the magnetoresistance was normalized with respect to values for the highest value of field (6 T) instead of being normalized with respect to the zero-field value, thus defining a MR ratio that can exceed 100%. The preparation method and different annealing conditions could be the reasons for the lower T_{MR} values (about 140 K) obtained in [5] compared with our data. Other reported T_{MR} temperatures for yttrium-doped Ca manganites range from 120 K (thin films prepared by laser ablation [10]) to 158 K (bulk samples prepared by a gel precursor technique [11]), whereas the structural parameters of our samples are similar to those reported in [5, 10, 11].

Qualitatively the influence of yttrium substitution can be understood in terms of the double-exchange mechanism [4]. In the perovskite structure Mn ions occupying B sites are surrounded by oxygen octahedra, whereas La cations are in A-site positions. For perfect cubic structure, the Mn–O–Mn bond angle is equal to 180 ° and undistorted MnO_6 octahedra form a three-dimensional network. Upon substitution of La by cations with a smaller radius, the MnO_6 octahedra are forced to rotate in order to compensate for the reduced size. This rotation of MnO_6 octahedra lowers the Mn–O–Mn bond angle and thus reduces the matrix element of electron hopping [4] between Mn^{3+} and Mn^{4+} ions. As was demonstrated in [12], the application of 'chemical pressure' lowers T_{ms} and is equivalent to the application of an external hydrostatic pressure. Also, hydrostatic pressure lowers the value of resistivity at T_{ms} and shifts the maximum to higher temperatures [11, 12]. Our results show the extreme sensitivity of magnetotransport properties of manganites to inhomogeneities, small lattice

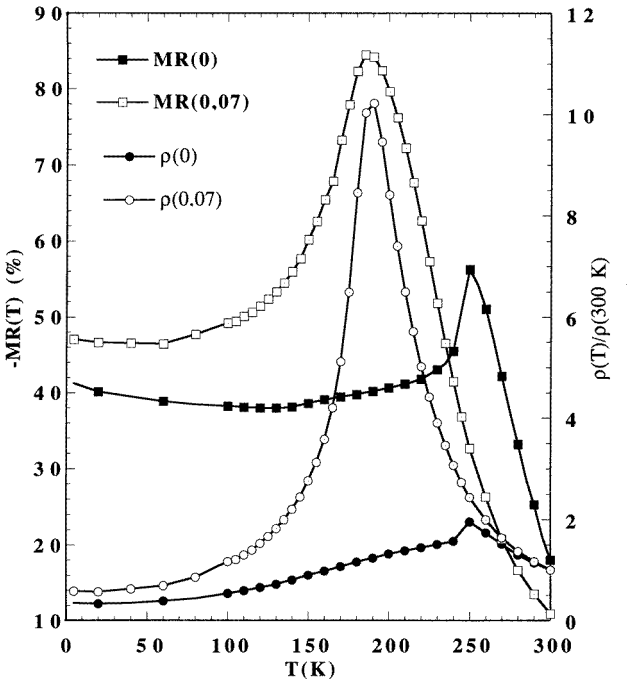

Figure 6. The influence of yttrium substitution on the resistivity $\rho(T, 0)$ and magnetoresistance MR of $La_{0.67-x}Y_xCa_{0.33}MnO_3$ for $x = 0$ and 0.07.

strains or chemical pressure resulting from the substitution of large La ions by smaller Y ions under different annealing conditions. The variation of properties may arise through the rearrangement of cations in the lattice which modifies the lattice parameters and distortion.

The present data show the existence of an optimum annealing time for obtaining maximum variations in $\rho(T)$ and MR(T). This may come:

(i) from a change in the crystallographic structure, particularly in the bond angles, following the ordering of cations and the increase in oxygen content, which influence the ordering temperature;

(ii) from the increase in Mn^{4+} proportion following oxygen content; and

(iii) from the suppression of defects and inhomogeneities in the sample, leading to a more resistive semiconducting phase and a less resistive metallic one. Data corresponding to the shortest annealing time indicate the existence of such inhomogeneities, which also lead to a curvature of the χ^{-1} curve and smearing of local Curie temperatures throughout the sample. However, the resistivity was then larger, even in the semiconducting state.

The first point may partly explain the rise in the Curie temperature with annealing time from 12 to 80 h. X-ray data show a slight increase in the lattice parameters during annealing. However, we were unable to deduce anything about the sense of evolution of the orthorhombic distortion. An optimized value of the Mn–O–Mn bond angle and of the electron hopping matrix element may result in some increase in the Curie temperature.

Concerning the second point, an important feature is the inherent extensive non-stoichiometry of lanthanum manganites $LaMnO_{3\pm\delta}$ in one or more sub-lattices, which is certainly dependent on annealing conditions. The dependence of oxygen non-stoichiometry

δ on the oxygen partial pressure for an annealing temperature of 1200 °C was studied in [13]. Annealing in the region of pressures $0 > \log P(O_2) > -2$ leads to $\delta > 0$, the excess being interpreted not as interstitial oxygen but as the formation of A- and B-site vacancies in equal amounts, as was confirmed by neutron diffraction [14] and electron microscopy [15, 16] studies.

Finally, the influence of local environmental effects on the electronic structure of Ca manganite arising from cation charge differences is quite large, as was emphasized in [17]. Model calculations of the local density of states (LDOS) performed in this last work for ordered solid solutions revealed strong spin-polarization differences in LDOSs of different Mn ions, related to the relative numbers of 2+ or 3+ cations surrounding the Mn ion. In reality the precise electronic structure will be defined by La/dopant ion disorder which, in turn, can be strongly dependent on annealing conditions.

4.2. Mechanisms of MR

Theoretical considerations about the origin of giant MR in manganites are not the subject of this paper, but the interpretation of the present data requires that we examine in more detail the mechanism of magnetoresistance. Various mechanisms have already been proposed. Among the most frequently invoked mechanisms are the spin-dependent scattering associated with the canting angle between manganese spins and magnetic polaron hopping. Millis *et al* [18] claim that double exchange alone does not explain the resistivity behaviour and suggest that a strong electron–phonon interaction plays an important role. Jahn–Teller distortions may have a large influence on interactions and thus on magnetic order. Meanwhile, the resistivity behaviour is clearly related to a semiconductor–metal transition near the Curie temperature. In a previous article [8], we related it to a band-crossing semiconductor–metal transition induced by the exchange field, like that occurring for instance in EuO [19]; we were able to reproduce the resistivity and MR behaviour in a phenomenological model with a few parameters.

In addition, recent band calculations [17, 20] seem to show that the ferromagnetic (hypothetical) state of $LaMnO_3$ and $CaMnO_3$ would be a half metallic state, in which the Fermi level for the majority spin (up-spin) band falls into a gap for the down-spin band. Thus one band would be metallic, the other semiconductor-like. This cannot be the case in mixed-valence systems, but nevertheless the ratio of the density of states (DOS) for the up-spin to that for the down-spin in the ferromagnetic solutions can be large. This factor is a most important one, which determines the magnitude of the giant magnetoresistance (GMR) in multilayers and heterogeneous granular systems, and may explain one of the contributions to MR in the present materials.

While describing the magnetization and magnetoresistance isotherms (figure 3), we remarked that there are different successive regimes for the MR in the ferromagnetic state, at least for sintered materials. The different contributions to the resistivity can be described in the following way.

4.2.1. MR related to magnetic domains. The first rapid drop in resistivity which occurs below 0.5 T is related to the technical magnetization. The amplitude of this term, being about 15% of the total resistivity at 5 K for the sample of figure 2, varies as a function of temperature roughly as the spontaneous magnetization. It may thus be attributed to a mechanism analogous to that of the GMR observed in multilayers or in granular materials, that is to the alignment of ferromagnetic entities under the field: layers and ferromagnetic clusters in multilayers and granular materials, domains or grains in the present case. If

manganites are close to being half-metallic systems, this will give a significant value to this term.

4.2.2. Influence of the magnetic induction. Above the technical saturation, there is a gentler decrease in the resistivity, which is associated with a further increase in the magnetic induction $B = \mu_0(H + M)$ and its effects on the band structure. The increase in magnetic induction leads to the following effects.

(i) The correlation function of Mn spins increases, related to the paramagnetic susceptibility above T_c and to the finite superposed susceptibility in the ferromagnetic state. We make no definitive statement about the underlying mechanism which relates the resistivity to the spin correlation function: according to the double-exchange model, they are related through the dependence of the carriers transfer integral on the angle between neighbouring moments.

(ii) The gap between the valence and conduction bands for the semiconducting state is reduced by the magnetic splitting, and a stronger and stronger overlap between them occurs in the ordered state; hence an increased number of carriers.

This induction-related term gives an initial decrease in resistivity as M^2 in the paramagnetic semiconducting state. Various types of fits have been tested in the ordered range, the best being a representation by the experimental law $\rho = A(1 - c\arctan(\alpha H)]$, where H is the applied magnetic field. These fits are experimental fits and have at present no theoretical justification. A detailed description of the fits, with numerical results, will be published in a forthcoming paper, with those for other compounds.

The A term, which is temperature-dependent, is related to the magnitude of the resistivity of the ferromagnetic phase, which is a function of the carrier density, their mobility and their coupling with the 3d spins. The carrier density is itself a function of temperature and magnetic induction through the exchange splitting of the bands. This dominant contribution is about 65% of the total resistivity at 5 K and 90% at T_c for the sample of figure 2. The factor within parentheses in the previous formula mainly arises from the variation of the spin correlation function. The fits with an 'arctangent law' are quite good from the lowest temperature to the Curie point and result in a nearly constant value of the parameter c. This type of law may arise from the competition between two characteristic energies of the system, namely the Zeeman energy and an energy related either to the semiconductor gap or to the energy necessary to promote one electron from one site to the next one. Nevertheless, α varies with temperature in the ferromagnetic range, which implies a re-normalization of this second energy scale with the magnetization, because the Mn local moment is not expected to experience large variations with temperature.

4.2.3. The residual resistivity. The extrapolation to infinite applied field gives a residual non-vanishing value for the resistivity. This residual value includes the phonon resistivity and a non-magnetic contribution which comes from the limited mean free path or mobility of electrons in the ferromagnetically aligned, but statistically disordered, solid solution. For some sintered materials, it may also come from insulating barriers at the grain boundaries. This term is minimized for 12 or 18 h annealing time: annealing improves the lattice; that is, it increases the intrinsic character and the magnitude of the resistivity in the semiconducting range, but lowers the residual value in the ferromagnetic range; hence an overall increase in the MR.

We now compare the relative MR for (La, Ca) manganites and Y-substituted solutions (figure 6). The magnitude of the resistivity is nearly the same in the paramagnetic

semiconducting (SC) range, which confirms, as observed before, that a similar gap exists in both systems. The incorporation of Y lowers the Curie point for reasons which have been invoked in the previous paragraph; thus the SC regime results in a much higher resistivity for lower T_c and hence a larger drop to the metallic regime. We may also invoke a larger B/T value at this temperature and a narrower Fermi–Dirac distribution, which makes the transition sharper. Also the magnetic ordering can be closer to a first-order transition due to distortion and magnetostriction effects. The proximity of such a transition is revealed by the sudden drop in resistivity and increase in magnetization just below T_c, which were also present in various earlier experimental data.

5. Conclusion

The substitution of La by Y in the $La_{1-x}Ca_xMnO_3$ manganite leads to a lowering of the Curie temperature, to the presence of a sharper peak of resistivity at T_c and to an increase in magnetoresistance amplitude. The variation of magnetic interactions is probably related to the influence of local strains and negative 'chemical pressure' on the distances and angles of the Mn–O–Mn bonds. Annealing has strong effects on the Curie temperature and also on the value of the magnetoresistance; the optimum effect was observed with annealing for 12 h at 1200 °C under oxygen.

The resistivity has been analysed and decomposed into three terms in the ferromagnetic range. The first one is related to the technical magnetization and is analogous to the GMR of granular materials. The second, dominating, contribution results from the influence of the magnetic induction on the correlation function for the Mn spins and on the band crossing of the paramagnetic semiconductor. The third one is a non-magnetic contribution due to the limited mobility of carriers and possibly to insulating barriers between metallic grains.

Acknowledgment

One of the authors (AN) acknowledges the receipt of a fellowship from the Commissariat à l'Energie Atomique.

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