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Crossover between Kondo and electron–electron interaction effects in $La_{0.75}Sr_{0.20}MnO_3$ manganite doped with Co impurities?

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Abstract

The resistivity minimum in manganites is still under debate. Recent publications discussed two possible scenarios: (i) electron–electron interaction in weak disordered systems and (ii) charge carriers tunnelling between antiferromagnetic coupled grains. In order to resolve this puzzle, we present a systematic study on the electrical resistivity, $\rho(T)$, which was carried out in ceramic samples of $La_{0.75}Sr_{0.20}MnO_3$ and $La_{0.75}Sr_{0.20}Mn_{1-c}Co_cO_3$ manganites over the temperature ranges 0.4–60 K and 4–60 K respectively. All compounds show a minimum in the resistivity at a characteristic temperature T_{min}, which in the Co-doped samples shifts towards higher temperatures as the Co concentration increases. T_{min} varies approximately as $c^{1/3}$. The application of an external magnetic field shows that the T_{min} decreases linearly as the field increases, and above 0.7 T remains field independent. In magnetic fields, where T_{min} is constant, T_{min} varies as $\sim c^{1/2}$. For temperatures below T_{min} the resistivity data can be fitted either with a $\sim -T^{1/2}$ or with a $-\ln T$ function, while for temperatures above the minimum the resistivity follows both a T^3 and a $T^{5/2}$ dependence. We believe that there is a crossover between a 'Kondo-like' scattering process and the 3D electron–electron interaction effects enhanced by disorder.

1. Introduction

Rare earth manganese perovskites of the type $La_{1-x}A_xMnO_3$, where A is a divalent alkali-earth element, like Ba, Sr or Ca, have been intensively studied during the last few years because they exhibit colossal magnetoresistance (CMR) effects near the ferromagnetic–paramagnetic transition T_c. These effects are very important both for basic science and for device applications [1–3]. The composition where the CMR effect is more pronounced is around $x \sim 0.3$. It is believed that the transport properties are correlated via the double exchange interaction, controlled by the hopping of the e_g electrons from M^{3+} to Mn^{4+} ions [4].

Measurements of a single crystal of bilayered manganite $La_{1.3}Sr_{1.7}Mn_2O_7$ [5], of stoichiometric single crystals and polycrystalline $La_{1-x}Sr_xMnO_3$ [6, 7], in non-stoichiometric polycrystalline $La_{0.95-x}Sr_xMnO_3$ [8], in stoichiometric polycrystalline $La_{1-x}Na_xMnO_3$ [9] compounds and in $La_{0.70}Ca_{0.30}MnO_3$ 1000 Å thick films grown on a (100) $LaAlO_3$ substrate at 700 °C [10] have shown that the low temperature resistivity exhibits a shallow minimum. Michalopoulou *et al* [8] have also found that the temperature $T_{\min}$, corresponding to the minimum of the resistivity, shifts to lower temperatures with increasing Sr content x, and varies approximately as $T_{\min} \sim x^{-2/5}$. There are two different approaches to explain the origin of this minimum: the first one considers the temperature-dependent Coulomb interaction between carriers strongly enhanced by disorder [5, 6, 8]; the second one focused on intergranular tunnelling, where charge carriers tunnel between antiferromagnetically coupled grains [7]. Tiwari and Rajeev [6], Michalopoulou *et al* [8] and Kumar *et al* [10] have excluded the Kondo effect, a phenomenon shown by a magnetic impurity put into a metal, as a possible cause because the investigated manganites, as strongly correlated systems, are in the ferromagnetic metallic state. In this state the spin degrees of freedom are completely frozen and hence there are no internal degrees of freedom any more. Electron tunnelling experiments [11] have shown also that the electron correlation effects are strong in the manganites.

Recently, Rozenberg and Auslender [12] have disputed the influence of electron–electron scattering with scattering from static inhomogeneities as the dominant mechanism for the upturn and the negative temperature coefficient of the resistivity in this class of materials.

Considering especially this controversy, we have (i) extended the measurements on the non-stoichiometric $La_{0.75}Sr_{0.20}MnO_3$ compound down to 0.4 K and (ii) measured the resistivity of compounds doped with cobalt between 4 and 60 K.

2. Experimental procedure

Polycrystalline non-stoichiometric $La_{0.75}Sr_{0.20}MnO_3$ and $La_{0.75}Sr_{0.20}Mn_{1-c}Co_cO_3$ bulk samples, with $c = 0.025$, 0.050, 0.075, 0.100, 0.150 and 0.200 Co, were prepared from perovskite powders by wet chemical processing [13]. High-purity powders of nitrates $La(NO_3)_3\ 6H_2O$, $Sr(NO_3)_2$, $Co(NO_3)_2\ 6H_2O$ and $Mn(NO_3)_2\ 4H_2O$ (Fluka, Germany) of a purity of 99.9% were mixed and cold pressed into rectangular bars. The compositional ratio of the samples is checked by inductively coupled plasma (ICP) atomic emission spectroscopy. The samples were sintered in air at 1300 °C for 24 h. The crystal structure of the manganite samples was characterized using a Siemens D 500 x-ray powder diffractometer using Cu Kα radiation, while they were magnetically characterized by means of a commercial DC SQUID (Quantum Design) magnetometer. The resistivity measurements were carried out in the temperature range 0.4–80 K for the $La_{0.75}Sr_{0.20}MnO_3$ sample, using a ^{3}He-evaporation cryostat and between 4 and 80 K for $La_{0.75}Sr_{0.20}MnO_3$ doped with 0.025, 0.050, 0.075 and 0.100 Co using the conventional four-point dc technique.

3. Results and discussion

Figure 1 shows the x-ray diffraction patterns for undoped and for some Co doped compounds ($c = 0.05$, 0.10, 0.15, 0.20). From the diffractograms one can see that both the number of the diffraction peaks, their relative intensities and their width do not undergo substantial change on substitution of Mn by Co ions within the resolution of the diffractometer. The diffraction

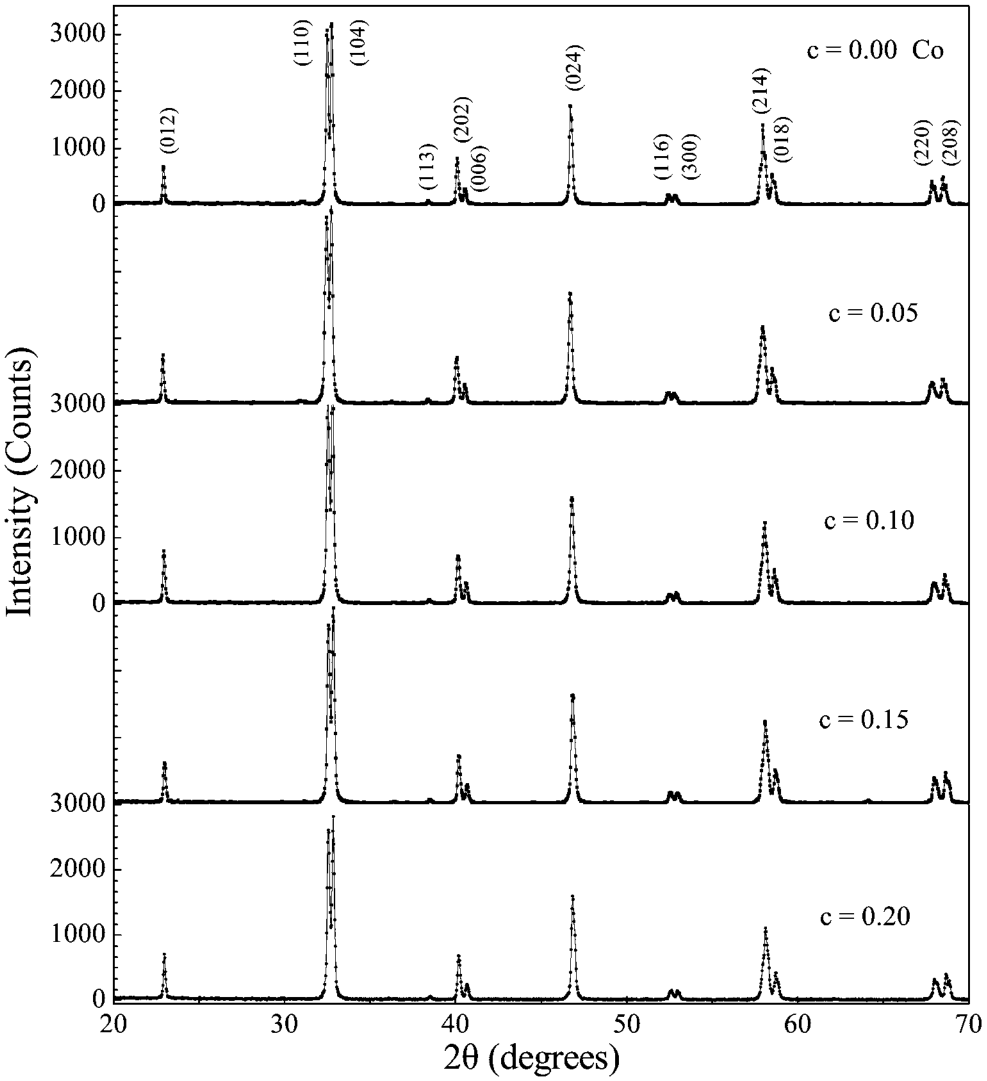

Figure 1. X-ray diffraction patterns of polycrystalline $La_{0.75}Sr_{0.20}MnO_3$ and $La_{0.75}Sr_{0.20}Mn_{1-c}Co_cO_3$ compounds fired at 1300 °C in air for 20 h.

data revealed that all samples are single-phase and crystallize in the perovskite structure. The samples were indexed on the basis of a hexagonal unit cell. However, one can see a shift of 2θ values when the Co content increases. This result indicates a change of the lattice constants a (5.518 Å for $c = 0.00$ Co) and c (13.358 Å for $c = 0.00$ Co) and of the unit cell volume V_c as the Co content increases. In more detail, the volume of the unit cell, V_c, first increases slightly as the Co content c increases, it goes through a weak maximum at about 0.05 and then decreases nearly monotonically as the Co content increases. The volume variation with respect to the undoped compound is about 1%. Similar behaviour is also exhibited by the lattice parameter of the $La_{0.70}Ca_{0.30}Mn_{1-c}Co_cO_3$ system [14]. Figure 2 shows both the volume V_c of the unit cell and the lattice parameter as a function of the Co content for $La_{0.75}Sr_{0.20}Mn_{1-c}Co_cO_3$ and $La_{0.70}Ca_{0.30}Mn_{1-c}Co_cO_3$ respectively. The dependence of unit cell volume V_c on the Co

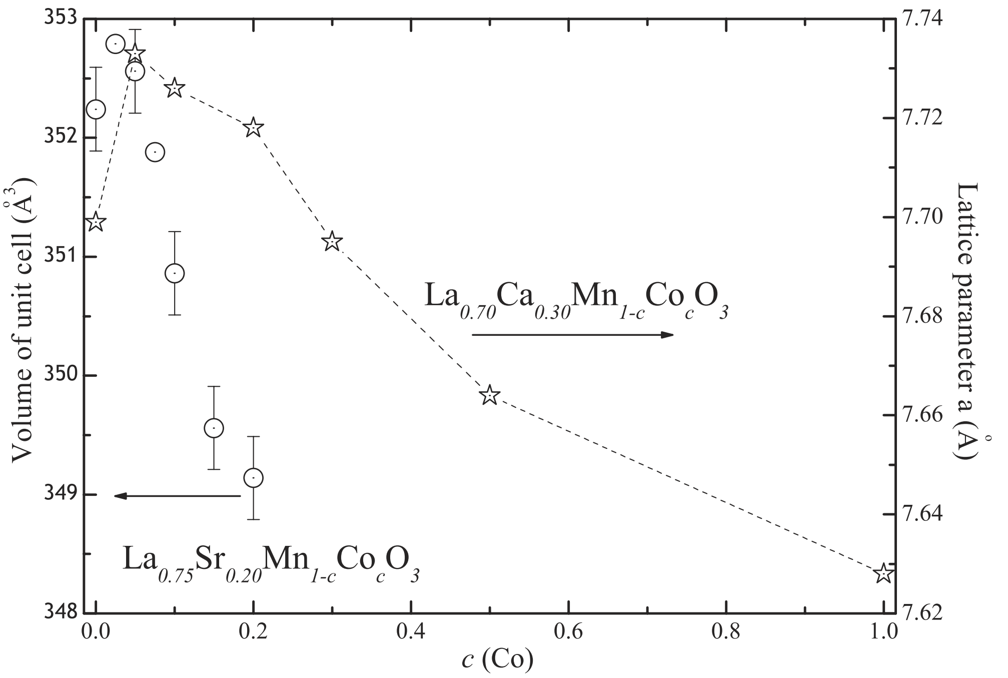

Figure 2. The co-doping dependence of the unit cell volume of $La_{0.75}Sr_{0.20}Mn_{1-c}Co_cO_3$ samples (open circles) and the lattice parameter of $La_{0.70}Ca_{0.30}Mn_{1-c}Co_cO_3$ system (open stars).

content can be related to the difference in the ionic radii of Co and Mn. The substitute Co^{3+} ions can appear either in the nonmagnetic low-spin state (LS) ($t_{2g}^6e_g^0$, $S = 0$) at room temperature and below or in the thermally excited high-spin (HS) ($t_{2g}^4e_g^2$, $S = 2$) magnetic state [15]. On the other hand the effective ionic radius of Co^{3+} (0.545 Å) in the LS-state differs very little from that of the Mn^{4+} (0.530 Å) ion, while the effective ionic radius of Co^{3+} (0.610 Å) in the HS-state differs very little from that of the Mn^{3+} (0.645 Å) ion [16]. From this aspect, it is expected that Mn^{4+} ions can be substituted by Co^{3+} ions in the LS state, and Mn^{3+} ions by Co^{3+} ions in the HS state. This assertion can be confirmed from the slight increase of the cell volume at low Co content ($c \leqslant 0.05$). On the other hand the decrease of the cell volume for $c \geqslant 0.05$ Co can be attributed to other reasons, like the formation of clusters.

The characterization of the magnetic properties of the samples has shown that the zero-field cooling magnetization M_{ZFC} at low magnetic fields (~4.5 mT) in pure manganite ($c = 0.00$) and in the slightly doped samples ($c \leqslant 0.05$) is nearly temperature independent for temperatures below T_c. This means that these samples show ferromagnetic long-range order. In contrast, the M_{ZFC} of the samples with a Co content $c \geqslant 0.05$ decreases slightly on cooling below T_c and drops at certain low temperatures. The drop of M_{ZFC} becomes more intense as the Co content increases. Similar behaviour has been observed in pure cobaltate [17, 18] and the drop of M_{ZFC} has been interpreted in terms of the ferromagnetic (short-range ordered) cluster glass model. Figure 3 shows the magnetization for undoped $La_{0.75}Sr_{0.20}MnO_3$ and with Co doped compounds ($c \leqslant 0.20$) as a function of the magnetic field at 5 K. All M–H curves show full saturation of the magnetic moments. The undoped compound shows the typical ferromagnetic metallic state, with the magnetization reaching saturation within 5 T. The complete parallel alignment of Mn^{3+}/Mn^{4+} spins is indicated by the value of M_s which

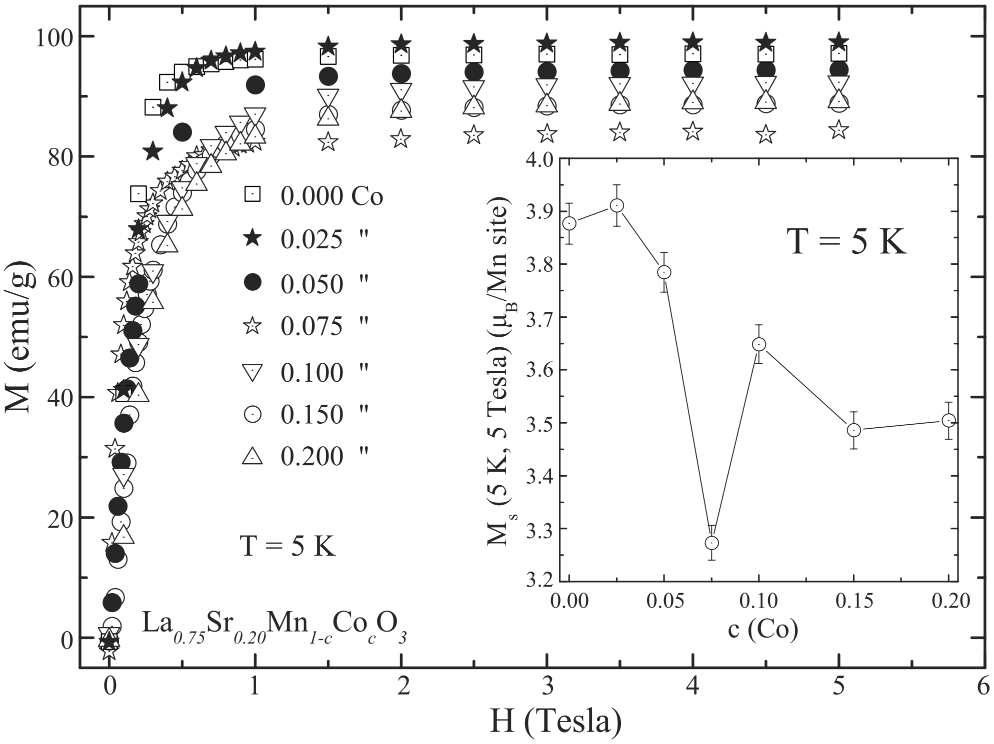

Figure 3. Magnetization isotherms of all $La_{0.75}Sr_{0.20}Mn_{1-c}Co_cO_3$ samples taken at 5 K.

approaches the theoretical spin-only value $(4 - x)\ \mu_B/Mn$ (inset of figure 3). Figure 3 shows also that the addition of Co to the $La_{0.75}Sr_{0.20}MnO_3$ sample does not change the ferromagnetic metallic state of the compounds but causes a change in M_s (5 K, 5 T) from the theoretical spin-only value $(4-x)\ \mu_B/Mn$ as c increases. The magnetization isotherms of doped samples do not exhibit obvious slopes in the high-field region. This observation suggests that there are few frozen magnetic moments in the samples at low temperatures. In more detail, M_s (5 K, 5 T) decreases slightly as the Co content c increases, showing a sharp minimum at 0.075 Co. This result indicates that the reduction of M_s can be attributed to the diminution in the density of moment-carrying Mn ions and to the modification of the mixed valence ratio Mn^{3+}/Mn^{4+}. The reduction of density of moment-carrying Mn ions can be referred to the contention that the substituted Co^{3+} ions behave non-magnetically. It must be mentioned here that when the inset of the plot of figure 3 is compared to figure 2 one can see a correlation between the cell volume V_c dependence on the Co content and the magnetization of saturation M_s. This is undoubtedly evidence that most of the Co^{3+} ions are substituted in the Mn^{4+} ion sites and are in the low-spin ($S = 0$) configuration ($t_{2g}^6e_g^0$). On other hand, Rivadulla *et al* [19] have shown that in $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$ system, the effective number of neighbours ferromagnetically coupled to Mn decreases approximately linearly with increasing Co content. From this result, they have concluded that Co ions do not participate in the double exchange interaction. This conclusion can also be accepted for the $La_{0.75}Sr_{0.20}Mn_{1-c}Co_cO_3$ system.

It must be mentioned here that although the resistivity measurements are extended up to room temperature the discussion is concentrated only on the low temperature range, where a minimum appears. The investigation is also restricted only to the samples with a Co

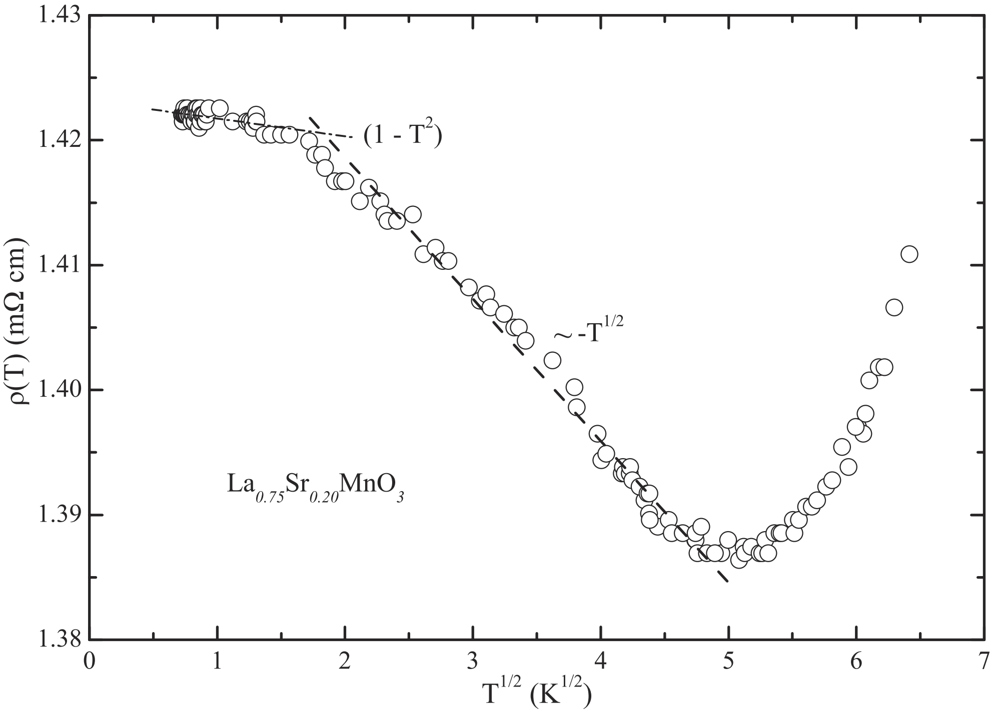

Figure 4. The electrical resistivity $\rho(T)$ versus $T^{1/2}$ for the non-stoichiometric $La_{0.75}Sr_{0.20}MnO_3$ compound. The dashed line is the least squares fit.

content $c \leqslant 0.10$, because these are, according to the resistivity measurements, in the metallic phase for temperatures below the Curie temperature T_c. Figure 4 shows the resistivity $\rho(T)$ as a function of the square root of the temperature, $T^{1/2}$, between 0.4 and 60 K for the undoped $La_{0.75}Sr_{0.20}MnO_3$ sample. The figure shows that the resistivity $\rho(T)$ decreases with temperature, goes through a minimum, then increases nearly as $-T^{1/2}$ and finally as $(1-T^2)$ at temperatures lower than 4 K. The dashed line is the best fit to $-T^{1/2}$, while the chain line is the $(1-T^2)$ dependence. It must be noted, however, that the resistivity data can be satisfied just as well with a logarithmic dependence. In figure 5 the same resistivity data are plotted against $\ln T$ between 0.4 and 60 K. One can see that the classical features of the Kondo effect are observed, namely the resistivity varies logarithmically over the temperature range between 4 and 20 K and flattens off at lower temperatures. For temperatures higher than 20 K the resistivity goes through a minimum and then increases as the temperature increases. At temperatures $T < 4$ K the resistivity shows a tendency to saturate. It is also difficult to properly distinguish between the $-T^{1/2}$ dependence of the electron–electron interaction effects and the $-\ln T$ dependence of the Kondo effect. The question now is:

(i) which of both laws holds, the square root or the logarithmic dependence, and
(ii) why the temperature corresponding to the minimum, T_{min}, shifts toward lower temperatures as the Sr content increases as we have shown earlier [8].

In our previous publications [8, 20] we have claimed that the minimum and the $-T^{1/2}$-dependence of the resistivity of non-stoichiometric $La_{0.95-x}Sr_xMnO_3$ compounds in the ferromagnetic metallic phase for temperatures $T > 4.2$ K may arise principally from 3D disorder-enhanced electron–electron interaction [21].

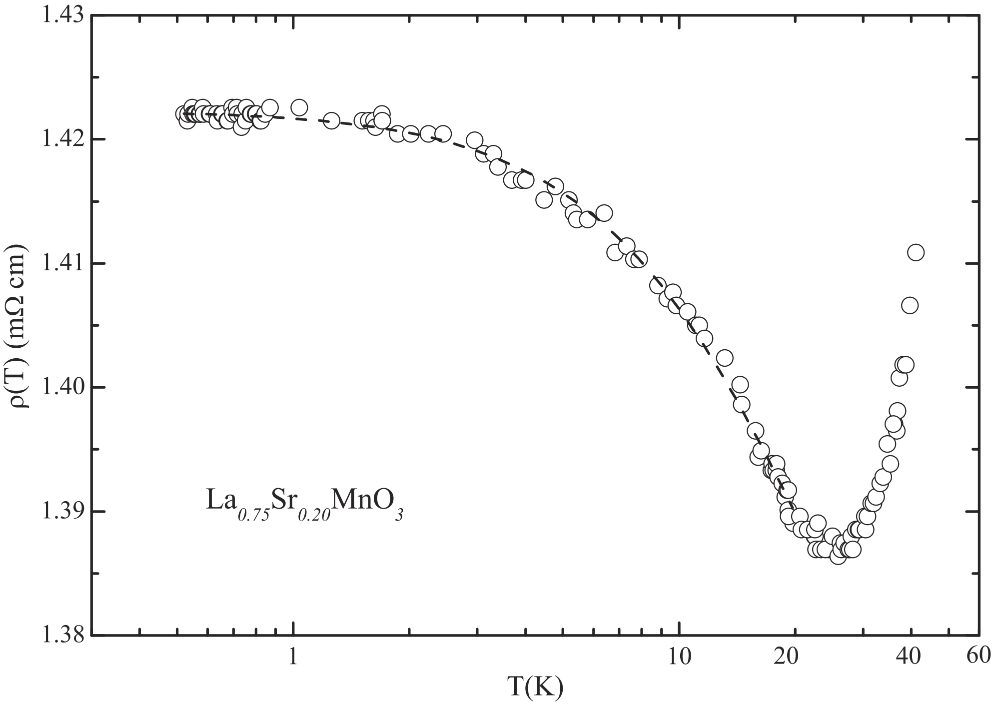

Figure 5. The electrical resistivity as a function of ln T for the La$_{0.75}$Sr$_{0.20}$MnO$_3$ compound. The dashed curve is the best fit to the Applebaum–Kondo equation (1).

The other possibility is to discuss the results in the framework of the Kondo scattering process. As was mentioned in the previous paragraph, three different characteristic temperatures ranges can be distinguished in figure 5. In the temperature range between 4 K and 20 K the resistivity is governed by pure Kondo ln T-behaviour. At low temperatures ($T < 4$ K) deviation from the ln T-dependence does occur, where the resistivity shows the tendency to saturate. For temperatures above 20 K the resistivity goes through a minimum and then increases as the temperature increases. The results show a close similarity to a Kondo system, like CuFe [22, 23], where interaction effects between the Fe impurities are assumed to be not negligible or to the ferromagnetic amorphous alloys (Fe$_{1-x}$Ni$_x$)$_{75}$P$_{16}$B$_6$A$_{l3}$ [24, 25]. If this behaviour is attributed to 'Kondo-like' scattering of e$_g$ carriers on unknown impurities then the resistivity data can be fitted in the low temperature interval 0.4–4 K to the n-channel Kondo model based on the Fermi liquid approach [26–28]. Within this approach, the low temperature resistivity has been derived assuming electron–hole symmetry around the Fermi level and is given by [29]

$$\rho_{\text{imp}}(T) = \rho_{\text{imp}}(0)[1 - c_2 T^2]. \tag{1}$$

The parameter $c_2 = (\pi^2/12T_L)^2(4n + 5)$ includes the effective number of channels $n = 2S$, where S the spin of the impurity and $T_L = (\text{`}T_K\text{'}/6)\pi(n + 2)$. '$T_K$' is the Sacramento and Schlottmann [28] definition of the characteristic Kondo temperature and $\rho_{\text{imp}}(0)$ corresponds to the unitarity bound and can be determined from extrapolation to $T = 0$. Figure 6 shows the resistivity of La$_{0.75}$Sr$_{0.20}$MnO$_3$ as a function of temperature between 0.4 K and 5 K. The dashed curve represents the best fit of the experimental data using equation (1), and is obtained taking c_2 as the fitting parameter. It is clear that there is a satisfactory agreement and the results

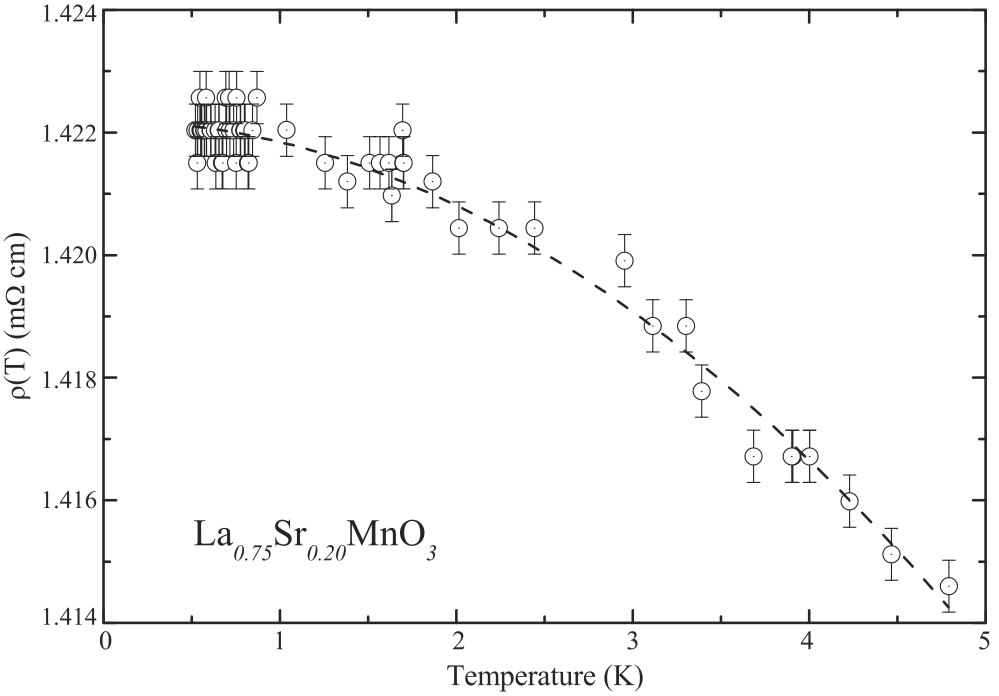

Figure 6. The low temperature resistivity of the $La_{0.75}Sr_{0.20}MnO_3$ compound as a function of T. The dashed curve is the Fermi liquid expression, equation (1).

can be well fitted by the T^2 law, confirming that the Fermi liquid picture is valid. The best-fit value of the parameter c_2 is $(0.000\,23 \pm 0.000\,02)$ K^{-2}. For $n = 1, 2$ and 3 channels it follows that 'T_K' takes up the values 104 ± 5, 93 ± 5 and 86 ± 5 K respectively.

On the other hand, from fitting the experimental data of figure 5 in the temperature interval 0.4–20 K to the Applebaum–Kondo approximate expression [30] given by

$$\rho(T) = A - B\left[\left(\frac{T}{\vartheta}\right)\ln\left(\frac{T}{\vartheta}\right)\right]^2, \tag{2}$$

one can calculate the parameters A and B, which are the temperature independent contributions due to potential scattering from magnetic and non-magnetic impurities, and the characteristic temperature, which in the Applebaum–Kondo formula corresponds to the Kondo temperature T_K. The dashed curve represents the best fit using the Applebaum–Kondo expression for the resistance of a dilute alloy containing magnetic impurities. As one can see, the result of the fit is very satisfactory. From the fitting values A and B one can calculate the potential scattering phase $\delta_v = 45°$. The fit procedure gives for the characteristic temperature the value $\vartheta \sim 110$ K, which is in satisfactory agreement with 'T_K' value deduced from equation (1) for the case of a one-channel Kondo model. It is interesting to note that it was attempted to fit the data to the Hamann–Fischer approximative expression [31, 32] with $S = 1/2$ but surprisingly no good fits were obtained. Some of the parameters were randomly varying over a wide range.

From the agreement between the experimental data and both the one-channel Kondo effect and the Applebaum–Kondo relation, one can conclude that this behaviour *can be caused by uncontrolled magnetic impurities*, which exist in the initially used nitrates. In order to confirm that this characteristic behaviour of the resistivity is of magnetic origin, we have measured

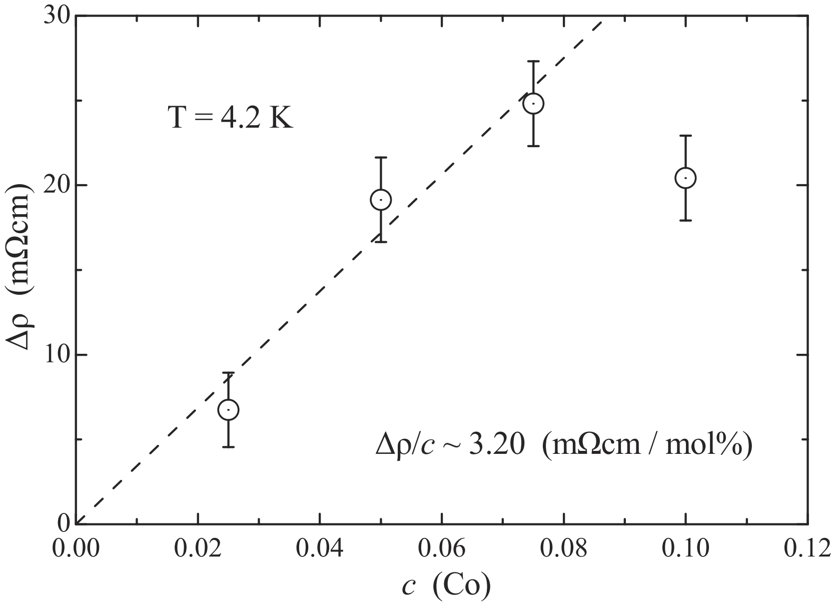

Figure 7. The resistivity difference $\Delta\rho$ of $La_{0.75}Sr_{0.20}Co_cMn_{1-c}O_3$ and $La_{0.75}Sr_{0.20}MnO_3$ compounds as a function of Co concentration at 4.2 K.

the resistivity of the non-stoichiometric $La_{0.75}Sr_{0.20}MnO_3$ compound, which was doped with 0.025, 0.05, 0.075 and 0.10 Co and sintered at 1300 °C for 24 h. Figure 7 shows the 'residual' resistivity $\Delta\rho$ (defined as $\Delta\rho = \rho(La_{0.75}Sr_{0.20}Mn_{1-c}Co_cO_3) - \rho(La_{0.75}Sr_{0.20}MnO_3)$) at 4.2 K as a function of the content c of Co doping. The figure exhibits an extraordinary result. There is a nearly linear relationship between the 'residual' resistivity and the concentration of Co. Such a linear behaviour is characteristic for dilute metallic alloys, where the impurities can be assumed as isolated and statistically distributed scattering centres. The deviation of the 'residual' resistivity of the $La_{0.75}Sr_{0.20}Mn_{0.90}Co_{0.10}O_3$ compound from linearity can be attributed to the high Co content, where other kinds of scattering centres are formed instead of statistically distributed ones, probably cluster type. Thus, it can be concluded that in most of these compounds the Co atoms are also distributed statistically and every Co atom scatters independently. The resistivity value for 1 mol% Co at 4.2 K is about 3.2 mΩ cm. For comparison the corresponding residual resistivity of dilute metallic AlCo, AuCo and CuCo alloys amounts about to 4.2, 5.75 and 6.3 $\mu\Omega$ cm/at.% respectively [33]. In figure 8 the resistivity as a function of $\ln T$ is plotted between 4 K and 60 K for $La_{0.75}Sr_{0.20}MnO_3$ compound together with the samples containing 0.025, 0.050, 0.075 and 0.100 Co respectively. The logarithmic temperature dependence is also evident for all compounds. One can see that the minimum shifts to higher temperatures, like in a usual Kondo system, as the concentration of Co increases.

Figure 9 shows the temperature $T_{\min}$, corresponding to the minimum, as a function of the Co concentration c in a double logarithmic plot (open circles). The dashed line corresponds to a linear least square fit. One can see that $T_{\min}$ varies approximately as $c^{1/3}$. It is obvious that these findings result solely from Co doping. It must be mentioned that the combination between the increasing and decreasing temperature-dependent parts of the resistivity gives rise to a minimum at $T_{\min}$. Since $T_{\min}$ varies approximately as $c^{1/3}$ with Co concentration, then according to Matthiessen's rule the total resistivity is assumed to be the sum of a $-c \ln T$ part for

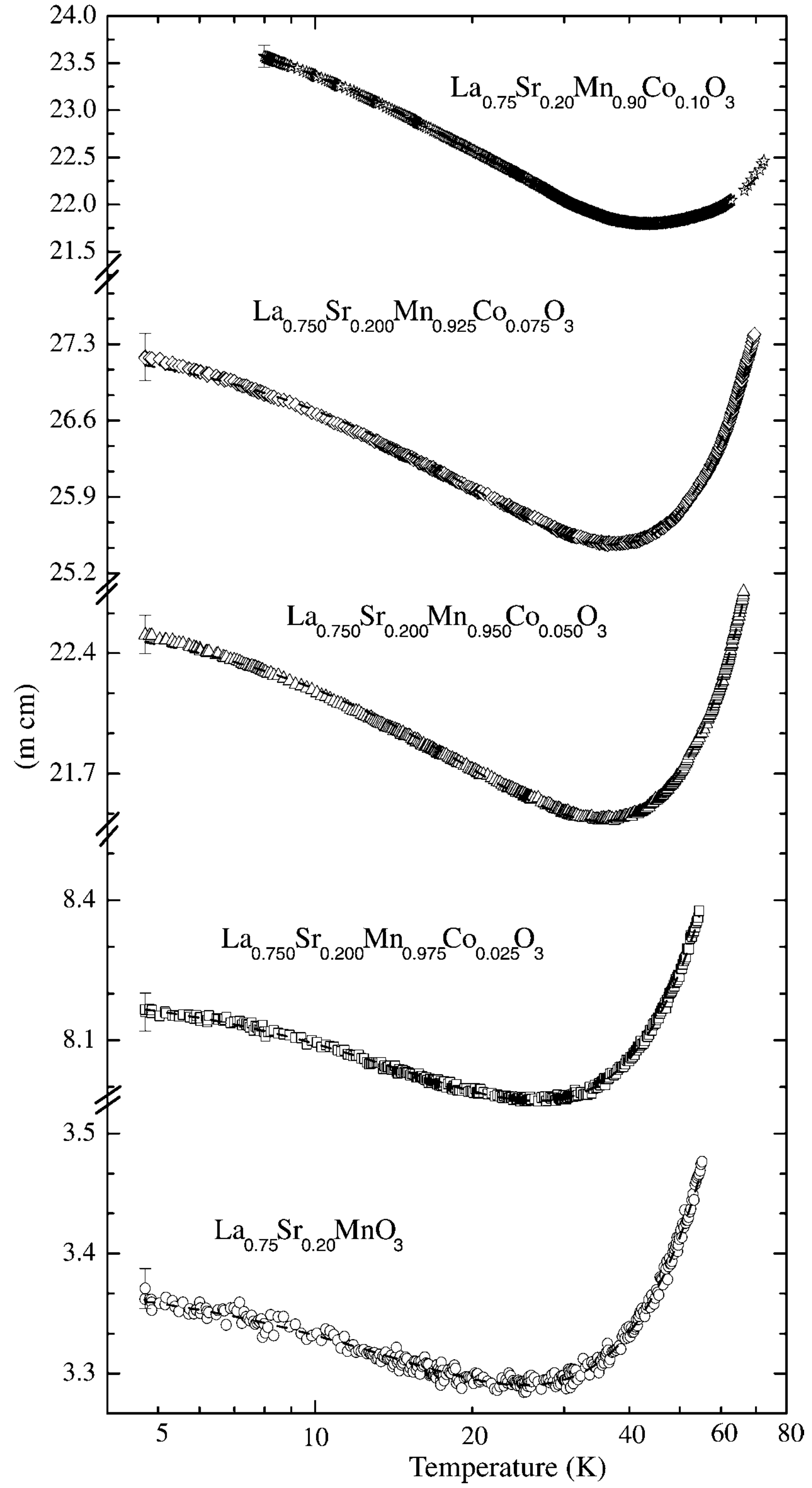

Figure 8. The electrical resistivity as a function of ln *T* for $La_{0.75}Sr_{0.20}MnO_3$ and with Co doped compounds. The curves are the best fits to the Applebaum–Kondo equation (2).

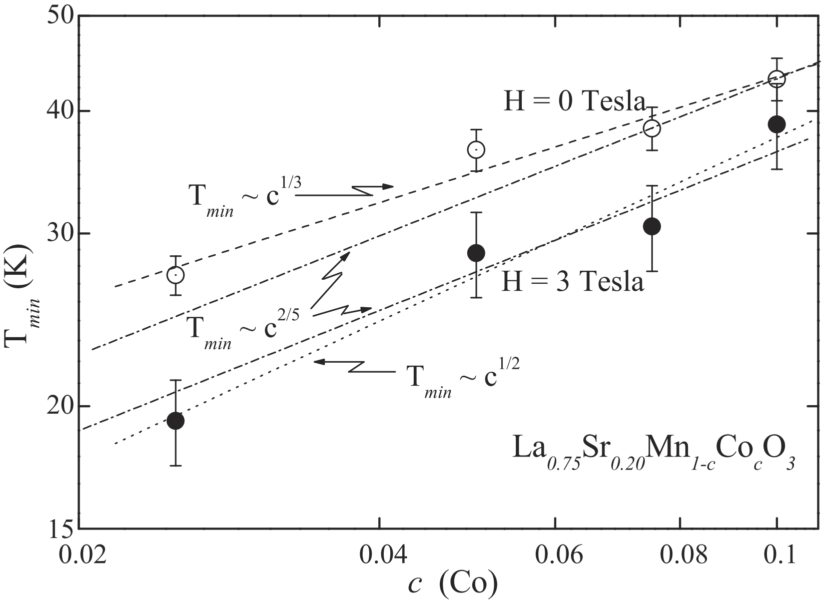

Figure 9. The temperature $T_{\rm min}$ corresponding to the minimum versus Co content. The dashed line represents $T_{\rm min} \sim c^{1/3}$, the dotted line $T_{\rm min} \sim c^{1/2}$, and the chain lines the $T_{\rm min} \sim c^{2/5}$ relation.

$T < T_{\rm min}$ and a part proportional to T^3 for $T > T_{\rm min}$. The T^3 dependence can be attributed to the unconventional one-magnon scattering process taking into account spin fluctuations. This scattering mechanism was proposed recently by Furukawa [34] and was proved experimentally by Michalopoulou *et al* [8] in the non-stoichiometric $La_{0.95-x}Sr_xMnO_3$ compounds. In the other case, if the decreasing part is due to disorder, then the total resistivity can be assumed to be the sum of a $-cT^{1/2}$ part for $T < T_{\rm min}$ and a part proportional to T^3 for $T > T_{\rm min}$. In this case, for the temperature corresponding to the minima of the resistivity a $T_{\rm min} \sim c^{2/5}$ dependence appears. The chain line in figure 9 corresponds to a $T_{\rm min} \sim c^{2/5}$ behaviour. It seems that the data are satisfied better with a $T_{\rm min} \sim c^{1/3}$ law. Thus, the total resistivity can be represented also as the sum between the Applebaum–Kondo relation and the $\sim T^3$ dependence:

$$\rho_{\rm tot} = c\left[A - B\left(\frac{T}{\vartheta}\right)^2 \ln\left(\frac{T}{\vartheta}\right)^2\right] + CT^3. \qquad (3)$$

The curves in figure 8 represent the predictions of equation (2) for the undoped and Co doped compounds. One can see that there is a good agreement between the experimental results and the expression (2).

According to the above, it is now possible to understand the presence of the minimum in the resistivity of manganites. It is certainly of magnetic origin and is due to a kind of Kondo scattering process of the e_g carriers on isolated magnetic impurities existing in the ferromagnetic compounds. The $T_{\rm min} \sim x^{-2/5}$ behaviour which was found previously in the undoped non-stoichiometric $La_{0.95-x}Sr_xMnO_3$ compounds [8] can be understood now as a dilution effect. Namely, if one assumes that there is a constant amount of unknown magnetic impurities in the parent compound $La_{0.95}MnO_3$, then after the replacement of La^{3+} cations with the divalent Sr^{2+} it can cause a dilution of the magnetic impurities and so a shift of the minimum to lower temperatures. Under these circumstances, it is believed that the magnetic impurities must exist in the $La(NO_3)_3\ 6H_2O$ nitrate.

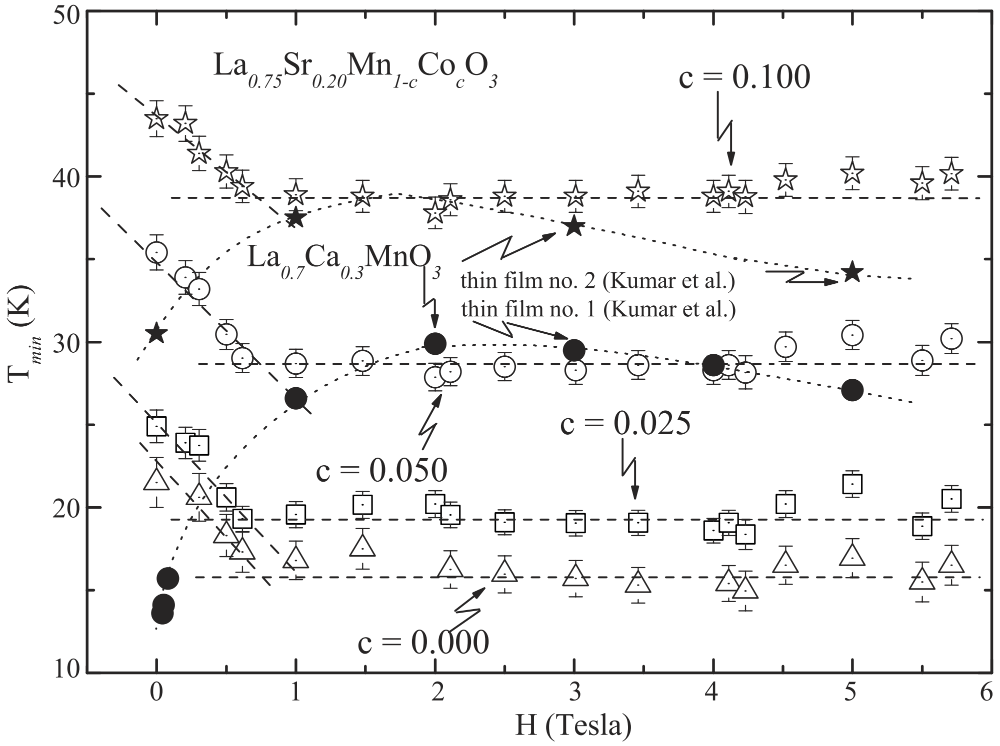

Figure 10. The temperature $T_{\min}$ corresponding to the minimum as a function of the external applied magnetic field.

We now try to explain why these peculiar properties of the present compounds are due to a ‘Kondo-like’ scattering, although the system, as mentioned above, is in the ferromagnetic state [35]. The ferromagnetic correlation induces ‘spin’ on the surrounding Co^{3+} site in the LS, which acts like a spin fluctuation. Then, the induced spin-like degrees of freedom cause the Kondo effect, a mechanism which is very similar to that of the ‘Kondo effect’ in high-T_c cuprates containing non-magnetic impurities such as Zn or Li [36, 37], where antiferromagnetic correlation plays a similar role as the ferromagnetic correlation mentioned in our problem.

In order to decide if the appearance of the resistivity minimum is due to a ‘Kondo-like’ effect or to the disorder, we consider the effect of an external applied magnetic field on the electrical resistivity and especially on the temperature $T_{\min}$. In figure 10, $T_{\min}$ is presented as a function of the magnetic field for the investigated samples. The plot shows that the initial $T_{\min}$ decreases linearly as the magnetic field H increases, i.e. $T_{\min}$ varies as $T_{\min}(H) = T_{\min}(0) - \alpha H$, and above 0.7 T is field independent. In the same figure the early results of Kumar *et al* [10] for $La_{0.70}Ca_{0.30}MnO_3$ 1000 Å thick films (full circles and stars) are also plotted for comparison. In contrast to the present results, Kumar *et al* [10] have found that for the $La_{0.70}Ca_{0.30}MnO_3$ films $T_{\min}$ increases sharply, goes through a maximum and then decreases slowly as the applied field increases. The field dependence of $T_{\min}$ in the present compounds can be explained as follows. As is mentioned above, the ferromagnetic correlation induces ‘spin’ on the surrounding Co^{3+} site in the LS, which acts like a spin fluctuation. Then, the induced spin-like degrees of freedom cause the Kondo effect, a mechanism, which is very similar to that of the 'Kondo effect' in high-T_c cuprates containing non-magnetic impurities. With the gradual application of an external magnetic field a freezing process of the 'spin' on the surrounding Co^{3+} sites begins. At fields above 0.7 T this state of the spin degrees of freedom is completely frozen out and the e_g free carriers can no longer suffer a 'Kondo-like' scattering. Simultaneously with the fluctuation freezing process, a second field independent scattering mechanism, which competes with the fluctuation freezing process, begins to appear. In order to clarify which scattering process is responsible for the field independence of T_{min}, we plotted in figure 9 the T_{min} values at a constant field of 3 T as a function of Co content (full circles). The dotted line is the best ordinary least squares fit to the data. It is clear that the data follow more closely a $T_{min} \sim c^{1/2}$ law instead of a $T_{min} \sim c^{1/3}$ or $T_{min} \sim c^{2/5}$ dependence (chain line). The $T_{min} \sim c^{1/2}$ law can be justified if it is assumed that the total resistivity in the magnetic field follows according to Matthiessen's rule a $\rho_{tot} = -cT^{1/2}+\alpha T^{5/2}$ temperature dependence. The first part comes, as is mentioned above, from the 3D coulombic interaction between carriers strongly enhanced by the disorder [5, 6, 8], while the second part can be attributed to the mechanism proposed by Wang and Zhang [38]. According to Wang *et al* in a nearly half-metallic ferromagnet the minority spin electrons close to the band edge at the Fermi energy ε_F are Anderson localized due to the disorder and thus only the majority electrons conduct current. Consequently, spin-flip scattering involving only one-magnon processes can occur with a finite probability. This single-magnon scattering process leads to a $\sim T^{2.5}$ temperature dependence of the resistivity. The question now is, why the resistivity in an external applied magnetic field obeys a $\sim T^{5/2}$ instead of a $\sim T^3$ dependence for temperatures above the minimum. It seems that the magnetic field freezes the Furukawa spin fluctuations which are responsible for the $\sim T^3$ dependence of the resistivity. With freezing of the Furukawa fluctuations the system must behave as fully polarized (true half-metallic ferromagnet). According to the Kubo and Ohata [39] ridge band picture, in such a fully polarized system the one-magnon scattering process is exponentially suppressed by a factor $\exp(\varepsilon_g/k_B T)$, where ε_g is the minority spin band gap at the Fermi energy. The second-order approximation (two-magnon process) leads to a $\sim T^{9/2}$ dependence of the resistivity, which is in contradiction to the present observation. But, if one assumes that there is a finite density of states of the minority spin at ε_F, as well as Anderson localization of minority spin electrons [38], then the single-magnon scattering process leads to a $\sim T^{5/2}$ dependence for the resistivity. It seems also that with the freezing of Furukawa fluctuations with the magnetic field the system is not fully polarized and behaves like a nearly half-metallic ferromagnet, where the single-magnon process proposed by Wang and Zhang [38] takes place. This means that, at fields above 0.7 T, the processes which are responsible for the resistivity minimum, are the 3D coulombic interaction between carriers strongly enhanced by the disorder and the above mentioned Wang and Zhang [38] mechanism. We believe therefore that there is a crossover between a 'Kondo-like' scattering process and the 3D electron–electron interaction effects enhanced by disorder.

According to the above discussion, we try to give an explanation why T_{min} in the $La_{0.70}Ca_{0.30}MnO_3$ thin films [10], in contrast to our results, first increases sharply, then at about 1.5 T goes through a broad maximum and finally decreases slowly as the applied magnetic field increases (see figure 10). We believe that in the temperature range below T_{min}, where the resistivity increases as the temperature decreases, this is due to the coexistence of both weak electron localization and electron–electron interaction effects [21]. The weak localization, being very sensitive effect to a magnetic field [40], is perfectly suppressed from an externally applied magnetic field of about 1.5 T and therefore only the electron–electron interaction enhanced by disorder remains, which is in a first-order approximation independent of the magnetic field.

4. Conclusion

The present low temperature electrical resistivity measurements on non-stoichiometric $La_{0.75}Sr_{0.20}MnO_3$ and $La_{0.75}Sr_{0.20}Mn_{1-c}Co_cO_3$ compounds provide evidence for a Kondo type scattering in the ferromagnetic metallic phase of manganites. The resistivity of the compounds shows a minimum, which depends on the content of Co. The temperature T_{min} corresponding to the resistivity minimum for the $La_{0.75}Sr_{0.20}Mn_{1-c}Co_cO_3$ compounds shifts to higher temperatures as the content of Co increases with the law $T_{min} \sim c^{1/3}$. The application of an external magnetic field shows that the temperature corresponding to the resistivity minimum at 0.7 T passes from a $T_{min} \sim c^{1/3}$ into a $T_{min} \sim c^{1/2}$ law, which means that there is a crossover between a 'Kondo-like' scattering process and the 3D electron–electron interaction effects enhanced by disorder.

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