Magnetization and resistivity in chromium doped manganites

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Abstract. We report measurements of the magnetic and electrical properties of sintered manganites of the form $La_{0.7}Ca_{0.3}Cr_xMn_{(1-x)}O_3$. We find that the peak in the conductivity moves rapidly to lower temperatures as the chromium content is increased and is completely absent for $x > 0.2$. The Curie temperature, as determined by magnetization measurements, is much less strongly suppressed, disappearing at $x \sim 0.7$. We interpret this behaviour in terms of the very different effects of the chromium in lifting spin and orbital degeneracy.

1. Introduction

Colossal magnetoresistance manganites have been intensely studied for the possible technological uses of the magnetoresistance, but these materials are also of scientific interest as examples of metallic conduction dominated by strong correlations (see [1] and references therein). There are several competing physical interactions which all have very similar energy scales: simple magnetic exchange interactions (both ferromagnetic and antiferromagnetic), structural 'buckling' distortions from a mismatch of atomic sizes, Jahn–Teller structural distortions and metallic 'double-exchange' interactions. It is a non-trivial matter to decide which of these can be safely neglected in any particular compound. Experiments provide a mixed response to this issue and must be interpreted carefully.

The atomic physics on the manganese site is dominant and electrons only hop freely between neighbouring atoms which have both magnetic moment and occupied orbitals carefully aligned, in order to avoid prohibitive penalties arising from Hund's rules. At high temperature the spins are disordered and the motion is curtailed, whereas at low temperature the spins are aligned in order to promote the motion and gain the associated bonding energy. Although this simple picture clearly explains the influence of an applied field on the conductivity, the magnitude of the effect combined with the dramatic structural dependence of the ferromagnetic transition [2], has led to the proposal that structural effects are also an integral part of the phenomenon [3]. Measurements of the Debye–Waller factor by neutron diffraction support this picture [4]. We have chosen to work with lanthanum and calcium compounds and have thereby reduced the 'buckling' effects found when rather smaller rare earths such as praseodymium are used, and gained a larger doping range than can be obtained with the other natural alkaline-earth metal, strontium [5].

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The parent compound $LaMnO_3$ provides a sequence of instructive phase transitions: below about 700 K the so-called O′ orthorhombic distortion appears and is presumably caused by a Jahn–Teller distortion associated with an *orbital* ordering. At about 140 K [6] there is a magnetic phase transition to an antiferromagnetic phase with ferromagnetic planes of atoms alternating in orientation along the z-axis, the antiferromagnetic ordering between planes being associated with a fourth order superexchange. This implies that the structural energy is much greater than that associated with the magnetic interactions and, although this is probably a justifiable conclusion, it should be borne in mind that there is a large difference in entropy between the orbital and magnetic orderings. There is also a clear comparability between the strength of the ferromagnetic and antiferromagnetic interactions.

When the material is doped by replacing lanthanum with calcium, however, there are rapid changes: the structural distortion transition temperature is quickly reduced, whereas the magnetic transition temperature quickly increases, until they merge at or around 250 K at a doping level of 20% calcium. At doping levels between 20 and 50% and at low temperatures, the material becomes a ferromagnetic conductor via the double exchange interaction. This behaviour is not unambiguous, but we take it to mean that the double-exchange interaction dominates *both* the super-exchange and the Jahn–Teller interactions.

This suggests that the orbital disorder is extracted in the ferromagnetic phase, and it is easiest to believe that it is removed fairly close to the transition temperature along with the spin disorder and that these are intimately associated with the onset of metallic conductivity.

The removal of spin disorder at the ferromagnetic transition is unambiguous, but not the orbital disorder. Orbital ordering is not a new field [7], but it is a rather inaccessible one experimentally. Magnetism takes precedence in interpretation for the manganites for the simple reason that there are well established experimental procedures for establishing its properties. Orbital ordering on the other hand has no natural probe and must be deduced from the structural anomalies which follow concomitantly with any classical ordering [8]. Although one might use orientational dependence of form-factors to try to investigate the orbital occupation [9], this is not a routine experiment and is not usually a viable alternative. For the current materials, where the metallic properties ensure that no classical long-range distortion is present, it has been supposed [10] that there may be a 'dynamical Jahn–Teller' distortion allied to the motion of the electrons. Chromium substitution is expected to interfere with these structural effects and provide an indirect probe of their importance.

In the present work, we have used the class of chromium doped manganites $La_{0.7}Ca_{0.3}Cr_xMn_{(1-x)}O_3$, to investigate the role of the orbital degeneracy in these compounds. We will argue that the chromium atoms do *not* play a role in the conductivity and the mobile electrons avoid these atoms. This avoidance is partly accomplished by the electrons entering particular orbitals which do not couple to neighbouring chromium atoms, and hence the orbital degeneracy is partially lifted by the dopants. The long-range ferromagnetism remains however, and so we can attempt to assess the ferromagnetic phenomenon in a reduced orbital presence. There have been previous investigations of chromium doped manganites [11] but, as we shall explain, we believe that the phenomena in those investigations are quite different from the current metallic regime.

We should emphasize that the measurements reported here were made on *sintered* samples, rather than melt grown single crystals. Such measurements are always potentially affected by intergranular effects. Although, therefore not totally unambiguous, we will argue that the main findings of this work are a consequence of the effect of chromium doping on the bulk material and are *not* the intergranular contacts.

2. Effect of chromium doping

Our theoretical analysis of the manganites is dealt with in detail in [12] where we use perturbation theory from the atomic limit to evaluate the nature and strength of the various interactions. The results of this study are in support of the picture outlined above for the $La_{1-x}Ca_xMnO_3$ series, i.e. double exchange strongest, Jahn–Teller distortion next strongest and super-exchange removing spin degeneracy where double exchange is not dominant. The above work did not, however, address the effect of chromium doping.

We assume in the present study that the chromium takes its Cr^{3+} form. This ion involves three electrons which fill the one-spin state of the t_{2g} orbitals in an analogous state to the Mn^{4+} ion. The lower positive charge on the Cr^{3+} ion makes it more stable than the Mn^{4+} ion and provides a weaker binding than the Mn^{4+} for an additional e_g electron, but it is in a better state to receive an initial fluctuation of an electron from an adjacent oxygen site than the Mn^{3+} because both its e_g orbitals are empty. The intermediate state, Cr^{2+}, corresponds quite directly to Mn^{3+}.

In the previously studied compound $LaMn_{1-x}Cr_xO_3$ [11], there is no Mn^{4+} and there is therefore no double exchange interaction. For the $LaMnO_3$ parent compound, the Jahn–Teller distortion dominates the behaviour at temperatures below $\sim$700 K and the orbital degeneracy is lifted, but not the spin degeneracy. Below $\sim$140 K the super-exchange favours ferromagnetic ordering in-plane and antiferromagnetic ordering between planes and spin degeneracy is also lifted. When a Cr^{3+} replaces an Mn^{3+} ion, it more readily hybridizes with an electron from a neighbouring oxygen, having no other e_g electron. We would expect the oxygen atoms to distort towards the chromium ion and, once moved, the surrounding manganese ions to rotate their occupied e_g orbitals somewhat to take advantage of the space provided. This would have two major consequences: firstly the local symmetric distortion would be expected to dominate the asymmetric Jahn–Teller distortion and hence weaken it; secondly, the magnetic interactions between the chromium ions and adjacent manganese ions would be enhanced via the super-exchange interaction and would provide ferromagnetic bonds in all six directions. These two consequences are exactly as found in the experimental system and as predicted by the authors of that investigation [11] for essentially similar reasons.

We turn now to the system $La_{0.7}Ca_{0.3}Cr_xMn_{1-x}O_3$ of interest in the current paper. From the behaviour of the chromium doped parent $LaMn_{1-x}Cr_xO_3$, one might predict strong ferromagnetic bonding between Cr^{3+} and Mn^{3+} and a subsequent strengthening of the ferromagnetic state, but we believe the physics to be quite different.

The oxygen ions adjacent to the chromium would still distort towards the chromium ion. The nearest neighbour manganese ions would behave rather differently. Because of the presence of Mn^{4+} ions, the Mn^{3+} ions, instead of being localized, are now mobile and reduce their energy dominantly by finding and exchanging with Mn^{4+} ions in the double-exchange interaction. Instead of orienting their orbitals towards the Cr^{3+} ions to make use of the distortion, we would now expect the occupied e_g orbitals of those manganese ions adjacent to a chromium ion to be oriented *away* from the chromium ions and pointing towards the neighbouring manganese ions which fluctuate between Mn^{3+} and Mn^{4+} as charge moves round the system. The manganese lattice would become ferromagnetic at low temperatures to permit this motion in essentially the same way as in the non-chromium-doped $La_{0.7}Ca_{0.3}MnO_3$ compound, albeit with a slightly reduced ferromagnetic transition temperature. One major difference is that the orbital degeneracy of the adjacent manganese ions is lifted by this new interaction. Naively we would expect this new interaction to be stronger and hence those manganese ions most strongly affected would lose their degeneracy at higher temperatures than in the chromium free material.

Due to the strong disorder introduced by the Cr^{3+} ions we would also expect a wide spread in the local fields and consequently a broad distribution in the temperatures at which this orbital degeneracy is extracted. In particular, manganese ions without a chromium neighbour would be on average further apart than in the chromium free compound and the strength of the interaction between these ions would be reduced. If the transition to the metallic state has anything to do with the lifting of orbital degeneracy, then we would expect the eventual transition to the metallic state to be suppressed to lower temperatures. On the other hand, the loss of a few neighbours is of little importance to the ferromagnetic transition which would remain close to its original temperature. We would therefore expect the magnetic and orbital transitions to *decouple*, with the observable ferromagnetic transition remaining at high temperature, while the transition to the metallic state is sharply reduced with chromium doping.

3. Experimental method

The $La_{0.7}Ca_{0.3}Mn_{1-x}Cr_xO_3$ $(0 \leqslant x \leqslant 1)$ samples were prepared by standard solid state reaction in air. Stoichiometric amounts of MnO_2, LaO_3, $CaCO_3$ and Cr_2O_3 were intimately mixed together, pelletized and heated at $1300\,°C$ for 20 hours. The resulting products were characterized by x-ray diffraction (Cu Kα radiation, Siemens D5000 diffractometer mode).

In the literature, the compounds $LaMn_{1-x}Cr_xO_3$ with $0.3 < x < 1$ are reported to show the orthorhombic $GdFeO_3$ type structure [13]; on the other hand the $La_{1-y}Ca_yMnO_3$ compounds with $y > 0.125$ are reported to show the cubic structure [14, 15]. We find that the $La_{0.7}Ca_{0.3}Mn_{1-x}Cr_xO_3$ $(0 \leqslant x \leqslant 1)$ XRD patterns can be indexed on a cubic lattice, although a broadening of the diffraction peaks for the samples $x = 0.1, 0.3, 1$ suggests the possibility of either compositional gradients or structural distortions within these samples. More detailed XPS studies are in hand to determine the oxidation state of the chromium, which for the present paper we take to be Cr^{3+}.

The magnetization measurements were made in a vibrating sample magnetometer in magnetic fields up to 12 T. Data were taken in two ways:

 (i) The specimen was cooled to 10 K in zero applied field (ZFC). The magnetic field was then increased to 12 T and decreased again to zero.
 (ii) The specimen was cooled to 4.2 K from room temperature in a magnetic field of 2 T (FC) and data then taken as the specimen was warmed.

Four-point resistivity measurements versus temperature were made in a continuous flow cryostat, using dc measuring currents from 1 μA to 1 mA, depending on the resistance of the sample. We were limited to a maximum resistance of 350 MΩ by the range of the multimeter used. At no stage did we observe any dependence of the resistivity on measuring current.

4. Results and discussion

In presenting these results we show data from selected samples which illustrate a particular feature or trend.

The zero field cooled magnetization versus magnetic field for $x = 0.1$ and $x = 0.5$ at 10 K and the field cooled magnetization versus temperature curves for the same specimens at 2 T are shown in figures 1(a) and (b). The form of the curves is qualitatively similar to that described for the manganites by many authors, having a typical ferromagnetic hysteresis loop and a broadly mean-field-like temperature dependence. For the $x = 0$ specimen, the magnetization reaches a maximum value of 3.6 μ_B per formula unit at an applied field of 1 T. This is very close to the saturation magnetization of 3.7 μ_B expected for this material
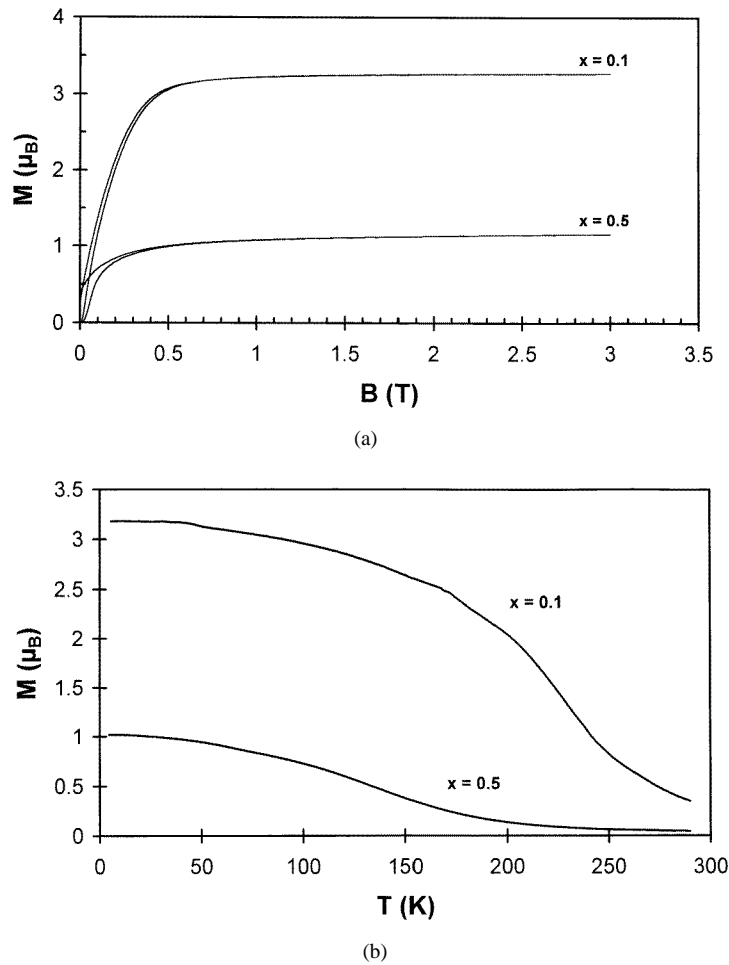
Figure 1. (a) Magnetic moment versus applied magnetic field at 10 K for $x = 0.1$ and $x = 0.5$. (b) Magnetic moment versus temperature at 2 T for $x = 0.1$ and $x = 0.5$.

by a simple application of Hund's rules to the Mn^{3+} and Mn^{4+} ions. By replotting the high temperature FC data as $1/M$ versus T we have obtained values for T_C which are rather close to the values we obtain by a simple extrapolation of the M/T data to $M = 0$. The sample with $x = 1$ shows a broad peak in the magnetization at around 170 K, probably associated with an antiferromagnetic transition [1].

In figure 2 we plot the Curie temperature obtained from the magnetization versus temperature data and also the moment at 12 T. We see that T_C decreases from 260 K for the undoped sample, at first rather slowly and then more rapidly above $x \sim 0.3$. The dependence of both T_C and M_s are consistent with our theoretical predictions. The Cr ions are unable to take part in the double-exchange interaction and so the electrons on the neighbouring Mn ions avoid the Cr ions and attempt to make a double-exchange interaction with their neighbouring Mn ions. The weakened double-exchange interaction is reflected in the progressive decrease in Curie temperature associated with increased Cr content. This rather weak dependence of T_C on Cr content for small values of x is again to be expected: the ferromagnetic exchange interaction between Mn ions is not strongly affected until a given manganese ion has Cr ions
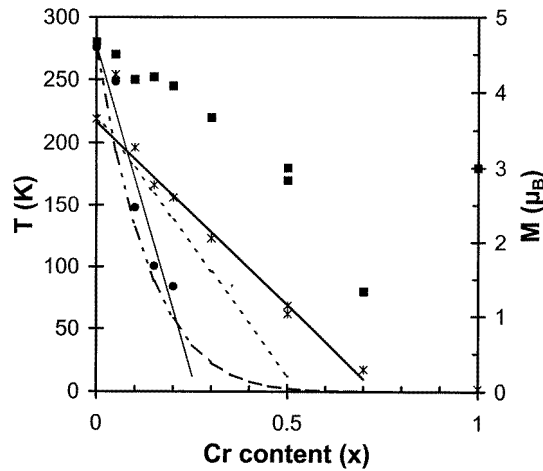
Figure 2. Dependence of various parameters on chromium fraction x. Magnetization at 12 T, M_s ($\star$); Curie temperature obtained from magnetization versus temperature data by plotting $1/M$ against T and extrapolating to $1/M = 0$ ($\blacksquare$); temperature of resistivity peak, T_p ($\bullet$); theoretical fit of M_s versus T from equation (1) (dotted line); linear fit to M_s data (thick solid line); linear fit to T_p data (thin solid line); the function $(1-x)^7$ (dash–dot line). This is the probability of finding a given manganese site atom as manganese in a random distribution multiplied by the binomial distribution for none of the six nearest neighbours being chromium. Probability $= 1$ corresponds to T_p at $x = 0$.

as a significant fraction of its nearest neighbours. The probability that a manganese atom has n chromium neighbours in a randomly doped alloy may be calculated directly from the binomial distribution. We find that for $x \sim 0.4$ the probability of a given Mn ion having Cr for at least half its nearest neighbours has increased to ~ 0.5, consistent with the behaviour shown in figure 2.

The magnetic *moment* drops somewhat more rapidly with temperature at low x and this is again in support of our theoretical interpretation. The inability of the Cr ions to make a double-exchange interaction with their neighbouring Mn ions results in a real space ordering of the e_g orbitals, on the adjacent Mn ions, leaving their *empty* $3_z^2 - 1$ orbitals pointing at the Cr ion. In the absence of an occupied orbital on either side of the intermediate oxygen, only the antiferromagnetic superexchange interaction remains, which results in a proportionate decrease in *total* moment. We can use this model to make an immediate prediction for the ferromagnetic moment of our system. Under the assumption that the compound is $La_{0.7}^{3+}Ca_{0.3}^{2+}Cr_x^{3+}Mn_{0.7-x}^{3+}Mn_{0.3}^{4+}O_3$ we are led to a ferromagnetic moment of

$$M = [4(0.7 - x) + 3 \times 0.3 - 3x]\mu_B = (3.7 - 7x)\,\mu_B. \tag{1}$$

This predicts a linear decrease in the total moment reaching zero at $x = 0.53$, compared with our observed linear decrease to zero at $x \sim 0.7$.

We should emphasize that this analysis is only strictly valid for low Cr doping levels where the number of Mn ions with Cr neighbours is small. Our prediction must break down when $x \sim x_c = 0.53$ and possibly much earlier, as the number of manganese atoms, and consequently the coordination number for the motion, is reduced and the motion weakened. Also, when chromium atoms neighbour each other, one might expect their mutual interaction to dominate and lessen the cancellation. Given these limitations, we believe the agreement with our theoretical predictions to be not unreasonable.

We also note that we are treating the moment at 12 T as the saturation moment which is inaccurate at large x where the moment clearly does not saturate. It is tempting to interpret the magnetization at high fields as the sum of a saturated moment from a subset of the Mn ions, whose proportion decreases as the ferromagnetism is suppressed by increasing Cr content, plus a paramagnetic moment from the remainder. This is not, however consistent with the increased hysteresis at large x which implies only a small paramagnetic contribution. In any case, our values for the magnetization of the higher x compositions should be treated as an underestimate.

We turn now to the behaviour of the resistivity. In figure 3 we show the dc resistivity versus temperature for all values of x. We first note that the changes in ρ (300 K) with x are not completely monotonic, which strongly suggests a role played by intergranular contacts. It is well known that intergranular contacts can have a substantial and, in weakly sintered materials, a dominant effect on the resistivity, and we must ask to what extent this is the case in the present samples.
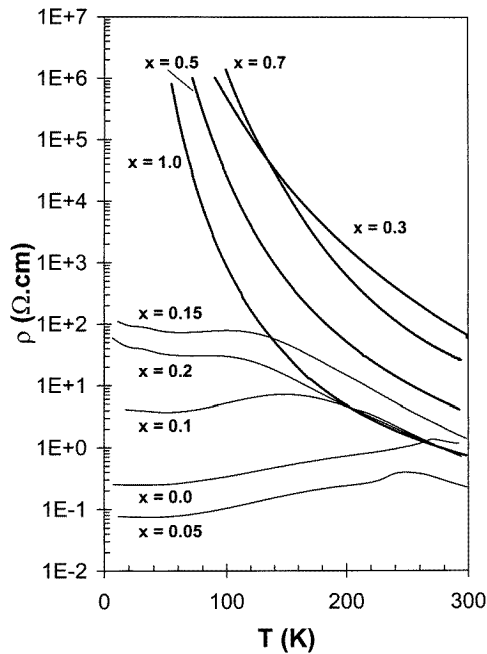

Figure 3. Resistivity versus temperature for all samples in zero applied magnetic field.

We see that the effect of the Cr doping is to cause a rapid suppression of the resistivity peak temperature T_p to lower temperatures. The suppression in temperature is accompanied by an increased rounding of the resistivity peak and for $x = 0.3$, the resistivity increases monotonically with decreasing temperature with no evidence of a peak within our observable range. Very similar behaviour has been reported in *cobalt* doped thin films [16] grown on LaAlO$_3$ substrates and which were presumably epitaxial, although the comparison with magnetization data was not made in that work and their interpretation was different. As a direct test of the role of intergranular contacts we prepared a separate series of samples at a sintering temperature of 1100 °C, which was the lowest temperature at which we were able to make sufficiently strong specimens for resistivity measurements. Despite differences in the

absolute resistivity from the first set of samples of up to three orders of magnitude, we found that the values of both the Curie temperature T_C (from the magnetization) and the resistivity peak temperature T_p were the same within 20%. The dependence of T_C and T_p on chromium doping was therefore the same, within experimental error, for the two sets of samples. We also note that in both sets of samples, T_p depends monotonically on the level of chromium doping, despite the large non-monotonic variations in absolute values of resistivity which we suggest *are* directly attributable to intergranular effects. Finally, as we shall see, we also obtain good agreement with our theoretical predictions and there is no obvious reason why the effect of Cr doping directly on the intergranular contacts should be in such good agreement with our predictions for the bulk, other than that the contacts are formed between the bulk grains whose properties we are seeking to investigate.

   Although we cannot completely preclude the possibility that our main results (i.e. the different dependences of T_C and T_p on chromium doping) are dominated by the effect of intergranular contacts, we therefore consider it unlikely and we will interpret them as representative of the bulk compounds for the purpose of the present discussion.

   First we observe that for the Cr doped samples, the T_C values derived from the behaviour of the magnetic moments is no longer identified with any particular trend in the resistivity curves. A significant feature of our results is that the resistivity shows a clear and strong delineation between the data for $x \leqslant 0.2$ and that for $x > 0.2$ in all aspects of its behaviour. For $x \leqslant 0.2$, we find a linear dependence of $\ln \rho$ on $1/T$ at temperatures below the resistivity peak. This is a well established feature of many manganites and implies the existence of a single activation energy. The temperature range in which this behaviour is observed in our samples is perforce limited, but if we tentatively associate it with such an energy we find values around 0.14 eV for $x = 0.05$–0.2, and about half this value for $x = 0$. For $x \geqslant 0.3$ no such linear dependence on $1/T$ is observed at any temperature, but we see from figure 4 that there is quite a good linear dependence of $\ln \rho$ on $1/T^{-1/4}$ for $x \geqslant 0.3$, implying that conduction in this regime is dominated by 3D variable range hopping [17]. We note that the slope is very similar for all the higher Cr doping levels.

   The temperature T_p of the resistivity peak drops rapidly with increasing x. A linear fit to the data extrapolates to zero at around $x = 0.25$, midway between the two regimes of different behaviour. This is shown clearly in figure 2. The transition temperature T_p will be proportional to the strength of the interaction which is driving the orbital order in those manganese whose orbital degeneracy has not already been lifted by the presence of a chromium neighbour. If we naively assume that this interaction strength is proportional to the number of manganese ions *without* a chromium neighbour, then simple application of the binomial distribution gives us the dash–dot line shown in figure 2. We emphasize that there are no variable parameters. We see that the agreement with the experimental data is really quite good for so simple a model and we take it as providing some support for our theoretical analysis.

   For the $La_{0.7}Ca_{0.3}MnO_3$ parent compound it is widely accepted that at high temperatures the compound is insulating and at low temperatures metallic, the peak in the resistivity at temperature T_p marking the transition between the two phases. It is also natural (and, indeed common) to associate the resistance peak intimately with the ferromagnetic transition which occurs at a temperature close to the peak. In our Cr doped compounds it is clear that the ferromagnetic peak is *separated* from the resistive transition and it is no longer natural to use the magnetism as an explanation of the metallic phase. Since we can no longer attribute the resistive transition directly to the magnetism, we have a choice of advocating the orbitals or simply focusing on the disorder as an explanation. Disorder is certainly important and probably accounts for the overall increase in low temperature resistivity with chromium doping and the variable range hopping behaviour observed for $x > 0.2$.
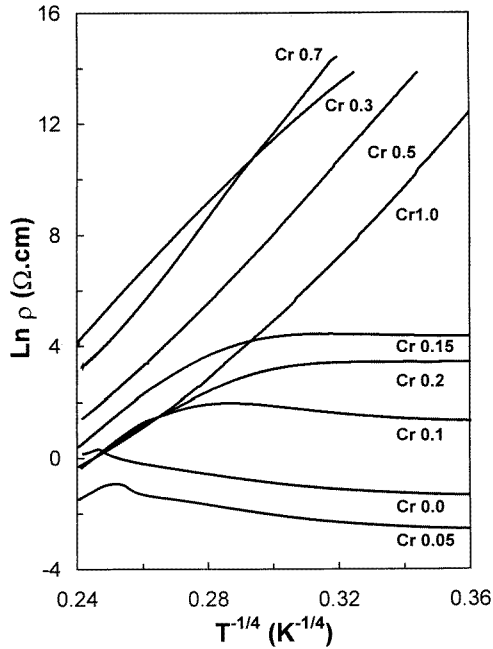
Figure 4. Resistivity on a logarithmic scale versus $T^{-1/4}$ for all samples in zero applied magnetic field.

The movement of a distinct bump in the resistivity to lower temperature is a separate issue and strongly suggests a distinct transition. In the $La_{0.7}Ca_{0.3}MnO_3$ parent compound we know that there is an orbital degeneracy which we expect to be lifted at a temperature close to the ferromagnetic transition. In our Cr doped compounds, however, the metallic phase appears to be restricted to a small window with $0 \leqslant x \leqslant 0.25$. As we have theoretically argued, chromium is expected to have its dominant role as an independent lifter of orbital degeneracy, thus separating the transition between insulating and metallic phases from the ferromagnetic transition. Although our evidence is necessarily indirect, we are therefore promoting the orbitals, rather than the ferromagnetism, as candidates to explain the resistive transition.

5. Conclusions

We see that both the saturation magnetization, M_s, and the magnetic transition temperature, T_C, fall rather slowly with Cr content, whereas the temperature T_p of the resistivity peak falls much more rapidly. Both these results are in good quantitative agreement with our model. We interpret the slow fall in M_s and T_C as evidence that the chromium ions do *not* order ferromagnetically with the manganese ions, as observed in the chromium doped parent compound $LaCr_xMn_{1-x}$, but order *anti*ferromagnetically with the manganese ions causing a proportionate reduction in the moment as given by equation (1) and also a reduction in the Curie temperature via a reduced strength in the ferromagnetic interaction.

The effect of Cr doping on the resistance, however, is much more dramatic, displaying a clear change in the properties between Cr doping levels above and below $x = 0.25$, with T_p dropping to zero as x approaches 0.25. We associate this with a real space ordering of the

manganese e$_g$ *orbitals* which causes a concomitant reduction in the magnetic response of the double-exchange interaction and the transition to the metallic state at a temperature roughly proportional to the number of Mn ions without Cr nearest neighbours.

Our results strongly suggest a *decoupling* of the ferromagnetic transition, which is associated with spin order, and the resistive transition, which is dependent on orbital order via the double-exchange interaction.

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