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Low-temperature transport properties of non-stoichiometric $\text{La}_{0.95-x}\text{Sr}_x\text{MnO}_3$ manganites

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Abstract

The low-temperature specific heat and electrical resistivity of the polycrystalline non-stoichiometric manganites $\text{La}_{0.95-x}\text{Sr}_x\text{MnO}_3$ have been investigated in the doping region $x = 0.00$ – 0.30 . The specific heat has terms proportional to T and T^3 . The resistivity of the samples decreases as $T^{1/2}$ with increasing temperature, goes through a minimum and then increases proportionally to T^3 . The temperature T_{\min} , corresponding to the minimum of the resistivity, shifts with Sr content as $T_{\min} \sim x^{-2/5}$.

1. Introduction

The transition metal oxides are systems with strong electron correlation and show a rich variety of physical phenomena. Among them, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ is a well-studied material in which an antiferromagnetic insulating phase at $x = 0$ changes to a metallic ferromagnetic one for $0.17 < x < 0.5$ [1]. Compounds of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x \geq 0.17$) are known to be conducting ferromagnets mediated by the double-exchange interaction [2, 3]. The nominal Mn^{3+} ions in the parent compound LaMnO_3 display the electron configuration $(t_{2g})^3 (e_g)^1$. Because of the strong Hund coupling and on-site Coulomb repulsion between e_g electrons, LaMnO_3 is an antiferromagnetic insulator. On replacing La with Sr atoms, Mn^{3+} ($3d^4$) ions change to the Mn^{4+} ($3d^3$) state without $(e_g)^1$ electrons. The vacant $(e_g)^1$ states of Mn^{4+} ions make it possible for $(e_g)^1$ electrons in surrounding Mn^{3+} ions to hop into the $(e_g)^1$ state of Mn^{4+} as long as the $(t_{2g})^3$ spins of neighbouring Mn^{3+} and Mn^{4+} ions are parallel. Thus a competition appears between a gain in the kinetic energy and a loss in the exchange energy of t_{2g} spins which favour antiferromagnetic coupling. With increasing number of mobile carriers on further doping with Sr atoms, the gain in the kinetic energy overcomes the loss of exchange energy, resulting in a transition to metallic ferromagnetism at about $x \sim 0.17$. The $(t_{2g})^3$ electrons of Mn ions can be viewed as localized spins ($S = 3/2$), while the $(e_g)^1$ state, which is strongly hybridized with the 2p states of oxygen, behaves as itinerant electrons with $S = 1/2$. The localized spins couple antiferromagnetically with each other and the strong exchange interaction (Hund coupling J_H) acts between the itinerant $(e_g)^1$ carriers and local $(t_{2g})^3$ spins. When hole doping

exceeds $x = 0.17$ [1], on replacing La^{3+} ions with Sr^{2+} a barely metallic ferromagnetic ground state is formed, which is perfectly spin polarized and is called a half-metallic state.

An unusual feature of this half-metallic state is the low-temperature behaviour of the electrical resistivity. It is known that in a conventional itinerant metallic weak ferromagnet where both spin channels conduct currents, the one-magnon scattering process gives rise to a T^2 -dependence on temperature of the resistivity [4,5]. For half-metallic systems, where there is a band gap at the Fermi energy ε_F , Kubo and Ohata [6] have shown that for one of the spin channels, the one-magnon scattering process is exponentially suppressed by a factor $T^2 \exp(-E_g/k_B T)$, where E_g is the minority-spin band gap at ε_F . On the other hand, the two-magnon scattering process results in a $T^{9/2}$ -dependence for the low-temperature resistivity. Furukawa [7], taking into account spin fluctuations at finite temperatures, which induce an incoherent minority band, has shown that the one-magnon scattering process is most relevant. This unconventional scattering mechanism gives a T^3 -dependency in the resistivity in the low-temperature region below 30 K. Recently, Calderon *et al* [8], by studying low-energy and low-temperature electronic properties of double-exchange systems, have found that the low-energy spin excitations are a linear combination of ion and electron spin waves. They have shown that static disorder in the hopping amplitude couples with the spin fluctuations and creates a resistivity which increases with temperature as $T^{3/2}$ and T^3 . They maintain that the $T^{3/2}$ -term is more important than the T^3 -term up to temperatures higher than the critical one and also that the magnitude of this resistivity is in agreement with experimental data.

The prominent feature for the polycrystalline manganites is the observation of a shallow minimum of the zero-field resistivity $\rho(0, T)$ which occurs at low temperatures ($T < 50$ K) [9,10]. Tiwari and Rajeev [9] have attributed this minimum to 3D electron–electron interaction strongly enhanced by disorder [11] and have excluded the Kondo effect as a possible cause because the manganites are ferromagnetic. On the other hand, Rozenberg *et al* [10] attributed it to the charge carriers tunnelling between antiferromagnetically coupled grains.

Since, the origin of the appearance of the resistivity minimum in manganites is not clear, we have carried out low-temperature resistivity measurements on non-stoichiometric $\text{La}_{0.95-x}\text{Sr}_x\text{MnO}_3$ in order to clarify the underlying effect and also to study the influence of the deficiency of La on the low-temperature properties. We also present complementary specific heat measurements on this system in the temperature range 4.2–30 K.

2. Experimental procedure

Polycrystalline $\text{La}_{0.95-x}\text{Sr}_x\text{MnO}_3$ samples were prepared by standard techniques of ceramic synthesis. Pure powders of La_2O_3 , SrO and MnO oxides were non-stoichiometrically mixed, cold pressed into rectangular bars and then fired in air at 1400 °C for 20 h. Powder x-ray diffraction studies, which were performed on pieces coming from the same part of the sample, indicated that the compounds are single phased and homogeneous. The specific heat measurements were performed from 4.2 to 30 K with a sensitive home-made calorimeter using the adiabatic technique. The resistivity measurements were carried out in the temperature range 4.2–40 K using the conventional four-point dc technique.

3. Results and discussion

Figure 1 shows the quantity C/T , which is the heat capacity of the parent $\text{La}_{0.95}\text{MnO}_3$ and Sr-doped compounds, as a function of T^2 in the temperature range 4.2–12 K. From this figure one can see that C/T for all compounds follows a T^2 -dependence on temperature.

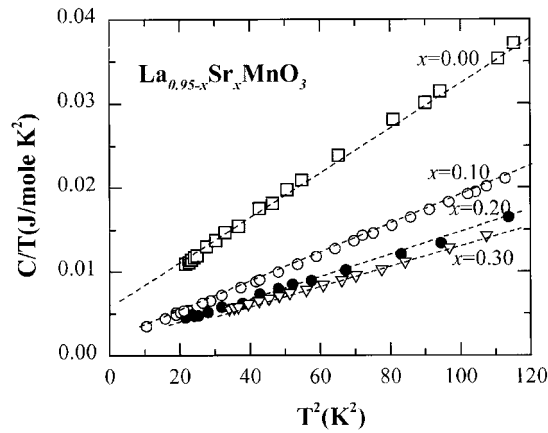


Figure 1. The low-temperature specific heat, plotted as C/T versus T^2 , for the $\text{La}_{0.95-x}\text{Sr}_x\text{MnO}_3$ system with $x = 0.00, 0.10, 0.20$ and 0.30 .

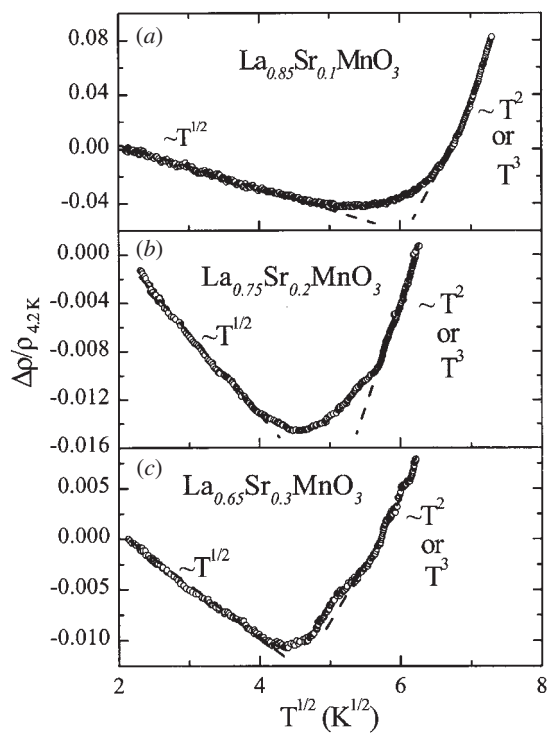


Figure 2. The temperature dependence of the normalized relative resistivity $\Delta\rho(T)/\rho_{4.2\text{ K}}$ on a square-root scale for $\text{La}_{0.95-x}\text{Sr}_x\text{MnO}_3$ with $x = 0.10, 0.20$ and 0.30 .

In figure 2 the normalized relative resistivity ($\Delta\rho(T)/\rho(4.2\text{ K})$) data for the present doped $\text{La}_{0.95-x}\text{Sr}_x\text{MnO}_3$ compounds are plotted as a function of $T^{1/2}$ in the temperature range 4.2–40 K, for three different Sr contents. It can be seen that at low temperatures the resistivity of the compound in the insulating phase, $\text{La}_{0.85}\text{Sr}_{0.1}\text{MnO}_3$, as well as those of the compounds in the metallic phase, $\text{La}_{0.75}\text{Sr}_{0.2}\text{MnO}_3$ and $\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_3$, decrease as $T^{1/2}$ with increasing temperature. Then they go through a minimum, which shifts towards lower temperatures with increasing Sr content and finally increases sharply with temperature. In the temperature region above the minimum, the resistivity data cannot be characterized by a defined power law. The data can be fitted either as T^2 or as T^3 . The resistivities of the compounds at 4.2 K are given in table 1, which shows that $\rho(4.2\text{ K})$ decreases as the Sr content increases.

Table 1. Summary of fitting results.

x (Sr)	$\rho(4.2\text{ K})$ ($\Omega\text{ cm}$)	γ ($\text{mJ mol}^{-1}\text{ K}^{-2}$)	$N(E_F) \times 10^{-47}$ (states $\text{J}^{-1}\text{ m}^{-3}$)	β ($\text{mJ mol}^{-1}\text{ K}^{-4}$)	Θ_D (K)	D (cm s^{-1})	F_σ^*
0.00		5.34	2.32	0.280	326		
0.10	2.05	1.68	0.76	0.172	382	1.25×10^{-4}	0.89
0.20	8.5×10^{-4}	1.69	0.77	0.127	423	0.30	0.91
0.30	2.7×10^{-4}	1.60	0.76	0.113	440	0.95	0.91

The specific heat of the parent compound $\text{La}_{0.95}\text{MnO}_3$ and of the doped $\text{La}_{0.95-x}\text{Sr}_x\text{MnO}_3$ manganites show the $C = \gamma T + \beta T^3$ variation normally expected of a metal. The linear term γT is due to free charge carriers, where γ is proportional to the density of states $N(E_F)$ at the Fermi level, while the βT^3 term arises from phonons with β proportional to the Debye temperature Θ_D . By fitting our specific heat data, the evolution of γ and β and therefore the density of states $N(E_F)$ and the Debye temperature Θ_D can be extracted as functions of Sr doping. The dashed lines through the data in figure 1 were generated using the fitting parameters shown in table 1. Surprisingly, over most of the temperature range measured, the specific heat of the parent compound $\text{La}_{0.95}\text{MnO}_3$ is a factor of about three larger than those of the metallic compounds $\text{La}_{0.75}\text{Sr}_{0.2}\text{MnO}_3$ and $\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_3$, although the system is an insulator as far as transport properties are concerned. Also, the specific heat of the $\text{La}_{0.85}\text{Sr}_{0.1}\text{MnO}_3$ sample is somewhat larger than those of the metallic samples. The γ -values of the samples in the ferromagnetic metallic region are about a factor of two smaller than those of the stoichiometric compounds $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ [12, 13]. In order to understand the origin of this unusual extra entropy of the antiferromagnetic electrically insulating samples, the contributions to the specific heat from various excitations have been estimated. According to Smolyaninova *et al* [14], the associated antiferromagnetic spin-wave contribution to the specific heat would be $C_{AFM} = (8\pi^2 R/15)(T/T_N)^3$, where R is the ideal-gas constant and T_N the Néel temperature. Using a Néel temperature $T_N = 130\text{ K}$ for our parent compound $\text{La}_{0.95}\text{MnO}_3$ [15], we estimate $C_{AFM} = 0.02 T^3\text{ mJ mol}^{-1}\text{ K}^{-1}$, which is about seven times smaller than the lattice contributions (βT^3) at 10 K measured in the metallic compounds $\text{La}_{0.75}\text{Sr}_{0.2}\text{MnO}_3$ and $\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_3$. Thus the large excess specific heat cannot be explained by antiferromagnetic spin-wave excitations. Also, the ferromagnetic spin-wave contribution to the specific heat $C_{FM} = 0.2 \times [0.113 V k_B (k_B T/D_s)^{3/2}] \sim 0.4 T^{3/2}\text{ mJ mol}^{-1}\text{ K}^{-1}$ is only about 4% of the lattice contribution at $T = 10\text{ K}$ [14]. V is the molar volume and $D_s = 75\text{ meV \AA}^2$ [16] is the spin-wave stiffness constant.

Recently Ghivelder *et al* [16], by means of a systematic study of the specific heat in a series of oxygen non-stoichiometric $\text{LaMnO}_{3+\delta}$ compounds have also found large γ -values for samples with oxygen excesses $\delta = 0.11$ and 0.15 . These authors have related the anomalous high linear coefficient γ to disorder effects that can affect spin and/or charge degrees of freedom. Accordingly, we also attribute our large γ -value of the parent compound to spin disorder, which can result from a probable non-stoichiometry as regards oxygen.

The present results on the electrical resistivity below the minimum cannot be explained by the above theories, which do not predict a $\sim -T^{1/2}$ -dependence.

It is known that in amorphous three-dimensional (3D) metallic systems the origin of the minimum and the $-T^{1/2}$ -dependence of the electrical resistivity at low temperatures may arise from weak localization [11] and from disorder-enhanced electron-electron interaction [11]. Weak localization can be ruled out since the effect of weak localization results from interference of complementary electron waves, whereas the strong spontaneous magnetic field in these

ferromagnetic compounds destroys the phase coherence of electron waves. So, a power-law $\sim -T^{1/2}$ -behaviour of the resistivity is expected to arise from 3D enhanced electron–electron interaction due to the disorder of the system. According to the 3D prediction of Alt’shuler and Aronov [17], the diffusion-channel (particle–hole) contribution to the correction of the zero-field resistivity is given by

$$\Delta\rho(T)/\rho_0 = -\rho_0(0.915e^2/4\pi^2\hbar)(4/3 - (3/2)F_\sigma^*)(k_B T/\hbar D)^{1/2}. \quad (1)$$

ρ_0 is the resistivity at 4.2 K, D the electron diffusion coefficient, which can be calculated from the Einstein relation $D = (1/2)e^2\rho_0 N(E_F)$ and F_σ^* is the electron screening parameter, which is given by the following relation:

$$F_\sigma^* = ((32/3)F)[(1 + (1/2)F)^{3/2} - 1 - (3/4)F]. \quad (2)$$

F is the Coulomb potential averaged over the Fermi surface, which in the free-electron model and Thomas–Fermi approximation is given by

$$F = \ln[1 + (2k_F/\kappa)^2]/(2k_F/\kappa)^2 \quad (3)$$

where $k_F = mv_F/\hbar \sim 0.61 \times 10^8 \text{ cm}^{-1}$ for the metallic compounds [18], $\kappa = [e^2 N(\epsilon_F)/\epsilon_0]^{1/2}$ being the inverse screening length and ϵ_0 the electrical field constant. Using the values of $N(\epsilon_F)$, the density of states, one can calculate the diffusion constant D , given in table 1, and the inverse screening length $\kappa = 1.48 \times 10^8 \text{ cm}^{-1}$. From equations (3) and (2) we obtain $F_\sigma^* = 0.72$. In order to examine whether the enhanced electron–electron interaction applies to our results, we fitted equation (1) to the low-temperature ($T < 20 \text{ K}$) resistivity data, where the $-T^{1/2}$ -law is obeyed. The theoretical fits are compared to the resistivity data in figure 2. As can be seen in figure 2, the theoretical fits are in quantitative agreement with the experimental data. By comparing the present values of the diffusion constant D with those of a normal metal like Cu ($D_{\text{Cu}} \sim 2.2 \times 10^2 \text{ cm}^2 \text{ s}^{-1}$), one can see that the carriers of the present manganites have a lower diffusivity than the electrons of a metal. The values of D of the present samples are about 3–4 orders of magnitude lower than those of pure noble metals and are very similar to those found for highly correlated systems like $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($D = 0.44 \text{ cm}^2 \text{ s}^{-1}$) [19] and LaNiO_3 ($D = 3 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$) [20]. From the fitting parameters and the calculated values of the diffusion constant D , one can estimate the effective screening parameter, which turns out to be $F_\sigma^* = 0.90$. This value is reasonably close to the calculated one. Consequently it appears that the $-T^{1/2}$ -dependence is due to 3D enhanced electron–electron interaction. This interaction can be attributed to the existence of some local lattice disorder in the present non-stoichiometric polycrystalline samples where the $(e_g)^1$ free charge carriers are scattered.

As has been mentioned above, it is difficult to distinguish between a $\sim T^2$ - and a $\sim T^3$ -dependence of the resistivity for the temperatures above T_{min} . These two laws correspond to different scattering mechanisms. In the case where the resistivity increases as $\sim T^2$, one can attribute this dependence to the Landau electron–electron scattering process [1]. Otherwise, if the resistivity varies as $\sim T^3$, then this temperature dependence can be attributed to the previously mentioned unconventional one-magnon Furukawa [7] scattering mechanism. The strong electron–electron interactions also enhance the incoherence of the minority band, which enlarges the T^3 -scaling region.

In order to clarify which of these scattering processes predominate, the well-known Matthiessen rule is used. According to Matthiessen’s rule the total resistivity can be represented as the sum of (i) the part decreasing as $-x^{-1}T^{1/2}$, due to enhanced electron–electron interaction, and (ii) the part increasing as T^2 , due to Landau electron–electron interaction or as T^3 , due to unconventional Furukawa one-magnon scattering, i.e. $\rho_{\text{tot}}(T) \sim -x^{-1}T^{1/2} + \alpha T^2$ or $\rho_{\text{tot}}(T) \sim -x^{-1}T^{1/2} + \alpha T^3$ respectively. The interplay of parts (i) and (ii) gives rise to the minimum of $\rho(T)$. The minimization of the total resistivity with respect to the temperature

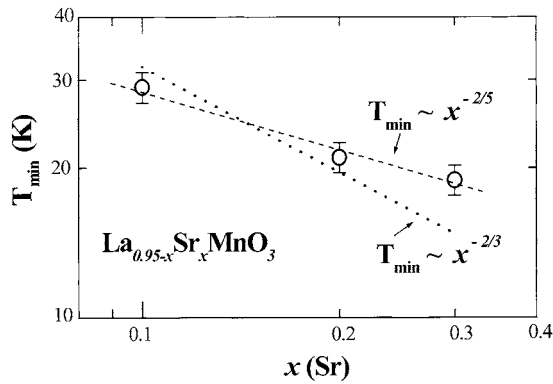


Figure 3. T_{\min} as a function of Sr content x .

gives a $T_{\min} \sim x^{-2/3}$ dependence on the Sr content for the first case and a $T_{\min} \sim x^{-2/5}$ dependence for the case where the resistivity above the minimum increases as T^3 . Figure 3 shows the temperatures T_{\min} , corresponding to the minima taken from the experimental curves, as functions of Sr content in a double-logarithmic plot. The $x^{-2/3}$ - and $x^{-2/5}$ -dependencies are also plotted in this figure. One can see that the experimental results for T_{\min} are better described by a $x^{-2/5}$ -law than by a $x^{-2/3}$ -dependence. From the $T_{\min} \sim x^{-2/5}$ dependence, one can conclude that above the minimum the unconventional Furukawa one-magnon scattering is the most likely mechanism.

An unconventional feature of the present investigation is the low-temperature resistivity of the $\text{La}_{0.85}\text{Sr}_{0.1}\text{MnO}_3$ sample. Although, according to the electronic phase diagram [1], the corresponding stoichiometric compound is a ferromagnetic insulator, the low-temperature resistivity behaviour of $\text{La}_{0.85}\text{Sr}_{0.1}\text{MnO}_3$ is similar to those of the compounds in the ferromagnetic metallic phase. This behaviour can be attributed to the deficiency of La^{3+} ions, which results in the creation of more Mn^{4+} ions in the compound and thus to an enhancement of the double-exchange interaction responsible for the metallic behaviour of the manganites.

4. Conclusions

The present measurements of the low-temperature specific heat and electrical resistivity of non-stoichiometric $\text{La}_{0.95}\text{MnO}_3$, $\text{La}_{0.85}\text{Sr}_{0.1}\text{MnO}_3$, $\text{La}_{0.75}\text{Sr}_{0.2}\text{MnO}_3$ and $\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_3$ manganites show some interesting behaviour. The relatively large specific heat linear coefficient γ of the parent compound $\text{La}_{0.95}\text{MnO}_3$ is attributed to spin disorder. The low-temperature resistivity behaviour can be better understood by considering 3D enhanced electron–electron interaction than by considering weak localization. The T^3 -dependence of the resistivity for temperatures above the minimum can be attributed to the unconventional one-magnon Furukawa scattering mechanism. The interplay of the two effects can lead to the existence of the minimum and to the shift of its position with Sr content as $\sim x^{-2/5}$.

References

- [1] Urushibara A, Moritomo Y, Arima T, Asamitsu A, Kido G and Tokura Y 1995 *Phys. Rev. B* **51** 14 103
- [2] Zener C 1951 *Phys. Rev.* **82** 403
- [3] Anderson P W and Hasegawa H 1955 *Phys. Rev.* **100** 675
- [4] Kasuya T 1959 *Prog. Theor. Phys.* **22** 227
- [5] Mannari I 1959 *Prog. Theor. Phys.* **22** 325
- [6] Kubo K and Ohata N 1972 *J. Phys. Soc. Japan* **33** 21

- [7] Furukawa N 2000 *J. Phys. Soc. Japan* **69** 1954
- [8] Calderin M J and Brey L 2001 *Phys. Rev. B* **64** 140403
- [9] Tiwari A and Rajeev K P 1999 *Solid State Commun.* **111** 33
- [10] Rozenberg E, Auslender M, Felner I and Gorodetsky G 2000 *J. Appl. Phys.* **88** 2578
- [11] Lee P A and Ramakrishnan T V 1985 *Rev. Mod. Phys.* **57** 287
- [12] Woodfield B F, Wilson M L and Byers J M 1997 *Phys. Rev. Lett.* **78** 3201
- [13] Okuda T, Asamitsu A, Tomioka Y, Kimura T, Taguchi Y and Tokura Y 1998 *Phys. Rev. Lett.* **81** 3203
- [14] Smolyaninova V N, Ghosh K and Greene R L 1998 *Phys. Rev. B* **58** R14 725
- [15] Michalopoulou A, Syskakis E and Papastaikoudis C at press
- [16] Ghivelder L, Castilo I A, Gusmao M A, Alonso J A and Cohen L F 1999 *Phys. Rev. B* **60** 12 184
- [17] Alt'shuler B L and Aronov A G 1985 *Electron-Electron Interactions in Disordered Systems* ed A I Efros and M Pollak (Amsterdam: North-Holland)
- [18] Hu C D 2001 *J. Phys. Soc. Japan* **70** 203
- [19] Fischer H E, Wilson S K and Cahill D G 1988 *Comments Condens. Matter Phys.* **14** 65
- [20] Rajeev K P and Raychaudhuri A K 1992 *Phys. Rev. B* **46** 1309