University of Groningen

Transport mechanisms in doped LaMnO₃

Palstra, T.T.M.; Ramirez, A.P.; Cheong, S.W.; Zegarski, B.R.; Schiffer, P.; Zaanen, J.

Published in:
Physical Review B

DOI:
[10.1103/PhysRevB.56.5104](https://doi.org/10.1103/PhysRevB.56.5104)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1997

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Palstra, T. T. M., Ramirez, A. P., Cheong, S. W., Zegarski, B. R., Schiffer, P., & Zaanen, J. (1997). Transport mechanisms in doped LaMnO₃: Evidence for polaron formation. *Physical Review B*, 56(9), 5104-5107. <https://doi.org/10.1103/PhysRevB.56.5104>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Transport mechanisms in doped LaMnO_3 : Evidence for polaron formation

T. T. M. Palstra

*Department of Chemical Physics and Materials Science Center, State University of Groningen, 9794 AG Groningen, The Netherlands
and Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974*

A. P. Ramirez, S-W. Cheong, and B. R. Zegarski

Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974

P. Schiffer

University of Notre Dame, Notre Dame, Indiana 46556

J. Zaanen

Lorentz Institute, University of Leiden, 2300 RA Leiden, The Netherlands

(Received 18 November 1996; revised manuscript received 9 April 1997)

We report electrical transport experiments on the colossal magnetoresistance compound $(\text{La,Ca})\text{MnO}_3$ over a wide range of composition and temperature. Comparison of thermopower and electrical resistivity measurements above the metal-insulator transition indicate a transport mechanism not dominated by spin disorder, but by small polaron formation. Additionally, we find that in the high-temperature limit the thermopower corresponds to backflow of spin entropy, expected from motion of positively charged particles in a rigid $S=2$ system, showing a remarkable independence of $S=3/2$ particle density. [S0163-1829(97)09334-X]

The recent observation of large magnetoresistance effects in thin films of doped LaMnO_3 has renewed the interest in the metal-insulator transition in these materials.¹⁻³ Since the metal-insulator transition temperature, T_{MI} , can be tuned to above room temperature, this opens possibilities to use this material not only for recording media but also for other types of magnetic switching applications. However, the emerging notion that magnetoresistance due to a metal-insulator transition decreases with increasing T_{MI} , necessitates a better understanding of the underlying basic transport mechanism to exploit the magnetoresistive properties of these materials fully. The microscopic nature of the transport mechanism is condensed into the description of double exchange, the simultaneous electron transfer of an electron on a Mn atom to an O atom of the surrounding oxygen octahedron, and another electron from this O atom to a neighboring Mn atom.⁴ This indirect exchange mechanism establishes, because of spin conservation in the exchange, a direct relation of the metallic state with the ferromagnetic coupling between the Mn spins. However, there is remarkably little known about the transport mechanism in the insulating state. Whereas spin disorder can contribute to the variations in the resistivity near T_c , only more recently the role of electron-phonon interactions on the localization has been put in a clearer perspective.⁵⁻⁷ This theoretical work was based on research on magnetic semiconductors like EuO, and only recently applied to doped LaMnO_3 . Still, it is not known if the metal insulator transition in doped LaMnO_3 is driven by changes in the carrier density or the mobility.

In order to gain insight into the nature of the transport mechanism, we have performed thermopower measurements on doped LaMnO_3 over a wide range of concentrations and temperatures in addition to the basic characterization by electrical resistivity and magnetic measurements. Thermopower

is in contrast to electrical resistivity relatively insensitive to effects of grain boundaries and disorder. We will show that for this material, thermopower provides unique insight into the transport mechanism. First, we show that the change of sign in the thermopower is not related to competition between electron and hole conduction, but accidental cancellation of the entropic term and the energy transport term of the thermopower. Secondly, the transport behavior above T_c is not dominated by spin disorder scattering, but by small polaron formation. From our measurements we can estimate the polaron binding energy and the energy scale for polaron interactions. Finally, the entropic contribution to the thermopower in the insulating state is in good agreement with the expectation for a polaron gas if only the spin entropy is considered. However, this state has to be more organized than a simple gas, because we find that the configurational entropy is at an extremum with respect to changes in the number of carriers.

Ceramic samples of $(\text{La,Ca})\text{MnO}_3$ were prepared by solid state reaction. Starting materials La_2O_3 , CaCO_3 , and MnO_2 were mixed in stoichiometric proportions and heated in air at 1250 °C for 5 h, and 1380 °C for 13 h, and then 1390 °C for 20 h with intermediate grinding. Powder x-ray diffraction shows clean single phase patterns. Transport experiments were performed in a commercially available temperature/magnetic field platform (PPMS/Quantum Design) and a resistance bridge operating at a frequency of 17 Hz (Linear Research LR400). Thermopower was measured between 80 and 475 K using a commercial setup (SB 100/MMR Technologies) using proprietary software and copper leads against a copper/constantan reference.

In Fig. 1 we show the electrical resistivity of $(\text{La,Ca})\text{MnO}_3$ between 10 and 350 K for doping levels between 10% and 60% Ca. The metallic behavior at low tem-

FIG. 1. Inverse temperature dependence of the electrical resistivity of ceramic samples $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ for $0.1 \leq x \leq 0.6$.

peratures and semiconducting behavior at high temperature have been reported much earlier.⁸⁻¹⁰ However, in contrast to earlier work, we concentrate in this paper solely on the behavior of the extrinsic semiconducting state above T_c . This regime was shown to hold to about 900 °C above which the conduction becomes intrinsic. In the extrinsic semiconducting state the resistivity can be fitted to $\rho(T) = \rho_0 \exp(\Delta_p/2k_B T)$ to obtain an estimate of the transport gap. The transition into the ferromagnetic state is accompanied by a transition into metallic behavior and is observed in the doping range $0.2 \leq x \leq 0.45$. The maximum Curie temperature is obtained for $x=0.33$ at 250 K. For lower doping levels ($x=0.10$) there is no transition into a metallic state despite a ferromagnetic component in the magnetization below 100 K. Probably the double exchange is here in competition with the superexchange which favors an antiferromagnetic spin state, rendering a canted magnetic structure and an insulating ground state. Also for doping concentrations $x > 0.5$ no metallic ground state is obtained. It was shown that for these concentrations a charge ordered ground state forms, which is insulating, exhibiting antiferromagnetic ordering at lower temperature.¹¹

We show the temperature dependence of the thermopower $S(T)$ of $(\text{La,Ca})\text{MnO}_3$ in Fig. 2. Also the thermopower has been reported previously over a much broader temperature regime, but no convincing quantitative models were provided.^{8,12} Again, in this paper we focus on the behavior of the extrinsic semiconducting state above T_c . The Curie temperature is here reflected by a jump in the thermopower. The metallic state exhibits a small thermopower less than a few $\mu\text{V/K}$. The thermopower changes sign near $x=0.3$ from apparent holelike behavior to electronlike transport, suggesting that the maximum T_c is somehow related to symmetry in electron and hole conduction. However, we will show that

FIG. 2. Inverse temperature dependence of the thermoelectric power of ceramic samples $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ for $0.1 \leq x \leq 0.9$.

the change of sign in $S(T)$ is fortuitous and does not have this physical significance. Our data indicate instead that the entire doping range is hole transport dominated, as expected from replacing trivalent lanthanum with divalent calcium.

The magnetic field dependence of the ferromagnetic-semiconducting transition has been studied¹³ extensively before in compounds like EuO . For this material it was proposed that electron-phonon interactions were responsible for the localization in the semiconducting state.⁶ For the manganates the insulating state is still poorly understood, and only recently the role of the electron-phonon interaction was demonstrated theoretically⁷ and experimentally.¹⁴ In this paper we focus therefore on the behavior of the extrinsic semiconducting regime. It was not realized that this regime provides a simple handle on the origin of localization. The basis for discussion of the transport mechanism in $(\text{La,Ca})\text{MnO}_3$ is the experimental observation that the thermopower can be deconvolved simply into two contributions. The temperature dependence in the extrinsic semiconducting state can be accurately fitted with a temperature independent term S_0 and a temperature dependent term

$$S = - \left| \frac{k_B}{e} \right| \cdot \frac{\Delta_S}{2T} + S_0 \quad (1)$$

for all doping concentrations $0.1 \leq x \leq 0.9$. This simple deconvolution is unusual for doped semiconductors, and allows interpretation of the thermopower in more detail. We show in Fig. 3 the results of this parametrization: S_0 , Δ_S , Δ_p for $0.1 \leq x \leq 0.6$. Regardless of further interpretation, this result shows that the high temperature state is in an entropy dominated regime. Equation (1) is in this case very general as it follows directly from the high-temperature expansion of the Kubo formula:

FIG. 3. Doping dependence x of the energy gaps derived by transport Δ_p and thermopower Δ_S and the high-temperature limit of the thermopower S_0 .

$$S = -\frac{S^{(2)}/S^{(1)}}{T} - \frac{\mu}{eT}, \quad (2)$$

where $S^{(2)}$ and $S^{(1)}$ are the energy-particle and particle-particle current correlation function and μ the chemical potential. In the high-temperature limit $S^{(2)}/S^{(1)} \ll \mu$ and the thermopower obtains its interpretation as entropy per carrier $-\mu/eT$. Hence the system is in a classical high-temperature state, and by analyzing S_0 and Δ_S one can infer some crude characteristics of the liquid. The negative value of Δ_S for $0.1 \leq x \leq 0.5$ suggests hole conduction in the Mn e_g band, as obtained by replacing trivalent La by divalent Ca. From Eq. (1) and Fig. 2 one can infer that the sign change in thermopower near $x=0.33$ is caused by cancellation of the temperature dependent and independent term, rather than symmetry of electron and hole conduction.

From Fig. 3 we see that the transport gap from thermopower is much smaller than the gap derived from resistivity measurements. Thermopower measures, in a simplified picture, the heat current associated with charge motion, which for usual semiconductors is the activation energy across the (kinetic) gap. If transport is dominated by one type of carrier, this results in an equality of the transport and thermopower gap. The vanishing value of Δ_S near $x=0.5$ can only be explained in a semiconductor model by symmetry of the holes and electrons, as expected, e.g., for a half filled band. The e_g band is however only one quarter filled at $x=0.5$. This would suggest a splitting of the e_g band, e.g., by a Jahn-Teller distortion of the $3d^4$ Mn³⁺ ion. However, we discount this explanation because it requires a rather good cancellation of both the prefactors (number of holes/electrons) and the respective gaps while still exhibiting acti-

vated behavior over a large temperature interval and a large range of concentrations. Therefore, we think that such a picture is not appropriate. Detailed Hall effect measurements could provide more information on this issue. However, these measurements are difficult because of the low mobility and the large temperature dependence of ρ_{xx} . We have thus far not yet been able to obtain experimental results for ρ_{xy} on either these ceramic samples or thin films.

A more appropriate interpretation of the disparity of Δ_S and Δ_p is in terms of lattice gas models, first discussed in the context of superionic solids and organic conductors.^{15,16} In these models the rate limiting step for charge transport is still the thermal activation of an electron above half the polaron binding energy E_p , which would exhibit only a modest x dependence. However, there is no heat transfer associated with the electron transfer since the polaron energy contribution in the chemical potential μ cancels the polaron energy term in $S^{(2)}/S^{(1)}$ [see Eq. (2)]. In this case one retains a temperature independent thermopower. This cancellation does not, in general, occur if particle-particle interaction are responsible for the heat transport. For instance, in lattice gas models the physical origin of Δ_S is the nearest neighbor (Coulomb) interaction V . More generally, Δ_S should originate from spin-polaron or polaron-polaron interactions. Its magnitude should give an estimate for the strength of those interactions. In addition, the vanishing value for Δ_S at $x=0.5$ is consistent with the effect of particle hole symmetry in the interacting problem.¹⁷ The spin-polaron interaction term was calculated by Liu and Emin¹⁸ for spin cluster models. They obtained a T^{-2} temperature dependence above T_c within their model. Our experimental result of a T^{-1} temperature dependence above T_c cannot support this model.

The description of colossal magnetoresistance effects has focussed on the double exchange mechanism, providing a link between the magnetic and transport properties. This leads to a description of scattering near and above T_c in terms of spin disorder. Whereas spin disorder scattering can reproduce the qualitative behavior near T_c , large quantitative discrepancies have been pointed out,⁷ such as the magnitude of the resistivity, and the doping dependence. Our experiments show unambiguously that above T_c a polaronic transport mechanism determines the electronic properties, although we cannot at this point distinguish between magnetic polarons or lattice polarons. Similar conclusions were obtained on thin film $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$.¹⁹

After discussing the temperature dependent term in the entropy, we now turn to the temperature independent term. The constant term S_0 has a very simple, unambiguous interpretation: in the high-temperature limit, when effects of interaction can be neglected, it measures the entropy carried by the mobile particles.¹¹ This quantity should know about the configurational entropy, thereby showing a strong x dependence, and the spin entropy. However, we find experimentally that S_0 is almost x independent. Assuming that each Ca results in a positively charged particle with a $S=3/2$ spin in the undoped $S=2$ spin system, we can use Heike's generalized formula for configurational degeneracy including the spin degeneracy,¹⁶ by taking the derivative of the degeneracy, g , with respect to the number of carriers $N_{3/2}$:

$$S = \frac{k_B}{|e|} \cdot \frac{\partial \ln(g)}{\partial N_{3/2}} = \frac{k_B}{|e|} \cdot \left[\ln \frac{x}{(1-x)} + \ln(4/5) \right]. \quad (3)$$

The first term is the conventional configurational term, and the second term represents the change in spin degeneracy by introducing carriers. For mobile electrons with spin=1/2 one obtains a spin contribution of $-k_B/|e| \cdot \ln(2) \approx -60 \mu\text{VK}$.¹⁶ Because we assume mobile positively charged particles moving in a rigid $S=2$ system with a spin degeneracy per site $g_S = 4^x \cdot 5^{(1-x)}$, we expect a backflow of spin entropy of $k_B/|e| \cdot \ln(4/5) \approx -20 \mu\text{VK}$, which is in good agreement with our experimental result. However, this implies that the configurational contribution to the thermopower, which is expected especially at low doping to be much larger than the spin contribution, is effectively quenched. This means that the configurational degeneracy is at an extremum with respect to changes in the carrier concentration. This can be interpreted either as the configurational entropy being minimized with respect to changes in number of carriers (charge ordering), or as the entropy being maximized as expected for systems near half filling. The latter state could possibly be realized by microscopic phase separation in regions near $x=0$ and $x=0.5$. The extraordinary aspect of our data is that the configurational entropic contribution to the thermopower is very small over the entire concentration range $0.1 \leq x \leq 0.6$.

With the above analysis we have made the simplifying assumption that each Ca adds one positively charge carrier into the system. This does not take into account the carriers induced by “self-doping,” i.e., carriers introduced by the

existence of vacancies on the La and Mn sites. Their concentration depends on the exact preparation conditions, especially the sintering temperature and oxygen partial pressure. It was shown by Tamura *et al.*²⁰ that for $x=0.2$ the vacancy concentration increases markedly only for extremely small oxygen partial pressures below 10^{-2} Pa at 1473 K. Mahendiran *et al.*²¹ show that the vacancy concentration is bigger for smaller x . Nevertheless, for small amounts of “self-doping” the spin entropy is unaffected, since it is determined by the ratio of the spin degeneracies and is independent of the doping concentration. Similarly, our experimental observation that the configurational term is independent of the doping concentration holds either for the nominal doping or the actual doping concentration.

In conclusion we have shown evidence that the transport mechanism above T_c is not dominated by spin disorder, resulting from the double exchange mechanism, but instead by small-polaron formation, presumably involving distortions of the Mn-O octahedra. The high-temperature limit of the thermopower is in agreement with backflow of spin entropy, expected from positively charged mobile particles, with spin $S=3/2$, in a rigid $S=2$ system. At the same time the doping independence of the Seebeck coefficient in the high-temperature limit hints at a remarkable collective nature of this fluid.

We acknowledge stimulating discussions with P. Littlewood, A. Millis, and B. Shraiman. J.Z. acknowledges support by the Dutch Royal Academy of Sciences (KNAW). We thank W. Bao for help with sample preparation.

-
- ¹J. H. Jonker and J. H. van Santen, *Physica (Amsterdam)* **16**, 599 (1950).
²R. von Helmholtz, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, *Phys. Rev. Lett.* **71**, 2331 (1993).
³S. Jin, M. McCormack, R. A. Fastnach, R. Ramesh, and L. H. Chen, *Science* **264**, 413 (1994).
⁴C. Zener, *Phys. Rev.* **81**, 440 (1951).
⁵R. M. Kusters, J. Singleton, D. A. Keen, R. McGreevy, and W. Hayes, *Physica B* **155**, 362 (1989).
⁶D. Emin, M. S. Hillary, and N-L. H. Liu, *Phys. Rev. B* **35**, 641 (1987); M. S. Hillary, D. Emin, and N-L. H. Liu, *ibid.* *Phys. Rev. B* **38**, 9771 (1988).
⁷A. J. Millis, P. B. Littlewood, and B. I. Shraiman, *Phys. Rev. Lett.* **74**, 5144 (1995).
⁸R. C. Miller, R. R. Heikes, and R. Mazelsky, *J. Appl. Phys.* **32**, 2202 (1961).
⁹T. Hashimoto, N. Ishizawa, N. Mizutani, and M. Kato, *J. Mater. Res.* **23**, 1102 (1988).
¹⁰P. E. Schiffer, A. P. Ramirez, W. Bao, and S.-W. Cheong, *Phys. Rev. Lett.* **75**, 3336 (1995).
¹¹A. P. Ramirez, P. Schiffer, S.-W. Cheong, C. H. Chen, W. Bao, T. T. M. Palstra, P. L. Gammel, D. J. Bishop, and B. Zegarski, *Phys. Rev. Lett.* **76**, 3188 (1996).
¹²J. Tanaka, M. Umehara, S. Tamura, M. Tsukioka, and S. Ehara, *J. Phys. Soc. Jpn.* **51**, 1236 (1982).
¹³T. Penney, M. W. Shafer, and J. B. Torrence, *Phys. Rev. B* **5**, 3669 (1972).
¹⁴T. A. Tyson, J. Mustre de Leon, S. D. Conradson, A. R. Bishop, J. J. Neumeier, H. Roder, and Jun Zang, *Phys. Rev. B* **53**, 13 985 (1996).
¹⁵S. M. Girvin, *J. Solid State Chem.* **25**, 65 (1978).
¹⁶P.M. Chaiken, in *Organic Superconductivity*, edited by V. Z. Kresin and W. A. Little (Plenum, New York, 1990).
¹⁷J. F. Kwak and G. Beni, *Phys. Rev. B* **13**, 652 (1976).
¹⁸N-L. H. Liu and D. Emin, *Phys. Rev. B* **30**, 3250 (1984).
¹⁹M. Jaime, M. B. Salomon, M. Rubinstein, R. E. Treece, J. S. Horwitz, and D. B. Chrisey, *Phys. Rev. B* **54**, 11 914 (1996).
²⁰S. Tamura and A. Yamamoto, *J. Mater. Sci.* **15**, 2120 (1980).
²¹R. Mahendiran, S. K. Tiwary, A. K. Raychaudhuri, T. V. Ramakrishnan, R. Mahesh, N. Rangavittal, and C. N. R. Rao, *Phys. Rev. B* **53**, 3348 (1996).