

Effect of doping Ca on polaron hopping in $\text{LaSr}_2\text{Mn}_2\text{O}_7$

S N BHATIA* and OSAMA A YASSIN

Department of Physics, Indian Institute of Technology, Powai, Mumbai 400 076, India

*Email: snbhatia@phy.iitb.ac.in

Abstract. From the transport studies in the bilayer manganites $\text{LaSr}_{2-x}\text{Ca}_x\text{Mn}_2\text{O}_7$, we have found the variable-range hopping model proposed by Viret *et al* to be inadequate to describe the transport of charge in these materials. The polarons appear to hop to their nearest neighbors with an activation energy, which in part is dependent on the magnetic interactions in the lattice.

Keywords. $\text{LaSr}_2\text{Mn}_2\text{O}_7$ manganite; Ca doping; polaron hopping; activation energy.

PACS No. 70.30.Vn

1. Introduction

Two mechanisms have been proposed for the charge transport in systems where the carriers are localized. The first proposed by Mott and Davis [1] involves hopping by the carriers called polarons to states of nearly equal energy. Such states are placed at random distances in the lattice due to the randomness in the potential. In the second process also, the conduction takes place by hopping by small polarons, but they hop only to the nearest neighbors and are assisted by the thermal energy. The resistivity, ρ , in this model is expected to follow the equation

$$\rho = \rho_0 T \exp(E_\rho/k_B T) \quad (1)$$

where E_ρ is the activation energy of the polarons and ρ_0 is a constant. In manganites the resistivity in the paramagnetic state shows the carriers to be localized. Both these models predict the temperature dependence of ρ equally satisfactorily. It is difficult to choose between the two models based on the data of resistivity alone. Also from the studies of monolayer manganites AMnO_3 , it has been observed that the magnetic properties of these compounds can be controlled by varying the size of the A-site ion. When Ca^{2+} is replaced by the larger Sr^{2+} ion, the Curie temperature T_C increases to ~ 370 K in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ [2]. The structurally distorted manganite $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (and also $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$) does not show either a metallic conductivity or a ferromagnetic ordering at any temperature, due to the A-site ion being small, while $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ becomes a ferromagnetic metal at 340 K [3]. We have also varied the magnetic state of the bilayer manganite $\text{LaSr}_2\text{Mn}_2\text{O}_7$ by substituting Sr with Ca. We have measured the resistivity and

thermoelectric power (TEP) of these manganites and have found the hopping to be thermally assisted. The TEP data further suggests these polarons to be magnetic in character.

Though Mott's model predicts correctly the temperature dependence of ρ , it has been found to be inadequate for these materials as it requires a very large randomness in the potential to predict the strong localization that is observed here. The potential is reduced considerably in the magnetic localization model proposed by Viret *et al* [4] according to which a magnetic random potential (MRP) arising due to the Hund's rule coupling $-J_{HS} \cdot S (=U_m)$ between the localized t_{2g} electrons (with spin S) and the spin (s) of the e_g electrons forming the conduction band is responsible for this localization of the carriers. The temperature dependence of resistivity is predicted to be

$$\rho = \rho_0 \exp(T_0/T)^{1/3} \quad (2)$$

(which is also characteristic of the variable range hopping in two-dimensional systems) both in the paramagnetic as well as the ferromagnetic regions. However, the characteristic temperature (T_0) is different, T_{op} and T_{of} , in the two regions and is given by

$$kT_{op} = 18\alpha^{-1}U_m v/(1-x)\varphi f \quad (T > T_C) \quad (3)$$

$$kT_{of} = kT_{op}[1 - \{M/M_S\}^{-1}] \quad (T < T_C) \quad (4)$$

where α^{-1} is the localization length of the carriers and the other symbols have their usual meanings [4]. In the paramagnetic state, the localized spins of the 3d orbital are randomly oriented in the absence of magnetic field. T_{op} therefore is predicted to have a (large) temperature independent value. Below T_C , the internal molecular field reduces these fluctuations, reducing thereby the value of T_0 to T_{of} . T_0 is thus expected to decrease at the onset of ferromagnetism. A similar decrease is expected with the external field.

2. Results and discussion

We have measured ρ and TEP of $\text{LaSr}_{2-x}\text{Ca}_x\text{Mn}_2\text{O}_7$ with $0 \leq x \leq 0.9$. The samples were prepared by the standard ceramic techniques and their phase purity was checked by X-ray diffraction. The details of sample preparation and measurement procedures are discussed elsewhere [5].

Above ~ 220 K, ρ shows a semiconducting behavior for all concentrations of Ca. It does not exhibit any discontinuity at the Curie temperature ~ 300 K. TEP is negative in the entire temperature range 220–600 K and decreases in magnitude with increase in x . We plotted $\ln \rho$ vs. $T^{-1/3}$. These plots were linear both above and below T_C . However at the Curie temperature there was no indication of any change in the value of T_0 as expected from eq. (2). For the magnetic random potential, TEP has not been formulated, but it is not expected to depend on the nature/type of disorder. It has been calculated for a random lattice potential (within the variable range hopping regime) for which it is proposed to vary with temperature as T^ν where $\nu = (3-m)/(3+m)$, when the density of states of the carriers varies as $(E - E_F)^m$ [6]. Plots of TEP vs. T^ν were not found to be linear for any value of m at all temperatures above T_C . On the other hand, following eq. (1), plots of $\ln \rho/T$ vs. $1/T$ were linear over the entire temperature interval 220–600 K with a decrease in the activation energy (E_ρ) at the magnetic ordering temperature as seen in figure 1. Further it is seen from

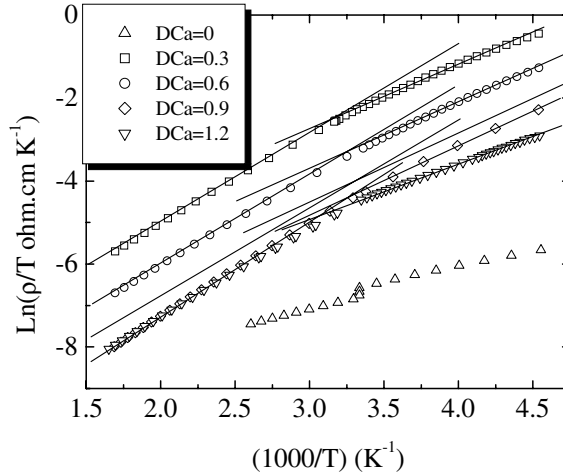


Figure 1. Activation energy change of the polarons at the Curie temperature for all concentrations of Ca.

the figure that E_p decrease with increase in Ca concentration. The TEP for such a hopping process is expected to vary as $1/T$. The present data showed a $A/T + B/T^2$ dependence for all concentrations of Ca (A and B are arbitrary constants). The presence of T^{-2} term together with the decrease in E_p at T_C observed here point towards a magnetic character of the polarons. Liu and Emin [7] have shown the TEP to vary as T^{-2} when the polarons hop amongst the magnetic clusters. Such clusters appear to be present in these samples as their susceptibility at high temperatures gives a large value for the Curie constant amounting to more than ten spins grouped together.

3. Conclusion

In conclusion we find the variable range-hopping model as proposed by Viret *et al* to be inadequate for the manganites studied here. The polarons appear to hop only to their [4] nearest neighbors. Their activation energy has a considerable contribution from the magnetic interaction in the lattice as it changes with the magnetic state of the samples.

References

- [1] N F Mott and E A Davis in *Electronic processes in non-crystalline materials* (Clarendon Press, Oxford, 1971)
- [2] J Fonticuberta *et al*, *J Appl. Phys.* **79**, 5181 (1996)
- [3] Y Moritomo, Y Tomioka and A Asamitsu, *Phys. Rev.* **B41**, 3297 (1995)
- [4] M Viret, L Ranno and J M D Coey, *J. Appl. Phys.* **81**, 4964 (1996)
- [5] O A Yassin, Ph.D. thesis (Indian Institute of Physics, Bombay, 2000)
- [6] I P Zvyagin in *Hopping transport in solids* edited by M Pollak and B Shklovskii (North Holland, Amsterdam, 1991) p. 147
- [7] N Liu and D Emin, *Phys. Rev.* **B30**, 13550 (1984)