Thermoelectric power measurements in Fe doped $La_{0.65}Ca_{0.35}MnO_3$

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Affia Aslam[1]**, S K Hasanain**[1,3]**, M Zubair**[1]**, M J Akhtar**[2] **and M Nadeem**[2]

[1] Physics Department, Quaid-I-Azam University, Islamabad, Pakistan
[2] Pakistan Institute of Nuclear Sciences and Technology, Nilore, Islamabad, Pakistan

E-mail: skhasanain@qau.edu.pk

Abstract
We report measurements of the thermoelectric power (TEP) on the
La$_{0.65}$Ca$_{0.35}$Mn$_{1-x}$Fe$_x$O$_3$ system for $0.00 \leqslant x \leqslant 0.07$. The ferromagnetic and
metallic transition temperatures are lowered and the TEP shows an increasingly
positive trend with the addition of Fe. We also observe a clear magnetic
contribution that manifests itself as a peak in the TEP close to the critical
temperature. The activation energies determined from the TEP are seen to
be insensitive to the Fe content. The data are interpreted firstly as showing
a decrease in the density of *active* holes, i.e. holes that can participate in the
hopping process, with increasing Fe content. Secondly the data suggest the role
of magnetic scattering due to the clusters formed by the antiferromagnetically
coupled Fe. Abrupt changes in the variation of the TEP are observed at the
concentration region $x \sim 0.04$ consistent with the hole density variation and
with previously reported transport and magnetic measurements.

1. Introduction

The ferromagnetic and metallic state in the large magnetoresistance manganates [1, 2] of the
type La$_{1-x}$Ca$_x$MnO$_3$ is well known to be weakened by the effects of both non-magnetic [3]
and magnetic [4–6] substituents at the Mn sites. In general these effects are related both to the
structural distortions introduced by the size difference of the impurity as well as to the purely
magnetic effects originating in the exchange interaction of the impurity and host Mn ions. The
two effects tend to become inter-linked since the structural changes produce carrier localization
that in turn affects the so-called double exchange interaction [7]. This latter interaction is well
known to be the source of the ferromagnetism in the CMR compounds. The case of Fe
impurities in the manganites [8–10] is particularly interesting since the Fe ions substitute for
the Mn as Fe^{3+} and have negligible size difference with the host Mn^{3+}. Hence the very strong

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[3] Author to whom any correspondence should be addressed.

weakening of the ferromagnetic, metallic state in the case of Fe is essentially a magnetic effect. The Fe^{3+} ion is in the state $S = 5/2$: hence, in the $La_{1-x}Ca_xMn_{1-y}Fe_yO_3$ system this results in both the t_{2g} and e_g spin-up sub-bands of Fe being completely filled [11]. The Fermi level, however, lies within the higher energy e_g spin-up sub-band of the Mn^{3+} and electron hopping between Fe and Mn is completely ruled out. The conduction continues to be defined by Mn^{3+} e_g states and hopping of the hole (on Mn^{4+}) between the Mn^{3+} and Mn^{4+}. Mossbauer measurements [10, 12, 13] have established that the Fe ions couple *antiferromagnetically* to the host Mn ions and indicate the presence of antiferromagnetically coupled clusters even below the ferromagnetic transition temperature T_c.

Previous experiments on Fe doped ferromagnetic compositions [8–12], including those of our own [14], have shown the lowering of the critical temperatures (by approximately 10–15 K/% Fe), increased resistivity and stronger localization of the charge carriers. In particular one observes [8, 14] a very pronounced decrease in the critical temperature and magnetic moment, and a very strong increase in the magnetoresistance at around 4% Fe content. This tendency of a sharp change in the properties around a particular composition prompted the suggestion [8] that the effect may be related to the Fe–Fe separation (at 4% concentration) acquiring an average value ($\sim$12 Å) that is close to the typical polaronic size of 12 Å [15]. This may lead to a strong disruption of the conduction and magnetic exchange processes. Thus it is clear that, even if the dominant effect of the Fe doping is to weaken the ferromagnetic double exchange due to its antiferromagnetic interaction with the Mn ions, it has profound effects on the polaronic transport activity. In the present work we explore the effects of Fe doping on thermoelectric power (TEP) of a ferromagnetic composition with particular reference to the model of small polaron hopping [16]. In this particular situation TEP is a more sensitive measurement than resistivity for identifying the role of various scattering mechanisms since it is not dominated by the presence of a few percolating paths. In particular, different scattering mechanisms often contribute to the TEP with opposite signs and temperature dependence, enabling their role to be separated out.

Our experiments on TEP in $La_{0.65}Ca_{0.35}Mn_{1-x}Fe_xO_3$ ($0.00 \leqslant x \leqslant 0.07$) complement the previously reported resistive and magnetic measurements on the same materials and yield new insight into the role of Fe in weakening the ferromagnetic and metallic state and its effects on hole concentration.

2. Experiment

The samples $La_{0.65}Ca_{0.35}Mn_{1-x}Fe_xO_3$, with $x = 0.0$, 0.02, 0.03, 0.04, 0.045, 0.05 and 0.07 were prepared in air by the standard solid state reaction technique described by us elsewhere [14] which also contains the x-ray analysis, resistive and magnetic characteristics of the samples. No appreciable change in the lattice parameters was observed with increasing Fe content. All the compositions studied here showed insulator to metallic transitions as well as the paramagnetic to ferromagnetic transitions. T_p is defined as the temperature where the peak occurs in the resistivity. The Curie temperature T_c was obtained from low field dc magnetization data and is defined as the midpoint of the ferromagnetic transition, i.e. where the magnetization has attained 50% of its low temperature, and approximately saturation, value. The values of these temperatures for various compositions are given in table 1. It was also observed that there are abrupt changes in magnetic moment and magnetoresistance at $x = 0.04$ [14]. The resistivity data for $T > T_p$ was fitted using two models: the polaronic model [16] and the variable range hopping (VRH) model [17]. It was observed that the VRH model gave, in general, a better fit to resistivity data almost all the way down to the resistivity peak than the polaronic model. The localization length $1/\alpha$ obtained from the fit to the VRH model showed

Table 1. Magnetic and transport properties of La$_{0.65}$Ca$_{0.35}$Mn$_{1-x}$Fe$_x$O$_3$: T_c magnetic critical temperature, T_p resistive critical temperature, T_s peak value in $S(T)$ curve, ε_a activation energy obtained from TEP, W activation energy obtained from resistivity and hole density $(1-c)$.

| x	T_c (K)	T_p (K)	T_s (K)	ε_a (meV)	W (meV)	Hole density $(1-c)$
0	265	270	250	—	129	—
0.02	235	245	223	12.9	145	0.44
0.03	218	222	203	7.8	152	0.37
0.04	210	208	206	12.5	125	0.43
0.045	185	191	195	14.5	—	0.42
0.05	175	185	190	11.4	112	0.39
0.07	140	135	146	10.7	131	0.37

a consistent decrease from 2.0 to 1.1 Å as x varied from 0.04 to 0.10 [14], while the hopping distance is estimated to be about 13.23 Å for $x = 0.04$. The estimate for the hopping distance corresponds to about 3–4 times the Mn–Mn separation, while the localization length is larger or comparable to the Mn^{3+} radius (i.e. 0.7 Å). Such values have been considered plausible for these polaronic systems [18]. These background characteristics of the materials establish that the conduction is describable as a hopping process where the carriers, presumably localized small polarons formed from the holes on the Mn^{4+} ions, move by hopping to nearby sites of favourable energies. Increasing Fe content weakens ferromagnetism, increases the resistivity and produces a higher degree of localization of the carriers, as evidenced by the decrease in the localization length.

TEP measurements for La$_{0.65}$Ca$_{0.35}$Mn$_{1-x}$ Fe$_x$O$_3$, with $x = 0.0$, 0.02, 0.03, 0.04, 0.045, 0.05 and 0.07 were performed by using the differential method with typical temperature differences of 1–1.5 K between the two ends of the sample. Sample length was typically in the range of 7–10 mm. The lead wires were made of copper while the voltage contacts were made with conducting silver paint. The temperatures were monitored using two copper–constantan thermocouples. Temperature was controlled to ±0.1 K. All the data shown were obtained during heating up the sample from the low temperature side, typically from 85 K up to room temperature. Background corrections and reproducibility were carefully checked for all the reported measurements.

3. Results and discussion

In figures 1 and 2 we show the combined data for the TEP for all the studied concentrations in the range 85–290 K. Several basic features are evident from these data. The undoped sample ($x = 0.0$) starts with the TEP $S \sim -18\ \mu$V K^{-1} at high temperature and smoothly declines towards zero, showing a more rapid decrease beginning at the critical temperature T_c (265 K). The negative values of S and the typical high temperature value of $S \sim -20\ \mu$V K^{-1} for a Ca composition in excess of 25% are widely reported [19, 20].

As x (the Fe content) is increased a systematic trend is observed. The value of S becomes more positive with the decrease in temperature, develops a peak at a temperature represented by the symbol T_s and then declines towards zero for all compositions. The low temperature behaviour where S decreases towards zero is consistent with the metallic behaviour exhibited in the resistivity. For $x \leqslant 4\%$ S is negative while for $x \geqslant 5\%$ it is almost entirely positive over the entire temperature range. For the 4 and 4.5% compositions there is almost complete overlap in $S(T)$ for $T < 175$ K which is below the T_c of both compositions. However, for the same two compositions there are very pronounced differences in the behaviour of S for higher
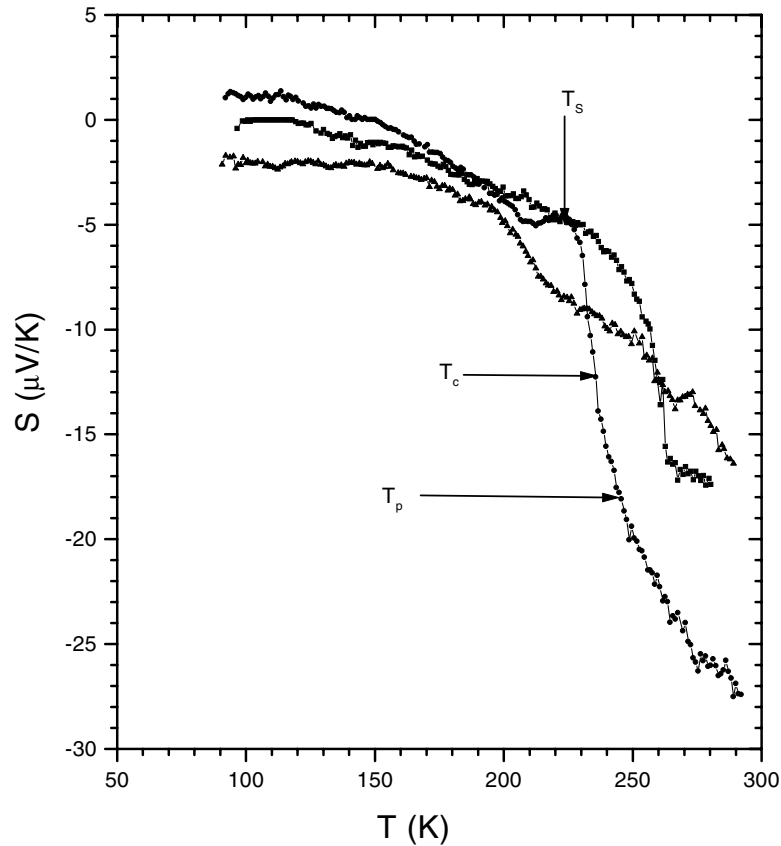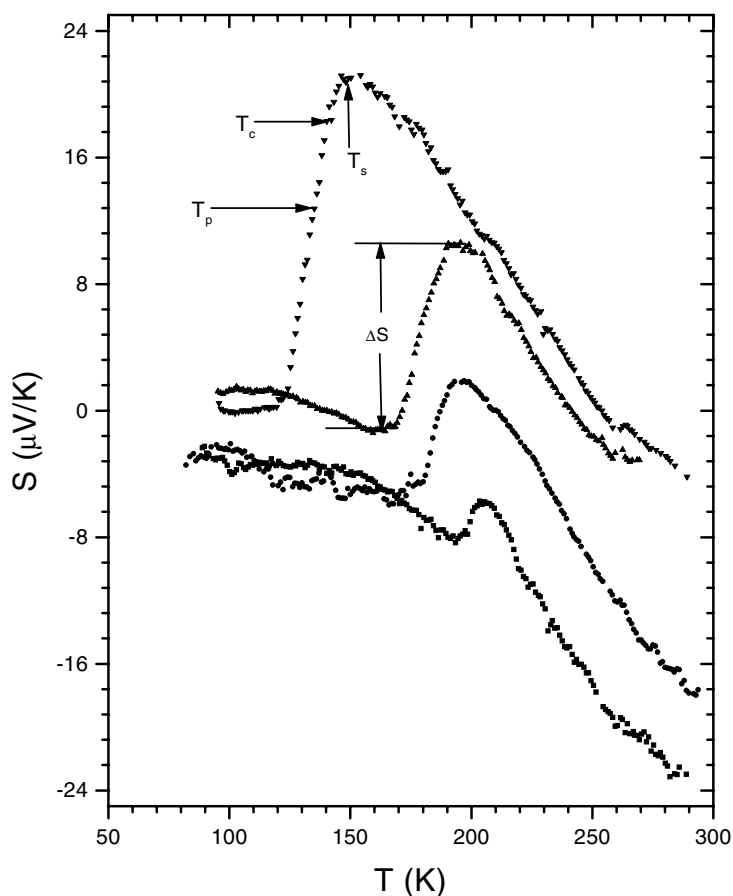
Figure 1. TEP $S(T)$ of the $La_{0.65}Ca_{0.35}Mn_{1-x}Fe_xO_3$ system for $0 \leqslant x \leqslant 0.03$: $x = 0.00$ (■), $x = 0.02$ (●), $x = 0.03$ (▲). T_s the temperature of the peak in $S(T)$, T_p the temperature corresponding to the resistivity peak and the Curie temperature T_c, as defined in the text, are shown for $x = 0.02$.

temperatures, i.e. in the paramagnetic and insulating phases. These differences are illustrated in figure 2 where it is evident that in this range of compositions $4 \leqslant x \leqslant 5\%$ there are large changes in S corresponding to small composition changes, in particular the crossover from completely negative to completely positive values over the entire temperature range.

Continuing with general observations on the variation of $S(T)$ with x we note the development of a pronounced peak at temperature $T_s \sim T_c$. For $x = 0.02$ this appears as a small bump and with increasing Fe content this becomes a very pronounced maximum. The peak temperature T_s while being close to the ferromagnetic transition temperature T_c and resistivity peak temperature T_p for the corresponding composition, is not entirely coincident with either. For compositions $x < 0.04$, T_s lies below T_c and T_p and for $x > 0.04$ the trend is reversed in the sense that the peak in S occurs at higher temperatures compared to both T_c and T_p, However, for $x = 0.04$ T_s is very close to T_c and T_p. It is also noticeable regarding this anomalous peak in S that, irrespective of the composition, its effect is to lead to a more positive value for S as the temperature is increased towards T_s.

We label the magnitude of this peak in the TEP as ΔS, which we define as the drop from the maximum to the point where the smooth decline towards zero takes over (see

Figure 2. TEP $S(T)$ of the La$_{0.65}$Ca$_{0.35}$Mn$_{1-x}$Fe$_x$O$_3$ system for $0.04 \leqslant x \leqslant 0.07$: $x = 0.04$ (■), $x = 0.045$ (●), $x = 0.05$ (▲), $x = 0.07$ (▼). The drop in the TEP ΔS, as defined in the text, is shown for $x = 0.05$. T_s, T_p and T_c, defined as in figure 1, are shown for $x = 0.07$.

figure 2 for a typical example of ΔS). The values obtained thus are plotted versus the concentration x in figure 3. It is noticeable that, while ΔS does in general increase with x, there is a sharp increase in its value at $x \geqslant 4\%$, which is consistent with the sharp changes in the magnetoresistance as well as the magnetic moment around this concentration [14]. For comparison, the magnetoresistance for these compositions at their respective T_c and $H = 15$ kOe are also included in figure 3. It is evident that the general trend of ΔS as a function of x is very similar to that of the magnetoresistance of the same compositions at the peak T_p. So it is suggested that this peak in S is being contributed by the magnetic scattering due to the Fe ions. In the case of the magnetoresistance measurements the external field suppresses the magnetic scattering close to the transition, while in the present case the development of the ferromagnetic order itself suppresses this scattering and its contribution to the TEP. Although in many metallic samples there is a peak in $S(T)$ curves at low temperatures due to phonon drag, this peak in thermopower usually appears at around $\theta_D/5$ [21], where θ_D is the Debye temperature. Since the Debye temperature for manganites is $\sim$375 K [21, 22], the peak due to phonon drag in manganites is expected to appear at 75 K, which is much lower than T_s, the temperature of the observed peaks in the thermopower.
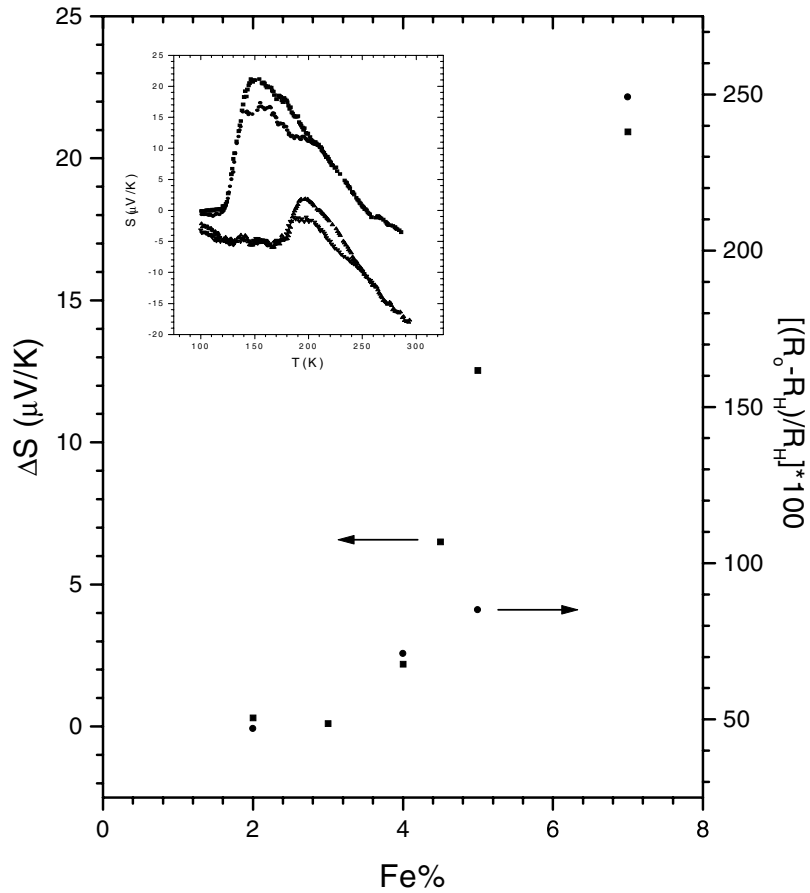
Figure 3. The drop in the TEP ΔS (■) and magnetoresistance (●) versus corresponding Fe concentration (x). Inset shows the dc field dependence of $S(T)$ for $x = 0.07$ and 0.045: $x = 0.07$ without field (■), $x = 0.07$ at $H_{dc} = 550$ Oe (●), $x = 0.045$ without field (▲), $x = 0.045$ at $H_{dc} = 550$ Oe (▼).

The magnetic origin of this peak was explored by the measurement of S in the presence of a small applied magnetic field. The behaviour of $S(T)$ for three different compositions was studied at 550 Oe applied field and qualitatively the same behaviour was observed in all three cases. Two of these compositions (i.e. for $x = 0.045$ and $x = 0.07$) are shown in the inset of figure 3. For both compositions, the two curves ($H = 0$ and $H > 0$) completely overlap below T_c, while above T_c the field suppresses the peak very significantly. While further work is underway to explore the effects at other fields, we base our discussion on the hypothesis that the suppression of the peak by applied fields is indicative of the magnetic scattering contributing strongly to the thermopower in the region close to the critical temperature ($T \geqslant T_c$). Presumably the applied field suppresses this scattering and consequently the value of S.

We shall now attempt to explain some of the main features observed in the thermopower peak structure, both as a function of temperature and the Fe concentration. As is well known, Fe ions have an antiferromagnetic interaction with their neighbours in these materials and there is clear evidence from Mossbauer measurements of the continued presence of clusters even

below the ferromagnetic T_c [10, 12, 13]. Also there is clear evidence from the Mossbauer measurements [8] that the Fe spins sharply sense the ferromagnetic transition, as evidenced by the sharp changes in the line shape and number. The effects of an antiferromagnetically coupled impurity in an otherwise ferromagnetic host matrix have been worked out for some cases [23]. A major result of the analysis was that in such cases, namely an antiferromagnetically coupled impurity in a ferromagnetic host matrix, the ground state is inhomogeneous, resulting in localized excitations where a reduction of the total spin takes place in the vicinity of the impurity. Simopoulos *et al* [12] have argued that their Mossbauer data is consistent with the picture of the Fe spin having the full value $S = 5/2$ at low temperatures and as the temperature is increased the localized states (where $S = 3/2$ and $1/2$) are increasingly populated. The contribution to the TEP which manifests itself as a peak near T_c could be an outcome of scattering from such spin inhomogeneities, which we may consider as clusters, which are expected to become more pronounced as the impurity (Fe) concentration increases. The presence of the peak at $T < T_c$ for small Fe content suggests that these excitations continue down to lower temperatures ($T < T_c$). This could be due to the fact that the corresponding (antiferromagnetic) clusters can be expected to be small; hence each of these may be strongly coupled *within* themselves (intra-cluster interaction). Hence the overall ferromagnetic alignment may not be able to overcome these small clusters of strongly coupled spins that continue to scatter the carriers even below T_c. As x is increased and the clusters become larger there would also be peripheral spins that are weakly coupled to the main cluster. With decreasing temperatures ($T \sim T_c$) and the growth of the ferromagnetic alignment in the matrix these weakly coupled spins could be absorbed in the ferromagnetic network, thereby weakening the antiferromagnetic clusters and resulting in less scattering from them. As T is lowered further more and more of the clusters are absorbed into the main ferromagnetic network. Thus the peak in S probably corresponds to the temperature where the antiferromagnetic clusters or localized excitations are not sustainable against the rapidly growing ferromagnetic correlations. After these clusters are absorbed into the main network the system exhibits the metal-like decrease to small values.

The general trend of increasingly positive values for S with increasing Fe content, in particular for $x \geqslant 0.04$, is very reminiscent of the behaviour of the samples of the type La$_{1-x}$Ca$_x$MnO$_3$ with increasing Ca content x [20]. We note that in this latter case, the smaller x compositions (small number of holes) have positive S, while with increased x (hole content) S tends to be negative. This suggests that the positive trend observed with increasing Fe content also originates from the same source, namely a decrease in the number of holes. While this is well accepted for the case of the $x = 0.0$ (undoped) system, i.e. adding Ca increases the hole concentration, there is some controversy regarding the effect in Fe doped systems. It is well established that Fe enters the system as Fe^{3+} and replaces the Mn^{3+} ions only [8, 10, 11]. The number of Mn^{4+} ions is generally accepted to remain unchanged. However, Gutierrez *et al* [24] argue that in the Fe doped La$_{0.7}$Pb$_{0.3}$MnO$_3$ system the effect of adding Fe is to decrease the Mn^{4+} concentration. Polaron formation and its hopping depend, of course, on both the concentrations, since it is the Mn^{3+} sites which are Jahn–Teller active and the distortion of the oxygen octahedra at these sites traps the carrier (hole) from the Mn^{4+} ion. Indeed the polaron in this case is the hole trapped at this distorted site [17]. Thus a decrease in either Mn^{3+} or Mn^{4+} from their undoped values (no Fe ions) would be deleterious to the formation of the polaron. We believe that even if the number of holes (Mn^{4+} ions) is considered to be independent of Fe content, the number of *active* holes, i.e. those which can hop to Mn^{3+} sites, will undoubtedly decrease with increasing Fe content: firstly, due to the increased Mn^{4+}–Mn^{3+} separation, on the average, and secondly the Fe spins cause spin deviations from ferromagnetic alignment in their neighbourhood and prevent the hopping which is spin dependent. Fe concentration

thereby increases the resistivity by cutting down the number of percolating paths available for holes [10]. Hence the variation of S as a function of Fe content is indicative of a decrease in the concentration of *active* holes, i.e. those which are able to hop to Mn^{3+} sites (as opposed to the total hole concentration).

However, the change from positive to negative S is a fortuitous development caused by the presence of two terms of opposite signs in TEP in the small polaron systems [25]. One term due to the spin entropy S_σ has, in the absence of magnetic ordering, a temperature-independent value of $\sim -19 \mu V\,K^{-1}$ [19]. The second contribution to S arises from the motion of charge carriers, in this case the small polarons. The general form of the temperature dependence of S at $T > T_c$ for the latter contribution is given by [19, 26]

$$S_c = (k_B/e)((\varepsilon_a/k_B T) + S_o) \tag{1}$$

where S_o is a temperature-independent constant. (In this relatively high temperature region where the CMR system is non-metallic and has polaronic conductivity the phonon drag term is not expected to be significant [27].) The energy ε_a appearing in this expression is different from the total activation energy (W) measured via resistivity which consists of two parts, $W_H + \varepsilon_a$. While the former (W_H) relates to the polaron binding energy, the latter ε_a is equal to the difference in energy between two identically distorted sites with and without a hole [26, 28]. The thermopower of small polaron hopping depends only on the latter, i.e. ε_a, and hence it is usual to measure much smaller activation energies via thermopower as compared to those measured resistively, in systems where small polaron hopping is the dominant conducting mechanism. In the high temperature limit ($\varepsilon_a/kT \ll 1$) the above expression for the thermopower for small polarons is given by the modified Heikes formula [29, 30]

$$S_c(T \to \infty) = (k_B/e) \ln(2(1 - c)/c) \tag{2}$$

where c is the number of electrons per available site and $(1 - c)$ is the hole concentration. The above expression is valid for the case of complete correlation which precludes double occupancy of a site due to the on-site Coulomb repulsion. To be able to translate the above discussion into quantitative assessments of hole carrier densities we adopted the following procedure. After subtracting the spin entropy contribution of $-19\ \mu V\ K^{-1}$ (assumed to be independent of Fe content) from the $S(T)$ data they were fitted to equation (1), as shown in figure 4. (From these fits the values of the activation energy ε_a were also obtained and are given in table 1.) The $S(T)$ fits above the respective critical temperatures were extrapolated to $T = 500$ K. The resulting values for S at 500 K were then used in Heikes' formula (equation (2)) to determine the hole density for each composition. The corresponding values are given in table 1 and shown in figure 5. One notes that there is a general trend of decreasing values of the hole densities with increasing Fe content. The trend is systematic with the density decrease from 0.44 to 0.37 ± 0.01 as x increases from 0.02 to 0.07. While these values of hole densities are generally on the higher side, one notes that these values, even in the best case, may depart from the nominal Mn^{4+} content due to various reasons. These include the effects of disproportion, oxygen non-stochiometry and cation vacancies [19, 31] which are common in air-annealed samples such as ours. What, however, is emphasized here is that within these limitations of the data the general trend is that the overall hole content appears to decrease from almost 44% to almost 37% as x varies from 2 to 7%.

We now discuss the values of the activation energies ε_a obtained from the fit to equation (2) and their variation with Fe content. (Since we did not have a sufficient number of data points above T_c for the $x = 0.00$ composition the activation energy could not be determined by this fit.) We find that the values are very sensitive to the region above the critical temperature chosen for fitting. The values decrease from 17 meV for $x = 0.02$ to 9 meV for $x = 0.07$ if the fitting is done from just above the critical temperature T_c (or from above T_s for $x > 4\%$) of each
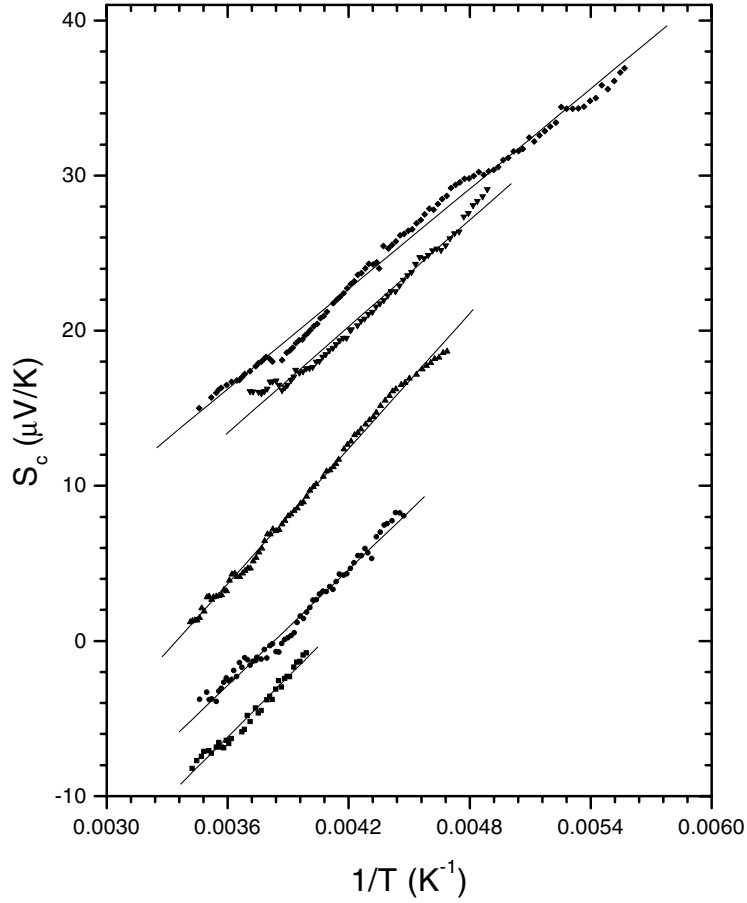
Figure 4. S_c versus $1/T$ for $T > T_c$ where S_c is the TEP value obtained after subtracting the spin entropy contribution. Symbols represent the experimental data while full lines represent the fit to equation (1): $x = 0.02$ (■), $x = 0.04$ (●), $x = 0.045$ (▲), $x = 0.05$ (▼), $x = 0.07$ (♦).

composition. However, if the fitting is made by excluding the region $1.0 < T/T_c < 1.10$ the values obtained for the activation energies are essentially constant (12 ± 2 meV). This suggests that, in the region where the magnetic effects are comparatively negligible, the activation energies are essentially independent of Fe concentration. Ogale *et al* [8] arrive at a similar conclusion for similar Fe compositions. The obtained thermopower activation energy ε_a is very small compared to the activation energies W obtained from the resistivity, which are in the range 110–140 meV. The difference between the two values, ε_a and W, is generally observed in the CMR system [19] and this is taken to be an indicator of conduction due to the hopping of small polarons as opposed to their band transport.

The general treatment of thermopower due to magnetic impurities, where the energy dependence of the conductivity is dominated by the variation of the density of states with E, takes the form [32]

$$S \sim (-\pi^2 k^2 T^2/3e)(\partial \ln D(E)/\partial E)_{E_F} \tag{3}$$

where $D(E)$ is the density of states and E_F is the Fermi energy. If the current carriers are holes ($e > 0$) then the observed positive sign of the magnetic contribution (ΔS) would imply
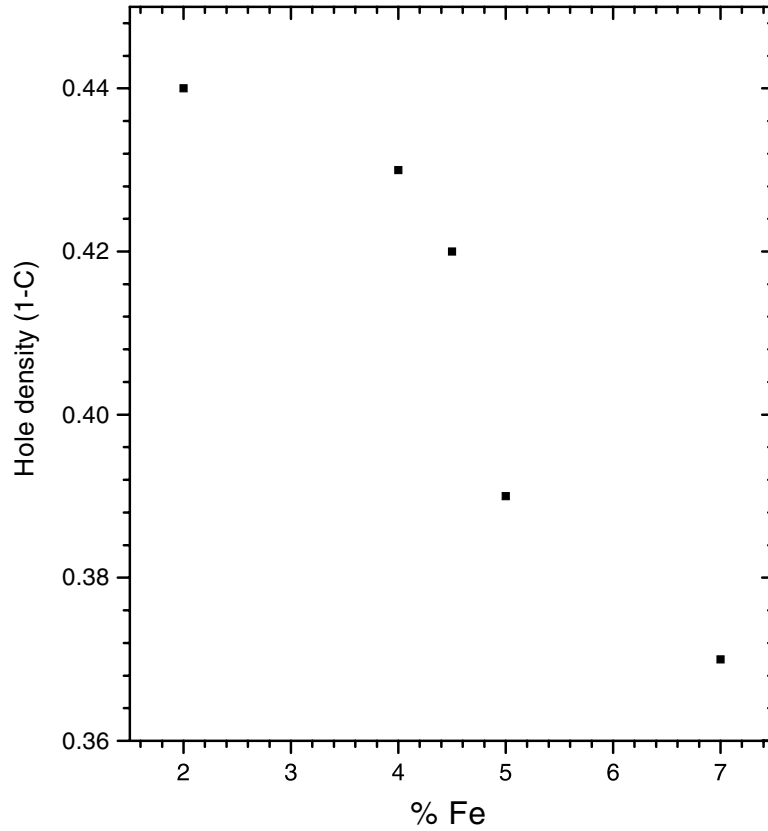
Figure 5. Hole density $(1 - c)$ obtained from the fit in figure 4 (as explained in the text) versus the corresponding Fe concentration (x).

from equation (3) that $(\partial \ln D(E)\partial E)_{E_F} < 0$, i.e. the density of states (of holes) is decreasing with increasing energy in the e_g sub-band.

4. Conclusions

Our study of the TEP in these compounds clearly supports the result that the effect of Fe doping is to reduce the number of holes available for the formation of polarons and hence leads to the observed increase in resistivity and the lowering of T_c. Sharp changes in the hole concentration around 4–5% are again consistent with the various other effects, e.g. magnetoresistance, critical temperature and magnetic moment, etc, which we have reported earlier. It thus appears that the abrupt changes in the T_c, magnetoresistance and saturation moment, etc, relate to the abrupt decrease in the effective or *active* hole density at $x \sim 0.04$ that profoundly affects the transport properties through its negative impact on the polaron density.

We have also shown for the first time a clear peak in the thermopower as Fe atoms are introduced. It is suggested that this peak is magnetic in origin, has a positive contribution to S and most probably arises from the scattering of the carriers by the localized excitations of the clusters formed by the Fe and its neighbours. The magnetic contribution to the TEP also grows rapidly around 4–5% and its variation with concentration is very similar to that

of the magnetoresistance. Finally we observe that the activation energies measured by the TEP, away from the magnetic region, are independent of the Fe concentration. Since this energy essentially reflects the energy difference of the two sites between which hopping takes place (i.e. the energy of the same site with and without a hole), the Fe independence of the activation energy implies that polaron characteristics are not affected by the Fe concentration. However, as the region closer to T_c is approached the magnetic interactions significantly affect the energy difference of these same states and we observe that the activation energies ε_a tend to decrease with increasing Fe content. We understand it as: that increased magnetic disorder that accompanies indicating the Fe doping diminishes the energy differences between a Jahn–Teller distorted site with and without a hole.

Further experiments are underway to explore the field dependence of S in more detail and also to study the effects of Fe dopants on the thermopower of compositions *away* from the strongly ferromagnetic region.

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