

A -site dependent percolative thermopower and Griffiths phase in $\text{Pr} (0.7 - x) \text{Ho} x \text{Sr} 0.3 \text{MnO}_3$ ($x = 0.0, 0.04, 0.08, \text{ and } 0.1$)

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A-site dependent percolative thermopower and Griffiths phase in $\text{Pr}_{(0.7-x)}\text{Ho}_x\text{Sr}_{0.3}\text{MnO}_3$ ($x=0.0, 0.04, 0.08, \text{ and } 0.1$)

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We report our analysis of thermopower $S(T)$ of $\text{Pr}_{(0.7-x)}\text{Ho}_x\text{Sr}_{0.3}\text{MnO}_3$ ($x=0, 0.04, 0.08, \text{ and } 0.1$) compounds within a percolative framework and correlate the results with the existence of a Griffiths phase. The Griffiths temperature, at which ferromagnetic metallic clusters nucleate above T_C , is evaluated. We further show that the Griffiths phase extends over a higher temperature range above T_C with increase in the variance of ionic radii of the A site. © 2005 American Institute of Physics. [DOI: 10.1063/1.1855613]

I. INTRODUCTION

$\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ belongs to a family of hole doped mixed valence manganite perovskite which exhibits colossal magnetoresistance (CMR).¹ The CMR effect was explained using the double exchange model² where electrons hop from singly occupied e_g orbital of Mn^{3+} ions to empty e_g orbital of neighboring Mn^{4+} . However, large changes in resistivity could not be explained within this framework³ and a localization mechanism not considered by this model was found to be necessary.³ Meanwhile, there is evidence from both experiments⁴ and theoretical calculations⁵ that polaron formation due to a strong Jahn–Teller interaction plays a major role in understanding the underlying physics in these materials. A competition between the double exchange mechanism, which tends to delocalize charge carriers in order to maximize the kinetic energy gain, and the electron phonon coupling, which tends to localize the carriers,⁶ results in the formation of insulating and metallic clusters which coexist above and below T_C . The metal-insulator transition can be thought of as due to percolation of ferromagnetic metallic clusters across T_C .

Several factors control the paramagnetic to ferromagnetic transitions in these systems, namely, the concentration

x of the alkaline earth, the average A-site radii $\langle r_A \rangle$, etc.⁷ However when these two are kept constant it is seen that the variance of the average A-site radius disorder $\langle \sigma^2 \rangle = \sum y_i r_i^2 - \langle r_A \rangle^2$ (r_i is the ionic radii size of the A-site ion of concentration y_i) plays an important role.⁸ It is seen that T_C decreases linearly as $\langle \sigma^2 \rangle$ increases. This random distribution of the A-site ions and hence charges (2+ due to Sr and 3+ due to rare earth) result in random charge trapping centers for the e_g electrons. This leads to regions with varying mobility, leading to an intrinsic phase separation in the lattice.

Combined effects of intrinsic randomness, doping, and tendency to phase separate and self-trapping of polarons were found to result in the formation of Griffiths–McCoy singularities leading to divergences in free energy and magnetization at a temperature T_G well above T_C the Curie temperature.⁹ The temperature range between T_G and T_C was termed as Griffiths phase. Recently Salamon *et al.*¹⁰ reported that the CMR effect in manganites is due to the presence of a Griffiths singularity and the percolating entities are nucleated by the intrinsic arbitrariness in the lattice below a temperature T_C^{rand} that occurs above the para-ferromagnetic Curie transition. This T_C^{rand} can be thought of as equivalent to T_G and occurs due to the nucleation of ferromagnetic clusters whose local transition temperature is higher than T_C .

In this work, we report our analysis of thermopower of $\text{Pr}_{(0.7-x)}\text{Ho}_x\text{Sr}_{0.3}\text{MnO}_3$ ($x=0, 0.04, 0.08, \text{ and } 0.1$) compounds

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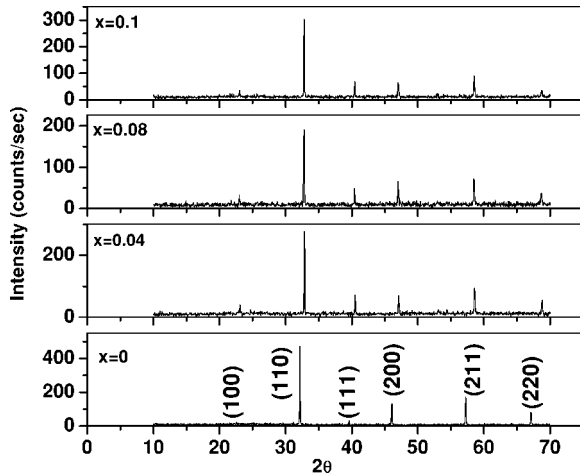


FIG. 1. X-ray diffractograms for $\text{Pr}_{(0.7-x)}\text{Ho}_x\text{Sr}_{0.3}\text{MnO}_3$ where $x=0, 0.04, 0.08,$ and 0.1 . The samples could be indexed to a pseudocubic structure.

within a percolative framework and correlate the results with the existence of a Griffiths phase, and evaluate T_C^{rand} from these analysis.

II. EXPERIMENT

The samples for the present study were prepared using the solid state route. The single-phase nature of the compounds was ascertained using x-ray diffraction using a Rich-Seifert diffractometer. The temperature variation of ac susceptibility was measured using a commercial ac susceptometer (Sumitomo, Japan). Thermoelectric power was measured by the standard dc technique using a home-made automated experimental setup.¹¹

III. RESULTS AND DISCUSSIONS

The x-ray diffractograms for all the samples are shown in Fig. 1. The samples are single phase in nature and could be indexed to a pseudocubic structure. Energy dispersion of x-ray analysis on these samples reveal that the samples are stoichiometric and the dopants are uniformly distributed in the sample. The temperature variation of ac susceptibility of the samples is shown in Fig. 2. The minimum in the temperature derivative of the ac-susceptibility plot was taken to be the Curie temperature T_C for all the samples. It is seen that T_C decreases with increase in A-site disorder (Table I). This is because, as the concentration of the Ho ion increases in the A-site, the disorder increases correspondingly. This leads to a decrease in the Mn–O–Mn bond angle leading to a lowering of the hopping integral.^{7,8}

Temperature variation of thermoelectric power $S(T)$ of all the samples is shown in Fig. 3. It is seen that while for the $x=0$ sample there is a slope change across T_C , a peak develops for the Ho doped samples. This peak becomes more and more prominent as $\langle\sigma^2\rangle$ increases and can be explained as follows. Above T_C , polaron formation occurs which leads to an activated behavior in $S(T)$. This high temperature behavior can be expressed as $S=S_0+k_B/e(E_S/k_B T)$ where S_0 is a constant representing the high temperature limit of thermopower and E_S is the activation energy.¹² Across T_C there is a change in the bandwidth and the mobility of the carriers

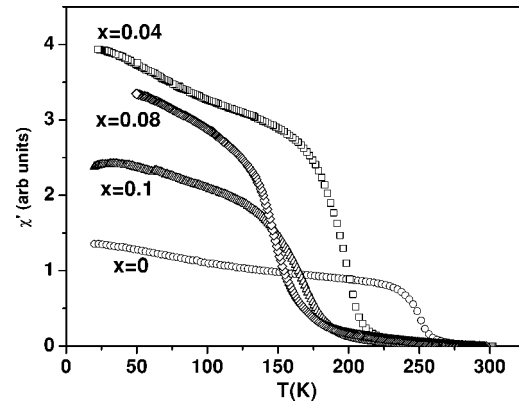


FIG. 2. Temperature variation of ac susceptibility.

increases. This manifests itself as a change in the slope in $S(T)$ as the sample is cooled. The peak in the $S(T)$ for $x > 0$ samples may arise due to the enhanced localization of carriers because of the A-site disorder. This results in increasing the activated behavior above T_C . This is supported by the fact that the value of activation energy increases with increase in $\langle\sigma^2\rangle$ (Table I). Once T_C is reached ferromagnetic ordering sets in and hence carriers get delocalized leading to a reduction in $S(T)$. Since competition between the two mechanisms, viz., the localization of carriers due to polaron formation and delocalization of the carriers due to the double exchange mechanism, results in percolative resistivity behavior;⁹ the thermopower may also thought to be percolative in nature.

The percolative nature of $S(T)$ has been analyzed using $S_{\text{total}}=pS_{\text{FMM}}(T)+(1-p)S_{\text{PMI}}(T)$, where p is the weighted metallic volume fraction and $S_{\text{FMM}}(T)$ and $S_{\text{PMI}}(T)$ being the contribution to $S(T)$ from the ferromagnetic metallic and paramagnetic insulating regions, respectively. A temperature dependence of $p=1/[1+\exp(-U/k_B T)]$ where $U=U_0(1-T/T_C^{\text{ep}})$ was used¹³ where T_C^{ep} is the transition temperature obtained from thermopower. The $S_{\text{PMI}}(T)$ was fitted to an expression $S_0+k_B/e(E_S/k_B T)$ where S_0 is a constant representing the high temperature limit of thermopower and E_S is the activation energy. $S_{\text{FMM}}(T)$ was fitted to a polynomial with T , T^2 , and T^3 terms.¹² The fits to the above model are shown in Fig. 3. It is seen that this model is able to fit the temperature variation in thermopower well, indicating the percolative nature of the thermopower. The value of transition temperature T_C^{ep} as obtained from the fit curve is given in Table I along with T_C . T_C^{ep} is found to be higher than T_C for all the Ho doped samples. The T_C^{ep} is plotted along with $1/\chi$ for the $x=0$ and $x=0.1$ samples alone for clarity in Fig.

TABLE I. Variance of the A-site disorder ($\langle\sigma^2\rangle$), lattice constant a , Curie temperature T_C , transition temperature from $S(T)$ T_C^{ep} , activation energy E_S , and $\Delta T=(T_C^{\text{ep}}-T_C)$ for $\text{Pr}_{(0.7-x)}\text{Ho}_x\text{Sr}_{0.3}\text{MnO}_3$ ($x=0, 0.04, 0.08,$ and 0.1).

x	$\langle\sigma^2\rangle \times 10^{-3} \text{ \AA}^2$	a (\AA)	T_C (K)	T_C^{ep} (K)	E_S (meV)	ΔT (K)
0	3.6	3.862	250	251	7.64	1
0.04	4.379	3.857	201	212	11.72	11
0.08	5.113	3.856	169	185	12.11	16
0.1	5.44	3.851	146	171	15.41	25

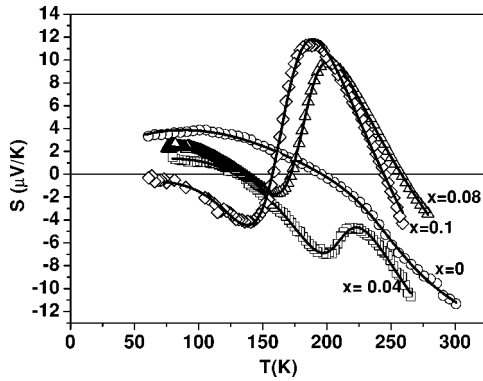


FIG. 3. Temperature variation of thermopower for $\text{Pr}_{(0.7-x)}\text{Ho}_x\text{Sr}_{0.3}\text{MnO}_3$. Symbols represent data points and line represents the fit to the percolative model.

4. The corresponding data for the other samples is listed in Table I. It is seen that while for the $x=0$ sample, T_C^{tep} coincides with T_C (marked by an up arrow in Fig. 4), the $x=0.1$ sample has $T_C^{\text{tep}} > T_C$. T_C^{tep} is found to coincide at a temperature where nonlinearity is seen in $1/\chi$ plot (Fig. 4).

According to Griffiths,¹⁴ ferromagnetic clusters start nucleating and begin interacting with each other at a temperature much above T_C at T_C^{rand} . The presence of these clusters leads to divergence in the susceptibility much above T_C and is seen as a kink in the $1/\chi$ vs T plot. As we cool the sample, the interaction amongst these clusters increases and leads to a long range ordering at T_C signaling the onset of ferromagnetic phase. Since transport is correlated with magnetism in these systems, the ferromagnetic interaction between these clusters leads to delocalization of the carriers which lowers the thermopower even before T_C is reached leading to a fall in $S(T)$ at T_C^{rand} which can be thought of as equivalent to T_C^{ep} . This leads to T_C^{ep} being much higher than T_C . Thus the onset of Griffiths phase, which is signaled by the presence of nonlinearity in $1/\chi$ vs T , coincides with T_C^{ep} (Fig. 4).

It is seen that the difference between T_C^{ep} and T_C increases with increase in $\langle \sigma^2 \rangle$. This may be due to the increase in localization centers for the carriers due to an increase in $\langle \sigma^2 \rangle$ which results in the formation of insulating spin clusters that coexist with the ferromagnetic clusters above T_C . Such clusters have been seen through synchrotron measurements in many manganites recently.¹⁵ These clusters impede the percolation of ferromagnetic clusters resulting in enhanced thermopower.

In conclusion, we have analyzed the thermoelectric power of $\text{Pr}_{(0.7-x)}\text{Ho}_x\text{Sr}_{0.3}\text{MnO}_3$ ($x=0, 0.04, 0.08$, and 0.1) within a percolative framework. It was seen that the thermoelectric transition temperature (T_C^{ep}) does not coincide with

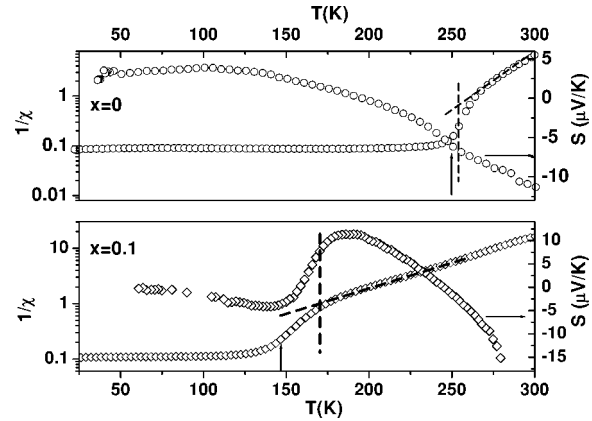


FIG. 4. $S(T)$ and $1/\chi$ plots for the $x=0$ and $x=0.1$ samples. The up arrow points to T_C . The dashed lines are guide to the eye. The dashed lines meet at T_C^{ep} .

T_C but is slightly above it for the $x > 0$ samples. This T_C^{ep} is ascribed to T_C^{rand} , the temperature at which ferromagnetic metallic clusters start nucleating above T_C . The difference between T_C and T_C^{ep} , the Griffiths phase regime, is found to increase as variance in A-site disorder increases.

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