Thermal/Electronic Transport Properties and Two-Phase Mixtures in La$_{5/8-x}$Pr$_x$Ca$_{3/8}$MnO$_3$

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We measured thermal conductivity $\kappa$, thermoelectric power $S$, and dc electric conductivity $\sigma$ of La$_{5/8-x}$Pr$_x$Ca$_{3/8}$MnO$_3$, showing an intricate interplay between metallic ferromagnetism (FM) and charge ordering (CO) instability. The change of $\kappa$, $S$ and $\sigma$ with temperature ($T$) and $x$ agrees well with the effective medium theories for binary metal-insulator mixtures. This agreement clearly demonstrates that with the variation of $T$ as well as $x$, the relative volumes of FM and CO phases drastically change and percolative metal-insulator transition occurs in the mixture of FM and CO domains.

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Immense resurgent activities on mixed-valent manganites reveal the importance of Jahn-Teller-type electron/lattice coupling in addition to the double exchange mechanism [1, 2]. Another important aspect of manganites is the existence of various-scale, real-space variation of physical properties or parameters. For example, even though the orthorhombicity of the average structure drastically decreases with the replacement of La by divalent ions in LaMnO$_3$, the large variation of local Mn-O bond lengths still remains intact [3]. In high divalent-ion doping ranges, charge ordering results in sheet-like arrangements of Mn$^{3+}$ and Mn$^{4+}$ ions with 10-30 Å length-scales [4]. Furthermore, ferromagnetic resonance experiments have shown the presence of two types of signals in ferromagnetic manganites, which was interpreted as evidence of electronic phase separation [6]. Various experiments suggest the existence of magnetic polarons or mobile ferromagnetic clusters at high temperature ($T$), which could be viewed as resulting from dynamic phase separation [6]. Recently, an electron diffraction study on low Curie temperature ($T_C$) manganites has revealed that there coexist ferromagnetic (FM)-metallic and CE-type charge-ordered (CO), insulating domains [8, 9]. It has been emphasized that this particular type of static phase separation is responsible for colossal magnetoresistance in low $T_C$ manganites. Various theoretical models for mixed-valent manganites also reveal the general tendency of static or dynamic electronic phase separation [10].

The transport properties of metal-insulator (M-I) mixtures have been perennial topics for both theoretical and experimental condensed matter physics [13]. Most of the experiments were performed on films with deposited M-I mixture [14] or artificial bulk M-I composites prepared under pressure [15]. The total electric and thermal conductivity and thermoelectric power of binary M-I mixtures were successfully explained by the effective medium theories [13, 15].

In this letter, we report the absolute values of the magnetization $M$, thermal conductivity $\kappa$, thermoelectric power $S$, and dc electric conductivity $\sigma$ of La$_{5/8-x}$Pr$_x$Ca$_{3/8}$MnO$_3$ with various $x$ and $T$. Various aspects of our results are consistent with the coexistence of FM and CO phases, whose relative volumes change with both $T$ and $x$, and the percolative M-I transition in FM-CO mixtures. Furthermore, the $T$ and $x$ dependence of $\sigma$, $\kappa$, and $S$ agrees well with the (general) effective medium theories for M-I mixtures.

High-quality polycrystalline specimens of La$_{5/8-x}$Pr$_x$Ca$_{3/8}$MnO$_3$ with $x=0.0$, 0.1, 0.2, 0.25, 0.3, 0.35, 0.375, 0.40, 0.42, and 0.625 have been prepared with the standard solid state reaction. We fixed the Ca concentration at 3/8 because our previous studies showed that $T_C$ is optimized at this particular Ca doping level [9]. $\sigma$ of all specimens with accurate geometry was measured with the standard four probe method, and $M$ was measured with a SQUID magnetometer. Both $\kappa$ and $S$ of the representative samples ($x=0.0$, 0.1, 0.25, 0.3, 0.35, 0.375, 0.40, 0.42, and 0.625) have been measured from 8 to 310 K with the steady state method. A radiation shield was used to obtain absolute $\kappa$ values [13].

The systematic $T$-dependent and $M/H$ curves are shown in Fig. 1. $M/H$ curves were measured in $H=2$ kOe, which was carefully chosen to align FM domains without influencing the CO insulating phase. These results indicate that La$_{5/8-x}$Pr$_x$Ca$_{3/8}$MnO$_3$ ($x=0.0$) is, basically, FM-metallic below 275 K, and that the ground state of Pr$_{5/8}$Ca$_{3/8}$MnO$_3$ ($x=0.625$) is CO-insulating below 225 K. The behaviors of $\sigma$ and $M/H$ for other $x$ compositions are systematically in-between those for $x=0.0$ and 0.625. Open circles (Fig. 1 (a)) represent the M-I transition points where $\sigma$ becomes (local) minimum [24]. Open circles in Fig. 1 (b) show the $M/H$ values at the M-I transition points determined from the curves. The average of those $M/H$ values (dotted line) is $17\pm2$ % of 8.1 emu/mol, the saturated $M/H$ value of $x=0.0$. Thus, with changing $T$, the M-I transition occurs when $M$ of each sample becomes about 17 % of that of $x=0.0$. 

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independent from $x$ value. If we assume that the $T$-dependent volume fraction $f(T)$ of the FM domain is proportional to $M(T)$ in H=2 kOe, the M-I transition with changing $T$ occurs when $f$ reaches $\sim 0.17$, close to the three-dimensional percolation threshold ($f_c$). This behavior can be also seen in the variation of $\sigma$ with $x$ for fixed $T$. In Fig. 2 (a), $\sigma$ vs. $M_s(T)/M_{0,0}(T)$ plot is shown at 10 and 100 K for various $x$. Interestingly, the samples with $M_s(T)/M_{0,0}(T) < 0.15$ are in the insulating regions of the curves in Fig. 1, while those with $M_s(T)/M_{0,0}(T) > 0.17$ are in the metallic regimes. Therefore, with variation of $x$, the M-I transition occurs when $M_s/M_{0,0} \approx 0.15-0.17$. These observations clearly suggest that the M-I transition with both $T$ and $x$ takes place when $f(T,x)$ ($=M_s(T)/M_{0,0}(T)$) becomes close to $f_c$. It is important to note that $M_{0,0}(T)$ contains the natural $T$-dependence of ferromagnetic moment so that $f(T,x)$ equals to $M_s(T)/M_{0,0}(T)$ (not $M_s(T)/M_{0,0}(T=0)$).

To gain further insights into the nature of the M-I transition, we measured $T$-dependent $\kappa$ and $S$ as shown in Fig. 3. First, we note that the estimated $\kappa_c$ from $\sigma$, using the Wiedemann-Franz law, is by two orders of magnitude smaller than the measured $\kappa(T)$ for all $x$, indicating the dominant phonon contribution. Furthermore, at high $T$ above $T_C$ or $T_{CO}$, $\kappa$ always increases when $T$ is raised, and the magnitude of $\kappa$ is in the range of 0.5-2 W/mK, comparable to that of amorphous solids [22]. This behavior has been attributed to local anharmonic lattice distortions associated with small polarons [22]. Related to this, $S(T)$ of all the samples at high $T$ follows the form $S_0 + E_g/\kappa B T$ with the gap energy $E_g$ systematically increasing from 4 meV ($x=0.0$) to 12 meV ($x=0.625$). These $E_g$ values are significantly smaller than the activation energies (125 meV: $x=0.0$ to 175 meV: $x=0.625$) associated with $\sigma(T)$. This difference can result from the small polaronic transport [23].

As shown in Fig. 3 (a), with increasing $x$, $\kappa(T)$ smoothly evolves from that of $x=0.0$ to that of $x=0.625$, and the $\kappa$ increase at $T_C$ becomes smaller. Consistently, $\kappa$ vs. $M_s(T)/M_{0,0}(T)$ at 10 and 100 K (Fig. 2 (b)) shows that $\kappa$ varies monotonically from the maximum ($\kappa_c$ of $x=0.0$) to the minimum ($\kappa$ of $x=0.625$). For $x=0.0$, $\kappa$ at $T_C$ increases suddenly, probably due to the suppression of local lattice distortions associated with small polarons. For $x=0.625$, $\kappa(T)$ behaves as in amorphous solids in the entire $T$ range, except for a slight increase at $T_{CO}$.

In comparison with $\kappa$ and $S$, $\sigma$ exhibits seemingly different behaviors with $x$. $S$ is very close to the metallic value, $S$ of $x=0.0$, even near $f_c$, where $\sigma$ ($\kappa$) is still significantly smaller than $\sigma$ ($\kappa$) of $x=0.0$. $S$ vs. $M_s/M_{0,0}$ at 100 K (Fig. 2 (c)) clearly demonstrates this tendency; $S$ is close to zero (slightly negative), and is insensitive to $M_s/M_{0,0}$ as long as $M_s/M_{0,0} \sim 10 \%$. In contrast, $\sigma$ for $M_s/M_{0,0} = 10 \%$ at 100 K is more than three orders of magnitude smaller than that of $x=0.0$. In fact, $T$-dependence of $S$ near $T_C$ is also consistent with this metallic $S$ behavior near $f_c$. With decreasing $T$ near $T_C$, $S$ starts to decrease, i.e., becomes metallic at $T$ higher than those for $\kappa$ and $\sigma$ changes. For example, in the heating curves of $x=0.35$, $S$ starts to decrease around 130 K, significantly higher than $T$ (100 K) for abrupt $\kappa$ increase or $T$ ($\sim 110$ K) for $\sigma$ minimum.

When thermal/electronic transport properties of our systems are viewed as those of M-I mixtures, the above peculiar $S$ behavior is, in fact, consistent with the theoretical prediction of effective thermoelectric power $S_E$ by Bergmann and Levy [18]. For an isotropic binary mixture, they showed that in terms of $\kappa$, $\sigma$, and $S$ of each component, $S_E$ is given by

$$S_E = S_M + (S_I - S_M) \left( \frac{\kappa_E/\kappa_M}{\kappa_I/\kappa_M} - 1 \right) / \left( \frac{\kappa_E/\kappa_M}{\sigma_I/\sigma_M} - 1 \right)$$

(1)

where the subscripts M and I refer to metallic and insulating components, respectively. $\kappa_E$ and $\sigma_I$ refer to effective thermal and electric conductivity, respectively, of the binary mixture. This equation has been successfully applied to explain $S$ behaviors of binary Al-Ge films [4]. When $\sigma_I/\sigma_M << \kappa_I/\kappa_M <$1 (which applies to our system) and for $f = f_c$, the above equation leads to $S_E \approx S_M$, which explains our experimental results noted above.

To quantitatively compare our results with Eq. (1), we calculated $S_E$ at every $T$ [21]. In this comparison, experimental $\sigma$ and $\kappa$, shown in Figs. 1 and 3, were used for $S_E$ and $\kappa_E$, and ($\sigma_1$, $\kappa_1$, and $S_1$) and ($\sigma_M$, $\kappa_M$, and $S_M$) are assumed to be identical with those of $x=0.0$ and 0.625, respectively. (For large $x$, it was difficult to measure $S$ at low $T$ due to high resistivity, so we assumed that $S_1$ changes as 1/$T$, and that $\sigma_1$ does exponentially.) The solid lines in Fig. 3 (b) depict the calculated $S_E$, using Eq. (1), for heating curves of $x=0.25, 0.35$, and 0.42. The calculated curves match with our experimental $S$ surprisingly well at all $T$ below $T_C$ or $T_{CO}$.

For $S_E$ (or $\kappa_E$) of a binary M-I mixture, Mclachlan [14] proposed the general effective medium (GEM) equation,

$$(1 - f) \left( \frac{\sigma_1^t/\sigma_M^t - \sigma_E^t/\sigma_M^t}{\sigma_M^t/A_1^t} \right) + f \left( \frac{\sigma_M^t - \sigma_E^t}{\sigma_M^t + A_M^t} \right) = 0$$

(2)

where $A = (1-f_c)/f_c$. The same equation also works for $\kappa$.

The critical exponent $t$ is close to 2 in three dimension. This equation has been successfully applied to isotropic inhomogeneous media in wide $f$ regions including percolation regime [4,14,17].

To apply the GEM equation to $\sigma(T)$, we assumed that $f(T,x) = M_s(T)/M_{0,0}(T)$, $S_M(T) = \sigma(T)$ of $x=0.0$, and $\sigma_I(T) = \sigma(T)$ of $x=0.625$. With the parameters $t=2$ & $f_c=0.17$, the calculated $\sigma_f$ for various $x$ are shown as solid lines in Fig. 4. At $T > \sim 80$ K, $\sigma_E(T)$ nicely matches the experimental $\sigma(T)$ even if $\sigma$ changes by 6 orders of
magnitude with $T$ and $x$. However, this agreement does not hold at very low $T$. The calculated $\sigma_E(T)$ at $T < 80$ K with the same parameters $t=2$ & $f_c=0.17$ significantly deviated from the experimental $\sigma(T)$. We found that at $T < 80$ K, the calculated $\sigma_E(T)$ matches the experimental $\sigma(T)$ better when $t$ is increased to $\sim 4$. This is more evident in the $x$ dependence of $\sigma$ at 10 and 100 K, as shown in Fig. 2 (a). $\sigma_E(100$ K), calculated with $t=2$ & $f_c=0.17$ (solid line), matches the experimental values (open circles) better than that with $t=4$ & $f_c=0.17$ (dotted line). However, $\sigma_E(10$ K), calculated with $t=4$ & $f_c=0.15$ (solid line), is closer to the experimental $\sigma$ (solid circles) than that with $t=2$ & $f_c=0.15$ (dashed line) [28]. (The change of $f_c$ in the range of 0.15-0.17 makes little difference.) These observations demonstrate that $t$, normally close to the three dimensional exponent of 2, becomes $\sim 4$ at very low $T$. A similar, drastic increase of $t$ has been noted in the case of tunneling transport for M-I mixtures [14,26], suggesting that the tunneling process between FM domains is important for $\sigma$ of our system at very low $T$ [27].

By using the GEM equation for $\kappa_E$, the $\kappa(T)$ for various $x$ can be calculated with the assumption that $\kappa_1(T) = \kappa(T)$ of $x = 0.625$, $\kappa_M(T) = \kappa(T)$ of $x = 0.0$, $t = 2$, and $f_c = 0.17$. The solid lines in Fig. 3 (a) represent the estimated $\kappa_E$ for $x = 0.1, 0.25, 0.35,$ and 0.42. In addition, the calculated $\kappa_E$ as a function of $M_f / M_0$ at 10 and 100 K is depicted as solid lines in Fig. 2 (b). Estimated $\kappa_E$ lines in Figs. 2 and 3 coincide with the experimental data well [28]. In order to confirm self-consistency, $S_E$ at 10 and 100 K is evaluated by using the calculated $\sigma_E$ and $\kappa_E$ (solid lines of Fig. 2 (a) and (b)), and the Eq. (1). The calculated $S_E$ (solid lines of Fig. 2 (c)) with the variation of $x$ is in good agreement with the experimental values.

The unambiguous agreement between the measured thermal/electronic transport properties and the calculated values based on Eqs. (1) and (2) strongly indicates that: (1) transport properties are dominated by thermal/electrical conduction in M-I mixtures, (2) the relative volume of the (FM) metallic phase is proportional to the measured $M(T,x)$, and (3) the $T$-dependent transport and magnetic properties of metallic and insulating phases are always that of $x = 0$ and 5/8, respectively. Combined with the earlier electron diffraction results [10], this successful agreement demonstrates that all of the thermal, electronic, and magneto-transport properties of $La_{5/3-x}Pr_xCa_{3/4}MnO_3$ are dominated by the percolative conduction through FM-metallic domains which is statically mixed with CO insulating domains. One surprising indication from our results is that at least in low $T_C$ materials ($x = 0.25$), the so-called Curie transition is, in fact, the M-I transition across percolation threshold, and the ordered FM moment changes smoothly near the percolative phase transition $T$.

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(slope changes) at the percolation points without showing metallic behavior just below the points. This originates from the drastic $T$-dependence of $\sigma$ of the insulating CO domains, as confirmed by the simulation results of $x=0.3$ in Fig. 4.

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FIG. 1. (a) $\sigma(T)$ of $\text{La}_{5/8-x}\text{Pr}_x\text{Ca}_{3/8}\text{MnO}_3$ for cooling (dotted lines) and heating (solid lines). (b) $M/H$ curves with zero field cooling. Open circles depict the M-I transition points determined from the data. $T$-dependent volume fraction of the FM domains, $f(T)$, for each $x$, was determined as $f(T,x) = M_x(T)/M_{0.0}(T)$.

FIG. 2. $S$, $\kappa$, and $\sigma$ values vs. $M_x/M_{0.0}$ at 10 and 100 K. The lines depict the theoretical predictions by Eqs. (1) and (2). The solid lines show the theoretical results with $t=4 \& f_c=0.15$ at 10 K and $t=2 \& f_c=0.17$ at 100 K. The dotted and dashed lines represent the theoretical results with $t=2 \& f_c=0.15$ at 10 K and with $t=4 \& f_c=0.17$ at 100 K, respectively. For the theoretical predictions (solid lines) of $\kappa$ at 10 and 100 K, $t=2 \& f_c=0.17$ were used.

FIG. 3. (a) $\kappa(T)$ for cooling (crosses) and heating (solid circles). The solid lines show the predictions of $\kappa(T)$ (heating) by Eq. (2) with $t=2 \& f_c=0.17$. (b) $S(T)$ of $\text{La}_{5/8-x}\text{Pr}_x\text{Ca}_{3/8}\text{MnO}_3$. Crosses represent cooling curves for $x=0.42$ and 0.35, and the other symbols represent heating data. ($S$ of $x=0.1$ is very close to that of $x=0.0$ and 0.25 below $T_C$ and omitted for clarity.) The solid lines show the predictions of Eq. (1) for $x=0.25$, 0.35, and 0.42 with heating.

FIG. 4. Theoretical predictions (solid lines) of $\sigma(T)$ by the GEM equation (Eq. (2)) with $t=2 \& f_c=0.17$ above $\sim 80$ K. Solid squares are the experimental data redrawn from Fig. 1.
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Fig. 4. K. H. Kim et al.