Mapping Colossal Magnetoresistance Phase Transitions with the Charge-Carrier Density Collapse Model

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We explain the observed specific heat anomaly (and hence entropy change) in the colossal magnetoresistive manganite Sm$_{0.55}$Sr$_{0.45}$MnO$_3$, by introducing phase separation into the current carrier density collapse theory via the notion of the ferromagnetic volume fraction. Within the same framework, we have also been able to explain the observed electrical resistivity of Sm$_{0.55}$Sr$_{0.45}$MnO$_3$ by using appropriate expressions governing the scattering mechanisms far away from the transition. Fitting specific heat and resistivity results has allowed us to separate the hopping activation energy of polaronic carriers and the bipolaron binding energy contributions to the exponential behaviour of resistivity in the paramagnetic phase.

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I. INTRODUCTION

The existence of a ferromagnetic-paramagnetic and metal-insulator transition in lanthanum manganites was established in the early 1950’s\cite{1,2} and was extensively studied thereafter. The magnetic transition which is associated with unusual transport properties, including large negative magnetoresistance, is observed in a family of doped manganites of perovskite structure, with the chemical formula Re$_{1-x}$A$_x$MnO$_3$, where Re is rare earth (La, Pr, Nd, Sm,...), and A is a divalent metal (Ca, Sr, Ba...). The recent resurgence of interest in these systems is related to the demonstration of a very large negative magnetoresistance in thin films\cite{3,4}, termed colossal magnetoresistance (CMR), which shows prospects of possible technological applications.

The metal-insulator transition in manganites has traditionally been attributed to the double exchange mechanism, which results in a varying bandwidth of electrons in the Mn$^{3+}$ d shell as a function of temperature and doping level\cite{5,7}. More recently it has been realized\cite{8,9} that the effective carrier-spin exchange interaction of the double-exchange model is too weak to lead to a significant reduction of the electron bandwidth. Millis et al\cite{8} proposed that there is in addition to the double exchange mechanism, a strong electron-phonon interaction arising from the Jahn-Teller splitting of the outer Mn d level, that plays a crucial role in the physics of manganites. X-ray-absorption fine structure of La$_{2/3}$Ca$_{1/3}$MnO$_3$ reveals differences between the nearest-neighbour Mn-O bond distributions at 80 K and above $T_c$. The single-site distribution at low temperature becomes a complex, multi-site distribution above $T_c$. The observed change is consistent with proposed small polaron related local Jahn-Teller distortions for $T>T_c$\cite{13}. A giant isotope effect\cite{10,11} suggest a very large electron phonon interaction, the sign anomaly of the Hall effect and the Arrhenius behaviour of the drift and hall mobilities, and the fact that polaron hopping satisfactorily accounts for resistivity in the paramagnetic phase\cite{12}, verify the polaronic nature of the charge carriers in perovskite manganites.

Low-temperature optical\cite{14,16}, electron energy-loss (EELS)\cite{17,18}, photoemission\cite{19,20}, and thermoelectric\cite{21} measurements showed that the ferromagnetic phase of manganites is not a conventional metal and confirmed that manganites were, in fact, charge-transfer doped insulators. EELS\cite{17,18} and O 1s x-ray absorption spectroscopy\cite{22} consistently show oxygen p holes as current carriers as opposed to d Mn$^{3+}$ electrons proposed in the double exchange theory. Moreover Hall effect measurements by Matl et al\cite{23} on La$_{1-x}$Ca$_x$MnO$_3$ have shown the carrier mobility near $T_C$ to be field independent. Also there are known classes of materials that exhibit colossal magnetoresistance in which it is guaranteed that the double exchange mechanism is non-existent such as pyrochlore manganites\cite{24} and chromium spinels\cite{25}. Like the perovskite manganites these compounds exhibit very large reductions in their electrical resistivity upon application of a magnetic field. However, unlike the perovskites there is no possibility for mixed valency, a prerequisite for the double exchange mechanism\cite{26}.

These observations strongly suggest that the double exchange mechanism is not the origin of colossal magnetoresistance.

These observations led to a novel theory of the ferromagnetic-paramagnetic phase transition driven by non-degenerate polarons in doped charge-transfer magnetic insulators, the so-called current-carrier density collapse (CCDC) theory\cite{27}. The CCDC theory takes into account the tendency of polarons to form local bound pairs (bipolarons) as well as the exchange interaction of p polaronic holes with d electrons. These bipolarons are practically immobile in manganites because of the strong electron-phonon interaction, in contrast with the case for cuprates, where bipolarons are mobile and responsible for in-plane transport\cite{28}. The argument behind the CCDC theory is that in the paramagnetic phase a fraction of polarons are bound into immobile bipolarons. As
temperature decreases within the paramagnetic phase, the density of bipolarons increases, resulting in fewer mobile polarons, and hence, the resistivity quickly increases, reaching a maximum at $T_c$. At some temperature $T_c$, non-degenerate polarons polarize the manganese spins via the p-d exchange interaction, $J_{pd}$, one of the polaron sub-bands falls below the energy of the bipolarons, thus causing pairs to break up, and the density of charge carriers (mobile polarons) increases suddenly. The occurrence of a deep minimum in mobile polaron density, near $T_c$ is the cause of the peak in resistivity, application of an external magnetic field will also cause a break up of bipolarons resulting in large negative magnetoresistance. The CCDC theory can explain physics of all colossal magnetoresistive materials including the pyrochlore manganites and chromium spinels.

Hall data by Westerburg et al. [29] has indeed shown a current carrier density collapse. Westerburg et al. [29] analysed the Hall data of $\La_{66}Ca_{33}MnO_3$ and $\La_{66}Sr_{33}MnO_3$ it was shown in both samples that with increasing temperature there is a sharp drop in the carrier density near the metal-insulator transition, further increase of temperature causes an increase in the density of carriers, such an observation is well explained by the CCCDC theory. A similar drop in the carrier density at the metal-insulator transition has been observed in $Nd_{65}Sr_{33}MnO_3$ [30]. There is other independent experimental evidence for the existence of bipolarons in perovskite manganites. Thermoelectric power measurements by Zhao et al. [31], show an isotope effect. If small polarons are bound to impurity centres, there would be no isotope effect in thermoelectric power measurements, whereas, if small polarons are bound into localized bipolarons states one would observe such an isotope effect, as the bipolaron binding energy is dependent upon the mass of isotopes. Perring et al. [32] have found short range antiferromagnetic order above $T_C$ in a so-called double perovskite, which may be evidence for the presence of singlet bipolarons.

A combination of low-energy electron diffraction and angle-resolved photoemission spectroscopy on some semiconducting interfaces has provided unambiguous evidence of a bipolaronic insulating state [33, 34]. There is also experimental evidence to support the existence of immobilized spin-singlet bipolarons in barium titanate perovskites [35, 36] which are of a very similar structure to the CMR perovskite manganites. Furthermore x-ray and neutron scattering measurements directly demonstrate the existence of short-range correlations of polarons in the paramagnetic phase of colossal magnetoresistive perovskite manganites [37, 40]. The polaron correlations are shown to have correlation lengths of approximately 10Å [40]. These short-range polaron correlations are shown to grow with decreasing temperature, but disappear abruptly at the ferromagnetic transition [37, 38, 40]. It is established that the temperature dependence of the polaron correlations is intimately related to the transport properties of the manganites [38, 40]. Also the polaron correlations collapse under an applied magnetic field [37, 40]. The polaron correlations are interpreted as bipolarons by Nelson et al. [39]. The experimental observations of polaron correlations in the paramagnetic phase of perovskite manganites are fully consistent with the formation of bipolarons within the CCDC theory.

Chipara et al. [41] claim that bipolarons are absent in, $La_{65}Ca_{33}MnO_3$ [41] as analysis of ESR measurements has not shown the presence of bipolarons. However Chipara et al. [41] also accept that low-spin bipolarons (singlets) have a zero spin and, accordingly, cannot be directly inferred from ESR data. We assume, as is usually the case, that the triplet states of bipolarons lie higher in energy than the singlet state, we therefore neglect the case of triplet bipolarons. The argument of Chipara et al. [41] regarding the absence of bipolarons, therefore becomes irrelevant.

While there is somewhat of a lack of spectroscopic evidence for the presence of bipolarons in perovskite manganites, given all of the experimental evidence regarding the observed carrier density collapse and correlated polarons that are observed only above $T_c$ the idea of such a bipolaronic insulating state in perovskites does not seem unreasonable. We believe that the CCDC theory is a much more complete theory of the colossal magnetoresistance phenomena, and other properties of these materials, when compared with the double exchange model. In this present paper we aim to show how the microscopic CCDC theory may describe the experimental specific heat and resistivity measurements in manganites, when used in conjunction with a generic phase separation model.

II. CCDC MODEL AND THE INTRODUCTION OF PHASE SEPARATION

Alexandrov and Bratkovsky [27] have proposed that the physics of perovskite manganites including the colossal magnetoresistance effect, can be explained by the current carrier density collapse theory (CCDC).

The grand thermodynamic potential of such a system has been calculated and has contributions from polarons, bipolarons, localized $\Mn^{+3}$ spins, and the double-counting term, respectively [27, 42]:

$$\Omega = \Omega_P + \Omega_{BP} + \Omega_S + \frac{1}{2}J_{pd}S\sigma_m$$

(1)

Normalizing the grand thermodynamic potential of the system by using the dimensionless temperature $t = 2k_BT/J_{pd}S$, magnetic field $h = 2\mu_BH/J_{pd}S$ and polaron binding energy $\delta = \Delta/J_{pd}S$, components of the grand thermodynamic potential are found as [27, 42]:

$$\Omega_P = -2\nu t\cosh\left(\frac{\sigma + h}{t}\right)$$

(2)
\[ \Omega_{BP} = -t \ln[1 + \nu^2 y^2 e^{2s/t}] \]  
\[ \Omega_S = -t \ln \left[ \frac{\sinh[(5/2)(m + 4h)/2t]}{\sinh[(1/2)(m + 4h)/2t]} \right] \]

Here we have taken the Mn\(^{+3}\) spin, \(S = 2\) due to strong Hund's coupling and the degeneracy factor, \(\nu\) is 3 due to the \(p\)-character of the polarons. If the bound pairs are extremely local objects, i.e. two holes on the same oxygen, then they will form a singlet. However, if these holes are localized on different oxygens, then they may well have parallel spins and form a triplet state. The triplet state is separated from the singlet state by an exchange energy, \(J_{st}\). We shall consider the simple case in which the separation of the triplets from the singlets, \(J_{st}\) is much larger than the critical temperature. In this case \(D=1\).

From the grand thermodynamic potential a series of mean field equations describing polaron density, chemical potential, manganese magnetization, and polaron magnetization, \(n\), \(\mu\), \(\sigma\) and \(m\), respectively has been found 27:

\[ n = 2\nu y \cosh \left[ \frac{\sigma + h}{t} \right] \]  
\[ y^2 = \frac{(x - n)}{2\nu^2} e^{-2s/t} \]

\[ m = ntanh \left[ \frac{\sigma + h}{t} \right] \]

\[ \sigma = B_2(m + 4h)/2t) \]

where \(y = e^{\mu/t}\) The polaron density can be found as a function of \(\sigma\) and temperature \(t\) by forming a quadratic equation by substituting Eq(6) into Eq(5). However one is left with a transcendental function to solve for \(\sigma\), to overcome this one may utilize the fact that the transition is first order in a homogeneous system in a wide range of \(\delta\). One can assume that the magnetization behaves as a step function that can become “smeared” due to disorder. Alexandrov et al 44 suggested that one should consider that different parts of a particular sample will exhibit differing values of \(\delta\) and therefore have different transition temperatures, and that a Gaussian distribution would provide a reasonable model for the spread of these transition temperatures. One can therefore say that the normalized magnetization (which we call the volume fraction, \(V\)) is equal to 1 minus the cumulative distribution function of transition temperatures. The volume fraction is then given by:

\[ V = \frac{1}{2} \text{erfc} \left[ \frac{t - t_c}{\Gamma} \right] \]

\[ \Gamma = s\sqrt{2}, \text{ where } s \text{ is the standard distribution of transition temperatures across the sample.} \]

We term the normalized magnetization as the volume fraction as it describes the fraction of the sample that remains in the ferromagnetic phase as the temperature is increased.

Broadening of the magnetic transition is in agreement with numerical studies by Mercaldo et al 144 who have shown that introducing quenched disorder, such as grain and crystalline boundaries into a three-dimensional pure system that exhibits a first order transition causes broadening of the temperature dependence of magnetization. Bulk samples of perovskite manganites usually exhibit crystallite size in the order of nanometers 15 46 48, thus leading to nanoscale phase separation in manganites 47.

## III. Transition Temperature and Volume Fraction of Sm\(_{0.55}\)Sr\(_{0.45}\)MnO\(_3\)

Egilmez et al 48 49 have produced samples of Sm\(_{0.55}\)Sr\(_{0.45}\)MnO\(_3\) annealed at different temperatures to produce different grain and crystallite size. Annealing at higher temperatures produced larger grains and crystallites, reducing the density of grain boundaries, and hence reduced disorder. The extra disorder in the low temperature annealed samples results in broadening of the transition and hence volume fraction, see Fig(2). The erfc function, Eq(9) corresponds to a Gaussian distribution of transition temperatures, however the magnetization data of Sm\(_{0.55}\)Sr\(_{0.45}\)MnO\(_3\) can be better fitted using combinations of polynomials and the erfc function. In general one can use any expression to describe the volume fraction, as in Fig(2).

One should remember that within the CCDC model that although the density of polarons is temperature and field dependent the total number of holes doped into the system is constant and equal to the doping concentration, \(N=x\). Utilizing the fact that Helmholtz free energy is continuous over a phase transition we may calculate, \(F = \Omega + \mu N\) in both the ferromagnetic and paramagnetic phases, by substituting \(\sigma = 1\) or 0 respectively into the expressions for \(\Omega\) and \(\mu\). The temperature at which these two functions cross over is the transition temperature. Fig(1) shows a plot of free energy in the CCDC model for both phases, with \(\delta = 0.65\) and \(x = 0.45\). This value of \(\delta\) was chosen such that a reasonable agreement between experimental specific heat data of Sm\(_{0.55}\)Sr\(_{0.45}\)MnO\(_3\) 48 49 and CCDC theory can be achieved (section(IV)). We have assumed \(\delta = 0.65\) for all samples of Sm\(_{0.55}\)Sr\(_{0.45}\)MnO\(_3\) to simplify the problem somewhat.

The normalized magnetization data for Sm\(_{0.55}\)Sr\(_{0.45}\)MnO\(_3\) 48, has been scaled such that
FIG. 1: A graph of the Helmholtz free energy, for $\delta = 0.65$ and $x = 0.45$, in the ferromagnetic and paramagnetic phases. The plot indicates $t_c \approx 0.2$.

The value of half volume fraction occurs at $t = 0.2$, see Fig[4].

FIG. 2: A graph of the volume fraction of $\text{Sm}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$, normalized such that the value of half volume fraction occurs at approximately, $t = 0.2$, as calculated for $\delta = 0.65$ and $x = 0.45$. Solid circles represent scaled data [48], lines represent expressions used to describe the volume fraction.

The transition temperature $T_c$ in $\text{Sm}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ samples only varies by a few degrees Kelvin [48], we can therefore look at the average conversion factor between the temperature in Kelvin and the normalized temperature $t$, which is $1.53 \times 10^{-3}$. This corresponds to an exchange energy between the carriers and localized spins of $J_{pd} = 56\text{meV}$, and hence the bipolaron binding energy is found to be $\Delta = 72.8\text{meV}$ as $\delta = 0.65$. The value of $J_{pd}$ found is in close agreement with the value of $60\text{meV}$ as estimated for perovskite manganites by [50].

IV. SPECIFIC HEAT AND ENTROPY OF $\text{Sm}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$

We can calculate the entropy of the system as:

\[
S = \frac{-\partial F}{\partial t} = \frac{-\partial \Omega}{\partial t} - x \frac{\partial \mu}{\partial t} = S \tag{10}
\]

In eq (10) $\Omega$ is the total grand thermodynamic potential found from the CCDC theory. By substituting $\sigma = 1$ or 0 into equation(10) and retaining the value of $\delta$ as 0.65, we may calculate the entropy of the ferromagnetic and paramagnetic phases respectively.

We suggest that the total entropy incorporating phase separation can be described as:

\[
S_{tot} = V S_f + (1 - V) S_p \tag{11}
\]

where $S_f$ and $S_p$ denote the entropy in the ferromagnetic and paramagnetic phases respectively, and $V$ is the volume fraction.

Differentiating once more we may calculate the specific heat.

\[
C_v = \frac{\partial S_{tot}}{\partial t} \tag{12}
\]

We fit our calculated specific heat under constant volume to the experimentally measured specific heat under constant pressure of $\text{Sm}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$, by assuming no thermal expansion. To fit to the experimental data an estimate of the lattice specific heat is required, typically the phonon blank method is used. The phonon blank method requires another sample to be prepared that does not exhibit the transition in question, this sample should have the same crystal structure and as close as possible a similar atomic mass. A possible phonon blank material for $\text{Sm}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ could be produced by replacing Mn for Ti atoms, the resultant material would not exhibit the ferromagnetic-paramagnetic transition, if this material possessed the same crystal structure as $\text{Sm}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ the specific heat of that sample would be very close to the lattice specific heat of $\text{Sm}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$. However no phonon blanks for $\text{Sm}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ were produced. In fact we are unaware of any published specific heat data for perovskite manganites including a phonon blank. We therefore simply take an estimate of the smooth lattice background specific heat, see Fig[3].

Figs[3] and [4] show that the theoretical specific heat is in reasonable agreement with the experimental results assuming our estimate of lattice specific heat is correct.
FIG. 3: Plots of specific heat of Sm_{0.55}Sr_{0.45}MnO_{3} annealed at (a)1200°C, (b)1300°C, (c)1400°C, (d)1500°C. Solid circles represent experimental specific heat data [48, 49], dashed lines correspond to our estimates of lattice specific heat, solid lines represent the addition of the lattice specific heat and the theoretical CCDC component.

We can calculate the entropy change associated with the anomalous part of the experimental data, Fig(4), by means of:

\[ S = \int \frac{C_v}{t} \, dt \]  

(13)

The entropy associated with the specific heat anomaly in the experimental data is plotted alongside the theoretically determined entropy in Fig(5).

We investigate the entropy change from \( t = 0.0465 \) to \( t = 0.3 \), as these temperatures are well below and above the transition respectively, hence all samples should exhibit the same entropy change over this temperature interval. The only role that the phase separation plays is to broaden the observed specific heat peak. Table(I) shows the entropy change associated with the anomalous part of the data for each sample.

| \( T_a (°C) \) | 1200 | 1300 | 1400 | 1500 |
|----------------|------|------|------|------|
| \( \Delta S_{\text{data}} (\text{JK}^{-1}\text{mol}^{-1}) \) | 12.9 | 12.8 | 12.4 | 13.0 |

TABLE I: Entropy change associated with the anomalous component of the experimental specific heat data of Sm_{0.55}Sr_{0.45}MnO_{3}, where \( T_a \) is the annealing temperature.

Averaging the data from table(I) we find the entropy change associated with the anomalous part of the experimental data from, \( t = 0.0465 \) to \( t = 0.3 \) as, \( \Delta S_{\text{data}} = 12.8 \pm 0.1\text{JK}^{-1}\text{mol}^{-1} \). This is in good agreement with
FIG. 5: Plots of entropy of Sm$_{0.55}$Sr$_{0.45}$MnO$_3$ annealed at (a) 1200°C, (b) 1300°C, (c) 1400°C, (d) 1500°C.

the theoretical entropy change over this temperature range, $\Delta S_{\text{CCDC}} = 12.802$ J/°C mol$^{-1}$.

Several authors report that the entropy change associated with the ferromagnetic-paramagnetic transition is much smaller than expected \[49, 53\] and hence unexplainable. Tanaka and Mitsuhashi\[51\] found a very small entropy change in La$_{0.8}$Ca$_{0.2}$MnO$_3$, Ramirez \[26\] states that this is approximately 10% of the expected value of $\approx 11$JK$^{-1}$mol$^{-1}$ (for localized spins), approximately twice as much entropy was found to reside under the ordering peak in La$_{0.67}$Ca$_{0.33}$MnO$_3$ by Ramirez et al \[52\]. The reasons for the entropy change being left unexplained up until now are that most authors \[49, 53\] have only considered local-moment degrees of freedom. The contribution to entropy of polarons acts to reduce the entropy change at $T_c$. Below $T_c$, polarons are unpaired, above $T_c$ the polarons are bound into immobile bipolarons, and hence the entropy of the charge carriers actually decreases at $T_c$. The total entropy change at $T_c$ will always be positive, it is simply that the contribution of carriers acts to reduce this increase, resulting in entropy changes that are smaller than has been expected \[49, 53\].

FIG. 6: Plots of electrical resistivity of Sm$_{0.55}$Sr$_{0.45}$MnO$_3$ annealed at (a) 1200°C, (b) 1300°C, (c) 1400°C, (d) 1500°C. Solid circles show the experimental data \[48, 49\], lines show fitted theoretical resistivity from equation (14).

A simple analytical expression for the resistivity of a binary mixture, which is consistent with comprehensive numerical simulations was proposed by Kabanov et al \[54\] and considered for use, when explaining the resistivity of mixed phase perovskite manganites \[33\];

$$\rho_{\text{eff}} = \rho_{\text{ferro}}^{V} \rho_{\text{para}}^{1-V}$$ \hspace{1cm} (14)

which is valid in a wide range of the ratios $\rho_{\text{para}}/\rho_{\text{ferro}}, V$ is the volume fraction. The resistivity is fitted in some-what of a generic manner, in as much that we are mixing the phases of a metal-like phase with that of an insulating phase. The expressions used are however, consistent with the physics of the CCDC model. Here we have used the expression governing the resistivity in the ferromagnetic phase as,

$$\rho_{\text{ferro}} = a T^{4.5} + c / \sinh^2 \left( \frac{\hbar \omega_0}{k_B T} \right).$$ \hspace{1cm} (15)

In fitting to the experimental data the coefficient c is found as 1(Ω cm) for all samples and $\hbar \omega_0$ has been fixed as: 50meV, which is a typical value for the phonon cut off in LCMO \[42\].

V. RESISTIVITY OF Sm$_{0.55}$Sr$_{0.45}$MnO$_3$

Using the same expressions governing the volume fraction, we fit the experimental resistivity data of Sm$_{0.55}$Sr$_{0.45}$MnO$_3$ \[48, 49\].
The expression for the ferromagnetic resistivity used here was suggested by Zhao et al.\[55\]. Kubo and Ohata\[56\] have studied the magnon scattering for half-metals where the spin-up (minority) and spin-down (majority) bands are well separated. In this case, one-magnon scattering is forbidden, and thus the two-magnon process plays a role in the low-temperature resistivity, which gives a contribution that is proportional to $T^5$. The term $c/\sinh^2 [\hbar \omega / k_B T]$ comes from the relaxation time of polarons calculated by Lang and Firsov. Jamie et al.\[58\] have ruled out electron-electron, and electron-phonon scattering mechanisms in the low temperature conductivity of manganites, that would give $T^2$ and $T^5$ contributions respectively. The resistivity of the paramagnetic phase can be well described by [43]:

$$\rho_{\text{para}} = bT e^{-\frac{E}{k_B T}}$$ (16)

We also include a residual resistivity $\rho_0$. The parameters used to fit the resistivity are shown in table II.

| $T_c$ (°C) | 1200 | 1300 | 1400 | 1500 |
|------------|------|------|------|------|
| $\rho_0$ (Ω cm) | 3 | 1 | 0.21 | 0.2 |
| $a$ (Ω cm K$^{-4.5}$) × 10$^{-10}$ | 38 | 17 | 4 | 0.07 |
| $b$ (Ω cm K$^{-1}$) × 10$^{-6}$ | 2.2 | 1.3 | 1.25 | 1.2 |
| $E$ (meV) | 138 | 131 | 123 | 116 |
| $E_a$ (meV) | 101.6 | 94.6 | 86.6 | 79.6 |

TABLE II: Parameters governing the resistivity of Sm$_{0.55}$Sr$_{0.45}$MnO$_3$ \[18\] [20].

It is clear that the peaks observed in the resistivity of Sm$_{0.55}$Sr$_{0.45}$MnO$_3$, Fig. 5, are broadened with increasing disorder and phase separation. One can also see that the resistivity is increased with the increasing disorder, this is simply due to increased scattering rates, as can be seen by the increase values of the constants $a$, $b$ and $\rho_0$ in table II with decreasing annealing time.

The high temperature mobility of polaronic carriers is likely to be dominated by hopping events due to polaron band narrowing,\[57\] [59], therefore $E$ has contributions from the bipolaron binding energy, $\Delta$, and the activation energy of polarons, $E_a$ as:

$$E = E_a + \Delta/2$$ (17)

By fitting the specific heat we have found $\Delta/2 = 36.4$meV, and from fitting the resistivity we have found $E$. This has allowed us to separate the polaron hopping activation energy and bipolaron binding energy from the exponential behaviour of the resistivity in the paramagnetic regime. See table I for values of polaron hopping activation energy. We can see that the hopping activation increases with an increasing density of grain boundaries (decreasing annealing temperature)\[48\]. This is what one would expect to see as the increasing levels of disorder act to localize the carriers resulting in a larger activation energy required for hopping.

VI. CONCLUDING REMARKS

Introducing Phase separation into the thermodynamics of the microscopic CCDC model by mixing the high and low temperature phases has allowed for the specific heat of Sm$_{0.55}$Sr$_{0.45}$MnO$_3$ samples produced by Egilmez et al.\[18\] [39] to be well explained. Up until now the entropy change associated with the ferromagnetic-paramagnetic transition in colossal magnetoresistive perovskite manganites has been left largely unexplained, however we find the entropy change from the CCDC theory and the experimental data to be in close agreement. The contribution to entropy of polarons acts to reduce the entropy change at $T_c$. Below $T_c$ polarons are unpaired, above $T_c$ the polarons are bound into immobile bipolarons, and hence the entropy of the charge carriers actually decreases at $T_c$. The total entropy change at $T_c$ will always be positive, it is simply that the contribution of carriers acts to reduce this increase, which results in an entropy change that is smaller than has been expected\[49\] [53]. Fitting specific heat data, in conjunction with a generic phase separated model of resistivity has allowed bipolaron binding energy and polaron hopping activation energy contributions to the exponential behaviour of resistivity to be separated. We hope that experimentalists working in the field of perovskite manganites try to produce phonon-blank materials such that the lattice contribution to specific heat of samples can be accurately determined.

We accept that the CCDC theory is not the only theory that hopes to explain the physics of colossal magnetoresistive materials, we have shown however for the first time that this theory may be used to explain the specific heat of perovskite manganites. More work is required, especially by experimentalists to either conclusively prove or disprove this model.

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