Specific heat and correlation between resistivity and thermoelectric power of GdBa$_2$(Cu$_{1-x}$Mn$_x$)$_3$O$_{7-\delta}$ HTSC system for $x \leq 0.02$

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**Abstract**

In this communication we present some theoretical results of specific heat and thermoelectric power of the superconductor GdBa$_2$(Cu$_{1-x}$Mn$_x$)$_3$O$_{7-\delta}$ (for $x \leq 0.02$). A model based on separate electronic and phononic contributions is used for the interpretation of the specific heat data while a narrow band model is used for the analysis of thermoelectric power. On the basis of these models two main conclusions have been drawn about the relative effects of different Mn contents: (1) the observed fluctuation effects near T$_c$ whose strength increases with increasing Mn content and (2) Mn produces mainly electronic effects for lower Mn contents, while for higher doping levels ($x > 0.0075$) Mn predominantly causes carrier-Mn scattering process.

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1. Introduction

The substitutional effects in high $T_c$ superconductors have been extensively investigated by several researchers. Primary aim of such studies has been essentially to explore the mechanism of superconductivity and to improve various properties so as to enhance the applicability of these materials. As far as transition metal ions are concerned, relatively less work seems to have been done on substitution of Mn, primarily due to its small solubility [1–7]. However, Mn doping is of great physical importance from the theoretical point of view due to some common features between various transition metal ions. Mn doping exhibits an unusual behavior in the sense that the superconducting transition temperature of the YBa$_2$Cu$_3$O$_{7-\delta}$ system is seen to only slightly affected by the Mn content. There are several reports on the measurements of the thermal behavior of YBa$_2$Cu$_3$O$_{7-\delta}$ with other dopants (Co, Zn, etc.) at Cu-sites. Loram et al. [8] have studied the specific heat of Co-doped YBa$_2$Cu$_3$O$_{7-\delta}$, while Sisson et al. [9] have studied the specific heat of Zn-doped YBa$_2$Cu$_3$O$_{7-\delta}$ system. As far as the thermoelectric power of doped Y- or Gd-based 123 systems is concerned, there exist studies with Zn [10], Pr [11], and Ca [12] doping.

In this paper we present theoretical studies on the GdBa$_2$(Cu$_{1-x}$Mn$_x$)$_3$O$_{7-\delta}$ superconducting system and highlight some important features of the specific heat (C$_P$) and thermoelectric power ($S$) [13,14] with a view to understand the role of Mn in GdBa$_2$(Cu$_{1-x}$Mn$_x$)$_3$O$_{7-\delta}$ on the basis of the connections of its effects on the specific heat and thermoelectric power. The Mn$^{k+}$ ion ($k = 2, 3, 4$) is magnetic. For $k > 2$, Mn will donate electrons to the overall system, which results in the reduction of the carrier (hole) density. Since the superconducting transition temperature T$_c$ is known to decrease with the reduction of carrier (hole) density with respect to the optimal doping case [15], a decrease in T$_c$ with Mn may be considered as an indication for the existence of Mn in valence states higher than +2.

2. Experimental techniques

Samples of the GdBa$_2$(Cu$_{1-x}$Mn$_x$)$_3$O$_{7-\delta}$ system in the nominal doping range $0 \leq x \leq 0.02$ were synthesized by a solid state reaction route. Synthesis details and measurement techniques for thermopower and specific heat have already been described elsewhere [13,14].
3. Results and discussion

Superconducting transition temperature $T_C$ deduced through resistivity measurements for our GdBa$_2$(Cu$_{1-x}$Mn$_x$)$_3$O$_7$–δ samples have already been reported [13]. Since the cuprate systems are d-wave superconductors [16], paramagnetic impurity is not expected to drastically reduce $T_C$. However we observe drastic reduction of $T_C$ for the sample with $x = 0.02$ which is either due to potential scattering [17] or due to reduction in the carrier (hole) density (caused by Mn$^{4+}$, $k > 2$ ions) [15]. In our earlier communication we have shown that the features of the thermoelectric power and thermal conductivity rule out the latter possibility [14]. The observed temperature dependence of the specific heat ($C_p$), of GdBa$_2$(Cu$_{1-x}$Mn$_x$)$_3$O$_7$–δ for different $x$ is described elsewhere [14]. The pristine sample ($x = 0.0$) shows a jump in $C_p$ of amount $\Delta C_p = 5.7$ mJ/gK. For $x = 0.005$ this jump reduces to 1.6 mJ/gK, and for $x = 0.0075$ it reduces further to 1.0 mJ/gK. Samples with $x = 0.01$ and 0.02, however, do not show any jump in $C_p$ at $T_C$. These values of $\Delta C_p$ suggest that either Mn induces gapless superconductivity for $x \geq 0.01$, or there are strong thermal fluctuations at and near $T_C$. The possibility of gapless superconductivity for $x > 0.01$ is ruled out by the behavior of the thermal conductivity of these samples [14].

For describing the specific heat in the normal state we use the following expression [18]:

$$C_p = \gamma T + A \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{e^{u}\nu^2}{(e^{u}-1)^2} \, du$$  \hspace{1cm} (1)

This equation describes the electronic (first term) and phononic contributions (second term) to the specific heat. Here $\gamma$ and $A$ are independent of temperature. In particular, $\gamma$ is proportional to the electronic density of states at the Fermi level ($N_F$) and $\theta_D$ is Debye temperature. Notice that Eq. (1) does not include the effect of jump in the specific heat at $T_C$. In fact, Eq. (1) is useful only for describing the experimental data except near $T_C$. Hence we have fitted the experimental data of $C_p$ with Eq. (1) by excluding a range of 10 K about $T_C$. Fig. 1 shows the temperature dependence of specific heat for various Mn-doped samples in the range 90–100 K.

The values of the parameters $\gamma$, $A$ and $\theta_D$ are shown in Table 1 for different Mn contents. Subtraction of the theoretical Eq. (1) values of $C_p$ from the experimental values provides us the jump structure of $C_p$ near $T_C$.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$A$ (mJ/gK)</th>
<th>$\gamma$ (mJ/gK$^2$)</th>
<th>$\theta_D$ (K)</th>
<th>$\mu$ (meV)</th>
<th>$W_\sigma$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>865.1</td>
<td>0.54</td>
<td>383.5</td>
<td>0.17</td>
<td>41.0</td>
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<td>0.005</td>
<td>842.3</td>
<td>0.59</td>
<td>393.5</td>
<td>1.35</td>
<td>34.0</td>
</tr>
<tr>
<td>0.0075</td>
<td>830.0</td>
<td>0.58</td>
<td>388.5</td>
<td>2.3</td>
<td>35.3</td>
</tr>
<tr>
<td>0.01</td>
<td>837.3</td>
<td>0.57</td>
<td>384.5</td>
<td>2.55</td>
<td>35.3</td>
</tr>
<tr>
<td>0.02</td>
<td>827.5</td>
<td>0.59</td>
<td>393.5</td>
<td>2.98</td>
<td>36.2</td>
</tr>
</tbody>
</table>

We now consider the role of Mn on the specific heat of the superconducting state of the GdBa$_2$(Cu$_{1-x}$Mn$_x$)$_3$O$_7$–δ system. From Table 1 we see that Mn does not have a strong effect in the Debye temperature $\theta_D$. On the basis of the $\gamma$ values (Table 1) we observe that the ratio $\Delta C_p/\gamma T_C$ is 0.111, 0.030 and 0.018 for the samples $x = 0.0$, 0.005 and 0.0075 samples, respectively. These values are one to two orders of magnitude lower than the ratio of 1.43 in the Bardeen–Cooper–Schrieffer (BCS) theory [19]. Such low values of $\Delta C_p/\gamma T_C$ for the $x = 0$ and $x > 0$ samples indicate strong effects of both the GdB$^{3+}$ ions and Mn$^{4+}$ ions in the considered system. In fact, for $x = 0.0$, $\Delta C_p/\gamma T_C$ is about 13 times smaller than the BCS value. Such a strong effect can be attributed to GdB$^{3+}$ ions because Mn$^{4+}$ ions are absent in the $x = 0.0$ sample. Further decrease in $\Delta C_p/\gamma T_C$ ratio with $x$ reflects the additional effect of Mn ions.

We now describe the behavior of thermoelectric power as a function of Mn content. In our previous study [14] we have analyzed the thermoelectric power on the basis of Gasumyants et al. [20] model. In this model one describes $S$ in terms of three parameters, namely $n$, $W_D$ and $W_\sigma$. Here, $n$, $W_D$, $W_\sigma$ denotes band filling, total effective bandwidth of the electronic states and the effective width of an energy interval for electronic conduction, respectively. In the present investigation, we have limited the temperature range up to 300 K. Hence, we have used only two parameters. The two-parameter version of the expression for $S$ as given by Gasumyants et al. [20] may be written as,

$$S = \frac{k_B}{e} \sinh W_\sigma \left( W_\sigma \sinh \mu^r + \mu^l (\cosh \mu^r + \exp W_\sigma) + \left( \cosh \mu^l + \cosh W_\sigma \ln \frac{1 + e^{W_\sigma - W_D}}{1 + e^{W_\sigma + W_D}} \right) \right)$$  \hspace{1cm} (2)

Here

$$\mu^r = \frac{\mu}{k_BT} = \ln \left( \frac{\sinh(nW_D)}{\sinh[(1-n)W_D]} \right), \quad W_\sigma = \frac{W_D}{2k_BT} \text{ and } W_\sigma = \frac{W_D}{2k_BT}$$  \hspace{1cm} (3)

In Eq. (2), $e$ is the electronic charge of the carrier. In Eq. (3), $\mu$ is the chemical potential and one can notice that $\mu$ is temperature dependent for given values of $n$ and $W_D$. In order to avoid this problem, one can notice that, in the limit $2k_BT \ll \mu^r$, $\mu^r$ approaches $(2n - 1)W_D/2k_BT$. Thus, $\mu^r$ becomes independent of $T$. Hence, for low temperatures we have estimated values of $\mu$ for different samples in the frame work of the narrow band picture. Notice that $S$ is an odd function of $\mu$. Using Eq. (2) we have fitted the experimental values of thermopower and thus obtained the values of $\mu$ and $W_\sigma$ for different samples. These values of $\mu$ and $W_\sigma$ are given in Table 1.

In the two-parameter version [14] of Gasumyants et al. [20], the ratio $\mu/W_\sigma$ plays effectively the same role as the ratio $W_D/W_\sigma$ in the three-parameter model [20]. In particular the slope of the $\mu/W_\sigma$ versus $x$ plot provides information about the strength of the carrier–Mn scattering rate. In fact larger (smaller) slope corresponds to smaller (larger) scattering rate. We plot $\mu/W_\sigma$ versus Mn content $x$ in Fig. 2. It is clear from this figure that the plot of $\mu/W_\sigma$ versus $x$ corresponds to two much different slopes – the first is the large

![](Fig_1.png)

Fig. 1. Variation of specific heat ($C_p$) of GdBa$_2$(Cu$_{1-x}$Mn$_x$)$_3$O$_7$–δ for $x \leq 0.02$ in the temperature range of 90–100 K. The inset shows variation of $C_p$ with $T$ between 70 and 300 K for the pristine sample.
slope (marked by “1” in Fig. 2) corresponding to the Mn content $x < 0.0075$, and the second is the small slope (marked by “2” in Fig. 2) corresponding to $x > 0.0075$. This means that the effect of Mn on the electronic conduction is much different below and above the Mn content $x = 0.0075$. Since, large slope (slope 1 in Fig. 2) corresponds to weak scattering processes, while small slope (slope 2 of Fig. 2) corresponds to strong scattering process; the scattering rate due to the Mn ions is rather weak for low Mn content. A possible reason for this is that for low $x$, Mn produces mainly electronic effects like change of carrier density and transfer of spectral weight from high energy regime to low energy regime [21]. With increasing Mn content the electronic effects get weaker and the carrier-Mn scattering process which determines the electronic conduction gets stronger. This is a possible explanation of the behavior of the slope of the $\mu / \rho_{0}$ versus $x$ plot in Fig. 2.

In order to clarify the correlation between two electrical transport properties of resistivity and thermoelectric power, we also plot residual resistivity ($\rho_{0}$) [extracted from the resistivity curves of Ref. [13]] versus the ratio $\mu / \rho_{0}$, which may provide valuable information about the conduction mechanism of charge carriers in the present system in Fig. 3. We see that the dependence of $\rho_{0}$ on $\mu / \rho_{0}$ has two distinct parts. The first is corresponding to a weak dependence of $\rho_{0}$ on $\mu / \rho_{0}$ for $x \leq 0.0075$, and the second to a strong dependence for $x \geq 0.0075$. The $x = 0.0075$ sample corresponds to the crossover between these two quite different parts.

From these observations it appears that the carrier conduction is governed by two different processes due to the presence of Mn in GdBa$_{2}$(Cu$_{1-x}$Mn$_{x}$)$_{3}$O$_{7-\delta}$ system. It has been found that the relation between $\rho_{0}$ and $\mu / \rho_{0}$ (Fig. 3) shows a crossover at $x = 0.0075$, implying different roles of Mn below and above this Mn content.

4. Conclusions

We have investigated specific heat and thermoelectric power of the Mn-doped GdBa$_{2}$Cu$_{3}$O$_{7-\delta}$ superconductors both in the superconducting state and in the normal state. The substitution of Mn in the system has been found to effectively suppress the specific heat jump observed in the pristine compound. Thermoelectric power data analysis suggests that for low Mn content ($x \leq 0.0075$) Mn$^{k+}$ ions cause mainly electronic effects in the system. A crossover takes place at $x = 0.0075$ so that for higher $x$ ($x > 0.0075$) Mn$^{k+}$ ions cause mainly scattering effects.

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References


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**Fig. 2.** Variation of $\mu / \rho_{0}$ with Mn content ($x$).

**Fig. 3.** Variation of $\rho_{0}$ with $\mu / \rho_{0}$.