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The influence of Mn doping on the thermal expansion of the high T_C superconductor $YBa_2(Cu_{1-x}Mn_x)_3O_y$

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Abstract

Measurement of the linear thermal expansion α has been carried out for Mn substituted $YBa_2(Cu_{1-x}Mn_x)_3O_y$ ($0 \leqslant x \leqslant 2\%$) using a high resolution dilatometer over the temperature range 10–300 K. Across the superconducting transition, the jump in the coefficient of linear thermal expansion $\Delta\alpha$ was found to decrease with increasing Mn content. For the pure sample, we observed a negative jump. While a threefold decrease in $\Delta\alpha$ with $x = 0.5\%$ was observed, only slight changes in the oxygen content and transition temperature have been noted, as a function of the Mn concentration. The above observations clearly suggest that the substituent Mn is being incorporated into the superconductors as a whole and not in the form of a local cluster. Further, from the Ehrenfest relations, the pressure dependence of T_C (dT_C/dP) and the discontinuity in the compressibility, ΔK, are expected to decrease with the Mn concentration.

1. Introduction

In order to understand the complex nature of superconductivity, numerous investigations are being carried out even many years after its discovery. In particular, substitution effects and the associated changes in the physical, chemical and electrical properties have been widely studied for both conventional and unconventional superconductors (high T_C). Among the substitutions involving various elements, in general, the addition of even a small amount of magnetic impurities leads to a significant reduction in the superconducting transition temperature, by breaking the Cooper pairs through spin flip/magnetic scattering in a conventional superconductor. In the case of high T_C superconductors such as $YBa_2Cu_3O_y$, the addition of a magnetic impurity is more complicated than that of non-magnetic impurities due

to the fact that the substituted magnetic impurities may lead to structural changes besides the pair-breaking effect. Many investigators have studied the substitution effects with magnetic and non-magnetic dopants at the Cu site in $YBa_2Cu_3O_y$ superconductors [1–7] and the primary aim of such studies is to understand the mechanism of superconductivity as well as to enhance the applicability of these materials by improving their chemical, physical and electrical properties. Depending on the specific atomic nature of a given dopant, the substituent occupies a chain or plane or both sites with or without a structural transition [1, 2]. It has been reported that dopants such as Fe and Co, which occupy chain sites, would induce a structural transformation from orthorhombic to tetragonal above certain critical concentrations [1, 2]. However, no such transformation is observed for Zn, which occupies a plane site, and Ni, which occupies both chain and plane sites [1, 5, 7].

Doping with Fe, Co, Ni, Zn, etc in $YBa_2Cu_3O_y$ not only alters the superconducting transition temperature T_C to a large extent, but also influences other physical properties such as the lattice components of the specific heat [8, 9] and the coefficient of thermal expansion [6–8, 10–13]. Thermal expansion is a useful tool for providing valuable information about the changes in the electronic and phononic properties across the superconducting transition [9, 14]. The close relation between the specific heat and thermal expansion of solids (Grüneisen formalism) can be effectively utilized for a detailed thermodynamic treatment (Ehrenfest relations) of phase transitions, and such studies have been widely carried out by many investigators on the dopants which occupy copper plane and chain sites in the high T_C superconductor $YBa_2Cu_3O_y$ [9, 14, 15]. These reports indicate that for dopants like Fe and Co, the jump in thermal expansion increases with the increase in dopant concentration [8, 11, 12]. On the other hand, such a jump decreases with the contents of dopants such as Ni and Zn [6, 7].

However, relatively little work seems to have been done on substitution of Mn, possibly due to the low solubility of Mn in $YBa_2Cu_3O_y$. However, Mn doping is of significant importance from the theoretical point of view owing to the distinct behaviours it exhibits as compared with other transition metal substitutions. For example, the transition temperature of $YBa_2Cu_3O_y$ is only slightly affected by the Mn substitution [15–19], while significant depression of T_C has been observed when Fe, Co, and Ni are substituted for Cu. In addition to this, Mn behaves like Fe or Co [20, 21] in as much as the occupancy of the copper chain site is concerned; whereas it behaves like Zn or Ni as far as the retention of orthorhombicity is concerned [1]. Recently we carried out a systematic study of the specific heat for a series of Mn doped $YBa_2Cu_3O_y$ samples [22]. In order to shed more light on the influence of Mn doping in the $YBa_2Cu_3O_y$ system, we have performed a detailed thermal expansion measurement on Mn substituted compounds $YBa_2(Cu_{1-x}Mn_x)_3O_y$ for $0 \leqslant x \leqslant 0.02$ in the temperature range 10–300 K. To the best of our knowledge, the present work represents the first comprehensive study of thermal expansion measurements on Mn substituted $YBa_2Cu_3O_y$ so far.

2. Experimental techniques

Samples of the $YBa_2(Cu_{1-x}Mn_x)_3O_{7-\delta}$ system in the nominal doping range $0 \leqslant x \leqslant 0.02$ were synthesized by the solid state reaction route. Stoichiometric quantities of Y_2O_3, $BaCO_3$, CuO, and MnO were thoroughly mixed and then calcined at 930 °C in air for 12 h. In order to improve the homogeneity, the mixing and calcination were repeated three times. The powder was then cold pressed into pellets and sintering was done in flowing oxygen for 72 h, which was followed by slow cooling to 450 °C and then slow cooling to room temperature. The transition temperature determination was done by electrical resistivity measurements using the standard four-probe technique. Crystallographic phase and lattice constants were determined by the XRD technique. The present investigated compositions have been found to be single

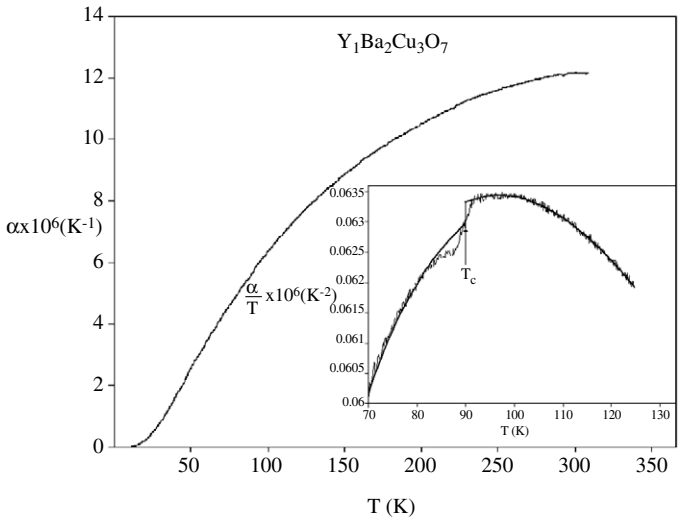

Figure 1. Temperature variation of α for a pure sample of $YBa_2Cu_3O_y$. The inset shows the behaviour of α/T in the vicinity of the superconducting transition.

Table 1. Various parameters of the $Y_1Ba_2(Cu_{1-x}Mn_x)_3O_y$ compounds.

x (%)	a (±0.001 Å)	b (±0.001 Å)	c (±0.001 Å)	T_C (K)	y (±0.03)
0	3.819	3.888	11.666	91.6	6.93
0.5	3.816	3.883	11.656	92.5	6.92
0.75	3.817	3.887	11.669	93	6.91
1.00	3.824	3.883	11.658	92	6.93
2.00	3.823	3.883	11.646	91	6.92

phase (orthorhombic) with no traceable impurities (within ±5%). The oxygen content of all the samples was found using the iodometric titration method. The lattice parameters along with the oxygen contents of all the samples are given in table 1.

Measurements of the linear thermal expansion coefficient were carried out using a capacitance dilatometer described elsewhere [23]. The dilatometer is sensitive enough for detecting changes of the order of about 10^{-8} K^{-1} in α for the present samples of about 5 mm length.

3. Results and discussion

All the samples on which measurements were performed show a typical metallic behaviour followed by a superconducting transition with a transition width of about 1–3 K. It is found that the transition temperature of Mn doped $YBa_2(Cu_{1-x}Mn_x)_3O_y$ compounds changes only slightly. Transition temperatures are shown in table 1. The temperature dependence of the thermal expansion coefficient $\alpha(T)$ in the temperature range 10–300 K for pure $YBa_2Cu_3O_y$ is depicted in figure 1. The inset shows α/T in the vicinity of the transition temperature.

Figure 2 shows the variations of the linear thermal expansion as a function of temperature with $x = 0.5\%$. The inset displays α/T in the vicinity of the transition temperature. A jump in the measured thermal expansion could be clearly seen, but smaller in comparison to the pure sample one.

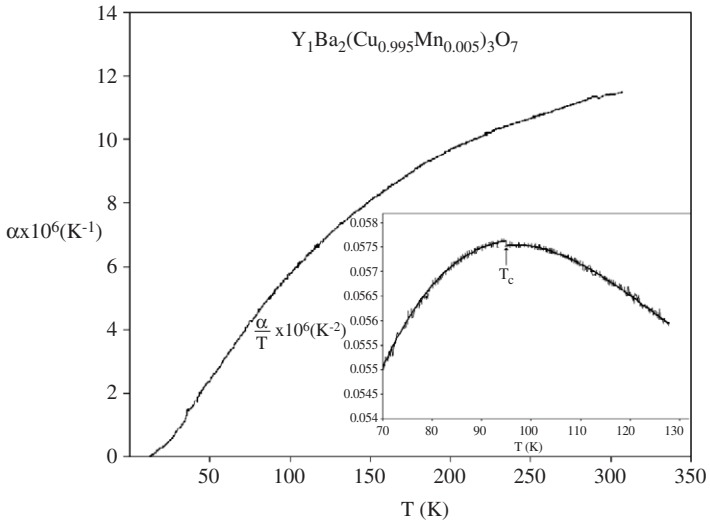

Figure 2. Temperature dependent variation of α for $x = 0.5\%$. The inset shows the behaviour of α/T in the vicinity of the superconducting transition.

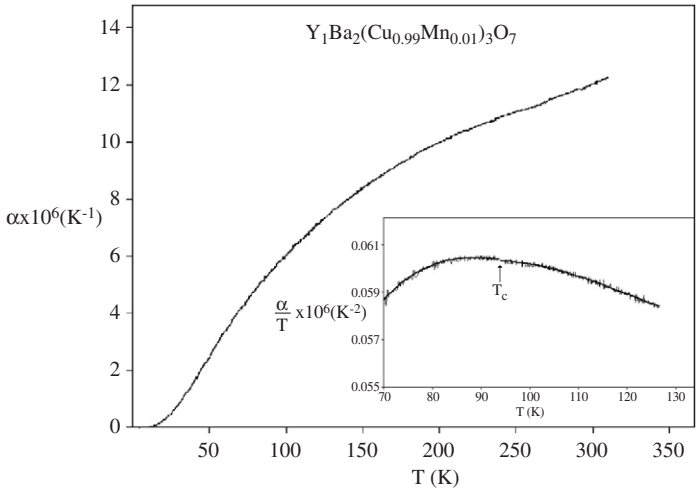

Figure 3. Temperature dependent variation of α for $x = 1\%$. The inset shows the behaviour of α/T in the vicinity of the superconducting transition.

Figure 3 shows the temperature variation of the thermal expansion for the sample with $x = 1\%$. In contrast to the pure and $x = 0.5\%$ sample cases, no apparent jump or discontinuity in $\alpha(T)$ could be noticed across the transition for the $YBa_2(Cu_{0.99}Mn_{0.01})_3O_y$ sample. Measurement of $\alpha(T)$ for the sample with $x = 2\%$ was also performed, similarly to that for the $x = 1\%$ sample; a smooth variation in the temperature range investigated was observed (figure not shown here).

The jump in the thermal expansion coefficient $\Delta\alpha$ at T_C was determined by extrapolating the two branches of α/T versus T curves at T_C. In the insets we plotted α/T instead of α because the jumps in thermal expansion are best seen in such a plot. In order to ascertain that

the values of $\Delta\alpha$ obtained are not due to the extrapolation procedure itself, this procedure was applied to α versus T data in the normal state region. It is satisfying to note that the difference of the two extrapolation values was less than 1.5×10^{-8} K^{-1} for all samples under evaluation. For the pure $YBa_2Cu_3O_y$ sample, a negative jump in thermal expansion coefficient of about $\alpha_{s-}\alpha_n = -6.7 \times 10^{-8}$ K^{-1} was estimated, which is in good agreement (as far as the magnitude is concerned) with the earlier report by Meingast *et al* [8]. With a small amount of Mn doping of 0.5%, the jump changes sign and decreases in magnitude to 2.2×10^{-8} K^{-1}. As the doping level increased to 1%, no jump in thermal expansion could be noticed within the experimental limits. Similar results have also been observed for the specific heat [22] and the jump in specific heat for the pure $YBa_2Cu_3O_y$ sample was observed to be 4.1 J mol^{-1} K^{-1}. With a small amount of Mn doping of 0.5%, the jump in specific heat was found to decrease to 3.5 J mol^{-1} K^{-1}, and for the sample with $x = 1\%$, no jump in specific heat was observed.

The pressure dependence, dT_C/dP, of T_C is related to the jump in linear thermal expansion coefficient $\Delta\alpha$ and the jump in specific heat which is given by one of the Ehrenfest relations:

$$\frac{dT_C}{dP} = T_C \frac{3\Delta\alpha}{\Delta C_P}. \tag{1}$$

Thus equation (1) gives an indirect method for determining dT_C/dP. Using another Ehrenfest relation one can calculate the discontinuity in the compressibility, ΔK as shown below:

$$\Delta K = 3\Delta\alpha \frac{dT_C}{dP}. \tag{2}$$

The pressure dependence dT_C/dP and ΔK were calculated for the samples using the recently published specific heat data of Rao *et al* [22]. We have obtained $dT_C/dP = (-0.55 \pm 0.04)$ K bar^{-1} for pure $YBa_2Cu_3O_y$, and the value of dT_C/dP decreases to (0.11 ± 0.04) K bar^{-1} for Mn doping of 0.5%. Similarly, ΔK was found to decrease from $(9 \pm 0.5) \times 10^{-8}$ bar^{-1} for the pure sample to $(0.75 \pm 0.5) \times 10^{-8}$ bar^{-1} for Mn doping of 0.5%. It should be mentioned that the samples used in [22] and those used in the present studies have been cut from the same piece of pellet. Direct measurements of dT_C/dP and ΔK for $YBa_2(Cu_{1-x}Mn_x)_3O_y$ system would be very instructive to compare with our present findings.

It is worth mentioning that the decrease of $\Delta\alpha$ with increasing Mn concentration has also been observed for Ni and Zn doped $YBa_2Cu_3O_y$ compounds [6–8]. In contrast, $\Delta\alpha$ has been found to increase with increase in Fe and Co concentration [6, 9, 10]. This suggests that $\Delta\alpha$ appears to correlate with the substitution site; that is, for dopants such as Fe, Co which occupy copper chain sites, $\Delta\alpha$ increases. In contrast, there is a decrease in $\Delta\alpha$ for dopants such as Ni and Zn, which occupy the copper plane sites.

4. Conclusions

The influence of Mn doping on the linear thermal expansion α of the high T_C superconductor $YBa_2(Cu_{1-x}Mn_x)_3O_y$ ($0 \leqslant x \leqslant 2\%$) was studied. The jump in thermal expansion $\Delta\alpha$ across the superconducting transition was found to disappear with increase in the Mn concentration. On substituting 0.5% of Mn into the Cu sites, $\Delta\alpha$ decreases by a factor of about 3 whereas the oxygen content and transition temperature do not change appreciably. No apparent jump or discontinuity in α could be noted across the transition with $x \geqslant 1\%$. This clearly demonstrates that these substituents are being incorporated into the superconductors as a whole and not in the form of a local cluster. The pressure derivative of T_C, dT_C/dP, was estimated to be 0.55 K bar^{-1} for pure $YBa_2Cu_3O_y$, and decreases to 0.11 K bar^{-1} for Mn doping of 0.5%. In

comparison with other transition metal substitutions, our present investigation suggests that Mn occupies presumably copper plane sites in the $YBa_2Cu_3O_y$ system.

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