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Effect of Ni doping on the thermal expansion of the high-T_c superconductor $YBa_2Cu_3O_y$

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Abstract. Thermal expansion measurements have been carried out for the Ni-substituted compounds $YBa_2(Cu_{1-x}Ni_x)_3O_y$ ($0 \leqslant x \leqslant 5\%$) with a high-resolution dilatometer using the three-terminal capacitance technique. The present set-up is sensitive enough to detect changes in α of less than 10^{-8} K^{-1}. Results indicate that the jump $\Delta\alpha$ in the coefficient of linear thermal expansion decreases with increase in Ni content. For $x = 1.5\%$, $\Delta\alpha$ decreases by a factor of 3 whereas T_c does not change appreciably. There is evidence that the temperature dependence of α for compounds with high Ni concentration depends on the conditions of sample growth.

1. Introduction

The addition of a magnetic impurity to a conventional superconductor results in the breaking up of Cooper pairs, and thereby a drastic reduction in the superconducting transition temperature is observed [1]. The addition of a magnetic impurity to the high-T_c superconductor $YBa_2Cu_3O_y$ is more complicated because of the presence of two copper sites, a plane and a chain. Different impurities have preferential occupancies, for instance impurities such as Fe, Co and Al occupy the plane sites whereas Ni, Zn, etc, occupy the chain sites [2–10]. The extent of the drop in T_c depends on the type of impurity added. In addition to this, depending on the magnetic impurity, there are changes in structure and oxygen content of the unit cell. In fact, experiments have also shown that, in the case of dopants which occupy copper plane sites, the pressure dependence of dT_c/dP of T_c increases whereas, for dopants occupying copper chain sites, there is a decrease in dT_c/dP [11–13]. dT_c/dP is related to the jump $\Delta\alpha$ in the thermal expansion coefficient α and the specific heat jump ΔC_p which is given by

$$\frac{dT_c}{dP} = \frac{\Delta\alpha T_c}{\Delta C_p}.$$

Hence the above relation suggests that the thermal properties such as specific heat and thermal expansion would depend on the nature of occupancies of the dopants. Thermal expansion in particular is of great importance since it provides an experimental tool for the study of the dynamics of lattice vibrations. Thermal expansion studies have been carried out by many investigators on the dopants which occupy copper plane sites, namely Fe- and Co-doped compounds of $YBa_2Cu_3O_y$ [14–16]. For these dopants the jump $\Delta\alpha$ increases with the increasing dopant concentration of the compounds. Little work seems to have been done on the dopants which occupy copper chain sites. The only report seems to have been given by Meingast *et al* [14] on two samples of Zn-doped $YBa_2Cu_3O_y$ compound

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with $x = 1\%$ and 2.5%. These results show a decrease in $\Delta\alpha$ with increasing dopant concentration. It was therefore interesting to carry out measurements of thermal expansion for doped compounds in which the dopants occupy copper chain sites.

This paper reports for the first time a detailed study of the linear thermal expansion of one such system, namely $YBa_2(Cu_{1-x}Ni_x)_3O_y$ for $0 \leqslant x \leqslant 5\%$ in the temperature range 77–300 K.

2. Experimental details

The standard solid state reaction technique [17] was used to prepare samples. Appropriate amounts of Y_2O_3, $BaCO_3$, CuO and NiO (all 99.9% pure) were mixed in an agate mortar and then sintered in air at 930 °C for 48 h. The product was reground, and sintering was repeated thrice to ensure homogeneous distribution of the substituent. Finally the powder was pressed into rectangular bars and annealed in flowing oxygen at 950 °C for 48 h. This was followed by cooling slowly to 450 °C where the sample was kept for 72 h and then slowly cooled to room temperature. X-ray diffraction studies were carried out with a Philips PW 1840/01/11 compact x-ray diffractometer system using CuKα radiation ($\lambda = 0.154\,05$ nm). The x-ray diffraction analysis of all the samples confirm that they were of a single-phase nature.

The transition temperature of each sample was determined by measuring the resistance in the temperature range 77–300 K using the standard four-probe technique. In order to determine the oxygen content, the iodometric titration technique suggested by Nazzal *et al* [18] was used. Titration for each sample was performed twice to check the reproducibility. High-purity argon gas was used to create an inert atmosphere. The accuracy in the determination of oxygen content was about ± 0.03. Thermal expansion measurements were carried out using a high-resolution capacitance dilatometer described elsewhere [19]. With our set-up we are able to resolve changes in α of the order of 10^{-8} K^{-1}.

3. Results and discussion

Figure 1 shows the transition temperature as a function of Ni concentration. These results indicate an almost linear decrease in T_c with increasing impurity concentration. There is qualitative agreement between the present results and the results reported in the literature [6, 20–22] but T_c-values obtained in the present work are slightly higher. Figure 2 shows the variation in oxygen content y of the unit cell with Ni concentration. The oxygen content y is almost independent of Ni concentration. The lattice constants are plotted in figure 3 as functions of the Ni concentration. It is evident from figure 3 that a decreases with increasing x; contrary to this, b increases; c, however, remains more or less constant. These results also indicate that the orthorhombic-to-tetragonal transformation is still taking place even at $x = 5\%$.

The temperature variation in the linear thermal expansion coefficient α in the temperature range 77–300 K for various Ni-doped compounds is shown in figure 4. Figure 5 shows the behaviour of α in the vicinity of the transition temperature. The present results on α do not show a sharp discontinuity in α around T_c; instead α increases gradually as the samples undergo the transition from the normal to the superconducting state. In contrast, in conventional superconductors such as Sn, a sharp discontinuity is observed in the thermal expansion coefficient at the transition temperature. This difference in behaviour is due to the broad transition widths (about 1 K) in high-T_c superconductors compared with the sharp widths (about 1 mK) in conventional superconductors. Therefore, to estimate the expected

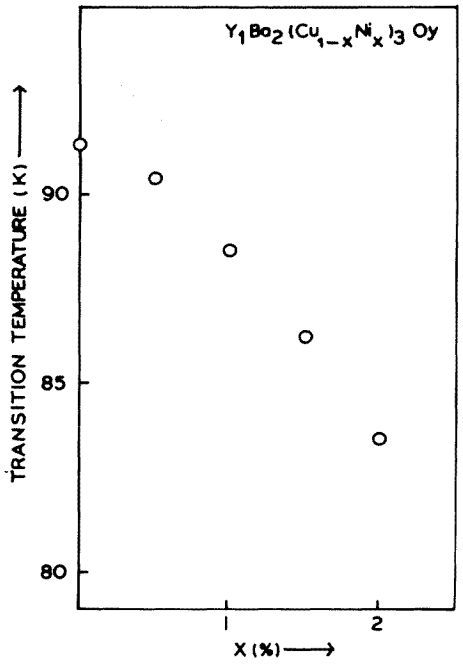

Figure 1. Variation in transition temperature with Ni concentration.

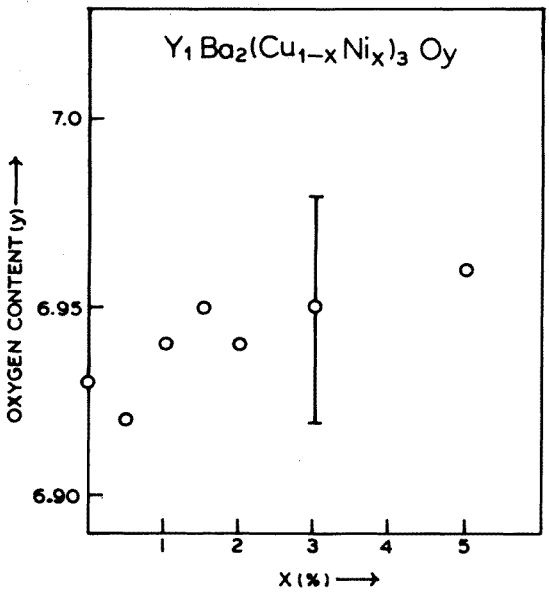

Figure 2. Oxygen content variation with Ni concentration.

jump $\Delta\alpha$ in the coefficient of linear thermal expansion α at the transition temperature T_c, the following procedure was adopted. Two polynomials in T, one for $T < T_c$ and the other for $T > T_c$, were fitted to the experimental data on $\Delta l/l_0$ as a function of

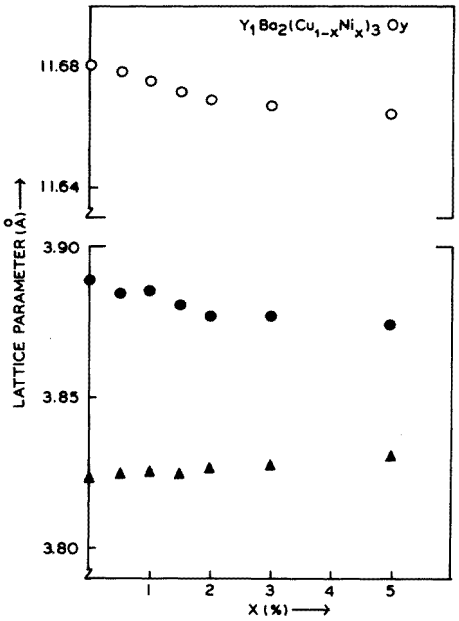

Figure 3. The variation in lattice constants with the Ni concentration of $YBa_2(Cu_{1-x}Ni_x)_3O_y$ compounds: ● , *a*; ▲, *b*; ○ , *c*.

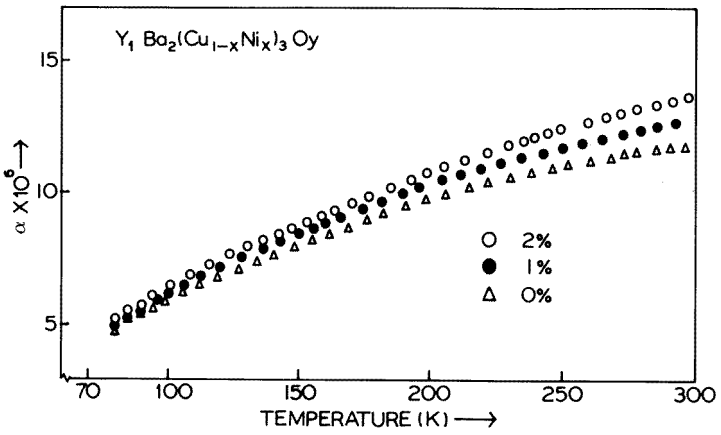

Figure 4. Temperature dependence of α for various Ni-substituted compounds.

temperature T (l_0 is the length of the sample at 77 K). Differentiation of the polynomials thus obtained gives α as a function of temperature. The jump in α at T_c, given by $\Delta\alpha$, was determined by extrapolating the two branches of the α versus T curves thus obtained (solid curves in figure 5) to T_c. The error in the determination of α is estimated to be about $\pm 1.5 \times 10^{-8}$ K^{-1}. The variation in $\Delta\alpha$ with Ni concentration is shown in figure 6. It is evident from the figure that $\Delta\alpha$ decreases with increasing Ni concentration. It is important to mention that replacing 1.5% Cu by Ni has little effect on the transition temperature; however, the decrease in $\Delta\alpha$ is almost a factor of 3. This clearly demonstrates that these

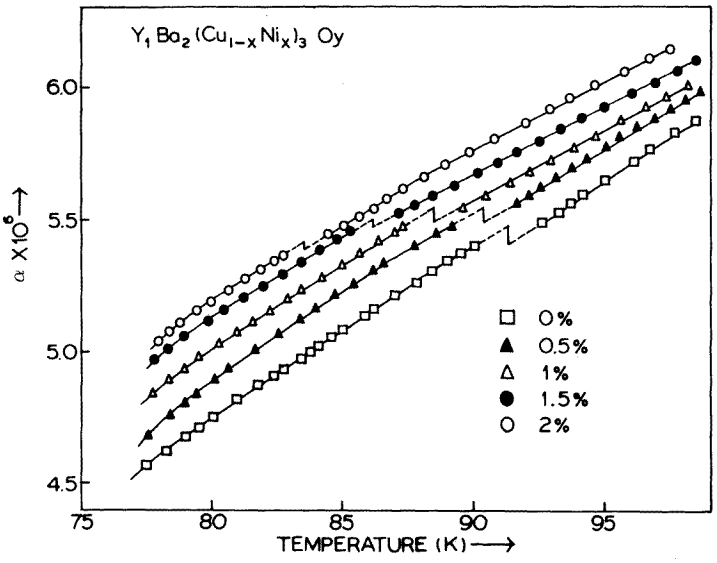

Figure 5. Temperature variation in α for the Ni-substituted compounds in the vicinity of the transition temperature.

substituents are being incorporated into the superconductor as a whole and not in the form of a local cluster. If Ni were substituted in the form of a local cluster, then it would not have any effect on $\Delta\alpha$ because thermal expansion is a bulk property.

There are reports of observations of anomalies in addition to the jump observed around T_c. For example Ruan *et al* [23] have observed a broad minima in α around 160 and 240 K. Meingast *et al* [14] have also reported some anomalies such as a jump in α at $T = 250$ K, hysteresis in the temperature region 50 K $< T <$ 250 K and irreversible length changes at low temperatures ($T <$ 45 K). The anomalous behaviour of α compounds having large Fe and Co concentrations has also been reported by Rao *et al* [15, 16] and they have attributed this to the presence of strain in the samples or to phase instabilities. In the present work the samples prepared with a higher Ni concentration (3% and 5%) did not show any anomalies in α. To study the effect of strain on the thermal expansion of these samples with a high impurity concentration of Ni, the above-mentioned well annealed samples were subjected to strain by keeping them at 200 °C for 8 h, followed by quenching to room temperature. The temperature of 200 °C was chosen because the temperature is low enough to prevent oxygen loss from the samples and moreover the idea was to subject the samples to small strains.

Figure 7 shows the variation in α as a function of temperature for quenched and unquenched samples of Ni with $x = 3\%$ and 5%. The quenched samples in general exhibit larger α-values compared with the unquenched samples and both the quenched samples show anomalies in the temperature range 200–280 K; however, no such anomalies are seen in either of the unquenched samples. The present results suggest that the presence of small strains in samples markedly affects the temperature dependence of the linear thermal expansion coefficient and perhaps leads to the types of anomaly observed in the present studies. It is important to mention that there is strong evidence for the phase instability of the $YBa_2Cu_3O_{7-\delta}$ system [24, 25] at low temperatures, particularly at 200 °C where aging for an extended length of time leads to decomposition into oxygen-ordered orthorhombic

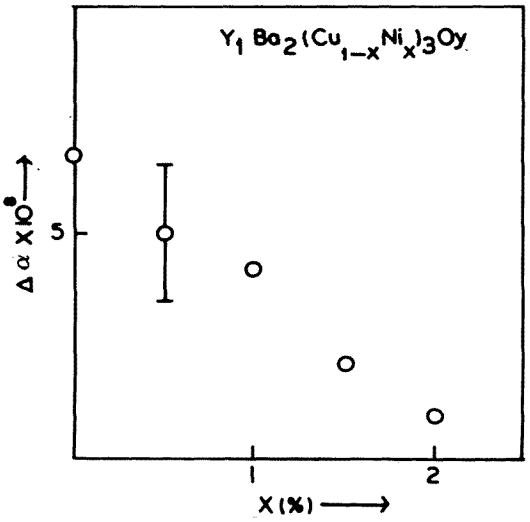

Figure 6. Dependence of α on Ni concentration.

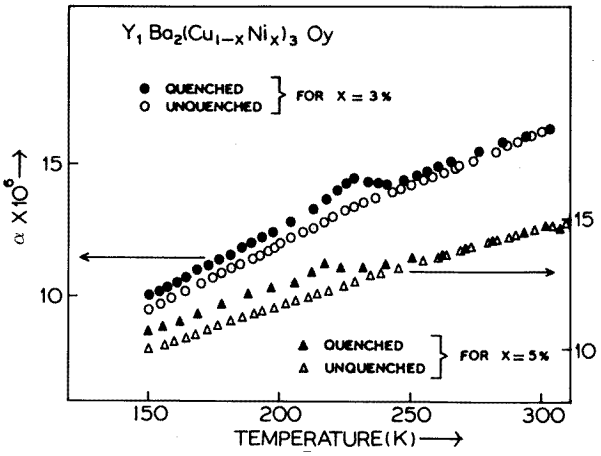

Figure 7. Temperature variation in α for Ni-substituted compounds with $x = 3\%$ and 5%.

and vacancy-ordered tetragonal phases. In the present investigations the samples were kept at $T = 200\,^{\circ}\mathrm{C}$ for only 8 h, and the phase decomposition during this aging period is likely to be very small. However, we do not rule out this effect and further investigations are needed to understand the nature of anomalies unambiguously. Such studies are being carried out and will be reported soon.

4. Conclusions

The dependence of the jump $\Delta\alpha$ on Ni concentration shows that $\Delta\alpha$ decreases with increase in Ni concentration. Meingast *et al* [14] have also observed a decrease in $\Delta\alpha$ for Zn-doped compounds. In contrast, $\Delta\alpha$ is observed to increase with increasing Fe and Co concentrations. This suggests that $\Delta\alpha$ appears to correlate with the substitution site; that

is, for dopants such as Fe and Co which occupy copper planes, $\Delta\alpha$ increases whereas, or dopants such as Ni and Zn occupying the copper chains, there is a decrease in $\Delta\alpha$.

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