# Influence of fluorine doping on the transport properties of $GdBa_2Cu_3O_{7-x}$

M. MURALIDHAR, T. SOMAIAH, D. MANGAPATHI RAO, F. M. AMANULLAH,
P. VEERESHAM, K. J. PRATAP, M. NAGABHOOSHANAM, V. HARI BABU
*Department of Physics, University College of Science, Osmania University,
Hyderabad 500 007, India*

Undoped and fluorine-doped materials of $GdBa_2Cu_3O_{7-x}F_x$ (with $x = 0$, 0.05, 0.1 and 0.2) were prepared at high temperature (950°C) by solid state reaction followed by oxygen treatment. X-ray diffractograms of the undoped sample showed single orthorhombic phase. Resistivity measurements showed that $T_c(0)$ decreases with fluorine concentration. Thermopower measurements indicated a peak just before the onset of the superconducting transition. The reasons for the decrease of $T_c$ and the anomalous behaviour of thermopower have been explained.

## 1. Introduction

Ever since the discovery of high-temperature super-conductivity $(T_c(0) = 30K)$ in the La–Ba–Cu–O system by Bednorz and Muller [1] and later 90 K superconductivity in the Y–Ba–Cu–O system by Wu *et al.* [2], there has been intense research activity on these high $T_c$ materials.

Several research groups replaced yttrium with rare earth atoms and they found that $T_c$ was not altered very little. Similarly, several others added small amounts of 3-d ions (chromium, manganese, iron, nickel, cobalt or zirconium) with the intention of replacing the copper ion. These doped compounds always showed a decrease in $T_c$. Several other workers tried to replace oxygen with fluorine, selenium, etc. To obtain higher $T_c$, Ovshinsky *et al.* [3] reported $T_c$ at 155 K by partial substitution of fluorine for oxygen. Radhakrishnan *et al.* [4] added $BaF_2$ as a dopant in $YBa_2Cu_3O_7$ compound and their results showed that fluorine did not enter the lattice. They also reported that there was no significant change in $T_c$. In the fluorine-implanted $YBa_2Cu_3O_7$ system, Narliker [5] observed a sudden drop in resistance to a very small value around 280 to 290 K; it then remained constant to 89 K and then dropped to zero. Meng Xian-Ren *et al.* [6] also observed zero resistance at 148.5 K in fluorine-implanted Y–Ba–Cu–O compound and this they attributed to a new superconducting phase. They also found that the new phase was quite unstable and it disappeared after three or more thermal cycles from room temperature (RT) to liquid nitrogen temperature (LNT). All these results suggest that fluorine plays an active role in these materials but the problem appears to be the stability of the new superconducting phase. All these studies have been confined to the Y–Ba–Cu–O system. We have studied the influence of fluorine on resistivity and thermopower of $GdBa_2Cu_3O_{7-x}$ material and the results are presented. It was observed that $T_c(0)$ gradually decreases with fluorine concentration and thermopower measurements indicate anomalous behaviour just before the onset of superconductivity. A possible explanation for these observations is given.

## 2. Experimental procedure

Undoped and fluorine-doped $GdBa_2Cu_3O_{7-x}F_x$ (with $x = 0, 0.05, 0.1$ and 0.2) compounds were synthesized by taking appropriate amounts of $Gd_2O_3$, $GdF_3$, $BaCO_3$ and $CuO$, such that gadolinium, barium and copper were in the molar ratio of $1:2:3$. The ground compounds were placed in a platinum crucible and reacted in air at high temperature (nearly 950°C) for 24 h. The compound so formed was cooled slowly and the process repeated. The material was powdered and pelletized by applying 4 to 5 tonne pressure. The pellets were then heated at 950°C in flowing oxygen and slowly cooled to room temperature. X-ray diffractograms of all the samples so prepared were recorded with a Phillips X-ray diffractometer employing $CuK\alpha$ radiation. Resistivity measurements were made by a four-probe technique in a glass cryostat kept in a glass dewar. For thermoelectric power measurements, a thick specimen (nearly 5 mm) was kept in good thermal contact between two copper blocks. The two copper blocks were again separated by two fused quartz rods and a low power heater was arranged around the upper copper block to maintain a temperature difference. Copper–constantan thermocouples were used to monitor $\Delta T$ between the two ends of the specimen. The thermo-induced voltage, $\Delta V$, was read with a digital micro-voltmeter with a sensitivity of 0 to $1 \mu V$.

## 3. Results

Fig. 1 shows the X-ray diffractograms (XRD) of undoped and fluorine-doped $GdBa_2Cu_3O_{7-x}$ for ($x = 0, 0.05$ and 0.1) samples. The XRD of undoped material shows that it has a single orthorhombic phase. The
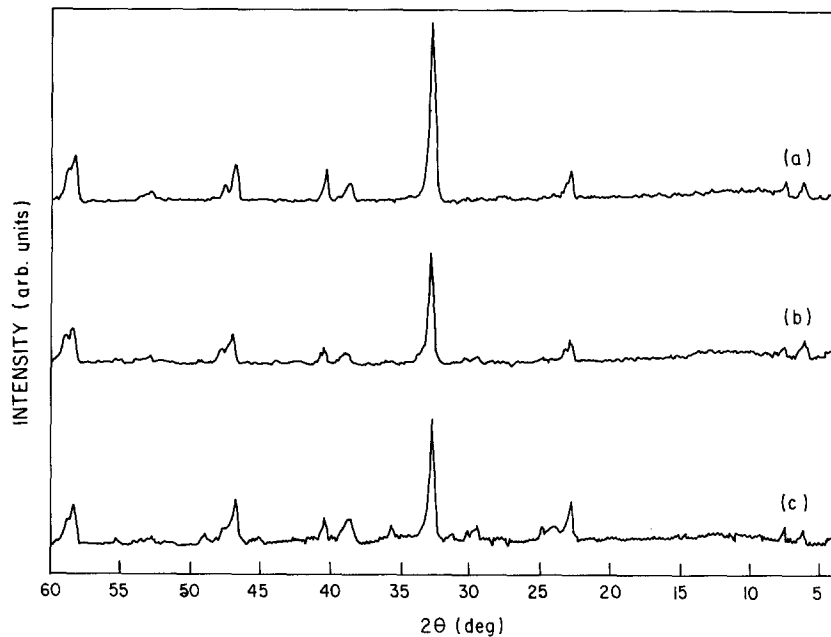
positions and intensities of the peaks are in good agreement with the reported values. The fluorine-doped samples, the intensity and position of the main peaks are found to change. In an undoped sample, the intense peak is obtained at $2\theta = 33°$, whereas its intensity decreased and shifted to $32.4°$ in $x = 0.1$ fluorine-doped sample. Additional peaks were also obtained at $2\theta$ equal to $29.8°$, $30.2°$, $35.8°$, $45.2°$ and $49°$. These peaks which were only just visible in the $x = 0.05$ fluorine-doped sample developed into well-defined peaks in the $x = 0.1$ doped sample. The decrease in the intensity of the main peak and the presence of additional peaks in the fluorine-doped samples suggest that additional phases have formed due to fluorine doping. The XRD of $GdF_3$ was also taken and a comparison showed that the additional peaks did not correspond to the $GdF_3$ phase.

The resistance of the samples has been studied as a function of temperature for the three samples ($x = 0.0$, 0.05 and 0.1) and the results are shown in Fig. 2. The superconducting transition was observed in all three samples above LNT but $T_c(0)$ decreased with

fluorine concentration. The observed $T_c(ON)$ and $T_c(0)$ of undoped and doped samples are given in Table I. The thermoelectric power (TEP) of three samples ($x = 0.0$, 0.05 and 0.1) as a function of temperature is shown in Figs 3a to c, respectively. The TEP drops to zero in all three samples. The transition temperatures obtained from these results are given in Table I. The graphs show that (i) the transition temperature decreases with fluorine doping, (ii) the value of thermopower at 220 K is almost the same (1.5 μV $K^{-1}$) in all three compounds, (iii) with decreasing temperature the thermopower decreases linearly until 120 K in undoped and 180 K in fluorine-doped compounds, (iv) below 120 K in undoped and 180 K in doped samples the thermopower is enhanced and reaches a maximum value ($S = 0.8 μV K^{-1}$ for $x = 0$, $S = 3.25 μV K^{-1}$ for $x = 0.05$ and $S = 3.5 μV K^{-1}$ for $x = 0.1$) just below the transition temperature.

## 4. Discussion

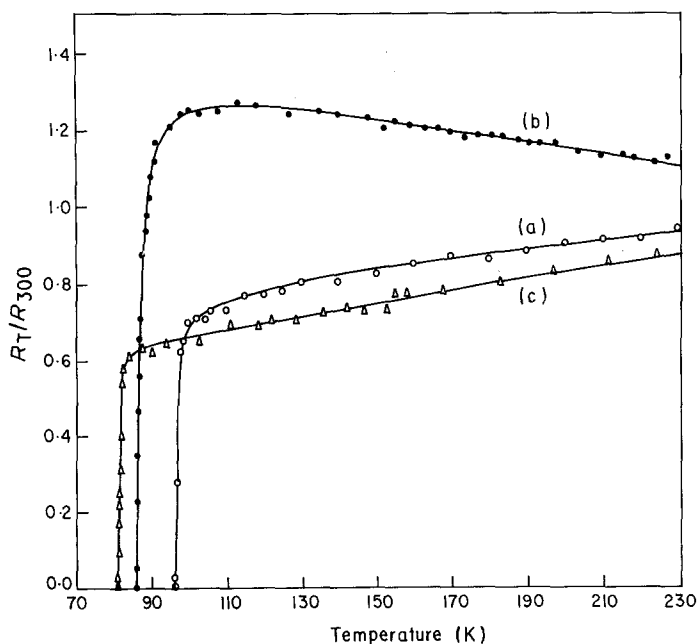The resistivity and thermopower data presented in Figs 2 and 3 show that $T_c$ decreases with increasing

TABLE I

| Serial no. | Compound | From resistivity | | From TEP |
|---|---|---|---|---|
| | | $T_c(\text{ON})$ (K) | $T_c(0)$ (K) | $T_c(\text{K})$ |
| 1. | $GdBa_2Cu_3O_7$ | 106 | 96 | 96 |
| 2. | $GdBa_2Cu_3O_{6.95}F_{0.05}$ | 96 | 86 | 90 |
| 3. | $GdBa_2Cu_3O_{6.9}F_{0.1}$ | 90 | 82 | 85 |

fluorine concentration. While preparing the fluorine-doped compound, the $Gd_2O_3$ concentration was reduced and $GdF_3$ was added in its place, in order to maintain the same gadolonium composition in all the compounds. Thus in the starting material itself, oxygen concentration is less. It has been established by several workers that $T_c$ is very sensitive to oxygen concentration and a decrease in oxygen concentration could lead to a decrease in $T_c$. Further XRD pattens showed the presence of additional phases in fluorine-doped samples. It has also been found that $GdF_3$ phases are not present and these additional phases probably could be due to the formation of some oxy-fluorides. If oxy-fluorides are formed, the effective concentration of oxygen present in the Cu–O phases could decrease and this may lead to a decrease in $T_c$.

The thermoelectric power of $YBa_2Cu_3O_7$ has been measured by a number of groups [7–10]. Similar to our results, they also observed an enhancement of the thermopower just above the superconducting transition temperature. Uher and Kaiser [8] suggested it to be a phonon drag truncated by the onset of supercon-

ductivity. Jha et al. [10] have also observed similar behaviour in $YBa_2Cu_3O_7$ cooled at different rates. This behaviour is very similar to the phonon drag peak expected at a temperature about $\theta_D/5$ where $\theta_D$ is the Debye temperature. Taking a reasonable value of $\theta_D$ as 400 K [11] the observed peak at its $1/T$-like fall are consistent with the phonon drag mechanism. The phonon drag mechanism should, in general, be reduced by alloying, due to an increase in the phonon scattering. However, Srinivasan et al. [9], who studied the thermopower of an alloy in which 20% yttrium was replaced by erbium, found no such reduction. Ausloos et al. [12] suggested another explanation which depends on the granular nature of these materials. Assuming a fraction of the grains to be superconducting, they were able to achieve the desired form of the temperature dependence of thermopower, S. Jha et al. [10] have suggested an alternating mechanism based on super-conducting fluctuations in the normal phase, rather than a phonon drag effect. It appears that no single mechanism described above is actually responsible for the enhancement in a strongly interacting supercon-ducting system like $YBa_2Cu_3O_7$, and we feel that more detailed studies are required before an exact mechanism could be postulated.

## Acknowledgements
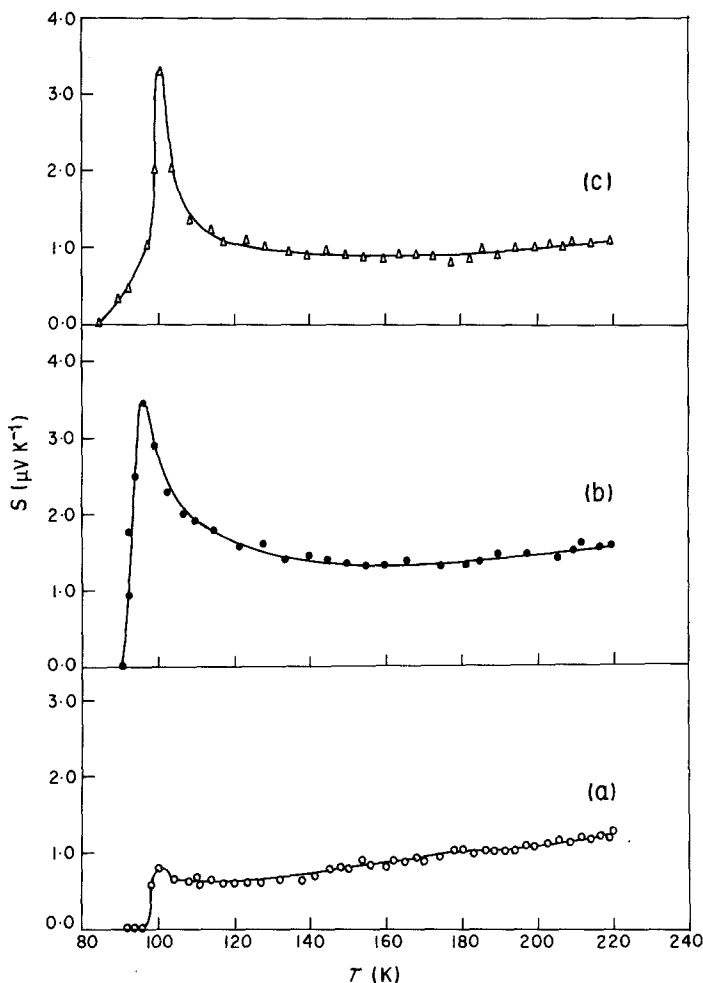
Figure 3 Thermoelectric power variation with temperature for (a) $GdBa_2Cu_3O_7$, (b) $GdBa_2Cu_3O_{6.95}F_{0.05}$, and (c) $GdBa_2Cu_3O_{6.90}F_{0.10}$.

## References

1. J. D. BEDNORZ and K. A. MULLER, *Z. Phys. B* **64** (1986) 189.
2. M. K. WU, J. R. ASHBURN, C. T. TORNG, P. H. HOR, R. L. MENG, L. GAO, Z. J. HUANG, Y. Q. WANG and C. W. CHU, *Phys. Rev. Lett.* **58** (1987) 908.
3. S. R. OVSHINISKY, R. T. YOUNG, D. D. ALLARD, G. DE MAGGIO and G. A. VANDER LEEDEN, *ibid.* **58** (1987) 2579.
4. T. S. RADHAKRISHNAN, S. KALAVATI, V. S. SASTRY, K. CHANDRASEKHARAN, C. R. VENKATESWARA RAO, M. PARANTHAMAN, U. V. VARADARAJU and G. V. SUBBA RAO, International Conference on low temperature Physics, Kyoto (1987).
5. A. V. NARLIKER, Lecture given at RRL, Hyderabad (1987).
6. MENG XIAN-REN, REN YON-RU, LINMING-ZHU, TU QING-YUN, LIN ZHEN-JIN, SANG LI-HUA DING, WEI-KING, FUMIN HUA, MENG QINGYUM, BICHANG-JIANG, LIXIA-HUI, QIN GUANLIANG and CHEN MON-YUANG, *Solid State Commun.* **64** (1987) 325.
7. A. MAWDSLEY, H. J. TRODAHL, J. TALLON, J. SARFATI and A. B. KAISER, *Nature* **328** (1987) 233.
8. C. UHER and A. B. KAISER, *Phys. Rev. B* **36** (1987) 5680.
9. R. SRINIVASAN, V. SANKARANARAYANAN, N. P. RAJU, S. NATARAJAN, U. V. VARADARAJU and G. C. SUBBA RAO, *Pramana J. Phys.* **20** (1987) L225.
10. S. R. JHA, Y. S. REDDY, D. K. SURI, K. D. KUNDRA, R. G. SHARMA and DEEPAK KUMAR, *ibid.* **32** (1989) 277.
11. M. F. CROMMIE, A. ZETTL, T. W. BARBEE and M. L. COHEN, *Phys. Rev. B* **37** (1988) 9734.
12. M. AUSLOOS, *Solid State Commun.* **65** (1988) 365.