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Investigation of novel high T_c superconducting oxides

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Abstract. Our results of microscopic and macroscopic studies of novel high T_c superconductors are discussed. They permit a straightforward comparison of the nature of the superconductivity in 40 K range (La_2CuO_4 type) and 90 K range ($YBa_2Cu_3O_7$ type) superconductors.

Keywords. High T_c superconductivity; RE–Ba–Cu–O system; lattice instability; macroscopic studies; microscopic studies

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Following the report of Bednorz and Muller (1986) and others (Uchida *et al* 1987; Chu *et al* 1987; Cava *et al* 1987) on the high T_c superconductivity in the La–Ba–Cu–O system in the 30 K range, we have put in efforts in increasing T_c as well as to understand some issues related to this new topic. Part of our results have already been published at various places (Dhar *et al* 1987; Grover *et al* 1987a, b; Nagarajan *et al* 1987a, b; Paulose *et al* 1987; Sampathkumaran *et al* 1987a, b). Since then we have carried out further detailed studies—both microscopic and macroscopic—in order to understand these systems better. We consider it worthwhile to summarize here our earlier findings reported in detail elsewhere and to have a fresh look at some of those experimental data along with new results. The characteristic temperatures of the resistance transition in our samples are listed in table 1. Our main findings are:

(i) The influence of various chemical substituents like Ca, Eu, Yb, Cd, Zn etc on the normal state resistive behaviour as well as on T_c of $La_{1·8}Sr_{0·2}CuO_4$ system was studied. The heat treatment during preparation was kept the same for all the specimens, a criterion to be necessarily satisfied to understand the normal state behaviour. We find that whenever there is a size mismatch between the substituent and La, T_c is depressed. However, both the size mismatch and the charge mismatch are found to be important for the semiconducting-like (localization) behaviour for the air-annealed specimens before the onset of superconductivity. Thus, both Ca and Eu depress T_c; and the degree of localization behaviour in the normal state for the Ca specimen is significant, scaling with Ca concentration, but not much affected by Eu substitution. The localization behaviour was also shown to be due to the oxygen vacancies (Grover *et al* 1987a). Annealing the specimens in oxygen resulted in a metallic behaviour of the resistivity in the normal state, at the same time raising T_c relative to the corresponding value in air-annealed specimens. Cd and Zn specimens were not found to superconduct, whereas Yb does not seem to enter the lattice.

Table 1. List of superconducting onset (T_0), midpoint (T_m), and zero resistance temperatures (T_c) of our specimens.

Compounds	T_0(K)	T_m(K)	T_c(K)
$La_{2-x}Ca_xCuO_4$			
$x = 0{\cdot}075$(air)	30	18	12
$0{\cdot}10(O_2)$	25	22	20
$0{\cdot}10$(air)	30	25	18
$0{\cdot}20$(air)	22	20	14
$0{\cdot}30$(air)	22	18	10
$La_{1{\cdot}8-x}Eu_xSr_{0{\cdot}2}CuO_4$			
$x = 0$(air)	36	29	26
$0{\cdot}1$(air)	36	28	25
$0{\cdot}1(O_2)$	38	30	25
$0{\cdot}2$(air)	24	15	9
$La_{1{\cdot}8-x}Yb_xSr_{0{\cdot}2}CuO_4$			
$x = 0{\cdot}1$(air)	36	29	23
$0{\cdot}1(O_2)$	40	32	26
$0{\cdot}2$(air)	39	32	28
$La_{1{\cdot}8}Pb_{0{\cdot}1}Sr_{0{\cdot}1}CuO_4$			
air-annealed	35	26	20
$Y_{1{\cdot}2}Ba_{0{\cdot}8}CuO_4(O_2)$	95	90	87
$Y_{1{\cdot}05}Ba_{1{\cdot}95}Cu_3O_y(O_2)$	95	92	91
-do- (air)	94	48	32
$Y_{1{\cdot}35}Ba_{1{\cdot}65}Cu_3O_y(O_2)$	100	90	53
$Y_{0{\cdot}9}Ba_{2{\cdot}1}Cu_3O_y(O_2)$	98	89	89
$Y_{0{\cdot}9}Ba_{1{\cdot}8}Sr_{0{\cdot}3}Cu_3O_y$(air)	96	85	82
$Y_{0{\cdot}9}Ba_{1{\cdot}8}Ca_{0{\cdot}3}Cu_3O_y$(air)	90	72	46
$Y_{0{\cdot}9}Ba_{1{\cdot}8}Ca_{0{\cdot}3}Cu_3O_y(O_2)$	98	83	81
$Y_{0{\cdot}9}Ba_{1{\cdot}5}Sr_{0{\cdot}6}Cu_3O_y$(air)	96	80	72
$Y_{0{\cdot}9}Ba_{1{\cdot}5}Ca_{0{\cdot}6}Cu_3O_y(O_2)$	98	81	79
$YBa_2Cu_3O_y(O_2)$	96	91	89
$EuBa_2Cu_3O_y$	98	92	85
$GdBa_2Cu_3O_y$	98	88	80
$NdBa_2Cu_3O_y$	90	78	69

(ii) During the period when there were attempts all over the world to raise T_c above 40 K, we investigated the compound $Eu_{1{\cdot}8}Sr_{0{\cdot}2}CuO_4$ (tetragonal) (following the clues from the results of high pressure experiments (Chu *et al* 1987) on $La_{1{\cdot}8}Ba_{0{\cdot}2}CuO_4$); this Eu compound turned out to be semiconducting. It is important to note that Eu_2CuO_4 itself crystallizes in the tetragonal form, unlike La_2CuO_4 (orthorhombic). Therefore, our observation may imply that those compounds on the verge of structural instability are more prone to high T_c superconductivity (Grover *et al* 1987a). This may mean that there are some soft

phonons in these La–Ba–Cu–O systems responsible for superconductivity. In other words, phonon-mediated superconductivity might dominate in this system.

(iii) There is no change in the ^{151}Eu Mössbauer isomer shift as a function of temperature in the superconducting $La_{1.7}Eu_{0.1}Sr_{0.2}CuO_4$ compound. This behaviour is quite different from that reported for Sn doped in $La_{1.85}Sr_{0.15}CuO_4$ (Giapintzakis *et al* 1987).

(iv) When attempts to increase T_c were on, Chu's group reported the observation of T_c at 80 K in the multiphase material at composition $Y_{1.2}Ba_{0.8}CuO_4$. Immediately after the publication of this work, we synthesized this specimen and reached a higher transition temperature with a much narrower transition width (Sampathkumaran *et al* 1987a). We performed a detailed study of this system (Paulose *et al* 1987). Our important observation was that there was a large difference between the DC magnetization values in the zero field cooled and field cooled states. We attributed this behaviour to the existence of spin-glass like metastable states in these superconductors (Paulose *et al* 1987). In concurrence with this conclusion subsequent to our study we came across a publication by Muller *et al* (1987) making similar observations.

(v) Attempts to identify the phase that is superconducting in the above multiphase Y–Ba–Cu–O system were made. We studied the compounds of the type $Y_xBa_{1-x}CuO_y$ following a clue in the X-ray diffraction pattern of our specimen of $Y_{1.2}Ba_{0.8}CuO_4$. From the correlation between the strength of the AC susceptibility (χ) signal and a particular set of X-ray diffraction lines, we concluded (Dhar *et al* 1987) that the compound $YBa_2Cu_3O_y (y \simeq 7)$ crystallizing in the $La_3Ba_3Cu_6O_{14}$ type structure gives rise to superconductivity well above 77 K. Simultaneously a few other groups from their studies arrived at a similar conclusion. We have observed extremely sharp transitions (< 2 K) in AC susceptibility as well as in electrical resistance in our specimens (Nagarajan *et al* 1987a).

(vi) Specimens of $YBa_2Cu_3O_y$ prepared in air following our method of preparation crystallize in the tetragonal structure with a lower $T_c (< 50$ K). However, those prepared in O_2 atmosphere crystallize in the orthorhombic structure with a higher $T_c (\sim 90$ K) (Dhar *et al* 1987; Nagarajan *et al* 1987a). Thus, our results show the existence of a correlation between the structure and the values of T_c. On the basis of these observations, we conclude that the Cu–O layers control superconductivity.

Following the above investigations, we have carried out more detailed magnetic response studies of $YBa_2Cu_3O_y$ as well as the influence of various chemical substituents (including rare-earths in the place of Y). These results viewed together with those for La–Ba–Cu–O system discussed above clearly bring out the different nature of superconductivity in the Y–Ba–Cu–O system. We also carried out Mössbauer, NMR and specific heat studies in some compounds. The results of these investigations are discussed below.

(i) The zero field cooled and field cooled specimens of $YBa_2Cu_3O_y$ also show spin-glass like magnetic response in the DC susceptibility (see figure 1). The lower critical fields are of the order of 400 Oe, 1·9 kOe and 2·2 kOe at 46 K, 26 K and 6 K respectively, as obtained from magnetization versus field plots.

(ii) AC susceptibility (χ) as a function of temperature for $YBa_2Cu_3O_y$ at various measuring fields is shown in figure 2. It is important to notice that the width of the transition is a sensitive function of the measuring field.

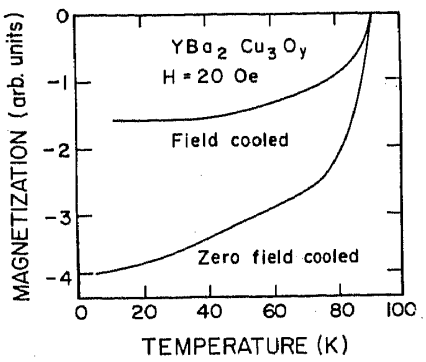

Figure 1. DC magnetization for the field-cooled and zero-field cooled specimens of $YBa_2Cu_3O_y$ sample.

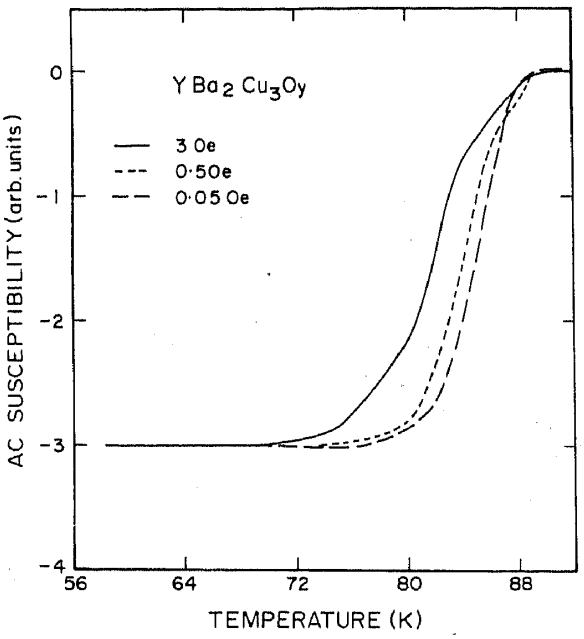

Figure 2. AC susceptibility as a function of temperature for the specimen $YBa_2Cu_3O_y$ at various measuring fields.

(iii) Total replacement of Ba by Ca and Sr showed the absence of superconductivity in $YBa_2Cu_3O_y$ down to 4·2 K. This behaviour is different from that of $La_{1.8}Ba_{0.2}CuO_4$, where the replacement of Ba by Sr, in fact, increases T_c. The size mismatch between Y^{3+} and Sr^{2+} is less than that between Y^{3+} and Ba^{2+}. It seems that the size mismatch between rare earth and alkaline ions results in better atomic ordering and favours higher values of T_c in this Y-based system.

(iv) Partial replacement of Ba by Sr and Ca in $YBa_2Cu_3O_y$ depresses T_c (see the resistance behaviour in figure 3). The air-annealed specimens of Ca-substituted samples show localization behaviour in the normal state. However, we do not find any relation between the degree of localization and size and charge imbalances as discussed above in the $La_{1.8}Sr_{0.2}CuO_4$ system. These observations essentially bring

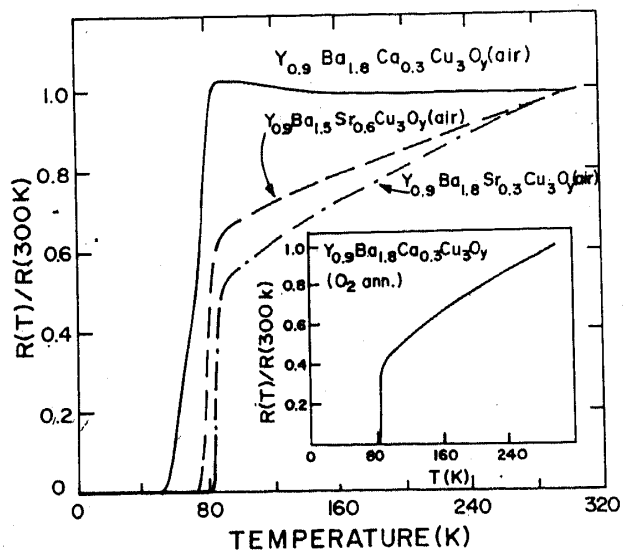

Figure 3. Resistance versus temperature for some specimens partially substituted by Ca and Sr in the place of Ba in the Y–Ba–Cu–O system.

out one of the major differences in the mechanisms of electrical conductivity between the 40 K and the 90 K superconductors.

(v) Following the work of Murphy *et al* (1987), we also synthesized the superconducting specimens with other rare earths (RE), $REBa_2Cu_3O_y$. The resistance data for some of the oxygen-annealed specimens are shown in figure 4. It is important to note that even the large magnetic moment values of rare earth ions do not drastically affect T_c in this class of compounds. This observation again brings out the different nature of superconductivity in this class of compounds. Though the width in the resistance transition is rather small in these rare-earth substituted specimens, AC susceptibility (see figure 5) shows a much broader transitions (for a reasonable field of measurement). In addition, T_c as inferred from the point where χ_{AC} starts becoming negative is always lower relative to that obtained from resistance studies (see figure 4). In the case of magnetic rare-earth ions, there is a paramagnetic contribution to susceptibility, which has to be overcome before the diamagnetic response becomes visible; this factor could be one reason for the lowering of T_c as obtained from susceptibility studies. However, this effect is absent in Y and Eu samples. This implies that there is a wide spectrum of temperature range, in which different regions of the sample undergo superconducting transition. In other words, the resistance measurements do not give any information regarding the homogeneity of the sample. In this connection, we would like to emphasize that only those samples which show a very sharp transition in χ_{AC} (as those reported by Nagarajan *et al* 1987b) should be employed for any serious measurement (like infrared studies to obtain superconducting gap).

(vi) We are also performing ^{63}Cu NMR measurements on the $REBa_2Cu_3O_y$ compounds to understand the hyperfine coupling between the rare-earth moments and ^{63}Cu nucleus in these systems. Our preliminary findings are quite interesting. In all the RE-substituted compounds measured till now (Y, Nd, Eu and Gd), a weak ^{63}Cu NMR resonance occurs at the same frequency (for a given field) and does not shift as a function of temperature down to 4·2 K. In short, the Knight shift

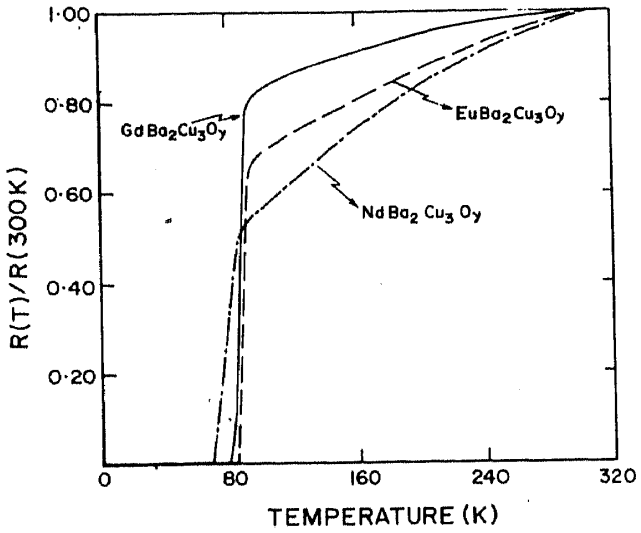

Figure 4. Resistance versus temperature for $REBa_2Cu_3O_y$ (RE = Nd, Eu and Gd) specimens.

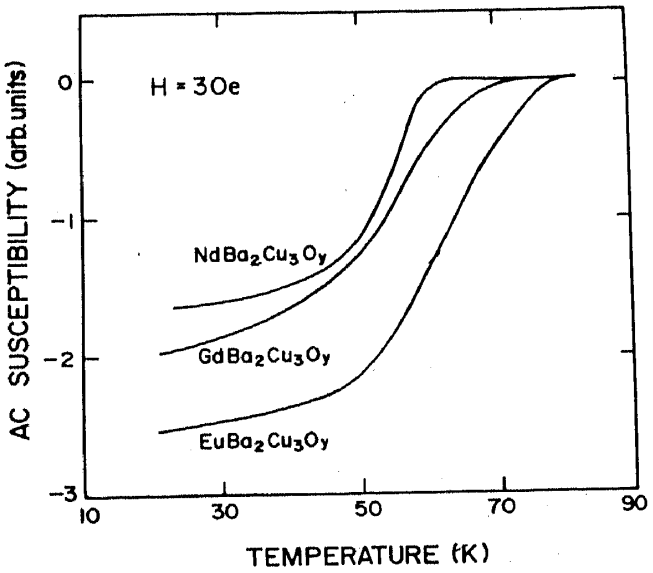

Figure 5. AC susceptibility as a function of temperature for $REBa_2Cu_3O_y$ (RE = Nd, Eu and Gd) specimens.

of ^{63}Cu, for some Cu ions, is temperature and rare-earth independent thereby implying the absence of coupling between the 4*f* electrons and ^{63}Cu nucleus. The shift is quite large ($> -0{\cdot}5\%$) and negative. This may suggest that Cu 3*d* shell is unfilled and the moment associated with 3*d* electrons is not of a localized nature. Due to a very large quadrupolar coupling constant for a major portion of Cu ions, as reported by Riesemeier *et al* (1987, private communication), we cannot observe the NMR signal of these Cu ions at our measuring frequency ($\sim$ 17 MHz). In any case, our results clearly suggest that there are different kinds of Cu ions with different co-ordination numbers (probably depending on the oxygen content).

(vii) Preliminary specific heat (C) studies in the temperature interval (4·2–18 K)

for the compound $YBa_2Cu_3O_y$ suggest that the electronic specific heat coefficient, γ, obtained using the relation $C = \gamma T + \beta T^3$, is about 15 mJ/mole K^2, a value typical of rare earth valence fluctuation materials. Measurements are being made on various specimens and the results will be published elsewhere (Nambudripad *et al* 1987).

(viii) ^{151}Eu Mössbauer measurements were carried out on $EuBa_2Cu_3O_y$ in order to see whether there are any electronic factors changing (as measured by ^{151}Eu isomer shift) across T_c and also to look for phonon anomalies at the Eu site as measured by Mössbauer resonance intensity. ^{151}Eu isomer shift is +0·6 mm/sec (with respect to EuF_3) and is practically temperature-independent. The results suggest that there is not much anomaly in the resonance intensity with decreasing temperature. This may mean that the phonon modes at the Eu site are not probably involved in the superconductivity. This is consistent with the fact that the magnetic rare-earth substitution does not alter superconductivity. Detailed results will be published elsewhere (Nagarajan *et al* 1987).

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