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Electromagnetic response of a single phase Y-Ba-Cu-O compound superconducting in the 90 K range

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Abstract. The results of x-ray diffraction, electrical resistance, DC and AC magnetization studies on two specimens of compositions $Y_{2\cdot1}Ba_{3\cdot9}Cu_6O_{14-\delta}$ and $Y_{1\cdot8}Ba_{4\cdot2}Cu_6O_{14-\delta}$ are presented. Our studies confirm that $La_3Ba_3Cu_6O_{14}$ type orthorhombic phase is responsible for superconductivity in the 90 K range. The heat treatment that yields high quality samples with sharp transition in electrical resistance as well as in AC magnetic susceptibility measurements is described. Magnetic response just below T_c is found to be sensitive to the measuring field.

Keywords. High temperature superconductivity; Y-Ba-Cu-O system; Electromagnetic response.

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The discovery of superconductivity by Wu *et al* (1987) above the boiling point of liquid nitrogen in a multiphase Y-Ba-Cu-O system has stimulated intense activity everywhere. This result was confirmed and improved upon (Ganguly *et al* 1987a; Sampathkumaran *et al* 1987; Umarji *et al* 1987; G V Subba Rao, Private Communication; S K Malik, Private Communication) and the phase that superconducts in the multiphase system was identified independently by several groups (Ganguly *et al* 1987b; Dhar *et al* 1987; Cava *et al* 1987; Beno *et al* 1987). In the course of our work towards isolating the single phase compound, we had synthesized and investigated the compounds belonging to the series $Y_{1-x}Ba_xCuO_y$ (Dhar *et al* 1987). On the basis of the correlation between the strength (as well as sharpness) of the diamagnetic response and the x-ray diffraction intensities of a particular set of lines, we arrived at the conclusion that the superconducting (T_c = 90 K) phase has the orthorhombic $La_3Ba_3Cu_6O_{14}$ type structure (Er-Rakho *et al* 1981). In this communication, we present the details of electrical resistance and magnetization measurements on a few specimens, close to the single phase composition, further characterizing the behaviour of the phase superconducting in the 90 K range. Extremely sharp transitions in the AC susceptibility and electrical resistance data have been observed for a particular heat treatment of our specimens. We think that this information is of technological importance.

The samples $Y_{2\cdot1}Ba_{3\cdot9}Cu_6O_y$ and $Y_{1\cdot8}Ba_{4\cdot2}Cu_6O_y$ (where $y = 14-\delta$) were prepared by a solid state reaction procedure. The stoichiometric amounts of Y_2O_3 (> 99%), CuO (> 99%) and $BaCO_3$ (AR grade) were thoroughly mixed in a medium of acetone and presintered at 700°C in air overnight. The presintered materials were then heated at 900°C for 2 days in air, with a few intermediate grindings. One portion of the reacted mixture for each sample was pelletized by

applying a pressure of about 4 tons and the pellet annealed at 900°C for 15 hr in a continuous flow of oxygen gas (hereafter referred to as oxygen-annealed specimen). The other portion of the reacted mixture was further heated at 900°C in oxygen atmosphere overnight prior to pelletizing. This pellet was also subsequently heated at 900°C for 15 hr (hereafter referred to as oxygen-presintered specimen).

The x-ray diffraction patterns obtained using CuK_α radiation for both the compositions are shown in figure 1. The oxygen-annealed and oxygen-presintered specimens at the same composition give nearly identical x-ray patterns. The majority of the sharp lines could be identified (Dhar *et al* 1987) with the $La_3Ba_3Cu_6O_{14}$ type (Er-Rakho *et al* 1981) distorted tetragonal structure. It has since been confirmed independently by several groups that the splitting visible in several of the intense lines corresponds to the orthorhombic nature (see, for instance, Schuller *et al* 1987). We find that the set of extra lines (marked by crosses in figure 1) belong to Y_2BaCuO_5 phase in the case of $Y_{2\cdot1}Ba_{3\cdot9}Cu_6O_y$ specimen, whereas they arise from $BaCuO_2$ type phase in $Y_{1\cdot8}Ba_{4\cdot2}Cu_6O_y$ specimen. Therefore, the perfect single phase compound could be synthesized at a composition intermediate between the above two specimens. This is consistent with many recent reports (Ganguly *et al* 1987b; Cava *et al* 1987; Beno *et al* 1987) which give the stoichiometry as $YBa_2Cu_3O_{6\cdot85}$.

DC electrical resistance measurements were performed on all the specimens by the conventional four-probe method. The detailed AC susceptibility and DC magnetization studies were carried out only on oxygen-presintered $Y_{2\cdot1}Ba_{3\cdot9}Cu_6O_y$ specimen.

Figure 2 shows AC susceptibility data in the oxygen-presintered specimen at stoichiometry $Y_{1\cdot8}Ba_{4\cdot2}Cu_6O_y$. The inset shows the temperature variation of AC susceptibility and resistance values on the same expanded scale. The rapid increase in diamagnetic response sets in at a temperature slightly lower (~ 2 K) than the fall in resistance values. It is satisfying to note that the width of the transition (defined as the variation from 10 to 90% value) in AC susceptibility and resistance data is very small (~ 2 K). The zero resistance state is obtained at 89 K and the mid-point is at 90 K.

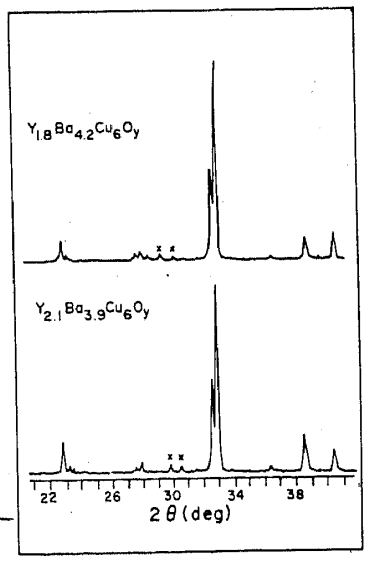

Figure 1. X-ray diffraction patterns of the specimens $Y_{1\cdot8}Ba_{4\cdot2}Cu_6O_y$ and $Y_{2\cdot1}Ba_{3\cdot9}Cu_6O_y$.

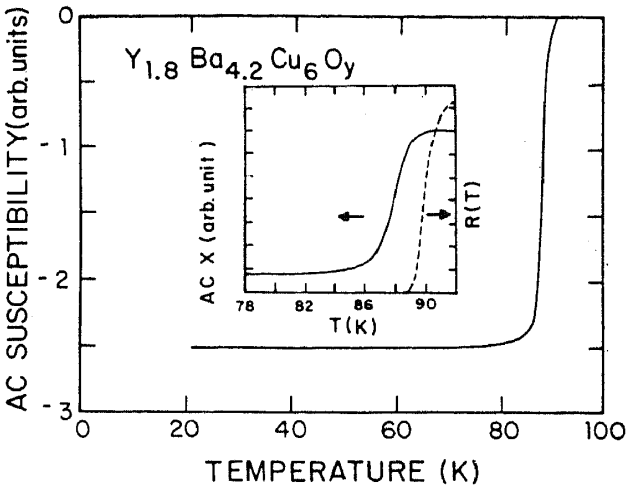

Figure 2. AC susceptibility (χ) in the temperature interval 20–100 K for the specimen $Y_{1.8}Ba_{4.2}Cu_6O_y$. Inset shows AC χ as well as the resistance data in the temperature interval 78–92 K for the same specimen.

Figure 3 displays the resistance data normalized to the 300 K value for the oxygen-presintered $Y_{2.1}Ba_{3.9}Cu_6O_y$ specimen. The zero resistance temperature, mid-point and 10 to 90% width values are 89 K, 90·5 and 2 K respectively. These values are the same as in oxygen-presintered $Y_{1.8}Ba_{4.2}Cu_6O_y$ specimen, thereby characterizing the parameters underlying the superconducting phase in two specimens. The inset of figure 3 affords a comparison of resistance behaviour near the transition in oxygen-presintered and oxygen-annealed specimens at the same composition. The latter shows higher zero resistance temperature (90 K). However, the comparison of the AC susceptibility data shows that in the oxygen-annealed specimen the transition is not only somewhat broadened but also shows a kink (see figure 3 in Dhar *et al* 1987) during the rapid fall. Similar differences have also been observed in the AC susceptibility response of the oxygen-presintered and oxygen-annealed specimens at composition $Y_{1.8}Ba_{4.2}Cu_6O_y$.

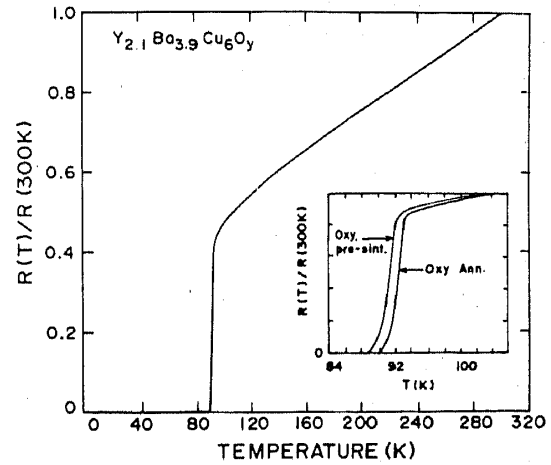

Figure 3. Resistance (4·2–300 K) normalized to the 300 K value for the oxygen presintered specimen of the sample $Y_{2.1}Ba_{3.9}Cu_6O_y$. Inset shows the difference in the resistance data for the oxygen-presintered and oxygen-annealed specimens of the same composition.

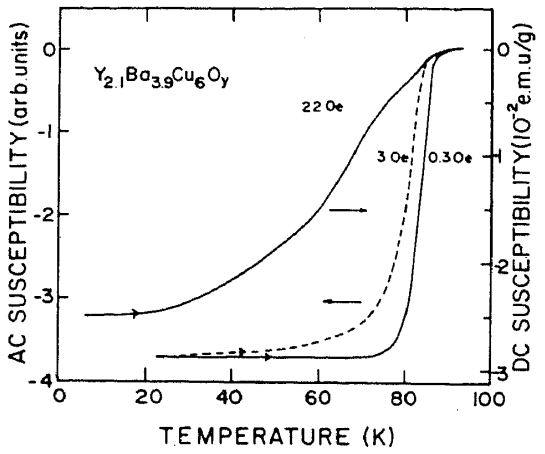

Figure 4. AC susceptibility (in two measuring fields 0·3 Oe and 3 Oe) and DC susceptibility (in a field of 22 Oe) as a function of temperature for the oxygen-presintered specimen of $Y_{2\cdot1}Ba_{3\cdot9}Cu_6O_y$.

These resuits imply that presintering the reaction product in oxygen atmosphere yields more homogeneous specimens.

Figure 4 shows the temperature variation of DC susceptibility measured in a field of 22 Oe and the AC susceptibility data recorded in fields of ~ 0·3 Oe (r.m.s.) and ~ 3·0 Oe (r.m.s.) at 320 Hz in $Y_{2\cdot1}Ba_{3\cdot9}Cu_6O_y$ (oxygen presintered specimen). The sample was first cooled down to the lowest temperature in earth's magnetic field and the measurements were made during the warm-up cycles. The different curves of figure 4 vividly show the sensitivity of the width of the transition in susceptibility data to the strength of the measuring field. Similar effect has also been seen recently by Ray Chaudhary *et al* (1987). Figure 5 contains the comparison of AC susceptibility data recorded in the same measuring field (~ 1 Oe r.m.s.) for specimen cooled down to the lowest temperature in the nominal zero field and 60 Oe field values. As earlier, the data were recorded during the warm-up cycle with the field on. The two curves of figure 5 demonstrate that as far as the widths of the transition in AC susceptibility data are concerned, the presence of steady DC magnetic field has less severe effect as compared to the measuring field.

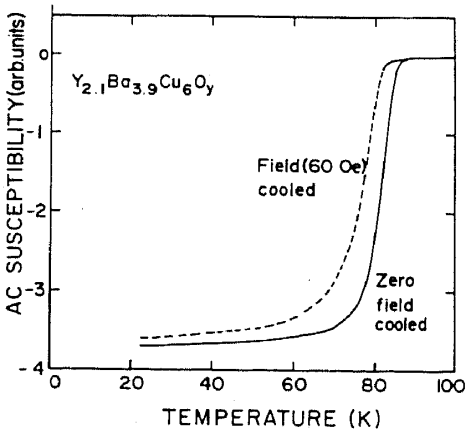

Figure 5. AC susceptibility of the oxygen-presintered specimen of the composition $Y_{2\cdot1}Ba_{3\cdot9}Cu_6O_y$ in the presence of DC field (60 Oe) as well as in the absence of this field.

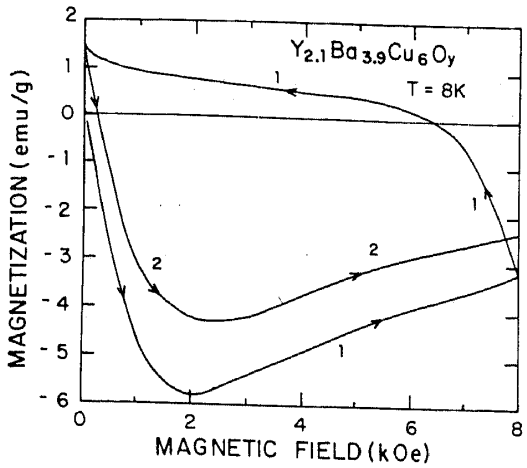

Figure 6. Magnetic hysteresis curve (measured up to a field of 8 kOe) for the oxygen-presintered specimen of $Y_{2.1}Ba_{3.9}Cu_6O_y$.

Figure 6 shows the magnetization versus field plot obtained at 8 K in oxygen-presintered $Y_{2.1}Ba_{3.9}Cu_6O_y$ specimen by cycling the field upto 8 kOe. The sample was cooled down to 8 K in nominal zero field before performing the measurements, the numbers labelling the curves in figure 6 connote the sequence of the cycling. The general shape and the hysteritic behaviour of the plot imply the irreversible type II nature of the specimen. The minimum in M versus H is observed at ~ 2 kOe field, this value is comparable to that observed earlier in oxygen-annealed multiphase specimen at composition $Y_{1.2}Ba_{0.8}CuO_4$ (see figure 5 in Paulose *et al* 1987). The magnitude of the magnetization value at the minimum position in the case of $Y_{2.1}Ba_{3.9}CuO_y$ is about 4 times the corresponding value in $Y_{1.2}Ba_{0.8}CuO_4$ (cf. figure 6 with figure 5 in Paulose *et al* 1987). This fact is qualitatively consistent with the ratio of the fractions of the superconducting phase present at the two compositions (Dhar *et al* 1987). Figure 7 depicts M versus H data at 8 K in $Y_{2.1}Ba_{3.9}CuO_y$ on an expanded scale. In this specimen, the deviation from linearity in M versus H behaviour sets in above 600 Oe whereas in the multiphase $Y_{1.2}Ba_{0.8}CuO_4$ a linear response could not be observed even below 50 Oe.

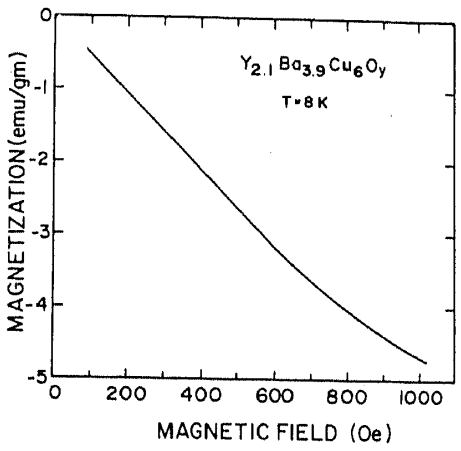

Figure 7. Magnetization as a function of the applied magnetic field at 8 K for the oxygen-presintered specimen of the $Y_{2.1}Ba_{3.9}Cu_6O_y$.

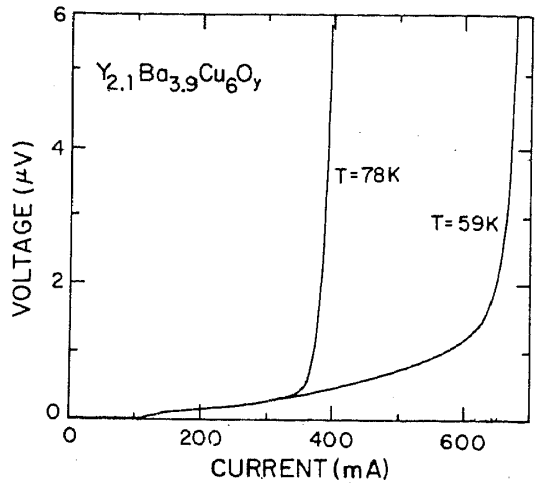

Figure 8. Current versus voltage characteristic of the oxygen-presintered specimen of $Y_{2\cdot1}Ba_{3\cdot9}Cu_6O_y$ at two temperatures.

Figure 8 presents the current versus voltage characteristics at 59 K and 78 K. It is interesting to note that the sample remains superconducting only upto 120 mA at both the temperatures; this corresponds to the critical current density of < 10 A/cm^2. Above this current value, the sample acquires a small finite resistance. At further higher value of current, which depends upon the temperature, another jump in resistance value is seen. The two-step increase in resistance value is curious, such a behaviour has not been observed in La-based compounds superconducting in the 30 K range (Grover *et al* 1987).

It is being increasingly argued (see, for instance, Müller *et al* 1987; Razavi *et al* 1987) that the response of the high T_c ceramic superconductors to the electromagnetic fields is analogous to that expected in granular superconducting materials. Most of the magnetic properties described above, like the dependence of the AC susceptibility on the measuring field, the difference in the DC field dependence of the AC susceptibility and the DC susceptibility etc., can be explained in terms of the collective behaviour of clusters containing loops of coupled superconducting grains (Ebner and Stroud 1985).

As a final remark, we may state here the results of various substitutional studies attempted on the stoichiometry of $Y_{2\cdot1}Ba_{3\cdot9}CuO_y$. The total replacement of Ba by Ca and Sr resulted in the absence of superconductivity down to 4·2 K. The partial replacement of Ba by small concentrations of Sr and Ca significantly lowers the superconducting T_c. For instance, the superconducting onset, mid-point and zero resistance temperature for two specimens are: $Y_{1\cdot8}Ba_{3\cdot6}Sr_{0\cdot6}Cu_6O_y$: 96 K, 85 K and 82 K and $Y_{1\cdot8}Ba_{3\cdot6}Ca_{0\cdot6}Cu_6O_y$: 90 K, 72 K and 46 K. The partial replacement of Y by La also lowers T_c. All substitutional specimens were synthesized in the oxygen atmosphere. We had earlier found (Dhar *et al* 1987) that the specimens heated in air had a tetragonal structure with T_c value lower than that of oxygen-annealed specimens giving rise to the orthorhombic phase. The fact that the air-annealed specimens are deficient in oxygen as compared to those synthesized in oxygen atmosphere, may imply that the oxygen deficiency stabilizes the tetragonal structure. When this manuscript was at a final stage, we came to know the work of Schuller *et al* (1987), reporting systematic high temperature x-ray diffraction studies

in the single phase specimens of $YBa_2Cu_3O_7$. These authors find the existence of a tetragonal to orthorhombic structural phase transition above 700 K. The authors also report that samples quenched from high temperatures giving rise to tetragonal phase have a lower T_c than those of slow-cooled specimens crystallizing in the orthorhombic structure. Our results (Dhar *et al* 1987) independently support these ideas.

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