Superconductivity above 200 K

1990 J. Phys.: Condens. Matter 2 8543

(http://iopscience.iop.org/0953-8984/2/42/030)

J. Phys.: Condens. Matter 2 (1990) 8543–8546. Printed in the UK

LETTER TO THE EDITOR

Superconductivity above 200 K

V N Moorthy, S K Agarwal, B V Kumaraswamy, P K Dutta,
V P S Awana, P Maruthikumar and A V Narlikar
National Physical Laboratory, Dr K S Krishnan Road, New Delhi 110012, India

Received 23 May 1990, in final form 28 June 1990

Abstract. For the first time both $R = 0$ and diamagnetic transitions have been observed together for the ErBaCuO system for $T > 200$ K, giving credence to earlier global reports of extra-high T_c. The problems of unstable aspects and rare reproducibility are believed to be linked with the small relative volume fraction of the extra-high-T_c entity estimated in the present study. The material considerations for achieving extra-high T_c are also indicated.

Although in the last two years the highest critical temperature (T_c) of stable superconductivity has remained unchanged at about 125 K in $Tl_2Ba_2Ca_2Cu_3O_x$, there have been a number of reports of transient resistance drops at temperatures of 200 K or above, from various laboratories all over the globe [1–5]. In the majority of instances these drops are partial, though there have been rare reports of complete resistance drops leading to an $R = 0$ state at such high temperatures [6–9]. The short-lived character of such observations has proved to be a prime deterring factor to further investigation of the phenomenon. Although such resistance drops, in some samples, have been related to the presence of extra-high-T_c superconducting phases through the observation of (i) an inverse AC Josephson effect [1, 4], (ii) non-linearity in the I–V characteristics [7, 9] and (iii) microwave absorption [10], there have been no convincing reports about the manifestation of the diamagnetic nature (Meissner effect), which is the deciding characteristic for confirming superconductivity at such high temperatures.

Consequently, extra-high-temperature superconductivity has been largely looked askance at, and such observations have been ascribed to all other types of transitions, namely, metal–insulator, magnetic, structural etc. In this letter we report for the first time the existence of extra-high-temperature superconductivity above 200 K as evidenced by a complete ($R = 0$) resistance drop and the simultaneous presence of substantial Meissner diamagnetism occurring at the same temperature.

The present study was carried out on $ErBa_2Cu_3O_7$ (the Er 1–2–3) system, where in earlier work Vijayaraghavan and co-workers [8] had reported a transient resistance drop with $R = 0$ at 260 K; but owing to its short-lived nature, superconductivity could not be fully established. The samples were synthesized by solid state processing using oxide ingredients of purity better than 4N; the materials considerations followed are given later in the paper. For R–T measurements the conventional four-probe technique was employed, using a Keithley constant-current source and a nanovoltmeter with a 1 mA current through the sample. The temperature of the sample was monitored using a PT-100 sensor in conjunction with a Keithley DMM. The measurement system was hooked

0953-8984/90/428543 + 04 \$03.50

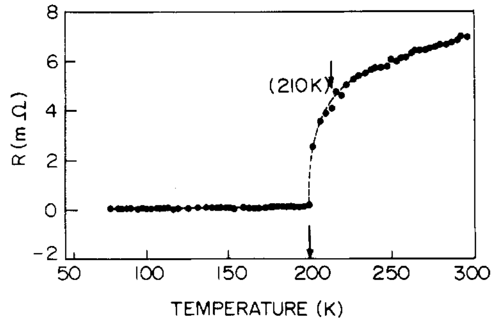

Figure 1. The resistance–temperature curve, showing $T_c(R = 0)$ at a temperature a little above 200 K and a T_c onset of about 210 K.

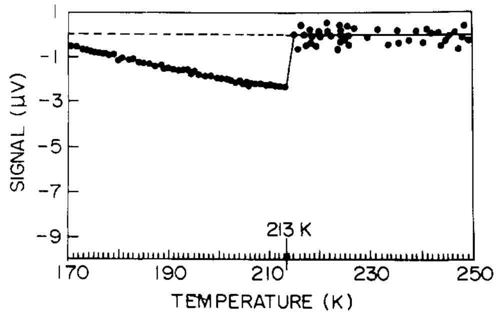

Figure 2. The diamagnetic susceptibility drop at about 210 K for the sample of figure 1.

up to a HP 216 System Controller for automatic data acquisition and control. Magnetic susceptibility data were acquired with the help of a fully computer-controlled Lakeshore 7000 AC susceptometer.

Figure 1 depicts the rare R–T behaviour of one of our Er 1–2–3 samples containing 1 at.%Ni nominally substituted for Cu. It showed a metallic behaviour from 300 K down to about 210 K, whereafter the resistance started to decrease and dropped to zero at a little above 200 K, in a relatively narrow range of about 10 K. The phenomenon was seen to persist after new contacts were made. As it is well known that such behaviour is short lived against thermal cyclings, the sample was immediately transferred to an AC susceptometer for studying susceptibility behaviour rather than further resistive studies being continued. Figure 2 shows the susceptibility signal of the field-cooled sample (field 400 A m^{-1}, 1000 Hz) as a function of temperature. The sample showed a major transition at about 90 K, which was not revealed in the R–T curve (figure 1), because $R = 0$ was achieved at a higher temperature of about 200 K. This transition is not shown in figure 2 as its diamagnetic signal was too large (300 μV) and was outside the temperature range of interest. Notably, a sharp diamagnetic signal was observed close to 210 K, coinciding with the resistive onset transition temperature of figure 1. By comparing the magnitude of the susceptibility drop at 210 K with that of the main 90 K phase, the superconducting volume fraction of the former relative to the latter is estimated to be around 1%. Simultaneous occurrence of both resistive (leading to $R = 0$) and diamagnetic transitions at the same temperature, observed for the first time, gives, we feel, strong credence to the existence of extra-high-T_c superconductivity above 200 K. The observed rounding off at the T_c onset in figure 1 is the characteristic feature linked with the high-temperature fluctuation effects, and has been commonly observed in Tl-based cuprate showing superconductivity at the relatively high temperature of 125 K. Incidently, the superconducting volume fraction of the extra-high-T_c phase in the present study, although small, is still about 100 times larger than reported for the 230 K phase in the Eu 1–2–3 system [6]. A slightly improved stability of the 210 K phase in our sample, as compared to earlier extra-high-T_c reports for Er 1–2–3 [8], may be related to the presence of a small concentration of Ni, which might be having some positive role in partly stabilizing the oxygen stoichiometry against thermal cycling, although its precise role is not clear. Interestingly, the 210 K transition which had disappeared with thermal cycling could be partly revived with an unstable T_c of 135 K (figure 3) by oxygenation at 600 °C for about six hours. It is worth noting the larger scatter of points above T_c in figures 2 and 3. This

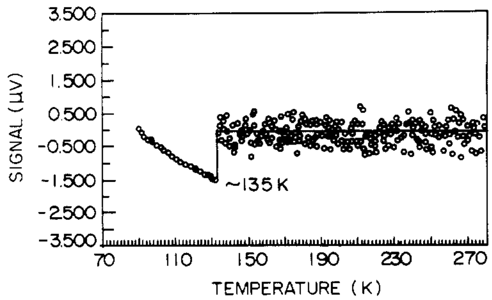

Figure 3. Restoration of the unstable T_c at 135 K by oxygenation.

is not surprising as the signal-to-noise ratio is signficantly reduced, owing to rather weak paramagnetic susceptibility in the normal state.

Large pressure effects on T_c in the La–Ba–Cu–O system containing a single Cu–O plane observed by Chu *et al* [11] led them to the successful idea of generating intense lattice pressures by replacing La, placed next to the Cu–O plane, by the smaller Y. This resulted in the discovery of Y 1–2–3, characteristic of three (two planar and one chain) low-dimensional Cu–O networks having a T_c of 90 K. In fact, it appears that this idea, perhaps fortuitously, has worked also for the genesis of Bi- and Tl-based 2–2–1–2 and 2–2–2–3 high-T_c systems. We find that when a cation of larger size, adjacent to Cu–O networks, is fully or partly replaced by a smaller cation (e.g., a partial replacement of Sr by Ca in Bi–Sr–Cu–O and of Ba by Ca in Tl–Ba–Cu–O) the resulting effect is the formation of an altered unit cell in which internal lattice stresses per Cu–O plane, produced by incorporation of a smaller cation, get reduced by formation of extra Cu–O planes [12]. The materials so formed have enhanced values of T_c. Although it is commonly believed that beyond three Cu–O planes T_c would saturate, the issue, as argued by Nakamura and Ogawa [13], remains far from settled, and instead what really seems to matter more is how to stabilize structures containing larger numbers of Cu–O stacks.

If we analyse a host of earlier observations of extra-high T_c, by others [2–10] as well as ourselves [1, 14], including the present report, we find that extra-high T_c is indicated in both pure and substituted 1–2–3 systems formed under specific conditions which seem to meet the aforesaid criteria [12]. The three independent reports [1, 7,10] of extra-high T_c, above 200 K, are for Y 1–2–3, where the larger Ba ion, placed adjacent to both Cu–O planes and a chain, is partly replaced by the smaller Sr ion. Ca is still smaller than Sr and its substitution (in place of Ba) has also yielded partial resistance drops at temperatures above 200 K [15]. On the other hand, the extra-high-T_c observations in pure systems such as of Eu 1–2–3 [6] and Er 1–2–3 [8] are, we believe [12], linked with a specific disordering effect in which the larger Ba ion is partly substituted by the smaller Eu and Er ions. Er is one of the smallest ions of the lanthanide series and, hence, at the Ba site it should give rise to relatively large lattice pressures on both Cu–O planes and chains. This motivated us to concentrate on Er 1–2–3 in the present study. We have been studying samples with nominal compositions having Ba deficiency, to enable Er or other Y-site cations to occupy the Ba site. It is interesting to note that the nominal composition of 5:6:11 for Y:Ba:Cu recently used by Chen *et al* [9], which yielded filamentary superconductivity above 200 K, is also essentially deficient in Ba and with a Y surplus. In our case, the observations of unstable partial resistance drops above 200 K were restricted to 5 to 8 of the 40 to 50 samples studied, while the present report represents the only instance with the resistance dropping to zero above 200 K.

To sum-up, although the phenomenon is unstable and also seems rare, the above study, beyond any reasonable doubt, lends strong support to the possibility of extra-high-T_c superconductivity above 200 K and, in a broad way, gives credence to the host of earlier reports [1–10], which had hitherto been considered inconclusive. As the superconducting volume fraction of the extra-high-T_c phase is small, it should be considered largely a matter of sheer chance that one finds a percolative interconnectivity leading to an $R = 0$ state, which accounts for the somewhat rare reproducibility of such observations. We feel that such an interconnectivity of extra-high-T_c entities preferentially—possibly comprising structures with increased numbers of Cu–O stacks—forms in narrow regions, possibly at the grain boundaries from where oxygen is more readily lost due to thermal contractions of the sample during cycling. In view of this, the efforts to enhance the pertinent superconducting volume fraction clearly seem to hold the key to the problem of stability and crystallographic identification of the extra-high-T_c phase.

The authors thank Professor S K Joshi, Director, National Physical Laboratory for his keen interest. The work was in part financially supported by the Commission of European Communities, Brussels under the Indo-French Programme.

References

[1] Gupta A K, Jayaram B, Agarwal S K, Gupta A and Narlikar A V 1987 *Phase Transitions* **10** 29
[2] Bourne L C, Cohen M L, Creager W N, Crommie M F, Stacy A M and Zettle A 1987 *Phys. Lett.* **120A** 494
[3] Narayan J, Shukla V N, Lukasiewicz, Biunno N, Singh N R, Schreiner A F and Pennycook S J 1987 *Appl. Phys. Lett.* **51** 940
[4] Chen J T, Wenger L E, McEwan C J and Logothetis E M 1987 *Phys. Rev. Lett.* **58** 1972
[5] Jostarndt H D, Galffy M, Freimuth A and Wohlleben A 1989 *Solid State Commun.* **69** 911
[6] Huang C Y, Dries L J, Hor P H, Meng R L, Chu C W and Frankel E B 1987 *Nature* **328** 403
[7] Ihara H, Terada N, Jo M, Hirabayashi M, Tokumoto M, Kimura Y, Matsubara T and Sugise R 1987 *Japan. J. Appl. Phys.* **26** L1413
[8] Ayyub P, Guptasarma P, Rajarajan A K, Gupta L C, Vijayaraghavan R and Multani M S 1987 *J. Phys. C: Solid State Phys.* **20** 1673
[9] Chen J T, Qian L X, Wang L Q, Wenger L E and Logothetis E M 1990 *Mod. Phys. Lett.* B at press
[10] Bhagat S M 1988 *Rev. Solid State Sci.* **2** 239
[11] Chu C W, Hor P H, Marg R L, Gao L, Huang Z J and Wang Y Q 1987 *Phys. Rev. Lett.* **58** 405
[12] Narlikar A V 1990 *Int. Conf. Superconductivity (Bangalore, 1990)*
[13] Nakamura K and Ogawa K 1990 *Studies of High Temperature Superconductors* vol 4, ed A Narlikar (New York: NOVA Science) p 87
[14] Jayaram B, Agarwal S K, Gupta A and Narlikar A V 1987 *Curr. Sci.* **56** 572
[15] Narlikar A V, Narasimha Rao C V and Agarwal S K 1990 *Studies of High Temperature Superconductors* vol 1, ed A Narlikar (New York: NOVA Science) p 341