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Photoinduced Changes in High Temperature Superconducting Films

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Abstract

Photoexcitation experiments performed in oxygen deficient but metallic $YBa_2Cu_3O_x$ *c*-axis oriented films revealed that the persistent photoinduced enhancement of conductivity and superconductivity are not restricted to the insulating side of the metal–insulator transition. A clear increase of the critical temperature T_c, which is accompanied by a decrease of the resistivity in the normal state ρ_{ab}, is observed for all studied oxygen contents ($6.4 \leqslant x \leqslant 6.6$). In this oxygen content range, the persistent photoinduced changes in T_c and ρ_{ab} have a strong dependence on the oxygen stoichiometry of the film. Several mechanisms which may explain the persistent photoinduced phenomena are discussed.

1. Introduction

Among the many high temperature superconductors, the most interesting materials are probably $RBa_2Cu_3O_x$ (RBCO; R = Y or rare earth). It is well known that the structural electrical and magnetic properties of YBCO are drastically changed when the oxygen content x decreases from $x = 7$ to $x = 6$. Besides the CuO_2 planes, common to all HTS, their crystalline structure contains CuO_x "chain" planes from which oxygen atoms can be easily removed [1]. As soon as oxygen vacancies are created, the remaining oxygen atoms rearrange themselves in a well-ordered chain structure for an oxygen content $x_n \geqslant 6.85$, the so-called Ortho I phase. For a lower oxygen content $6.5 \leqslant x_n \leqslant 6.8$, the ordering of oxygen atoms gives rise to an Ortho II phase in which a superstructure consisting of one full and two empty chains appears. Finally, the chain planes are depleted of oxygen atoms, and the structure becomes tetragonal for $x_n < 6.5$ [2]. The oxygen ordering in the chain planes is a unique property of all RBCO materials. It produces an increase in the carrier density in the CuO_2 planes at a fixed oxygen content [3, 4] and gives rise to interesting phenomena such as the characteristic plateau structure in the $T_c(x_n)$ curve near 60 K, and the surprising changes observed in the superconducting [5, 6] and normal state properties [6] of YBCO samples during annealing at room temperature after a rapid quench of the sample from high temperatures.

Photoexcitation is an alternate way to increase the carrier density in RBCO without changing the oxygen concentration. A transient photoinduced enhancement of the surface conductivity, after pulsed laser excitation, by more than ten orders of magnitude and with a decay time of the order of nanoseconds, was reported for insulating YBCO single crystals [7]. The observations of similar photoinduced conductivity changes for different illumination levels compared to changes produced by increasing the oxygen concentration led to the conclusion of photodoping by light illumination [8].

On the other hand, measurements performed in insulating YBCO ($x_n \leqslant 6.4$) films (thickness ~ 1000 Å) led to the discovery [9] of the effect of persistent photoconductivity (PPC) at temperatures below 270 K. It was shown that photoexcitation reduces the resistivity of the material over the whole temperature range $0 < T < 300$ K with an abrupt decrease in the resistivity at low temperatures, suggesting the possibility of photoinduced enhancement of superconductivity [10]. The decay time of the PPC was found to be of the order of days at room temperature, and no signs of decay were observed below $T \sim 270$ K [10]. All these experiments were carried out on samples in the insulating side of the metal–insulator transition ($x \leqslant 6.4$).

Recently, we have shown that photoexcitation of oxygen deficient, but not insulating YBCO films, produces an enhancement of the superconducting transition temperature [11]. We also demonstrated that the enhancement of superconductivity is accompanied by a corresponding decrease in the resistivity and Hall coefficient during photoexcitation, indicating an increase in the carrier density [12]. At room temperature, all these changes relax back to their equilibrium values with characteristic times of the order of days, which are comparable to the relaxation times due to oxygen ordering measured in quenched oxygen deficient films [6]. These results obtained in metallic films strongly suggest that persistent photoinduced phenomena in YBCO are not restricted to the insulating side of the M–I transition [13].

The above-mentioned measurements were performed on different films. After the illumination and due to constraints in the experimental setup, the films were brought to room temperature during a short period of time (approx. half an hour) before inserting them in another cryostat to measure the changes in $\rho(T)$ and T_c. Since the annealing at room temperature may produce some relaxation of the observed photoinduced changes, it is difficult to determine the precise relationship between the oxygen content and the photoinduced changes in ρ and T_c.

In this paper we discuss recent photoexcitation experiments performed in one YBCO film with T_c's varying

between 15 K and 50 K. All the measurements before and after illumination have been carried out *in situ*, without bringing the film to room temperature (see Section 2.2 below). The results show that persistent photoconductivity and photoinduced enhancement of superconductivity are clearly observed in these metallic films, corroborating that the M–I transition plays no role in the existence of persistent photoinduced phenomena in YBCO. The photoinduced changes show a strong dependence on the oxygen content of the film at low oxygen concentrations.

2. Experimental

2.1. *Preparation of oxygen deficient YBCO films*

The fully oxidized YBCO films are prepared using a planar magnetron sputtering system. The films are deposited on MgO (100) substrates in the 90° off-axis configuration in a mixed Ar/O_2 (80/20) sputtering gas with a total pressure of 400 mTorr and at a substrate temperature $T_S = 740\,°C$. After deposition, the film is annealed *in situ* during 15–30 minutes at $T_S = 500\,°C$ and $P_{O_2} = 1$ atm to allow full oxidation. These *in-situ* prepared films are c-axis oriented with $T_c(R = 0) \approx 89$ K and $\Delta T_c \leqslant 1$ K. More details about the preparation technique have been published elsewhere [14].

Oxygen deficient YBCO films with a nominal oxygen content $6.4 \leqslant x_n \leqslant 7$ are prepared using the oxygen partial pressure-temperature (P_{O_2}–T) phase diagram for bulk material [15]. Several P_{O_2}–T phase diagrams have been published [16–19]. For reasons to be discussed elsewhere [20] we adopted for the present work the P_{O_2}–T phase diagram reported in [19]. The film is placed in a small stoichiometric YBCO ceramic box which in turn is placed inside a quartz tube and evacuated to $P = 10^{-6}$ Torr at room temperature. After this, it is filled with oxygen to $P_{O_2} = 10$ Torr for $x_n > 6.5$ or $P_{O_2} = 5$ Torr for $x_n < 6.45$ and the temperature is increased to the appropriate $T_{ann}(x_n)$ to obtain the desired oxygen content x_n. Once the pressure P_{O_2} inside the tube is stabilised (usually after 2–3 hrs at T_{ann}) the sample is slowly cooled (2–3 °C/min) while the P_{O_2} is decreased as to follow the corresponding P_{O_2}–T phase line. Finally, the samples are quenched to room temperature in $P_{O_2} = 75$ mTorr and from a quenching temperature $T_Q(x_n)$. By this method, we obtain in a controlled and reproducible way YBCO thin films with a homogeneous oxygen content.

2.2. *Photoexcitation experiments*

The illumination of the oxygen deficient YBCO film was performed using an Ar–ion laser ($\lambda = 488$ nm) with an output power of 0.5 W. The measured power on the films was 0.46 W/cm^2. The film was illuminated during 8 hours, which corresponds to a total dose $Q = 3.4 \times 10^{22}$ ph/cm^2. The 1000 Å thick oxygen deficient YBCO film was patterned using classical photolithography and wet etching techniques producing a four-point pattern with a bridge with dimensions 35 μm × 1 mm. The $R(T)$ curves were measured in a He flow cryostat with optical access in which the temperature can be varied between 5 K and 300 K. After measuring the $R(T)$ curve for the non-illuminated film during the warming-up cycle, the sample was cooled down to 100 K and illuminated *in situ* at this temperature during 8 hours. The sample was then cooled down below T_c and the $R(T)$ curve was again recorded during the warming-up cycle (up to $T \simeq 250$ K). In this way the sample was always kept at temperatures below 250 K after the illumination, avoiding any possible room temperature relaxation of the photoinduced phenomena.

3. Results

Figure 1 shows the resistivity as a function of temperature for the YBCO film, before and after illumination. The film has been successively treated according to the method

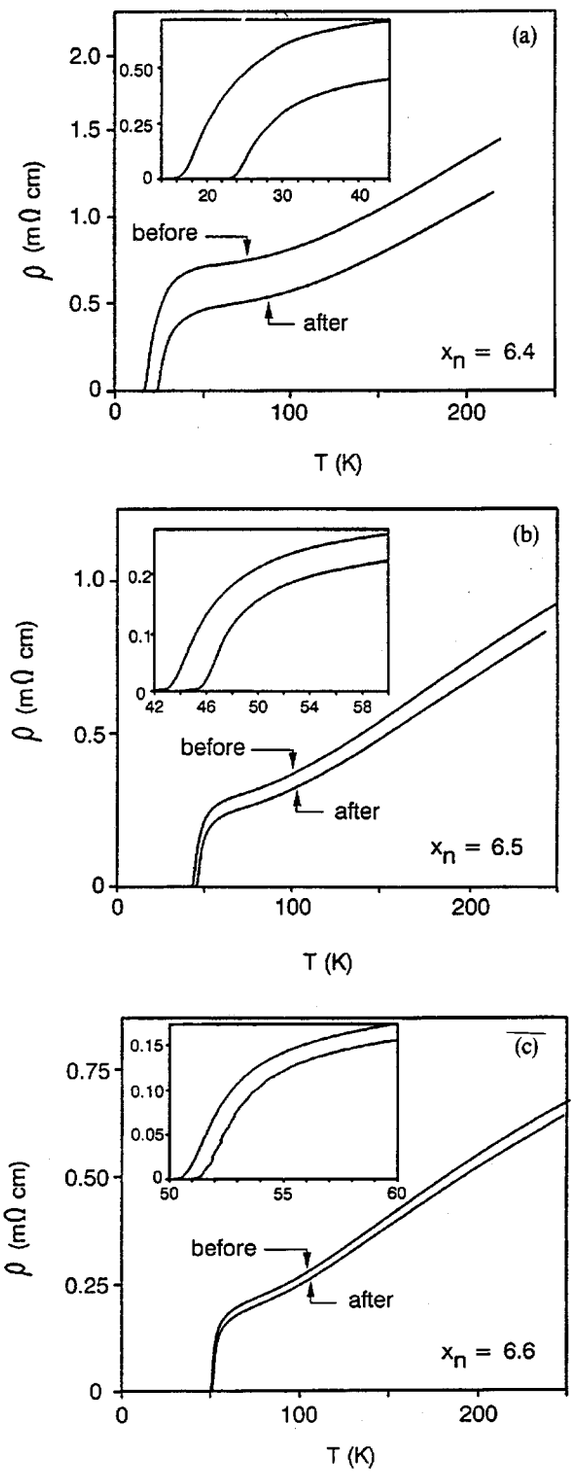

Fig. 1. Electrical resistivity ρ *vs.* temperature before and immediately after laser illumination for one YBCO film with different oxygen stoichiometries: (a) $x_n = 6.4$; (b) $x_n = 6.5$; and (c) $x_n = 6.6$. The insets show the region near T_c in an expanded scale.

described in Section 2.1 in order to obtain the different nominal oxygen contents $x_n = 6.4$ [Fig. 1(a)], $x_n = 6.5$ [Fig. 1(b)] and $x_n = 6.6$ [Fig. 1(c)]. After the oxygen depletion treatment, the sample has been kept at room temperature for at least three days in order to allow complete relaxation of the oxygen ordering effects [6]. Clearly, the illumination produces a decrease of the resistivity throughout the entire temperature range for all oxygen contents. Notice that the resistivity change is weakly temperature dependent for $T > T_c$. The insets in Fig. 1 show in an expanded scale the superconducting transitions before and after illumination. We note a clear enhancement of the superconducting transition even for the sample with a high critical temperature $T_c \simeq 50\,\mathrm{K}$ [Fig. 1(c)]. The pronounced rounding of the transitions near the normal state, which is likely to be due to an increased contribution of two-dimensional fluctuations at low x_n, considerably hinders the definition of the transition widths, and in particular, the onset of the superconducting transition. However, in all cases there is a parallel shift of the transition towards higher temperatures without changes in its shape. In other words, the same absolute shift of T_c [i.e. $\delta T_c = T_c$(after illumination) $- T_c$(before illumination)] is obtained irrespective of the definition of T_c.

In Fig. 2 we have plotted T_c before and after illumination [Fig. 2(a)] and the total increase of T_c, δT_c after 8 hours of illumination [Fig. 2(b)] as a function of oxygen content x_n. It is clear that δT_c is larger at lower oxygen contents and has a well-defined and strong dependence on x_n in the oxygen content range $6.4 < x_n < 6.6$. Assuming that T_c varies linearly with the hole concentration [22], we can make a rough estimate of the increase in the nonequilibrium carrier density δn_h during photoexcitation. We obtain $\delta n_h \simeq 0.006$ for $x_n = 6.4$, $\delta n_h \simeq 0.003$ for $x_n = 6.5$ and $\delta n_h \simeq 0.001$ for $x_n = 6.6$. Although not much significance has to be given to these absolute values, it is interesting to note that this estimate indicates that the photoinduced carriers, which are responsible for the observed changes in T_c, are produced in small amounts [23].

Figure 3 shows the resistivity measured at $T = 100\,\mathrm{K}$ before and after illumination [Fig. 3(a)], and the total decrease in resistivity $\delta\rho$ [Fig. 3(b)], both as a function of oxygen content x_n. Notice that the same trend, i.e. larger photoinduced changes at lower oxygen contents, is also valid for the $\rho(x_n)$ data.

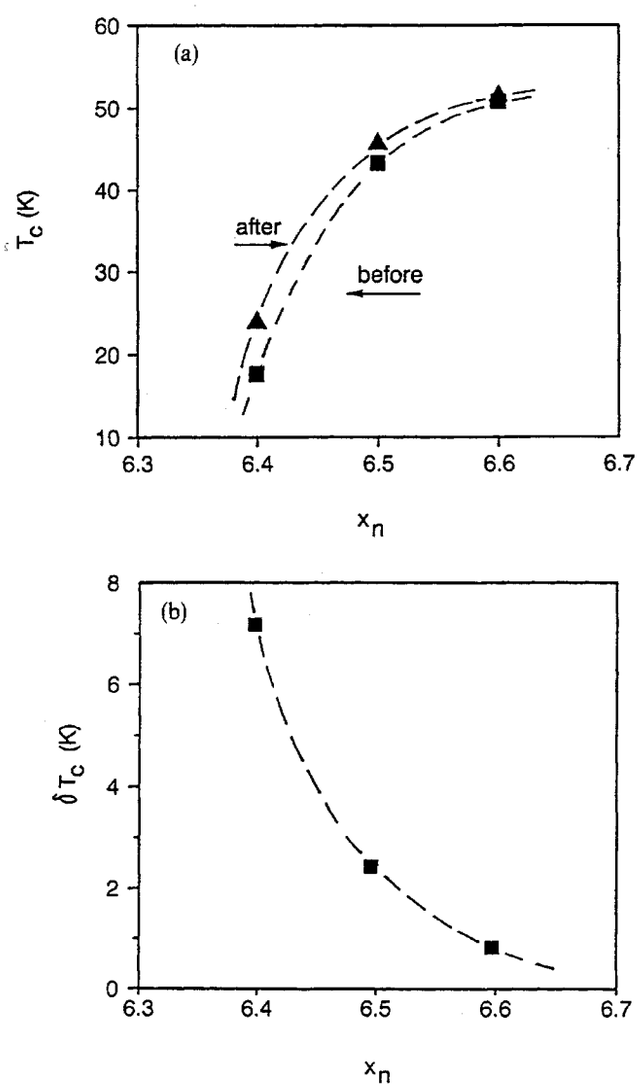

Fig. 2. (a) Critical temperature T_c *vs.* the oxygen content before and after illumination for the same YBCO film shown in Fig. 1. (b) Total increase in T_c after 8 hr of laser illumination as a function of oxygen content.

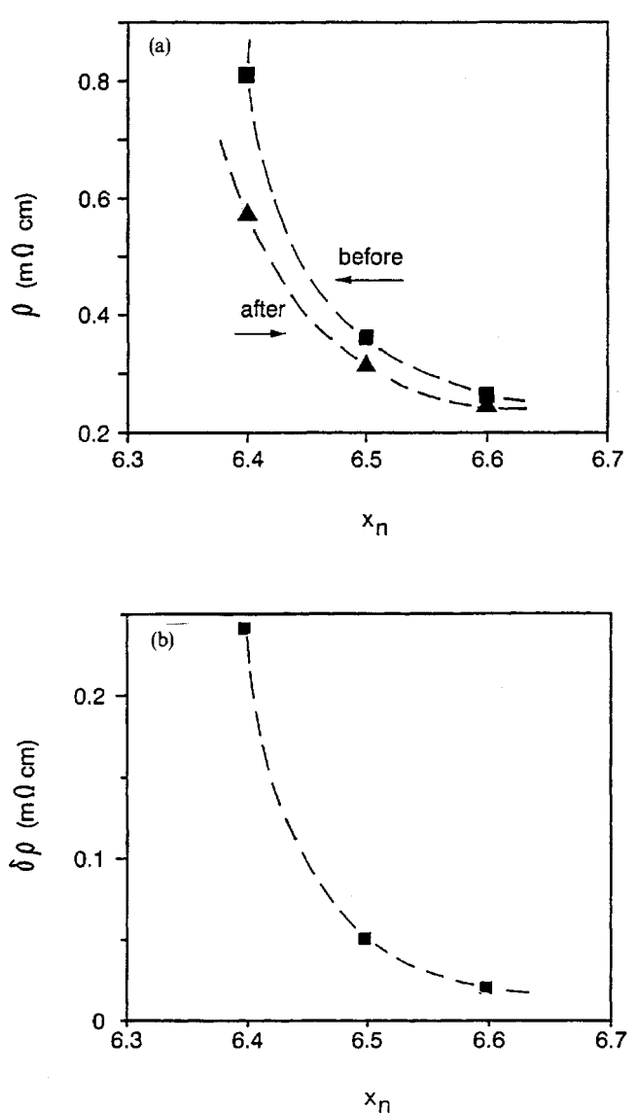

Fig. 3. (a) Resistivity at 100 K *vs.* the oxygen content before and after illumination for the YBCO film. (b) Total decrease in resistivity $\delta\rho$ as a function of the oxygen content.

Finally, it is worth mentioning here that in all cases the T_c and $\rho(T)$ values measured before illumination are recovered after ~ 3 days of annealing at room temperature.

4. Discussion

The microscopic mechanism underlying the observed photoinduced phenomena remains unclear at the present time. One possible explanation is related to the photoexcitation phenomena observed in low T_c granular In–CdS [24] films and in Sn–CdS–Sn junctions [25], i.e. changes in the conductivity of the photosensitive (CdS) intergranular material. Assuming that the superconductivity in the YBCO films is granular in character, an analogous effect might be present during the laser irradiation. It should be noted, however, that granular In–CdS films exhibit a decrease in the width of the normal to superconducting transition, but no change in the onset critical temperature after illumination. In contrast, our results show a parallel shift of the $R(T)$ curves and a clear increase in T_c after illumination. Moreover, a rather peculiar behaviour of the intergranular material must be assumed in order to explain the oxygen content dependence of the photoinduced phenomena using this granular model.

Another possibility comes from the analogy with the well-known photoinduced phenomena in semiconductors. Since the electrical properties of insulating YBCO can be rather well described by the formalism developed for semiconducting material, it was reasonable to assume the same mechanism [9, 10, 21] in order to explain the persistent photoinduced phenomena. According to this model an electron–hole pair is photoinduced by absorption of one photon in the CuO_2 planes. While the hole increases the carrier density in these planes, the electron is transferred via some mechanism to the CuO_x chain planes, where it is trapped by an oxygen vacancy. Our results, however, clearly indicate that the photoinduced phenomena are also observable in YBCO films well inside the metallic region of the T–x_n phase diagram and cast therefore serious doubts about the applicability of the proposed microscopic mechanism to explain the persistent photoinduced phenomena in YBCO. An alternate and more plausible explanation is the occurrence of photoassisted oxygen ordering, i.e., the local rearrangement of oxygen atoms around Cu1 ions induced by the illumination. It is usually assumed that Cu1 ions have a 2+ oxidation state when they are threefold (chain end) or fourfold (Cu in a chain) coordinated, and 1+ oxidation state when they are twofold coordinated (empty chain). Assuming that the produced photoelectrons contribute to change the valence state of a Cu1 ion from Cu^{++} to Cu^{+} and taking into account that the situation in which a Cu^{+} ion is fourfold or threefold coordinated is energetically unfavourable [26], it follows that the system will locally relax to a new configuration inducing the ordering of oxygen atoms in longer chain fragments. The produced hole will contribute to the increase of the carrier density in the CuO_2 planes. In the absence of enough thermal energy this situation will persist in time, explaining the observed persistent photoinduced phenomena. When the temperature is raised, the oxygen atoms will disorder again with characteristic times equal to the ones observed in phenomena related to the oxygen ordering process [5, 6]. Notice that this simple physical picture applies naturally for all oxygen concentrations $x_n < 7$, and that the photoinduced changes will depend on oxygen content in a similar way as they do for the oxygen ordering effects. Finally, if this photoassisted oxygen ordering mechanism is correct, persistent photoinduced phenomena should only be present in high T_c materials containing chain planes in their crystalline structure.

5. Conclusions

In summary, we have shown that measurable persistent photoinduced changes in the resistivity and critical temperature are clearly observed in metallic YBCO films with T_c's as high as 50 K. These changes, (*i*) are more pronounced at the low oxygen concentrations, (*ii*) are a decreasing function of the oxygen content, (*iii*) have long relaxation times at room temperature irrespective of the oxygen content.

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References

1. Beno, M. A., Soderholm, L., Capone, D. W. II, Hinks, D. G., Jorgensen, J. D., Grace, J. D., Schuller, I. K., Segre, C. U. and Zhang, K., Appl. Phys. Lett. **51**, 57 (1987).
2. For an early report see, for instance: Khachaturyan, A. G. and Morris, J. W., Phys. Rev. Lett. **59**, 2776 (1987).
3. McCormak, R., de Fontaine, D. and Ceder, G., Phys. Rev. **B45**, 12976 (1992).
4. Uimin, G. and Rossat-Mignod, J., Physica **C199**, 251 (1992).
5. Veal, B. W., Paulikas, A. P., Hoydoo You, Hao Shi, Fang, Y. and Downey, J. W., Phys. Rev. **B42**, 6305 (1990).
6. Libbrecht, S., Osquiguil, E., Wuyts, B., Maenhoudt, M., Gao, Z. X. and Bruynseraede, Y., Physica **C206**, 51 (1993).
7. Yu, G., Heeger, A. J., Stucky, G., Herron, N. and McCarron, E. M., Solid State Commun. **72**, 345 (1989).
8. Yu, G., Lee, C. H., Heeger, A. J., Herron, N. and McCarron, E. M., Phys. Rev. Lett. **67**, 2581 (1991).
9. Kirilyuk, A. I., Kreines N. M. and Kudinov, V. I., Pis'ma Zh. Eksp. Teor Fiz. **52**, 696 (1990) [JETP Lett. **52**, 49 (1990)].
10. Kudinov, V. I., Kirilyuk, A. I., Kreines, N. M., Laiho, R. and Lähderanta, E., Phys. Lett. **A151**, 358 (1990).
11. Nieva, G., Osquiguil, E., Guimpel, J., Maenhoudt, M., Wuyts, B., Bruynseraede, Y., Maple, M. B. and Schuller, I. K., Appl. Phys. Lett. **60**, 2159 (1992).
12. Nieva, G., Osquiguil, E., Guimpel, J., Maenhoudt, M., Wuyts, B., Bruynseraede, Y., Maple, M. B. and Schuller, I. K., Phys. Rev. **B46**, 14249 (1992).
13. Bruynseraede, Y., Osquiguil, E., Maenhoudt, M., Wuyts, B., Nieva, G., Guimpel, J., Lederman, D. and Schuller, I. K., in: "Proceedings of the Second Internatonal Conference on Macroscopic Quantum Phenomenona (FCMQP-2)" (Edited by Š. Beňačka and M. Kedro) (Czechoslovakia 1992), p. 253.
14. Wuyts, B., Gao, Z. X., Libbrecht, S., Maenhoudt, M., Osquiguil, E. and Bruynseraede, Y., Physica **C203**, 235 (1992).
15. Osquiguil, E., Maenhoudt, M., Wuyts, B. and Bruynseraede, Y., Appl. Phys. Lett. **60**, 2159 (1992).
16. Gallagher, P. K., Adv. Cer. Mater. **2**, 632 (1987).
17. Verweii, H., Ann. Phys. Fr. **13**, 349 (1988).
18. Hammond, R. H. and Bormann, R., Physica **C162–164**, 703 (1989).
19. Tetenbaum, M., Curtiss, L. A., Tani, B., Czech, B. and Blander, Physica **C158**, 371 (1989).
20. Maenhoudt, M., Osquiguil, E., Wuyts, B., Gao, Z. X., Libbrecht, S. and Bruynseraede, Y., (unpublished).

21. Kudinov, V. I., Kirilyuk, A. I. and Kreines, N. M., Pis'ma Zh. Eksp. Teor. Fiz. **56**, 101 (1992) [JETP Lett. **56**, 102 (1992)]; Kudinov, V. I., Chaplygin, I. L., Kirilyuk, A. I., Kreines, N. M., Laiho, R., Lähderanta, E. and Ayache, C., Phys. Rev. **B47**, 9017 (1993).
22. Zhang, H. and Sato, H., Phys. Rev. Lett. **70**, 1697 (1993).
23. From Refs [2], [4] and [22] it can be estimated that the total amount of holes per unit cell necessary to bring the YBCO material from insulating ($x \leqslant 6.4$) to superconducting with $T_c = 90\,\mathrm{K}$ ($x = 7$) is $\delta n_h \approx 0.15$.
24. Deutsher, G. and Rappaport, M. L., Phys. Lett. **71A**, 471 (1979).
25. Giaver, I., Phys. Lett. **20**, 1286 (1968); Dynes, R. C. and Fulton, T., Phys. Rev. **B3**, 3015 (1971).
26. Rushan, H., Zizhao, G., Daole, Y. and Liao Qing, Phys. Rev. **B41**, 6683 (1990).