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Improvement of the superconducting properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ by thermal treatment

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Résumé. — Les propriétés supraconductrices du matériau à haute température critique $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ont été optimisées grâce à une étude systématique de l'influence du dernier recuit. Cette étude a été effectuée, à l'air, sur des pastilles frittées. Les mesures de susceptibilité en courant alternatif font apparaître des transitions étroites, environ 2 K, avec une température de début de transition proche de 91 K, si le dernier traitement thermique est effectué dans un domaine de température très étroit, proche de 440 °C, durant quelques heures. Les échantillons ainsi obtenus sont particulièrement homogènes et leur stoechiométrie en oxygène est voisine de 7. Des recuits à température plus élevée conduisent à un abaissement du $T_c$ et à un élargissement de la transition. En outre un refroidissement lent des échantillons n’apparaît pas nécessaire. Le traitement thermique décrit, simple et totalement réversible, s’applique également à d’autres composés $\text{REBa}_2\text{Cu}_3\text{O}_{7-x}$ ($\text{RE} = \text{terre rare}$).

Abstract. — Superconducting properties of the high $T_c$ superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ were optimized through a systematic study of the influence of the last thermal treatment of sintered pellets in open air. A.c. susceptibility measurements used to test the superconducting behaviour show sharp transitions, about 2 K wide, with onset temperatures near 91 K, when annealing is performed in a very narrow temperature range, near 440 °C, for a few hours. The samples obtained are very homogeneous, with an oxygen content close to 7. Higher annealing temperatures lead to lower $T_c$ and transition broadening. Moreover, slow cooling appears to be unnecessary. The described thermal treatment, very easy in application and completely reversible, also applies to other $\text{REBa}_2\text{Cu}_3\text{O}_{7-x}$ materials ($\text{RE} = \text{rare earth}$).

1. Introduction.

The recent discovery by Bednorz and Müller [1] of high temperature superconductivity in the La-Ba-Cu-O system of layered copper oxides initiated an intense research for even higher $T_c$ in related systems: thus a superconducting transition around 90 K was reported in the Y-Ba-Cu-O system [2]. The stoichiometry of the superconducting phases was soon defined either from phase-diagram studies [3-5] or from structural determinations [6-9]. Such materials are of major interest for future technological applications so we started a program of thin-film elaboration [10] using a d.c. sputtering device designed for complex compounds deposition. When preparing target materials, we noticed that the superconducting transition temperature $T_c$ of these compounds is strongly dependent on their oxygen content which can be controlled by annealing conditions such as the temperature or the speed of cooling. Such a behaviour has actually been reported by a number of other groups [11-13]. Our aim was, however, to define a quick method which could
permit a reproducible preparation of good quality samples. With this in mind we have performed a systematic study of the influence of annealing conditions on the critical temperature of YBa$_2$Cu$_3$O$_{7-x}$.

In order to test the samples quality, an a.c. susceptibility method was chosen, mainly for three reasons: first, because of its sensitivity to the purity and homogeneity of the bulk, contrary to resistive methods; a second, because abnormally large transition widths were frequently encountered in the literature, which may be an indication of multiphase samples usually due to unsuitable heat treatments; and third, because it is a very quick and neat method to measure superconducting transitions without attaching any probe or wire to the sample, and thus allowing to cycle the same specimen over and over again through subsequent thermal treatments. One of our aims in this work was a rapidity in the characterization technique, so $T_c$ measurements were strictly limited to the range above the nitrogen boiling point.

This work follows the report by four of us to the French Patent Office in May 1987 [14].

2. Experimental.

The samples were synthesized from stoichiometric amounts of BaCO$_3$, Y$_2$O$_3$ and CuO; the starting powders were mixed and grounded in acetone, heated for 2 hours at 970°C in an alumina boat under air atmosphere and quenched in air. The powder obtained was reground and a lot of identical pellets (150 mg, diam. = 3.6 mm, $l = 4$ mm) pressed at a uniaxial pressure of 1 kb were sintered for two hours at 970°C, and air-quenched. To obtain the orthorhombic phase [6-9], these pellets were annealed for two hours at 650°C and quenched in air. Up to this stage, all the pellets were treated together in order to guarantee the validity of further comparisons. A last annealing was performed on each pellet individually according to different procedures. This last heat treatment constitutes the main part of our work, and it is thoroughly described in the results section.

Samples were characterized by means of a standard mutual-inductance bridge operating at 119 Hz. The in-phase signal was recorded with the temperature slowly varying between 120 K and 77 K. Temperature equilibrium was not searched but instead a standardized cooling procedure was used for all the samples: the experimental rig was first precooled on a nitrogen dewar and the sample centred in the middle of the pick-up coil by maximizing its signal at 77 K. The rig was then extracted out of the dewar and allowed to warm up to 120 K and immersed quickly back into the dewar. Exchange-gas pressure in the double-chamber rig was always maintained at 100 mm Hg. By this procedure, samples could attain 77 K in approximately one hour. Hysteresis during the warm-up and cool-down sequence due to the thermal inertia of the whole set-up was lower than 2 K. However, reproducibility of the transition curve for the same sample using the same cooling procedure was better than 0.1 K, thus ensuring reliable comparisons between all samples tested in this work. The a.c. current in the primary coil was kept below 100 $\mu$A, which allowed the narrowest transition width. The corresponding a.c. field was estimated to be lower than 2-10 mOe. By increasing the current above this value, vortices were swept in and out of the sample, leading to wider transitions, and eventually to saturation effects [15].

3. Results.

Since a DTA (differential thermal analysis) curve of a powdered non-superconducting YBa$_2$Cu$_3$O$_{7-x}$ sample has shown a peak near 450°C (which must reflect an oxygen gain as shown by thermogravimetric data [13]), a systematic study of thermal treatment in that temperature domain was performed. Each pellet was air-annealed in a flat-bottom platinum boat for two hours at a given temperature in the range 360-600°C, and then quickly cooled down by putting the boat on a large aluminium block in order to avoid further evolution. The results of this isochrone treatment are shown in figure 1. All the samples annealed in the temperature range of 360-600°C show superconducting transitions or — at least — the beginning of it. Below 400°C, transitions are very broad, although their onset seems to occur always at 91 K. In the range 400-460°C for the annealing temperature, transitions are very narrow (2.5 K between 10% and 90% of the amplitude), and $T_c$ stays constant ($T_c = 88$ K at the midpoint). For annealing temperatures above 460°C, the critical temperature quickly goes down, even though the transition width remains small. Cell parameters, refined from an X-ray diagram obtained after grinding a pellet annealed at 440°C for two hours, are: $a = 3.819$ Å, $b = 3.884(4)$ Å, $c = 11.675(7)$ Å, and $V = 173.2$ Å$^3$. From reference [16] these unit cell parameters correspond to an oxygen stoichiometry close to 7.

Special attention was drawn on the existence of a small “step” in the upper part of the transition. No spurious phase was ever found by X-ray analysis and no extra peak was observed in the imaginary part ($X''$) of the a.c. susceptibility, indicating that this anomaly is an intrinsic effect. We have recently shown [15] that this effect is due to the granular structure of these superconductors; but under certain preparation conditions [17] it may be suppressed in bulk samples, leading to inductive transition widths below 0.2 K, without affecting $T_c$.

These results are summarized in figure 2 where
Inductive transitions for pellets annealed two hours at different temperatures, $T_{\text{ann}}$ (360 °C $< T_{\text{ann}} < 600 °C$). Transitions denoted by index 440 °C correspond to the range 400 °C $< T_{\text{ann}} < 460 °C$. The midpoint of the transition temperature is plotted versus the annealing temperature: a plateau, corresponding to the best samples, is clearly seen in the range 400-460 °C.

In order to confirm that full transitions were obtained above 77 K, measurements were also performed down to helium temperatures. The same rig used at liquid nitrogen temperatures was now immersed into a helium dewar, and the amplitude of the in-phase signal recorded between 4.2 K and 15 K. No other contribution was detected for our best samples. Samples which were not fully superconducting at 77 K attained — on the other hand — full amplitude at helium temperatures. Comparison with a Pb sample of same dimensions showed that the Meissner effect in the Y-Ba-Cu-O samples was of the order of 80% of that of lead. This value is comparable to the one obtained in sintered samples of superconductors like Chevrel phases. Quality of the best samples was also checked by using a SHE Corp. SQUID susceptometer or by resistivity measurements (a quasi-linear $\rho(T)$ behaviour above $T_c$, and a very sharp transition at 91 K was observed [18]. The results obtained were similar to those found in the literature and they will be published elsewhere [17].

In order to determine the kinetics of oxygen insertion, a lot of pellets, treated as before (2 hours at 970 °C followed by 2 hours at 650 °C) were annealed for diverse durations at 440 °C. The corresponding superconducting transitions are shown in figure 3. The critical temperature (midpoint) is reported versus annealing time in figure 4. It can be seen that, for pellets of size and weight as indicated,
equilibrium is completely reached in about 2 hours. Larger samples have also been tested under these thermal conditions, without changing our conclusions substantially, provided that the sample’s dimensions remain within the same range.

4. Discussion.

The oxygen content has not been determined independently in this work. One of our starting pellets (annealed for two hours at 650 °C and air-quenched) was checked by using the SQUID susceptometer down to liquid helium: the transition is broad and the onset appears at 78 K ($T_c = 63$ K at the mid-point), the refined cell parameters are: $a = 3.827(1)$ Å, $b = 3.882(2)$ Å, $c = 11.688(4)$ Å, $V = 173.6$ Å³. When comparing these results with references [13, 16] it appears that our starting pellets would have an oxygen stoichiometry close to 6.7. This result agrees also quite well with ATG [19] and equilibrium data [20] from which the expected oxygen content would be close to 6.65.

The oxygen content starts to increase very slowly at low annealing temperatures, and it seems to be incomplete at $T_{\text{ann}} < 400$ °C. In addition, oxygen ordering probably does not occur at these temperatures. On the other hand, oxygen starts to be lost when $T_{\text{ann}} < 400$ °C, which is consistent with results of reference [19], for instance.

Moreover, for annealing temperatures above 460 °C, the superconducting transition is shifted toward lower values although its width remains narrow. So, it would appear that wide superconducting transitions previously reported may reflect some inhomogeneities of the oxygen content inside the same sample, arising from the non-equilibrium of the material. Such a behaviour would appear if intermediate cooling rates were used. In order to determine the influence of slow cooling, additional experiments were performed. For instance, a sample such as those described above was cooled down slowly from 440 °C to 20 °C in 17 hours. A wider transition was obtained, although its onset remains unchanged.

It is important to insist, at this point, that the thermal treatment proposed in this work is completely reversible, that is, superconducting samples which were annealed at 440 °C for 2 hours would become non-superconducting (above 77 K) if reannealed above 600 °C. On the other hand, non- or poorly-superconducting samples (i.e. low $T_c$ or wide transitions) would become « good-quality » samples ($T_c = 90$ K, $\Delta T_c < 2$ K) if reannealed at 440 °C $\leq T_{\text{ann}} \leq 460$ °C. Thus, cycling the sample pellet (prepared at 970 °C + 650 °C) through the last annealing temperature is completely reversible: this means that the oxygen is taken in and out of the host structure.

In order to check the influence of the metallic composition on the superconductive transition, some non-stoichiometric pellets were tested. Deviations from the 1:2:3 composition induce a large transition broadening but there is no clear indication for the existence of a second superconducting phase. In fact a strong porosity increase occurring for out-stoichiometry samples was pointed out [5]. A striking behaviour is the dependence of the low temperature part of the diamagnetic response on the intensity of
applied magnetic field (Fig. 5) : this is astonishingly similar to that of model systems of weakly-coupled classical superconducting grains [21]. A quantitative description of this behaviour in the framework of coherence transition has been given [15]. This granular aspect was recently confirmed by several other authors [22, 23]. In particular, a strong dependence of the transition width with the sample's apparent density was pointed out [24].

In addition, some thermal treatments were performed under pure oxygen atmosphere. In fact there is very little difference in the resulting behaviour : the last annealing temperature can be increased of about 40 °C. A slightly narrower transition ($\Delta T_c = 1.5$ K) was observed for samples annealed at 480 °C.

5. Conclusion.
In this work, we show that the midpoint transition temperature measured by inductive methods is very sensitive to the annealing temperature which controls the oxygen concentration. Using a proper thermal treatment we were able to obtain well defined samples characterized by very narrow superconducting transitions, both inductively and resistively.

In addition to a very high quality attainable, the annealing process which we propose [14] has the advantages of simplicity, speed samples are obtained within 8 hours) and very good reproducibility (almost a hundred tested samples gave the same inductive response). All these points are of clear interest either for the elaboration of reliable samples in view of physical measurements or for a future large-scale preparation.

The same thermal treatment proposed in this work has been extended to other (RE)$_2$Ba$_2$Cu$_3$O$_{7-x}$ compounds, and lead to equally good results [17].

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