Staircase superconducting structure and oxygen intercalation in $YBa_2Cu_3O_{7-\delta}$ single crystals

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ac susceptibility studies of single crystals of $YBa_2Cu_3O_{7-\delta}$ have been carried out with an ac field parallel or perpendicular to the surface of these crystals. The analysis of the results gives evidence for a staircase structure in which oxygen deficiencies increase towards the sample core. As a consequence, the oxygen mobility appears to be extremely anisotropic, favoring the c axis.

INTRODUCTION

Single crystals of the high-T_c materials (Refs. 1 and 2) $YBa_2Cu_3O_{7-\delta}$ prepared by different techniques such as the flux method[3] or the mineralization process[4] are now intensively studied. However, the crucial problem of the oxygen intercalation is still not well controlled in single crystals. This can lead to inhomogeneous oxygen distributions across the sample, a possibility of fundamental consequences, especially for careful investigations of anisotropic properties of single crystals.

In this paper we present a low-field ac susceptibility study of several single crystals of $YBa_2Cu_3O_{7-\delta}$ prepared by a flux method with typical dimensions of $2\times2\times0.1$ mm^3. This study leads to a very coherent picture of the superconducting structure and oxygen distribution in our samples. We have also performed a study in larger fields which allows us to investigate the mechanism of superconductivity development across twin boundaries.[5]

EXPERIMENTAL TECHNIQUES

The crystals were obtained by a flux method similar to the one mentioned in Ref. 3. The starting components with molar composition $BaO:YO_{1.5}:CuO=31.5:2:66.5$ were heated in air at 1020 °C during 5 h in an alumina crucible. A rapid cooling (1020→960 °C) was followed by a slow cooling down to 880 °C (50°/h). Then the crucible was removed from the furnace. The single crystals were intercalated by a cooling down from 700 to 200 °C in 60 h under an oxygen pressure of 20 bars. The obtained c-lattice parameter was $c=11.686$ Å. The ac susceptibility setup has been previously described in Ref. 6. The measurements were performed between 1.2 and 100 K at a frequency of 107 Hz for different values of an excitation field ($h_{ac}=0.1$ to 2 Oe) parallel or perpendicular to the ab basal plane of several crystals of the same batch. For clarity, we present in this paper our results for one of those crystals. All the others give very similar results.

SUSCEPTIBILITY RESULTS

Figures 1 and 2 show some results obtained for $h_{ac}=2$ Oe. When the field is parallel to the basal plane, the imaginary susceptibility $X''(T)$ shows a distribution of peaks ranging between 64 and 85 K [Fig. 1(a)]. Similarly to the case of inhomogeneous superconducting systems,[7]

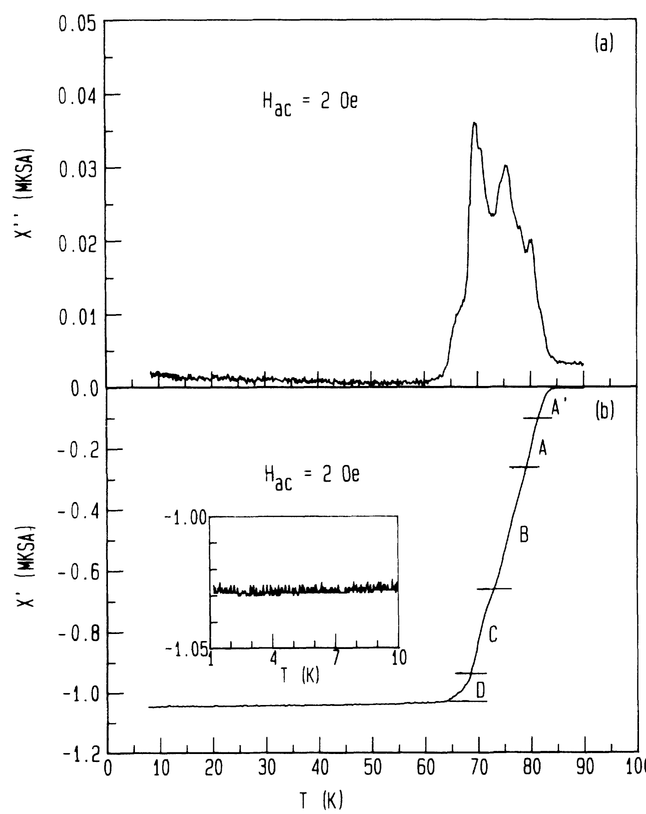

FIG. 1. $X''(T)$ and $X'(T)$ for H_{ac} (2 Oe) parallel to the ab basal plane show different superconducting phases A', A, B, C, D. The inset shows the $X'(T)$ variation at low temperature.

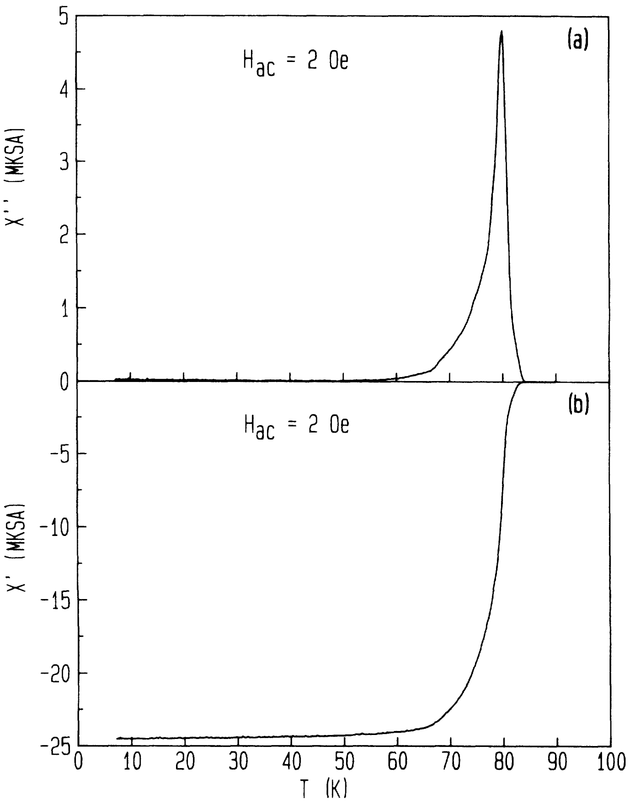

FIG. 2. $X''(T)$ and $X'(T)$ for H_{ac} (2 Oe) parallel to the c axis show only the A superconducting phase.

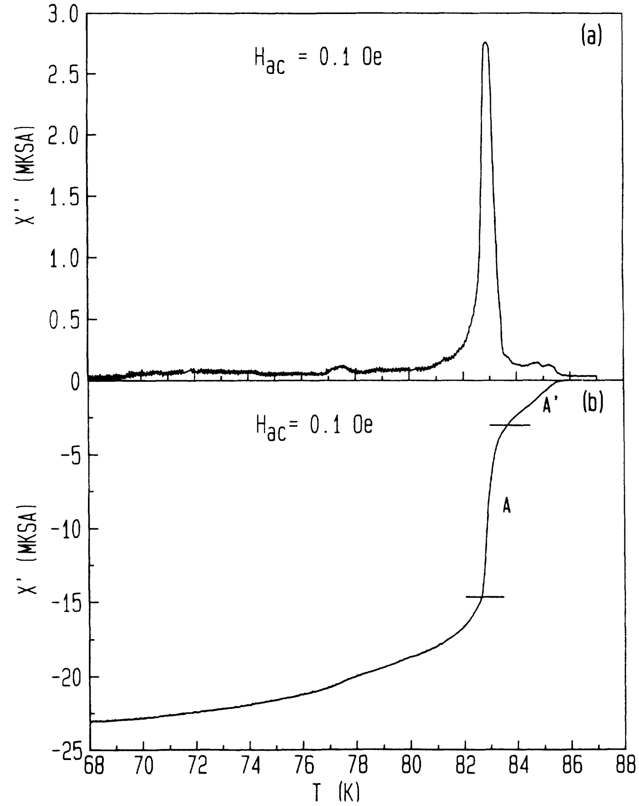

FIG. 3. For H_{ac} (0.1 Oe) parallel to the c axis $X''(T)$ shows the great contribution of phase A and a very smaller one for the other phases A', B, C, D.

these X'' peaks characterize different superconducting phases.

In the same temperature region, a careful analysis of the real contribution to the susceptibility $X'(T)$ reveals slight steps at positions corresponding with the $X''(T)$ maxima; at least four different phases (A, B, C, D) can be resolved in the ac field of 2 Oe applied in the basal plane. When the same field is applied along the c axis, we essentially observe a single X'' peak at 80 K together with an inflection point on $X'(T)$ [Fig. 2(a)]. This corresponds to a superconducting transition at $T_c=80$ K. A more detailed investigation can be performed by lowering the ac field. For $h_{ac}=0.1$ Oe, the broadened low temperature part of the X'' peak observed at 2 Oe can be resolved [Fig. 3(a)], together with a main peak at 82.8 K (instead of 80 K) we observe now several much smaller peaks, as well, above and below this temperature. It is interesting to see a correspondence between the temperatures of these peaks and those (A, B, C, D) observed in Fig. 1(a); only a slight shift of about 2.8 K takes place, which is due to a difference in the values of the applied field.

Now we will see that a comparison of the X'' and X' anomalies for h_{ac} parallel and perpendicular to the basal plane allows us to determine the main features of the geometrical arrangement of the different superconducting phases of our single crystal. These differences (see above and also see Figs. 1–3) can be understood in detail if one considers a platelike structure (Fig. 4) where the lowest-T_c phases are sandwiched between two extreme layers of the $T_c \simeq 80$-K phase. In such a case, this phase will strongly screen the inner ones leading to very small X'' contribution when h_{ac} is parallel to the c axis. On the opposite, when h_{ac} is parallel to ab, there is no preferential screening, and the X'' peaks are of comparable amplitudes suggesting that the relative volumes of corresponding superconducting phases are also comparable. This has been checked by an experimental simulation: two plates of NbZr ($T_c=10.9$ K) separated by a NbTi plate ($T_c=9.3$ K), all of them being of equal volume, give the susceptibility response shown in Fig. 5. The striking similarity with the results of Figs. 1–3 gives further support to the plate-

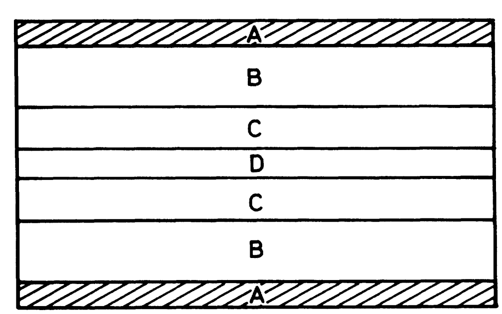

FIG. 4. A schematic view of the platelet structure of the sample.

let structure of superconducting phases of our single crystal. Within this interpretation, the supplementary weak peaks at 84.8 and 85.2 K [Fig. 3(a)] correspond to superconducting phases A' (Figs. 1 and 3) which (i) cannot be screened by the A superconducting phase, which has a smaller transition temperature (82 K at 0.1 Oe), and (ii) do not screen this 82-K phase, because the X'' susceptibility of this phase is very large.

As a consequence, the highest T_c phases A' at 84.8 and 85.2 K, cannot have an extended platelet structure. They form islands of relatively small volume, which are presumably located at crystal edges. Now let us go further in our analysis by considering some quantitative aspects. The relative proportions of the phases $(A, \ldots, D)$ are clearly related to their contributions to X' for h_{ac} parallel to ab, i.e., to the differences $\Delta X'$ between consecutive steps, or equivalently, between the different T_c values given by the X'' peaks. The obtained thicknesses (given in μm) are as follows (see also Fig. 4):

$$e_A \simeq 9, \; e_B \simeq 21 e_c \simeq 15, \; e_D \simeq 4 \; .$$

This platelet structure suggests the existence of transition regions (more or less disordered) between adjacent superconducting phases which presumably also contain staking faults and [001] twin boundaries. If normal, these regions could give a contribution to χ_{ac} at the onset of coherence (proximity effect) as it has already been observed in multifilamentary superconductors.[8] No similar effect was found even at low temperatures down to 1.2 K [see inset of Fig. 1(b)] thus supporting the idea that all these regions are already superconducting when the last transition occurs near 70 K. Nevertheless, more refined effects based on the development of superconductivity across twin boundaries [001] and [1$\bar{1}$0] will be reported and dealt with in a next paper.[5]

In our evaluation of the different phases thickness, we have neglected the demagnetizing field effect ($h_{ac} \parallel ab$). This cannot be justified when h_{ac} is parallel to the c axis. It is well known that, in the limit of a film of thickness e, and mean length a, the demagnetizing field coefficients are given by

$$N_{\parallel} = \frac{\pi}{4} \frac{e}{a} \quad \text{for } h_{ac} \parallel ab \; ,$$

$$N_{\perp} = 1 - \frac{\pi e}{2a} + \ldots \quad \text{for } h_{ac} \perp ab \; .$$

For our sample we get $N_{\parallel} \simeq 3.9 \times 10^{-2}$ and $N_{\perp} \sim 0.92$. The measured low-temperature susceptibility (below 70 K where the last transition occurs), $X_{\parallel}^{m} = -1.05$ and $X_{\perp}^{m} = -23$ give $X_{\parallel} = -1.01$ and $X_{\perp} = -1.04$ after demagnetizing field corrections. When the ac field is applied along the c axis, the distortions of flux lines around the sample, occurring below 82 K, are imposed by the two extreme superconducting layers ($T_c = 82$ K) and are almost independent of the nature of inner layers: The obtained value $X_{\perp} \simeq -1$ is therefore due to a complete shielding effect. On the other hand, when the temperature decreases from 82 K, in presence of an ac field parallel to the ab plane, the flux lines going through the inner layers are progressively expelled in correlation with the superconducting transitions of these inner layers. The screening effect is not important here, and the value $X_{\parallel} \sim -1$ indicates that almost all the volume of the sample is superconducting.

An obvious consequence of our observation of layered superconducting phases concerns the mechanisms of oxygen intercalation. The thickness distribution of different phases with given T_c is plotted in Fig. 6. Using a standard $T_c(\delta)$ curve[9,10] for disordered $CuO_{1-\delta}$ planes we get the oxygen concentration profile along the sample thickness given in Fig. 6. These curves show that in the intercalation process, most oxygen atoms enter the crystals from the two outer crystal surfaces parallel to the ab plane; if the oxygen was also entering the film from the four sample edges, then an edge surface superconducting circuit

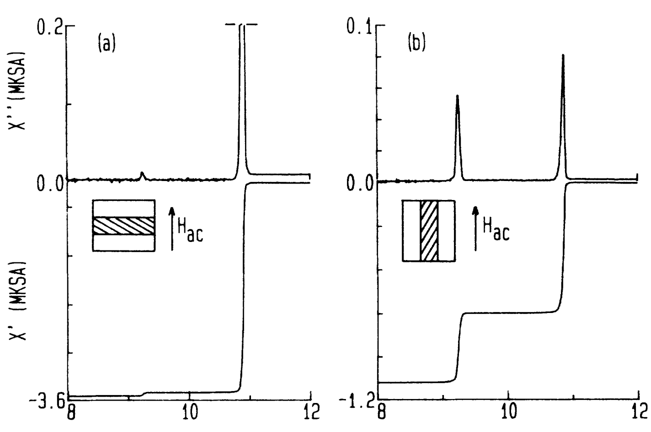

FIG. 5. Simulation of the screening effect with NbTi plate sandwiched between two NbZr plates. (a) h_{ac} (1 Oe) perpendicular to the plates. The signal $\Delta X'$ corresponding to the transition of NbTi plate is around 1.8% of the whole transition. (b) For H_{ac} (0.1 Oe) parallel to the plates the transition of NbTi is around the expected value of 36% (no screening effect in this case).

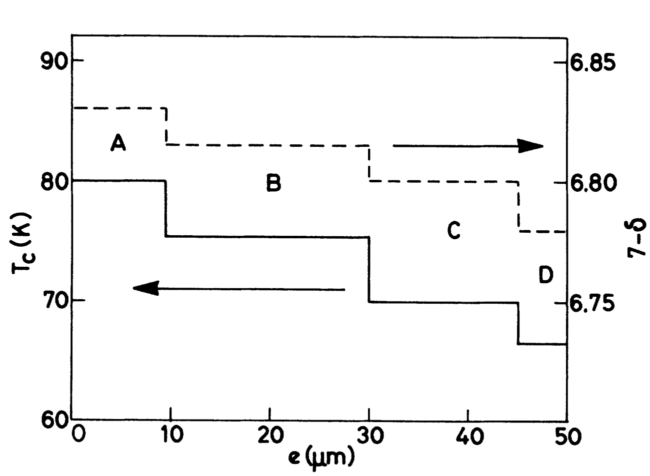

FIG. 6. The critical temperature and the composition of oxygen as a function of the depth e(μm) with the origin ($e = 0$) located at the sample's surface.

would be there and screen more or less completely the inner parts of the sample for $h_{ac}\parallel$ or $\perp$ to *ab*. We do not observe such screenings (see Fig. 1). As a consequence, during the intercalation process, the oxygen mobility appears to be extremely anisotropic: Almost all the oxygen diffuses along the *c* axis and nothing perpendicular to this axis, whatever the mean oxygen concentration of considered layers. This result, which might seem surprising at first sight, could be due to a progressive and partial filling of $CuO_{1-\delta}$ planes of the inner part of the sample by a mechanism in which oxygen vacancies in different sites migrate step by step in average along the *c* axis toward the sample surface. Another possibility would be the formation of a nonsuperconducting oxygen diffusion barrier of unknown composition on the overall small surface of the crystal edges. But this possibility does not question the previous diffusion mechanism of oxygen along the *c* axis. Nevertheless it would be interesting to perform ionic conductivity experiments in $YBa_2Cu_3O_{7-\delta}$ single crystals to provide a more direct evidence for our result. Moreover, a characteristic staircase profile of the oxygen concentration along the *c* axis instead of a continuous one was rather unexpected. This would suggest that a continuous δ composition is not allowed, and only discrete values of δ corresponding to a superstructure on oxygen vacancies in the orthorhombic phase are permitted.

CONCLUSION

Careful ac susceptibility experiments performed on several single crystals of $YBa_2Cu_3O_{7-\delta}$ show the existence of a succession of superconducting layers parallel to the *ab* plane with temperature transitions T_c decreasing from the outer to the inner part of the sample. Such a staircase superconducting behavior shows that oxygen intercalation is spatially modulated and would involve a large anisotropy in the oxygen mobility, favoring diffusions along the *c* axis. This conclusion could be very helpful for a microscopic understanding of the intercalation process in $YBa_2Cu_3O_{7-\delta}$. Furthermore, we stress the important role the existence of staircase superconducting layers can play in the investigations of anisotropic properties of $YBa_2Cu_3O_{7-\delta}$ single crystals. The influence of twin domain boundaries can be revealed in larger ac fields (see Ref. 5).

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