CRITICAL PARAMETERS OF HIGH T_c COMPOUNDS

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Upper critical fields of $XBa_2Cu_3O_{7-\delta}$ with X = Y, Er, Gd, Ho, Eu or $Y_{1-x}Pr_x$ have been measured using pulsed magnetic fields up to 26 T. As long as the high temperature superconductivity is present, the superconducting coherence length calculated from the critical field data, remains comparable to the size of the unit cell (~1 nm). Oxygen evolution experiments have been used to control the depletion of oxygen sites corresponding to different activation energies. The variation of the critical parameters has been determined as a function of the oxygen deficiency δ for the $YBa_2Cu_3O_{7-\delta}$ compound.

1. Introduction

Recently, it has become clear that there exists a very strong correlation between the oxygen content and the critical parameters (critical temperature T_c, critical field B_c, critical current density J_c) of the high T_c compound $YBa_2Cu_3O_{7-\delta}$ [1]. The transition temperature T_c strongly depends upon the oxygen deficiency δ. For large enough δ values, the orthorhombic superconducting phase is replaced by an insulating tetragonal phase [2, 3]. An exact knowledge of the role which is played by the oxygen deficiency and disorder will probably provide important information about the microscopic origin of the superconductivity.

Even when the ideal oxygen stoichiometry has been obtained, the critical current density J_c derived from electrical transport measurements is still very small for polycrystalline samples ($<10^3$ A/cm^2) at liquid nitrogen temperature. On the other hand, the critical current density derived from magnetization measurements ($\sim10^6$ A/cm^2) is much larger than the current density obtained from direct transport measurements. This difference can be explained as being a consequence of the Josephson tunneling which occurs between the weakly-coupled grains, preventing the existence of large superconducting current densities on a macroscopic scale [4]. Very close to T_c, the Josephson effect dominates the electronic properties. In a small magnetic field ($B \sim 10^{-3}$ T), the resistance already jumps to a finite value. On the other hand, the strong superconducting order within the grains is confirmed by the large critical fields B_c at which the normal state resistance is restored. The slope of this upper critical field near T_c is of the order of -3 T/K [5] indicating a very small superconducting coherence length of the order of 1 nm in these high T_c materials.

We have measured in detail the critical parameters T_c and B_c of stoichiometric $YBa_2Cu_3O_{7-\delta}$ samples. When the Y is replaced by another trivalent rare earth element (Er, Ho, Gd, Eu), the critical parameters remain basically unaffected. However, when the Y is partially replaced by Pr which has also a stable tetravalent state, the superconducting transition temperature is depressed and for a Pr concentration larger than 0.5, these compounds become insulators [6, 7].

In a second set of experiments, we have performed extensive oxygen evolution experiments which reveal the strong influence of a reduced oxygen site occupancy on the critical parameters of the high T_c compounds. Up to now, the exact role of the oxygen occupancy of the various inequivalent sites is still unclear. In particular, changes in the oxygen stoichiometry of $YBa_2Cu_3O_{7-\delta}$ have been shown to produce an orthorhombic to tetragonal phase transition, together with a depression of the superconducting transition temperature T_c and an increase of the normal state resistivity ρ [2, 3]. Whether the

structural phase transition occurs exactly at an oxygen stoichiometry of 6.5 (only Cu^{2+} present) and whether the disappearance of superconductivity coincides exactly with this phase transition has not yet been uniquely established [3].

In order to identify the binding energy of the different oxygen sites in the unit cell we have studied in detail the oxygen evolution from samples that are known to contain only Cu–O planes (La_2CuO_4, $La_{2-x}Sr_xCuO_4$), samples that contain Cu–O planes and chains ($YBa_2Cu_3O_{7-\delta}$, $LaBa_2Cu_3O_{7+\delta}$, $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$) and samples composed of different phases (Bi–Ca–Sr–Cu–O compounds). Comparison of different high and low T_c ceramic superconductors indicate the presence of an additional 600°C desorption peak for the superconductors containing Cu–O chains. The superconductors that only contain two-dimensional Cu–O planes show a single desorption peak around 800°C. The absence of the 600°C peak in the desorption spectrum of the Bi compound may indicate that there are no chains present in this structure [8]. The results of the evolution experiments allow us to selectively deplete different oxygen sites by annealing the samples in vacuum at the appropriate temperature. In this way, we can make a detailed link between the structural phase and the occurrence of the high T_c superconductivity in $YBa_2Cu_3O_{7-\delta}$.

2. Critical parameters of stoichiometric compounds

The $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ samples with $x = 0$, 0.06, 0.09, 0.12, and 0.20 as well as the Er, Ho, Gd and Eu 123 compounds were prepared at Argonne National Laboratory (U.S.A.). We refer to Soderholm et al. [6] for the details of the sample preparation. The upper critical field B_c has been defined as the field where 50% of the normal state resistance is recovered. Due to the important broadening of the resistance versus magnetic field curves close to T_c, this procedure is no longer valid for $T/T_c > 0.98$. Possible deviations from the linear critical field slope due to

fluctuation effects can therefore not be detected in our polycrystalline samples.

In a first experiment, the influence of replacing the Y in the 123 compound by the other trivalent rare earth elements Er, Gd, Ho and Eu has been studied. While the T_c value remains close to 90 K for the Er, Gd and Ho compounds, T_c is reduced to 84 K for the Eu compound. The weakening of the superconducting order by introducing the Eu is also confirmed by a reduction of the critical field slope near T_c, as shown in fig. 1, where we have plotted the critical field data as a function of temperature. From the critical field slope near T_c we calculate that for all of the 123 compounds the zero temperature coherence length $\xi(T \to 0)$ is of the order of 1 nm, in agreement with the results obtained by other experimental groups [5].

In a second experiment, Y was partially replaced by Pr [6, 7]. Pr is a rare earth element having also a stable tetravalent state, while most of the rare earth elements have only a stable trivalent state. Using resistivity measurements in zero field, it was shown that for a Pr concentration larger than 0.5, these compounds become insulators. At the same time, T_c gradually decreases from 90 K to 0 K when the Y concentration decreases from 1 to 0 [6, 7]. In the samples with a 0.5 Pr concentration, the Pr^{4+} adds one extra electron to the structure and completely removes the presence of Cu^{3+}. The situation is very similar to the formation of insulating $YBa_2Cu_3O_{7-\delta}$ when the oxygen deficien-
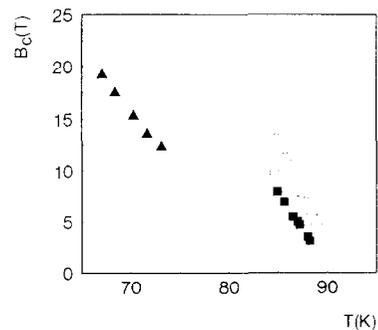

Fig. 1. Temperature dependence of the upper critical field B_c of the high T_c compound $XBa_2Cu_3O_{7-\delta}$ with X = Y(○), X = Er (□), X = Gd (△), X = Ho (■) and X = Eu (▲).
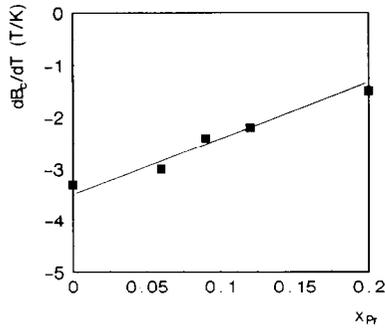
Fig. 2. Critical field slope dB_c/dT in the vicinity of T_c as a function of the Pr content x_{Pr} in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ compounds.

Fig. 3. Temperature dependence of the upper critical field B_c for $YBa_2Cu_3Y_{7-\delta}$ (■) and a Bi–Sr–Ca–Cu–O (▲) compound.

cy $\delta \simeq 0.5$ [2] (see section 3). In fig. 2 we have plotted the variation of the critical field slope near T_c for the different Pr contents. The decrease of the absolute value of this slope with increasing Pr concentration corresponds to an increase of the coherence length $\xi(T\to 0)$ from 1.4 nm to 2.3 nm when the Pr concentration is increased from 0 to 0.2. This increase of the coherence length cannot be a consequence of a reduced elastic mean free path. In a dirty type II superconductor, a smaller mean free path would imply an increase of the upper critical field slope. The replacement of Y by Pr rather decreases the superconducting coupling and consequently increases the intrinsic coherence length which varies inversely proportional to the superconducting transition temperature. This is in agreement with the observation that l_c rapidly decreases with increasing Pr concentration. This would also indicate that the metal–insulator transition in the Pr compounds is driven by electronic correlation effects rather than by disorder-induced Anderson localization.

In fig. 3 we have compared the critical field data for the $YBa_2Cu_3O_{7-\delta}$ to the critical field data obtained for a Bi–Sr–Ca–Cu–O compound. To obtain the Bi compound, the appropriate amounts of Bi_2O_3, $CaCO_3$, $SrCO_3$ and CuO powders have been mixed in atomic ratios Bi/Sr/Ca/Cu = 1/1/1/2. The pressed pellets of the mixture have been annealed at 890°C for 20 min, followed by a slow furnace cooling [9]. Although the resulting Bi compound contains several phases, the dominating phase ($T_c \simeq 80$ K) is
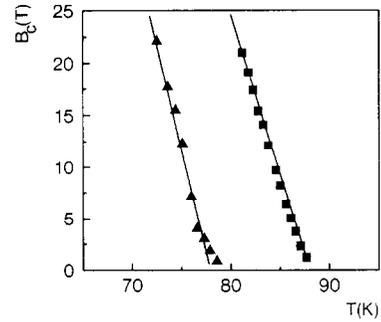
characterized by upper critical fields which are comparable to the fields obtained for the $YBa_2Cu_3O_{7-\delta}$ compound. From the data shown in fig. 3, we can also conclude that both the Y and the Bi compound are characterized by a very small superconducting coherence length (~ 1 nm).

3. Critical parameters of oxygen deficient samples

3.1. Oxygen evolution from high T_c compounds

We have performed a series of gas evolution experiments to study the changes in chain and plane oxygen occupancy in $YBa_2Cu_3O_{7-\delta}$ and their effect on the superconductivity. All the samples discussed in this section were prepared at Argonne National Laboratory using standard powder metallurgy techniques. Structural information has been obtained from X-ray diffraction. The samples were also characterized by critical temperature and resistivity measurements [2, 3, 7, 10]. Oxygen evolution was measured by placing the ceramic material in an evacuated quartz tube and recording the pressure and temperature as the sample was heated from room temperature to above 900°C [11]. In order to rule out spurious effects due to the evolution of impurity gases, the evolved gases were analyzed using a mass spectrometer. All our data have been corrected to take into account the gas evolution from the walls of the vacuum chamber.
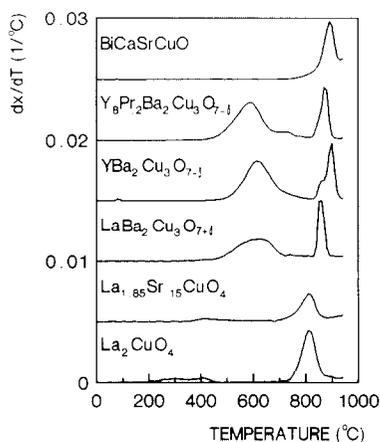
Fig. 4. Temperature derivatives of the number of oxygen atoms evolving from different ceramic superconductors.

Fig. 4 shows a comparison of typical oxygen evolution curves (shifted for clarity along the y-axis), for different ceramic superconductors. The y-axis is directly proportional to the temperature derivative of the number of oxygen atoms evolved from the sample. The spectra are characterized by sharp high temperature peaks around 800°C in *all* the samples and a broad low temperature peak around 600°C in *some* of the samples. Only the samples that contain Cu–O chains ($YBa_2Cu_3O_{7-\delta}$, $LaBa_2Cu_3O_{7+\delta}$, $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$) also exhibit the low-temperature peak. We therefore identify this peak with the oxygen evolution from the chains commonly designated as the O1 site. A detailed comparison of our evolution data with neutron diffraction data confirms this assignment [2, 11]. The fact that the peak around 600°C is broad, indicates the presence of oxygen with slightly different binding energies, possibly due to the presence of oxygen vacancies or oxygen atoms occupying the O5 site which should be un-occupied in the ideal orthorhombic structure. The La_2CuO_4 and $La_{2-x}Sr_xCuO_4$ samples which are known not to contain Cu–O chains [12], also lack the low-temperature 600°C evolution peak. Note that this peak is also absent in the Bi–Ca–Sr–Cu–O samples. Of course, the presence of Bi–O chains with a large binding energy cannot be ruled out by our experiment.

The high-temperature peak (800°C) looks quite similar among all samples, with a splitting clearly observable for the $YBa_2Cu_3O_{7-\delta}$ samples. The similarity of this evolution peak for the different systems clearly indicates that this oxygen is evolving from the other oxygen containing planes. Comparison with neutron diffraction data reveals that this peak corresponds to evolution from the Ba–O planes (O4 site). The identification of the third peak has not been made since the existing neutron data do not allow a unique interpretation. We would also like to stress that our identification of the peaks with a particular site is completely based on the neutron scattering results [2, 13]. Therefore, any change in the interpretation of the neutron data may also affect the interpretation presented here.

3.2. Destruction of high T_c superconductivity in oxygen deficient samples

In the present experiments, part of the oxygen has been removed from the samples by annealing them for a fixed amount of time at 400°C. The amount as well as the origin of the removed oxygen during the 400°C annealing can be determined by recording the oxygen evolution up to 900°C. The inset of fig. 5 shows such an evolution curve obtained for an $YBa_2Cu_3O_{7-\delta}$ sample heated at a rate of 10°C/min after 6 h of annealing at 400°C. The integrated amount of oxygen corresponding to the 600°C peak, is shown in fig. 5 as a function of the annealing
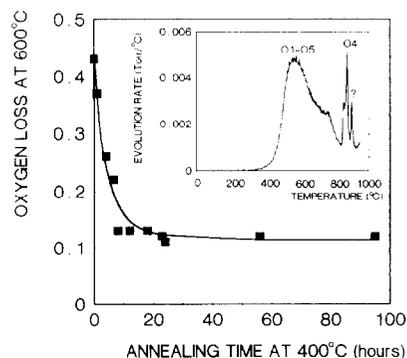

Fig. 5. Evolution of the O1 and O5 ("chains") occupancy versus annealing time at 400°C. Note the fast decrease of this occupancy for annealing times shorter than 10 h. The inset shows a typical evolution curve as described in the text.

time at 400°C. Up to 10 h of annealing, we observe a rapid decrease of the 600°C peak, followed by a plateau which persists up to 90 h of annealing. The variation of the second peak, which is centered near 860°C, is radically different. As shown in fig. 6 this second peak remains nearly unaffected up to 10 h of annealing at 400°C, followed by a gradual decrease for larger annealing times. Our data indicate that for a 400°C anneal, the O1–O5 oxygen atoms escape from the sample during the first 10 h, while the O4 oxygen occupancy remains constant. For larger annealing times, the chain occupancy remains fixed at 0.12, while the O4 occupancy slowly decreases. X-ray diffraction measurements show that the sample with a chain occupancy of 0.12 has a fixed orthorhombic distortion which is almost independent of the occupancy of the O4 site. We believe the residual concentration of 0.12 not to be a "magic" number [14], but determined by a thermodynamic equilibrium between the different site occupancies. Since this equilibrium will depend on the annealing temperature, we can explain the discrepancy observed between different experiments.

After each annealing at 400°C, we have determined the critical temperature T_c using rf susceptibility measurements. Measuring the diamagnetic response of the oxygen deficient sample turns out to be a better method to define the superconducting transition when compared to classical resistance measurements. Indeed, an inhomogeneous evolution of the oxygen may result in a percolating path through the sample for which the resistively determined T_c value deviates considerably from the average T_c value for the material.

The variation of T_c as a function of the annealing time at 400°C is shown in fig. 7 and turns out to be quite interesting. The T_c value decreases rapidly down to 60 K and then levels off. A comparison of figs. 5, 6 and 7 is quite revealing, showing that the change in the superconducting transition temperature is largely determined by the "chain" occupancy (sites O1–O5) and almost independent of the O4 occupancy.

At this point, two interpretations of our experiments are possible. If the superconductivity is caused by a geometrical ordering of the chains, the chain occupancy will dominate the superconducting behavior, while the O4 occupancy has only a minor effect. If the presently more "popular" viewpoint is adopted, which claims that the only role of the chains is to provide holes to the conductive Cu–O planes [15], our results imply that the hole concentration in our samples is dominated by the removal of oxygen from the chains.

It is important to note that our present results bring into agreement contradictory results concerning the exact oxygen deficiency δ for which the orthorhombic–tetragonal transition occurs and $T_c \rightarrow 0$. Our results indicate that the superconductivity is closely related to the chain occupancy and is almost independent of the O4
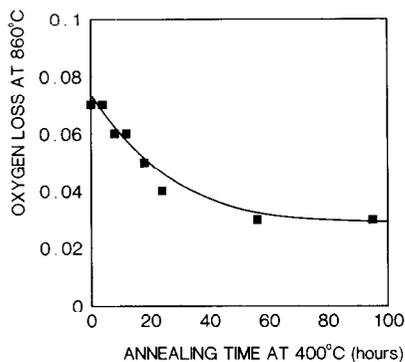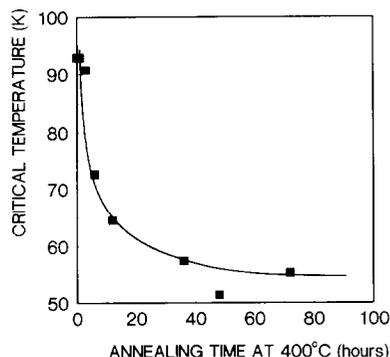
Fig. 6. Evolution of the O4 occupancy versus annealing time at 400°C. Note that the oxygen concentration of these sites remains constant for annealing times shorter than 10 h.

Fig. 7. Decrease of the transition temperature T_c as a function of the annealing time at 400°C.

occupancy as long as this occupancy is high enough to maintain electrical conduction. Conclusions from experiments which are based on the total oxygen stoichiometry can therefore be misleading and could strongly depend on the particular sample preparation method.

4. Conclusion

Our detailed measurements of the upper critical field in $XBa_2Cu_3O_{7-\delta}$ samples have demonstrated that for $X = Y$, Er, Gd, Ho and Eu the critical field slope in the vicinity of T_c is of the order of -3 T/K. This implies that for all these high T_c compounds the superconducting coherence length remains comparable to the size of the unit cell (~ 1 nm). For $X = Y_{1-x}Pr_x$, an important decrease of the absolute value of the critical field slope occurs with increasing Pr concentration. The tetravalent Pr atoms destroy the superconducting order and give rise to an increase of the intrinsic coherence length.

By making a detailed study of the oxygen evolution from various high T_c compounds, it has become possible to identify the low-temperature peak with evolution from the O1–O5 sites and the high-temperature peak with the O4 site. This allows us to selectively deplete the oxygen chains. Our results show that the evolution kinetics proceeds by an initial large change in the chain occupancy while the other occupancies are constant, followed by a gradual decrease of the O4 site occupancy with the chain occupancy remaining constant. The superconducting transition temperature and the orthorhombic distortion are found to be mainly determined by the chain occupancy which may explain the discrepancy between experiments with equal total oxygen stoichiometry.

Acknowledgements

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