Oxygen Deficient $YBa_2Cu_3O_{7-\delta}$: Two Superconducting Phases

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A set of oxygen deficient powder and granular samples of $YBa_2Cu_3O_{7-\delta}$ ceramics was studied by means of thermogravimetric and magnetically modulated microwave absorption methods. Especially the last method has turned out to be a powerful method, which was used to determine the dependence of critical temperature T_c on the oxygen parameter δ. Using these methods it has been shown that the removing of oxygen evokes the inhomogeneous oxygen distribution in the samples and a change in carrier concentration till to the loss of superconducting properties. A superconducting phase with $T_c = 60$ K, which occurs in oxygen deficient $YBa_2Cu_3O_{7-\delta}$ sample, is an unstable phase.

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1. Introduction

Oxygen stoichiometry in $YBa_2Cu_3O_{7-\delta}$ (YBCO) decides on copper charged state and charge carrier concentration [1, 2]. The concentration of oxygen affects YBCO superconducting properties, hence it is relevant to understand the mechanism of spin pairing and phase diagram of high-temperature superconductors (HTCS). Inhomogeneous charge and spin distribution seems to be the origin of strong carrier density fluctuations, responsible for the appearance of superconducting phase transition at a given T_c. The oxygen content in YBCO is characterised

by two parameters: x-oxygen content in the sample and δ-concentration of oxygen vacancy at O(1) site in the elementary unit cell ($\delta = 7 - x$). The parameter δ changes while the sample is heated in vacuum or in the noble gas atmosphere. Thermogravimetric studies show that the oxygen parameter δ linearly depends on the loss of weight Δm as $\delta = -0.41666\Delta m$ [3]. The 1.65% loss of weight corresponds to the change in δ from 0 to 0.7. Oxygen desorption is accompanied by the expansion of the unit cell along the c-axis direction [4, 5]. The dependence $\delta(c)$ is described as $\delta = 74.688[(c/11.670) - 1]$ and gives δ parameter with 10% accuracy. If the process takes place close to the transition from orthorhombic to tetragonal phase, which is an order–disorder transition for oxygen at O(1) and O(5) sites, the oxygen parameter can be determined from the volume of the elementary unit cell [6].

Despite extensive studies on oxygen deficient samples [7], there are still questions regarding the mechanism of removing the oxygen and homogeneity of superconducting phase in the whole range of possible oxygen concentration. In the present study the oxygen deficiency and relevant phenomena are intensively investigated by means of the magnetically modulated microwave absorption (MMMA) method. The phenomenon of MMMA is associated with a loss of microwave energy due to the Cooper pair excitation to a quasi-particle state. The method can serve to determine the critical temperature T_c of the transition from normal to superconducting state, critical Josephson field H_{cJ} and to investigate the flux pinning phenomenon as the width of MMMA hysteresis loop is proportional to the number of trapped fluxions [8, 9]. It is also especially useful below the percolation threshold, where transport measurements cannot be applied, and low concentrations of superconducting phase do not allow measuring the magnetic susceptibility.

Here, the changes observed in the temperature dependences of MMMA and the changes of sample properties at different levels of oxygen concentration point to at least two-phase model of YBCO as oxygen is removed [10].

2. Experimental

YBCO powder from Superconductive Components Inc. with a grain size of 1–10 μm was the master sample. *In situ* oxygen desorption on a thermogravimetric analysis (TG) balance was performed to determine the set of four temperature values, at which the rate of oxygen loss is not fast. During the TG analysis the powder was heated at the rate of 5 K/min in controlled $Ar/5\%H_2$ atmosphere. The set of oxygen deficient samples was prepared by heating the powder for 10 min in argon atmosphere at temperatures determined from the TG analysis and then quenched to room temperature.

Another sample was a highly granular piece of YBCO ceramics characterised by mass of $\sim$ 10 mg, porosity of 30%, and average diameter of the grains equal 5 μm. The sample was placed in a quartz tube and heated under vacuum to

523 K. After 10 min of heating the tube with the sample was sealed and cooled to room temperature. Immediately after cooling the critical temperature T_c of the sample was measured. The next measurements of T_c were performed after heating the sample during 10 min in selected higher temperatures up to the limit of 773 K. For the accurate measurements of the critical temperature T_c and thus the determination of small changes in δ parameter the MMMA non-contact method was used. The technical details of the method can be found elsewhere [8, 11].

The MMMA measurements were performed using an X band EPR spectrometer equipped with Oxford helium-flow ESR 900 cryostat. The second modulation of the applied magnetic field was used. The frequency of the second modulation was equal 100 kHz and its amplitude was 1 mT. There was a standard configuration of the magnetic fields in microwave cavity, i.e. the microwave magnetic field was perpendicular to the applied magnetic field and to the field of second modulation.

3. Results and discussion

Figure 1 presents TG curve for the powder sample. Using the data from Fig. 1 the set of oxygen deficient samples was prepared by heating the powder for 10 min in argon atmosphere at temperatures determined from the TG analysis, i.e. 523 K, 803 K, 833 K, and 898 K and then quenched to room temperature.

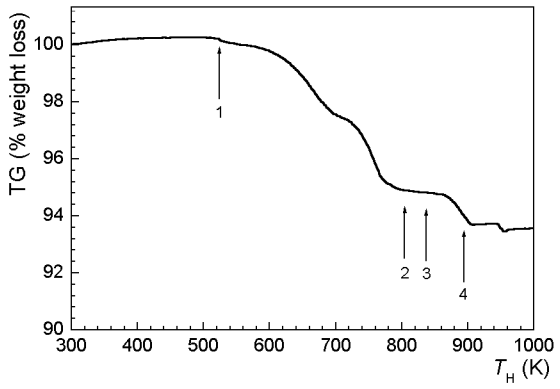

Fig. 1. The weight of YBCO powder vs. temperature of heating (TG curve) in $Ar/5\%H_2$ atmosphere. The rate was 5 K/min.

Figure 2 presents MMMA signals versus temperature for 4 oxygen deficient powder YBCO samples, heated at 4 previously selected temperatures (i.e. 523 K, 803 K, 833 K, and 898 K). Each oxygen loss due to heating destroys adequately the superconducting state. For a heating temperature of $T_1 = 523$ K the critical temperature is still $T_c \approx 90$ K as for the untreated sample of YBCO. Higher temperatures of 803 K and 833 K were resulted in decrease in T_c to 60 K ($\delta \approx 0.3$)

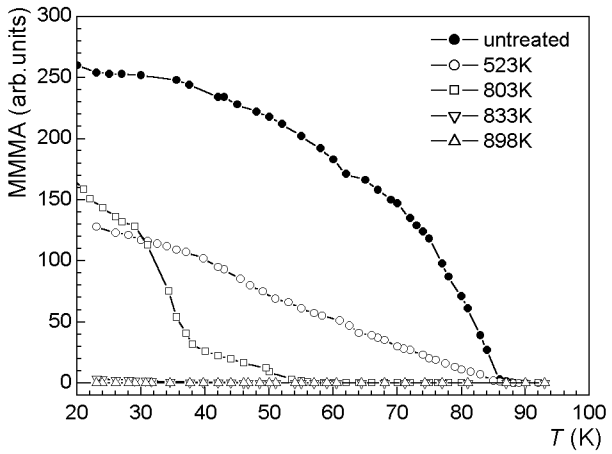

Fig. 2. The amplitude of MMMA vs. temperature for untreated and deoxygenated YBCO at different temperatures.

and in reduction of MMMA signal amplitude. There is no MMMA signal associated with superconductivity for $T_4 = 898$ K.

The granular YBCO sample was heated more carefully. The heating temperature was increased from 523 K to 773 K. The interval between two consecutive temperatures selected for heating the sample was equal 20 K, especially in the range of 673–773 K. After each of the heating cycle the critical temperature T_c was measured using MMMA. The results obtained are presented in Fig. 3. The critical temperature remains constant and equal $T_c = 90$ K for heating temper-

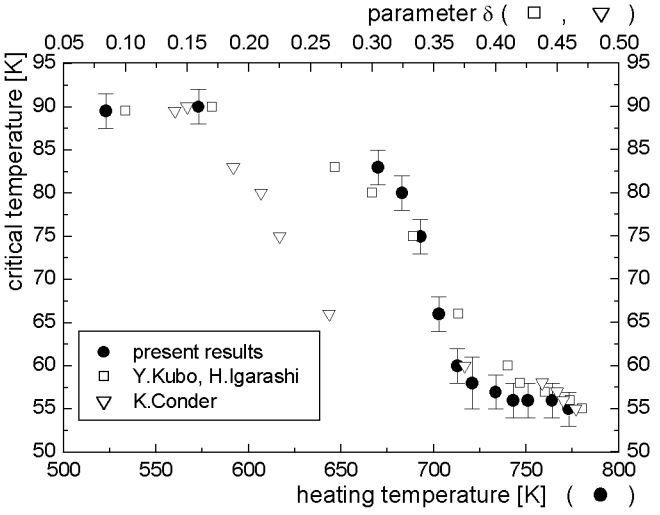

Fig. 3. The critical temperature T_c vs. heating temperature T_H and versus δ coefficient after data of Kubo et al. [12] and Conder [13].

atures up to 573 K. The sharp drop of critical temperature begins at a heating temperature of 673 K and ends at 723 K, where T_c reach the value of 55 K. For even higher heating temperatures up to 773 K there is the plateau of critical temperature because the 90 K YBCO phase is converted to 60 K phase.

The overall dependence of critical temperature T_c on heating temperature is similar to the dependence of weight loss versus heating (see Fig. 1). It proves that the loss of oxygen is the most important factor influencing the temperature of transition to superconducting state T_c.

The present results are compared in the same Fig. 3 with the data reported by Kubo et al. [12] and Conder [13]. The last two authors determined also the relations between δ-coefficient and critical T_c and heating temperature T_H. Our results seem well correspond to the data obtained by Kubo et al. However there is some disagreement with the data of Conder. The reason for the disparity is probably due to a different oxygen diffusion rate caused by differences in the structure of the samples like, for example, size and shape of the grains, and sample porosity [13].

Careful investigation of MMMA signal dependence on temperature and magnetic field presented in Fig. 4 allowed one to discover two different transitions in

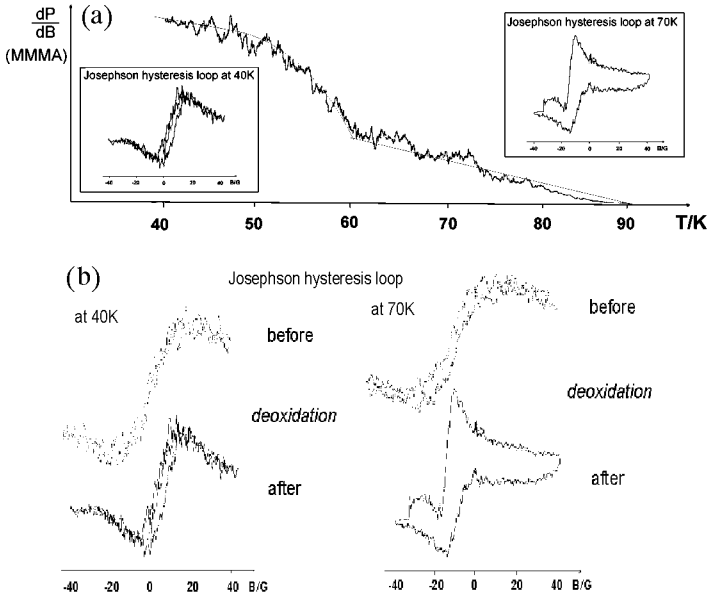

Fig. 4. The amplitude of MMMA signal for oxygen deficient sample exhibiting the presence of two superconducting phases with: T_c = 60 K and T_c = 90 K. Microwave hysteresis loops show a strong pinning above 60 K (a). The flux pinning below 60 K is less effective than in an intermediate phase between 60 and 90 K (b).

the samples with δ-coefficient above ≈ 0.3. They are evidenced by abrupt changes in amplitude of MMMA vs. temperature $A_{\mathrm{MMMA}}(T)$. The high-temperature transition occurs near 90 K, where MMMA increases whereas the low-temperature transition appears close to 60 K. Obviously, the two transitions correspond to two different YBCO phases present in the same sample. Moreover, from 90 K to 60 K the amplitude A_{MMMA} depends almost linearly on temperature, whereas below 60 K $A_{\mathrm{MMMA}}(T)$ is like the one for untreated YBCO containing pure 90 K phase — Fig. 4a.

Beside the temperature dependences of MMMA the microwave hysteresis loops were registered for temperatures 40 K and 70 K, i.e. below the low- and high-temperature transition, respectively. There is a substantial difference in width for both loops (40 K and 70 K) compared to loops for untreated YBCO sample observed at the same temperatures — Fig. 4b. The loop at 70 K in oxygen deficient sample corresponds to the linear $A_{\mathrm{MMMA}}(T)$ dependence. This loop is broad. A very narrow hysteresis loop was recorded at 40 K.

The broader microwave hysteresis loop implies a stronger magnetic flux trapping in the sample because the microwave hysteresis width ΔH is directly related to the mean value of magnetic flux $\langle H\rangle_{\mathrm{trap}}$ trapped inside the sample: $\Delta H = p\langle H\rangle_{\mathrm{trap}}$ [9]. Here, p is a coefficient dependent on the structure and geometry of the sample. The magnetic flux can be trapped in a form of inter- or intragranular flux, which corresponds to the pinning of Abrikosov or Josephson vortices, respectively. The present case is even more complex as the sample is composed of two superconducting phases, i.e. 60 K phase and 90 K phase. The microwave hysteresis loop recorded at 70 K is due to the pinning in 90 K phase only, whereas the 60 K phase contributes to the total pinning and influences microwave hysteresis measured at 40 K. Thus, the low temperature microwave hysteresis is an additive effect of the pinning forces in the two superconducting phases.

The trapping of intragranular flux due to Abrikosov vortices pinning is especially affected by the oxygen content in the sample and to the process of oxygen desorption. It is because one of the effective pinning centres for the vortices are oxygen vacancies. The oxygen vacancies are effectively generated during deoxygenation process and this is why 60 K phase is much richer in pinning centres than 90 K phase. The elementary pinning force of an Abrikosov vortex by oxygen vacancy, $f_{\mathrm{pin}} = 10(\mu_0 H_c^2)\pi r_d^2$ [14, 15], is proportional to the thermodynamic field H_{c} and the radius of vacancy r_d. The density of vacancies and their size are not the only parameters determining the total pinning force. The other ones are material parameters like: the coherence length ξ and the penetration depth λ. This is because the condensation energy $\mu_0 H_c^2 \pi r_d^3/2$ and so the pinning in Larkin–Ovchinnikov model [16] is equal to $\Phi_0^2 r_d^3/(4\pi\mu_0\lambda^2 4\xi^2)$ (where Φ_0 is the flux quantum). As ξ and λ parameters are different for 60 K and 90 K phase (for example: $\lambda = 2550 \pm 125$ Å and 1415 ± 30 Å for 60 K and 90 K phase, respectively [17]), therefore it is difficult to say which phase dominates in the total pinning. Anyway, the pinning in 90 K

phase increases as the temperature decreases and additionally at low temperatures 60 K phase becomes superconducting and contributes to the pinning. The increase in the total pinning force should expand a microwave hysteresis width very much. The opposite effect is observed.

The behaviour of microwave hysteresis width, however, can be well explained in terms of pinning of intergranular flux in a form of Josephson vortices. The vortices are coreless and thus pinned in intergranular voids and grains of normal phase. The elementary pinning force is proportional to the strength of intergranular Josephson junctions and the number of pinning centres to the porosity of the sample and to the amount of normal phase. Here, the porosity of the sample is constant contrary to the amount of the normal phase, which is temperature dependent. At a temperature of 70 K the 60 K phase is obviously normal and contributes to the total pinning. However, it becomes superconducting at 40 K and Josephson vortices are pinned in intergranular voids, only. Therefore the total pinning force and trapping of magnetic flux decreases and a narrow microwave hysteresis occurs. Opposite, in the range of linear $A_{\mathrm{MMMA}}(T)$ dependence in 60 K < T < 90 K, the higher total number of vortices pinned is expected.

The effect of "ageing" observed in the deoxygenated samples ($\delta \approx 0.3$) points also to two-phase transition to superconducting state for an oxygen deficient sample. After 3 weeks of keeping the powder sample in argon atmosphere the phase with $T_c \approx 60$ K disappeared. The recovery of strong MMMA signal at $T_c \approx 90$ K was observed, which means that 60 K phase was replaced by 90 K phase as a result of "free" oxygen redistribution in the sample. The explanation of the effect is that the oxygen leaves O(1) sites without leaving the sample, hence the ageing process gives oxygen back at O(1) site. Thus one can conclude that the 60 K phase is unstable. We reported the similar effects of oxygen and charge redistribution for artificially inhomogeneous superconductors [18].

4. Conclusions

The results presented in this paper show that the oxygen loss in YBCO is an inhomogeneous process. The deoxygenation under high temperature and vacuum or noble atmosphere removes oxygen atoms from O(1) sites in YBCO structure. Simultaneously a decrease in transition temperature down to 60 K is observed. The 60 K phase seems to be unstable due to "ageing" effects associated with the recovery of oxygen atoms to O(1) sites and the recovery of 90 K phase. There are two superconducting phases with two different transition temperatures equal 60 K and 90 K in the samples heated at intermediate temperatures.

The observed evolution and the changes of MMMA signal with temperature are due to superconducting transitions of the two phases and to the intergranular flux pinning in the form of Josephson vortices. The contribution from the pinned Abrikosov vortices can be neglected.

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