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Implication for phase separation in an overdoped Y-Ca-Ba-Cu-O superconducting system♣

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A series of polycrystalline, oxygenated $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ (x=0; 0.025; 0.05; 0.1 and 0.2) samples is investigated by XRD and magnetic measurements. It is established that increasing Ca content leads to T_c suppression, thus supporting the sample overdoping. The width of magnetization loops ($\Delta M(H)_{T=const}$) is reduced. However $\Delta M(H)_{T=const}$ is a measure of the intragranular critical current in a magnetic field. Its suppression may indicate a decrease in the pinning ability of the material and/or the quality of the superconducting condensate. The main pinning centers in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ are the oxygen vacancies, but their amount increases with x. Therefore, $\Delta M(H)_{T=const}$ reduction suggests that phase separation appeares and the number of Cooper pairs decreases when the overdoping is stronger. This assumption is also supported by an observed degradation of the Meissner volume fraction with increasing carrier concentration, which obviously excludes the role of the magnetic field.

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1. Introduction

It has been found that in overdoped (OD) cuprates, the ratio n_s/m^* (n_s – the superconducting carrier density, m^* - the effective mass) decreases with increasing carrier doping [1, 2]. A reliable explanation of this fact is the appearance of phase separation into the superconducting and the normal metal ground state. Two types of holes appear in the OD region. In one of them, holes condense into the low energy superconducting state. The other extra holes are expelled from the superconducting islands to the surrounding area, forming a non-superconducting metallic sea. The bulk superconductivity is established due to the Josephson coupling (or proximity effect) between the islands [3, 4]. In this sense, the OD HTSC systems are fundamentally different from conventional BCS superconductors, where all the normal-state charge carriers participate in the superconducting condensate [3-5]. This picture is supported by the observation of percolative superconductivity in OD single crystals (LSCO, Tl-2201) [4]. In the 1-2-3 superconducting system, the large OD state cannot be reached with oxygen doping only. Usually, a heterovalent substitution is used for this purpose. Schmehl et al. [6] showed that Ca substitution on the Y position increases the carrier concentration in YBCO thin films up to x=0.3. Improvement of the grain-boundary transparency by Ca doping has been explained with Ca segregation and raising the carrier concentration in depleted inter-grain regions [7].

Recently, it has been shown that a small quantity of Ca (2-4%) increases the pinning in Y(Ca)BCO samples [7, 8]. As is known, Ca substitution creates oxygen vacancies, which are effective pinning centers [9]. Increasing the Ca concentration raises the number of oxygen vacancies [10] and pinning centers.

In this study, we investigate magnetic hysteresic loops of polycrystalline samples with different levels of overdoping, in order to find a correlation between the level of doping and pinning in the OD region.

2. Experimental details

A series of polycrystalline $Y_{1-x}Ca_xBa_2Cu_3O_z$ (x=0; 0.025; 0.05; 0.1 and 0.2) samples was prepared by a standard solid-state reaction method. One of the samples with x=0.2 was additionally oxygenated for 50 hours at 450˚C, in order to obtain a highly OD specimen. Samples were characterized by the XRD method with $Cu_{k\alpha}$ radiation. Magnetic measurements (hysteresis curves and

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ac magnetic susceptibility) were performed with a MagLab Oxford 7000 susceptometer. All investigated samples had rectangular shapes and very similar dimensions. The magnetic field was parallel to the longest dimension of the samples. The estimated demagnetization factor was small enough that the geometric effect could be neglected.

3. Results and discussion

According to XRD analysis, all investigated samples were single-phase, with an orthorhombic crystal structure. The limiting composition for single-phase $Y_{1-x}Ca_xBa_2Cu_3O_z$ material is about x=0.2 [11]. In this case, neutron diffraction data show that substitution on the Y site is only 0.16, but this is enough for heavily OD samples to be produced.

Using the correlation between the lattice parameters and oxygen content in the non-substituted 1-2-3 phase [12], we determined the oxygen content in the $YBa_2Cu_3O_z$ sample. The **z** value was found to be about 7.05 i.e. the sample was slightly OD, which was confirmed by the low T_{onset} of 91.4 K determined from ac susceptibility measurements. The unit cell lattice parameter **a** for substituted samples was stable and almost unchanged. The lattice parameter **b** decreased very slightly with increasing Ca content, supporting the assumption that the oxygen concentration in the chains is almost unchanged [13]. Thus the oxygen vacancies, which appear in substituted samples, are predominantly located in the Cu-O_2 planes, and can effectively keep the pancake vortices.

In Fig.1, the real part of the AC magnetic susceptibility as a function of temperature ($\chi_1{}'(T)$) is presented for all investigated samples. The $\chi_1{}'$ is normalized to the maximal value (χ'_{1max}) for the each specimen. The temperature at which the first non-zero diamagnetic signal appeared is accepted as T_{onset}. With increasing Ca concentration, T_{onset} decreases and intra- and inter-granular transitions are shifted to the lower temperatures. This is an indication of the overdoping of the samples. In underdoped samples, the critical temperature increases with Ca, as shown in [14]. In order to verify the overdoping of Ca substituted samples, we additionally oxygenated the $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_z$-(a) sample for 50 hours at 450˚C. It was established that $T_{c\text{-}midpoint}$ of the obtained $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_z$-(b) sample decreases by approximately 10 K, which confirms the overdoping of the initial sample (a).

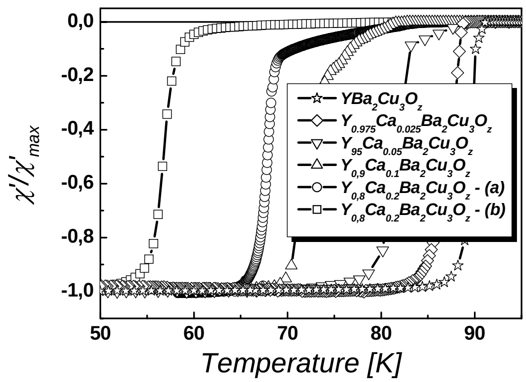

Fig. 1. Temperature dependence of the normalized real part of the fundamental AC magnetic susceptibility for all investigated samples at H_{ac}=1 Oe and f=1000 Hz. The maximum $\chi_1{}'$ value for the corresponding sample is taken for normalization.

The carrier concentration, p, in the Cu-O_2 planes was evaluated by the empirical dependence $T_c/T_{cmax}=1-82.6(p-0.16)^2$ [11]. T_{cmax} for the non- substituted sample was accepted to be 93.5 K.

Assuming the critical temperature suppression with 0.4 K per at. % Ca substitution, we estimate T_{cmax} values for the substituted samples. The T_{cmax} value for x=0.2 was determined to be 85.5 K, which matches well the experimentally found value of 85 K [15]. Sample $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_z$-(b) had the highest carrier concentration, p=0.186, being the most OD. $Y_{0.95}Ca_{0.05}Ba_2Cu_3O_z$ had the smallest carrier concentration, p=0.172, but was also OD. The other samples had p valued between these two limits.

In Fig. 2, the M(H) dependencies are presented at 4.2 K, for all investigated samples. According to the Bean critical state model, the intra-granular critical current at a given field (H) can be determined from the width of the hysteresis curve $J_c=15\Delta M/d$, where $\Delta M = M^+ - M^-$ is the difference of the magnetic moments between the ascending and descending field branches of the hysteresis loop in emu/cm^3, and d is the average grain size within the ceramic samples, in cm. The critical current of two samples with similar ΔM will be determined from d. Thus, the finer grain structure of the Ca substituted samples will result in a higher J_c (samples $Y_{1-x}Ca_xBa_2Cu_3O_z$ with x=0; 0.05 in Fig. 2).

The magnetization is defined as $M=B/\mu_0-H$, where H is the external magnetic field and B is the average magnetic induction in the bulk supercon-ductor. For $H<H_{c1}$ (H_{c1} – lower critical field), the superconducting surface current expels the magnetic field from the sample's volume (the Meissner state) and a linear relation M(H) holds for a cylindrical sample. The magnetization continues to grow to its maximum value at the field H_p (penetration field), where the flux front reaches the center of the sample. M(H) could deviate slightly from the straight line of perfect diamagnetism, as a result of surface

effects. Thus for any superconductor, a penetration peak appears in the first magnetization curve. When the field decreases from a high value (from both the positive and negative sides) a large magnetization peak appears near the zero field, due to the establishment of a large superconducting current. This huge central peak envelops the penetration peak. For a percolative superconducting system, due to the difficulty of establishing a high current density near the zero field, the penetration and the central peak may disappear. For fields $H \geq H_p$, the Bean model predicts a constant magnetization $M = -H_p/2$. In fact, the magnetization decreases, which reflects the reduction of the critical current density with increasing applied field. When the external field starts to decrease, the gradient of the local field near to the sample edge changes its sign, but has the same absolute value as before. The magnetization becomes positive in the case where there is a magnetic field trapped in the superconductor by the pinning centers.

From, Fig. 2, several important facts can be seen. Sample $Y_{0.975}Ca_{0.025}Ba_2Cu_3O_z$ has the largest M(H) curve and the highest trapped magnetic field, as a result of the strongest pinning (A). A linear M(H) dependence with a constant

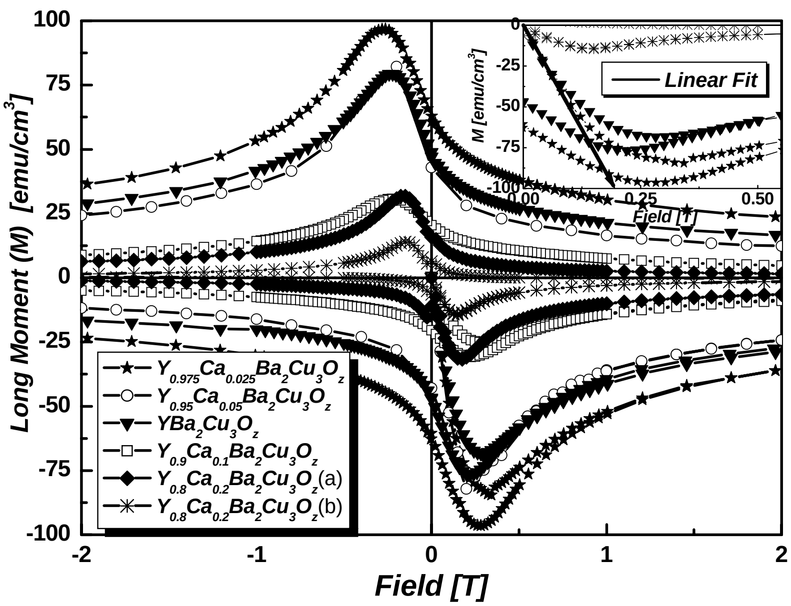

Fig. 2. Magnetization hysteresis loops for all investigated samples at 4.2 K. The inset shows the deviation from the linear fit, (which determines the H_{c1} in the case where the surface barrier is ignored). For the $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_z$-(b) sample, the flux penetration starts immediately after the field is increased from zero.

slope is observed for substituted specimens with low Ca content, and for non-substituted ones as well ($Y_{1-x}Ca_xBa_2Cu_3O_z$ with x=0; 0.025 and 0.05) (B). For the highly OD samples $Y_{1-x}Ca_xBa_2Cu_3O_z$- (x=0.1; 0.2), the common linear slope is absent, indicating that H_{c1} is almost zero (C). For $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_z$-(b), the penetrating peak is the smallest and the magnetization becomes zero when the external field is reduced, changing its sign (D). Finally, the penetration peak coincides with the central peak, as seen in the inset (E). The last of these facts suggests that the smallest critical current density in the $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_z$-(b) sample is due to the percolative superconductivity. Probably, superconducting islands are formed in the sea of fermions. In HTSC, due to the short coherent length, the energy cost for creation of phase boundaries is small, and facilitates phase separation [3]. In case of slight overdoping, the non-superconducting regions are small and their dimensions probably are comparable with the coherent length ξ. As a result, a broad M(H) curve is observed due to the effective pinning. When the doping considerably exceeds the optimal concentration, the volume of non-superconducting regions increases. They are not able to pin the flux vortices any more, and the critical current is significantly suppressed. In fact, the critical current is a parameter highly dependent upon the material processing. However, the experimental results show that the quality of the superconducting condensate is strongly influenced by the level of overdoping.

In order to exclude the magnetic field influence in the M(H) measurements, we performed the $\chi(T)$ measurements presented in Fig. 3. Two pieces from the same sample, one from the surface and the other from the volume, were investigated at a small ac field amplitude (1 Oe).

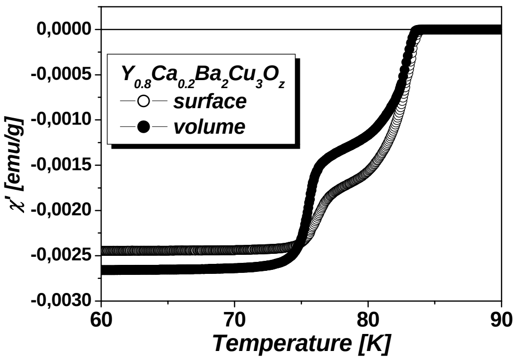

Fig. 3. Temperature dependence of the AC magnetic susceptibility for surface and volume samples at H_{ac}=1 Oe and f=1000 Hz.

The absolute value of $\chi_1{}'$ at the measured lowest temperature 4.2 K was smaller for the sample taken from the surface, despite the higher oxygen content in it. This fact also suggests a decrease in the superconducting volume fraction in the sample with the higher hole concentration, as a result of the presence of non-paired carriers.

In conclusion, we demonstrate that in OD polycrystalline samples, the $Y_{1-x}Ca_xBa_2Cu_3O_z$ critical temperature, T_c and critical current, $J_c(H)$ decrease with increasing carrier concentration p. This is explained by the appearance of percolative superconductivity in heavily OD specimens. Increasing the level of overdoping enlarges the non-superconducting regions, and they cease being effective as pinning centers. The highest critical current is achieved for the substituted sample with a small Ca content. In this case, the non-superconducting regions should be small enough to be strong pinning centers.

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