PROXIMITY EFFECT IN BULK $LaBa_2Cu_3O_{7-y}$
SAMPLES WITH $Ag$ ADDITIONS

E. Nazarova, A. Zahariev, A. Angelow, K. Nenkov
Institute of Solid State Physics, 72 Trackia Blvd., 1784 Sofia, BG
March 21, 2022

Abstract

Bulk $LaBa_2Cu_3O_{(7-y)}$ samples with different $Ag$ additions were investigated. It was shown that $Ag$ does not enter the crystallographic structure of the superconductor and segregates on the grain boundary region. Current path in these samples occurs through the proximity connected grains and this was confirmed from the temperature dependence of the critical current density and mutual inductance. By using the theory developed for the thin film structures we conclude that growing of the $Ag$ content increased the effective cross section and the normal metal thickness. The first one prevails at low concentration increasing the current. The second dominates at higher concentration leading to saturation or even lowering of the critical current.

1 Introduction

Thin film structures prepared from low and high temperature superconducting (HTSC) materials, based on the proximity effect, were widely discussed in literature [1], [2],[3],[4]. Is it possible a proximity coupling to occur between the grains through normal metal inclusions in bulk HTSC samples? It is difficult to answer to this question having in mind low value and high anisotropy of coherence length ($\xi$) in HTSC. Nevertheless there were found some indications for the existence of the proximity effect in bulk samples [4],[3],[7]. The more frequently used experiments proving the existence of proximity junction like I-V and $dI/dV$ curves, temperature dependence of normal layer coherence length ($\xi_n$) or exponential decay of $I_c$ with increasing of the normal layer thickness, $L$, are not applicable to the case of bulk samples. The aim of this work is to indicate that the critical current in bulk samples with normal metal inclusions can be governed by the proximity effect. This is very important from practical point of view because similar conditions can exist in Ag-sheathed tapes and wires.
2 Experimental

The investigated samples were prepared by the solid state reaction method described in detail previously \[8\]. Five samples with different Ag additions (2 wt%, 5 wt%, 10 wt%, 15 wt% and 20 wt%) and one without Ag additions were examined. The specimens were characterized by X-ray diffraction analysis using DRON 4M powder diffractometer with Cu \( \alpha \) radiation and Scanning Electron Microscope Philips 515 with EDX analysis. Temperature dependence of critical current at zero magnetic field was measured in a specially designed device. The necessary temperature was maintained by thermoregulator within ±0.15 K with an accuracy of ±0.01 K. The appearance of 10\( \mu \)V/cm voltage is accepted as a critical current criterion. The ”screening” method (according to \[9\]) was used for the mutual inductance determination.

3 Results and discussions

\( \text{LaBa}_2\text{Cu}_3\text{O}_{7-y} \) samples with starting composition 1:2:3 usually contain a small amount of \( \text{BaCuO}_2 \) impurity phase \[10\], \[11\]. X-ray diffraction analysis of our undoped samples also detected the presence of \( \text{BaCuO}_2 \). The impurity phase is not observed for the Ag doped samples. A very small shift (less than 0.05 degree) of the main orthorhombic peaks was observed for the Ag doped samples. This shift corresponds to the change of ”c” lattice parameter from 11.8329 A for undoped sample to 11.8256 A for 20 wt% Ag doped sample. Such deviation, however, cannot be due to Ag incorporation in 1:2:3 unit cell because it is shortening and very small. Ag is melted during the process of sample synthesis and incorporates significant amount of oxygen. It is more reasonable to think that the inclusion of this oxygen in 1:2:3 phase is able to produce the observed reduction in ”c” lattice parameter.

SEM investigations also support the Ag segregation. EDX analysis in the superconducting grains shows nominal compositions close to 1:2:3 stoichiometry and no Ag within detectable limits has been found. Ag additions are statistically uniformly distributed through the specimen between the grains.

Therefore we assume that Ag inclusions do not enter the crystallographic structure of \( \text{LaBa}_2\text{Cu}_3\text{O}_{7-y} \). During the synthesis process Ag moves out of growing grains and segregates on the grain boundary regions. Similar results were observed for the Ag doped \( \text{YBCO} \) samples \[12\], \[13\] and \( \text{Bi} – 2223 \) phase \[14\].

For doped and undoped samples different grain boundary conditions exist. The variations of the grain boundary content significantly influences the critical current of the samples. Grain boundaries of undoped samples mainly contain the insulating impurity phase. It is reasonable to expect that current path occurs through the superconductor – insulator – superconductor (S-I-S) system. In doped samples, with the increasing of the Ag content, the current flows predominantly through the Ag coupled grains. These samples can be considered as a superconductor – normal metal – superconductor (S-N-S) system on the level of individual grains. In case of individual junction the \( I_c(T) \) dependence over temperature range below \( T_c \) provides a clear inside into the nature of the junction. This
dependence can be used to distinguish $S-N-S$ devices from other junction types.

In our samples we have normal metal barriers with different thickness and electron mean free path is not limited from the thickness of the normal interlayer as in the thin film structures. The average dimension of the Ag particles determined from the width of the Ag x-ray diffraction pick is of order of 30 nm for the sample with 20 wt%. The normal metal coherent length $\xi_n$ determines the mean size of the Cooper pair in the normal metal barier.

Assuming that the carrier mean free path $l_n$ in the normal metal is determined from the dimensions of the Ag particles both limits: ”clean” ($l_n > \xi_n$) and ”dirty” ($l_n < \xi_n$) will be present at nitrogen temperatures in our unusual for the proximity studies samples. But only $S-N-S$ junctions in ”dirty” limit will support the transport current facilitating the grains connection in the specimens. In fact normal metal thickness, $L$, has to be of order of $\xi_n$ for achieving a intergranular current close to intragranular one. By decreasing the temperature, $T$, normal metal coherence length will increase according to the relation [15]:

$$\xi_n = \left(\frac{h v_n l_n}{6 \pi k T} \right)^{\frac{1}{2}},$$  \hspace{1cm} (1)

where $v_n$ is the Fermi velocity of normal metal and $k$ is the Boltzman constant. At nitrogen temperatures $\xi_n$ will be about 15 nm and will increase up to 66 nm at 4 K for $l_n$ equal to the average partial size of Ag. Some of the $S-N-S$ transitions being in ”clean” limit at nitrogen temperature will turn to ”dirty” limit at lower temperatures. This will increase to some extent the number of $S-N-S$ connections able to support high intergranular current.

The systematic theoretical investigation of the behavior of $S-N-S$ thin film structures was carried out first by De Gennes[16]. An expression has been derived for $I_c$ as a function of temperature $T$ and $L$:

$$I_c(T, L) = \frac{\pi A |\Delta_i|^2 L}{2 e R_n k T \xi_n} \exp \left( -\frac{L}{\xi_n} \right),$$  \hspace{1cm} (2)

where $\Delta_i$ is the superconducting gap of the normal interlayer interface, $A$ is the cross section of the individual $S-N-S$ transition, $R_n$ is the normal layer resistance, $T_c$ is the superconductor transition temperature and $e$ is the electron charge. Eq. (2) was derived using dirty limit ($l_n < \xi_n$) boundary conditions.

Following Delin at all [15] for an $S-N-S$ structure prepared from a high $-T_c$ superconductor and a noble metal as interlayer, $\Delta_i^2$ will have the form:

$$\Delta_i^2 = \Delta^2 \frac{2}{\pi^2 \gamma^2} \frac{T_c - T}{T},$$  \hspace{1cm} (3)

where $\Delta$ is the superconductor energy gap far from the interface region and $\gamma$ is the so called interface parameter. The value of $\gamma$ is given by the ratio

$$\gamma = \left( \frac{N_n \rho_s}{N_s \rho_n} \right)^{\frac{1}{2}},$$  \hspace{1cm} (4)
where $N_n$ and $N_s$ are the normal metal and superconductor density of states, respectively, and $\rho_n$ and $\rho_s$ are their resistivities, respectively. For high – $T_c$ superconductor – noble metal (Ag) junction $N_n \gg N_s$ ($N_n = 5.85.10^{28}m^{-3}$ and for YBCO $N_s = 5.0.10^{27}m^{-3}$) and $\rho_n \ll \rho_s$ ($\rho_n \approx 0.0084.10^{-6}\Omega.m$ and for YBCO $\rho_s = 0.77.10^{-6}\Omega.m$ at 77K) therefore $\gamma \gg 1$ ($\gamma \approx 1078$).

Substituting Eq.(4) and Eq.(3) in Eq.(2) and assuming a BCS temperature dependence of the energy gap $\Delta(T)$ in the HTSC material:

$$\Delta(T) \approx 3.2 \kappa T_c \left(1 - \frac{T}{T_c}\right)^{\frac{1}{2}},$$

an useful expression for $I_c(T, L)$ is obtained:

$$I_c(T, L) = \frac{(3.2)^2 \sqrt{6k^\frac{3}{2}AT^\frac{1}{2}}(T_c - T)^2}{e\rho_n\gamma^2(\pi\hbar\upsilon_n l_n)^\frac{1}{2}} \exp \left[-L \left(\frac{6\pi kT}{\hbar\upsilon_n l_n}\right)^{\frac{1}{2}}\right].$$

Eq.(3) present the temperature dependence of the critical current across the $S - N - S$ structure. We will use this equation to explain our experimental results. Dividing both sides of Eq.(3) by the sample cross section, in the left side we obtain the critical current density through the sample. It is seen that temperature dependence of the critical current density is following:

$$J_c(T) \propto (T_c - T)^2 \exp(-T^\frac{1}{2}).$$

The term $(T_c - T)^2$ will dominate this dependence because the exponential and $T^\frac{1}{2}$ terms have a weak influence. This is shown in the Fig.1. It present $J_c(T)$ experimental dependencies for the Ag doped samples. The experimental data for sample with 20 wt% Ag are fitted twice: fit 1 - by the $(T_c - T)^2$ term only, and fit 2 - by the temperature dependence according to (4). Both fits show very close results which give us reason to use the simple one ignoring in fact $\xi_n(T)$. It was found also that the quadratic fit (straight lines) gives the least mean square deviation from the data for 5 to 20 wt% Ag doped samples, when the fits of type $(T_c - T)^n$ with $n \leq 2$ were examined.

For the sample with 2 wt% Ag experimental results can be fitted better with linear temperature dependence. The quadratic fit is also possible. At this concentration it is difficult to create the current path entirely through the Ag connected grains. More frequently the connection occurs through the insulating phase and this dependence resembles $J_c$ vs. $(T_c - T)$ for undoped samples. For the comparison, on the Fig.2 $J_c$ vs. $(T_c - T)$ is presented for undoped sample. The line gives the best linear fit to the data. The temperature dependence of current across the $S - I - S$ Josephson junction is described by the Ambegaokar - Baratoff dependence [14]. For values $T < T_c$ but close to $T_c$ a linear temperature dependence occurs. By lowering the temperature the current reaches the saturation. In fact Ag additions change the mechanism of current flow on the basis of the proximity effect and its value increased.

In the Fig.3 $\sqrt{J_c}$ vs. $(T_c - T)$ plots are shown for Ag doped samples. It is seen that with increasing of the Ag content the slopes of the lines increase and a tendency to a saturation can be noticed too. According to Eq.(3) $A$ and $L$ quantities can be influenced by the Ag amount. For our samples $A$ has a meaning of an effective cross section. With increasing
of the Ag amount both quantities A and L could increase too. At small Ag concentrations the first one prevails raising the value of critical current density in the sample. At higher concentration A goes to a saturation and L increasing begins to dominate, lowering the probability for the proximity connection between the grains. This leads first to a saturation and then to a current decreasing when \( L > (2 - 3)\xi_n \). This can serve as a basis of explanation of the observed saturation tendency in our case and the lowering of the critical current density reported by some authors [7], [12], [18] when the Ag additions come nearer to some critical concentration. This concentration is technologically dependent.

In the Fig.4 normalized mutual inductance is presented as a function of temperature for the non doped sample and sample with 20 wt% Ag additions. It is seen that in wide temperature interval below \( T_c \) the sample with Ag has a lower mutual inductance than non doped. As the mutual inductance is proportional to the density of superconducting electrons, \( n_s \) [9], it is lowered in the sample with Ag due to the lowering of \( n_s \) in normal metal inclusions. Ag particles with different thickness L exist in the sample. By lowering the temperature below \( T_c \), they will be able to connect superconducting grains when their thickness L becomes of order of \( \xi_n \) according to Eq.(1).

These investigations are important from the point of view of practical applications of HTSC materials in wires and tapes. For example the "powder in tube" method, which is widely used for tapes preparation, ensure the existence of HTSC materials/silver interface. During the heat treatment process of the tape preparation, Ag diffusion between the superconducting grains on the interface region is possible. Investigations of transport current distributions in Ag sheathed Bi – 2223 based tapes showed that high current densities are observed in a thin layer ((2 – 3)\( \mu \)m width) located close to the silver, which is roughly 10 - 15 % of the total superconducting area [19]. Therefore, when the preparation technology ensures the formation of Ag particles with dimensions of order of \( \xi_n \), the current path through the specimens will be determined by the proximity effect. Grain boundaries containing normal metal with various thickness can exist in doped samples. The current path, however, will be through the boundaries with the thickness of order of \( \xi_n \).

In conclusion we investigate bulk 1:2:3 HTSC material with normal metal (Ag) inclusions with an average dimension of order of \( \xi_n \). It was shown that the current path in these samples is based on the proximity coupling between the grains. We establish that \( J_c(T) \) dependence below \( T_c \) is quadratic which is typical for \( S - N - S \) structures. Mutual inductance measurements also support this type of intergranular current. By using the theory developed for thin film structures we analyze the experimental results for the samples with different Ag amount. When the Ag additions increased the number of proximity coupled grains and normal metal thickness increased, too. If the first one dominates the critical current in the sample will increase, while the domination of the second leads to a saturation or current decreasing when \( L > (2 - 3)\xi_n \). The value of the current through connected in series \( S - N - S \) transitions is limited by the grains with the smallest cross section, A, and the largest thickness, L.
4 Acknowledgment

The authors are grateful to Dr. Ram Kossowsky supporting the presentation of the work at the NATO ARW.

This work was partly supported by the National Foundation "Scientific Research" under Grant 421.

References

[1] R. Simon and P. M. Chaikin, Phys. Rev. B, 23 (9) (1981) 4463.
[2] M. A. M. Gijs, D. Scholten, Th van Rooy and A. M. Gerrits Phys. Rev. B, 41 (16), (1990) 11627.
[3] G. Deutscher, R. W. Simon, J. Appl. Phys., 69 (7), (1991) 4137.
[4] H. Z. Durusoy, D. Lew, L. Lombardo, A. Kapitulnik, T. H. Geball, M. R. Beasley, Physica C 226, N3-4 (1996) 253.
[5] G. Lubberts, J. Appl. Phys., 68 (2), (1990) 688.
[6] R. Pinto, P. R. Apte and S. P. Pai, Physica C 207 (1993) 13.
[7] J. Jung, M. A-K Mohamed and J. P. Franck, Supercond. Sci Technol., 4 (1991) S217.
[8] E. Nazarova, M. Kostova, A. Zahariev and I. Iordanov, Cond. Matt. and Mater. Comm., 2 (1995) 31.
[9] J. H. Claassen, Magnetic Susceptibility of Superconductors and Other Spin Systems, ed. by R. A. Hein et al., Plenum Press, NY, 1991 pp 405-422.
[10] T. Wada, N. Susuki, A. Maeda, T. Yabe, K. Uchinokura, S. Uchida, S. Tanaka, Phys. Rev. B, 39 (1989) 9126.
[11] Y. Song, J. Golben, S. Chittipedi and R. Gaines, Phys. Rev. B, 28 (1988) 4605.
[12] J. P. Singh, H. J. Leu, R. B. Poeppel, E. Van Voortees, G. T. Goudey, K. Winsley, Donglu Shi, J. Appl. Phys., 66 (1989) 3154.
[13] J. J. Lin, T. M. Chen, Y. D. Yao, J. W. Chen, Y. S. Gou, Jap. J. Appl. Phys., 29 (1990) 497.
[14] K. Kawasaki, H. Ikeda, R. Yoshizaki and K. Yoshikawa, ICMC Conf., Kitakyshu, May 21-24, 1996.
[15] K. A. Delin, A. W. Kleinsasser, Supercond. Sci. Technol., v.9, N4 (1996) 227.
[16] P. G. De Gennes, Rev. of Mod. Phys. 36 (1964) 225.
[17] V. Ambegaokar, A. Baratoff, Phys. Rev. Lett., 10 (1963) 486.
[18] M. Itoh, H. Ishigaki, T. Ohyama, T. Minemoto, H. Nojiri, M. Motokawa, J. Mater. Res., 6, N11 (1991) 2272.

[19] U. Welp, D. O. Gunter, G. W. Crabtree, W. Shong, U. Balachandran, P. Haldar, R. S. Sokolowski, V. K. Vlasko-Vlasov, V. I. Nikitenko, Nature, 376 (1995) 44.
Fig. 1. The temperature dependence of critical current density for Ag doped samples.
Fig. 2. $J_c$ vs. $(T_c - T)$ for undoped sample. The line shows the best linear fit.
Fig. 3. $J_c^{1/2}$ vs. $(T_c - T)$ for Ag doped samples.
Fig. 4. Normalized mutual inductance versus temperature for the indicated samples.