

Effects of hole doping and chemical pressure on the average superconducting kinetic energy of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals

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Abstract. We reported on $M_{ZFC}(T)$ and $M_{FCC}(T)$ reversible dc magnetizations of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{Y}_{0.99}\text{Ca}_{0.01}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{YBa}_{1.75}\text{Sr}_{0.25}\text{Cu}_3\text{O}_{7-\delta}$ single crystals with a strong focus on the effects of Ca and Sr doping on the average superconducting kinetic energy density, $k(T)$ of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The $k(T)$ is used as a relevant tool to provide physical information about the HTSC pairing mechanism. The determination of the $k(T)$ from $M_{ZFC}(T)$ and $M_{FCC}(T)$ data is supported by virial theorem of superconductivity [$k(T) = -\mathbf{M}\cdot\mathbf{B}$]. The $M_{ZFC}(T)$ and $M_{FCC}(T)$ measurements were performed with a SQUID magnetometer to $H \leq 50\text{kOe}$ applied parallel to the c axis of the samples. The results show that the samples present a common $k(T)$ behavior that is characterized by a maximum value for $T \ll T_c$ that gradually decreases as the temperature rises towards to the T_c , becoming null to $T \leq T_c$. The magnetic field affects smoothly the $k(T)$ data behavior. The $k(T)$ results contrasting of our samples shows that the Ca and Sr doping promotes a reduction of its amplitude. A possible explanation to this feature could be associated to the fact that the hole doping character promoted by Ca doping and the chemical pressure effect motivated by Sr doping affects considerably the superconducting pairing mechanism of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

1. Introduction

According to the BCS theory the superconductor electronic state gets kinetic energy during the condensation of Cooper pairs [1-4]. Infrared experiments performed in high temperature superconductors (HTSC) detects a large spectral amount transferred to the HTSC superfluid condensate, supportive of a kinetic energy driven mechanism [1-4]. The average kinetic energy density, $k(T,B)$ can be obtained from zero field cooled, $M_{ZFC}(T)$ and field cooled cooling, $M_{FCC}(T)$ dc magnetizations measurements through the application of the virial theorem of superconductivity (VTS) given by [1-4].



$$k(T, B) = \left\langle \frac{\hbar^2}{2m} \left| \left(\nabla - \frac{2\pi}{\Phi_0} A \right) \psi \right|^2 \right\rangle = -\vec{M} \cdot \vec{B} \quad (1)$$

In the equation 1 the symbol $\langle \dots \rangle$ represents the spatial average, \hbar^2 , $2m$ and Φ_0 are phenomenological constants, ψ is the superconductor order parameter, M is the equilibrium magnetization and B is the vector magnetic field induction.

The $k(T)$ study can be applied as a relevant tool to get some relevant physical information about superconductor order parameter behaviour on the superconducting-normal transition [1-4]. In particular the VTS equation was applied to determination of the $k(T, B)$ behaviour of the some low and high temperatures superconductors. For instance, the $k(T)$ behaviour reported to Pb-In alloys [1] and Nb [2] samples for $T \leq T_c$ are in agreement to the Abrikosov treatment of the Ginsburg-Landau theory and to the general BCS theory predictions. Otherwise the identification of the $k(T, B) > 0$ for $T > T_c$ have been reported for underdoped $\text{YBa}_2\text{Cu}_3\text{O}_x$ [2] and optimally doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [2] single crystals as well as a $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ sample[3]. The authors of these studies elect the pseudogap effect as responsible for this behaviour eliminating the thermal fluctuations as an alternative explanation. In a recent study performed with $\text{Sm}_2\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramic samples [5] the microstructural aspects of the samples (granularity) were associated to the $k(T, B)$ behaviour.

An alternative manner of modify the superconducting state of a superconductor material is to promote the partial chemical substitution at its structure. The hole doping character or the chemical pressure mechanism promoted respectively by partial substitutions of Y for Ca and of Ba for Sr in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ structure are potential examples of the last predictions [6-8]. The Ca doping solubility limit at Y site is almost 15% as the Sr doping solubility limit at the Ba site is almost 50% [7-8]. The Ca (+2) and Y (+3) atoms have diferent valences which justify the hole doping character introduced by this particular doping. In contrast, the Sr atom radius is smaller than the Ba atom radius which supports the chemical pressure effects on the superconducting state of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [7-8].

Motivated by the last questions about the $k(T, B)$ behaviour we decided to plan a dc magnetization experimental study in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{Y}_{0.99}\text{Ca}_{0.01}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{YBa}_{1.75}\text{Sr}_{0.25}\text{Cu}_3\text{O}_{7-\delta}$ single crystals focusing on the effects of Ca and Sr chemical doping on the $k(T, B)$ behaviour.

2. Sample preparation and experimental procedures

The single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO), $\text{Y}_{0.99}\text{Ca}_{0.01}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ [Y(Ca)BCO] and $\text{YBa}_{1.75}\text{Sr}_{0.25}\text{Cu}_3\text{O}_{7-\delta}$ [YB(Sr)CO] were grown by self-flux method [6-8]. The selected single crystals were submitted to an extra oxygen process to improve their superconducting temperature transition, T_c [6-8]. The picked samples had their structure and superconducting transition characterized respectively by x-ray diffraction (XRD) and zero field cooled DC magnetization, $M_{\text{ZFC}}(T)$ [6-8]. The figure 1 displays their XRD results.

It is possible identify the characteristic YBCO-123 orthorhombic crystalline structure along their c crystallographic axis. The c lattice parameters obtained from the XRD analysis to the samples were $c = (11.65 \pm 0.01)\text{\AA}$ to the YBCO, $c = (11.65 \pm 0.01)\text{\AA}$ to the Y(Ca)BCO and $c = (11.58 \pm 0.01)\text{\AA}$ to the YB(Sr)CO. The estimation of the superconducting transition of the samples through of $M_{\text{ZFC}}(T)$ measurements to $H = 10\text{Oe}$ applied parallel to the c axis of the single crystals resulted in the following T_c values $(93.4 \pm 0.2)\text{K}$ to the YBCO, $(91.8 \pm 0.2)\text{K}$ to the Y(Ca)BCO and $(87.9 \pm 0.1)\text{K}$ to the YB(Sr)CO. The results presented to the c crystallographic axis and superconducting transition of the samples are in agreement with those reported by literature [6-8]

The isofield dc magnetization measurements were performed with a quantum design SQUID magnetometer. The usual zero field cooled, $M_{\text{ZFC}}(T)$ and field cooled cooling, $M_{\text{FC}}(T)$ dc magnetizations were recorded while dc magnetic fields up to 50kOe were applied parallel to c axis of samples ($H // c$).

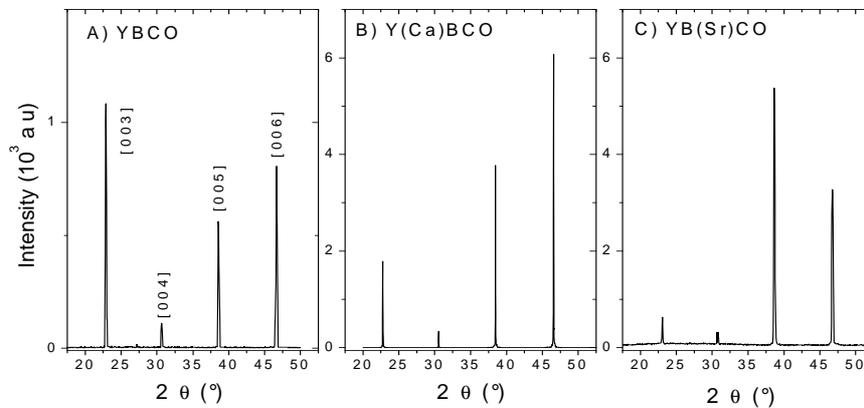


Figure 1. The XRD of the A)YBCO, B) Y(Ca)BCO and C) YB(Sr)CO samples obtained for monochromated $CuK\alpha$ radiation oriented to their c axis.

The magnetization measurement procedure consisted in first cooling down the sample to temperatures well below T_c in zero field (ZFC). Then the zero field cooled magnetization, $M_{ZFC}(T)$ was measured under constant magnetic field while slowly warming the sample (0.4 K/min or less) up to temperatures well above T_c . Subsequently the field cooled cooling magnetization, $M_{FCC}(T)$ was measured while cooling (0.4 K/min or less) the sample back to low temperatures in the same field (FCC) [6-8].

The samples size was determined with a SEM inset of a FIB, JIB 4SOU model from JEOL Company. The possible demagnetization factor contribution to the $M(T)$ data was checked. The geometrical factors were estimated on the basis of the calculation in reference [9] and the paramagnetic signal contribution of sample holder was measured to all the applied dc magnetic fields and its magnetic contribution was subtracted from $M_{ZFC}(T)$ and $M_{FCC}(T)$ data.

3. Results and discussion

The figure 2 displays a representative result of the $\Delta M(T)$ data to the Y(Ca)BCO sample while a $H = 10\text{kOe}$ is applied parallel to c axis of the sample. The $T_{irr}(H)$ temperature is put in evidence. Otherwise its insets highlight the correspondently $M_{ZFC}(T)$ and $M_{FCC}(T)$ dc magnetizations results when the $T_c(H)$ and $T_{irr}(H)$ temperatures are indicated.

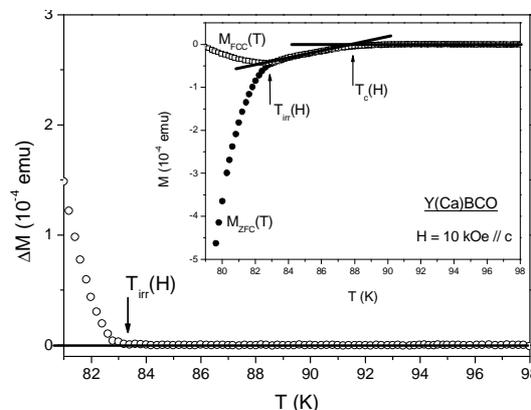


Figure 2. The determination of $T_{irr}(H)$ and $T_c(H)$ temperatures from the $M_{ZFC}(T)$ and $M_{FCC}(T)$ dc magnetizations (inset) when the $H = 10\text{kOe}$ is applied parallel to the c axis of the Y(Ca)BCO sample.

In the figure 2 the $T_{irr}(H)$ is the temperature which leaves the zero base line of the $\Delta M(T)$ plot [$\Delta M(T) = M_{FCC}(T) - M_{ZFC}(T)$]. The $T_c(H)$ is determined by the intersection between the linearly extrapolated $M_{ZFC}(T)$ and $M_{FCC}(T)$ dc magnetizations in the normal and superconducting phases, as illustrated by the inset of figure 2.

The $T_{irr}(H)$ defines the limit below which pinning effects become important. We carried out our analyses in the temperature regime above $T_{irr}(H)$ in which the experimental data describe the equilibrium magnetization with no ambiguity [1-5].

We assume that GL theory describes the equilibrium magnetization adequately in most of the reversible superconducting regimes of our samples [5]. Then using the VTS [1-5] we plot in figures 3A and 3B the $k(T,B)$ versus (TT_c^{-1}) for YBCO, Y(Ca)BCO and YB(Sr)CO samples where the normalized $T_c(H)$ is indicated by arrows in the plots. In particular the figure 3A shows the $k(T,B)$ results to $0.1T \leq H \leq 1T$ as well as figure 3B to $1T \leq H \leq 5T$.

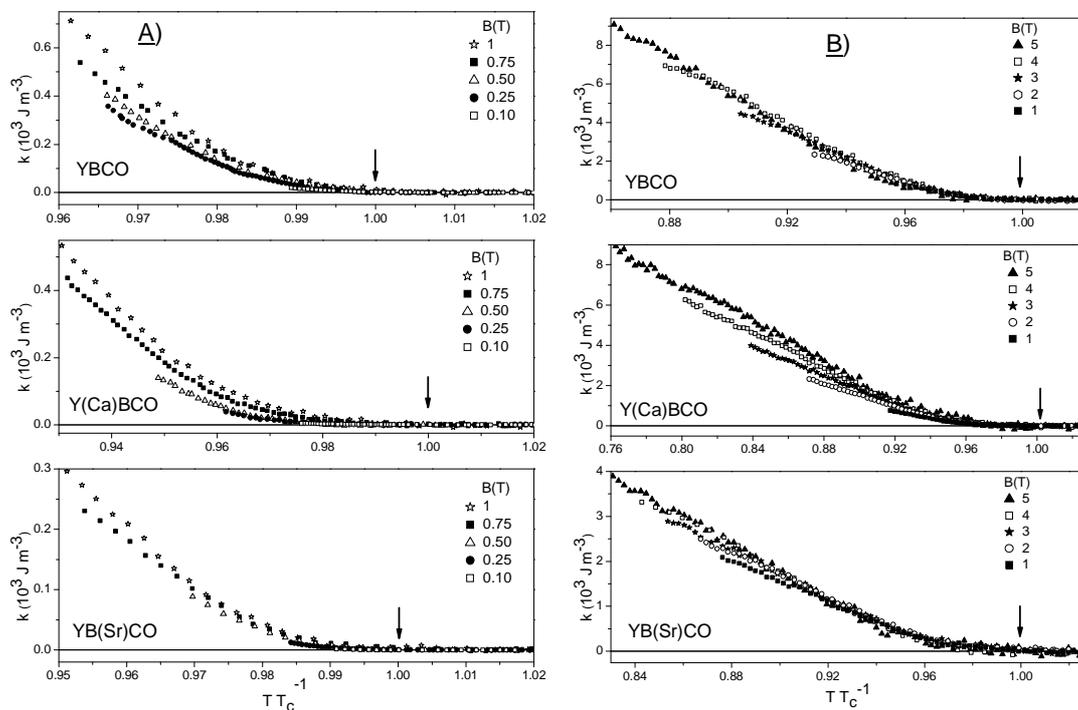


Figure 3. The $k(T,B)$ behavior for YBCO, Y(Ca)BCO and YB(Sr)CO samples to $0.1T \leq H \leq 5T$.

The results showed in the figure 3 are not on the same range because the reversible magnetization regime is sample dependent and according to the VTS in the light of Abrikosov theory the $k(T,B)$ data is evaluated to all the reversible magnetization regime. The results show that the samples presents a common $k(T,B)$ behavior that is characterized by a $k(T,B)$ maximum value for $T \ll T_c$ that gradually decreases as the temperature rises towards to the T_c , becoming null to $T \leq T_c$.

The magnetic field affects smoothly the $k(T,B)$ versus TT_c^{-1} profile of our single crystals as compared to the response observed for this quantity in microstructural modified $Sm_2Ba_2Cu_3O_{7-\delta}$ ceramic samples [5]. In particular, the figure 3 shows that the $k(T,B)$ profile of the doped single crystals is more affected by the magnetic field application then that displayed by the pure sample especially to $B \geq 1T$. This behavior is compatible to that observed to microstructural modified $Sm_2Ba_2Cu_3O_{7-\delta}$ ceramic samples where the $k(T,B)$ profile of the $Sm_2Ba_2Cu_3O_{7-\delta}$ sample with more microstructural defects is more affected by the applied magnetic field.

In contrast to the reported results that identify the $k(T,B) > 0$ for $T > T_c$ in underdoped $\text{YBa}_2\text{Cu}_3\text{O}_x$ [2] and optimally doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [2] single crystals as well as a $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$ sample [3] the results displayed in the figure 3 do not show a significant contribution of the $k(T,B)$ to $T \geq T_c$.

The contrasting between $k(T)$ results of the YBCO sample with those to Y(Ca)BCO and YB(Sr)CO samples at the same T/T_c^{-1} shows that the Ca and Sr doping promotes a reduction of its amplitude as well as produces the enlargement of the $k(T,B)$ temperature regime. These peculiarities are more pronounced to the YB(Sr)CO sample.

We realized a dc magnetization experimental study in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{Y}_{0.99}\text{Ca}_{0.01}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{YBa}_{1.75}\text{Sr}_{0.25}\text{Cu}_3\text{O}_{7-\delta}$ single crystals with a strong focus on the effects of Ca and Sr chemical doping on the $k(T,B)$ behaviour. The Sr and Ca doping does not change significantly the $k(T,B)$ versus TT_c^{-1} profile but strongly reduces the $k(T,B)$ intensity at the same time that collaborates to the enlargement of the $k(T,B)$ temperature regime. Otherwise we could not identify a $k(T,B)$ behavior that supports the pseudogap behavior. We conclude that the chemical pressure effects introduced by 12,5 % of Sr doping [6] were more nocive to the superconducting state of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystal than the 1% of Ca doping [8]. If we connect the lower T_c value of our doped single crystals to the suppression of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconducting state then it will be possible to suggest that the significant reduction of the $k(T,B)$ magnitude observed to the doped single crystals is associated to the proportional breaking of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconducting paring mechanism promoted more efficiently by 12,5% of Sr doping than 1% of Ca doping.

Acknowledgments

The authors would like to thanks to the PRONEM 03/2011 (under contract: 11/2042-7) scientific program for partially financing this work.

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