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

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Abstract. In this brief communication we applied the $M_{\text{ZFC}}(T)$ and $M_{\text{FCC}}(T)$ reversible dc magnetizations to get the average superconducting kinetic energy density, $k_S(T,B)$, of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{Y}_{0.95}\text{Ca}_{0.05}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{YBa}_{1.75}\text{Sr}_{0.25}\text{Cu}_3\text{O}_{7-\delta}$ ceramic samples with the aim of study the effects of Ca and Sr doping on the $k_S(T,B)$. The $M_{\text{ZFC}}(T)$ and $M_{\text{FCC}}(T)$ measurements were performed with a SQUID magnetometer from quantum design to dc magnetic fields up to 50kOe. The determination of the $k_S(T,B)$ from reversible dc magnetization is supported by virial theorem of superconductivity $[k_S(T,B) = -M_B]$. The $k_S(T,B)$ results show an common temperature profile for all the samples which is smoothly affected by the magnetic field. On the other hand the $k_S(T,B)$ results to $T \geq T_c$ could not be associated to the pseudogap phenomenon. The Ca doping affects more effectively the $k_S(T,B)$ behaviour then Sr doping. A possible explanation to this feature could be associated to the fact that the hole doping promoted by Ca doping depress more considerably the superconducting state and enhances the granular character of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor than the chemical pressure effect promoted by Sr doping.

1. Introduction
The average superconducting kinetic energy density, $k_S(T,B)$ study can be applied as a tool to get some relevant physical information about the amplitude behaviour of superconductor order parameter, $\psi(r,T)$ which is consider a physical quantity of first importance to understand the nature of the superconducting state of HTSC. [1-4].

In particular, at the literature is possible to select some experimental works which acquire the $k_S(T,B)$ from the zero field cooled, $M_{\text{ZFC}}(T)$ and field cooled cooling, $M_{\text{FCC}}(T)$ reversible dc magnetizations through the use of the virial theorem of superconductivity (VTS) [2,5,6]. The VTS was theoretically developed by Doria and collaborators to a large $k$ superconductor by rewriting the classical virial theorem at the light of Ginzburg-Landau (G-L) theory [1-6].

According to the VST the connection between $k_S(T,B)$ and isothermal reversible magnetization is given by the following equation [1-4]:

\[ k_S(T,B) = -M_B \]
\begin{equation}
    k_s(T, B) = \frac{\hbar^2}{2m} \left( \nabla \frac{2\pi}{\Phi_0} A \right)^2 = |M| B
\end{equation}

In the equation (1) the symbol \( \langle \ldots \rangle \) represents the spatial average, \( M \) is the equilibrium magnetization, \( B \) is the magnetic field induction and \( \hbar^2, 2m \) and \( \Phi_0 \) are phenomenological constants.

The \( k_s(T, B) \) data, obtained from VST, of a type II superconductor enlarges the application of its reversible magnetization to the comprehension of the superconductor state. For instance, the study of in-field \( k_s(T, B) \) in conventional and HTSC type II superconductors is used to check the agreement of the expectations derived from the Abrikosov treatment of the G-L theory with \( k_s(T, B) \) experimental results as well as the general BCS predictions [2,4,6]. On the other hand the investigation of the \( k_s(T, B) \) data behaviour at the light of Abrikosov and London theories is successful applied to get a satisfactory estimation of superconductor fundamental quantities like the Ginzburg-Landau parameter, \( k \), the penetration length, \( \lambda(0) \) and the upper critical field, \( B_{c2}(T) \) [1,5,6].

A recent dc magnetization experimental study performed with SmBa\(_2\)Cu\(_3\)O\(_7\)-\(\delta\) ceramic samples showing different microstructural aspects reveals that the \( k_s(T, B) \) behaviour was strongly affected by distinct granular character of these samples [5]. On the other hand, in underdoped YBa\(_2\)Cu\(_3\)O\(_7\)-\(\delta\) single crystals [2] the pseudogap phenomenon is correlated to the observation of \( k_s(T, B) > 0 \) to \( T \geq T_c \). However at the literature there is not consensus about it [2,5,6].

An alternative way of modify the granular character of structure and the physical characteristics of superconducting-normal transition of HTSC materials is to promote partial chemical substitution in their structure [7-11]. In the case of YBa\(_2\)Cu\(_3\)O\(_7\)-\(\delta\), the hole doping character and the chemical pressure mechanism promoted respectively by partial substitutions of Y for Ca and of Ba for Sr are potentials examples. [7-10].

Motivated by last specified questions we propose a dc magnetization experimental study where the Ca and Sr doping effects on the \( k_s(T, B) \) behaviour of YBa\(_2\)Cu\(_3\)O\(_7\)-\(\delta\), Y\(_{0.95}\)Ca\(_{0.05}\)Ba\(_2\)Cu\(_3\)O\(_7\)-\(\delta\) and YBa\(_{1.75}\)Sr\(_{0.25}\)Cu\(_3\)O\(_7\)-\(\delta\) ceramic samples will be evaluated through the application of VTS to \( M_{ZFC}(T) \) and \( M_{FCC}(T) \) reversible dc magnetizations, obtained to \( H \leq 50\text{kOe} \).

2. Samples characterization and experimental procedures

The YBa\(_2\)Cu\(_3\)O\(_7\)-\(\delta\) [YBCO], Y\(_{0.99}\)Ca\(_{0.09}\)Ba\(_2\)Cu\(_3\)O\(_7\)-\(\delta\) [Y(Ca)BCO] and YBa\(_{1.80}\)Sr\(_{0.20}\)Cu\(_3\)O\(_7\)-\(\delta\) [Y(BaSr)CO] ceramic samples were prepared from high purity Y\(_2\)O\(_3\), CaCO\(_3\), BaCO\(_3\), SrCO\(_3\) and CuO by solid state reaction [7,9,10]. After thoroughly mixing the powders in an agate mortar the first reaction was made by slowly heating to 950°C and stabilized there for 4h. The product was ground to fine powders and pressed to pellets of 1 cm in diameter and 1mm in thickness. It was sintered at 950°C during 8h in oxygen atmosphere then slowly cooled through 700°C and from 450°C to 250°C in 24h.

The samples had their structure and superconducting transition characterized by x-ray diffraction (XRD), electrical resistivity, \( \rho(T, H) \) and dc magnetization, \( M(T, H) \). The figure 1 displays the XRD results to the identified samples. The previous results confirm that the amount of Y and Ba partially substituted for Ca and Sr do not changed significantly the orthorhombic crystalline structure of YBa\(_2\)Cu\(_3\)O\(_7\)-\(\delta\). The lattice parameters values of samples are highlight in the figure. Their values are in agreement with those reported in the literature [7-10].

In particular, the same samples were used to the resistivity and magnetization measurements. The samples were made in a parallelepiped shape of about 10 mm\(^2\) in rectangular area and about 2 mm in thickness. The four electrical contacts were fixed at rectangular area of these samples. The \( \rho(T, H) \) measurements were performed with ac low current-low frequency PPMS inset while dc magnetic fields up to 600Oe were simultaneously applied parallel to the longest dimension of the samples and to the measurement current density \( (H // J) \) [8,10].
Figure 1. The XRD of YBCO, (YCa)BCO and YB(Sr)CO samples obtained for CuKα radiation.

The ρ(T,H) was recorded while the temperature was decreased in a very slowly rate (≤ 0.4 k/min) from $T >> T_c$ what allowed that a high number of data points could be recorded in the temperature range of the samples transition and the temperature derivative of the resistivity $[d\rho(T)/dT]$ could be numerically determinate. In the figure 2, for the identified samples, the upper panels display the $\rho(T,H)$ data and the lower panels display their correspondent $d\rho(T,H)/dT$ data to $H \leq 600\text{Oe}$.

Figure 2. The $\rho(T,H)$ and $d\rho(T,H)/dT$ curves of the YBCO, YB(Sr)CO and (YCa)BCO where the superconducting granular character of samples is put in evidence.
The $T_c$ of the samples approximately corresponds to the temperature that marks the maximum value of the $d\rho(T,H)/dT$ plots showed in the lower panels of the figure 2 [8,10]. The $T_c$ value for the samples is displayed at the lower panels of the figure 2. These are in agreement with those reported from literature [6-10].

Other aspect showed by the superconducting transition of the samples in the lower panels of the figure 2 is the temperature asymmetric of the $d\rho(T,H)/dT$ data. This asymmetry is characterized by a main peak followed by a hump as the temperature is decreased like observed to the Y(BaSr)CO sample in this figure. The application of a 600Oe magnetic field affects considerably the temperature position and temperature profile of the hump then the main peak.

The behavior described at last paragraph is the signature of a granular superconductor [8,10,11]. At this scenario while the main peak of the $d\rho(T,H)/dT$ data marks the pairing critical temperature within the superconducting grains, $T_c(H)$ its hump profile points out the coupling process of superconducting grains which proceeds the coherence transition phenomenon [11]. The application of a lower magnetic field in a granular superconductor is well known to be responsible to distort the G-L order parameter phase within the junctions between the superconducting grains thereby weakening the coupling energy and the pinning strength of the Josephson flux dynamics while lets almost intact the superconducting transition within the grains which is governed by the Abrikosov flux dynamics [8,10,11].

Adopting the temperature range of the hump as a practical criterion to compare the effect of the chemical doping on the granular aspect of superconducting transition of our samples displayed in the figure 2 [11], it is possible to identify that both partial chemical substitutions improved the granularity feature in the YBa$_2$Cu$_3$O$_{7-\delta}$ samples in which the Ca doping was more effectively than Sr doping.

The isofield dc magnetization measurements were performed with a quantum design SQUID magnetometer. The usual zero field cooled, $M_{ZFC}(T)$ and field cooled cooling, $M_{FCC}(T)$ dc magnetizations were recorded up to $\mu_0H = 5T$. The magnetization measurement action consisted in first cooling down the sample to temperatures well below $T_c$ in zero field (ZFC). Then the zero field cooled magnetization, $M_{FCC}(T)$ 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) [8,10,11]. 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 [12].

3. Results and discussion

The figure 3 displays a representative result of the $\Delta M(T)$ data when the magnetic irreversibility temperature, $T_{irr}(H)$ is put in evidence while a $\mu_0H = 5T$ is applied to the Y(BaSr)CO sample. Its inset highlight the correspondently $M_{ZFC}(T)$ and $M_{FCC}(T)$ dc magnetizations and distinguish the $T_c(H)$ from the $T_{irr}(H)$ [5].

In the figure 3, the $T_{irr}(H)$ is defined as the temperature that approximately sets the deviate from 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 $M_{FCC}(T)$ and $M_{ZFC}(T)$ dc magnetizations in the normal and superconducting phases of the inset of figure 3 [5]. The $T_{irr}(H)$ defines the limit below which pinning effects become important [8,10]. 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 [1-6].

Presuppose that GL theory describes the equilibrium magnetization adequately in most of the reversible superconducting regimes of our samples [5] and applying VTS [1-6] we plot in the figure 4 the $k_{B}(T,B)$ versus $TT_c^{-1}$ to $1T \leq \mu_0H \leq 5T$ for YBCO, YB(Sr)CO and Y(Ca)BCO samples where the normalized $T_c(H)$ is indicated by arrows in the plots.
Figure 3. The determination of $T_{\text{irr}}(H)$ and $T_c(H)$ temperatures from the $M_{\text{ZFC}}(T)$ and $M_{\text{FCC}}(T)$ dc magnetizations data (inset) to $\mu_0H = 5T$ applied to the Y(BaSr)CO sample.

The results of the figure 4 show that the samples display a common $k_S(T,B)$ behavior which is characterized by the observation of a higher $k_S(T,B)$ value for $T << T_c$ that gradually decreases as the temperature rises towards to the $T_c$, becoming null to $T \geq T_c$ [5]. The magnetic field affects smoothly the $k_S(T,B)$ versus $TT_c^{-1}$ profile specially to the YBCO and Y(BaSr)CO samples. The contrasting between $k_S(T,B)$ results of YBCO sample with those to Y(Ca)BCO and Y(Br)CO samples shows that the Ca and Sr doping promotes a considerable reduction of $k_S(T,B)$ magnitude. This effect can be associated to the different granularity aspect introduced by the Sr and Ca doping on the superconducting state of YBCO, as discussed at the section 2. The profile of the results of the figure 4 to the chemically doped samples is in agreement with those reported to this quantity in microstructural modified SmBa$_2$Cu$_3$O$_7$-$\delta$ ceramic samples [5,8,10].

On the other hand the $k_S(T,B)$ data of our samples do not show a $k_S(T,B) > 0$ for $T > T_c$. In the literature the identification of this behavior to an underdoped YBa$_2$Cu$_3$O$_x$ single crystal is understood as the signature of a pseudogap phenomenon [2,6].

We realized a dc magnetization experimental study in YBa$_2$Cu$_3$O$_{7-\delta}$, Y$_{0.95}$Ca$_{0.05}$Ba$_2$Cu$_3$O$_{7-\delta}$ and YBa$_{1.75}$Sr$_{0.25}$Cu$_3$O$_{7-\delta}$ ceramics samples focusing on the effects of Ca and Sr chemical doping on the $k_S(T,B)$ behaviour. The XRD and electrical magnetoresistivity results show that the Sr and Ca doping do not alter significantly the orthorhombic crystalline structure of YBa$_2$Cu$_3$O$_{7-\delta}$ but in contrast it enhances its superconducting granular character.

The analysis of Sr and Ca doping effect on the $k_S(T,B)$ behavior of YBa$_2$Cu$_3$O$_{7-\delta}$ superconductor support that the chemical doping do not change significantly the $k_S(T,B)$ profile but reduces strongly its magnitude. It could be associated to the different superconducting granular character introduced by Sr and Ca doping on the YBa$_2$Cu$_3$O$_{7-\delta}$ structure. On the other hand, the $k_S(T,B)$ results of our samples to $T > T_c$ could not be associated to the pseudogap phenomenon what suggests that the hole doping or the chemical pressure mechanism do not play the same role as the oxygen deficiency at the YBa$_2$Cu$_3$O$_{7-\delta}$ structure.
Figure 4. The \( k_S(T, B) \) behavior to the for YBCO, Y(Ca)BCO and YB(Sr)CO samples to \( 1 \text{T} \leq \mu_0 H \leq 5 \text{T} \).

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References
[1] Doria M M, Salem-Sugui Jr S, de Oliveira I G et al 2002 Phys. Rev. B 65 14450902
[2] Salem-Sugui Jr S, Doria M M, Alvaraga A D et al 2007 Phys. Rev. B 76 132502
[3] Doria M M, Gubernatis J E and Rainer D 1989 Phys. Rev. B 39 9573
[4] Doria M M 2009 J Supercond Nov Mag 22 325
[5] Pena A J P, Martinez D B, Parra Vargas C A, et al 2013B J Phys 25 1250
[6] Doria M M and Salem-Sugui Jr S 2008 Phys. Rev. B 78 134527
[7] Luo J L, Loram J W, Cooper J R and Tallon J 2000 Physica C 341-348 1837
[8] Vieira V N and Schaf J 2002 Phys. Rev. B 65 144531-9
[9] Liyanawadugge N P, Singh S K et al 2012 Supercond. Sci. Technol. 25 035017
[10] Vieira V N, Riegel I C and Schaf J 2007 Phys. Rev. B 76 024518-7
[11] Vieira V N, Schaf J and Pureur P 2002 Phys. Rev. B 66 0224506
[12] Osborn J A 1945 Physical Review 67 11