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Josephson coupling between superconducting clusters in $Bi_2Sr_2CaCu_2O_{8+\delta}$ crystals

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Abstract. – Diamagnetic moments for two $Bi_2Sr_2CaCu_2O_{8+\delta}$ crystals were measured at different fields H and temperatures. For the higher fields two distinct transition temperatures T_g and T_J are seen, with $T_g > T_J$. By increasing H the line $T_g(H)$ shifts very slowly while $T_J(H)$ shifts much faster to lower temperatures, displaying a clear upward curvature well described by a theory based on Josephson coupling between superconducting clusters. We show further that $T_J(H)$ is dependent on sample homogeneity, which is correlated with oxygen distribution in the high-T_c superconductors.

The study of high-temperature superconductors (HTSc) has been relatively difficult due to their rich crystal chemistry that gives rise to anisotropic properties and to strong sensitivity on sample composition and purity level [1, 2]. By early 1990 a number of good-quality single crystals of these new superconductors were grown and brought the hope for obtaining its intrinsic properties. However, it was soon observed that the distribution of oxygen atoms in those HTSc single crystals was often found to be inhomogeneous, resulting in various oxygen-deficient regions or clusters [3, 4]. By now, it is clear that the oxygen distribution influences superconductivity in several ways, which could inadvertently be taken as intrinsic manifestations of pure single crystals. An interesting case is the upward curvature in the upper critical field line, $H_{c2}(T)$, which has received much attention from both experimentalists [5–10] and theoreticians [11–13]. A number of explanations have been suggested for this anomaly, such as the presence of $d(x^2 - y^2)$ pairing [11, 13], Bose-Einstein condensation of charged bosons [9, 10], or thermal/quantum fluctuation of flux lines [12]. It has been indicated also that it is very difficult to determine $H_{c2}(T)$, due to rounded transition curves for underdoped and optimally doped samples [10, 14]. Interestingly, several experimental results [6, 7, 9] have shown relatively sharp resistive-transition curves which are shifted to temperatures much lower than T_c when an applied magnetic field is increased. The $H_{c2}(T)$ line, as determined from these experiments, showed an upward curvature which was related by the authors to the oxygen overdoping effect in their Tl:2201 and Bi:2201 samples. Similar behavior of the H_{c2} line has been observed [5, 10] also in underdoped crystals of $YBa_2Cu_3O_{7-\delta}$, with $0.53 \le \delta \le 0.63$, displaying decreased values of T_c in the range 4 K–40 K.

Geshkenbein, Ioffe and Millis [15] have proposed a phenomenological theory that explains the upward curvature of $H_{c2}(T)$ observed in overdoped samples of $Tl_2Ba_2CuO_{6+\delta}$. According to them, the measured $H_{c2}(T)$ is related to a bulk superconducting phase coherence, formed through Josephson coupling between superconducting clusters (or grains) that occurs at a temperature T_J. These clusters are assumed to have superconducting transition temperature T_g and they are dispersed throughout the sample matrix which is expected to have a transition temperature T_c such that $T_c < T_g$. In a recent report [16] Wen *et al.* showed that the temperature dependence of diamagnetic moment for a $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$ ($x = 0.25$) single crystal could be well described by the phenomenological model proposed by Geshkenbein *et al.* [15]. It was indicated by Wen *et al.* that the upward curvature of $H_{c2}(T)$ determined previously by resistive measurements may not be an intrinsic property of HTSc.

We present in this paper measurements of the diamagnetic moment, at different fields and temperatures, for two $Bi_2Sr_2CaCu_2O_{8+\delta}$ single crystals. Our results corroborate the model of Josephson coupling between clusters, and further indicate that the coupling temperature T_J depends on the oxygen content and its distribution inside the samples. We thus conclude that the observation of an upward curvature in the $H_{c2}(T)$ line most probably is not indicating an intrinsic property in some particular samples of overdoped or underdoped HTSc.

We have studied single crystalline samples of nominal composition $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) grown by conventional self flux method with Bi_2O_3 in excess [17]. The crystals are shiny with typical dimensions of $1.5\times1.0\times0.04\,\mathrm{mm}^3$. X-ray diffraction of both samples shows only $(00l)$ peaks belonging to the Bi:2212 phase, with no indication of impurity phases. One of the single crystals, labeled as A, was kept as grown and the other, labeled as B, was annealed in flow of oxygen at 450 °C for ten days, to ensure a more homogeneous composition throughout the sample. The superconducting properties were measured by using a Superconducting Quantum Interface Device (SQUID) made by Quantum Design Co. The magnetic moment M of both samples was measured as a function of temperature in FCC (Field Cooled measured on Cooling) and ZFC (Zero Field Cooled) processes, under several applied fields H ranging from 5 Oe to 50 kOe and parallel to the crystal $\hat{c}$ axis. A few FCW (Field Cooled measured on Warming) curves were taken too, helping to analyze the flux dynamics as discussed ahead. For clarity only ZFC measurements of $M(T)$, under several magnetic fields, are shown in fig. 1(a) for sample A and fig. 1(b) for sample B. Both samples display a relatively sharp one-step transition for $H = 5\,\mathrm{Oe}$, whose onset is around 70 K for sample A and 82 K for sample B. Under higher fields both samples display two distinct transitions, the first starting at a temperature identified as T_g, where the $M(T)$ curve departs from the normal-state base-line, and the second starting at relatively lower temperature identified as T_J, the Josephson coupling temperature. This latter transition is increasingly sharper for $H > 50\,\mathrm{Oe}$ in sample A and $H > 1\,\mathrm{kOe}$ in sample B. We observe also that while T_g shifts with field very slowly, T_J shifts much faster to lower temperatures, thus suggesting different fundamental origins.

Both samples show fan-shaped $M(T)$ curves in the region near $T_g(H)$ as shown in the enlarged view presented in the insets of fig. 1. The $M(T)$ curves follow a scaling law based on fluctuations in the amplitude of the superconducting order parameter, given by [18]

$$\frac{M}{(TH)^n} = F\left[A\,\frac{T - T_g(H)}{(TH)^n}\right], \tag{1}$$

where F is a universal scaling function, A is a temperature- and field-independent coefficient, and n is 2/3 or 1/2, respectively for a 3D or 2D system. For both of our samples the 2D exponent $n = 1/2$ produced the best scaling fits, as shown in fig. 2. We employed in these fits the basic linear relationship $T_g(H) = T_{g0} + H/S_H$, with $S_H = \mathrm{d}H_{c2}/\mathrm{d}T = -20\,\mathrm{kOe/K}$.

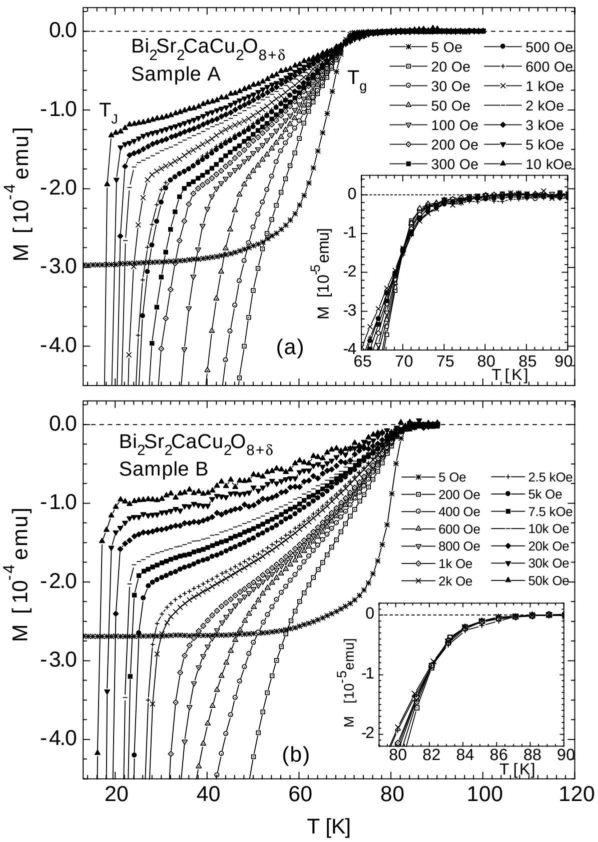

Fig. 1 – Magnetic moment as a function of temperature for (a) sample A and (b) sample B, measured in ZFC processes under several applied fields. For $H = 5$ Oe there is only one transition (T_{g}) and for higher fields two transitions (T_{g} and T_{J}) are clearly identified. The inset blows up the region near T_{g}, revealing a fan-shaped behavior of the M *vs.* T curves near the transition onset.

The good verification of this fluctuation scaling provides strong indication that $T_{\mathrm{g}}(H)$ is an intrinsic property of a bulk superconductor, similarly to results [19–21] from various bulk HTSc that display only one transition. Hence, the data of transitions associated with $T_{\mathrm{g}}(H)$ can be used to determine the intrinsic $H_{\mathrm{c}2}(T)$ lines, as shown on the right side of fig. 3. The slope of these critical lines ($S_H \approx -20\,\mathrm{kOe/K}$) compares well with reported values [20] for bulk Bi-2212 and it contrasts with the very small slopes of the $H_{\mathrm{J}}(T)$ curves (left side of fig. 3) for $H \lesssim 1.0\,\mathrm{kOe}$.

The $H_{\mathrm{J}}(T)$ curves were obtained by plotting the lower transition points $T_{\mathrm{J}}(H)$ extracted from figs. 1(a) and (b). Similarly to the so-called $H_{\mathrm{c}2}(T)$, determined previously in resistive measurements of overdoped [6, 7] Tl:2201 and Bi:2212 and underdoped [10] YBCO samples, our $H_{\mathrm{J}}(T)$ curves also show upward curvatures. The continuous lines going nicely through the $H_{\mathrm{J}}(T)$ data points (see fig. 3) represent the fitted expression for the coupling field [15]

$$H_{\mathrm{J}}(T) = H_0\, \frac{T_{\mathrm{J}}^0}{T}\, e^{-T/T_0}\,, \tag{2}$$

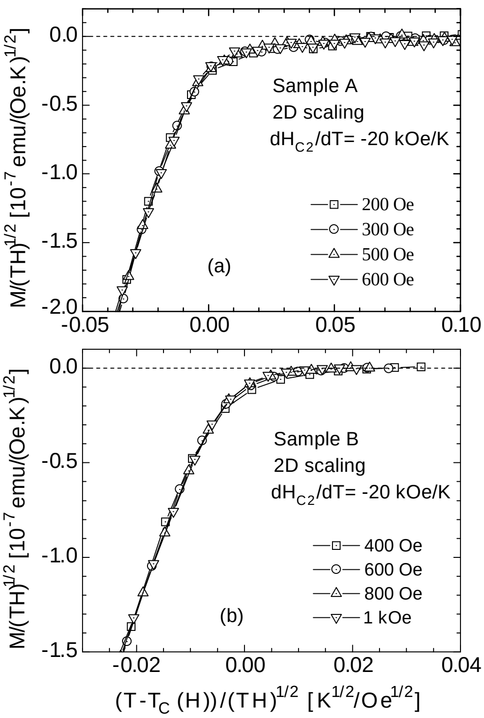

Fig. 2 – Test of the 2D fluctuation scaling according to eq. (2) for (a) sample A and (b) sample B. The above plots were obtained for some of the M *vs.* T curves shown in the inset of fig. 1, using $\mathrm{d}H_{\mathrm{c2}}/\mathrm{d}T = -20$ kOe/K.

where $H_0 = \phi_0/(\pi dR)$, $T_{\mathrm{J}}^0 = \sqrt{Z}E_{\mathrm{J}}^0/k_{\mathrm{B}}$, d is the spacing between clusters of size R, k_{B} is the Boltzmann constant, $\phi_0 = 2.07 \times 10^{-7}\,\mathrm{Gcm}^2$ is the flux quantum and the Josephson energy scale is given by

$$E_{\mathrm{J}}^0 = \eta^2 \frac{v_{\mathrm{F}}}{2\pi d} (p_{\mathrm{F}} R) N_{\mathrm{c}} \,. \tag{3}$$

Here N_{c} is the number of superconducting planes contained in a typical cluster, v_{F} and p_{F} are the Fermi velocity and momentum, respectively, and $\eta \approx (R/d)^{\frac{1}{2}}$. According to Geshkenbein *et al.* [15] the clusters become coupled at $T_{\mathrm{J}} = ZE_{\mathrm{J}}/k_{\mathrm{B}}$, where E_{J} is the Josephson coupling energy between two superconducting clusters (or grains) immersed in a normal matrix [22] and $Z \sim 6$ is the effective number of clusters assumed to be the first neighbors of a given cluster, for $T > T_0$, with $T_0 = \hbar\, v_{\mathrm{F}}/(k_{\mathrm{B}}\, d)$.

It is seen from fig. 3 that the fitted theoretical curves give a remarkably good description of the experimental data pertaining to the lower transition temperature T_{J} (fig. 1). Two free parameters were used to fit eq. (2) to the data, the coefficient $C = H_0\, T_{\mathrm{J}}^0$ and the exponent T_0. By definition they are constant for a given sample, changing their values only when the cluster properties $(R, d, T_{\mathrm{g}}(H))$ change. We found $C = 1.34 \times 10^7\,\mathrm{Oe\,K}$, $T_0 = 4.32\,\mathrm{K}$ for sample A and $C = 5.2 \times 10^7\,\mathrm{Oe\,K}$, $T_0 = 4.23\,\mathrm{K}$ for sample B. Using [15] $v_{\mathrm{F}} = 1.52 \times 10^7\,\mathrm{cm/s}$ (= 1 eV Å) the average distance between clusters $d = \hbar\, v_{\mathrm{F}}/(k_{\mathrm{B}}\, T_0)$ becomes $d \approx 2690\,$Å for sample A and $d \approx 2750\,$Å for sample B. An evaluation of the cluster size R can be made using the superconducting volume fraction at temperature T_{J} relative to the total diamagnetic shielding at $T = 5\,\mathrm{K}$. Employing the $M(T)$ curve for $H = 100\,\mathrm{Oe}$, we found a superconducting fraction

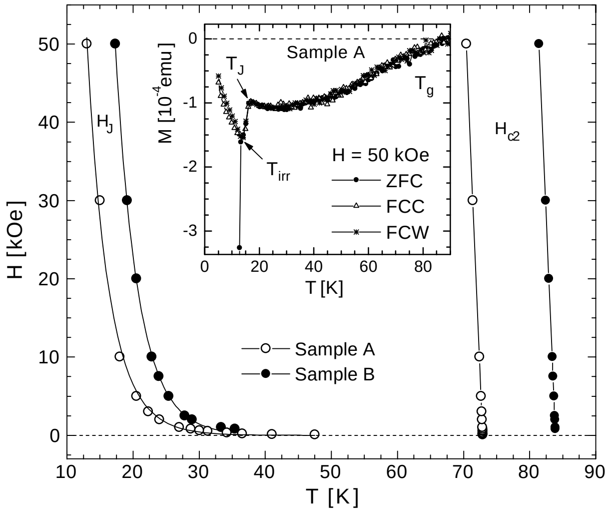

Fig. 3 – On the left-hand side are plotted the data points corresponding to the lower-temperature transitions at T_J (see fig. 1). The solid lines going through these points represent the coupling field $H_\mathrm{J}(T)$ given by eq. (2). On the right-hand side appears a plot of the $H_{\mathrm{c}2}(T)$ lines as obtained by the fluctuation scaling analysis (eq. (1)). The inset shows a detail of the typical reversible region above T_irr, tested with ZFC, FCC and FCW measurements for different fields (only $H = 50$ kOe, for sample A, is shown here).

around 0.04 for sample A which is related to the total cluster volume at $T_\mathrm{J} = 41$ K. After a simple geometrical reasoning, one gets $R \approx 0.19\,d$, implying $R \approx 510\,\text{Å}$ for sample A. This value is consistent with a dilute system hypothesis ($R^2/d^2 \ll 1$), used by Geshkenbein *et al.* [15] in deriving eq. (2). It can also be shown that $R_\mathrm{B} \approx 2.0\,R_\mathrm{A}$, where subscripts A and B refer to the sample labels. This relationship between cluster sizes is readily found if we use the fitted values $(H_0\,T_\mathrm{J}^0)_\mathrm{B} \approx 3.9 \times (H_0\,T_\mathrm{J}^0)_\mathrm{A}$ and the required proportionality $(R/N_\mathrm{c})_\mathrm{A} = (R/N_\mathrm{c})_\mathrm{B}$. Since d is roughly the same for both samples, we conclude that sample B must contain a bigger volume fraction of clusters which in fact is obtained from the $M(T)$ measurements. All these figures regarding the assumed cluster distribution suggest a more homogeneous and optimized composition of sample B as should in fact be expected, since it was annealed for a longer time, aiming at an improved quality [2] concerning its superconducting properties. A microstructural characterization of the samples using high-resolution transmission electron microscopy (HRTEM) is highly desirable, although particular care has to be exercised in order to minimize self-heating effects which could drastically change the local oxygen distribution [4, 23]. Compositional modulation in a nanometric scale has indeed been revealed by HRTEM studies on YBCO [4] and BISCCO [24, 25] crystals. The Bi compounds show a varied microstructure which displays, for instance, mixed regions of Bi:2212 ($T_\mathrm{c} \sim 83\,\mathrm{K}$) and Bi:2201 ($T_\mathrm{c} \sim 20\,\mathrm{K}$), dependent on post-reaction annealing time and temperature [24, 25].

For samples showing upward curvature in the critical field line, several different authors have also observed a consistent narrowing of the resistive transition width when H is increased [6, 7, 9]. A similar narrowing is present also in our magnetic transitions, for $T \leqslant T_\mathrm{J}(H)$ (see fig. 1). We propose that, in such cases, the magnetic-field increase narrows the *distribution* of values for relevant parameters of the cluster system, mainly $T_\mathrm{g}(H)$ and d, that more directly affect the Josephson coupling energy [15]. Consequently, the transition width to a

Josephson coupled state becomes more narrow and robust. We have observed also a systematic reduction of the superconducting fraction at $T_{\mathrm{J}}(H)$ when H increases, for both of our samples. This could mean that a field increase drives a fraction of clusters in the sample to the normal state (those having lower T_{g} values), and a smaller and more uniform system of *effective* clusters is formed, having relatively higher values of $T_{\mathrm{g}}(H)$ and d.

The inset of fig. 3 displays an important result showing that our $M(T)$ curves are totally reversible between $T_{\mathrm{g}}(H)$ and $T_{\mathrm{J}}(H)$, similar to previous works where Josephson coupling between clusters was proposed [15, 16]. Actually the reversible region extends further, from the onset of transition down to the irreversibility temperature (T_{irr}) where the ZFC, FCC and FCW curves become separated. For clarity we show only the measurement at $H =$ 50 kOe for sample A, but similar results were obtained for several fields on both samples. The observed reversibility strongly supports the model of cluster distribution as well as the evaluated cluster sizes, $R_{\mathrm{A}} \lesssim 510\,\text{Å}$ and $R_{\mathrm{B}} \lesssim 1020\,\text{Å}$. This may happen because for $T > T_{\mathrm{J}}(H)$ the penetration depth is [26] $\lambda_{ab} > 2700\,\text{Å} \gg R$, thus making the occurrence of vortices in the clusters energetically unfavorable. The reversible diamagnetic response may arise from induced shielding currents in the clusters surface. Below $T_{\mathrm{J}}(H)$ the superconducting volume fraction grows rapidly favoring vortices nucleation, and for $T \leqslant T_{\mathrm{irr}}$ vortex pinning begins to occur. Following these ideas, the identification of an anomalous irreversibility line may sound reasonable, as proposed by Seidler *et al.* [5] to explain transitions measured in underdoped YBCO samples. However, a close inspection of their excellent data reveals the same upward curvature perfectly described by eq. (2). Seidler *et al.* presented a nice fit to their data using $T \propto \ln(H_0/H)$ which indeed is a good approximation of eq. (2), $H_{\mathrm{J}} \approx H_0 \exp[-T/T_0]$, for $T \sim T_{\mathrm{J}}^0$. Therefore, $T \approx T_0 \ln(H_0/H_{\mathrm{J}})$ and, consequently, the straight lines fitted to the data appearing in fig. 2 of ref. [5] could be interpreted as showing smaller slopes $1/T_0$ for the samples annealed for longer time intervals. This would mean that smaller spacings between clusters ($d \propto 1/T_0$) were obtained in the more homogeneous and ordered YBCO samples, as should be expected from the operating oxygen kinetics [5, 23].

Concluding, we have presented magnetic transition measurements on Bi-2212 crystals that strongly support the model of Josephson coupling between clusters having higher transition temperatures than the sample matrix, typically expected for overdoped or underdoped HTSc. Several experimental works [5–10] done on these type of materials have shown critical field lines with upward curvature that seems to follow also this model. In principle this phenomenon can occur in any type of inhomogeneous superconductor. Its demonstration for conventional low-T_{c} materials, that usually have more stable physicochemical properties and allow a simpler microstructural characterization, would be of great interest.

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REFERENCES

[1] Fisk Z. and Sarrao J. L., *Annu. Rev. Mater. Sci.*, edited by E. N. Kaufmann (1997) pp. 35-67.

[2] Majewski P., *Adv. Mater.*, **6** (1994) 460.

[3] Daeumling M. *et al.*, *Nature*, **346** (1990) 332.

[4] Horiuchi S., *Jpn. J. Appl. Phys.*, **31** (1992) L1335.

[5] Seidler G. T. *et al.*, *Physica C*, **183** (1991) 333.
[6] Mackenzie A. P. *et al.*, *Phys. Rev. Lett.*, **71** (1993) 1238.
[7] Osofsky M. S. *et al.*, *Phys. Rev. Lett.*, **71** (1993) 2315.
[8] Walker D. J. C. *et al.*, *Phys. Rev. B*, **51** (1995) 9375.
[9] Alexandrov A. S. *et al.*, *Phys. Rev. Lett.*, **76** (1996) 983.
[10] Gantmakher V. F. *et al.*, *Sov. Phys. JETP*, **88** (1999) 148.
[11] Joynt R. *et al.*, *Phys. Rev. B*, **41** (1990) 4271.
[12] Kotliar G. and Varma C. M., *Phys. Rev. Lett.*, **77** (1996) 2296.
[13] Kim W. *et al.*, *Phys. Rev. B*, **58** (1998) R607.
[14] Nikulov A. V., *Phys. Rev. Lett.*, **78** (1997) 981.
[15] Geshkenbein V. B. *et al.*, *Phys. Rev. Lett.*, **80** (1998) 5778.
[16] Wen H. H. *et al.*, *Phys. Rev. Lett.*, **82** (1999) 410.
[17] da Silva R. R., private communication.
[18] Ullah S. and Dorsey A. T., *Phys. Rev. Lett.*, **65** (1990) 2066.
[19] Welp W. *et al.*, *Phys. Rev. Lett.*, **67** (1991) 3180.
[20] Li Q. *et al.*, *Phys. Rev. B*, **48** (1993) 9877.
[21] de Lima O. F. and de Andrade R. jr., *Physica C*, **248** (1995) 353.
[22] Tinkham M., *Introduction to Superconductivity* (McGraw-Hill, New York) 1996.
[23] Veal B. W. *et al.*, *Phys. Rev. B*, **42** (1990) 6305.
[24] Horiuchi S. *et al.*, *Physica C*, **168** (1990) 205.
[25] Eibl O., *Physica C*, **168** (1990) 249.
[26] Nideröst M. *et al.*, *Phys. Rev. Lett.*, **81** (1998) 3231.