Thermodynamic relevance of nanoscale inhomogeneities in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$

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Using finite size scaling we analyze specific heat and London penetration depth data to estimate the spatial extent of the superconducting grains in so called high-quality Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ single crystals. Contrary to the previously investigated type II superconductors, YBa$_2$Cu$_3$O$_{7-\delta}$, MgB$_2$, 2H-NbSe$_2$ and Nb$_{77}$Zr$_{23}$, where the lower bound for the length scale of the grains ranges from 182 A to 814 A, our analysis uncovers nanoscale superconducting grains. This clarifies the relevance of the spatial variations in the electronic characteristics observed in underdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ with scanning tunneling microscopy for bulk and thermodynamic properties and establishes their spatial extent.

Since the discovery of superconductivity in cuprates by Bednorz and Müller [1] a tremendous amount of work has been devoted to their characterization. Bismuth based cuprates deserved special attention due to their potential for applications. The issue of inhomogeneities and their characterization is essential for several reasons, including: First, if inhomogeneity is an intrinsic property, a re-interpretation of experiments, measuring an average of the electronic properties, is unavoidable. Second, inhomogeneity may point to a microscopic phase separation, i.e. superconducting grains, embedded in a nonsuperconducting matrix. Third, there is neutron spectroscopic evidence for nanoscale cluster formation and percolative superconductivity in various cuprates [2,3]. Fourth, nanoscale spatial variations in the electronic characteristics have been observed in underdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ with scanning tunneling microscopy (STM) [4–7]. They reveal a spatial segregation of the electronic structure into 3nm diameter superconducting domains in an electronically distinct background. On the contrary, a large degree of homogeneity has been observed by Renner and Fischer [8]. As STM is a surface probe the relevance of these observations for bulk and thermodynamic properties remains to be clarified. Fifth, in YBa$_2$Cu$_3$O$_{7-\delta}$, MgB$_2$, 2H-NbSe$_2$ and Nb$_{77}$Zr$_{23}$ considerably larger grains have been established. The magnetic field induced finite size effect revealed lower bounds ranging from $L = 182$ to $814$ A [9]. This letter concentrates on the interpretation of issues by providing clear evidence for the existence of superconducting grains with spatial nanoscale extent.

It is well-known that systems of spatial extent, i.e. isolated superconducting grains, undergo a rounded and smooth phase transition [10]. As in an infinite and homogeneous system the transition temperature $T_c$ is approached the correlation length $\xi$ increases strongly and diverges at $T_c$. However, when superconductivity is restricted to grains with length scale $L$, $\xi$ cannot grow beyond $L$. In type II superconductors, exposed to a magnetic field $H$, there is an additional limiting scale $L_H = \sqrt{\Phi_0/(aH)}$ with $a \approx 3.12$, related to the average distance between vortex lines [9]. Indeed, as the magnetic field increases, the density of vortex lines becomes greater, but this cannot continue indefinitely, the limit is roughly set on the proximity of vortex lines by the overlapping of their cores. Due to these limiting length scales the phase transition is rounded and occurs smoothly. As a remnant of the singularity in the thermodynamic quantities of the homogeneous system at $T_c$, these quantities exhibit a so called finite size effect, i.e. a maximum or an inflection point at $T_p$ where $\xi(T = T_p) = L_m$ and $L_m = L$ when $L < L_H$, while $L > L_H$ for $L_m = L_H$. We have shown that in YBa$_2$Cu$_3$O$_{7-\delta}$, MgB$_2$, 2H-NbSe$_2$ and Nb$_{77}$Zr$_{23}$, in the range of attained fields, the condition $L > L_H$ is satisfied. As the experimental data do not extend to low fields, the actual extent of the grains may exceed the resulting lower bounds ranging from $L = 182$ to $814$ A [9]. On the contrary, the specific heat measurements reveal that in the Bismuth- and Thallium based cuprates $T_p$ does not shift up to 14T, for fields applied parallel or perpendicular to the c-axis [11–13]. Thus, in these materials the condition $L < L_H = \sqrt{\Phi_0/(aH)} = 69$ A applies, uncovering nanoscale superconducting grains, consistent with the length scale of the inhomogeneities observed with STM spectroscopy [4–7].

To refine this rough estimate we perform a detailed finite size scaling analysis of the specific heat [13] and the London penetration depth data [14] of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ single crystals. It uncovers isolated superconducting grains with length scale $L_c \approx 92$ A along the c-axis and $L_{ab} \approx 68$ A in the ab-plane. The latter value is comparable with the spatial segregation of the electronic structure into 30A diameter superconducting domains in an electronically distinct background observed with STM spectroscopy [4–7]. As STM is a surface probe, our analysis establishes that these grains are not merely an artefact of the surface, but a bulk property with spatial extent, giving rise to a rounded thermodynamic phase transition which occurs smoothly. While there are many questions to be answered about the intrinsic or extrinsic origin of the inhomogeneity, the existence and the nature of...
a macroscopic superconducting state, we establish that a finite size scaling analysis yields spatial extent of the inhomogeneity which prevents the occurrence of a homogeneous and macroscopic superconducting phase.

Approaching $T_c$ from below the transverse correlation length $\xi^t_i$ in direction $i$ increases strongly. However, due to the limiting length scales $L_t$ and $L_{H_i} = \sqrt{\Phi_0/(aH_i)}$, it is bounded and cannot grow beyond

$$\xi^t_i(t_p) = \xi^t_{bi} \left| t_p \right|^{-\nu} = \left\{ \begin{array}{ll} \sqrt{L_jL_k}, & i \neq j \neq k \\ \sqrt{\Phi_0/(aH_i)} = L_{H_i} & \end{array} \right\}, \quad \nu \leq 1$$

where $t_p = 1 - T_p/T_c$ and $\nu$ denotes the critical exponent of the transverse correlation length. Beyond the mean-field approximation it differs from $\nu = 1/2$ and $a \approx 3.12$ is a universal constant [9]. As a remnant of the singularity at $T_c$ the thermodynamic quantities exhibit a so-called finite size effect, i.e. a maximum or an inflection point at $T_p$. Two limiting regimes, characterized by

$$L_{H_i} = \sqrt{\frac{\Phi_0}{aH_i}} = \left\{ \begin{array}{ll} < \sqrt{L_jL_k}, & i \neq j \neq k \\ > \sqrt{L_jL_k}, & \end{array} \right\},$$

(2)

can be distinguished. For $L_{H_i} < \sqrt{L_jL_k}$ the magnetic field induced finite size effect limits $\xi^t_i$ to grow beyond $L_{H_i}$, while for $L_{H_i} > \sqrt{L_jL_k}$ the superconducting grains set the limiting length scales. Since $L_{H_i}$ can be tuned by the strength of the applied magnetic field, both limits are experimentally accessible. $L_{H_i} < \sqrt{L_jL_k}$ is satisfied for sufficiently high and $L_{H_i} > \sqrt{L_jL_k}$ for low magnetic fields. Thus, the occurrence of a magnetic field induced finite size effect requires that the magnetic field and the length scales of the superconducting grains satisfy the lower bound $H_i > \Phi_0/(aL_j)$.

To derive detailed estimates we analyze the single crystal data for the specific heat coefficient of Junod et al. [13] for $\text{Bi}_{2.12}\text{Sr}_{1.71}\text{Ca}_{1.22}\text{Cu}_{1.95}\text{O}_{8+\delta}$. In Fig.1 we displayed the data for fields applied parallel to the c-axis. In zero field there is a broad peak around $T = 14T$. In the thermodynamic quantities exhibit a so-called finite size effect limits $(\Phi_0/(aH_i)) = \frac{1}{\xi^t_i(t_p)} = \sqrt{L_jL_k}$ (Eq.(1)). Accordingly, $H_i \rightarrow 0$ corresponds to limit $z \rightarrow 0$. Here the scaling function $G(z)$ is a universal scaling function of its argument and $G(0) = 1$ [9,15]. $\alpha$ denotes the critical exponent and $A^\pm$ the critical amplitude of the specific heat, where $\pm = sign(1 - T_p/T_c)$ and $B^\pm$ accounts for the regular background. Strictly speaking this scaling form applies to a neutral superfluid. However, there is strong evidence that for the accessible temperature range cuprates fall effectively into this 3D-XY universality class [9,15,16]. At $T_p$ the transverse correlation length is fixed by $\xi^t_i(t_p) = \sqrt{L_jL_k}$. Accordingly, $H_i \rightarrow 0$ corresponds to limit $z \rightarrow 0$. Here the scaling function $G(z)$ adopts the form [15], $G(z) = 1 + cz (-1 + \ln(z))$, where $c$ is a universal constant. At $T_p$ and for fields applied along the c-axis the relative reduction of the specific heat coefficient, $\Delta \gamma(t_p, H_c) = (c(t_p, H_c) - c(t_p, H_c = 0))/T_p$, adopts then the scaling form

$$\Delta \gamma(t_p, H_c) = bH_c (-1 + \ln(dH_c)),$$

(6)

where

$$b = \frac{A^- cL_aL_b}{T_p \Phi_0, \quad dH_c = z = \frac{H_cL_aL_b}{\Phi_0}. \quad \Phi_0(). \quad \Phi_0().$$

Hence the reduction is controlled by the length scales of the superconducting grains in the ab-plane.
this scaling form applies in the limit $H_c \to 0$, we restricted the fit to the experimental data displayed in Fig.2 to the low field data points. The fit yields $b = 8 \times 10^{-5} J/(K^2 \cdot \text{gat})$, and $d = 0.012 \, T^{-1}$ so that

$$\sqrt{L_a L_b} = 50 \text{A},$$

consistent with the upper bound, $L_{ab} < 69 \text{A}$ (Eq.(3)), derived from the absence of a shift of $T_p$ up to 14T. When the magnetic field is applied parallel to the a-axis, the scaling variable is $z = (H_a \xi_c^2)/\Phi_0 \approx \left(\alpha (\xi_c^2)^2\right)/\Phi_0 = \left(\alpha (\xi_c^2/\gamma^2)^2\right)/\Phi_0$, where $\gamma$, defined by $\gamma^2 = \xi_c^2/\xi_{ab}^2 = (\lambda_c/\lambda_{ab})^2$, measures the anisotropy. Thus, in this field direction the scaling variable entering Eq.(6) is $z = H_{ab}L_{ab}^2/\Phi_0$. As $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ is highly anisotropic ($\gamma > 100$) the reduction should be very small. This behavior, reflecting the large anisotropy, was also found experimentally [13].

![FIG. 2. $\Delta T_c(\xi_c, H_c)$ versus magnetic field $H_c$ applied parallel to the c-axis of a Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ single crystal, derived from Junod et al. [13]. The solid line is Eq.(6) with the parameters listed in the text.](image)

Next we turn to the zero field transition to estimate the critical correlation volume $V_c^\gamma = \xi_{ab}^\gamma \xi_{bc}^\gamma \xi_{cc}^\gamma$. This quantity is essential to derive, in combination with the volume of the superconducting grains, $V_{gr} = L_a L_b L_c$, an independent estimate of the reduced temperature $t_p$, where the finite size effect sets in. In Fig.3 we compare the measured temperature dependence of the zero field specific heat coefficient with the expected critical behavior of the homogenous counterpart. The solid lines in Fig.3 are Eqs.(4) and (5) with $H = 0$ and the parameters $T_c = 85.7K$, $A^- = A^+/(T_c \alpha) = -0.0472$, $B^- = 0.15693$, $B^+ = 0.16022$ in J/K$^2$ gat, $A^+/A^- = 1.07$ and $\alpha = -0.013$.

To estimate the correlation volume we note that $A^- = T_c \alpha \, \tilde{A}^-$, $A^-(cm^{-3}) = (10^4/k_B/V_{gat}) A^- (\text{mJ/K/cm}^3)$ and $V_{gat} = 9.1\text{cm}^3$ gives for the critical amplitude of the specific heat the estimate $A^- = 4.2 \times 10^{-3} \text{A}^-$. The universal relation [9], $A^-\xi_{ab}^\gamma \xi_{bc}^\gamma \xi_{cc}^\gamma = A^- V_c^\gamma = (R^-)^3$, where $R^- = 0.815$, yields then the correlation volume $V_c^\gamma \approx 129A^3$ compared to $680A^3$, the value for optimally doped YBa$_2$Cu$_3$O$_{7-\delta}$ [9].

Finally we turn to the finite size effect in the London penetration depth. Considering again the 3D-XY critical point, extended to the anisotropic case, the penetration depths and transverse correlation lengths in directions $i$ and $j$ are universally related by [15,17]

$$\frac{1}{\lambda_i(T)} \frac{1}{\lambda_j(T)} = \frac{16\pi^3 k_B T}{\Phi_0^2 \sqrt{\xi_i(T) \xi_j(T)}}. \quad (9)$$

When the superconductor is inhomogeneous, consisting of superconducting grains with length scales $L_i$, embedded in a nonsuperconducting medium, $\xi_i^\gamma$ does not diverge but is bounded by $\xi_i^\gamma \xi_j^\gamma \leq L_k^2$, where $i \neq j \neq k$. The resulting finite size effect is clearly seen in the microwave surface impedance data for $\lambda_{ab}^2(T=0)/\lambda_{ab}^2(T)$ versus $T$ of Jacobs et al. [14], displayed in Fig.4. The solid curve indicates the leading critical behavior of the homogeneous system. A characteristic feature of this finite size effect is the occurrence of an inflection point at $T_p \approx 87K$, giving rise to an extremum in $d\left(\lambda_{ab}^2(T=0)/\lambda_{ab}^2(T)\right)/dT$. Here Eq.(9) reduces to

$$\frac{1}{\lambda_{ab}^2(T_p)} \approx \frac{1}{\lambda_a(T_p)} \frac{1}{\lambda_b(T_p)} = \frac{16\pi^3 k_B T_p}{\Phi_0^2 L_c}. \quad (10)$$

With $\lambda_{ab}^2(T=0) = 1800\text{A}$ as obtained from $\mu$SR measurements [18], $T_p \approx 87K$ and $\lambda_{ab}^2(T=0)/\lambda_{ab}^2(T_p) = 0.066$ we find...
$L_c \approx 68A$, \hspace{1cm} (11)

compared to $L_{ab} \approx 50A$ (Eq.(8)) and consistent with the upper bound $\sqrt{L_{ab}L_c} < 69A$ (Eq.(3)). This yields for the volume of the superconducting grains, $V_{gr}$, the estimate $V_{gr} = L_{ab}^2 L_c \approx 1.7 \times 10^5A^3$. Together with the correlation volume $V_c^T \approx 129A^3$ we find for the reduced temperature $t_p$, where rounding and shifting of the transition sets in, the value $|t_p| = (V_c^T/V_{gr})^{1/3} \approx (V_c^T/V_{gr})^{1/2} \approx 0.027$, consistent with the rounding of the peak in the specific heat coefficient displayed in Fig.3. Thus, although the superconducting grains are of nanoscale only, the very small correlation volume makes the critical regime attainable. Clear evidence for 3D-XY critical behavior was also observed in epitaxially grown Bi2212 films [16].

FIG. 4. Microwave surface impedance data for $\lambda_{ab}^2 (T = 0)/\lambda_{ab}^2 (T)$ (O) and $d (\lambda_{ab}^2 (T = 0)/\lambda_{ab}^2 (T))/dT$ (□) versus $T$ of a high-quality Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ single crystal taken from Jacobs et al. [14]. The solid line is $\lambda_{ab}^2 (T = 0)/\lambda_{ab}^2 (T) = 1.2 (1 - T/T_c)^{2/3}$ and the dash-dot line its derivative with $T_c = 87.5K$, indicating the leading critical behavior of the homogeneous system. The dotted line is the tangent to the inflection point at $T_p \approx 87K$, where $d (\lambda_{ab}^2 (T = 0)/\lambda_{ab}^2 (T))/dT$ is maximum.

In contrast to YBa$_2$Cu$_3$O$_{7-\delta}$, MgB$_2$, 2H-NbSe$_2$ and Nb$_{77}$Zr$_{23}$, where the lower bounds for the length scale $L$ of the superconducting grains ranges from 182 A to 814 A [9], we have seen that the data for Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ single crystals uncovers the existence of nanoscale superconducting grains. This finding is consistent with the spatial variations in the electronic characteristics observed in underdoped Bi-2212 with STM [4–7]. However, our analysis has shown that nanoscale superconducting grains are not merely an artefact of the surface, but a bulk property with spatial extent, giving rise to finite size effects and with that to a rounded thermodynamic phase transition which occurs smoothly. While there are many questions to be answered about the intrinsic or extrinsic origin of the inhomogeneity, the existence and the nature of a macroscopic superconducting state, we established that a finite size scaling analysis yields the spatial extent of the inhomogeneity which prevents the occurrence of a homogeneous and macroscopic superconducting phase.

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[10] M. E. Fisher, in Critical Phenomena, Proceedings of the 1970 International School of Physics Enrico Fermi, Course 51, edited by M. S. Green (Academic, New York, 1971), p. 1.