Absence of gross static inhomogeneity in cuprate superconductors

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Recent scanning tunnelling microscopy (STM) studies on $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) revealed the presence of severe inhomogeneity with a length scale $L_0 \approx \xi_0$, the coherence length. Other studies have been interpreted in terms of mesoscale or nanoscale phase segregation. Here we analyze heat capacity and NMR data on Bi-2212 and $(Y,Ca)Ba_2Cu_3O_{7-\delta}$ and find no evidence of phase segregation or gross inhomogeneity. For Bi-2212 the coherence scale L_0 increases with doping from $5\xi_0$ to $17\xi_0$ and the hole density inhomogeneity decreases from 0.028 to 0.005 holes/Cu. We conclude that STM measurements considerably overstate the inhomogeneity in bulk Bi-2212.

The possible importance of inhomogeneity in the physics of high-temperature superconducting (HTS) cuprates has been stressed since their first discovery. Despite their highly variable disorder[1–4] the cuprates display a universal phase behavior.[5,6] Their physical properties vary systematically with doping in much the same way for each compound provided that the disorder lies outside of the active CuO_2 planes. More fundamentally, inhomogeneity of intrinsic electronic origin has been discussed widely, most notably various nanoscale stripe phases in which the background spins separate spatially from doped charges to form quasi-one-dimensional structures.[7] There is thus much scope in HTS materials for significant extrinsic and intrinsic spatial inhomogeneity.

Recent high-resolution scanning tunnelling microscope (STM) studies[8,9] at 4.2 K have provided dramatic evidence of apparent electronic inhomogeneity on the surfaces of Bi-2212. These reveal a patchwork of contrasting regions with length scale ≈ 14 Å, comparable with the coherence length ξ_0, some having well-defined coherence peaks and others having strongly reduced coherence peaks shifted to higher energies. The $\sim 50\%$ spread in the magnitude of the superconducting (SC) energy gap, Δ_0, was shown to correlate with a similar spread in the local density of states.[8] These variations were attributed to a distribution of local hole concentration, p, arising from oxygen disorder and a full width at half maximum (FWHM) spread of $\triangle p \approx 0.08$ holes/Cu was inferred by comparing the distribution in SC gap with the p dependence of Δ_0 deduced from photoelectron spectroscopy. It was suggested that such inhomogeneity may be quite general and may reflect ''an intimate relationship with superconductivity'' in the cuprates.[8] However, it cannot be presumed that such behavior reflects the nature of the bulk electronic state. STM is strictly a surface probe sensitive to just the outermost CuO_2 layer. Little is known about surface reconstruction in this material, the location of additional oxygen atoms in the cleaved BiO layer,[1] or the role of the $\sim 5\%$ Bi atoms incorporated into the underlying SrO layer. We argue here from thermodynamic measurements and NMR data that the bulk electronic state is much more homogeneous than was concluded from STM.

A quantitative measure of the degree of doping inhomogeneity in the HTS cuprates can be inferred from NMR linewidths. NMR is a bulk probe which is sensitive to the local electronic state near the probe nucleus. While the NMR-linewidth will not detect rapidly varying disorder with time-scale $< 10^{-8}$ sec, it is sensitive to the static or slowly varying inhomogeneity seen in STM. In Fig. 1 we show the ^{89}Y Knight shift $^{89}K_s$, at 300 K for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ (Y,Ca-123) at six different values of δ and p spanning the SC phase diagram.[10] The p values were obtained from thermopower measurements and T_c values are also plotted. As is well known, the Knight shift varies systematically with doping and the figure reveals a slope of 580 ppm/hole. Doping inhomogeneity will therefore induce a *minimum* line width of $580 \times \triangle p$ ppm. Other contributions, such as local moments[11] and the effect of disorder on the chemical shift will also add to the linewidth. We may thus use the observed linewidth to determine the *maximum* doping inhomogeneity (if all the linewidth came only from $\triangle p$).

The vertical bands in the figure show the FWHM, $\triangle p$, determined in this way.[12] We have used the magic-angle-spinning data of Balakrishnan *et al.*[13] for $YBa_2Cu_3O_{7-\delta}$ (Y-123) and of Williams *et al.*[14] for $YBa_2Cu_4O_8$ (Y-124). In the last case the linewidth is extremely narrow, about 100 Hz, giving $\triangle p \lesssim 0.0069$. It is clear that this class of HTS is remarkably homogeneous yet they exhibit the same generic thermodynamic and ground-state behavior as Bi-2212.[15] Similar conclusions have recently been drawn by Bobroff *et al.*[16] from NMR studies of Y-123.

Heat capacity studies on HTS cuprates provide several checks against electronic inhomogeneity. These include (i) the value of the specific heat coefficient, $\gamma \equiv C_p/T$ at $T = 0$; (ii) its value, γ_n, at high temperature in the normal state; (iii) the magnitude and doping dependence of the jump, $\triangle \gamma$, in γ at T_c; and (iv) the transition width. For example, mesoscale segregation into SC and normal metallic phases will result in normal states in the gap manifested by a nonzero value of γ at $T = 0$. Progressive segregation will see $\gamma(0)$ rising steadily, filling out the d-wave gap. On the other hand, mesoscale segregation into insulating and normal metallic phases will result in a progressive reduction in the
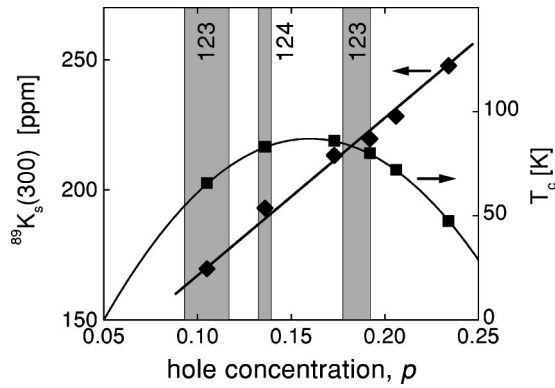
FIG. 1. The doping dependence of the ^{89}Y Knight shift at 300 K for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$. From this the NMR line-width is used to estimate a maximum FWHM, Δp, in doping state shown for Y-123 and Y-124 by the vertical bands.

FIG. 2. The specific heat coefficient $\gamma(T)$ for a series of doping states for Bi-2212 ($0.13 \leqslant p \leqslant 0.21$) (Ref. 17) and (Y,Ca)-123 ($0.084 \leqslant p \leqslant 0.23$) (Ref. 18). Arrows indicate increasing doping, bold curves denote critical doping, $p=0.19$ and dashed curves optimal doping, $p=0.16$.

high-temperature value of γ_n as states are removed. Here we focus on the thermodynamic data for Bi-2212 because this is the system in which the STM inhomogeneity was observed. To this we add data for Y,Ca-123, a very different system, to show that our observations are generic to the cuprates.

Ceramic samples (≈ 2 gm) of $Bi_{2.1}Sr_{1.9}CaCu_2O_{8+\delta}$ (Ref. 17) and $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ (Ref. 18) were synthesized using standard solid-state reaction and were oxygen loaded by slow cooling and annealing for many days at 325 °C in flowing oxygen. The electronic heat capacity was measured using a high-precision differential technique described elsewhere.[19] The samples were then alternately annealed and quenched into liquid nitrogen and the heat capacity remeasured so as to track the thermodynamic state as a function of the progressively depleted oxygen content. Changes in the oxygen stoichiometry were determined from the mass changes and these concurred rather precisely with changes in the phonon specific heat. Values of p were determined from T_c values using the approximate parabolic phase curve, $T_c(p)$, given by[5]

$$T_c(p) = T_{c,max}[1 - 82.6(p - 0.16)^2]. \tag{1}$$

Similar studies have correlated such values of p with the thermopower for both Bi-2212 (Ref. 20) and (Y,Ca)-123.[21]

Figure 2 shows a series of $\gamma(T)$ curves for each sample at closely spaced p values from deeply underdoped to deeply overdoped. Dashed curves denote optimal doping where T_c maximises while the thick curves denote critical doping ($p_{crit}=0.19$) where the pseudogap abruptly closes. Apart from small impurity-induced upturns for $T<10$ K $\gamma(0)$ remains close to zero across the entire doping range $0.084 \leqslant p \leqslant 0.23$ in (Y,Ca)-123 and $0.13 \leqslant p \leqslant 0.21$ in Bi-2212, while the values of $\gamma(T)$ at high temperature are constant, independent of doping and characteristic of a uniform normal metal. These observations rule out the two types of mesoscale segregation discussed above. We note that the ^{17}O Knight shift in overdoped Y,Ca-123 also approaches zero at $T=0$,[10] in agreement with the thermodynamic data and independently confirming the absence of unpaired quasiparticles. Significant gap filling in the single layer cuprates
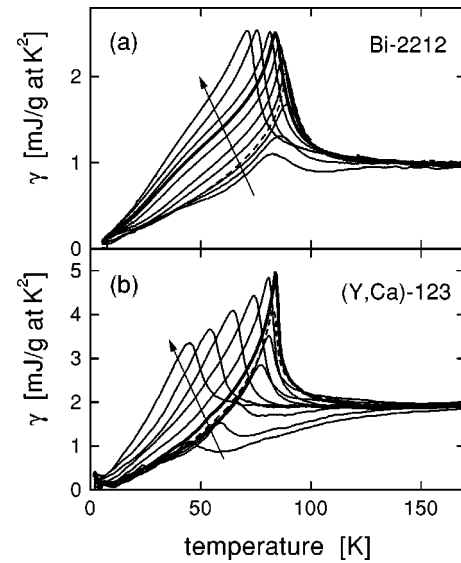
Tl-2201 (Ref. 22) and La-214 (Ref. 23) only occurs in the most heavily overdoped region $p \geqslant 0.24$. This may reflect the increased role of pair breaking relative to a rapidly decreasing superconducting gap, and does not necessarily indicate segregation.

Figure 2 also reveals rather sudden changes in $\gamma(T,p)$ with doping. The jump $\Delta\gamma$ at the transition changes only slowly across the deeply overdoped region but, starting at $p_{crit}=0.19$, the magnitude of $\Delta\gamma$ falls very rapidly with further reduction in doping. Adjacent curves are separated by about $\Delta p \approx 0.008$ and the observed sudden collapse of the specific heat anomaly suggests that any spread in doping state arising from nanoscale inhomogeneity must be less than this value. Consistent with this inference the transition widths remain quite narrow and we now focus on this issue in more detail.

A finite transition width Δt_m may arise from a spread, Δp, in doping over *mesoscopic* regions (due for example to a spread, Δx, in local donor density, x). Here

$$\Delta t_m = \Delta T_c/T_c = T_c^{-1}|dT_c/dp| \times \Delta p, \tag{2}$$

which falls to a minimum at optimum doping $p = p_{opt} = 0.16$. On the other hand, a finite transition width Δt_{fs} independent of $|dT_c/dp|$, will result from inhomogeneity on a much shorter length scale, ξ the coherence length, due to *finite-size* effects.[24–26] In the thermodynamic limit the coherence length, $\xi(T)$, diverges as $t = T/T_c - 1 \rightarrow 0$ according to the power law $\xi(T) = \xi_0/|t|^\nu$, where $\nu = 0.67$ ($\approx 2/3$) for three-dimensional (3D) XY fluctuations. Where the system is inhomogeneous this divergence is cut off by the spatial length scale of the inhomogeneity L_0,[24–26] and as a consequence the divergence of critical fluctuations is suppressed within
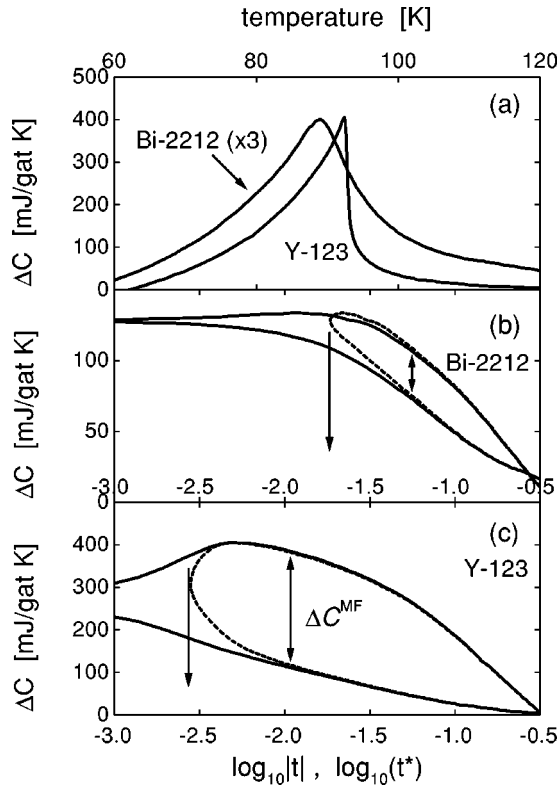
FIG. 3. (a) The specific heat anomaly near T_c for Bi-2212 and YBa$_2$Cu$_3$O$_{6.92}$, both with $p \approx 0.18$. Panels (b) and (c) show ΔC vs $\log_{10}|t|$ (solid curve) and vs $\log_{10}(t^*)$ (dashed curve), where $t^* = (t^2 + \Delta t^2)^{1/2}$. Single-head arrows show the transition width, Δt, and double-head arrows show the mean-field jump in specific heat, ΔC^{MF}.

$$\triangle t_{fs} = (\xi_0 / L_0)^{3/2}. \tag{3}$$

It is immediately apparent that, if $L_0 \approx \xi_0$ as inferred from STM,[8,9] then the transition broadening must be comparable to the magnitude of T_c, which is clearly not the case. In fact, typical transition widths of ≈ 2–3 K require that $L_0/\xi_0 > 10$. For any doping state we can estimate the transition width from the finite cutoff of the fluctuation-induced heat capacity as $|t| \to 0$ and we will see that it is indeed small.

Figure 3(a) shows the specific heat near the T_c of Bi-2212 and pure YBa$_2$Cu$_3$O$_{6.92}$, both at a similar doping state $p \approx 0.18$. In the 3D XY model the logarithmic divergence of the specific heat near T_c is given by $\Delta C_p = A^- \ln|t| + \triangle C_p^{MF}$ for $t < 0$ and $A^+ \ln|t|$ for $t > 0$. Here $\triangle C_p^{MF}$ is the mean-field step, $A^- \approx A^+ = 4k_B/[9\pi^2\Omega(0)]$, and Ω is the coherence volume.[27] A semilog plot of $\triangle C_p$ versus $\ln|t|$ gives two parallel lines offset by the mean-field step, $\triangle C_p^{MF}$. In practice this plot [shown in Fig. 3(b) for Bi-2212 and in Fig. 3(c) for Y-123] exhibits a negative curvature for sufficiently small $|t|$ due to the finite-size cutoff in critical fluctuations or other sources of broadening. The effect of a spread in T_c may be modeled by replacing t by $t^* = (t^2 + \triangle t^2)^{1/2}$ in the above expressions for $\triangle C_p$.[25] This is illustrated in Figs. 3(b) and 3(c) by selecting values of the half-width $\triangle t$ that just avert negative curvature. Since $\triangle t_{fs}$ and $\triangle t_m \lesssim \triangle t$ the measured broadening $\triangle t$ yields a lower limit to L_0/ξ_0 and an upper
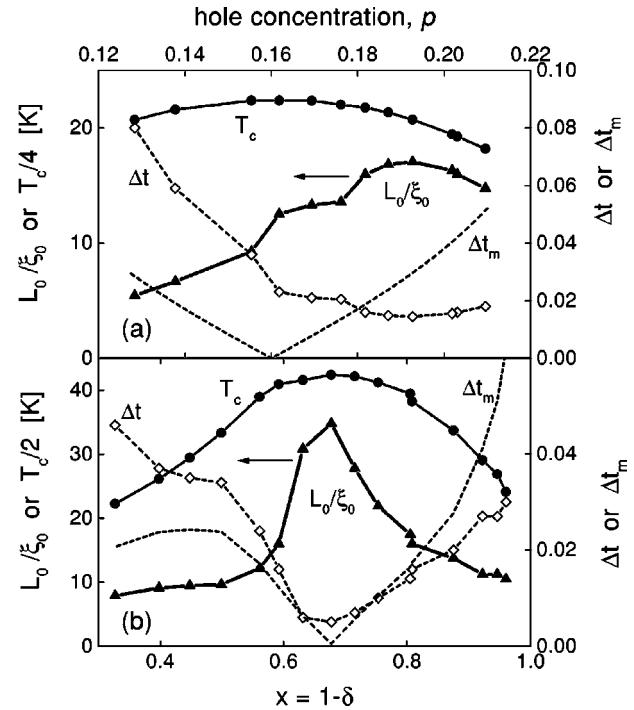

FIG. 4. The half-width of the transition Δt and lower limits for L_0/ξ_0 derived from Eq. (3) for (a) Bi-2212 and (b) (Y,Ca)-123. Values of Δt_m calculated using Eq. (2) are shown in (a) for $\Delta p = 0.005$ and in (b) for $\Delta x = 0.01$.

limit to $\triangle p$ [Eqs. (2) and (3)]. From the figures one finds $\triangle t = 0.018$ and $\triangle C_p^{MF} = 34$ mJ/g at K for Bi-2212; and $\triangle t = 0.0028$ and $\triangle C_p^{MF} = 266$ mJ/g at K for YBa$_2$Cu$_3$O$_{6.92}$. These values for $\triangle t$ translate to $L_0 \geqslant 16\xi_0$ and $50\xi_0$, respectively, values which are very much larger than those inferred from the STM results.

The same analysis may be carried out for each investigated doping level in Y$_{0.8}$Ca$_{0.2}$Ba$_2$Cu$_3$O$_{7-\delta}$ and in Bi-2212. Figure 4 shows the measured broadening $\triangle t$ and the corresponding lower limit to L_0/ξ_0 plotted as a function of p in the case of Bi-2212 and of oxygen content, $x = 1 - \delta$, for (Y,Ca)-123. In the former case lower-limit values of L_0/ξ_0 range from 17 at critical doping ($p_{crit} = 0.19$) down to 5 in the most heavily underdoped samples. For (Y,Ca)-123, though less than for pure Y-123, values of L_0/ξ_0 are still as high as 35. Even in the most extreme cases the length scale is almost an order of magnitude longer than that inferred from the STM studies. In Fig. 4 we also show the transition width Δt_m obtained from Eq. (2) that would result from a doping inhomogeneity $\Delta p = 0.005$ for Bi-2212 and $\Delta x = 0.01$ for (Y,Ca)-123. In the latter case Δt_m follows $\triangle t$ rather well across the phase diagram indicating a spread in oxygen content of $\triangle x \approx \pm 0.01$ for this compound. This corresponds to a spread $\triangle p = \pm 0.0021$[5] In Bi-2212 the transition width $\triangle t$ does not correlate with Δt_m, confirming the existence of short-length-scale inhomogeneity. Nevertheless we can conclude that the spread in p does not exceed ≈ 0.005 at $p = 0.21$ and ≈ 0.028 at $p = 0.13$, significantly less than the value inferred from the STM data.
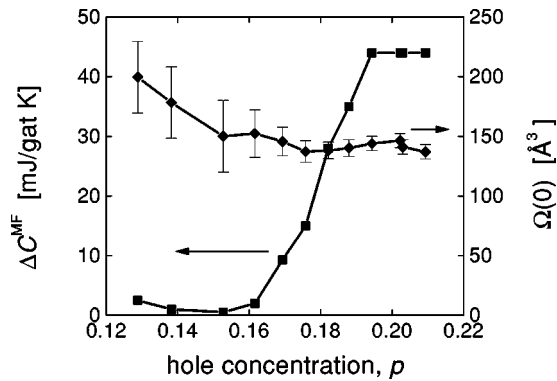
In Fig. 5 we plot the magnitude of the deduced mean-field

FIG. 5. The doping dependence of the mean-field jump, ΔC^{MF}, in specific heat for $Bi_{2.1}Sr_{1.9}CaCu_2O_{8+\delta}$ determined from the fluctuation analysis as in Fig. 2(b) for each annealing state. The coherence volume $\Omega(0)$ from the amplitude $A^+ = 4k_B/[9\pi^2\Omega(0)]$ is also shown.

step, $\triangle C_p^{MF}$, for Bi-2212. This remains rather constant on the overdoped side but falls extremely sharply at $p_{crit} = 0.19$ as the pseudogap opens and, remarkably, is essentially zero by optimal doping. A mere change of $\Delta p = 0.03$ results in the complete collapse to zero of the mean-field step. This abrupt change again implies a high degree of bulk electronic homogeneity, even in the case of Bi-2212. With $\triangle C_p^{MF} \approx 0$ for $p \lesssim 0.16$ the specific heat anomaly becomes symmetric about T_c because its weight arises *purely* from critical fluctuations. We note that there is no significance in the fact that the mean-field step reaches zero at p_{opt}. This is not the case in Y-123 and we expect that the collapse in $\triangle C_p^{MF}$ would be even more abrupt in a system with weaker interlayer coupling than Bi-2212. The coherence volume $\Omega(0)$ is also shown in the figure. The values are consistent with $\xi_{ab} \approx 17$ Å and $\xi_c \approx 0.5$ Å.

We conclude that specific heat and NMR data indicate levels of inhomogeneity much lower than those inferred from STM studies. In the doping range considered there are no phase-separated "normal" or "insulating" regions coexisting with superconductivity. Y-123 and Bi-2212 reveal thermodynamic features which change abruptly with doping indicating a spread in local hole concentration no more than $\triangle p \approx \pm 0.01$. Such features, also found in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$, $Tl_{0.5}Pb_{0.5}Sr_2Ca_{1-x}Y_xCu_2O_7$, and $La_{2-x}Sr_xCuO_4$, are generic to the cuprates and suggest (for $p > 0.125$) a remarkable degree of bulk electronic homogeneity in spite of considerable disorder in the non-CuO_2 layers. An analysis of critical fluctuations near T_c indicates a spread of local donor densities no greater than $\triangle x \approx \pm 0.01$ for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ and $\approx \pm 0.02$ for Bi-2212, while the latter compound exhibits a sudden and complete collapse of the mean-field step between critical and optimal doping.

We believe that the STM data can be reconciled with the above conclusions. Differential conductance plots in Fig. 3 of Lang *et al.*[10] show that the spectra at low bias voltage ($< \pm 20$ meV) are remarkably *uniform* as a function of position. Since the density of states in this energy region is determined by the *k*-dependent SC gap $\Delta(\varphi) = \Delta_0\cos(2\varphi)$ over a large portion of the Fermi surface centered on the nodes near (π,π) this necessarily implies a *uniform* prefactor Δ_0 and a *uniform* doping state p. It is only the presence or absence of coherence peaks that is position dependent, suggesting a site-sensitive *scattering rate*, or an interference effect, for the heavily damped quasiparticles near $(\pi,0)$. Such effects might not show up in thermal measurements. However, the specific heat does reveal a states-conserving SC gap. There is therefore no *overall* lost weight in the SC coherence peaks. We conclude that the nature of the inhomogeneity revealed by STM is radically different from that implied in Refs. 8 and 9, and is not inconsistent with our data.

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