Inhomogeneous superconductivity in both underdoped and overdoped regimes of high-$T_c$ cuprates

Y Koike, T Adachi, Y Tanabe, K Omori, T Noji and H Sato

Department of Applied Physics, Tohoku University, 6-6-05 Aoba, Aramaki, Aoba-ku, Sendai, 980-8579, Japan

E-mail: koike@teion.apph.tohoku.ac.jp

Abstract. Our recent experimental works on the inhomogeneity of superconductivity in both underdoped and overdoped regimes of La$_{2-x}$Sr$_x$CuO$_4$ are reviewed. In order to estimate the superconducting (SC) volume fraction in a sample, bulk-sensitive magnetic-susceptibility and specific-heat measurements have been carried out, using La$_{2-x}$Sr$_x$CuO$_4$ single crystals of good quality with $x = 0.05-0.3$. As a result, it has been found that the SC volume fraction is not 100% in both underdoped and overdoped regimes, suggesting the occurrence of a phase separation into SC and non-SC regions. Moreover, strong vortex-pinning effects have been observed in moderate magnetic fields in the overdoped regime, suggesting that the phase separation in the overdoped regime is not macroscopic but microscopic.

1. Introduction

Since the observation of a spatially inhomogeneous superconducting (SC) gap or pseudo-gap in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ by scanning-tunneling-microscopy (STM) [1,2], the inhomogeneity of the electronic state in the underdoped regime of high-$T_c$ cuprates has attracted great interest. It is true that the SC coherence length in the underdoped regime is so short that the SC fluctuation is expected to be large. However, such static spatial inhomogeneity as observed by STM is not simply understood. Moreover, STM measurements are very sensitive to the surface electronic state, which may sometimes be rather different from the bulk one. Therefore, the inhomogeneity must be confirmed using a bulk-sensitive probe.

In the overdoped regime of Tl$_2$Ba$_2$CuO$_{6+\delta}$ (TBCO), on the other hand, old muon-spin-relaxation ($\mu$SR) measurements revealed that the SC carrier density divided by the effective mass decreased with increasing hole-concentration [3,4]. A similar result was obtained in the overdoped regime of (Y,Ca)Ba$_2$Cu$_3$O$_{7-\delta}$ (YCBCO) [5]. These suggest that a phase separation into SC and non-SC regions takes place in the overdoped regime of high-$T_c$ cuprates [6].

In this paper, we review our recent experimental works on the inhomogeneity in both underdoped and overdoped regimes, using bulk-sensitive probes such as magnetic-susceptibility, $\chi$, and specific-heat and using La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) single crystals of good quality with $x = 0.05-0.3$ [7-12]. Mainly, we have estimated the SC volume fraction in each crystal. We have also investigated vortex-pinning effects in the overdoped regime. The origin of the phase separation is discussed.

2. Experimental

Single crystals of LSCO were grown by the traveling-solvent floating-zone method. As-grown single-crystals in the overdoped regime were annealed in oxygen gas, so that the oxygen deficiency $\delta$ in La$_2$.
\( \chi_{\text{Sr,CuO}_4} \) was estimated from the iodometric titration to be less than 0.01. The chemical composition of the single crystals was analyzed by the inductively coupled plasma optical emission spectrometry (ICP-OES). The quality of the single crystals was checked by the x-ray back-Laue photography to be good. For the study of the inhomogeneity of superconductivity, it is indispensable to use single crystals of good quality with spatially homogeneous compositions. The homogeneity was checked to be good from the width of the x-ray diffraction peaks and also using an electron probe microanalyzer (EPMA).

For \( \chi \) measurements, single crystals were formed into almost the same rectangular shape in order to make the demagnetizing-field effect on the \( \chi \) value identical to each other. The \( \chi \) measurements were performed using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS). Specific-heat measurements were carried out by the thermal relaxation method (Quantum Design, PPMS).

3. Results and discussion

3.1. Magnetic susceptibility

In order to estimate the SC volume fraction in a phase-separated sample including non-SC regions, \( \chi \) measurements on warming after zero-field cooling are not suitable, because shielding SC currents flowing near the surface mask non-SC regions included inside the sample. In fact, values of \( \chi \) at the lowest measured temperature 2 K on zero-field cooling, were almost the same among all measured SC samples regardless of the degree of phase separation, indicating that shapes, namely, demagnetizing-field effects of all measured samples were almost identical to each other. From \( \chi \) measurements on field cooling, the SC volume fraction can be evaluated, because vortices are trapped in non-SC regions at low temperatures below the SC transition temperature, \( T_c \), on field cooling so that the absolute value of \( \chi \) at 2 K, \( |\chi_{2K}| \), decreases depending on the non-SC volume fraction.

![Figure 1. Temperature dependence of the magnetic susceptibility, \( \chi \), in both (a) underdoped and (b) overdoped regimes of \( \text{La}_2-x\text{Sr}_x\text{CuO}_4 \) single crystals in a magnetic field of 10 Oe parallel to the c-axis on field cooling [7,10,11].](image)

3. Results and discussion

3.1. Magnetic susceptibility

In order to estimate the SC volume fraction in a phase-separated sample including non-SC regions, \( \chi \) measurements on warming after zero-field cooling are not suitable, because shielding SC currents flowing near the surface mask non-SC regions included inside the sample. In fact, values of \( \chi \) at the lowest measured temperature 2 K on zero-field cooling, were almost the same among all measured SC samples regardless of the degree of phase separation, indicating that shapes, namely, demagnetizing-field effects of all measured samples were almost identical to each other. From \( \chi \) measurements on field cooling, the SC volume fraction can be evaluated, because vortices are trapped in non-SC regions at low temperatures below the SC transition temperature, \( T_c \), on field cooling so that the absolute value of \( \chi \) at 2 K, \( |\chi_{2K}| \), decreases depending on the non-SC volume fraction.

![Figure 1. Temperature dependence of the magnetic susceptibility, \( \chi \), in both (a) underdoped and (b) overdoped regimes of \( \text{La}_2-x\text{Sr}_x\text{CuO}_4 \) single crystals in a magnetic field of 10 Oe parallel to the c-axis on field cooling [7,10,11].](image)
Figures 1(a) and (b) show the temperature dependence of $\chi$ in both underdoped and overdoped regimes of LSCO single crystals in a magnetic field of 10 Oe parallel to the c-axis on field cooling [7,10,11]. In the underdoped regime, it is found that the value of $|\chi_{2K}|$ increases with increasing x, exhibits a maximum at $x = 0.09$, decreases and exhibits a minimum at $x = 0.115$ and increases again. In the overdoped regime, on the other hand, $|\chi_{2K}|$ decreases with increasing x. The x dependence of $|\chi_{2K}|$ is clearly seen in Fig. 2(b). It is hard to estimate the SC volume fraction exactly from the value of $|\chi_{2K}|$, because unremovable crystal imperfections trap vortices in some degree even in a conventional SC material whose SC volume fraction is 100%. Anyway, since the quality of the used LSCO single crystals is good and not so different from each other, it is said that the SC volume fraction decreases with decreasing x below $x = 0.09$ in the underdoped regime and also decreases with increasing x over $x = 0.18$ in the overdoped regime, suggesting that a phase separation into SC and non-SC regions takes place in both underdoped and overdoped regimes. Moreover, it is found that the SC volume fraction decreases around $x = 0.115$, which is in good correspondence to the dip of $T_c$ shown in Fig. 2(a). Therefore, the decrease around $x = 0.115$ is concluded to be due to the growth of non-SC regions of a static stripe order of holes and spins which tends to be stabilized around $x = 0.115$ in LSCO [13,14].

![La$_{2-x}$Sr$_x$CuO$_4$](image)

**Figure 2.** Sr-concentration, x, dependence of (a) the superconducting transition temperature, $T_c$, defined as the cross point between the extrapolated line of the steepest part of the Meissner diamagnetism and zero susceptibility, and (b) the absolute value of the magnetic susceptibility at 2 K, $|\chi_{2K}|$, in a magnetic field of 10 Oe parallel to the c-axis on field cooling for La$_{2-x}$Sr$_x$CuO$_4$ single crystals. Solid lines are to guide the reader’s eyes.
3.2 Specific heat
Specific-heat measurements at low temperatures in zero field are effective for the estimation of the SC volume fraction, because the specific heat, $C$, is given by $C = \gamma T + AT^2 + \beta T^3$ in a d-wave superconductor including non-SC metallic regions. Here, the first, second and third terms are due to non-SC metallic regions, d-wave SC regions and phonons, respectively. In the underdoped regime of high-$T_c$ cuprates, the second term is negligibly small [15]. Therefore, the non-SC metallic volume fraction is estimated from the $C/T$ vs. $T^2$ plot shown in Fig. 3. Figure 4 shows the $x$ dependence of $\gamma$, regarded as the electronic specific-heat coefficient in the non-SC metallic regions, together with $\gamma$’s in the overdoped regime obtained by Wang et al. [16] using our single crystals. It is found that the $\gamma$ value is not zero even in SC crystals with $x = 0.05 - 0.26$. These values are consistent with formerly reported several values of $\gamma$ [17-19]. In Fig. 4, normal-state values of $\gamma$, $\gamma_n$, obtained by Momono et al. [15] using partially Ni-substituted polycrystalline samples are also plotted. Since $\gamma$ is proportional to the density of states at the Fermi level in the non-SC metallic regions, these results indicate that the non-SC metallic regions increase with decreasing $x$ in the underdoped regime, while they increase with increasing $x$ in the overdoped regime. These are consistent with the results of $\chi$ described in 3.1 that the SC volume fraction decreases with decreasing $x$ below $x = 0.09$ in the underdoped regime and also decreases with increasing $x$ in the overdoped regime. However, no increase in $\gamma$ is observed around $x = 0.115$, though the SC volume fraction decreases in the $\chi$ measurements. This may be understood assuming that $\gamma = 0$ in non-SC static stripe-ordered regions, because the value of $\gamma_n$ is reduced around $x = 0.115$ [15]. The origin of the residual small value of $\gamma$ between $x = 0.10$ and 0.18 is not clear at present.

![Temperature dependence of the specific heat, C, in the underdoped regime of La$_{2-x}$Sr$_x$CuO$_4$ single crystals plotted as C/T vs. T$^2$.](image-url)
Figure 4. Sr-concentration, x, dependence of the electronic specific-heat coefficient, $\gamma$, for La$_{2-x}$Sr$_x$CuO$_4$ single crystals. Values of $\gamma$ in the overdoped regime were obtained by Wang et al. [16] using our single crystals. Normal-state values of $\gamma$, $\gamma_n$, obtained by Momono et al. [15] using polycrystalline samples are also plotted. Solid lines are to guide the reader’s eyes.

3.3 Magnetic susceptibility in high magnetic fields

Figure 5 displays the temperature dependence of $\chi$ in various magnetic fields up to 7 T parallel to the c-axis on warming after zero-field cooling for the overdoped LSCO [12]. It has been found that $\chi$ exhibits a plateau in a moderate temperature-range in the SC state in moderate magnetic fields of $\sim 1$ T. This behavior has clearly been observed for $x = 0.198 - 0.219$, while it has disappeared for $x \geq 0.238$. Moreover, a so-called second peak has markedly appeared in the magnetization curve, M vs. H, in the overdoped regime of LSCO, as shown in Fig. 6. The second peak has often been observed in commercial bulk superconductors of REBa$_2$Cu$_3$O$_{7-\delta}$ (RE: rare earth elements) including a small amount of the second phase of RE$_2$BaCuO$_5$ [20,21]. Neither plateau in $\chi$ vs. T nor second peak in M vs. H is observed in a layered conventional superconductor NbSe$_2$ [22]. These behaviors suggest the occurrence of a strong vortex-pinning for $x = 0.198 - 0.219$.

These strong vortex-pinning effects cannot be explained simply as being due to the oxygen deficiency in a crystal, because the oxygen deficiency is almost identical to each other in the overdoped LSCO crystals. Neither are they explained as being due to the crystal structure, because the crystal structures of $x = 0.198$ and 0.219 in the SC state are different from each other; the former is orthorhombic, while the latter is tetragonal. After all, the strong vortex-pinning effects are explained as being due to microscopic phase separation into SC and non-SC metallic regions as follows. That is, in a microscopically phase-separated sample, microscopic weak SC regions appear around the boundary between intrinsic SC regions and non-SC metallic regions due to the proximity effect. The superconductivity of the weak SC regions is destroyed earlier than that of the intrinsic SC regions with increasing temperature or field so that the weak SC regions operate as strong pinning centers for vortices, resulting in strong vortex-pinning in a moderate range of temperature or field. The strong vortex-pinning near the surface of a sample on warming after zero-field cooling brings about the plateau in $\chi$ vs. T and the second peak in M vs. H. These strong vortex-pinning effects are guessed to be markedly observed in a microscopically phase-separated sample where a large number of weak SC regions are ubiquitously distributed. Therefore, it is reasonable that the vortex-pinning effects are weak for $x = 0.178$ where intrinsic SC regions are dominant and that they are weak also for $x \geq 0.238$.
where non-SC metallic regions are dominant. Accordingly, the present experimental results strongly suggest that a *microscopic* phase separation into SC and non-SC metallic regions takes place in the overdoped LSCO.

![Graph](a) Temperature dependence of the magnetic susceptibility, \( \chi \), for a La\(_{2-x}\)Sr\(_x\)CuO\(_4\) single crystal with \( x = 0.198 \) in magnetic fields of \( 0.001 \leq H \leq 7 \) T parallel to the c-axis on warming after zero-field cooling [12]. (b) Magnified plots of \( \chi \) in (a) [12].

![Graph](b) Magnetization curve, M vs. \( H \), parallel to the c-axis up to 7 T for a La\(_{2-x}\)Sr\(_x\)CuO\(_4\) single crystal with \( x = 0.198 \) at various temperatures [12]. Arrows indicate so-called second peaks.
3.4 Origin of phase separation

In the underdoped regime of LSCO, our $\chi$ and specific-heat measurements have revealed that a phase separation into SC and non-SC regions occurs not only near the surface of a sample but also in the bulk. As described in 1, the SC coherence length is so short in the underdoped regime that the SC fluctuation is expected to be large. Usually, however, it is not easy to stabilize the phase separation, namely, static spatial inhomogeneity. Therefore, a kind of disorder may induce the stabilization, as theoretically pointed out by Yanase [23]. In order to confirm it, measurements in an underdoped high-$T_c$ cuprate cleaner than LSCO are necessary.

The origin of the non-SC regions in the underdoped regime is another important issue. Former $\mu$SR results in the underdoped regime of LSCO and $Y_{1-x}Ca_xBa_2Cu_3O_6$ by Niedermayer et al. [24] remind us that the non-SC regions are in a spin-glass state. In fact, it is theoretically pointed out that local coexistence of a spin-glass state with nanoscale SC puddles may take place, using phenomenological models for the antiferromagnetic (AF) vs. d-wave superconductivity competition and Monte Carlo techniques [25]. In the underdoped regime, on the other hand, the origin of the pseudo-gap has not yet been clarified; whether it is due to the appearance of preformed pairs of electrons or due to another order. Moreover, a static stripe order tends to be stabilized around $x = 0.115$ in LSCO. In future, therefore, it is important to clarify the relation between the non-SC regions, pseudo-gap and static stripe order.

In the overdoped regime as well, our $\chi$ and specific-heat measurements have revealed that a phase separation into SC and non-SC regions takes place in the bulk. This is supported by the NMR result by Ohsugi et al. [26] that the residual spin Knight shift in the SC ground state increases with increasing $x$ in the overdoped regime of LSCO. Moreover, the occurrence of a phase separation in the overdoped regime is suggested not only from old $\mu$SR measurements in TBCO [3,4] and YCBCO [5] as described in 1 but also from old $\chi$ measurements on field cooling in TBCO by Kubo et al. [27,28]. Therefore, it appears that the phase separation in the overdoped regime is universal in the high-$T_c$ cuprates.

As for the origin of the phase separation in the overdoped regime, there are two possible scenarios [8]. One is due to the decrease of the SC condensation energy in the overdoped regime estimated from specific-heat measurements by Matsuzaki et al. [29]. That is, the decrease of the SC condensation energy is caused by the so-called flat energy-band around $(\pm \pi, 0)$ and $(0, \pm \pi)$ in the reciprocal lattice space rising above the Fermi level in the overdoped regime [30], so that the free energy in the SC state may compete with that in the normal state, leading to the phase separation. The other is due to the generation of Cu-3d holes. That is, holes may enter not only the O-2p orbital but also the Cu-3d orbital in the lower Hubbard band in the overdoped regime, though the lower Hubbard band may not be so definite in the overdoped regime. Holes doped into the Cu-3d orbital tend to be localized, resulting in the appearance of free Cu spins and pair-breaking around themselves. On the other hand, holes doped into the Cu-3d orbital disturb the AF correlation between Cu spins, producing free Cu spins and destroying the superconductivity around themselves as in the case of Zn partially substituted in LSCO [31]. In any case, both of them may bring about local destruction of superconductivity, leading to a microscopic phase separation. The appearance of Cu free spins in the overdoped regime has been confirmed from old $\chi$ measurements [32] and the suppression of the AF correlation in the overdoped regime has also been confirmed from the inelastic neutron scattering experiment [33]. It is a forthcoming issue to clarify which scenario is realized. Finally, it is noted that the decrease in $T_c$ with increasing $x$ in the overdoped regime is guessed to be due to a large proximity effect between intrinsic SC and non-SC metallic regions in a microscopically phase-separated sample.

4. Conclusions

Our $\chi$ and specific-heat measurements in LSCO have revealed that a phase separation into SC and non-SC regions takes place in the bulk in both underdoped and overdoped regimes. Especially in the overdoped regime, the phase separation has been found to be microscopic and universal in the high-$T_c$ cuprates. As for the origin of the phase separation in the underdoped regime, it is guessed to be due to
the short SC coherence length based on the strong-coupling superconductivity, but it is not clear at present whether some disorder is necessary for the phase separation or not. In the overdoped regime, on the other hand, the origin of the phase separation is guessed to be due to the decrease of the SC condensation energy or the generation of Cu-3d holes. In conclusion, a model assuming a spatially uniform SC state is insufficient to understand the superconductivity in the high-$T_c$ cuprates quantitatively.

Acknowledgments
Authors are indebted to K. Takada and M. Ishikuro for their help in the ICP-OES analysis. The $\chi$ measurements were carried out at Center for Low Temperature Science, Tohoku University. Our works were supported by the Iketani Science and Technology Foundation and also by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References
[1] Pan S H, O’Neal J P, Badzey R L, Chanmon C, Ding H, Engelbrecht J R, Wang Z, Eisaki H, Uchida S, Gupta A K, N. K –W, Hudson E W, Lang K M and Davis J C 2001 Nature (London) 413 282
[2] Lang K M, Madhavan V, Hoffman J E, Hudson E W, Eisaki H, Uchida S and Davis J C Nature (London) 415 412
[3] Uemura Y J, Keren A, Le L P, Luke G M, Wu W D, Kubo Y, Manako T, Shimakawa Y, Subramanian M, Cobb J L and Marker J T 1993 Nature (London) 364 605
[4] Niedermayer Ch, Bernhard C, Binninger U, Glückler H, Tallon J L, Ansaldo E J and Budnick J 1993 Phys. Rev. Lett. 71 1764
[5] Bernhard C, Tallon J L, Blasius Th, Golnik A and Niedermayer Ch 2001 Phys. Rev. Lett. 86 1614
[6] Uemura Y J, 2003 Solid State Commun. 126 23
[7] Omori K, Adachi T, Tanabe Y and Koike Y 2007 Physica C 460–462 1184
[8] Tanabe Y, Adachi T, Noji T and Koike Y, 2005 J. Phys. Soc. Jpn. 74 2893
[9] Tanabe Y, Adachi T, Noji T, Sato H and Koike Y 2006 AIP Conf. Proc. 850 419
[10] Adachi T, Tanabe Y, Noji T, Sato H and Koike Y 2006 Physica C 445–448 14
[11] Tanabe Y, Adachi T, Omori K, Sato H and Koike Y 2007 Physica C 460–462 376
[12] Tanabe Y, Adachi T, Omori K, Sato H, Noji T and Koike Y 2007 J. Phys. Soc. Jpn. 76 113706
[13] Torikai E, Tanaka I, Kojima H, Kitazawa K and Nagamine K 1990 Hyperfine Int. 63 271
[14] Suzuki T, Goto T, Chiba K, Shinoda T, Fukase T, Kimura H, Yamada K, Ohashi M and Yamaguchi Y 1998 Phys. Rev. B 57 R3229
[15] Momono N, Ido M, Nakano T, Oda M, Okajima Y and Yamaya K 1994 Physica C 233 395
[16] Wang Y, Yan J, Shan L, Wen H -H, Tanabe Y, Adachi T and Koike Y, 2007 Phys. Rev. B 76 064512
[17] Nohara M, Suzuki H, Isshiki M, Mangkorntong N, Sakai F and Takagi H 2000 J. Phys. Soc. Jpn. 69 1602
[18] Wen H -H, Liu Z, Zhou F, Xiong J, Ti W, Xiang T, Komiyama S, Sun X and Ando Y 2004 Phys. Rev. B 70 214505
[19] Loram J W, Mirza K A, Liang W Y and Osborne 1989 Physica C 162–164 498
[20] Higuchi T, Yoo S I and Murakami M 1999 Phys. Rev. B 59 1514
[21] Jirsa M, Muralidhar M, Murakami M, Noto K, Nishizaki T and Kobayashi N 2001 Supercold. Sci. Technol. 14 50
[22] Tanabe Y, Adachi T, Omori K, Sato H, Noji T, Sasaki T, Kobayashi N and Koike Y J. Phys. Chem. Solids (in press)
[23] Yanase Y 2006 J. Phys. Soc. Jpn. 75 124715
[24] Niedermayer Ch, Bernhard C, Blasius T, Golnik A, Moodenbaugh A and Budnick J I 1998 Phys. Rev. Lett. 80 3843
[25] Alvarez G, Mayr M, Moreo A and Dagotto E 2005 Phys. Rev. B 71 014514
[26] Ohsugi S, Kitaoka Y and Asayama K 1997 Physica C 282-287 1373
[27] Kubo Y, Shimakawa Y, Manako and Igarashi H 1991 Phys. Rev. B 43 7875
[28] Kubo Y, Kondo T, Shimakawa Y Manako T and Igarashi H 1992 Phys. Rev. B 45 5553
[29] Matsuzaki T, Momono N, Oda M and Ido M 2004 J. Phys. Soc. Jpn. 73 2232
[30] Ino A, Kim C, Nakamura M, Yoshida T, Mizokawa T, Fujimori A, Shen Z –X, Kakeshita T, Eisaki H and Uchida S 2002 Phys. Rev. B 65 094504
[31] Mahajan A V, Alloul H, Collin G and Marucco J F 1994 Phys. Rev. Lett. 72 3100
[32] Oda M, Ohguro, Yamada N and Ido M 1989 J. Phys. Soc. Jpn. 58 1137
[33] Wakimoto S, Zhang H, Yamada K, Swainson I, Kim H and Birgeneau R J 2004 Phys. Rev. Lett. 92 217004