Anomalies at magic charge densities in under-doped La$_{2-x}$Sr$_x$CuO$_4$ superconductor crystals prepared by floating-zone method

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Abstract

This is a brief review about our recent years work on floating-zone growth of high-quality La$_{2-x}$Sr$_x$CuO$_4$ superconductor crystals and our observations of intrinsic anomalous superconducting properties at magic doping levels of $x=1/16$ and $x=1/9$ in the under-doped La$_{2-x}$Sr$_x$CuO$_4$ crystals. Interesting results of charge dynamics studies obtained on our crystals are also briefly discussed.

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The physical properties of cuprate superconductors strongly depend on charge doping levels [1–4]. Sr(cation)-doped La$_{2-x}$Sr$_x$CuO$_4$ (SD-La$_{2}$14) is known to be one of the cuprate superconductors that exhibit wide charge doping range while having a simple layered structure with single CuO$_2$ planes. However, although the overall density of doped holes in the CuO$_2$ planes of SD-La$_{2}$14 can be continuously tuned by substitution of Sr$^{2+}$ cations for La$^{3+}$ ones, the free-carrier and superfluid densities cannot be simply accounted for by the doping levels due to the observed charge inhomogeneity [5–7] and intrinsic electronic phase separations both in the superconducting [8] and non-superconducting [9] regimes. Furthermore, even at the same doping level the type, cation or anion, of the dopant has a strong influence on the doped hole states in the CuO$_2$ planes. Soft (anion) dopants tend to reveal the real intrinsic electronic properties of doped hole and hard dopants (cation) will destroy the delicate electronic phase separations [8]. Indeed, while never observed in strontium and oxygen co-doped La$_{2-x}$Sr$_x$CuO$_4$+δ (CD-La$_{2}$14), hole localization at special hole concentrations of $p=0.06(\sim 1/16)$ and $p=0.1(\sim 1/9)$ was observed around room temperature by Hall effect measurements in O(anion)-doped La$_3$CuO$_4$+δ (OD-La$_{2}$14) system [10]. A model based on the formation of 2D Wigner lattices in the cuprates at $p=1/16$ and $p=1/8$, with $T_C=15$ and 30 K, respectively, was proposed from far-infrared charge dynamics study of CD-La$_{2}$14 [11]. The existence and the competition between different 2D charge ordered Wigner lattices have also been clearly seen in SD-La$_{2}$14 [12], not only in samples with oxygen dopants. These subtle 2D charge orderings are independent of the types of dopants and therefore are robust and intrinsic to high $T_C$ cuprates. All of the above observations were done in polycrystalline samples. To further pursue the detailed studies on intrinsic electronic properties around those specific hole-doping levels is extremely important for the ultimate understanding of the occurrences and mechanism of high $T_C$. High-quality crystals are indispensable for this purpose.

By using traveling-solvent floating-zone (TSFZ) technique and focusing on the problem of intrinsic electronic superconducting phase separations, we have succeeded in preparing a series of large and high-quality underdoped La$_{2-x}$Sr$_x$CuO$_4$ ($x=0.063–0.125$) single crystals covering these special doping levels [13]. The as-grown ingots were of a typical size of 5–6 mm in diameter and 110 mm in...
length, as shown in Fig. 1. Polished crystals pieces were carefully checked by optical microscopy using polarized and normal light, revealing that large single-grain crystals were obtained. The compositions of the grown crystals were checked by the inductively coupled plasma atomic emission spectroscopy (ICP-AES). Shown in Fig. 2 are powder XRD patterns of the crystals. All the observed Bragg reflections can be indexed using appropriate unit cell dimensions and no impurity phases were detected in the samples within experimental resolution (~1%). Experiments of X-ray rocking curves were performed on representative La$_{1.91}$Sr$_{0.09}$CuO$_4$ ($x=0.09$) crystal using a double-crystal diffractometer in order to check the crystal quality. The full-width-at-half-maximum (FWHM) is as small as 0.10°.

Another evidence for the high-quality of the crystal comes from the experiments of Rutherford backscattering spectrometry combined with ion-beam channeling effect (RBS-channeling) [13]. The RBS-channeling minimum yield is only $\chi_{\text{min}}=3.8\%$. Moreover, the backscattering counts of the aligned spectrum increase very slowly with depth. This is a strong indication that the defect density in the crystal is very low.

The superconducting transitions of the crystals were characterized by dc magnetic measurements using SQUID magnetometer (Quantum Design, MPMS-XL) [14]. Shown in Fig. 3 are the Meissner (field-cooled) and the shielding (zero-field-cooled) signals of all the six crystal samples. The data were measured in a low field of 5 Oe on warming with $c$-axis of the crystals along the magnetic field and were corrected for demagnetizing factors. Given in Fig. 4 are the onset superconducting transition temperature, the transition width and the Meissner fraction as function of the hole concentration $x$. The critical temperature, $T_C$, shows a familiar evolution with $x$ but a ‘plateau’ appears around $x=1/9$. It is of much interest to note that the superconducting (SC) transition width as well as volume fraction behaves by no means monotonically but anomalously. Around the doping levels of $x=1/16 (=0.0625)$ and $x=1/9 (=0.111)$, the SC transitions are much sharper ($\Delta T = 2$ K) than those away from the ‘magic numbers’ with $\Delta T \geq 6$ K, and the Meissner fraction drops remarkably, accompanying the $T_C$ plateau, to a minimum in the vicinity of $x=1/9$. The shielding signals exhibit the same broadening trend for the doping levels away from the magic numbers and they all have 100% volume fraction. This indicates that there are no macroscopic inhomogeneity and/or weak links.

As mentioned above, our careful examinations on the representative $x=0.09$ crystal showing a broad SC transition indicate that this crystal is of high crystal quality [13]. We therefore ruled out the possibility that such transition broadening may result from crystalline imperfection and concluded that the anomalous doping dependences in this series of crystals are intrinsic properties of the system [14]. We note that the superconducting transition temperatures are 15 and 30 K around the two special doping levels of $x=1/16$ and $x=1/9$, respectively (see Fig. 4). They are exactly the two intrinsic $T_C$’s observed earlier [8]. In other

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**Fig. 1.** As-grown ingot of $x=0.125$ LSCO crystal.

**Fig. 2.** Powder XRD patterns for this series of La$_{2-x}$Sr$_x$CuO$_4$ single crystals.

**Fig. 3.** Meissner curves (symboled lines) and shielding curves (bare lines) of La$_{2-x}$Sr$_x$CuO$_4$ single crystals with various under-doping levels ($x=0.063$–0.125).
words, these two intrinsic superconducting phases with \( T_C = 15 \) and 30 K are preferentially formed at around the magic doping levels. That can naturally explain the single sharp SC transitions near the two magic doping levels and the broadening of the transition while away from the magic dopings. The 15 K SC transition of our crystal at \( x = 1/16 \) is the same \( T_C \) that was previously observed in cation and anion co-doped system at exactly the same carrier concentration where the formation of a \( p(4 \times 4) \) 2D Wigner lattice was proposed [11,12].

In the meantime, we have also collected further evidences and confirmed our proposed 2D charge ordering [11,12] states through charge dynamics studies on our series of SD-La214 crystals. Based on detailed far-infrared studies and especially the observation of characteristic collective modes at \( \omega \approx 18 \) and 22 cm\(^{-1}\), the ab-plane charge dynamics in under-doped SD-La214 can be understood through a composite charge model that only a very small fraction of the total holes contributes to the free charge transport and superconductivity while the rest of the holes are in an ordered bound state forming 2D electronic (charge) lattices. In this composite charge picture, the free-carriers innately coexist with the underlying 2D charge lattice that is formed at \( \sim 200 \) K, which is much higher than \( T_C \), in the CuO\(_2\) planes [15]. Other interesting results have also been obtained by applying various probes to our crystals. For instance, by high-resolution ARPES experiments on \( x \approx 1/16 \) SD-La214 crystal, an anomalous change at \( \sim 70 \) meV in the nodal scattering rate was clearly observed above \( T_C \) [16], revealing complicated charge dynamics in normal state in SD-La214. It was also found by high-resolution ARPES that there exists a remarkably sharp nodal quasiparticle peak at all dopings only at low energy below 70 meV. However, this sharp quasiparticle peak disappears completely in antinodal regions in the underdoping regime [17]. This indicates that there exists some extra strong scattering operating primarily on antinodal electrons in underdoped SD-La214, which may be related to the Fermi surface topology [17]. Nernst signal measurements indicated that, in the underdoping regime, the superconducting condensation is established simultaneously with the coherent motion of Cooper pairs along the \( c \)-axis, while in the normal state the Nernst effect is of a strict 2D nature [18]. We find that all of the above results are consistent with the recently proposed composite charge model [15] with an intrinsically coherent \( c \)-axis charge transport [19].

In summary, we have found from dc magnetic measurements that in underdoped \( La_{2-x}Sr_xCuO_4 \) crystals the superconducting transition width and Meissner fraction exhibit intrinsic anomalies around ‘magic number’ doping levels of \( x = 1/16 \) and 1/9, and have confirmed the existence of intrinsic superconducting phases with \( T_C = 15 \) and 30 K, respectively. These anomalies can be understood in light of our recently proposed composite charge model [15] of intrinsic electronic superconducting phases [8]. Recent high-resolution ARPES experiments on our \( La_{2-x}Sr_xCuO_4 \) crystals also revealed complicated charge dynamics in the cuprate.

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