Observation of room-temperature spontaneous chemical phase segregation in overdoped $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals

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The occurrence and development of phase inhomogeneity in $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals have been investigated by measuring their superconducting transition patterns using a high-sensitivity ac magnetometer. We find that the overdoped $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals, even if they were single-phased immediately after a high-temperature annealing process, show progressively pronounced multiple superconducting transitions with time as they were kept at room temperature in a dry air atmosphere. The results reveal that the oxygen dopants in the crystal are still mobile at room temperature. These dopants tend to rearrange and thus form different phases, at a characteristic time scale of one or two weeks or so. Moreover, the diamagnetic loops in the newly segregated phase are very weak, presumably due to the existence of additional inhomogeneity down to a nanometer scale. Our results also show that the optimally doped $Bi_2Sr_2CaCu_2O_{8+x}$ crystals seem capable to remain in a single transition with storage time.

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That the cuprates are of a single phase at a given temperature and a carrier concentration is an essential assumption in the widely used phase diagrams,[1,2] based on which many experimental aspects in the normal and superconducting states have been correlated and discussed. However, it is often a primary difficulty to obtain single crystals with high structural perfection and doping uniformity, yet with large enough size suitable for many experiments. Besides the electronic phase separation,[3,4] chemical phase separation at mesoscopic or even larger scales, often related to the inhomogeneous distribution or domain formation of oxygen vacancies or dopants, has also been observed in many families of the cuprates,[5,6] for example, in La_2CuO_{4+x},[7–10] in lightly Sr-doped $La_{2-x}Sr_xCuO_4$,[11] in $Nd_{2-x}Ce_xCuO_{4-y}$,[12] and in underdoped $YBa_2Cu_3O_{7-x}$ where vacancy ordering domains of different types form at the chain layers.[13,14] Phase inhomogeneity has also been observed in $Bi_2Sr_2CaCu_2O_{8+x}$ by low-temperature scanning tunneling microscopic studies.[15–17] With all these observations, however, one still cannot rule out the possibility that the phase separation is an extrinsic effect, avoidable if the crystals are grown up and annealed properly. In this paper, through investigating the time evolution of the diamagnetic signal, we show that the oxygen dopants in originally single-phased overdoped $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals tend to redistribute spontaneously at room temperature, which eventually and unavoidably leads to the occurrence of phase separation and inhomogeneity in the titled compound.

The $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals were synthesized using a self-flux method. The as-grown crystals have an onset superconducting transition temperature of $\sim$89 K. They were proven to be of high structural quality and stoichiometric purity with the resolution limits of x-ray diffraction and energy dispersion x-ray studies. To further guarantee the uniformity of the crystal, only those tiny pieces of crystalline sheets (typically $0.5\times0.5\times0.05$ mm^3, $\sim10^{-2}$ mm^3 in volume) cleaved and cut from the center of larger uniform ones were used for investigation. Each crystal was carefully annealed to maintain a certain and uniform level of overdoping. Then its susceptibility was measured in a weak ac magnetic field (0.3–60 G) using a high-sensitivity vibration-sample magnetometer specially designed for measuring submillimeter-sized specimens.[18] This magnetometer uses a double-synchronous detection technique, with a high-frequency ac magnetic field at 10 kHz (at which the $Bi_2Sr_2CaCu_2O_{8+x}$ crystal is fully penetrated in the normal state), and a low-frequency vibration of the sample at 4.4 Hz. It reaches a resolution of 1×10^{-8} emu in susceptibility (or 3×10^{-10} emu in magnetic moments) for a sample of volume 1 mm^3 in a field of 30 G. With such sensitivity we are able to resolve any minority superconducting phase whose total volume is as small as 10^{-7} mm^3, yet without suppressing the superconductivity. Our measurement on optimally doped $Bi_2Sr_2CaCu_2O_{8+x}$ crystals reveals a single sharp transition (will be shown in Fig. 4), which proves the reliability of this homemade setup on the one hand and the high quality of the pristine crystals used in this experiment on the other hand.

Figure 1 shows the superconducting transitions of two overdoped $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals, samples 1 and 1′, measured immediately after an annealing treatment in O_2 atmosphere at 550 °C for 52 h. Sample 1 was measured in the $B\perp c$ configuration in which the crystalline sheets were parallel to the axis of a quartz-tube sample holder. In order to mount the sample into the quartz tube in the $B\perp ab$ configuration, a small piece of sample, named as sample 1′, was cut from sample 1. The 10–90% transition width for sample 1′ is $\sim$1 K in a field of 0.6 G perpendicular to the *ab* plane, which demonstrates that an overdoped crystal could be in a uniform single phase.

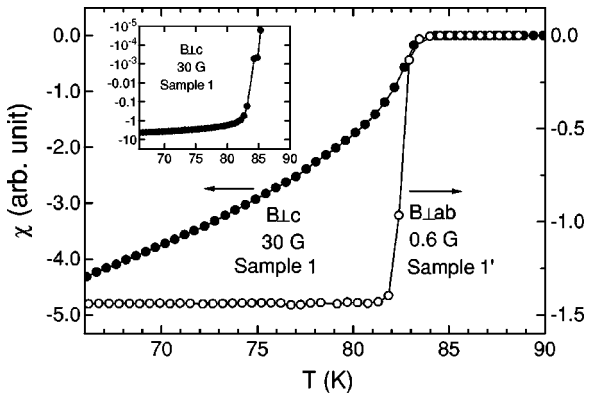

FIG. 1. The superconducting transition pattern of overdoped $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals measured immediately after an annealing treatment in O_2 atmosphere at 550 °C, showing a single-sharp transition. The inset is a semilogarithmic plot of the data (according to their inverted absolute values) in the $B\perp c$ configuration, which helps to distinguish the existence of any secondary superconducting phase in this configuration. Sample 1′ is a small piece cut from sample 1.

For the case of $B\perp c$, the diamagnetic signal at low temperatures reflects the nature of intrinsic Josephson couplings between different CuO_2 layers.[19] In a logarithmic scale (see the inset of Fig. 1 and the caption therein) the temperature dependence of the susceptibility is very steep in the transition regime but relatively ''flat'' in the Josephson coupling regime. The crossover between the two regimes takes place at ~82.5 K for sample 1.

Although the overdoped crystals show a single sharp superconducting transition if measured immediately after the annealing treatment, multiple transitions with different significance are always seen after the crystals have been kept for some period of time at room temperature and in a dry air environment protected by silica gel, which is a common way of sample storage in most of the laboratories. In our experiment, nine overdoped crystals have been examined, seven of them eventually exhibited a multiple transition pattern, and two of them underwent significant broadening in transition width, after they having been stored for a certain period of time.

Figure 2 shows the time evolution of transition pattern for sample 2 in the $B\perp c$ configuration [panel (b)], and for sample 2′ in the $B\perp ab$ configuration [panel (a)] (where sample 2′ was a small piece taken from sample 2 at the end of the three-month period). These crystals were annealed in O_2 atmosphere at 450 °C for 48 h. It can be seen that the 88-K phase grew up significantly with time.

Two years after the first annealing, sample 2′ and the remaining part of sample 2 were annealed again using exactly the same conditions as before. Single sharp superconducting transition was restored, also shown in Fig. 2.

The reversible change in volume of a higher-T_c phase should reflect the change in local oxygen content and/or arrangement in the crystals. Our results therefore reveal that the balanced oxygen content in an overdoped $Bi_2Sr_2CaCu_2O_{8+x}$ is a function of the temperature and the oxygen partial pressure of the crystal's environment. The

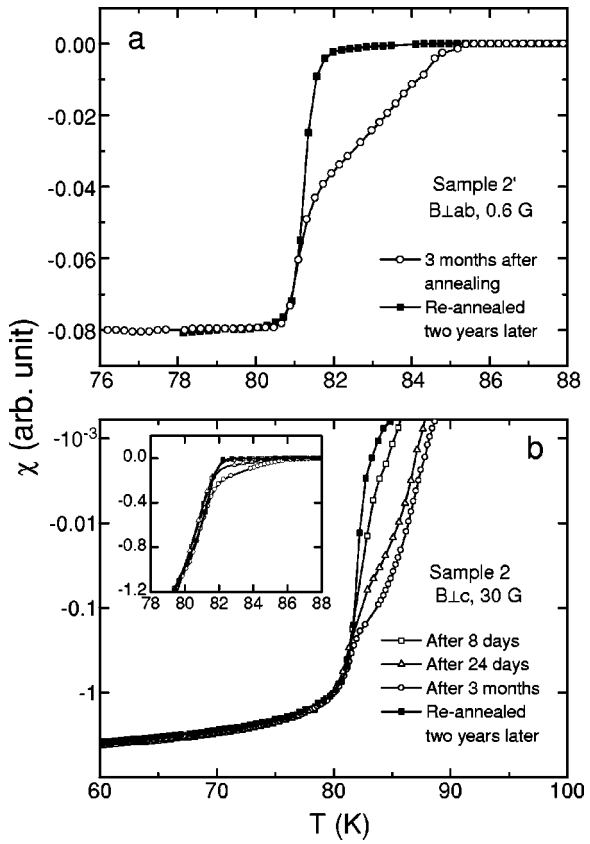

FIG. 2. The time evolution of the transition patterns of overdoped $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals. A higher-T_c phase gradually grew up as the crystals were kept at room temperature in a dry air atmosphere after an annealing treatment. Three months later, the newly segregated phase reached ~10% of the total ac diamagnetic signal (around 82 K) for the case of $B\perp c$ [panel (b)], and up to ~50% for the case of $B\perp ab$ [panel (a)]. Two years later, the samples were re-annealed following exactly the same conditions as before. A single-sharp superconducting transition was restored.

uniform oxygen content (as told by a single sharp superconducting transition at low temperatures) maintained during a high-temperature annealing process in O_2 atmosphere must become over saturated when the crystal is cooled down to room temperature. This is why the oxygen dopants tend to redistribute and even to escape from the crystal, which finally creates the higher-T_c phase. In this scenario, the newly formed phase is likely distributed near the edge of the crystals.

The distinct multiple-transition pattern indicates the formation of two types of domains in the ab plane of the crystal, each having a different oxygen content. The mechanism of such domain formation might be similar to that of the vacancy ordering domains in underdoped $YBa_2Cu_3O_{7-\delta}$,[13,14] where different types of domains correspond to different staging structures of oxygen vacancies. Such distributions are energetically more favored than just a random one.[20] A nontrivial mobility for the oxygen dopants is another key factor for the occurrence of spontaneous phase separation at room temperature.

Figure 3 shows the field dependence of the transition pattern of sample 2′ three months after the annealing, and

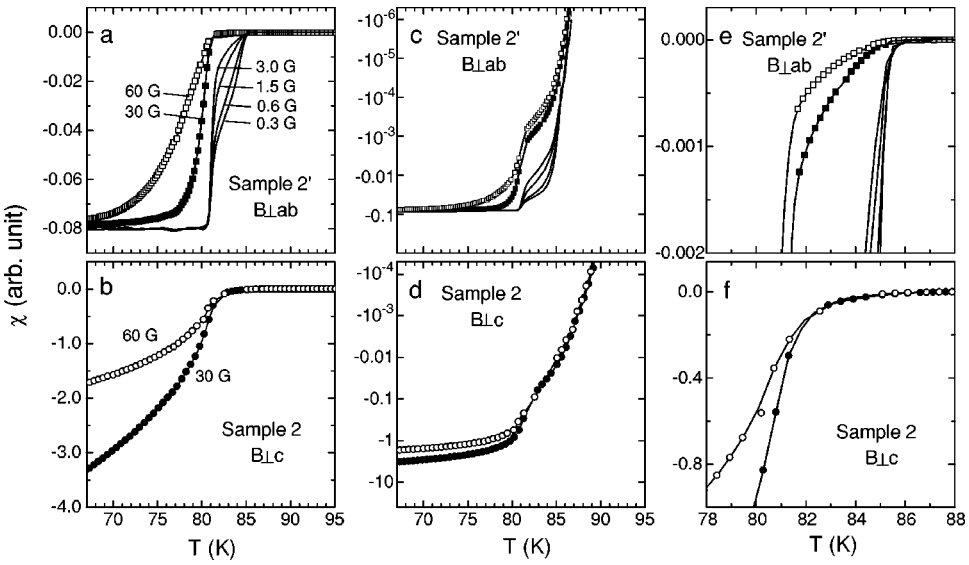

FIG. 3. The field dependence of the multiple transitions of overdoped $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals. Panels (a) and (b) are the susceptibility in the $B\perp ab$ and $B\perp c$ configurations, respectively. Panels (c) and (d) are the semilogarithmic plots of the data in panels (a) and (b), and panels (e) and (f) display the details of the onset-transition regions.

sample 2 24 days after the annealing. Two transitions can be recognized in weak magnetic fields, one onsets at ~81.6 K and the other above 86 K. The nucleating and growing up of the superconducting domains below 86 K build up substantially large or enormous amount of diamagnetic loops in the *ab* plane of the crystal. However, these loops are very weak, as they can be drastically suppressed by a field of ~1 G, and almost washed out by a field of a few tens G. Compared to the 81.6-K phase therefore the diamagnetization around 86 K should arise from a Josephson-like weak superconductivity, reflecting the existence of additional inhomogeneity in the *ab* plane of the newly segregated phase down to the coherence length scale.[21]

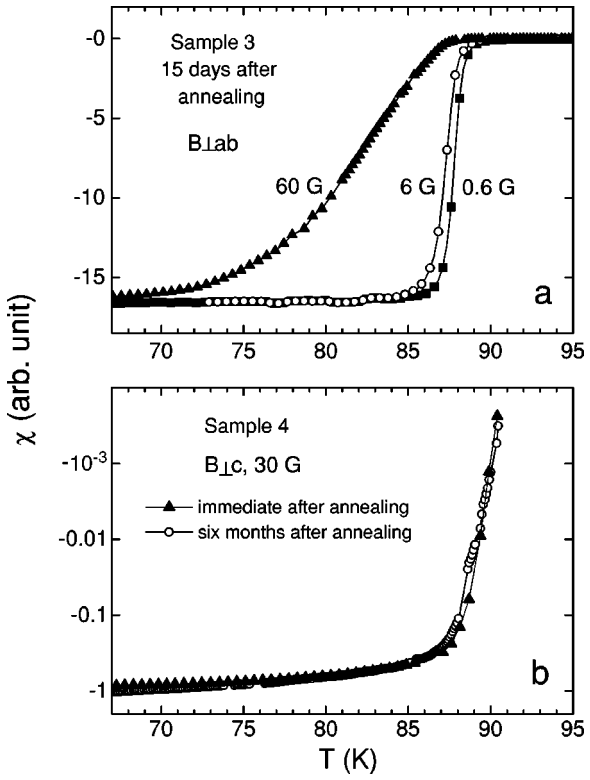

FIG. 4. The transition patterns of two optimally doped crystals of $Bi_2Sr_2CaCu_2O_8$ 15 days (sample 3) and six months (sample 4) after being annealed in Ar atmosphere at 600 °C. Their transition patterns remain nearly the same, showing no significant field dependence at a level of a few gauss.

The diffusion process of the dopants to a lower-energy distribution is presumably driven by the thermal energy which is significantly lower at room temperature compared to that during high-temperature annealing. This factor makes the diffusion process hardly completed, giving rise to the additional inhomogeneity in the *ab* plane. This picture seems consistent with the recent observation of energy gap inhomogeneity at nanometer scale using scanning tunneling microscopy.[15–17] With the best single crystals they obtained, Pan and co-workers found that the superconducting energy gap of $Bi_2Sr_2CaCu_2O_{8+x}$ compound is inhomogenous from place to place down to the nanometer scale, though the lattice is highly perfect.

Finally, Fig. 4 shows the transition patterns of two optimally doped $Bi_2Sr_2CaCu_2O_{8+x}$ crystals (the 88-K phase) 15 days (sample 3) and six months (sample 4) after being annealed in Ar atmosphere (600 °C, two weeks). These crystals were from the same batch as samples 1 and 2. Their transition pattern remained nearly the same after the six months period, and showed no significant field dependence at a level of a few Gauss. Therefore the evolution to multiple transitions is much insignificant in optimally doped crystals. This is consistent with the fact that $Bi_2Sr_2CaCu_2O_{8+x}$ material usually does not become underdoped. Even if the crystal keeps losing oxygen, the influence on T_c is insignificant, as for optimally doped crystals its T_c sits on the top of the T_c vs carrier concentration parabolic curve.

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