The normal state magnetic susceptibility of $La_2CuO_{4+\delta}$ with excess oxygen

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Abstract

The ceramic $La_2CuO_{4+\delta}$ with excess oxygen is found to have two superconducting phases, whose T_c's are 32 K (36 K) of the low T_c phase and 45 K of the high T_c phase, respectively. In this paper we report the normal state susceptibilities of the two kinds of almost single superconducting phases. The susceptibility of the high T_c phase was found to be similar to that of the optimum doped $(LaSr)_2CuO_4$. The susceptibility gradually decreased with decreasing temperature from 300 K. This shows that the high T_c phase is a bulk superconductor. On the other hand, the low T_c phase showed different behavior. The susceptibility increased with decreasing temperature above 255 K. Then, two small humps appeared around 210-255 K, indicating two antiferromagnetic phases which have different Néel temperatures. Moreover, the susceptibility showed a Curie type increase from about 210 K down to the superconducting transition temperature.

Key words: high T_c superconductivity; $La_2CuO_{4+\delta}$; excess oxygen

As well known, the La_2CuO_4 without excess oxygen is an insulating and antiferromagnetic substance. It becomes a superconductor by doping excess oxygen. Hirayama et al. have succeeded in preparing two kinds of almost single superconducting phases by the electrochemical oxidation method at 60-70 °C[1], whose T_c's are 32 K (36 K) of the low T_c phase and 45 K of the high T_c phase, respectively. The T_c of the low T_c phase is changed from 32 K to 36 K by annealing at about 200 K. They observed the specific heat jump at the superconducting transition temperature T_c in the high T_c phase[2], indicating a bulk superconductor. On the other hand, Wells et al. reported that the $La_2CuO_{4+\delta}$ with excess oxygen has stage structure of excess oxygen from the neutron experiment with single crystal[3]. Hirayama et al. concluded that the low T_c phase has the stage-6 structure and the high T_c one is the stage-4 from the values of δ[1]. In this paper, we have studied the normal state magnetic susceptibilities of the two single phases.

The stoichiometric ceramic La_2CuO_4 was prepared by the usual solid-state reaction. Then it was treated with electrochemical oxidation at 60-70 °C. The detail of the electrochemical oxidation method is presented in the Ref.[1]. The dc susceptibility was measured using a commercial superconducting quantum interference device magnetometer (MPMS2, Quantum Design, USA). Both bulk and powdered samples were used for measurements. The magnetic field was applied parallel to the longer side of the bulk samples, and the demagnetization factor correction was not applied.

Fig.1 shows the temperature dependence of susceptibility of the high T_c phase from 300 K down to 50 K. The susceptibility decreased with decreasing temperature. This behavior is similar to that of the optimum doped $(LaSr)_2CuO_4$. The magnitude of the susceptibility change was also comparable with the optimum doped one. There was a small peak at about 260 K, probably due to the existence of the separated

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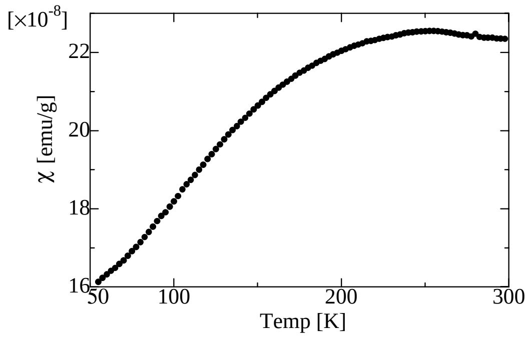

Fig. 1. Temperature dependence of the susceptibility of the high T_c phase. The origin of the ordinate is arbitrary.

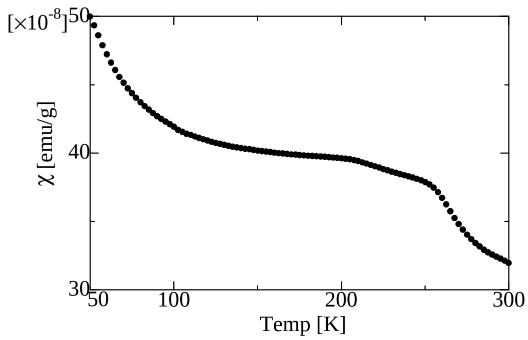

Fig. 2. Temperature dependence of the susceptibility of the low T_c phase. The origin of the ordinate is arbitrary.

antiferromagnetic phase. However, the amount of the remained antiferromagnetic phase is considered to be very small, because the peak is very small. This result shows that the high T_c phase is a bulk superconductor. The present result of the bulk nature is also consistent with the observation of the specific heat jump at the superconducting transition temperature by Hirayama et al[2].

Fig.2 shows the temperature dependence of susceptibility of the low T_c phase. The susceptibility showed a steep increase with decreasing temperature above about 255 K. Then two humps appeared at about 255 K and 210 K. Below the second hump, a Curie type susceptibility increase was observed down to the transition temperature T_c of superconductivity. These behaviors are considered to be a result of superposition of three kinds of susceptibilities: two antiferromagnetic susceptibilities with peaks at Néel temperatures of about 255 K and 210 K (something like one in Fig.3), and a Curie type one with no Néel temperature down to about 50 K at least. The first hump at 255 K is considered to be caused by the remained antiferromagnetic phase (the oxygen poor phase which is separated from the superconducting phase). Because the low T_c phase includes small amount of the antiferromagnetic phase.

Fig.3 shows the temperature dependence of susceptibility of the La_2CuO_4 which is annealed at 600

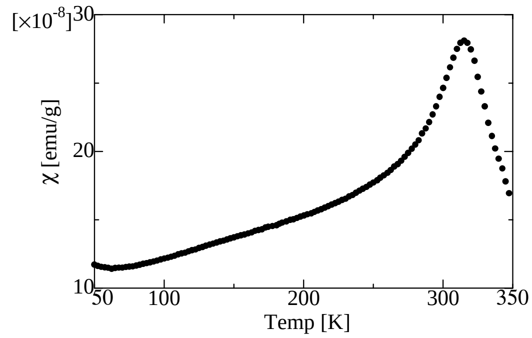

Fig. 3. Temperature dependence of the susceptibility of the La_2CuO_4 without excess oxygen. The origin of the ordinate is arbitrary.

°C in vacuum. The magnetic property of this sample, La_2CuO_4 without excess oxygen, is well known. The Néel temperature is decreased with adding a small amount of the excess oxygen. Below the Néel temperature, the susceptibility decreases smoothly down to about 50 K.

It is anomalous that the low T_c phase has the second hump and the Curie type behavior in the susceptibility. The second hump suggests that there are two kinds of antiferromagnetic substances with different Néel temperatures. One should be the oxygen poor phase. The origin of the second hump is still to be resolved. As for the Curie type susceptibility, some magnetic impurities might be considered to be included in materials. However, both in the high T_c phase and the La_2CuO_4 annealed in vacuum, no such Curie type behavior was observed, although they were all made from the same materials. Therefore the Curie type behavior suggests that substantial amount of free copper ions is included in the low T_c phase. The electronic state in the low T_c phase might be much different from that of the high T_c one.

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