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Emergence of two superconducting phases (33 K and 40 K) and their relation to structural phase transitions in crystalline $La_2CuO_{4.011}$

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Adiabatic calorimetry revealed three structural phase transitions existing in $La_2CuO_{4.011}$ single crystal; the higher-order type at 287 K, the Martensitic type at 265 K, and the first-order type at 222 K. The phase stable between 222 and 265 K can be supercooled easily and shows superconductivity with the onset at 33 K, while the phase stable below 222 K does that at 40 K. The annealing effects on the structural phase transitions are discussed in correlation with different appearances of the superconducting transition temperature and of the Meissner fraction.

I. INTRODUCTION

Most of the high-T_c superconductors showing oxygen nonstoichiometry, the configuration of the nonstoichiometric oxygens, and the associated change in the crystal structure have influences on the electronic state and superconductivity. La_2CuO_4 being relatively simple in crystal structure and a prototype of the Cu-based superconductors, many investigations have been devoted to the stoichiometric and oxygen-nonstoichiometric crystals. It is well known that in the system with excess oxygens phase separation occurs into two phases of oxygen-rich phase (metallic and superconductive) and oxygen-poor phase (insulating and antiferromagnetic).[1,2] In view of the fact that the phase separation requires long-distance diffusion of excess oxygens and thus proceeds as a thermal activation process, how the crystal has been cooled from high temperature has influences on the contents of excess oxygen δ of the two phases, the configuration of excess oxygens, the grain size of each phase, and consequently the superconductivity. The detailed properties of the configurations and the rearrangement rates of excess oxygens, however, have hardly been clarified, and even the phase separation temperature is still open to a question.[1-5] In such a situation, the reason for the interrelation between the properties of superconductivity such as Meissner fraction and transition temperature T_c and the thermal treatments such as cooling rate and thermal annealing still remains ambiguous.[5-8] Furthermore, the distinction is ambiguous whether each thermal annealing enhances the progress of some structural phase transition, the grain size of each phase, or the phase separation.

Ahrens *et al.*[6] pointed out that the superconducting T_c of $La_2CuO_{4.032}$ crystals was sensitive to the cooling rate around 195 K, and the T_c of a slowly cooled sample, ~33 K, was 4 K higher than that of a rapidly cooled one, ~29 K. The result was explained as due to freezing-in of the phase separation process halfway in the nonequilibrium state, since the diffusion rate of excess oxygens would become small as the temperature decreased. Then, the metallic phase in the rapidly cooled sample has a smaller δ than that in the slowly cooled one. The small δ, meaning dilute hole concentration, leads to a lowering of the T_c. Reyes *et al.* used a ^{139}La nuclear quadrupole resonance (NQR) technique to probe the local structure around lanthanum ions in $La_2CuO_{4.03}$ crystals, and observed the appearance of a broad NQR signal in the metallic phase below 200 K in association with the above-stated change in T_c.[7] Kremer *et al.*[5,8] have investigated the annealing effects at some temperatures on the Meissner fraction of $La_2CuO_{4.017}$ crystals, and suggested the freezing-in of the diffusion of hole clusters around 180 K as well as that of excess oxygens around 220 K. Thus, most of the researchers have related the effects of the cooling rate and annealing below room temperature to the freezing-in or -out of the diffusion of excess oxygens concerning the phase separation.

We have previously measured the heat capacities of a $La_2CuO_{4.035}$ single crystal under adiabatic conditions,[4] and found three structural phase transitions at 295 K, 265 K, and around 210 K. No spontaneous enthalpy relaxation was observed due to freezing-in of the diffusional process of excess oxygens. Furthermore, the phase transition around 265 K was found out to be of the martensitic type, indicating that microcrystals and therefore many defects were expected to be produced through the transition. These suggest the possibility that the effects of annealing and cooling rates are related to the progress of these structural phase transitions and to the grain growth of the crystals. This suggestion is quite in contrast to the above understanding based on the freezing-in of the diffusional process of excess oxygens. In the present study, we first clarified the phase behavior of $La_2CuO_{4.011}$ crystals through precise heat capacity measurements and examined Meissner fractions of the samples annealed at dif-

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ferent temperatures and for different periods, so that the interrelation between the thermal treatments and the superconductivity could be clarified definitely. In fact, it resulted that the annealing effect around 200 K could be explained by the progress of the phase transition but not of the phase separation.

II. EXPERIMENTAL DETAILS

A $La_2CuO_{4.011}$ single crystal was grown by a procedure described previously.[4] The amount of excess oxygen content was adjusted through a high-temperature treatment under an atmosphere of controlled oxygen-gas pressure. The valence of copper was determined by the iodometric titration technique and the excess oxygen content was calculated from this value.

The heat capacity of the sample was measured by the intermittent heating method under adiabatic conditions using a high-precision adiabatic calorimeter in the temperature range of 13–300 K:[9] The former equilibrium temperature T_f of a calorimeter cell loaded with a sample was rated for 10 min, a specified quantity of electrical energy ΔE corresponding to the temperature rise of 0.5–3 K was supplied into the cell in 1–20 min, and then the latter equilibrium temperature T_l was rated for 10 min. The latter rating served as the former rating in the next sequence of the measurement, and the procedure of this sequence was repeated until some desired temperature was reached. The gross heat capacity of the cell was evaluated to be $\Delta E/(T_l - T_f)$ at the average temperature $(T_f + T_l)/2$. In case where nothing anomalous happens in the sample, no temperature drift is observed in the temperature-rating periods. In cases where a phase separation associated with oxygen composition or a first-order phase transition takes place, on the other hand, spontaneous temperature drifts due to heat evolution or absorption of the sample are observed in the rating periods at the temperatures where the diffusion rate of the oxygen or the transition rate become close to the experimental time scale of 10^2–10^6 s. The rates of spontaneous endothermic drifts observed around 220 K were taken to be those at 8 min after each energy supply. Then the temperatures T_f and T_l for the evaluation of the heat capacity were taken to be those at 10 min after each energy supply, and thus the heat capacity value derived involved the contribution due to progress of the process responsible for the endothermic drift during the energy supply and the latter temperature rating for 10 min. The mass of the sample used was 11.2354 g ($\widehat{=}$ 0.027 701 mol). The imprecision and the inaccuracy of the measurements with the apparatus were estimated previously to be within ±0.06% and ±0.3%, respectively.[9]

Magnetic susceptibility was measured with a superconducting quantum interference device (SQUID) magnetometer in the temperature range of 5–50 K. The experiment was carried out only under application of a magnetic field of 50 Oe during all the cooling processes and the magnetic susceptibility measurements. A demagnetization correction was not made in the data processing.

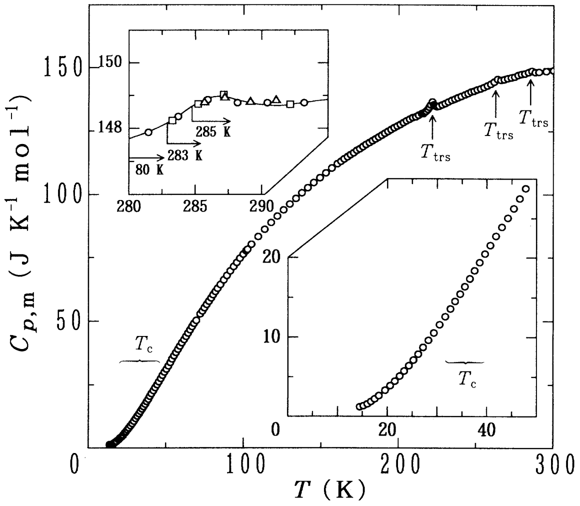

FIG. 1. Heat capacities of a $La_2CuO_{4.011}$ single crystal. The upper-left and lower-right insets show the results around 280 K and in the superconducting-transition temperature region, respectively, on enlarged scales. Temperatures in the upper inset indicate the lowest temperatures that each sample has experienced just before the measurements: ○, 80 K; □, 283 K; △, 285 K.

III. RESULTS AND DISCUSSION

A. Thermal properties

Figure 1 shows experimental heat capacities of a $La_2CuO_{4.011}$ single crystal. Three heat capacity anomalies were observed at 287 K, around 265 K, and at 222 K. No heat capacity anomaly was detected in the superconducting-transition temperature region, as shown in the lower-right inset of the figure on an enlarged scale. The upper-left inset of the figure shows the heat capacities around 287 K where open circles, squares, and triangles represent the results of the samples precooled to 80, 283, and 285 K, respectively, from 300 K. In view of the fact that the three sets of data are located on a single curve within their experimental errors and that no spontaneous temperature drift has been observed around 287 K immediately after the precooling treatments or during the heat capacity measurements on heating, this anomaly is understood to be a second-order phase transition as observed at 295 K in $La_2CuO_{4.035}$.[4]

Figure 2 shows the heat capacities around 265 K, where open circles, triangles, diamonds, squares, and inverted triangles represent the values obtained on heating the samples precooled to 80, 257, 259, 261, and 265 K, respectively, from 280 K and a dashed line stands for the base line used for estimating the anomalous parts of the heat capacities. All of the five sets of data were located on different curves depending on the low-temperature limit of each precooling, and meanwhile no appreciable spontaneous temperature drift was observed, even just after the precooling, or during the heat capacity measurements on heating. The latter indicates that the transition proceeds in a short time to a certain quasiequilibrium state. These are characteristics observed in quite the same tempera-

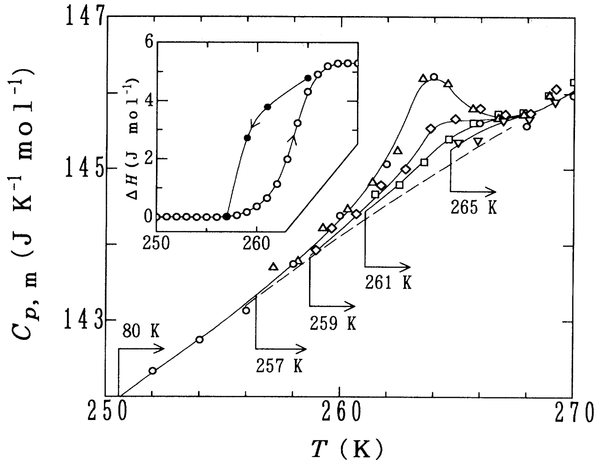

FIG. 2. Thermal hysteresis in the heat capacities observed around 265 K. Temperatures in the figure indicate the lowest temperatures that each sample has experienced just before the measurements and a dashed line represents the base line for estimating the excess part of heat capacity. The inset shows the temperature dependences of the enthalpy of transition: ○, in the heating direction; ●, in the cooling direction.

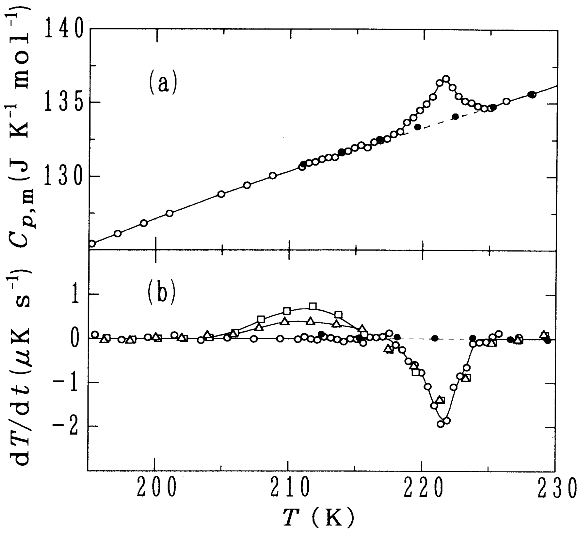

FIG. 3. Heat capacities (a) and spontaneous temperature drift rates (b) observed around 222 K in the intermittent heating process: ●, precooled from 270 K to 212 K; □, △, ○, annealed at 210 K for 0, 4, and 50 h, respectively, after precooling from 270 K to 180 K.

ture region in $La_2CuO_{4.035}$ (Ref. 4) and of the martensitic phase transitions. The inset of Fig. 2 shows a hysteresis loop of the enthalpy of transition between in the heating and cooling directions. The total transition enthalpies of $La_2CuO_{4.011}$ and $La_2CuO_{4.035}$ crystals are estimated to be about 5 and 14 $J\,mol^{-1}$, respectively. On considering that the transition temperature is independent of the composition and that the part of the crystal undergoing the transition increases with increasing the excess oxygens, the martensitic transition is interpreted to proceed in the oxygen-rich phase. An antiferromagnetic phase transition takes place, as reported before,[4] at around 265 K in the oxygen-poor phase in the sample. One may consider that the transition contributes considerably to the observed enthalpy of transition. The transition, however, does not contribute appreciably as was shown in the result of $La_2CuO_{4.002}$ (see Fig. 1 in Ref. 4), since the orientation of each spin becomes ordered within the *ab* plane much above the transition temperature T_N and changes only a little to produce their antiferromagnetic arrangement along the *c* axis at T_N.[10]

Figures 3(a) and 3(b) show the heat capacities and the spontaneous temperature drift rates observed in the temperature-rating periods of the measurements around 222 K, respectively. The sample quenched at 20 $K\,min^{-1}$ from 270 K to 150 K (squares in the figure) exhibited heat evolution starting at around 205 K and ceasing at 217 K and subsequently heat absorption in the range between 217 K and 225 K. When annealed at 210 K for 4 h after precooling to 180 K, the sample exhibited a smaller heat evolution effect around 210 K, but almost the same magnitude of heat absorption effect around 222 K as the quenched sample did. In the case where the sample was annealed at 210 K for 50 h, the heat evolution entirely disappeared and a larger heat absorption effect was observed than in the previous cases. Meanwhile, the sample precooled from 270 K to 212 K showed neither anomalies of heat capacity nor spontaneous heat evolution or absorption effects around 222 K at all. It is concluded from these that the anomaly at 200–225 K is attributed to a first-order phase transition; namely, the heat evolution around 210 K corresponds to the high-temperature to low-temperature phase transition and the heat absorption effect around 222 K to the opposite process. The observation that the sample precooled from 270 K to 212 K undergoes no transition from the high- to low-temperature phase at 212 K is understood as due to absence of the nucleus of the low-temperature phase. The understanding is reasonable in that a first-order transition proceeds as two processes of the nucleation of a new phase and the growth and that the nucleation tends to proceed in the low-temperature range (away from the transition point) where the Gibbs energy difference between the two phases becomes large.[11,12] The enthalpy and entropy of the transition were evaluated to be 8 $J\,mol^{-1}$ and 0.04 $J\,K^{-1}\,mol^{-1}$, respectively, for $La_2CuO_{4.011}$. They are quite small, suggesting that the transition is of the displacive type such as associated with a tilting of CuO_6 units.

The anomaly in 200–225 K is obviously considered to be related to the annealing effects around 200 K observed by many researchers.[5–8] Judging from the following situations, however, the anomaly would have nothing to do with a relaxation phenomenon like freezing-in or -out of the diffusion process of excess oxygens. First, as has been indicated by many experiments,[1,2] there are two phases with different oxygen compositions even above 225 K. It is very unlikely that another phase separation into more than two phases occurs at 222 K concerning the oxygen composition. Second, if the anomaly was attributed to the phase separation, considering that the endothermic drifts were observed only at 217–225 K with the maximum drift rate at 222 K as indicated with open circles in Fig. 3, the phase diagram should be such that the oxygen composition does not change below 217 K but does suddenly above 217 K. Such a phase separation is very hard to be realized. And, as shown with open triangles in Fig. 3, the spontaneous exothermic drift due to oxygen diffusion appeared only above 205 K even in the presence of the nucleus of the low-temperature phase. This indicates that the characteristic time of oxygen diffusion comes into the calorimetric time scale of 10^2–10^6 s at 205 K on heating. In such a situation, we should have observed endothermic drifts in a temperature range of a few tens kelvin above 217 K but not over only 8 K. The reason is that the phase separation is accompanied by the diffusion of oxygen atoms over a long distance and the time scale of such a process comes close to the calorimetric time scale in a wide range as will be exemplified in the very phase separation phenomenon in the $La_2NiO_{4+\delta}$ system.[13]

B. Magnetic properties

Figure 4 shows the results of magnetic susceptibility measurements under 50 Oe. When the sample was quenched at about 25 K min^{-1} from 320 K to 5 K, the Meissner fraction started to appear at around 30 K and increased gradually with decreasing temperature and sharply below around 20 K. The two samples annealed at 250 K and then quenched to 5 K exhibited the diamagnetic Meissner effect starting at 33 K, and the longer annealing there gave rise to the larger effect while holding the starting temperature at the same 33 K. The samples annealed at 210 K after being precooled to 5 K showed the Meissner effect starting at 40 K. The difference in the annealing periods between 20 h and 42 h did not make much difference in the Meissner fractions. The most remarkable point is that the two phases stable in between 222 K and 265 K and below 222 K give definitely different superconducting-phase transition temperatures, 33 K and 40 K, respectively. This indicates also that the first-order phase transition at 222 K takes place in the oxygen-rich metallic phase in the crystal. It is noted that the superconducting-transition temperature would change with small structural modifications of ions under essentially the same arrangement of excess oxygens.

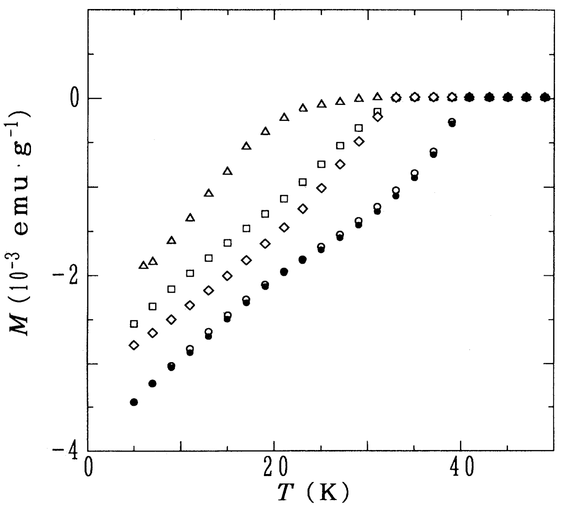

FIG. 4. Magnetization of a $La_2CuO_{4.011}$ crystal in the temperature range of 5–50 K under magnetic field of 50 Oe: △, quenched at 25 K min^{-1} from 320 K to 5 K; □, ◇, annealed at 250 K for 3 and 18 h, respectively, and then quenched; ○, ●, annealed at 210 K for 20 and 44 h, respectively, after quenching from 320 K to 5 K.

The other interesting feature is concerned with the annealing effect at 250 K after cooling from 320 K. Assuming that the anomaly around 265 K is ascribed to the martensitic phase transition as stated above, the transition is expected to proceed relatively fast but to produce microcrystalline particles due to the presence of the interfacial energies between the mother and daughter phases in the course of the transition. Then at 250 K, which is below the transition temperature region, the whole sample is necessarily in the low-temperature phase stable in between 222 K and 265 K. In fact, the enthalpy of the martensitic transition did not depend on the annealing period below 257 K. The annealing at 250 K is thus considered only to enhance the grain growth of the crystals. The annealing effects observed on the superconducting-transition temperature T_c and on the Meissner fraction are consistent with the above understanding. The T_c was independent of the annealing period: This is reasonable since crystalline particles with sizes above a certain magnitude give the same T_c. If the annealing at 250 K enhanced the diffusion of excess oxygens and the establishment of equilibrium δ at the temperature, on the other hand, the T_c would change with the annealing. The Meissner fraction increased with an increase in the annealing period: This is reasonable since the fraction depends on the grain size of the crystals. Namely, the annealing at 250 K is understood to help the removal of the defects, dislocations, and/or grain boundaries produced through the martensitic transition.

Recently, Chou *et al.* reported two superconducting phases with $T_c \approx 32$ K and 40 K, respectively, in an electrochemically oxidized $La_2CuO_{4+\delta}$ single crystal.[14] It is noted that the two temperatures are in good agreement with those found in phases stable above and below 222 K, respectively, in the present substance. More detailed information is desired to be obtained about the interrelation between the oxygen-rich metallic region of the present sample and the elecrochemically oxidized sample with large δ.

IV. CONCLUSION

Three structural phase transitions and two superconducting transitions were found in a $La_2CuO_{4.011}$ single crystal, though the phase separation process in which the two phases were formed of high and low excess-oxygen compositions was not detected. The transition at 265 K was concluded to be of the martensitic type and to proceed in the metallic oxygen-rich phase, consequently suggesting that the above phase separation potentially occurs at above 265 K. The suggestion should be confirmed in the future by high-temperature calorimetry and so on. The transition at 222 K was found to proceed also in the metallic region and between the two phases which brought superconductivity at 33 K and 40 K, respectively. This result is quite interesting in that the same superconducting-transition temperatures T_c have been reported in an electrochemically oxidized crystal with large excess-oxygen composition and in that a structural change of a displacive type could cause the large difference in the T_c. Raman scattering studies and so on are attractive for examining how the structures such as the Cu-apical oxygen distance change through the transition as attributable to different T_c's.

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