

Pressure dependence of phase-transition temperatures in oxygenated single-crystalline $\text{La}_2\text{CuO}_{4.035}$

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The pressure dependence of the phase-transition temperatures for oxygenated $\text{La}_2\text{CuO}_{4.035}$ single crystals was investigated in the pressure range < 14 kbar. Three successive phase transitions, one at 295 K with second-order character, one around 265 K with martensitic-transition character, and the other around 222 K with first-order character, were found to be suppressed under pressure. The pressure coefficient of the superconducting temperature dT_c/dp turned from -0.5 to $+0.7$ K/kbar when the three successive phase transitions were suppressed by pressure.

The phase transitions and phase transformations in oxygenated $\text{La}_2\text{CuO}_{4+\delta}$ are very interesting from the viewpoints of physics and chemistry. Previously, many reports^{1–10} have focused on the phase diagram for this system, i.e., phase separation, phase transition, and magnetic phase transition with the change in δ . These results are summarized as follows. (1) The miscibility gap does appear in the range $\delta \geq 0.01$. (2) The tetragonal ($I4/mmm$)-orthorhombic ($Bmab$) transition temperature decreases with the increase in δ . (3) A phase-separation-like behavior becomes prominent below 260 K for the oxygenated samples. There are two ways of understanding the “phase separation” results obtained around 260 K from the neutron-diffraction analysis of single and polycrystalline $\text{La}_2\text{CuO}_{4+\delta}$ samples that were oxygenated both by high oxygen pressure treatment and electrochemical oxidation techniques. One hypothesis is that the separation of the $Bmab$ phase into an oxygen-poor $Bmab$ phase and an oxygen-rich $Fmmm$ phase occurs below 260 K. Around this temperature, a sharp peak appears in the magnetic susceptibility corresponding to an antiferromagnetic ordering of lightly tilted Cu spins. Another theory is that the $Bmab$ phase separates into oxygen-poor and oxygen-rich $Bmab$ phases. The oxygen ion is thought to migrate through the lattice, since the phase-separation behaviors are considered to be caused by the disproportionation of excess oxygen ions.

Recently our calorimetric and resistometric studies^{11,12} revealed that oxygenated single-crystalline samples show a rather interesting transition behavior. When excess oxygen is introduced in the sample, second-order transitions, martensitic phase transitions, and first-order transitions appear above 200 K. However, precise adiabatic heat-capacity measurements below 320 K could not detect the glass transition that would indicate the freezing of the positional disorder of migrating ions. In the oxygenated sample, the following three successive phase transitions occur: a second-order transition at 295 K ($\delta=0.035$) and 287 K ($\delta=0.011$), martensitic transition at 250–270 K, and a first-order transition around 222 K. From the results of the magnitude of enthalpy change and temperature drift after several precooling conditions, we could not confirm the sign of oxygen diffusion, although previous reports indicate that phase separation does occur in the vicinity of 260 K. Therefore, we concluded that these three phase transitions have displacive

characters. Recently, Kremer and co-workers^{4,7,8} reported that the phase separation is of an electronic and percolative nature, based on resistivity and susceptibility measurements below 420 K.

Another interesting phenomenon for the $\text{La}_2\text{CuO}_{4+\delta}$ sample is the change in the superconducting transition temperature by the annealing around 200 K.^{4,5,7} Ahrens *et al.*⁵ pointed out that T_c depends on the cooling rate around 195 K. The slowly cooled sample and rapidly cooled samples, respectively, show T_c 's ~ 33 and 29 K. For this change, freezing-in of the hole clusters at 180 K as well as the excess oxygen ions around 220 K has been proposed.^{4,7} NQR measurements for ^{139}La also revealed the appearance of a metallic phase below 200 K.⁶ The origin of the annealing effect for $\text{La}_2\text{CuO}_{4+\delta}$ has been elucidated in our previous report;¹² that is, the experience of the first-order phase transition at 222 K increases the superconducting transition temperature from 32 K (quenched sample) to 40 K (annealed at 200 K).

Such a complicated state for the interpretation of phase separation transition is related to the presence of a very small amount of excess oxygen. Since we have found that all the phase transitions above 200 K have the displacive character, it is very interesting to investigate the effect of external pressure on the phase transitions and the relationship between the phase transition temperatures at higher temperature and superconducting transition temperature. In this paper, we report the results of pressure dependence of the resistivity measurements for oxygenated $\text{La}_2\text{CuO}_{4.035}$.

The single crystalline sample with a 6-mm diameter and a 30-mm length was prepared by the traveling solvent floating zone method. The details of the experimental conditions are almost the same as reported in the previous paper.^{11,13} Stoichiometric mixture of La_2O_3 (99.99% pure) and CuO (99.99% pure) were thoroughly mixed and calcined at 1123 K. Then the calcined powder was pressed into a cylindrical shape with a 6-mm diameter and sintered at 1373 K and used as both the feed and seed rods. Growth conditions involve growth rate of 1.0 mm h^{-1} , solvent composition of 78 mol % CuO , and 0.2 MPa O_2 gas. Oxygenation of the pristine crystal was carried out by the heat treatment under 600 atm of pure oxygen gas for a week. The oxygen content of the obtained sample was determined by the

iodometry and the composition was found to be $\text{La}_2\text{CuO}_{4.035}$. Measurements of resistance were carried out along both the a and c axes of the crystal with a cooling and heating rate of 0.6 K/min. Since the size of the single crystal used for the resistance measurement was too small to calculate the exact resistivity, we did not transform the raw resistance data to the resistivity. Maximum pressure applied for the sample was 18 kbar at room temperature and the pressure was monitored by the change in the resistance of the manganese wire. Resistance measurements were carried out for pressures 0.0, 1.3, 3.0, 4.7, 6.6, 8.3, and 11.0 kbar at 273 K and 0.0, 3.8, 6.6, 11.1, and 13.1 kbar around T_c . The pressure loss for the employed high pressure vessel with the temperature decrease from room temperature to helium temperature was about 4 kbar. Details of the experimental procedure for high pressure are given in our previous paper.^{14,15}

Figure 1 shows the pressure dependence of the resistance along the a and c axes above 180 K. As found in our previous reports,^{11,12} three successive phase transitions are observable at 295, 250–270, and below 222 K at ambient pressure. The value in the figure show the pressures at 273 K. The inset in Fig. 1(b) shows the pressure change with temperature. The temperature of the second-order transition at 295 K first increases up to 305 K with increasing pressure then vanishes. The temperature of the martensitic transition around 250–270 K increases with pressure then vanishes. Although the resistance change corresponding to the first-order transition at 222 K is not so clear compared to other two phase transitions, very small slope change and temperature hysteresis loop could be observed in the temperature range 222 and 190 K. This phase transition disappears at pressures greater than 8 kbar. Figure 2 shows the variation of superconducting transition temperature with pressure. The pressure dependence of T_c changes from -0.5 to $+0.7$ K/kbar at the pressure of 4 kbar which corresponds to the pressure 8 kbar at 273 K. The rise in the transition temperatures for two successive phase transitions above 250 K and their disappearance at higher pressure may be interpreted as follows. As mentioned above, all three phase transitions above 200 K have the displacive character, i.e., accompanying no diffusion or migration of oxygen ions. We should assume that the disproportionation of the sample into excess-oxygen-rich and excess-oxygen-poor regions would occur between the temperatures of the $I4/mmm$ - $Bmab$ transition and 320 K, which was the maximum temperature of our heat-capacity measurement.¹¹ The nature of the second-order transition at 295 K is not clear at all since the structured change and thermal anomaly are very small. When this phase transition disappears with increasing pressure, metallic conductivity appears at all temperatures above 200 K. Since we cannot detect the phase transition in the resistivity along the a axis at 295 K, this second-order transition induces a two-dimensional character although the mechanism of the transition is completely obscure. The martensitic phase transition synchronously disappears as well as the second-order transition when the pressure increases. This phase transition is observed along both a and c axes. According to the neutron

diffraction data,¹⁰ reflection lines of (006), (014), and (100) show the changes in both integrated intensity and line width at 260 K. These changes have been interpreted as due to the phase separation into oxygen-rich $Bmab$ phase and nearly stoichiometric antiferromagnetic $Bmab$ phase or due to the effect of small domain. The change or jump in lattice parameter along the c axis is most prominent around 260 K. If we accept their second view for the

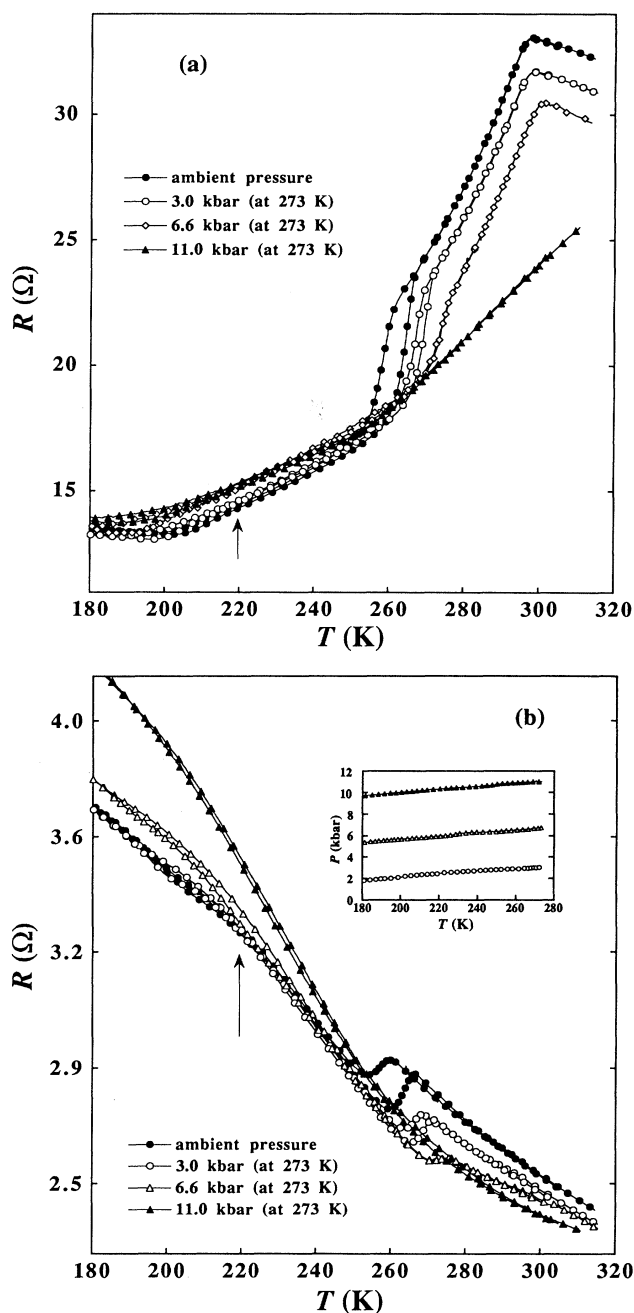


FIG. 1. Typical curves for the temperature dependence of resistance of $\text{La}_2\text{CuO}_{4.035}$ along the c direction (a) and the a direction (b) above 180 K. Arrows in this figure show 222 K where first-order phase transition occurs. The inset shows the pressure monitored by the manganese wire.

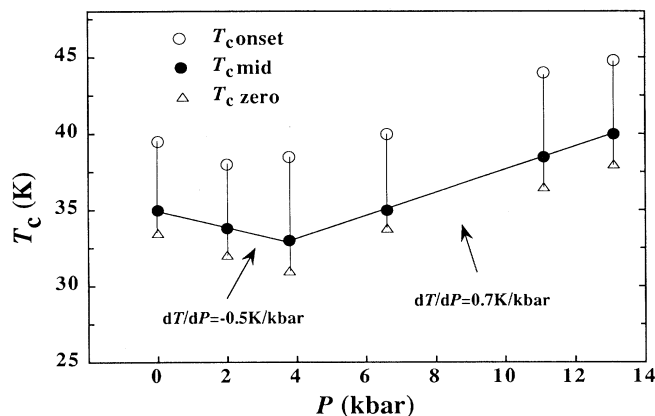


FIG. 2. Pressure dependence of the superconducting transition temperature. The pressure of the abscissa indicates the pressure at the superconducting transition temperature.

neutron diffraction data, i.e., the formation of a small domain in the crystal below 260 K, the formation might be attributed to the cooperative Jahn-Teller distortion of Cu^{2+} ions along the c axis due to the localization of holes with decreasing temperature in the oxygen-poor region. Since such a phase transition is considered to produce the interfacial energy between the mother and daughter phases and proceed fairly fast, martensitic character may be observed, i.e., the transition proceeds in a short time to a certain quasi equilibrium state. Application of the external pressure enhances the phase transition temperatures as shown in Fig. 1. This implies that the external stress works to cancel the internal stress induced by the transition. Figure 3 shows the pressure dependence of the martensitic transition temperature determined for the resistive change with temperature along the c axis. This figure clearly shows that martensitic transition temperature disappears at 8 kbar. Therefore, 8 kbar and 273 K are the critical pressure and temperature where the deformation stress of the mother phase becomes equal to the stress required to induce the transition. Above this temperature under 8 kbar, the mother phase would suffer from elastic deformation before the external stress induces the transition.

Comparing the results in Figs. 1 and 2, we can recognize the close relation between the sign of dT_c/dp versus phase transitions above 200 K. When three phase transitions remain under pressure ($p < 8$ kbar at 273 K), negative pressure dependence appears. On the contrary, when these phase transitions disappear ($p > 8$ kbar) positive temperature dependence appears. Therefore, we can conclude here that application of pressure plays the same role as electrochemical oxidation and annealing at 200 K, which enhances the superconductivity transition temperature up to 40 K.

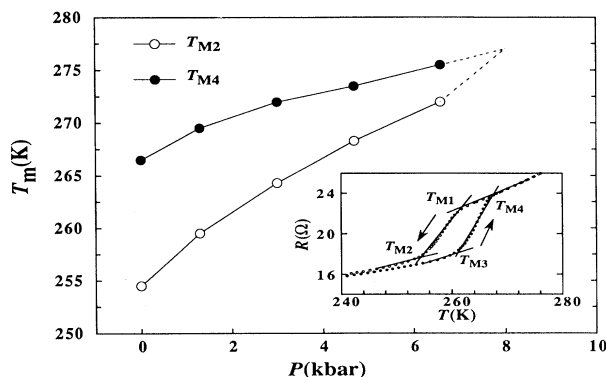


FIG. 3. Pressure dependence of the martensitic transition temperature determined from the resistivity along the c axis. The inset shows the definition of T_{Mn} ($n = 1, 2, 3, 4$).

In conclusion, the effect of application of isostatic pressure on the resistance of $\text{La}_2\text{CuO}_{4.035}$ single crystal is prominent in the phase transitions above 200 K. At a pressure greater than 8 kbar, phase transitions above 200 K disappear. When the sample experiences these phase transitions at higher temperatures, it shows pressure dependence of T_c , $dT_c/dp = -0.5$ K/kbar. On the contrary, when the sample does not experience these phase transitions at higher temperature, it shows a positive temperature dependence of $+0.7$ K/kbar. Using the compressibility data for La_2CuO_4 ,¹⁶ the volume change due to a compression up to 10 kbar is about 0.7%. This small volume decrease with pressure would be effective for the displacive phase transition at $T > 200$ K. Pressure dependence of T_c may reflect the effects not only the external pressure but also the internal pressure required for the displacive transition at high temperature, especially the martensitic phase transition at 265 K. Recently, we have investigated the electrical properties of electrochemically oxidized single crystalline, $\text{La}_2\text{CuO}_{4+\delta}$ and found that phase transitions above 200 K are clearly depressed with increasing δ .¹⁷ The small dT_c/dp for the electrochemically oxidized $\text{La}_2\text{CuO}_{4+\delta}$ (Ref. 18) and $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ (Ref. 19) may imply that the T_c under pressure may saturate in the higher pressure region $p > 15$ kbar. Inelastic neutron scattering experiment for the single crystalline $\text{La}_2\text{CuO}_{4+\delta}$ may elucidate the mechanism of phase transition.

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