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Superconductivity in the Ladder Material $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$

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We have observed superconductivity in the ladder material $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$ under pressures of 3 GPa and 4.5 GPa by means of electrical measurements. The superconducting transition temperatures T_c (onset) are 12 K and 9 K at 3 and 4.5 GPa, respectively. The superconducting volume fraction was obtained to be about 5% from magnetization measurement under 3.5 GPa at 4.2 K, indicating the bulk nature of the superconductivity in this system.

KEYWORDS: superconductivity, ladder system, $(Sr, Ca)_{14}Cu_{24}O_{41-\delta}$ high-pressure experiment

All high-T_c superconductors found so far are composed of two-dimensional (2D) CuO_2 planes. In this letter we report a new superconductor containing not CuO_2 planes but quasi-one dimensional (1D) Cu_2O_3 ladders.

The ladder, which is described as spin 1/2 chains antiferromagnetically interacting along legs and rungs, was proposed as an interesting intermediate step between 1D and 2D systems.[1-5] Daggoto *et al.* and Rice *et al.* suggested that the ladder system is in a spin liquid state and has a gap in the spin excitation spectrum (spin gap).[1,2] They also concluded that when holes are lightly doped, the spin gap would remain and superconductivity possibly occurs. Experimentally the existence of the spin gap has generally been recognized.[6-8] Hiroi and Takano reported that the ladder material $LaCuO_{2.5}$ showed clear insulator-metal transition upon hole carrier doping by substitution of Sr^{2+} for La^{3+} but no sign of superconductivity was observed.[9] By NMR and μSR measurements, the ground state of this material has been shown to be a three-dimensional (3D) Néel state rather than a spin liquid state, probably due to the relatively strong inter-ladder coupling.[10,11] Therefore, there remains unsolved whether superconductivity can be realized in a doped-ladder system.

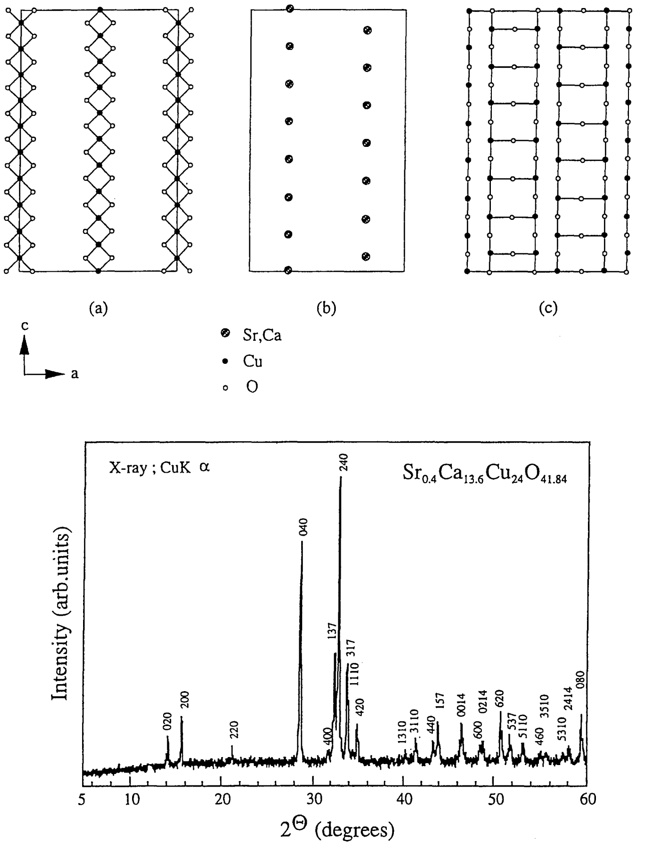

Fig. 1. Upper panel: The crystal structure of $(Sr, Ca)_{14}Cu_{24}O_{41-\delta}$ divided to each layer. (a) The layer containing 1D-CuO_2 chains, (b) (Sr, Ca) layer, (c) Cu_2O_3 layer (two-leg ladder). Lower panel: X-ray powder diffraction pattern of $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$.

The ladder material $(Sr, Ca)_{14}Cu_{24}O_{41-\delta}$ was first reported by McCarron *et al.* and Siegrist *et al.*[12,13] This phase is composed of 1D-CuO_2 chains (1D-chain), (Sr, Ca) layers and Cu_2O_3 layers (two-leg ladder) (see upper panel of Fig. 1) and the crystal symmetry is orthorhombic. The layers are stacked along the *b*-axis (perpendicular to the paper of Fig. 1) in the sequence (Sr, Ca) layer-ladder-(Sr, Ca) layer-1D-chain-(Sr, Ca) layer, with a spacing of ~ 1.6 Å. NMR and neutron scattering experiments have shown the existence of a spin gap in both the 1D-chain and ladder sites of $Sr_{14}Cu_{24}O_{41-\delta}$.[14-17] The value of the spin gap (36 meV according to neutron scattering results) of the ladder is comparable with that of the ladder material $SrCu_2O_3$.[7,15,16] The main feature of this material is that the Cu formal valence is +2.25 i.e., hole carriers are inherently doped and the conductivity increases with increasing Ca content.[18] The electrical resistivity of $Sr_4Ca_{10}Cu_{24}O_{41-\delta}$ single crystal (this composition represents the Ca-substitution limit when

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synthesized under 1 atm O_2) at room temperature is as low as $\sim 10^{-3}$ ($\Omega \cdot$ cm) parallel to the ladder direction.[19] However, the T-dependence of the electrical resistivity remains semiconducting. We report in this letter that the Ca-substitution limit can be extended up to 13.6 under an O_2 partial pressure of $P_{O_2} = 400$ atm using a furnace for hot isostatic pressing (HIP) and that a $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$ sample shows superconductivity under pressures of 3 GPa and 4.5 GPa.

A sample with nominal composition $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41-\delta}$ was synthesized from $SrCO_3$, $CaCO_3$ and CuO powders with purities higher than 99.9%. The powder mixture was calcined at 1000°C for 50 h under flowing O_2 and ground 4 times. Then, the resultant pellet was sintered at 1200°C for 8 h in 20%O_2+80%Ar at a total pressure of 2000 atm ($P_{O_2} = 400$ atm) using a furnace for HIP. The oxygen content was determined by the inert gas fusion-infrared absorption method.

A cubic-anvil apparatus[20] was used for the susceptibility and electrical resistivity measurements. The sample was placed in a teflon cell filled with a fluid pressure transmitting medium, a mixture of Fluorinert FC70 and FC77, to maintain hydrostatic pressure.

Electrical resistivity measurements were carried out using the standard four-probe method. Magnetic susceptibility data were obtained from AC susceptibility measurements carried out using primary and secondary coils wound around the sample. The data were collected as output signals of a lock-in amplifier.

The X-ray powder diffraction pattern of $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$ is shown in the lower panel of Fig. 1. All peaks could be indexed, showing that this sample is single phase. The lattice parameters a, b and c are 11.14, 12.44 and 27.02 Å, respectively, at ambient pressure. The c-axis length was calculated from (0 0 $7n$) (n=integer) reflections which indicate the c-axis length of the ladder because the 1D-chain and ladder are linked incommensurately.[12, 13] Figure 2 shows the T-dependence of the electrical resistivities under pressures of 0, 1.5, 2 and 3 GPa. The values of the electrical resistivities at room temperature decrease monotonically with increasing pressure. The T-dependence of the electrical resistivities under 0 and 1.5 GPa is almost flat above 200 K and shows a broad maximum at ~110 K. A similar broad peak has also been observed in the nearly metallic ladder compound $(Sr_{0.4}Ca_{0.6})_{14}Cu_{19.2}Co_{4.8}O_{41-\delta}$.[21] Therefore, this similar broad peak may be a characteristic feature of this system just before the metallic state, although the origin is unclear. Finally the electrical resistivities increase again below ~60 K and ~30 K, respectively, under 0 and 1.5 GPa. The T-dependence of the electrical resistivity under 2 GPa is metallic above 150 K and shows similar behavior to that under 1.5 GPa below 150 K. The superconducting transition occurs at 12 K under 3 GPa with metallic behavior above T_c and the zero resistivity temperature is 8 K. Fig. 3 shows the T-dependence of the electrical resistivities under 3, 4.5 and 6 GPa below 50 K. It can be clearly seen that the values of T_c (onset) are decrease from 12 K to 9 K with increase in the applied pressure from 3 to 4.5 GPa. Finally, the superconducting transition disappears at an applied pressure of 6 GPa.

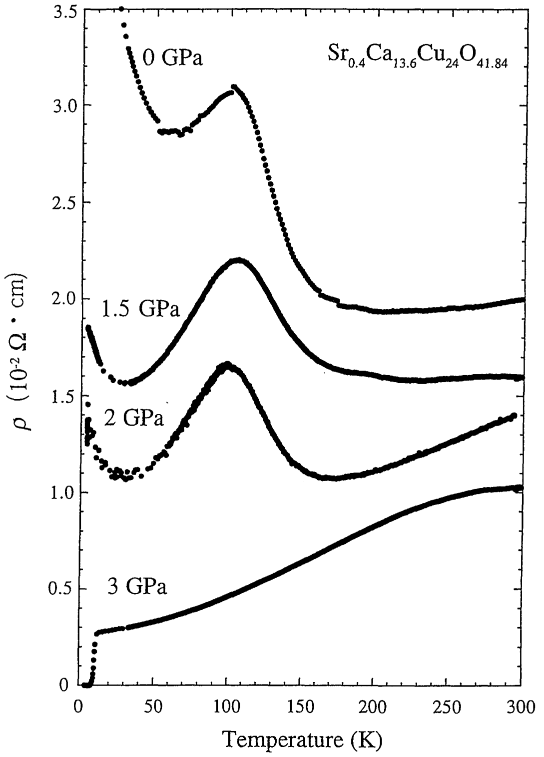

Fig. 2. T-dependence of the electrical resistivities ρ of $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$ under pressures of 0, 1.5, 2 and 3 GPa.

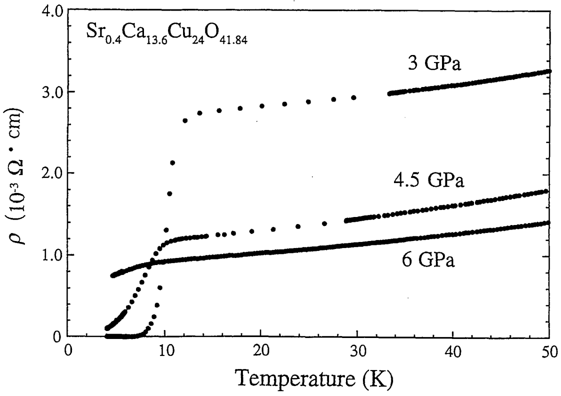

Fig. 3. T-dependence of the electrical resistivities ρ of $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$ under pressures of 3, 4.5 and 6 GPa below 50 K.

The change in the electrical property with pressure variation is in contrast to that of high-T_c copper oxide superconductor (HTCS). In the case of HTCS, the application of pressure does not cause the insulator-superconductor-metal transition unless the doping concentration is varied. To discuss the transport properties in detail, it is necessary to clarify in which sites, 1D-chain or ladder, the mobile hole carriers mainly responsible for the superconductivity are located. Kato *et al.* assumed that hole carriers are almost entirely situated at 1D-chain sites in non-Ca-doped $Sr_{14}Cu_{24}O_{41-\delta}$ and they are released into ladder sites with increasing Ca content, accompanying the shrinkage of the lattice and the increase in conductivity.[22] This assumption is supported by bond-valence-sum calculations.[22] If this assumption is true, a sufficient number of hole carriers to yield metallic conduction

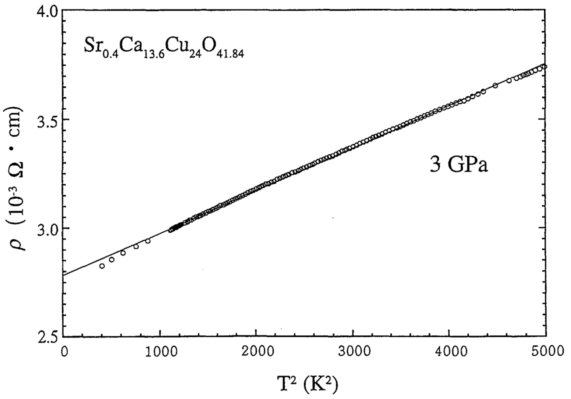

Fig. 4. T^2 plot of electrical resistivity ρ of $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$ under pressure of 3 GPa. The solid line shows the linear fitting.

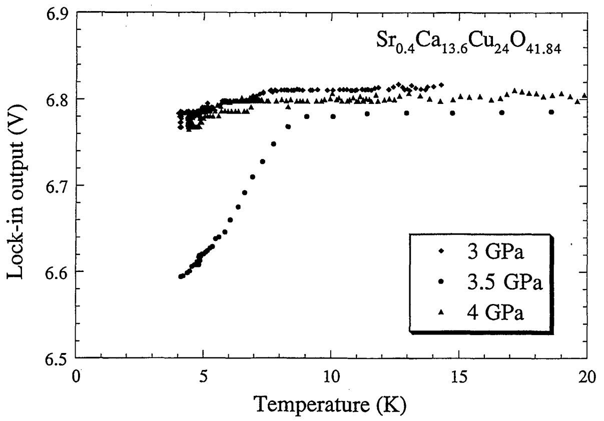

Fig. 5. Output signals of a lock-in amplifier (AC susceptibility) under 3, 3.5 and 4 GPa.

and also superconductivity are released into ladder sites when pressure is applied, because the lattice should be shrunk by applying pressure as well as by Ca-doping. On the other hand, Kitaoka *et al.* claim based on NMR and NQR measurements, that the hole carriers are situated almost entirely in the ladder sites.[23] In this case, sufficient hole carriers for superconductivity already exist in the ladder sites but are localized by the random potential, and the transfer energy increases enough to screen the random potential under application of pressure and superconductivity appears.

Next, we note that the electrical resistivity under 3 GPa between 20 and 70 K is proportional to T^2 as shown in Fig. 4. This is reminiscent of the behavior of an "over-doped" region in HTCS. Actually T_c decreases when pressures above 3 GPa are applied as shown in Fig. 3. Therefore, T_c should be increased to a greater degree in this system when the carrier concentration is optimum.

Figure 5 shows the T-dependence of the output signals of the lock-in amplifier (AC susceptibility) under 3, 3.5 and 4 GPa. A diamagnetic signal was observed at 9 K under 3.5 GPa. The superconducting volume fraction was calculated to be about 5% at 4.2 K under 3.5 GPa from comparison measured for Pb under the same conditions, demonstrating the bulk nature of the superconductivity of this compound. The rather small Meissner volume fraction may be due to the deviation from the optimum carrier concentration for superconductivity, which is indicated by the T^2-type electrical resistivity. Under 3 and 4 GPa, only weak diamagnetic signals were observed. In the case of electrical measurements, superconductivity can be observed when only one superconducting path passes through the sample. Therefore, superconductivity was observed over a wider pressure range by electrical measurement than by magnetic measurement. This demonstrates that bulk superconductivity in this system is realized in a very narrow pressure range, i.e., around 3.5 GPa.

To verify the spin gap under pressure, NMR and neutron scattering measurements should be performed under pressure.

In summary, we have observed superconductivity in the ladder material $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$ under pressures of 3 GPa and 4.5 GPa. The results of magnetization measurements suggest that the bulk superconductivity in this system is realized in a very narrow pressure range, i.e., around 3.5 GPa.

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