Substitution Effects of Cobalt on the Electrical Resistivity of $Sr_{14}Cu_{24}O_{41}$

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Abstract

Substitution effects of cobalt for copper on the electrical resistivity in two-legged ladder compound, $Sr_{14}Cu_{24-x}Co_xO_{41}$ are investigated. Polycrystalline samples of single phase with cobalt concentration up to $x = 5$ are prepared. The electrical resistivity of $Sr_{14}Cu_{24-x}Co_xO_{41}$ for all x shows semiconductive behavior. It is found, however, that for cobalt concentration with $x \geq 3$ the value of the resistivity decreases with cobalt concentration x. The effect of cobalt substitution with $x = 5$ on resistivity is almost equivalent to that of Ca substitution for Sr with $y = 6$ in $Sr_{14-y}Ca_yCu_{24}O_{41}$.

Key words: $Sr_{14}Cu_{24}O_{41}$; substitution effect; carrier doping

The compound $Sr_{14}Cu_{24}O_{41}$ has a unique crystal structure with two leg Cu_2O_3 ladders and CuO_2 chains. This compound has attracted much attention, particularly because superconductivity was discovered in a highly Ca substituted sample, $Sr_{14-x}Ca_xCu_{24}O_{41}$ under high pressure [1]. The parent compound $Sr_{14}Cu_{24}O_{41}$ shows semiconductive behavior in electrical resistivity, although in this parent compounds holes inherently exist. As Ca is substituted for Sr, the electrical resistivity decreases although nominal number of holes is unchanged, because the Sr ion and Ca ion are isovalent. It is generally accepted that the decrease of resistivity with the increase of Ca is realized by the redistribution of holes, which are initially localized in chains, to the ladders [2,3]. However, it is not certain that the exact roles of Ca substitution are fully understood. And we are not aware of another effective method of hole doping to the ladders in this compound. However, before the discovery of superconductivity in this compound a metal-insulator transition is reported for $(Sr_{0.4}Ca_{0.6})_{14}Cu_{24-x}Co_xO_{41-\delta}$ with cobalt substitution after high pressure O_2 annealing [4]. This result is not simply understandable, because the valence of cobalt ion is supposed to be +3 and this should rather lead to the decrease of hole number even after high-pressure O_2 annealing.

This compound is also unique from the standpoint of magnetism. It is revealed that both the ladders and the chains have spin gaps. In the system which has a spin gap like spin Peierls compounds, it is reported that slightly doped impurity induces antiferromagnetism without destroying the spin gap. In $Sr_{14-y}Ca_yCu_{24}O_{41}$ with high Ca concentration an antiferromagnetism is observed at a low temperature, e.g. at 2 K for y=11.5, which is low compared to the spin gap energies of both chains and ladders [5]. This antiferromagnetism is regarded as a similar phenomenon mentioned above, but the true nature is yet to be revealed. To better understand these points, it is helpful to investigate the effect of the substitution of other elements for copper site on the transport properties and magnetism. Recently the effects of nonmagnetic ion substitution for Cu in $Sr_{14}Cu_{24}O_{41}$ were reported[6]. When Ga and Zn were substituted for Cu, the decrease of resistivity was observed. In this paper we report the electrical resistivity and magnetic susceptibility measurements for cobalt substituted samples $Sr_{14}Cu_{24-x}Co_xO_{41}$.

Polycrystalline samples of $Sr_{14}Cu_{24-x}Co_xO_{41}$ with

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$0 \leq x \leq 5$ were prepared by usual solid state reaction. Starting materials were $SrCO_3$, $CaCO_3$, CuO and CoO with purities higher than 99.9 %. They were mixed and heated in flowing oxygen at between 950 and 990 °C. Some of them were annealed in Ar. Samples with cobalt concentration $x \leq 5$ were confirmed to be single phases by X-ray diffraction measurements. We tried to prepare samples with higher cobalt concentration, but did not succeed. Electrical resistivity was measured by the usual dc four probe method. Magnetic susceptibility was measured with a SQUID magnetometer.

The lattice parameters were obtained by X-ray powder diffraction measurements. For cobalt substitution the lattice parameters of a, b and c axes keep almost constant, respectively. However, slight tendency for decrease of the lattice parameters for all axes with the increase of the cobalt concentration is seen. For instance, lattice parameter of a axis is about 11.48 Å and the change of the lattice parameter between $x = 0$ and $x = 5$ is less than 0.01 Å. While the lattice parameter of a axis of $Sr_{14-y}Ca_yCu_{24}O_{41}$ decreases by 0.2 Å from $y = 0$ to $y = 5$.

The results of the temperature dependence of the resistivity of $Sr_{14}Cu_{24-x}Co_xO_{41}$ are shown in Fig. 1. All samples show semiconductive behavior. As shown in the figure for lower cobalt concentration with $x \leq 2$ the value of resistivity increases with substituting cobalt. We feel that for lower cobalt concentration the value of resistivity is rather sensitive to annealing condition. Samples after annealing in Ar shows lower resistivity than that with $x = 0$, but the change is not large. For higher cobalt concentration with $x \geq 3$ the resistivity decreases as cobalt concentration increases. The decrease of the resistivity is not small. Comparing the resistivity at 150 K with the parent compound $Sr_{14}Cu_{24}O_{41}$, the decrease of the resistivity by cobalt substitution with x=5 is almost equivalent to that by Ca substitution for Sr with $y = 6$ in $Sr_{14-y}Ca_yCu_{24}O_{41}$.

The temperature dependence of magnetic susceptibility was measured. As the concentration of cobalt increases, the susceptibility increases with x systematically, due to the contribution of a Curie-Weiss term originated from the moment of cobalt ions. Because of the large Curie-Weiss term, it is difficult to extract more information on the nature of the chain and the ladder. This systematic variation seems to reflect that cobalt is substituted effectively. No trace of antiferromagnetic transition nor other anomaly was detected down to 2 K for all samples.

The large decrease by the substitution of cobalt for copper was found. The decrease of the resistivity is not small. Cobalt is seemed to be effectively substituted judging from the experimental facts. It is not clear why this large change in resistivity occurs. Although we did not confirm the change of the oxygen content, considering the valence of cobalt, it is natural to think that the total number of holes does not increase by cobalt substitution. Since the conduction is mainly determined by the ladders, we assume reasonably that the cobalt replaces the copper belonging to the chain. Considering the small change in lattice constant, the ladder is not so much disturbed by cobalt substitution. This result suggests that the decrease of the resistivity is caused by some instability that the parent compound might have [6,7].

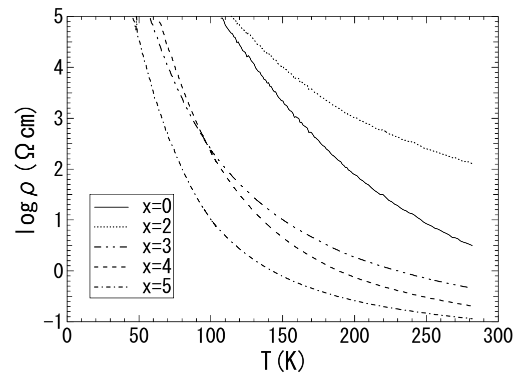

Fig. 1. Temperature dependence of the electrical resistivity for $Sr_{14}Cu_{24-x}Co_xO_{41}$ with $0 \leq x \leq 5$.

Acknowledgements

The authors thank the Materials Design and Characterization Laboratory, Institute of Solid State Physics, University of Tokyo for using the facilities.

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