Carrier density control in the $\text{La}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_{6+y}$ system

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Abstract. The effect of strontium and oxygen content variation is systematically studied in the $\text{La}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_{6+y}$ system. The reason for the absence of superconductivity in this system is discussed.

Keywords. Carrier density control; La–Sr–Cu–O.

1. Introduction

Empirical rules extracted from the currently known high T_c copper oxides seem to suggest the following necessary conditions for the occurrence of superconductivity; the presence of two-dimensional copper oxygen layers and the carrier density in the appropriate range. In the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system, for instance, superconductivity occurs for the range $0.05 < x < 0.3$, the transition temperature being highest for $x \approx 0.15$. A question may be asked whether these conditions are *necessary* and/or *sufficient* for the occurrence of high temperature superconductivity. The former part of the question is closely related to another question, whether the mechanisms of high temperature superconductivity is the same for the copper oxides and bismuth oxides. Another class of systems relevant to the question are $\text{La}_4\text{BaCu}_5\text{O}_{13-y}$ (Michel *et al* 1988), and $(\text{La}_{8-x}\text{Sr}_x)\text{Cu}_8\text{O}_{20-y}$ (Torrance *et al* 1988), having three-dimensional structure. The $\text{La}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_{6+y}$ system (Michel and Raveau 1984), which has two-dimensional copper oxygen double layers similar to those of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$, may be relevant to the latter part of the question. This system shows metallic behaviour at least around room temperature. Although it satisfies the above conditions, superconductivity is not found in this system down to 0.3 K. In this paper, we report a systematic study of this system by varying strontium and oxygen contents.

2. Structure and synthesis

The ideal structure of $\text{La}_2\text{SrCu}_2\text{O}_6$ is shown in the inset of figure 1. This structure is realized in $\text{La}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_{6+y}$ for $-0.05 < x < 0.2$. In non-ideal structures, La and Sr atoms are partially interchanged. Excess oxygen atoms occupy the site between the two CuO_2 planes. In an isostructural $\text{La}_{2-x}\text{Ca}_x\text{Cu}_2\text{O}_{6+y}$ system, the range of Ca content is much narrower, because La and Ca with their different ionic radii do not exchange their sites so easily as the La and Sr case. The range of oxygen off-stoichiometry is also much narrower for the Ca compounds, because the Ca layers do not readily accommodate excess oxygen atoms.

Samples were prepared by the standard solid-state reaction of La_2O_3 , SrCO_3 and CuO . The final heat treatment was done at 1060°C for all samples with different

Figure 1. Temperature dependence of resistivity of $\text{La}_{1.9}\text{Sr}_{1.1}\text{Cu}_2\text{O}_{6+y}$ samples with different y prepared by quenching from different temperatures. The inset shows the ideal structure of $\text{La}_2\text{SrCu}_2\text{O}_6$.

strontium contents. Best phase purity was obtained for the range of strontium content $0.05 < x < 0.15$. The compounds in the range of $0.0 < x < 0.15$ were single-phase in the X-ray criteria. Outside this range, X-ray peaks of impurity phases, particularly $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, became discernible.

3. Effect of oxygen stoichiometry

For a systematic study of the effect of oxygen stoichiometry, a batch of samples with the strontium concentration $x = 0.1$, $\text{La}_{1.9}\text{Sr}_{1.1}\text{Cu}_2\text{O}_{6+y}$ was prepared. Samples with different oxygen content were prepared from them by quenching from different annealing temperatures. After annealing in an oxygen flow in a vertical furnace at different temperatures for 20 h, the samples were quenched into liquid nitrogen. Figure 1 shows the temperature dependence of the resistivity of $\text{La}_{1.9}\text{Sr}_{1.1}\text{Cu}_2\text{O}_{6+y}$ quenched from different temperatures. All the samples show metallic behaviour around room temperature, but an upturn of resistivity is seen at low temperatures. Samples quenched from higher temperatures show higher resistivities at room temperature and higher slopes of resistivity upturn at low temperatures. The temperature coefficient of resistivity around room temperature remains metallic even for the sample quenched from the highest temperature, $T_q = 1000^\circ\text{C}$. The hole number per copper atom estimated from the Hall coefficient assuming single carrier conduction is 0.056 for this sample, which is in good agreement with $0.5x = 0.05$. Thus, the excess oxygen content is $y \approx 0$ in this high temperature-quenched sample. The behaviour of this high T_q sample is very similar to that of $\text{La}_{1.9}\text{Ca}_{1.1}\text{Cu}_2\text{O}_6$, which has virtually no excess oxygen. On the other hand, for the furnace-cooled $\text{La}_{1.9}\text{Sr}_{1.1}\text{Cu}_2\text{O}_{6+y}$ sample, the oxygen content was determined by iodometry as $y = 0.25$. This corresponds to a hole number per copper of 0.30. Thus, this furnace-cooled sample may be classified as an “overdoped” system in comparison to other copper oxide systems which show high temperature superconductivity.

Figure 2. Hall coefficient of $\text{La}_{1.9}\text{Sr}_{1.1}\text{Cu}_2\text{O}_{6+y}$ at room temperature as a function of the quenching temperature, T_q .

Figure 2 shows the Hall coefficient of $\text{La}_{1.9}\text{Sr}_{1.1}\text{Cu}_2\text{O}_{6+y}$ at room temperature as a function of T_q . The increase of Hall coefficient occurs for $T_q > 500^\circ\text{C}$. Thermogravimetric analyses show that the oxygen loss takes place above 450°C in $\text{La}_{1.9}\text{Sr}_{1.1}\text{Cu}_2\text{O}_{6+y}$. The T_q -dependence shown in figure 2 is consistent with this result. The data in figure 2 prove that the high temperature quenching process indeed decreases the hole density in this system.

Based on the chemical estimate and the Hall measurement, we can conclude that the present series of $\text{La}_{1.9}\text{Sr}_{1.1}\text{Cu}_2\text{O}_{6+y}$ samples with different T_q cover a rather wide (from “underdoped” to “overdoped”) range and that the system does not undergo superconducting transition at any hole density.

4. Effect of strontium content variation

The temperature dependences of Hall coefficients for $\text{La}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_{6+y}$ with different x -values (furnace-cooled) are shown in figure 3. Except for the sample with $x = -0.05$, the Hall coefficient is positive and its temperature dependence is weak. The drastically different behaviour of the $x = -0.05$ sample should be taken with caution at the present stage, because this sample contains $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ as an impurity phase. Elementary valence counting tells us that the hole number per copper in $\text{La}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_{6+y}$ is given by $0.5x + y$. The roughly constant Hall coefficient for $0.05 < x < 0.2$ may suggest that the oxygen content changes accordingly to compensate the change in the strontium content. The trend of the Hall coefficient toward negative sign with decreasing strontium content as seen in the $x = 0$ and -0.05 samples is opposite to the behaviour expected from the valence counting. Such behaviour may be related with the fact that the sign of Hall coefficient is negative for the three-dimensional copper oxide systems, $\text{La}_4\text{BaCu}_5\text{O}_{13-y}$ and $\text{La}_{8-x}\text{Sr}_x\text{Cu}_8\text{O}_{20-y}$ (Tamegai and Iye 1989). The excess oxygen in the $\text{La}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_{6+y}$ system would make the system more three-dimensional by connecting two neighbouring copper oxygen planes.

Figure 3. Temperature dependence of Hall coefficient in the $\text{La}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_{6+y}$ system with different strontium contents, x .

5. Conclusions

The $\text{La}_2\text{SrCu}_2\text{O}_6$ system is an outstanding exception among the layered copper oxides, in the sense that it does not show superconductivity despite that it appears to satisfy the general structural and carrier density requirements for the occurrence of high temperature superconductivity. The reason for the absence of superconductivity in the $\text{La}_2\text{SrCu}_2\text{O}_6$ system, is most likely to be sought in the detrimental effect of excess oxygen atoms inserted between CuO_2 planes. One may compare this strong suppressing effect of the midplane oxygen atoms with the relatively mild suppression of transition temperature by copper site substitutions, or the lack of magnetic pair breaking in the rare earth substitution in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ system. The low temperature upturn of resistivity in the $\text{La}_2\text{SrCu}_2\text{O}_6$ system is suggestive of weak carrier localization. While the localization effect certainly acts to suppress the potential superconductivity, whether it explains the absence of superconductivity in the $\text{La}_2\text{SrCu}_2\text{O}_6$ remains to be seen. In this context, it would be interesting if one can dope the $\text{La}_2\text{SrCu}_2\text{O}_6$ system without introducing excess oxygen atoms, or prepare samples with ordering of excess oxygen atoms.

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