Study on the normal state resistivity of doped Ru-1222 system

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The present work investigates the effect of Sb substitution on the transport properties $Ru_{1-x}Sb_xSr_2Gd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ system. The onset superconducting transition temperature is found to decrease with Sb substitution. The normal state resistivity data could be described by 3D variable range hopping in lower temperature region (below T_M) and small polaron hopping model in higher temperature region (above T_M).

1. Introduction

Recent discovery of the coexistence of superconductivity and ferromagnetism in a hybrid ruthenate-cuprate $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ (Ru-1222) with layered perovsikite has attracted a great deal of interest in the properties of this material [1–4]. The Ru-1222 material exhibits ferromagnetic order at a rather high temperature, $T_M = 180$ K, and becomes superconductive at $T_c = 42$ K, within the ferromagnetic order state [1]. The crystal structure of Ru-1222 evolves from the $YBa_2Cu_3O_7$ (YBCO) superconductors. The Ru ions substitute Cu(1), and only one distinct Cu site [corresponding to Cu(2)] exists with five fold pyramidal coordination. The *Y* layer in YBCO is replaced by inserting fluorite type $Gd_{1.4}Ce_{0.6}O_2$ layers, thus shift alternate perovskite blocks by (a+b)/2. The superconductivity in Ru-1222 is belived to be associated with the CuO_2 layers where some carriers are created by some Ru^{5+}/Ru^{4+} charge transfer and the ferromagnetism is proposed to originate from the canting of Ru moments in the RuO_2 layers that give a net moment perpendicular to the c-axis [1]. The RuO_2 layer in this material is at the origin of not only the ferromagnetism but also the carrier-creation mechanism. Therefore, cationic substitution for Ru in $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$should provide some important insights into the understanding of the novel properties in Ru-1222. In our previous works, we have studied the effect of doping of Ru on structural, transport and magnetic properties of Ru-1222 [5–7]. In this paper, we focus on the effects of Sb substitution for Ru on the normal state properties in Ru-1222.

2. Experimental

Polycrystalline samples of the $Ru_{1-x}Sb_xSr_2Gd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ (x = 0, 0.02, 0.05, 0.07) were synthesized by a solid-state reaction method with the starting stoichiometric powders of RuO_2, Sb_2O_3, $SrCO_3$, Gd_2O_3, CeO_2, and CuO. The mixture were thoroughly ground and die-pressed into pellets before preliminary reaction in air at 1000°C for 36 h. The resulting samples were reground, repelleted, and heated at 1070°C in flowing oxygen for a further 60 h, and finally slow cooled to room temperature. XRD patterns were measured with a Mac Science MXP18AHF X-ray diffractometer using Cu $K\alpha$ radiation. The resistance of the samples was measured using a standard four-probe method down to 4.2 K.

3. Results and discussion

The XRD patterns for the samples $Ru_{1-x}Sb_xSr_2Gd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ reveal that they are all single-phase 1222 type materials [5].

Fig. 1 shows the temperature dependence of the resistivity ρ(T) for samples $Ru_{1-x}Sb_xSr_2Gd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ (x = 0, 0.02, 0.05, 0.07). The superconducting transitions are observed in all the four samples, although the zero-resistance temperature $T_{c(0)}$ for x = 0.07 lies below 4.2 K. The onset superconducting transition temperature $T_{c(onset)}$ decreases with increasing Sb content x, and all four samples are semiconductor-like above $T_{c(onset)}$. The $T_{c(onset)}$ plotted against x is shown in Fig. 2. It can be seen that $T_{c(onset)}$ decreases with Sb doping. As Sb^{3+} substitutes Ru^{5+}, the hole concentration

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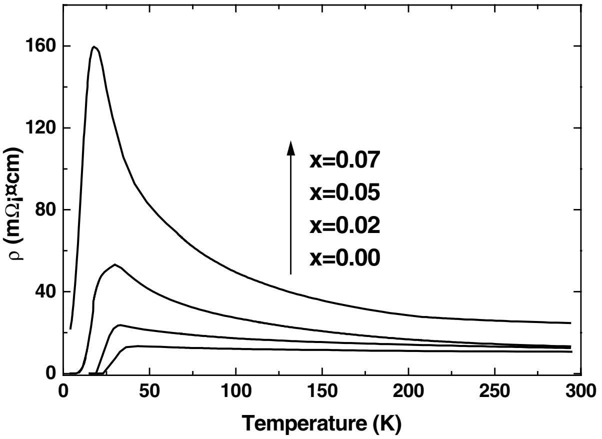

Figure 1 Variations of resistivity with temperature for $Ru_{1-x}Sb_xSr_2Gd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ samples.

in the CuO_2 planes should increase with Sb doping. In this case, the normal state resistivity of Sb doped samples should be more metal-like, and $T_{c(onset)}$ is expected to increase with Sb doping. However, the observed variations indicated that all Sb doped samples show semiconducting-like behavior and the $T_{c(onset)}$ decreases with Sb doping. The normal state resistivity (ρ_n) at 250 K plotted against x is also shown in Fig. 2. It is evident that $T_{c(onset)}$ decreases with the increase of ρ_n of samples, which may be due to the disorder-induced localization. On the other hand, there may exist magnetic trapping or scattering of the holes [8] due to the distortion of the RuO_6 octahedra in Ru-1222 [9], which has also been reported for $RuSr_2GdCu_2O_{10-\delta}$ (Ru-1212) [10, 11]. Ru-1212 is a material closely related to the Ru-1222 system. Sb doping could introduce more distortion of the RuO_6 octahedra, and lead to more magnetic trapping or scattering of the holes. Both the disorder scattering and the magnetic scattering or trapping hamper the movement of carriers and result in the hole localization. Consequently, though it increases the hole concentration, Sb doping creates enough disorder which results in the hole localization to exceed the effect of hole concentration increasing to transport properties.

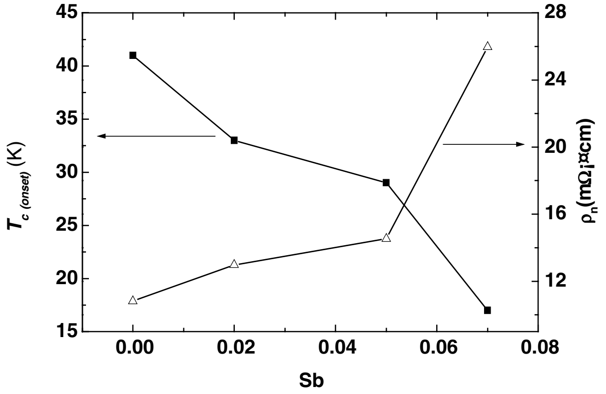

Figure 2 Sb content dependence of the onset superconducting transition temperature $T_{c(onset)}$ and normal state resistivity ρ_n measured at 250 K.

From above analysis, we can see that Sb doping not only causes a change in the microstructure but also leads to disorder to the $Ru_{1-x}Sb_xSr_2Gd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ system, which results in the increase of normal state resistivity. A careful study of the unusual normal state properties of copper oxide superconductors could improve our understanding of superconductivity and helps identify the connection between the superconductive state and the normal state. For the samples $Ru_{1-x}Sb_xSr_2Gd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$exhibiting semiconducting-like behavior in the region of normal state, we investigated the possibility of a semiconducting behavior or a variable-range-hopping (VRH) process [12]. The VRH mechanism of resistivity is given as

$$\rho = \rho_0 \exp(T_0/T)^{1/d+1} \tag{1}$$

here d is the space dimensionality for hop and $d =$ 1, 2, 3 for one, two and three dimensional system respectively. T_0 is the parameter depending on the localization length and the density of states at the Fermi level. We have examined the resistivity data for samples $Ru_{1-x}Sb_xSr_2Gd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ in the normal state region in terms of VRH theory, and found that $d = 3$ fits well to our data (see Fig. 3). It is also observed that the plots of $ln\rho$ versus $T^{-1/4}$ could be described by a single straight line below T_M (180 K) for all samples. The $ln\rho$

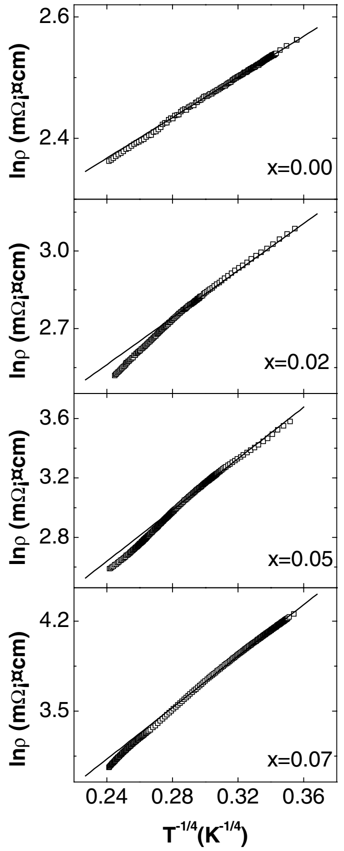

Figure 3 ln ρ~$T^{-1/4}$for $x = 0$, 0.02, 0.05 and 0.07 samples. The solid line corresponds to the best fit with VRH model below T_M (Equation 1).

TABLE I The values of the parameters T_0 and α^{-1}obtained from VRH fitting the low temperature resistivity

x	T_0 (10^3 K)	α^{-1} (Å)
0.00	1.67	14.4
0.02	4.54	10.2
0.05	8.66	8.3
0.07	10.01	7.9

deviates from the linearity at higher temperatures. The value of T_0 is found to increase with increasing x for all samples (Table I). T_0 can be described as

$$T_0 = 16\alpha^3/k_B N(E_F) \tag{2}$$

here $\alpha^{-1}$is the localization length, k_B is the Boltzmann constant, $N(E_F)$ is the density of localized states of the Fermi level which remains almost a constant. The increasing T_0 means the localization length (α^{-1}) decreases with increasing x. This implies that the degree of hole localization is enhanced with increase in disorder. To obtain the absolute value for localization length (α^{-1}) in terms of Equation 2 we need the $N(E_F)$ which could be approximated by the free electron model [13] with

$$N(E_F) = (m^*\hbar^2\pi^2)(3\pi^2 n)^{1/3} \tag{3}$$

here m^* is the effective carrier mass which is about 10 m_e since we are dealing with a strongly correlated system. n is the carrier concentration. As $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ shows the best superconducting behavior in $RuSr_2(Gd_{1+x}Ce_{1-x})Cu_2O_{10-\delta}$ system [2], it is assumed $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ is an optimally doped material with a hole content of 0.16 per CuO_2 plane and 0.32 per chemical unit cell. Hence, α^{-1}can be evaluated from Eq. 2 and 3. We can see that the localization length (α^{-1}) (Table 1) is within only a few unit cells, which indicate that VRH mechanism conforms reasonably to the conducting behavior of Ru-1222 system in the studied temperature region.

At high temperatures (above T_M), it is further observed that the resistivity data could be fitted with the small polaron hopping model [14]. This model suggests that the localized charge carriers (holes) can jump between adjacent sites if sufficient energy is acquired. The process is thus thermally activated and its temperature dependence can be described by

$$\rho = AT \exp(E/k_B T) \tag{4}$$

here E is the activation energy for hopping. In Fig. 4 we show the fitting results in terms of small polaron hopping model. The values of E obtained from the fitting results are 246 , 306 , 367 , 401 K for $x = 0.00, 0.02, 0.05, 0.07$ respectively. We can see that E increases with increasing x, which may arise from the enhanced degree of disorder due to Sb doping.

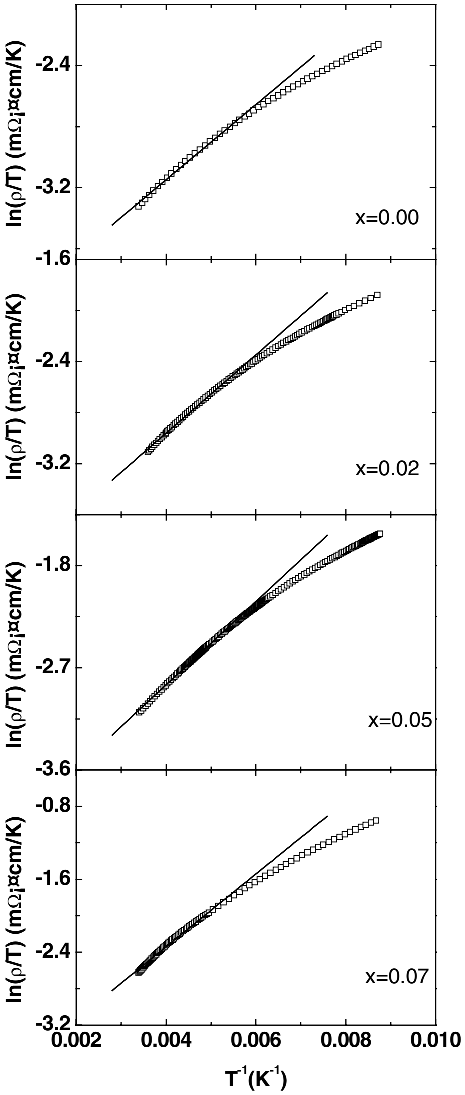

Figure 4 $\ln(\rho/T) \sim T^{-1}$for $x = 0$, 0.02, 0.05, and 0.07 samples. The solid line corresponds to the best fit with the small polaron hopping model above T_M (Equation 4).

4. Conclusions

It is found that Sb doping suppresses apparently superconductivity of the Ru-1222 system, this may reflect the increase in hole localization due to disorder effects resulted from Sb doping. The normal state resistivity at low and high temperature ranges can be described by variable range hopping (VRH) model and small polaron hopping model, respectively.

Acknowledgments

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