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Thermoelectric power of the La214 system doped with trivalent metals (Fe, Ga, Co, Cr, Mn, and Al)

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Abstract. The thermoelectric power (TEP) of the La214 system doped with trivalent metals (Fe, Ga, Co, Cr, Mn, and Al) was investigated systematically. The TEPs for the samples doped with 3d metals and sp metals show different temperature-dependent behaviours. The broad maximum in the $S(T)$ - T curve notably shifts to higher temperature upon 3d-metal (Fe, Co, Mn, and Cr) doping, while for the sp-metal (Ga and Al) doping, the broad peak is nearly unchanged. Magnetic scattering is proposed as the main factor influencing the TEP. Other possible factors are analysed and discussed in this paper.

It has been widely recognized that the temperature dependence of the thermoelectric power, $S(T)$, is an important probe of the high- T_c superconductors. A wealth of efforts have been devoted to this field. Some universal characteristics of the thermoelectric power (TEP) for high- T_c copper oxides were observed. For example, there is a universal correspondence of the room temperature TEP with the hole concentration; the zero-temperature-extrapolated value (S_0) is nonzero, which differs from the case for the conventional metals; for the materials including all of the Bi [1], Tl [2], and Hg [3] series, the TEP is linearly temperature dependent below room temperature, and the slope is not a strong function of either the material or the hole concentration. The most prominent exception is provided by the Y123 systems, whose TEP is both weaker and nonlinearly temperature dependent, and for which the slope can change from positive to negative with decreasing oxygen content [4–6]. This behaviour has been clarified as being related to the chain contribution [7]. A broad maximum in the $S(T)$ - T curve of the high- T_c superconducting cuprates below room temperature was observed prevalently, especially for the La214 system [8]; this has attracted attention widely. Many models have been proposed to account for the transport properties [9–14], and each has met with success in describing some features. But there is still no consensus on the behaviour of the TEP of high- T_c superconducting cuprates.

The La214 system provides a good stage on which to study the normal-state transport properties, especially TEP, because the La214 system possesses a simple crystal structure and single CuO₂ sheets, which avoids any contribution to the TEP from 'charge reservoirs' in the nonsuperconductive intergrowth layers. Zhou and Goodenough [15] systematically

investigated the TEP of copper oxides with single CuO_2 sheets and found that the doping of the magnetic ion at non-Cu sites has little influence on the TEP, while for the cases of elemental substitution at the Cu sites of the La214 system, only Zn and Ni dopings have been widely studied [16–18]. The shapes of the $S(T)$ – T curves are similar, and with increasing dopant (Zn or Ni) concentration, the TEP value increases for the Ni-doped system and decreases for the Zn-doped system; this may be attributed to the changes of carrier concentration caused by doping.

Previously there have been many reports on the magnetic properties and superconductivity of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ superconductors doped with 3d and sp metals [19–22]. One of the important results from this research is that the Ni doping has less effect on the spin correlation in the CuO_2 plane compared with doping with Fe, Zn, and Ga, and thus has only a weak influence on T_c . Ishikawa *et al* [23] analysed the spin-correlation energy of the La214 system doped with different elements, and pointed out that Co doping increases the spin-correlation energy, while Ni doping does not influence the energy. In addition, it is known that Ni shows an effective moment of $0.7\mu_B$ in the La214 system [24], close to that of Cu^{2+} ($0.8\mu_B$). Therefore the effect of magnetic elemental doping at the Cu site on the thermoelectric power cannot be well displayed in Ni-doped systems.

Recently we investigated the TEP of the La214 system doped with trivalent ions (Fe, Co, Mn, Cr, Ga, and Al) and found different variations in the shapes of the $S(T)$ – T curves for 3d- and sp-metal doping. Since the substitution of trivalent ions for Cu^{2+} changes the carrier concentration greatly, double doping (Co and Sr replacing Cu and La, respectively) is employed to nearly compensate for the strong decrease of carrier concentration induced by doping with trivalent ions.

Ceramic samples of $\text{La}_{1.85-x}\text{Sr}_{0.15+x}\text{Cu}_{1-x}\text{M}_x\text{O}_y$ ($M = \text{Fe, Co, Mn, Cr, Ga, Al}$) and $\text{La}_{1.6-x}\text{Sr}_{0.4+x}\text{Cu}_{1-x}\text{M}_x\text{O}_4$ ($M = \text{Fe and Ga}$) were prepared from La, Cu, Ga, Fe, Co, Cr, Al, and Mn oxides and Sr carbonates in the appropriate ratios. La_2O_3 powder was preheated to 1173 K in a furnace for five hours, and cooled to room temperature before weighing. The well-ground mixtures were pre-heated in air at 1273–1493 K for 40 h, with an intermediate grinding. Then the mixture was reground and pressed into dish-shaped pellets. The pellets were sintered in air at 1323–1523 K for one day. In order to ensure that the samples were homogeneous, the pellets were pulverized and re-pressed into pellets, sintered at 1323–1523 K for 24 hours, and then the pellets were cooled down to and kept at 1073 K in the furnace for 40 h. Finally, the samples were cooled down to room temperature.

The x-ray diffraction (XRD) analysis was carried out using a Rigaku-D/max- γ A diffractometer using high-intensity Cu $K\alpha$ radiation to screen for the presence of impurity phase and the changes in structure. The thermoelectric power, $S(T)$, was measured by a differential method. The temperature at the two ends of the measured sample was controlled automatically within a precision of 0.01 K. The emf of the sample was indicated by a Keithley 181 Nanovoltmeter with an error of the TEP measurement smaller than $0.1 \mu\text{V K}^{-1}$.

XRD analysis indicates that all of the prepared samples remain single phase. Figures 1(a) and 1(b) show the temperature dependence of the thermoelectric power for samples of $\text{La}_{1.85-x}\text{Sr}_{0.15+x}\text{Cu}_{1-x}\text{Fe}_x\text{O}_4$ ($0 \leq x \leq 0.13$) and $\text{La}_{1.85-x}\text{Sr}_{0.15+x}\text{Cu}_{1-x}\text{Ga}_x\text{O}_4$ ($0 \leq x \leq 0.10$). For the ‘parent compound’ $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, one can find that the shape of the $S(T)$ – T curve and the TEP value are very similar to those from previous reports [8]. For the Fe- and Ga-doped samples, the TEP values decrease gradually with increasing x . According to the work of Tallon *et al* [25], it can be speculated that upon doping the charge-carrier concentration of the two systems is slightly enhanced. Another interesting phenomenon is that Fe and Ga dopings lead to different modifications of the shapes of the $S(T)$ – T curves. For the Ga-doped system, the TEP curves shift down upon doping, and the temperature, T_m , corresponding to

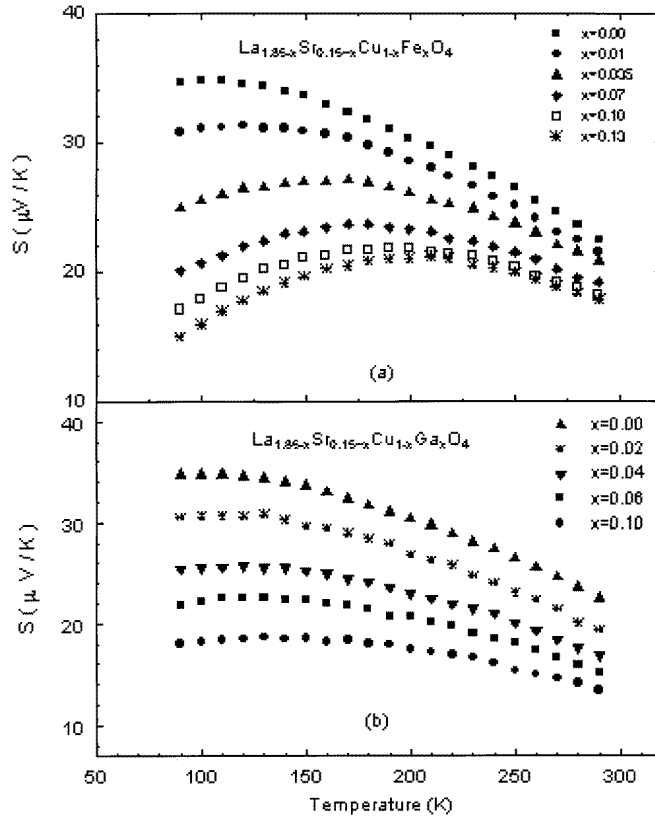


Figure 1. The temperature dependence of the thermoelectric power S for the compounds $\text{La}_{1.85-x}\text{Sr}_{0.15+x}\text{Cu}_{1-x}\text{M}_x\text{O}_4$; (a) $M = \text{Fe}$; (b) $M = \text{Ga}$.

the broad maximum in the $S(T)$ - T curve is nearly unchanged, which is similar to the case for the Zn-doped system reported previously [26, 27]; however, for the Fe-doped samples, T_m increases notably with Fe doping and the TEP at high temperatures becomes much more weakly temperature dependent, i.e., the slope (absolute value) of the $S(T)$ - T curves at high temperature decreases remarkably.

In order to account for the different variations of the TEPs for Fe- and Ga-doped systems, it is necessary to understand the nature of Fe^{3+} and Ga^{3+} ions as well as the effects of dopings with them on the electronic structure and crystal structure. First, Fe^{3+} is half-filled as regards 3d electrons ($3d^5$), while Ga^{3+} is full as regards 3d electrons ($3d^{10}$). The 3d electrons of Fe can hybridize strongly with the planar carriers. This interaction changes the shape of the ϵ - k dispersion curves near ϵ_F as a function of temperature, which can induce a marked change of the TEP. The Ga^{3+} ion, full as regards 3d electrons, only shows much weaker d-p hybridization with oxygen, so its doping has less influence on the TEP. Second, the Fe^{3+} ion has a strong magnetic moment ($4.9\mu_B$), while Ga^{3+} is a nonmagnetic ion. Although previous work [15, 28] has indicated that the TEP of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is independent of magnetic field, and that even the magnetic elemental doping at non-Cu sites ($(\text{La}_{1-x}\text{Nd}_x)_{1.85}\text{Sr}_{0.15}\text{CuO}_4$) does not influence the shape of $S(T)$ - T curves, these features do not seem to rule out the possibility that strongly local moments in the CuO_2 plane may influence the TEP. It is known that the doping with Fe^{3+} ($S = 5/2$) not only changes the spin state at the site where the Cu is replaced by Fe, but also

produces a strongly local moment in the conductive sheets. On one hand, the local magnetic moment scatters the conducting carrier. On the other hand, the introduction of a local moment (Fe^{3+}) may favour the formation of spin polarons or a decrease of the size of the polarons [29], which will lead to a decrease of the slope of the $S(T)$ - T curves, while the substitution of Ga ($3d^{10}$, $S = 0$) for Cu only produces a spin vacancy.

Third, structural analysis shows that Fe and Ga dopings change the lattice parameters in different fashions, which reflects the different interactions in these two systems. One of the results of the analyses, that the magnetic scattering may play a major role in influencing the T_m , is consistent with our previous study on $\text{Bi}_2\text{Sr}_{2-x}\text{CuO}_6$ samples [30].

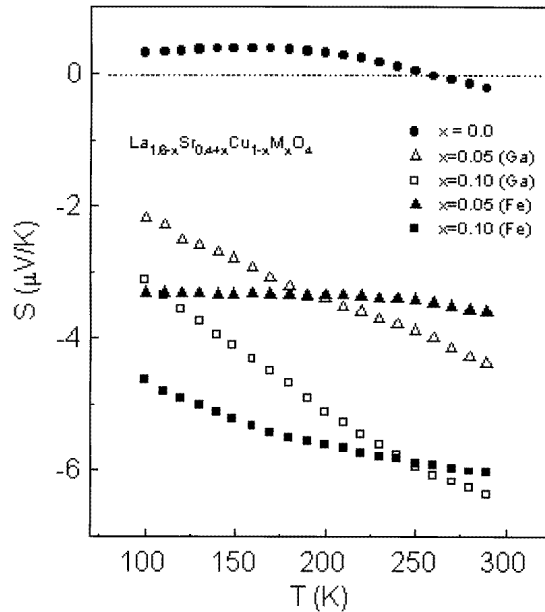


Figure 2. Thermoelectric power S versus temperature T for $\text{La}_{1.6-x}\text{Sr}_{0.4+x}\text{Cu}_{1-x}\text{M}_x\text{O}_4$ ($M = \text{Fe}$ and Ga).

Figure 2 shows the influence of Fe and Ga dopings on S versus T for overdoped $\text{La}_{1.6-x}\text{Sr}_{0.4+x}\text{Cu}_{1-x}\text{M}_x\text{O}_4$ ($M = \text{Fe}, \text{Ga}$). One can find that, upon doping, the TEP values for Fe- and Ga-doped systems all decrease to negative values. Although the broad peak in the $S(T)$ - T curves disappears, the different temperature dependences of the TEPs are still observed clearly. The absolute value of the slope of the $S(T)$ - T curve for a Fe-doped sample is much smaller than that for the corresponding Ga-doped sample. This difference is not associated with the contribution of antiferromagnetic (AF) spin fluctuations, because in this system the AF spin fluctuations are completely suppressed. Obviously this discrepancy also originates from the different interactions between dopants and charge carriers or from the different magnetic behaviours of the dopants, as analysed above.

Besides the Fe- and Ga-doped systems, we also investigated systematically systems doped with Cr, Mn, Co, and Al. Figure 3 shows typical $S(T)$ - T curves for $\text{La}_{1.75}\text{Sr}_{0.25}\text{Cu}_{0.9}\text{M}_{0.1}\text{O}_{4-\delta}$ ($M = \text{Fe}, \text{Co}, \text{Mn}, \text{Cr}, \text{Ga}, \text{Al}$) samples. For comparison, the TEP of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ is also given in this figure. Oxygen content analysis by the iodometric titration method gives $0 \leq \delta \leq 0.01$ for all of these samples, which means that the oxygen content is nearly unchanged. The dopings with Co and Al, like those with Fe and Ga, decrease the TEP value

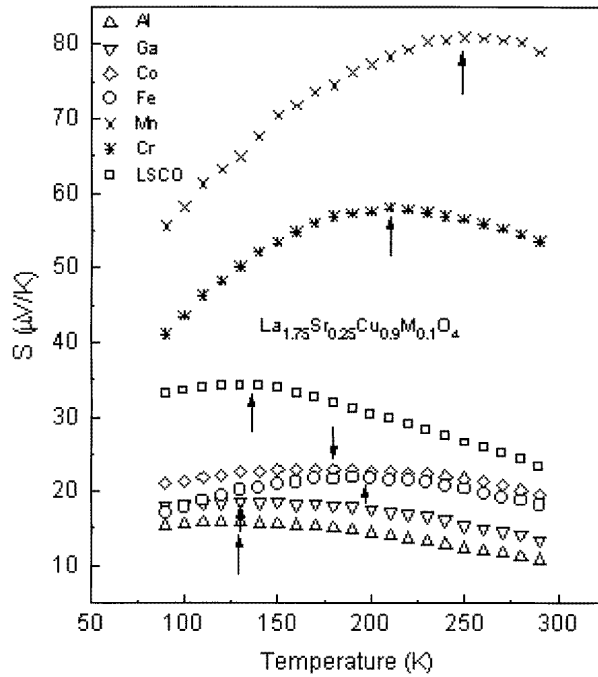


Figure 3. The thermoelectric power S as a function of temperature T for $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ and $\text{La}_{1.75}\text{Sr}_{0.25}\text{Cu}_{0.9}\text{M}_{0.1}\text{O}_{4+\delta}$ ($M = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ga}, \text{and Al}$).

gradually, while Cr and Mn dopings increase the TEP value. These changes may be related to the degree of carrier localization.

Another phenomenon that should be noted is the broad peaks in the $S(T)$ – T curves, as denoted by arrows in figure 3. The shapes of the $S(T)$ – T curves for Ga- and Al-doped samples are similar, and T_m is about 130 K—close to that for the $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ sample. In fact, the variation of $S(T)$ for $\text{La}_{1.85-x}\text{Sr}_{0.15+x}\text{Cu}_{1-x}\text{Al}_x\text{O}_4$ with increasing x is very similar to that for the Ga-doped system (see figure 1(b)), and that for the Co-doped system is very similar to that for the Fe-doped system. The T_m -values for the samples doped with Fe, Co, Mn, and Cr all increase significantly.

Regardless of the carrier concentration, it is found that the effects of 3d-metal (Fe, Co, Cr, and Mn) dopings on the TEP are very different from those of sp-metal (Ga, Al) dopings. This difference cannot be accounted for by phonon drag or mass-enhancement models. It is known that both Fe and Ga dopings (see figure 1) introduce impurity into the systems. According to the model of mass enhancement by impurity scattering, the scatterings from Fe and Ga should be similar, and the broad peaks in the $S(T)$ – T curves should be enhanced. However, just the opposite is observed.

To summarize, the effects of doping on the thermoelectric power S for the La214 system doped with 3d and sp metals have been presented above. A notable difference between $S(T)$ for magnetic elemental doping and $S(T)$ for nonmagnetic elemental doping was clearly observed. It is suggested that magnetic scattering plays a major role in influencing the TEP. Some other possible explanations were also analysed. These observations may present useful clues as regards the understanding of the transport properties of high- T_c copper oxides. Further efforts to clarify the basic effect of elemental doping on TEP are still needed.

Acknowledgments

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