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Different effects of Fe and Ga doping on T_c between the Bi2201 system and the La214 system

Xu Gaojie†‡, Pu Qirong‡, Ding Zejun‡ and Zhang Yuheng†

† Structure Research Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

‡ Department of Astronomy and Applied Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

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Abstract. Single-phase samples $Bi_{1.8}Pb_{0.2}Sr_{1.6+x}La_{0.4-x}Cu_{1-x}M_xO_y$ and $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}M_xO_y$ (M = Fe^{3+}, Ga^{3+}) were synthesized by the solid state reaction method. The crystal structure, transport properties and spin dynamics were investigated by means of x-ray diffraction (XRD), resistivity, thermoelectric power (TEP) measurement and the electron spin resonance (ESR) spectrum. It is found that Fe doping suppresses T_c more effectively in the La214 system than in the Bi2201 system, while Ga doping shows a similar effect on T_c in both the Bi2201 system and the La214 system. The different effects of Fe doping on the broad peaks in $S(T)$–T curves between the La214 system and the Bi2201 system are clearly observed, while Ga doping shows a similar influence on the broad peaks in $S(T)$–T curves. ESR results show that a strong ESR signal from Fe^{3+} spins was detected in the La214 system, but no ESR signals were observed in the Bi2201 system. It is suggested that there exist different spin dynamic behaviours between the two systems. The superconductivity and transport properties are discussed based on these experimental results.

1. Introduction

Cation substitution for Cu sites and non-Cu sites of cuprate oxides has provided important clues to the basic mechanism responsible for superconductivity. One knows that conventional superconductors are very sensitive to magnetic element doping, and a little magnetic ion doping can suppress superconductivity completely. The superconductivity of high T_c cuprate oxides seems not so sensitive to magnetic element doping at the non-Cu site as conventional superconductors. For element doping at the Cu site in CuO_2 sheets, both magnetic and non-magnetic ions can destroy the superconductivity with a few per cent dopant concentration. It has been demonstrated that the suppression of cation substitution on superconductivity originates from a magnetic pair-breaking mechanism [1]. Ishikawa *et al* pointed out that magnetic ion (such as Co^{3+}) doping enhances the nearest-neighbour spin correlation, while non-magnetic ion (Ga^{3+}, Zn^{2+}) doping decreases the spin correlation energy [2]. These results indicated that magnetic and non-magnetic element doping at the Cu site should show different influences on superconductivity and normal-state (NS) properties. Our experimental results show that the substitution of Fe for Cu suppresses the superconductivity completely at Fe concentration more than 4 at.% in the Bi2201 system, which is contrast to that in the La214 system (Fe content less than 2 at.%). On the other hand Fe doping shows different effects on the NS transport properties between the Bi2201 system and the La214 system. It is known that Fe ($3d^6\ 4s^2$) is trivalent (Fe^{3+}, $3d^5$) in the $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_y$ system and the $Bi_2Sr_2Cu_{1-x}Fe_xO_y$

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system, which was determined from the ^{57}Fe Mössbauer spectroscopy [3, 4]. In order to clarify the above great discrepancy, we analyse the electronic spin states of Fe^{3+} in the two systems, as well as the different chemical environments of CuO_2 sheets between the two systems.

2. Experimental methods

The polycrystalline samples of $Bi_2Sr_{1.6+x}La_{0.4-x}Cu_{1-x}M_xO_y$ (M = Fe, Ga, $0 \leqslant x \leqslant 0.4$) and $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}M_xO_y$ (M = Fe and Ga, $0 \leqslant x \leqslant 0.13$) were synthesized by a conventional solid state reaction method using high-purity powder of Bi_2O_3, $SrCO_3$, CuO, Fe_2O_3, Ga_2O_3 and La_2O_3. First, the appropriate mixtures of the powders were well ground and calcined for 40 hours in air at about 800–850 °C for the $Bi_2Sr_{1.6+x}La_{0.4-x}Cu_{1-x}M_xO_y$ system and 1000 °C for the $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}M_xO_y$ system with an intermediate grinding; then, the two series of powders were pressed into pellets and sintered at 880–880 °C and 1030–1100 °C respectively in air for another day; finally, the sample was cooled down to room temperature in the furnace.

Powder x-ray diffraction (XRD) patterns were obtained on a Rigaku-D/max-γA rotating target x-ray diffractometer with Cu Kα radiation ($\lambda = 0.154\,18$ nm). Lattice parameters were determined from the d-values of the XRD peaks by a standard least-squares refinement method. Resistivity as a function of temperature was measured by a four-probe method in a closed-cycle helium cryostat. Thermoelectric power (TEP), $S(T)$, was measured by a differential method [5]. The temperature at two ends of the measured sample was controlled automatically within the precision of 0.01 K, and the temperature gradient between both ends of the sample was 2 K. The emf of the sample was indicated by a Keithley 181 nanovoltmeter with an error of TEP measurement smaller than 0.1 μV K^{-1}. The electron spin resonance (ESR) experiments were carried out at 100 K by a Bruker (ER-200D-SRC) reflection X-band-type spectrometer. Microwave frequency and magnetic field were measured using a frequency counter and a proton NMR gaussmeter, respectively.

3. Experimental results

Every sample was carefully characterized by XRD and confirmed to be single phase. The oxygen content was not determined, but it should remain nearly unchanged, since double doping was performed in these systems. Fe and Ga dopants definitely substitute for the Cu site as demonstrated by the fact that the samples with Fe and Ga doping remain single phase. The fitting result of lattice parameters shows that Fe and Ga doping in both Bi2201 and La214 systems leads to the lattice constants a and b increasing monotonically and c decreasing.

Figures 1 and 2 show the temperature dependence of resistivity for Fe and Ga doped Bi2201 systems. Overall, the two systems exhibit similar transport behaviour. Both Fe and Ga doping can suppress the superconductivity completely at low dopant level. A metal–semiconductor transition takes place as the dopant concentration $x \geqslant 0.05$. The room temperature resistivity (ρ_0) increases with doping. Comparing the Fe doped system with the Ga doped system carefully we can find that the effect of Fe and Ga doping on superconductivity and ρ_0 is very different.

Figure 3 shows T_c as a function of dopant concentration x for Fe and Ga doped Bi2201 and La214 systems. One can see that Fe doping destroys the superconductivity completely with the lowest Fe concentration (x_c) about 4.5 at.% in the Bi2201 system and less than 2 at.% in La214 system, i.e. the suppression rate is about 7 K/at.% and 15 K/at.%, respectively. For Ga doped systems, x_c is about 3 at.% for both systems. This marked discrepancy between Fe

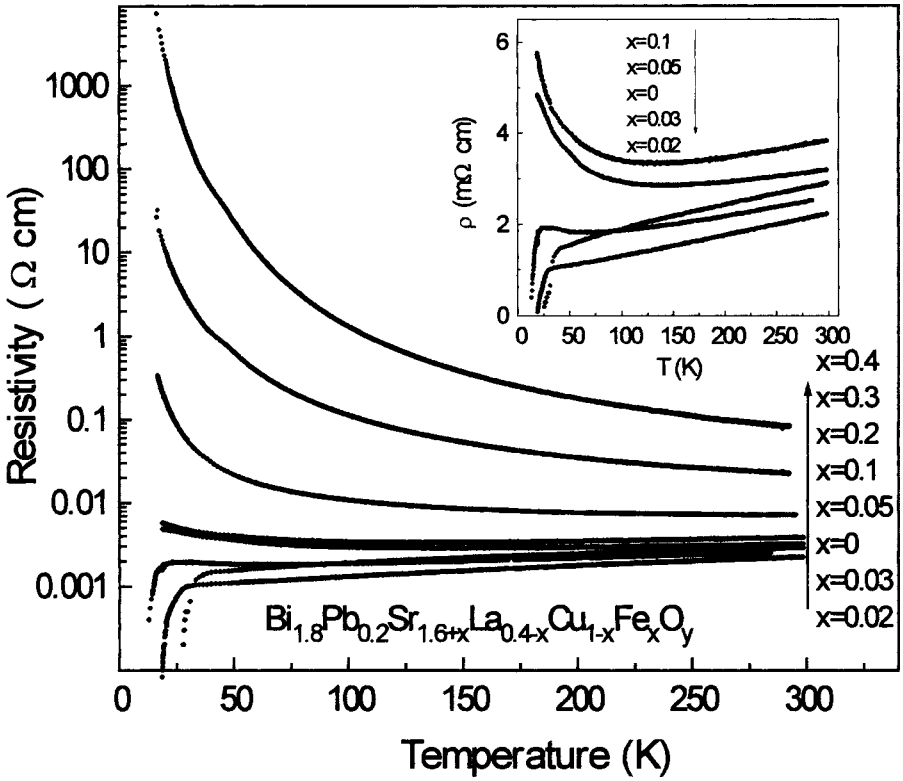

Figure 1. Temperature dependence of resistivity for samples $Bi_{1.8}Pb_{0.2}Sr_{1.6+x}La_{0.4-x}Cu_{1-x}Fe_xO_y$. The inset is the enlarged $\rho(T)$–T curves for the samples with $x = 0$, 0.02, 0.03, 0.05 and 0.1.

doped Bi2201 and La214 systems may be related to the different chemical environment and spin correlation.

Figures 4(a) and (b) show the temperature dependent TEP for Fe and Ga doped Bi2201 systems. Fe doping leads to the room temperature TEP (S_0) decreasing first, and then increasing as $x \geqslant 0.20$, while Ga doping increases the S_0 monotonically. The TEP for all the samples shows negative temperature dependence. The absolute value of dS/dT decreases gradually with increasing dopant (Fe or Ga) concentration. In these two systems we do not observe a shift of the broad peak in $S(T)$–T curves, and Fe and Ga doping results in a similar change in TEP. However, for the doped La214 system, Fe doping causes the broad maximum (corresponding temperature T_m) to shift up to high temperature from 110 to 220 K as x increases from 0 to 0.13, while the T_m for the Ga doping system is nearly unchanged (as shown in figures 5(a) and (b), which have been described elsewhere [6]).

To understand the different effects of Fe doping on the physical properties analysed above, we investigate the spin dynamics of the two Fe doped systems. Figure 6 shows the EPR signals at 100 K for the samples of the $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_y$ system and $Bi_2Sr_{1.6+x}La_{0.4-x}Cu_{1-x}Fe_xO_y$. The g factor corresponding to these lines is approximately 2.0, indicating the dominance of Fe^{3+} spins. It is found that the ESR signal intensifies gradually with increasing Fe content for the La214 system, while for the Bi2201 system no obvious ESR signals were observed for the samples with dopant Fe content changing from $x = 0$ to $x = 0.4$. Previous experimental results have indicated that Fe^{3+} in the doped La214 system is

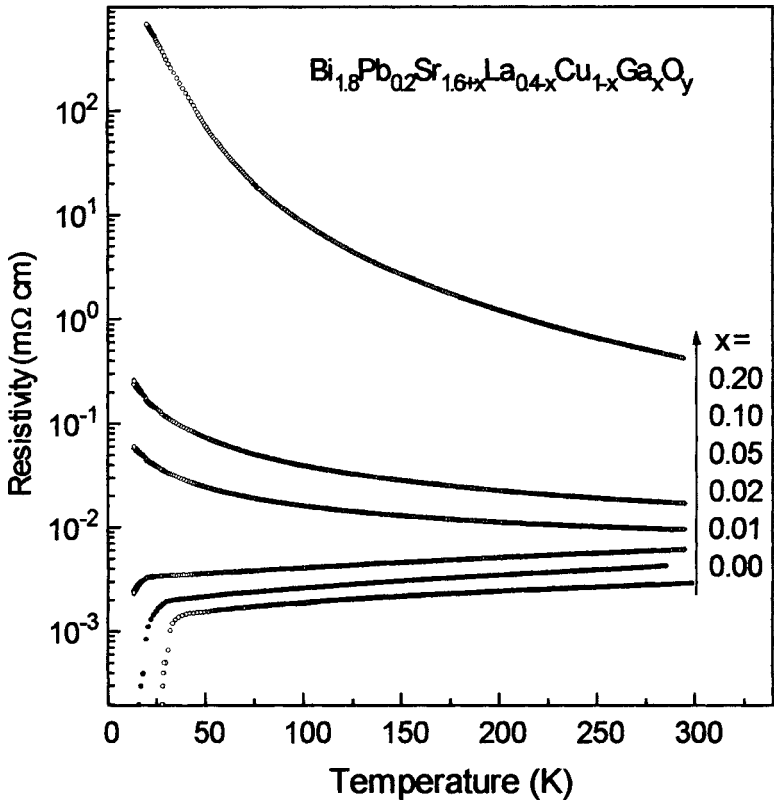

Figure 2. Temperature dependence of resistivity for samples $Bi_{1.8}Pb_{0.2}Sr_{1.6+x}La_{0.4-x}Cu_{1-x}Ga_xO_y$.

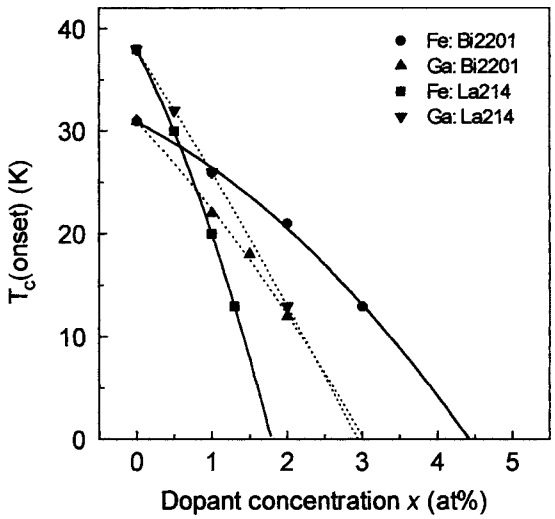

Figure 3. Superconducting transition onset temperature, T_c^{onset}, as a function of dopant (Fe, Ga) content x for the doped Bi2201 and La214 systems.

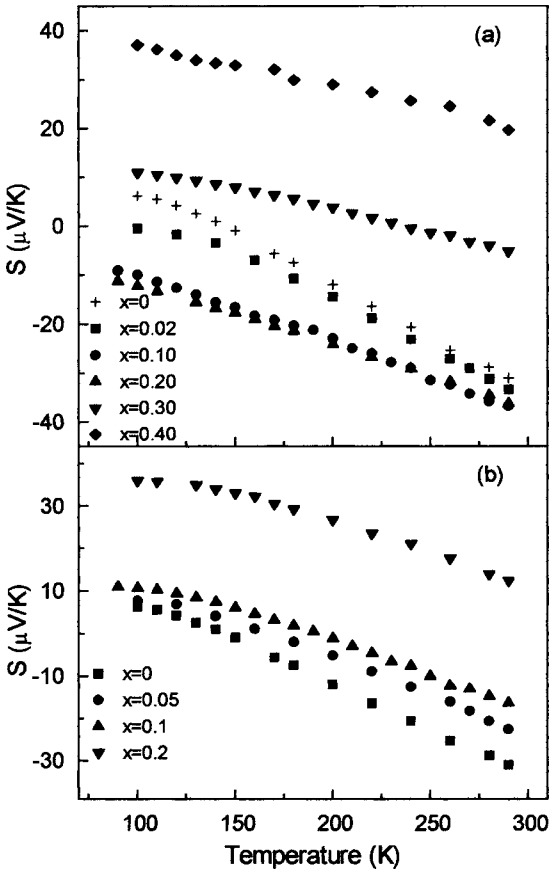

Figure 4. Thermoelectric power as a function of temperature for samples $Bi_{1.8}Pb_{0.2}Sr_{1.6+x}La_{0.4-x}Cu_{1-x}M_xO_y$: (a) M = Fe, (b) M = Ga.

in a high-spin state with an effective local magnetic moment of 4.9 μ_B [7], which is consistent with the ESR results, whereas in the Bi2201 system we do not detect the Fe^{3+} ESR signals, which implies that the spin dynamics of the CuO_2 plane of the Bi2201 system is different from that of the La214 system.

4. Discussion

In order to account for the ESR results of Fe doped Bi2201 system, one can easily think of two different spin states of Fe^{3+}. It is known that the 3d orbitals in an octahedron are split into the triplet (t_{2g} = xy, yz and xz) and doublet (e_g = z^2 and $x^2 - y^2$) groups, separated by the crystal field splitting energy (Δ_0). The Fe^{3+} ion can be in a high-spin state ($t_{2g}^3\ e_g^2$, S = 5/2) or a low-spin state (t_{2g}^5, S = 1/2), which depends on crystal field splitting energy (Δ_0) and pairing energy (P) of two electrons in the same orbital. Fe^{3+} is in a high-spin state in the La214 system and may be in a low-spin state in the Bi2201 system. This explanation seems to give cause for the ESR results, but it is in disagreement with a previous report, i.e. the fitting result of previous susceptibility data from $Bi_2Sr_2Cu_{1-x}Fe_xO_y$ gave an effective magnetic moment of 5.13 μ_B per Fe atom [4], which implies Fe^{3+} in a high-spin state. On that

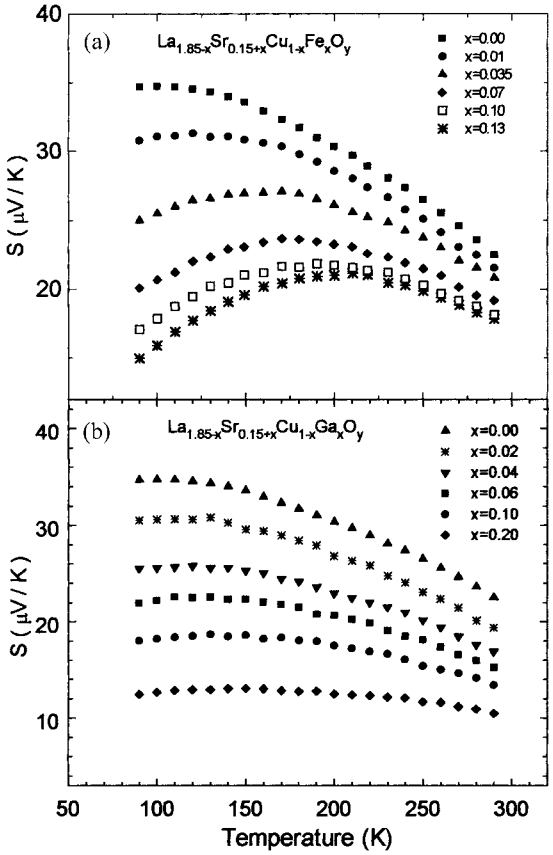

Figure 5. Temperature dependence of thermoelectric power for (a) $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_y$, (b) $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Ga_xO_y$.

account, another alternative explanation should be given. Spectroscopic evidence suggests that in $La_{2-x}Sr_xCuO_4$ the introduced extra holes reside near the O site and form O^- [8]. Due to the extra hole located at O of the CuO_6 (FeO_6) octahedron, the symmetry of the CuO_6 (FeO_6) octahedron reduces. This distortion changes the spin orientation of Cu^{2+} or Fe^{3+} and destroys the Fe–O–Cu AF super-exchange interaction. The localized Fe^{3+} spins form a strong local magnetic moment. For the Fe doped Bi2201 system, on one hand the Bi_2O_2 layers are a charge carrier reservoir and the hole does not reside at the O site; on the other hand the CuO_2 plane is under compression, which favours these to nearly remain a constant length of the in-plane Cu–O bond upon doping. Hence, an effective Fe–O–Cu AF super-exchange interaction can form. This kind of spin correlation makes Fe^{3+} spins align with reversed orientation between contiguous Fe^{3+}. The density of electrons in the CuO_6 (FeO_6) octahedron of the Fe doped Bi2201 system is greater than that in the Fe doped La214 system. The greater number of electrons make the electron–electron interaction strengthen. Thus the relaxation rate decreases for the Bi2201 system. It is known that previous attempts to investigate the spin dynamics of La_2CuO_4 by Cu^{2+} electron-paramagnetic resonance (EPR) measurements failed [9], because of strong Cu–O–Cu spin correlation. The Fe doped Bi2201 system discussed above may be similar to that case, so no ESR signals were observed. Our previous study on $Bi_2Sr_{2-x}CuO_y$ has indicated that the localized Cu^{2+} spins induced by structural distortion could be easily

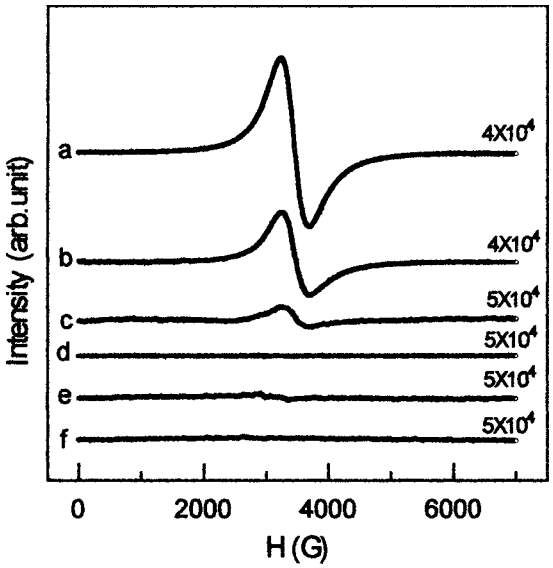

Figure 6. Electron spin resonance spectra at 100K for samples $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_y$ (a: $x = 0.13$, b: $x = 0.07$, c: $x = 0.02$, d: $x = 0$) and $Bi_{1.8}Pb_{0.2}Sr_{1.6+x}La_{0.4-x}Cu_{1-x}Fe_xO_y$ (e: $x = 0.4$, f: $x = 0$).

detected by ESR measurement [10]. Based on this result it is suggested that Fe^{3+} spins in the Bi2201 system tend to de-localize.

From the above analysis one can see that the chemical environment of Cu (in the CuO_2 plane) in the La214 system is different from that in the Bi2201 system, and the doped Fe^{3+} shows variable spin correlation characteristics in the two systems. Fe^{3+} spins in $La_{1.85-x}Sr_{0.15+x}Cu_{1-x}Fe_xO_y$ are localized, which is different from that in $Bi_2Sr_{1.6+x}La_{0.4-x}Cu_{1-x}Fe_xO_y$. So T_c goes to zero at an Fe concentration x_c of 1.8 at.% for the La214 system and 4.3 at.% for the Bi2201 system. Ga^{3+} ($3d^{10}$) replacing Cu^{2+} in La214 and Bi2201 systems only creates spin vacancies in the CuO_2 sheet. Therefore, Ga doping destroys the superconductivity completely at nearly the same dopant level in the both systems.

Local spin scattering also influences the transport properties markedly. In the above La214 system the doping of Fe^{3+} influences the temperature dependent broad peak in the $S(T)$–T curve more strongly than the doping of Ga^{3+}. For the Bi2201 system the $S(T)$–T curves show a similar variation between Fe doping and Ga doping. In fact, it has already been suggested that the temperature-linear resistivity may be caused by the spin fluctuation scattering [11, 12]. Our previous study on $La_{1.6-x}Sr_{0.4+x}Cu_{1-x}M_xO_y$ (M = Fe and Ga) has shown that although the carrier concentration of the samples lies in the overdoped region, the different effects of Fe and Ga doping on TEP still exist [6]. Local spin scattering influence on T_m has also been observed in $Bi_2Sr_{2-x}CuO_y$ (2201) and $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ (2212) systems [10, 13]. In these systems the localized Cu^{2+} spins were detected by ESR spectroscopy. The increase of the fraction of localized Cu^{2+} spins not only leads to a rapid resistivity increase and a metal–insulator (MI) transition, but also causes the broad peak strikingly to shift to high temperatures.

Our experimental results indicate that although both La214 and Bi2201 possess simple crystal structure (average structure) and a single CuO_2 plane, their spin dynamic behaviours are different. Because the spin dynamics and the mobility of free carriers in these materials are

strongly interdependent, Fe doping shows different effects on the superconductivity and NS transport properties between Bi2201 and La214 systems.

Acknowledgment

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