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Abstract. Thermoelectric power (TEP) values of $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+y}$ single crystals were measured in the liquid nitrogen temperature range. A non-Fermi-liquid model—the Nagaosa–Lee model (NL model)—has been applied to explain the observed results. It is found that experimental data follow the NL model well.

1. Introduction

Because thermoelectric power (TEP) is sensitive to electronic structure, conduction mechanism, scattering processes etc, the measurement of TEP has been used as an important method for studying the normal state properties of high-temperature superconductors (HTSCs) [1–8]. The behaviour of TEP of HTSC materials, especially behaviour of single-phase polycrystalline samples, has been well recognized. Their relationships with doping and temperatures show some common features. It is possible to use room-temperature TEP as a probe to determine the doping state of any HTSC materials [9]. A number of models have been proposed to explain the TEP behaviour of oxide superconductors, but it is difficult to distinguish which model is superior to others only using data measured from polycrystalline samples. Experimental data from single crystals are necessary. In this paper, we report the TEP of single-crystals $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+y}$ ($x = 0$, 0.1, 0.2, 0.3, 0.4) in the liquid nitrogen temperature range. Results were analysed based on one of the theoretical models—the Nagaosa–Lee model—and compared with the results of polycrystal $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+y}$ to discuss the applicability of the NL model to HTSC systems.

2. Experiment

Single crystals of the $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+y}$ system were grown by spontaneous nucleation from eutectic melts. A detailed description of crystal growth can be found in our earlier paper [8]. X-ray diffraction patterns show all the crystals possess pure 2212 phase. T_c was determined by the standard four-probe method to be 80, 90, 86, 62 and 50 K [10]. TEP was measured by a differential method [8]. Two Lake Shore silicon diodes were used both as temperature control sensors and as thermometers. The temperature was controlled by a Lake Shore DRC-93CA temperature controller. The temperature difference

between the two ends of sample was 2–3 K during the measurement. A Keithley 182 sensitive digital voltmeter was used to measure the thermal voltage. The TEP of the copper lead was subtracted from the sample data to obtain the absolute TEP. Thin, platelike crystals with typical size $4 \times 2 \times 0.1$ mm^3 were carefully chosen. Two copper wires were connected to samples by silver paste. Measured TEP is along the *ab* plane.

3. Results and discussion

Figure 1 shows the TEP of $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+y}$ single crystals versus temperature T. The TEP values (S) of five samples are all positive in the whole temperature range studied. S increases with x. For the undoped sample ($x = 0$), S has a negative slope. It increases almost linearly as T decreases, passing through a maximum at $\sim$110 K, and then begins to drop. The drop becomes rapid after the sample undergoes the superconducting transition. When the sample is near the optimal hole concentration ($x = 0.1$), the S–T curve shows similar trends as that of the $x = 0$ sample, but the slope is much smaller and the maximum occurs at about 210 K. For the sample with $x = 0.2$, S remains almost unchanged in the high-temperature range (300–220 K) then falls gradually above T_c. No maximum that generally appears in the S–T curve of superconducting samples [1, 2] is observed. When the nominal Ce concentration increases to 0.3 or 0.4, T_c decreases rapidly and S becomes large. It has a weak temperature dependence in the higher-temperature region and then decreases gradually.

It has long been recognized that the normal properties of HTSCs cannot be fully understood in the framework of a simple Fermi liquid. Several non-Fermi models have been proposed. One of them is the Nagaosa–Lee model [11]. The NL model is based on a uniform resonating-valence-bond (RVB) state. The physical implication of this kind of state is that the strong electron–electron correlation results in the separation of charge degrees of freedom from spin degrees of freedom. The conduction in the normal state is mediated by holons, which can be taken to be spinless bosons of charge e, and the magnetic fluctuations in the normal metal are fermion solitons (spinons) with a pseudo-Fermi surface, no charge, and spin 1/2. Both of these excitations are solitons of the two-dimensional Cu–O layers, involving rearrangements of the entire layer wave functions and as such cannot tunnel from one layer to another. The only three-dimensional objects are real electrons, which can tunnel between layers but must then break up into holon–spinon pairs of excitations. NL considered the coupling of the uniform RVB state to the gauge field and pointed out that the TEP should include two contributions: the Fermi part S_F and the Bose part S_B. That is

$$S = S_F + S_B. \tag{1}$$

recall $S_F \sim -(k_B/e)k_B T/E_F$ and $S_B \sim (k_B/e)[1 - \ln(2\pi p/mk_B T)]$; S can be expressed as

$$S = \frac{k_B}{e}\left[1 - F \ln \frac{2\pi pG}{T} - \frac{T}{H}\right] \tag{2}$$

where p is the hole concentration per Cu ion. F, G ($\sim$m^{-1}), H ($\sim E_F$) are fitting parameters. It is expected that S_B will dominate and S will be near k_B/e.

We analysed our TEP results on the basis of equation (2). The best-fit curves for all the samples are presented in figure 1. It is seen that the experimental points fit well with the expression (2). The best-fit parameters and errors are given in table 1.

In the NL model, values for parameters G and H are expected to be of the order of the exchange energy $J \sim 1000$ K. From table 1 we can see that, except the value of G for the
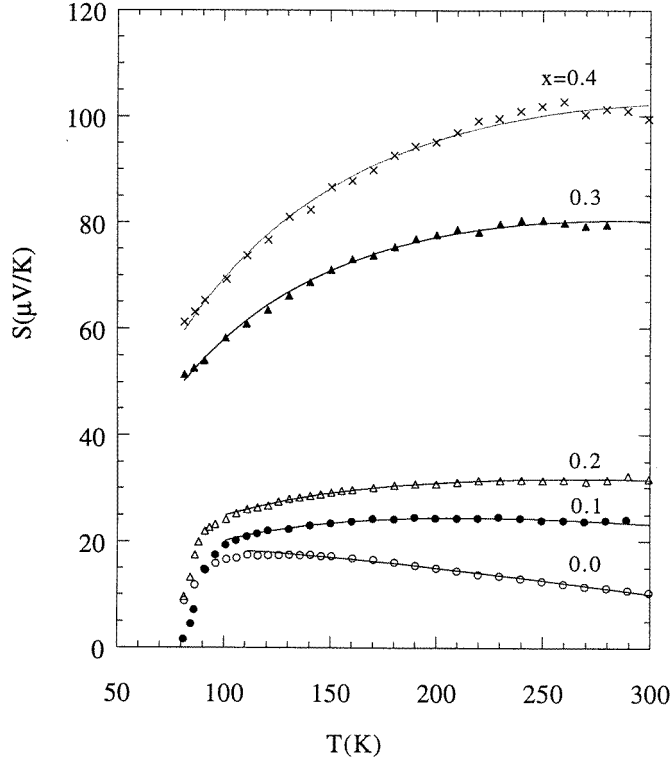
Figure 1. Thermoelectric power of $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+y}$ single-crystalline samples. Solid lines are best-fitting curves to equation (2).

Table 1. Best-fit parameters to equation (2).

x	T_c (K)	F	G (K)	H(K)	$S_{F,270K}$ $(\mu V\ K^{-1})$	$S_{B,270K}$ $(\mu V\ K^{-1})$
0.0	80	0.0594 ± 0.0173	$1.345 \times 10^7 \pm 0.263 \times 10^6$	1230.38 ± 131.67	-18.93	32.48
0.1	90	0.2230 ± 0.0156	1818.91 ± 913.66	948.84 ± 73.635	-24.54	48.27
0.2	86	0.2222 ± 0.0136	1585.66 ± 487.86	1201.25 ± 103.61	-19.39	50.59
0.3	62	0.6443 ± 0.0262	465.74 ± 3.3732	442.76 ± 31.715	-52.6	131.70
0.4	50	0.7684 ± 0.0428	504.04 ± 2.5994	428.68 ± 46.475	-54.32	154.32

$x = 0$ sample, all the values of G and H are of about the same order as anticipated by the model. The NL model is essentially valid for underdoped samples, whereas the $x = 0.0$ sample is in the overdoped region. This may be the reason why the G value of the $x = 0.0$ sample is much higher than expected from the model. In order to show the contributions of holons and spinons, parameters S_F and S_B were calculated from the fitting (table 1) and plotted against x (figure 2). S_F is negative, and roughly decreases with x, while S_B is positive, and increases with x. For each sample, $|S_B|$ is larger than $|S_F|$. This indicates the main contribution to TEP is from holons. When the doping level is a little higher ($x = 0.3$, 0.4), TEP values are near $k_B/e = 86.25\ \mu V\ K^{-1}$.
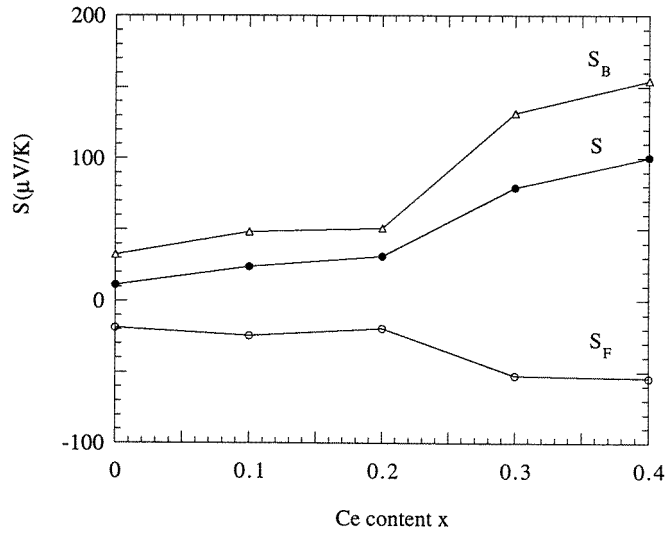
Figure 2. Plot of S_B, S_F and S against Ce content x at $T = 270$ K. Solid lines are guides to the eyes.

Comparing to the TEP of $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+y}$ polycrystals [8], it is found that, for samples with the same Ce concentration, S values of single crystals are much larger than those of polycrystals. Take the undoped specimen ($x = 0$) as an example. The general features of the S–T curves are similar for the $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+y}$ single crystal and polycrystal. However they have opposite signs near room temperature and S of the single crystal is about 14 μV K^{-1} larger than that of the polycrystal before the sample becomes a superconductor. The large and positive TEP in the $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+y}$ single crystal and the small and negative TEP in the $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+y}$ polycrystal near room temperature has been observed by many researchers [2–6].

As assumed from the NL model, holons and spinons are two-dimensional solitons. Equation (2) only considers conduction along the ab plane. To describe the TEP of polycrystals, the contribution of S_c should be considered. According to the two-band model [12],

$$S = \frac{\sigma_{ab}S_{ab} + \sigma_c S_c}{\sigma_{ab} + \sigma_c} \tag{3}$$

where S_{ab} (σ_{ab}) and S_c (σ_c) are the in-plane and out-of-plane TEP (conductivity) respectively. For the Bi-2212 system, $\sigma_{ab} \gg \sigma_c$, $S_{ab} \sim S_c$ [5], so $S \approx S_{ab}$. That is, because of the large anisotropy in HTSC, the TEP of polycrystals roughly represents the in-plane TEP. Thus, theoretically, the NL model is also applicable to polycrystalline samples. Nevertheless, when the NL model was applied to polycrystalline samples, though experimental results follow equation (2) well and H values are about of the same order as J, G values are either too large or too small [8].

Let equation (2) change to the following form:

$$S = \frac{k_B}{e} \left[1 - F \ln(2\pi pG) + F \ln T - \frac{T}{H} \right] \tag{4}$$

for each sample, p, F, G and H are constants. It is clear from equation (4) that the variation

of G only shifts the whole S–T curve to higher or lower position without changing its relationship with temperature. If G is forced to take the value $G_0 \sim 1000$ K, to obtain reasonable fitting to experimental results, an extra term $\Delta S = -(k_B/e)F \ln(G/G_0)$ should be added

$$S = S_0 + \Delta S \tag{5}$$

where S_0 has temperature dependence and values expected by the NL model. Expression (5) qualitatively explains the TEP difference between Bi$_2$Sr$_2$Ca$_{1-x}$Ce$_x$Cu$_2$O$_{8+y}$ polycrystals and single crystals. It shows the TEP of sintered samples and the *ab* plane TEP are not identical, which is inconsistent with the result predicted by the two-band model. The inconsistency suggests, to explain the TEP behaviour of polycrystalline samples, some scattering mechanisms such as boundary scattering should not be ignored.

From the TEP point of view, the NL model applies to BSCO systems, especially single crystals, well. Yet the NL model proposes there exists a temperature T_g, well above the superconducting transition temperature T_c, at which a spin gap opens. NMR [13] and inelastic neutron scattering [14] demonstrated the existence of T_g in the underdoped region in YBCO (123 and 124) and LSCO systems. Indirect measurements such as resistivity–T, Hall coefficient–T [15], specific heat–T [16] and TEP–T [7, 17] relationships have suggested the presence of some cross-over temperature T^* in the underdoped samples in the two systems. In our Ce-doped Bi-2212 systems, the increment of TEP caused by the opening of a spin gap was not observed. In other doped Bi and Tl systems, to our knowledge, spin-gap-like behaviours have not been reported. Maybe the spin gap was depressed by doping in these two systems [18].

4. Conclusions

Thermoelectric power values of Bi$_2$Sr$_2$Ca$_{1-x}$Ce$_x$Cu$_2$O$_{8+y}$ single crystals were measured in the liquid nitrogen temperature range. TEP values are all positive for five samples. S increases as Ce content x increases. Experimental data fit equation (2), proposed by the NL model, well. Best-fit parameters G and H are of the order of the exchange energy $J \sim 1000$ K. Two contributions, a Fermi part S_F and a Bose part S_B, were calculated. For each sample, $|S_B|$ is larger than $|S_F|$. This indicates the main contribution to TEP is from holons. When the doping level is a little higher ($x = 0.3, 0.4$), TEP values are near $k_B/e = 86.25$ μV K^{-1}. All these results are consistent with the model. After adding a term to equation (2), reasonable fitting parameters can also be obtained for experimental data measured from polycrystalline samples. However, the cross-over temperature T^* proposed by the NL model was not observed in our system. More detailed research is necessary.

Acknowledgments

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