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Thermopower of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_y$ ($\text{R} = \text{Gd}, \text{Pr}$) single crystals

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Abstract

The temperature and carrier concentration dependence of the thermopower (TEP) S in $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_y$ ($\text{R} = \text{Gd}, \text{Pr}$) single crystals were carefully studied. Upon Gd or Pr doping, the superconductivity changes systematically from overdoping to underdoping with the TEP increasing monotonically. $S(T)/S(T_{\text{scale}})$ against T/T_{scale} for all the underdoped crystals can be well scaled into a universal curve, where T_{scale} is the temperature at which S begins to deviate from T -linear behaviour. This scaling behaviour is assumed to correlate with the opening of the pseudogap. Furthermore, the temperature dependence of the TEP is analysed and discussed in terms of two different two-band models and the Nagaosa–Lee model.

1. Introduction

It is well appreciated that understanding of the normal-state transport properties, which is a rich resource to provide information on the band structure, Fermi level, carrier concentration and their interaction, is crucial to elucidate the underlying mechanism of high- T_c superconductors (HTSCs) [1]. For instance, the in-plane resistivity keeps a T -linear dependence over a wide temperature range above T_c in an optimally doped sample. The Hall coefficient R_H drops rapidly as $R_H \propto 1/T$ with increasing temperature. Complementary to resistivity and Hall effect, the thermopower (TEP) is sensitive to the topological structure of the Fermi level and other elementary excitations, and thus much information on electron properties can be obtained from the TEP. In cuprate superconductors, a nearly universal relationship between the TEP value at room temperature, the hole concentration on the CuO_2 planes and the transition temperature has been brought forth by Obertelli *et al* [2] and used as a gauge to determine the hole concentration. Although some common features of the TEP have been found in La, Y, Bi, Tl and Hg systems over the years [2–19], there has been no satisfactory explanation for the behaviour of the TEP up to now, and a wealth of theoretical models and experiments remain controversial. Furthermore, the significant changes of the electric properties near the Fermi level E_F are still unclear and worth being investigated. So, it is necessary to find the

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most reliable explanation for the TEP behaviour of HTSCs. On the other hand, in the HTSCs, it is natural to take into account the influence induced by incorporating the dopant itself on the Fermi level. The $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (Bi2212) superconductor has been widely studied [3, 10–15, 20–23] since not only can it be prepared over a wide doping range, but also it has no complex Cu–O chain which might affect the electronic state. Nonisovalent substitution for the Ca of Bi2212 by rare-earth elements (R) is a fruitful way to directly change the charge carriers and the band spectrum, and hence the transport behaviour. However, previous work on rare-earth element substitution at the Ca site has mainly been focused on polycrystalline samples whose inhomogeneities and grain-boundary effect could mask many intrinsic phenomena. Therefore, research on single crystals is necessary for the TEP of the Bi2212 system and has great advantage over polycrystalline samples in providing more significant information. In this work, we measured the TEP on single crystals of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_y$ ($\text{R} = \text{Gd}, \text{Pr}$). The shift of S with the carrier concentration and the broad maximum of S were discussed. A scaling behaviour, $S(T)/S(T_{\text{scale}})$ against T/T_{scale} , can be established for all the underdoped crystals. The temperature T_{scale} may be assigned to the opening of the pseudogap. In addition, the validity of several models in describing the temperature and doping dependence of the TEP was also analysed.

2. Experiment

Single crystals of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_y$ ($\text{R} = \text{Gd}, \text{Pr}$) were grown from Bi-rich melts by a directional solidification method with the atomic ratio of the grown melts of 2.4 Bi:2.0 Sr:(1 – x) Ca:(x) R:2.0 Cu. The detailed growth process has been described elsewhere [20, 21]. To ensure homogeneity of the crystals with regard to composition, structure and oxygen content, bright crystal sheets of similar size with ab -plane dimensions of 3 mm \times 1 mm and thickness around 30 μm were chosen as candidates for the present experiments. All the R-doped crystals were annealed in air at 400 °C for 2 days before the TEP measurements to improve the oxygen homogeneity. The actual R content of the single crystals was determined by energy dispersive x-ray analysis (EDX) using a scanning electron microscope (Stereocan 440, Leica). The experimental uncertainty was smaller than 5%. The thermopower was measured by a differential method in the temperature range from 90 K to 290 K. During the measurement, the crystals were mounted on the top of two well separated copper blocks. The temperature at the two ends of the crystals was controlled automatically within the precision of 0.01 K and the temperature gradient between them was kept at 2 K. The emf of the crystals was obtained by a Keithley 181 nano-voltmeter with an error less than 0.1 μV . Calibrated by pure Pb, the error of the TEP measurement system was smaller than 0.1 $\mu\text{V K}^{-1}$.

3. Results and discussion

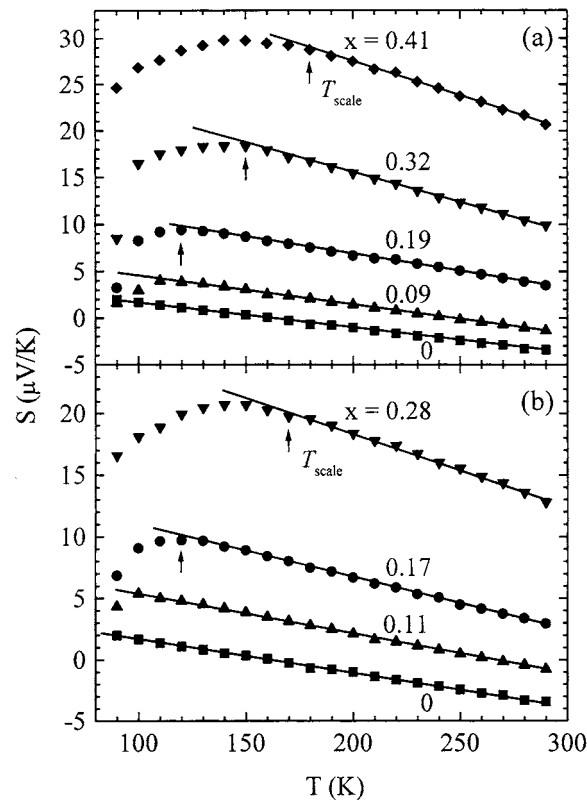
The superconducting transition temperature T_c of Bi2212 single crystals was determined by the zero-resistivity measurements. The changes of T_c with R-doped content are listed in table 1. T_c was found to vary from the overdoped to the underdoped region with R doping. It is well known that such a change is induced by the hole-filling effect on the CuO_2 plane [21, 22], for the valence of the rare-earth ion is higher than that of the Ca ion. There is a universal parabolic formula between the T_c and the carrier concentration p [24]

$$T_c/T_{c,\text{max}} = 1 - 82.6(p - 0.16)^2. \quad (1)$$

Based on this formula, one can calculate the carrier concentration for all the R-doped crystals, as shown in table 1.

Table 1. Doping content x dependences of T_c obtained from resistivity measurements and p calculated from the T_c using equation (1) for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_y$ ($R = \text{Gd}, \text{Pr}$) single crystals.

R	Composition	T_c (K)	p
Gd	$x = 0$	84	0.180
	$x = 0.09$	87	0.163
	$x = 0.19$	83	0.144
	$x = 0.32$	78	0.120
	$x = 0.41$	63	0.104
Pr	$x = 0.11$	88	0.157
	$x = 0.17$	82	0.144
	$x = 0.28$	73	0.121

**Figure 1.** Temperature dependence of the thermopower for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_y$ single crystals with (a) Gd doping and (b) Pr doping. For different underdoped crystals, the positions of T_{scale} where S begins to deviate from T -linear behaviour are indicated by arrows.

The temperature dependence of the TEP S for the superconducting single crystals of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_y$ ($R = \text{Gd}, \text{Pr}$) is shown in figures 1(a) and (b). The data shift systematically with R-doping concentration. The larger the doping content, the larger the magnitude of S . This systematic variation is mainly due to the decrease of carrier concentration with R doping. The values of S at room temperature are negative for high p and linearly increase with decreasing temperature. A usual confusion is that a shift towards more negative values

with increasing carriers is almost opposite to that implied by the simple expectation that the TEP reflects the carrier sign, as the Hall effect shows. However, it should be pointed out that this expectation is not reliable since even in some simple metals the sign of the TEP unambiguously differs from that of the carriers. Kaiser *et al* [25] supposed the presence of more than one type of carrier to explain the coexistence of a positive Hall effect and a negative TEP. Furthermore, Kubo *et al* [26] pointed out that the changes in sign of the Hall coefficient and the TEP both could arise from the existence of a van Hove singularity (VHS). For samples with low carrier concentration, S increases with decreasing temperature, passes through a broad maximum at T_{\max} about 100–150 K and then drops at the low temperature region. The broad maximum shifts to high temperature with reduction of the hole concentration. This behaviour follows a common feature of the temperature and doping dependence of S for HTSCs. Troadahl [13] regarded the maximum of S as the contributions from large T -independent phonon drag within the conventional Fermi-liquid theory. In this picture, the TEP is the sum of a negative diffusion contribution S_d varying linearly with T and a positive phonon-drag TEP S_g varying little with T above 100 K. The zero-offset thermopower S_0 , which denotes the value of the linear $S(T)$ extrapolated to $T = 0$ K, is simply the saturation value of S_g . The positive S_0 obtained from our experiments decreases with increasing doping level, as shown in figure 2, which is similar to that reported by Choi and Kim on the $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+z}$ system [6] and can be properly explained as the expanding out of the cylindrical hole-like Fermi surface [13].

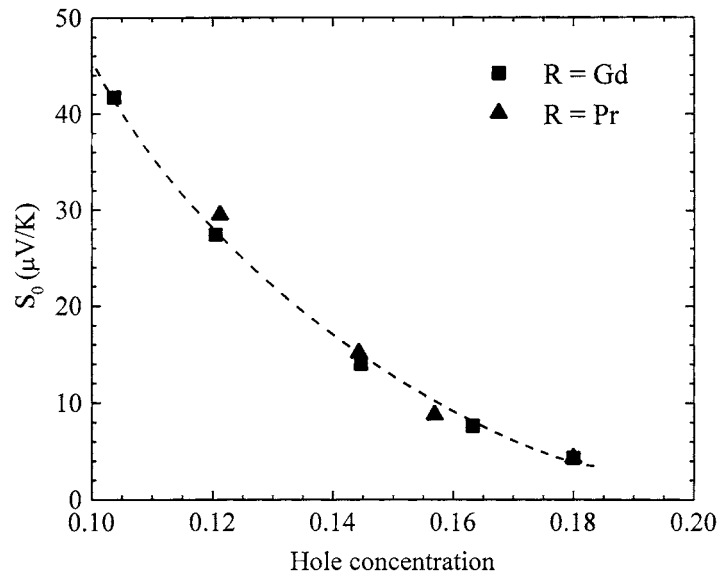


Figure 2. The hole concentration dependence of the zero-offset thermopower S_0 for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_y$ ($\text{R} = \text{Gd}, \text{Pr}$) single crystals. The dashed lines are guides for the eyes.

As shown in figure 1, the TEP keeps a T -linear behaviour at high temperature with negative slope dS/dT whose absolute value increases with the decrease of carrier concentration. The characteristic temperature T_{scale} , below which S begins to deviate from linear behaviour, was found to decrease monotonically with increasing hole concentration for all the underdoped crystals as shown in figure 3. To obtain more information, we plotted $S(T)/S(T_{\text{scale}})$ as a function of T/T_{scale} and found that all data above T_{scale} can be well scaled into a single curve as shown in figure 4. This scaling behaviour may be associated with the normal state pseudogap with T_{scale} being the pseudogap characteristic temperature. Recently, a gaplike feature in the

electric spectrum of low energy excitation and a series of characteristic temperatures have been found in the underdoped HTSCs, from NMR [27], optical conductivity [28] and thermopower [9, 12]. This pseudogap is supposed to be associated with a phenomenon affecting the density of states or the antiferromagnetic excitations [29]. The relationship between this scaling characteristic temperature and the carrier concentration has been found very close to those found by scaling the NMR Knight shift and neutron scattering [12, 29]. Scaling on other normal-state transport properties of HTSCs has also been established and found to be similar to ours. Hwang *et al* [30] found that the Hall coefficient $R_H(T)$ of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ can be scaled to a universal function as $R_H(T) = R_H^0 + R_H^* f(T/T_H^*)$: $R_H(T)$ is temperature dependent below a characteristic temperature T_H^* and temperature independent (R_H^0) above T_H^* . Uchida *et al* [31, 32] found the scaling behaviour of the in-plane resistivity $\rho_{ab}(T)/\rho_{ab}(T_\rho^*)$ against T/T_ρ^* for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ which deviated from the linear behaviour below a temperature T_ρ^* well above T_c . It is generally believed that the opening of the pseudogap causes the decrease of the resistivity at the characteristic temperature T_ρ^* . Mandal *et al* [4] also scaled $S(T)/S(T^*)$ and T/T^* for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+y}$ and $\text{Tl}_2\text{Ba}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+y}$ systems; however, here T^* is the temperature where S shows a peak, which is different to our scaling.

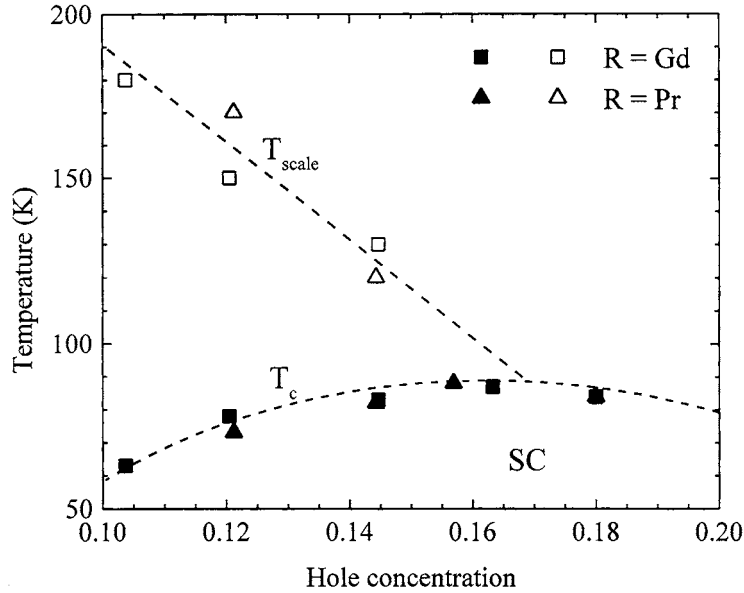


Figure 3. Hole concentration dependence of T_{scale} and T_c for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_y$ ($\text{R} = \text{Gd}, \text{Pr}$) single crystals. The dashed lines are guides for the eyes.

The above qualitative analysis shows that the deviation of the TEP from T -linear dependence can be associated with opening the pseudogap. On the other hand, we will quantitatively discuss the data on the basis of some other proposed models. It should be underlined that during fitting with these models, we have not considered the data near T_c because the steep drop in the TEP near T_c may originate from thermodynamic superconducting fluctuation [33].

A two-band model was proposed by Xin *et al* [18], which concluded the TEP comes from a combined contribution from the valence band holes in the CuO_2 planes and the conduction band electrons in the semiconducting BiO layers, hence the TEP can be approximately expressed as

$$S = AT + (BE_g/2k_B + CT) e^{-E_g/2k_B T} \quad (2)$$

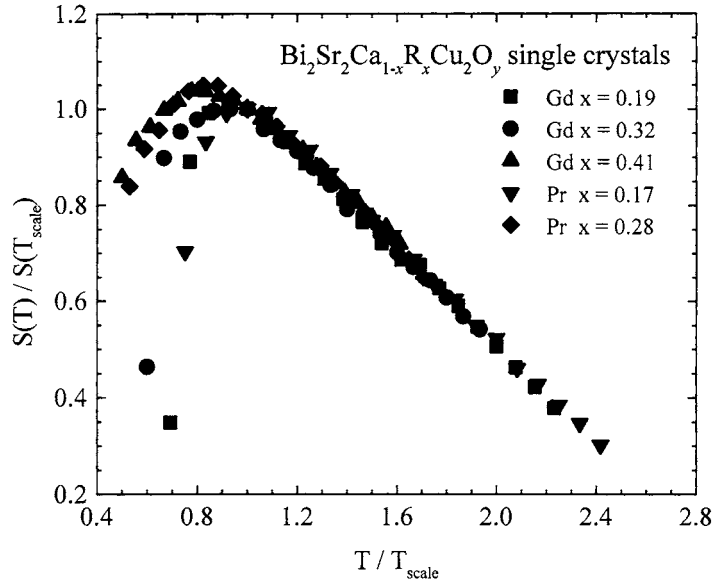


Figure 4. S/S_{scale} versus T/T_{scale} for underdoped $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_y$ ($R = \text{Gd}, \text{Pr}$) single crystals.

where A , B , C are constants, and E_g is the semiconductor gap of the BiO layers. This model can fit our TEP data well as shown in figure 5. Another two-band model with a T -linear term [33] was suggested from the similar TEP behaviour of HTSCs and CeNi_x [34]. The contributions to the TEP arise from a normal band and a localized narrow band at E_0 with a peak width Γ superimposed on the broad band and can be concluded as

$$S = \frac{\beta T}{\gamma^2 + T^2} + \alpha T \quad (3)$$

with

$$\beta = \frac{2(E_0 - E_F)}{e} \quad \text{and} \quad \gamma^2 = 3 \frac{(E_0 - E_F)^2 + \Gamma^2}{\pi^2 k_B^2}. \quad (4)$$

Here, α , β and γ are fitting parameters. In addition, a model based on a gauge field theory for a uniform RVB model was proposed by Nagaosa and Lee (NL) [35]. They assumed the transport properties could be determined from the sum of the spinless boson contribution and the spin carrying fermion contribution. After comparing with experimental results, Ikagawa *et al* [36] gave the expression of TEP based on the NL model as

$$S = \frac{k_B}{e} \left[1 - F \ln \left(\frac{2\pi p G}{T} \right) - \frac{T}{H} \right] \quad (5)$$

where F , G and H are fitting parameters and H is proportional to E_F . The latter two models can also fit our TEP data very well, similar to that shown in figure 5.

The best fitting parameters in the three models mentioned above are listed in tables 2, 3 and 4 respectively and found to show a systematic variation tendency. The increase of the semiconducting gap E_g in equation (2) with doping is expected since it depends on the intercalation of excess oxygen in the BiO layers [14, 15] and the increase of excess oxygen with R doping has been confirmed by many experiments. The parameter of A in equation (2) is inversely correlated with the contribution from the mobile holes in the CuO_2 planes, thus the

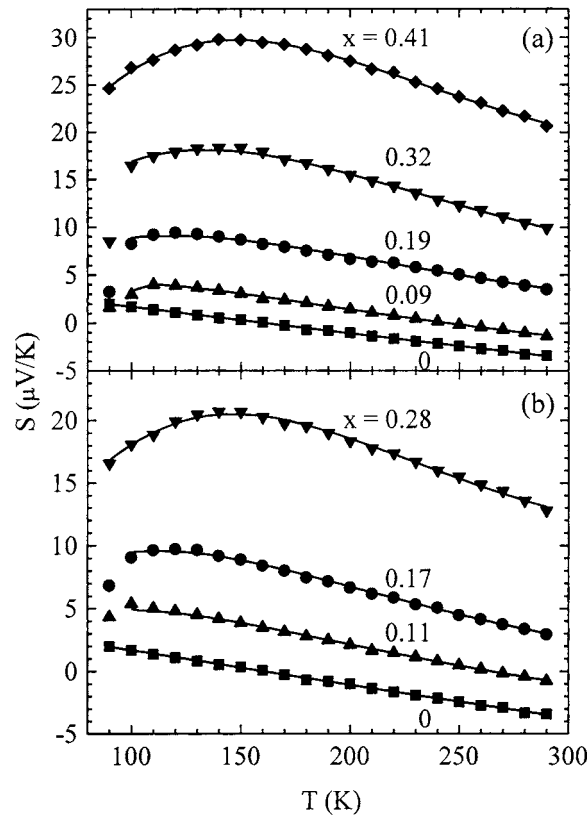


Figure 5. The fit curves of the thermopower for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_y$ single crystals with (a) Gd doping and (b) Pr doping corresponding to equation (2).

Table 2. The best fit parameters A , B , C and E_g in equation (2) for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_y$ ($R = \text{Gd}, \text{Pr}$) single crystals. E_g is the semiconducting gap of the BiO layers.

R	Composition	A ($\mu\text{V K}^{-1}$)	B ($\mu\text{V K}^{-1}$)	C ($\mu\text{V K}^{-1}$)	E_g (eV)
Gd	$x = 0$	0.0337	-0.0925	-0.0297	0.0481
	$x = 0.09$	0.0645	-0.1342	-0.0544	0.0512
	$x = 0.19$	0.1140	-0.3213	-0.0815	0.0600
	$x = 0.32$	0.1976	-0.4291	-0.0719	0.0720
	$x = 0.41$	0.2961	-0.6769	-0.0188	0.0791
Pr	$x = 0.11$	0.0719	-0.1512	-0.0555	0.0538
	$x = 0.17$	0.1250	-0.2496	-0.0786	0.0591
	$x = 0.28$	0.1977	-0.5825	0.1374	0.0881

great increase in A just indicates the variation of the hole concentration. Moreover, although these three models are all based on the multiband or multicarrier model in contrast to the single-band model [2], the starting points concerning the band structure are ultimately different and the physical information from those parameters needs more support from other evidence. The intrinsic contribution to the TEP of HTSCs needs further study.

Table 3. Fit parameters α , β and γ to the two-band model with a T -linear term and the estimated values of $E_0 - E_F$ and Γ in terms of equation (3).

R	Composition	α ($\mu\text{V K}^{-2}$)	β (μV)	γ (K)	$E_0 - E_F$ (K)	Γ (K)
Gd	$x = 0$	-0.0185	609	86	3.53	155
	$x = 0.09$	-0.0181	1283	106	7.44	192
	$x = 0.19$	-0.0146	2666	121	15.45	218
	$x = 0.32$	-0.0336	7360	161	42.67	289
	$x = 0.41$	-0.0390	12 624	177	73.18	312
Pr	$x = 0.11$	-0.0178	1432	103	8.30	187
	$x = 0.17$	-0.0210	3111	129	18.04	234
	$x = 0.28$	-0.0412	10 074	187	58.40	334

Table 4. Fit parameters F , G and H to the Nagaosa–Lee model in terms of equation (5) for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_y$ (R = Gd, Pr) single crystals.

R	Composition	F	G (K)	H (K)
Gd	$x = 0$	0.0212	1.52×10^{21}	2303
	$x = 0.09$	0.0494	7.37×10^9	1666
	$x = 0.19$	0.0840	1.76×10^6	1220
	$x = 0.32$	0.2294	2006	567
	$x = 0.41$	0.3994	446	378
Pr	$x = 0.11$	0.0391	6.79×10^{11}	1737
	$x = 0.17$	0.0726	7.06×10^6	1196
	$x = 0.28$	0.2912	974	498

4. Conclusion

The temperature dependence of the thermopower S for the $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_y$ (R = Gd, Pr) single crystals shifts to higher values with the R-doping concentration and deviates from linear behaviour below a scaling temperature T_{scale} for all the underdoped crystals. The T_{scale} is assumed to relate to the opening of the pseudogap. The quantitative analyses of the data were studied in the frame of the two different two-band models and the Nagaosa–Lee model. Although good fitting results can be obtained, it should be pointed out that the present models are still questionable in a physical picture.

Acknowledgments

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