Lorenz number in the optimally doped and underdoped superconductor EuBa$_2$Cu$_3$O$_y$

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The temperature dependences of the Hall-Lorenz numbers (L_{xy}) in a EuBa$_2$Cu$_3$O$_y$ (Eu-123) single crystal before and after oxygen reduction are reported. The study is based on data on the normal state longitudinal and transversal transport coefficients. Namely, the temperature dependences of the electrical resistivity, Hall coefficient, longitudinal thermal conductivity, and transverse thermal conductivity are presented. The set of measurements was performed for an optimally doped sample ($y \approx 7$), then the oxygen content in the the same crystal was reduced to $y \approx 6.65$, and the measurements were repeated. For both cases L_{xy}'s are about two times larger than the Sommerfeld value of the Lorenz number and depend weakly on temperature in a range 300–160 K. Below $T \approx 160$ K the Hall-Lorenz number for the optimally doped sample slowly drops, while the value of L_{xy} for the oxygen reduced sample begins to rise. Such results suggest that the electronic system in the investigated compound may be considered as a metallic one with pseudogaps that open at the Fermi level.

A relation between thermal and electrical conductivities known as the Wiedemann-Franz (WF) law is a sensitive probe of fundamental properties of the electronic system. The value and temperature dependence of the Lorenz number (L), defined in the WF law as

$$L \equiv \frac{\kappa_{el}}{\sigma T}\left(\frac{e}{k_B}\right)^2,\tag{1}$$

where κ_{el} is the electronic thermal conductivity, σ is the electrical conductivity, k_B is Boltzmann's constant, can bear testimony to the nature of the ground state of the electronic system. In the standard Fermi liquid theory L is equal to the Sommerfeld value $L_0 = \pi^2/3$ as far as the mean free paths for transport of charge and entropy are identical. Deviations from the WF law may be regarded as a mark of an exotic nature of the electronic ground state. For example spin-charge separation,[1,2] i.e., fractionalization of electrons for neutral spin-1/2 fermions called "spinons" and spinless charge-e bosons called "holons," is considered as a reason of violation of the WF law in the cooper oxide superconductor $(Pr,Ce)_2CuO_4$.[3] If charge carriers are bipolarons the Lorenz number will be strongly suppressed ($L \approx 0.15\, L_0$) and approximately proportional to the temperature.[4,5] On the other hand, results derived in the framework of the marginal Fermi-liquid approximation show L to be temperature independent, but still smaller than Sommerfeld's value ($L \approx 0.68\, L_0$).[6]

Unfortunately, the pure electronic Lorenz number can not be experimentally evaluated on the basis of measurements of the longitudinal transport coefficients, since heat in solids is usually carried by both electrons and phonons. Thus the measured total thermal conductivity is the sum of the electronic (κ_{el}) and phonon (κ_{ph}) components, $\kappa = \kappa_{el} + \kappa_{ph}$, where in high-$T_c$ cuprates κ_{ph} provides a significant contribution to κ and cannot be neglected.[7,8]

In this paper we use a unique method of a separation of the electronic component from the total thermal conductivity

as proposed by Zhang *et al.*[9] It is based on measurements of the transverse thermal and electrical conductivities (κ_{xy} and σ_{xy}), since these coefficients appear to be purely electronic.[9–11] Our studies of the longitudinal and transverse transport effects have been performed in the normal-state of a EuBa$_2$Cu$_3$O$_7$ (optimally doped) and EuBa$_2$Cu$_3$O$_{6.65}$ (underdoped) single crystals. The determined Hall-Lorenz numbers (L_{xy}) for both samples are almost identical and weakly temperature dependent in the range 300–160 K. Below $T \approx 160$ K the L_{xy} coefficient for the optimally doped sample slowly drops, while the value of L_{xy} for the underdoped sample begins to rise. The values of both Hall-Lorenz numbers significantly exceed the Sommerfeld value. To explain the properties of the examined compound we suppose that a pseudogap opens at the Fermi level in the optimally doped sample, while two different pseudogaps appear in two temperature regions for the oxygen reduced crystal.

Single crystals of EuBa$_2$Cu$_3$O$_y$(Eu-123) were grown from CuO-BaO flux in ZrO$_2$ crucibles by the slow cooling method.[12] To avoid any substitution of Ba by Eu the growth was carried out in a reduced atmosphere of 100 mbar air. The crystal selected for measurements was about 2 mm long, 1.1 mm wide, and 0.18 mm thick (along the crystallographic c axis). It was twinned, therefore the coefficients measured along the ab plane should represent values averaged between the a and b crystallographic directions. The magnetically measured superconducting transition of the sample had an onset of ≈ 94.5 K and a midpoint of 94.0 K. The oxygen content y was estimated to be close to 7 [on the basis of the T_c value and the in-plane thermoelectric power value at room temperature $S_{ab}(300\,\text{K}) \approx -2\,\mu\text{V}/\text{K}$].[13–15] As described below a second set of measurements was performed on the same specimen annealed in air for 12 days at $T = 500\,^\circ\text{C}$ to reduce its oxygen content. After the reduction treatment the critical temperature (T_c) dropped to about 61 K (measured magnetically) and its thermoelectric power was equal to $S_{ab}(300\,\text{K}) \approx 30\,\mu\text{V}/\text{K}$. Both values suggest[13–15] that the oxygen content has dropped to ≈ 6.65.

Electrical resistivity was measured using a four-point technique. The Hall coefficient measurements were performed by a standard method in a magnetic field of 13 T. The longitudinal and transverse thermal conductivities were measured in a single experiment. One edge of a sample was glued to a heat sink, and a carbon heater was painted on the opposite edge. Using this heater a longitudinal temperature gradient ($\nabla_x T$) was generated. The transverse temperature gradient ($\nabla_y T$) was measured perpendicularly to $\nabla_x T$ and to the magnetic field applied along the c axis of a crystal. Both gradients were measured with a pair of Chromel-Constantan thermocouples. Typically $\nabla_x T$ and $\nabla_y T$ were of the order of magnitude of 1 K/mm and 10 mK/mm, respectively. $\nabla_x T$ at $B=0$ T was used to calculate the longitudinal thermal conductivity. We usually observed $\nabla_y T \neq 0$ at $B=0$ T due to slightly asymmetric positions of the thermocouple junctions. This inconvenience was eliminated by varying the magnetic field between -13 and $+13$ T and by using, for calculations of the transversal thermal conductivity, only the slope $\Delta[\nabla_y T(B)]/\Delta B$. Typically, $\Delta[\nabla_y T(B)]/\Delta B$ was of the order of 0.1 mK/(mm T). To obtain reliable results, B was inverted several times with various $\nabla_x T$ at every considered temperature.

As was already mentioned, our studies are based on an analysis of the longitudinal and the transverse transport coefficients. The longitudinal thermal and electrical conductivities (κ_{xx} and σ_{xx}) were measured in absence of a magnetic field, while for the measurement of the transverse thermal and electrical conductivities (κ_{xy} and σ_{xy}) a magnetic field was applied. It is worth it to underline that all investigations were performed on one and the same EuBa$_2$Cu$_3$O$_y$ single crystal, which was examined before and after oxygen reduction. In Fig. 1 we show the temperature dependences of the electrical coefficients: $\sigma_{xx}(T)$ and $\sigma_{xy}(T)$. The longitudinal electrical conductivity is presented as the electrical resistivity ($\rho=1/\sigma_{xx}$) in the upper panel (a). The transverse electrical conductivity is shown in the inset as a result of multiplication the Hall coefficient (R_H) by the square of σ_{xx} [$\sigma_{xy}/B = R_H(\sigma_{xx})^2$]. It is the valid formula, since the crystal is twinned, thus $\sigma_{xx}=\sigma_{yy}$. The temperature dependence of R_H is presented in the bottom panel (b). All curves relate to the same Eu-123 single crystal: at the beginning it was optimally doped (solid lines), but after annealing in air it became underdoped (dashed lines). As expected, the electrical resistivity rises (about three times) at room temperature in the oxygen reduced sample. The critical temperature, defined as a point where curvature of $\rho(T)$ changes sign, drops from 94.5 K (optimally doped) to 62.5 K (underdoped). The Hall coefficient in the underdoped sample is about six times larger (at $T=300$ K) than it was before oxygen reduction. However, the temperature dependences of R_H and ρ for the oxygen reduced sample still have the same characteristics as those observed for the optimally doped one.

There are also no qualitative differences between thermal conductivities presented in Fig. 2. For both samples the longitudinal thermal conductivity in the normal state slowly rises when the temperature decreases—see panel (a). κ_{xx} for reduced sample is almost two times smaller (at room temperature) than it was for the optimally one. Also the trans-
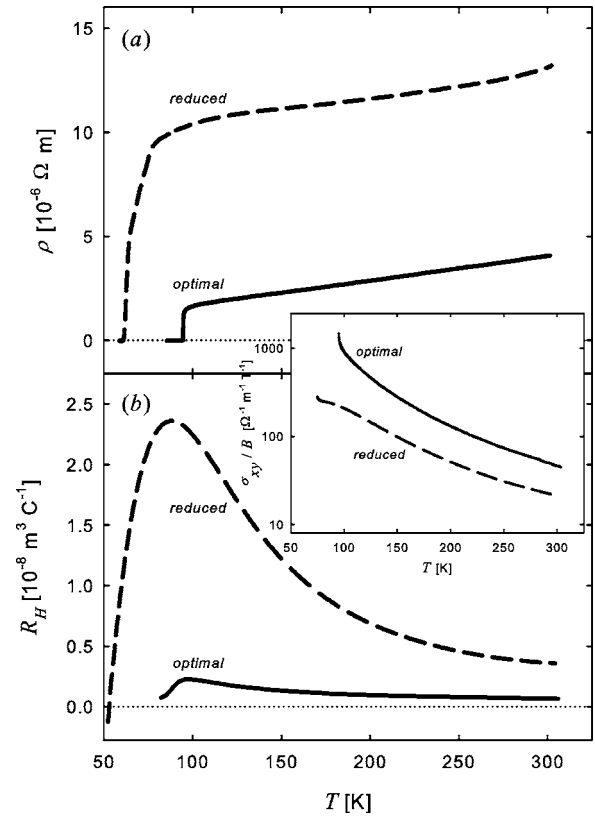

FIG. 1. Temperature dependences of the electrical transport coefficients for the EuBa$_2$Cu$_3$O$_7$ (optimal—solid lines) and EuBa$_2$Cu$_3$O$_{6.65}$ (reduced—dashed lines) single crystals. The longitudinal electrical resistivities are presented in the upper panel (a), and the Hall coefficients are placed in the bottom panel (b). The inset shows the transverse electrical conductivities calculated as: $\sigma_{xy}/B = R_H(\sigma_{xx})^2$.

verse thermal conductivity $\kappa_{xy}=\nabla_y T \kappa_{xx}/\nabla_x T$ is lower in the reduced sample by a factor of 2 at room temperature. The $\kappa_{xy}(T)$ dependences for both samples can be fitted by a power function aT^b, where the parameter b is equal to -1.14 for the optimally doped, and -1.21 for the underdoped sample. These values agree with results of measurements of the transverse thermal conductivity in an optimally doped YBa$_2$Cu$_3$O$_y$ (YBCO) single crystal performed by Zhang et $al.$[9] ($b=-1.21$), and independently by Matusiak et $al.$[11] ($b=-1.19$).

The above presented coefficients can be used to calculate the Hall-Lorenz number from the modified WF law[9]

$$L_{xy} \equiv \frac{\kappa_{xy}}{\sigma_{xy}T}\left(\frac{e}{k_B}\right)^2.$$ (2)

Results of evaluation of the Hall-Lorenz numbers for optimally doped (solid points) and oxygen reduced (open points) samples are presented in Figure 3. It is noticeable that both curves are practically the same above $T \approx 160$ K. Below this temperature the Hall-Lorenz number for the optimally doped sample decreases slowly, while $L_{xy}(T)$ in the oxygen reduced sample increases to significantly higher values. The results of measurements of the optimally doped Eu-123 specimen are
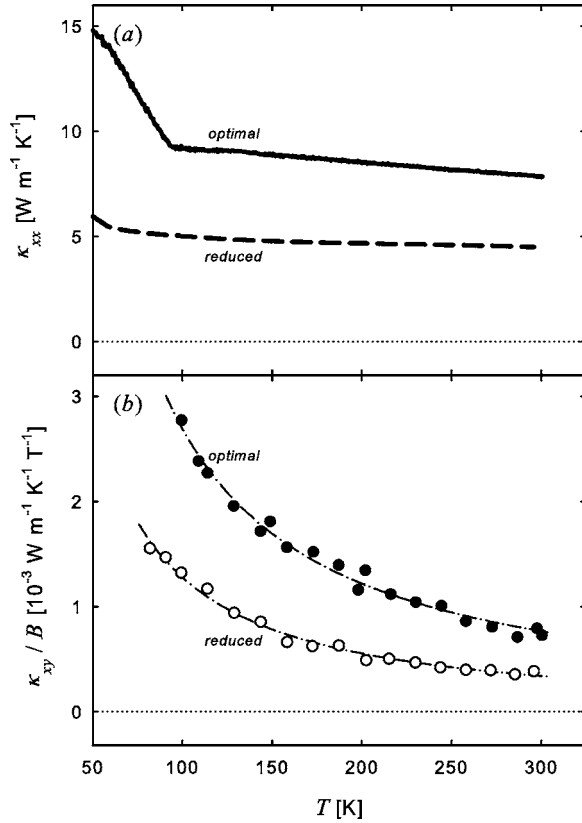
FIG. 2. Temperature dependences of the thermal conductivities for the $EuBa_2Cu_3O_7$ (optimal—solid lines, solid points) and $EuBa_2Cu_3O_{6.65}$ (reduced—dashed lines, open points) single crystals. The longitudinal coefficients are presented in the upper panel (a), and the transverse coefficients are placed in the bottom panel (b); the dash-dotted lines, which are drawn along κ_{xy} points show functions aT^b beeing best power fits with exponents equal to $b_{opt}=-1.14$ and $b_{red}=-1.21$.

very close to the data obtained previously for optimally doped YBCO single crystal.[11] A possible reason for the difference between our results and those reported for YBCO in Ref. 9 might be that different amounts of out-of-plane impu-
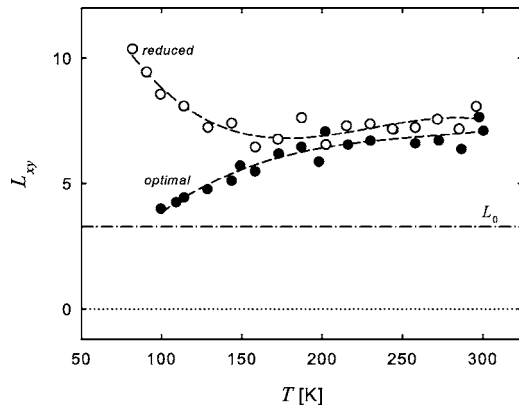

FIG. 3. Temperature dependences of the Hall-Lorenz numbers for the $EuBa_2Cu_3O_7$ (optimal—solid points) and $EuBa_2Cu_3O_{6.65}$ (reduced—open points) single crystals; the dashed lines are guides for the eye.

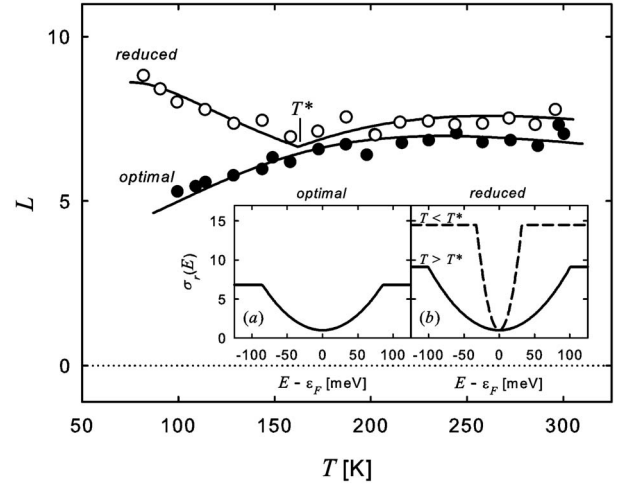FIG. 4. Temperature dependences of the Lorenz numbers for the $EuBa_2Cu_3O_7$ (optimal—solid points) and $EuBa_2Cu_3O_{6.65}$ (reduced—open points) single crystals; the solid lines present results of the L's calculations, which are based on the assumption that a depletion of the reduced electrical resistivity appears at the Fermi level. In the inset (a) the shape of the depletion assumed for $EuBa_2Cu_3O_7$ is shown, while in the inset (b) the shapes of two wells assumed in two temperature regions for $EuBa_2Cu_3O_7$ are presented—for $T > T^*$ it is the solid line, and for $T \leqslant T^*$ it is the dashed line.

rities existed in the two $YBa_2Cu_3O_{6.95}$ crystals used in Ref. 9, one for κ_{xy} and the second one for σ_{xy} measurements. This is discussed in detail in Refs. 6 and 11.

The difference in behavior below $T \approx 160$ K between the Hall-Lorenz numbers in the optimally doped and underdoped specimens has to mirror a change in the electronic structure, since L_{xy} is a purely electronic factor. There are no phonon contributions to the transverse thermal and charge conductivities. In the Boltzmann equation approach, the Hall-Lorenz number is equal to the regular Lorenz number if charge carriers scatter elastically.[9] Otherwise, i.e., when inelastic scattering appears, which usually disturb the heat current more effectively than the charge current,[16] L_{xy} may be compared to L by the ratio

$$a_L \equiv \frac{L^2}{L_{xy}} \qquad (3)$$

The a_L factor is expected to be nearly constant, since $L \sim \langle l_s \rangle / \langle l_e \rangle$ and $L_{xy} \sim \langle l_s^2 \rangle / \langle l_e^2 \rangle$,[9,17] where (l_s) and (l_e) are different mean free paths defined for the transport of entropy and charge, respectively. Because the values of the Hall-Lorenz numbers for both optimally doped and underdoped sample tend to saturate at high temperatures, we suppose that the room temperature is high enough to assume that charge carriers are scattered mostly elastically. Thus we write $L_{xy}(300) \approx L(300)$ and calculate the Lorenz numbers from Eq. (3), where $a_L \approx L_{xy}(300)$. The temperature dependences of L for both specimens are shown in Fig. 4. Remarkable are the large values of L's at room temperature, which are about two times larger than the Sommerfeld value of the Lorenz number expected for a regular Fermi-liquid system: L_0

$=\pi^2/3$. It would be consistent with experimental studies of the thermal transport in other cuprates at temperatures lower than T_c and in high magnetic fields. They also suggest that the Lorenz number in these compounds can exceed the Sommerfeld value.[3,18] One of possible reasons of the enhancement of the Lorenz number in 1-2-3 high-T_c superconductors is a pseudogap that opens at the Fermi level, as was indicated in Ref. 19. A very similar consideration was carried out by Goff[20,21] to explain the anomaly in the Lorenz number[22–24] of chromium. Goff has suggested that the unusual $L(T)$ dependence in Cr is a result of an anomalous distribution of the electronic states about the Fermi level (ε_F). For the calculation the Klemens' moments method[25] was used, which treats the Boltzmann equation in a way that the resulting transport coefficients become integral functions of energy only. It is assumed that the same relaxation times describe both electrical and thermal transport, the phonon system is in equilibrium and the Fermi level is chosen as the reference energy. The transport coefficients are expressed using moments of the function $\sigma(\in)$ called specific conductivity,[25] where $\in$ is the reduced energy ($\in = E/k_B T$). The nth moment is defined as

$$M_n = -\int_{-\infty}^{+\infty} \sigma(\in) \in^n \frac{\partial f^0}{\partial \in} d\in, \quad (4)$$

where f^0 is the equilibrium Fermi-Dirac distribution function: $f^0(\in) = (e^{\in} + 1)^{-1}$.

In this approach the Lorenz number becomes

$$L = (k_B/e)^2 (M_2/M_0) - S^2. \quad (5)$$

Since the relaxation time of individual scattering mechanisms may be separated for an energy and temperature dependence: $\tau^{-1}(E, T) = f(E)g(T)$, a reduced specific conductivity: $\sigma_r(E) = \sigma(E)/\sigma(0)$ can be defined,[20] which tends to be temperature independent. Then, the transport coefficients may be rewritten in terms of new integrals $G_n(T)$, where: $M_n = \sigma(0)G_n(T)$, and $G_n(T) = -\int_{-\infty}^{+\infty} \sigma_r(\in) \in^n (\partial f^0/\partial \in) d\in$. If the retardation effect of the internal electric field on the thermal conductivity is neglected, (it is, at most, an effect of the order of magnitude of a few percent in our samples), the Lorenz number becomes

$$L = (k_B/e)^2 (G_2/G_0). \quad (6)$$

Goff considered in his studies two models of electronic structures containing a depletion of the reduced specific conductivity about the Fermi level. They were supposed to be a parabolic-shaped well in a single band model[20] or a parabolic and BCS-like gap in model of two electronic subsystems.[21] Such a depletion of $\sigma_r(\in)$ may be related to a decrease of the density of states, and therefore it is a structure very similar to the pseudogap observed in high-T_c superconductors.[26,27] We suggest that this phenomenological approach can be successfully used to explain our experimental data.

The $L(T)$ data of the optimally doped sample, presented in Fig. 4 have been fitted with a numerically calculated function $G_2(T)/G_0(T)$ [Eq. (4)], which has two free parameters (a width and a depth) describing a paraboliclike pseudogap. A model of the electronic structure used in the calculation is shown in the inset (a) in Fig. 4. Despite that the shape of the well was arbitrarily chosen and that it was assumed to be temperature independent we have obtained a satisfactory agreement between the fit and the experimental data. Moreover, the estimated width of the supposed pseudogap ($2\Delta = 170$ meV) is of the same order of magnitude as reported for so called "large pseudogap" in YBCO.[28]

While in the optimally doped crystal we observe an influence of the large pseudogap only, the growth of the $L(T)$ value in the underdoped sample below the temperature $T^* \approx 160$ K suggests an opening of the another, narrower, pseudogap. The appearance of two distinct pseudogaps seems to be characteristic for the high-T_c superconductors phenomenon, and it has been observed in many experiments.[26–30] Thus to describe this feature we have assumed in our calculations that the large pseudogap is simply replaced by the "small pseudogap" at $T^* \approx 160$ K. Both pseudogaps are presented in the inset (b) in Fig. 4. The estimated width of the small pseudogap $2\Delta = 65$ meV and the temperature where it opens are similar to those observed previously for underdoped YBCO single crystals with $T_c \sim 60$ K.[31]

In summary, we have investigated transport properties in the normal state of a $EuBa_2Cu_3O_y$ single crystal. The sample was examined in two different oxidation states: first as an optimally doped one ($y \approx 7, T_c = 94.5$ K), next, after oxygen reduction treatment, as an underdoped one ($y \approx 6.65, T_c = 62.5$ K). The measured temperature dependences of the longitudinal and transverse electrical, as well as thermal conductivities have been used to calculate temperature dependences of the Hall-Lorenz number (L_{xy}). For both crystals we have found the values of L_{xy} significantly enhanced—at room temperature they are about two times larger than the Sommerfeld value of the Lorenz number. The $L_{xy}(T)$ dependences for the optimally doped as well as underdoped sample are almost identical at high temperatures. Namely, the values of both L_{xy}'s decrease slowly from room temperature down to about 160 K. Below this temperature L_{xy} for the optimally doped crystal still drops, while the value of L_{xy} for the underdoped sample rises. To explain their behavior a phenomenological model of the electronic structure of the material was proposed. The main feature of this model is a depletion of the density of states present at the Fermi level. In our opinion, we see a manifestation of one pseudogap for the optimally doped crystal, and two different pseudogaps for the underdoped one.

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