

Lorenz Number in High T_c Superconductors: Evidence for Bipolarons

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The strong electron-phonon interaction in cuprates has gathered support over the last decade in a number of experiments. While phonons remain almost unrenormalized, electrons are transformed into itinerant bipolarons and thermally excited polarons when the electron-phonon interaction is strong. We calculate the Lorenz number of the system to show that the Wiedemann-Franz law breaks down because of the interference of polaron and bipolaron contributions in the heat flow. The model fits numerically the experimental Hall Lorenz number, which provides direct evidence for bipolarons in the cuprates.

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The discovery of high-temperature superconductors [1,2] has broken constraints on the maximum T_c predicted by the conventional theory of low-temperature superconducting metals and alloys. Understanding the pairing mechanism of carriers and the nature of the normal state in cuprates and other novel superconductors has been a challenging problem of condensed matter physics. A number of theoretical models have been proposed, which rely on different nonphononic mechanisms of pairing (see, for example, [3,4]). On the other hand, over the last decade, increasing evidence for the electron-phonon interaction has been provided by isotope effect measurements [5], infrared [6–8] and thermal conductivity [9], neutron scattering [10], and more recently by angle-resolved photoemission spectroscopy [11,12].

To account for the high values of T_c in the cuprates, one has to consider electron-phonon (e -ph) interactions, which are larger than those used in the intermediate coupling theory of superconductivity [13]. Regardless of the adiabatic ratio, the Migdal-Eliashberg theory of superconductivity and the Fermi liquid have been shown to break down at the e -ph coupling constant $\lambda \approx 1$ [14]. The many-electron system collapses into the small (bi)-polaron regime at $\lambda \gtrsim 1$ with well-separated vibration and charge-carrier degrees of freedom. Although it might have been thought that these carriers would have a mass too large to be mobile, the inclusion of the on-site Coulomb repulsion and the poor screening of the long-range e -ph interaction do lead to *mobile* intersite bipolarons [15,16]. Above T_c the Bose gas of these bipolarons is nondegenerate and below T_c their phase coherence sets in and superfluidity of the doubly charged $2e$ bosons can occur. In this picture, the thermally excited single polarons coexist with the Bose gas.

There is much evidence for the crossover regime at T^* and normal-state charge and spin gaps in the cuprates [17]. These energy gaps could be understood as being half of the binding energy Δ and the singlet-triplet gap of preformed bipolarons, respectively, [18]. Many other experimental observations were explained using the bipolaron model [19].

These include the Hall ratio, the Hall angle, ab and c -axis resistivities, magnetic susceptibility, and angle-resolved photoemission. The bipolaron model provides parameter-free fits of critical temperatures, upper critical fields, explains a remarkable increase of the quasiparticle lifetime below T_c [20], and the symmetry of the order parameter [21] in many cuprates. Further evidence for bipolarons comes from a parameter-free estimate of the renormalized Fermi energy ϵ_F [22], which yields a value well below 100 meV. It is so small that pairing is certainly *individual* in most cuprates; i.e., the bipolaron size is smaller than the intercarrier distance. This is the case in a (quasi)two-dimensional system, if

$$\epsilon_F \lesssim \pi\Delta. \quad (1)$$

The normal-state pseudogap, experimentally measured in many cuprates, was found as large as $\Delta/2 \gtrsim 50$ meV [17], so that Eq. (1) is well satisfied in underdoped and probably also in optimally doped cuprates. One should notice that a coherence length in the charged Bose gas is *not* the size of a boson. It depends on the interparticle distance and the mean-free path, [18], and might be as large as in the BCS superconductors. Hence, it is incorrect to apply the ratio of the coherence length to the intercarrier distance as a criterion of the BCS-Bose liquid crossover. The criterion of real-space pairing is given by Eq. (1).

Direct evidence for the existence of charged $2e$ Bose liquid in the normal-state cuprate materials is highly desirable. In 1993 Alexandrov and Mott [23] discussed the thermal conductivity κ ; the contribution from the carriers given by the Wiedemann-Franz ratio depends strongly on the elementary charge as $\sim (e^*)^{-2}$ and should be significantly suppressed in the case of $e^* = 2e$ compared with the Fermi-liquid contribution. As a result, the Lorenz number, $L = (e/k_B)^2 \kappa_e / (T\sigma)$, differs significantly from the Sommerfeld value $L_e = \pi^2/3$ of the standard Fermi-liquid theory, if carriers are bipolarons. Here κ_e , σ , and e are the electronic thermal conductivity, the electrical conductivity, and the elementary charge, respectively. Reference [23] predicted a very low Lorenz

number L_b for bipolarons, $L_b = 6L_e/(4\pi^2) \approx 0.15L_e$, due to the double charge of carriers, and also due to their nearly classical distribution function above T_c .

Unfortunately, the extraction of the electron thermal conductivity has proven difficult since both the electron term κ_e and the phonon term κ_{ph} are comparable to each other in the cuprates. Some experiments have attempted to get around this problem in a variety of methods [24–26]. In particular, Takenaka *et al.* [24] found that κ_e is constant or weakly T dependent in the normal state of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$. This approximately T -independent κ_e therefore implies the violation of the Wiedemann-Franz law (since the resistivity is found to be a nonlinear function of temperature) in the underdoped region. The breakdown of the Wiedemann-Franz law has been seen also in other cuprates [27,28].

More recently a new way to determine the Lorenz number has been realized by Zhang *et al.* [29], based on the thermal Hall conductivity. The thermal Hall effect allowed for an efficient way to separate the phonon heat current even when it is dominant. As a result, the ‘‘Hall’’ Lorenz number, $L_H = L_{xy} = (e/k_B)^2 \kappa_{xy}/(T\sigma_{xy})$, has been directly measured in $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ because transverse thermal κ_{xy} and electrical σ_{xy} conductivities involve only the electrons. Remarkably, the measured value of L_{xy} just above T_c is about the same as predicted by the bipolaron model, $L_{xy} \approx 0.15L_e$. However, the experimental L_{xy} showed a strong temperature dependence, which violates the Wiedemann-Franz law. This experimental observation is hard to explain in the framework of any Fermi-liquid model.

In this Letter we propose a theory of the Lorenz number in the cuprates explaining the experimental results by Zhang *et al.* [29]. Our particular interest lies in the conclusions that the Wiedemann-Franz law is violated in the cuprates in the temperature range below the crossover temperature T^* . Here we demonstrate that the Wiedemann-Franz law breaks down because of the interference of polaron and bipolaron contributions to the heat transport. When thermally excited polarons are included, the bipolaron model explains the violation of the Wiedemann-Franz law in the cuprates and the Hall Lorenz number as seen in the experiment.

$$c_{xx} = c_{yy} = \frac{\sigma_p}{2e^2} [T\Gamma_p + \Delta/2 + e\phi + 2A(T\Gamma_b + 2e\phi)],$$

$$c_{yx} = -c_{xy} = \frac{\sigma_p}{2e^2} [\Theta_p(T\Gamma_p + \Delta/2 + e\phi) + 2A\Theta_b(T\Gamma_b + 2e\phi)],$$

$$d_{xx} = d_{yy} = \frac{\sigma_p}{e^2} \left\{ T\gamma_p + \Gamma_p(\Delta - \mu/2 + e\phi) + (\Delta/2 + e\phi) \frac{\Delta - \mu}{2T} + A[T\gamma_b + \Gamma_b(2e\phi - \mu) - 2e\phi\mu/T] \right\},$$

$$d_{yx} = -d_{xy} = \frac{\sigma_p}{e^2} \left\{ \Theta_p \left[T\gamma_p + \Gamma_p(\Delta - \mu/2 + e\phi) + (\Delta/2 + e\phi) \frac{\Delta - \mu}{2T} \right] + A\Theta_b [T\gamma_b + \Gamma_b(2e\phi - \mu) - 2e\phi\mu/T] \right\}.$$

Here

$$\Gamma = \frac{\int_0^\infty dEE^2 \partial f_0 / \partial E}{T \int_0^\infty dEE \partial f_0 / \partial E} = \frac{2\Phi(z, 2, 1)}{\Phi(z, 1, 1)}$$

Thermally excited phonons and (bi)polarons are well decoupled in the strong-coupling regime of the electron-phonon interaction [18], so that the conventional Boltzmann equation for renormalized carries can be applied. We make use of the τ approximation [30] in an electric field $\mathbf{E} = \nabla\phi$, a temperature gradient ∇T , and in a weak magnetic field $\mathbf{B} \perp \mathbf{E}, \nabla T$. The bipolaron and single-polaron nonequilibrium distributions are found as

$$f(\mathbf{k}) = f_0(E) + \tau \frac{\partial f_0}{\partial E} \mathbf{v} \cdot \{ \mathbf{F} + \Theta \mathbf{n} \times \mathbf{F} \}, \quad (2)$$

where $\mathbf{v} = \partial E / \partial \mathbf{k}$, $\mathbf{F} = (E - \mu) \nabla T / T + \nabla(\mu - 2e\phi)$ and $f_0(E) = [y^{-1} \exp(E/T) - 1]^{-1}$ for bipolarons with the energy $E = k^2/(2m_b)$, and the Hall angle $\Theta = \Theta_b = 2eB\tau_b/m_b$, and $\mathbf{F} = (E + \Delta/2 - \mu/2) \nabla T / T + \nabla(\mu/2 - e\phi)$ and $f_0(E) = \{y^{-1/2} \exp[(E + \Delta/2)/T] + 1\}^{-1}$, $E = k^2/(2m_p)$ and $\Theta = \Theta_p = eB\tau_p/m_p$ for thermally excited polarons. Here $m_{b,p}$ are the bipolaron and polaron masses of *two-dimensional* carriers, $y = \exp(\mu/T)$, μ is the chemical potential, $\hbar = c = k_B = 1$, and $\mathbf{n} = \mathbf{B}/B$ is a unit vector in the direction of the magnetic field. Equation (2) is used to calculate the electrical and thermal currents induced by the applied thermal and potential gradients as

$$j_\alpha = a_{\alpha\beta} \nabla_\beta (\mu - 2e\phi) + b_{\alpha\beta} \nabla_\beta T, \quad (3)$$

$$w_\alpha = c_{\alpha\beta} \nabla_\beta (\mu - 2e\phi) + d_{\alpha\beta} \nabla_\beta T. \quad (4)$$

Equation (3) defines the current with the polaronic conductivity $\sigma_p = e^2 \tau_p n_p / m_p$, where the kinetic coefficients are given by

$$\begin{aligned} a_{xx} &= a_{yy} = \frac{1}{2e} \sigma_p (1 + 4A), \\ a_{yx} &= -a_{xy} = \frac{1}{2e} \sigma_p (\Theta_p + 4A\Theta_b), \\ b_{xx} &= b_{yy} = \frac{\sigma_p}{e} \left[\Gamma_p + \frac{\Delta - \mu}{2T} + 2A(\Gamma_b - \mu/T) \right], \\ b_{yx} &= -b_{xy} \\ &= \frac{\sigma_p}{e} \left[\Theta_p \left(\Gamma_p + \frac{\Delta - \mu}{2T} \right) + 2A\Theta_b (\Gamma_b - \mu/T) \right]. \end{aligned} \quad (5)$$

Equation (4) defines the heat flow with the coefficients given by

and

$$\gamma = \frac{\int_0^\infty dEE^3 \partial f_0 / \partial E}{T^2 \int_0^\infty dEE \partial f_0 / \partial E} = \frac{6\Phi(z, 3, 1)}{\Phi(z, 1, 1)}$$

are numerical coefficients, expressed in terms of the Lerch transcendent $\Phi(z, s, a) = \sum_{k=0}^\infty z^k / (a+k)^s$ with $z = y$ in Γ_b , γ_b , and $z = -y^{1/2} \exp[-\Delta/(2T)]$ in Γ_p , γ_p , and $A = m_p \tau_b n_b / (m_b \tau_p n_p)$ is the ratio of the bipolaron and polaron contributions to the transport, which strongly depends on the temperature. For simplicity we neglect the spin gap, which is small in the optimally doped cuprates [17]. Then the bipolaron singlet and triplet states are nearly degenerate, so that the bipolaron and polaron densities are expressed as

$$n_b = \frac{2m_b T}{\pi} |\ln(1-y)|, \quad (7)$$

$$n_p = \frac{m_p T}{\pi} \ln \left[1 + y^{1/2} \exp\left(-\frac{\Delta}{2T}\right) \right]. \quad (8)$$

Using the kinetic coefficients Eqs. (5) and (6) we obtain

$$\rho = \frac{1}{\sigma_p(1+4A)}, \quad (9)$$

$$R_H = \frac{1 + 4A\Theta_b/\Theta_p}{en_p(1+4A)^2}, \quad (10)$$

$$L = \frac{L_p + 4AL_b}{1+4A} + \frac{A[2\Gamma_p - \Gamma_b + \Delta/T]^2}{(1+4A)^2}, \quad (11)$$

$$L_H = \frac{L_p + 4AL_b\Theta_b/\Theta_p}{1 + 4A\Theta_b/\Theta_p} + \frac{A(4A + \Theta_b/\Theta_p)[2\Gamma_p - \Gamma_b + \Delta/T]^2}{(1+4A)^2(1+4A\Theta_b/\Theta_p)} \quad (12)$$

for the in-plane resistivity, the Hall ratio, the Lorenz number, and the Hall Lorenz number, respectively, where $L_p = (\gamma_p - \Gamma_p^2)$ and $L_b = (\gamma_b - \Gamma_b^2)/4$ are the polaron and bipolaron Lorenz numbers. In the limit of a pure polaronic system (i.e., $A = 0$) the Lorenz numbers, Eqs. (11) and (12) are $L = L_H = L_p$. In the opposite limit of a pure bipolaronic system (i.e., $A = \infty$) we obtain a reduced Lorenz number [23] $L = L_H = L_b$. However, in general our Eqs. (11) and (12) yield the *temperature dependent* Lorenz numbers that differ significantly from both limits. The main difference originates in the second terms on the right-hand side of Eqs. (11) and (12), which describe an interference of polaron and bipolaron contributions in the heat flow. In the low-temperature regime, $T \ll \Delta$, this contribution is exponentially small because the number of unpaired polarons is small. However, it is enhanced by the factor $(\Delta/T)^2$ and becomes important in the intermediate temperature range $T_c < T < T^*$. The contribution appears as a result of the recombination of

a pair of polarons into the bipolaronic bound state at the cold end of the sample, which is reminiscent to the contribution of the electron-hole pairs to the heat flow in semiconductors [30]. These terms are mainly responsible for the breakdown of the Wiedemann-Franz law in the bipolaronic system.

It has been shown that the bipolaron model nicely fits the temperature dependencies of the in-plane [31] and out-of-plane [32] resistivities and the Hall ratio in the cuprates. Here we show that it also fits the Hall Lorenz number measured by Zhang *et al.* [29]. To reduce the number of fitting parameters we take the charge pseudo-gap $\Delta/2 = 600$ K, as found by Mihailovic *et al.* [17] for nearly optimally doped $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ in their systematic analysis of charge and spin spectroscopies. According to Ref. [33] the main scattering channel above T_c is due to the particle-particle collisions with the relaxation time $\tau_{b,p} \propto 1/T^2$. The chemical potential is pinned near the mobility edge, so that $y \approx 0.6$ in a wide temperature range, if the number of localized states in the random potential is about the same as the number of bipolarons [33]. This is the case in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, where every excess oxygen ion x can localize the bipolaron. As a result, there is only one fitting parameter in L_H , Eq. (12), which is the ratio of the bipolaron and polaron Hall angles Θ_b/Θ_p . The model well fits the experiment, Fig. 1, with a reasonable value of $\Theta_b/\Theta_p = 0.44$. It also quantitatively reproduces the (quasi)linear in-plane resistivity and the inverse Hall ratio, as observed in the cuprates (upper inset of Fig. 1 and Refs. [31,33]).

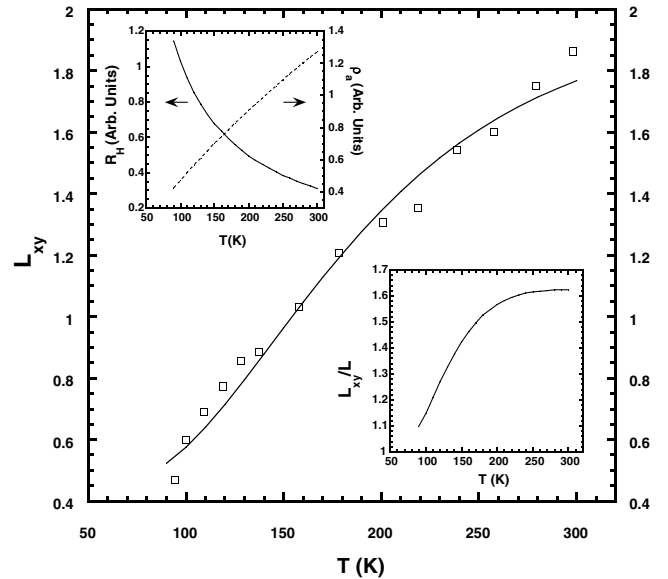


FIG. 1. The experimental Hall Lorenz number [29] in $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ fitted by the bipolaron theory, Eqs. (11) and (12), with $\Theta_b/\Theta_p = 0.44$. The upper inset shows the linear in-plane resistivity and the Hall ratio. The lower inset shows the ratio of the Hall Lorenz number to the Lorenz number as a function of temperature.

The lower inset of Fig. 1 shows a slightly lower Lorenz number compared to the Hall Lorenz number produced by our calculations. Because the thermal Hall conductivity directly measures the Lorenz number in the framework of our model, it can be used to measure the lattice contribution to the heat flow as well. When we subtract the electronic contribution determined by using the Lorenz number, the lattice contribution to the diagonal heat flow appears to be much higher than is anticipated in the framework of any Fermi-liquid model.

We notice that some recent measurements [34] on $Tl_2Ba_2CuO_{6+\delta}$ suggest that the Wiedemann-Franz law holds perfectly well in the overdoped region and therefore conclude that the Fermi liquid prevails at this doping range. Alexandrov and Mott [18] suggested that there might be a crossover from the Bose-Einstein condensation to a BCS-like *polaronic* superconductivity across the phase diagram. Thus Proust *et al.*'s results [34] are still compatible with the (bi)polaron picture. If the Fermi liquid does exist at overdoping then it is likely that the heavy doping causes an "overcrowding effect" where the polarons find it difficult to form bipolarons due to the larger number of competing holes [18].

We conclude that by the necessary inclusion of thermally excited polarons as the temperature rises, the bipolaron model predicts the Lorenz number very close to experiment in underdoped and optimally doped cuprates. Our consideration leads to good fits for the experimental Hall Lorenz number, Hall ratio, and the in-plane resistivity. The interference of the polaron and bipolaron contributions to the energy flow breaks down the Wiedemann-Franz law and results in the unusual temperature dependence of the Lorenz number.

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