

Determining the Wiedemann-Franz Ratio from the Thermal Hall Conductivity: Application to Cu and YBa₂Cu₃O_{6.95}

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The Wiedemann-Franz (WF) ratio compares the thermal and electrical conductivities in a metal. We describe a new way to determine its value, based on the thermal Hall conductivity. The technique is applied to copper and to untwinned YBaCuO. In the latter, we uncover a T -linear dependence and suppression of the Hall-channel WF ratio. We discuss the implications of this suppression. The general suppression of the WF ratio in systems with predominant electron-electron scattering is discussed.

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The electron fluid in a metal is an excellent conductor of both electric charge and entropy. In familiar metals such as Au, Pb, and Cu, the thermal conductivity of the electrons is so large that the phonons account for less than 1% of the heat current at any temperature T . Wiedemann and Franz (WF) observed that the ratio of the thermal and electrical conductivities is very nearly the same in many metals [1]. This ratio is expressed as the Lorenz number, which is conveniently written in dimensionless form as

$$\mathcal{L} = \frac{\kappa_e}{T\sigma} \left(\frac{e}{k_B} \right)^2, \quad (1)$$

where κ_e is the electronic thermal conductivity, σ is the electrical conductivity, e is the elementary charge, and k_B is Boltzmann's constant. In standard transport theory, \mathcal{L} equals the Sommerfeld value $\pi^2/3$ if the mean-free-paths (mfp) are assumed identical for charge and heat transport. Indeed, in all conventional metals, the observed \mathcal{L} is rather close to this number above 273 K [2]. However, below ~ 273 K, the observed \mathcal{L} falls significantly below this value, implying that the heat current is more strongly scattered relative to the charge current. Because \mathcal{L} compares directly the charge and entropy currents, it has contributed strongly to our current understanding of how the two currents are affected by distinct scattering processes in conventional metals [3].

In solids, the observed thermal conductivity κ is the sum of the electronic and phonon conductivity κ_{ph} , viz. $\kappa = \kappa_e + \kappa_{\text{ph}}$. In conventional metals where $\kappa_{\text{ph}} \ll \kappa_e$, one may use κ instead of κ_e to evaluate \mathcal{L} with negligible error. However, in conductors with relatively small carrier densities, κ_{ph} is often much larger than κ_e . These conductors (with resistivities ρ exceeding 100 $\mu\Omega$ cm) include many interesting systems such as the cuprates, doped fullerenes, quasicrystals, and newer materials such as CaB₆ [4]. Recent theoretical discussions of charge versus entropy currents are most applicable to these conductors. Ironically, their WF ratio seems experimentally inaccessible using conventional techniques. Hence, a fresh experimental approach is desirable.

The thermal Hall effect provides a rather efficient way to screen out the phonon heat current (even when it is dominant). In zero field, the observed thermal current \mathbf{J}_Q is parallel to the temperature gradient $-\nabla T$ (applied $\parallel \hat{\mathbf{x}}$). A field $\mathbf{H} \parallel \hat{\mathbf{z}}$ generates a Lorentz force that acts only on the electronic component of \mathbf{J}_Q . This produces a transverse Hall current parallel to $\pm \hat{\mathbf{y}}$ (depending on the sign of the charge carriers). Thus, the transverse Hall conductivity κ_{xy} involves only the electrons (the phonon current is strictly unaffected by \mathbf{H}). By forming the ratio in Eq. (1) with κ_{xy} and the electrical Hall conductivity σ_{xy} , we may measure directly the "Hall" Lorenz number $\mathcal{L}_{xy} \equiv [\kappa_{xy}/T\sigma_{xy}](e/k_B)^2$. At sufficiently high T , \mathcal{L}_{xy} approaches the Sommerfeld value [5].

We have applied the technique to a detwinned crystal of optimally doped cuprate YBa₂Cu₃O_{6.95} (YBCO) with a critical temperature $T_c = 93.3$ K, and to elemental Cu. A longitudinal gradient $-\nabla T$ is applied $\parallel \mathbf{a}$ of the YBCO crystal ($\partial_x T \sim 2$ K), and the transverse gradient $-\partial_y T$ is measured using a pair of thermocouples (chromel-constantan) versus field ($\mathbf{H} \parallel \pm \mathbf{c}$). The Hall signal $-\partial_H T$ is the field-*odd* component of $-\partial_y T$ [6]. κ_{yx} is computed as $[\partial_H T / \partial_x T](\kappa_{xx}\kappa_b/\kappa_a)$. We measured $\kappa_a = \kappa_{xx}$, and used the anisotropy κ_b/κ_a previously measured in another crystal from the same batch (see Ref. [7]). The copper sample was cut from oxygen-free high-conductivity (OFHC) stock, but was not vacuum annealed to further reduce lattice disorder.

First, we discuss the T dependence of κ_{xy} in Cu, and compare \mathcal{L}_{xy} with the standard Lorenz number (see Ref. [8] for early data on κ_{xy}). Figure 1 displays traces of κ_{xy} versus H between 60 and 350 K measured in sample 1. In order to calculate \mathcal{L} and \mathcal{L}_{xy} , we have also measured its electrical conductivity σ and Hall conductivity σ_{xy} . (Below 50 K, where κ_{xy} and σ_{xy} display increasing curvature vs H , \mathcal{L}_{xy} is obtained from their values in the limit of weak-fields.)

The values of κ vs T in sample 1 are in close agreement with a compilation by Powell *et al.* [9]. However, in

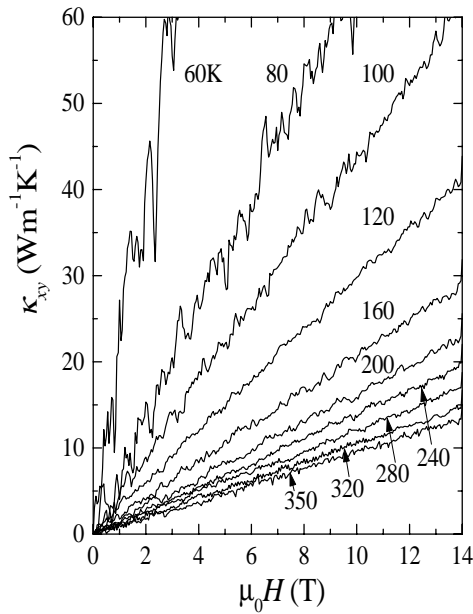


FIG. 1. The field dependence of κ_{xy} (electronlike) in unannealed OFHC copper at selected T in sample 1 (dimensions $4 \text{ mm} \times 0.3 \text{ mm} \times 50 \text{ }\mu\text{m}$). A gradient $\delta_x T \sim 0.4 \text{ K}$ is applied along the sample length ($\parallel \hat{x}$ at 14 T corresponds to a Hall temperature difference $\delta_y T$ across the sample width of $\sim 1.6 \text{ mK}$).

samples that have been carefully annealed, the peak value (at 20 K) may be twice as large [see Berman and MacDonald (BM) [10]].

Figure 2 shows that \mathcal{L} and \mathcal{L}_{xy} in our sample start at values slightly higher than the Sommerfeld value at 350 K, and decrease with falling T , with \mathcal{L}_{xy} decreasing slightly faster. In Cu, the Debye temperature θ_D is 343 K. Both Lorenz numbers reach a minimum near 60 K, and increase again at lower T . For comparison, we show (broken line) \mathcal{L} reported by BM [10]. The minimum is deeper and occurs at a lower T (20 K). As discussed later, this is consistent with its higher purity.

In conventional metals, electronic currents are limited by scattering of electrons by phonons (at finite T). Large-angle scattering involving phonons with large wave vectors \mathbf{q} ($q > k_F$, the Fermi wave vector) are equally disruptive of the charge and heat currents. By contrast, small-angle scattering ($q \ll k_F$) relaxes only the heat current, leaving the charge current relatively unaffected [3]. In terms of ℓ_S and ℓ_e (the mean-free paths for entropy and charge transport, respectively) we may express \mathcal{L} as $(\pi^2/3)\langle \ell_S \rangle / \langle \ell_e \rangle$, where $\langle \dots \rangle$ denotes averaging over the Fermi surface (FS). At high temperature ($T \geq \theta_D$), we have $\ell_S \sim \ell_e$ because large-angle scattering is dominant. As T decreases below θ_D , the phonon population is increasingly skewed towards the small- q limit, so that ℓ_e increases relatively faster than ℓ_S .

This accounts for the decrease in \mathcal{L} in Fig. 2. At very low T , when elastic scattering from impurities dominates, ℓ_e and ℓ_S are again equal, and \mathcal{L} returns to the Som-

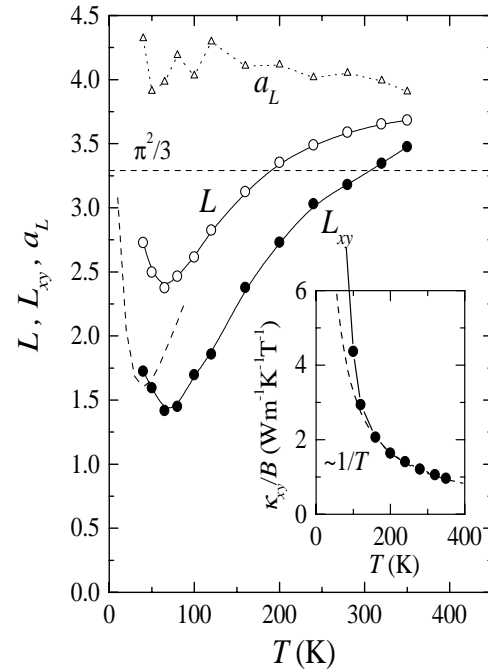


FIG. 2. The T dependence of the conventional Lorenz number \mathcal{L} (open) and Hall-Lorenz number \mathcal{L}_{xy} (solid circles) measured in OFHC copper (sample 1). Both \mathcal{L} and \mathcal{L}_{xy} decrease from their high- T asymptotic values ($\sim 10\%$ higher than the Sommerfeld value), with the latter falling faster. To compare the two rates, we plot (open triangles) the quantity $a_L = \mathcal{L}^2 / \mathcal{L}_{xy}$. The near constancy of a_L implies that $\mathcal{L}_{xy} \sim \mathcal{L}^2$ (see text). The inset shows the T dependence of κ_{xy}/B measured in the limit $B \rightarrow 0$. The broken line varies as $1/T$.

merfeld value. In our sample, this turnaround occurs near 60 K, whereas in the cleaner sample of BM, it occurs at 20 K. In comparing \mathcal{L} with \mathcal{L}_{xy} , we find that both display a minimum at nearly the same T . However, on the high- T side, \mathcal{L}_{xy} falls faster with decreasing T . The two rates are compared via $a_L \equiv \mathcal{L}^2 / \mathcal{L}_{xy}$. The near constancy of a_L is consistent with the expectation [5] that $\mathcal{L} \sim \langle \ell_S \rangle / \langle \ell_e \rangle$, whereas $\mathcal{L}_{xy} \sim \langle \ell_S \rangle^2 / \langle \ell_e \rangle^2$. Hence, \mathcal{L}_{xy} falls faster because it involves the squares of the mfp's. In Cu, the Hall-Lorenz number approaches the same WF ratio at high T , so that it provides information comparable to \mathcal{L} . Moreover, additional information on scattering processes may be derived from its low T behavior.

Thermal conductivity measurements have produced a wealth of information on the superconducting state of the cuprates. In YBCO, they provided early evidence favoring an unconventional pairing symmetry [11,12], and long lifetimes for the quasiparticles at low temperatures [13]. The contributions of the chains to κ_b [7] and the effect of hole doping [14] also have been investigated. Above T_c , however, the problem of estimating κ_{ph} has been a serious obstacle to the extraction of κ_e . In fact, neither the magnitude nor the T dependence of κ_e in the normal state may be regarded as experimentally established. Hence, the present technique is especially appropriate. While the behavior of κ_{xy} in YBCO was investigated previously [13,15,16] in the

superconducting state, the rapid attenuation of the thermal Hall signal precluded measurements above ~ 100 K. The improved resolution now allows κ_{xy} to be determined reliably up to 320 K. Figure 3 displays the H dependence of κ_{xy} at selected temperatures from 95 to 320 K. It is worth a second remark that, as κ_{xy} derives no contribution from the phonons, the raw experimental curves directly mirror the electronic heat current. We proceed to compare it with the charge current. In the normal state of YBCO, σ_{xy} is known to vary as $1/T^3$. This produces the anomalous T dependence of the Hall coefficient R_H that is so characteristic of the cuprates [17]. It is interesting to ask if the same dependence is observed in κ_{xy}/T (dividing by T to remove the heat capacity contribution). As shown in Fig. 4 (open symbols), the T dependence of the κ_{xy}/B is well-fitted to $T^{-1.2}$. Hence, we find that κ_{xy}/T actually has a weaker dependence than σ_{xy} .

When we calculate \mathcal{L}_{xy} , we find that it varies linearly with T (solid circles in Fig. 4). In addition to this unusual T dependence, its value from 95 to 320 K is significantly smaller than the Sommerfeld value.

In some previous reports, values of \mathcal{L} (often close to the Sommerfeld value) were obtained using a variety of arguments to subtract κ_{ph} from κ . However, these arguments are suspect for the following reasons. In the cuprates, κ_{ph} is strongly decreased by lattice disorder associated with dopants (κ is 2 to 4 times larger in the pristine parent compound La_2CuO_4 compared with doped compounds [14]). Moreover, within the plane, κ_{ph} is strongly anisotropic. In both $\text{YBa}_2\text{Cu}_3\text{O}_7$ and its two-chain variant $\text{YBa}_2\text{Cu}_4\text{O}_8$,

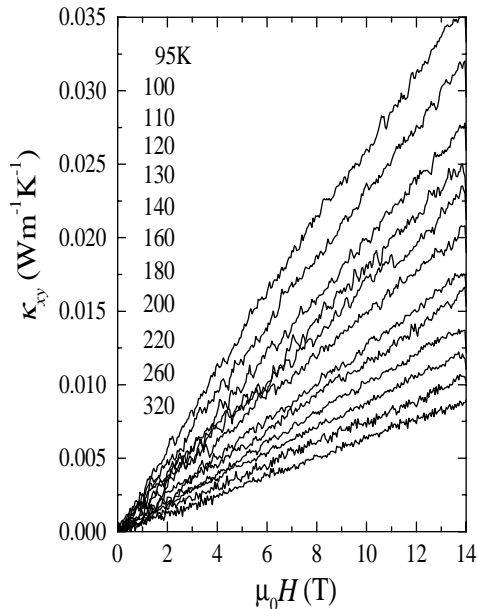


FIG. 3. The field dependence of κ_{xy} (holelike) measured in untwinned $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ at selected T (with $\mathbf{H} \parallel \mathbf{c}$). Each trace is in sequence with values of T indicated. At 320 K and 14 T, the value of κ_{xy} corresponds to a Hall signal of 1.5 mK (in an applied gradient $\delta_x T \sim 2\text{K}$).

κ_{ph} is significantly larger along \mathbf{b} (the chain axis) compared with \mathbf{a} , because of the anisotropy in elastic constants [18]. These factors make comparisons between doped and undoped crystals, or between κ measured along the axes \mathbf{a} and \mathbf{b} in the same sample, quite unreliable. A different approach is to extrapolate the value of κ_e of quasiparticles in the superconducting state to temperatures just above T_c . A recent experiment [15] reports extrapolated values of κ_e in the range 0.8–1.0 W/mK at T_c . With $\rho_a = 100 \mu\Omega \text{ cm}$, this gives $\mathcal{L} = 1.1\text{--}1.4$, which is closer to our \mathcal{L}_{xy} than to the Sommerfeld value.

Aside from the overall suppressed scale, the nominally T -linear dependence of \mathcal{L}_{xy} is also unusual. An extrapolation (broken line in Fig. 1) shows that it intersects the Sommerfeld value near 500 K. We note that the acoustic phonons in YBCO have a maximum energy of 20 mV. Above 200 K, the dominant acoustic phonons should have sufficient momenta to span the full FS ($\Theta_D = 420$ K is higher because of the large unit cell). Certainly, by 320 K, we should have $\langle \ell_S \rangle = \langle \ell_e \rangle$ if electron-phonon scattering is the dominant mechanism for relaxing the two currents. Hence, the small values of \mathcal{L}_{xy} and the high temperature scale at which it attains the Sommerfeld value (500 K) seem incompatible with dominant electron-phonon scattering.

In contrast, a suppressed WF ratio may be expected in systems with dominant electron-electron (ee) scattering.

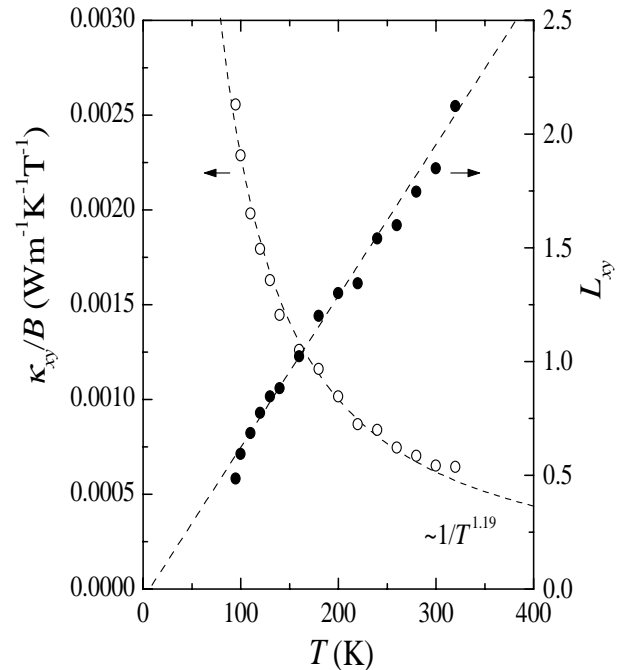


FIG. 4. The T dependence of the Hall-Lorenz number \mathcal{L}_{xy} (solid circles) in untwinned $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ determined from $\kappa_{xy}/T\sigma_{xy}$ (\mathcal{L} is unavailable for comparison). Linear extrapolation of \mathcal{L}_{xy} (broken line) shows that it attains the Sommerfeld value $\pi^2/3$ near 500 K. The open circles represent the weak-field values of κ_{xy}/B derived from Fig. 3 (fit to curve $1/T^{1.19}$ is shown).

A discussion of this point illustrates how normal (N) and umklapp (U) scattering processes influence the WF ratio. As in the case of lattice thermal conduction [19,20], N processes leave the total momentum of the electron gas unchanged, so that the charge current cannot relax without U processes. However (unlike lattice conduction), N -process ee scattering *does* relax the heat current because it causes a redistribution of energy between hot and cold electrons [21]. This distinction implies that systems in which ee scattering is dominant have a strongly reduced Lorenz number. Moreover, because the relative weights of N versus U processes are not determined by Θ_D in ee scattering, this reduction could prevail to very high T . These issues are intimately related to behavior of the WF ratio. Hence, the T dependences of κ_{xy} and \mathcal{L}_{xy} displayed in Fig. 4 should place strong constraints on transport models for YBCO.

In summary, we have described measurements of the Hall-Lorenz number, obtained as the ratio of κ_{xy}/T to σ_{xy} . In Cu, this method gives results comparable to direct measurements of \mathcal{L} . However, in systems in which lattice conduction is not small, the Hall-Lorenz experiment provides a direct comparison of the heat and charge currents of the charge carriers. A quantitative understanding of the information derived from \mathcal{L}_{xy} awaits comparison with microscopic calculations. In view of the increased interest in systems with dominant ee scattering, we expect the high-temperature WF ratio to play an increasingly prominent role.

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