In-plane thermal conductivity and Lorenz number in $YBa_2Cu_3O_{7-y}$

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We make a tentative proposal to extract the electronic contribution to the in-plane thermal conductivity $\kappa_{el}(T)$ of $YBa_2Cu_3O_{7-y}$ in the normal state. We have measured $\kappa_{ab}(T)$ for single crystals with various oxygen contents ($6.06 \leqslant 7-y \leqslant 6.93$). The systematic study of the oxygen-content dependence of κ_{ab} for the insulating phase enables us to estimate the phononic contribution $\kappa_{ph}(T)$ for the metallic phase to some extent. Based on the estimated κ_{ph}, we examined κ_{el} from the view point of whether the Wiedemann-Franz law holds or not. The estimated κ_{el} appears to show only a weak T dependence and no significant change at a characteristic temperature T^* below which the electrical conductivity $\sigma_{ab}(T)$ is enhanced possibly due to the opening of a spin gap. The difference between κ_{el} and σ_{ab} suggests the violation of the Wiedemann-Franz law below T^*. We discussed the ambiguity of our analyses and other possible interpretations of the present result as well as the picture of the charge transport speculated from the above suggestion. [S0163-1829(97)02934-2]

I. INTRODUCTION

A striking feature in the charge transport of high-T_c superconductors is the systematic deviation from the T-linear behavior in the in-plane resistivity $\rho_{ab}(\rho_a)(T)$ commonly observed below a characteristic temperature T^* well above T_c in the underdoped cuprates $YBa_2Cu_3O_{7-y}$,[1,2] $YBa_2Cu_4O_8$,[3] and $La_{2-x}Sr_xCuO_4$.[4] This characteristic behavior provides us with a clue to elucidate the mechanism of the charge transport or an interplay between charge and spin excitations.[1,2]

In order to get further insight into this issue, we have investigated the in-plane thermal conductivity $\kappa_{ab}(T)$ of $YBa_2Cu_3O_{7-y}$ using single crystals with various oxygen contents in the range $6.06 \leqslant 7-y \leqslant 6.93$. The thermal conductivity of $YBa_2Cu_3O_{7-y}$ has so far been studied by many researchers.[5] However, the previous works focused on the superconducting state.[6–13] Much less attention has been paid to its magnitude and T dependence in the normal state to make a detailed comparison between thermal and electrical conductivity. Here we make an attempt to establish the relation between the thermal and electrical conduction by studying how the characteristic behavior in ρ_{ab} below T^* is reflected in κ_{ab}.

In metals the thermal and electrical relaxation are closely related to each other and the investigations of similarities and differences between them—generally it is carried out based on Lorenz number $L_e(T) \equiv \kappa(T)/\sigma(T)T$—has enabled us to identify the mechanism of the charge transport.[14–16] In high-T_c superconductors, however, electronic (κ_{el}) and lattice (κ_{ph}) components of the in-plane thermal conductivity are both substantial, which has prevented us from understanding the thermal transport of the charge carriers.[9–13]

In order to determine κ_{el}, we have attempted to estimate κ_{ph} for the metallic phase by the detailed investigation of κ_{ab} for the insulating phase. The present study indicates that at high temperatures the T dependence of κ_{ab} should be attributed primarily to κ_{ph}, suggesting that κ_{el} shows a weak T dependence over the whole T region in the normal state and hence the Wiedemann-Franz (WF) law does not hold below T^* while it holds above T^*. Examining the $\mathbf{q}$ dependence of the scattering process based on the failure of the WF law and differences between the spin-gap structures around $\mathbf{q}=0$ and $\mathbf{Q}$ indicated by NMR experiments, it is suggested that the charge carriers are scattered predominantly by the processes with small momentum change.

II. EXPERIMENTS

Single crystals of $YBa_2Cu_3O_{7-y}$ were grown by a self-flux method using a Y_2O_3 crucible.[17,18] The oxygen content was controlled by annealing them at 600 °C for 12 h in a sealed quartz tube together with about 10 g of polycrystalline $YBa_2Cu_3O_{7-y}$ and determined by the iodometric titration of these polycrystals. After annealing, the crystals were slowly cooled in order to reduce oxygen disorder in the chain site.[1] In order to make the analyses and discussions more convincing, we have also investigated the a-b anisotropy of the thermal conduction for detwinned $YBa_2Cu_3O_{6.68}$ and the in-plane thermal conductivity of $YBa_2(Cu_{0.99}Zn_{0.01})_3O_{6.93}$. The twin defects were removed by applying uniaxial stress ($\sim 10^2$ kgf/cm^2) at 450 °C for 40 h. The annealing condition mentioned above was crucial to avoid introducing twin defects into the twin-free crystals.[2] The observation by a polarized optical microscope and single-crystalline x-ray diffraction confirm that the detwinning was perfect. The Zn content was examined by electron-probe microanalysis (EPMA).

The thermal conductivity was measured by a steady-state method. The specimen was anchored on a copper heat sink and a 120 Ω strain gauge was placed as a heater with silver paste. The temperature gradient across the specimen ΔT (0.3–0.5 K) was measured by a differential Chromel-

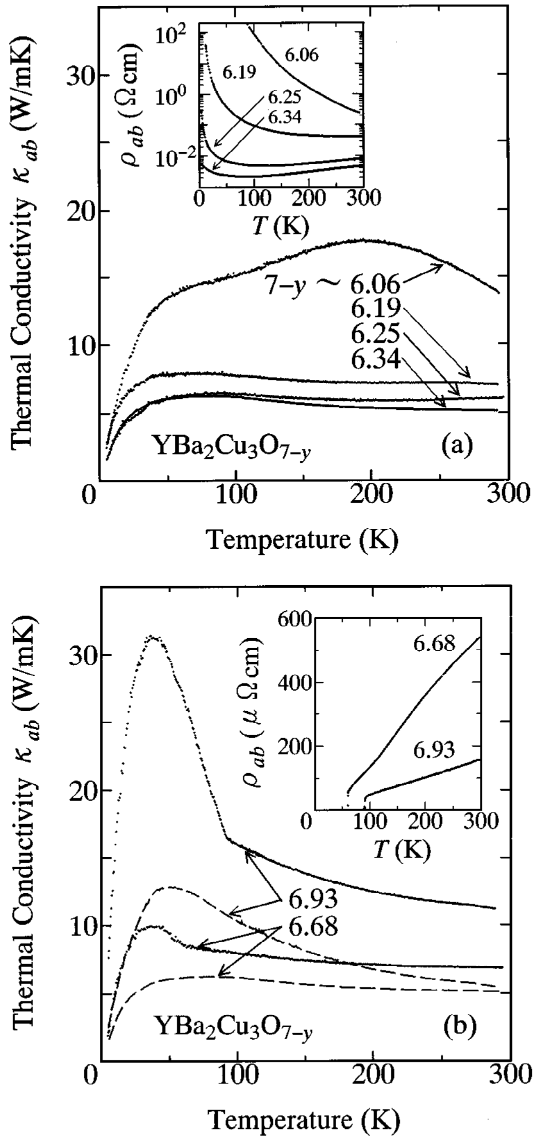

FIG. 1. In-plane thermal conductivity κ_{ab} of $YBa_2Cu_3O_{7-y}$ plotted as a function of temperature for the insulating compounds ($6.06 \leqslant 7-y \leqslant 6.34$) (a) and for the metallic compounds ($7-y \sim 6.68$ and 6.93) (b). The dashed curve shown in (b) represents the estimated phonon contribution κ_{ph} described in the text. Insets show the in-plane resistivity ρ_{ab} measured on the same crystal.

Constantan thermocouple attached to the specimen using varnish.

The experimental results are shown in Fig. 1(a) for κ_{ab} of insulating $YBa_2Cu_3O_{7-y}$ ($6.06 \leqslant 7-y \leqslant 6.34$) and in Fig. 1(b) for κ_{ab} of metallic $YBa_2Cu_3O_{7-y}$ ($T_c \sim 63$ K and 92 K for $7-y \sim 6.68$ and 6.93, respectively). The results of κ_a and κ_b for twin-free $YBa_2Cu_3O_{6.68}$ and κ_{ab} for $YBa_2(Cu_{1-z}Zn_z)_3O_{6.93}$ ($z = 0$ and ~ 0.01, $T_c \sim 80$ K) are displayed in Fig. 2 and Fig. 3, respectively. The major source of uncertainty in the thermal conductivity measurements is heat loss. The vacuum below 10^{-6} torr and adopting a fine (25 μm) Constantan wire as a lead reduce heat losses via residual gases and lead to below 1% of the measured value. Nevertheless, a strong T dependence ($\propto T^3$) of heat loss via radiation still limits the accuracy of the measurement especially at high temperatures. In order to overcome this difficulty, we have used a thick single crystal with a large cross section (typically $1\times1\times0.2$ mm^3).[19] In the present work, the ρ_{ab} measurements confirm that the crystals used here have the same quality as the thinner one used for the previous resistivity measurements.[1,20] The insets in Fig. 1 show ρ_{ab} measured on the same crystal used for the κ_{ab} measurement. Our carefully designed experimental setup enables us to obtain highly reproducible and systematic thermal conductivity data.

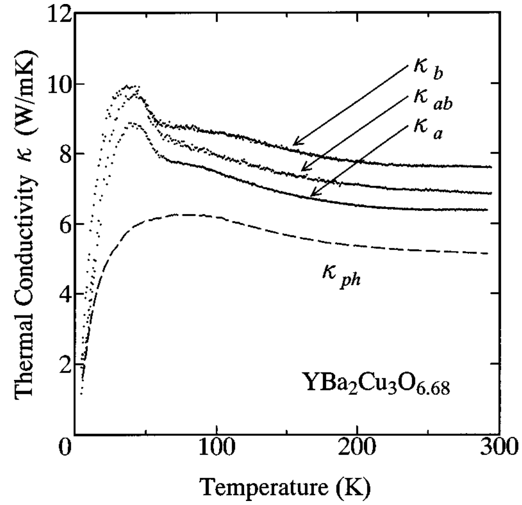

FIG. 2. Temperature dependence of in-plane thermal conductivity components κ_a and κ_b measured on a detwinned $YBa_2Cu_3O_{6.68}$. For a comparison, κ_{ab} and estimated κ_{ph} of $YBa_2Cu_3O_{6.68}$ are also shown by a solid and a dashed curve, respectively. The a-b anisotropy is attributable to the electronic components.

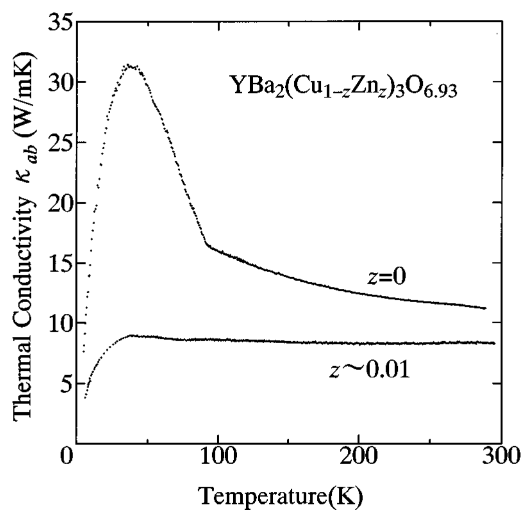

FIG. 3. Temperature dependence of κ_{ab} measured on $YBa_2(Cu_{1-z}Zn_z)_3O_{6.93}$ for $z = 0$ and ~ 0.01 ($T_c \sim 80$ K). The in-plane thermal conductivity is drastically suppressed by Zn substitution. In the normal state, T^{-1}-like behavior due to the phonon-phonon U process almost disappears. This can be interpreted as that the Zn ions disturb the phononic system of the CuO_2 plane as a main heat channel. In the superconducting state, on the other hand, the abrupt peak observed for pure crystal almost disappears, contrary to $L^*\sigma_1 T$ which shows a peak clearly below T_c. This suggests the existence of some process which contributes to W^{el} but not to ρ_{ab}.

III. RESULTS

A. Insulating phase

In insulators, heat is carried by phonons and, in some cases, by magnons. Because ρ_{ab} measured in this work is at least 5×10^{-3} Ω cm, an electronic contribution is roughly estimated to be less than 2% of the measured value, assuming the WF law $\kappa=L_0\sigma T$ [L_0 is the Lorenz number of a degenerate Fermi gas, $(\pi^2/3)(k_B/e)^2\simeq2.45\times10^{-8}$ WΩ/K^2]. Therefore, we can ignore the electronic contribution for the present oxygen-content range.

The most notable feature of κ_{ab} is the two structures for the sample with the lowest oxygen content ($7-y\sim6.06$): a shoulder at ~80 K and a broad peak at ~200 K. The thermal conductivity of an ordinary insulating crystal is characterized by a T^3 rise at low temperatures dominated by boundary scattering which crosses over to a T^{-1} tail at high temperatures due to a phonon-phonon umklapp(U) process.[14] In the present case, the peak at ~200 K is hardly explained within the framework of the conventional lattice thermal conductivity. The origin of this ''double-peak'' structure is still in dispute as is discussed later (Sec. IV A). However, it is more essential that this structure is not remarkable except in the neighborhood of $7-y=6$. This structure is rapidly suppressed by oxygenation and for the partially oxygenated compounds κ_{ab} is characterized solely by the broad peak at ~80 K which is a typical lattice thermal conductivity of an ordinary insulator. Therefore, the shoulder at $\sim$ 80 K for $\sim$ 6.06 should be considered due to the same origin of the broad peak for the partially oxygenated compounds—the crossover from a T^3 rise to a T^{-1} tail. The effect of the double-peak structure appears to be notable only for the higher-T region. In this sense, we may argue the y dependence of κ_{ph} based on the lower-temperature part of κ_{ab}. For the range 6.19–6.34, we measured κ_{ab} on the *same* crystal with various oxygen contents, which enables us to make systematic and quantitative discussions on the y dependence of $\kappa_{ab(ph)}$.

The decrease of $\kappa_{ab(ph)}$ with oxygenation is probably due to the increase of phonon-defect scatterings by the randomness in the chain layer. However, the present result shows that the drastic suppression by oxygen introduction is remarkable only in the neighborhood of $7-y=6$ and further oxygenation does not change κ_{ab} so strongly. In fact, κ_{ab} is almost the same for $\sim$ 6.25 and 6.34 except the slight difference near room temperature probably due to the remnants of the double-peak structure. This suggests that for the intermediate compositions the phononic state as a heat channel is the same regardless of oxygen content. In addition, it is noteworthy that T^{-1}-like behavior is clearly observed for $\sim$ 6.34 where the chain layers are considerably disordered. These features can be explained consistently by the picture that heat flows mainly through nearly perfect other layers and hence the randomness in the chain layers has rather indirect effects on the in-plane κ_{ph}.

A minor role of the chain layer as a heat channel is supported by the result that the a-b anisotropy of the in-plane thermal conductivity measured on a twin-free crystal arises from the electronic contribution (Fig. 2 for the 60-K material and Ref. 8 for the 90-K material). The difference between κ_a and κ_b can roughly be scaled with the difference between ρ_a and ρ_b.[21] The in-plane phononic components should be isotropic.

Impurity effect on κ_{ab} suggests that a main heat channel is CuO_2 plane. Zinc substitution suppresses κ_{ab} so drastically that in the normal state T^{-1}-like behavior, due to a phonon-phonon U process, almost disappears (Fig. 3). The NMR study indicates that the Zn ions are substituted selectively for the planar Cu(2),[22] and hence this result can be understood by the fact that the Zn substitution affects the phononic system of the CuO_2 plane as a main heat channel, which is consistent with the fact that κ_{ab} is drastically suppressed by a slight oxygenation for the nearly stoichiometric region.

B. Metallic phase

For the 90-K material, κ_{ab} is characterized by a pronounced peak below T_c and a clear T^{-1}-like tail in the normal state. For the 60-K material, the overall feature is not affected by the oxygen reduction, though its magnitude and T dependence are suppressed compared with the 90-K material. The weak T dependence of κ_{ab} in the normal state reported previously is probably due to the radiation heat loss and/or less integrity of the specimens.

First, we examine κ_{ab} in the normal state. The result of κ_{ab} for the insulating phase provides us with the following picture of κ_{ph} at high temperatures: κ_{ph} can be described as $\kappa_{ph}=(W_0^{ph}+\alpha T)^{-1}$. Here W_0^{ph} and αT are phonon thermal resistivities due to the phonon-defect and phonon-phonon processes, respectively. The y dependence of κ_{ph} is dominated by the randomness in the chain layers. For the intermediate compositions κ_{ph} is not sensitive to the oxygen content and can be commonly characterized by the T^{-1}-like tail. These features indicate that T^{-1}-like behavior of κ_{ab} for the two metallic samples should be attributed to not electronic but *phononic* origin. If we roughly estimate the electronic contribution assuming the WF law, the decrease of κ_{ab} for the 60-K material is hardly explained by increase of ρ_{ab} alone[20,23] and hence the increase of W_0^{ph} by introducing the randomness into the chain layers should be taken into account.

Turning to the superconducting state, the main subject is whether the pronounced peak below T_c is electronic or phononic in origin.[24] The present result supports the former because the peak for the 90-K material is larger than κ_{ab} for the $O_{6.06}$ crystal. The phonon mean free path should be considered originally suppressed by some scatterers other than charge carriers, probably by slight nonstoichiometry (randomness in the chain layer). Some researchers claim the phononic origin based on the result that κ_{ab} of the crystal reduced further than $\sim$ 6.06 is larger than that of the 90-K material. However, the 90-K material ($\sim$ 6.93) contains the randomness in the chain layers. In the neighborhood of the stoichiometric composition κ_{ab} is considered to be drastically suppressed by the randomness in the chain layers and hence κ_{ab} of the 90-K material should be compared with the $O_{6.06}$ crystal rather than the stochiometric $YBa_2Cu_3O_6$ because of the similar structural integrity.

IV. ANALYSES

A. Origin of the double-peak structure

We examine two candidates for the origin of this anomalous structure. One is heat conduction by the spin waves in the CuO_2 plane.[25] The contribution of magnon (κ_{mg}) is suggested by the following facts: (1) The peak temperature is comparable to the Néel temperature of the material. (2) A similar broad peak at $\sim$200 K is observed for $PrBa_2Cu_3O_{7-y}$ (Ref. 26) in which few holes are doped into the CuO_2 plane for any oxygen content and the planes remain to be a charge-transfer (CT) insulator.[27,28] (3) The drastic suppression of this peak by oxygen introduction or by a small concentration ($<$2.5 at. %) of Zn and Ni impurities[12] is consistent with the fact that the spin-correlation length in the plane decreases rapidly with hole doping into the planes or by substituting Cu with these impurities, respectively.[29]

As an alternative interpretation of this double-peak structure, the anomalous phonon damping mechanism due to tilt distortion of the CuO polyhedra is proposed.[30] Cohn *et al.* claimed that this interpretation has the following advantages over the magnetic origin: (1) weak magnetic field dependence and (2) absence of this structure in κ_{ab} for the T' compound Pr_2CuO_4,[26,31] which has no apical oxygen. However, these facts might be explained also by spin-wave contribution as follows: (1) The magnetic coupling is much stronger than the effect of an ordinary magnetic field. (2) In the case of Pr_2CuO_4, κ_{ab} is larger than that of La_2CuO_4 or $YBa_2Cu_3O_6$ probably because of a larger contribution of the lattice component due to better stoichiometry. Assuming κ_{mg} is nearly the same between Pr_2CuO_4 and $YBa_2Cu_3O_6$, κ_{ph} in Pr_2CuO_4 is about twice as large as that in $YBa_2Cu_3O_6$.

B. Separation of electronic and lattice contributions

The present experimental result indicates that the T dependence of κ_{ab} should be attributed primarily to κ_{ph}. The subject in this section is to examine the magnitude and T dependence of the electronic contribution κ_{el}. It is plausible to discuss κ_{el} within the Boltzmann transport theory. It limits $\kappa_{el} \leq L_0 \sigma T$, where the equal sign represents the WF law.[14] We examine whether the estimation of κ_{el} assuming the WF law is consistent or not with the speculation of κ_{ph} deduced from the y dependence of κ_{ab} for the insulating phase.

The WF law appears hold where T linearity of ρ_{ab} is observed because it yields a T-independent κ_{el} and hence is self-consistent with the above conclusion that the T dependence of κ_{ab} is dominated by κ_{ph}. For the 90-K material, κ_{el} is estimated to be more than 40% of κ_{ab} from $L_0 T/\rho_{ab}$. Therefore, if κ_{el} would show a remarkable T dependence, the T dependence of κ_{ab} would be affected also by the electronic contribution.

The central concern is if the enhancement of σ_{ab} below T^* leads to a similar enhancement of κ_{el} for the 60-K material. The present study is, if anything, negative to this, suggesting violation of the WF law below T^*. κ_{el} appears to be almost T independent or, at least, to show a weaker T dependence than that estimated from the enhancement of σ_{ab} assuming the WF law.

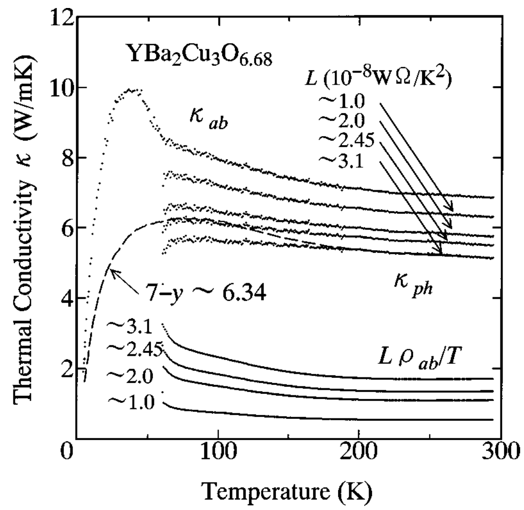

FIG. 4. The measured κ_{ab} and the estimated κ_{el} and κ_{ph} assuming the WF law with various values of Lorenz number for $YBa_2Cu_3O_{6.68}$. For comparison, κ_{ab} for $\sim$ 6.34 is also shown by a dashed curve. For the reasonable values of L, κ_{ph} is T independent or decreases with temperature decreases, which is contradictory to the prediction based on the results of κ_{ab} for the insulating phase. The T dependence of κ_{ab} is primarily attributed to κ_{ph}.

If we estimate κ_{el} to be $L_e T/\rho_{ab}$, κ_{ph} $(=\kappa_{ab}-\kappa_{el})$ is T independent or decreases with decreasing temperature unless we adopt the substantially small value of L_e compared with the Sommerfeld value L_0 and/or that measured on various metals[32] (Fig. 4). This behavior is usually observed for the heavily disordered phononic systems like amorphous solids or disordered alloys, where the phonon mean free path is so short that it is not sensitive to additional scattering processes.[14] This is contrary to the present experiment, suggesting that the phononic system of a main heat channel is rather indirectly affected by the randomness in the chain layers and hence κ_{ph} shows persistently T^{-1}-like behavior. For the intermediate compositions κ_{ph} is almost y independent and hence we may regard κ_{ab} for $\sim$ 6.34 as the "common" κ_{ph} for the partially oxygenated compounds with oxygen content ranging from $\sim$6.25 to $\sim$6.68 (the 60-K material). The above estimated κ_{ph} is rather suppressed compared with κ_{ab} of $\sim$ 6.34 [the dashed curve in Figs. 1(b) and 4].

Assuming κ_{ab} for $\sim$ 6.34 to be equal to κ_{ph} for the 60-K material, κ_{el} can be determined as a difference between the measured κ_{ab} and the above-estimated κ_{ph} (Fig. 5). It follows that in the normal state κ_{el} is almost T independent, in contrast to the dashed curve $L^* T/\rho_{ab}$ (L^* is chosen to coincide with κ_{el} at 300 K, $\sim$ 3.1×10^{-8} W Ω/K^2). The difference is more clearly envisaged in terms of the Lorenz number $L_e = \kappa_{el}\rho_{ab}/T$ (Fig. 6). One can rule out the contribution of the CuO chains to κ_{ab} by observing the difference in κ_a and ρ_a measured on the twin-free $YBa_2Cu_3O_{6.68}$. This indicates that this feature is inherent to the CuO_2 plane.

If κ_{ph} of the 60-K material is substantially suppressed compared with κ_{ab} of $\sim$ 6.34, it probably originates from the electron (charge carrier)-phonon interaction. However, this effect is considered to make only a minor contribution in this system by the following reason. The phonon thermal resistivity due to electron scattering, W_{el}^{ph}, is generally re-

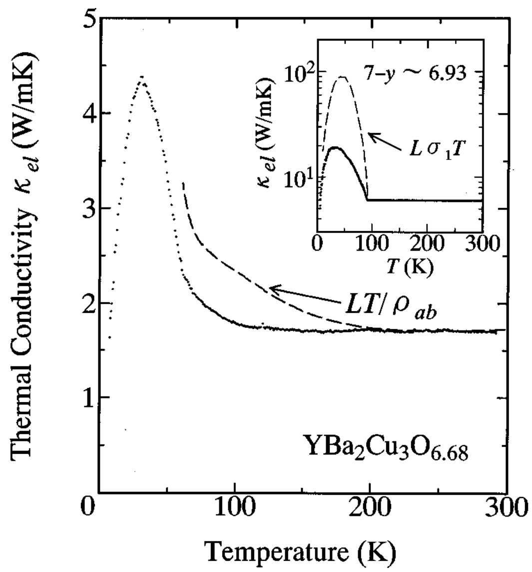

FIG. 5. Temperature dependence of the estimated electronic component of the in-plane thermal conductivity, $\kappa_{\rm el}$, for the 60-K material. The details of the estimation are described in the text. The dashed curve shows L^*T/ρ_{ab} (L^* is chosen to coincide with $\kappa_{\rm el}$ at 300 K, $\sim 3.1\times10^{-8}$ W Ω/K^2). The inset shows $\kappa_{\rm el}$ (solid curve) and $L^*\sigma_1 T$ (dashed curve) for the 90-K material. σ_1 is taken from Ref. 34.

lated to the electrical resistivity due to phonon scattering, $\rho_{\rm ph}^{\rm el}$. In the conventional picture this relation is expressed as

$$W_{\rm el}^{ph}=\frac{\rho_{\rm ph}^{\rm el}}{L_0T}\frac{\pi n_a^2}{3} \tag{1}$$

at high temperatures (n_a is the number of electron per unit cell).[14] Previous studies indicate that the electron-phonon interaction plays only a minor role on the electrical resistivity,[1,33] and hence $W_{\rm el}^{\rm ph}$ can be ignored in the present case.

The phonon-magnon (spin fluctuation) interaction may also have some contribution to $W^{\rm ph}$. However, because boson-boson scattering hardly persists at low temperatures, a phonon-magnon coupling, if any, cannot contribute to $W^{\rm ph}$. At high temperatures, if the spin scattering is dominant, $\kappa_{\rm ph}$ will increase monotonically with increasing oxygen content because the magnetic fluctuation or the magnetic order is destroyed by hole doping. Therefore, the phonon-magnon interaction seems to make only a minor contribution to $W^{\rm ph}$ because the y dependence of $\kappa_{\rm ph}$ is controlled by the randomness in the chain layers.

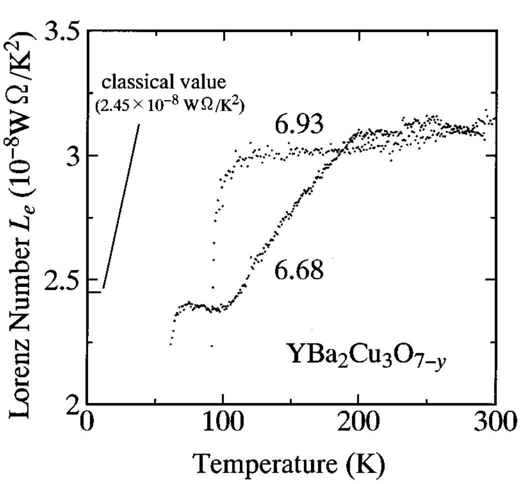

FIG. 6. Temperature dependence of the Lorenz number $L_e=\kappa_{\rm el}/\sigma_{ab}T$ estimated for $YBa_2Cu_3O_{7-y}$ in the metallic phase. For the 60-K material, L_e is T dependent below T^* while it is T independent above T^*, suggesting the failure of the WF law below T^*.

The effect of the anomalous double peak may still remain persistently at near room temperature for $\sim$ 6.34. However, this effect tends to weaken the T^{-1}-like behavior and hence $\kappa_{\rm ph}$ for the 60-K material shows more clearly the T^{-1}-like behavior than κ_{ab} for $\sim$ 6.34, which leads to a strengthening of the violation of the WF law.

Next, we make a rough estimation of $\kappa_{\rm el}$ at the superconducting state. It appears that the WF law holds over the whole T region as far as ρ_{ab} shows T linearity. Then, for the 90-K material we estimate $\kappa_{\rm el}$ and $\kappa_{\rm ph}$ in the normal state to be $L^*T/\rho_{ab}=6.0$ W/mK and $\kappa_{ab}-\kappa_{\rm el}=(W_0^{\rm ph}+\alpha T)^{-1}$, respectively. A least-squares fit yields $\alpha=5.50\times10^{-4}$ m/W and $W_0^{\rm ph}=4.48\times10^{-2}$ mK/W. The estimated $\kappa_{\rm ph}$ at high temperatures is smoothly connected to κ_{ab} of the $O_{6.06}$ crystal which is considered to represent $\kappa_{\rm ph}$ of the 90-K material at the low-T region. $\kappa_{\rm el}$ in the superconducting state is determined as a difference between κ_{ab} and this $\kappa_{\rm ph}$. Thus estimated $\kappa_{\rm ph}$, $\kappa_{\rm el}$, and L_e are shown in Fig. 1(b) (dashed curve), the inset of Fig. 5, and Fig. 6, respectively. Then, we can make a parallel analysis on the charge (quasiparticle) transport in the superconducting state by formally comparing $\kappa_{\rm el}$ with the real part of the microwave conductivity, $\sigma_1(T)$. Reflecting the enhancement of the relaxation time and a rapid decrease in the quasiparticle density, σ_1 shows a pronounced peak below T_c, which reaches a value more than 20 times the normal-state value.[34] It turns out that the estimated $\kappa_{\rm el}$ is smaller than $L^*\sigma_1 T$ below T_c, as in the case of $\kappa_{\rm el}$ in the normal state below T^* for the underdoped compounds (Inset of Fig. 5). Thus, a common mechanism might be working which violates the WF law when either superconducting or spin gap opens.

We cannot completely exclude other possibilities of interpreting the experimental results. (1) Ignoring $W_{\rm el}^{\rm ph}$ may be an oversimplification even if the electron-phonon interaction makes only a minor contribution to the carrier scattering. Therefore, the present interpretation might be altered according to a more precise estimation of $W_{\rm el}^{\rm ph}$: The WF law may hold also below T^*. In any case, it seems to be sure that the WF law holds at least above T^* or where ρ_{ab} shows the T-linear behavior. (2) A question arises whether L_e is much smaller than the Sommerfeld value L_0. For example, the Lorenz number of the nondegenerate Bose gas with charge $2e$ is $\sim\frac{1}{4}L_0$ (Ref. 35) (Sec. V). However, the present result is negative to this picture. Considering the possibility of the electron-phonon interaction and/or remnants of the double-peak structure, κ_{ab} for $\sim$ 6.34 does not appear to underestimate $\kappa_{\rm ph}$ for the 60-K material. Therefore, L_e hardly becomes small comparable to $1/4L_0$, for example.

V. DISCUSSION

Based on the correlation between T^* and the onset of a spin gap, we speculated that the in-plane charge transport is dominated by the spin excitations and the enhancement of σ_{ab} below T^* is due to the decrease in the density of the spin excitations upon opening the spin gap.[1] If the spin gap has a *different* effect on the thermal and electrical conduction, as is suggested by the present result that $\kappa_{\rm el}$ appears to show a weak T dependence also below T^*, it might be necessary to take into account different scattering processes between electrical and thermal conduction.

The results of NMR experiments show that the Knight shift ΔK, proportional to the uniform susceptibility $\chi(\mathbf{q}=0)$, is suppressed below T_K which is higher than the temperature T_R at which the nuclear relaxation $(T_1T)^{-1}$, proportional to the staggered susceptibility $\chi(\mathbf{q}=\mathbf{Q})$ with $\mathbf{Q}=(\pi,\pi)$ (antiferromagnetic wave number), shows a peak.[36] The characteristic temperature T^* in the charge transport is rather close to T_K,[2,37,38] and so the electrical conduction seems to be dominated by the process with small momentum change.

The intimate relation between σ_{ab} and $\chi(0)$ leads to the following picture of the in-plane charge transport. Above $T^*(\sim T_K)$ both σ_{ab} and $\kappa_{\rm el}$ are dominated by spin excitations with small momentum and so the WF law holds. On the other hand, below T^*, where the spin excitations around $\mathbf{q}=0$ are suppressed, excitations with larger momentum, for example, $\mathbf{q}\sim\mathbf{Q}$, become dominant, which incidentally coincides with the wave number of the nodes in a $d_{x^2-y^2}$-like spin gap.[39] In this case, the present experimental result can be explained if the process with a large momentum change contributes to the thermal resistance ($W^{\rm el}$) but not to the electrical resistance (ρ_{ab}).

Contrary to this, if the WF law does hold also below T^*, it indicates that the spin gap has the *same* effect on the thermal and electrical conduction. One possible explanation is that the relaxation process depends only upon the frequency of the scattering.

However, $\mathbf{q}$ dependence of scattering process, especially the connection between σ_{ab} and $\chi(0)$, is suggested also by studies of Zn-substitution effects on charge and spin excitation. A recent study[20] indicates that Zn substitution does not affect the T-dependent part of ρ_{ab} but only increases the T-independent residual resistivity. The NMR (Refs. 22 and 40) and neutron scattering[41,42] studies of the Zn-substitution effect indicate that the spin gap feature is sensitive to Zn around $\mathbf{q}=\mathbf{Q}$, while it is not around $\mathbf{q}=0$.

If the scattering process below T^* which contributes only to the thermal conductivity originates from spin excitations around $\mathbf{q}=\mathbf{Q}$, Zn substitution, which fills up the spin gap around $\mathbf{q}=\mathbf{Q}$, suppresses $\kappa_{\rm el}$ below T^* (or T_c) further than the estimation taking into account only the elastic scattering by Zn ions. The above picture is not contradictory to the present experimental result. In Fig. 3, $L^*\sigma T$, which is estimated using ρ_{ab} and σ_1 for Zn-substituted $YBa_2Cu_3O_7$ taken from Ref. 20 and Ref. 43, respectively, is also shown. Below T_c ($\sim$ 80 K) $L^*\sigma T$ exhibits a peak clearly while the measured κ_{ab} shows little change at T_c, suggesting the existence of some process which contributes to $W^{\rm el}$ but not to ρ_{ab}.

The mechanism of the charge transport related to $\chi(0)$ appears to be hardly explained within the framework of the Fermi-liquid picture. Some theorists propose non-Fermi-liquid models as an alternative. One of them is that based on the uniform resonating valence bond (RVB) state,[44] where one electron dissociates into a spinon-holon pair in the CuO_2 plane and they are coupled through a gauge field. In this context, the in-plane electrical current is carried by holons which are scattered by the long-wavelength (small-momentum) fluctuation of the gauge field. This mechanism yields T-linear resistivity. These fluctuations are suppressed by the spinon condensation (singlets) and hence the resistivity is reduced in the spin gap region. On the other hand, the in-plane thermal current is carried by spinons in this model, so that the WF law is not necessarily to be obeyed.

The bipolaron model is proposed as another non-Fermi-liquid model of high-T_c superconductors.[35] In this model, the current is carried by charged spin bipolarons, which form a condensed Bose gas below T_c and a nondegenerate gas above it. Extended (free) bipolarons whose density is proportional to T are scattered by localized bipolarons. This relaxation rate is proportional to T^2 because only localized bosons within the energy shell of $k_{\rm B}T$ near the mobility edge contribute to the scattering and the number of the final state is proportional to T, so that the in-plane resistivity is expected to be linear in T. The magnetic properties are dominated by a singlet-triplet exchange of bipolarons: Below the characteristic temperature T^* which coincides with T_K, the triplet bipolarons turn into the singlet one, and so the spin degree of freedom is frozen. If singlets are lighter than triplets, this model can explain also the deviation from the T-linear behavior of the in-plane resistivity below T^*. However, in this scenario the failure of the WF law below T^* cannot be explained because the scattering mechanism itself is not altered at T^*. In addition, this model treats the carriers as a nondegenerate Bose gas with charge $2e$ and hence predicts that the Lorenz number is $3(k_{\rm B}/2e)^2\simeq 1/4L_0$, which is not favored by this study.

The superconducting and spin gaps have the same influence on the charge transport in the sense that they radically change the Lorenz number. However, for the 60-K material, where T^* does not coincide with T_c, the difference between the effects of the superconducting gap and that of the spin gap becomes apparent: $\kappa_{\rm el}$ appears to show a peak below T_c while it does not show an appreciable change at T^*. A surface resistance study by Kitano *et al.* suggests that σ_1 for the 60-K $YBa_2Cu_3O_{6.7}$ material also shows a peak below T_c (Ref. 45) as well as ρ_{ab} deviates from the T-linear behavior below T^*. In both cases, the peaks below T_c for the 60-K material are suppressed compared with that for the 90-K material. These differences originate probably from the differences between quasiparticles and normal carriers and/or superconducting and spin gaps.

VI. SUMMARY

We have proposed and examined a tentative approach to determine the electronic contribution to the in-plane thermal conductivity of metallic $YBa_2Cu_3O_{7-y}$ using κ_{ab} data measured on single crystals with various oxygen contents in the range $6.06 \leqslant 7-y \leqslant 6.93$. The present results suggest that the WF law does not hold below T_c or the characteristic temperature T^* which is close to the spin gap temperature at $\mathbf{q}=0$. Different T dependence between thermal and electrical relaxation indicates that the charge carriers are scattered dominantly by the spin excitations with small momentum.

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[1] T. Ito, K. Takenaka, and S. Uchida, Phys. Rev. Lett. **70**, 3995 (1993).

[2] K. Takenaka, K. Mizuhashi, H. Takagi, and S. Uchida, Phys. Rev. B **50**, 6534 (1994).

[3] B. Bucher, P. Steiner, J. Karpinski, E. Kaldis, and P. Wachter, Phys. Rev. Lett. **70**, 2012 (1993).

[4] Y. Nakamura and S. Uchida, Phys. Rev. B **47**, 8369 (1993).

[5] For a review, see C. Uher, in *Physical Properties of High Temperature Superconductor III*, edited by D. M. Ginsberg (World Scientific, Teaneck, NJ, 1992), p. 159.

[6] S. J. Hagen, Z. Z. Wang, and N. P. Ong, Phys. Rev. B **40**, 9389 (1989).

[7] Joshua L. Cohn, Stuart A. Wolf, and Terrell A. Vanderah, Phys. Rev. B **45**, 511 (1992).

[8] R. C. Yu, M. B. Salamon, Jian Ping Lu, and W. C. Lee, Phys. Rev. Lett. **69**, 1432 (1992).

[9] M. B. Salamon, Fang Yu, and V. N. Kopylov, J. Supercond. **8**, 449 (1995).

[10] K. Krishana, J. M. Harris, and N. P. Ong, Phys. Rev. Lett. **75**, 3529 (1995).

[11] Joshua L. Cohn, Phys. Rev. B **53**, R2963 (1996).

[12] A. V. Inyushkin, A. N. Taldenkov, and T. G. Uvarova, Phys. Rev. B **54**, 13 261 (1996).

[13] Robert Gagnon, Song Pu, Brett Ellman, and Louis Taillefer, Phys. Rev. Lett. **78**, 1976 (1997).

[14] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, Oxford, 1960); R. Berman, *Thermal Conduction in Solids* (Oxford University Press, Oxford, 1976).

[15] For the case of Na, see J. G. Cook, M. P. Van der Meer, and M. J. Laubitz, Can. J. Phys. **50**, 1386 (1972).

[16] G. K. White and R. J. Tainsh, Phys. Rev. Lett. **19**, 165 (1967); J. T. Schriemph, A. I. Schindler, and D. L. Mills, Phys. Rev. **187**, 959 (1969).

[17] H. Takei, H. Asaoka, Y. Iye, and H. Takeya, Jpn. J. Appl. Phys. Part 1 **30**, 1102 (1991).

[18] Ruixing Liang, P. Dosanjh, D. A. Bonn, D. J. Baar, J. F. Carolan, and W. N. Hardy, Physica C **195**, 51 (1992).

[19] If the contact thermal resistance is ignored heat loss via radiation is estimated as follows: at 300 K for the typical specimen,

$$\frac{\dot{Q}_{\rm rad}}{\dot{Q}_{\rm spec}}=\frac{4\sigma T^3}{\kappa}\,\frac{S_{\rm cross}+S_{\rm side}}{S_{\rm cross}}l<2\%.$$

Here, σ is the Stefan-Boltzman constant, equal to 5.67×10^{-12} W/cm^2 K^4, $\dot{Q}_{\rm rad(spec)}$ is the heat flow rate through radiation (specimen), $S_{\rm cross(side)}$ is the cross-section (side) area of the specimen, and l is the length of the specimen [I. Yoshida (unpublished)]. In order to reduce the contact resistance, we used silver paste as contacts.

[20] K. Mizuhashi, K. Takenaka, Y. Fukuzumi, and S. Uchida, Phys. Rev. B **52**, R3884 (1995).

[21] If the WF law holds and we adopt $L_e\sim3.1\times10^{-8}$ WΩ/K^2 which is estimated by ρ_{ab} and $\kappa_{\rm el}$ in this study, the difference between the two phonon components, $\kappa_b^{\rm ph}-\kappa_a^{\rm ph}$, is estimated to be $\sim$ 0.5 W/mK at 300 K, which is less than 10% of the estimated $\kappa_{\rm ph}$. The anisotropy of the phonon components is much less than that expected from the large structural anisotropy of the chain layer.

[22] H. Alloul, P. Mendels, H. Casalta, J. F. Marucco, and J. Arabski, Phys. Rev. Lett. **67**, 3140 (1991).

[23] V. W. Wittorff, N. E. Hussey, J. R. Cooper, Chen Changkang, and J. W. Hodby (unpublished).

[24] J. L. Cohn, V. Z. Kresin, M. E. Reeves, and S. A. Wolf, Phys. Rev. Lett. **71**, 1657 (1993); R. C. Yu, M. B. Salamon, and J. P. Lu, *ibid.* **71**, 1658 (1993).

[25] Y. Nakamura, S. Uchida, T. Kimura, N. Motohira, K. Kishio, K. Kitazawa, T. Arima, and Y. Tokura, Physica C **185-189**, 1409 (1991).

[26] A. Inyushkin, A. Taldenkov, S. Shabanov, and T. Uvarova, Physica C **235-240**, 1487 (1994).

[27] K. Takenaka, Y. Imanaka, K. Tamasaku, T. Ito, and S. Uchida, Phys. Rev. B **46**, 5833 (1992).

[28] R. Fehrenbacher and T. M. Rice, Phys. Rev. Lett. **70**, 3471 (1993).

[29] H. Sato, Prog. Theor. Phys. **13**, 119 (1955).

[30] J. L. Cohn, C. K. Lowe-Ma, and T. A. Vanderah, Phys. Rev. B **52**, R13 134 (1995).

[31] Y. Nakamura and S. Uchida (unpublished).

[32] For example, see N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (W. B. Saunders Company, Philadelphia, 1976), p. 21.

[33] M. Gurvitch and A. T. Fiory, Phys. Rev. Lett. **59**, 1337 (1987).

[34] D. A. Bonn, Ruixing Liang, T. M. Riseman, D. J. Baar, D. C. Morgan, Kuan Zhang, P. Dosanjh, T. L. Duty, A. MacFarlane, G. D. Morris, J. H. Brewer, W. N. Hardy, C. Kallin, and A. J. Berlinsky, Phys. Rev. B **47**, 11 314 (1993).

[35] N. F. Mott, Physica C **205**, 191 (1993); A. S. Alexandrov, A. M. Bratkovsky, and N. F. Mott, Phys. Rev. Lett. **72**, 1734 (1994).

[36] M. Takigawa, A. P. Reyes, P. C. Hammel, J. D. Thompson, R. H. Heffner, Z. Fisk, and K. C. Ott, Phys. Rev. B **43**, 247 (1991).

[37] H. Y. Hwang, B. Batlogg, H. Takagi, H. L. Kao, J. Kwo, R. J. Cava, J. J. Krajewski, and W. F. Peck, Jr., Phys. Rev. Lett. **72**, 2636 (1994).

[38] T. Nakano, M. Oda, C. Manabe, N. Momono, Y. Miura, and M. Ido, Phys. Rev. B **49**, 16 000 (1994).

[39] A. G. Losser, Z.-X. Shen, D. S. Dessau, D. S. Marshall, C. H. Park, P. Fournier, and A. Kapitulnik, Science **273**, 325 (1996).

[40] G.-q. Zheng, T. Odaguchi, T. Mito, Y. Kitaoka, K. Asayama, and Y. Kodama, J. Phys. Soc. Jpn. **62**, 2591 (1993).

[41] K. Kakurai, S. Shamoto, T. Kiyokura, M. Sato, J. M. Tranquada, and G. Shirane, Phys. Rev. B **48**, 3485 (1993).

[42] H. Harashina, S. Shamoto, T. Kiyokura, M. Sato, K. Kakurai, and G. Shirane, J. Phys. Soc. Jpn. **62**, 4009 (1993).
[43] D. A. Bonn, S. Kamal, Kuan Zhang, Ruixing Liang, D. J. Baar, E. Klein, and W. N. Hardy, Phys. Rev. B **50**, 4051 (1994).
[44] N. Nagaosa and P. A. Lee, Phys. Rev. Lett. **64**, 2450 (1990); N. Nagaosa, J. Phys. Chem. Solids **53**, 1493 (1992).
[45] H. Kitano, T. Shibauchi, K. Uchinokura, A. Maeda, H. Asaoka, and H. Takei, Phys. Rev. B **51**, 1401 (1995).