Theory of Thermoelectric Power in High-$T_c$ Superconductors

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We present a microscopic theory for the thermoelectric power (TEP) in high-$T_c$ cuprates. Based on the general expression for the TEP, we perform the calculation of the TEP for a square lattice Hubbard model including all the vertex corrections necessary to satisfy the conservation laws. In the present study, characteristic anomalous temperature and doping dependences of the TEP in high-$T_c$ cuprates, which have been a long-standing problem of high-$T_c$ cuprates, are well reproduced for both hole- and electron-doped systems, except for the heavily under-doped case. According to the present analysis, the strong momentum and energy dependences of the self-energy due to the strong antiferromagnetic fluctuations play an essential role in reproducing experimental anomalies of the TEP.

The thermotransport phenomena in high-$T_c$ cuprates exhibit various anomalous behaviors. In particular, the thermoelectric power (TEP), expressed by the Seebeck coefficient $S$, is known to show characteristic temperature and doping dependences above $T_c$, namely (i) $dS/dT < 0$ in hole-doped compounds such as YBa$_2$Cu$_3$O$_{7-x}$ (YBCO) or La$_{2-x}$Sr$_x$CuO$_4$ (LSCO), and $S$ is positive in the under-doped systems at room temperatures \cite{2}. (ii) $S$ is negative in electron-doped compounds like Nd$_{2-x}$Ce$_x$CuO$_4$ (NCCO) and LaPr$_{1-x}$Ce$_x$CuO$_4$ (PCCO), and $dS/dT > 0$ in the under-doped compound at higher temperatures $T \gtrsim 200$ K \cite{3}. In both cases, $|S|$ increases drastically as the doping decreases. Thus, a conventional Fermi liquid type behavior, $S \propto T_c$, is totally violated in high-$T_c$ cuprates for a wide range of temperatures. In particular, a qualitative particle-hole symmetric behavior of the TEP, i.e., $S_{LSCO} \sim -S_{NCCO}$ for the same carrier doping weight $x$ as was reported in ref. \cite{4}, is very mysterious because both LSCO (YBCO) and NCCO have similar large hole-like Fermi surfaces according to angle-resolved photoemission spectroscopic (ARPES) studies \cite{5}.

From an academic point of view, the TEP is a unique and important phenomenon in that it sensitively reflects the properties of the quasiparticles away from the Fermi surface, whereas electronic transport phenomena are caused by the quasiparticles on the Fermi surface. Thus, the characteristic non-Fermi liquid behavior of the TEP in high-$T_c$ cuprates suggests that the excited states of quasiparticles in high-$T_c$ cuprates are significantly anomalous. In this respect, the theoretical study of the TEP is quite important.

Up to now, several theoretical studies on the TEP for models with strong Coulomb interactions have been performed based on the dynamical mean field theory (DMFT) \cite{6}. These studies found that the energy dependence of the relaxation time is important for the TEP in strongly correlated systems. However, in high-$T_c$ cuprates, it is known that the momentum dependence of the relaxation time is also prominent, and the vertex correction (VC) in terms of the current plays an essential role for transport phenomena. These features are totally dropped in DMFT. Thus, for the present purpose, we have to develop a theory for the TEP by taking the momentum dependence into account.

In this letter, we study the TEP in high-$T_c$ cuprates on the basis of the antiferromagnetic (AF) fluctuation theory. We take the momentum and energy dependences of the relaxation time into account, and include all of the VC’s required by the Ward identity, i.e., the conserving approximation \cite{8}. Our study reproduces the main futures of the experimental TEP for both hole- and electron-doped compounds. According to the present analysis, the approximate particle-hole symmetry for the TEP is caused by the ”alternation of cold spots”, as is the case with the Hall coefficient \cite{10}.

In the present study, we calculate the self-energy $\Sigma_k(\epsilon)$ using the fluctuation-exchange (FLEX) approximation which is a kind of self-consistent spin-fluctuation theory \cite{11}, because it works well for high-$T_c$ cuprates for $|1-n| < 0.1$ above the spin pseudo-gap temperature \cite{12}. Here, we study the square lattice tight-binding model whose dispersion is given by $\epsilon_k^0 = 2t(\cos k_x + \cos k_y) + 4t' \cos k_x \cos k_y + 2t''(\cos 2k_x + \cos 2k_y)$, where $t$, $t'$ and $t''$ denote the nearest-, next-nearest- and third-nearest-neighbor hopping integrals. The parameters are chosen as $(t,t',t'') = (-1.0,0.17,-0.2)$ for YBCO and NCCO \cite{9}, and $(-1.0,0.15,-0.05)$ for LSCO \cite{6}, respectively.

First, we discuss the linear response theory for the TEP. In 1964, Luttinger derived a general expression for the TEP based on the linear response theory \cite{13}. Although his original formula was given by a complicated three-particle correlation function, Jonson and Mahan later obtained a much simplified formula for a system with impurities and adiabatic phonons \cite{14}. In the same way, the formula for the TEP of a Hubbard model with on-site Coulomb interaction $U$ is derived as follows \cite{15}:

$$S = -L_{xx}/eT\sigma_{xx}, \quad L_{xx} = \Phi(\omega + i0)/|\omega|_{\omega \rightarrow 0},$$

where $\Phi(\omega + i0)$ is given by the analytic continuation of the following function:

$$\Phi(\omega) = \int_0^\beta d\tau e^{-\omega \lambda} \tau \omega \langle T_{\tau}j_x(0)j_x(\tau) \rangle,$$
where $j_k$ is the current operator, $T_\tau$ is a $\tau$ ordering operator, and $\omega_\lambda$ is a conductivity and $-e$ ($e > 0$) is the charge of an electron. Recently, we performed the analytic continuation exactly as for the most singular terms with respect to the inverse of the damping rate of the quasiparticles [10]. The result is

$$L_{xx} = \sum_k \int \frac{d\epsilon}{\pi} \left( -\frac{\partial f}{\partial \epsilon} \right) c_{\epsilon k x}(\epsilon) \left[ |G_k(\epsilon)|^2 J_{k x}(\epsilon) \right] - \text{Re} \left\{ G_k^*(\epsilon) \right\} v_{\epsilon k x}(\epsilon),$$

(4)

$$J_{k x}(\epsilon) = v_{\epsilon k x}(\epsilon) + \sum_{k'} \int \frac{d\epsilon'}{4\pi i} T_{22} \left( k | k' \epsilon' \right) |G_k(\epsilon')|^2 J_{k' x}(\epsilon'),$$

(5)

where $v_{\epsilon k x}(\epsilon) = (\partial/\partial \epsilon_{\epsilon k})(\epsilon_k^0 + \text{Re} \Sigma_k(\epsilon_k^0))$, $f(\epsilon) = (1 + \exp((\epsilon - \mu)/T))^{-1}$, and $G_k(\epsilon)$ is the Green function. Here, $J_{k x}(\epsilon)$ is the total current with the VC from the irreducible four-point vertex $T_{22}$, which was introduced by Eliashberg in ref. [17] for the first time. The derivation of eq. (4) based on the Fermi liquid theory will be given elsewhere [10].

In calculating a transport coefficient, it is known that the conservation laws should be satisfied to avoid unphysical results [13]. For this purpose, the Ward identity between $T_{22}$ in eq. (5) and the self-energy $\Sigma_k(\epsilon)$ has to be taken into account [13,8]. Note that $T_{22}$ within the FLEX approximation is given in ref. [8]. We stress that the relaxation time approximation cannot reproduce the seemingly non-Fermi liquid behaviors of $R_H$ and the magnetoresistance ($\Delta \rho/\rho$): These long-standing mysteries of the magnetotransport phenomena were recently solved by taking account of the VC for $J_k$ in refs. [8] and [10] for $R_H$ and in refs. [8] and [13] for $\Delta \rho/\rho$, from the standpoint of the nearly AF Fermi liquid. Moreover, anomalous temperature and pressure dependences of $R_H$ in $\kappa$-BEDT-TTF organic superconductors are well reproduced according to the same mechanism [20]. Thus, it is important to determine whether the spin-fluctuation theory with satisfying the conservation laws is also successful for the thermotransport phenomena.

As for the conductivity, we calculate $\sigma_{xx}$ based on the conserving approximation as explained in ref. [10]. According to the FLEX approximation, $\sigma_{xx} \propto 1/\gamma_{\text{cold}}$ because the VC gives only a qualitative correction for $\sigma_{xx}$. As a result, the famous $T$-linear resistance in high-$T_c$ cuprates is reproduced for a wider range of temperatures [9].

Before calculating the TEP, we consider the behavior of eq. (4) by using the quasiparticle representation of the Green function, $G_k(\omega + i\delta) = z_k/(\omega - \epsilon_k^0 + i\gamma_k)$. Here, $\epsilon_k^0 = z_k(\epsilon_k^0 + \text{Re} \Sigma_k(\epsilon_k^0) - \mu)$, $\gamma_k = -2\text{Im} \Sigma_k(\epsilon_k^0 + i\delta) > 0$, and $z_k = (1 - \partial \Sigma_k(\epsilon)/\partial \epsilon)^{-1}$ is the renormalization factor. Then, eq. (4) is simplified as

$$L_{xx} = \int \frac{dk}{2\pi i} \int \frac{dk}{\pi} \frac{1}{z_k} \left( 1 - \frac{\partial f}{\partial \epsilon} \right) \frac{\epsilon_k^0}{\gamma_k(\epsilon_k^0)} \times v_{\epsilon k x}(\epsilon_k^0) J_{k x}(\epsilon_k^0),$$

(6)

where $k_{\parallel} [k_{\perp}]$ is the momentum along [perpendicular to] the Fermi surface. At sufficiently low temperatures, eq. (6) becomes

$$L_{xx} = \frac{(\pi T)^2}{6} \int \int \frac{dk}{2\pi \pi} \frac{1}{\gamma_k(\epsilon_k^0)} \frac{\partial}{\partial \epsilon} \left[ v_{\epsilon k x}(\epsilon_k^0) J_{k x}(\epsilon_k^0) \right].$$

Thus, $L_{xx}$ given by eq. (6) is enhanced by $z_k^{-1}$.

When the temperature dependences of $\gamma_k(\epsilon_k^0)$, $v_{\epsilon k x}(\epsilon_k^0)$ and $J_{k x}(\epsilon_k^0)$ are negligible like in a conventional Fermi liquid, then $L_{xx} \propto T^2/\gamma$ and $S \propto T$ are obtained. However, the temperature dependences of these functions are usually large at higher temperatures in strongly correlated systems. For example, in heavy Fermion systems, a huge $\epsilon$ dependence of $\gamma(\epsilon)$ due to the Kondo resonance causes a prominent non-Fermi liquid behavior on $S$ around the Kondo temperature $T_K$ [11]. In the present study, we find that the temperature dependences of the anisotropy of $\gamma_k(\epsilon_k^0)$ in eqs. (6) or (7) are primarily responsible for highly enhanced TEP in (under-doped) high-$T_c$ cuprates. Thus, we analyze the behavior of $\gamma_k(\epsilon_k^0)$ below.

![Fermi surface in YBCO/LSCO](image)

FIG. 1. Fermi surface in YBCO/LSCO. AFBZ stands for the AF Brillouin zone boundary. The cold spot, at which $\text{Im} \Sigma_k(0)$ takes the smallest value on the Fermi surface, is located near $(\pi/2, \pi/2)$ [(0, $\pi$)] in YBCO [NCCO].

Figure 1 shows the Fermi surface without interaction, together with the contour given by $\epsilon_k^0 = \pm \delta \epsilon$ ($\delta > 0$). According to the ARPES measurement, the position of the cold spot, where $\gamma_k$ takes the smallest value, is near $(\pi/2, \pi/2)$ in YBCO and near $(\pi, 0)$ in NCCO. This "cold spot alternation" was first predicted using the FLEX approximation in ref. [10] prior to the ARPES measurement [11,12]. According to the analysis in ref. [10], this finding leads to the opposite sign of the Hall coefficient in hole-
and electron-doped compound, although they have similar hole-like Fermi surfaces. Later in this article, this finding also explains the opposite sign of the TEP in hole- and electron-doped compound.

![Graph](image)

FIG. 2. Obtained relation between $\gamma_k \equiv \text{Im}\Sigma_k'(\epsilon_k^*)$ and $\epsilon_k^*$ at $T = 0.02$. We see that $\partial \gamma_k(\epsilon_k^*)/\partial k_\perp > 0$ ($< 0$) around the cold spot for YBCO (NCCO), where $k_\perp$ is normal to the Fermi surface.

Next, we examine the $(k, \epsilon)$-dependence of the self-energy $\Sigma_k(\epsilon)$ given by the FLEX approximation. Here we use $U = 8$ for YBCO and $U = 6$ for NCCO. Figure shows the obtained $\gamma_k(\epsilon_k^*)$ vs $\epsilon_k^*$ near the Fermi surface, along $(0, 0) \rightarrow (\pi, \pi)$ and $(0, \pi) \rightarrow (\pi, \pi)$. Here, $\epsilon_k^*$ is the solution of $\text{Re}\{1/G_k(\epsilon_k^*)\} = 0$. We stress that $\gamma_k(\epsilon_k^*)$ is highly asymmetric, and $\partial \gamma_k(\epsilon_k^*)/\partial k_\perp > 0$ [ < 0] at the cold spot in YBCO [NCCO], where $k_\perp$ is the momentum normal to the Fermi surface. (Note that $\gamma_k(\epsilon_k^*) \propto \{\epsilon_k^*\}^n$ and $n \sim 2$ if the self-energy is $k$-independent.) This finding naturally explains why the sign of $S$ in a hole-doped compound and that in an electron-doped compound are different, according to eq. for $L_{xx}$.

Here, we analyze the origin of the asymmetric behavior of $\gamma_k(\epsilon_k^*)$ in terms of the nearly AF Fermi liquid: In high-$T_c$ cuprates, the spin propagator is well expressed in the following functional form:

$$\chi_q(\omega) = \chi_Q/(1 + \xi^2(q - Q)^2 - i\omega/\omega_{sf}), \quad (8)$$

where $Q = (\pi, \pi)$, $\xi$ is the AF correlation length, and $\chi_Q \propto \omega_{sf}^{-1} \propto \xi^2$. According to the standard AF fluctuation theory, $\xi^2 \propto T^{-1}$ in two-dimensional systems. If we assume $\omega_{sf} \gg T$ for simplicity, then $\gamma_k(\epsilon) = \text{Im}\Sigma_k(\epsilon - i0)$ around the cold spot is approximately given by

$$\gamma_k(\epsilon) \propto \frac{1}{|q_k|} \frac{\xi^3(T^2 + (\epsilon/\pi)^2)}{1 + \xi^2(2\Delta k)^2} |^{3/2}, \quad (9)$$

within the one-loop approximation. Here, $\Delta k$ is the distance between $k$ and the antiferromagnetic Brillouin zone (AFBZ) boundary, as shown in Fig. 1. Equation (9) gives an analytical explanation for the numerical results shown in Fig. (According to the FLEX approximation, $\xi \lesssim 1/\Delta k$ for $n \leq 0.9$. By considering Fig. 1 eq. (9) directly indicate that (i) the inside region of the AFBZ provides the positive contribution for $S$ because $\partial \gamma_k(\epsilon_k^*)/\partial k_\perp > 0$ in the presence of strong AF fluctuations. At the same time, (ii) the outside of the AFBZ provides the negative contribution because $\partial \gamma_k(\epsilon_k^*)/\partial k_\perp < 0$.

![Graph](image)

FIG. 3. Temperature dependences of the TEP calculated with full VC’s for $L_{xx}$. Here, $T = 0.1$ corresponds to $\sim 500$ K. We put $U = 8$ for YBCO, $U = 6$ for NCCO and $U = 5.5$ for LSCO. For NCCO, the VC’s play a qualitatively essential role, and $|S(n = 1.10)| > |S(n = 1.15)|$ is realized only when the VC’s are taken into account. In contrast, the VC’s are less important for YBCO and LSCO.

In Fig. we show numerical results of the TEP derived from eq. according to the conserving approximation. The TEP without the VC for $L_{xx}$, which is given by replacing $J_{xx}(\epsilon)$ with $\gamma_{xx}(\epsilon)$ in eq. (4), is also plotted in Fig. Here, $T = 0.02$ corresponds to $\sim 100$ K. In YBCO.
(U = 8), dS/dT < 0 for n = 0.80 ∼ 0.92, nd S becomes positive at room temperatures for optimally- and under-doped case (n ≥ 0.85). This result is consistent with that of experiments [23]. We stress that S ≈ a ∗ T and a < 0 for a smaller interaction (U = 3.5) as shown in Fig. 3, which indicates the importance of the correlation effect on S.

On the other hand, S is always negative and |S| increases as n approaches 1 in NCCO, and dS/dT > 0 in under-doped systems for higher temperatures. These results are consistent with those of experiments [23]. We stress that the VC for Jk enhancement of the anomalous temperature dependence of S strongly in the case of NCCO, as shown in Fig. 3. Finally, dS/dT < 0 is also reproduced in the case of YBCO, and |S| for YBCO is larger than |S| for YBCO or NCCO, if we compare the same filling cases. However, we see that the qualitative behavior of S is the same if the Fermi surface is hole-like. We note that S given by eq. (4) becomes zero at T = 0 if the ground state is metallic. This finding indicates that dS/dT should change to positive below T = 0.02 for both YBCO and LSCO.

Finally, we discuss the following quantity to understand qualitatively the temperature and doping dependence of S for YBCO:

\[ L_{xx}^{\text{in}} = \sum_{\mathbf{k}} \int \frac{de}{\pi} \left( -\frac{\partial f}{\partial \epsilon} \right) \epsilon v_{kz}(\epsilon) \left[ \cdots \right] , \]  

(10)

where [ · · · ] is the same as that of eq. (4). In Fig. 4, we show \( S_{\text{in}} \equiv -eL_{xx}^{\text{in}}/T \sigma_{xx} \) together with \( S_{\text{out}} \equiv S - S_{\text{in}} \). Apparently, \( S_{\text{in}[\text{out}] \) represents the contribution from the inside [outside] region of the AFBZ. As we expected analytically, \( S_{\text{in}} > 0 \) and \( S_{\text{out}} < 0 \) is actually observed, and \( |S_{\text{in}}| > |S_{\text{out}}| \) for YBCO at lower temperatures because the cold spots exist inside the AFBZ. In Fig. 4, we see a conventional behavior \( S_{\text{out}} \propto T \) approximately. On the other hand, \( S_{\text{in}} \sim \text{const.} \) is realized because \( 1/\gamma_{k}(\epsilon_{k}) \) around the cold spot becomes much asymmetric as the temperature decreases, as shown in Fig. 3. According to eq. (4), we see that \( \partial \gamma_{k}/\partial k_{\perp} \propto \xi^{2} \Delta k \cdot \gamma_{k} \) for \( \xi \Delta k \lesssim 1 \), and \( \partial \gamma_{k}/\partial k_{\perp} \propto (\Delta k)^{-1} \cdot \gamma_{k} \) for \( \xi \Delta k \gtrsim 1 \). Thus, the k-dependence of \( 1/\gamma_{k}(\epsilon_{k}) \) near the cold spot is prominent in the case of \( \gamma \sim (\Delta k_{\text{cold}})^{-1} \), which is realized in YBCO for \( n = 0.9 \) at low temperatures according to our previous study [23]. Moreover, S is enhanced by \( \gamma^{-1} \), which increases slowly as the temperature decreases. As a result, the approximate behavior \( S(= S_{\text{in}} + S_{\text{out}}) \propto T + a \) (a > 0) as well as the change of the sign of S in YBCO is realized.

This situation is very contrastive to that for the Hall coefficient. We consider \( R_{\parallel}^{\text{in}} \) which comes from the inside region of the AFBZ, and \( R_{\parallel}^{\text{out}} \equiv R_{\parallel} - R_{\parallel}^{\text{in}} \). As shown in Fig. 4, \( |R_{\parallel}^{\text{in}}| \gg |R_{\parallel}^{\text{out}}| \) for 0.1 ≥ T ≥ 0.02, which means that \( R_{\parallel} \) is almost determined by the electronic property at the cold spot. As a result, the simple scaling relations \( R_{\parallel} \sim \xi^{2} \) and \( \Delta \rho \cdot \rho \sim \xi^{4} \) are realized in high-\( T_{c} \) cuprates [21-23].

In summary, we analyzed the anomalous behavior of the TEP in high-\( T_{c} \) cuprates in a conserving manner. In our numerical calculation based on the spin-fluctuation theory, the main features of the TEP are reproduced successfully, at least for \( |n - n_{c}| \gtrsim 0.1 \) above the spin pseudo-gap temperature. The main origin is that the quasiparticle damping rate, \( \gamma_{k}(\epsilon_{k}) \), becomes more anisotropic near the Fermi surface as the temperature is decreased, reflecting the growth of AF fluctuations. In conclusion, the seemingly non-Fermi liquid behavior of the TEP is well understood in terms of the nearly AF Fermi liquid picture. In particular, the difference in the sign of the TEP in electron- and hole-doped systems is naturally explained by the "cold spot alternation" mechanism. Conversely, the success of the present study means that the AF fluctuation theory provides a reliable description for the excited states of quasiparticles, which determine the thermotransport phenomena.

Before concluding the study, we comment that compounds with large figure of merit, \( Z = \sigma_{xx}S^{2}/\kappa \) (\( \kappa \) being the thermal conductivity), attract great attention nowadays because of their applicability in electricity generators or refrigerators [14,15]. Thus, theoretical study of the TEP phenomena in strongly correlated systems will become much more important in the near future.

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[1] S. D. Obertelli, J.R. Cooper, and J.L. Tallon: Phys. Rev. B 46 (1992) 14928.
[2] J. Takeda, T. Nishikawa, and M. Sato: Physica C 231 (1994) 293.
[3] P. Fournier, X. Jiang, W. Jiang, S.N. Mao, T. Venkatesan, C.J. Lobb, and R.L. Greene: Phys. Rev. B. 56
(1997) 14149.

[4] N. P. Armitage, D. H. Lu, D. L. Feng, C. Kim, A. Damascelli, K. M. Shen, F. Ronning, and Z.-X. Shen: Phys. Rev. Lett. 86 (2001) 1126.

[5] N.P. Arimitage et. al.: preprint [cond-mat/0107244].

[6] H. Schweitzer and G. Czycholl: Phys. Rev. Lett. 67 (1991) 3724.

[7] G. Pálsson and G. Kotliar: Phys. Rev. Lett. 80 (1998) 4775.

[8] G. Baym and L.P. Kadanoff: Phys. Rev. 124 (1961) 287.

[9] H. Kontani, K. Kanki and K. Ueda: Phys. Rev. B 59 (1999) 14723.

[10] K. Kanki and H. Kontani: J. Phys. Soc. Jpn. 68 (1999) 1614.

[11] N.E. Bickers and S.R. White: Phys. Rev. B 43 (1991) 8044.

[12] T. Dahm and L. Tewordt: Phys. Rev. B 52 (1995) 1297.

[13] H. Kontani: to appear in J. Phys. Soc. Jpn. (2001), No.7 [cond-mat/0011327].

[14] J. M. Luttinger: Phys. Rev. 135 (1964) A1505.

[15] M. Jonson and G. D. Mahan: Phys. Rev. B 42 (1990) 9350.

[16] H. Kontani: in preparation.

[17] G. M. Eliashberg : Sov. Phys. JETP 14 (1962) 886.

[18] K. Yamada and K. Yosida: Prog. Theor. Phys. 76 (1986) 621.

[19] H. Kontani: Phys. Rev. B 64 (2001) 054413.

[20] H. Kontani and H. Kino: Phys. Rev. B 63 (2001) 134524.

[21] T. Moriya, Y. Takahashi and K. Ueda: J. Phys. Soc. Jpn. 59 (1990) 2005.

[22] B. P. Stojković and D. Pines: Phys. Rev. B 55 (1996) 857.