Enhancement of the thermoelectric power by electronic correlations in bad metals: a study of the Kelvin formula

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Abstract

In many strongly correlated electron metals the thermoelectric power has a non-monotonic temperature dependence and values that are orders of magnitude larger than for elemental metals. Kelvin proposed a particularly simple expression for the thermopower in terms of the temperature dependence of the chemical potential. We consider a Hubbard model on an anisotropic triangular lattice at half filling, a minimal effective Hamiltonian for several classes of organic charge transfer salts. The finite temperature Lanczos method is used to calculate the temperature dependence of the thermopower using the Kelvin formula. We find that electronic correlations significantly enhance the magnitude of the thermopower and lead to a non-monotonic temperature dependence. The latter reflects a crossover with increasing temperature from a Fermi liquid to a bad metal. Although, the Kelvin formula gives a semi-quantitative description of some experimental results it cannot describe the directional dependence of the sign of the thermopower in some materials.

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I. INTRODUCTION.

Strongly correlated electron materials have attracted interest as candidate thermoelectric materials because they can exhibit values of the Seebeck coefficient $S$ as large as $100 \, \mu V/K$. Understanding and describing the temperature dependence of $S$ in strongly correlated materials represents a significant theoretical challenge. Both the magnitude and the temperature dependence of $S$ is distinctly different than in elemental metals. At low temperatures $S$ increases linearly with temperature, with a large slope, and reaches a maximum value of order $k_B/e \simeq 86 \, \mu V/K$ ($k_B$ is Boltzmann's constant and $e$ is the charge of an electron). With increasing temperature $S$ decreases and can even change sign. These qualitative features are seen in diverse materials including organic charge transfer salts, cuprates, heavy fermion compounds, cobaltates, and iron pnictides. This is illustrated in Figure 1 with experimental results for an organic metal. Behnia, Jaccard, and Floquet showed that for a wide range of materials that the slope of the temperature dependence of $S$ and the specific heat capacity at low temperatures were proportional to one another. For heavy fermion materials, this observation can be explained in terms of a slave boson treatment of the Kondo lattice model.

Understanding the thermopower in strongly correlated electron materials has recently attracted increasing theoretical interest. Shastry and coworkers have argued that the high frequency limit of the Kubo formula for the thermopower actually gives a good approximate value to the dc limit. This approach has the advantage that the thermopower (a transport property) can actually be evaluated from an equal-time expectation value (an equilibrium property). Peterson and Shastry have shown that the thermopower is approximately given by the Kelvin formula, the derivative of the entropy with respect to the particle number; which via a thermodynamic Maxwell identity equals the derivative of the chemical potential with respect to temperature. Recent Dynamical Mean-Field Theory (DMFT) calculations for the Hubbard model and the Falicov-Kimball model show that in the bad metal regime the Kelvin formula is a reasonable approximation. The Kelvin formula has the significant advantage that a transport property can be calculated from an equilibrium thermodynamic property. It also illuminates the physical significance of work by Jaklič and Prelovšek who showed that for the $t - J$ model the entropy as a function of doping is a maximum close to optimal doping. This means that the thermopower should change sign at optimal doping, as is observed experimentally in the cuprates.

Figure 1 shows the measured temperature dependence of the thermopower of an organic metal.
Figure 1. (color online) Temperature dependence of the thermoelectric power in the organic metal $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. The two different curves correspond to two different directions in the crystal. Experimental data is taken from Ref. 2. Note the non-monotonic temperature dependence and that the thermopower is comparable to $k_B/e = 86 \mu$V/K. For temperatures below about 50 K the thermopower is approximately linear in temperature, as expected in a Fermi liquid. The inset shows a schematic of the electron and hole Fermi surfaces deduced from a tight-binding band structure$^{18}$. Transport in the $a$ and $c$ directions will be dominated by holes and electrons, respectively.

The authors also calculated the thermopower using a Boltzmann equation and a band structure obtained with the Huckel approximation. They obtained values that were about five times smaller than the experiment. However, they found that if all the hopping integrals were reduced by about a factor of five that the results were comparable to experiment. Similar results were obtained earlier by Mori and Inokuchi$^{19}$. Merino and McKenzie suggested that the non-monotonic temperature dependence arose from a crossover with increasing temperature from a renormalised Fermi liquid to a bad metal$^{20}$. They showed this was consistent with results of calculations for a Hubbard model based on Dynamical Mean Field Theory.
II. THE KELVIN FORMULA

Starting from a Kubo formula Peterson and Shastry showed that if one interchanges the thermodynamic and the static limits that the thermopower is given by the temperature derivative of the chemical potential

\[ S_K = -\frac{1}{e} \left( \frac{\partial \tilde{S}}{\partial N_{el}} \right)_{T,V} = \frac{1}{e} \left( \frac{\partial \mu}{\partial T} \right)_{N,V} , \]

where \( e \) is the magnitude of the charge of an electron, \( \tilde{S} \) is the entropy, and \( N_{el} \) is the particle number. Note that this result is independent of the direction of the thermal gradient in the crystal. Hence, it will be unable to explain the origin of the different signs shown in Figure 1. As a result of the third law of thermodynamics, the entropy should vanish as the temperature goes to zero for all \( N_{el} \) and so \( S_K(T) \to 0 \) as \( T \to 0 \).

III. HUBBARD MODEL

For numerical calculations we consider a system at fixed temperature \( T \) and chemical potential \( \mu \), and model it with a (grand canonical) Hubbard model on the anisotropic triangular lattice,

\[ \hat{H}_{el} = -\sum_{i,j,s} t_{i,j} \hat{c}_{i,s}^\dagger \hat{c}_{j,s} + U \sum_i \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow} - \mu \hat{N}_{el}. \]

This is a minimal effective Hamiltonian for several classes of organic charge transfer salts when at half filling. \( \hat{N}_{el} \equiv \sum_{i,s} \hat{n}_{i,s} \) is the total electron number operator, \( t_{i,j} = t \) for nearest neighbour bonds in two directions and \( t_{i,j} = t' \) for nearest neighbour bonds in the third direction. Electronic spin is denoted with \( s (\uparrow \text{ or } \downarrow) \).

For fixed half filled system the chemical potential changes with temperature and \( \mu(T) \) is fixed by the constraint that

\[ \langle \hat{N}_{el} \rangle = N, \]

where \( N \) is the number of lattice sites, ensuring half-filling, and \( \langle \hat{A} \rangle \) denotes the grand canonical thermal average, \( \langle \hat{A} \rangle \equiv \text{Tr}[\hat{A}\exp(-\beta\hat{H}_{el})]/Z \) with \( Z \) being the thermodynamic sum \( Z = \text{Tr}[\exp(-\beta\hat{H}_{el})] \). Here we have also used \( \beta = 1/(k_B T) \).

Our numerical results for finite lattices were obtained by the finite-temperature Lanczos method (FLTM)\textsuperscript{22}, which we previously used to determine several thermodynamic quantities of this Hubbard model\textsuperscript{23}. We showed that there was a transition from a metal to a Mott insulator with increasing \( U/t \), with the critical value depending on the amount of frustration \( t'/t \). In the metallic
phase as the temperature increased there is a crossover from a Fermi liquid (with a specific heat and entropy that increased linearly with temperature) to a bad metal, characterised by an entropy of order $k_B \ln(2)$. The coherence temperature associated with this crossover, was substantially reduced by strong correlations, having a value of order $t/10$.

IV. RESULTS

In Fig. 2 we show how the thermopower estimated with Kelvin formula $S_K$ shows a large enhancement with increasing electronic interactions $U$ at low $T$. In comparison to the non-interacting ($U = 0$) system the enhancement can be an order of magnitude and originates in electronic correlations. The largest magnitude of $S_K$ is reached for $T \sim T_{coh} \sim 0.1t$ which is much lower than the Fermi energy. Below $T_{coh}$ one enters a coherent Fermi liquid regime in which one expects a linear temperature dependence of $S_K$, extrapolating to zero at zero temperature, in accordance with the third law of thermodynamics. This regime is hard to reach numerically and our results only indicate it with $S_K$ tending to 0 at $T \to 0$ for $T < T_{coh}$. In Fig. 2 we linearly extrapolated $S_K$ to 0 for $T \to 0$ by hand to demonstrate the expected behaviour.

A. Non-interacting fermions

In a non-interacting fermion system the chemical potential, at temperatures much less than the Fermi temperature can be estimated via Sommerfeld expansion leading to

$$\mu(T) = E_F - \frac{\pi^2}{6} (k_B T)^2 \frac{g'(E_F)}{g(E_F)}.$$  \hspace{1cm} (4)

Here $g(E_F)$ is the density of states (DOS) at the Fermi energy ($E_F$) and $g'(E_F)$ is its slope. Substituting Eq. (4) in the Kelvin formula gives $S_K$ that is linear in temperature, with a magnitude of order, $(k_B/\epsilon)(k_B T/E_F)$, which for elemental metals will be very small. We show in Fig. 2 that the Sommerfeld expansion, Eq. (4), gives a good low $T$ estimate for non-interacting electrons, up to about $T = 0.3t$. The non-interacting density of states is shown in Fig. 3.

B. Fermi liquid regime

When using the Kelvin formula one should however be careful, since it may not be a good approximation in some regimes. For example, its weakness for $T < T_{coh}$ can be understood by
Figure 2. (color online) Enhancement of the thermopower by strong correlations. The temperature dependence of the Kelvin thermopower $S_K$ is shown for several different values of the Hubbard $U$. All results are for the isotropic triangular lattice, $t' = t$. As the Mott metal-insulator transition ($U_c \approx 7.5t$) is approached the magnitude of the thermopower increases to values that are an order of magnitude larger than for non-interacting electrons ($U = 0$) for temperatures of about $T \sim t/10$. The maximum in $|S_K|$ at low temperatures corresponds to the crossover from a Fermi liquid at low temperatures to a bad metal at higher temperatures. This maximum is also seen in the specific heat and the spin susceptibility. The curves have been linearly extrapolated from their value at $T = 0.06t$ to zero at zero-temperature. Also shown is the linear temperature dependence obtained by a Sommerfeld expansion for non-interacting electrons.

starting with the Mott formula\textsuperscript{13,14}

$$S_{\text{Mott}} = -T \frac{\pi^2 k_B^2}{3e} \frac{d}{d\mu} \ln[g(\mu)v_{k,x}^2 \tau_{k,\mu}]|_{\mu \rightarrow E_F}.$$  

(5)

Here, $v_{k,x}^2 \tau_{k,\mu}$ denotes the average of the quasi-particle velocity at wave vector $k$ in the $x$ direction ($v_{k,x}$) times the quasi-particle lifetime ($\tau_{k,\mu}$) over a surface in reciprocal space at energy equal to $\mu$. To obtain the Kelvin formula from $S_{\text{Mott}}$ one needs to neglect the $\mu$ dependence of $v_{k,x}^2 \tau_{k,\mu}$ in Eq. (5) leading to

$$S_K = -T \frac{\pi^2 k_B^2}{3e} \frac{d}{d\mu} \ln[g(\mu)]|_{\mu \rightarrow E_F}.$$  

(6)

This is the same result as obtained for the non-interacting case via Eq. (4) and also represents
Figure 3. (color online) Energy dependence of the density of states $g(\epsilon)$ for the tight-binding band structure associated with non-interacting electrons with $t' = t$. For half filling $\mu = E_F = 0.82t$ at zero temperature, and $g(E_F) = 0.14/t$ and $g'(E_F) = 0.056/t^2$. The latter determines the slope of the Kelvin thermopower versus temperature for non-interacting electrons. Reversing the sign of $t'$ or both $t$ and $t'$, corresponds to a particle-hole transformation and reverses the sign of this derivative ($g'(E_F)$).

the low-temperature Kelvin formula in a coherent regime with well defined quasi-particles. The problem with the Kelvin formula in a Fermi liquid regime is in neglecting the $\mu$ dependence of the velocity in the term $v_{k,x}^2 \tau_{k,\mu}$, while keeping the $\mu$ dependence of the density of states $g$, which is also related to the velocity since $g \propto 1/v$. It is also unlikely that in a Fermi liquid regime that $\tau$ would cancel the $\mu$ dependence of $v_{k,x}^2$ in $v_{k,x}^2 \tau_{k,\mu}$. That the Kelvin formula is more appropriate for higher temperatures and in the incoherent regime was already pointed out in Ref. 14, while in the low temperature regime it only gives a rough approximation. This is explicitly found in recent Dynamical Mean-Field Theory (DMFT) calculations for the Hubbard model\textsuperscript{15} and the Falicov-Kimball\textsuperscript{16} model.
C. Effect of dimerization

In Fig. 1 the measured thermopower of an organic metal in two different directions is shown. The opposite signs for the two directions was argued\cite{2} to originate in the finite dimerization of the hopping (alternating hopping $t - \delta t$, $t + \delta t$, ...) in two directions on the triangular lattice. Such a dimerisation splits the band into two bands, one electron and the other hole like\cite{18,25}. Each band dominates the thermopower in its own direction and leads to opposite signs of the thermopower for the two directions. Due to the band splitting the density of states is also split. However, it turns out that just the density of states cannot capture the change of sign and that $v^2$ term discussed in Sec. IV B needs to be included to reproduce the opposite signs. The Boltzmann transport equation approach in Ref. 2 does take these terms into account and captures the correct signs.

D. Comparison to experiment

For comparison of the experimental data shown in Fig. 1 and our results shown in Fig. 2 we set the energy scale $t = 50$ meV $\sim 580$ K as appropriate value obtained by Density Functional Theory for organic charge transfer salts\cite{26-29}. We note that with our definition of hopping parameters in Eq. (2) we should for organics either take both $t$ and $t'$ negative\cite{26,28,29} or positive $t$ and negative $t'$\cite{27}, but both changes correspond at half-filling to particle-hole transformation (with additional shift in $k$ space for the later) and therefore only reverse the sign of $S_K$ shown in Fig. 2. Then we estimate from Fig. 2 that the maximal thermopower would appear at roughly $T_{coh} = 60$ K, which is in agreement with experiment. We also capture the qualitative $T$ dependence of the thermopower. However, as already discussed in Sec. IV C, the Kelvin formula does not have the potential to describe the orientational dependence shown in Fig. 1, which originates in the finite dimerization of the lattice.

V. CONCLUSION

In conclusion, we have shown with the Kelvin formula, which is a good approximation in the bad metallic regime, that the thermopower is strongly enhanced by electronic correlations at low $T$, even by an order of magnitude compared to the weak or non-interacting electron limit. Comparing with experimental data for an organic charge transfer salt, we capture qualitatively the temperature dependence and overall magnitude of the thermopower. On the other hand, the Kelvin formula can
not capture the orientational dependence of $S$ observed in experiment, for which one would need to employ a Kubo formula and introduce dimerization of the lattice into the model. We leave this as a future challenge.

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