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

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In many strongly correlated electron metals the thermoelectric power has a nonmonotonic temperature dependence and values that are orders of magnitude larger than for elemental metals. Inspired by Kelvin, Peterson and Shastry derived a particularly simple expression for the thermopower in terms of the temperature dependence of the chemical potential, now known as the Kelvin formula. 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 nonmonotonic temperature dependence. The latter reflects a crossover with increasing temperature from a Fermi liquid to a bad metal. Although, the Kelvin formula gives a semiquantitative description of some experimental results it cannot describe the directional dependence of the sign of the thermopower in some materials.

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 [1]. 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 Boltzmanns 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 [2], cuprates [3,4], heavy fermion compounds [5], cobaltates [6], strained rare earth nickelates [7], and iron pnictides [8]. This is illustrated in Fig. 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 [9]. For heavy fermion materials, this observation can be explained in terms of a slave boson treatment of the Kondo lattice model [10].

Understanding the thermopower in strongly correlated electron materials has recently attracted increasing theoretical interest [1,11]. Shastry and coworkers have argued [12–14] 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 [15] 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 [16] and the Falicov-Kimball [17] model show that although the Kelvin formula is unreliable at low temperatures in the bad metal regime it can be 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 [18] 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 [3,4], and found theoretically within cellular DMFT [19].

Figure 1 shows the measured temperature dependence of the thermopower of an organic metal [2]. The authors also calculated the thermopower using a Boltzmann equation and a band structure obtained with the Huckel approximation. They were able to reproduce the two signs of the thermopower, which arose from the electron and hole parts of the Fermi surface. However, they obtained values that were about five times smaller than the experiment. But, 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 [21]. Merino and McKenzie suggested that the nonmonotonic temperature dependence arose from a crossover with increasing temperature from a renormalized Fermi liquid to a bad metal [22]. They showed this was consistent with results of calculations for a Hubbard model based on dynamical mean field theory.

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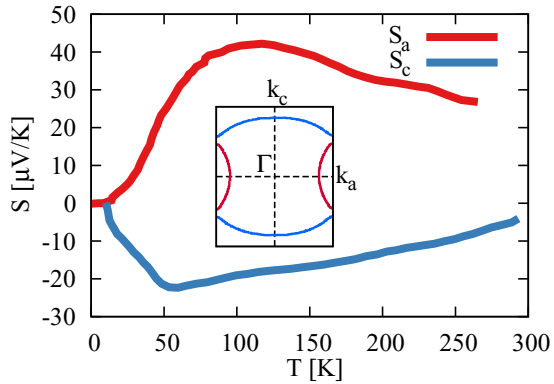FIG. 1. (Color online) Temperature dependence of the thermo-electric power in the organic metal κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. The two different curves correspond to two different intralayer directions in the crystal. Experimental data is taken from Ref. [2]. Note the nonmonotonic temperature dependence and that the thermopower is comparable to $k_B/e = 86$ μV/K. For temperatures below about 50 K the thermopower is approximately linear in temperature, as expected in a Fermi liquid. The material becomes a superconductor below $T_c = 12$ K. The inset shows a schematic of the electron (blue) and hole (red) Fermi surfaces deduced from a tight-binding band structure [20]. Transport in the a and c directions will be dominated by holes and electrons, respectively.

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 [15]

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

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 Fig. 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 μ, and model it with a (grand canonical) Hubbard model on the anisotropic triangular lattice,

$$\hat{H}_{el} = -\sum_{i,j,s} t_{i,j} c_{i,s}^{\dagger} c_{j,s} + U \sum_i \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow} - \mu \hat{N}_{el}. \quad (2)$$

At half filling, this is a minimal effective Hamiltonian for several classes of organic charge transfer salts, including the κ-(BEDT-TTF)$_2$X family [23]. $\hat{N}_{el} \equiv \sum_{i,s} \hat{n}_{i,s}$ is the total electron number operator, $t_{i,j} = t$ for nearest neighbor bonds in two directions and $t_{i,j} = t'$ for nearest neighbor bonds in the third direction. Electronic spin is denoted with s ($\uparrow$ or $\downarrow$).

For the organic charge transfer salts, such as the compound whose data is shown in Fig. 1, the values of U/t and t'/t

determine whether the ground state is a metal, Mott insulator, antiferromagnet, spin liquid, or superconductor. These parameters can be varied with pressure or chemical substitution, leading to a rich phase diagram. Accurately determining the parameters from electronic structure calculations, such as those based on Huckel or density functional theory [24] is challenging, and reviewed in detail in Ref. [23].

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

$$\langle \hat{N}_{el} \rangle = N, \quad (3)$$

where N is the number of lattice sites, ensuring half-filling. $\langle \hat{A} \rangle$ 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 were obtained by the finite-temperature Lanczos method (FTLM) [25], which employs finite lattices, averaging over starting random vectors to obtain finite-T results. In addition we use also twisted boundary conditions to reduce the finite-size effects. We used this method previously to determine several thermodynamic quantities of the Hubbard model [26]. 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, characterized by an entropy of order $k_B \ln(2)$, associated with noninteracting localized spins. The coherence temperature associated with this crossover was substantially reduced by strong correlations, having a value of order $t/10$, near the metal-insulator transition.

IV. RESULTS

In Fig. 2 we show the thermopower estimated with Kelvin formula S_K, calculated for 16 lattice sites. It shows a large enhancement with increasing electronic interactions U at low T. In comparison to the noninteracting ($U = 0$) 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 (measured from the band edges). 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. One can estimate T_{coh} from S_K as the temperature at which S_K has maximal absolute value or as the end of a linear-in-T regime. These roughly agree with the estimate $T_{coh} \sim 0.1t$ from the specific heat [26]. T_{coh} is expected to increase with decreasing U, and this is nicely seen in the specific heat [26] and also in Fig. 3, but is less clear in Fig. 2.

To investigate the possible role of finite size effects we show in Fig. 3 also S_K results for smaller $N = 14$ and $N = 12$ cluster sizes. It is evident from the figures that although the high T results are robust, there are still some finite size effects
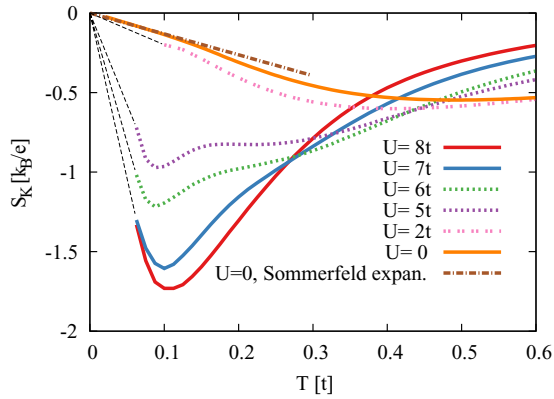
FIG. 2. (Color online) Enhancement of the thermopower by strong correlations. The temperature dependence of the Kelvin thermopower S_K is shown for several different values of the Hubbard U. All results are for the isotropic triangular lattice, $t' = t$. As the Mott metal-insulator transition ($U_c \simeq 7.5t$) [26] is approached the magnitude of the thermopower increases to values that are an order of magnitude larger than for noninteracting 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 [26] and the spin susceptibility. The curves have been linearly extrapolated from their value at $T = 0.06t$ to zero at zero-temperature. All results shown are for a 16-site cluster. Also shown is the linear temperature dependence obtained by a Sommerfeld expansion for noninteracting electrons [27].

at lower T. In particular the maximum slightly shifts to lower T and the low-T S_K still increases with increasing system size. However, the main features in our results, namely, increase with U, nonmonotonicity in T, and values of the order k_B/e, are observed for all cluster sizes.

The MIT is expected to affect the thermopower and it is interesting to see whether one can observe some change in S_K due to the MIT. We show in Fig. 4 how for several T above T_{coh} S_K changes with increasing U and that a minimum is observed for $U \sim 7.5t$, where the MIT is expected [26]. However, there is no clear signature of the MIT. This is
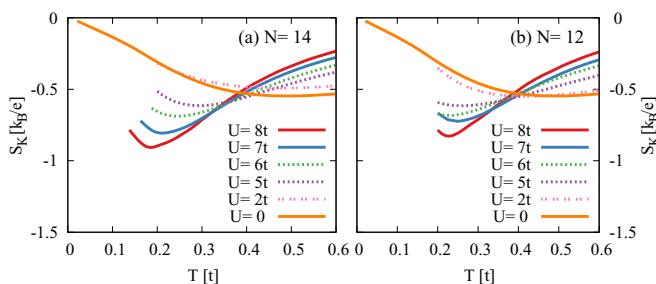

FIG. 3. (Color online) Limited finite-size effects. The same quantities as shown in Fig. 2 are plotted here for smaller 12- and 14-site clusters. All the main features, namely, that S_K increases with U at low temperatures, is nonmonotonic in T, and is of the order of k_B/e close to the MIT, are present. However, at lowest T there are still some finite size effect and S_K still seems to slightly increase with system size.
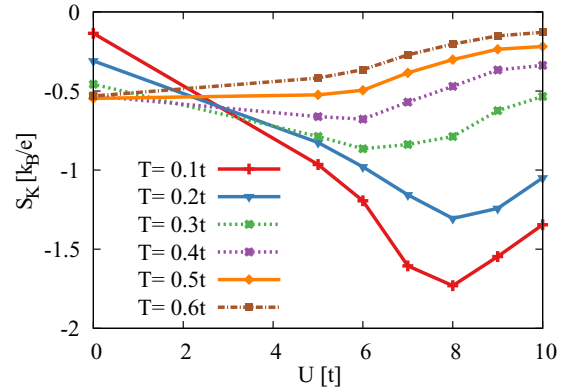

FIG. 4. (Color online) The dependence of S_K on U for several different fixed temperatures T is shown. It is seen how correlations increase S_K at low temperatures, with possibly a signature of the MIT near the critical $U_c \sim 7.5$ [26].

similar to what is observed for the specific heat, entropy, and spin susceptibility, which exhibit a smooth crossover as one goes from the metal to Mott insulator. It is not clear what the temperature dependence and magnitude of the thermopower should be in the Mott insulator. We are unaware of any theoretical predictions for finite U. In a conventional semiconductor the thermopower is given by $S = -k_B/e[\Delta/T + 5/2]$, where Δ is the charge gap [see for example, Eq. (A20) in Ref. [28]]. However, this formula does not seem to be a very good description of our results for the Kelvin thermopower. For $U = 8t$, we previously estimated that $\Delta/t \sim 0.1 - 0.2$ [26]. Specifically, the formula gives too larger values and diverges as T goes to zero. But, we should not necessarily expect this formula to be relevant since it assumes well-defined quasiparticles with nondispersive scattering.

V. NONINTERACTING FERMIONS

In a noninteracting fermion system the chemical potential, at temperatures much less than the Fermi temperature, can be estimated via the Sommerfeld expansion leading to [27]

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

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 a S_K that is linear in temperature, with a magnitude of order, $(k_B/e)(k_B T/E_F)$, 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 noninteracting electrons, up to about $T = 0.3t$. The noninteracting density of states is shown in Fig. 5.

VI. 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 $T < T_{\mathrm{coh}}$ can be understood by starting with the Mott formula [14,15]

$$S_{\mathrm{Mott}} = -T \frac{\pi^2 k_B^2}{3e} \frac{d}{d\mu} \ln \left[g(\mu) \overline{v_{k,x}^2 \tau_{k,\mu}} \right]|_{\mu \to E_F}. \tag{5}$$
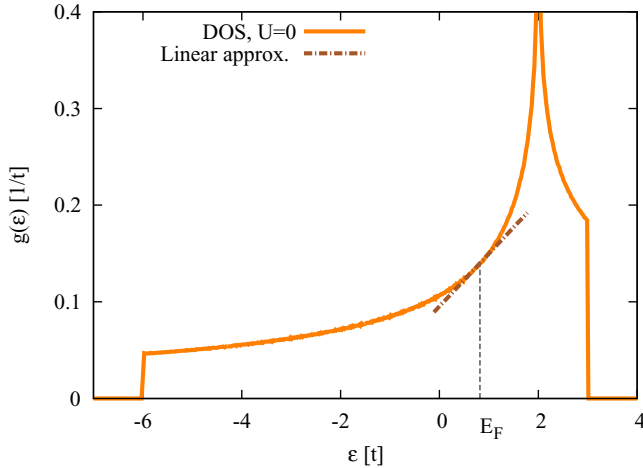
FIG. 5. (Color online) Energy dependence of the density of states $g(\epsilon)$ for the tight-binding band structure associated with noninteracting electrons with $t' = t$. For half filling $\mu = E_F = 0.82t$ at zero temperature, and $g(E_F) = 0.14/t$ and $g'(E_F) = 0.056/t^2$. The latter determines the slope of the Kelvin thermopower versus temperature for noninteracting electrons. Reversing the sign of t', or both t and t', corresponds to a particle-hole transformation and reverses the sign of this derivative [$g'(E_F)$].

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

$$S_K = -T \frac{\pi^2 k_B^2}{3e} \frac{d}{d\mu} \ln[g(\mu)]|_{\mu \to E_F}. \qquad (6)$$

This is the same result as obtained for the noninteracting case via Eq. (4) and also represents the low-temperature Kelvin formula in a coherent regime with well-defined quasiparticles. The problem with the Kelvin formula in a Fermi liquid regime is in neglecting the μ dependence of the velocity in the term $\overline{v_{k,x}^2 \tau_{k,\mu}}$, while keeping the μ 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 τ would cancel the μ dependence of $v_{k,x}^2$ in $\overline{v_{k,x}^2 \tau_{k,\mu}}$. That the Kelvin formula is more appropriate for higher temperatures and in the incoherent regime was already pointed out in Ref. [15], while in the low-temperature regime it only gives a rough approximation. This is explicitly found in recent DMFT calculations for the Hubbard model [16] and the Falicov-Kimball [17] model. It has also been shown that Kelvin formula fails near the critical point of a one-dimensional exactly solvable model [29].

VII. 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 [2] to originate in the finite dimerization of the hopping (alternating hopping $t - \delta t$, $t + \delta t, \ldots$) in two directions on the triangular lattice. Such a dimerization splits the band into two bands, one electron

and the other hole like [20,30]. 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 above 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.

VIII. 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 ~ 580 K as appropriate value obtained by Density Functional Theory for organic charge transfer salts [24,31–34]. We note that with our definition of hopping parameters in Eq. (2) we should for organics either take both t and t' negative [24,32,33] or positive t and negative t' [31], but both changes correspond at half-filling to a 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 $T_{\text{coh}} = 60$ K, which is in agreement with experiment, in particular with S_c for the material in Fig. 1.

We also capture the qualitative T dependence of the thermopower. However, as already discussed above, 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. Dimerization can also significantly alter the absolute values and sign of S and is therefore needed for reconciliation of the experimental, e.g., $S_c \simeq 22$ μV/K at maximum, and theoretical, $S_K \simeq 86$ μV/K at maximum, values.

IX. CONCLUSION

We have shown with the Kelvin forumla, 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 noninteracting 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 cannot 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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