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Strongly enhanced thermal transport in a lightly doped Mott insulator at low temperature

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We show how a lightly doped Mott insulator has hugely enhanced electronic thermal transport at low temperature. It displays universal behavior independent of the interaction strength when the carriers can be treated as nondegenerate fermions and a nonuniversal “crossover” region where the Lorenz number grows to large values, while still maintaining a large thermoelectric figure-of-merit. The electron dynamics are described by the Falicov-Kimball model which is solved for arbitrary large on-site correlation with a dynamical mean-field theory algorithm on a Bethe lattice. We show how these results are generic for lightly doped Mott insulators as long as the renormalized Fermi liquid scale is pushed to very low temperature and the system is not magnetically ordered.

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Introduction Thermoelectric materials are attracting significant attention, because of their potential for various power generation or refrigeration applications which involve so-called green technologies. The mass application of the thermoelectric devices is hampered by their low efficiency and the aim of current research is to produce materials with better thermoelectric conversion efficiency. At high temperatures, the efforts are directed towards nanostructured semiconductors [1] with reduced thermal conductivity. At low temperatures, the focus is on the materials with strongly correlated electrons, like Kondo insulators and systems with a Mott-Hubbard gap to enhance the thermopower in metallic systems.

Here, we present a theory for the charge and thermal transport in a slightly doped Mott insulator that is described by the Falicov-Kimball model. The exact solution is obtained from dynamical mean-field theory (DMFT) and it shows that for large correlation and small doping the figure-of-merit is unusually large. This behavior is expected to also hold in more general doped Mott insulators, like those described by the Hubbard model if they are sufficiently frustrated away from magnetic order and if the operating temperature lies well above the renormalized Fermi temperature. Even the presence of magnetic order is unlikely to strongly modify this effect, since the magnetic order rarely has a large effect on charge and heat transport in strongly correlated materials[2]. The numerics, however, requires quite high precision to determine the transport for such low doping values, which is why this problem can only be solved within the Falicov-Kimball model with current state-of-the-art methods.

Theoretical description To discuss this thermoelectric phenomena, we use transport equations which express the charge and the internal energy current densities, $\mathbf{J}(\mathbf{x})$ and $\mathbf{J}_E(\mathbf{x})$, in terms of the generalized forces [3]. The coefficients of these generalized forces, $N_{ij}(T)$, are given by various current-current correlation functions which have to be calculated for the model at hand. The electrical

conductivity σ , the Seebeck coefficient (or thermopower) α , and the thermal conductivity κ_e are then obtained as

$$\sigma(T) = e^2 N_{11}(T), \quad (1)$$

$$\alpha(T) = \left(\frac{k_B}{e}\right) \frac{N_{12}(T)}{T N_{11}(T)}, \quad (2)$$

$$\kappa_e(T) = \left(\frac{k_B}{e}\right)^2 \frac{\sigma(T)}{T} D(T), \quad (3)$$

where $D = N_{22}/N_{11} - N_{12}^2/N_{11}^2$ gives the effective Lorenz number $\mathcal{L}(T) = \kappa_e/(\sigma T) = (e/k_B)^2 D(T)/T^2$. The dimensionless figure-of-merit of a particular thermoelectric material is $ZT = \alpha^2 \sigma T / \kappa$, where $\kappa = \kappa_e + \kappa_{ph}$ is the overall thermal conductivity due to the electronic and the lattice degrees of freedom. The electronic figure-of-merit can be expressed as $ZT = \alpha^2 / \mathcal{L}$ and an efficient thermoelectric material has $ZT > 1$. We do not consider the phonon contribution to the thermal conductivity further here.

We next show how to exactly evaluate the transport coefficients for the spinless Falicov-Kimball model [4] with a large on-site Coulomb interaction. The Hamiltonian on an infinite-coordination ($Z \rightarrow \infty$ with Z the coordination number in this equation only and not to be confused with the figure of merit ZT) Bethe lattice is

$$\mathcal{H} = -\frac{t^*}{\sqrt{Z}} \sum_{\langle ij \rangle} (c_i^\dagger c_j + h.c.) - (\mu + \frac{U}{2}) \sum_i c_i^\dagger c_i + U \sum_i c_i^\dagger c_i w_i, \quad (4)$$

where c_i^\dagger (c_i) creates (destroys) a conduction electron at site i , t^* is the renormalized hopping, μ is the chemical potential shifted so that $\mu = 0$ corresponds to half-filling, U is the interaction between localized and itinerant electrons, and w_i is a classical variable equal to 0 if a localized electron is not at site i and equal to 1 if the localized electron is at site i . We consider the upper Hubbard band filling $n_c \ll 1$ and the average filling of the localized electrons $\langle w_i \rangle \simeq 1/2$. (The total conduction electron

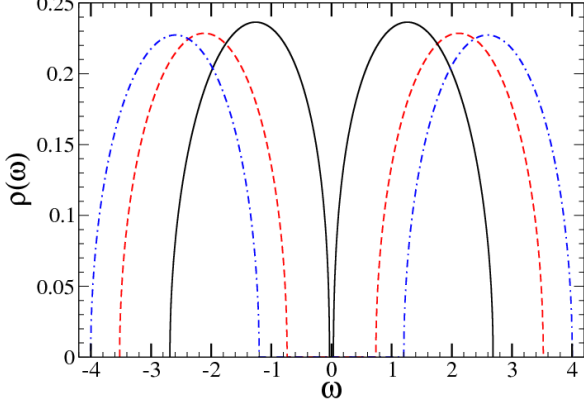


FIG. 1: (Color online) The density of states plotted as a function of energy for $U = 2.2$ (full line), $U = 4$ (dashed line), and $U = 5$ (dashed-dotted line). The lower and the upper gap-edges are at $\omega_-(U)$ and $\omega_+(U)$, respectively.

filling is $1/2 + n_c$.) These parameters lead to a Mott-insulating state when U is larger than $2t^*$ and $\mu = 0$. For $\langle w_i \rangle = n_c$, we find similar behavior as obtained in the Hubbard model at high temperatures where the coherent Fermi liquid state is destroyed [5]. The sum over i and j in the kinetic-energy term is over nearest neighbor pairs and $h.c.$ denotes the hermitian conjugate. This model is appropriate for doped Mott insulators where the dopants provide carriers without producing impurity levels in the gap, as is often seen in many semiconductors.

To calculate the thermal transport, we need to evaluate a series of Kubo formulas for the relevant transport coefficients. This is greatly simplified because the Falicov-Kimball model satisfies the Jonson-Mahan theorem [6, 7]. Thus, the transport coefficients can be written as [8],

$$N_{mn}(T) = \int_{-\infty}^{\infty} d\omega \left(-\frac{\partial f(\omega)}{\partial \omega} \right) \omega^{m+n-2} \Lambda_{tr}(\omega), \quad (5)$$

with the transport function given by

$$\Lambda_{tr}(\omega) = \frac{4}{3\pi^2} \int d\epsilon \rho_0(\epsilon) (4t^{*2} - \epsilon^2) [\text{Im } G(\epsilon, \omega)]^2, \quad (6)$$

where the noninteracting density of states is

$$\rho_0(\epsilon) = \frac{1}{2\pi t^*} \sqrt{4t^{*2} - \epsilon^2}, \quad (7)$$

and $G(\epsilon, \omega)$ is the “band-energy-dependent” Green’s function (ϵ is the noninteracting band energy) which we calculate within DMFT [9]. (One should note that there is no momentum on a Bethe lattice, and instead, one should think of the band-energy as analogous to the independent variable of momentum.) The integral in Eq. (6)

can be performed exactly, resulting in

$$\Lambda_{tr}(\omega) = \frac{1}{3\pi^2} \text{Im}^2[G(\omega)] \frac{|G(\omega)|^2 - 3}{|G(\omega)|^2 - 1}. \quad (8)$$

The local Green’s function, $G(\omega) = \int d\epsilon \rho_0(\epsilon) G(\epsilon, \omega)$ satisfies a simple cubic equation [10], which allows for the numerics to be carried out to high precision (*i.e.*, there is no self-consistent iterative algorithm needed to solve the problem). In this equation, and in the following, we set $t^* = 1$ as our energy unit. Note that because the density of states at the band edge grows like the square root of frequency, the transport density of states is linear near the band edge as one goes into the band and vanishes as one goes into the gap. Similar results are obtained for a three-dimensional cubic lattice (within DMFT), as has been checked for a few points in parameter space.

Numerical results The energy dependence of the renormalized density of states $[\rho(\omega) = -\text{Im}G(\omega)/\pi]$ of a Mott insulator is shown in Fig. 1 for several values of U , with $\mu = 0$. The density of states for the Falicov-Kimball model does not depend on temperature, and since the cubic equation for $G(\omega)$ depends only on $\omega + \mu$, U , and the average filling of the localized electrons, the density of states for this lightly doped Mott insulator is identical to that of the Mott insulator, except the origin is shifted, as the chemical potential changes (when $\langle w_i \rangle = 1/2$). For $U > 2$, the DOS is split into a lower and upper Hubbard band of width W and with a separation between the maxima approximately equal to U . The shape of the Hubbard bands is nearly independent of U (for $U > 2$) and only the gap, which extends from $\omega_-(U)$ to $\omega_+(U)$, increases with U .

The temperature dependence of the chemical potential, obtained for various values of U and several (small) values of n_c is shown in Fig. 2. At zero doping, the system is electron-hole symmetric and the chemical potential is in the middle of the gap, $\mu(T) = 0$. At finite electron doping, the zero-temperature chemical potential is in the upper Hubbard band, just above the band edge, as can be seen by comparing $\mu(0)$ in Fig. 2 with $\omega_+(U)$ in Fig. 1. For $n_c \ll 1$, the values of $\mu(0)$ are approximately given by $\omega_+(U) \approx (U - W)/2$. The low-temperature behavior of $\mu(T)$ is demonstrated in the inset of Fig. 2. The data show that after an initial parabolic decrease, $\mu(T)$ is nearly linear up to a characteristic temperature T_μ . For $T > T_\mu$, the decrease of $\mu(T)$ slows down, because excitations across the gap restore the electron-hole symmetry and the chemical potential approaches the high-temperature limit, $\mu(T) \rightarrow 0$. For a given U , the characteristic temperature T_μ increases with n_c . This is shown in Fig. 2 by the full, dashed, and dashed-dotted arrows which indicate T_μ obtained for $U = 4$ and $n_c = 10^{-6}$, 10^{-5} , and 10^{-4} , respectively.

The observed behavior follows from the fact that $\mu(T)$ is close to the bottom of the upper Hubbard band at low temperatures and that the excitations across the gap

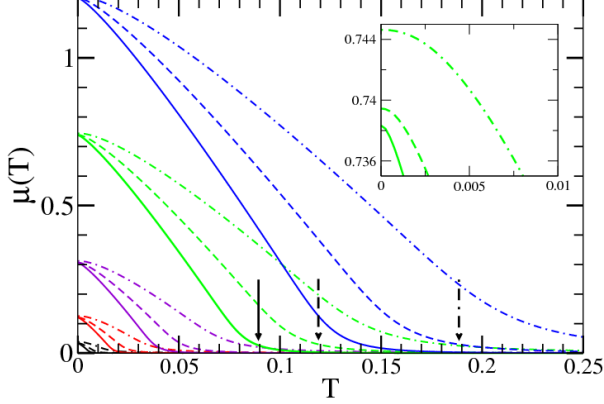


FIG. 2: (Color online) Chemical potential plotted as a function of temperature. The black, red, purple, green, and blue curves are calculated for $U = 2.2, 2.5, 3, 4$, and 5 , respectively. The full, dashed, and dashed-dotted curves correspond to the concentrations of $n_c = 10^{-6}, 10^{-5}$, and 10^{-4} electrons above half filling. The characteristic temperature T_μ , obtained for $U = 4$, is indicated by the full, dashed and dashed-dotted arrows. The inset show the low-temperature behavior obtained for $U = 4$.

establish a symmetric state at high temperatures, where $\mu \approx 0$. Thus, for a given n_c , an increase of U shifts $\mu(0)$ and T_μ to higher values and translates $\mu(T)$ upwards, as shown in Fig. 2. If we increase n_c keeping U constant, a higher temperature is needed to restore the electron-hole symmetry, so that T_μ increases with n_c .

To calculate the transport integrals in Eq. (5) we adjust $\mu(T)$ to yield the target filling of particles and measure the energy at each temperature with respect to $\mu(T)$. Since neither $\rho(\omega)$ nor $\Lambda_{tr}(\omega)$ change their shape, the transport coefficients in Eq. (5) are easy to compute. At high temperatures, $T \geq T_\mu(U)$, the behavior is universal, *i.e.*, the transport coefficients are independent of n_c , for a given U . This is revealed most clearly by the effective Lorenz number, $\mathcal{L}(T)$, plotted in the uppermost panel of Fig. 3. The curves $\mathcal{L}(T)$ obtained for a given U and various n_c merge for $T \geq T_\mu$, due to the fact that at such high temperatures $\mu \simeq 0$ and all the systems we are concerned with become (nearly) electron-hole symmetric.

At the lowest temperatures, $T \leq T_1$, the Lorenz number is given by the usual value, $\mathcal{L}(T) \simeq \mathcal{L}_0 = (\pi^2/3)(k_B/e)^2$, expected from the Wiedemann-Franz (WF) relation for degenerate fermions. The characteristic temperature T_1 depends on the distance of the $T = 0$ chemical potential from the upper Hubbard band edge $\mu(0) - \omega_+(U)$. For very low doping, this temperature is physically irrelevant and we do not show it on the figure. Another type of universality sets in when the chemical potential is in the gap and the lower Hubbard band

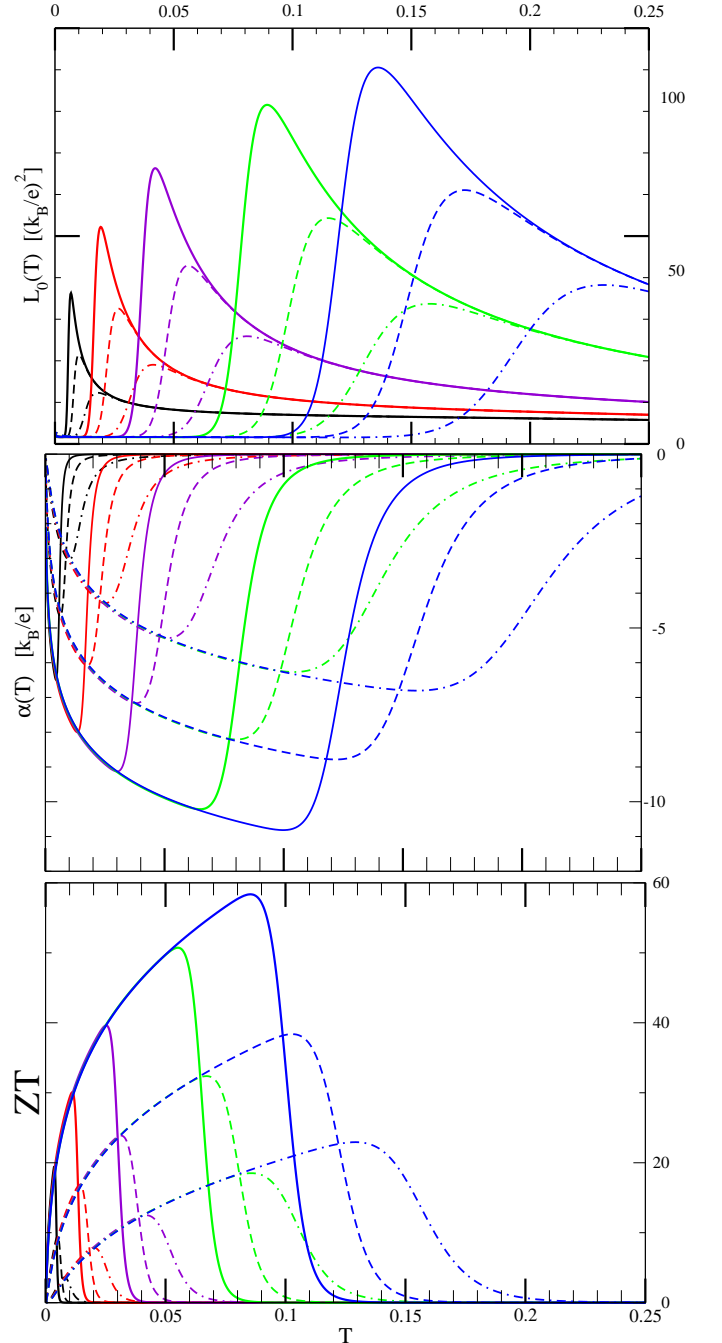


FIG. 3: (Color online) Lorenz number in units of $[k_B/e]^2$, thermopower in units of $[k_B/e]$, and thermoelectric figure of merit ZT are plotted as a function of temperature for the same parameters as in Fig. 2.

starts affecting the transport. Figure 3 shows that, for a given U , the Lorenz number becomes independent of n_c for a wide range of temperature $T_1 \ll T < T_0$, where T_0 depends on the size of the Mott-Hubbard gap. Here, the Fermi gas is nondegenerate and the WF relation holds with the smaller classical value $\mathcal{L}_0 = 2(k_B/e)^2$.

Curiously, for $T_1 \ll T < T_0$, the thermopower and

the figure of merit also assume universal forms, independent of U , which can be seen by the overlapping curves in Fig. 3. This low-temperature universality arises because the shape of $\Lambda_{tr}(\omega)$ around $\omega = \mu$ does not depend strongly on U . The universality is lost for $T \geq T_0$, when the excitations across the gap become important.

For $T_0 \leq T \leq T_\mu$, there is a crossover from the low- to the high-temperature regime. Here, the transport coefficients vary in a non-universal way, which is also revealed most clearly by the effective Lorenz number. It grows rapidly for $T \geq T_0(n_c)$, attains a maximum at about $T \simeq T_\mu$, and then decays slowly. Well above T_μ , where κ and σ assume their high-temperature universal forms, $\mathcal{L}(T)$ is independent of n_c .

We now consider in more detail the results for thermopower and the figure-of-merit, shown in Fig. 3. At very low temperatures, the slope of $\alpha(T)$ is determined by the logarithmic derivative $d \ln \Lambda_{tr} / d\omega|_{\omega=\mu}$ which is large for low doping, since $\mu(T)$ is close to the band edge. Here, $\alpha(T)$ grows rapidly and α/T increases as n_c decreases but, for a given n_c , it does not depend on U . At higher temperatures, the presence of the Mott-Hubbard gap leads to novel features. Unlike in ordinary semiconductors, $\alpha(T)$ continues to grow when the temperature renormalization brings $\mu(T)$ below the bottom of the upper Hubbard band. When that happens, the states below the chemical potential do not contribute to N_{12} and $\alpha(T)$ grows to very large values for large U and $T \leq T_0$. Eventually, for $T_0 < T \simeq T_\mu$, the system becomes nearly electron-hole symmetric and $\alpha(T)$ drops to very small values.

The figure-of-merit becomes very large in the proximity of the metal-insulator transition. For $U \geq 20$ and doping which gives less than 10^{-19} conduction electrons ($n_c \approx 10^{-4}$), we find $ZT > 200$! The maximum of ZT occurs at a temperature at which the WF relation holds for nondegenerate fermions and the thermal conductivity is very low, so that the thermal current due to any additional degrees of freedom will greatly reduce the thermoelectric efficiency. However, the temperature range in which $ZT > 1$ increases with U and n_c . For larger doping, a relatively large ZT is found in a broad temperature range, even for moderate U . By tuning the concentration of conduction electrons, one can find a temperature window in which $\mathcal{L}_0 \ll \mathcal{L}(T)$ and $ZT \gg 1$. Here, the electronic thermal conductivity is not small and the large ZT values should be physically relevant, if one were to include phonon effects to the thermal conductivity. This occurs, typically for temperatures of the order of T_μ .

Summary and conclusions We presented a theory for the charge and heat transport of a "bad metal" described by the Falicov-Kimball model. Using DMFT, we show that the transport coefficients of a lightly doped Mott insulator exhibit universal features at low temperatures, $T_1 \ll T \leq T_0$, and at high temperatures, $T \geq T_\mu$. In the crossover region, $T_0 \leq T \leq T_\mu$, the effective Lorenz

number becomes very large and the WF relation is not obeyed. The thermopower and the figure of merit grow to very large values close to $T \approx T_0$. In this region, the system might be optimal for use in thermoelectric devices.

The low-temperature thermoelectric properties are enhanced because the renormalized transport density of states of a lightly doped Mott insulator is very asymmetric close to the gap. As the temperature increases, the chemical potential drops below the bottom of the conduction band, such that the asymmetry of the electron and hole currents becomes even more pronounced, and the thermopower is further enhanced. At about $T \simeq T_\mu$, the chemical potential approaches the center of the gap, the system nearly acquires electron-hole symmetry, and the thermopower drops to small values. We could not obtain similar effects with non-interacting electrons or in a Fermi liquid.

The ZT of a strongly correlated system with just a few electrons in the upper Hubbard band turns out to be surprisingly large. This finding is not restricted to a Bethe lattice; large ZT is obtained for a three- d cubic lattice as well. We point out that the maximum of ZT occurs at temperatures at which the WF relation holds for non-degenerate fermions and the thermal conductivity is low, so that the thermoelectric efficiency of a real system described by our model would be greatly affected by other degrees of freedom that can transport heat. However, for large U and moderate n_c , there is a broad temperature interval, $T_0 \leq T \leq T_\mu$, in which ZT is moderately large, even though the electronic thermal conductivity and \mathcal{L} are not small and in this regime, phonons will not affect the ZT values as much.

One might ask whether such features are generic for all Mott insulators, or specific to the Falicov-Kimball model. It turns out, the Hubbard model will share this behavior for small enough doping and large U . This is because in this regime the renormalized Fermi temperature is reduced towards zero, so a Fermi liquid won't form here and the system behaves as a "bad metal" [5]. In this interesting regime where the thermoelectric effects can be so large, the Hubbard model acts similar to the Falicov-Kimball model. (It is still possible that a too large phonon thermal conductivity, that magnetic order which modifies the transport density of states, or localization effects due to disorder in lightly doped systems will reduce this effect, but there should be a regime where it will still be able to be seen [11].) We hope that this work will inspire experimental groups to look for this kind of phenomena as a new route towards low-temperature thermoelectric refrigeration.

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