Thermoelectric Response Near the Density Driven Mott Transition

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(Received 15 September 1997)

We investigate the thermoelectric response of correlated electron systems near the density driven Mott transition using the dynamical mean field theory. [S0031-9007(98)06111-0]

Thermoelectric effects which are responsible for the direct conversion of heat energy into electrical energy and vice versa have recently received renewed attention [1]. So far optimal thermoelectric response has been achieved in traditional doped semiconductors, but recent improvements in both the synthesis of correlated electron systems and the theoretical methods for treating them have generated new interest in the thermoelectric properties of correlated materials.

The thermoelectric performance of a material reflects its ability to convert applied voltages into temperature gradients while minimizing the irreversible effects of Joule heating and thermal conduction. This can be quantified by the so-called dimensionless figure of merit denoted here by $Z_T T$:

$$Z_T T = \frac{S^2 \sigma T}{\kappa + \kappa_L}. \tag{1}$$

Here σ is the electrical conductivity, S the thermopower (or Seebeck coefficient), T the temperature, κ the electronic contribution to the thermal conductivity, and κ_L the lattice thermal conductivity. In weakly correlated systems the Seebeck coefficient can be interpreted as the logarithmic derivative of the conductivity with respect to the Fermi energy. In strongly correlated electron systems, S is a more difficult quantity to interpret and is the subject of this Letter.

We consider a system of fermions doped away from a Mott insulating state, where the magnetic correlations are weak so that the magnetism is not the driving force behind the metal to insulator transition. This situation is realized experimentally in titanate and vanadate perovskite compounds [2]. For example, $La_{1-x}Y_xTiO_3$ is ferromagnetic for x near 1 and antiferromagnetic at small values of x, but in all these compounds the Néel and Curie temperatures are quite small, of the order of 130 K and less [3], so we focus on the paramagnetic phase of the doped Mott insulator.

The experimental motivation for our study was mainly provided by the work of Y. Tokura's group, which has demonstrated that in the class of ternary perovskites, one can control to a large extent various parameters such as orbital degeneracy, bandwidth, and carrier concentration to provide an experimental realization of the filling driven Mott transition [2], in a wide region of parameters.

To approach this problem we use the dynamical mean field theory (DMFT) [4–8], which has successfully described many aspects of the physics of three dimensional transition metal oxides. The goal of our study is to understand qualitatively the thermoelectric response of a doped Mott insulator and to derive explicit formulas for the transport coefficients which are valid at very low and high temperatures. Using these insights and numerical results we discuss the figure of merit of this particular kind of material. An early numerical calculation of the Seebeck coefficient in the large d Hubbard model appeared in Ref. [7].

We consider perfect periodic solids described by the N-fold degenerate Hubbard model:

$$H = -\sum_{\langle ij \rangle \sigma} t_{ij} c_{i\sigma}^+ c_{j\sigma} + \frac{U}{2} \sum_{j\sigma \neq \sigma'} n_{j\sigma} n_{j\sigma'} - \mu \sum_{j\sigma} n_{j\sigma} \tag{2}$$

and ignore electron-phonon interactions. The index σ can be thought of as a spin or an orbital index, and will run from 1 to N. The single band case corresponds to $N = 2$. We now summarize the relevant aspects of the DMFT. The transport properties are obtained from a Green's function with a frequency dependent but momentum independent self-energy:

$$G(k, \omega) = G(\epsilon_k, \omega) = \frac{1}{\omega + \mu - \epsilon_k - \Sigma(\omega)}, \tag{3}$$

where ϵ_k is the dispersion relation. The self-energy, is computed by solving an Anderson impurity model in a bath described by a hybridization function $\Delta(i\omega)$. Regarded as a functional of the hybridization function it obeys the self-consistency condition [5,6]

$$\frac{1}{i\omega + \mu - \Delta(i\omega) - \Sigma(i\omega)} = \int d\varepsilon \, G(\varepsilon, i\omega) D(\varepsilon), \tag{4}$$

where $D(\varepsilon)$ is the bare density of states, $D(\varepsilon) = \sum_k \delta(\varepsilon - \epsilon_k)$. The transport coefficients that govern the electrical and thermal responses of the model are given in terms of current-current correlation functions. Within the DMFT they reduce to averages over the spectral density $\rho(\epsilon, \omega)$ [7]:

$$\sigma = \frac{e^2}{T} A_0, \quad S = \frac{-k_B}{e} \frac{A_1}{A_0}, \quad \kappa = k_B^2 \left(A_2 - \frac{A_1^2}{A_0} \right), \tag{5}$$

where

$$A_n = \frac{\pi}{\hbar V} \sum_{k,\sigma} \int d\omega \, \rho_\sigma(k,\omega)^2 \left(\frac{\partial \epsilon_k}{\partial k_x}\right)^2$$

$$\times \left(-T \frac{\partial f(\omega)}{\partial \omega}\right)(\beta\omega)^n$$

$$= \frac{N\pi}{\hbar k_B} \int_{-\infty}^{\infty} d\omega \, d\varepsilon \, \frac{\rho^2(\varepsilon,\omega)(\omega\beta)^n}{4\cosh^2(\frac{\beta\omega}{2})} \Phi(\varepsilon). \quad (6)$$

In this expression the relevant information about the bare band structure is contained in the spectral density, ρ, and the transport function Φ,

$$\Phi(\varepsilon) = \frac{1}{V} \sum_k \left(\frac{\partial \epsilon_k}{\partial k_x}\right)^2 \delta(\varepsilon - \epsilon_k). \quad (7)$$

The DMFT expressions bear superficial similarity with recent work of Mahan and Sofo [9], if we identify their transport function which we denote $\Sigma_{MS}(\varepsilon)$ as

$$\Sigma_{MS}(\omega + \mu) = \left(\frac{N\pi}{\hbar}\right) \int d\varepsilon \, \rho^2(\varepsilon,\omega)\Phi(\varepsilon). \quad (8)$$

Reference [9] stressed the relevance of correlated materials to thermoelectricity and suggested that the optimal response is obtained when Σ_{MS} takes the form of a delta function like peak at the Fermi level. The DMFT allows us to derive explicit expressions for Σ_{MS} starting from microscopic Hamiltonians. Near the Mott transition, the low energy spectral function does assume a deltalike form at low temperatures. We find, however, that the optimum of the figure of merit is achieved at high temperatures, when the quasidelta-functionlike resonance at the Fermi level is absent.

In electronic systems near a Mott transition there are two widely separated energy scales: the bare bandwidth D, which sets the scale for incoherent excitations, and the coherence temperature T_{coh} where Fermi-liquid-like properties begin to be observed. T_{coh} vanishes as we approach half filling. As a result, when we decrease the temperature, starting from very high temperatures we expect two crossovers to take place, one when $k_B T \approx D$ and the other when $T \approx T_{coh}$. We assume in this analysis that the interaction energy U is much larger than the bare bandwidth; i.e., we are close to the the $U = \infty$ limit.

At very low temperature the Fermi-liquid picture is applicable and momentum space offers a natural description of the transport processes. The only states that contribute come from a narrow region around the Fermi surface, which in the local mean-field picture shows up as a narrow Kondo-like resonance near the Fermi level. At very high temperatures the entire Brillouin zone is equally important and a real-space picture of the transport is more appropriate. The transport is then entirely due to incoherent motion of charge carriers. We discuss these two asymptotic regimes below.

Low temperature regime.—In this regime we use Fermi liquid ideas to parametrize the transport coefficients in terms of a few parameters, which contain all the effects of the interactions: $\gamma = \text{Im}\,\Sigma(0)$ is the scattering rate at the Fermi level, $Z = (1 - \frac{\partial\,\text{Re}\,\Sigma}{\partial\omega}|_{\omega=0})^{-1}$ is the quasiparticle residue at the Fermi level and $\tilde{\mu} = \mu - \text{Re}\,\Sigma(0)$ is the effective chemical potential. Close to the Mott transition there is only one effective scale controlling the low-temperature physics, and therefore the scattering rate behaves as $A(k_B T)^2/Z^2 D$ where A is a dimensionless constant [10]. Performing a low-temperature expansion of Eq. (6) and substituting into (5), we obtain

$$\sigma = \frac{Ne^2 D Z^2 \Phi(\tilde{\mu}) E_0}{2A(k_B T)^2} \qquad \kappa = \frac{k_B N D Z^2}{2A(k_B T)} \Phi(\tilde{\mu}) E_2. \quad (9)$$

We find that the thermopower and the figure of merit do not depend on γ and are given by

$$S = -\frac{k_B}{e}\left(\frac{k_B T}{Z} \frac{d\ln\Phi(\tilde{\mu})}{d\tilde{\mu}}\right)\frac{E_2}{E_0}, \quad (10)$$

$$Z_T T = \frac{E_2}{E_0}\left(\frac{k_B T}{Z} \frac{d\ln\Phi(\tilde{\mu})}{d\tilde{\mu}}\right)^2. \quad (11)$$

Here the numbers E_n are given by

$$E_n = \int_{-\infty}^{\infty} \frac{x^n dx}{4\cosh^2(\frac{x}{2})[1 + (\frac{x}{\pi})^2]}. \quad (12)$$

Numerical calculation gives $E_0 = 0.82$ and $E_2 = 1.75$. Note that the Wiedeman-Franz law holds here as it does for transport dominated by impurity scattering. However, since the scattering rate is energy dependent around the Fermi surface, the ratio of σT and κ is not equal to the classical Lorenz number. The physical content of Eq. (11) is transparent. Correlations enhance the figure of merit relative to that of a noninteracting system with the same density of states by a factor of $\frac{1}{Z^2}$ which in this context can be thought of as the square of the mass enhancement. This factor is expected to be large and in fact diverges as we approach the density driven Mott transition in $La_x Sr_{1-x} TiO_3$ [2]. Note, however, that expression (11) is valid only in the low-temperature regime because it is restricted to $\beta Z D \gg 1$. Thus the figure of merit will be very low in the low-temperature regime unless the logarithmic derivative of the transport functions becomes appreciable. Unlike the density of states, however, the transport function does not have any Van Hove singularities, and the only singular points in the logarithmic derivative are at the band edges where the transport function vanishes.

High temperature regime.—To describe this region we observe that the spectral function shifted by the value of the chemical potential

$$\tilde{\rho}(\epsilon,\omega) = \rho(\epsilon, \omega - \mu) \quad (13)$$

converges to a well-defined shape, centered around $\omega = 0$ as the temperature tends to infinity. This agrees with a rigid-band interpretation of the lower Hubbard band, except that the carriers in this band are completely incoherent near the band edge. The high-temperature behavior of the chemical potential can also be found analytically and is given by $\beta\mu = \ln(\frac{n}{N(1-n)})$. We can now obtain the leading high-temperature behavior of the transport coefficients by inserting the scaling form (13) with $\tilde{\rho}$ temperature independent and expanding to lowest order in β the equations for the coefficients A_n. The results are parametrized in terms of the moments

$$\gamma_m = \frac{a}{D^{m+1}} \int d\epsilon \, d\omega \, \omega^m \tilde{\rho}^2(\epsilon, \omega)\Phi(\epsilon), \qquad (14)$$

which we evaluate numerically. To leading order in β we find

$$\sigma = \left(\frac{e^2}{a\hbar}\right)\pi N(D\beta)\gamma_0 \frac{\frac{n}{N}(1-n)}{[\frac{n}{N} + (1-n)]^2}, \qquad (15)$$

$$S = \left(\frac{k_B}{e}\right)\ln\left(\frac{n}{N(1-n)}\right), \qquad (16)$$

$$\kappa = \left(\frac{k_B D}{a\hbar}\right)\pi N(D\beta)^2\gamma_2 \frac{\frac{n}{N}(1-n)}{[\frac{n}{N} + (1-n)]^2}. \qquad (17)$$

Near the Mott transition the density and degeneracy dependence of the moments γ_0 and γ_2 is given by $\gamma_m = \tilde{\gamma}_m(1 - n + \frac{n}{N})^2$ where the $\tilde{\gamma}_m$'s are constants, $\tilde{\gamma}_0 \approx 0.05$ and $\tilde{\gamma}_2 \approx 0.01$. The factor in parenthesis is simply the total integrated spectral weight of the Green's function. The high-temperature equation that we get for the thermopower corresponds to the well-known Heikes formula [11] generalized for degeneracy N. Comparison with numerical solutions of the dynamical mean-field equations reveals that for the resistivity, the high-temperature expansion formula is quite accurate over a very wide temperature range and breaks down only at temperatures of the order of T_{coh}. This is surprising, since the high-temperature expansion is *a priori* valid only for $\beta D \ll 1$. This result gives some insight into the origin of the linear resistivity which was observed in early studies of the Hubbard model in infinite dimensions [12]. Furthermore, if one keeps the next term in the high-temperature expansion of the thermopower, one can fit the numerical data over a comparable region. Notice that the thermopower close to the Mott transition is holelike, which agrees with the picture of holes in a paramagnetic spin background [13].

The high-temperature expression for the figure of merit is to lowest order in β given by

$$Z_T T = \frac{\pi\tilde{\gamma}_0 \ln^2(\frac{n}{N(1-n)})n(1-n)}{\frac{\kappa_L}{\kappa_D} + \pi\tilde{\gamma}_2(D\beta)^2 n(1-n)}, \qquad (18)$$

where $\kappa_D = \frac{k_B D}{a\hbar}$. Here the lattice contribution to the thermal conductivity has been included since the electronic

contribution tends to zero in the high-temperature region. As temperature increases the figure of merit increases monotonically to a constant value that goes linearly with the bandwidth, D, of the system. At any finite temperature, however, the equation above gives a figure of merit that increases monotonically with D to a maximum which is at a bandwidth larger than $k_B T$ and thus outside the region of validity of our formula. Thus we conclude that the optimum figure of merit is obtained when the bandwidth is of the order of the temperature.

We now turn to quantitative calculations of the thermopower in the intermediate temperature range which is the range most pertinent to experiments and possible applications. The best characterized system in the class of materials that we seek to describe is the $La_{1-x}Sr_x TiO_3$ system with x small. We model this system with a Hubbard model on a three dimensional hypercubic lattice with half-bandwidth $D = 0.5$ eV and interaction strength $U = 2.0$ eV in the Mott insulating end of the series ($x = 0$). We take into account the x dependence of the bandwidth by using the fact that the Ti-O-Ti bond angle θ changes with doping. The bandwidth then depends on θ through $D(\theta) = D(180°)\cos^2\theta$. To select the bond angles corresponding to a given doping we use data for ab-plane bond angles from [14]. The results from the calculations of S, using iterated perturbation theory (IPT), with this choice of parameters is displayed in Fig. 1.

We notice here that in the high temperature end of the data the values of the thermopower are actually close to what Heikes formula predicts, thus indicating that the high-temperature thermopower can be used as a rough estimate of the carrier density. At lower temperature we see a marked decrease in the magnitude of the thermopower which heralds the transition into the Fermi-liquid regime where the thermopower is small and electronlike. We note, however, that for doping values lower than 0.1 the thermopower is already holelike above 300 K which indicates that the quasiparticle peak has almost disappeared
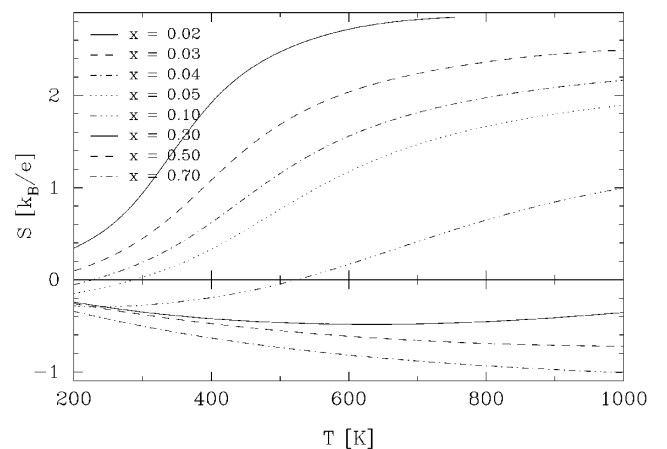

FIG. 1. Thermopower vs temperature for several values of doping in the $La_{1-x}Sr_x TiO_3$ system.

and that the carriers are completely incoherent. This regime does not appear for smaller values of the interaction U when the system is below the Mott transition. The thermopower near the Mott transition therefore seems to be a sensitive indicator of the character of the carriers (i.e., localized vs itinerant).

Since bandwidth and carrier concentration can be controlled to a large degree in this class of materials, we use our results to assess the prospects for a large figure of merit in this class of systems. We are not aware of any measurements of the thermal conductivity in the titanate compounds, so for the purpose of obtaining an order of magnitude estimate of the figure of merit we use a value of 2.0 W/mK for κ_L based on measurements carried out recently in the manganite oxides [15].

The results from the numerical calculation of the figure of merit in the intermediate temperature region are displayed in Fig. 2. The data for $T = 0.05$ and $T = 0.10$ were obtained with IPT modified for finite doping [16]. For the $T = 0.20$ data we use the infinite U noncrossing approximation (NCA). This approach has also been shown to give results in good agreement with exact methods at high temperatures [17,18].

The behavior of the figure of merit can be understood qualitatively as follows. It vanishes at a density $n_0(T)$ where the Seebeck coefficient vanishes. At very high temperature this occurs at $n_0 = \frac{N}{1+N}$ according to Eq. (16). As temperature is lowered, $n_0(T)$ moves towards half filling, and is given by the condition $T_{\mathrm{coh}}(n) \approx T$. This is due to the formation of the coherent quasiparticles which give a negative contribution to the thermopower. For densities lower than $n_0(T)$ the system is Fermi-liquid-like and we find a low figure of merit, closer to the Mott transition at temperature higher than $T_{\mathrm{coh}}(n)$ the figure of merit is larger.

The lowest temperature results show little density dependence below n_0. This is because both the logarithmic derivative of the transport function and the quasiparticle residue depend essentially linearly on the doping, and therefore the figure of merit varies little with density. The $T = 0.1$ data seem to be displaying a similar trend as the $T = 0.05$ data but the system is essentially out of the Fermi-liquid regime at that temperature.

To conclude, we have investigated the thermoelectric coefficient and the thermoelectric figure of merit near the density driven Mott transition. We provided simple expressions for the transport coefficients of this model, obtaining a qualitative understanding of the thermoelectric coefficient. In the light of our results, a large figure of merit in this class of systems seems rather unlikely. It would require very small doping, and a very small value of the bare half-bandwidth parameter D, to be able to access the high temperature regime $T > D$ where the figure of merit is of order unity. We have argued, however, that the
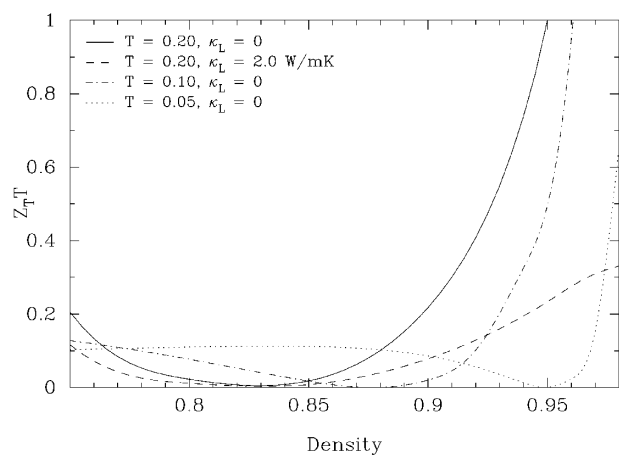

FIG. 2. Figure of merit vs temperature for several values of doping. Data for $T = 0.1$ and 0.05 from IPT with $U = 4.0$. Data for $T = 0.2$ from NCA.

thermopower is a sensitive probe of the degree of itinerary of the carriers, and an experimental investigation of the thermoelectric response in the region where large mass enhancement has been observed [2] is highly desirable.

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