

Optimal doping and entropic origin of giant thermopower in doped Mott insulators

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We study the Seebeck coefficient of the Hubbard model on the 3-dimensional FCC lattice at various fillings and interaction strength using dynamical mean-field theory for the one-band Hubbard model. It is shown to exhibit a giant Seebeck coefficient at strong coupling that feeds off the electronic frustration of the FCC lattice. In addition, we find that there is an optimal doping. The high-frequency limit of the thermopower gives a reliable estimate of the DC limit at weak to intermediate couplings, while the Kelvin approach is useful in the strongly interacting case. The latter result shows that in doped Mott insulators, the enhancement of the thermopower can be understood on entropic grounds for all temperatures.

The search for better thermoelectric materials has focussed on strongly correlated materials in recent years, going beyond traditional semiconductor systems. Narrow band correlated oxide systems in quasi two dimensional systems such as sodium cobaltate Na_xCoO_2 [1] show large thermoelectric power (or Seebeck coefficient) $S \sim 100\mu V/K$, at $\sim 100^0K$. Mott Hubbard physics is invoked to understand this extraordinary scale of S in Na_xCoO_2 and $Sr_xLa_{1-x}TiO_3$ [2], often in the limit of zero bandwidth or atomic limit $t \rightarrow 0$, [2–4]. More recent excitement has centered around $FeSb_2$ (a Kondo insulator or a correlated band insulator)[5, 6], a three dimensional compound with a colossal Seebeck coefficient $S \sim 45,000 \mu V/K$ that is of great interest for thermoelectric cooling at cryogenic temperatures.

For more traditional classes of thermoelectric materials such as the semiconductor Bi_2Te_3 , the Bloch-Boltzmann transport theory points to a way to optimize the band structure for thermoelectric applications [7]. In the case of strongly correlated materials, the situation is much more complicated due to the fragility of the quasiparticles. New approaches to calculating the Seebeck coefficient for correlated matter are necessary, and some promising ideas have been put forward recently by Shastry and coworkers [8–11]. In these works, bypasses to the usual difficulties of computing the Kubo formulas are proposed and, among other results, it has been argued that electronic frustration can amplify the Seebeck coefficient considerably beyond Bloch-Boltzmann (band) theory expectations.

Amongst frustrated electronic structures, the FCC lattice is important because of its prevalence in materials. It has optimal thermopower according to the Bloch-Boltzmann theory [7], when the chemical potential coincides with the sharp peak in the density of states. Here we show, instead, that the largest thermoelectric effects appear at low temperatures provided the system is sufficiently correlated that the half-filled case is insulating. Under these conditions we find that as a function of doping there is an entropically driven maximum in the See-

beck coefficient with magnitude much larger than the prediction of Bloch-Boltzmann theory.

Model and methods : The dynamical mean-field theory (DMFT) has proven its accuracy for the Hubbard model and predictive power for real materials [12, 13]. We apply it to study the one-band Hubbard model on the FCC lattice where the single particle dispersion is given by $\varepsilon_{\mathbf{k}} = -4t[\cos(k_x)\cos(k_y) + \cos(k_x)\cos(k_z) + \cos(k_y)\cos(k_z)]$.

For integrals over the Brillouin zone entering the self-consistency relation, we devised an adaptive 3d Gaussian quadrature for a cube. To solve the impurity problem of DMFT, we use two different methods. 1) The numerically exact continuous time quantum Monte Carlo method (CTQMC) [14], a finite temperature approach that relies on the Monte Carlo summation of all diagrams obtained from the expansion of the partition function in powers of the hybridization Δ . This method does not have errors associated with time discretization or bath parametrization and is therefore exact within statistical errors but computationally expensive. 2) Iterated Perturbation Theory (IPT), an approximation method that relies on an interpolation from 2^{nd} order perturbation theory for the Anderson impurity problem [15]. The interpolation preserves the correct high-frequency limit for the self-energy and is exact in both the non-interacting and the atomic limits. At finite temperature, we use the condition of Refs.[16] and [17] to fix the bath occupation number. We only consider paramagnetic solutions. We find that G computed with IPT accurately fits CTQMC even at not too high frequency. We have compared them extensively in the most difficult case, namely for $U = 16t$. The system there is in the vicinity of the Mott transition. Deviations between the two methods will be smaller in the weak and strong coupling limits since IPT is constructed to reproduce these limits exactly. We found that CTQMC and IPT give also similar temperature dependent chemical potentials $\mu(T)$ results which will be important for thermopower calculation. In this paper, we focus on the computationally more efficient IPT.

Thermopower. While the methods of solution for

DMFT are formulated in Matsubara frequency, transport properties require real-frequency information. For example, a general formula for the thermopower may be written down using linear response theory [8] as

$$S(q_x, \omega) = \frac{\chi_{\hat{J}_x(q_x), K(-q_x)}(\omega)}{T \chi_{\hat{J}_x(q_x), \rho(-q_x)}(\omega)}, \quad (1)$$

where the susceptibility of any two operators A, B is given by $\chi_{A,B}(\omega) = i \int_0^\infty dt e^{i\omega t - 0^+ t} \langle [A(t), B(0)] \rangle$ and where ρ , $K = H - \mu \hat{N}$ and \hat{J}_x are the charge density, the (grand canonical) Hamiltonian and the current operator respectively at finite wave vectors. In the *fast* limit where $\mathbf{q} \rightarrow 0$ first and then $\omega \rightarrow 0$, the infinite size system has arbitrarily closely spaced energy levels and enough time to *adjust* to the applied inhomogeneous field. This is the relevant limit for transport. [18] To evaluate the resulting equations, one needs analytically continued Green's functions and vertex corrections. In the DMFT limit the latter vanish for one band models [19, 20] but one still needs analytical continuation of single-particle Green's functions, which can be done to obtain meaningful results in the simplest cases [17]. We also use two new approximate methods that have been proposed to compute the thermopower [8, 11], namely the *superfast limit* S^* and the Kelvin formula S_{Kelvin} . They have the advantage that they do not require analytical continuation. In addition, they have different physical content that will help us identify the origin of enhanced thermopower.

Consider first the superfast limit of Eq.(1), $S^* = \lim_{\omega \gg \omega_c} \lim_{\vec{q} \rightarrow 0} S(q, \omega)$, where ω_c is the largest characteristic frequency in the problem. In the case of the Hubbard model, we would identify $\omega_c = \max\{W, U\}$ with W the bandwidth. In terms of the thermoelectric operator Φ^{xx} and the stress tensor τ^{xx} that appears in the f-sum rule [8], the quantity S^* is equal $\frac{\langle \Phi^{xx} \rangle}{T \langle \tau^{xx} \rangle}$. Since the Seebeck coefficient is a ratio of transport coefficients where the scattering rate cancels in the relaxation time approximation, it is conceivable that the result may have a weak dependence on frequency. It turns out that S^* captures much of the many body content of the exact S_{Kubo} when the characteristic ω_c is not too large. [8] For the Hubbard model, the commutators can be evaluated exactly and the correlation functions evaluated solely in terms of the single-particle Green's function [21, 22]

$$\langle \Phi^{xx} \rangle = \frac{q_e}{\beta} \sum_{\mathbf{k}, n, \sigma} e^{i\omega_n 0^+} G_\sigma(\mathbf{k}, i\omega_n) \left\{ \Sigma_\sigma(\mathbf{k}, i\omega_n) \frac{\partial^2 \varepsilon_{\mathbf{k}}}{\partial k_x^2} + \frac{\partial}{\partial k_x} \left(\frac{\partial \varepsilon_{\mathbf{k}}}{\partial k_x} (\varepsilon_{\mathbf{k}} - \mu) \right) \right\},$$

with q_e the (negative) charge of the electron. While one can show that $\lim_{T \rightarrow 0} \langle \Phi^{xx} \rangle = 0$ when $U = 0$, for interacting systems it was found in numerical calculations [9, 10] and from Fermi liquid theory that $\lim_{T \rightarrow 0} \langle \Phi^{xx} \rangle \neq 0$ and

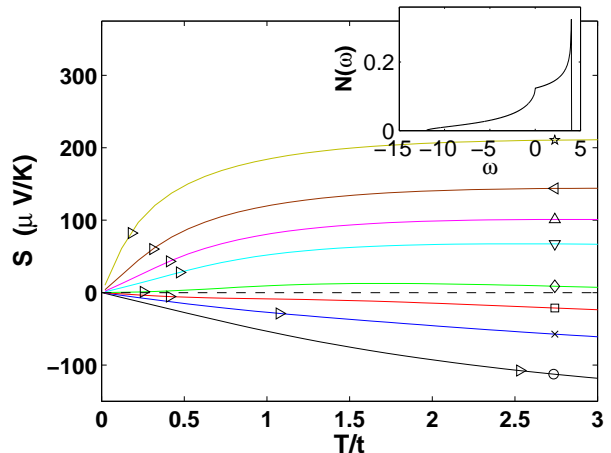


FIGURE 1: (Color online) S in $\mu V/K$ for $U = 0$ as a function of T/t for different values of density : $n = 0.2$ (black (\circ)), 0.4 (blue (\times)), 0.6 (red (\square)), 0.8 (green (\diamond)), 1.2 (cyan (∇)), 1.4 (magenta (\triangle)), 1.6 (brown (\triangleleft)) and 1.8 (khaki (\star)).

hence, S^* diverges as T vanishes. At large frequency there are reactive parts to the energy transport that should not be considered part of the thermal current. We thus eliminate the constant term $\lim_{T \rightarrow 0} \langle \Phi^{xx} \rangle \equiv \langle \Phi^{xx} \rangle_0$ by fitting the low temperature part of $\langle \Phi^{xx} \rangle$ to $\langle \Phi^{xx} \rangle_0 + bT^2$, a functional form derived from the Sommerfeld expansion that empirically remains valid in the presence of strong interactions. We then define the thermopower in the super fast limit by

$$S^{**} = \frac{1}{T} \frac{\langle \Phi^{xx} \rangle - \langle \Phi^{xx} \rangle_0}{\langle \tau^{xx} \rangle}. \quad (2)$$

We also consider the slow limit of the general formula for thermopower, Eq. (1). As noted earlier [8, 11], this leads to a finite and interesting answer that is termed the Kelvin formula

$$S_{Kelvin} = \lim_{\vec{q} \rightarrow 0} \lim_{\omega \rightarrow 0} = \frac{k_B}{q_e} \left(\frac{\partial S}{\partial N} \right)_{T, V} = - \frac{k_B}{q_e} \left(\frac{\partial \mu}{\partial T} \right)_{V, N} \quad (3)$$

where S is the entropy and where the last form follows from a Maxwell relation. The formulas for S^{**} and S_{Kelvin} approach S_{Kubo} from two different limits.

Results : The results for the Seebeck coefficient in the band limit ($U = 0$) are displayed in Fig. 1 along with the non-interacting density of states as an inset. The bare bandwidth is $16t$. The horizontal triangles \triangleright in this plot indicate the temperature denoted as T_ℓ , below which the leading term of the Sommerfeld expansion for the $U = 0$ case is 90% of the full answer. Below T_ℓ the thermopower is essentially linear, as can be seen from the numerical results. The low temperature thermopower changes sign near the van Hove singularity located around $n = 0.8$ in the density of states. The absolute value of the thermopower is maximum in the large T limit, and for an almost empty or almost filled band where the largest deviations from particle-hole symmetry occur. The sharp

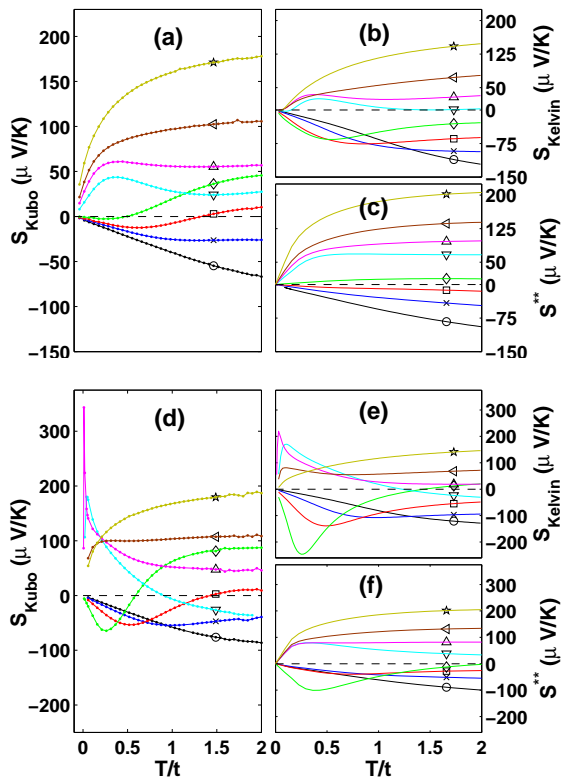


FIGURE 2: (Color online) S_{Kubo} , S_{Kelvin} and S^{**} as a function of T/t as calculated with IPT for $U = 8t$ (a), (b), (c) and $U = 32t$ (d), (e), (f) for different values of density : $n = 0.2$ (black (\circ)), 0.4 (blue (\times)), 0.6 (red (\square)), 0.8 (green (\diamond)), 1.2 (cyan (∇)), 1.4 (magenta (\triangle)), 1.6 (brown (\triangleleft)) and 1.8 (khaki (\star)).

peak in the density of state near the filled band causes this enhancement.

The exact Kubo formula in DMFT is given solely by the bubble for both the conductivity and thermal transport [19, 20]. We performed the analytical continuation on the self-energy using Padé N points algorithm that can be found in [23] and calculated S_{Kubo} using the real frequency equations as for example in [17]. We consider two representative values $U = 8t$ (weak to intermediate coupling) and $U = 32t$ (strong coupling), respectively well below and well above the Mott transition. Figs. 2(a),(b),(c) and (d),(e),(f) for $U = 8t$ and $32t$ show that as one increases U , the thermopower for densities far from half-filling, namely $n = 0.2, 0.4$ and $1.6, 1.8$, there is very little change of U from the free electron value, since carriers can avoid each other at small densities.

At densities $n = 0.6, 0.8$ and $n = 1.2, 1.4$, for weak coupling $U = 8t$ the thermopower is still near its non-interacting value Fig.1. The only qualitative change is a sign change as a function of T but the absolute values are not changed considerably. In contrast, for the same densities at strong coupling $U = 32t$ there are strong deviations from the $U = 0$ results. At half-filling

the system is an insulator with a large gap and vanishing thermopower. Upon doping, it develops a large Seebeck coefficient with non-trivial T dependence even below T_ℓ defined in Fig.1. The sign change as a function of filling of the low temperature thermopower now occurs closer to half-filling $n = 1$ instead of around $n = 0.8$ for $U = 0$ (see Fig. 1). The maximum magnitude of thermopower that is obtained at low temperature for example for $n = 0.8$, $S \approx -65\mu V/K$ at $T = 0.25t$, or for $n = 1.2$, $S \approx 180\mu V/K$ at $T = 0.04t$, or for $n = 1.4$, $S \approx 345\mu V/K$ at $T = 0.01t$ represent at least an order of magnitude increase with respect to the non-interacting case. The appearance of pronounced peaks at low temperature that are absent in the non-interacting limit reflects, as pointed out in Ref. [17], the fact that Fermi liquid coherence is recovered only at very low temperature in the presence of strong correlations.[12] Frustration apparently is a factor that contributes to make the Fermi liquid coherence temperature low, and also plays a role in the $t - J$ model on the triangular lattice as discussed elsewhere.[30].

It is instructive to compare $S^{**}(T)$ and $S_{Kelvin}(T)$ with $S_{Kubo}(T)$ Figs. 2(b),(e) and (c),(f). One finds that for weak to intermediate coupling ($U = 8t$), S^{**} seems to give a good estimate while for strong coupling ($U = 32t$) it is S_{Kelvin} that compares well. We must note that the differences in height of the sharp peaks in S_{Kubo} and S_{Kelvin} at $U = 32t$ come from the difficulty to obtain pronounced peaks from numerical differentiation involved in the calculation of S_{Kelvin} .

We now focus on the low T region. In the spirit of non-interacting system in 3d one could write the following phenomenological form for S at low T involving two different Fermi temperature

$$S \approx Sgn(S) \frac{k_B \pi^2 T}{|q_e| 2 T_f^{(1)}} \left(1 - \left(\frac{T}{T_f^{(2)}} \right)^2 \right). \quad (4)$$

We wrote explicitly the sign of the thermopower to be able to define a positive $T_f^{(1)}$. Fig. 3 shows $Sgn(S)/T_f^{(1)}$ as calculated from the non-interacting S , and for S_{Kubo} , S^{**} and S_{Kelvin} in two cases, $U = 8t$ (a) and $U = 32t$ (b). This illustrates the two main results of this paper i.e. (1) for weak to intermediate coupling S^{**} is a good indicator of the behavior of S while for strong coupling S_{Kelvin} is the right indicator. (2) In the strong coupling limit we find a clear signature of the existence of an optimal doping both for electron and hole doping. Indeed one can see from the Kubo results in Fig. 3(b) that for $n < 1$, $1/T_f^{(1)}$ is largest as doping approaches half-filling before changing sign. For $n > 1$, there exists an even clearer optimal doping (largest $1/T_f^{(1)}$) but this time occurring at intermediate doping ($\sim 40\%$). This optimal doping appears for $n > 1$, which is most favorable for S at $U = 0$. This is where the effect of frustration is maximum and thus where the entropy can vary most with filling.

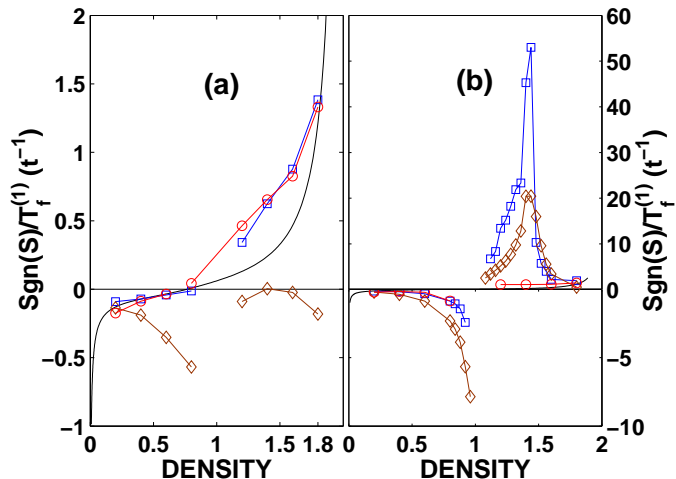


FIGURE 3: (Color online) $Sgn(S)/T_f^{(1)}$ for $U = 8t$ (a) and $U = 32t$ (b) as a function of the density with the non-interacting value (black solid line) : S_{Kubo} (blue (\square)), S_{Kelvin} (brown (\diamond)) and S^{**} (red (\circ)).

The fact that S^{**} is less reliable for the Hubbard model at strong coupling, contrary to the $t - J$ model, [30] was expected from the fact that large U makes ω_c too far from the $\omega = 0$ limit. However, as shown from the $T_f^{(1)}$ results, S^{**} should be a good estimate in the weak coupling limit where ω_c is smaller. The relationship between entropy and thermopower has been discussed in the linear low temperature regime and multiband systems experimentally [24–26] and theoretically [27]. In the very high temperature regime, Heikes formula suggests this relationship. The results of Fig. 2 show that the recently proposed S_{Kelvin} Eq. (3) gives a good estimate for the thermopower for the Hubbard model in the doped Mott insulator at both low and high temperatures. This demonstrates that in the strong coupling regime, entropy drives the thermopower for the entire range of temperature.

Estimates of the temperature scale for real materials give for V_2O_3 [28] $t \approx 580K$, for $FeSi$, [29], $t \approx 152K$, and $t \approx 100K$ for Na_xCoO_2 [30]. Hence the peaks that we find for $T < t$ as well as the strong temperature dependence up to about $T \sim t$ are in a physically relevant temperature range not far from room temperature.

Using the Kubo formula and two new approaches to compute the thermopower with DMFT, we have shown that sharp peaks in the T dependence of Seebeck coefficients and absolute values of several $k_B/|q_e|$, in other words in the hundreds $\mu V/K$, can be obtained by doping FCC materials that are Mott insulators at half-filling. For doped Mott insulators, the Kelvin formula gives a reasonable estimate of the thermopower without the need for analytical continuation. This clearly shows that large thermopower can be explained on entropic grounds over the whole doping and temperature range. We found that

there exists an optimal doping at low temperature on both side of half filling. The largest thermopower occurs for $n > 1$, where electronic frustration is largest. This should be of interest for the search of materials with good thermoelectric properties.

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