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We illustrate how the electronic charge reconstruction near the interfaces of metal-strongly-correlatedbarrier-metal devices can lead to a significant enhancement of the thermoelectric response due to the breaking of particle-hole symmetry. We show how one can achieve effective Seebeck coefficients larger than 150  $\mu$ V/K and effective electronic figures-of-merit ZT higher than 1. Our work shows that electronic thermoelectric transport properties can be significantly enhanced from inhomogeneities created by the rearrangement of charge near the interfaces, and that bulk figures-of-merit cannot generically be employed to determine the figure-of-merit of a multilayered nanostructure.

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## **1** Introduction

Seebeck and Peltier discovered two different thermoelectric effects in the early 1800s: Seebeck [1] discovered that when two metals are joined together and placed in a thermal gradient, that a voltage develops, while Peltier [2] found that electrons moving through a material carry both charge and heat. These effects are generically small – a temperature difference of 10 K will yield a voltage difference of  $10-100 \ \mu\text{V}$  in ordinary metals. Doped semiconductors were recognized to be good candidate materials for thermoelectric effects in the 1950s [3], and a significant period of research activity took place to optimize their properties resulting in the discovery of Bi–Te–Sb alloys, which are used in most commercial devices for refrigeration and power generation. Nevertheless, thermoelectric power generation and refrigeration remains a niche market, where the reliability, durability, and the vibration isolation of the devices are more important than their efficiency; thermoelectric devices typically operate at a small fraction of the maximal allowed Carnot efficiency.

The usefulness of a bulk material for deployment in a thermoelectric device is summarized by the socalled figure-of-merit  $ZT = \sigma S^2 T / \kappa$ , where  $\sigma$  is the dc conductivity, S is the Seebeck coefficient, T is the temperature, and  $\kappa$  is the thermal conductivity. The best materials used in thermoelectric devices have ZT values near 1 [4]. Some new materials have been found that have ZT values near 2 [5], but they have not yet been commercialized. If ZT could be increased to 4, refrigerators would have similar efficiency to conventional coolant-based refrigerators, and power generators would become competitive with steam turbines. While there is no theoretical maximum to the figure-of-merit, it has proved to be difficult to find ways to increase its magnitude. This is because an increase in the conductivity usually leads to a corresponding increase in the thermal conductivity, and the thermopower is not easy to tune.

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Since the thermal conductivity includes both electronic and phononic pieces, much work in enhancing the figure-of-merit has focused on finding ways to reduce the phonon contribution to the thermal conductivity, but leaving the electronic transport unchanged. This electron-crystal-phonon-glass approach [6] has been used by introducing rattling modes into skudderudites or clathrates or by introducing phonon scattering via multilayered interfaces with widths on the order of nms [7].

In this work, we take a different approach, and examine whether one can *enhance* the electronic contributions to thermoelectric phenomena by creating appropriate multilayered nanostructures. As an example, we consider a particle-hole symmetric (half-filled) ballistic metal for the leads of the device, with a barrier that is a particle-hole symmetric Mott insulator. Since both pieces of the device are particle-hole symmetric, they are thermoelectrically inert, with S = 0 in the bulk. If the chemical potentials of the two materials do not match, then there will be an electronic charge reconstruction that will break the overall particle-hole symmetry of the device, and allow it to have a thermoelectric response. If we can tune the electrochemical potential that arises from the rearrangement of charge in such a way, that it lies close to the upper or lower Hubbard band edges, then we have a near-optimal situation for enhancing the Seebeck coefficient, since the local density of states will be quite asymmetric. This procedure works remarkably well, as described below, and it opens the door to a new strategy for enhancing the thermoelectric performance of devices. Since the multilayered structures should also reduce the phonon thermal conductivity, due to additional interface scattering, one expects these systems to be able to work quite well as thermoelectric elements.

### 2 Formalism

The many-body formalism for solving the inhomogeneous dynamical mean-field theory of a multilayered nanostructure is complex, and cannot be derived in detail here. Instead, we will describe the basic ideas, and refer to other publications where detailed derivations can be found [8-11].

The systems we wish to model are composed of ballistic metal leads (no scattering whatsoever) which surround a strongly correlated barrier region. For simplicity, we take the lattice sites to lie at the positions of a simple cubic lattice, and we assume the same hopping between any two lattice sites (both interplane and intraplane). Inhomogeneity is allowed only in the longitudinal (z) direction, where the planes can be described by different models. In the leads, we simply take a tight-binding single-band model on a semi-infinite simple cubic lattice at half filling  $\mu = 0$ , while the barrier is described by the Falicov–Kimball model [12] at half filling for both the mobile and localized particles; in the Falicov–Kimball model mobile electrons are described by a tight-binding model but they also interact with localized particles with an interaction strength U (we choose the spinless version of the model). In the bulk, the Falicov-Kimball model on a simple cubic lattice has a Mott metal-insulator transition at  $U \approx 4.9t$ , where t is the nearest-neighbor hopping integral. For concreteness we will measure all energies in units of t, and we will set t = 0.25 eV, which corresponds to a bare bandwidth of 3 eV.

In the bulk, both the ballistic metal leads and the Falicov–Kimball model barrier have vanishing Seebeck coefficient S = 0, because they are particle-hole symmetric. Hence they have no thermoelectric response. Our idea is to imagine that the chemical potential of the barrier is mismatched with that of the metal leads by an amount denoted  $\Delta E_f$  (because the metal leads extend to infinity in each direction, they determine the chemical potential of the device). As we shift the band of the barrier upwards in energy, we break the particle-hole symmetry of the system, and allow it to have a thermoelectric response (the parameter  $\Delta E_f$  is *added* to the chemical potential on each plane). Because the bulk Mott insulator has a well defined gap, if we can tune the density of states of the barrier to lie right at the upper band edge of the lower Hubbard band, or the lower band edge of the upper Hubbard band, then we have an opportunity for a large thermoelectric response because we are maximizing the particle-hole asymmetry. Furthermore, as we have DOS near the chemical potential, the system is likely to display metallic characteristics rather than insulating ones, so it is possible that the phonon contribution to the thermal conductivity will not overwhelm the electronic contribution, and the electronic estimate of the figure of merit may be close to the actual value that can be achieved in devices.

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This description has so far ignored the notion of electronic charge reconstruction, which plays an important role in these devices [10, 13, 14]. If the barrier is not located at its bulk chemical potential, electrons will spill out of or into the barrier. This will create a screened dipole layer at each metal-barrier interface, which will ultimately determine the total number of electrons transfered. The rearrangement of charge also creates an electrical potential energy, which must be included in the many-body theory.

Finally, we need to be able to calculate the charge and heat transport, which can be done by using a real-space version of the Kubo formula [15, 16] (it must be in real space because the system lacks translational invariance along the longitudinal direction). These transport coefficients can be determined by utilizing the Jonson–Mahan theorem [10, 11, 17] in a real-space format. Details for how to do so appear elsewhere.

We find the Green's functions and the self-energies from a self-consistent iterative approach to inhomogeneous dynamical mean-field theory with the Potthoff–Nolting algorithm [8]. The electronic charge reconstruction is determined in a semiclassical fashion, where the Coulomb potential energy is found from a classical solution of Poisson's equation, and this then determines the electrochemical potential on each plane, which is input into the inhomogeneous dynamical mean-field theory to find the electron charge on each plane. Solving these problems self-consistently is much more difficult than when there is no charge reconstruction, and we typically need 3000-6000 iterations to reach a convergence of one part in  $10^8$ .

#### **3** Numerical results

In Fig. 1, we plot false-color plots of the local electronic density of states for different planes as a function of frequency (horizontal axis). We take 30 self-consistent planes in each metal lead, which are cou-



**Fig. 1** (online colour at: www.pss-b.com) Density of states for half of the nanostructure in a false color plot; top panel is for  $\Delta E_f = 0$ , middle for  $\Delta E_f = -1$  and bottom for  $\Delta E_f = -3$ . Note how the mismatch of the chemical potentials makes the bands more and more asymmetric, but how the center of the barrier lies close to the particle-hole symmetric case.

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**Fig. 2** (online colour at: www.pss-b.com) (a) Electronic charge reconstruction and (b) potential at T = 300 K for various  $\Delta E_{\rm f}$  values. Note the similarity in shape of the charge profiles, and how the potential energy increases in magnitude as the mismatch increases.

pled to bulk metal to make the semi-infinite lead, and the barrier region is 20 atomic planes thick. Since the device is mirror symmetric, we show only half of the device, with the metal leads lying to the upper part of the figure and the barrier to the bottom. Panel (a) is for the particle-hole symmetric case where the chemical potentials match at all T. The barrier is described by a Mott insulator with U = 6, which creates a gap of about 200 meV and a barrier height of about 100 meV. Note how the density of states has a deep trench near zero frequency, and how the presence of the barrier introduces Friedel-like oscillations within the density of states of the metal lead. In Panel (b), we have a shift of the chemical potentials by one unit  $\Delta E_f = -1$  and in panel (c) the shift is 3 units  $\Delta E_f = -3$ . Note how the density of states becomes asymmetric due to the shifts, and how the Coulomb potential energy tends to bring the central planes of the barrier closer to the chemical potential of the leads.

In Fig. 2, we plot the electronic charge profile and potential energy at T = 300 K for various chemical potential mismatches. We choose the effective dielectric constant so that the screening length for the charge rearrangement is on the order of two lattice spacings. Note how the size of the charge rearrangement grows with the mismatch [panel(a)], but appears to have the same shape for the different cases. The electronic potential energy grows with the mismatch as expected, but the maximal magnitude of the potential energy (at the center of the barrier) is always smaller in magnitude than the mismatch.

In Fig. 3, we show the temperature dependence of the charge profile and the potential energy for  $\Delta E_{\rm f} = -0.5$ . Note how the system has a substantial temperature dependence even at relatively low temperatures. This illustrates the importance of self-consistently solving for the electronic charge reconstruction at each temperature. It also shows that the temperature evolution of these devices may produce dif-



Fig. 3 (online colour at: www.pss-b.com) (a) Electronic charge reconstruction and (b) potential at  $\Delta E_{\rm f} = -0.5$  for various temperatures values. Note how the charge rearrangement can depend strongly on the temperature.

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Fig. 4 (online colour at: www.pss-b.com) (a) Seebeck coefficient, (b) Lorenz number, and (c) figure-of-merit versus temperature for various  $\Delta E_{\rm f}$ values. The figure of merit is highest at low temperatures for moderate chemical potential mismatches. As the mismatch grows, the peak maximum drops, and moves to higher temperature.

ferent behavior than seen in bulk systems, because there is this additional temperature dependence to the "scattering potential".

The main results for the thermoelectric transport are shown in Fig. 4. We plot the Seebeck coefficient in panel (a). Note how the peak is reduced in magnitude, and moves to higher energies as the mismatch is increased. In metallic systems, achieving a Seebeck coefficient larger than 156  $\mu$ V/K will create a figure-of-merit larger than 1. Here we can get large Seebeck coefficients in numerous different temperature ranges simply by tuning the chemical potential mismatch. The effective Lorenz number [18] satisfies  $\mathcal{L} = R/(R_{th}T)$ , using the resistance R of the junction, the thermal resistance  $R_{th}$  and the temperature T. In a metallic system at low temperature, the Lorenz number is equal to  $\pi^2/3$ . In all cases we consider, we see this result, although the temperature dependence of the Lorenz number can be significant. In cases where it dips below  $\pi^2/3$ , which occurs for all systems for some temperature range, the thermoelectric properties can be enhanced. When it becomes larger, the thermoelectric properties are degraded. In panel (c), we plot an effective device  $ZT = S^2/\mathcal{L}$ . Note how there is a robust low-temperature region where ZT is larger than one. As the mismatch increases in magnitude, the ZT value has its maximum pushed to higher T, but it also has its maximum value lowered. This tracks most closely with the behavior of the Seebeck coefficient.

The reason why we see a maximum to the Seebeck coefficient (as a function of the chemical potential mismatch), is because the band edge for the Mott insulator moves continuously with the chemical potential mismatch (and it approaches a fixed location deep within the barrier). The band edge passes by the chemical potential close to the  $\Delta E_f = -0.25$  case, which is why it has such a large thermoelectric response. As  $\Delta E_f$  becomes more negative, the response gets reduced, as we expect. As  $\Delta E_f$  approaches zero, we can find very large Seebeck coefficients and ZT values, which occur at lower and lower temperatures. But the conductances are so low, that it becomes a bad approximation to neglect the phonon thermal conductance, and the actual figure-of-merit is probably reduced significantly. Of course, when  $\Delta E_f = 0$ , the Seebeck coefficient and ZT both vanish for all T.



#### 4 Conclusions

In this work, we have considered the thermal transport when two bulk materials, both with vanishing Seebeck and Peltier coefficients, are joined in a sandwich structure to create a device. Because the chemical potentials of the materials do not generically match, there is an electronic charge reconstruction, which breaks the particle-hole symmetry of the system and creates a thermoelectric response. Surprisingly, if the barrier material is a small-gap Mott insulator, one can generate a significant effect, if the bands are tuned so that the electrochemical potential lies close to one of the strongly correlated electron band edges. Indeed, we can easily generate electronic figures of merit larger than 1 over fairly wide temperature ranges. As the mismatch of the bands increases further, the effect is pushed to higher temperatures, but tends to shrink in overall magnitude.

There are two important comments to make about this work. First, we have only calculated the electronic contribution to the thermoelectric figure-of-merit. If the thermal conductance from the phonons is large enough, the phonons can form a thermal short for the conduction of heat, which will dramatically reduce the overall figure of merit by sharply increasing the total thermal conductance. As the devices become more metallic, which occurs as the mismatch is made larger, this problem is reduced, because the electronic contribution to the thermal conductance becomes important and can dominate the phonon piece. Second, we have made no attempt to try to optimize the effect in terms of selection of materials for the various parts of the device (which governs the interaction strength and the band mismatches) or for the thicknesses of the different layers (which is how one tunes the effect for a given material), so it may be possible that even larger enhancements can be found as the result of an optimization study.

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