Doping dependence of thermopower and thermoelectricity in strongly correlated materials

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The search for semiconductors with high thermoelectric figure of merit ¹ ² ³ has been greatly aided by theoretical modeling of electron and phonon transport, both in bulk materials ⁴ and in nanocomposites ⁵ ⁶ ⁷. Recent experiments ⁴ ⁸ ⁹ have studied thermoelectric transport in “strongly correlated” materials derived by doping Mott insulators, whose insulating behavior without doping results from electron-electron repulsion, rather than from band structure as in semiconductors. Here a unified theory of electrical and thermal transport in the atomic and “Heikes” limit is applied to understand recent transport experiments on sodium cobaltate and other doped Mott insulators at room temperature and above. For optimal electron filling, a broad class of narrow-bandwidth correlated materials are shown to have power factors (the electronic portion of the thermoelectric figure of merit) as high at and above room temperature as in the best semiconductors.

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The efficiency of a thermoelectric material for refrigeration or electrical generation is determined by its thermoelectric figure of merit

\[
ZT = \frac{TS^2\sigma}{\kappa},
\]

where \(T\) is the temperature, \(\sigma\) is the electrical conductivity, \(S\) the thermopower and \(\kappa\) the thermal conductivity. The same transport coefficients that determine a material’s utility for thermoelectric applications are also of importance for fundamental materials science; for example, thermopower measurements are frequently used to measure the sign of the dominant charge carriers in a material. Most thermoelectrics currently in use ² are bulk semiconductors such as Bi₂Te₃, with \(ZT \approx 1\) at room temperature.

In recent years, strongly correlated oxides have been studied as candidate thermoelectric materials. Research in this direction was sparked off by the observation of high thermopower (∼ 125 µV/K) at room temperature coupled with a low electrical resistivity in the material Na₂CoO₂ ³ ⁴. Other materials including Sr₂La₁₋ₓTiO₃ and several superconducting cuprates ⁵ ⁶ were found to have promising values of thermopower at room temperature. These materials are strongly correlated with an interaction energy scale \(U\) that is much larger than the bandwidth set by the hopping \(t\). Theoretical calculations on such materials are difficult and often specific only to certain ranges of parameters ⁷ ⁸ ⁹ ¹⁰ ¹¹.

The “power factor” \(TS^2\sigma\) appearing in the numerator of \(ZT\) is determined by properties of the charge carriers (electrons or holes), while \(\kappa\) is dominated by phonons for most viable thermoelectric materials. Although applications of oxides as thermoelectric materials are currently limited by their relatively high thermal conductivity, recent advances in reducing phonon thermal conductivity in semiconductor thermoelectrics ³ ⁶ ¹⁴ should lead to more dramatic gains in oxides, where the original thermal conductivity is higher. Hence, understanding which oxides can have power factors as high or higher than the best semiconductors is an important step toward realizing the potential of this material class.

In this paper, we extend the calculation of the thermopower of correlated systems in the atomic limit ¹² ¹³ ¹⁴ to the electrical and thermal conductivities and obtain the power factor and electronic \(ZT\), as functions of doping and temperature. Although the optimum band structure for thermoelectric efficiency in a semiconductor was determined by Mahan and Sofo ⁴, the dominant role of electron-electron interactions in correlated materials requires entirely different theoretical methods. The power factor is found to display maxima at doping values of 5% and 88% from the Mott insulator consistent with recent experiments on Na₂CoO₂ ³. We discuss the effect of multiple orbitals in closing and comment on the search for high-efficiency thermoelectric oxides.

We describe a strongly correlated system by the Hubbard model, which consists of a lattice with electrons capable of hopping from a site, with a single orbital, to its nearest neighbors with an energy (hopping parameter) \(t\). Double occupancy incurs an energy cost of \(U\) per site. This surprisingly complex model has been used to study the physics of superconductivity, spin and charge ordering, and the Mott transition seen in a variety of oxides. The Mott insulator appears at the occupancy of one electron per site. At temperature \(T\), the atomic limit is defined as the approximation \(t \ll (k_BT/U)\). Systems with narrow bandwidths (e.g., Na₂CoO₂) are best suited for this type of analysis. In this limit, \(\sigma\), \(S\) and \(\kappa\) are
Here $\beta = 1$ is the Mott insulator and $\rho$ for a triangular lattice.

The expression for the thermal conductivity $\kappa$ is of sub-leading order at high temperature ($k_B T \ll U$) but not in the Heikes limit $k_B T \ll U$, where it is the leading term. It should be noted that both $\sigma$ and $\kappa$ depend on a relaxation time $\tau$ as in Drude theory, while $S$ and $ZT$ do not. There are further simplifications in the Heikes limit $k_B T \ll U$:

$$S = -\frac{k_B}{e} \log \left[ \frac{(1 - \rho)}{\rho} \right],$$

$$\sigma = \frac{e^2 A \beta}{2} \rho (1 - \rho),$$

$$\kappa = \frac{\sigma \tau^2}{e^2 T},$$

and

$$ZT = \frac{\epsilon^2 S^2}{\kappa_B (\beta \epsilon)^2},$$

The above expressions are for $\rho \leq 1$ and can be extended to $\rho \geq 1$ by making the substitution $\rho \rightarrow 2 - \rho$. We note that the thermopower has no temperature dependence and is independent of material parameters in this limit; it changes sign by going through a resonance at the Mott insulator $\rho = 1$. Experimental data on $Na_xCoO_2$ is compared with theory in Fig. 1. The electronic $ZT$ is divergent close to the Mott insulator but adding a phonon contribution to $\kappa$ keeps it finite. This is illustrated with the material parameters for $Na_xCoO_2$ [17], as an example in Fig. 2.

The chemical potential $\mu$ is expressed in terms of the doping $\rho$ as

$$e^{\beta \mu} = \frac{\rho - 1 + \sqrt{(\rho - 1)^2 + \rho (2 - \rho) e^{-\beta U}}}{(2 - \rho) e^{-\beta U}}.$$

$\rho = 1$ is the Mott insulator and $\rho = 0$ and $\rho = 2$ correspond to completely empty and full bands respectively and are both band insulating limits. The second term in the expression for the thermal conductivity $\kappa$ is of sub-leading order at high temperature ($k_B T \sim U$) but not in the Heikes limit $k_B T \ll U$, where it is the leading term. It should be noted that both $\sigma$ and $\kappa$ depend on a relaxation time $\tau$ as in Drude theory, while $S$ and $ZT$ do not. There are further simplifications in the Heikes limit $k_B T \ll U$:

$$\sigma = \frac{e^2 A \beta}{2} \rho (1 - \rho),$$

$$\kappa = \frac{\sigma \tau^2}{e^2 T},$$

and

$$ZT = \frac{\epsilon^2 S^2}{\kappa_B (\beta \epsilon)^2},$$

The relaxation time $\tau = 2 \times 10^{-15} \text{ s}$ for $Na_xCoO_2$ is...
extracted from the conductivity measurements \[3\]. \(x=0\) corresponds to the Mott insulator \(\rho = 1\). A plot of the theoretical \(TS^2\sigma\) for \(\text{Na}_x\text{CoO}_2\) is shown in Fig. 3. The value of \(TS^2\sigma\) \((\approx 1 - 2\text{Wm}^{-1}\text{K}^{-1})\) is indeed observed in experiments. The main result of the above calculation is a robust maximum in the power factor at dopings of \(\rho = 0.12\) and \(\rho = 1.88\) and secondary maxima close to the Mott insulator at \(\rho = 0.95\) and \(\rho = 1.05\). These maxima arise from competition between the (large) thermopower and (small) conductivity near the Mott \((\rho = 1)\) and band \((\rho = 0\) and \(\rho = 2)\) insulators. \(\rho = 1.88\) corresponds to \(x=0.88\) for \(\text{Na}_x\text{CoO}_2\), where a peak in the power factor has indeed been observed in recent experiments over a range of temperatures \[4\]. Although we have used \(\text{Na}_x\text{CoO}_2\) to enable comparison with experimental data, the fact that the main features are reproduced in the Hubbard model shows that any material with roughly similar values of \(t, U\), and \(\tau\) will have the same features.

![Theoretical estimate for \(\text{Na}_x\text{CoO}_2\) at 300 K](image)

**FIG. 3:** The power factor \((TS^2\sigma)\) as a function of doping for \(\text{Na}_x\text{CoO}_2\) as predicted by theory. There are maxima at \(\rho \approx 0.12, \rho \approx 0.95, \rho \approx 1.05\) and \(\rho \approx 1.88\). The last two values can be realized in the material in principle at doping values \(x=0.05\) and \(x=0.88\). The positions of the peak are independent of the material parameters in this calculation and a peak at \(x=0.88\) has indeed been seen in experiments on \(\text{Na}_x\text{CoO}_2\).

The location of the doping peak depends only weakly on temperature and for \(\text{Na}_x\text{CoO}_2\) and shifts appreciably only at \(T \geq 700\text{ K}\). The theoretical position of the peak is independent of material dependent parameters. In reality however, factors like the effect of phonons on electron transport (phonon drag and polarons), orbital degrees of freedom, etc. could change the location of the peak. As mentioned earlier, the above theory initially assumed the atomic limit and hence is best applied to narrow-bandwidth systems. For other correlated systems, one might need to consider terms beyond leading order in the calculation of transport coefficients. However, the existence of a peak in the power factor is quite general and has been observed in other candidate thermoelectric materials, such as \(\text{La}_{x}\text{Sr}_{1-x}\text{TiO}_3\) (for which polaronic effects are known to be important), close to the band insulator \[10\].

We finally examine the effects of multiple orbitals per site on thermoelectric transport. This model is applicable to certain strongly correlated materials like chromium and magnesium based oxides \[18\]. We consider a multiple-orbital Hubbard model with \(N\) degenerate orbitals per site and a single value of the hopping parameter (for concreteness), and extend the calculation for the thermopower \[16\] to include \(\sigma, \kappa, ZT\) and \(TS^2\sigma\). There is a correlation energy of \(U\) for each pair of carriers occupying the same site. In the Heikes limit, we obtain the following expressions for the transport coefficients:

\[
\sigma = \frac{e^2 AN\beta}{\rho} (1-\rho), \quad (12)
\]

\[
S = -\frac{k_B}{e} \log \left[ \frac{N(1-\rho)}{\rho} \right], \quad (13)
\]

\[
\kappa = \frac{\sigma N^2 t^2}{e^2 T}, \quad (14)
\]

\(TS^2\sigma\) for an arbitrary system at a fixed temperature \(T\) is shown in Fig. 4. There are still strong maxima as a function of doping, though displaced slightly from the single-orbital \((N=1)\) value. This is due mainly to the logarithmic dependence of \(S\) on \(N\). The overall magnitude increases for large \(N\), as the presence of more hopping channels increases the conductivity.

![The value of the power factor at a particular temperature for an arbitray system, as a function of doping for a multiple-orbital Hubbard model](image)

**FIG. 4:** The value of the power factor at a particular temperature for an arbitrary system, as a function of doping for a multiple-orbital Hubbard model. All material dependent parameters are assumed to be the same for the different values of \(N\). Larger \(N\) implies more conducting channels giving a larger conductivity and hence a larger value of \(TS^2\sigma\). The peaks shift with increasing \(N\) but not by much owing to a weak logarithmic dependence of the thermopower on \(N\).
To conclude, we have investigated the thermoelectric properties of strongly correlated systems by studying the Hubbard model. We have shown that in the absence of phonon heat conduction, $ZT$ can diverge at values of doping close to the Mott and band insulators. The calculated power factor and thermopower agree with experiments on Na$_x$CoO$_2$. We have in particular demonstrated the existence of a doping maximum 88\% away from the Mott insulator, also been seen in experiments and have investigated the effect of multiple orbitals on it. The prediction of a large power factor and the presence of a doping maximum should aid in searches for better thermoelectric oxides.

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