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Abstract. Transport properties of strongly correlated materials, such as vanadates, cobaltates, cuprates, Kondo semiconductors, and organic salts are poorly understood, despite an overwhelming amount of experimental data. One common feature of these vastly different materials is that they are formed by doping the parent compound away from a Mott-Hubbard insulating state. Starting from this observation, and the general properties of the transport relaxation time of a doped Mott-Hubbard systems, we calculate the transport coefficients from the Kubo formula. Our analysis shows that the resistivity and thermopower of such systems exhibit simple universal features which depend on the concentration of the charge carriers.

1. Introduction

The transport properties of strongly correlated materials, such as oxides in the families of vanadates[1, 2], cobaltates[3, 4, 5] or cuprates [6, 7, 8, 9], valence fluctuators such as $YbAl_3$[10], Kondo metals and semiconductors such as CeB_6[11, 12], FeSi [13] or $FeSb_2$[14, 15], and organic charge transfer salts[16, 17] are widely studied, as it is believed that some of these systems might be useful for thermoelectric applications. The oxides with a large power factor are considered for the thermoelectric recovery of waste heat in the industrial processes, because they are stable at high temperatures, abundant, and non-toxic. The valence fluctuators and Kondo systems are considered for low-temperature cooling, because their Peltier coefficient often has a maximum around 100 K. However, the thermoelectric efficiency of these materials has to be improved if they are to be used in real devices. It is clear that the optimization and the search for new materials would benefit from an understanding of their transport coefficients.

In this paper, we focus on the thermoelectric properties of a particular class of compounds obtained by doping away the parent material from a Mott-Hubbard insulating state. For temperatures above 100 K, where the scattering of the charge carriers becomes incoherent and the mean free path is very short, the thermopower $S(T)$ and the resistivity $\rho(T)$ of such strongly correlated systems exhibit some universal features which depend on the concentration of carriers. At very low concentrations (lightly doped Mott insulators) the thermopower has a pronounced low-temperature peak that shifts to higher T with doping, the resistivity is very large and has a sharp low-T upturn. The sign of $S(T)$ is negative for electron and positive for hole doping. At moderate carrier concentration (bad metals) $S(T)$ has a small low-T peak that shifts to lower temperature with doping and changes sign at high enough temperatures. Here, $\rho(T)$ increases linearly in a broad temperature range without any sign of saturation. Such a behavior of $\rho(T)$ is often used to define a bad metal. At the highest carrier concentration (dirty metals) $S(T)$ is

positive for electron doping (negative for hole doping) and $\rho(T)$ shows a well resolved T^2 term. Here, both $S(T)$ and $\rho(T)$ are monotonic functions of temperature.

A doping-induced transformation of a Mott-Hubbard insulator into an 'underdoped' bad metal and, then, into an 'overdoped' dirty metal is seen most clearly in vanadates[1, 2] cobaltates[3, 4] and cuprates[6, 7, 9]. In other materials, like iron silicides FeSi[13] and FeSb$_2$[18, 15], sodium doped cobalt oxide Na$_x$CoO$_2$[5], misfit cobaltites[19], and several other oxides[20], the carrier concentration is more difficult to change and the transport coefficients of each particular system exhibits only one of the above described features. The fact that the universal behavior is observed in so many vastly different compounds points to a common cause and, here, we show that the universality follows from the general features of the transport relaxation time of doped Mott-Hubbard systems.

The paper is organized as follows. In the next section, we calculate the resistivity and thermopower of doped Mott-Hubbard insulators using the Kubo formula and the general form of the transport relaxation time. Then, we present the results obtained for various concentrations of the charge carriers and show that calculated $S(T)$ and $\rho(T)$ capture the main features of the experimental data. The last section summarizes our results.

2. Calculations

The Kubo formula gives the electrical conductivity $\sigma(T) = \sigma_0 L_{11}(T)$ and the thermopower $S(T) = S_0 \left[L_{12}/(TL_{11}) - \mu/T \right]$, where σ_0 is a material specific constant, $S_0 = k_B/e$, and μ is the chemical potential, in terms of the transport integrals L_{mn}. Typical models of strong correlations, like the Hubbard model, Falicov-Kimball model, and periodic Anderson model, satisfy the Jonson-Mahan theorem[21], so that the transport integrals can be written as[22]

$$L_{mn}(T) = \sum_\sigma \int_{-\infty}^{\infty} d\omega \, \left(-\frac{\partial f(\omega)}{\partial \omega} \right) \, \omega^{m+n-2} \, \tau_\sigma(\omega) \, . \tag{1}$$

The summation is over the spin states σ and $\tau_\sigma(\omega)$ is the exact transport relaxation time which includes the velocity factors, averaged over the Fermi surface, and the effects of vertex corrections, if present. The derivative of the Fermi function, $(-df(\omega)/d\omega)$, is sharply peaked around the chemical potential, so that the integral is cut-off outside the Fermi window $|\omega| \geq k_B T$. In what follows, we set $k_B = \hbar = 1$ and measure all energies with respect to μ. In the absence of the magnetic field, all spin states are equivalent and the spin label can be dropped.

The transport relaxation time of the typical models of strong correlations, exhibits the following features[23, 24]: $\tau(\omega)$ is non-negative within narrow energy bands and vanishes outside. Thus, it must have at least one maximum within each band. In a Fermi liquid, $\tau(\omega)$ diverges as $T \to 0$ and $\omega \to 0$, and the resistivity, $\rho(T) = 1/\sigma_{dc}(T)$, follows at low temperatures a T^2 law. If there is residual scattering in the material, due to disorder or impurity scattering, $\tau(\omega)$ and $\rho(T)$ remain finite even at $T = 0$. For temperatures *above* the Fermi liquid scale, the transport relaxation time of strongly correlated metals typically has two maxima, located in the upper and the lower Hubbard band, separated by a large gap. At physically relevant (intermediate) temperatures, the width of the Fermi window is much smaller than the gap between the Hubbard bands and neither the shape nor the maxima of $\tau(\omega)$ change appreciably with temperature. Since the chemical potential of a strongly correlated metal is either within the lower or the upper Hubbard band, we calculate the resistivity focusing on $\tau(\omega)$ with just a single broad maximum at ω_0, neglecting the excitations across the gap.

The value of the integral in Eq. (1) crucially depends on the overlap between $(-df/d\omega)$ and $\tau(\omega)$, i.e., on temperature and doping. Temperature broadens the Fermi window, while doping changes the number of carriers, so that ω_0 gets shifted with respect to $\mu = 0$. Apart from that shift, we assume that $\tau(\omega)$ is unchanged by doping. This is a rather drastic approximation,

because we know from model calculations[23, 24] that the value and the shape of $\tau(\omega)$ around ω_0 are doping-dependent. However, the comparison with the exact solution of the Falicov-Kimball[24, 25] and Hubbard model[23, 26] shows that the approximate solution, which is easy to find for any doping, captures the main features of the microscopic models.
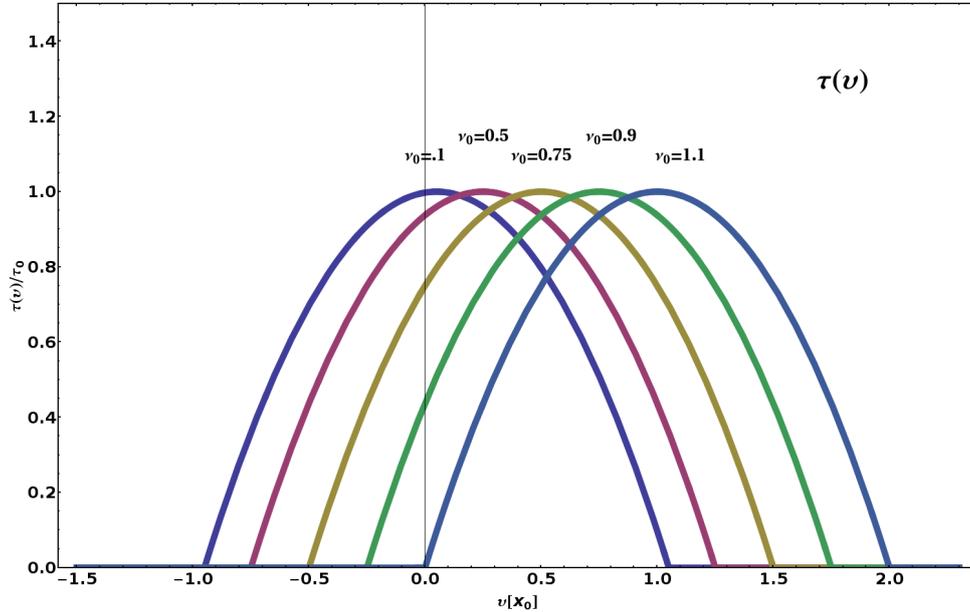

Figure 1. Rescaled relaxation time $\tau(\nu)/\tau_0$ of electron-doped systems is plotted as a function of rescaled frequency $\nu = \omega/x_0$ relative to the chemical potential, indicated by the vertical line at $\nu = 0$. (For definition of the scaling factors see the text.) The right-most curve ($\nu_0 = 1.1$) corresponds to a lightly doped Mott insulator, the left-most curve ($\nu_0 = 0.1$) describes a dirty metal, and the intermediate curves ($\nu_0 = 0.5, 0.75, 0.9$) correspond to a bad metal.

To estimate the transport integrals we use a simple model which neglects the asymmetry of $\tau(\omega)$ around ω_0 and make the lowest order expansion,

$$\tau(\omega) \approx \tau_0 - \tau_1(\omega - \omega_0)^2 , \qquad (2)$$

where $\tau_0 = \tau(\omega_0)$ and $\tau_1 = d^2\tau(\omega)/d\omega^2\big|_{\omega \to \omega_0}$. In this approximation, $\tau(\omega)$ is a parabolic function for $\Lambda_- < \omega < \Lambda_+$ and $\tau(\omega) = 0$ otherwise. The cutoffs $\Lambda_\pm$ are obtained by setting $\tau(\omega) = 0$ in Eq. (2) which yields $\Lambda_\pm = \omega_0 \pm x_0$, where $x_0^2 = \tau_0/\tau_1$ is inversely proportional to the curvature of $\tau(\omega)$ at ω_0. For $\Lambda_- \leq \mu \leq \omega_0$, the transport coefficients of electron-doped systems mainly depend on the low-energy part of $\tau(\omega)$, because the Fermi window renders the high-energy part irrelevant. The parameter $x_0 = \omega_0 - \Lambda_-$ defines an effective bandwidth relevant for the transport properties reminiscent of the Kondo scale. To perform the integration we introduce the new energy and temperature variables, $\nu = \omega/x_0$ and $\tilde{T} = T/x_0$, and write the relaxation time as, $\tau(\nu)/\tau_0 = 1 - (\nu - \nu_0)^2$, where $\nu_0 = \omega_0/x_0$. Integrating by parts, and using $\tau(\Lambda_-) = \tau(\Lambda_+) = 0$, yields

$$L_{mn}(\tilde{T}) = 2\tau_0 \, x_0^{m+n-2} \int_{\nu_0-1}^{\nu_0+1} d\nu \, f(\nu) \, \frac{d[\nu^{m+n-2}\tau(\nu)]}{d\nu} , \qquad (3)$$

where $f(\nu) = 1/[1 + \exp(\nu/\tilde{T})]$, $d\tau_a/d\nu = 2(\nu - \nu_0)$, and we took the spin degeneracy into account. The transport integrals are not reduced to the usual Fermi-Dirac integrals, because the limits are finite. However, the integrand is a regular function and the numerical evaluation

is straightforward. The approximate transport relaxation times used in this calculations is plotted in Fig. 1 for several values of ν_0, corresponding to a few typical band fillings. The right-most curve (ν_0=1.1) corresponds to a lightly doped Mott insulator, the intermediate curves (ν_0=0.5, 0.75, 0.9) correspond to bad metals, and the left-most curve (ν_0= 0.1) describes an electron-doped dirty metal. For ν_0=0, the symmetry point of $\tau(\nu)$ is right at ω=0, such that the thermopower vanishes. However, for $|\nu_0| \ll 1$, the parabolic approximation is insufficient, because in this concentration range the sign of thermopower is strongly dependent on the asymmetry of $\tau(\nu)$. In what follows, we use Eqs.(2) and (3) to obtain the temperature dependence of the resistivity and thermopower in various concentration regimes, neglecting the temperature dependence of the chemical potential.
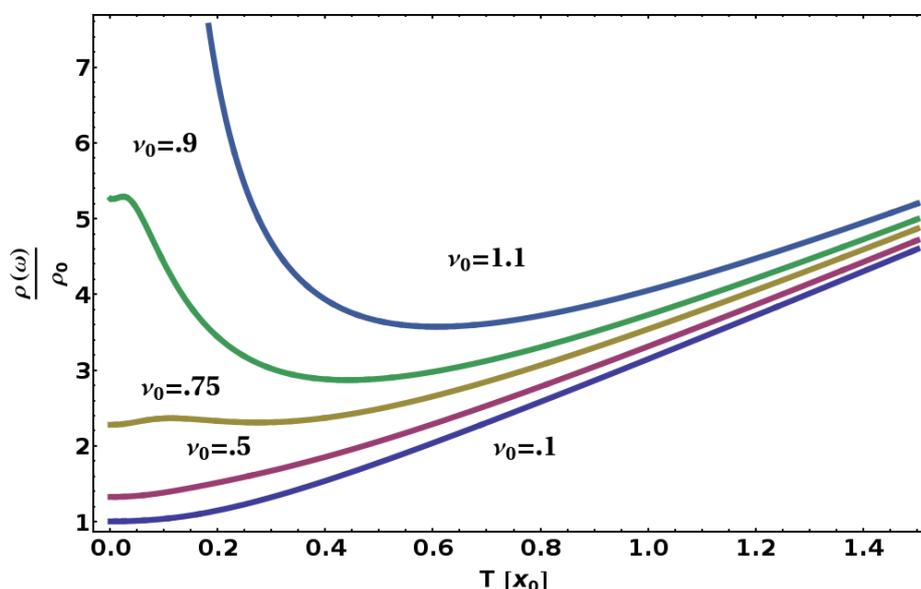

Figure 2. The rescaled resistivity obtained from Eq. (3) plotted as a function of rescaled temperature, for various concentrations of the charge carriers. The parameters are the same as in Fig. 1.

3. Results and discussion

The renormalized resistivity, $\rho(\tilde{T})/\rho_0$ and thermopower $S(\tilde{T})/S_0$, where $\rho_0 = 1/(\sigma_0\tau_0)$ and $S_0 = k_B/|e|$, are shown in Figs. 2 and 3 for electron-doped systems and the same values of ν_0 as in Fig. 1. We find three different types of behavior, depending on the relative position of ω_0 with respect to μ, i.e., on the number of charge carriers.

For $\nu_0 \geq 1$, when the chemical potential is below the band-edge, the low-temperature resistivity is very large and it decreases rapidly as temperature increases. At about $T \simeq \omega_0/2$ the resistivity drops to a minimum and at about $T \simeq \omega_0$, it assumes a linear form. Unlike the resistivity, which has a finite residual value, the thermopower must vanish at $T = 0$, so that $S(T)$ exhibits a very large low-temperature peak. The peak decreases and moves to higher energies as doping increases. At fixed doping, for $T \geq \omega_0$, the thermopower decays logarithmically above the peak, which is typical of lightly doped Mott insulators. For $\nu_0 \leq 1$, when the chemical potential is above the band edge but below ω_0, the low-temperature resistivity starts, at $T = 0$, from a finite value and grows to a well pronounced maximum, which is reduced and shifted to lower temperature as ν_0 is reduced (doping is increased). The minimum still occurs at about

$T \simeq \omega_0/2$ and, for $T \geq \omega_0$, the resistivity becomes a linear function in a broad temperature range. The thermopower has a peak in the same temperature range as $\rho(T)$ and follows the same concentration dependence as $\rho(T)$ but the peak of $S(T)$ is much less pronounced, which is typical of bad metals. For $\nu_0 \ll 1$, the maximum of $\tau(\nu)$ is close to the chemical potential and $\rho(T)$ increases parabolically from its zero-temperature value, as found in dirty metals. At higher temperatures, $T > \omega_0$, there is a crossover to the linear behavior. Since the chemical potential is very close to the maximum of $\tau(\nu)$, the thermopower of dirty metals is very small.
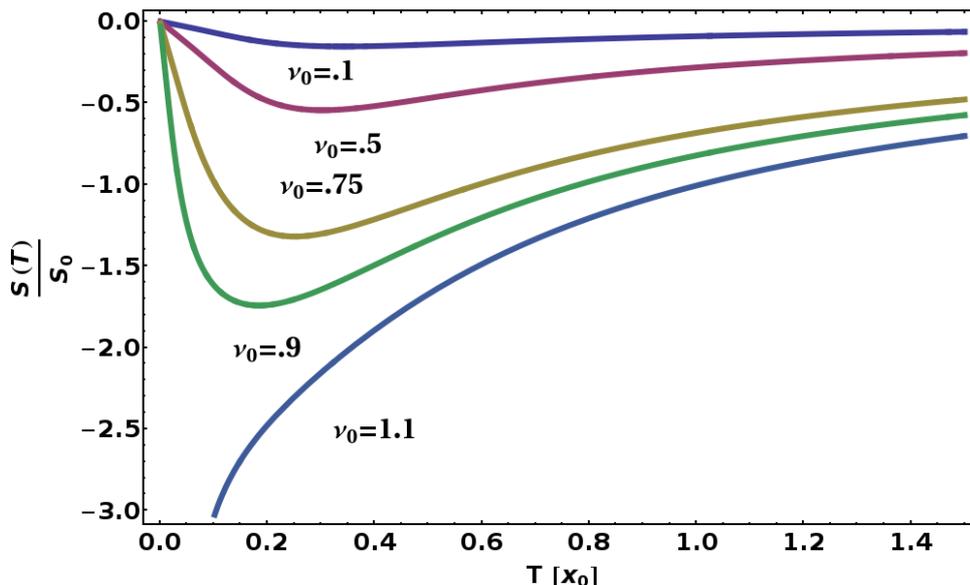

Figure 3. Thermopower of electron-doped systems, obtained from Eq. (3), is plotted as a function of rescaled temperature, for various concentrations of the charge carriers. The parameters are the same as in Fig. 1.

Our simple model shows that the sign of $S(T)$ is doping-dependent. For $\nu_0 > 0$ ($\nu_0 < 0$) and $T \ll \omega_0$, there are more (less) electrons than holes in the system (see Fig.1), so that the low-temperature thermopower is negative (positive). However, for small ν_0, the temperature dependence of $\mu(T)$ and the asymmetry of $\tau(\nu)$ can easily change the relative number of electrons and holes within the Fermi window, and flip the sign of $S(T)$, as often seen in experimental data. Temperature at which this happens cannot be obtained from the simplified model but requires detailed calculations which provide sufficiently accurate results for $\mu(T)$ and $\tau(\nu)$.

4. Summary and conclusions

In summary, using a model with the parabolic form of the transport relaxation time, we have shown that the resistivity and thermopower of doped Mott-Hubbard systems exhibit simple universal features and that, depending on the concentration of the charge carriers, the strongly correlated materials can be classified into three distinct groups. In lightly doped insulators, the low-temperature resistivity is exponentially large and the thermopower is sharply peaked at temperature T_S. Here, doping decreases the magnitude of $\rho(T)$ and $S(T)$, and increases T_S, as seen in $La_{1-x}Sr_xVO_3$ for $x \leq 0.18$ [2] and in $La_{1-x}Sr_xCoO_3$ for $x \leq 0.18$ [4]. A higher concentration of the charge carriers produces a bad metal with a quasi linear resistivity and thermopower which has a small peak that shifts to lower temperatures as doping increases. Finally, a large enough doping produces a dirty metal with a Fermi liquid-like resistivity, $\rho(T) \simeq \rho_0 + AT^2$, and the thermopower is negative for electron- and positive for hole-

doped systems. In this concentration range, both $\rho(T)$ and $S(T)$ are monotonic functions of temperature. Such a behavior is found in $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ for $x \geq 0.30$ [2], $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ for $x \geq 0.25$ [4], and overdoped oxides[7].

The symmetric transport relaxation time cannot explain the sign-change of $S(T)$ which is found at high enough temperatures in the underdoped oxides[6, 7], $\text{La}_{1-x}\text{Sr}_x\text{VO}_3$ for $0.18 \leq x \leq 0.30$ [2], and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ for $0.18 \leq x \leq 0.25$ [4]. To explain this observation we have to take into account the temperature dependence of $\mu(T)$ and the detailed shape of $\tau(\nu)$, i.e., we need a proper microscopic calculations. For the Falicov-Kimball model, the simplest model which yields the Mott-Hubbard transition and admits a solution at arbitrary filling, the concentration dependence of the temperature at which $S(T)$ changes sign has been obtained by the dynamical field theory [25]. In lightly doped insulators, this yields an exponential dependence on the concentration of the charge carriers and, in and bad metals, a linear dependence. This agrees with the experiments on cuprates[9] and is expected for other oxides as well. It would be interesting to perform similar calculations for the Hubbard and the periodic Anderson models which apply to a broader class of strongly correlated systems than the Falicov-Kimball model.

Acknowledgments

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