Thermoelectric power of single-orbital and two-orbital Hubbard models on triangular lattices

Xian-Lu Gu a,b, Feng Lu c, Da-Yong Liu a, Liang-Jian Zou a,*

a Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, P.O. Box 1129, Hefei 230031, China
b Graduate School of the Chinese Academy of Sciences, Beijing 100049, China
c Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT

The thermoelectric power of the single-orbital and two-orbital correlated electron systems on a two-dimensional triangular lattice is investigated by the dynamical mean field theory with the exact diagonalization solver at finite temperature. It reveals that for the hole doping case, the geometrical frustration together with the Coulomb interaction greatly enhances thermoelectric power, in comparison with the electron doping case. In an anisotropic triangular lattice, we find a large thermoelectric power in the direction with small hopping integral in the anisotropic systems. In the two-orbital systems, we show that though the orbital entropy contributes to thermoelectric power, Hund’s rule coupling may suppress the large thermoelectric power.

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1. Introduction

In the past decade, the discovery of large thermoelectric power (TEP) in layered compound Na0.5CoO2 at x=0.5 [1] and in 0.75 < x < 0.84 [2], together with the superconductivity in hydrated compounds [3], has stimulated great interest in researching the properties of triangular compounds. Besides Na0.5CoO2, [Bi1–xCo0.3Ca2O4] δ CoO2 [4] which also contains triangular CoO2 layer, exhibits good thermoelectric performance. It is well known that the antiferromagnetically interacting spins are frustrated in triangular lattice. It is interesting why these compounds with triangular CoO2 layers have larger TEP than the square/cubic lattice, and whether other narrow-band triangular compounds have much better thermoelectric properties.

In order to hunt for new and efficient materials for application, much effort has been put into studying the TEP in strongly correlated systems. Experimentally, the large TEP in doped triangular cobaltates was attributed to the spin entropy enhancement [4–6]. Theoretically, the TEP of strongly correlated electron systems have been investigated in the one-dimensional Hubbard model [7,8] and in the t–J model [9]. These studies focused on the thermoelectric properties in the high temperature regime [10,11]. For example, the Heikes formula [12] was obtained in the high temperature limit. In addition, several authors [13,14] recently attempted to examine the TEP in the case of atomic limit (the strongly correlated limit). Numerically, some authors [15–17] studied the TEP in the single- and two-orbital Hubbard models on the Bethe or the hypercubic lattices by the dynamical mean field theory (DMFT). Nevertheless, a systematic path to greatly improve the thermoelectric properties still lacks for experimentists, in spite of much intensive theoretical research over the past 10 years.

To provide an overall insight into the TEP in triangular lattices and a systematic way to improve the efficiency of the thermoelectric materials, it needs to systematically study the finite-temperature TEP of two-dimensional (2D) triangular lattice in the strong correlation regime. Especially, it is necessary to explore the influences of many parameters and fields on the TEP, such as temperature, doping, Coulomb interaction, lattice geometrical frustration, spin entropy, orbital entropy and so on. Meanwhile, although a few of highly anisotropic triangular compounds have been discovered in recent years, there are few theoretical research on TEP in these anisotropic triangular compounds. In contrast, the anisotropic TEP in other systems has been found in several experiments [18–20]. Therefore, it is worthy to pay more attention to uncovering the thermoelectric behavior of 2D anisotropic triangular lattice.

In this paper, we study the behaviors of the TEP on isotropic and anisotropic triangular lattices within 2D single-orbital and two-orbital Hubbard models, and present the temperature and Coulomb interaction dependence of TEP based on the linear response theory using the DMFT with the exact diagonalization...
(ED) approach. We show that in the strong correlation regime and in finite temperature, the TEP in the hole-doped triangular lattice is much larger than that in the hole-doped square lattice; the orbital entropy gives large contribution to TEP; and Hund’s coupling is unfavorable of large TEP. We also find that in anisotropic triangular lattice, the TEP along the weak coupling direction is considerably enhanced compared with that in the strong coupling direction. The rest of the paper is organized as follows: In Section 2, we investigate the thermoelectric behaviors of triangular lattice based on single-orbital Hubbard model; in Section 3, the results of two-orbital Hubbard model are obtained; finally, we give a brief conclusion in Section 4.

2. TEP in single-orbital Hubbard models

The Hamiltonian of single-orbital Hubbard model on 2D triangular lattice reads

\[ H = \sum_{\langle i,j \rangle} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} - \mu \sum_{\sigma} n_{i\sigma}, \]

where \( c_{i\sigma}^\dagger \) (\( c_{i\sigma} \)) is the creation (annihilation) operator of electron with \( \sigma \) spin at the \( i \) site, \( n_{i\sigma} \) is the fermion number operator, \( \langle i,j \rangle \) are the nearest-neighbor sites, \( U \) is the on-site Coulomb interaction and \( t_{ij} \) is the hopping parameter between \( i \) and \( j \) sites. As shown in Fig. 1, \( t \) and \( t' \) are nearest-neighbor hopping parameters along the \( x \) and \( \pm \pi/3 \) direction, respectively. The bare band structure of the triangular lattice is

\[ \epsilon_k = -2\cos(k_x a) - 4\tau \cos(k_y a/2) \cos(k_y a\sqrt{3}/2). \]

The anisotropic thermoelectric power is expressed \([16,21]\) as

\[ S_{xy}(yy) = -\frac{k_B}{e} \frac{A^{xy}_{n}}{A^{0}_{n}}, \]

where

\[ A^{xy}_{n} = \frac{\pi}{V N_h} \sum_{k \sigma} \int d\omega \rho_{\sigma}(k,\omega)^2 \left( \frac{\partial \epsilon_k}{\partial \omega} \right)^2 \left( -T \frac{\partial^2 \rho_{\sigma}(k,\omega)}{\partial \omega^2} \right) \Phi_{xy}(\omega). \]

In Eq. (4), \( \rho_{\sigma}(k,\omega) \) is the spectral function of the carriers with spin \( \sigma \), \( \rho(\omega) \) is the density of states (DOS), and \( \Phi_{xy}(\omega) \) is the transport function.

\[ \Phi_{xy}(\omega) = \frac{1}{V} \sum_k \left( \frac{\partial \epsilon_k}{\partial \omega} \right)^2 \delta(\omega - \epsilon_k). \]

As a comparison, we first study the TEP in the isotropic systems with \( t' = t \). We find that the TEP along the \( x \) direction \( S_{xx} \) is equal to \( S_{yy} \) along the \( y \) direction. In this case, we denote \( S_{xx} = S_{yy} = S \).
seen in Fig. 2 for isotropic triangular lattice and in Fig. 3 for isotropic square lattice.

The Coulomb interaction dependence of TEP in an isotropic triangular lattice is presented in Fig. 2. The $S(U)$ curves are calculated for the electron densities from $n=0.2$ to $1.8$. We note that when $n < n_0$ ($n_0$ is about 0.75 in the present triangular lattice), $S < 0$, the TEP is electron-like and is nearly independent of the Coulomb interaction. On the contrary, $S > 0$ for $n > n_0$, the TEP is hole-like. In addition, the Coulomb interaction strongly enhances the TEP in a large electron density region ($1.0 \leq n \leq 1.6$). As a comparison, the Heikes formula predicts that the critical doping $n_c$ is $\frac{2}{3}$ in the correlated electronic systems in the high-$T$ and large $U$ limits [12]. Obviously, the TEP is enhanced through the enhancement of effective mass when the electron–electron correlation is switched on [16,17,22]. It shows that the Coulomb interaction plays very important role in the enhancement of the TEP for hole-doped triangular lattice. As is well known, the sign of TEP reveals the type of charge carriers (electrons or holes). When the electron density reaches $n_0$, the TEP becomes positive. This shows that the holes give larger contribution to TEP than electrons for $n > n_0$. Comparing the electron-like curves ($n_e=n,n<n_0$) with the hole-like ones ($n_h=2-n,n>1$) at the same carrier concentration ($n_h=n_e$), for example, in the electron doping case $n=0.2$ and 1.8 (i.e. $n_h=0.2$), or $n=0.4$ and 1.6 (i.e. $n_h=0.4$), etc., we find that the absolute values of TEP in hole doped system is considerably larger than that in the electron doped system. As shown in Fig. 3, the bandwidth of the hole doped system is much narrower than that of the electron doped system. The enhancement of TEP in hole-doped triangular lattice arises from the band narrowing and the increase of the effective mass of the carriers [16,17,22]. This shows that there would be large TEP in hole doped (or p-type doped) triangular compounds.

As shown in Fig. 2, an especial interest occurs at half-filling $n=1.0$. The TEP smoothly varies with the increase of $U$ away from the quantum critical point $U_c$. The system undergoes a Mott–Hubbard metal–insulator transition at the critical Coulomb interaction $U_c \approx 9t$ at $n=1.0$. We note that the TEP greatly varies with $U$ and is strongly enhanced near the quantum critical point of the metal–insulator transition, which comes from the contribution of the excitations between the down and upper Hubbard bands. This is in agreement with the results of the early study [15]. Furthermore, Fig. 2 gives a good agreement in the magnitude order with the large enhancement of the TEP in hole-doped Na$_2$CoO$_2$ for heavy Na doping [2].

In order to identify the different behavior between the triangular and square lattices, we also present the Coulomb interaction dependence of TEP on a 2D isotropic $(t'/t=1)$ square lattice for various electron densities from $n=0.2$ to 0.9 in Fig. 4. The TEP vanishes at half-filling [23]. When the hole concentration is equal to the electron concentration, the absolute value of TEP in the hole doping system is equal to that in the electron doping system, demonstrating the particle–hole symmetry in 2D square lattice. Therefore, we plot the thermoelectric behaviors of 2D square lattice only for the electron doping cases in Fig. 4. As seen from Fig. 4, the TEP is nearly independent of the Coulomb interaction when $n$ is far away from half-filling. However, the TEP is highly dependent on the Coulomb interaction near the half-filling. It considerably increases with the Coulomb interaction at $n=0.8$ and 0.9. This behavior is attributed to the fact that the entropy density increases with the Coulomb interaction when the carrier concentration is around the half-filling [24].

Comparing Fig. 2 with Fig. 4, one clearly finds that the TEP of 2D triangular lattice is considerably larger than that of 2D square lattice for the same hole concentration. The emergence of different thermoelectric behaviors can be attributed to the effect of the particle–hole asymmetry associated with the triangular lattice, which influences the charge dynamics in strongly correlated electron systems [25]. Therefore, the triangular compound is more advantageous to obtain large TEP than square lattice. Thus, besides the spin entropy contribution [5], the band narrowing effect of the hole carriers induced by the Coulomb interaction is also responsible for the large TEP in Na$_2$MnO$_2$.

Next, we consider the situations of anisotropic triangular lattices, denoting the ratio $t'/t$ as the anisotropy strength. In Fig. 5, we present the temperature dependence of TEP $S_{xx}$ and $S_{yy}$ on 2D anisotropic triangular lattice for $n=1.0$, $U=3t$, at $t'/t=1.0,7.0,5.0$ and 0.1, respectively. There are rich thermoelectric behaviors in anisotropic triangular lattice in Fig. 5. There are two limit cases: one is the isotropic case at $t'/t=1$, the other is the extremely anisotropic for $t'/t=0$ or $\infty$. In the limit of $t'/t=1$, $S_{xx}=S_{yy}$ increases with temperature and exhibits linear temperature dependence at low temperature; and $S(T\rightarrow0)\rightarrow0$, which arises from the Fermi liquid. In the limit of $t'/t=0$, the system exhibits one-dimensional behavior in the x-direction, and the model is topologically equivalent to 2D square lattice without geometrical frustration [26]. In this case, the system is the particle–hole symmetry in the x-direction, so $S_{xx}$ vanishes for half-filling. In Fig. 5, the evolution of TEP is consistent with this behavior.

However, $S_{xx}$ is significantly different from $S_{yy}$ when $t' \neq t$. $S_{yy}$ increases with the ratio of $t'/t$, while $S_{xx}$ decreases with the ratio of $t'/t$. $S_{yy}/S_{xx}$ becomes very large as the anisotropy ratio $t'/t$ is very small. The more the anisotropy of the system is, the larger the $S_{yy}/S_{xx}$ is. The TEP in the direction with large hopping integral will be greatly suppressed in the anisotropic systems, as seen in Fig. 5(a)–(d). Recently, Shelimova et al. [18] found a significant anisotropy TEP in PbSb$_2$Te$_4$ and PbBi$_2$Te$_4$ single crystals. They showed that the out-of-plane TEP with weak coupling is several times larger than the in-plane TEP. Our results qualitatively agree with this observation. Therefore, we anticipate that there would be anisotropic and large TEP in the newly found anisotropic triangular compound, $\alpha$-Na$_2$MnO$_2$ [27].
3. TEP in two-orbital Hubbard models

Koshibae et al. [10] investigated the contribution of the orbital degeneracy to the TEP in the high temperature limit. In order to study the orbital effect on TEP at finite temperature, we further consider the two-orbital Hubbard model in isotropic triangular lattice, which reads

\[ H = \sum_{\langle ij \rangle} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_{\mu \nu} n_{i\mu\uparrow} n_{i\nu\downarrow} + U \sum_{\langle \sigma \sigma' \rangle} n_{i\sigma} n_{i\sigma'} + J \sum_{\langle \mu \nu \rangle} c_{i\mu\uparrow} c_{i\mu\downarrow} c_{i\nu\downarrow} c_{i\nu\uparrow} + J_u \sum_{\mu \nu} c_{i\mu\uparrow} c_{i\mu\downarrow} c_{i\nu\downarrow} c_{i\nu\uparrow}. \]  

Here, \( c_{i\mu\sigma}^\dagger (c_{i\mu\sigma}) \) is the creation (annihilation) operator of electron with spin \( \sigma (= \uparrow, \downarrow) \) and orbit \( \mu = 1,2 \) at the \( i \) site, \( n_{i\mu\sigma} \) is the fermion number operator, \( t_{ij} \) is the hopping parameter between the \( \mu \) and \( \nu \) orbitals of the nearest-neighboring sites, \( U(U') \) is the intraband (interband) Coulomb interaction, \( J \) is the Hund's rule coupling and \( J_u \) is the pair-hopping coupling. In our paper, we impose the condition \( J = J' \) and \( U = U' + 2J \) and assume \( t_{ij} = t_{ij'} = t, t_{ij'\sigma} = 0 \). The TEP expression of the two-orbital Hubbard model reads

\[ S = -\frac{k_B A_n}{e} \]  

where

\[ A_n = \frac{\pi}{V_N} \sum_{k\sigma} \int dk \rho_{\mu\sigma}(k) \left( \frac{\partial \epsilon_{2k}}{\partial k} \right)^2 \left( -T \frac{\partial f(\omega)}{\partial \omega} \right)^n. \]  

Fig. 5. Temperature dependence of thermoelectric power on a two-dimensional triangular lattice for electron density \( n = 1.0, U = 3.0t \) and \( t'/t = 1.0 \) (a), \( t'/t = 0.7 \) (b), \( t'/t = 0.5 \) (c), \( t'/t = 0.1 \) (d).

Fig. 6. Hund's rule coupling dependence of TEP on a two-dimensional triangular lattice for different Coulomb repulsion strengths \( U = 5.0t \), \( 6.0t \), and \( 7.0t \) at electron density \( n = 1.0 \) and \( k_BT = 0.1t \).
Fig. 6 shows the evolution of TEP with Hund’s rule coupling $J$ for $n=1.0$ and $U=5.0t$, $6.0t$, $7.0t$, respectively, at $k_BT=0.1t$. The TEP decreases with the increase of Hund’s rule coupling. Hund’s rule coupling is expected to suppress the TEP by suppressing the spin and orbital fluctuations and reducing the spin and orbital entropy. Such an negative effect of the Hund’s rule coupling on thermoelectric behavior suggests that spin and orbital degeneracies play an important role in the TEP. In this situation, the role of Hund’s coupling acts as an effective magnetic field to align spins in the same direction and to distribute electrons in different orbits, thus removes the spin and orbital degeneracies. Therefore, the dependence of TEP on $J$ is very similar to the magnetic-field dependence of TEP found by Wang et al. [5].

In Fig. 7, we display the temperature dependence of TEP of the two-orbital Hubbard model for $U=3t$, $J=0a t$, $n=0.1$ (a), $n=0.2$ (b), $n=0.3$ (c), and $n=0.4$ (d) respectively. The results of the single-orbital Hubbard model are also displayed for comparison. From Fig. 7, it is found that the absolute value of TEP in the two-orbital model is significantly larger than that in the single-orbital model for the same electron density. Such a large TEP is ascribed to the contribution of orbital entropy. Due to the orbital fluctuations, it gives large contributions to the orbital entropy and causes the large TEP. This result qualitatively demonstrates that the orbital entropy plays an important role in enhancing the TEP [10,28].

4. Conclusions

Our results have shown that the frustrated structure together with strong electron–electron correlation and multi-orbital character is responsible for the large value of TEP in the hole doped triangular lattice. It suggests that the experimentalists may find the most potential thermoelectric material in such compounds. Furthermore, we find that there would be large TEP in the direction with small hopping integral in the anisotropic systems, which gives us a new guiding principle to search for or design new and efficient thermoelectric materials.

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