

# Electron interaction-driven peculiarities of strongly correlated system thermopower

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Peculiar thermoelectric properties of narrow-band materials with strong electron correlations [1,2] suggest their use for energy harvesting and other high-demand technologies. Studies of the layered cobaltites [3,4] and weakly electron-doped titanates [5] reveal thermopower values much larger than those typical for semiconductors. Interpreting these peculiarities requires a detailed characterization of band structure and electron correlations in these perspective materials.

We use the theoretical model of electron subsystem for strongly correlated compound with a peculiar density of electronic states (DOS). The energy spectrum is calculated within the unperturbative approach [6]. The chemical potential and Seebeck coefficient are calculated numerically for a number of realistic DOS forms for non-integer band fillings.

## Theoretical approaches for calculation of electronic contribution to thermopower

Recently, some progress has been achieved [7,8] in understanding of the temperature dependence of electron contribution to thermopower  $S$  in materials with narrow energy bands. In particular, it has been shown for intermediate correlation strength that the optimal approach is the modification of the so-called Kelvin formula [8]. At the same time, in paper [9] within DMFT approach it has been proven for single-band Hubbard model that thermopower has non-monotonic temperature dependence and tends asymptotically to values predicted by the Mott-Heikes formula.

A standard definition for electronic thermopower is

$$S = -\frac{L_{12}}{e|L_{11}|T}$$

where  $L_{kn}$  are kinetic coefficients, satisfying Onsager relations ( $\sigma = e^2 L_{11}$  being the electrical conductivity),  $T$  is temperature. Sign of  $S$  determines whether electrons or holes are the majority carriers. Using Sommerfeld expansion at condition  $E_F < k_B T$  we obtain the following expression (Mott formula)

$$S = -\frac{\pi^2 k_B^2 T}{3|e|} \frac{d \ln \sigma(E)}{dE} \Big|_{E=E_F}$$

where  $E_F$  is Fermi energy. For a consistent analysis of thermopower peculiarities in narrow band materials we have to consider models, which take into account the peculiar properties of their electronic subsystems, namely strong electron interactions, orbital degeneracy of energy levels and realistic electronic density of states.

## Model Hamiltonian: a non-degenerated band

Following papers [6,10] we chose the initial form of Hamiltonian for non-degenerate band in Hubbard-operators representation as

$$H = H_0 + H_1 + H'_1 + H_2,$$

where

$$\begin{aligned} H_0 &= -\mu \sum_i (X_i^1 + X_i^4 + 2X_i^2) + U \sum_i X_i^2, \\ H_1 &= \sum_{ij\sigma} t_{ij}(n) X_i^{\sigma 0} X_j^{\sigma 0} + \sum_{ij\sigma} \tilde{t}_{ij}(n) X_i^{\sigma 1} X_j^{\sigma 2}, \\ H'_1 &= \sum_{ij} t_{ij}^{(0)} (X_i^{10} X_j^{22} - X_i^{10} X_j^{22} + h.c.), \\ H_2 &= -\sum_{ij\sigma} \frac{J_{ij}^{(0)}}{2} ((X_i^{\sigma 0} + X_j^{\sigma 0})(X_j^{\sigma 1} + X_j^{\sigma 2}) + X_i^{\sigma 0} X_j^{\sigma 0}). \end{aligned}$$

Extension of the canonical transformation method for this model leads to the effective Hamiltonian which differs substantially from that of the Hubbard model. Let us apply a canonical transformation [6] to exclude hybridization processes  $\tilde{H} = e^S H e^{-S}$

where  $S$  is chosen in the following form

$$S = \sum_{ij} L_{ij} ((X_i^{10} X_j^{22} - X_i^{10} X_j^{22}) - h.c.)$$

The effective Hamiltonian can be represented as

$$\begin{aligned} H &= -\mu \sum_i (X_i^1 + X_i^4 + 2X_i^2) + U \sum_i X_i^2 + \\ &+ \sum_{ij\sigma} t_{ij}(n) X_i^{\sigma 0} X_j^{\sigma 0} + \sum_{ij\sigma} \tilde{t}_{ij}(n) X_i^{\sigma 1} X_j^{\sigma 2} - \\ &- \sum_{ij\sigma} \frac{J_{ij}^{(0)}}{2} ((X_i^{\sigma 0} + X_j^{\sigma 0})(X_j^{\sigma 1} + X_j^{\sigma 2}) + X_i^{\sigma 0} X_j^{\sigma 0}) - \\ &- \sum_{ij\sigma} \frac{t_{ij}^{(0)} t_{ij}^{(n)}}{U} (X_i^{\sigma 0} X_j^{\sigma 0} - X_i^{\sigma 0} X_j^{\sigma 0} - X_i^{\sigma 1} X_j^{\sigma 2}) - \\ &- \sum_{ij\sigma} \frac{t_{ij}^{(n)} t_{ij}^{(k)}(n)}{U} (X_i^{\sigma 0} X_j^{\sigma 0} X_k^{\sigma 0} - X_i^{\sigma 0} X_j^{\sigma 0} X_k^{\sigma 0}) - \\ &- \sum_{ij\sigma} \frac{t_{ij}^{(k)}(n) t_{ij}^{(k)}(n)}{U} (X_i^{\sigma 0} X_j^{\sigma 0} X_k^{\sigma 2} - X_i^{\sigma 0} X_j^{\sigma 0} X_k^{\sigma 2}). \end{aligned}$$

Exclusion of the pair creations and annihilations have led to three new terms, the first corresponding to the indirect exchange interaction, other two describing electron hoppings. The exchange mechanism is induced by virtual transitions of  $|\downarrow\sigma\rangle$ -states to  $|\uparrow\downarrow\rangle$ -states and stabilizes antiparallel orientation of  $|\downarrow\sigma\rangle$  and  $|\uparrow\bar{\sigma}\rangle$ .

## Model Hamiltonian: a doubly orbitally degenerated band

In analogue to the above consideration of the non-degenerated band we transform the model for the doubly degenerated one. The initial Hamiltonian for the doubly degenerated model [11] of  $e_g$ -band in the limiting case of strong Hund's rule coupling in the formalism of  $X_i^{\alpha\beta}$ -operators reads as

$$\begin{aligned} H &= H_0 + H_a + H_b + H_{ab}, \\ H_0 &= -\mu \sum_i (X_i^{\gamma 1} + X_i^{\gamma 4} + 2X_i^{\gamma 1} + 2X_i^{\gamma 4}) + (U - J_H) \sum_i X_i^{\gamma\sigma}, \\ H_a &= \sum_{ij\sigma} t_{ij}(n) X_i^{\gamma\sigma 0} X_j^{\gamma\sigma 0}, \\ H_b &= \sum_{ij\sigma} \tilde{t}_{ij}(n) X_i^{\sigma\alpha 0} X_j^{\sigma\alpha 0}, \\ H_{ab} &= \sum_{ij} \left( \frac{t_{ij}^{(n)}(X_i^{\beta 1,0} X_j^{\alpha 1,1} - X_i^{\gamma 1,1} X_j^{\alpha 1,0})}{X_i^{\alpha 1,0} X_j^{\beta 1,1} - X_i^{\beta 1,0} X_j^{\alpha 1,1} + h.c.} \right) \end{aligned}$$

$H_a$  and  $H_b$  describe the system at fixed number of holes and Hund's doublets (at a constant temperature),  $H_{ab}$  describes the processes of pair creation and annihilation of holes and doublets in the nearest neighboring sites. Let us exclude hybridization by the canonical transformation, with

$$S = \sum_{ij} (L_{ij} ((X_i^{\beta 1} X_j^{\alpha 1,1} - X_i^{\gamma 1,1} X_j^{\alpha 1,0}) + X_i^{\alpha 1,0} X_j^{\beta 1,1} - X_i^{\beta 1,0} X_j^{\alpha 1,1}) - h.c.)$$

where  $L_{ij}$  is determined by the condition  $[SH_0] + H_{ab} = 0$ . In second order in the hopping integral we obtain

$$\begin{aligned} H &= H_0 + \sum_{ij\sigma} t_{ij}(n) X_i^{\gamma\sigma 0} X_j^{\gamma\sigma 0} + \sum_{ij\sigma} \tilde{t}_{ij}(n) X_i^{\sigma\alpha 0} X_j^{\sigma\alpha 0} - \\ &- \sum_{ij\sigma} \frac{t_{ij}^{(n)} t_{ij}^{(n)}}{U - J_H} (X_i^{\gamma\sigma 0} X_j^{\sigma\alpha 0} + X_i^{\sigma\alpha 0} X_j^{\gamma\sigma 0}) - \\ &- \sum_{ij\gamma\sigma} \frac{t_{ij}^{(n)} t_{ij}^{(k)}(n)}{U - J_H} (X_i^{\gamma\sigma 0} X_j^{\sigma\alpha 0} X_k^{\gamma\sigma 0} - X_i^{\gamma\sigma 0} X_j^{\sigma\alpha 0} X_k^{\gamma\sigma 0} + \\ &+ X_i^{\sigma\alpha 0} X_j^{\sigma\alpha 0} X_k^{\gamma\sigma 0} - X_i^{\sigma\alpha 0} X_j^{\sigma\alpha 0} X_k^{\gamma\sigma 0}). \end{aligned}$$

From the above effective Hamiltonian one can see that for the realization of the virtual superhopping, real holes at electron concentrations  $n < 1$  or Hund's doublets at  $n > 1$  are needed. At  $n=1$  the concentration of these states is proportional to  $\exp(-U/KT)$ . In systems where one can control the electron concentration, the superhopping may affect the magnetic ordering stabilization which, in its turn, modifies the energy spectrum considerably.

## Quasiparticle energy spectra

Following paper [6] we use the projection procedure in the Green function equations of motion for the case  $n < 1$ , when one can neglect the processes with doubly occupied states and obtain

$$G_k^{\sigma}(E) = \frac{1}{2\pi} \frac{1 - n_{\sigma}}{E - \tilde{E}_k^{\sigma}}$$

where the quasiparticle energy spectrum

$$\tilde{E}_k^{\sigma} = -\mu + \alpha_{\sigma} t_k(n) + \beta_{\sigma} - zJn_{\sigma} + zJn_{\sigma}$$

contains the correlation narrowing factor

$$\alpha_{\sigma} = 1 - n_{\sigma} + \frac{n_{\sigma} n_{\bar{\sigma}}}{1 - n_{\sigma}}$$

and the correlation shift of the band center

$$\beta_{\sigma} = -\frac{1}{1 - n_{\sigma}} \sum_k t_k(n) (X_i^{\sigma 0} X_j^{\sigma 0})_k$$

Likewise, for the case  $n > 1$  we consider the doublon Green function

$$\tilde{G}_k^{\sigma}(E) = \frac{1}{2\pi} \frac{n_{\sigma}}{E - \tilde{E}_k^{\sigma}}$$

where the spectrum of the upper quasiparticle subband is

$$\tilde{E}_k^{\sigma} = -\mu + U + \tilde{\alpha}_{\sigma} t_k(n) + \tilde{\beta}_{\sigma} - zJn_{\sigma} + zJn_{\sigma}$$

where

$$\tilde{\alpha}_{\sigma} = n_{\sigma} + \frac{(1 - n_{\sigma})(1 - n_{\bar{\sigma}})}{n_{\sigma}}$$

and

$$\tilde{\beta}_{\sigma} = -\frac{1}{n_{\sigma}} \sum_k t_k(n) (X_i^2 X_j^2)_k$$

Using the same approach, Green function and energy spectrum have been calculated for the doubly degenerated band at electron concentrations  $n < 1$

$$\alpha_k^{\sigma}(E) = \frac{1}{2\pi} \frac{1 - n + n_{\sigma}}{E - \tilde{E}_k^{\sigma}}$$

$$\tilde{E}_k^{\sigma} = -\mu + \alpha_{\sigma} v_k(n) + \beta_{\sigma}$$

$$\alpha_{\sigma} = 1 - n + n_{\sigma} + \frac{2n_{\sigma} n_{\bar{\sigma}} + n_{\sigma} n_{\sigma}}{1 - n + n_{\sigma}}$$

$$\beta_{\sigma} = -\frac{1}{1 - n + n_{\sigma}} \sum_k t_k(n) \left( (X_i^{\sigma 0} X_j^{\sigma 0})_k + (X_i^{\sigma 0} X_j^{\sigma 0})_k + (X_i^{\sigma 0} X_j^{\sigma 0})_k \right).$$

For  $n > 1$  the corresponding results are

$$\tilde{G}_i^{\sigma}(E) = \frac{1}{2\pi} \frac{n_{\sigma} + n_{\bar{\sigma}}}{E - \tilde{E}_i^{\sigma}}$$

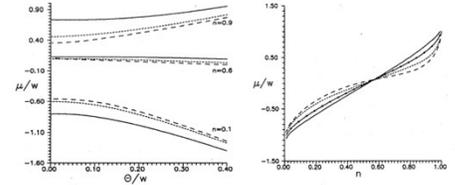
$$\tilde{E}_i^{\sigma} = -\mu + U - 3J' + \tilde{\alpha}_{\sigma} v_k(n) + \tilde{\beta}_{\sigma}$$

$$\tilde{\alpha}_{\sigma} = n_{\sigma} + n_{\bar{\sigma}} + \frac{n_{\sigma}}{n_{\sigma} + n_{\bar{\sigma}}}$$

$$\tilde{\beta}_{\sigma} = \frac{1}{n_{\sigma} + n_{\bar{\sigma}}} \sum_k t_k(n) (X_i^{\sigma\sigma} X_j^{\sigma\sigma})_k$$

## Results and discussion

In a wide interval of temperature and carrier concentration values the dependence of  $S$  on temperature can be determined by the corresponding dependence of the chemical potential, which is calculated numerically with use of the obtained analytical expressions for Green functions and quasiparticle energy spectra.

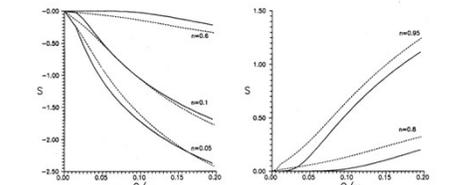


Temperature dependence of the chemical potential at different band fillings. Solid curve corresponds to model rectangular DOS, short-dashed curve is for bcc lattice, long-dashed curve is for sc lattice.

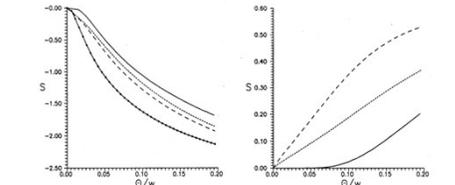
Concentration dependence of the chemical potential for different DOS forms. Solid curve is for rectangular DOS, the dotted one - semi-elliptical DOS, short-dashed curve - sc lattice, long-dashed curve - bcc lattice.

Let us neglect both the diffusion component and the phonon drag thermopower to write down Kelvin formula for the low-temperature estimate of the thermopower  $S = \frac{1}{e} \frac{d\mu}{dT}$ . When the electronic conductivity is known, the Heikes-Mott formula can also be used

$$S = -\frac{\pi^2 k_B^2 T}{3e\sigma(E)} \left( \frac{d\sigma}{dE} \right)_{E=E_F}$$

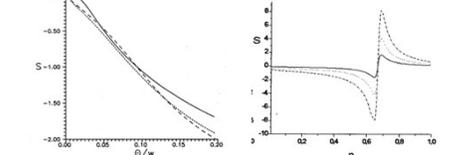


Temperature dependence of the thermopower at different band fillings (left panel for  $n < 2/3$  and the right one for  $n > 2/3$ ). Solid curves correspond to model rectangular DOS, dashed curves are built with semi-elliptical DOS.



Temperature dependence of the thermopower at  $n=0.1$ . Solid curve corresponds to rectangular DOS, other curves correspond to DOS with asymmetry parameter ( $\alpha=0.3$  for short-dashed,  $\alpha=0.5$  for long-dashed,  $\alpha=0.9$  for dotted curve).

Temperature dependence of the thermopower at  $n=0.8$ . Solid curve corresponds to rectangular DOS, other curves correspond to DOS with asymmetry parameter ( $\alpha=0.3$  for short-dashed,  $\alpha=0.5$  for long-dashed curve).



Temperature dependence of the thermopower at  $n=0.1$ . Solid curve corresponds to rectangular DOS, short-dashed curve is for sc lattice, long-dashed curve is for bcc lattice.

Filling-controlled thermopower changes. Solid curve corresponds to  $k_B T = 0.02w$ , dotted curve is for  $k_B T = 0.05w$ , dashed corresponds to  $k_B T = 0.1w$ .

## Conclusions

Distinct types of Seebeck coefficient temperature behavior have been observed for the model of electron subsystem with strong correlations. These distinctions can be attributed to different electron interaction regimes to be realised in some regions of electron band-filling and strongly influenced by the DOS form.

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