

Thermoelectric power of high- T_c superconductors using extended Hubbard model

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Abstract. The thermoelectric power (TEP) for a one dimensional lattice has been studied by using the extended Hubbard model in the limit $U \neq \infty$, where U is the on-site Coulomb interaction. A new expression for TEP, derived in this study, has been found to successfully reproduce the experimental results of the insulating samples of different hole- and electron-doped high temperature superconducting systems.

Keywords. Hubbard model; thermoelectric power.

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1. Introduction

Hubbard model [1] basically deals with the theory of correlation effects in transition metals having narrow d-bands. This model has been successfully used to explain the metal-insulator (M-I) transition behaviour of transition metals. Hubbard model has also been extensively used for the analysis of transport properties of many conducting salts of organic compounds, e.g., *N*-methylphenazinium-tetracyanoquinodimethane (NMP-TCNQ) etc. [2, 3] and high-temperature superconducting (HTSC) samples [4–6], both of which show M-I transitions [7, 8].

In some earlier papers [9a, 10], we have reported the method of measurement and the analysis of TEP of HTSC samples by using Hubbard model and also other existing models. TEP of HTSC samples by using Hubbard model has also been studied by Cooper *et al* [11]. The Hubbard Hamiltonian [11], which has been used in these studies, has the form

$$H = U \sum_i n_{i\uparrow} n_{i\downarrow} - t \sum_{i,\sigma} (C_{i,\sigma}^\dagger C_{i+1,\sigma} + \text{H.C.}), \quad (1)$$

where U is the on-site Coulomb interaction, t is the nearest-neighbour tight-binding transfer integral, $C_{i,\sigma}^\dagger$ ($C_{i,\sigma}$) creates (destroys) an electron of spin σ at the i th site, and $n_{i,\sigma} = C_{i,\sigma}^\dagger C_{i,\sigma}$ is the corresponding number operator with $n_i = n_{i\uparrow} + n_{i\downarrow}$.

A systematic analysis of the results of these studies [9a–11] leads to the following conclusions:

- (1) For some hole-doped HTSC systems, e.g., La-214 [11] and Bi-2212 [9a], the experimental data on TEP at low carrier (hole) concentration can be explained

reasonably well on the basis of Hubbard model but marked deviations occur at higher concentrations.

- (2) For some other hole-doped HTSC systems, e.g., Tl-2212 [10] a large difference between theoretical and experimental values are observed even at low carrier concentrations.

These findings show that Hubbard model as used in these studies has only limited success. One of the shortcomings of this model is the neglect of the intermolecular electron repulsion in the Hamiltonian given by eq. (1), which, as has been shown by Kwak and Beni [12] in the study of TEP of conducting salts of organic compounds, e.g., NMP-TCNQ etc., has significant influence on the TEP of these samples. To take account of the influence of the intermolecular electron repulsion, Kwak and Beni [12], have modified the Hamiltonian given by eq. (1) to the form

$$H = U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_i n_i n_{i+1} - t \sum_{i,\sigma} (C_{i,\sigma}^\dagger C_{i+1,\sigma} + \text{H.C.}), \quad (2)$$

where V represents the intermolecular electron repulsion. This modified form of the Hamiltonian has often been referred to as the extended Hubbard model and it is this form that has been used in our present study of TEP of HTSC samples. However, as mentioned, the study of Kwak and Beni [12] is restricted to conducting salts of NMP-TCNQ only and therefore our first objective is to use the Hamiltonian of eq. (2) in the study of HTSC samples. The logic behind this investigation is that since both NMP-TCNQ and HTSC samples show M-I transitions [7, 8] we expect the extended Hubbard model of Kwak and Beni [12] to be equally applicable in the study of TEP of HTSC samples. However, our study differs from Kwak and Beni in the limits of U . In the analysis of Kwak and Beni [12], to reduce the complexity of calculations, Kwak and Beni have considered the limit $U = \infty$ for the study of TEP of a Hubbard chain with arbitrary electron density and restricted their study to bands less than half-filled so that $n_i = 0$ or 1 . We, in this paper, use the extended Hubbard model in the limit $U \neq \infty$. The physical significance of this limit is to include also the cases for which n_i may have values other than 0 or 1. To our knowledge this study represents the first investigation on TEP of HTSC systems with extended Hubbard model in the limit $U \neq \infty$.

Our investigation shows that although the above form of the Hamiltonian, given by eq. (2), is successful in explaining the TEP behaviour of the insulating samples of electron-doped $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ system [13], it completely fails to reproduce the experimental results of hole-doped samples. However, if the V -dependent term in the Hamiltonian given by eq. (2) is taken as negative (attractive), we find that TEP behaviour of the insulating samples of our (hole-doped) Bi-2212 and Tl-2212 systems, as reported earlier [9a, 10] can be successfully explained. Thus our results suggest that for hole-doped samples the V -dependent term cannot be identified with intermolecular electron repulsion, but may be identified with an intersite attractive interaction as has been proposed by Mandal and Poddar *et al* [14] in the study of hole-doped systems using single band Hubbard model. Therefore, the negative V -dependent term may be considered as an effective intersite attractive interaction potential originating from electron-phonon interaction as proposed by Mandal *et al* [9b].

The section-wise breakup of the paper is as follows. In § 2 we give the basic formalism. In § 3 we discuss the application of the expression obtained for TEP in the study of

experimental data of TEP of the insulating samples of different hole- and electron-doped HTSC systems.

2. Thermoelectric power

Following the method of Beni [2] and restricting to a one-dimensional lattice and using Kubo's formulas [15] for the transport coefficient of a many-body system, TEP, S , may be defined [2] as

$$S = \frac{-S^{(2)}/S^{(1)} + \mu/e}{T}, \quad (3)$$

where e is the absolute value of electronic charge, μ , the chemical potential and

$$S^{(1)} = \frac{1}{2}\beta e^2 \int_0^\infty \langle v v(\tau) + v(\tau)v \rangle d\tau \quad (4)$$

and

$$S^{(2)} = \frac{1}{2}\beta e \int_0^\infty \langle Qv(\tau) + v(\tau)Q \rangle d\tau \quad (5)$$

are the correlation functions with

$$v(\tau) = e^{-i\tau H} v e^{i\tau H}. \quad (6)$$

In eqs (4) and (5), $\beta = (kT)^{-1}$, k is the Boltzmann constant, T is the absolute temperature, v and Q are the velocity and the energy-flux operators respectively and $\langle \dots \rangle$ represents thermal averages. The operators v and Q are given by

$$v = \text{Lt}_{q \rightarrow 0} \frac{1}{\hbar q} \sum_j [n_j, H] e^{iq(j\alpha)}, \quad (7)$$

and

$$Q = \text{Lt}_{q \rightarrow 0} \frac{1}{\hbar q} \sum_j [h_j, H] e^{iq(j\alpha)}, \quad (8)$$

where $\sum_j h_j = H$, $\sum_j n_j = N$, the total number operator, α , the lattice constant and q is determined by periodic boundary conditions.

Perturbation theory has been used to determine the correlation functions $S^{(1)}$ and $S^{(2)}$. Using the Hamiltonian given by eq. (2) in eqs (7) and (8) one obtains

$$v = \frac{\alpha t}{i\hbar} \sum_{i,\sigma} C_{i,\sigma}^\dagger C_{i-1,\sigma} + \text{H.C.}, \quad (9)$$

and

$$Q = \frac{U\alpha t}{i\hbar} \sum_{i,\sigma} n_{i,-\sigma} C_{i,\sigma}^\dagger C_{i-1,\sigma} + \text{H.C.} \\ + \frac{iV\alpha t}{\hbar} \sum_{i,\sigma} C_{i,\sigma}^\dagger C_{i+1,\sigma} (n_{i-1,\sigma} + n_{i+2,\sigma}) + \text{H.C.}, \quad (10)$$

where the t^2 -terms have been dropped, as usually done in the narrow-band approximation. Using the same approximation, the full Hamiltonian H in $S^{(1)}$ and $S^{(2)}$ may be replaced by the unperturbed Hamiltonian

$$H_0 = U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_i n_i n_{i+1}. \quad (11)$$

Using eqs (4)–(6), the expression for $S^{(2)}/S^{(1)}$ has been found to be

$$\frac{eS^{(2)}}{S^{(1)}} = \frac{\int_0^\infty d\tau \text{Tr}[e^{-\beta(H_0 - \mu \sum_i n_i)} (Qe^{-iH_0\tau} v e^{iH_0\tau} + e^{-iH_0\tau} v e^{iH_0\tau} Q)]}{\int_0^\infty d\tau \text{Tr}[e^{-\beta(H_0 - \mu \sum_i n_i)} (v e^{-iH_0\tau} v e^{iH_0\tau} + e^{-iH_0\tau} v e^{iH_0\tau} v)]}. \quad (12)$$

The traces of the above equation may be obtained in a straight forward way by using

$$e^{-iH_0\tau} C_{j,\sigma} e^{iH_0\tau} = e^{i\tau\{Un_{j-\sigma} + V(n_{j-1,\sigma} + n_{j+1,\sigma})\}} C_{j,\sigma}. \quad (13)$$

Considering only four adjacent sites $|i-1, i, i+1, i+2\rangle$ for the calculation of the traces and after some lengthy algebra we obtain from eq. (12)

$$\begin{aligned} \frac{eS^{(2)}}{S^{(1)}} = & U \{ x^2 e^{-\beta U - 2\beta V} + x^3 (e^{-2\beta U - 5\beta V} + e^{-\beta U - 4\beta V}) + x^4 e^{-2\beta U - 6\beta V} \} / \\ & \{ 1 + x(1 + e^{-\beta U - \beta V}) + x^2 (e^{-\beta U - \beta V} + e^{-\beta U - 3\beta V}) \\ & + x^3 (e^{-2\beta U - 4\beta V} + e^{-\beta U - 4\beta V} + x^4 e^{-2\beta U - 6\beta V}) \}, \end{aligned} \quad (14)$$

where $x = e^{\beta\mu}$. Using (14) in (3) we obtain,

$$\begin{aligned} S = & -\frac{k}{e} [\beta U \{ x^2 e^{-\beta U - 2\beta V} + x^3 (e^{-2\beta U - 5\beta V} + e^{-\beta U - 4\beta V}) + x^4 e^{-2\beta U - 6\beta V} \} / \\ & \{ 1 + x(1 + e^{-\beta U - \beta V}) + x^2 (e^{-\beta U - \beta V} + e^{-\beta U - 3\beta V}) \\ & + x^3 (e^{-2\beta U - 4\beta V} + e^{-\beta U - 4\beta V} + x^4 e^{-2\beta U - 6\beta V}) \} - \ln x]. \end{aligned} \quad (15)$$

This is the expression for TEP of extended Hubbard model in the limit $U \neq \infty$. It may be noted that if one uses $V = 0$ in eq. (15), the final expression reduces to the TEP of the narrow-band Hubbard chain at arbitrary electron density as obtained by Beni (eq. (12), [2]).

For the determination of S , we also need an expression for the chemical potential, which depends on the grand-partition function. To derive the expression for grand-partition function we consider the lattice as a one dimensional chain and each lattice site to have four possible states, $|00\rangle$, $|0\uparrow\rangle$, $|0\downarrow\rangle$ and $|\uparrow\downarrow\rangle$. Also we consider only the nearest neighbours and each of the nearest neighbours to have only $|0\uparrow\rangle$ or $|0\downarrow\rangle$ configuration, i.e., the nearest neighbours have only one electron per site. Under this condition the grand-partition function has been found to be

$$Z = (1 + 4xe^{-\beta V} + 2x^2 e^{-2\beta V - \beta U})^N = z^N, \quad (16)$$

where N is the number of lattice sites. The number condition is given by

$$\frac{\partial z}{\partial x} = \rho \frac{z}{x}, \quad (17)$$

where $\rho = N_e/N$ is the electron density and N_e is the number of electrons. From eqs (16) and (17) we obtain

$$x = \frac{-(1 - \rho)e^{-\beta V} + \{(1 - \rho)^2 e^{-2\beta V} + (\rho/2)(2 - \rho)e^{-\beta U - 2\beta V}\}^{1/2}}{(2 - \rho)e^{-\beta U - 2\beta V}}. \quad (18)$$

This equation, together with eq. (15), completes the determination of S .

We now use the above results for the analysis of TEP of HTSC samples. For HTSC samples $U \cong 5 \text{ eV}$ [9b, 14, 16]. This shows that U is very large for these samples compared to the value of kT at room temperature ($kT = 0.026 \text{ eV}$ at $T = 300 \text{ K}$). If we use $U \gg kT$ in eqs (15) and (18), they reduce to

$$S = \frac{k}{e} \ln x \quad (19)$$

and

$$x = \frac{\rho}{4(1 - \rho)e^{-\beta V}} \quad (20)$$

respectively.

3. Results and discussion

The plots of S versus kT/V , as obtained from eq. (19) for different values of ρ (0.002, 0.004, 0.006 and 0.008) are shown in figure 1. The inset of the same figure shows

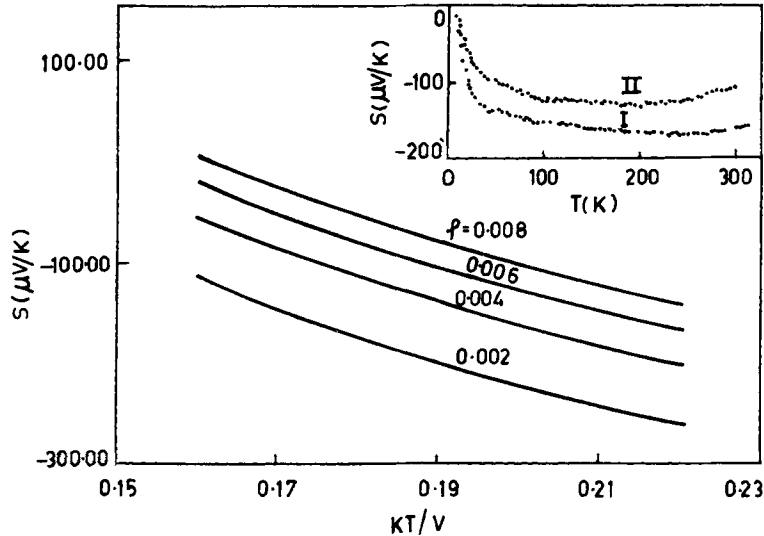


Figure 1. Theoretical curves of kT/V vs S for $\rho = 0.002, 0.004, 0.006$ and 0.008 obtained by using eq. (19). The experimental curves (reproduced from figure 1 of Xu *et al* [13]) of S vs T for $\text{Nd}_{0.99}\text{Ce}_{0.01}\text{CuO}_4$ and $\text{Nd}_{0.975}\text{Ce}_{0.025}\text{CuO}_4$, denoted by I and II respectively, are shown in the inset (see text).

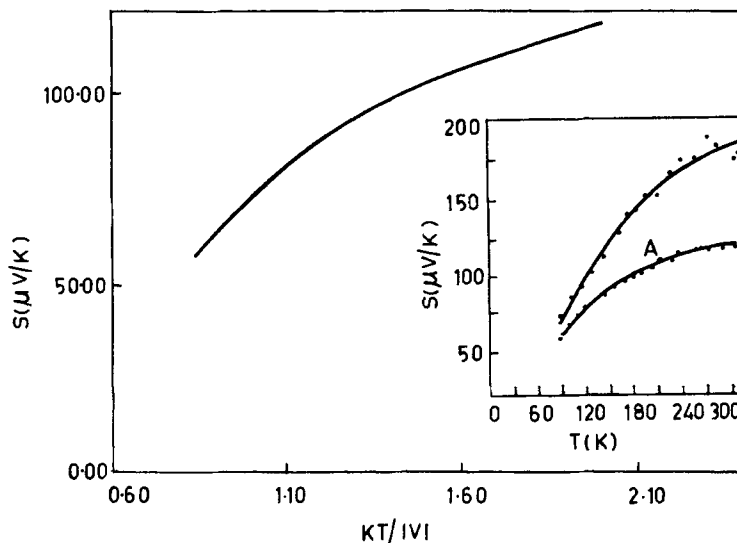


Figure 2. The variation of S with $kT/|V|$ for $\rho = 0.962$, calculated by using eq. (19). The curves A of inset shows the experimental curve of S vs T for $\text{Tl}_2\text{Ba}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_2\text{O}_{8+y}$ sample (reproduced from figure 4(c) of Keshri *et al* [10]).

the experimental curves of S versus T of figure 1 of Xu *et al* [13] for the insulating samples $\text{Nd}_{1.99}\text{Ce}_{0.01}\text{CuO}_4$ and $\text{Nd}_{1.975}\text{Ce}_{0.025}\text{CuO}_4$ of the electron-doped HTSC system $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$. It is seen that S versus kT/V curves of figure 1 resemble the experimental curves of inset of figure 1. This shows that eq. (19), which gives the expression for S in the limit $U \neq \infty$, is successful to produce the experimental results of the insulating samples of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ system. However, we have not come across any other data of temperature variation of TEP of electron-doped samples, with known carrier density, to test its general validity.

We have also used eq. (19) for the explanation of experimental curves of TEP of the insulating samples of our hole-doped HTSC systems, $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+y}$ [9a] and $\text{Tl}_2\text{Ba}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+y}$ [10]. The experimental data (figure 4c) of Keshri *et al* [10] of S versus T for the insulating sample $\text{Tl}_2\text{Ba}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_2\text{O}_{8+y}$ has been shown in the inset of figure 2 by curve A. The hole density ($p = 1 - \rho$) of this sample is 0.038 which corresponds to $\rho = 0.962$. The S versus $kT/|V|$ curve for $\rho = 0.962$, as obtained using eq. (19) with negative V , is shown in figure 2. It may be noted that the S versus $kT/|V|$ curve of figure 2 exactly resembles the curve A of inset of figure 2 for nearly the entire range of temperature (90–250 K) considered in this study. Figure 2 may also be used to estimate the value of V for $\text{Tl}_2\text{Ba}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_2\text{O}_{8+y}$ sample in the temperature range of 90–250 K. By taking the value of S at any temperature T within this range from the inset of figure 2, the value of $kT/|V|$ corresponding to the same value of S within this range may be determined from figure 2. As T is known, the value of V is easily known. Following this procedure the value of V in the temperature interval $T = 90$ –250 K has been found to be -0.01 eV.

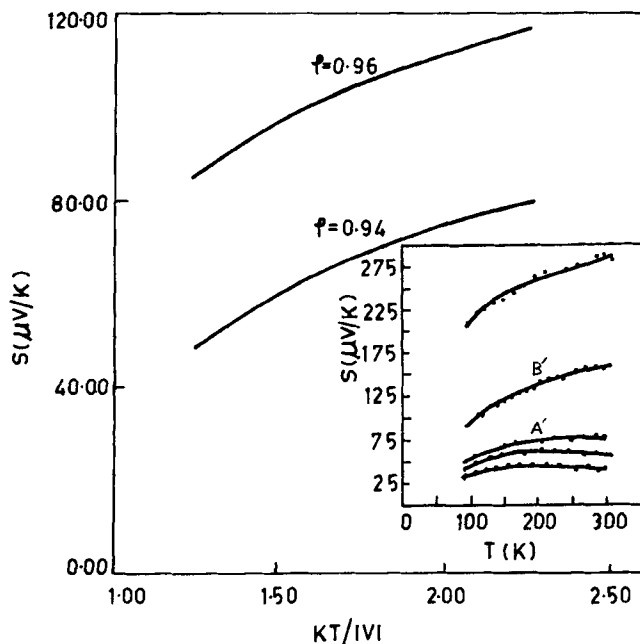


Figure 3. S vs $kT/|V|$ curves for $\rho = 0.94$ and 0.96 , calculated by using eq. (19). The curves A' and B' of the inset represent the experimental curves of S vs T for $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Y}_{0.6}\text{Cu}_2\text{O}_{8+y}$ and $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.3}\text{Y}_{0.7}\text{Cu}_2\text{O}_{8+y}$ samples respectively (reproduced from figure 4(b) of Mandal *et al* [9a]).

The experimental results of TEP (reproduced from figure 4(b) of [9a] of the insulating samples $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Y}_{0.6}\text{Cu}_2\text{O}_{8+y}$ (with $p = 0.06$, i.e. $\rho = 0.94$) and $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.3}\text{Y}_{0.7}\text{Cu}_2\text{O}_{8+y}$ with ($p = 0.04$, i.e. $\rho = 0.96$), are shown in the inset of figure 3 by the curves A' and B' respectively. The plots of S versus $kT/|V|$ for $\rho = 0.94$ and 0.96 , as obtained from eq. (19) with negative V , are shown in figure 3. A comparison of the plots of figure 3 with the plots of the inset of figure 3 shows that, in the low temperature region, eq. (19) with negative V is also successful to reproduce the experimental data of TEP of $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Y}_{0.6}\text{Cu}_2\text{O}_{8+y}$ and $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.3}\text{Y}_{0.7}\text{Cu}_2\text{O}_{8+y}$. By using the same procedure, as discussed for $\text{Tl}_2\text{Ba}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_2\text{O}_{8+y}$, the values of V , in the temperature interval $T = 90\text{--}150$ K have been found to be -0.007 eV and -0.005 eV for $\rho = 0.94$ and 0.96 respectively.

4. Conclusions

A new expression (eq. (19)) for TEP has been derived on the basis of extended Hubbard model in the limit $U \neq \infty$ for a one-dimensional lattice. The temperature dependence of TEP of the insulating samples of hole-doped HTSC systems can be explained reasonably well with this expression if the V -dependent term in the extended Hubbard model Hamiltonian is identified with the intersite attractive interaction potential due to electron-phonon interaction as proposed by Mandal *et al* [9a].

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