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Thermoelectric power of the extrinsic Mott semiconductor*

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The thermoelectric power for the non-half-filled band Mott semiconductor is calculated for the single-band Hubbard model both in the absence and presence of coupling of the electrons to the vibrational degrees of freedom of the sites. The results for the very-near-half-filled band are studied in detail and compared with results for a conventional semiconductor. The thermoelectric power changes sign as a function of temperature. The quarter-filled-band case is also discussed.

I. INTRODUCTION

In a previous paper,[1] the thermoelectric properties of a half-filled-band model were obtained in the very-narrow-bandwidth regime. The strong electron-electron interaction was accounted for as in the Hubbard model and intrasite vibrations were coupled to the electrons as well. The one-electron spectral weight function and the frequency-dependent conductivity were found to be Gaussian broadened.

The Gaussian behavior resulted from a short-time expansion of the vibrational displacement parameter. This approximation was used to simulate (with a single Einstein oscillator) the linewidths that would result from a more complete and realistic treatment of the many modes (including dispersion) of a planar organic molecule. The exact calculation of the spectral weight function for the Einstein oscillator spectrum yields an infinite number of δ-function peaks with spectral weights given by a Poisson distribution. A straightforward calculation yields

$$\frac{1}{2\pi}A(\omega)=e^{-\Gamma/2\Omega}\sum_{n=0}^{\infty}\frac{(\Gamma/2\Omega)^{n}}{n!}\,\delta(\omega-U_1+\tfrac{1}{2}\Gamma-n\Omega)+e^{-\Gamma/2\Omega}\sum_{n=0}^{\infty}\frac{(\Gamma/2\Omega)^{n}}{n!}\,\delta(\omega+\tfrac{1}{2}\Gamma+n\Omega)\;. \tag{1.1}$$

In Eq. (1.1), $A(\omega)$ is the usual on-site one-electron spectral weight function[1] and it has been evaluated at zero temperature. $\frac{1}{2}\Gamma$ is the small-polaron binding energy, Ω is the Einstein oscillator frequency, and $U_1=U-\Gamma$, where U is the intrasite mutual Coulomb repulsion. Equation (1.1) is to be compared with Eq. (3.18) of Paper I, which approximates the two δ-function series in Eq. (1.1) by Gaussian peaks at $\omega=U_1$ and $\omega=-\Gamma$. In Eq. (1.1) the δ-function peaks have spectral weights given by the Poisson distribution

$$e^{-\Gamma/2\Omega}(\Gamma/2\Omega)^{n}/n!\;.$$

For $\Gamma/2\Omega\gg 1$, the Poisson distribution is peaked at $n\simeq\Gamma/2\Omega$ and (its envelope) approximates a Gaussian function. We see that the largest spectral weights will be associated with $\omega=U_1$ and $\omega=-\Gamma$.

In Paper I, the thermoelectric power (TEP) was formulated in site space for the strongly interacting model Hamiltonian. An expression was derived for the energy current, and the TEP was calculated using the quantum statistical formalism.

The intrinsic Mott semiconductor contains, on the average, one electron per site. The TEP was calculated for this case both in the presence and absence of phonons, and it was found to be exactly zero in each case. In the case of a noninteracting one-dimensional cosine band, Chaikin *et al.*[2] noted that the TEP vanished for the half-filled band. On the other hand, it can easily be seen that the TEP is linear in T for the non-half-filled cosine band. This is the result expected for metals, and the half-filled band appears to be a pathological case.

Small deviations from the half-filled band can be expected even in high-purity materials. For the TEP, then, the study of the almost-half-filled band becomes important since the TEP can be sensitive to impurities and changes in carrier concentration. We also note that for some models of interest the TEP is zero in the perfect half-filled band—an apparent consequence of particle-hole symmetry. As we have seen, for the metallic case the TEP reveals its signature (linear T dependence) for the non-half-filled-band case. In this paper we calculate the TEP in the non-half-filled band of strongly correlated electrons.

We recall some pertinent results from Paper I. The TEP α is given by the relation

$$\alpha=-(1/T)(\mu/e-\Xi/\sigma)\;. \tag{1.2}$$

Here μ is the chemical potential, e is the electric charge (a negative quantity), and σ is the appropriately calculated dc conductivity. Ξ is a transport coefficient related to the electrical response associated with a thermal gradient according to the relation

$$\langle J\rangle = \sigma[E-(T/e)\nabla(\mu/T)] + \Xi(-\nabla T/T) . \qquad (1.3)$$

α is then the ratio of the effective electric field $E-(1/e)\nabla\mu$ to the thermal gradient ∇T that produces the former at zero net current ($\langle J\rangle = 0$). Unlike in Paper I, here we use the customary sign convention for the TEP.

The quantum-mechanical expression for Ξ is

$$\Xi = \frac{\beta}{2L}\int_{-\infty}^{\infty} d\tau\, \langle J J^q(\tau)\rangle . \qquad (1.4)$$

Here J is the one-dimensional current operator in site space:

$$J = ieab\sum_{l,\sigma}(C^\dagger_{l+1\,\sigma} C_{l\sigma} - C^\dagger_{l\sigma} C_{l+1\,\sigma}) , \qquad (1.5)$$

and J^q is the energy-current operator (derived in Paper I):

$$J^q = ib^2 a\sum_{l,\sigma}(C^\dagger_{l+2\,\sigma} C_{l\sigma} - C^\dagger_{l\sigma} C_{l+2\,\sigma})$$
$$+\frac{ibUa}{2}\sum_{l,\sigma}(C^\dagger_{l+1\,\sigma} C_{l\sigma} - C^\dagger_{l\sigma} C_{l+1\,\sigma})(n_{l+1-\sigma}+n_{l-\sigma})$$
$$+\frac{ibVa}{2}\sum_{l,\sigma}(C^\dagger_{l+1\,\sigma} C_{l\sigma} - C^\dagger_{l\sigma} C_{l+1\,\sigma})(Q_{l+1}+Q_l) . \qquad (1.6)$$

$\beta = (kT)^{-1}$ and L is the crystal volume. $J^q(\tau) = e^{iH\tau} J^q e^{-iH\tau}$ and the angular brackets denote the thermal average. The parameters in the electric and energy-current operators are related to the model Hamiltonian

$$H = \frac{\Omega}{2}\sum_l (P_l^2 + Q_l^2) + V\sum_l Q_l(n_{l\uparrow}+n_{l\downarrow})$$
$$+ U\sum_l n_{l\uparrow}n_{l\downarrow} - b\sum_{l,\sigma}(C^\dagger_{l+1\,\sigma} C_{l\sigma} + C^\dagger_{l\sigma} C_{l+1\,\sigma}) . \qquad (1.7)$$

Q_l and P_l are the coordinate and momentum operators that describe the vibrational degree of freedom at the lth molecular site; V is the coupling energy to the electrons; $n_{l\sigma}$ is the occupation-number operator for an electron on the lth site with spin σ; b is the one-electron transfer integral; $C_{l\sigma}$ destroys an electron on the lth site with spin σ; and $n_{l\sigma} = C^\dagger_{l\sigma} C_{l\sigma}$. The parameter a is the intersite spacing.

In Paper I, the bandwidth was taken to be the smallest energy in the model. The conductivity and TEP were calculated to second order in the bandwidth. This approach is consistent with the treatment of the single small polaron[3] in the nonadiabatic regime $\Omega > t$.

Our present calculation is a straightforward extension of the calculation of the TEP in Paper I. The chemical potential and the relevant thermal averages are calculated for the non-half-filled-band case.

In Sec. II the analysis is carried out for the case of $V=0$. This is just the narrow-band Hubbard model. It is found that α can be expressed as

$$\alpha = -(k/e)[x/(1+R^2 e^x) + \ln R] . \qquad (1.8)$$

Here k/e is the ratio of Boltzmann's constant to the electric charge ($\simeq -86\ \mu V/^\circ K$); $x=\beta U$; and

$$R = \frac{\xi + [\xi^2 + (1-\xi^2)e^{-x}]^{1/2}}{1-\xi} , \qquad (1.9)$$

where $\xi = \langle n_{l\uparrow} + n_{l\downarrow}\rangle - 1$. This expression is analyzed in detail for the nearly-half-filled band $|\xi| \ll 1$ and the quarter-filled band $\xi = -\frac{1}{2}$. Note that for the half-filled band, α vanishes identically.

The TEP in the presence of coupling to phonons is straightforwardly evaluated in the non-half-filled-band case by following the methods of Paper I and Sec. II. The resulting expression for α is

$$\alpha = -\frac{k}{e}\left(\ln\mathcal{R} + y\frac{(\mathcal{R}^2 e^y - \frac{1}{2})e^{-U_2^2/4S} + \mathcal{R}e^{y-\Gamma^2/4S} + \frac{1}{2}\mathcal{R}^2 e^{2y-U^2/4S}}{\mathcal{R}^2 e^{y-U_2^2/4S} + (\mathcal{R}e^y + \mathcal{R}^3 e^{2y})e^{-\Gamma^2/4S} + \mathcal{R}^2 e^{2y-U^2/4S}}\right) . \qquad (1.10)$$

Here

$$\mathcal{R} = \frac{\xi + [\xi^2 + (1-\xi^2)e^{-y}]^{1/2}}{1-\xi} , \qquad (1.11)$$

$y = \beta(U-\Gamma)$, $U_2 = U - 2\Gamma$, $S = \frac{1}{2}V^2\coth(\frac{1}{2}\beta\Omega)$, $\Gamma = V^2/\Omega$. Limiting cases of this expression are discussed and compared with those in Sec. II.

II. EXTRINSIC MOTT SEMICONDUCTOR

In the absence of vibrational coupling, the problem is that of calculating the transport coefficient Ξ to second order in b in the Hubbard model. The conductivity has been calculated to this order for the half-filled-band case by Bari and Kaplan,[4] and we shall extend their result to the non-half-filled-band case.

We must determine the chemical potential and partition function for the non-half-filled band for $b=0$. This is straightforwardly obtained by writing

$$Z = \mathrm{Tr}\exp\left[-\beta U\sum_l n_{l\uparrow}n_{l\downarrow} + \beta\mu\sum_l (n_{l\uparrow}+n_{l\downarrow})\right]$$
$$= (1 + 2e^{\beta\mu} + e^{2\beta\mu-\beta U})^{N_s} , \qquad (2.1)$$

where N_s is the number of sites. The average number of particles per site is just $N_s\langle n_{l\uparrow} + n_{l\downarrow}\rangle = \partial/\partial(\beta\mu)\ln Z$. We define ξ as the carrier-per-site deviation from half-filled band

$$\xi = \langle n_{l\uparrow} + n_{l\downarrow} \rangle - 1 \ . \qquad (2.2)$$

Then

$$1 + \xi = \frac{2\zeta + 2\zeta^2 e^{-\beta U}}{1 + 2\zeta + \zeta^2 e^{-\beta U}} \qquad (2.3)$$

or

$$\zeta = e^{\beta U} R \ , \qquad (2.4)$$

where R is given by Eq. (1.8) and $\zeta = e^{\beta\mu}$.

The dc conductivity for the non-half-filled band is straightforwardly obtained following the methods of Ref. 4, and is given by

$$\sigma = (4e^2 a^2 b^2 \beta\eta / Z^2)(Re^{\beta U} + R^3 e^{2\beta U}) \pi\delta(\omega) \ , \qquad (2.5)$$

where η is the number density. For the half-filled-band case, $R = e^{-\beta U/2}$ and Eq. (2.5) agrees with the result obtained in Ref. 4.

The transport coefficient Ξ in Eq. (1.4) is also straightforwardly evaluated. We use Eq. (1.6) for the energy current with $V = 0$. The second term in Eq. (1.6) leads to the contribution to Ξ that is second order in b. We find that

$$\Xi = (4ea^2 b^2 \beta\eta U / Z^2) R^3 e^{2\beta U} \pi\delta(\omega) \ . \qquad (2.6)$$

We combine Eqs. (2.5) and (2.6) and obtain

$$\frac{\Xi}{\sigma} = \frac{U}{e} \frac{R^3 e^{2\beta U}}{Re^{\beta U} + R^3 e^{2\beta U}} \ . \qquad (2.7)$$

The thermoelectric power follows from Eqs. (1.2), (2.4), and (2.7) and is given by Eq. (1.8).

In the very-near-half-filled-band case, $|\xi| \ll 1$, the TEP takes a particularly simple form in the high- and low-temperature regimes that are determined by [according to Eq. (1.9)] $\xi^2 e^{\beta U}$.

Case I. $|\xi| \ll 1$ *and* $\xi^2 \gg e^{-\beta U}$

This is the very-low-temperature regime and the TEP is given by

$$\alpha \simeq \mp (k/e) \ln|2\xi| \ . \qquad (2.8)$$

The upper (lower) sign corresponds to the slightly greater (less) than half-filled band, and since $e < 0$ the TEP is negative (positive) when the number of carriers is slightly greater (less) than the number of sites.

We note the appearance of twice the excess concentration of carriers in the semiconductor in Eq. (2.8). In analogy to the results for the ordinary semiconductor[5] one might have anticipated $(k/e)\ln\xi$ rather than $(k/e)\ln 2\xi$. However, the latter is a characteristic result of the narrow-band Hubbard model and the counting of states therein. This point was noted by Adler[6] in connection with the Hall effect in the Hubbard model.

Case II. $|\xi| \ll 1$ *and* $\xi^2 \ll e^{-\beta U}$

This is the high-temperature regime, and the TEP is given by

$$\alpha \simeq -(k\xi/e)(e^{\beta U/2} + 1)(1 - \tfrac{1}{2}\beta U) \ . \qquad (2.9)$$

We see that the thermoelectric power is positive (negative) for the slightly greater (less) than half-filled-band case.

Hence [by comparing Eqs. (2.8) and (2.9)], we see that the TEP must change sign as a function of temperature for the very-nearly-half-filled band.

In the case of a quarter-filled band, the TEP is negative and varies monotonically from $(k/e)\ln 2$ to $(k/e)\ln 3$ as kT increases from zero to infinity.

III. DISCUSSION

The thermoelectric power for the case of electron-phonon coupling is given by Eq. (1.10). In the limit $V \to 0$, Eq. (1.10) reduces to Eq. (1.8). However, the presence of vibrational coupling in the second term of Eq. (1.10) does not allow us to reduce that expression in the very-nearly-half-filled case to expressions as simple as Eqs. (2.8) and (2.9); i.e., the relative sizes of the vibrational overlap terms, $\exp(-\Gamma^2/4S)$, $\exp(-U_2^2/4S)$, and $\exp(-U^2/4S)$, must also be taken into account.

We study Eq. (1.8) for the particular choice of $\xi = e^{-6}$. In this case—the TEP in the absence of vibrational coupling—Eq. (1.8) varies monotonically from $\alpha \simeq -5.31k/|e|$ at $T = 0$ to $\alpha \simeq 0.002k/|e|$ at $T = \infty$. The TEP changes sign for $kT/U \simeq \frac{1}{2}$. In the low-temperature regime given by $\xi^2 \gg e^{-\beta U_1}$, we have also estimated the contribution to the TEP for the second term in Eq. (1.10). We find that for the choice of parameters taken in Paper I, $\Gamma = \Omega = \frac{1}{5} U$,

$$|\alpha - (k/e)\ln 2\xi| \approx \tfrac{1}{2} y \, e^{12-y} \ ,$$

where, since $\xi = e^{-6}$, $e^{-12} \gg e^{-y}$. Hence we see that the corrections to the TEP from the vibrational coupling are small in this regime and for this choice of parameters.

For the special case $U = \Gamma$, the TEP in the presence of vibrational coupling [Eq. (1.10)] becomes

$$\alpha = -(k/e)\ln[(1+\xi)/(1-\xi)] \ . \qquad (3.1)$$

For $\xi \ll 1$, $\alpha \simeq -2(k/e)\xi$ and the TEP is positive (negative) for the greater (less) than half-filled band. For the quarter-filled band, $\alpha = (k/e)\ln 3$.

In summary, we have calculated the TEP for an extrinsic Mott semiconductor in both the presence and absence of coupling of the electrons to intramolecular vibrations. Because of impurities and possibly incomplete charge transfer, TCNQ (tetracyanoquinodimethan) charge-transfer salts that are believed to be Mott insulators will not be exactly half-filled band systems. Therefore the study of the nearly-half-filled band becomes important, especially for the TEP. This is also true for some transition-metal oxides, such as lithium-doped nickel oxide.

Note added in proof. Equation (1.8) has been independently derived by G. Beni. G. Beni and C. Coll III have independently arrived at the result given in the Appendix. I thank Professor C. Coll III for informing me of these facts.

APPENDIX

The vanishing of the TEP under general conditions of particle-hole symmetry can be seen in the following way. From Eqs. (1.2) and (1.4) and with the conductivity σ given by

$$\sigma = \frac{\beta}{2L}\int_{-\infty}^{\infty} d\tau \langle J J(\tau)\rangle \,,$$

$$\alpha = \frac{1}{T\sigma}\frac{\beta}{2L}\int_{-\infty}^{\infty} d\tau \left\langle J\left(J^q(\tau) - \frac{\mu}{e}J(\tau)\right)\right\rangle \,. \qquad \text{(A1)}$$

we see that the TEP can be expressed as The integrand of Eq. (A1) contains the correlation of the electric current operator with a quantity which can be regarded as the free-energy current operator. Quite generally this quantity $(J^q - \mu/e)J)$ can be obtained from the free-energy density defined by

$$H - \mu N = \int dr[h(r) - \mu n(r)] \,, \qquad \text{(A2)}$$

where $h(r)$ is the energy density and $n(r)$ is the particle-number density; the integral is taken over the volume of the system. We then have the continuity equation

$$\frac{\partial}{\partial\tau}[h(r) - \mu n(r)] + \operatorname{div}\left(j^q(r) - \frac{\mu}{e}j(r)\right) = 0 \,, \qquad \text{(A3)}$$

where

$$J^q - \frac{\mu}{e}J = \int dr\left(j^q(r) - \frac{\mu}{e}j(r)\right) . \qquad \text{(A4)}$$

If $H - \mu N$ is particle-hole symmetric, then it follows from Eqs. (A2), (A3), and (A4) that $J^q - (\mu/e)J$ must also be particle-hole symmetric. The integrand of Eq. (A1) should not depend (is invariant) on whether the averages are calculated in terms of an electron representation or a hole representation; i.e.,

$$\langle J[J^q(\tau) - (\mu/e)J(\tau)]\rangle_{\text{electrons}} = \langle J[J^q(\tau) - (\mu/e)J(\tau)]\rangle_{\text{holes}} \,. \qquad \text{(A5)}$$

On the other hand, the electric current operator changes sign under a particle-hole transformation. Hence, given that $J^q(\tau) - (\mu/e)J(\tau)$ is invariant under a particle-hole transformation, we are led to the conclusion that the right-hand side of Eq. (A5) is also equal to the negative of the left-hand side and consequently that the correlation function is zero. Thus if $H - \mu N$ is invariant under a particle-hole transformation, the TEP is zero.

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[1] R. A. Bari, Phys. Rev. B 9, 4329 (1974); referred to here as Paper I.

[2] P. M. Chaikin, J. F. Kwak, T. E. Jones, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 31, 601 (1973).

[3] T. Holstein, Ann. Phys. (N.Y.) 8, 329 (1961); 8, 343 (1961).

[4] R. A. Bari and T. A. Kaplan, Phys. Rev. B 6, 4623 (1972).

[5] K. D. Schotte, Z. Phys. 196, 393 (1966).

[6] D. Adler, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1968), Vol. 21, p. 44.