Thermoelectric power of isolated narrow bands in the presence of correlation effects*

Adam Lewis
Gordon McKay Laboratory, Harvard University, Cambridge, Massachusetts 02138
(Received 7 July 1975)

The results of the one-dimensional thermoelectric power calculations of Bari and Beni in the regime where the correlation energy is much greater than kT are rederived using simpler arguments which are applicable to three-dimensional systems. The qualitative behavior of the thermopower at the lowest temperatures (kT much smaller than the bandwidth) is discussed.

Recently, Bari[1] and Beni[2] used a one-dimensional model to derive an expression for the thermoelectric power for systems in which the correlation energy U is large compared to the bandwidth. Starting with Hubbard's Hamiltonian, the calculation was based on Kubo's generalized transport equations. The purpose of this note is to rederive their results for $U \gg kT$ using simple thermodynamic arguments which are independent of the dimensionality of the system. Some consideration is given to one effect a finite bandwidth may have on the temperature dependence of the thermopower.

The probability that a state at energy ϵ is occupied by an electron is the Fermi-Dirac factor

$$f(\epsilon) = \{1 + N \exp[(\epsilon - \mu)/kT]\}^{-1}, \tag{1}$$

where N is the "impurity-level spin degeneracy"[3] and μ is the temperature-dependent chemical potential. In a band of zero width (the approximation used in Refs. 1 and 2) all states have an equal probability of occupancy ρ. Thus $\rho = f(\epsilon)$ and Eq. (1) gives

$$\epsilon - \mu = kT \ln[(1-\rho)/N\rho]. \tag{2}$$

If conduction occurs only via states in this one band, then the Peltier heat, the energy carried by each charge carrier, is just $\epsilon - \mu$. The Peltier coefficient Π is the Peltier heat per charge carrier,[4]

$$\Pi = (\epsilon - \mu)/e, \tag{3}$$

where e is the charge on the electron. The thermopower S is given by[5]

$$S = \Pi/T, \tag{4}$$

and for a band of zero width is therefore[6]

$$S = -(\epsilon - \mu)/|e|T. \tag{5}$$

This if the familiar result for the thermopower of a unipolar semiconductor[4] except the "kinetic-energy" term is missing because a zero bandwidth has been assumed. Combining (2) and (5) gives

$$S = -(k/|e|)\ln[(1-\rho)/N\rho]. \tag{6}$$

The density of states derived from Hubbard's Hamiltonian consists of two narrow bands. The singly occupied states form the lower band and the states with two electrons per site are higher in energy by U. In the limit $U/kT \to \infty$ (electrons cannot be thermally excited out of the lower band and the bands are "isolated") conduction occurs in one band only, and now ρ is the temperature-independent fractional occupancy of the appropriate band.

If the number of electrons is smaller than the number of sites, and in the limit $U/kT \to \infty$, only the lower Hubbard band is of interest. The appropriate value of the degeneracy factor N can be derived from the partition function [Eq. (2.1) of Ref. 1] for the zero-bandwidth Hubbard model,

$$Z = (1 + 2e^{\beta\mu} + e^{2\beta\mu - \beta U})^{N_s}, \tag{7}$$

where N_s is the number of sites, $\beta = (kT)^{-1}$, and ϵ is taken to be zero at the lower band. In the limit $U/kT \to \infty$, the number condition[1,2] applied to (7) gives

$$\rho = (1 + \tfrac{1}{2} e^{-\beta\mu})^{-1}. \tag{8}$$

Comparing (1) with (8) shows that $N = \frac{1}{2}$ for states in the lower Hubbard band. Thus,

$$S = -(k/|e|)\ln[(2-2\rho)/\rho], \tag{9}$$

which changes sign at $\rho = \frac{2}{3}$ and is Eq. (17) of Ref. 2. If the number of electrons exceeds the number of sites and $U/kT \to \infty$ only the upper band is of interest. In this case, the partition function (7) and number condition give $N = 2$ and

$$S = -(k/|e|)\ln[(1-\rho)/2\rho], \tag{10}$$

which is the same as Eq. (2.8) of Ref. 1.

Consider now one effect of making the bandwidth Δ finite, but keeping $U/kT \to \infty$. The thermopower for $kT \gg \Delta$ given by (6) is independent of the conduction mechanism. This will not be true at the lowest temperatures where $\Delta \gg kT$ since the probability of occupancy is not the same for each state. S will then depend on the details of the conduction mechanism and will be model dependent. Nevertheless, writing $g(E)$ for the density of states, it is found that

$$S \propto -T^n \left.\frac{\partial \ln g(E)}{\partial E}\right|_{\mu} \tag{11}$$

for conduction limited by phonon scattering in a normal metal[4] ($n=1$) and for conduction by phonon-assisted hopping in amorphous semiconductors[7] ($n=\frac{1}{2}$). It seems reasonable then that S for conduction at the lowest temperatures in a narrow band will have a similar dependence on $g(E)$. In this case, the derivative term can be very large and a thermopower of order 100 μV/K cannot be ruled out. Since the thermopower goes smoothly from its value at $kT \ll \Delta$ to its value at $kT \gg \Delta$, a consideration of (6) and (11) shows that a peak, a zero crossing[8] or both may occur in the plot of S versus temperature.

Although it is not the intention of this note to propose an isolated narrow band scheme for specific systems, it is interesting to point out that a peak near 20 K followed by a flattening out for $T \gtrsim 100$ K has recently been reported[9] for the thermopower of the salt hexamethylene-tetraselenafulvalenium tetracyanoquinodimethanide (HMTSF-TCNQ). A zero crossing at 40 K followed by a tendency to level off near 200 K was reported[10] in the transverse (nonmetallic) direction of tetrahiafulvalene-tetracyanoquinodimethane (TTF-TCNQ). Finally, in measurements down to 50 K, the thermopower in both the metallic and transverse directions of the salt $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$ is temperature independent for $T > 150$ K but becomes more negative at lower temperatures.[11]

---

*Research supported by NSF Contracts Nos. DMR-7203020 and GH-38830X and the Joint Services Electronic Program Contract No. N00014-75-C-0648.

[1]R. A. Bari, Phys. Rev. B 10, 1560 (1974).
[2]G. Beni, Phys. Rev. B 10, 2186 (1974).
[3]J. S. Blakemore, *Semiconductor Statistics* (Pergamon, New York, 1962), p. 118ff.
[4]H. Fritzsche, Solid State Commun. 9, 1813 (1971).
[5]R. D. Barnard, *Thermoelectricity in Metals and Alloys* (Wiley, New York, 1972).
[6]Equation (5) was derived by G. L. Sewell [Phys. Rev. 129, 597 (1963)] for conduction by hopping in a narrow band.
[7]I. P. Zvyagin, Phys. Status Solidi B 58, 443 (1973).
[8]A zero crossing is predicted for S by the theory in Refs. 1 and 2 for $\Delta = 0$ at $kT \sim \frac{1}{2}U$ for $\rho > \frac{2}{3}$ in the lower Hubbard band. The mechanism giving rise to the zero crossing at $kT \sim \Delta$ in this work has a different origin.
[9]A. N. Bloch, D. O. Cowan, K. Bechgaard, R. E. Pyle, R. H. Banks, and T. O. Poehler, Phys. Rev. Lett. 34, 1561 (1975).
[10]J. F. Kwak, P. M. Chaikin, A. A. Russel, A. F. Garito, and A. J. Heeger, Solid State Commun. 16, 729 (1975).
[11]D. Kuse and H. R. Zeller, Solid State Commun. 11, 355 (1972).