The B factor in multilayer thermionic refrigeration

C. B. Vining

ZT Services, 2203 Johns Circle, Auburn, Alabama 36830-7113

G. D. Mahan

Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996-1200, and Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6030

(Received 2 April 1999; accepted for publication 14 September 1999)

The figure of merit for multilayer thermionic refrigeration is discussed in terms of an effective B factor, which has a similar definition as the B factor in thermoelectrics. We show that high efficiencies for cooling or power generation are only obtained with very high values of this B factor. Such high values can only be attained because of the low thermal conductivity of multilayers. The B factor for thermionics is usually less than the one for thermoelectrics. © 1999 American Institute of Physics. [S0021-8979(99)05824-7]

I. INTRODUCTION

Solid state refrigeration has traditionally used thermoelectric materials. ^{1,2} The efficiency of the refrigerator is determined by the dimensionless figure of merit ZT= $\sigma TS^2/K$, where σ is the electrical conductivity, K is the thermal conductivity, and S is the Seebeck coefficient. Increasing ZT increases the efficiency of the refrigerator. Chasmar and Stratton³ showed that ZT, in turn, was determined by a dimensionless parameter which they called β but is now called B. It will be defined below, but depends upon electron mobilities, effective masses, etc. The larger the value of B, then the larger is ZT and the larger is the efficiency.

Recently, one of us co-invented the concept of multilayer thermionic emission as a possible solid state refrigerator.^{4,5} It is a form of evaporative cooling. Electrons which are thermally excited above an energy barrier are swept away by a small voltage. In a solid state environment, the efficiency is relatively high if the temperature differences are small across a single barrier. Macroscopic cooling is obtained by having multiple barriers. Because the temperature and voltage difference across each barrier are small, the equations of thermionic emission can be linearized and become ordinary differential equations. In that limit, one can make an analogy between thermionic cooling and thermoelectric cooling.⁵ In Refs. 4 and 5 it was shown that one could define an effective ZT for multilayer thermionic cooling. Here we wish to show that one can also define an effective B parameter for this system. Relatively high efficiencies are obtained only for high values of B. That is, the thermionic cooling is more efficient than the thermoelectric cooling only if the effective B parameter is higher. We denote these parameters as B_{TE} and B_{TI} for the thermoelectric and thermionic cooling, respectively.

II. B FACTORS

From Refs. 4 and 5 the effective figure of merit for multilayer thermionic cooling is

$$ZT = \frac{(b+2)^2}{2 + Z_0 e^b},\tag{1}$$

$$\frac{1}{Z_0} = B_{\text{TI}} = \frac{m^* k_B (k_B T)^2 L}{2 \,\pi^2 \hbar^3 K_L},\tag{2}$$

where L is the thickness of a single layer, K_L is the thermal conductivity of the lattice, and $b = e \phi/k_B T$ where $e \phi$ is the work function in thermionic emission. The similar equation for thermoelectrics^{2,6} for a semiconductor with nondegenerate statistics is

$$ZT = \frac{(2-\eta)^2}{2 + e^{-\eta}/B_{\rm TF}},\tag{3}$$

$$B_{\rm TE} = \frac{m^* k_B (k_B T)^2 \lambda_T}{2 \, \pi^{3/2} \hbar^3 K_I},\tag{4}$$

$$\lambda_T = \tau v_T = \tau \sqrt{\frac{2k_B T}{m^*}},\tag{5}$$

$$\frac{B_{\rm TI}}{B_{\rm TE}} = \frac{L}{\lambda_T \sqrt{\pi}},\tag{6}$$

where $\eta = \mu/k_BT$ and μ is the chemical potential of the semiconductor in relation to the band edge. The parameter B_{TE} is that of Chasmar and Stratton³ for a thermoelectric material with nondegenerate statistics. The other parameters are: λ_T is the electron mean free path, v_T is the thermal velocity, and τ is the average lifetime for scattering. The choice of v_T for thermal velocity is somewhat arbitrary, but the conclusions do not change if we use other choices.

The two formulas (1) and (3) have identical structure. The coefficients $-\eta$ and b are varied to optimize ZT, so that $-\eta$ and b wind up with similar values of one to three.

Multilayer thermionic refrigeration only works if the electrons traverse the barrier layer ballistically, which suggests that $L < \lambda_T$. Then $B_{TI} < B_{TE}$ and the B factor for thermionic cooling is not larger than for a similar thermoelectric device with the same thermal conductivity.

There are, however, other differences in the theory of thermoelectrics and thermionics. Let us examine Eq. (3) in more detail. The figure of merit for thermoelectric materials with nondegenerate statistics is called $(ZT)_n$ and is taken from Ref. 3

$$(ZT)_n = \frac{[(\nu + 5/2) - \eta]^2}{(\nu + 5/2) + e^{-\eta}/B_{TE}},\tag{7}$$

where ν is a parameter which describes the energy dependence of the electron lifetime $(\tau(E) \propto E^{\nu})$. If the important scattering is from impurities, then the mean free path is $1/\lambda = n_i \sigma$ where n_i is the impurity concentration and σ is the cross section. If the cross section is a constant, independent of electron energy, then the lifetime is $1/\tau = n_i \sigma v_k$, where $v_k \propto \sqrt{E}$ is the velocity. Note that scattering theory requires that σ has to be a constant for low energy scatterers. However, there could be energy variation for scattering by energetic particles. The choice $\nu = -1/2$ does best fit the data of Seebeck versus doping. In this case $\nu = -1/2$, $\nu + 5/2 = 2$ and the two formulas (1) and (7) are remarkably similar if we map $\eta \rightarrow -b$.

There is a problem with this mapping. Neither (1) nor (6) are accurate in all cases of interest. Equation (1) fails when the effective work function is either too large or negative. When the work function is sufficiently large $(b \ge 1)$, Eq. (1) is unreliable because it neglects intrinsic carriers in the barrier regions. In the case that b < 0, carriers become trapped in an energy well rather than excited over them. In a roughly similar way, Eq. (6) fails when the chemical potential becomes too negative or too positive. When it is very negative $(\mu \le k_B T)$, minority carrier contributions become important. In the case $\mu > 0$ degenerate statistics prevail. Both effects are neglected in Eq. (6). Nonetheless, the B factor for thermionics is not going to be bigger than the B factor of thermoelectrics.

III. DISCUSSION

Recent theoretical⁸⁻¹⁰ and experimental¹¹⁻¹³ work has shown that the phonon thermal conductivity K_L in multilayers, perpendicular to the layers, can be as much as ten times smaller than the thermal conductivity of the materials in the layers. This result was predicted theoretically and has been confirmed in several experiments. For materials with very low thermal conductivity, as typically used in thermoelectrics, the reduction in the multilayer is only a factor of 3 or 4. The increased thermal resistance is due to the thermal impedance of the interfaces.

This large decrease in K_L has the potential to significantly increase the efficiency of solid state refrigerators. In Eq. (4) the phonon part of the thermal conductivity enters directly into the denominator of the formula for $B_{\rm TE}$ and $B_{\rm TI}$. Reducing K_L by a factor of 3 raises $B_{\rm TE,TI}$ by this same factor. The value of ZT increases by a similar factor. This is the origin of the large increase in the efficiency predicted for multilayer thermionic emission.

If one could build a multilayer device without potential barriers, so that it electronically behaved as a three dimensional homogeneous device, then one would get a similar enhancement of B in thermoelectrics. Such an enhancement was reported in Ref. 14 for superlattices of Bi_2Te_3/Sb_2Te_3 . They report isotropic conduction which suggests no barriers due to band offsets. Yet the thermal conductivity is reported to be very low due to interface resistance. The effect of this device is that the effective B is greatly increased, and values of ZT are in the range 3-4. When one builds a multilayer thermoelectric device without barriers due to band offsets, it has a very high effective value of ZT.

However, such multilayers usually also introduce periodic potential barriers to the flow of electrons and holes. These barriers exist in both semiconductor multilayers, due to band offsets, as well as in alternate layers of metals and semiconductors due to Schottky barriers. Such barriers will impede the flow of electrons, and hence reduce the electrical conductivity. However, thermionic emission uses these periodic potential barriers as a method of filtering out the low energy electrons. ^{15,16} Only the energetic electrons can move in the direction perpendicular to the layers, and hence they provide efficient refrigeration.

Thus the essential feature of multilayer thermionic refrigeration is to utilize the very low values of thermal conductivity found for multilayers when the heat flow is perpendicular to the layers. If the interfaces generate barriers to the flow of electrons, the thermionic emission modeling shows the optimum value for the barrier height $e \phi(b=e\phi/k_BT)$ which is needed for efficient refrigeration and power generation.

G.D.M. acknowledges a research Grant from the Office of Naval Research (N00014-98-1-0741-Mahan), research support from the University of Tennessee, and from Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp. for the U.S. Department of Energy under Contract No. DE-AC05-96OR22464.

- ¹G. D. Mahan, B. C. Sales, and J. Sharp, Phys. Today (March, 1997).
- ²G. D. Mahan, in *Solid State Physics*, edited by H. Ehrenreich and F. Spaepen (Academic, New York, 1998), Vol. 51, p. 81.
- ³R. P. Chasmar and R. Stratton, J. Electron. Control 7, 52 (1959).
- ⁴G. D. Mahan and L. M. Woods, Phys. Rev. Lett. 80, 4016 (1998).
- ⁵G. D. Mahan, J. O. Sofo, and M. Bartkowiak, J. Appl. Phys. 83, 4683 (1998).
- ⁶H. J. Goldsmid, Electronic Refrigeration (Pion, London, 1986).
- ⁷G. D. Mahan, J. Appl. Phys. 65, 1578 (1989).
- ⁸P. Hyldgaard and G. D. Mahan, Phys. Rev. B 56, 10754 (1997).
- ⁹G. Chen, Phys. Rev. B 57, 14958 (1998).
- ¹⁰G. Chen and M. Neagu, Appl. Phys. Lett. 71, 2761 (1997).
- ¹¹G. Chen, C. L. Tien, X. Wu, and J. S. Smith, J. Heat Transfer **116**, 325 (1994).
- ¹²W. S. Capinski and H. J. Maris, Physica B **219–220**, 699 (1996).
- ¹³ S. M. Lee, D. G. Cahill, and R. Venkatasubramanian, Appl. Phys. Lett. **70**, 2957 (1997).
- ¹⁴ R. Venkatasubramanian and T. Colpits, Mater. Res. Soc. Symp. Proc. 478, 73 (1997).
- ¹⁵ L. W. Whitlow and T. Hirano, Proceedings of the 12th International Conference on Thermoelectrics (edited by K. Masuura, Japan, 1993), 1994, pp. 39-43.
- ¹⁶D. M. Rowe and G. Min, Proceedings of the 13th International Conference on Thermoelectrics edited by B. Mathiprakasam and P. Heeman (AIP, New York, 1994), #316, pp. 339-342.