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SUPERLATTICES IN THERMOELECTRIC APPLICATIONS

J. O. Sofo and G. D. Mahan

DEPARTMENT OF PHYSICS AND ASTRONOMY,
UNIVERSITY OF TENNESSEE, KNOXVILLE, TN

and

SOLID STATE DIVISION
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Superlattices in Thermoelectric Applications

J. O. Sofo and G. D. Mahan

Solid State Division, Oak Ridge National Laboratory, P.O.Box 2008, Oak Ridge, TN 37831-6030,

and

Department of Physics and Astronomy, The University of Tennessee, Knoxville, TN 37996-1200

Abstract

The electrical conductivity, thermopower and the electronic contribution to the thermal conductivity of a superlattice, are calculated with the electric field and the thermal gradient applied parallel to the interfaces. Tunneling between quantum wells is included. The broadening of the lowest subband when the period of the superlattice is decreased produces a reduction of the thermoelectric figure of merit. However, we found that a moderate increase of the figure of merit may be expected for intermediate values of the period, due to the enhancement of the density of states produced by the superlattice structure.

During the last two years, several papers were published analyzing the application of quantum well superlattices to improve the efficiency of thermoelectric coolers.[1, 2, 3, 4] Experimental work is being done seeking the confirmation of the theoretical predictions.[5, 6] To our knowledge, the first proposal that a superlattice structure may be a highly efficient thermoelement was done by Mensah and Kangah.[1] However, calculation of the transport properties of superlattices have been previously reported.[7,, 8, 9] The first quantitative result was given by Hicks[2] where a huge increase of the thermoelectric figure of merit is predicted as the width of the quantum wells is reduced. The thermoelectric figure of merit is a measure of the quality of a material to be used as a thermoelement[10] and is defined as

$$Z = \frac{S^2\,\sigma}{\kappa}\,, \tag{1}$$

where S is the thermopower, σ the electrical conductivity and κ the thermal conductivity. Z has units of inverse temperature and is usually referred as the dimensionless quantity ZT where T is the absolute temperature. Hicks' calculation was welcome by both the workers on thermoelectric devices and those in the field of semiconductors superlattices. The former are seeking for creative ideas to break the traditional barrier of $ZT \approx 1$, and the latter welcome a new application for a very well developed technique.

In this communication, we want to revisit the calculation of the transport coefficients involved in Eq. (1) for a superlattice. We incorporate two elements in the model of superlattice that change the prediction of a *huge* increase in the thermoelectric figure of merit. These are the tunneling probability between quantum wells and the finite thermal conductivity of the material forming the barriers. The quantum mixing between quantum wells produce a broadening of the lowest subband that changes the density of states from a two-dimensional shape to a three-dimensional one. On the other hand, as was pointed out by Mahan and Lyon,[4] the finite thermal conductivity of the barriers produces a parasitic effect of backflow of heat, without helping the thermoelectric pumping. As a result, we found that as we decrease the period of the superlattice, there is a moderate increase in ZT until it reaches a maximum, and a further reduction of the period reduces the figure of merit.

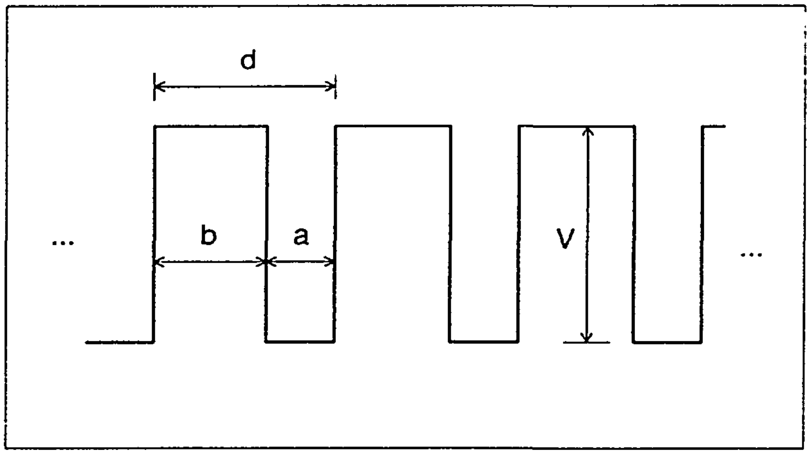

Figure 1: Potential profile for the conduction band of the superlattice used in the calculation.

The dynamics of electrons in the conduction band of the superlattice is described using the envelope function approximation.[11] Thus, neglecting the electron-electron interaction, the problem is reduced to the study of electrons with effective mass components m_x, m_y, and m_z in a potential profile as shown in Fig. 1. The energy levels in the superlattice are given by

$$\varepsilon_s(k_x, k_y, k_z) = \frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 k_y^2}{2m_y} + E_s(k_z) \ , \tag{2}$$

where k_x and k_y are the wave vectors in the x and y direction (parallel to the plane of the interfaces) and $E_s(k_z)$ is the dispersion relation of the subband s of the superlattice. This dispersion relation is given by the solutions to the equation[12]

$$\cos(k_z d) = \cos(qa)\ \cosh(Kb) + \frac{K^2 - q^2}{2qK}\ \sin(qa)\ \sinh(Kb) \ , \tag{3}$$

where

$$q = \left(\frac{2m_z E}{\hbar^2}\right)^{1/2} \quad \text{and} \quad K = \left[\frac{2m_z(V - E)}{\hbar^2}\right]^{1/2} \ , \tag{4}$$

for energies E lower than the conduction band offset V. Here a is the well width, b the barriers width and $d = a + b$ the superlattice period, as illustrated in Fig. 1.

The low field transport coefficients are defined by

$$\begin{aligned} \mathrm{J} &= \sigma \mathrm{E} + \sigma S \nabla T \ , & (5) \\ \mathrm{J}_Q &= -T\sigma S \mathrm{E} - \kappa_0 \nabla T \ , & (6) \end{aligned}$$

where J is the electric current, J_Q the heat current, E the electric field, T the temperature, σ the electrical conductivity, and S the thermopower. The thermal conductivity, usually measured at zero electric current, is given by

$$\kappa = \kappa_0 - T\sigma S^2 + \kappa_l \ , \tag{7}$$

where κ_l is the lattice contribution to the thermal conductivity. In the case of a superlattice this transport coefficients can be calculated as

$$\sigma = \frac{e^2}{4\pi^3} \sum_{s=0}^{\infty} \int_{-\infty}^{+\infty} dk_x \int_{-\infty}^{+\infty} dk_y \int_{-\pi/d}^{+\pi/d} dk_z\ \tau\, v_x^2 \left(-\frac{\partial f_0}{\partial \varepsilon}\right)_{\varepsilon=\varepsilon_s(\mathbf{k})} \ , \tag{8}$$

$$\sigma S = \frac{ek_B}{4\pi^3}\sum_{s=0}^{\infty}\int_{-\infty}^{+\infty} dk_x \int_{-\infty}^{-\infty} dk_y \int_{-\pi/d}^{+\pi/d} dk_z\, \tau\, v_x^2 \left(-\frac{\partial f_0}{\partial \varepsilon}\right)_{\varepsilon=\varepsilon_s(\mathrm{k})} \left(\frac{\varepsilon_s(\mathrm{k})-\mu}{k_B T}\right) , \tag{9}$$

$$\kappa_0 = \frac{k_B^2 T}{4\pi^3}\sum_{s=0}^{\infty}\int_{-\infty}^{+\infty} dk_x \int_{-\infty}^{-\infty} dk_y \int_{-\pi/d}^{+\pi/d} dk_z\, \tau\, v_x^2 \left(-\frac{\partial f_0}{\partial \varepsilon}\right)_{\varepsilon=\varepsilon_s(\mathrm{k})} \left(\frac{\varepsilon_s(\mathrm{k})-\mu}{k_B T}\right)^2 , \tag{10}$$

where e is the electron charge, f_0 the Fermi function, v_x the group velocity of the electron in the x direction, τ the relaxation time, k_B the Boltzmann constant, μ the chemical potential and we assume the electric field and the temperature gradient applied in the x direction. The summation runs over the different subbands produced by the superlattice structure. In what follows we will only consider the lowest energy band with $s = 0$.

We will calculate these coefficients in the simplest possible form in order to make more evident the effects produced by the superlattice structure. Assuming a constant relaxation time we can carry out the integration over the momentum components parallel to the interfaces, obtaining that,

$$\sigma = \frac{e\,\mu_x}{2\pi d}\left(\frac{2k_B T}{\hbar^2}\right)(m_x m_y)^{1/2}\, I_0(\mu, T) , \tag{11}$$

$$\sigma S = \frac{k_B\,\mu_x}{2\pi d}\left(\frac{2k_B T}{\hbar^2}\right)(m_x m_y)^{1/2}\, I_1(\mu, T) , \tag{12}$$

$$\kappa_0 = \frac{k_B \hbar^2 \tau}{4\pi d}\left(\frac{2k_B T}{\hbar^2}\right)^2 \left(\frac{m_y}{m_x}\right)^{1/2} I_2(\mu, T) : \tag{13}$$

where we have defined

$$I_0(\mu, T) \equiv \frac{1}{2\pi}\int_{-\pi}^{+\pi} dx\, F_0(\zeta) , \tag{14}$$

$$I_1(\mu, T) \equiv \frac{1}{2\pi}\int_{-\pi}^{+\pi} dx\, [2F_1(\zeta) - \zeta F_0(\zeta)] , \tag{15}$$

$$I_2(\mu, T) \equiv \frac{1}{2\pi}\int_{-\pi}^{+\pi} dx \left[3F_2(\zeta) - 4\zeta F_1(\zeta) + \zeta^2 F_0(\zeta)\right] , \tag{16}$$

with

$$\zeta = \frac{\mu - E_0(x/d)}{k_B T} .$$

We have used a notation as close as possible to the one used by Hicks [2] in order to facilitate the connection between both approaches. In the formulas above, $\mu_x = e\tau/m_x$ is the mobility in the x-direction and F_l the Fermi integrals defined by

$$F_l(\zeta) = \int_0^{\infty} dx \frac{x^l}{e^{(x-\zeta)} + 1} . \tag{17}$$

These Fermi integrals for integer l are related to the polylogarithms functions and can be easily evaluated.[13]

From the given formulas of the transport coefficients we obtain our first result. In the limit of decoupled quantum wells, i.e. when the barriers are wide (or the conduction band offset large) the lowest subband is flat, and we obtain expressions for the transport coefficients similar to those in Ref. [2] (Eqs. (12), (13), and (14)), with the difference that instead of having the width of the quantum well a in the denominator, our expressions have the period of the superlattice d. This difference gives the proper dependence of the transport coefficients on the parameters of the superlattice. Under the assumption of a constant relaxation time the conductivity can be written as $\sigma = \frac{e^2\tau}{m_x}\, n$ where n is the density of electrons. If the width of the well and the chemical potential are kept fixed while increasing the width of the barriers, the density of electrons n should decrease and in the same proportion the conductivity σ should decrease. This dependence is not reflected in the expressions of Ref. [2].

In order to calculate the thermoelectric figure of merit of the superlattice we need the lattice contribution to the thermal conductivity. Neglecting transversal heat flow across the interfaces,[4] the lattice thermal conductivity of the superlattice can be written as

$$\kappa_l = \frac{a\,\kappa_l^{(a)} + b\,\kappa_l^{(b)}}{a+b}\,, \tag{18}$$

where $\kappa_l^{(a)}$ and $\kappa_l^{(b)}$ are the lattice thermal conductivity of the well and barriers respectively.

The thermoelectric figure of merit can be calculated as

$$ZT = \frac{I_1^2/I_0}{I_2 - I_1^2/I_0 + 1/B'}\,, \tag{19}$$

where $I_n \equiv I_n(\mu, T)$ and

$$B' = \frac{1}{2\pi d}\left(\frac{2k_BT}{\hbar^2}\right)(m_x m_y)^{1/2}\,\frac{k_B^2 T \mu_x}{e\,\kappa_l}\,. \tag{20}$$

Again, in the case of a flat lowest subband, where

$$I_0 = F_0\,,$$

$$I_1 = 2F_1 - \zeta\, F_0\,,$$

and

$$I_2 = 3F_2 - 4\zeta\, F_1 + \zeta^2 F_0\,,$$

our result is similar to that of Ref. [2] but instead of the well width a in the denominator of B' we found the period of the superlattice d. We can obtain their result for B' if we assume a flat lowest subband and zero lattice thermal conductivity for the material forming the barriers of the superlattice. This situation is far from any experimental realization.

In what follows, all our results have been calculated for a superlattice where the wells are made of Bi_2Te_3 — one of the best thermoelectric materials known at room temperature.[2] We have chosen the orientation of the layers perpendicular to the a_0-axis of the material. Therefore, we use a mobility in the x direction $\mu_x = 1200$ cm^2/V sec, the effective mass in the direction of the superlattice is $m_z = 0.32 m_0$, where m_0 is the free electron mass. The other effective mass components have been taken as $m_x = 0.021 m_0$ and $m_y = 0.081 m_0$. The thermal conductivity for this layers $\kappa_l^{(a)} = 15$ mW/cm K is a reasonable value for Bi_2Te_3 at room temperature. For the material of the barrier we assume a conduction band offset $V = 1$ eV as a typical value for semiconductors. The results presented here does not depend in a critical way on the assumed value of this parameter.

As can be seen from our formulation, assuming $\kappa_l^{(b)} = 0$ is one of the possibles ways of avoiding the parasitic effect of the barriers. A way very difficult to realize in practice. This was previously discussed by Mahan and Lyon.[4]

Another way is to reduce the barrier width b in order to decrease the amount of material that do not contribute to the thermoelectric heat current. In Fig. 2 we show this effect. We plot the thermoelectric figure of merit times the temperature of the superlattice (ZT) as a function of the well width, for three different values of the barrier width b= 20, 45 and 90 Å. The calculation has been done for 100. 200

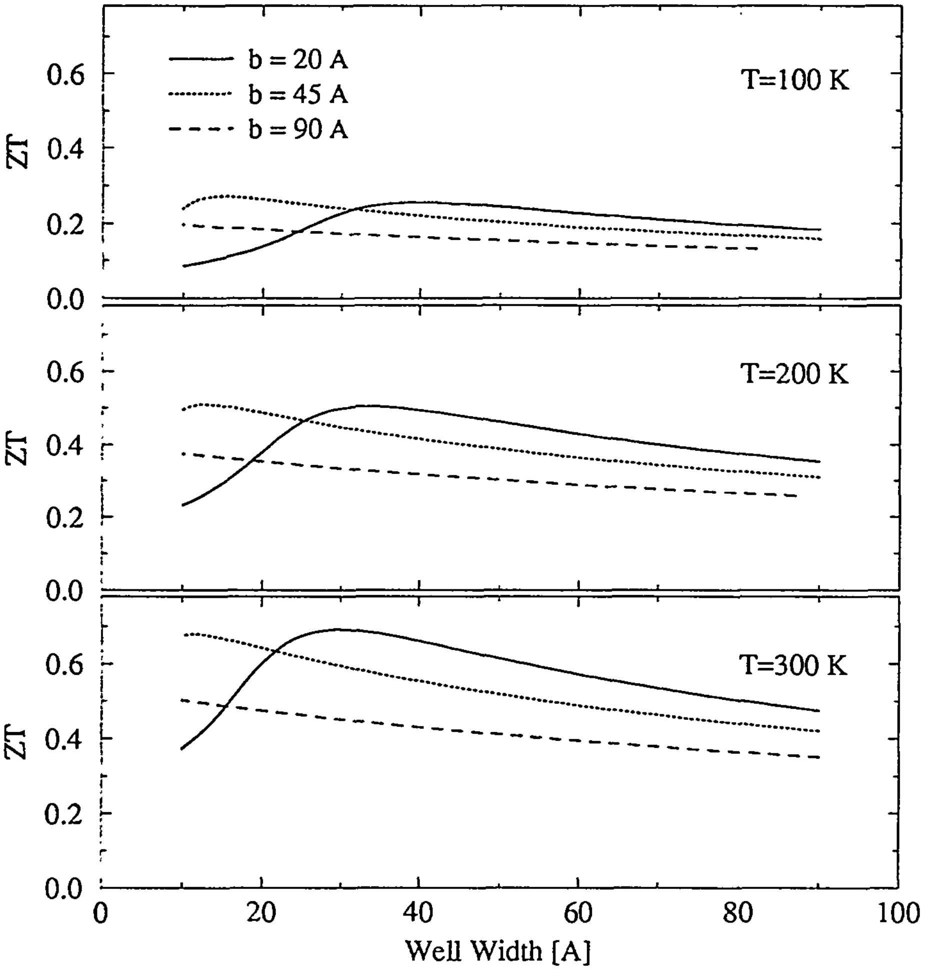

Figure 2: Thermoelectric figure of merit times the temperature (ZT) vs. the width of the well a for three different thicknesses of the barriers at temperature T=100, 200, and 300K. The lattice thermal conductivity is assumed to be the same for both materials.

and 300 K as indicated in the figure. The chemical potential has been adjusted in order to maximize the figure of merit in each case. We assume that the lattice thermal conductivity is the same in both layers. Except for the case of a barrier of 20 Å, the general behavior is an increase of ZT as we reduce the width of the wells a or the width of the barriers b. As long as the lowest subband can be considered as dispersionless (flat) reducing a or b reduces the period of the superlattice d, increasing B' and therefore, ZT. In our problem, the lowest subband can be considered flat when the chemical potential lies above its top at a distance grater than the typical thermal energy. A square density of states, like in a two-dimensional electron system, is very favorable for the thermoelectric efficiency. Electrons above and below the Fermi level have opposite contribution to the thermopower as can be seen in Eq. (9). Reducing the period of the superlattice without tunneling between quantum wells is as increasing the density of states without changing its squared shape. Therefore, this is a method of increasing the number of carriers per unit volume, without reducing the thermopower of the system. However, this method is impossible to be realized in this system. As can be seen from the curve corresponding to the thiner barriers (b=20 Å) ZT increases until the mixing between states in different quantum wells produces a broadening of the lowest subband, becoming a three dimensional density of states (as expected!) and reducing the thermoelectric figure of merit. As can be seen from Fig. 2, the behavior at the three temperatures shown is the same, with an overall reduction of the figure of merit as the temperature decreases.

To make more clear the argument presented in the last paragraph we present in Fig. 3(a) the behavior of ZT as a function of the barriers width b for a fixed wells width a=15 Å. The full line show the result of our calculation, while the dashed line shows the result of neglecting the tunneling between wells. Both approximation coincides when the barriers are thick and the figure of merit is low. When the barriers thickness decrease, the approximation of independent quantum wells shows a divergence because of the piling up of two-dimensional layers without quantum mixing. The proper consideration of the subband broadening gives a reduction of the figure of merit when the chemical potential enters into the three-dimensional like density of states of the lowest subband. This is shown in Fig. 3(b) where the short dashed lines represent the band edges of the lowest subband, and the full line is the chemical potential that maximizes ZT in each case. The conduction band offset is also shown as a long dashed line to set the proper scale of energies involved.

The other way of increasing the figure of merit of the superlattice is to reduce the lattice thermal conductivity of the barriers $\kappa_l^{(b)}$. However this may be difficult, considering that we want to use a good thermoelectric material in the well. The thermal conductivity of this layer will be low for a crystalline solid, of the order of the value we have used in our calculation ($\kappa_l^{(a)} \approx$10 mW/cm K). If we want to use for the barriers a material with a lattice thermal conductivity ten times lower than that, we will be searching in the range of values characteristic of polymers and not of crystalline solids.

Our calculation was done considering only the lowest subband of the superlattice because the well known fact that one band materials are better thermoelectrics. This assumption is confirmed in Fig. 4 where we plot ZT as function of the chemical potential in a superlattice with barriers width b=50 Å and well width a=50 Å, assuming a band offset of 1eV. In the figure we can see two peaks. The arrows show the subbands bottom. The first peak, much higher than the second, corresponds to the chemical potential near the first subband. The second peak appears when the chemical potential reaches the second subband. From the difference between both peaks it is clear that only the first subband has to be included in the search for good thermoelectric superlattices.

In summary, we have presented the calculation of the thermoelectric figure of merit for superlattices. We use a simple model in order to show the effects arising from the superlattice structure itself. We show that there is an improvement of the figure of merit, produced by the enhancement of the density of states at the bottom of the lowest subband. This enhancement is produced by the increase of the

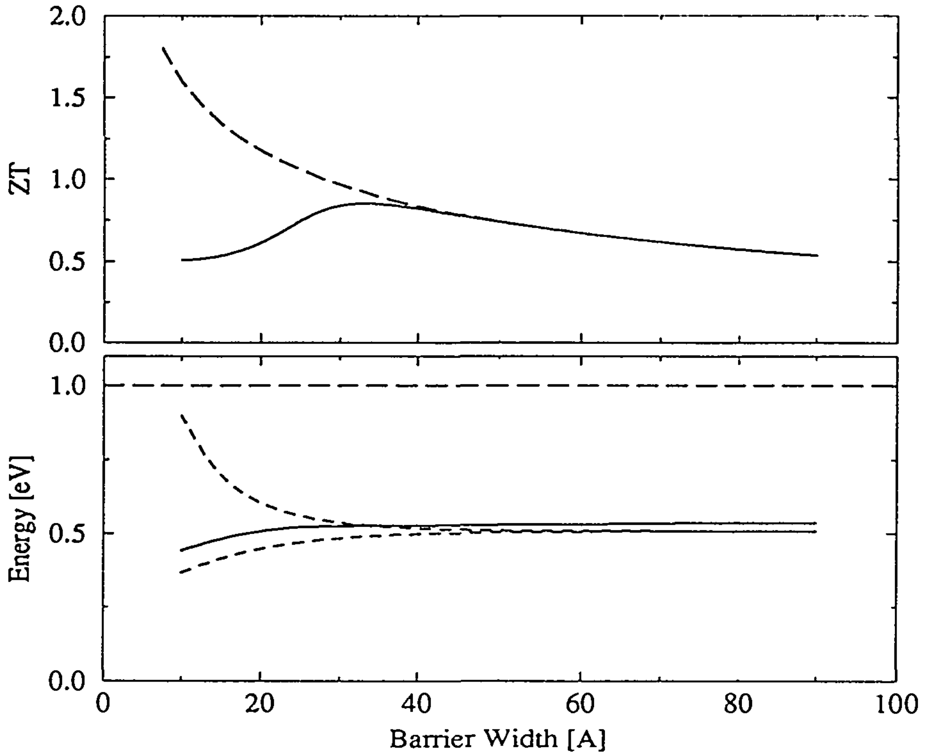

Figure 3: (a) ZT vs. barriers width b for a fixed well width a=15 Å. The dashed line is the result of neglecting the tunneling between quantum wells, considering the independent. Th efull line is the result of our calculation, considering the broadening of the lowest subband. (b) The chemical potential that maximizes ZT (full line) corresponding to the calculation shown in (a), displayed together with the lowest subband band edges (short dashed lines), to show the correlation between the reduction of ZT and the chemical potential entering between the limits of the subband.

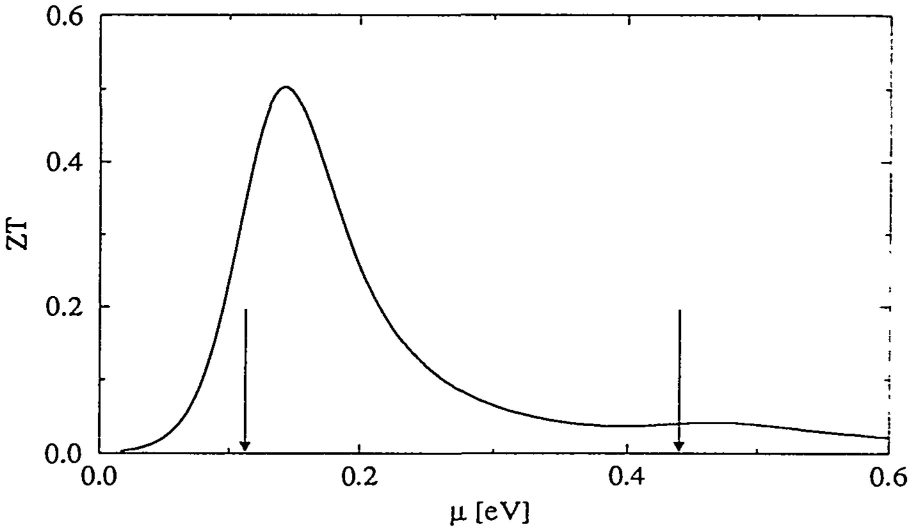

Figure 4: ZT vs. chemical potential for a superlattice. The arrows show the position of the subbands bottom edge. In the calculation the barriers and the wells are 50Åwidth. The temperature is 300 K and the band offset 1eV.

effective mass in the direction of the superlattice. The improvement is obtained by a reduction of the period of the superlattice. However, a further reduction of the period reduces ZT because of the broadening of the lowest subband, approaching a three-dimensional like density of states. From our calculation of the transport coefficients becomes clear that the correct normalization is given by the period of the superlattice and not by the width of the well. This is an important point to be considered in experimental works searching for the apparent a^{-1} behavior that emerges from the formulas given in Ref. [2].

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