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### Thermoelectric figure of merit as a function of carrier propagation angle in semiconducting superlattices

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Superlattices have been a fruitful approach for enhancing the figure of merit, ZT, of thermoelectric materials. Generally, superlattice transport is measured either parallel or perpendicular to the superlattice planes. We show here that the figure of merit is a function of carrier propagation angle in the superlattice and that ZT generically exhibits a maximum at an oblique angle, near  $\theta \approx \pi/6$ . © 2011 American Institute of Physics. [doi:10.1063/1.3633112]

Thermoelectric devices, which convert electric fields into thermal gradients and vice versa, hold great promise for increasing energy sustainability and providing cleaner forms of energy. To be economically competitive, the target for thermoelectric materials is that the figure of merit used to characterize efficiency should reach  $ZT \approx 3$ .<sup>1</sup> Approaches involving the use of thin-film structures,<sup>2</sup> such as those based on quantum-confinement effects,<sup>3</sup> phonon-blocking/electrontransmitting superlattices,<sup>4–6</sup> and heterostructures,<sup>7,8</sup> are promising candidates for ZT enhancement. Superlattices in particular have made great strides,<sup>9–15</sup> with ZT = 2.4 reported in p-type Bi<sub>2</sub>Te<sub>3</sub>/Sb<sub>2</sub>Te<sub>3</sub> superlattices at 300 K.<sup>9</sup>

One difficulty in raising ZT is that the phonon and electron transport properties cannot be independently tuned since they arise from the same underlying crystal structure. Furthermore, it has generally been thought that the best directions in a superlattice are the cross-plane direction and the direction parallel to the planes and that the best of these two orientations is the one with the highest mobility.<sup>3</sup> However, because ZT is a rational function of multiple response functions, its optimization can be at an intermediate carrier propagation angle, where none of the individual parameters are optimized. We show below that enhancements of 5%–15% are possible at *oblique angles in superlattices*, with ZT reaching a maximum near  $\theta \approx \pi/6$ .

As a theoretical model, we consider the infinite superlattice with a simple cubic crystal structure, which is sufficient to address the issue of optimal angle of propagation in a superlattice. The superlattice periodicity is along the z direction with p number of type 1 atoms and q number of type 2 atoms in one unit cell, as shown in Fig. 1. The electrons and phonons are taken to interact only through the relaxation time.

First, we consider the phonon contribution to *ZT*. We use a nearest neighbor, harmonic approximation, and take the spring constant between two ions to be the same for longitudinal and transverse displacements, and the off-diagonal elements of the spring constant tensor are neglected. We set the spring constant between type 1 ions to be  $K_1$ , between type 2 ions to be  $K_2$ , and between type 1 and type 2 ions to be  $K_3$ . Because of the periodicity of the superlattice system, the canonical Hamiltonian equation becomes an eigenvalue equation  $MA_j = \omega^2 A_j$ . Here  $A_j$  is a vector with p + q elements, with each element being the amplitude of the oscilla-

tion of the ion at each site in one unit cell; *j* denotes the x, y, and z directions; and  $\omega$  is the angular frequency. *M* is a matrix with p + q dimension, whose nonzero elements for one wave vector  $\mathbf{k} = (k_x, k_y, k_z)$ 

$$M_{i,i-1} = \begin{cases} -K_3/m_1 exp(-ik_z c), i = 1; \\ -K_1/m_1 exp(-ik_z c), 2 \le i \le p; \\ -K_3/m_2 exp(-ik_z c), i = p + 1; \\ -K_2/m_2 exp(-ik_z c), p + 2 \le i \le p + q; \end{cases}$$

$$M_{i,i} = \begin{cases} K_1/m_1 \eta + K_3/m_1, i = 1, p; \\ K_1/m_1(\eta + 1), 2 \le i \le p - 1; \\ K_2/m_2 \eta + K_3/m_2, i = p + 1, p + q; \\ K_2/m_2(\eta + 1), p + 2 \le i \le p + q - 1; \\ K_2/m_2(\eta + 1), p + 2 \le i \le p - 1; \\ -K_3/m_1 exp(ik_z c), i = p; \\ -K_2/m_2 exp(ik_z c), p + 1 \le i \le p + q - 1; \\ -K_3/m_2 exp(ik_z c), i = p + q; \end{cases}$$
(1)

where  $\eta = 5 - 2\cos(k_x c) - 2\cos(k_y c)$ , *c* is the distance between nearest neighbors,  $m_1$  and  $m_2$  are the masses of type 1 and type 2 ions respectively, and the indices of *M* run from i = 1 to p + q, with  $M_{1,p+q} \equiv M_{1,0}$  and  $M_{p+q,1} \equiv M_{p+q,p+q+1}$ . Solving this equation for  $\omega(\mathbf{k})$  yields p + q bands, each 3fold degenerate due to our approximation that the spring constants are the same for longitudinal and transverse displacements. Then the thermal conductivity tensor due to phonons can be derived from semiclassical theory<sup>16</sup>



FIG. 1. (Color online) The geometry of the simplified cubic superlattice system in our theoretical model. The system size is infinite. The superlattice periodicity is along the z direction, with p = 4 type 1 atoms and q = 4 type 2 atoms as an example. One unit cell contains p + q atoms, as denoted by the rectangle box in the figure. The x-y plane has monatomic translational symmetry. The unit vector **n** specifies the direction of transport.

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$$\mathbf{K}_{p} = -\sum_{n} \int \frac{3d\mathbf{k}}{8\pi^{3}} \varepsilon_{n}^{2}(\mathbf{k}) \tau_{p} \frac{\partial g_{n}^{0}}{\partial \varepsilon_{n}} \frac{1}{T} \mathbf{v}_{n}(\mathbf{k}) \mathbf{v}_{n}(\mathbf{k}), \qquad (2)$$

where *n* is the band index,  $\varepsilon = \hbar \omega$  is the energy,  $\mathbf{v} = \nabla_{\mathbf{k}} \omega$  is the group velocity,  $\tau_p$  is the phonon relaxation time, and  $g^0$  is the Bose-Einstein distribution.

We now consider the electron contribution to ZT. We use a tight-binding approximation in which the coupled orbital is assumed to be non-degenerate per spin at a single atomic site and to couple symmetrically to all six nearest neighbor atoms. The onsite energy of type 1 atoms is  $\varepsilon_1$ , and that for type 2 atoms is  $\varepsilon_2$ . The overlap energy between neighboring type 1 sites is  $\Delta_1$ , between neighboring type 2 sites is  $\Delta_2$ , and between neighboring type 1 and type 2 sites is  $\Delta'$ . Then the time-independent Schrödinger equation reduces to the eigenvalue equation  $H_{\alpha\beta}a_{\beta} = Ea_{\alpha}$  with dimensionality p + q, where  $a_{\alpha}$  is the coefficient associated with the wavefunction at each site and E is the eigenenergy of the electron in the whole superlattice system. The non-zero elements of the matrix H are

$$H_{i,i-1} = \begin{cases} -\Delta' exp(-ik_{z}c), i = 1; \\ -\Delta_{1}exp(-ik_{z}c), 2 \le i \le p; \\ -\Delta' exp(-ik_{z}c), i = p + 1; \\ -\Delta_{2}exp(-ik_{z}c), p + 2 \le i \le p + q; \end{cases}$$

$$H_{i,i} = \begin{cases} \varepsilon_{1} - \Delta_{1}\zeta, 1 \le i \le p; \\ \varepsilon_{2} - \Delta_{2}\zeta, p + 1 \le i \le p + q; \\ \varepsilon_{2} - \Delta_{2}\zeta, p + 1 \le i \le p - 1; \\ -\Delta_{1}exp(ik_{z}c), 1 \le i \le p - 1; \\ -\Delta' exp(ik_{z}c), p + 1 \le i \le p + q - 1; \\ -\Delta' exp(ik_{z}c), p + 1 \le i \le p + q - 1; \\ -\Delta' exp(ik_{z}c), i = p + q; \end{cases}$$
(3)

where  $\zeta = 2\cos(k_xc) + 2\cos(k_yc)$  and the indices of H run from i=1 to p+q, with  $H_{1,p+q} \equiv H_{1,0}$  and  $H_{p+q,1} \equiv H_{p+q,p+q+1}$ . Solving this eigenvalue equation yields p+q electronic bands, and each band has two-fold spin degeneracy. Then from the semi-classical theory of transport,<sup>16</sup> we have the electrical conductivity tensor  $\Sigma = L^{11}$ , the thermal conductivity tensor of the electrons  $\mathbf{K}_e = \mathbf{L}^{22} - \mathbf{L}^{21}(\mathbf{L}^{11})^{-1}\mathbf{L}^{12}$ , and the thermopower tensor  $\mathbf{Q} = (\mathbf{L}^{11})^{-1}\mathbf{L}^{12}$ . The total thermal conductivity tensor is  $\mathbf{K} = \mathbf{K}_e + \mathbf{K}_p$ .  $\mathbf{L}^{11}$ ,  $\mathbf{L}^{12}$ ,  $\mathbf{L}^{21}$ , and  $\mathbf{L}^{22}$  are given by  $\mathbf{L}^{11} = \mathcal{L}^{(0)}$ ,  $\mathbf{L}^{21} = T\mathbf{L}^{12} = -\frac{1}{e}\mathcal{L}^{(1)}$  and  $\mathbf{L}^{22} = \frac{1}{e^2T}\mathcal{L}^{(2)}$ , with  $\mathcal{L}^{(\alpha)}$  given by

$$\mathcal{L}^{(\alpha)} = e^2 \sum_{n} \int \frac{d\mathbf{k}}{4\pi^3} \left(-\frac{\partial f_n^0}{\partial E_n}\right) (E_n(\mathbf{k}) - \mu)^{\alpha} \mathbf{v}_n(\mathbf{k}) \mathbf{v}_n(\mathbf{k}) \tau_e, \quad (4)$$

where -e is the electronic charge, *n* is the band index, *E* is the energy of electron,  $\mathbf{v} = 1/\hbar \nabla_{\mathbf{k}} E$  is the group velocity,  $\mu$  is the chemical potential,  $\tau_e$  is the electron relaxation time, and  $f^0$  is the Fermi-Dirac distribution.

We now have all the tensors needed in order to calculate the figure of merit. Because the x-y plane has monatomic translational symmetry, we only need to specify the transport direction with the unit vector  $\mathbf{n} = (\sin\theta, 0, \cos\theta)$  as shown in Fig. 1, where  $\theta$  is the polar angle with respect to the z axis. The electrical conductivity, thermal conductivity, thermopower, and figure of merit as functions of  $\theta$  are given by  $\sigma(\theta) = (\mathbf{\Sigma}\mathbf{n}) \cdot \mathbf{n}, \quad \kappa(\theta) = (\mathbf{K}\mathbf{n}) \cdot \mathbf{n}, \quad S(\theta) = (\mathbf{Q}\mathbf{n}) \cdot \mathbf{n}, \quad \text{and} \quad Z(\theta)T = \frac{\sigma(\theta)S(\theta)^2}{\kappa(\theta)}T, \text{ respectively.}$ 

In the following calculations, we use input parameters which are both reasonable microscopically and also yield results close to those measured for the Bi<sub>2</sub>Te<sub>3</sub>/Bi<sub>2</sub>Te<sub>2 83</sub>Se<sub>0 17</sub> superlattice.<sup>9</sup> While the crystal structure we use has a different symmetry from that of the Bi<sub>2</sub>Te<sub>3</sub>/Bi<sub>2</sub>Te<sub>2.83</sub>Se<sub>0.17</sub> superlattice, our cubic approximation is sufficient to test the conjecture that varying the angle of propagation can enhance ZT. We have set the lattice constant c = 4 Å,<sup>17</sup> and the masses are  $m_1 = 160u$ and  $m_2 = 158u$  in atomic mass units. For spring constants, we have taken  $K_1 = 11.9$  N/m,  $K_2 = 11.0$  N/m, and  $K_3 = (K_1 + K_2)/2$ . The spring constants are estimated from a Lennard-Jones potential.<sup>16</sup> We take the values of the energy levels being hybridized to form the bands to be  $\varepsilon_1 = -0.68 \text{ eV}$ and  $\varepsilon_2 = -0.71$  eV. The overlap energies are taken to be  $\Delta_1 = -\varepsilon_1/12$ ,  $\Delta_2 = -\varepsilon_2/12$ , and  $\Delta_{3'} = (\Delta_1 + \Delta_2)/2$ . We take p = 4 and q = 20, consistent with the thickness ratio used in Ref. 9. We use  $\mu = -1.03$  eV for the chemical potential and T = 300 K for the room temperature. We use  $\tau_p = 1$  ps for the phonon relaxation time (dominated by anharmonic effects) and  $\tau_e = 50$  fs for the electron relaxation time (dominated by the electron-phonon interaction).

In Fig. 2 we show the computed thermoelectric properties as a function of carrier propagation angle in the superlattice. Fig. 2(a) shows our computed electrical conductivity as a function of angle, which varies within the range (3-11) $\times 10^4 \Omega^{-1} m^{-1}$ , overlapping the experimentally reported range  $(8-10) \times 10^4 \Omega^{-1} m^{-1.9}$  The thermal conductivity in the cross-plane direction is reported to be  $\kappa \approx 0.6 \text{ Wm}^{-1} \text{ K}^{-1.9}$ consistent with our Fig. 2(b). Notice that our results for the thermopower (Fig. 2(c)) indicate that it is negative, which is



FIG. 2. (Color online) Thermoelectric properties of the  $Bi_2Te_3/Bi_2Te_{2.83}Se_{0.17}$  superlattice with the parameters used in this paper. (a) Electrical conductivity as a function of angle. (b) Thermal conductivity as a function of angle. (c) Thermopower as a function of angle. (d) Figure of merit as a function of angle.

appropriate to the n-type superlattice  $Bi_2Te_3/Bi_2Te_{2.83}Se_{0.17}$ . Our calculated thermopower in the cross-plane direction is  $-268 \ \mu\text{V}$ , close to the experimental result  $-250 \ \mu\text{V}$ .<sup>9</sup> We find that ZT = 1.22 in the cross-plane direction, close to the value ZT = 1.4 reported in  $Bi_2Te_3/Bi_2Te_{2.83}Se_{0.17}$  superlattices.<sup>9</sup>

Now that we have shown that our minimal theoretical model yields physically reasonable properties, we can study the thermoelectric properties of our superlattices as a function of carrier propagation angle. From Fig. 2,  $\sigma$ ,  $\kappa$ , and *S* are monotonic response functions with respect to the angle of carrier propagation. Since *ZT* is a rational function of these response functions,  $Z(\theta)T = \frac{\sigma(\theta)S(\theta)^2}{\kappa(\theta)}T$ , *ZT* can be a nonmonotonic function of  $\theta$ . Indeed, as shown in Fig. 2(d), the maximum value of *ZT* is neither in the cross-plane direction nor in the direction parallel to the planes. Rather, the maximum figure of merit appears at about  $\theta \approx \pi/6$ , with an enhancement of 10% over the cross-plane direction.

For completeness, we also explore other ways that ZT may be enhanced within this model. One possibility is to change the thickness ratio of the layers in the superlattice (with other parameters the same as those used in Fig. 2). As shown in Fig. 3(a), p = 4 and q = 20 has the best figure of merit (many other sets of p and q have also been calculated though not presented here), which means the ratio used in the experiments for Bi<sub>2</sub>Te<sub>3</sub>/Bi<sub>2</sub>Te<sub>2.83</sub>Se<sub>0.17</sub> is one optimized ratio. Another approach is to change the chemical potential, via, e.g., light doping. As shown in Fig. 3(b), the maximum figure of merit ZT with chemical potential  $\mu = -1.04$  eV is improved 3.5% over the maximum value of ZT obtained with  $\mu = -1.03$  eV, indicating that a small decrease of the chemical potential (within a certain range) could result in noticeable ZT enhancements. Therefore, we predict that further light doping of both constituents in the superlattice can also improve the figure of merit.

It is evident in Fig. 3 that the cross-plane direction is not the direction in which ZT is optimized and that instead ZT is optimized at oblique angles in each case. We have calculated many other sets of parameters, and we find that ZT is typically optimized at nonzero angles. This means that the non-zero angle maximum figure of merit is quite a generic phenomenon in superlattice systems. Our most important conclusion is therefore that ZT can be enhanced in existing superlattices via transport at an oblique angle, typically by 5%-15%. As a consequence, by a selection of better angle, the impressive experimental result ZT = 2.4 in Bi<sub>2</sub>Te<sub>3</sub>/Sb<sub>2</sub>Te<sub>3</sub> is anticipated to be further enhanced, up to ZT = 2.7 or higher. For other superlattices based on different materials,<sup>5,10–13</sup> the same prediction of ZT enhancement at an oblique angle can also be made due to its generality. Transport at an oblique angle may be achieved via, e.g., polishing a superlattice at an oblique angle with subsequent overlay of contacts.

One may imagine that in a real system with thermal losses, the enhancement of ZT at oblique angles is less since the phonon thermal conductivity may be affected by thermal leakage in the direction transverse to electronic carrier propagation. A "worst case scenario" may be calculated by approximating the phonon thermal conductivity as a constant, equal to its maximum possible value (that of the inplane direction). While this extreme limit decreases the maximum ZT (which still occurs at an oblique angle), it decreases ZT in the cross-plane direction even more, with the



FIG. 3. (Color online) The figure of merit as a function of angle for (a) different thicknesses of the two materials, and (b) different chemical potentials, with all the other parameters kept unchanged from those used in Fig. 2 in both cases, respectively.

result that the maximum ZT relative to the cross-plane direction is further enhanced over the ideal case.

In conclusion, we have developed a theoretical model investigating the thermoelectric properties of superlattices in order to predict thermoelectric properties at general angles of carrier propagation in superlattices. The results of our model are consistent with extant experimental results on such properties as electrical conductivity, thermal conductivity, thermopower, and cross-plane figure of merit in, e.g., Bi<sub>2</sub>Te<sub>3</sub>/Bi<sub>2</sub>Te<sub>2.83</sub>Se<sub>0.17</sub> superlattices. We have shown theoretically that the figure of merit in superlattices is optimized at an oblique angle rather than in the cross-plane direction or in the direction parallel to planes. By using superlattices for thermoelectric figure of merit can be enhanced by 5%–15% or more over the in-plane and cross-plane directions.

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- <sup>1</sup>B. C. Sales, Science 295, 1248 (2002).
- <sup>2</sup>T. M. Tritt, M. G. Kanatzidis, H. B. Lyon, and G. D. Mahan, Mater. Res. Soc. Proc. **478**, 73 (1997).
- <sup>3</sup>L. D. Hicks and M. D. Dresselhaus, Phys. Rev. B 47, 12727 (1993).
- <sup>4</sup>R. Venkatasubramanian, Naval Res. Rev. **58**, 31 (1996).
- <sup>5</sup>S. M. Lee, D. G. Cahill, and R. Venkatasubramanian, Appl. Phys. Lett. 70, 2957 (1997).
- <sup>6</sup>A. Shakouri, **Proc. IEEE 94**, 1613 (2006).
- <sup>7</sup>G. D. Mahan and L. M. Woods, Phys. Rev. Lett. 80, 4016 (1998).
- <sup>8</sup>A. Shakouri and J. E. Bowers, Appl. Phys. Lett. **71**, 1234 (1997).
- <sup>9</sup>R. Venkatasubramanian, E. Siivola, T. Colpitts, and B. O'Quinn, Nature **413**, 597 (2001).
- <sup>10</sup>V. Rawat, Y. K. Koh, D. G. Cahill, and T. D. Sands, J. Appl. Phys. **105**, 024909 (2009).
- <sup>11</sup>M. Zebarjadi, Z. Bian, R. Singh, A. Shakouri, R. Wortman, V. Rawat, and T. Sands, J. Electron. Mater. 38(7), 960 (2009).
- <sup>12</sup>V. Rawat and T. D. Sands, J. Appl. Phys. 100, 064901 (2006).
- <sup>13</sup>S. Cho, Y. Kim, S. J. Youn, A. DiVenere, G. K. L. Wong, A. J. Freeman, J. B. Ketterson, L. J. Olafsen, I. Vurgaftman, J. R. Meyer, and C. A. Hoffman, Phys. Rev. B 64, 235330 (2001).
- <sup>14</sup>I. Chowdhury, R. Prasher, K. Lofgreen, G. Chrysler, S. Narasimhan, R. Mahajan, D. Koester, R. Alley, and R. Venkatasubramanian, Nat. Nano-technol. 4, 235 (2009).
- <sup>15</sup>Y. Wang, C. Liebig, X. Xu, and R. Venkatasubramanian, Appl. Phys. Lett. 97, 083103 (2010).
- <sup>16</sup>N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Brooks/Cole, Belmont, CA, 1976).
- <sup>17</sup>D. R. Lide, editors, CRC Handbook of Chemistry and Physics, 79th ed., (CRC Press, Boca Raton, FL, 1998).