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# Thermoelectric figure of merit of strongly correlated superlattice semiconductors

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The Anderson lattice Hamiltonian was solved using the slave-boson mean-field approximation to get the energy bands of a strongly correlated semiconductor. The transport properties were calculated in the relaxation-time approximation, and the thermoelectric figure of merit was obtained for the strongly correlated semiconductor and a variety of superlattice structures. We found that at room temperature the dimensionless quantity $ZT$, thermoelectric figure of merit multiplied by temperature, can reach nearly 1.4 for a quantum wire lattice structure. We believe that it may be possible to find high values of the figure of merit for strongly correlated superlattice semiconductors. [S0163-1829(99)50624-3]

For a material to be a good thermoelectric cooler, it must have a high value of the thermoelectric figure of merit $Z$[1], which is defined as $Z=Q^2\sigma/K$, where $Q$ is the thermopower (Seebeck coefficient), $\sigma$ is the electrical conductivity, and $K$ the thermal conductivity. The best thermoelectric material now known is $Bi_2Te_3$, which has $ZT\approx 1$ at room temperature.[1] No materials are found at lower temperature with $ZT$ larger than 1. Recently, much work has been done on strongly correlated semiconductors (also referred to as Kondo insulators), and some authors suggested that this class of materials may be a good candidate for thermoelectric materials.[2–4] Some experiments have been carried out to try to find good thermoelectric materials from strongly correlated semiconductors,[2,5] however, so far there has been no satisfactory result.

The strongly correlated semiconductors can be characterized as mixed-valence semiconductors with band gaps of less than 1000 K.[6] The small value of the gap and its significant temperature dependence have been shown to be consistent with a band structure where the hybridization between local $f$ or $d$ electrons and the conduction band is strongly renormalized by many-body effects due to the large on-site $f$ or $d$ electron Coulomb repulsion.[7,8] Near the chemical potential the resulting bands are almost flat.[4,9] This is a close approximation of the ideal electronic structure suggested by Mahan and Sofo[3] for thermoelectric materials, where the transport distribution function is a $\delta$ function centered about 2–3 kT from the Fermi energy.[3]

In this paper we calculate the transport properties of a strongly correlated semiconductor with an indirect gap of approximately 600 K, which we will see has properties very similar to those suggested by Mahan and Sofo[3] for good thermoelectric materials. Additionally we will show that a superlattice system might increase the thermoelectric figure of merit as argued by some authors.[10] Here, we also consider the superlattice structure of the strongly correlated semiconductor, because the indirect gap for them is proportional to $V^2/W$ (where $V$ is the hybridized matrix element and $W$ is the bandwidth of the conduction electrons), one may expect a wider indirect gap for a superlattice structure. Additionally, the DOS (density of states) will also be modified, thereby, influencing thermoelectric behavior. We expect that the correlations and the superlattice structure will improve the thermoelectric figure of merit.

Our calculation follows the method used by Sanchez-Castro, Bedell, and Cooper.[4,9] We start with the Anderson lattice Hamiltonian, which can be written as

$$H=\sum_{k\sigma}\epsilon_k^0 c_{k\sigma}^\dagger c_{k\sigma}+\sum_{i\sigma}\epsilon_f f_{i\sigma}^\dagger f_{i\sigma}+\frac{1}{2}\sum_{i\sigma\sigma'}U f_{i\sigma}^\dagger f_{i\sigma} f_{i\sigma'}^\dagger f_{i\sigma'}$$
$$+\frac{1}{\sqrt{N_s}}\sum_{ik\sigma}(Ve^{-i\mathbf{k}\cdot\mathbf{R_i}}c_{k\sigma}^\dagger f_{i\sigma}+\text{c.c.}), \quad (1)$$

where $c_{k\sigma}^\dagger$ is a creation operator for a conduction electron with wave vector $\mathbf{k}$ located in the first Brillouin zone and with spin $s=\pm\frac{1}{2}$; $f_{i\sigma}^\dagger$ is a creation operator for a localized $f$ electron centered at $\mathbf{R_i}$ in the ith unit cell; and $N_s$ is the number of unit cells in the crystal. We consider the case $U=\infty$, two electrons per primitive cell, and degeneracy $N=2$. We treat the $U=\infty$ Anderson lattice Hamiltonian using a slave-boson formalism. Here $f_{i\sigma}^\dagger$ is represented as the bilinear product $f_{i\sigma}^\dagger=\hat{f}_{i\sigma}^\dagger b_i$, where $\hat{f}_{i\sigma}^\dagger$ is a slave fermion creation operator representing the $|f_\sigma^{(1)}\rangle_{\mathbf{R_i}}$ configuration, and $b_i^\dagger$ is a slave-boson creation operator representing the $|f_\sigma^{(0)}\rangle_{\mathbf{R_i}}$ configuration. In terms of the slave-boson operators, the $U=\infty$ Anderson lattice Hamiltonian is rewritten as

$$H'=\sum_{k\sigma}\epsilon_k^0 c_{k\sigma}^\dagger c_{k\sigma}+\sum_{i\sigma}\epsilon_f\hat{f}_{i\sigma}^\dagger\hat{f}_{i\sigma}$$
$$+\frac{1}{\sqrt{N_s}}\sum_{ik\sigma}(Ve^{-ik\cdot R_i}c_{k\sigma}^\dagger b_i^\dagger\hat{f}_{i\sigma}+\text{c.c.})$$
$$+\sum_i\lambda_i\left(\sum_\sigma\hat{f}_{i\sigma}^\dagger\hat{f}_{i\sigma}+b_i^\dagger b_i-1\right), \quad (2)$$

where a time independent auxiliary boson field $\lambda_i$ is added, which couples to the system through the last term in the Hamiltonian and enforces the constraint of no multiple occupancy of an $f$ site. Furthermore, the mean-field approximation is applied to the slave-boson Hamiltonian by replacing the boson field with the expectation value over the coherent equilibrium states, namely, $r=\langle b_i\rangle$ and $\Lambda=\langle\lambda_i\rangle$. Now the resulting Hamiltonian has a renormalized hybridization matrix element $\tilde{V}=rV$ and a renormalized $f$ level position $\tilde{\epsilon}_f$

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$=\epsilon_f+\Lambda$. After changing to the Bloch representation for the $f$ electrons given by $\hat{f}^{\dagger}_{k\sigma}=(1/\sqrt{N_s})\Sigma_i e^{-ik\cdot R_i}\hat{f}^{\dagger}_{i\sigma}$, a canonical transformation is performed to the hybridized band creation operators as follows:

$$\begin{bmatrix} a^{\dagger}_{k1\sigma} \\ a^{\dagger}_{k2\sigma} \end{bmatrix} = \begin{bmatrix} \alpha_{k\sigma} & \beta_{k\sigma} \\ -\beta_{k\sigma} & \alpha_{k\sigma} \end{bmatrix} \begin{bmatrix} \hat{f}^{\dagger}_{k\sigma} \\ c^{\dagger}_{k\sigma} \end{bmatrix},$$

where $a^{\dagger}_{k1\sigma}=\alpha_k\hat{f}^{\dagger}_{k\sigma}+\beta_k c^{\dagger}_{k\sigma}$ and $a^{\dagger}_{k2\sigma}=-\beta_k\hat{f}^{\dagger}_{k\sigma}+\alpha_k c^{\dagger}_{k\sigma}$, and with

$$\alpha_k^2=\frac{1}{2}\left(1+\frac{\epsilon_k^0-\tilde{\epsilon}_f}{E_k}\right) \tag{3}$$

and

$$\beta_k^2=\frac{1}{2}\left(1-\frac{\epsilon_k^0-\tilde{\epsilon}_f}{E_k}\right). \tag{4}$$

In terms of the hybridized band operators, the mean-field Hamiltonian simplifies to

$$H^{MF}=\sum_{kn\sigma}\epsilon_{kn}a^{\dagger}_{kn\sigma}a_{kn\sigma}+N_s\Lambda(r^2-1), \tag{5}$$

where $n=1,2$ is the band index and $\epsilon_{kn}$ is the hybridized band energy given by

$$\epsilon_{kn}=\frac{1}{2}[\epsilon_k^0+\tilde{\epsilon}_f+(-1)^n E_k], \tag{6}$$

and

$$E_k=[(\epsilon_k^0-\tilde{\epsilon}_f)^2+4r^2V^2]^{1/2}. \tag{7}$$

The resulting partial density of states are given by

$$\rho_{c\sigma}(\omega)=\frac{1}{N_s}\sum_k \delta\left(\omega-\frac{\tilde{V}^2}{\omega-\tilde{\epsilon}_{f\sigma}}-\epsilon_{k\sigma}\right), \tag{8}$$

and

$$\rho_{f\sigma}(\omega)=\frac{\tilde{V}^2}{(\omega-\tilde{\epsilon}_{f\sigma})^2}\rho_{c\sigma}(\omega). \tag{9}$$

The equations for determining the expectation values of the boson fields are obtained by minimizing the mean-field energy with respect to $r$ and $\Lambda$, respectively. The resulting equations to determine $r$, $\Lambda$, and the chemical potential $\mu$ are[11,12]

$$1-r^2=\frac{1}{N_s}\sum_{k\sigma}[\alpha^2_{k\sigma}n_F(\epsilon_{k1\sigma})+\beta^2_{k\sigma}n_F(\epsilon_{k2\sigma})], \tag{10}$$

$$\Lambda=\frac{1}{N_s}\sum_{k\sigma}\frac{V^2}{E_{k\sigma}}[n_F(\epsilon_{k1\sigma})-n_F(\epsilon_{k2\sigma})], \tag{11}$$

and

$$\frac{1}{N_s}\sum_{k\sigma}[n_F(\epsilon_{k1\sigma})+n_F(\epsilon_{k2\sigma})]=2, \tag{12}$$

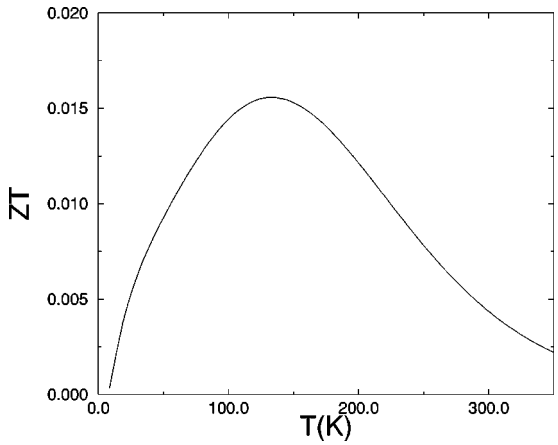


FIG. 1. The temperature dependence of the dimensionless quantity $ZT$ for bulk material in which the conduction band is a tight-binding band.

where $n_F$ is the Fermi-Dirac distribution function.

The relaxation-time approximation[13] is used in our calculation, thus the electrical conductivity $\sigma$, the thermopower $Q$, and the thermal conductivity $\kappa$ are given by $\sigma=L_0$, $Q=-(k_B/|e|)(L_1/L_0)$, and $\kappa=(k_B^2T/e^2)(L_2-L_1L_0^{-1}L_1)$, where $L_m$ is

$$L_m=-\frac{e^2}{V}\sum_{kn\sigma}\frac{\partial n_F(\epsilon_{kn\sigma})}{\partial\epsilon_{kn\sigma}}\tau(\epsilon_{kn\sigma})\mathbf{v}_{kn\sigma}\mathbf{v}_{kn\sigma}\left(\frac{\epsilon_{kn\sigma}-\mu}{k_BT}\right)^m. \tag{13}$$

For the case of a small number of impurities, the electronic relaxation time is given by

$$\frac{1}{\tau_{kn\sigma}}=\frac{\pi}{\hbar}\frac{N_{imp}}{N_s}|V_0|^2\left(\frac{\partial\epsilon_{kn\sigma}}{\partial\epsilon^0_{k\sigma}}\right)^2\rho(\epsilon_{kn\sigma}), \tag{14}$$

where

$$\frac{\partial\epsilon_{kn\sigma}}{\partial\epsilon^0_{k\sigma}}=\beta_k^2(\alpha_k^2) \tag{15}$$

for $n=1(2)$ and $N_{imp}$ is the total number of impurities. We have assumed a value of $(N_{imp}/N_s)V_0^2=0.09$ eV$^2$ for the impurity potential so that the electrical conductivity is of the same order as the material FeSi at room temperature.

We are now in a position to calculate the thermoelectric figure of merit for bulk material. At first, the dispersion relation of the conduction band is assumed to be a tight-binding band expressed as follows:

$$\epsilon^0_{k\sigma}=\frac{W}{6}[\cos(k_xa)+\cos(k_ya)+\cos(k_za)]. \tag{16}$$

To perform our calculation, we consider a cubic lattice with a lattice constant $a^3=83$ Å$^3$, $W=5.0$ eV, $V^2=0.4$ eV$^2$, and $\epsilon_f=0.67$ eV below the conduction Fermi energy, so that the indirect gap is 640 K at $T=0$ K , consistent with the value found for FeSi.

In Fig. 1 the dimensionless quantity $ZT$ as a function of temperature is shown. We find that $ZT$ is no higher than 0.02, and it is similar to the measurement on FeSi.[2]

In a tight-binding model we have particle-hole symmetry. The contributions to the thermopower, $Q$, are opposite for the particles and holes leading to small values of $Q$ and $ZT$. One way of increasing $ZT$ is to look for materials that are not particle-hole symmetric. We can approximate this effect in our calculation by introducing a nearly parabolic band structure for the conduction band of the Anderson lattice Hamiltonian. The parameters of this band structure are adjusted to give good agreement with the transport properties in the bulk three-dimensional (3D) case.

The figure of merit $Z$ has been calculated for (i) a three-dimensional bulk material, (ii) a 2D multilayered superlattice, and (iii) a 1D quantum wire superlattice, using a conduction band that is nearly parabolic. For a suitably fabricated superlattice, the conduction electrons are confined to move within 2D quantum wells or within 1D quantum wires, and the electrons occupy only the lowest subband of the quantum well or wire. Here we assume infinite potential barriers and zero barrier widths, following the same assumption as that of Hicks and Dresselhaus.[10] The dispersion relation for the conduction electrons in 3D is chosen to be

$$\epsilon_k^0 = \epsilon_0 + \frac{W}{3\left(\frac{\pi}{a}\right)^2}[f(k_x)+f(k_y)+f(k_z)], \tag{17}$$

where

$$f(k) = \frac{1}{2}\left[k^2 + \left(\frac{2\pi}{a}-k\right)^2\right] - \left[\left(\frac{\left[k^2-\left(\frac{2\pi}{a}-k\right)^2\right]}{2}\right)^2 + U_0\right]^{1/2} \tag{18}$$

and we let $W=6.0$ eV, $U_0 = 0.1[3(\frac{\pi}{a})^2/W]^2$ eV$^2$. In the 2D case, the dispersion relation becomes

$$\epsilon_k^0 = \epsilon_0 + \frac{W}{3\left(\frac{\pi}{a}\right)^2}[f(k_x)+f(k_y)] \tag{19}$$

and in the 1D case, the dispersion relation is

$$\epsilon_k^0 = \epsilon_0 + \frac{W}{3\left(\frac{\pi}{a}\right)^2} f(k_x), \tag{20}$$

where $\epsilon_0$ is a constant reference energy. In our calculation, we will assume that $\epsilon_f$ is 0.67 eV below the conduction electron Fermi energy so that the indirect gap at $T=0$ K is 640 K for the 3D case.

In Fig. 2 we show the transport properties versus temperature for the three cases: (1) The bulk 3D case; (2) the 2D planes forming a layered superlattice (hereafter referred to as 2D); and (3) the 1D quantum wire superlattice (hereafter referred to as 1D). In the last two of these examples we are calculating the transport for a superlattice embedded in a 3D structure. In Fig. 3 we show results of our calculation of the dimensionless quantity $ZT$ as function of temperature. We find that at low temperature, $ZT$ is very large, however, it has

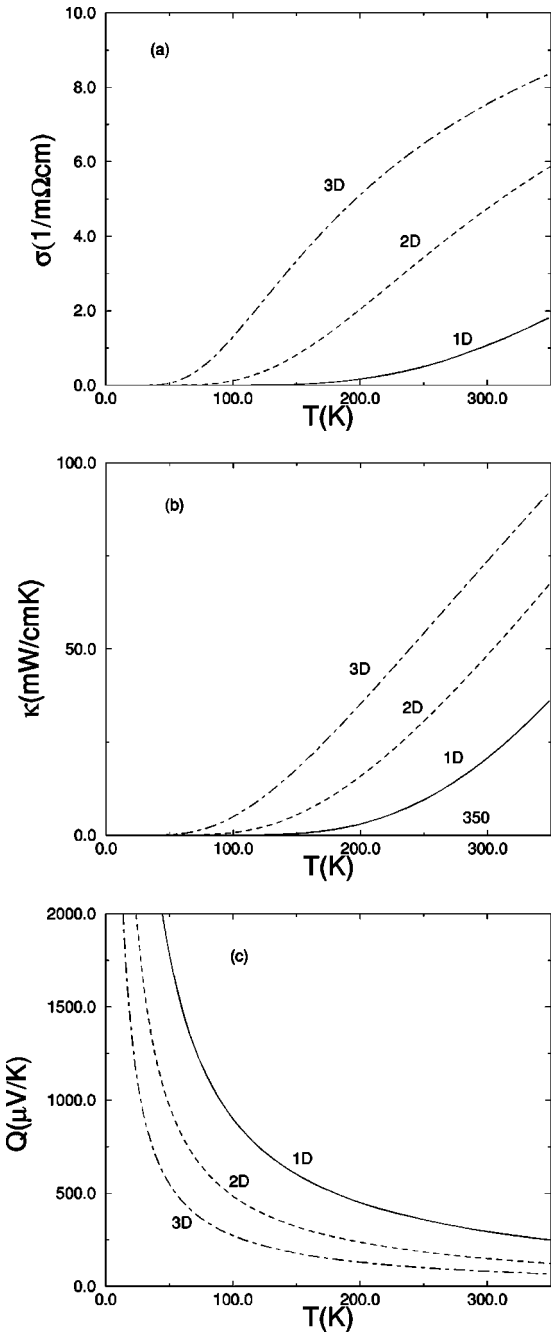


FIG. 2. The transport properties [(a) electrical conductivity, (b) thermal conductivity, (c) thermopower] for 3D, 2D, and 1D cases in which the conduction band is nearly parabolic band.

to be noted that in our calculation, we have not included lattice thermal conductivity, which will dominate the total thermal conductivity at low temperature, thus $ZT$ could be dramatically decreased. At room temperature, the electronic thermal conductivity is larger than or comparable to the lattice thermal conductivity. Moreover, for superlattice systems, the phonons can be scattered by the interfaces and this could reduce the lattice thermal conductivity. Therefore we expect that at higher temperature our calculation should be a good estimate for $ZT$.

In Fig. 3 we plot $ZT$ for the 3D, 2D, and 1D cases. At $T=300$ K, $ZT=0.2$ for the bulk 3D material with an indirect gap of 640 K. If we now form a superlattice with 2D planes

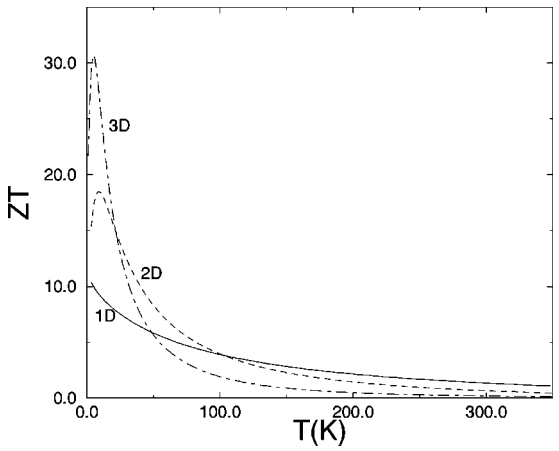


FIG. 3. The temperature dependence of the dimensionless quantity $ZT$ for 3D, 2D, and 1D cases in which the conduction band is nearly parabolic band.

or 1D wires of correlated semiconducting material we get the value of 0.65 and 1.4, respectively, for $ZT$. To get a feel for the importance of the correlations we performed similar calculations in the superlattice structures with an ordinary semiconductor system. We chose an indirect gap for this semiconductor to be 640 K and adjust the effective mass of the electron and hole bands to give $ZT=0.2$ for the 3D bulk case at $T=300$ K. For the 2D and 1D bulk cases we find 0.24 and 0.4, respectively, for $ZT$. As one might expect, the correlations do play an important role and they become more important in lower dimensional superlattice structures.

The calculations we have performed suggest that an increased thermoelectric figure of merit is expected for superlattice structures of correlated semiconducting materials. While the calculations are somewhat idealized they do hint at important features one should look for in designing these materials. The band structure for the conducting electrons should not be particle-hole symmetric. The strong correlations are important so materials with relatively flat $f$ or $d$ bands like $Ce_3Bi_4Pt_3$ or FeSi should be used. If superlattice structures can be fabricated from these materials it would be interesting to explore the role of doping on these materials. For example the best thermoelectric materials come from doping $Bi_2Te_3$ with Sb or Se. These materials, however, have not shown much improvement in the $ZT$ in a superlattice structure. It would seem from our calculations that the search for new thermoelectric materials should include strongly correlated semiconductors.

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