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Thermoelectric performance of granular semiconductors

Andreas Glatz[1] and I. S. Beloborodov[2]
[1]*Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA*
[2]*Department of Physics and Astronomy, California State University Northridge, Northridge, California 91330, USA*
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We study the effects of doping and confinement on the thermoelectric properties of nanocrystalline semiconductors. We calculate the thermopower and figure of merit for temperatures less than the charging energy. For weakly coupled semiconducting grains it is shown that the figure of merit is optimized for grain sizes of order 5 nm for typical materials, and that its value can be larger than one. Using the similarities between granular semiconductors and electron or Coulomb glasses allows for a quantitative description of inhomogeneous semiconducting thermoelectrics.

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The understanding and optimization of thermoelectric materials is of great importance for emerging energy technologies, since these materials promise to serve as a reliable and maintenance free way of electrical energy conversion. Although there have been extensive research efforts in the last several decades, the progress in this quest has been limited until recently. However, these materials were still used, despite their inefficiency, by, e.g., long-term space expeditions for conversion of nuclear heat to electricity due to its reliability.

It was found that for further improvement in efficiency *inhomogeneous/granular* thermoelectric semiconductors are especially suited.[1] These materials are now accessible for next generation thermoelectric devices and technologically important due to the possibility of direct control of the system parameters. The dimensionless *figure of merit*, $ZT = S^2\sigma T/\kappa$, is the preferred measure for the performance or efficiency of thermoelectric materials, where S is the thermopower and σ and κ the electric and thermal conductivities, respectively.[2,3] Recently, ZT values of 2.4 in layered nanoscale structures[4] at 300 K, and 3.2 for a bulk semiconductors with nanoscale inclusions[5] at about 600 K were reported. These high values of ZT are in the range for applications and, therefore, call for the development of a detailed theory of granular semiconducting thermoelectrics.

In this paper, we develop a theory for the thermopower S and figure of merit ZT of granular semiconductors (see Fig. 1) and show that the latter can be of order one or even larger (which is the required order for applications) and predict the optimal morphology of the samples for best performance. Using the similarities between of granular semiconductors and Coulomb glasses allows for a quantitative description of the thermoelectric properties.

Each semiconducting nanocrystal is characterized by two energy scales: (i) the mean energy level spacing $\delta = 1/(na^d)$, where n is the density of states at the Fermi surface, a is the grain size, and d is the dimensionality of a grain, and (ii) the charging energy $E_c = e^2/(\epsilon_r a)$ with ϵ_r being the dielectric constant. In semiconductors the density of states n is of about two orders of magnitude smaller than that in metals. Thus, in semiconducting dots δ can be of order of the charging energy, $\delta \sim E_c$, in contrast to metallic granular materials where typically $\delta \ll E_c$.[6] We emphasize that in our Ref. 6 we studied the case of metallic granular systems which are important for low temperature, but not for energy conversion applications. The physics described in these references is also completely different and the performance of granular semiconductors is many orders of magnitude higher than that of granular metals.

The internal conductance of a grain is taken larger than the intergrain tunneling conductance, g_t, which controls macroscopic transport properties of the sample.[7] In this paper, we consider $g_t \ll 1$, i.e., smaller than the quantum conductance, which is the typical experimental situation.[4,5] Our considerations are valid for temperatures $T < E_c$.

In the case of diagonal (short range) Coulomb interaction, the total probability for an electron tunneling through many grains via elastic or inelastic co-tunneling can be written as the product, $P = \Pi_{i=1}^{N} P_i$, of the individual probabilities of single elastic/inelastic co-tunneling events through single grains with $N = r/a$ is the number of grains. The probability P is related to the localization length ξ as $P \sim e^{-r/\xi}$.

Semiconducting nanocrystal arrays are described by the Hamiltonian

$$\mathcal{H} = \sum_i \mathcal{H}^{(i)} + \sum_{\langle ij\rangle,p,q} [t_{ij}^{pq}\hat{c}^{\dagger}_{i,p}\hat{c}_{j,q} + \text{H.c.}], \qquad (1)$$

where i, j are the grain indexes and the summation in the second term of the r.h.s. of Eq. (1) is performed over nearest

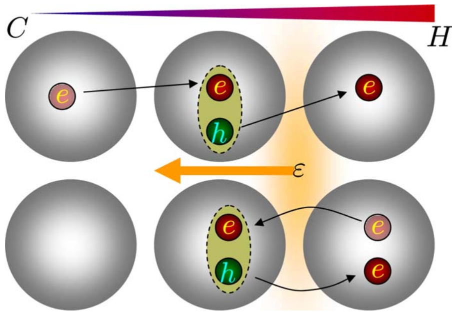

FIG. 1. (Color online) Sketch of a nanogranular material showing typical electron (e) and hole (h) transport. In the upper row of grains an inelastic electron tunneling process is shown and in the lower row a co-tunneling loop responsible for the electronic part of the heat transport is presented. The energy (ε) transport goes from the "hot" (H) to the "cold" (C) side.

neighbors. The term $\mathcal{H}^{(i)}$ is the Hamiltonian for the single grain i including the free-electron energy and the diagonal Coulomb interaction, and the second term is the tunneling Hamiltonian between the adjacent grains i and j with t_{ij} being random tunneling matrix elements and $\hat{c}^{\dagger}_{i,p}[\hat{c}_{i,p}]$ the creation [annihilation] operator for an electron in the state p on the ith grain. Due to the large mean-energy level spacing in semiconducting grains $\delta \sim E_c$, only a few terms of the k-sums are important.

In Ref. 8, it was shown that the probability for elastic $P_i^{\rm el}$ and inelastic $P_i^{\rm in}$ co-tunneling through an array of weakly coupled semiconducting grains has the form

$$P_i^{\rm el} = \frac{1}{[\tau \max(\delta,E_c)]^2}, \quad P_i^{\rm in} = \frac{e^{-2\delta/T}}{[\tau \max(\delta,E_c)]^2}, \tag{2}$$

where τ is the electron escape time from a grain. Thus, for the elastic/inelastic localization length we obtain

$$\xi^{\rm el} \sim \frac{a/2}{\ln[\tau \max(\delta,E_c)]}, \quad \xi^{\rm in} \sim \frac{a/2}{\ln[\tau \max(\delta,E_c)] + \delta/T}. \tag{3}$$

The localization length $\xi^{\rm el/in}$ is related to the characteristic temperature scale $T_0 = e^2/(\epsilon_r \xi^{\rm el/in})$, which is of order $E_c \ln P_i^{-1}$. Below we derive the thermopower, S, thermal conductivity, κ, and figure of merit, ZT for granular semiconductors using Eq. (3).

One remark is in order: The thermopower S of lightly doped compensated semiconductors was investigated in the past.[9–12] However, all previous studies were concentrated on the Mott variable range hopping (VRH) regime, with conductivity being $\sigma(T) \sim \exp(-T_M/T)^{1/4}$, where T_M is the Mott temperature.[13] In granular materials the Mott VRH regime is hard to observe. Indeed, in semiconductors the Efros-Shklovskii (ES) law[14,15] may turn into the Mott behavior with an increase in temperature. This happens when the typical electron energy ε involved in a hopping process becomes larger than the width of the Coulomb gap Δ_c, i.e., when it falls into the flat region of the density of states where Mott behavior is expected. To estimate the width of the Coulomb gap Δ_c, one compares the ES expression for the density of states $n(\Delta_c) \sim (\epsilon_r/e^2)^d |\Delta_c|^{d-1}$ with the density of states (DOS) in the absence of the long-range part of the Coulomb interaction, n_0 ($d=2,3$ is the dimensionality of a sample). Using the condition $n(\Delta_c) \sim n_0$ we obtain $\Delta_c = (n_0 e^{2d}/\epsilon_r^d)^{1/d-1}$. Inserting the value for the bare DOS, $n_0 = 1/E_c \xi^d$, into the last expression we finally obtain $\Delta_c \sim E_c$. This means that there is no flat region in the DOS for $T < E_c$.

Here, we discuss two effects: (i) we calculate the thermopower S of granular semiconductors taking into account the shift of the chemical potential $\Delta\mu = a_1(\nu - 1/2)T_0$ with ν being the electron filling factor (ν is related to the compensation level of semiconductors, here, we concentrate on n-type doped semiconductors with $1/2 < |\nu| < 1$), a_1 a dimensionless numerical coefficient, and the asymmetry of the DOS $\Delta n = a_2(\nu - 1/2)T_0^{-1}$ with a_2 being a numerical constant; (ii) we show that even in the absence of the chemical potential shift, $\Delta\mu = 0$, and asymmetry of DOS, $\Delta n = 0$, the thermopower S is still finite, although small, due to co-tunneling processes. We start with the former case.

To calculate the thermopower of granular materials in the regime of weak coupling between the grains it is necessary to take into account electrons and holes because the contributions of electrons and holes cancel in the leading order. In general the thermopower is proportional to the average energy transferred by charge carriers and can be written as[9–12]

$$S = -\frac{1}{2eT}[\langle \varepsilon - \tilde{\mu} \rangle_e + \langle \varepsilon - \tilde{\mu} \rangle_h]. \tag{4}$$

Here, the subscripts e and h refer to electrons and holes and $\tilde{\mu} = \mu + \Delta\mu$ is the shifted chemical potential. The expression in the square brackets of the r.h.s. of Eq. (4) describes the average energy transferred by charge carriers (electron or hole) measured with respect to the shifted chemical potential $\tilde{\mu}$. The average energy in Eq. (4) can be calculated as follows

$$\langle \varepsilon - \tilde{\mu} \rangle_{e/h} = \frac{\int_0^\infty d\varepsilon (\varepsilon - \tilde{\mu}) n(\varepsilon - \tilde{\mu}) f_{e/h}(\varepsilon - \tilde{\mu}) e^{-(\varepsilon - \tilde{\mu})^2/2\Delta^2}}{\int_0^\infty d\varepsilon n(\varepsilon - \tilde{\mu}) f_{e/h}(\varepsilon - \tilde{\mu}) e^{-(\varepsilon - \tilde{\mu})^2/2\Delta^2}}. \tag{5}$$

Here, $f_{e/h}(\varepsilon)$ is the Fermi function for electrons or holes, $\Delta = \sqrt{T_0 T}$ the typical transfer energy in one hop, and $n(\varepsilon)$ is energy dependent the DOS. As we will see later, it is crucial to take into account the asymmetry of the DOS and the shift of the chemical potential in order to obtain a finite result in Eq. (4).

The DOS, $n(\varepsilon)$ in Eq. (5) for $\tilde{\mu} - \Delta_c < \varepsilon < \tilde{\mu}$ has the following form[10]

$$n(\varepsilon) \propto |\varepsilon - \tilde{\mu}|^{d-1}[1 - (\varepsilon - \tilde{\mu})\Delta n], \tag{6}$$

and is constant, n_0, outside the Coulomb gap region, $\varepsilon < \tilde{\mu} - \Delta_c$ and $\varepsilon > \tilde{\mu}$, where $\Delta_c \sim E_c$ is the width of the Coulomb gap.[14] The shift of the chemical potential $\Delta\mu = \tilde{\mu} - \mu$ and the asymmetry of the DOS, Δn, are explicitly defined above Eq. (4).

To support our choice for the expression of the DOS $n(\varepsilon)$ in Eq. (6) we numerically compute the DOS for a two-dimensional (2D) Coulomb glass model to simulate the whole system of semiconducting grains (see Refs. 16 and 17 for details) at arbitrary filling factor ν using first principles. The result of the simulations is shown in Fig. 2. These simulations clearly indicate that for a filling factor $\nu \neq 1/2$, the DOS is asymmetric and the chemical potential is shifted. Using these results we can identify the dimensionless numerical coefficients $a_1 \simeq 2.9$ and $a_2 \simeq 0.4$ by a simple linear fit. We note that $a_1 \gg a_2$, thus, the contribution to the thermopower caused by $\Delta\mu$ in Eq. (7) is dominant.

Now, we can calculate Eq. (5) and the analog contribution for holes using Eq. (6) for the DOS together with the numerically found values for $a_{1,2}$.[18] Finally we derive the expression for the thermopower S of granular semiconductors in the limit of weak coupling between the grains

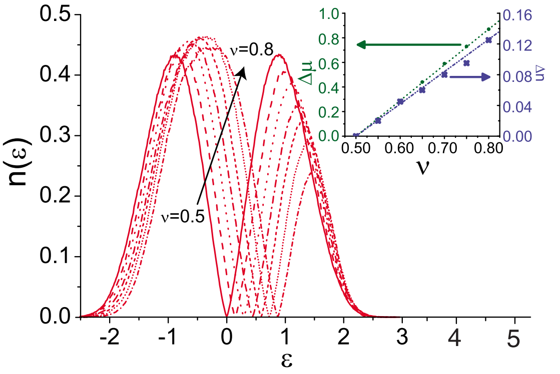

FIG. 2. (Color online) Simulation results for the density of state $n(\varepsilon)$ vs energy for different filling factors ν, indicated by the arrow across the curves from $\nu=0.5$ to $\nu=0.8$ in steps of $\Delta\nu=0.05$ ($\nu>1/2$ corresponds to n-type doped semiconductors). The simulations were done for a 2D Coulomb glass model, simulating the whole weakly coupled granular sample[16,17] for a system size of 500^2. The inset shows the dependence of the shift of the chemical potential $\Delta\mu$ and the asymmetry of the density of states Δn on ν (see text). Using these data we extract the numerical coefficients $a_1\approx 2.9$ and $a_2\approx 0.4$ in Eq. (7) by linear fitting.

$$S = -\frac{d[\Delta\mu + \Delta n T_0 T]}{eT} = \frac{1/2-\nu}{e} d\left[a_1\frac{T_0}{T} + a_2\right]. \tag{7}$$

We note that the r.h.s. of Eq. (7) vanishes for filling factor $\nu=1/2$, i.e., for compensated semiconductors.

Equation (7) is valid for temperatures $T<T_0=E_c \ln P_i^{-1}$ and weak coupling between the grains $g_t<1$. Under this condition, the electric conductivity σ is[7,8]

$$\sigma \simeq 2e^2 a^{2-d} g_t e^{-\sqrt{T_0/T}}. \tag{8}$$

The thermal conductivity κ consists of two parts: the electron, κ_e and phonon, κ_{ph}. The phonon contribution κ_{ph} at temperatures $T\leq\Theta_D$, where Θ_D is the Debye temperature is given by[19,20]

$$\kappa_{ph} \sim l_{ph}^{2-d} T[T/\Theta_D]^{d-1}, \tag{9}$$

where $l_{ph}=\lambda_F \exp(\Theta_D/[aT/\lambda_F])$ is the phonon mean-free path in granular semiconductors with λ_F being the Fermi length. [For $a\simeq 10$ nm, $\lambda_F\simeq 1$ Å, $\Theta_D\sim 450$ K, one obtains $l_{ph}\simeq 1$ nm at $T\simeq 200$ K] The main contribution to the electric part κ_e of the thermal conductivity κ appears due to a single closed co-tunneling loop (see Fig. 1). An electron executing a co-tunneling loop brings back its charge to the starting grain and, hence, there is little change in the electrical conductivity and therefore the classical activation term is absent. However, there is no requirement that the returning electron has exactly the same energy (due to inelastic processes). The leading contribution to κ_e is proportional to g_t^2 and is depicted in the diagram shown in Fig. 3(a). The analytical result corresponding to this process can be estimated as follows

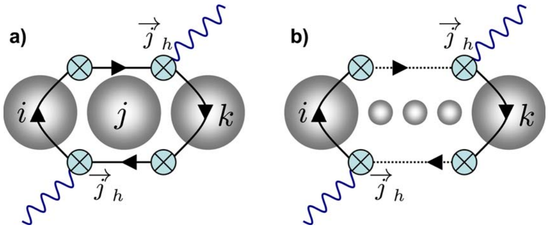

FIG. 3. (Color online) Diagrams describing lowest (a) and higher (b) order co-tunneling processes (multiple tunneling events are indicated by the dotted lines). The solid lines denote the propagator of electrons. The tunneling vertices are described by the circles. The wavy lines indicate the external coupling to the heat vertices.

$$\kappa_e \sim g_t^2 a^{2-d} T \frac{e^{-2\delta/T}}{[\tau \max(\delta, E_c)]^2}, \tag{10}$$

where we used Eq. (2) for the inelastic co-tunneling probability P_i^{in}. Since at relatively high temperatures the phonon contribution κ_{ph} to thermal conductivity is dominant, we can neglect the contribution κ_e in the following.

Substituting Eqs. (7) and (9) into the expression for the figure of merit $ZT\simeq S^2\sigma T/\kappa_{ph}$ we obtain the result

$$ZT \sim \frac{2d^2 g_t e^{-\sqrt{T_0/T}}[\Delta\mu/T + \Delta n T_0]^2}{(\lambda_F/a)^{2-d}(T/\Theta_D)^{d-1}} e^{(d-2)\Theta_D\lambda_F/Ta}. \tag{11}$$

Here the expressions for $\Delta\mu$ and Δn are given above Eq. (4). Using Eq. (11) we can calculate the temperature T^* at which ZT has its maximum value, given by the solution of the quadratic equation $T^*=\frac{4}{T_0}[\alpha+(d+1)T^*]^2$, where $\alpha=(2-d)\Theta_D\lambda_F/a$. In $d=2$ we get $T^*_{2D}=T_0/[4(d+1)]$, while in three-dimensional (3D) the existence of a maximum depends on the values of α and T_0.

In Fig. 4 we plotted the figure of merit ZT for a two and three-dimensional system, using typical parameters for granular semiconductors: $\lambda_F\simeq 1$ Å, $\Theta_D\simeq 450$ K, $T_0\simeq 2E_c$, $\varepsilon_r\simeq 4$, and $g_t\simeq 0.1$. Figure 4(a) shows the temperature dependence of ZT for two different filling factors $\nu=0.6, 0.65$ for a grain size of $a\simeq 5$ nm (For this size and the above dielectric constant we get $E_c\sim 800$ K. In Refs. 4 and 5 the grain sizes between 20 and 50 nm were investigated). We clearly see that the figure of merit can well exceed one. However, we remark that ZT depends inversely proportional on the numerical coefficient of κ_{ph}, which is assumed to be one here. Figure 4(b) shows the grain size dependence of ZT at fixed temperature $T=200$ K. At this temperature for the above system parameters, the figure of merit is optimal for grain sizes $a^*_{3D}\simeq 4$ nm in 3D and $a^*_{2D}\simeq 6$ nm in 2D.

Now, we concentrate on the compensated regime (filling factor $\nu=1/2$). In this case Eq. (7) predicts zero thermopower S. Thus, the fundamental question exists what mechanism may lead to a finite thermopower in this case. We start our consideration with the fact that the thermopower S can be expressed in terms of the thermoelectric coefficient η and the electric conductivity σ as $S=\eta/\sigma$. Thus, to calculate the thermopower S one has to know the thermoelectric coefficient η. To estimate $\tilde{\eta}$ we use the diagram shown in Fig.

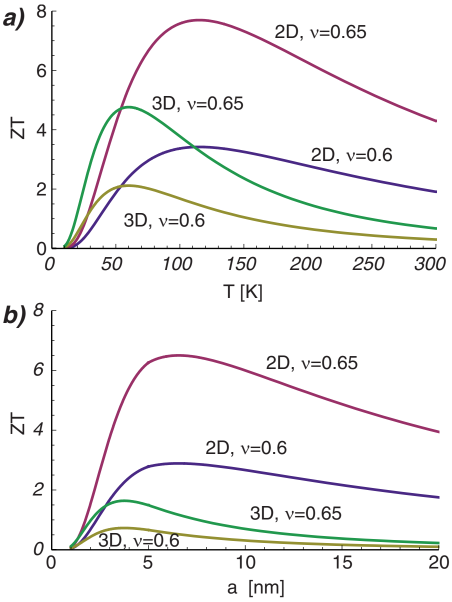

FIG. 4. (Color online) Plots of the figure of merit ZT vs temperature T (a) and grain size a (b) for two (2D) and three (3D) dimensional samples and two different filling factors $\nu=0.6, 0.65$ (n-type doped granular semiconductors). Typical material parameters are given in the text. In a), the grain size is chosen to be $a=5$ nm and in b), the temperature is fixed at 200 K. One sees that ZT can be optimized by choosing appropriate grain sizes: For the used parameters, these sizes are about 4 nm in 3D and 6 nm in 2D.

3(b) (here the tilde indicates the compensated case). Since the dominant contribution to $\tilde{\eta}$ vanish due to particle-hole symmetry, to obtain a nonzero result it is necessary to take into account the fact that the tunneling matrix elements t and the density of states n depend on energy. In the leading order, the corrections to both quantities are proportional to T/E_F, where E_F is Fermi energy.[6] As a result, the thermoelectric coefficient is given by the expression

$$\tilde{\eta} \sim e a^{2-d} g_t [T/E_F] e^{-\sqrt{T_0/T}}, \tag{12}$$

where the temperature scale T_0 was defined below Eq. (3). Substituting Eqs. (8) and (12) into the expression for thermopower we obtain $\tilde{S} \sim (1/e)(T/E_F)$.

It follows that the thermopower $\tilde{S}$ is finite although small, leading to a small figure of merit as well, since $ZT \sim \tilde{S}^2$. Using Eqs. (7) and the expression for $\tilde{S}$ one can see that the ratio of two thermopowers for compensated $[\nu=1/2]$ and for n-type $[\nu>1/2$, Eq. (7)] regimes is of order $\tilde{S}/S \sim T^2/(T_0 E_F) \sim 10^{-3}-10^{-2} \ll 1$.

In conclusion, we studied the effects of doping and confinement on the thermoelectric properties of granular semiconductors. In a recent experiment,[21] it was shown that confinement effects substantially enhance the thermopower in nanogranular PbSe. We showed that the figure of merit ZT is optimized for typical material parameters at grain sizes of 5 nm and can be larger than one—for $ZT>3$ these materials become important for applications.[1] Doping effects lead to a shift of the chemical potential and asymmetry of the density of states which is related to the physics of Coulomb glasses. We also discussed the case of compensated (half filling, $\nu=1/2$) granular semiconductors. We showed that in this regime the thermopower is finite, but rather small.

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