PHYSICAL REVIEW B **81**, 155415 (2010)

Violation of the Wiedemann-Franz law in quasi-one-dimensional organic crystals

Anatolie Casian
Department of Computers, Informatics and Microelectronics, Technical University of Moldova, MD-2004 Chisinau, Republic of Moldova

(Received 31 October 2009; revised manuscript received 9 January 2010; published 6 April 2010)

The charge and energy transport in some highly conducting quasi-one-dimensional organic crystals is studied. Two electron-phonon interactions and scattering on impurity are considered. It is found that the Wiedemann-Franz law is strongly violated. The Lorentz number is diminished for a large interval of Fermi energy: (1) due to faster decrease in thermal conductivity than the electrical conductivity when the conduction band width is decreased, and (2) due to strong dependence of relaxation time on carrier energy. The Lorentz number becomes dependent on crystal purity and may be reduced by up to ten times and even more in comparison with ordinary materials. This is favorable for the increase of thermoelectric figure of merit *ZT*. It is predicted that in really existing crystals of tetrathiotetracene-iodide, when after the optimization of carrier concentration $ZT=1.4$ is expected, the Lorentz number is reduced by 1.6 times with respect to the usual value.

DOI: 10.1103/PhysRevB.81.155415 PACS number(s): 72.15.Jf, 72.80.Le, 73.63.−b, 84.60.Rb

I. INTRODUCTION

Presently, large application of thermoelectric converters of energy is limited by their low efficiency. The latter is determined by low thermoelectric figure of merit *ZT* of used materials. In order to increase *ZT*, it needs to increase in the same material the electrical conductivity σ, the thermopower (Seebeck coefficient) S, and to diminish the thermal conductivity κ at operating temperature T. However, this strategy applied to known bulk materials has not yet produced materials with $ZT > 1$ at room temperature, because σ, S and κ are not independent each of other.

Recently, significant increase in *ZT* has been obtained in thermoelectric materials prepared as low-dimensional structures or composites.[1] The growth of *ZT* is determined first, by the growth of electronic density of states, which leads to the growth of the thermoelectric power factor $P=\sigma S^2$ and, second, by additional scattering of phonons at interfaces of structure which leads to the decrease in thermal conductivity.

Really, an increase in P has been measured in n- and p-type PbTe/PbEuTe quantum-well superlattices.[2,3] However, theoretical investigations[4–7] have shown rather limited possibilities to increase P and *ZT* in such structures. The increase in *ZT* has been obtained,[8–11] but mainly due to the reduction of lattice thermal conductivity, than the increase in power factor. A 100-fold reduction in κ has been obtained in arrays of Si nanowires, yielding $ZT=0.6$ at room temperature[12] and[13] $ZT \sim 1$ at 200 K. The phonon contribution to κ is reduced to the limit of amorphous Si.

Note that from the theoretical point of view there is no an upper limit for *ZT*. Therefore, it is clear that mainly by the increase of P it will be possible to obtain really high values of *ZT*. But the increase in σ leads to the increase in carriers' contribution κ_e to the total thermal conductivity k, in accordance with the Wiedemann-Franz law. This law is generally valid in ordinary materials at high temperatures. In the Q1D organic crystals the temperatures near the room one can be considered as high because such T is significantly greater than the Debye temperature which is rather low, $\sim 85-100$ K. Therefore, it is necessary to search new materials with more complicated internal interactions that would overcome this difficulty. This problem is very important and urgent.

The aim of this paper is to show that under certain conditions the Wiedemann-Franz law is strongly violated in Q1D organic crystals and the Lorentz number may be significantly less then in ordinary materials for a large interval of carriers' concentrations. This is favorable for thermoelectric applications of such materials, because it gives a possibility to increase *ZT*. It will be demonstrated for concrete Q1D organic crystals of tetrathiotetracene-iodide, TTT_2I_3. Note also that the TTT_2I_3 crystals can be considered as nanostructured bulk materials, because they consist of conducting chains of molecules the distances between the chains being of the order of one nanometer.

II. ELECTRON-PHONON AND ELECTRON-IMPURITY INTERACTIONS

Let us consider a Q1D organic crystal of a tetragonal symmetry formed from linear chains of molecules. The lattice constant along the chains is considerably smaller than between the chains. As a result, the overlap of conduction electrons wave functions along chains is much greater than that of electrons from different chains. Accordingly, the transport mechanism along chains is of the band type and between chains is of hopping type. In the transport processes the latter is of less importance and can be neglected. Usually the ratio of longitudinal electrical conductivity along chains to the transversal one across the chains is of the order of 10^3. Thus, the electrons are moving in a 1D conduction band.

The Hamiltonian of a linear chain of molecules in the tight-binding and nearest-neighbors approximations takes the form[14]

$$H=\sum_k \varepsilon(k)a_k^\dagger a_k+\sum_q \hbar\omega_q b_q^\dagger b_q + \sum_{k,q}[A_1(k,q)+A_2(q)]a_k^\dagger a_{k-q}(b_q^\dagger+b_{-q}) + \frac{Id}{Na}\sum_{k,p}\sum_{l=1}^{N_i}\exp(ipr_l)a_k^\dagger a_{k-p}. \tag{1}$$

Here the first term is the energy operator of the free electrons with the projection of wave vector k along the chains and the energy $\varepsilon(k)=2w(1-\cos ka)$, where $|w|$ and a are the energy of an electron transfer between the nearest molecules and the lattice constant along chains, $a_k^\dagger(a_k)$ are the creation (annihilation) operators of such carrier. The second term in Eq. (1) is the energy of longitudinal acoustic phonons with the projection q of the wave vector along the chains and the frequency $\omega_q=2v_s a^{-1}|\sin qa/2|$, where v_s is the sound velocity along the chains. The third term in Eq. (1) represents the electron-phonon interactions. Two mechanisms of such interactions are considered. The matrix element $A_1(k,q)$ describes the interaction caused by the fluctuations of the transfer energy $|w|$, due to intermolecular vibrations (phonons)

$$A_1(k,q) = 2i\hbar^{1/2}w'(2NM\omega_q)^{-1/2}[\sin ka - \sin(k-q)a], \tag{2}$$

where M is the mass of molecule, N is the number of molecules in the basic region of the chain. This interaction is similar to that of deformation potential and the coupling constant is proportional to the derivative w' of w with respect to the intermolecular distance.

The matrix element $A_2(q)$ describes the interaction, due to fluctuations of the polarization energy of molecules surrounding the conduction electron, caused by the same phonons

$$A_2(q) = 4i\hbar^{1/2}e^2\alpha_0 a^{-5}(2NM\omega_q)^{-1/2}\sin qa. \tag{3}$$

Here e is the charge of carrier. The coupling constant of this interaction is proportional to the average polarizability α_0 of the molecule. So as α_0 is roughly proportional to the volume of molecule, this interaction is important for crystals formed from big molecules. Such are, usually, the Q1D organic crystals.

The last term in Eq. (1) describes the scattering of carriers on impurities that always exist in crystals. For simplicity the impurities are considered neutral and pointlike. In Eq. (1) N_i is the number of impurities with the random coordinate r_l along the chain, I and d are the effective height and width of the impurity potential, p is the transferred wave vector between a carrier and the impurity. In order to obtain the Hamiltonian of crystal it needs to sum up in Eq. (1) on all chains in the basic region of the crystal.

This model will be applied to the Q1D organic crystals of tetrathiotetracene-iodide, $\mathrm{TTT_2I_3}$, for which the conduction band width[15–17] $\Delta=4w=0.64$ eV $\sim 25k_0T_0$, (k_0 is the Boltzmann constant, $T_0=300$ K) is rather large that justifies the application of band model. The Coulomb interaction between carriers is neglected in Eq. (1) because it is strongly screened by highly polarizable molecules.

III. CHARGE AND ENERGY TRANSPORT

Let us consider the charge and energy transport under the action of a weak electric field E and a temperature gradient ∇T, applied along the chains of the Q1D crystal in the above presented model. The electrical I_e and thermal I_Q current densities are determined as

$$I_e = \sigma E - \sigma S\,\nabla T, \quad I_Q = T\sigma S E - K\,\nabla T, \tag{4}$$

where K is the electronic thermal conductivity at zero electric field. The usual electronic thermal conductivity at zero electric current κ_e is defined by $k_e=K-T\sigma S^2$. The current densities from Eq. (4) can be calculated using the expressions

$$I_e = \frac{2ez}{Nabc}\sum_k v_k f_k^1, \quad I_Q = \frac{2z}{Nabc}\sum_k [\varepsilon(k)-E_F]v_k f_k^1, \tag{5}$$

where f_k^1 is the deviation from equilibrium distribution function of carriers, v_k is the velocity of carrier, a, b, and c are the lattice constants, z is the number of chains through the transversal section of the unit cell, E_F is the Fermi energy. In Eq. (5) the summing up on all chains is carried out.

We will study the transport at temperatures T close to room temperature. As it is shown in Ref. 14 at such T the scattering processes on acoustic phonons can be considered elastic. The linear kinetic equation takes the form of Boltzmann equation and is solved as in Ref. 14. We obtain the following expressions for electrical conductivity σ and electronic thermal conductivity κ_e:

$$\sigma = R_0, \quad \kappa_e = (e^2T)^{-1}[R_2 - (R_1)^2/R_0], \tag{6}$$

where R_n are the transport integrals,

$$R_n = -\frac{2e^2az}{\pi\hbar^2bc}\int_0^\Delta (E-E_F)^n[E(\Delta-E)]^{1/2}\tau(E)f_0'dE. \tag{7}$$

Here E is the carrier energy, $0\le E\le\Delta$, $f_0'(E)$ is the derivative of Fermi distribution function with respect to E, and $\tau(E)$ is the relaxation time. So as the conduction band width is not too large, the integration in Eq. (7) is carried out on all energies in the band. Replacing the phonon distribution function by its high-T limit, we obtain for the relaxation time

$$\tau(E) = \frac{\hbar M v_s^2 w^2[E(\Delta-E)]^{1/2}}{2a^2k_0Tw'^2\gamma^2[(E-E_0^{s,p})^2+4w^2\gamma^{-2}D]}, \tag{8}$$

where γ is the ratio of amplitudes of above mentioned electron-phonon interactions $\gamma=2e^2\alpha_0/(a^5|w'|)$ and characterizes the relative role of these interactions, $E_0^{s,p}=2w(\gamma\pm1)/\gamma$ is the resonance energy (for s- and p-type bands, respectively), which corresponds to the maximum of $\tau(E)$, when $0\le E_0^{s,p}\le\Delta$. The dimensionless parameter D in Eq. (8) describes the scattering of carriers on impurities. It has the meaning of ratio of relaxation time $\tau_0(E)$, determined only by the electron-phonon interaction of deformation potential type, caused by w' (when $\gamma=0$, $D=0$), to the relaxation time $\tau_{im}(E)$, determined only by the carriers' scattering on impurities,

$$D = \tau_0(E)/\tau_{im}(E) = n_{im}I^2d^2Mv_s^2/(4a^3k_0Tw'^2), \tag{9}$$

where n_{im} is the linear concentration of impurity. So as D is proportional to n_{im}, it can be made much less than unity, if the crystal purity is sufficiently high.

Earlier, we have shown theoretically[18–20] that in some highly conducting Q1D organic crystals it is expected to obtain very high values of $ZT\sim20$. This increase can be achieved mainly due to significant mutual compensation[14,21] of both above mentioned electron-phonon interactions for a narrow strip of states in the conduction band. As a result, the relaxation time $\tau(E)$ as a function of carrier energy E takes the form of Lorentzian which can be rather sharp. Note that the model of the best thermoelectric material proposed by Mahan and Sofo[22] is characterized by a narrow distribution of the energy of carriers participating in the transport process of the Dirac delta function form. It was proposed in Ref. 22 to use the carriers' density of states close to a Lorentzian of very narrow width that could come from the contribution of electronic f-levels of rare-earth elements. We propose to use the Lorentzian form of relaxation time [Eq. (8)] that has a number of advantages: (1) high values of relaxation time ensure high values of mobility and of electrical conductivity; (2) sharp dependence on carrier energy ensures high values of the thermopower S, leading in such a way to significant growth of the power factor P; (3) as it will be shown further, the Lorentz number can be diminished under certain conditions and this can give important contribution to the growth of ZT. Recently, high values of ZT have been predicted in the one-molecule contact,[23] where the transmission function takes also the form of a Lorentzian. A violation of the Wiedemann-Franz law has been predicted in a single-electron transistor,[24] in some heavy-fermions compounds,[25] in weakly disordered Luttinger liquids,[26] but these systems do not refer to thermoelectric applications.

IV. LORENTZ NUMBER

The Lorentz number is defined as

$$L = \kappa_e / \sigma T. \tag{10}$$

It has been modeled for different values of E_F, γ, and D at room temperature.

First, we find that in the case of only the electron-phonon interaction caused by w' (small molecules, α_0 is negligible small) and nondegenerate gas L can be calculated analytically. For a large conduction band ($w \gg k_0 T_0$) it follows from Eq. (10) the usual result for scattering on acoustic phonons $L=2(k_0/e)^2$. For strongly degenerate gas, when the approximation method of calculation of integrals with $f_0'(E)$ can be applied, we also obtain from Eq. (10) a usual result $L=(\pi^2/3)(k_0/e)^2$. These limited cases are seen in the Fig. 1 as horizontal parts of solid line, calculated numerically after Eq. (10) with $\gamma=0$ and $D=0$ for a large conduction band ($w=1.6$ eV) and the other parameters as for the dashed line. The latter is calculated for a narrower conduction band with the parameters of Q1D organic crystal of tetrathiotetracene-iodide, TTT_2I_3: $w=0.16$ eV, $w'=0.26$ eV Å^{-1}, $M=6.5\times10^5 m_e$ (m_e is the mass of free electron), $a=18.46$ Å, $b=18.35$ Å, $c=4.96$ Å, ($\boldsymbol{c}$ is the direction of chains), $v_s=1.5\times10^5$ cm/s, the lattice thermal conductivity $\kappa_l=0.6$ W m^{-1} K^{-1}. The dimensionless Fermi energy $\varepsilon_F=E_F/2w$ is varied between $-0.5(E_F=-6\ k_0T_0)$ and unity ($E_F=12k_0T_0$). It is seen (dashed line in Fig. 1) that even in crystals formed from small molecules, when only one interaction mechanism is involved and the mutual compensation[14] of mentioned electron-phonon interactions does not take place, the Wiedemann-Franz law is violated

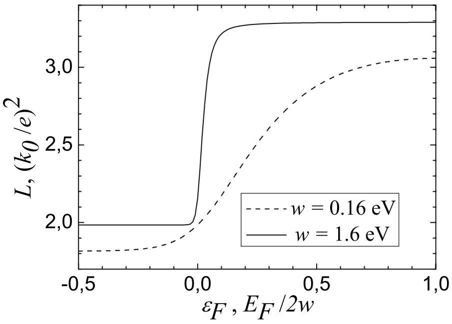

FIG. 1. Lorentz number L as a function of ε_F for the case of only the interaction caused by w'. The solid and dashed lines are for a large and a narrower conduction bands.

and L is diminished in the whole interval of ε_F variation. The analysis shows that it is occurred because with the decrease of conduction band width κ_e decreases faster than σ. The diminution of L is more significant for $\varepsilon_F \sim 0.1-0.3$. So, for $\varepsilon_F=0.1$, L is reduced by 1.5 times in comparison with the case of large band. It is favorable for thermoelectric applications of such materials.

Let us consider in more details the Q1D "synthetic metal" TTT_2I_3. It has been investigated many years ago[15–17] with the aim to create a high critical temperature T_c organic superconductor. After the discovery of high T_c cuprates and the understanding that for a superconducting transition the Q2D gas of carriers is required, the investigations of TTT_2I_3 were stopped. Recently it was found[27] that these crystals may have prospect thermoelectric properties. It has been shown theoretically that in really existing such crystals it is possibly to increase the figure of merit ZT up to 1.4 at room temperature, if the carriers concentration is diminished by approximately 2.5 times with respect to the concentration in stoichiometric crystals. More over, the crystals have needlelike form as almost ready legs for thermocouples. When the crystals are obtained from solution,[17] they have in the same batch $\sigma \sim 800-1800$ Ω^{-1} cm^{-1}, whereas being grown from gas phase,[16] they have $\sigma \sim 10^3-10^4$ Ω^{-1} cm^{-1} at room temperature. The electrical conductivity σ is very sensitive to crystal purity and perfection. If only the electron-phonon interaction caused by w' is considered, it is difficult to explain such high values of σ. In this case it would expect unreal small value of w' in such materials. Therefore, we will consider both electron-phonon interactions and their mutual compensation (i.e., put $\gamma \neq 0$), as in Ref. 14. In mixed valence compound TTT_2I_3 the carrier concentration is $n=1.2\times10^{21}$ cm^{-3} which corresponds to ε_F a little less than 0.4. Only the TTT chains are conducting and the carriers are holes. The compound admits the formation of nonstoichiometric crystals with increased or diminished iodine contents and holes concentration, respectively.

The parameter γ is not known in TTT_2I_3 because the molecule polarizability α_0 is not known. In the Fig. 2 the dependences of L on D are presented for $\varepsilon_F=0.1$, 0.2, 0.3, and 0.4. We have put $\gamma=1.7$ that corresponds to $\alpha_0=45$ Å^3. For comparison, in antracene $\alpha_0=25$ Å^3, but TTT molecule is bigger and α_0 must be greater too. It is seen that L is additionally diminished in comparison with the values of dashed line in

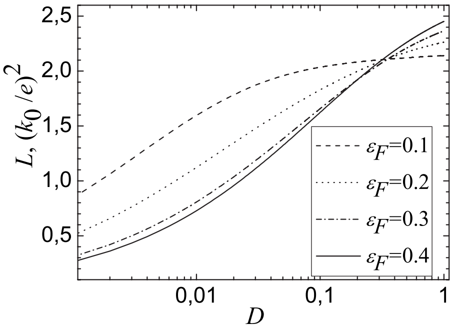

FIG. 2. Lorentz number L as a function of dimensionless parameter D for different values of ε_F and $\gamma = 1.7$.

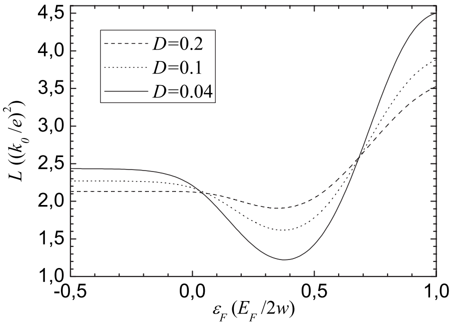

FIG. 4. Lorentz number L as a function of ε_F for TTT_2I_3 crystals with $\gamma = 1.7$ and different degree of purity.

Fig. 1. The diminution is especially strong in purer crystals (for smaller D) at higher values of ε_F. So, at $\varepsilon_F \sim 0.4$ and $D = 10^{-3}$ it results from Fig. 2 $L = 0.3(k_0/e)^2$. This means that L is 11 times less than in ordinary materials and 9 times less than for dashed line from Fig. 1 in presence of only one electron-phonon interaction. This additional diminution is determined by the stronger energy dependence of relaxation time than in the case of only the deformation potential interaction.

The dependence of relaxation time on carrier energy is presented in Fig. 3 for $\gamma = 1.7$ and different degrees of crystal purity ($D = 0.2$, 0.1, and 0.04): the dashed and dotted lines correspond to existing crystals of TTT_2I_3 with $\sigma = 5 \times 10^3$ and 10^4 Ω^{-1} cm^{-1}, respectively, but the solid line is calculated for slightly purer crystals with $\sigma = 2 \times 10^4$ Ω^{-1} cm^{-1} at room T. For comparison, in Fig. 3 the case of only the deformation potential interaction ($\gamma = 0$, $D = 0$) is also presented—by the dash-doted line. In the last case the energy dependence of relaxation time is rather smooth and L corresponds to dashed line in Fig. 1. When $\gamma = 1.7$, the relaxation time has a maximum which grows with the decrease of D and becomes even sharp at $D = 0.04$ (solid line in Fig. 3). The maximums occur at ε close to 0.4, or $E \sim 0.128$ eV $\sim 5k_0T_0$. As it is seen form Fig. 4, near this value of ε_F the Lorentz number has a minimum which also is more pronounced for smaller values of D. For $D = 0.04$ the minimum is $L = 1.2(k_0/e)^2$ or is by 2.7 times less than in ordinary materials.

The minimums of L are determined by the carriers with energies around the maximums of relaxation time. The contribution of these carriers to the charge transport leads to an increase in σ, which obtains high maximums at $\varepsilon_F \sim 0.4$, due to the growth of relaxation time. Simultaneously κ_e grows too, but not so strongly as σ, due to narrower interval of energy of carriers that give main contribution to the energy transport. In the limit when the Lorentzian in Eq. (8) is transformed in δ function, $\kappa_e \to 0$, because all carriers participating in the transport have the same energy. The maximums of κ_e are relatively lower and larger than those of σ and are displaced to higher values of Fermi energy $\varepsilon_F \sim 0.6$. Such behavior of σ and κ_e explains also the growth of L for $\varepsilon_F < 0.05$ and especially for $0.75 < \varepsilon_F < 1$. In these intervals of Fermi energy σ decreases faster than κ_e, due to larger maximums of κ_e than of σ as functions of ε_F and to the displacement of κ_e maximum to higher values of ε_F.

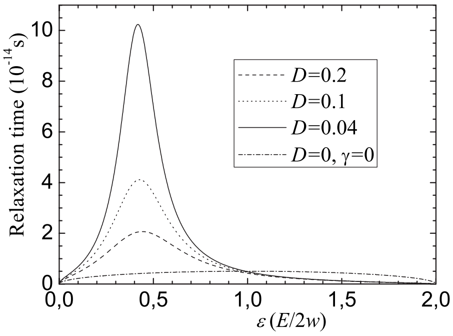

FIG. 3. Relaxation time as a function of carrier energy in unities of $2w$ for $\gamma = 1.7$ (dashed, dotted and solid lines), and $\gamma = 0$ (dash-dotted line).

The analysis shows that in TTT_2I_3 crystals at usual carriers concentration n (ε_F a little less than 0.4) ZT weakly depends on D and is only ~ 0.1, because the thermopower is small and the power factor P is only ~ 10 μW cm^{-1} K^{-2}. Nevertheless, the diminution of L can give important contribution to the increase in ZT for lower values of ε_F. For this it needs to diminish the carriers' concentration. Thus, the calculations show that when n is diminished from 1.2×10^{21} cm^{-3} by 2.5 times (to $\varepsilon_F = 0.1$, $D = 0.1$), and $ZT \sim 1.4$ is expected[27] in really existing TTT_2I_3 crystals the Lorentz number becomes $\sim 2(k_0/e)^2$ in comparison with the usual value of $\sim 3.2(k_0/e)^2$ at given Fermi energy, i.e., L is diminished by 1.6 times. The calculated parameters in this case are $\sigma = 2.1 \times 10^3$ Ω^{-1} cm^{-1}, $S = 194$ μV/K, $\kappa_e = 1.0$ W m^{-1} K^{-1}.

In purer crystals with higher values of σ the diminution of L will be more over, as it is seen in Fig. 2. This means that highly conducting Q1D organic crystals, as synthetic metal TTT_2I_3, are very prospect materials for thermoelectric applications.

V. CONCLUSION

In conclusion, we have investigated theoretically the charge and energy transport in some highly conducting quasi-one-dimensional organic crystals with the application to the thermoelectric properties of tetrathiotetracene iodide, TTT_2I_3, crystals. The interactions of charge carriers with acoustic phonons determined both by the variation of energy transfer of the carrier from a molecule to the nearest one along the one-dimensional chains (interaction of deformation potential type) and by the variation of polarization energy of molecules surrounding the carrier (interaction of polaron type) are considered. The scattering on impurities is also taken into account. We found a strong violation of the Wiedemann-Franz law. The Lorentz number L is diminished into a large interval of Fermi energy and is increased in other intervals as compared with the usual values. The diminution of L is determined, first, by a faster decrease of thermal conductivity than the electrical conductivity when the conduction band width is decreased and, second, by stronger dependence of relaxation time on carrier energy. The Lorentz number becomes dependent on crystal purity and may be reduced up to ten times and even more in comparison with ordinary materials. It is favorable for thermoelectric applications of such materials. The calculations show that in really existing crystals of TTT_2I_3, when after the optimization of carriers concentration the value of the thermoelectric figure of merit $ZT=1.4$ is expected, L is diminished by 1.6 times in comparison with the usual value at given Fermi energy. It is expected that in purer crystals with higher values of σ the diminution of L will be more over.

ACKNOWLEDGMENTS

Discussions with Z. Dashevsky and E. B. Yagubskii are acknowledged. The work was supported by Grant No. 305b/s of the Academy of Sciences of Moldova.

---

[1] M. S. Dresselhaus, G. Chen, M. Y. Tang, R. G. Yang, H. Lee, D. Z. Wang, Z. F. Ren, J.-P. Fleurial, and P. Gogna, Adv. Mater. **19**, 1043 (2007).

[2] T. C. Harman, P. J. Taylor, M. P. Walsh, and B. E. LaForge, Science **297**, 2229 (2002).

[3] T. C. Harman, D. L. Spears, D. R. Calawa, S. H. Groves, and M. P. Walsh, *Proceedings of 16th International Conference on Thermoelectrics, Dresden, Germany* (IEEE, Piscataway, NJ, 1997), pp. 416–423.

[4] A. Casian, I. Sur, H. Scherrer, and Z. Dashevsky, Phys. Rev. B **61**, 15965 (2000).

[5] A. Casian, Z. Dashevsky, V. Kantser, H. Scherrer, I. Sur, and A. Sandu, Phys. Low-Dimens. Struct. **5/6**, 49 (2000).

[6] D. A. Broido and T. L. Reinecke, Phys. Rev. B **64**, 045324 (2001).

[7] I. Sur, A. Casian, and A. Balandin, Phys. Rev. B **69**, 035306 (2004).

[8] H. Beyer, J. Nurnus, H. Böttner, A. Lambrecht, T. Roch, and G. Bauer, Appl. Phys. Lett. **80**, 1216 (2002).

[9] R. Venkatasubramanian, E. Siivola, T. Colpitts, and B. O'Quinn, Nature (London) **413**, 597 (2001).

[10] S. Ghamaty, J. C. Bass, and N. B. Elsner, in *Thermoelectrics Handbook, Macro to Nano*, edited by D. M. Rowe (CRC Press, Boca Raton, FL, 2006), Chap. 57.

[11] T. C. Harman, M. P. Walsh, B. E. Laforge, and G. W. Turner, J. Electron. Mater. **34**, L19 (2005).

[12] A. I. Hochbaum, R. Chen, R. D. Delgado, W. Liang, E. C. Garnett, M. Najarian, A. Majumdar, and P. Yang, Nature (London) **451**, 163 (2008).

[13] A. I. Boukai, Y. Bunimovich, J. Tahir-Kheli, J.-K. Yu, W. A. Goddard III, and J. R. Heath, Nature (London) **451**, 168 (2008).

[14] A. Casian, V. Dusciac, and Iu. Coropceanu, Phys. Rev. B **66**, 165404 (2002).

[15] L. C. Isett, Phys. Rev. B **18**, 439 (1978).

[16] B. Hilti and C. W. Mayer, Helv. Chim. Acta **61**, 501 (1978).

[17] I. F. Shchegolev and E. B. Yagubskii, in *Extended Linear Chain Compounds*, edited by I. S. Miller (Plenum Press, New York, 1982), Vol. 2, pp. 385–435.

[18] A. Casian, Z. Dashevsky, H. Scherrer, V. Dusciac, and R. Dusciac, in *Proceedings of 22nd International Conference on Thermoelectrics*, edited by H. Scherrer and J.-C. Tedenac (IEEE, Piscataway, NJ, 2004), pp. 330–335.

[19] A. Casian, in *Thermoelectric Handbook, Macro to Nano*, edited by D. Rowe (CRC Press, Boca Raton, FL, 2006), Chap. 36.

[20] A. Casian, J. Thermoelectr. **3**, 45 (2007).

[21] A. Casian, A. Balandin, V. Dusciac, and Iu. Coropceanu, Phys. Low-Dimens. Struct. **9/10**, 43 (2002).

[22] G. D. Mahan and J. O. Sofo, Proc. Natl. Acad. Sci. U.S.A. **93**, 7436 (1996).

[23] P. Murphy, S. Mukerjee, and J. Moore, Phys. Rev. B **78**, 161406(R) (2008).

[24] B. Kubala, J. König, and J. Pekola, Phys. Rev. Lett. **100**, 066801 (2008).

[25] K.-S. Kim and C. Pepin, Phys. Rev. Lett. **102**, 156404 (2009).

[26] A. Garg, D. Rasch, E. Shimshoni, and A. Rosch, Phys. Rev. Lett. **103**, 096402 (2009).

[27] A. Casian, J. Stockholm, V. Dusciac, and V. Nicic, J. Nanoelectron. Optoelectron. **4**, 95 (2009).