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CONTEMPORARY MATERIALS FOR HEAT HARVESTING

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ABSTRACT
In this paper, we have introduced new contemporary materials for heat harvesting, based on thermoelectric effect (or Seebeck effect): rear earth mono-pnictides and graphene. Measure of effectiveness for transformation of heat to electricity is represented with zT factor, which measure heat harvesting potential. zT factor is related with heat and electric conductivity coefficients. For better understanding of these processes, it is necessary to comprehend all mechanisms of electron and phonon scattering in thermoelectric materials. Theory of electron and hole (or carriers) scattering was introduced trough modified Boltzman transport equation, and theory predicted results are in a good agreement with experimental data.

1. INTRODUCTION

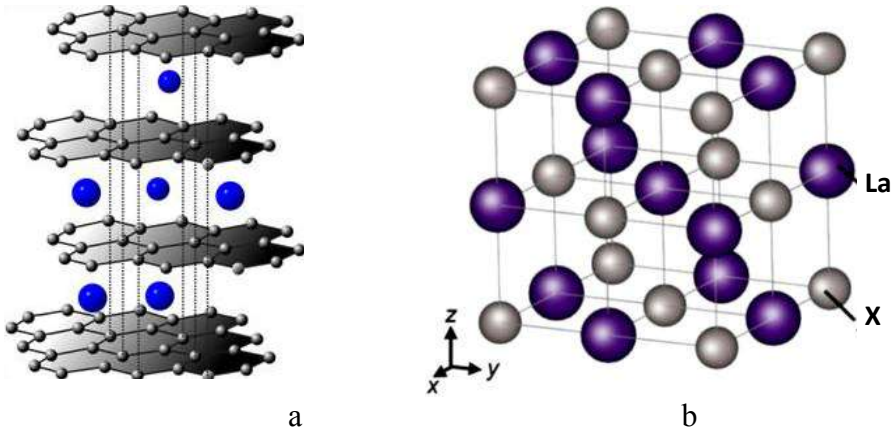
Thermoelectric effect is phenomena characteristic for some materials that are capable for getting electricity directly from heat. When we place thermoelectric material in some heat flux, where on different sides of thermoelectric exist different temperatures – then on those sides appear electric potential difference. The effect exhibit many materials, but most common are semiconductors (Bi_2Re_3, PbTe, SiGe) doped with various admixtures to amplify effect. The converting heat to electricity efficiency is expressed with dimensionless *zT* factor [1]:

$$zT = \frac{S^2 T}{\rho \kappa}, \qquad (1)$$

Where ρ and κ are coefficients of electric resistivity and thermal conductivity, respectively; S – Seebeck constant (characteristic of material); T – temperature.
From the equation (1) one can see that materials with high zT factor must conduct the electric current well, but at the same time to conduct heat poorly. These requirements are opposite in most materials and for better understanding we must analyze mechanisms of heat and electric conductivity, i.e. electron and phonon transport trough crystals. Owing to this, thermal coefficient have two components: $\kappa = \kappa_e + \kappa_{ph}$. Although phonons have greater significance in heat capacity, for the transport phenomena electrons are of much greater importance [2]. The analysis of transport processes in conducting crystals is usually analyzed by solving the Boltzmann transport equation in the approximation of the relaxation time. If these processes are analyzed micro-theoretically, for example by applying Green's methods [3], then again, relaxation times occur as inevitable quantities and without them transport coefficients of interest cannot be determined. The relaxation times can be determined depending on the different sizes, e.g. energy (wave vector), concentration of the (quasi)particles involved in transport processes, temperatures, etc. The dependence of the relaxation time on temperature is especially important, since the desired transport coefficients are determined as a function of temperature. This is significant because of the relatively simple experimentally measurement of these coefficients and the comparison of their values and behavior with predictions of theoretical mechanisms.

2. NEW THERMOELECTRIC MATERIALS: GRAPHENE AND RARE EARTH MONO-PNICTIDES

Graphene is true 2D material [4], made of one-layer carbon atoms, mutually interconnected in hexagonal structure, with thickness of just one carbon atom (Fig 1a). Graphite with thickness of 1 mm contain about 3 million layers of graphene. Graphene have unique properties: it is optically transparent, but also so dense that smallest gas atoms could not get through; this is the thinnest but strongest known material; with very high electrical conductivity (even better than Cu). The last physical property is the most interesting regarding thermoelectric effect.
The next contemporary materials of interest with thermoelectric potential are lanthanum compounds [5], with general formula LaX, where X=P, As, Sb and Bi (Fig 1b), and the most potential among them is LaP. Although researchers have shown these materials are still far below the characteristics of PbTe (where $zT \approx 2.2$) it is considered that with fine-tuning of charge carriers concentration and increase of temperatures – they could achieve higher values of zT factor.



a b

Figure 1. a) graphene; b) lanthanum mono-pnictides LaX

The key role for specific and high electric conductivity is 2D structurally shape, which is obviously evident in graphene, but also exist (and one can see and imagine various planar structures) in mono-pnictides. Concentration of charge carriers play significant role on *zT* factor, and that is experimentally proved and represented on Fig.2.

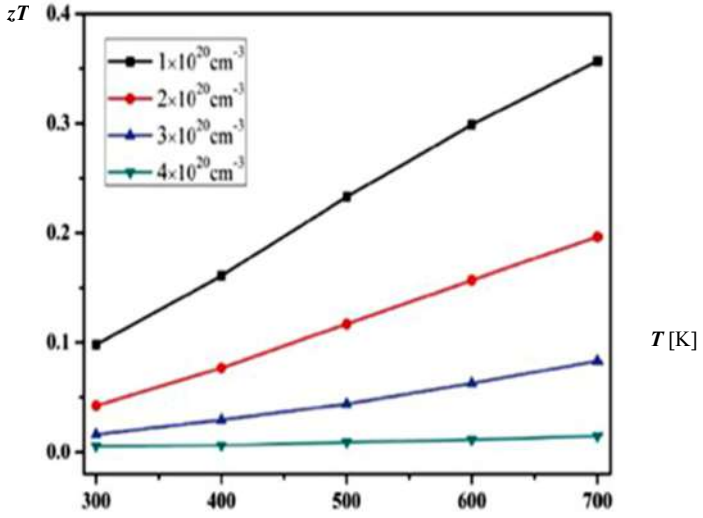


Figure 2. zT factor dependence from temperature for various concentration of charge carriers [5]

It is considered that electrons have planar character of movement when they find themselves in homogenous electric filed or in temperature gradient. Significance for understanding electron transport processes laying in transport coefficient and knowledge of electron scattering. We will first introduce how are electrical and heat conductance calculated for the 2D planar structures using Boltzmann equation, and then various mechanisms for electron scattering processes are given.

3. APPLICATION OF BOLTZMANN EQUATION

Final values of transport coefficient are consequence of imperfection of crystal structure. Without imperfection in ideal crystals, electric conductivity will be infinite. In equilibrium states (without influence of any physical interaction), electrons in graphene have Fermi-Dirac distribution $f_0 \equiv f_{FD}(\varepsilon, \varepsilon_F)$, where ε is electron energy and ε_F is Fermi level energy. In any physical field or temperature gradient function of electron distribution changes and depend from coordinate and energy (or wave vector) of electron. New function $f(\vec{r}, \vec{k})$ is find by solving Boltzmann transport equation in time relaxation approximation. For the stationary case, Boltzmann equation become [6]:

$$\dot{\vec{r}} \cdot \nabla_{\vec{r}} f + \dot{\vec{k}} \cdot \nabla_{\vec{k}} f = I_{\text{col}} \qquad (2)$$

where I_{col} is so-called collision integral, and could be expressed through time relaxation as:

$$I_{\text{col}} = -\frac{f - f_0}{\tau(\vec{k})} = -\frac{f_1}{\tau(\vec{k})}. \qquad (3)$$

Time of relaxation is time measured from the moment of perturbation on system (when electron is scattered) to the moment of re-established equilibrium state. This time period is very short $10^{-12} - 10^{-14}$ s. Assumptions for usage of time relaxation approximation are that $|f_1| \ll |f_0|$ and that change of electron energy within one act of scattering very small compared with $k_B T$, (k_B is Boltzman constant) . Other conditions to implement this approximation into kinetic processes are [7,8]:

- Wavelength of electron is much smaller when compared with electron mean free path $\lambda \ll l$
- Uncertainty of electron energy is small compared with electron mean energy $\hbar/\tau_0 \ll \bar{\varepsilon}$
- Change of electron energy in external field (E) and at distance of de Broglie wavelength (λ) is much smaller from electron mean energy $\ll \bar{\varepsilon} \cong k_B T$.

Electrical conductivity of graphene could be written as [9,10]:

$$\sigma = \frac{e^2 v_F^2}{2} \int_0^{\infty} n(\varepsilon)\tau(\varepsilon)\left(-\frac{\partial f_0}{\partial \varepsilon}\right) d\varepsilon , \qquad (4)$$

where $\tau(\varepsilon)$ is relaxation time; $n(\varepsilon)$ is electron concentration; $f_0 = \left(e^{\frac{\varepsilon-\mu}{k_B T}} + 1\right)^{-1}$ is Fermi-Dirac function of distribution; μ is electron chemical potential. Here $\tau(\varepsilon)$ is overall time of relaxation, which is according Matthiessen's rule [11]:

$$\frac{1}{\tau} = \sum_i \frac{1}{\tau_i} , \qquad (5)$$

where index "i" refers to different mechanisms of electron scattering. Similarly to the equation (4), we could calculate heat conductivity coefficient of graphene [12]:

$$\kappa = \frac{1}{4\pi L_z k_B T^2} \int_{\omega_{\min}}^{\omega_{\max}} (\hbar\omega_s)^2 \frac{e^{\frac{\hbar\omega_s}{k_B T}}}{\left(e^{\frac{\hbar\omega_s}{k_B T}} - 1\right)^2} \tau(\omega_s) \frac{v}{u} \omega_s d\omega_s , \qquad (6)$$

where $s \in (LA, TA, ZA)$ refers to phonon polarization branch; L_z - graphene thickness; ω_s - frequency of phonon polarization branch; v and u – are group and phase speed of phonon respectively; $\tau(\omega_s)$ - phonon relaxation time.

As one can see from equations (4) and (6) transport coefficients depend on relaxation times of elementary excitations. Graphene is usually strongly bounded to substrate and mobility of electron will depend from charged impurities (generally in SiO_2) and (always present on $T>0$ temperatures) phonon sub-system. All these processes determine relaxation times and in final transport coefficients whose determine electrical and heat conduction properties.

4. RELAXATION TIMES OF ELECTRON SCATTERING

Processes of electron flow through 2D crystalline structures such are graphene are followed by various scattering mechanisms. We will in this paper explain and analyze several scattering mechanisms [13,14]:

- Scattering on neutral impurities.

For this process relaxation time of electron could be defined as [8]:

$$\frac{1}{\tau(\varepsilon_k)} = \frac{n_i U_0^2 \hbar v_F k}{4\hbar^3 v_F^2} = \frac{n_i U_0^2 \varepsilon_k}{4\hbar^3 v_F^2} . \qquad (7)$$

- Scattering on charged impurities.

Mechanism for the scattering processes on charged impurities depends on the type of the potential of the impurity. In the case of long-range Coulomb potential relaxation time is [15,16]:

$$\frac{1}{\tau(\varepsilon_k)} == \frac{n_i}{4\hbar}\left(\frac{2\pi e^2}{\varepsilon_r}\right)^2 \frac{1}{\varepsilon_F}\frac{\varepsilon_F}{\varepsilon_k} = \frac{1}{\tau_1}\frac{\varepsilon_F}{\varepsilon_k} , \qquad (8)$$

but for the scattering processes on the charged impurities with screening potential, relaxation times is [16]:

$$\frac{1}{\tau(\varepsilon_k)} = \frac{2\pi n_i}{\hbar}\int_0^{2k}\frac{q^2}{k^3}\sqrt{1-\left(\frac{q}{2k}\right)^2}\,dq\int_0^{\infty}\left(\frac{2\pi e^2}{\varepsilon_r}\right)^2\frac{1}{\left(q+q_s(T)\right)^2}\frac{k'dk'}{\left(2\pi\right)^2}\frac{1}{\hbar v_F}\delta\left(k-k'\right). \qquad (9)$$

- Scattering on vacancies.

We assume that vacancy (empty space in crystalline lattice) have spherical shape. Relaxation time is [17,18]:

$$\frac{1}{\tau(\varepsilon_k)} = \frac{n_i\pi^2\hbar v_F^2}{\varepsilon_k \ln^2\frac{\varepsilon_k R}{\hbar v_F}}. \qquad (10)$$

- Scattering on phonons.

The main difference in scattering processes between impurities and phonons is that number of impurities is constant value, and number of phonons is constantly changing. In theory of scattering of electrons on phonons, matrix element of scattering is different and relaxation time highly depend on temperature [19]. For the $T \ll T_{BG}$, where $T_{BG} = 2v_p\hbar k_F / k_B$ is Bloch-Gruneisen temperature (on the temperature above T_{BG} phonons are degenerate system of quasi-particles), relaxation time is:

$$\frac{1}{\tau(\varepsilon_k)} = \frac{D^2}{\pi\rho v_F}\frac{k_B T}{\left(\hbar v_p\right)^2}\frac{1}{k}\int_0^{2k}\frac{dq}{2k}\sqrt{1-\frac{q^2}{4k^2}} = \frac{D^2}{\pi\rho v_F}\frac{k_B T}{\left(\hbar v_p\right)^2}k\frac{\pi}{4}, \qquad (11)$$

and for the $T \gg T_{BG}$ relaxation time become:

$$\frac{1}{\tau(\varepsilon_k)} = \frac{1}{2\pi\hbar}\frac{2\varepsilon_F}{\left(\hbar v_F\right)^2}\frac{D^2\hbar}{2\rho v_p}\int_0^{2k} qdq\frac{2\hbar v_p q}{k_B T}\frac{q^2}{2k^3}\sqrt{1-\frac{q^2}{4k^3}}N_q\left(N_q+1\right). \qquad (12)$$

5. THERMOELECTRIC FORCE

Thermoelectric force is defined with all above defined transport coefficients and corresponding relaxation times.

$$Q_x = -\frac{k_\mathrm{B}}{e}\frac{\int_{-\frac{\mu}{k_\mathrm{B}T}}^{\infty} x(\mu+k_\mathrm{B}T\,x)\;\tau(x,T)\frac{\mathrm{e}^x}{(\mathrm{e}^x+1)^2}dx}{\int_{-\frac{\mu}{k_\mathrm{B}T}}^{\infty}(\mu+k_\mathrm{B}T\,x)\;\tau(x,T)\frac{\mathrm{e}^x}{(\mathrm{e}^x+1)^2}dx}, \qquad (13)$$

where μ is chemical potential, $\tau(x,T)$ - relaxation time with $x=\varepsilon-\mu$ and dispersion law $\varepsilon=\hbar v_F k$. We have take into account all mechanisms of relaxation times. For particular numerical calculation of thermoelectric force (equation 13) and for numerical calculation we have used available values od parameters in [20,21]. Results are graphicaly showed on Fig.3. One can see from the above graph that thermoelectric force arise with the temperature, and this result is with good agreement with experimental data [10,22].

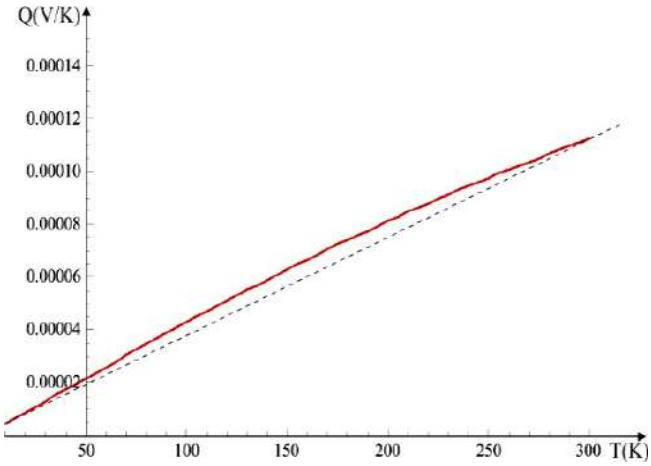


Figure 3. Thermoelectric force dependence from temperature for calculated all scattering processes

6. CONCLUSIONS

In this paper are presented results of research of thermoelectric properties of rare-earth mono-pnictides and monolayer graphene. These materials show exceptional efficiency in transformation of heat to electric energy, which make them perspective for heat waste harvesting (or recovery of heat).

Although heat transport include electron and phonon mechanism, we have concluded that electron transport processes are much more important for thermoelectric properties from phonon mechanism and narrowed our research to electron scattering in graphene (or similar 2D crystalline structure). We have used Boltzman transport equation in time relaxation approximation and showed how scattering processes and mechanisms influence onto relaxation time and consequently onto electrical and heat conductivity coefficients. We have calculated relaxation times for scattering on charged and neutral impurities, on vacancies and phonons. All these processes, along with values of charge carrier's concentrations, significantly influence on zT factor and finally on thermoelectric force. We have obtained that those parameters increase with temperature, which is in agreement with the available experimental data.

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