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QUANTUM-DIMENSIONAL EFFECTS IN THERMOELECTRIC CHARACTERISTICS OF LEAD CHALCOGENIDES NANOSTRUCTURES

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Abstract: On the basis of theoretical model of quantum well (QW) with infinitely high walls it was investigated thermoelectric parameters depending on the thickness of the layer of nanostructures IV-VI (PbS, PbSe, PbTe) in the approximation of changing Fermi energy. There have been shown that the dependences of the Seebeck coefficient, electrical conductivity and thermoelectric power factor on well width for lead chalcogenides nanofilms are in good agreement with the experimental data. So, that proves the correctness of used model.

Keywords: lead chalcogenides, nanostructures, quantum size effects.

1. INTRODUCTION

The ability of nanostructured materials to improve thermoelectric (TE) figure of merit has received increasing attention [3, 5]. Reducing the dimension of the material creates conditions for quantum size effect, which leads to an increase in the density of states near the Fermi energy. This allows to maintain high conductivity σ at relatively low Fermi energy E_F, where there are high values of Seebeck coefficient S. Tangible influence of quantum effects on the thermoelectric properties is possible only if the size of the structure in the direction of confinement is comparable with the de Broglie wavelength of carriers. This condition, in particular, holds for structures in the form of quantum wells [7, 8, 9].

The aim of this work was the theoretical explanation of the behavior of a number of thermoelectric (TE) parameters on the width of quantum wells (QW) for lead chalcogenides (PbS, PbSe, PbTe) [7, 8, 9].

2. THEORETICAL MODEL

For quantum well (QW) with high walls, electrons are limited in the direction OZ, and in the OX- and OY-directions their movement is free. Electronic wave function and energy eigenvalue, provided by parabolic energy bands, are defined by expressions [10]:

$$\psi = (\frac{2}{\Omega})^{\frac{1}{2}} \exp(ik_x x + jk_y y)\sin(\frac{n\pi z}{d}), \quad (1)$$

$$E = \frac{\pi^2\hbar^2}{2m_z^* d^2} n^2 + \frac{\hbar^2 k^2}{2m_p^*}, \tag{2}$$

where $k^2 = k_x^2 + k_y^2$, m_z^* - effective mass of the electron along the direction of limitation; $m_p^* = \sqrt{m_x^* m_y^*}$, m_x^*, m_y^* - effective mass of the electron along the axes *ox* and *oy*, Ω – total volume of the layer, *d* – well width, *n* – quantum number which takes integer values.

Number of quantized levels that are below a given energy, is defined by the first part of (2):

$$E_n = \frac{\pi^2\hbar^2}{2m_z^* d^2} n^2 \tag{3}$$

Substituting the value of the Fermi energy (E_F) in (3), we can find the width *d*, where below the Fermi level there is the specified number of levels *n*. The difference between the values of this width for the next two levels will determine the period of oscillations Δd, which is equal to the width d_{min}, where the bottom of the lowest subband coincides with the energy E_F. Thus, from (3) it follows:

$$\Delta d = d_{мін} = \frac{\lambda_F}{2} = \frac{h}{\sqrt{8m_z^* E_F}} \tag{4}$$

From (4) we can see, that the change of the Fermi level value leads to the change of the oscillation period. The Fermi energy value can be expressed through the well width (*d*) and the concentration of carriers in the conduction band [2]:

$$E_F = \varepsilon_1 \frac{(n_0+1)(2n_0+1)}{6} + \frac{\pi\hbar^2}{m^*}\frac{n_{el}}{n_0} d, \tag{5}$$

where ε_1 – the first quantized level, which is determined by the formula (3), when $n = 1$; $n_0 = [(E_F/\varepsilon_1)^{1/2}]$ – the integer part of number $(E_F/\varepsilon_1)^{1/2}$; m^* – carriers effective mass, which is defined as $m^* = (m_\perp^2 m_\parallel)^{1/3}$ [2]; n_{el} – electronic concentration.

If the Fermi level coincides with the bottom of the band n_0, then $E_F(d_0) = \varepsilon_1 n_0^2$. At such the width $(E_F(d_0)/\varepsilon_1)^{1/2}$ – integer. Substituting this value in (5) for d_{n0} is obtained:

$$d_{n_0} = d_0 n_0 \left[1 - \varepsilon_1 \frac{(n_0+1)(2n_0+1)}{6n_0^2}\right]^{1/3}, \tag{6}$$

where $d_0 = (\pi/2n_{el})^{1/3}$. The number n_0 at a given width *d* is the integer part from the solution of equation (6) relatively to n_0, when $d_{n0} = d$.

Thus, the substitution of the integer part from the solution of equation (6) relatively to n_0, when $d_{n0} = d$, in (5) makes it possible to build the ratio $E_F(d)$. Based on the directly proportional dependence of the perpendicular component of the effective mass on energy [2]:

$$m_z^* = m_{z0}^* \left(1 + 2 E_F / \varepsilon_g\right), \tag{7}$$

where m_{z0}^*, ε_g – *z*-component of the effective mass at low concentrations and bandgap, it can be argued that near the Fermi energy the ratio between m_z^* and *d* has the same character as $E_F(d)$.

In the case of quantum well thermoelectric transport coefficients may be obtained from the Boltzmann equation, which is written under the assumption that the electron distribution function in the steady state is stable and may be changed only by the action of external forces and fields. Then the system of electrons comes back to equilibrium due to different relaxation processes with characteristic relaxation times. For quasi-two-dimensional system it can be written [4]:

$$\sigma = \frac{e^2}{T}\Gamma^1, \tag{8}$$

$$S = \frac{E_F}{eT} + \frac{1}{eT}\frac{\Gamma^2}{\Gamma^1}, \tag{9}$$

where σ – conductivity, S – Seebeck coefficient, E_F – the Fermi energy, e – electron charge, T – absolute temperature.

The transport coefficient Γ is defined by the semiclassical approach, whereby particles are limited in potential well. The temperature gradient and electric field are directed along the axis *OX*. Then:

$$\Gamma^1 = -\zeta^{(0)}, \tag{10}$$

$$\Gamma^2 = \zeta^{(1)}, \tag{11}$$

where :

$$\zeta^{(s)} = \frac{2T}{\pi a}\sqrt{\frac{m_y^*}{m_x^*}}\frac{1}{\hbar^2}\sum_{n=1}^{E_n \le E_F}\int_0^\infty E^s \tau\varepsilon\left(\frac{\partial f}{\partial \varepsilon}\right)d\varepsilon\,. \tag{12}$$

Here f – Fermi distribution function, $\varepsilon = E\text{-}E_n$, τ – relaxation time, which in the case of scattering on acoustic phonons is independent from energy [4] ($\tau = \tau_0$), so it can be taken outside the integral.

Under this condition the expressions for the Seebeck coefficient S and electrical conductivity σ can be written as:

$$S = \frac{k_B}{e}\left[\frac{E_F}{k_B T} - \frac{A_1 + A_2}{A_3}\right], \tag{13}$$

$$\sigma = \frac{1}{2\pi d}\frac{2k_B T}{\hbar^2}\sqrt{\frac{m_x^*}{m_y^*}}e^2\tau_0 A_3, \tag{14}$$

where:

$$A_1 = \left(\sum_{n=1}^{En \le E_F}\int_0^\infty x^2\left(-\frac{\partial f_n}{\partial x}\right)dx\right), \tag{15}$$

$$A_2 = \left(\sum_{n=1}^{En \le E_F} E'\int_0^\infty x\left(-\frac{\partial f_n}{\partial x}\right)dx\right), \tag{16}$$

$$A_3 = \left(\sum_{n=1}^{En \le E_F}\int_0^\infty x\left(-\frac{\partial f_n}{\partial x}\right)dx\right) \tag{17}$$

Fermi distribution function has the known form:

$$f_n = \frac{1}{e^{x-\eta_n}+1}, \tag{18}$$

where $x = \varepsilon / k_B T$ – reduced carrier energy and $\eta_n = \xi - E_n'$. Here $\xi = E_F / k_B T$ and $E_n' = E_n / k_B T$, k_B – Boltzmann constant.

The relaxation time in (15) can be estimated based on the mobility μ of *n*-type carriers in the bulk samples [1]:

$$\mu = e\tau_0 / m . \tag{19}$$

3. RESULTS AND DISCUSSION

Based on the experimental dependences [7-9], which show nonmonotonic, oscillatory character of the TE parameters change with changing the thickness of the condensate (Fig. 1), is natural to assume that such behavior is due to the quantization of energy carriers by restricting their movement in the potential well.

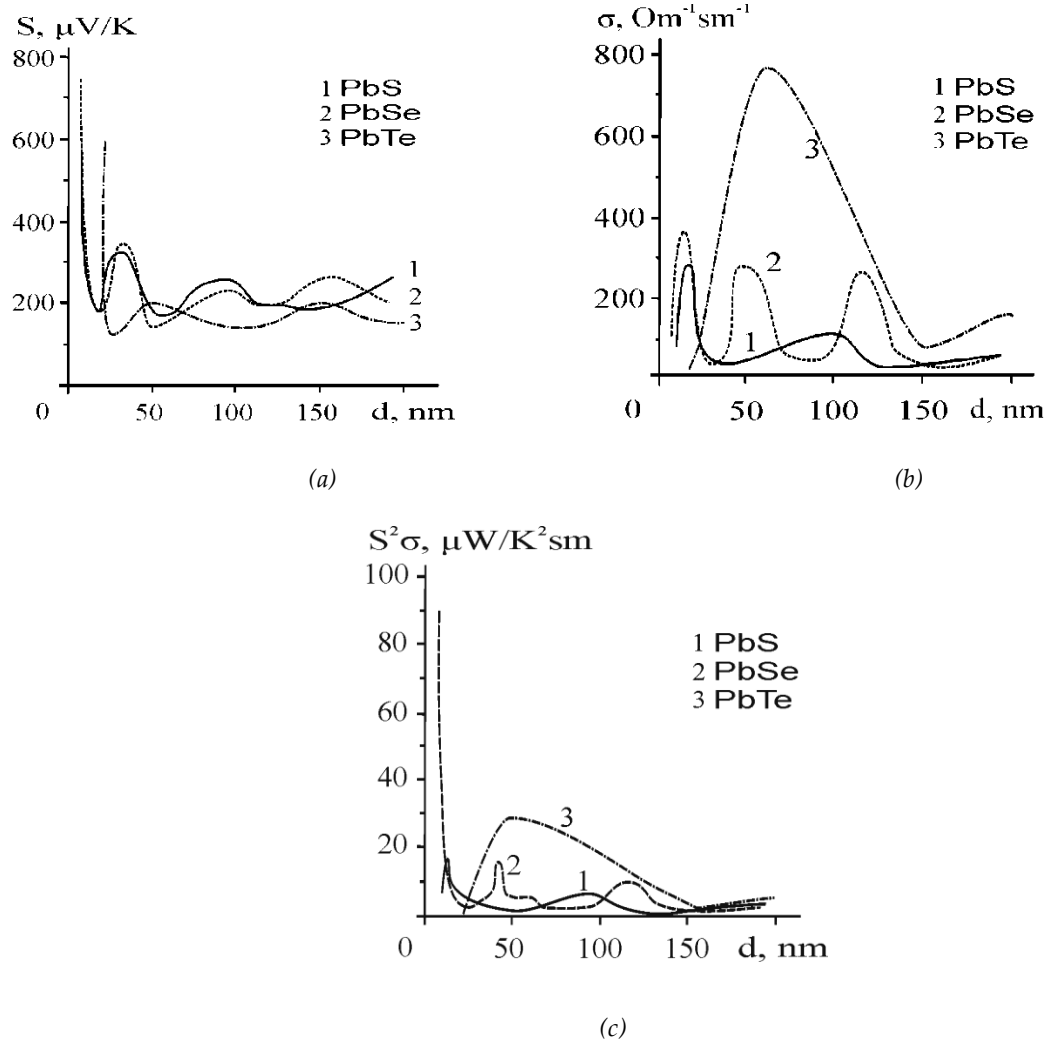


Fig. 1. Experimental dependences of the Seebeck coefficient S (a), electric conductivity σ (b) and TE power factor $S^2\sigma$ (c) on the thickness of the nanofilms PbS, PbSe, PbTe on substrates KCl, covered with a layer of EuS, at T=300 K [7-9]

Increasing the well width on the value of Fermi half-wave leads to new subband below the Fermi energy. At the width of the new band filling in the density of states it is observed the jump, which leads to oscillating behavior.

Consideration of the Fermi energy d-dependence (Fig. 2) in formulas (13)-(18) and z-component of the effective mass in the ratios (16)-(19) allowed us to obtain the corresponding dependences of the Seebeck coefficient S and electrical conductivity σ on the well width for nanofilms of lead

chalcogenides (Fig. 3, a, b). The formula (3) shows that the number of levels below the Fermi energy is determined by d-dependence of the effective mass and actually by E_F, as well as by the well width d. The calculations take into account a change of the Fermi energy, and change of the number of levels below it, depending on the well width. Calculating the electrical conductivity σ by (15) it was assumed that $m_x^* = m_y^*$. In the theoretical model the quantum well width was considered to be equal to the thickness of the condensate in the experimental dependences of relevant parameters. The calculation was carried out in the approximation of constant concentration and carrier mobility across all the range of well width. The values of the last were selected based on relevant experimental measurements (table, according to the data in Fig.1). The resulting dependences of TE coefficients on the width of lead chalcogenides QW are characterized by nonmonotonic oscillating behavior (Fig. 2, 3).

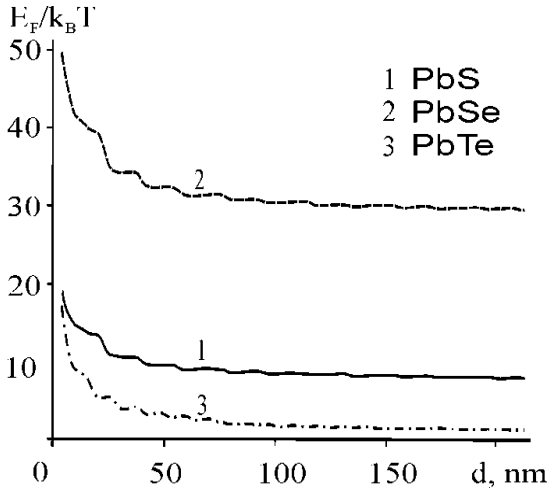
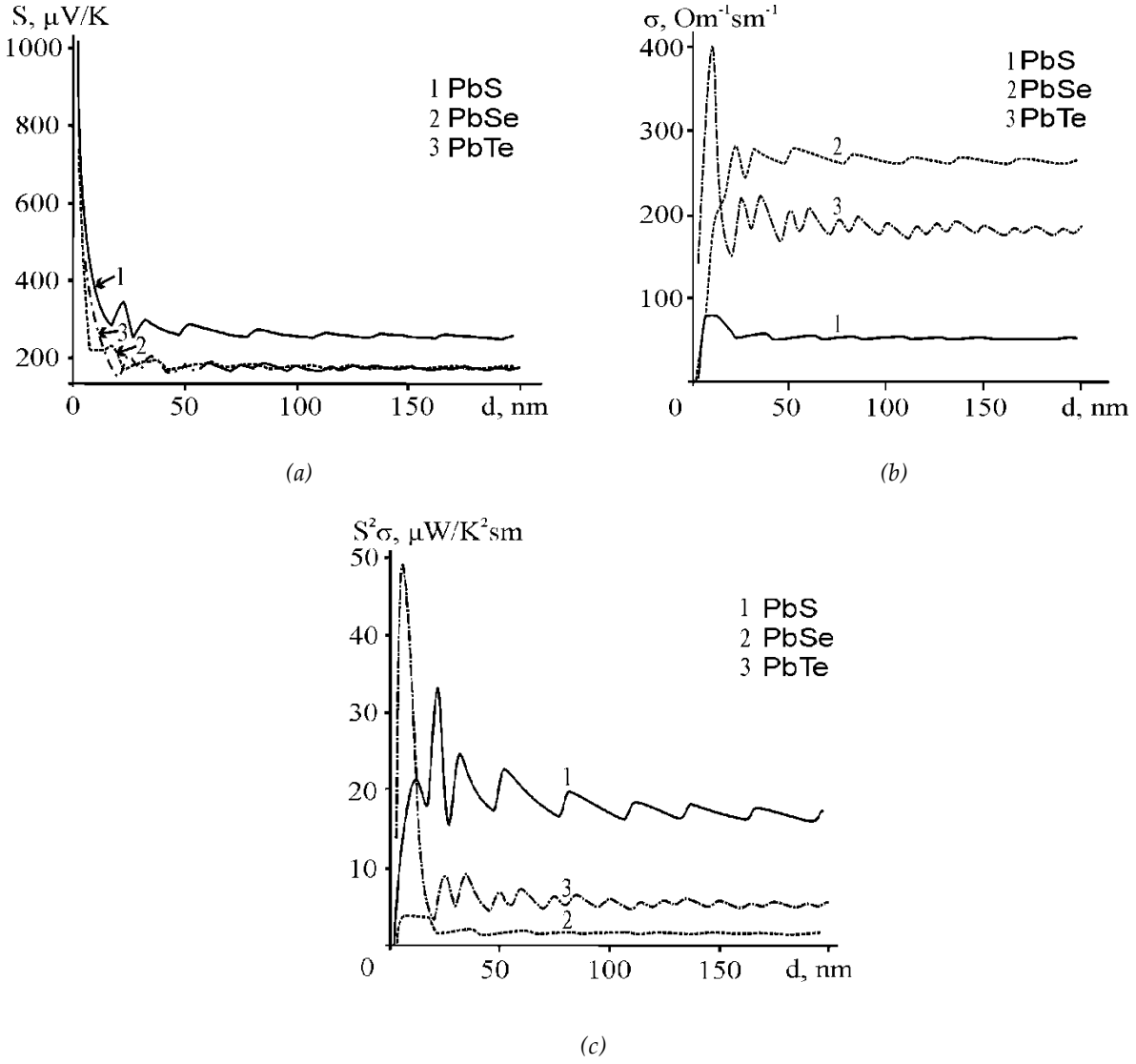


Fig. 2. Calculated values of the Fermi energy E_F in units of k_BT on the width of QW PbS, PbSe, PbTe at T=300 K

	PbS	**PbSe**	**PbTe**
μ, $cm^2/V{\cdot}s$	70	200	1096
n, cm^{-3}	$2{,}5{\cdot}10^{18}$	$4{\cdot}10^{18}$	$0{,}72{\cdot}10^{18}$

Tab. 1. The values of carriers mobility (μ) and concentration (n) for films of n-type lead chalcogenides, which were used in the calculations of thermoelectric coefficients

The dependences of TE parameters on the well width for films of different compounds of lead chalcogenides distinguish by average value of TE parameters throughout the studied range of thicknesses as well as by size and position of extrema (Fig. 3). However, the change character of the curves is identical. So, for all structures at small values of the well width (less than 20 nm) there was revealed the high values of Seebeck coefficient and very low values of conductivity. Increasing the well width leads to a decrease of the value of the Seebeck coefficient and to increase of the value of electrical conductivity. Thus, all these dependencies go to saturation. Note, that this character of theoretical curves change (Fig. 3) is fully consistent with the experimental data (Fig. 1) [7-9], what proves the correctness of the chosen calculation model.



(a) *(b)* *(c)*

Fig. 3. Theoretical dependences of the Seebeck coefficient S (a), electric conductivity σ (b) and TE power factor $S^2\sigma$ (c) on the width of QW for films PbS (1), PbSe (2), PbTe (3) in the model of infinitely deep potential well at T = 300 K

As it is seen from the relation (4) the period of oscillation is inversely proportional to the value of the Fermi energy. Descending character of the Fermi energy (Fig. 2) indicates that with increasing the well width it has place a growth of oscillation period of d-dependences for TE parameters (Fig. 3). The lowest average Fermi energy was obtained for lead telluride (Fig. 2, curve 3). Therefore, PbTe should be characterized by the largest average oscillations period Δd, what is also fully confirmed by experiment (Fig. 1, curve 3) [7-9].

Fig. 3 shows the d-dependences of thermoelectric power factor $S^2\sigma$. In general we can say that the maximum meanings $S^2\sigma$ are smaller than the experimental ones (Fig. 1, c) [6]. Only for compound PbTe the maximum value $S^2\sigma$ is higher than experimental, but this value corresponds to a very small well width, for which no experiment was carried out. On the one hand the cause of this mismatch may be not taking into consideration the limited height of the potential barrier, and on the other hand - the availability of additional experimental factors, which, along with the phenomenon of quantum size effect, influence on the oscillation amplitude of d-dependences of thermoelectric characteristics.

Taking into account the limited height of the potential barriers and calculation the thermal conductivities for lead chalcogenides nanostructures, to determine the d-dependences of thermoelectric figures of merit for relevant structures, will be accomplished in our subsequent works.

4. CONCLUSIONS

For the model of quantum well (QW) with infinitely high walls there were presented the expressions for the Fermi energy and effective mass on the QW width. On this basis, the character of change of oscillation period for the density of states with increasing the well width was defined.

There have been calculated and built the dependences of the Seebeck coefficient, electrical conductivity and thermoelectric power factor for lead chalcogenides nanofilms on their thickness. It was shown that the resulting oscillation character of their profiles are in good agreement with the experimental data.

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Фреїк Д.М., Юрчишин І.К., Потяк В.Ю. Квантово-розмірні ефекти термоелектричних параметрів наноструктур халькогенідів свинцю. *Журнал Прикарпатського університету імені Василя Стефаника*, **1** (1) (2014), 65–72.

На основі теоретичної моделі квантової ями (КЯ) з нескінченно високими стінками досліджено залежності термоелектричних параметрів від товщини шару наноструктур IV-VI (PbS, PbSe, PbTe) в наближенні змінної енергії Фермі. Показано, що залежності коефіцієнта Зеєбека, електропровідності і термоелектричного коефіцієнта потужності від ширини ями для наноплівок халькогенідів свинцю добре узгоджуються з експериментальними даними, що доводить правильність використаної моделі.

Ключові слова: халькогеніди свинцю, наноструктури, квантово-розмірні ефекти