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Frequency spectrum and group velocities of acoustic phonons in PbI_2 nanofilms

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Using the elastic continuum approach, an energy spectrum and spectral dependences of a group velocities of confined acoustic phonons in planar quasi-two-dimensional nanostructures (nanofilms) of hexagonal symmetry of the 2H-PbI_2 type were studied by methods of the theory of elasticity. It is shown that the energy and propagation velocity of vibrational modes for all branches of the phonon spectrum in these type nanostructures are nonlinear functions of a magnitude of a wave vector and a thickness of the nanofilm.

The obtained results can be used to analyze an influence of acoustic phonons on a course of phenomena of thermal and electrical conductivity, carrier scattering and optical absorption in nanostructures, components of which are thin layers of lead iodide.

Keywords: nanostructure, nanofilm, phonon, spectrum, frequency, group velocity.

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Introduction

Despite the fact that the properties of lead iodide and nanostructures based on it have been studied for a long time the interest in them has not decreased today. This is due to the fact that the combination of unique properties of this layered semiconductor with unique properties of low-dimensional structures is a very promising direction in the design of new generations of electronic and electro-optical devices for a wide range of purposes [1-4]. The need to develop this area stimulated an in-depth study of peculiarities of physical processes in such structures. As a result, a number of works have been published in recent years, in which the results of both experimental and theoretical studies of various properties of ultrathin films of lead iodide are presented. In particular, the structure of the phonon spectrum and regularities of the heat transfer phenomenon were studied in works [5-7], and the transformation of the energy spectrum of the electronic system due to its interaction with optical phonons and changes in the exciton absorption band in such structures were studied in works [8-10].

However, the theoretical aspects of the influence on the interaction of electrons with acoustic phonons, what is an important factor influencing the processes of electrical conductivity, optical absorption, radiation, luminescence and Raman scattering in quasi-two-dimensional structures are currently poorly covered.

The reason for this is the presence of certain difficulties in the calculation to describe the influence of acoustic phonons on these processes. These include the difficulties associated with divergence of integrals series contained in the structure of the corresponding electron-phonon interaction functions, as well as the absence of explicit laws of dispersion for different branches of the acoustic phonons spectrum in quasi-two-dimensional nanostructures.

To construct dispersion curves in such structures, numerical calculations are usually used (see, for example, [11, 12]), and when calculating quantities that characterize a phenomenon or process, are limited to regularities valid for bulk (three-dimensional) crystals. However, to consistently describe the electron-phonon interaction, it is necessary to use functions that describe the dispersion dependences for all branches of the phonon spectrum (see, for example, [8-10, 13]). Thus, the problem of establishing such functions is relevant for the development of the theory of electron-phonon interaction in nanostructures.

To solve this problem, we have proposed in [14] the simple way to establish the dispersion dependences of frequencies and velocities of acoustic phonons in the flat quasi-two-dimensional crystalline nanostructure, the nanofilm. It is based on the idea of developing in Fourier series for amplitudes of components of the displacement vector for elastic vibrations of atoms in the crystal lattice, which makes it possible to find solution of the equations of motion and the dispersion law of their frequency in analytical form.

In this paper, the dispersion and dimensional dependences of the frequency spectra ω and group velocities v for all branches of confined acoustic phonons in $2H$-PbI_2 nanofilms of different thickness d are studied for the first time on the basis of this method.

I. Frequency spectrum of acoustic phonons in the $2H$-PbI_2 nanofilm

The paper [14] presents the analytical expressions obtained in the approximation of the elastic continuum for the study of the dispersion laws for all modes of acoustic phonons in the nanofilm of the hexagonal symmetry crystal. In the case of shear vibrations, the dependence of the frequency ω of elastic vibrations of atoms in the nanofilm of thickness d on the magnitude of the wave vector q is described by the formula

$$\omega_n^{sh}(q) = \sqrt{\frac{c_{66}q^2 + c_{44}(n\pi/d)^2}{\rho}}\,, \tag{1}$$

in the case of dilatation (SA-polarization) and flexural (AS-polarization) modes are described by expressions, respectively,

$$\omega_n^{SA/AS}(q) = \sqrt{\frac{F_{1n}(q) \pm \sqrt{F_{2n}(q)}}{2\rho}}\,. \tag{2}$$

Herein $n = 1, 2, \ldots$ is the quantum number (number of the vibrational state), ρ is crystal density,

$$F_{1n}(q) = (c_{11}+c_{44})q^2 + (n\pi/d)^2(c_{33}+c_{44})$$

and

$$F_{2n}(q) = (c_{11}-c_{44})^2 q^4 + 2(n\pi/d)^2[2(c_{33}+c_{44})^2 - \\ -(c_{11}-c_{44})(c_{33}-c_{44})]q^2 + (n\pi/d)^4(c_{33}-c_{44})^2$$

are auxiliary functions, the values of which are determined by the corresponding set of elastic constants c_{ij}.

In the case $n = 0$ formulas (1) and (2) determine the law of frequency dispersion, respectively, TA_2- and LA/TA_1-modes of normal vibrations in a three-dimensional (bulk) crystal are linear functions $\omega_0^{sh}(q) \equiv \omega^{TA_2} = \sqrt{c_{66}/\rho}\,q$, $\omega_0^{SA}(q) \equiv \omega^{LA} = \sqrt{c_{11}/\rho}\,q$ and $\omega_0^{AS}(q) \equiv \omega^{TA_1} = \sqrt{c_{44}/\rho}\,q$. Dimensional quantization states ($n > 0$) are quasi-optical, the frequencies of all phonon modes in the long-wavelength range ($q \to 0$) tend to non-zero values, proportional to $n\pi/d$ with coefficients of proportionality, respectively: $\sqrt{c_{44}/\rho}$ in the case of shear and flexural vibrations phonon modes, and $\sqrt{c_{33}/\rho}$ in dilatation phonon modes.

Using the obtained relations, as well as the values that determine the structure and mechanical properties of lead iodide 2H-polytype (wurtzite, lattice parameters $a_0 = 4{,}5$ Å, $c_0 = 6{,}98$ Å, $\rho = 6{,}16$ g/cm^3 [15]) and the values of the elastic constants (in GPa) of this crystal determined according to [16]: $c_{11} = 27{,}7$; $c_{33} = 20{,}2$; $c_{44} = 6{,}2$; $c_{66} = 3$; $c_{12} = 9{,}6$; $c_{13} = 11{,}3$, we calculated the dispersion dependences of the frequencies of acoustic phonons in nanofilms of type $2H$-PbI_2 for different thickness character of these dependencies is illustrated in Fig. 1, which shows the results of calculating the energy $\hbar\omega_n(q)$ for the first four components of the spectra for each the acoustic phonons modes in the nanofilm of the certain thickness $d = Nc_0$ (N is the number of $2H$-PbI_2 layer packets). Their peculiarity is the appearance of quasi-optical phonon states with energies $\hbar\omega_n$ ($n = 1, 2, \ldots$), different from the energy of the corresponding type of acoustic vibrations in the bulk crystal $\hbar\omega_0$, as well as the dependence $\hbar\omega_n(q)$ is nonlinear. These peculiarities are most pronounced in the long-wavelength range ($q \to 0$), but differently for different branches of the spectrum (see Fig. 1). They are the smallest in the component of the shear vibrations phonon mode (Fig. 1 *a*), more significant in AS- (Fig. 1 *b*) and the largest in the case of SA-phonons (Fig. 1 *c*). As we move to the short-wavelength range, the differences between the values of the frequencies ω_n of states with different quantum numbers $n = 1, 2, \ldots$ decrease in all branches of the spectrum. In this case, the frequencies ω_n of each of the modes for acoustic phonons in the nanofilm asymptotically approach to the values characteristic of the corresponding vibrations (longitudinal LA or transverse TA_1 or TA_2) in the bulk $2H$-PbI_2 crystal. The rate of this approximation is the lowest in the case of the shear vibrations mode (Fig. 1 a), higher in AS-phonons (Fig. 1 b) and the highest in the case of SA-phonons (Fig. 1 c).

The dependences of the frequency spectrum on the thickness of the nanofilm are illustrated in Fig. 2. Analysis of the change in energies of phonon states calculated at fixed value of q for different values of the nanofilm thickness d shows that the distances between the dispersion curves are nonlinearly decreasing functions of the nanofilm thickness. The rate of decrease for the energy $\hbar\omega_n$ with increasing the nanofilm thickness is different. It is the lowest in the phonon mode of AS-polarization (Fig. 2 *b*) and the highest for SA- phonons (Fig. 2 *c*).

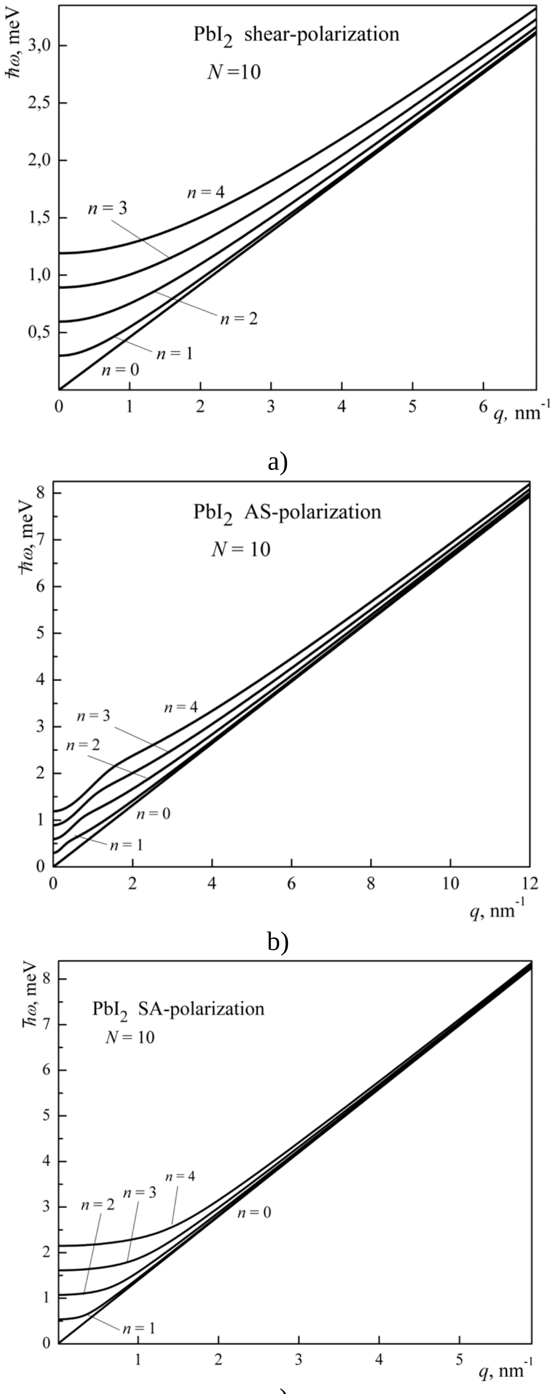
II. Velocity spectrum of acoustic phonons in the 2H-PbI_2 nanofilm

The analytical expressions obtained in [14]

$$\upsilon_n^{sh}(q) = \frac{c_{66}q}{\sqrt{\rho(c_{66}q^2 + (\frac{\pi n}{d})^2 c_{44})}} \tag{3}$$

$$\upsilon_n^{SA/AS}(q) = \{[(c_{11}+c_{44})\sqrt{F_{2n}(q)} \pm (\frac{n\pi}{d})^2[2(c_{13}+c_{44})^2 - (c_{11}-c_{44})\times \\ \times(c_{33}-c_{44})]]q \pm (c_{11}-c_{44})^2 q^3\}\times[2\rho F_{2n}(q)(F_{1q}(q) \pm \sqrt{F_{2n}(q)})]^{-1/2} \tag{4}$$

for calculating the group velocities of acoustic phonons in the nanofilm of the hexagonal symmetry crystal made it

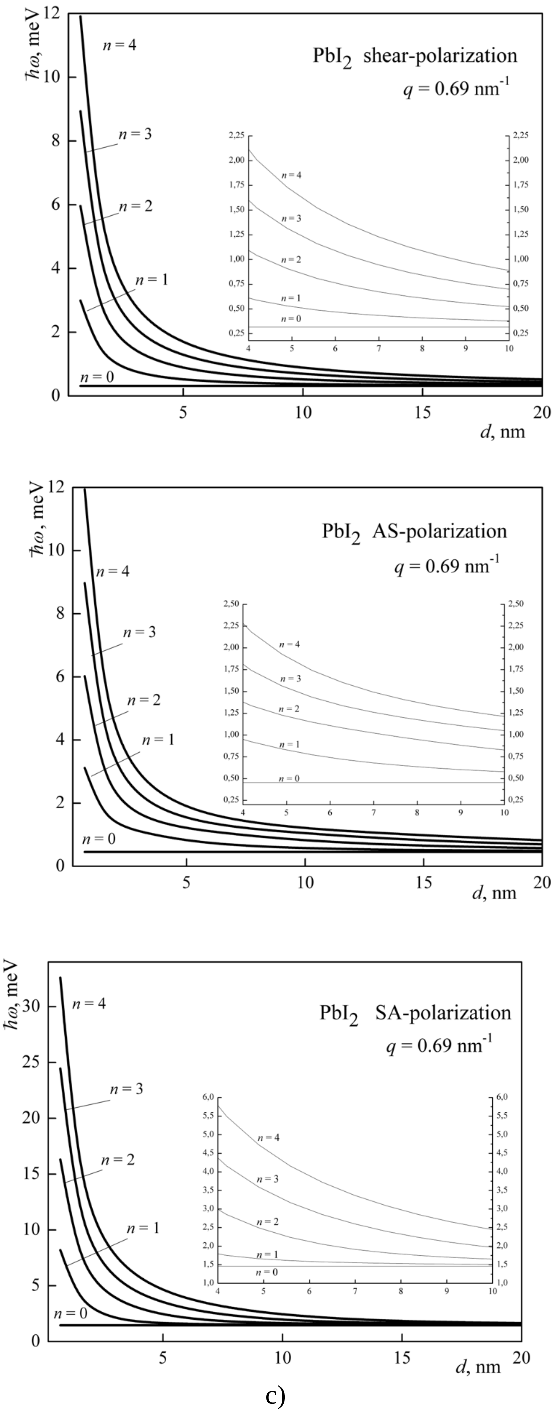


a)

b)

c)

Fig. 1. Dispersion dependences of the energy for phonon modes of different polarization: shear (*a*), flexural (*b*) and dilatational (*c*) vibrations in the 2*H*-polytype nanofilm of lead iodide with thickness in *N* layer packets of PbI$_2$.

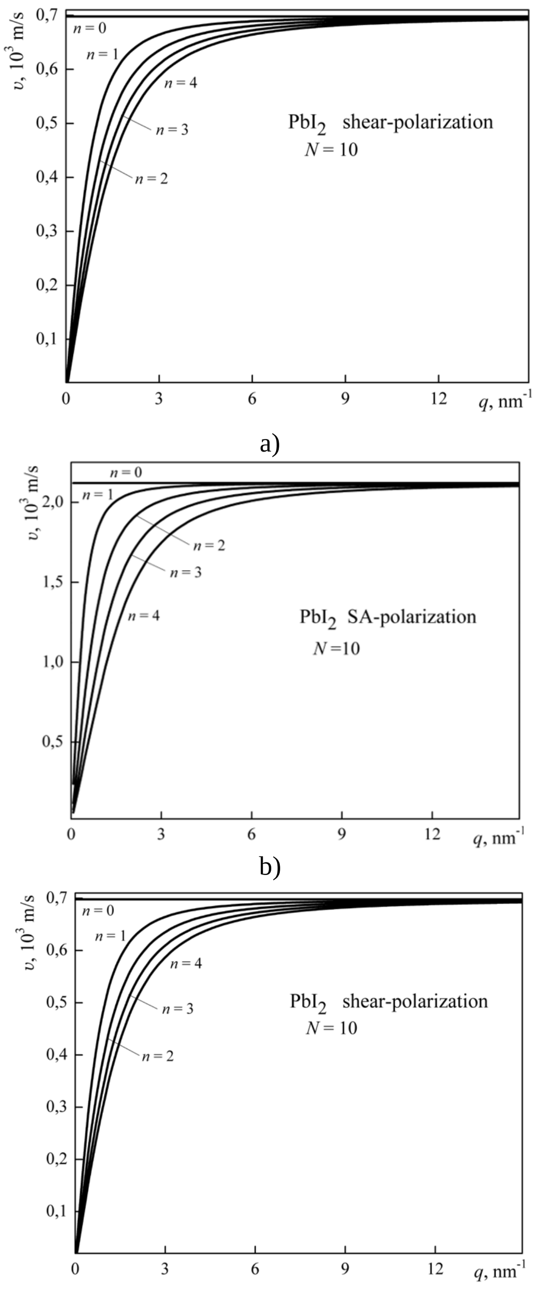


c)

Fig. 2. Dependence of phonon modes energy on the thickness of the 2*H*-PbI$_2$ nanofilm: *a*) shear, *b*) flexural, *c*) dilatational vibrations.

possible to investigate their dispersion and dimensional dependences on the example of 2*H*-PbI$_2$ nanofilms. The calculation of the dependences $v_n(q)$ by formulas (3) and (4) showed that in contrast to the bulk crystal, where the group velocities *LA*-, *TA*$_1$- and *TA*$_2$- modes of acoustic phonons of the corresponding polarization relative to the plane of the PbI$_2$ layer packet are constant: $\upsilon_{LA} \equiv \upsilon_0^{SA} = \sqrt{c_{11}/\rho} = 2121$, $\upsilon_{TA_1} \equiv \upsilon_0^{AS} = \sqrt{c_{44}/\rho} = 1003$ and $\upsilon_{TA_2} \equiv \upsilon_0^{sh} = \sqrt{c_{66}/\rho} = 698$ m/s, for the nanofilm consisting of *N* packets, their values are quantized and become dependent on the wave vector (Fig. 3). In this case, the propagation velocities of shear vibrations and dilatational phonons are smaller than their corresponding values in the bulk crystal (Fig. 3 *a*, *b*). The difference between $v_n(q)$ and v_0 is bigger if the wave vector *q* is smaller and the quantum number *n* is bigger. The dependences $v_n(q)$ are monotonically increasing; at bigger *q* their values are asymptotically, from below, approaching to values of v_{TA2} and v_{LA} respectively.

The dispersion dependence of the group velocities $v_n(q)$ of flexural phonons is non-monotonic. Bigger q causes their sharp increase from infinitely small values to maximal ones, which exceed the velocity of transverse TA_1-phonons in the bulk crystal. Further the increase q leads to smaller $v_n(q)$, which also asymptotically approaches to the value of v_{TA1}, but from above (Fig. 3 c).The differences of values for group velocities of different quantum states for each branches of the acoustic phonons spectrum between themselves and values of corresponding velocities in the bulk crystal are changed according to the change of the nanofilm thickness (Fig. 4). They are most pronounced in ultrathin films with the thickness of several PbI$_2$ layer packets (3-4) in the case of shear vibrations phonon modes (Fig. 4 *a*) but several tens (50-100) in flexural (Fig. 4 *b*) and dilatation (Fig. 4 c). Further increasing the nanofilm thickness decreases this difference: sharp (≈ 7 m/s at 1 nm) in the case of dilatation phonons, slower (≈ 5 m/s at 1 nm) in the shear vibrations modes and the slowest (≈ 3 m/s at 1 nm) in flexural (see inserts in Fig. 4 *c*, *a*, *b*).

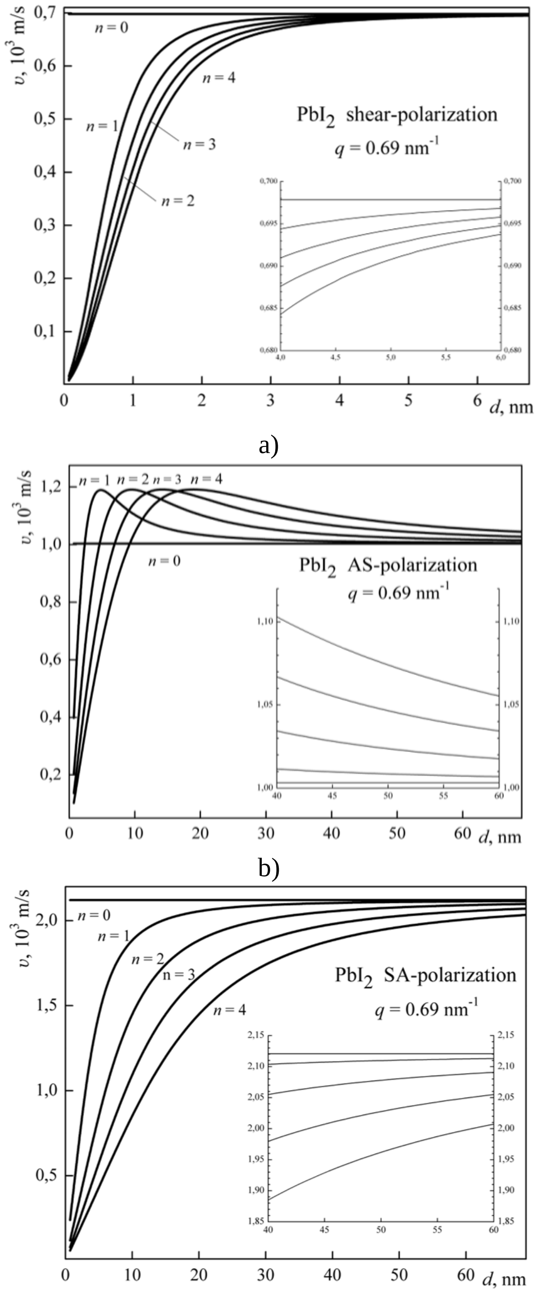


a)

b)

c)

Fig. 3. Dispersion dependences of group velocities for phonon modes of different polarization: shear (*a*), dilatational (*b*) and flexural (*c*) vibrations in the 2H polytype nanofilm of lead iodide with thickness in N layer packets of PbI$_2$.



a)

b)

c)

Fig. 4. Dependences of group velocities of phonon modes on the thickness of the 2*H*-PbI$_2$ nanofilm: *a*) shear, *b*) flexural, *c*) dilatational vibrations.

Conclusions

The proposed method makes it possible to analyze the dispersion dependences for frequencies of confined acoustic phonons and their propagation velocities in nanofilms with the crystal lattice of hexagonal symmetry (wurtzite), as well as their transformations on changing film thickness. It can also be used to study the processes of heat transfer, electron scattering, electrical conductivity and optical absorption in nanofilms with this type of symmetry.

Analysis of dispersion curves for energies and group velocities of all modes of confined acoustic phonons, performed on the example of 2*H*-PbI_2 nanofilms of different thickness, shows the nonlinear nature of changes in these values with changes in both phonon wavelength and nanofilm thickness. The first circumstance can be decisive in determining the influence of acoustic phonons on the processes determined by electron-phonon interaction in nanostructures whose components are 2*H*-PbI_2 nanofilms, and the second one allows tuning the physical properties of such nanostructures by selecting its thickness.

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[1] W. S. Yang, B.-W. Park, E. H. Jung et al., Iodide management in formamidinium-lead-halide-based perovskite layers for efficient solar cells, Science 356(6345), 1376 (2017); https://doi.org/10.1126/science.aan2301.

[2] Z. Razaq, A. Fadhel, Preparation and Study the Physical Properties of PbI2 by using Thermal Evaporation to use in Nuclear Detector, Indian Journal of Natural Sciences 9(50), 14793 (2018); https://doi.org/10.13140/RG.2.2.31708.44162.

[3] Y. Sun, Zh. Huang, Z. Zhou et al., Band Structure Engineering of Interfacial Semiconductors Based on Atomically Thin Lead Iodide Crystals, arXiv:1810.08927v2 (2019); [cond-mat.mes-hall]. https://arxiv.org/ftp/arxiv/papers/1810/1810.08927.pdf.

[4] K. Tvingstedt, O. Malinkiewicz, A. Baumann, et al., Radiative efficiency of lead iodide based perovskite solar cells, Science Reports 4, 6071 (2015); https://doi.org/10.1038/srep06071.

[5] P. Guo, C. C. Stoumpos, L. Mao, et al., Cross-plane coherent acoustic phonons in two-dimensional organic-inorganic hybrid perovskites, Nature Commun. 9, 2019 (2018); https://doi.org/10.1038/s41467-018-04429-9.

[6] R. Ran, C. Cheng, Z.-Y. Zeng et al., Mechanical and thermal transport properties of monolayer PbI2 via first-principles investigations, Phil. Mag. 99(10), 1277 (2019); https://doi.org/10.1080/14786435.2019.1580818.

[7] L. Pedesseau, J. Even, C. Katan et al., Vibrational properties of 2H-PbI2 semiconductors studied via Density Functional Theory calculations, Thin Solid Films 541, 9 (2013); https://doi.org/10.1016/j.tsf.2012.10.129.

[8] O. Pugantseva, V. Kramar, VIII International School-Conference (Publ. Hous "Ukrpol" Ltd., Drohobych, 2013), P. 106-107.

[9] V. Kramar, O. Pugantseva, A. Derevyanchuk, Spatial confinement, self-polarization and exciton–phonon interaction effect on the location of exciton line in lead iodide nanofilms, Low Temp. Phys. 40(8), 766 (2014); https://doi.org/10.1063/1.4892649.

[10] A.V. Derevyanchuk, O.V. Pugantseva, V.M. Kramar, Temperature changes in the function of the shape inherent to the band of exciton absorption in nanofilm of layered semiconductor, Semicond. Phys. Quant. Electron.&Optoelectronics 17(2), 188 (2014); https://doi.org/10.15407/spqeo17.02.188.

[11] E. P. Pokatilov, D. L. Nika, A. A. Balandin, Phonon spectrum and group velocities in AlN/GaN/AlN and related heterostructures, Superlattices and Nanostructures 33, 155 (2003); https://doi.org/10.1016/S0749-6036(03)00069-7.

[12] E.P. Pokatilov, D.L. Nika, A.A. Balandin, Confined electron-confined phonon scattering rates in wurtzite AlN/GaN/AlN heterostructures, J. Appl. Phys. 95, 5626 (2004); https://doi.org/10.1063/1.1710705.

[13] M.V. Tkach, V.M. Kramar, Electron-phonon interaction and the mechanisms of electron spectrum renormalization in a flat nanofilm, Ukr. J. Phys. 53(8), 810 (2008); http://archive.ujp.bitp.kiev.ua/files/journals/53/8/530812p.pdf.

[14] Yu.V. Lutsiuk, V.M. Kramar, Analytical Calculation of Frequency Spectrum and Group Velocities of Acoustic Phonons in Quasi-two-dimensional Nanostructures, J. Nano- Electron. Phys. 12(5), 05033 (2020); https://doi.org/10.21272/jnep.12(5).05033.

[15] T. Minagawa, Common polytypes of PbI2 at low and high temperatures and the 2H-12R transformation, Acta Cryst. A31, 823 (1975); https://doi.org/10.1107/S0567739475001787.

[16] O. Madelung, U. Rössler, M. Schulz (ed.), Lead diiodide (PbI2) Grüneisen parameters, effective charge, force constants (Springer-Verlag, Berlin Heidelberg, 1998).

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Частотний спектр і групові швидкості акустичних фононів у наноплівках PbI_2

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У наближенні пружного континууму методами теорії пружності досліджено енергетичний спектр і спектральні залежності групових швидкостей обмежених акустичних фононів у плоских квазідвовимірних наноструктурах (наноплівках) гексагональної симетрії типу 2H-PbI_2. Показано, що енергія і швидкість поширення коливних мод усіх гілок фононного спектра в наноструктурах такого типу є нелінійними функціями величини хвильового вектора та товщини наноплівки.

Отримані результати можуть бути використані для аналізу впливу акустичних фононів на перебіг явищ тепло- та електропровідності, розсіювання носіїв і оптичного поглинання у наноструктурах, компонентами яких є тонкі шари дийодиду свинцю.

Ключові слова: наноструктура, наноплівка, фонон, спектр, частота, групова швидкість.