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The Role of Acoustic Phonons in the Formation of Thermophysical Properties of PbI_2 Nanofilms

Based on the dispersion dependences of acoustic phonon frequencies in hexagonal quasi-two-dimensional nanostructures, previously obtained by us in the elastic continuum approximation, the heat capacity, entropy, free energy (Helmholtz), and thermal diffusion coefficient of nanometer-thick planar structures (nanofilms) of lead diiodide were calculated. The dependence of these quantities on the nanofilm thickness and temperature, as well as the role of different branches of the phonon spectrum in the formation of the thermophysical properties of such structures, was investigated. The results of calculating the heat capacity, entropy, free energy, and thermal diffusion coefficient of lead diiodide nanofilms indicate that all of them depend on the nanofilm thickness. This dependence is especially pronounced in ultrathin (up to 8 PbI_2 layered packages thick) nanofilms. The absolute values of all these quantities increase with a rise in temperature in nanofilms of any thickness. In the low-temperature range, the rate of increase is slower for thinner nanofilms. At temperatures above the Debye temperature, the growth of heat capacity and entropy slows down; the $C_V(T)$ dependence practically disappears, and the rate of growth of entropy S decreases the more, the greater the nanofilm thickness. Due to the difference in the rates of change of entropy in nanofilms of different thickness, in the region $T \sim 400$ K, the inversion of the S(T) dependence occurs – the entropy acquires values that are the greater, the thinner the nanofilm. The rate of change of the free energy upon reaching the Debye temperature acquires its greatest value, so that with a subsequent rise in temperature, the free energy changes linearly at a rate whose value is practically independent of the nanofilm thickness. It has been shown that phonons with transverse polarizations – displacement and bending – have the greatest influence on thermophysical

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processes controlled by heat capacity, entropy, and free energy. Thermal diffusion, like thermal conductivity, is determined primarily by longitudinal – dilatation – phonons.

Keywords: nanostructures, nanofilm, lead diodide, acoustic phonons, thermophysical properties, heat capacity, thermal diffusion, free energy, entropy.

Introduction

Global warming processes are increasingly highlighting the problem of reducing the negative impact of human activity on the environment due to the growth of thermal waste from production processes. One of the promising methods for reducing heat emissions into the atmosphere from both energy-intensive industrial facilities and powerful heat engines, as well as from the operation of low-power equipment or household appliances, is the use of thermoelectric waste heat recuperators [1]. Employees of the Institute of Thermoelectricity of the NAS of Ukraine have developed a number of thermoelectric generators that convert waste heat energy into electricity [2–4]. The authors of [5] proposed a method for increasing the efficiency of thermoelectric converters by creating multilayer thermoelectric unipairs – film thermoelectric modules on a thin flexible substrate. According to the authors, this approach could enable thermoelectric generators that can be used in low-power solar energy microsystems. This would allow converting not only light but also heat generated by the solar cell design into electrical energy.

A similar idea was proposed in [6] regarding efficiency increase of new generation solar energy systems using hybrid organic-inorganic solar cells based on thin films of perovskite lead-containing organohalides. The precursor for their creation is PbI_2, which is combined with methylammonium $CH_3NH_3^+$ (MA), formamidinium $HC(NH_2)_2^+$ (FA) or their solution $FA_xMA_{1-x}PbI_3$ [7–9]. Usually, lead diiodide is introduced in excess to passivate the surfaces at the perovskite grain boundaries. This promotes better crystallization of the perovskite, and therefore increases the efficiency of solar cells. According to the authors [6], in the presence of a temperature gradient, nanoscale layers of excess PbI_2 formed at the grain boundaries can generate a thermo-emf, the source of which is the heat absorbed by the solar cell structure. Adding it to the photostimulated emf of the cell can increase its efficiency.

The rapid development of perovskite solar energy technologies determines the high relevance of in-depth study of the physical properties of layered nanostructures XI_2 (X = Si, Ge, Sn, Pb) and the features of the course of physical processes in them [10–12]. The most suitable for their creation are considered to be germanium, tin and lead diiodides, the last of which – PbI_2 – is distinguished by a sufficiently high stability [12–14]. In addition, simple technologies for obtaining nanostructures on its basis have been developed. In particular, planar crystalline structures of hexagonal symmetry with a thickness of several layers of lead diiodide are obtained by vapor deposition methods [11, 15], growth from colloidal solutions [16], or mechanical exfoliation from the bulk 2H-PbI_2 crystals [17]. This makes it particularly attractive for creating various electronic devices based on them: planar light sources [16] and solar cells [18], high-temperature X- and γ-radiation detectors [19, 20], and also for thermoelectric needs [6].

Considering the possibility of practical application of the thermoelectric properties of nanosized PbI_2 structures [6, 21], it seems important to study other thermophysical, in particular thermodynamic, properties of such systems.

The purpose of this article is to study the role of the components of the frequency spectrum of acoustic phonons in the formation of the values of thermodynamic functions (free energy F and entropy S), molar heat capacity C_V and thermal diffusion coefficient of nanofilms (NFs) of lead diiodide *2H*-PbI_2 of different thicknesses, as well as in temperature changes of these quantities.

1. Problem statement and research model selection

The influence of acoustic phonons on the thermal properties of NFs is possible because heat exchange in them is carried out mainly due to phonons of this type. The spectra of frequencies and group velocities of such structures are significantly rearranged when their thickness changes. In particular, its decrease leads to a decrease in the averaged velocities of acoustic phonons and, as a result, reduces the thermal conductivity of NFs [21]. Naturally, their other properties also undergo changes. Therefore, by appropriately selecting the size, it is possible to obtain nanostructures with the necessary thermal, electrical, optical, etc. properties, that is, to solve the problems of phonon engineering [22, 23].

A consistent study of possible changes in the properties of NFs, in the formation of which acoustic phonons participate, requires knowledge of the spectral dependences of their frequencies and group velocities. We have proposed a method for their explicit determination [24] and have carried out specific calculations of the values of these quantities using the example of PbI_2 NFs for each of the branches of the spectrum of acoustic phonons in them [25]. The validity of using the obtained analytical expressions for frequencies and group velocities, in our opinion, is confirmed by the agreement of the results of calculations based on them of the dynamics of temperature changes in the thermal conductivity of lead diiodide NFs of different thicknesses [21] with the data of other authors on the thermal conductivity of massive and monolayer PbI_2 (see references in [21]).

Similarly, it is possible to analyze the size-temperature dependences of other thermophysical quantities. In particular, having the dispersion dependences of the frequencies of the components of the acoustic phonon spectrum in NFs of a given thickness, it is possible to calculate the temperature dependences of the heat capacity, entropy, and free energy of such structures [26].

For this purpose, we used the formula [26], adapted for calculating the molar heat capacity at constant volume C_V, entropy S and free energy F. After the transition in them from the sum over discrete values of the two-dimensional (in the plane of the film) wave vector of the phonon to the corresponding integral, they take the form

$$C_V(T) = \frac{Ra^2}{4\pi}\sum_{\alpha}\sum_{n}\int_0^{q_{\max}} \{(\frac{\hbar\omega_n^{\alpha}(q)}{k_BT})^2 \frac{\exp(\frac{\hbar\omega_n^{\alpha}(q)}{k_BT})}{[\exp(\frac{\hbar\omega_n^{\alpha}(q)}{k_BT})\text{-}1]^2}\} qdq\,, \tag{1}$$

$$S(T) = \frac{Ra^2}{4\pi}\sum_{\alpha}\sum_{n}\int_0^{q_{\max}} \{\frac{\hbar\omega_n^{\alpha}(q)}{2k_BT} cth(\frac{\hbar\omega_n^{\alpha}(q)}{2k_BT})\text{-}\ln[2sh(\frac{\hbar\omega_n^{\alpha}(q)}{2k_BT})]\} qdq\,, \tag{2}$$

$$F(T) = \frac{RTa^2}{8\pi}\sum_{\alpha}\sum_{n}\int_0^{q_{\max}} \{\frac{\hbar\omega_n^{\alpha}(q)}{k_BT} + 2\ln[1\text{-}\exp(\text{-}\frac{\hbar\omega_n^{\alpha}(q)}{k_BT})]\} qdq\,. \tag{3}$$

Here k_B and R are, respectively, the Boltzmann constant and the universal gas constant; a is the lattice period in the film plane; $\hbar\omega_n^{\alpha}(q)$ is the energy of the n-th branch pf the phonon state with quasimomentum q (α is the index determining the polarization of the displacement vector oscillations); T is the temperature. As functions $\omega_n^{\alpha}(q)$ of all possible types of acoustic vibrations characteristic of nanostructures of hexagonal symmetry – *shear*, *flexural, AS polarization* and *dilatational, SA* polarization [27] we used spectral dependences obtained in [24].

Knowledge of these quantities makes it possible to estimate other thermodynamic characteristics of NFs, for example, the thermal diffusion coefficient and heat capacity at constant pressure.

2. Results and discussion

The results of calculations obtained by us on the example of nanofilms of a layered crystal of hexagonal symmetry PbI_2 (polytype 2*H*, density $\rho = 6.16$ g/cm^3, lattice parameters: $a = 4.55$ Å, $c = 6.98$ Å) using relations (1–3) and dependences $\omega_n^{\alpha}(q)$ obtained in [25] are shown in Fig. 1–3.

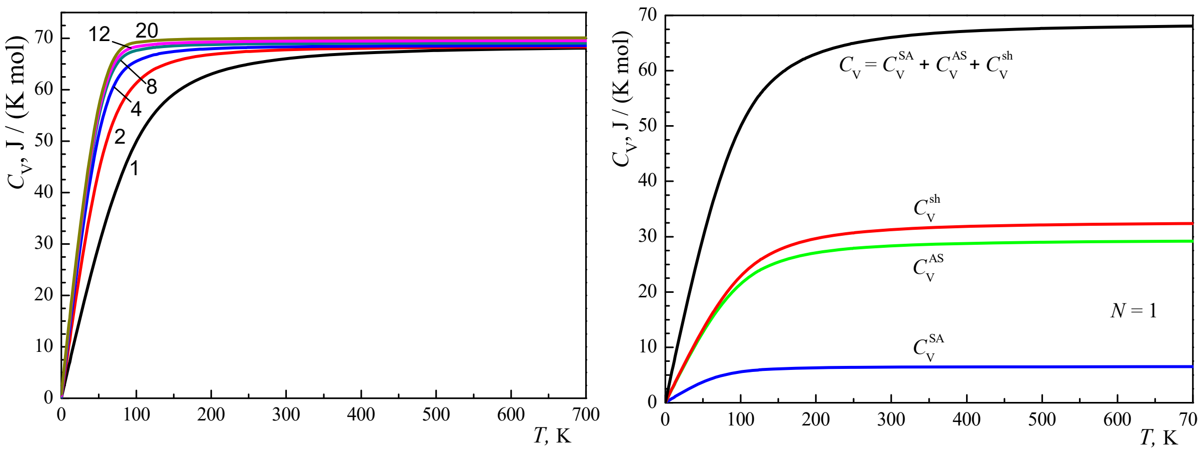
2.1. Heat capacity

The temperature dependences of the molar heat capacity C_V of NFs of different thickness $d = Nc$ (N is the number of PbI_2 layer packages forming the film) are shown in Fig. 1, *a*.

The plots of the $C_V(T)$ dependence have a standard form – its value decreases rapidly towards zero in the temperature range below the Debye temperature θ_D, and practically does not change at significantly higher temperatures (Fig. 1, *a*). Analysis of the obtained results shows that with a decrease in the thickness of the NFs, the value of θ_D increases from 100 to 125 K, which is consistent with both the measured value of $\theta_D = 99.4$ K in the bulk PbI_2 samples [28] and the calculated value of $\theta_D = 123$ K for monolayer PbI_2 in [6].

At any temperature, the heat capacity is the smaller, the thinner the NF. The dependence of the NF heat capacity on its thickness is nonlinear and significant for ultrathin films (up to 8

PbI$_2$ layers). Thus, the calculated value of the heat capacity of a monolayer (N = 1) film at 300 K is 66.09 J/(mol·K), which is in good agreement with the corresponding value of 67.85 J/(mol·K) obtained as a result of ab initio calculations by the authors [26]. With increasing thickness, the heat capacity of the NF increases.At the same time, the growth rate decreases, so that in films with a thickness of more than 14 nm ($N > 20$) the C_V value is little different from the value of 70 J/(mol·K). Comparison with the value of the heat capacity of a bulk PbI$_2$ crystal at room temperature of 81.51 J/(mol·K) [29] shows that in this case our calculations give a significantly underestimated result. However, from the above comparisons it is clear that the regularity established by us - a decrease in heat capacity with a decrease in the NF thickness - is confirmed by independent studies of other authors.



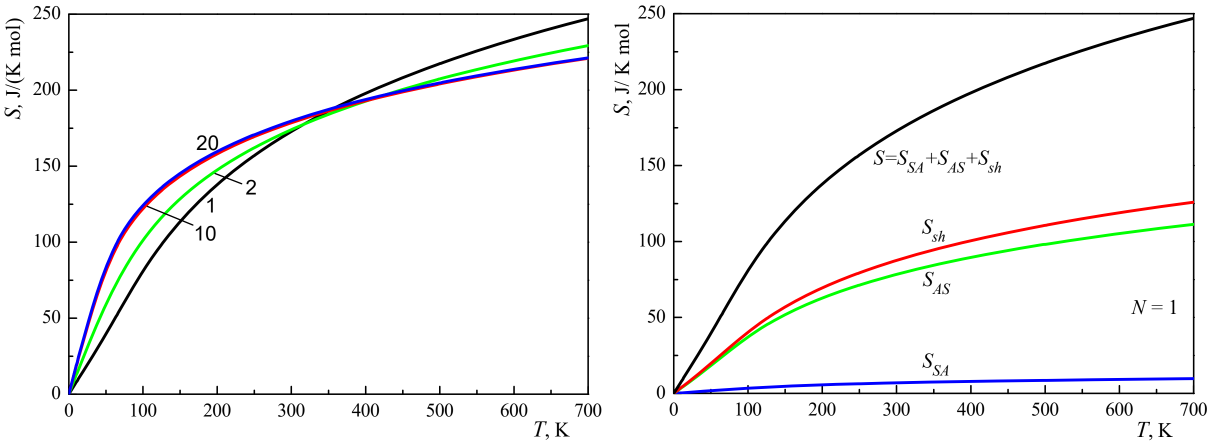
a) *b*)

Fig. 1. Temperature dependences of a) molar heat capacity C_V of NFs with a thickness of N layered packages PbI$_2$ (the value of N is indicated next to the corresponding curve); b) contributions to its value due to acoustic oscillations of shear (sh), bending (AS), and stretching (SA) polarization in a monolayer (N = 1) PbI$_2$ film

The role of different branches of the acoustic phonon spectrum in the formation of the heat capacity value and the dynamics of its changes was also investigated. General conclusions on this issue are illustrated by the plot of the heat capacity dependence on temperature, obtained on the example of a monolayer PbI$_2$ NF (Fig. 1, *b*). The phonon states of the longitudinal (*SA*) polarization branch make the smallest contribution to the heat capacity C_V, the frequencies and group velocities of which exceed the corresponding values of the phonons of the transverse branches of the spectrum [25]. The contributions of the vibrational states of the transverse polarizations – shear (*sh*) and bending (*AS*) – are much larger in magnitude and differ little from each other, which is explained by the closeness of the values of their frequencies and group velocities. The differences in the values of the contributions of different branches of the phonon spectrum of NF are explained by the fact that at $T \leq \theta_D$ the population of the corresponding vibrational states is the smaller, the higher the frequency.

2.2. Entropy

Temperature changes in the entropy of the acoustic phonon system in PbI_2 NF of different thicknesses, calculated by formula (2), are shown in Fig. 2, *a*. The dependencies *S(T)* and *S(d)* are found to be nonlinearly increasing functions. In the region $T \leq \theta_D$, the rate of temperature increase of entropy is greater, the greater the NF thickness. A further increase in temperature causes a decrease in the rate of change of entropy. Since the Debye temperature in NF of different thicknesses is different, the slowdown in the temperature increase of entropy begins earlier in those whose thickness is greater. As a result, in the vicinity of room temperatures, the ratio of entropy values in NF of different thicknesses changes – the thinner the NF, the greater the entropy values.



a) *b)*

Fig. 2. Temperature dependences of the entropy S of PbI_2 NF of different thickness (a) and contributions to its value due to acoustic vibrations of different polarization in the monolayer film (b)

The role of different branches of the acoustic phonon spectrum in the formation of the NF entropy value is similar to their role in the formation of the heat capacity – the largest contribution is made by phonons of transverse polarization (Fig. 2, *b*).

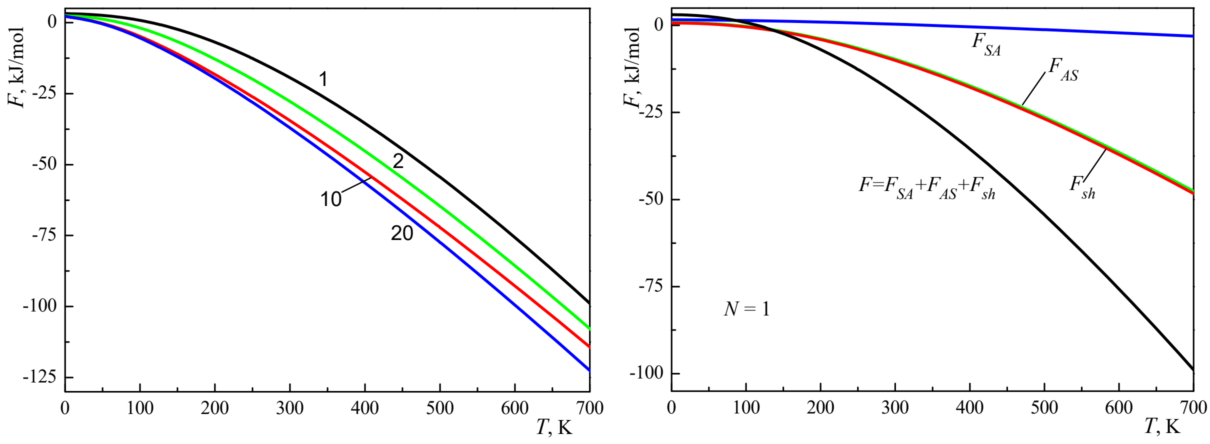
We also note that the results of our calculations are in satisfactory agreement with the known literature data on the entropy value of monolayer and bulk PbI_2. In particular, the entropy values obtained by us for NF with a thickness exceeding 7 nm ($N > 10$) differ little from each other and at 300 K are approximately 179.88 J/(mol·K).

This result is close to the experimentally determined value of the entropy of a bulk PbI_2 crystal, which according to [30] is 174.849 J/(mol·K), and according to [31] – 175.008 J/(mol·K).

Comparison of the temperature dependence of the entropy value of a single-layer PbI_2 NF (Fig. 2, $N = 1$) with the data of ab initio calculations [26, Fig. 4] gives grounds to assert that in this case too, satisfactory agreement of the results has been achieved at least at temperatures above room temperature, where the discrepancy does not exceed 2 %. In the low-temperature region, the entropy values calculated by us are smaller than the data [26], the lower the temperature (up to 23% at 50 K).

Free energy

The results of the study of the dependence of the free energy of the acoustic phonon system on temperature in PbI_2 NF of different thicknesses are shown in Fig. 3, *a*. The *F(T)* dependences are found to be decreasing (nonlinearly in the interval $0 < T \leq \theta_D$ and practically according to a linear law in the region of high temperatures) functions. An increase in the NF thickness leads to an increase in the rate of change of the function *F(d)* in the region of temperatures below room temperature. However, this difference is significant in ultrathin ($N \leq 10$) films. An increase in the NF thickness above 14 nm ($N \geq 20$) has practically no effect on the value of the free energy in the entire temperature range.



a) *b)*

Fig. 3. Temperature dependences of the free energy F of PbI_2 NF of different thicknesses (a) and contributions to its value due to acoustic vibrations of different polarization in the monolayer film (b)

The influence of different branches of the acoustic phonon spectrum on the value of the free energy of the NF, similar to their influence on the heat capacity and entropy, is different. The largest (approximately the same in magnitude) contribution to the value of the free energy is given by phonons of transverse polarization (Fig. 3, *b*).

Analysis of the plot of the temperature dependence of the free energy of a single-layer PbI_2 NF (Fig. 3, $N = 1$) shows that the results obtained by us are underestimated compared to the results of similar calculations by no more than 30% [see 26, Fig. 4]. We have not found any data on the free energy of a larger NF, as well as a bulk PbI_2 crystal.

2.3. Thermal diffusion

The availability of the results of calculating the heat capacity in the NF of different thickness presented here makes it possible to estimate another quantitative characteristic of thermal processes in PbI_2 NF – the thermal diffusion coefficient. The coefficients of thermal diffusion (k) and thermal conductivity (κ) are important physical parameters necessary for simulation and optimization in the manufacturing process of photoacoustic devices, related to each other and to the value of the specific heat capacity by the ratio $\kappa = k\rho c_V$ [29].

Using the heat capacity values obtained here and the results of calculations of the thermal conductivity coefficient [21], the dependence of the thermal diffusion coefficient of PbI_2 NF on their thickness (N) and temperature T was investigated (Table 1).

Table 1

The values of the thermal diffusion coefficient k (in units of 10^{-6} m²/s) of the NF with a thickness of N PbI_2 layers were calculated and compared with the data of other authors

T, K	100	200	300	400	500	600	700
$N = 1$	0.989	0.215	0.085	0.042	0.025	0.025	0.025
$N = 2$	1.72	0.405	0.127	0.067	0.041	0.041	0.041
$N = 4$	1.84	0.591	0.181	0.087	0.051	0.051	0.051
$N = 8$	2.575	0.598	0.212	0.102	0.060	0.060	0.060
$N = 12$	2.651	0.618	0.214	0.102	0.060	0.060	0.060
$N \geq 20$	2.665	0.658	0.220	0.103	0.065	0.064	0.063
[29] (200 μm)	–	–	2.48±0.2	–	–	–	–
[29] (250 μm)	–	–	2.5±0.04	–	–	–	–
[33] (extrapolation)	–	0.561	0.300	0.188	0.152	0.124	–

It can be seen that, similar to other quantities studied here, the thermal diffusion coefficient increases nonlinearly with increasing NF thickness but decreases with a rise in temperature. The rate of these changes is significant in the case of ultrathin (up to 8 PbI_2 layers) NF and not too high (up to 400 K) temperatures.

Comparison of the values of the thermal diffusion coefficient obtained by us with the data of other authors is possible only for the case of PbI_2 films with a thickness of more than 14 nm ($N \geq 20$) due to the lack of such information for ultrathin NF. The value of the thermal diffusion coefficient determined by the authors [29] on the basis of photoacoustic spectrometry data at 300 K is an order of magnitude higher than the corresponding value calculated by us. At the same time, its values measured by the Laser Flash Analysis method in millimeter-thick crystals [33] are in fairly good agreement with the results of our calculations (see Table 1).

Conclusions

1. All the studied characteristics of thermophysical processes in PbI_2 NF depend on their thickness. The absolute values of the heat capacity C_V, free energy F, thermal diffusion coefficient k and (at $T \leq 400$ K) entropy S are nonlinearly increasing functions of the NF thickness. Their growth rate is the highest in the thinnest NF and monotonically decreases with increasing thickness. This behavior of the indicated thermophysical characteristics of

NF is explained by the dependence of the frequency spectra of acoustic phonons on the NF thickness.

2. The heat capacity, entropy and thermal diffusion coefficient in NF of any thickness increase with a rise in temperature. In so doing, in the temperature range below the Debye temperature θ_D, their growth rate is the lowest in the thinnest NF. At $T >> \theta_D$, the temperature growth of the heat capacity and entropy slows down, the dependence of C_V on temperature practically disappears (right side of Fig. 1, a), and the growth rate $S(T)$ decreases the stronger, the greater the NF thickness. Due to the dependence of the Debye temperature on the NF thickness, the $C_V(T)$ functions reach their largest values at temperatures that are the higher, the thinner the NF. For the same reason, in the region $T \sim 400$ K, the inversion of the $S(T)$ dependence occurs in the NF of different thickness – the entropy acquires values that are the higher, the thinner the NF (right side of Fig. 2, *a*).
3. At $T << \theta_D$ the absolute values of the free energy increase slightly with temperature. The rate of such increase is greater, the greater the NF thickness. Upon reaching the Debye temperature, it reaches its maximum value, so that at $T >> \theta_D$ the free energy changes directly proportionally to the temperature with a rate whose magnitude is practically independent of the NF thickness (right side of Fig. 3, *a*).
4. The phonon branches of transverse polarizations of shear (*sh*) and bending (*AS*) have the greatest influence on thermophysical processes controlled by the values of heat capacity, entropy, and free energy, the contribution of which to the values of the indicated quantities is approximately the same (Fig. 1–3, *b*). The magnitude of the contribution of phonons of longitudinal – *SA*-polarization is an order of magnitude smaller than the contribution of phonons of each of them.
5. The temperature and dimensional changes of the thermal diffusion coefficient *k* are similar. The difference is that the largest contribution to its value is made by longitudinal phonons (*SA*-polarization). The reason for this is that they play a decisive role in the formation of the value of the thermal conductivity coefficient κ [21] and, at the same time, their contribution to the value of the heat capacity is small, while $k \sim \kappa/c_V$. Therefore, the phenomena of thermal diffusion, as well as thermal conductivity [21], are determined mainly by dilatation phonons.
6. Our results are generally consistent with the data of independent studies by other authors. This gives grounds to assert the ability of the methodology we used for theoretical study of the thermophysical properties of NF.

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Роль акустичних фононів у формуванні термофізичних властивостей наноплівок PbI_2

На основі дисперсійних залежностей частот акустичних фононів у гексагональних квазідвовимірних наноструктурах, раніше отриманих нами у наближенні пружного континууму, розраховано теплоємність, ентропію, вільну енергію (Гельмгольца) та коефіцієнт термодифузії плоских структур нанометрової товщини (наноплівок) дийодиду свинцю. Досліджено залежність цих величин від товщини наноплівки та температури, а також роль різних гілок фононного спектра у формуванні термофізичних властивостей таких структур. Результати розрахунку теплоємності, ентропії, вільної енергії та коефіцієнта термодифузії наноплівок дийодиду свинцю свідчать, що усі вони залежать від товщини наноплівки. Ця залежність особливо виразна у надтонких (товщиною до 8 шаруватих пакетів PbI_2)

наноплівках. Абсолютні значення усіх указаних величин зростають із збільшенням температури у наноплівках будь-якої товщини. У діапазоні низьких температур швидкість їх зростання тим менша, чим тонша наноплівка. При температурах понад температуру Дебая зростання теплоємності та ентропії уповільнюється; залежність $C_V(T)$ практично зникає, а швидкість зростання ентропії S зменшується тим сильніше, чим більша товщина наноплівки. Унаслідок відмінності швидкостей зміни ентропії у наноплівках різної товщини в області $T \sim 400$ K відбувається інверсія залежності $S(T)$ – ентропія набуває значень тим більших, чим тонша наноплівка. Швидкість зміни величини вільної енергії по досягненні температури Дебая набуває свого найбільшого значення, так що з подальшим зростанням температури вільна енергія змінюється за лінійним законом із швидкістю, величина якої практично не залежить від товщини наноплівки. Показано, що найбільший вплив на термофізичні процеси, контрольовані значеннями теплоємності, ентропії та вільної енергії, мають фонони поперечних поляризацій – зсуву та згину. Явище ж термодифузії, як і теплопровідності, визначається переважно поздовжніми – дилатаційними фононами.

Ключові слова: наноструктури, наноплівка, дийодид свинцю, акустичні фонони, термофізичні властивості, теплоємність, термодифузія, вільна енергія, ентропія.

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