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REVIEW OF RESULTS OF THEORETICAL APPROACHES TO PHONON ENGINEERING OF THERMODYNAMIC PROPERTIES FOR DIFFERENT QUANTUM STRUCTURES

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Summary: Application of nano-structures requires a knowledge of their fundamental physical (mechanical, electro-magnetic, optical, etc.) characteristics. Thermodynamic properties associated with phonon displacements through the nanosamples are particularly interesting. Independent of the type of lattices, the thermodynamics of their subsystems (electrons, excitons, spin waves, etc.) is determined when the subsystem is in thermodynamic equilibrium with phonons. Phonons are collective mechanical oscillations of molecules or atoms and represent the most important system of excitations. Besides, the acoustical characteristics as well as conductive and superconductive properties etc. could not be realistically explained without phonons.

In this paper we will try to observe the difference between the characteristics of different nano-crystalline structures: ultrathin films, composite films, i.e. superlattices, nanorods and quantum dots, we were interested in whether the quantum size effects (quantum confinement), quantum (de)coherence and influence of boundary conditions, strengthen or weaken in nanosamples. Finally, this paper describes how the dimensional confinement of phonons in nanostructures leads to modifications in the electronic, optical, acoustic, superconducting and thermodynamic properties of quantum.

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Thermal properties of nanostructures have recently attracted a lot of attention. The influence of size effects on thermal conductivity is becoming extremely important for device design and reliability. On the basis of the calculated dispersion law and distribution of phonon states in nanoscopic crystals, free energy and entropy will be calculated. Internal energy as well as heat capacitance will also be analyzed.

Keywords: phonons, Green's function, ultrathin films, superlattices, quantum wires–nanorods, quantum dots, energy spectra, thermodynamic behavior, specific heat, thermal conductivity

Introduction

Over the last decade, we have witnessed a rapid development of nanotechnology, i.e. production technologies of structures with nanodimensions.[3] The trend of rapid development of nanotechnologies is not accidental since nanostructures possess physical characteristics that are substantially different from the physical characteristics of the structures which are larger in size. Nanostructures are characterized by a series of qualitatively new effects. Superconductive, thermal insulating, acoustic and other features that characterize nanomaterials are better than those in bulk structures. It is also expected that the use of nanostructured elements may increase the sensitivity of measuring instruments which in turn leads to new experimental findings. All of the above mentioned leads to the conclusion that nanomaterials can be a good basis for further development of physics. In a way, nanostructure effects are connected to the effects in bulk structures, similarly to the relationship between quantum and classical effects. Therefore, further and even faster development of the science of nanostructure materials and nanotechnology is to be expected.

The precise structuring of materials to the dimensions of the order of nanometer is of great importance in electronics, optoelectronics, high temperature superconductivity, biology, medicine, environmental protection and many other scientific and technological disciplines. Theoretical and experimental studies of properties of low-dimensional systems (thin films, superlattices, quantum wires and quantum points, Fig.1), have become very intense in recent decades, so it could be concluded that they represent one of the key directions of research in modern condensed matter physics.

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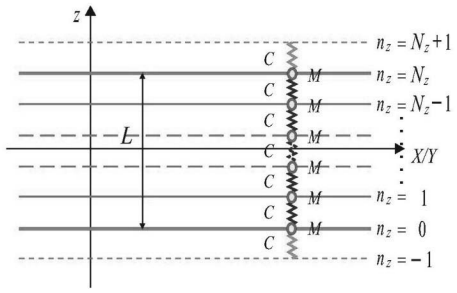

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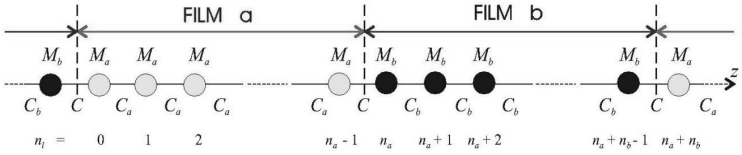

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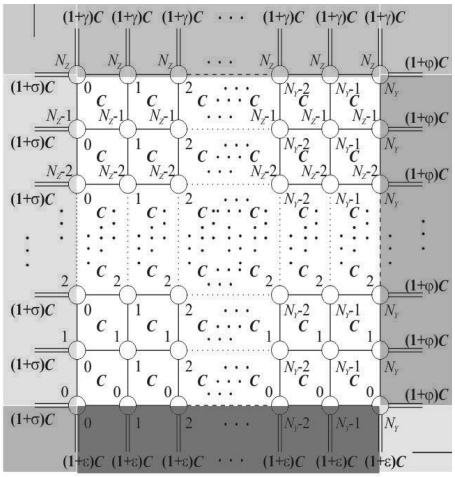

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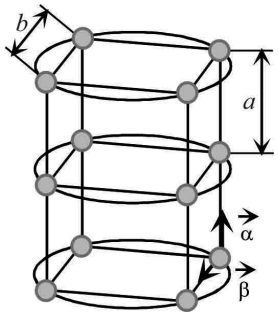

QUANTUM DOT

Figure 1: Different models of crystalline quantum structures

The development of sophisticated techniques for the growth control of very thin layers caused intensive research of the nano-crystalline structures. One of the basic principles for their production is based on a process of self-construction or self-assembly,[4] which is one of the "bottom-up" techniques, in which atoms or molecules arrange themselves into low-dimensional structures on the basis of mutual physical-chemical interactions. Although the self-assembly has been known for many years, its use in industry is still at the beginning. Improved knowledge of thermodynamics and kinetics of the nano-scale processes, with the advancement of characterization techniques and computer modeling, should lead to the development of complex systems.

Nanoscience continues to advance at a dramatic pace and is making revolutionary contributions in diverse fields, including electronics, optoelectronics, quantum electronics, materials science, chemistry, and biology. The technologies needed to fabricate nanoscale structures and devices are advancing rapidly. These technologies have made possible the design and study of a vast array of novel devices, structures and systems confined dimensionally on the scale of 10 nm or less in one or more dimensions.[5] Moreover, nanotechnology is continuing to mature rapidly and will no doubt lead to further revolutionary breakthroughs like those exemplified by quantum-dot semiconductor lasers operating at room temperature, intersubband multiple quantum-well and quantum wire lasers, double-barrier quantum-well diodes operating in the terahertz frequency range, single-electron transistors and memories.

1. Theoretical Modelling

Application of nano-structures requires a knowledge of their fundamental physical (mechanical, electromagnetic, optical, etc.) characteristics.[6] Thermodynamic properties[7] associated with phonon displacements through the nano-samples are particularly interesting. Independent of the type of lattices, the thermodynamics of their subsystems (electrons, excitons, spin waves, etc.)

4 Nanoscale Assembly -- Chemical Techniques, Ed. W. T. S. Huck, *Springer*, New York (2005); Self-Organized Nanoscale Materials, Eds. M. Adachi, D. J. Lockwood, *Springer*, New York (2006).; J. P. Šetrajčić, S. K. Jaćimovski, V. D. Sajfert, Phonon Contribution to Heat Capacitance of Nanolayered Crystalline Structures, *Mod. Phys. Lett.*B **29**/4, 1550008 (2015); doi: 10.1142/S0217984915500086.

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7 M. C. Tringides, M. Jałochovski, E. Bauer, Quantum Size Effect in Metallic Nanostructures, *Physics Today*, April (2007), pp. 50–54.; M. G. Cottam, D. R. Tilley, Introduction to Surface and Superlattice Excitations, *University Press*, Cambridge (1989); V. D. Sajfert, J. P. Šetrajčić, S. K. Jaćimovski, B. S. Tošić, Thermodynamic and Kinetic Properties of Phonons In Cylindrical Quantum Dots, *Physica* E **353**, 479-491 (2005).

is determined when the subsystem is in thermodynamic equilibrium with phonons.[8] Phonons are collective mechanical oscillations of molecules or atoms and represent the most important system of excitations. The reason is simple: phonons are present in all systems and their influence, more or less, changes behavior of all other objects or excitations of the system. The mentioned influence reflects primarily in the fact that they play the role of a thermostat of the system and determine its thermodynamics. Besides, the acoustical characteristics as well as conductive and superconductive properties etc. could not be realistically explained without phonons.[9] All quoted is well known and all applications of phonons in bulk structures have been intensively exploited for more than a century.

The fact which must be specifically mentioned is that the role of phonons in nanostructures is much more impressive than in bulk structures. The main fact concerning phonon properties in nanostructures is the absence of the so-called acoustical phonons, i.e. the phonons whose energy tends to zero when phonon momentum tends to zero. An activation energy different from zero is necessary for exciting phonons in nanostructures. Such unexpected characteristics require revision of all conclusions obtained regarding bulk theories of phonons. Therefore, the contribution of phonon subsystems to thermodynamic and energy transferring analysis is the first step in the research of nano-structure properties.[10]

This paper describes a major aspect of the effort to understand nanostructures, namely the study of phonons and phonon-mediated effects in structures with nanoscale dimensional confinement in one or more spatial dimensions. During the last two decades there has been a steady effort to understand the optical and acoustic phonons in nanostructures such as the superlattice, quantum wires, nanotubes and quantum dots. The central theme of this paper is the description of the acoustic phonons of optical type in these nanostructures. As a preliminary to describing the dispersion relations and mode structures for phonons in nanostructures, phonon amplitudes are quantized in terms of the harmonic oscillator approximation, and anharmonic effects leading to phonon decay are described in terms of the dominant phonon decay channels. These elastic and discontinued models are applied to describe the deformation potential and interactions in a variety of nanostructures including quantum wells, nanowires and quantum dots. Finally, this paper describes how the dimensional confinement of phonons in nanostructures leads to modifications in the electronic, optical, acoustic, superconducting and thermodynamic properties of the quantum.

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10 S. M. Stojković and J. P. Šetrajčić, Superconductive Characteristics of Materials: Bulk Samples and Thin Films, *NBP: Journal of Criminalistics and Law* **3**/1, 39-67 (1998); LJ. Budinski-Petković, U. Kozmidis-Luburić, M. Ćetković, Lj. Mašković and B. S. Tošić, Phonons in Cylindric Microschips, *NBP: Journal of Criminalistics and Law* **5**, 69 (2000).

Research of the influence of phonons with quantum size and confinement effects in nanostructures is not new. It has been conducted for almost two decades. It is known[11] that acoustic phonons affect practically all electronic, thermal and optical properties of semiconductors. They are carriers of heat and together with optical phonons constrain the mobility of electrons in the areas of medium and high temperatures. Reduction of sizes in nanostructures leads to the so-called confinement of phonons due to which the phonon branches are quantized (dimensional quantization) and a substantive modification of their energy spectrum, group velocity and polarization occur. Due to the reflections from the inner surface of the structure, phonon modes hybridize and cease to be purely longitudinal or purely transverse, and their group velocity is reduced compared to the case in the bulk structure.

Dependence of energy on the wave vector is highly nonlinear and linear approximation of the laws of dispersion of phonons in small size nanostructures makes no sense. Changing the phonons dispersion law due to confinement severely affects the kinetic effects conditioned by the interaction of acoustic phonons with electrons, dotted defects, phonon-phonon interaction. Managing transport properties of acoustic phonons through the modification of their energy spectrum in nanostructures was named phonon engineering.[12]

The concept of phonon engineering is based on the corresponding changes to the phonon spectrum in order to improve the electric and thermal transport properties of the given nanostructure. In homogeneous layers and nanowires, phonon engineering can be realized on the account of changes in the size of the nanostructure or changes in the quality of exterior surfaces. In this sense, the most advantageous are composite materials composed of layers with different phonon properties. In these structures, general hybridized phonon modes occur, which may originate from the phonon properties of the individual layers or as averaged modes of different layers. By changing the thickness of the layers as well as the types of materials that go into the composite, a different degree of hybridization of the phonon modes can be achieved and thus change thermal transport properties of the structure in a wide range.

A demonstration of phonon engineering is given in a series of papers for the three-layer film heterostructures and coated nanowires.[13] In these structures, the phonon modes are divided into three groups: fluctuations in the inner layer of the

11 A. A. Balandin, et.al., Significant Decrease of the Lattice Thermal Conductivity due to Phonon Confinement in a Free-standing Semiconductor Quantum Well, *Phys. Rev*. B **58**/3, 1544 (1998); A. A. Balandin, D. L. Nika, Phononics in Low-Dimensional Materials, *Materials Today* **15**/6, 266 (2012); J. M. Ziman, Electrons and Phonons: The Theory of Transport Phenomena in Solids, *Oxford University Press*, New York (2001).

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coating and general oscillations as a whole. Redistribution of atom displacements between layers leads to attenuations of electron-phonon interaction and to the increase of the mobility of electrons in materials that are coated with other materials[14].

Another direction of development of phonon engineering is the optimization of thermal transport at the nanolevel. By targeted changing of the phonon spectra, the density of states and group velocity of phonons, thermal conductivity of nanostructures can be increased or decreased. Depending on what material is used as a coating, thermal conductivity can be altered.[15]

Unlike in the previous papers,[16] here we will try to observe the difference between the characteristics of different nano-crystalline structures: ultrathin films, composite films, i.e. superlattices, nanorods and quantum dots, we were interested in whether the quantum size effects (quantum confinement), quantum (de)coherence and influence of boundary conditions, strengthen or weaken in nanosamples.

2. Results and Discussion

While the theoretical study of the structures which are larger in size generally requires solving differential equations with constant coefficients, difference equations appear in the research of nanostructures, but their coefficients depend on the spatial coordinates due to the necessity to introduce the boundary conditions and the breaking of spatial translational symmetry in the equation,

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as well as the impact of vacancies and impurities. The most commonly used mathematical structure in solving the problem of difference equations are translational operators,[17] because their use enables the most efficient reaching of solutions.

The major part of this paper deals with the application of the mentioned methodology of solving difference equations and the problem of structures with broken symmetry along a single crystallographic direction. Furthermore, nanostructures that are translationally invariant in only one direction and structures that do not possess translational invariance have also been studied. The method of Green's functions is generally used here because this method is self-consistent, i.e. it solves both the dynamic and thermodynamic sides of the problem. Other methods are used for either one or the other. For example, the dynamic characteristics of the problem can be determined by using the wave function, but in order to solve thermodynamics, one has to resort to the methods of statistical physics. Regardless of this, in some sections of the second part, the structure problems were solved by using the wave functions of nanostructures.

It should be noted that the methodology for calculating the Green's function[18] in the conditions of broken symmetry has already been developed, where such a breaking of symmetry can be along one direction, along two directions and along all three spatial directions. When the problem of calculating the Green's functions for the structures with broken symmetry is concerned, there are a lot of inconsistencies today because of the fact that in such structures Green's functions depend on individual spatial variables, rather than on their difference, as is the case with the structures with ideal symmetry.

Thermal properties of nanostructures have recently attracted a lot of attention. The influence of size effects on thermal conductivity is becoming extremely important for device design and reliability.[19] The problem of thermal management

17 .P.Šetrajčić, V.M.Zorić, N.V.Delić, D.Lj.Mirjanić, S.K.Jaćimovski, Phonon Participation in Thermodynamics and Superconductive Properties of Thin Ceramic Films, Ch.15, pp.317-348, In Thermodynamics, Ed. M.Tadashi, *InTech*, Vienna (2011); J.P.Šetrajčić, D.Lj.Mirjanić, S.M.Vučenović, D.I.Ilić, B.Markoski, S.K.Jaćimovski, V.D.Sajfert, V.M.Zorić, Phonon Contribution in Thermodynamics of Nano-Crystalline Films and Wires, *Acta Phys Pol.* A **115**, 778 (2009); S.K.Jaćimovski, B.S.Tošić, J.P.Šetrajčić, V.M.Zorić, V.D.Sajfert, D.I.Ilić, Thermodynamics of Mechanical Oscillations in Crystalline Superlattices, *Int.J.Mod.Phys.*B **21**(6), 917-930 (2007); S.K. Jaćimovski, J. P. Šetrajčić, M.S.Jaćimovski and V.V.Stojanović, Phonon Contribution in Thermodynamics and Transport Properties of Ultrathin Ceramic Films, *Acta Phys.Pol.* A **126**/3, 811 (2014); J.P.Šetrajčić, V.D.Sajfert, D.Lj.Mirjanić, S.M.Vučenović, Operator Method for Solving the Difference Equations, *Proceedings 5th WSEAS International Conference on Applied Mathematics*, **488**/148, 1-4 (2004).

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is even more severe for photonic devices such as vertical cavity surface emitting lasers. On the other hand, to improve performance of thermoelectrics, one needs to achieve low thermal conductivity. These are two contradictory demands, but both can be approached with appropriate modification of phonon modes, e.g. phonon engineering.

On the basis of the calculated dispersion law and distribution of phonon states in nanoscopis crystals, free energy and entropy will be calculated. Internal energy as well as heat capacitance will also be analyzed. Low-temperature behavior of these quantities will be compared to the corresponding ones of bulk-structures. It was shown that heat capacitances of nano-layered structures in low-temperature region were higher than the same quantities of the corresponding bulk sample. In the middle and the highest temperature region, temperature behaviour was inverse: heat capacitance of layered structures was lower than those of the corresponding bulk ones. The consequences were discussed with relation to the better superconductive properties of nano-materials.

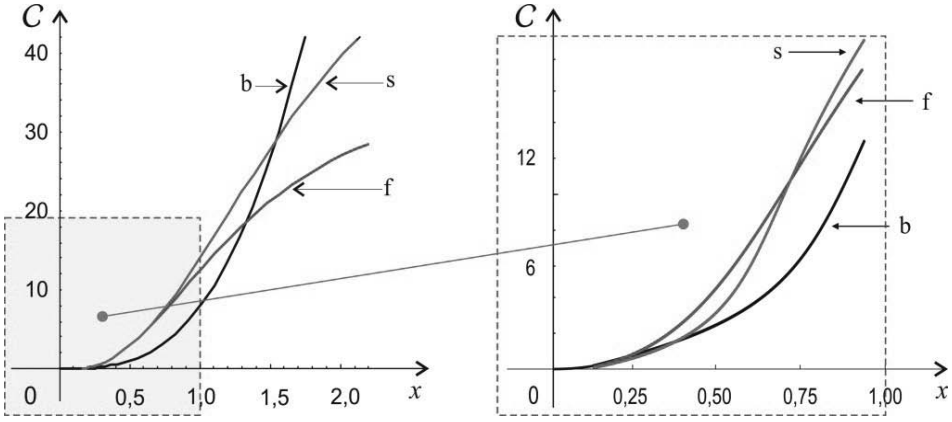

Figure 2: Temperature behaviour of specific heats of ultrathin film and superlattice in comparison to bulk ones

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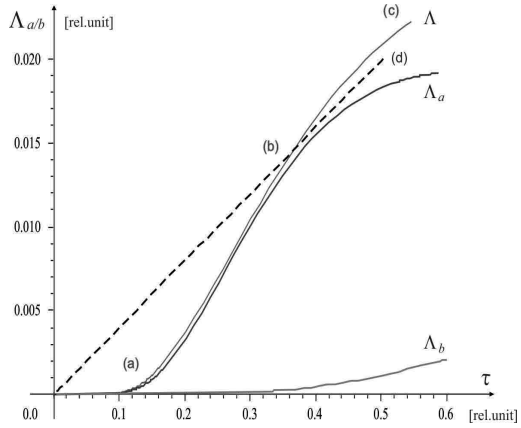

Figure 3: Low temperature behaviour
of the thermal conductivity coefficients of nanodots

As observed in[20] the thermal conductivity reduction, while having a negative effect on thermal management of electronic devices has a positive effect on thermoelectric devices, which require materials with high electrical conductivity, the Seebeck coefficient, low thermal conductivity and superconductivity.

The authors of the paper[21] report on the experiments using a conventional semiconductor thin film where thermal conductivity in-planes decreases with decreasing thickness because the thermal transport in such structures is mostly limited by the phonon scattering from the film boundaries. An opposite dependence can be observed in few-layer graphenes where the transport is limited mostly by the lattice anharmonicity.[22] Our results generally correspond to the reported data of experimental researches of the lateral thermal conductivity of nitride/silicon/oxide membranes measured with a suspended microstructure,[23] where reduction in thermal conductivity cannot be attributed entirely to boundary scattering and structure imperfections, and is likely to be related to modification of phonon modes and corresponding change in the thermal transport.

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Conclusion

Temperature analysis of phonon contribution to the thermodynamic characteristics behavior of nano-layered structures (ultrathin film, superlattice, nanorods and quantum dots) was carried out in detail. The main results follow.

The results of the analyses of phonons in ultrathin films can be summarized as follows:

1) Comparing the mean specific heat of film (introduced by above convention) with the specific heat of ideal structure we found that the specific heat curves have two intersections points and these intersections are quoted in this work. From $T = 0$ K up to first intersection point specific heat of film is several orders of magnitude less than the specific heat of the ideal structures. The same is valid for thermal conductivities: the low temperature thermal conductivity of the film is noticeably less than that of the ideal structure. It emphasizes that at the low temperatures the films process thermal insulation properties extremely well.

2) At the temperatures higher than the second intersection temperature point the thermal conductivity of the film is less than that of the ideal structure but their differences are not extremely high.

3) In the temperature interval, which lies in domain (50 – 100 K) approximately, the specific heat of the film as well as thermal conductivity is insignificantly higher than these characteristics of the ideal structure.

It was very interesting for us, and a bit unexpected, that the differences in the corresponding thermodynamic quantities, relative to the bulk-structure, are more pronounced in single (solo) ultrathin films, than in multilayered films – superlattices. This is imposed as a very important conclusion. Effects of dimensional quantization and confinement, which are important for nano-films (in parallel films, i.e. superlattices, they are amplified), are damped and their behavior is closer to the behavior of corresponding quantities in bulk-structures.

Consequently, the paper shows that the apparent changes in the dispersion law of acoustic phonons in nanostructures caused by quantum size and confinement effects have a direct implication on the significant reductions of their thermal characteristics in relation to the ones in the bulk structures. The volume of the reduction certainly depends on the boundary conditions of nanostructures: for films – on the thickness, i.e. the number of crystallographic planes, as well as on the values of boundary parameters (phonon interactions) on the surface-planes, and for superlattices – on the period, the transmission ratio and the value of boundary parameters (phonon interactions) on the surfaces of the primitive cell. These dependencies are not presented in the paper because this is an ongoing reserach and their impact is being tested and will be the subject of our next report. Here we focus only on the general guidelines and outlined tendencies and analytical application of the Green's functions method to the testing of the share of phonons in thermal behavior of nanostructures, and qualitative indicators of possible effects of the fundamental confinement effects to the macroscopic properties of the samples have been obtained.

The exposed method for calculation of Green's function of spatially deformed structure appears here, first. The usual approach in analyses of spatially deformed structures, consisting in calculation of spatially diagonal Green's functions in the broken symmetry direction cannot reproduce the spatial dependence of such structures. In this approach the spectral dependence of physical characteristics of deformed structures was lost. The new method presented here doesn't suffer this failure.

The spatial dependence of density and of diffusion coefficient of axial phonons in quantum dots were analysed in this paper. It turned out that the maximum of density change as well as the maximum of diffusion occur in the middle of quantum dots, while on the boundaries they are minimal. It should also be noted that specific heat, as well as the thermal conductivity of quantum dots, is exponentially small at low temperatures.

We are of opinion that the conditions for appearance of high temperature superconductivity as well as of thermal insulation properties are fulfilled in cylindrical quantum dots.

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PREGLED REZULTATA TEORIJSKIH PRISTUPA FONONSKOM INŽENJERINGU TERMODINAMIČKIH OSOBINA RAZLIČITIH KVANTNIH STRUKTURA

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Sažetak: Primena naostruktura zhteva poznavanje njihovih osnovnih fizičkih (mehaničkih, elektromagnetnih, optičkih, itd.) karakteristika. Termodinamičke osobine su povezane sa ponašanjem fononskog podsistema koji uvek postoji. Fononi su kolektivne mehaničke oscilacije molekula ili atoma kristalne rešetke i predstavljaju najvažniji sistem ekscitacija u ovim strukturama.Nezavisno od tipa kristalne rešetke termodinamika njenih podsistema (elektrona, eksitona, spinskih talasa itd.) je određena kada je odgovarajući podsistem u termodinamičkoj ravnoteži sa fononima. Uloga fonona u nanostrukturama je značajnija nego u tzv. balk strukturama, posebno što je u nanostrukturama (filmovi, superrešetke, žice, tačke) kretanje fonona ograničeno u nekoliko dimenzija. Zbog ograničenosti dimenzija kod nanostruktura se javljaju novi efekti kao što je dimenziono kvantovanje, konfiniranje fonona itd. Uticaj graničnih uslova na zakon disperzije fonona dovodi do promene karakteristika termodinamičkih i transportnih osobina. Dakle, menjanjem graničnih uslova se može uticati na toplotne i transportne osobine ovih struktura, što se danas popularno naziva fononski inženjering. U radu su analizirani i upoređivani toplotni kapaciteti i koficijenti toplotne provodnosti (kao merljive veličine) za razne strukture, kako na niskim tako i na visokim temperaturama, kao i posledice na njihovu praktičnu primenu.