

DIFFERENCES IN THERMODYNAMIC PROPERTIES OF PHONON NANO-LAYERED CRYSTALLINE STRUCTURES

S. K. Jaćimovski¹, J. P. Šetrajić², V. M. Zorić², D. I. Ilić³, B. S. Tošić⁴, V. D. Sajfert⁵

¹ Faculty of Electrical Engineering, University of Belgrade, Serbia,

² Department of Physics, Faculty of Sciences, University of Novi Sad, Vojvodina, Serbia,

³ Faculty of Technical Sciences, University of Novi Sad, Vojvodina, Serbia,

⁴ Vojvodina Academy of Science and Arts, Vojvodina, Serbia,

⁵ Technical Faculty "Mihajlo Pupin", University of Novi Sad, Vojvodina, Serbia

Abstract

Using the method of two-time dependent Green's functions applying to bounded and translational perturbed systems, the phonon spectra and thermodynamic characteristic of film-structures and superlattice are analyzed. Free and internal energy of the system as well as specific heat and entropy are found. The temperature behavior of layered structures specific heat is compared to that of bulk-structures.

Keywords: phonons, ultrathin film, superlattice, thermodynamics.

1. Introduction

Application of nano-structures requires knowing of thermodynamic characteristics of these systems and their subsystems (electrons, excitons, etc) when these subsystems are in thermodynamic equilibrium with phonons [1, 2]. Free energy, entropy and specific heat of ultrathin films and superlattices (consisting of two periodically repeating films) will be analyzed and low-temperature behavior will be compared to the corresponding quantities of bulk structure [3 -5].

2. Thermodynamic characteristics

We begin from the well-known expression of the Hamiltonian for the phonon subsystem in the nearest neighbor's approximation, which depends on the \vec{u}_n^α -the small movements of atom in place \vec{n} from its equilibrium position in direction α and \vec{p}_n^α -the corresponding momentum. We assume that the symmetry is disturbed along z direction, while translational symmetry of cubic structure is conserved in XY planes. On the Figs.1 and 2 the nano-film and superlattice model of phonons are presented schematically in z direction, only.

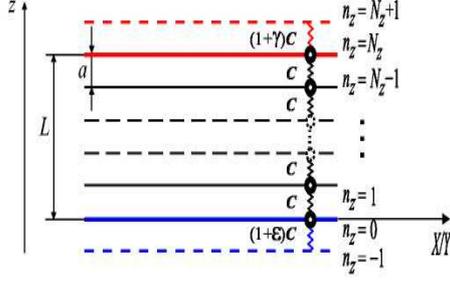


Figure 1: Phonon nano-film model

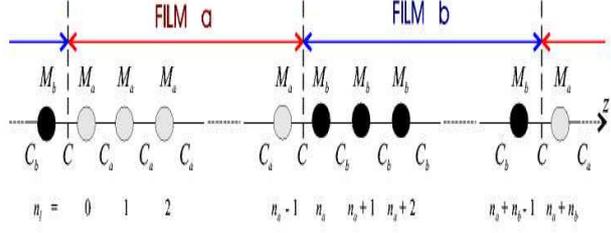


Figure 2: Phonon superlattice model

The corresponding Green's function [6]:

$$G_{\bar{n},n_i;\bar{m},m_i}(t-t') \equiv \langle\langle u_{\bar{n},n_i}(t) | u_{\bar{m},m_i}(t') \rangle\rangle \Theta(t-t') < [u_{\bar{n},n_i}(t), u_{\bar{m},m_i}(t')] \rangle \quad (1)$$

have the equation of the motion of the form:

$$-M_i \omega^2 G_{\bar{n},n_i;\bar{m},m_i}(\omega) = -\frac{i\hbar}{2\pi} \delta_{\bar{n},\bar{m}} \delta_{n_i,m_i} + \frac{1}{i\hbar} \langle\langle [p_{\bar{n},n_i}, H] | u_{\bar{m},m_i} \rangle\rangle_{\omega} \quad (2)$$

After evaluating the commutators figuring in higher order Green's function [4, 5] and applying the partial configuration Fourier transformation one obtains the system of non-homogeneous algebraic-differential equations for Green's functions for film and for superlattice. These equations can be reduced to there of simple cubic lattices with help of substitutions connected with the lattice constants. We obtain the solvable systems of algebraic-difference equations. The unknown Green's functions are: $G_{\bar{n},m} = D_m / D$, where D_m and D are the variable, respectively the system's determinants. The poles of Green's functions, determining the dispersion laws of phonons are found by equating the determinant D to zero. By expanding determinant through numerical calculations only [3, 6, 7], we give adequate number of values for frequencies ω_k . In this way, we found the dispersion law of phonons in nano-layered crystalline structures.

The quadratic structure of Hamiltonian corresponds to the system of non-interacting phonons and the free energy of the system can be taken as the sum of partial free energies. General expressions for free energy and corresponding entropy are:

$$F = \sum_k \sum_{\alpha} \ln \left(1 - e^{-\frac{\hbar \omega_{k\alpha}}{\theta}} \right); \quad S = -\frac{\partial F}{\partial T}; \quad \theta \equiv k_B T. \quad (3)$$

The phonon frequencies are $\omega_k = \Omega \sqrt{A + B a^2 k^2}$, where $\Omega_{\alpha}^2 \equiv \frac{C_{\alpha}}{M}$, $A = \rho + 2\alpha$, $B = \alpha$.

After calculations [7, 8], we obtain the entropies (per elementary cell), for nano film:

$$S_{nf} = \frac{3k_B}{2\pi} \left(\frac{\Delta}{E_0} \right)^2 \left\{ \left[\ln(1 - e^{\Delta/\theta}) - \varepsilon^2 (1 - e^{\varepsilon \Delta/\theta}) \right] + 3 \left[Z_1 \left(\frac{\Delta}{\theta} \right) - \varepsilon^2 Z_1 \left(\varepsilon \frac{\Delta}{\theta} \right) \right] + \dots \right\} \quad (4)$$

and similarly for nanolattice. Here $Z_r(X) = \sum_{j=1}^{\infty} j^{-r} e^{-jX}$ are the Dyson's functions, $E_0 = \hbar\Omega$,

$$\Delta_{m;n} = \hbar\Omega\sqrt{A + Bak_{\min;\max}}, \quad \varepsilon = \Delta_n / \Delta_m, \quad \Omega = \sqrt{C_{a/b} / M_{a/b}}, \quad \text{and } N = N_x N_y (N_z + 1).$$

Indices nf and sl are in relation to nano films as well as superlattices, respectively. The analyzes shown that all phonon excitations of multilayer nanostructures posses energy gap. As a consequence the free energy and entropy at low temperatures are lower than in corresponding bulk system. Internal energy and specific heat are:

$$U = \sum_{k\alpha} E_{k\alpha} \left(e^{\frac{E_{k\alpha}}{\theta}} - 1 \right)^{-1}; \quad C = -\frac{\partial U}{\partial T} \quad (5)$$

In this way we found the following expression for nano film:

$$C_{nf} = \frac{3k_B}{2\pi} \left(\frac{\Delta}{E_0} \right)^2 \left\{ \frac{\Delta}{\theta} \left[\ln(e^{\Delta/\theta} - 1)^{-1} - \varepsilon^3 (e^{\varepsilon\Delta/\theta} - 1)^{-1} \right] + 3 \left[Z_1 \left(\frac{\Delta}{\theta} \right) - \varepsilon^2 Z_1 \left(\varepsilon \frac{\Delta}{\theta} \right) \right] + \dots \right\} \quad (6)$$

and similarly for the nano lattice. Whether the acoustical phonons were investigated in nanostructures, the specific heat is exponentially small at the low temperatures. The practical aspects of this effect were discussed in previous section. The phonon contribution into specific heat of ultrathin film, superlattice and bulk structures (in accordance with data from [5,7]) is numerically analyzed. Nanostructures are considered for "cut off" case, i.e. the deformations of boundary parameters of the system were not taken into account. Exposed numerical estimates of the specific heat are presented on the Fig.3.

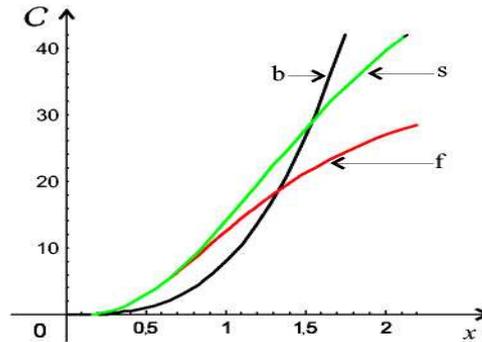


Figure 3: Low-temperature behaviour of specific heats nano and bulk structure

By C is denoted relative specific heat, while x denotes relative temperature:

$$C_{b/fls} \equiv \frac{C_{b/fls}}{C_0}; \quad C_0 = \frac{k_B}{2} \left(\frac{\Delta}{E_0} \right)^3; \quad x \equiv \frac{\theta}{\Delta}; \quad \Delta \approx 50k_B \quad (7)$$

It is seen on Fig.3 that the superlattice above 35 K has higher specific heat than ultrathin film. It means that its thermal conductivity is higher.

3. Conclusions

Our analysis has shown that it is expectable for ultrathin films and superlattices to be better superconductors than the corresponding bulk structure. Experimentally confirmation of this can be found in [9-11]. At the temperatures below 10 K and above 80 K the specific heat of the bulk structure is higher than those of ultrathin film and superlattice. It means that in the temperature ranges quoted bulk possesses higher thermal conductivity, and higher electrical conductivity. This is of practical interest, because between 10 and 80 K ultrathin films and superlattices have lower electrical resistance and they can be used for save of electric energy.

The main low-thermodynamic characteristics of nanostructures are considerably lower than those of the bulk structure and consequently, their superconductive characteristics are better than those of bulk structures.

Acknowledgements

This work was partially supported by the Serbian Ministry of Science and Technology: Grant No 1795 or ON 131044.

References

1. M. C. Tringides, M. Jaločovski, E. Bauer, *Quantum Size Effect in Metallic Nanostructures*, Physics Today, (2007)
2. M. G. Cottam, D. R. Tilley, *Introduction to Surface and Superlattice Excitations*, Univ. Press, Cambridge (1989)
3. S. K. Jaćimovski, J. P. Šetrajčić, V. M. Zorić, B. S. Tošić, V. D. Sajfert, D. I. Ilić, Int. J. Mod. Phys. B 6, 916 (2007)
4. S. K. Jaćimovski, D. I. Ilić, I. K. Junger, J. P. Šetrajčić, Novi Sad J. Math. 1, 55 (2001)
5. S. Lazarev, M. R. Pantić, S. M. Stojković, B. S. Tošić, J. P. Šetrajčić, J. Phys. Chem. Sol. **61**, 931 (2000)
6. G. Rickayzen, *Green's Functions and Condensed Matter*, Acad. Press, London (1980)
7. J. P. Šetrajčić, S. K. Jaćimovski, D. Raković, D. I. Ilić, in "Electrical and Computer Engineering Series: Advances in Simulation, Systems Theory and Systems Engineering" (Eds. N. E. Mastorakis, V. V. Kluev, D. Koruga), WSEAS Press (2003)
8. J. P. Šetrajčić, V. M. Zorić, S. M. Vučenović, D. Lj. Mirjanić, V. D. Sajfert, S. K. Jaćimovski, D. I. Ilić, Materials Science Forum **555**, 291 (2007)
9. D. H. Santamore, M. C. Cross, arXiv:cond.mat. 0011373 (2001)
10. W. E. Bies, R. Radke, H. Ehrenreich, arXiv:cond.mat. 0005028 (2000)
11. A. J. Bulen, K. E. O'Hara, D. G. Cahill, arXiv:cond.mat. No 0008084 (2001)