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Phonon Participation in Thermodynamics and Superconductive Properties of Thin Ceramic Films

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1. Introduction

The scope of our study in this paper is limited to the analysis of the phonons, i.e. phonon behavior in thin layered structures or crystalline films, which implies the existence of two boundary surfaces perpendicular to a preferred direction. Besides that, these film-structures could be doped by foreign atoms from one or both sides of the boundary surfaces in which way the internal configuration of the atom distribution is disturbed.

Since elastic constants and atomic masses define phonon spectra and states, we conclude that they must be different in the film-structures with respect to the corresponding ones in the ideal unbounded and translational invariant crystalline structures. The change of mass distribution along one direction and the existence of the finite structure width along that direction introduces additional boundary conditions into the analysis of the phonon behavior. We shall study the thin film "cut-off" from the ideal tetragonal crystalline structure with lattice constants $a_x = a_y = a$ and $a_z = 3a$. This structure has a finite width in the z -direction, while XY -planes are assumed to be infinite, meaning that the structure possesses two infinite boundary surfaces (parallel to the unbounded XY -planes) lying at $z = 0$ and $z = L$ (Fig. 1). The number of the atoms located along z -direction is assumed to be N_z , and it is also assumed that torsion constants $C_{\alpha\beta}$ ($\alpha \neq \beta$) can be neglected with respect to the elongation constants $C_{\alpha\alpha}$ (Tošić et al., 1987). These structures will be titled the ideal crystalline films. The doping (by sputtering) of the ideal film with guest atoms (impurities) along z -direction, from one or mutually from both boundary surfaces, produces the film with disturbed internal distribution of atoms. Such structures will be entitled asymmetrically or symmetrically deformed crystalline films, respectively.

We have decided to study phonon behavior in the above mentioned film-structures for two reasons. Phonons are the basic elementary excitations in the condensed matter which have the decisive role in the creation of Cooper pairs of electrons in the low-temperature superconductivity. On the other hand, although the existence of phonons

and Cooper pairs in the high-temperature superconductive ceramics is experimentally established (Chang & Esaki, 1992), the very mechanism of the superfluid charge transfer is not yet resolved (Bednorz & Müller, 1988). Taking into account the technical and technological treatments for the production of these high-temperature superconductors – they are small-grain crystalline structures (of small dimensions with pronounced boundaries) produced by doping, more precisely sputtering by guest atoms in certain stoichiometric ratio (Šetrajčić et al., 1990; Harshman & Mills, 1992), it is necessary to formulate the corresponding theoretical model. The simplest model for the bounded structures is the ideal crystalline film. Within the framework of this model we shall study only and exclusively the influence of the system boundaries onto spectra and states of phonons and their contribution to the basic physical properties of the system. In order to consider also the influence of the doping, we shall study the spectra and states of phonons in the deformed films and estimate what has the stronger influence to the change of the system behavior: the existence of the boundary surfaces or the disturbance of the internal distribution and type of atoms inside the system.

Fig. 1. Sight of crystalline film-structure model

The starting point of our study will be the standard Hamiltonian of the phonon system (Mahan, 1983; Jones & March, 1985) in the nearest neighbors' approximation:

$$H_{ID} = \frac{1}{2} \sum_{\vec{n}} \frac{p_{\vec{n}}^2}{M_{\vec{n}}} + \frac{1}{4} \sum_{\vec{n}, \vec{\lambda}} C_{\vec{n}, \vec{\lambda}} (\vec{u}_{\vec{n}} - \vec{u}_{\vec{n} + \vec{\lambda}})^2, \quad (1)$$

where: $\vec{p}_{\vec{n}}$ and $\vec{u}_{\vec{n}}$ – are the momentum and displacement of the atom of mass $M_{\vec{n}}$ at the crystal site $\vec{n} = a(n_x \vec{e}_x + n_y \vec{e}_y + 3n_z \vec{e}_z)$, while $C_{\vec{n}, \vec{\lambda}} \equiv C_{\vec{\lambda}, \vec{n}}$ – is Hooke's elastic constants between the atom at the site $\vec{n}$ and its neighboring atoms at the site $\vec{m} = \vec{n} + \vec{\lambda}$, $\vec{\lambda} = a(\vec{e}_x + \vec{e}_y + 3\vec{e}_z)$.

One of the most important aims is to study if the minimal frequencies of the atoms in the film are non-vanishing, i.e. does the phonon energy spectrum possesses the gap. In the structures where such gap exists, there can arise the damping or the elimination of the acoustical phonons (Tošić et al., 1987; Šetrajčić et al., 1990) so that there exist only the phonons of optical type. This would result in the film behavior like a "frozen" structure until certain corresponding activation temperature is reached – the temperature necessary for the creation of the phonons in the film (Djajić et al., 1987), since bellow that temperature, real (acoustical) phonons can not be present¹.

¹For example, electrons would move in such a structure without friction up these temperatures, i.e. they would behave like ideal conductors.

Taking this into account, the presence of the phonon gap might represent the possible explanation of the fact (CRC HCP, 1989) that thin films represent better ordered thermodynamical systems and that they have higher critical superconductive temperature than the corresponding bulk structures. Since the change in the properties of the anisotropic structures, is caused by the change in the dispersion law, it is necessary to study the behavior of relevant physical quantities in order to obtain a more complete picture about these processes.

In Section 2 we first derive the dispersion law for phonons and calculate the possible phonon states in the above mentioned crystalline films, with separate study of the situation in the ideal (non-deformed), and in (symmetrically and asymmetrically) deformed films and the results are compared to the corresponding ones for unbounded structures with no breaking of the symmetry of the internal distribution of the atoms (ideal infinite structures). The Section 3 is devoted to the determination of the strength and the analysis of the diversity of the influences (the presence of boundaries, the type and manner of the doping, etc.) onto the changes of energy spectrum and specific moments in the population of the phonon states resulting from it, compared to the results with the known ones – for non-deformed bulk-structures. The conclusion gives the summary of the most important results and the discussion of the level of impact of boundary and deformation parameters.

2. Dispersion law and states of phonons in films

The Hamiltonian of the phonon subsystem of the model film-structure in the nearest neighbors approximation (Tošić et al., 1995) is given in the form expression 1, where:

$$-\frac{N_\beta}{2} \leq n_\beta \leq \frac{N_\beta}{2}; \quad N_\beta \sim 10^8; \quad \beta \in (x, y); \quad 0 \leq n_z \leq N_z; \quad N_z = \frac{L}{3a} \sim 20,$$

so that it can be written in the expanded form as:

$$\begin{aligned} H_{FS} = & \frac{1}{2} \sum_{\alpha} \sum_{n_x, n_y} \sum_{n_z=0}^{N_z} \frac{(p_{n_x, n_y, n_z}^{\alpha})^2}{M_{n_x, n_y, n_z}} + \frac{1}{4} \sum_{\alpha} \sum_{n_x, n_y} \left\{ C_{-1}^{\alpha} (u_{n_x, n_y, 0}^{\alpha})^2 + \right. \\ & + C_0^{\alpha} \left[(u_{n_x+1, n_y, 0}^{\alpha} - u_{n_x, n_y, 0}^{\alpha})^2 + (u_{n_x-1, n_y, 0}^{\alpha} - u_{n_x, n_y, 0}^{\alpha})^2 + \right. \\ & + (u_{n_x, n_y+1, 0}^{\alpha} - u_{n_x, n_y, 0}^{\alpha})^2 + (u_{n_x, n_y-1, 0}^{\alpha} - u_{n_x, n_y, 0}^{\alpha})^2 + \\ & + (u_{n_x, n_y, 1}^{\alpha} - u_{n_x, n_y, 0}^{\alpha})^2 + (u_{n_x, n_y, 0}^{\alpha})^2 \left. \right] + \\ & + C_1^{\alpha} \left[(u_{n_x, n_y, 1}^{\alpha} - u_{n_x, n_y, 2}^{\alpha})^2 + (u_{n_x, n_y, 1}^{\alpha} - u_{n_x, n_y, 0}^{\alpha})^2 \right] + \\ & + \sum_{n_z=1}^{N_z-1} C_{n_z}^{\alpha} \left[(u_{n_x+1, n_y, n_z}^{\alpha} - u_{n_x, n_y, n_z}^{\alpha})^2 + (u_{n_x-1, n_y, n_z}^{\alpha} - u_{n_x, n_y, n_z}^{\alpha})^2 + \right. \end{aligned}$$

$$\begin{aligned}
& + \left(u_{n_x, n_y+1, n_z}^\alpha - u_{n_x, n_y, n_z}^\alpha \right)^2 + \left(u_{n_x, n_y-1, n_z}^\alpha - u_{n_x, n_y, n_z}^\alpha \right)^2 \Big] + \\
& + \sum_{n_z=2}^{N_z-2} C_{n_z}^\alpha \left[\left(u_{n_x, n_y, n_z+1}^\alpha - u_{n_x, n_y, n_z}^\alpha \right)^2 + \left(u_{n_x, n_y, n_z-1}^\alpha - u_{n_x, n_y, n_z}^\alpha \right)^2 \right] + \\
& + C_{N_z-1}^\alpha \left[\left(u_{n_x, n_y, N_z-1}^\alpha - u_{n_x, n_y, N_z}^\alpha \right)^2 + \left(u_{n_x, n_y, N_z-1}^\alpha - u_{n_x, n_y, N_z-2}^\alpha \right)^2 \right] + \\
& + C_{N_z}^\alpha \left[\left(u_{n_x+1, n_y, N_z}^\alpha - u_{n_x, n_y, N_z}^\alpha \right)^2 + \left(u_{n_x-1, n_y, N_z}^\alpha - u_{n_x, n_y, N_z}^\alpha \right)^2 + \right. \\
& + \left(u_{n_x, n_y+1, N_z}^\alpha - u_{n_x, n_y, N_z}^\alpha \right)^2 + \left(u_{n_x, n_y-1, N_z}^\alpha - u_{n_x, n_y, N_z}^\alpha \right)^2 + \\
& + \left. \left(u_{n_x, n_y, N_z-1}^\alpha - u_{n_x, n_y, N_z}^\alpha \right)^2 + \left(u_{n_x, n_y, N_z}^\alpha \right)^2 \right] + C_{N_z+1}^\alpha \left(u_{n_x, n_y, N_z}^\alpha \right)^2 \Big\}.
\end{aligned} \tag{2}$$

This Hamiltonian describes the film-structure model presented at the Fig.1. It enables further theoretical analysis of the properties, specific effects and changes in the phonon behavior in above mentioned translational non-invariant systems. All changes and specific effects which can occur in the system, will be treated as a strict consequence of the contribution of the mechanical vibrations of the atoms of the crystal lattice under the influence of the presence of boundary surfaces and asymmetric distribution of the atoms along one preferred (z) crystallographic direction in that system.

2.1 Ideal film-structures

The concept of the ideal film means here the model of the crystal bounded by two parallel surfaces which can "breathe" (no rigid walls) along one crystallographic direction (which we choose for the positive direction of z-axis) perpendicular to the boundary surfaces and unbounded in the two other remaining directions. Furthermore, besides boundaries, there are no other defects in the ideal film, so inside the boundaries we encounter single atom tetragonal structure.

The Hamiltonian, expression 2, adapted to the above mentioned model can be separated into two parts: the first one H_S , which includes "surface" terms and the second one H_B , which includes "bulk" terms subject to the conditions (see Fig.1):

$$M_{n_x, n_y, n_z} \equiv M; \quad C_{n_x n_y n_z; n_x \pm 1, n_y n_z}^\alpha = C_{n_x n_y n_z; n_x n_y \pm 1, n_z}^\alpha = C_{n_x n_y n_z; n_x n_y n_z \pm 1}^\alpha \equiv C_\alpha.$$

Since there are no layers for $n_z \leq -1$ and for $n_z \geq N_z + 1$, we must include the following condition, too:

$$u_{n_x, n_y, l}^\alpha = 0; \quad l \leq -1 \wedge l \geq N_z + 1 \quad (\text{i.e. } l \notin [0, N_z]).$$

If we would assign $C_{-1}^\alpha = C_{N_z+1}^\alpha = 0$, then the boundary atoms (for $n_z = 0$ and $n_z = N_z$) would be "frozen", i.e. we would have the effects of rigid walls (Maradudin, 1987). In this way, the expression for the total Hamiltonian of the ideal crystalline film obtains the following form:

$$H_{IF} = H_S + H_B, \tag{3}$$

where:

$$\begin{aligned}
 H_S = & \frac{1}{2M} \sum_{\alpha} \sum_{n_x, n_y} \left[\left(p_{n_x, n_y, 0}^{\alpha} \right)^2 + \left(p_{n_x, n_y, N_z}^{\alpha} \right)^2 \right] + \\
 & + \frac{1}{4} \sum_{\alpha} C_{\alpha} \sum_{n_x, n_y} \left[2 \left(u_{n_x, n_y, 0}^{\alpha} \right)^2 + 2 \left(u_{n_x, n_y, N_z}^{\alpha} \right)^2 + \right. \\
 & + \left(u_{n_x, n_y, N_z-1}^{\alpha} - u_{n_x, n_y, N_z}^{\alpha} \right)^2 + \left(u_{n_x, n_y, 1}^{\alpha} - u_{n_x, n_y, 0}^{\alpha} \right)^2 + \\
 & + \left(u_{n_x, n_y, 0}^{\alpha} - u_{n_x+1, n_y, 0}^{\alpha} \right)^2 + \left(u_{n_x, n_y, 0}^{\alpha} - u_{n_x-1, n_y, 0}^{\alpha} \right)^2 + \\
 & + \left(u_{n_x, n_y, 0}^{\alpha} - u_{n_x, n_y+1, 0}^{\alpha} \right)^2 + \left(u_{n_x, n_y, 0}^{\alpha} - u_{n_x, n_y-1, 0}^{\alpha} \right)^2 + \\
 & + \left(u_{n_x, n_y, N_z}^{\alpha} - u_{n_x+1, n_y, N_z}^{\alpha} \right)^2 + \left(u_{n_x, n_y, N_z}^{\alpha} - u_{n_x-1, n_y, N_z}^{\alpha} \right)^2 + \\
 & \left. + \left(u_{n_x, n_y, N_z}^{\alpha} - u_{n_x, n_y+1, N_z}^{\alpha} \right)^2 + \left(u_{n_x, n_y, N_z}^{\alpha} - u_{n_x, n_y-1, N_z}^{\alpha} \right)^2 \right];
 \end{aligned} \quad (4)$$

$$\begin{aligned}
 H_B = & \frac{1}{2M} \sum_{\alpha} \sum_{n_x, n_y} \left(p_{n_x, n_y, n_z}^{\alpha} \right)^2 + \frac{1}{4} \sum_{\alpha} C_{\alpha} \times \\
 & \times \sum_{n_x, n_y} \left\{ \sum_{n_z=1}^{N_z-1} \left[\left(u_{n_x+1, n_y, n_z}^{\alpha} - u_{n_x, n_y, n_z}^{\alpha} \right)^2 + \left(u_{n_x-1, n_y, n_z}^{\alpha} - u_{n_x, n_y, n_z}^{\alpha} \right)^2 + \right. \right. \\
 & + \left. \left(u_{n_x, n_y+1, n_z}^{\alpha} - u_{n_x, n_y, n_z}^{\alpha} \right)^2 + \left(u_{n_x, n_y-1, n_z}^{\alpha} - u_{n_x, n_y, n_z}^{\alpha} \right)^2 \right] + \\
 & + \sum_{n_z=2}^{N_z-2} \left[\left(u_{n_x, n_y, n_z+1}^{\alpha} - u_{n_x, n_y, n_z}^{\alpha} \right)^2 + \left(u_{n_x, n_y, n_z-1}^{\alpha} - u_{n_x, n_y, n_z}^{\alpha} \right)^2 \right] + \\
 & \left. + \left(u_{n_x, n_y, N_z-1}^{\alpha} - u_{n_x, n_y, N_z-2}^{\alpha} \right)^2 + \left(u_{n_x, n_y, 1}^{\alpha} - u_{n_x, n_y, 2}^{\alpha} \right)^2 \right\}.
 \end{aligned} \quad (5)$$

We have decided to use the approach of Heisenberg's equations of motion (Tošić et al., 1992; Šetrajčić et al., 1992; Šetrajčić & Pantić, 1994) for the determination of possible frequencies (energy spectrum) and the states of phonons. We start from the following system of the equations of motion for the phonon displacements:

– for $n_z = 0$

$$\begin{aligned}
 \ddot{u}_{n_x, n_y, 0}^{\alpha} = & \Omega_{\alpha}^2 \left(u_{n_x+1, n_y, 0}^{\alpha} + u_{n_x-1, n_y, 0}^{\alpha} + u_{n_x, n_y+1, 0}^{\alpha} + \right. \\
 & \left. + u_{n_x, n_y-1, 0}^{\alpha} + u_{n_x, n_y, 1}^{\alpha} - 6u_{n_x, n_y, 0}^{\alpha} \right) = 0;
 \end{aligned} \quad (6)$$

– for $1 \leq n_z \leq N_z - 1$

$$\begin{aligned}
 \ddot{u}_{n_x, n_y, n_z}^{\alpha} = & \Omega_{\alpha}^2 \left(u_{n_x+1, n_y, n_z}^{\alpha} + u_{n_x-1, n_y, n_z}^{\alpha} + u_{n_x, n_y+1, n_z}^{\alpha} + \right. \\
 & \left. + u_{n_x, n_y-1, n_z}^{\alpha} + u_{n_x, n_y, n_z+1}^{\alpha} + u_{n_x, n_y, n_z-1}^{\alpha} - 6u_{n_x, n_y, n_z}^{\alpha} \right) = 0;
 \end{aligned} \quad (7)$$

– for $n_z = N_z$

$$\ddot{u}_{n_x, n_y, N_z}^\alpha - \Omega_\alpha^2 \left(u_{n_x+1, n_y, N_z}^\alpha + u_{n_x-1, n_y, N_z}^\alpha + u_{n_x, n_y+1, N_z}^\alpha + u_{n_x, n_y-1, N_z}^\alpha + u_{n_x, n_y, N_z-1}^\alpha - 6u_{n_x, n_y, N_z}^\alpha \right) = 0. \quad (8)$$

where $\Omega_\alpha = \sqrt{\mathcal{C}_\alpha/M}$. The solution of this system of N_z+1 homogeneous differential-difference equations for phonon displacements can be looked for in the form of the product of an unknown function (along z -axis) and harmonic function of the position (within XY -plane) known from the bulk solutions, i.e.

$$u_{n_x, n_y, n_z}^\alpha(t) = \sum_{k_x, k_y, k_z=-\infty}^{+\infty} \int d\omega e^{ia(k_x n_x + k_y n_y) - it\omega} \Phi_{n_z}^\alpha; \quad \Phi_{n_z}^\alpha \equiv \Phi_{n_z}^\alpha(k_z, \omega). \quad (9)$$

Substituting this expression into the equations 6–8 we obtain:

$$\begin{aligned} R\Phi_0^\alpha + \Phi_1^\alpha &= 0 \\ \Phi_0^\alpha + R\Phi_1^\alpha + \Phi_2^\alpha &= 0 \\ \cdot &\cdot \cdot \\ \Phi_{n_z-1}^\alpha + R\Phi_{n_z}^\alpha + \Phi_{n_z+1}^\alpha &= 0 \\ \cdot &\cdot \cdot \\ \Phi_{N_z-2}^\alpha + R\Phi_{N_z-1}^\alpha + \Phi_{N_z}^\alpha &= 0 \\ \Phi_{N_z-1}^\alpha + R\Phi_{N_z}^\alpha &= 0 \end{aligned} \quad (10)$$

where:

$$R \equiv W_\alpha^2 - 4\mathcal{F}_{k_x k_y} - 2; \quad W_\alpha \equiv \frac{\omega}{\Omega_\alpha}; \quad \mathcal{F}_{k_x k_y} \equiv \sin^2 \frac{ak_x}{2} + \sin^2 \frac{ak_y}{2}. \quad (11)$$

In this way the system of $N_z + 1$ differential-difference equations 6–8 turns into a system of $N_z + 1$ homogeneous algebraic difference equations 10. In order that this system possesses nontrivial solutions, its determinant:

$$\mathcal{D}_{N_z+1}(R) = \begin{vmatrix} R & 1 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 \\ 1 & R & 1 & 0 & \cdots & 0 & 0 & 0 & 0 \\ 0 & 1 & R & 1 & \cdots & 0 & 0 & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & \ddots & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & 0 & \cdots & 1 & R & 1 & 0 \\ 0 & 0 & 0 & 0 & \cdots & 0 & 1 & R & 1 \\ 0 & 0 & 0 & 0 & \cdots & 0 & 0 & 1 & R \end{vmatrix} \quad (12)$$

must vanish. The roots (poles) of this determinant represent one of the forms of Chebyshev's polynomials of the second order (Cottam & Tilley, 1989) and can be written in the form:

$$\mathcal{D}_{N_z+1}(R) \equiv \mathcal{D}_{N_z^I-1}(R) = \frac{\sin(N_z^I \zeta)}{\sin \zeta}; \quad N_z^I = N_z + 2; \quad \zeta \neq 0,$$

where: $R = 2\cos \zeta$. Above mentioned condition ($\mathcal{D}_{N_z+1}(R_\nu) = 0$) is satisfied for:

$$\zeta_\nu = \frac{\pi \nu}{N_z^I}; \quad \nu = 1, 2, 3, \dots, N_z^I - 1, \quad (13)$$

whose substitution into expressions 11 leads to the expression for demanded (possible) unknown phonon frequencies:

$${}^I\omega_{k_x k_y}^\alpha(\mu) = 2\Omega_\alpha \sqrt{\mathcal{G}_\mu^I + \mathcal{F}_{k_x k_y}}, \quad (14)$$

where:

$$\mathcal{G}_\mu^I \equiv \sin^2 \frac{ak_z(\mu)}{2}; \quad k_z(\mu) = \frac{\pi}{a} \frac{\mu}{N_z^I}; \quad \mu \equiv N_z^I - \nu = 1, 2, 3, \dots, N_z^I - 1. \quad (15)$$

One must notice that contrary to k_x and k_y which range from 0 to π/a , one has:

$$\begin{aligned} k_z^{\min} &\equiv k_z(1) = \frac{\pi}{a} \frac{1}{N_z^I} > 0; \\ k_z^{\max} &\equiv k_z(N_z^I - 1) = \frac{\pi}{a} \frac{N_z^I - 1}{N_z^I} < \frac{\pi}{a}, \end{aligned} \quad (16)$$

because $N_z^I \ll (N_x, N_y)$.

If one divides the system of equations 10 by $\Phi_0^\alpha \equiv \Phi_0^\alpha(k_z)$ and rejects the last equation, this system is obtained in the new form:

$$\begin{aligned} R_\nu + \varrho_1 &= 0, & \text{for } n_z &= 0 \\ 1 + R_\nu \varrho_1 + \varrho_2 &= 0, & \text{for } n_z &= 1 \\ \varrho_{n_z-1} + R_\nu \varrho_{n_z} + \varrho_{n_z+1} &= 0, & \text{for } 2 \leq n_z \leq N_z - 1 \end{aligned} \quad (17)$$

where $R_\nu \equiv 2 \cos \zeta_\nu$ and:

$$\varrho_{n_z} \equiv \varrho_{n_z}^\alpha = (\Phi_0^\alpha)^{-1} \Phi_{n_z}^\alpha \implies \Phi_{n_z}^\alpha = \Phi_0^\alpha \nearrow_{n_z}^\alpha. \quad (18)$$

The last of the equations 18 is satisfied for:

$$\varrho_{n_z} = (-1)^{n_z} \{P \sin(n_z \zeta_\nu) + Q \sin[(n_z - 1) \zeta_\nu]\}, \quad (19)$$

and using this and expression 13 it follows:

$$\varrho_1 = -P \sin(\zeta_\nu); \quad \varrho_2 = P \sin(2\zeta_\nu) + Q \sin(\zeta_\nu).$$

Substituting these expressions into the first and second equation in the system of difference equations 18 we arrive to the unknown coefficients $P \equiv P_\nu = R_\nu \sin^{-1} \zeta_\nu$ and $Q \equiv Q_\nu = -\sin^{-1} \zeta_\nu$, while returning them into expressions 19 and 18, it follows:

$$\Phi_{n_z}^\alpha(k_z) = (-1)^{n_z} \frac{\sin[(n_z + 1) \zeta_\nu]}{\sin \zeta_\nu} \Phi_0^\alpha. \quad (20)$$

According to above calculations – combining 9, 20 and standard normalization (Callaway, 1974), one can easily obtain the final expression for phonon displacements in the form:

$$\begin{aligned} {}^I u_{n_x, n_y, n_z}^\alpha(t) &= \sum_{k_x k_y} \sum_{\mu=1}^{N_z^I-1} {}^I \mathcal{N}_{n_z}^\alpha(k_x k_y, \mu) \times \\ &\times e^{ia(k_x n_x + k_y n_y) - it \omega_{k_x k_y}^\alpha(\mu)} \sin[(n_z + 1) ak_z(\mu)]; \\ {}^I \mathcal{N}_{n_z}^\alpha(k_x k_y, \mu) &= (-1)^{n_z} \sqrt{\frac{\hbar}{MN_x N_y N_z^I \omega_{k_x k_y}^\alpha(\mu)}}. \end{aligned} \quad (21)$$

Comparing the result obtained here with the corresponding one for ideal infinite structures, one can conclude that mechanical vibrations in the ideal unbounded structure are plane waves in all spatial directions, while in the thin film they represent the superposition of the standing waves in z -direction and plane waves in XY -planes. It is also evident that the displacement amplitude in the films is $\sim 10^4 \sqrt{2/N_z^I}$ times larger² than the amplitude in corresponding unbounded structures.

Using expression 14 one can determine the dispersion law for phonons in thin undeformed ideal film³:

$${}^I E_{k_x k_y}^\alpha(\mu) \equiv \hbar^I \omega_{k_x k_y}^\alpha(\mu) = E_I^\alpha \sqrt{\mathcal{G}_\mu^I + \mathcal{F}_{k_x k_y}}, \quad (22)$$

where $E_I^\alpha = 2\hbar \Omega_\alpha$ and which is valid together with expressions 11 and 15.

We represent graphically this energy spectrum at the Fig.2 vs XY -plane vector $k^2 = k_x^2 + k_y^2$:

$$\mathcal{E}_\mu^z \equiv \left(E_{k_x k_y}^z(\mu) / E_I^z \right)^2 = {}^I \mathcal{E}_{k_z(\mu)}^z \left(\mathcal{F}_{k_x k_y} \right).$$

Fig.2 represent energy spectrum of phonons in the ideal (ultrathin $N_z = 4$) crystalline films vs. two-dimensional (XY planar) wave vector. Within the band of bulk energies with continual spectrum (bulk limits are denoted by solid dashed lines) one can notice five allowed discrete phonon energies in the film studied (thin solid lines). One can notice the narrowing of the energy band and the existence of the energy gap.

Fig. 2. Phonon spectra in the ideal ultrathin crystalline films

²For very thin films $N_z^I \sim 10$, so the factor of the amplitude increase can achieve even 2000.

³Most common treatment is that using classical procedure, for example, second quantization method (Callaway, 1974), on the basis of expressions 3-??, 14 and 20, the Hamiltonian H_{IF} is diagonalized, and then the energy spectrum in the form 22 is readily obtained.

One can clearly see from the plot explicate discreteness of the allowed energy levels of phonons in the ideal film with respect to the continuum of these values for the corresponding bulk-structures. All three acoustic frequencies in bulk-structures vanish when three-dimensional (spatial) vector $k = |\vec{k}|$ vanishes, while the minimal frequencies of phonons in the thin ideal film-structure are:

$$\Delta_i \equiv (\omega_\alpha^l)_{\min} \equiv \omega_\alpha^l(k_x = k_y = 0, k_z = k_z^{\min}) \approx \Omega_\alpha \frac{\pi}{N_z^l} > 0. \quad (23)$$

On the other hand, maximal values of the frequencies of acoustic branches in the ideal infinite crystal tend to the value $(\omega_\alpha^b)_{\max} = 2\Omega_\alpha \sqrt{3}$ when $k_\alpha \rightarrow \pi/a$, $\alpha = x, y, z$, while in the studied ideal film they are:

$$(\omega_\alpha^l)_{\max} \equiv \omega_\alpha^l(k_x = k_y = \frac{\pi}{a}, k_z = k_z^{\max}) \approx 2\Omega_\alpha \sqrt{3} \left[1 - \frac{\pi^2/12}{(N_z^l)^2} \right] < (\omega_\alpha^b)_{\max}. \quad (24)$$

It can be also seen from the same figure that the width of the energy band in the film is narrower. From expressions 23 and 24 we can determine the total narrowing of the band of allowed energies of the phonons in the film-structures with respect to the bulk band:

$$\mathcal{W}_\alpha^l \equiv \hbar \{ (\omega_\alpha^b)_{\max} - [(\omega_\alpha^l)_{\max} - (\omega_\alpha^l)_{\min}] \} \approx \hbar \Omega_\alpha \frac{\pi (N_z^l + 1)}{(N_z^l)^2} > 0. \quad (25)$$

The functional behavior and the physical explanation, as well as the effects that might be caused by the existence of the frequency threshold 23 and the band narrowing 25 will be exposed in the next Section after the analysis of the phonon behavior in the deformed structures.

2.2 Deformed film-structures

During sputtering perpendicular to the boundary surfaces (Cava et al., 1987; Chu et al., 1987; Politis et al., 1987; Segre et al., 1987; Dietrich et al., 1987; Kuwahara, 1992; Notzel et al., 1992), the atoms that are introduced locate themselves along z -axis since this is energetically most convenient: $a_z = 3a$ and $a_x = a_y = a$. For that reason the effective mass of the atom (as well as the elongation constant), at some site in the crystalline lattice, will depend on its relative position (with respect to the origin of z -axis), i.e. on the lattice index in the z -direction, but not in x and y directions:

$$M_{\vec{n}} \equiv M_{n_x, n_y, n_z} = M_{n_z}.$$

Using the Heisenberg equations of motion for u and p with the Hamiltonian (given by expression 2), taking into account above mentioned conditions, one arrives to the system of $N_z + 1$ homogeneous differential-difference equations for the phonon displacements:

– for $n_z = 0$

$$\begin{aligned} \ddot{u}_{n_x, n_y, 0}^\alpha &= \frac{C_0^\alpha}{M_0} \left(u_{n_x+1, n_y, 0}^\alpha + u_{n_x-1, n_y, 0}^\alpha + u_{n_x, n_y+1, 0}^\alpha \right. \\ &+ \left. u_{n_x, n_y-1, 0}^\alpha + u_{n_x, n_y, 1}^\alpha - 5u_{n_x, n_y, 0}^\alpha \right) + \\ &+ \frac{C_1^\alpha}{2M_0} \left(u_{n_x, n_y, 1}^\alpha - u_{n_x, n_y, 0}^\alpha \right) - \frac{C_{-1}^\alpha}{2M_0} u_{n_x, n_y, 0}^\alpha, \end{aligned} \quad (26)$$

– for $1 \leq n_z \leq N_z - 1$

$$\begin{aligned} \ddot{u}_{n_x, n_y, n_z}^\alpha &= \frac{\mathcal{C}_{n_z}^\alpha}{2M_{n_z}} \left[2 \left(u_{n_x+1, n_y, n_z}^\alpha + u_{n_x-1, n_y, n_z}^\alpha + u_{n_x, n_y+1, n_z}^\alpha + u_{n_x, n_y-1, n_z}^\alpha \right) + \right. \\ &+ u_{n_x, n_y, n_z+1}^\alpha + u_{n_x, n_y, n_z-1}^\alpha - 10u_{n_x, n_y, n_z}^\alpha \left. \right] + \\ &+ \frac{\mathcal{C}_{n_z+1}^\alpha}{2M_{n_z}} \left(u_{n_x, n_y, n_z+1}^\alpha - u_{n_x, n_y, n_z}^\alpha \right) + \frac{\mathcal{C}_{n_z-1}^\alpha}{2M_{n_z}} \left(u_{n_x, n_y, n_z-1}^\alpha - u_{n_x, n_y, n_z}^\alpha \right), \end{aligned} \quad (27)$$

– for $n_z = N_z$

$$\begin{aligned} \ddot{u}_{n_x, n_y, N_z}^\alpha &= \frac{\mathcal{C}_{N_z}^\alpha}{M_{N_z}} \left(u_{n_x+1, n_y, N_z}^\alpha + u_{n_x-1, n_y, N_z}^\alpha + u_{n_x, n_y+1, N_z}^\alpha + \right. \\ &+ u_{n_x, n_y-1, N_z}^\alpha + u_{n_x, n_y, N_z-1}^\alpha - 5u_{n_x, n_y, N_z}^\alpha \left. \right) + \\ &+ \frac{\mathcal{C}_{N_z-1}^\alpha}{2M_{N_z}} \left(u_{n_x, n_y, N_z-1}^\alpha - u_{n_x, n_y, N_z}^\alpha \right) - \frac{\mathcal{C}_{N_z+1}^\alpha}{2M_{N_z}} u_{n_x, n_y, N_z}^\alpha. \end{aligned} \quad (28)$$

The solution of this system of equations can be looked for in the form of the product of an unknown function in z -direction and plane harmonic waves in XY -planes:

$${}^D u_{n_x, n_y, n_z}^\alpha(t) = \sum_{k_x, k_y, k_z=-\infty}^{+\infty} \int d\omega e^{ia(k_x n_x + k_y n_y) - it\omega} \Psi_{n_z}^\alpha; \quad \Psi_{n_z}^\alpha \equiv \Psi_{n_z}^\alpha(k_z, \omega). \quad (29)$$

Calculating corresponding derivatives and introducing them into equation 27 we obtain the difference equation for the unknown functions $\Psi_{n_z}^\alpha$:

$$\begin{aligned} 2 \left(M_{n_z} \omega^2 - 4\mathcal{C}_{n_z}^\alpha \mathcal{F}_{k_x k_y} \right) \Psi_{n_z}^\alpha + \mathcal{C}_{n_z}^\alpha \left(\Psi_{n_z+1}^\alpha + \Psi_{n_z-1}^\alpha - 2\Psi_{n_z}^\alpha \right) + \\ + \mathcal{C}_{n_z+1}^\alpha \left(\Psi_{n_z+1}^\alpha - \Psi_{n_z}^\alpha \right) + \mathcal{C}_{n_z-1}^\alpha \left(\Psi_{n_z-1}^\alpha - \Psi_{n_z}^\alpha \right) = 0 \end{aligned} \quad (30)$$

valid for $n_z = 1, 2, 3, \dots, N_z - 1$. For $n_z = 0$, using the same procedure, one obtains from equation 26 the first (upper) boundary equation:

$$\begin{aligned} 2 \left(M_0 \omega^2 - 4\mathcal{C}_0^\alpha \mathcal{F}_{k_x k_y} \right) \Psi_0^\alpha + \mathcal{C}_0^\alpha \left(\Psi_1^\alpha - 2\Psi_0^\alpha \right) + \\ \mathcal{C}_1^\alpha \left(\Psi_1^\alpha - \Psi_0^\alpha \right) - \mathcal{C}_{-1}^\alpha \Psi_0^\alpha = 0 \end{aligned} \quad (31)$$

and for $n_z = N_z$, using equation 28, the second (lower) boundary equation:

$$\begin{aligned} 2 \left(M_{N_z} \omega^2 - 4\mathcal{C}_{N_z}^\alpha \mathcal{F}_{k_x k_y} \right) \Psi_{N_z}^\alpha + \mathcal{C}_{N_z}^\alpha \left(\Psi_{N_z-1}^\alpha - 2\Psi_{N_z}^\alpha \right) + \\ + \mathcal{C}_{N_z-1}^\alpha \left(\Psi_{N_z-1}^\alpha - \Psi_{N_z}^\alpha \right) - \mathcal{C}_{N_z+1}^\alpha \Psi_{N_z}^\alpha = 0. \end{aligned} \quad (32)$$

The procedure for the determination of the allowed phonon states using the above equations is extremely complicated⁴. For that reason we are going to perform the transition to continuum

⁴In fact, it is not known or elaborated in the literature for this, completely general case.

(continuum approximation), i.e. transition from the discrete to continual variables, and expand the corresponding quantities into the Taylor's series:

$$n_z \longrightarrow z; \quad \Psi_{n_z}^\alpha \longrightarrow \Psi_\alpha(z); \quad M_{n_z} \longrightarrow M(z); \quad a_z \longrightarrow a(z); \quad C_{n_z}^\alpha \longrightarrow C_\alpha(z).$$

Besides that, as a consequence of sputtering, i.e. clustering of foreign atoms around the atoms of the basic matrix (Tošić et al., 1987; Šetrajčić et al., 1990; Tošić et al., 1992; Ristovski et al., 1989), the mass of the basic matrix must be substituted by the corresponding reduced mass:

$$M^{-1}(z) = \mathcal{M}_m^{-1} + n(z) \mathcal{M}_d^{-1}, \quad (33)$$

where: $\mathcal{M}_m$ – is the mass of the basic matrix, $\mathcal{M}_d$ – the mass of doping atoms and $n(z)$ – their number at the site z (measured from the lower boundary surface of the crystalline film).

After these transformations and introduction into the difference equation 30, it becomes a second order differential equation:

$$\frac{d^2 \Psi_\alpha(z)}{dz^2} + C_\alpha^{-1}(z) \frac{dC_\alpha(z)}{dz} \frac{d\Psi_\alpha(z)}{dz} - \left[\frac{4\mathcal{F}_{k_x k_y}}{a^2(z)} - \frac{M(z)\omega^2}{C_\alpha(z)a^2(z)} \right] \Psi_\alpha(z) = 0. \quad (34)$$

Further solving of this differential equation demands the specification of the functional dependence of the quantities $M(z)$, $C_\alpha(z)$ and $a(z)$, and they depend not only on the procedure of the sputtering of the basic matrix – ideal crystalline film-structure, but also on the number, type and distribution of the sputtered atoms.

2.2.1 Asymmetrical deformation

Taking into account that the production of oxide superconductive ceramics includes the sputtering with foreign atoms (Cava et al., 1987; Chu et al., 1987; Politis et al., 1987; Segre et al., 1987; Dietrich et al., 1987; Kuwahara, 1992; Notzel et al., 1992; Johnson, 1995), we shall assume that it is performed perpendicularly to one (upper) of the boundary surfaces of the model film-structure. For this reason, doping atoms cluster along z -direction, from this upper surface towards lower boundary surface and let us assume the (approximate) parabolic distribution of such "weighted" atoms, i.e. their reduced masses:

$$M(z) \longrightarrow M_A(z) = A_M^A + B_M^A (z - L)^2.$$

Using boundary conditions:

$$M_A(0) = \mathcal{M}_m; \quad M_A(L) = \frac{\mathcal{M}_m \mathcal{M}_d}{\mathcal{M}_d - n \mathcal{M}_m},$$

we determine the unknown coefficients A_M^A and B_M^A , so that we obtain:

$$M_A(z) = \frac{\mathcal{M}_m}{\mathcal{O}_M^A} \left[1 - (1 - \mathcal{O}_M^A) \left(1 - \frac{z}{L} \right)^2 \right]; \quad \mathcal{O}_M^A = 1 - n \frac{\mathcal{M}_m}{\mathcal{M}_d}. \quad (35)$$

The sputtering of the basic matrix causes also (parabolic) change of the lattice constant:

$$a(z) \longrightarrow a_A(z) = A_a^A + B_a^A (z - L)^2,$$

with boundary conditions:

$$a_A(0) = a_z; \quad a_A(L) = \frac{a_z}{n},$$

from which it follows:

$$a_A(z) = a_z \left[1 - \frac{n-1}{n} \frac{z}{L} \left(2 - \frac{z}{L} \right) \right]. \quad (36)$$

Since Hooke's constants may be expressed as $C_\alpha(z) = \text{const}(\alpha) a^{-\gamma}(z)$, using expression 36 one can write:

$$C_\alpha^A(z) = C_\alpha \left[1 + \gamma \frac{n-1}{n} \frac{z}{L} \left(2 - \frac{z}{L} \right) \right]. \quad (37)$$

Furthermore, instead of $a_A(z)$ and $C_\alpha^A(z)$ we shall use their values averaged over the total film width (L):

$$\begin{aligned} \overline{a_z^A} \equiv \overline{a_A(z)} &= \frac{1}{L} \int_0^L a_A(z) dz = f_n^A a_z; \quad f_n^A \equiv \frac{n+2}{3n}; \\ \overline{C_\alpha^A} \equiv \overline{C_\alpha^A(z)} &= \frac{1}{L} \int_0^L C_\alpha^A(z) dz = g_n^A C_\alpha; \quad g_n^A \equiv 1 + 2\gamma \frac{n-1}{3n}. \end{aligned} \quad (38)$$

To simplify the solution of the last differential equation, besides 35 and 38, it is convenient to change variable $z \rightarrow \eta$: $1 - z/L = \Lambda \eta$, so that it becomes:

$$\frac{d^2 \Psi_\alpha^A}{d\eta^2} + \mathcal{K}_\alpha^A \left\{ \left[1 - \left(\Lambda_\alpha^A \right)^2 \left(1 - \mathcal{O}_M^A \right) \eta^2 \right] \omega^2 - 4 \frac{\mathcal{O}_M^A}{\mathcal{M}_m} \overline{C_\alpha^A} \mathcal{F}_{k_x k_y} \right\} \Psi_\alpha^A = 0. \quad (39)$$

Introducing new notations:

$$\mathcal{K}_\alpha^A = \frac{L^2 \left(\Lambda_\alpha^A \right)^2 \mathcal{M}_m}{\overline{a_z^A}^2 \overline{C_\alpha^A} \mathcal{O}_M^A}; \quad \Lambda_\alpha^A = \sqrt{\frac{\overline{a_z^A} \Omega_\alpha^A}{L \omega}}; \quad \Omega_\alpha^A = \Omega_\alpha \tau_\alpha^A(n); \quad \tau_\alpha^A(n) = \sqrt{\frac{g_n^A \mathcal{O}_M^A}{1 - \mathcal{O}_M^A}} \quad (40)$$

and

$$\begin{aligned} {}^A \mathcal{Q}_{k_x k_y}^\alpha(\omega) &= \frac{L}{\overline{a_z^A}} \left[\frac{\omega}{\Omega_\alpha^A} \left(1 - \mathcal{O}_M^A \right)^{-1} - 4 \frac{\Omega_\alpha^A}{\omega} \mathcal{F}_{k_x k_y} \right] \equiv \\ &\equiv 2s + 1; \quad s = 0, 1, 2, \dots, \end{aligned} \quad (41)$$

the above differential equation can be turned into Hermit-Weber one (Callavay, 1974):

$$\frac{d^2 \Psi_\alpha^A}{d\eta^2} + \left[{}^A \mathcal{Q}_{k_x k_y}^\alpha(\omega) - \eta^2 \right] \Psi_\alpha^A = 0, \quad (42)$$

with the solution:

$$\Psi_\alpha^A \equiv \Psi_\alpha^A(\eta) \longrightarrow {}^A \Psi_s^\alpha(\eta) = \mathcal{N}_s^\alpha \mathcal{H}_s(\eta) e^{-\eta^2/2}, \quad (43)$$

where $\mathcal{H}_s(\eta)$ – is Hermitian's polynomial of the order s . In order that atomic displacements remain finite, it is necessary that ${}^A \mathcal{Q}_{k_x k_y}^\alpha(\omega)$ satisfies the identity condition (expressed by 41) which, in fact, insures the physics-chemical (crystallographic) stability of the model

film-structure. This identity allows the determination of the allowed vibrational frequencies of the system:

$${}^A\omega_{k_x k_y}^\alpha(s) = \frac{\Omega_\alpha^A}{2} \left[\mathcal{G}_s^A + \sqrt{(\mathcal{G}_s^A)^2 + \mathcal{F}_{k_x k_y}} \right], \quad (44)$$

where $\mathcal{F}_{k_x k_y}$ is defined in 11, and

$$\mathcal{G}_s^A \equiv \frac{2s+1}{\overline{N_z^A}}; \quad \overline{N_z^A} = \frac{L}{a_z^A} (1 - \mathcal{O}_M^A)^{-1}.$$

It is clear from this expression that none of the possible frequencies ${}^A\omega_{k_x k_y}^\alpha(s)$ vanishes, neither for $s = 0$, nor for (dimensionless) twodimensional vector $q = a^{-1} \sqrt{k_x^2 + k_y^2} \rightarrow 0$.

Since we have solved Hermite-Weber's equation 42 without taking into account the boundary conditions, it must be supplied by two boundary equations 31 and 32, for $z = 0$ and $z = L$, i.e. its solution 43 must satisfy these supplementary conditions. The substitution of 43 into 31 for $z = 0 \Rightarrow \eta = (\Lambda_\alpha^A)^{-1}$ and $q = 0$ gives:

$$\left\{ 2 - \mathcal{O}_M^A \left[\frac{{}^A\omega_0^\alpha(s)}{\Omega_\alpha^A} \right]^2 \right\} \mathcal{H}_s \left(\frac{1}{\Lambda_\alpha^A} \right) = \exp \left\{ \left(1 - \frac{\overline{a_z^A}}{2L} \right) \frac{{}^A\omega_0^\alpha(s)}{\Omega_\alpha^A} \right\} \mathcal{H}_s \left(\frac{L - \overline{a_z^A}}{\Lambda_\alpha^A L} \right). \quad (45)$$

By analogous procedure, solution expressed by 43 with boundary equation 32, for $z = L \Rightarrow \eta = 0$ and $q = 0$, gives:

$$\left\{ 2 + \left(1 - \mathcal{O}_M^A \right) \left[\frac{{}^A\omega_0^\alpha(s)}{\Omega_\alpha^A} \right]^2 \right\} \mathcal{H}_s(0) = \exp \left\{ \frac{\overline{a_z^A}}{2L} \frac{{}^A\omega_0^\alpha(s)}{\Omega_\alpha^A} \right\} \mathcal{H}_s \left(\frac{\overline{a_z^A}}{\Lambda_\alpha^A L} \right). \quad (46)$$

Using the relation $\mathcal{H}_s(x+c) = \mathcal{H}_s(x) + (2c)^s$ one can write:

$$\mathcal{H}_s \left(\frac{L - \overline{a_z^A}}{\Lambda_\alpha^A L} \right) = (-1)^s \mathcal{H}_s \left(\frac{\overline{a_z^A}}{\Lambda_\alpha^A L} \right) + \left(\frac{2}{\Lambda_\alpha^A} \right)^s,$$

after which the equations 45 and 46 turn into a single one:

$$\begin{aligned} & \left\{ 2 - \mathcal{O}_M^A \left[\frac{{}^A\omega_0^\alpha(s)}{\Omega_\alpha^A} \right]^2 \right\} \left[\exp \left\{ \frac{{}^A\omega_0^\alpha(s)}{\Omega_\alpha^A} \right\} \mathcal{H}_s \left(\frac{1}{\Lambda_\alpha^A} \right) + (-1)^{s+1} \mathcal{H}_s(0) \right] = \\ & = \left\{ (-1)^s \left[\frac{{}^A\omega_0^\alpha(s)}{\Omega_\alpha^A} \right]^2 \mathcal{H}_s(0) + (\Lambda_\alpha^A)^{-s} \exp \left\{ \frac{\overline{a_z^A}}{2L} \frac{{}^A\omega_0^\alpha(s)}{\Omega_\alpha^A} \right\} \right\}. \end{aligned} \quad (47)$$

It is obvious from here that the parameters $\mathcal{M}_m$, $\mathcal{M}_d$, n , L and quantum number s are not mutually independent. In fact, for given values, from expression 44 they define the conditions for the existence of phonon states with the energies $\hbar {}^A\omega_{k_x k_y}^\alpha(s)$. From this equation, one can determine for which value of quantum number s the function ${}^A\omega_0^\alpha(s)$ attains minimal value. A graphical-numerical solving method gives $s_{min} = 2$. Numerical calculations and estimates were performed for the compound $\text{La}(\text{Ba}_{2-\varepsilon}\text{La}_\varepsilon)\text{Cu}_3\text{O}_{7+\delta}$, where it was taken $n = 3$, $\gamma = 12$, $\mathcal{O}_M^A = 1/0,83$, $\varepsilon = 0,125$, $\delta = 0,11$, $v_z \approx 3$, $a_z \approx 1,2$; all based on data from

(Šetrajčić et al., 1990; Cava et al., 1987; Chu et al., 1987; Politis et al., 1987; Segre et al., 1987; Dietrich et al., 1987; Kuwahara, 1992; Notzel et al., 1992; Johnson, 1995) and (Ristovski et al., 1989; Djajić et al., 1991; Šetrajčić et al., 1994). Due to the discreteness of the solutions (2.43) and the initial model, their total number must be equal to $N_z + 1$. It follows from here that the quantum number s is bounded also from above: $s_{max} = N_z + 2$, i.e. $s \in [2, N_z + 2]$. Substituting of the solution expressed by 43 into difference equation 30, and normalizing it, the expression for the phonon displacements becomes:

$$\begin{aligned}
 {}^A u_{n_x, n_y}^\alpha(z, t) &= \sum_{k_x k_y} \sum_{s=2}^{N_z-2} {}^A \mathcal{N}_{n_z}^\alpha(k_x k_y, s) \mathcal{H}_s(z) e^{-2(1-z/L)^2/(2\Lambda_\alpha^A)^2} \times \\
 &\times e^{i[a(k_x n_x + k_y n_y) - t {}^A \omega_{k_x k_y}^\alpha(s)]}; \\
 {}^A \mathcal{N}_{n_z}^\alpha(k_x k_y, s) &\equiv (-1)^{n_z} \sqrt{\frac{\hbar}{M_z N_x N_y N_z^A {}^A \omega_{k_x k_y}^\alpha(s)}}; \quad N_z^A = N_z + 4.
 \end{aligned} \tag{48}$$

The analysis of this expression shows that, contrary to phonon displacements in ideal unbounded structures (plane waves in all three spatial directions), and similar to the ideal films (superposition of standing wave and plane waves), here they represent the superposition of the plane waves in XY -planes and collective vibrational harmonic motion along z -direction. The amplitude of the phonon displacements is here $\sim 10^4 \sqrt{2/N_z^A}$ times larger than the corresponding one in the bulk structures, and approximately equal (in fact slightly smaller) than in the ideal films⁵.

According to all above mentioned, it follows from expression 44 that the dispersion law for phonons in the asymmetrically deformed crystalline films has the following form:

$${}^A E_{k_x k_y}^\alpha(s) \equiv \hbar {}^A \omega_{k_x k_y}^\alpha(s) = E_A^\alpha \left[\mathcal{G}_s^A + \sqrt{(\mathcal{G}_s^A)^2 + \mathcal{F}_{k_x k_y}} \right], \tag{49}$$

where $E_A^\alpha \equiv \hbar \Omega_\alpha^A/2$, and $s = 2, 3, 4, \dots, N_z^A - 2$. Graphical presentation of this dispersion law in the form ${}^A \mathcal{E}_s^z \equiv [{}^A E_{k_x k_y}^z(s)/E_A^z]^2 = {}^A \mathcal{E}_s^z(\mathcal{F}_{k_x k_y})$ is given in the Fig.3.

Fig.3 represent the energy spectrum of phonons in the asymmetrically deformed (ultrathin $N_z = 4$) crystalline films vs. two-dimensional (XY planar) wave vector. Besides the narrowing of the energy band with five discrete levels and the presence of the energy gap (with respect to the bulk band denoted by solid dashed lines) a shift of this band outside bulk limits can be noticed, corresponding to the appearance of the localized phonon modes.

One can see from this plot that non of the allowed energies, i.e. possible frequencies ${}^A \omega_q^\alpha(s)$ does not vanish for $q \rightarrow 0$, implying that the presence of boundaries together with the deformation of the atom distribution of the parabolic type (expressed by 35–38) leads to the appearance of the energy gap in the phonon spectrum, i.e. to the possible creation of the phonons of only the optical type. Contrary to the dispersion law for phonons in unbounded and nondeformed structures, where minimal and maximal frequency of the acoustic phonon

⁵See the comment below the expression 22.

Fig. 3. Phonon spectra in the asymmetrically deformed ultrathin crystalline films

branches tend to 0, and $2\Omega_\alpha\sqrt{3}$, respectively, they have the following values here⁶:

$$(\omega_\alpha^A)_{min} \equiv {}^A\omega_0^\alpha(2) = \omega_\alpha^A(k_x = k_y = 0; s = 2) = \frac{5}{N_z^A}\Omega_\alpha^A > (\omega_\alpha^I)_{min}; \tag{50a}$$

$$(\omega_\alpha^A)_{max} \equiv \omega_\alpha^A\left(k_x = k_y = \frac{\pi}{a}; s = N_z^A - 2\right) \approx \frac{2(2N_z^A - 3)}{N_z^A}\Omega_\alpha^A < (\omega_\alpha^I)_{max}. \tag{50b}$$

It is evident from the same figure that the width of the allowed phonon energies band in the film is smaller⁷. Using expressions 49 and 50 one can determine the total narrowing of the energy band of phonons in the asymmetrically deformed film-structure with respect to the phonon bulk-band⁸:

$$\begin{aligned} \mathcal{W}_\alpha^A &\equiv \hbar \{ (\omega_\alpha^B)_{max} - [(\omega_\alpha^A)_{max} - (\omega_\alpha^A)_{min}] \} \approx \\ &\approx \hbar \Omega_\alpha \left[2\sqrt{3} - \frac{4N_z^A - 11}{N_z^A} \tau_\alpha^A(n) \right] > \mathcal{W}_\alpha^I. \end{aligned} \tag{51}$$

More detailed analysis, functional behavior and physical interpretation as well as the possible effects caused by the existence of the frequency threshold in formula 49 and narrowing of the frequency range in expression 51 will be presented in the next Section.

⁶Compare with the expressions 23 and 24.
⁷It is also evident that this band is shifted so it leaves the bulk limits. This result which might mean the appearance of the localized phonon modes is not discussed here in particular, since it occurs for the higher values of the planar two-dimensional (XY) wave vector, for which the validity of the continual – long wavelength approximation might be questioned.
⁸See expression 25.

2.2.2 Symmetrical deformation

In the case of symmetrical sputtering (sputtering of the basic matrix – ideal crystalline film, by foreign atoms mutually perpendicular to both boundary surfaces of the film) within the framework of the parabolic approximation will be:

$$\begin{aligned} M(z) &\longrightarrow M_s(z) = A_M^s + B_M^s \left(z - \frac{L}{2}\right)^2; \\ a(z) &\longrightarrow a_s(z) = A_a^s + B_a^s \left(z - \frac{L}{2}\right)^2. \end{aligned} \quad (52)$$

The constants A and B are determined from the boundary conditions:

$$\begin{aligned} M_s(0) &= M_s(L) = n^{-1} \frac{\mathcal{M}_d}{\mathcal{O}_M^s}; \quad \mathcal{O}_M^s = 1 + n^{-1} \frac{\mathcal{M}_d}{\mathcal{M}_m}; \\ M_s\left(\frac{L}{2}\right) &= \mathcal{M}_m; \quad a_s(0) = a_s(L) = \frac{a_z}{n}; \quad a_s\left(\frac{L}{2}\right) = a_z \end{aligned}$$

(n is the number of sputtered atoms of the mass $\mathcal{M}_d$ around the atom of the mass $\mathcal{M}_m$ of the basic – unsputtered matrix), so that we obtain:

$$M_s(z) = \frac{\mathcal{M}_m}{\mathcal{O}_M^s} \left[\mathcal{O}_M^s - \left(1 - 2\frac{z}{L}\right)^2 \right]; \quad (53a)$$

$$a_s(z) = a_z \left[1 - \frac{n-1}{n} \left(1 - 2\frac{z}{L}\right)^2 \right]. \quad (53b)$$

Due to $\mathcal{C}_\alpha^s(z) = \text{const}(\alpha) a_s^{-\gamma}(z)$, where γ – is the decay exponent of the interatomic potentials with distance, sputtering will also cause the change of the Hooke's constants of elongation:

$$\mathcal{C}_\alpha^s(z) = \mathcal{C}_z^\alpha \left[1 + \gamma \frac{n-1}{n} \left(1 - 2\frac{z}{L}\right)^2 \right]. \quad (54)$$

In order to simplify further analysis, just as in the previous case, instead of 53b and 54 we shall use their values averaged over the total film width (L):

$$\begin{aligned} \overline{a_z^s} \equiv \overline{a_s(z)} &= f_n^s a_z; \quad f_n^s = \frac{2n+1}{3n}, \\ \overline{\mathcal{C}_\alpha^s} \equiv \overline{\mathcal{C}_\alpha^s(z)} &= g_n^s \mathcal{C}_z^\alpha; \quad g_n^s = 1 + \gamma \frac{n-1}{3n}. \end{aligned} \quad (55)$$

The notations a_z and $\mathcal{C}_z^\alpha$ in the expressions 53 and 54 are related to the corresponding quantities for the unsputtered matrix.

Now we can proceed to the solving of the equation 34. We introduce expressions 53a and 55 in it and perform the change of variable $z \rightarrow \zeta$: $(L - 2z)/(2L) = \Lambda_\alpha^s \zeta$, after which it takes the form:

$$\begin{aligned} \frac{d^2 \Psi_\alpha^s}{d\zeta^2} + \mathcal{K}_\alpha^s \left\{ \left[\mathcal{O}_M^s - 4 \left(\Lambda_\alpha^s \right)^2 \zeta^2 \right] \omega^2 - 4 \frac{\mathcal{O}_M^s}{\mathcal{M}_m} \overline{\mathcal{C}_\alpha^s} \mathcal{F}_{k_x k_y} \right\} \Psi_\alpha^s &= 0, \\ \mathcal{K}_\alpha^s &= \frac{L^2 \left(\Lambda_\alpha^s \right)^2 \mathcal{M}_m}{\overline{a_z^s}^2 \overline{\mathcal{C}_\alpha^s} \mathcal{O}_M^s}; \quad \Lambda_\alpha^s = \sqrt{\frac{\overline{a_z^s} \Omega_\alpha^s}{2L\omega}}; \quad \Omega_\alpha^s = \Omega_\alpha \tau_\alpha^s(n); \quad \tau_\alpha^s(n) = \sqrt{g_n^s \mathcal{O}_M^s}. \end{aligned} \quad (56)$$

Since the atoms in the studied film (along z -direction) represent the system of mutually coupled linear harmonic oscillators, above equation is reduced to the well-known (Callaway, 1974) Hermite-Weber's equation:

$$\frac{d^2 \Psi_\alpha^s}{d\zeta^2} + \left[{}^s Q_{k_x k_y}^\alpha(\omega) - \zeta^2 \right] \Psi_\alpha^s = 0, \quad (57)$$

with:

$${}^s Q_{k_x k_y}^\alpha(\omega) = \frac{L}{2a_z^s} \left(\mathcal{O}_M^s \frac{\omega}{\Omega_\alpha^s} - 4 \mathcal{F}_{k_x k_y} \frac{\Omega_\alpha^s}{\omega} \right). \quad (58)$$

In order to secure the crystal stability of the structure, the displacements of the atoms for any film width must remain finite, so we must introduce the restriction:

$${}^s Q_{k_x k_y}^\alpha(\omega) = 2r + 1; \quad r = 0, 1, 2, \dots \quad (59)$$

On the other hand, this is just the quantum-mechanical condition for the convergence of the solutions of the equation 57, which in this case can be expressed as:

$$\Psi_\alpha^s \equiv \Psi_\alpha^s(\zeta) \longrightarrow {}^s \Psi_r^\alpha(\zeta) = {}^s \mathcal{N}_r^\alpha \mathcal{H}_r(\eta) e^{-\zeta^2/2}, \quad (60)$$

where $\mathcal{H}_r(\zeta)$ – is the Hermitian's polynomial of order r in terms of ζ .

Equating the condition equations 58 and 59, one obtains the expression for the possible phonon frequencies in the form:

$${}^s \omega_{k_x k_y}^\alpha(r) = \frac{\Omega_\alpha^s}{2} \left[\mathcal{G}_r^s + \sqrt{(\mathcal{G}_r^s)^2 + \mathcal{F}_{k_x k_y}} \right], \quad (61)$$

where the function $\mathcal{F}_{k_x k_y}$ is defined by formula 11, while

$$\mathcal{G}_r^s \equiv \frac{2r+1}{N_z^s}; \quad \overline{N_z^s} = \frac{L}{a_z^s} \mathcal{O}_M^s.$$

One can easily see by a simple analysis of this expression that allowed phonon frequencies express their discreteness, that they depend on all the parameters of the system ($L, n, \gamma, \mathcal{M}_m, \mathcal{M}_d, a_z$ and $\mathcal{C}_z^\alpha$) and that their minimal values do not vanish neither for $r = 0$, nor for $(k_x, k_y) \rightarrow 0$.

Due to the presence of the boundaries, the solution 60 obtained without taking into account the presence of the boundaries of the studied system, must be additionally supplied by two boundary equations 31 and 32. Since we assume the symmetric conditions at the boundaries, these two equations are identical and after the substitution 60 they give:

$$\begin{aligned} & \exp \left\{ \frac{{}^s \omega_0^\alpha(r)}{\Omega_\alpha^s} \left(1 - \frac{\overline{a_z^s}}{L} \right) \right\} \mathcal{H}_r \left(\frac{2\overline{a_z^s} - L}{2\Lambda_\alpha^s} \right) = \\ & = \left\{ \frac{3}{2} - \left[\frac{{}^s \omega_0^\alpha(r)}{\Omega_\alpha^s} \right]^2 \frac{1}{n} \frac{\mathcal{M}_d}{\mathcal{M}_m} \right\} \mathcal{H}_r \left(-\frac{L}{2\Lambda_\alpha^s} \right). \end{aligned} \quad (62)$$

One can see from here that the parameters of the studied system $\mathcal{M}_m, \mathcal{M}_d, r, n$ and L (or N_z) are not mutually independent. In fact, for given values and through expression 61

they determine the conditions of the existence of phonon states with the energies $\hbar^s \omega_q^\alpha(r)$. Numerical solving and combination of the equations 61 and 62 allow us to determine the lowest possible energy state with $r = r_{min}$ and $q = 0$. These calculations⁹ have shown that the value of the quantum number r_{min} can not be lower than 1. Due to the discreteness of the solutions (formula 61) and the initial model, their total number must be equal to $N_z + 1$. It follows from here that the quantum number r must be bounded from above, too: $r_{max} = N_z + 1$, i.e. $r \in [1, N_z + 1]$.

Substituting the solution expressed by 60 into 29 and normalizing it, the expression for the phonon displacements becomes:

$$\begin{aligned} {}^s u_{n_x n_y}^\alpha(z, t) &= \sum_{k_x k_y} \sum_{r=1}^{N_z^s-2} {}^s \mathcal{N}_{n_z}^\alpha(k_x k_y, r) \mathcal{H}_r(z) e^{-(1-2z/L)^2/(2\Lambda_\alpha^s)^2} \times \\ &\times e^{i[a(k_x n_x + k_y n_y) - t {}^s \omega_{k_x k_y}^\alpha(r)]}; \\ {}^s \mathcal{N}_{n_z}^\alpha(k_x k_y, r) &\equiv (-1)^{n_z} \sqrt{\frac{\hbar}{M_z N_x N_y N_z^s {}^s \omega_{k_x k_y}^\alpha(r)}}; \quad N_z^s = N_z + 3. \end{aligned} \quad (63)$$

The analysis of this expression shows that contrary to the phonon displacements in the ideal unbounded structures (plane waves in all three spatial directions), similar to ideal films (superposition of the standing and plane wave) and in the same way as in asymmetrically deformed films, they represent here the superposition of the plane waves in XY-planes and the collective oscillatory harmonic motion along z-direction. The amplitude of the phonon displacements is of order $\sim 10^4 \sqrt{2N_z^{-1}}$ times higher than the corresponding one in the bulk structures, and approximately the same as in the ideal crystalline films¹⁰. The largest difference between the bulk and film structures is for the thin films. We must mention also, that any relevant difference between the ideal and deformed film-structures appears only for ultrathin films, but the quantitative analysis of this dependence within their framework of of this analysis (continual approximation), can not be reliably performed¹¹.

According to all the above results, the solution expressed by 61 leads to the dispersion law of phonons in symmetrically deformed crystalline films:

$${}^s E_{k_x k_y}^\alpha(r) \equiv \hbar^s \omega_{k_x k_y}^\alpha(r) = E_s^\alpha \left[\mathcal{G}_r^s + \sqrt{(\mathcal{G}_r^s)^2 + \mathcal{F}_{k_x k_y}} \right], \quad (64)$$

where $E_s^\alpha = \hbar \Omega_\alpha^s / 2$ and $r = 1, 2, 3, \dots, N_z^s - 2$. The plot of this dispersion law in the form:

$${}^s \mathcal{E}_k^z \equiv \left[\frac{{}^s E_{k_x k_y}^z(r)}{E_s^z} \right]^2 = {}^s \mathcal{E}_{k_x k_y}^z(\mathcal{G}_r^s)$$

is given at the Fig.4.

The Fig.4 represent the energy spectrum of phonons in the symmetrically deformed (ultrathin $N_z = 4$) crystalline films vs. two-dimensional (XY planar) wave vector. Besides the narrowing

⁹Estimates were based on the data from Refs. (Šetrajčić et al., 1990), (Cava et al., 1987; Chu et al., 1987; Politis et al., 1987; Segre et al., 1987; Dietrich et al., 1987; Kuwahara, 1992; Notzel et al., 1992; Johnson, 1995) and (Ristovski et al., 1989; Djajić et al., 1991; Šetrajčić et al., 1994) for the compound

Fig. 4. Phonon spectra in the symmetrically deformed ultrathin crystalline films

of the energy band with five discrete levels and the presence of the energy gap (with respect to the bulk band denoted by thin dashed lines) a shift of this band outside bulk limits can be noticed, corresponding to the appearance of the localized phonon modes.

It is clear from this plot that none of the allowed energies ${}^sE_q^\alpha(r)$ does not vanish when two-dimensional vector $q \equiv a\sqrt{k_x^2 + k_y^2} \rightarrow 0$, meaning that the presence of boundaries together with the deformation of the parabolic type (expressions 52–55) of the atom distribution leads to the appearance of the energy gap in the phonon spectrum, i.e. to the possible creation of phonons of only optical type. As compared to the acoustic phonon energies in unbounded and nondeformed structures, here the minimal and maximal frequencies (compare with formula 50):

$$(\omega_\alpha^s)_{min} \equiv {}^s\omega_0^\alpha(1) = \omega_\alpha^s(k_x = k_y = 0; r = 1) = \frac{3}{N_z^s} \Omega_\alpha^s > (\omega_\alpha^A)_{min}; \tag{65a}$$

$$(\omega_\alpha^s)_{max} \equiv \omega_\alpha^s\left(k_x = k_y = \frac{\pi}{a}; r = N_z^s - 2\right) \approx \frac{2(2N_z^s - 3)}{N_z^s} \Omega_\alpha^s < (\omega_\alpha^A)_{max}. \tag{65b}$$

It is also evident from the same figure that there arises a narrowing of the band of allowed phonon energies in the studied film¹². On the basis of formulas 64 and 65 one can

La(Ba_{2-ε}La_ε)Cu₃O_{7+δ}, where it was taken $n = 3$, $\gamma = 12$, $\varepsilon = 0,125$, $\delta = 0,11$, $v_z \approx 3$, $a_z \approx 1,2$.

¹⁰See the comment below the expression 21.

¹¹The doubts that these results are the consequence of the applied (parabolic) approximation are rejected after testing on the simplest possible examples of three- and five-layered structures (Šetrajčić et al., 1990; Djajić et al., 1991), which can be also solved exactly.

¹²Besides that there is a visible shift of this band and its leaving the bulk limits. This results in the

determine the total narrowing of the energy band of phonons in the symmetrically deformed film-structures with respect to the phonon bulk-band (compare also with expression 51):

$$\begin{aligned}\mathcal{W}_\alpha^S &\equiv \hbar \{(\omega_\alpha^B)_{max} - [(\omega_\alpha^S)_{max} - (\omega_\alpha^S)_{min}]\} \approx \\ &\approx \hbar \Omega_\alpha \left[2\sqrt{3} - \frac{4N_z^S - 9}{N_z^S} \tau_\alpha^S(n) \right] > \mathcal{W}_\alpha^A.\end{aligned}\quad (66)$$

The analysis of the functional behavior and physical interpretation, as well as the possible effects caused by the existence of the frequency threshold 65 and narrowing of the frequency range 66 will be presented in the next Section.

3. Energy gap and state density of phonons in ultrathin films

The basic property of the energy spectra of the phonons in the studied crystalline films is the narrowing of the allowed energy band¹³. Physically, the most interesting result of our calculations of the dispersion law is the presence of the energy gap, i.e. the existence of the acoustical phonons of the optical type. Analyzing the expressions 14, 44 and 61, and also the formulas 23, 50a and 65a, it is visible that:

$$\Delta_\alpha^F \equiv \hbar (\omega_\alpha^F)_{min} \sim (N_z^F)^{-1}; \quad F \equiv \{I, A, S\}, \quad (67)$$

i.e. that the size of the gap decreases hyperbolically with the number of atomic XY layers (parallel to boundary surfaces) and that in the classical limit ($N_z^F \rightarrow \infty$) it vanishes. In Fig.5 we show this dependence for the studied types (nondeformed and deformed) crystalline film-structures.

Fig.5 shown the dependence of the size of energy gap or phonon activation temperature on the film width (i.e. the number of perpendicular layers) of particular film types: *I* – ideal crystalline film-structures, *A* – asymmetrically deformed crystalline film-structures, *S* – symmetrically deformed crystalline film-structures.

It can be clearly seen from the figure that for the same film width larger value of the gap belongs to deformed films (especially the symmetric ones) and that the effect is most expressed for ultrathin films ($N_z \leq 10$), meaning that the doping process can (in relatively small amount) to increase the effect (appearance of the gap) which is the consequence of the finiteness of (one of) the dimensions of the system¹⁴.

Since the films studied are produced by "cutting them out" of the ideal infinite tetragonal structure with simple unit cell, it is clear that only acoustical phonon branches can appear. The existence of the gap, as the basic characteristic of the optical phonon branches, does not

phenomenon of localized phonon modes, which will not be discussed here in detail, since they appear for higher values of the perpendicular (*z*) wave-vector, for which the validity of the applied continual – long-wavelength approximation is questioned.

¹³See the expressions 25, 51 and 66 and notice that it is exclusive consequence of the boundness of the system – finite film width. Doping (within the framework of the parabolic model), can increase this effect only slightly, but for $L \rightarrow \infty$ (i.e. for $N_z \gg 10$) the narrowing magnitude $\mathcal{W} \rightarrow 0$.

¹⁴These, at first sight, puzzling conclusions become rather realistic on the basis of the general discussion based on the uncertainty relations. It is well-known that any micro-particle moving within the bounded region of space, can not possess zero energy. Applying the uncertainty relations $\Delta p_z \Delta z \geq \hbar/2$ and taking $\Delta z = N_z a_z = L_z$ and $\Delta p_z = \Delta E/v$, where *v* is the speed of sound, we obtain: $\Delta E \geq \hbar v/(2L_z)$. In bulk structures with $L_z \sim 1$ cm and $v = 4 \cdot 10^3$ m/s, it follows that $\Delta E \sim 10^{-10}$ eV, and this value is practically undetectable. On the other hand, in exceptionally thin films with the width $L \sim 10^{-7}$ cm, we find $\Delta E \sim 1$ meV, which is observable, experimentally accessible quantity.

Fig. 5. Phonon energy gap vs. ultrathin film thickness

mean the elimination of the acoustical ones (as was the explanation in Refs. (Tošić et al., 1987; Šetrajčić et al., 1990; Djajić et al., 1987), but a completely new physical effect – the appearance of the acoustical phonons of the optical type. This agrees with the classical (thermodynamic) limit: for $N_z \rightarrow \infty$ it also follows that $T_{ac} \rightarrow 0$.

One can assign to the energy gap corresponding activation temperature:

$$T_{ac}^F = \frac{\Delta_F}{k_B} \equiv \frac{\Omega_\alpha}{k_B} \varphi_F(N_z) \approx \begin{cases} 35 \text{ K,} & \text{for ideal } (F = I) \text{ nondeformed films;} \\ 38 \text{ K,} & \text{for asymmetrically } (F = A) \text{ deformed films;} \\ 40 \text{ K,} & \text{for symmetrically } (F = S) \text{ deformed films,} \end{cases} \quad (68)$$

for the typical values of the parameters¹⁵ according to data from Refs. (Cava et al., 1987; Chu et al., 1987; Politis et al., 1987; Segre et al., 1987; Dietrich et al., 1987; Kuwahara, 1992) and (Notzel et al., 1992; Johnson, 1995; Ristovski et al., 1989; Djajić et al., 1991; Šetrajčić et al., 1994). According to all the above mentioned, physical interpretation which could be assigned to these temperatures might be the following: No phonons can appearing in the crystalline film-structure up to T_{ac} ,¹⁶ and this structure behaves as completely “frozen”. For phonon

¹⁵Following experimental data we have chosen: $\mathcal{M}_m = (2 - x)\mathcal{M}_Y + \mathcal{M}_{Cu} + (4 - \delta)\mathcal{M}_O$, $\mathcal{M}_d = (x - \delta)\mathcal{M}_{Ba}$ for the compound $Y_{2-x}Ba_{x-\delta}CuO_{4-\delta}$, $x, \delta \in (0, 5, 1, 0)$, $n = 4$, $\gamma = 12$, $a_z \approx 1, 2 \text{ nm}$, $v \approx 3 \cdot 10^3 \text{ m/s}$; we gave a detailed explanation in our Refs. (Šetrajčić et al., 1992; 1994).

¹⁶This is the consequence of the existence of boundary surfaces in the system studied. The very effect of the sputtering, although not decisive, definitely contributes to this effect, especially for the symmetrical doping.

states to be created, energy must be brought to the system from outside (thermal, mechanical, etc) at least in the amount of the gap size. This could be also an acceptable explanation of the well-known effect (CRC HCP, 1989; Notzel et al., 1992) that superconductive critical temperature of the films is always higher than in the corresponding bulk structures.

From the plot (Fig.5) and from 68 one can notice two trends. The first one that the appearance of the activation temperature (energy gap) is the consequence of the existence of finite (small) film width, i.e the boundness of the structure. The sputtering which disturbs the symmetry of the distribution of atoms in the film along the direction in which the film is bounded (two parallel boundary surfaces) can only enhance this effect¹⁷, and can not cause it in any way:

$$\Delta_S > \Delta_A > \Delta_I \gg \Delta_B \equiv 0 \quad (69)$$

(compare the expressions 23, 50a and 65a with ω_{min}).

The calculations of the energy bandwidth also support the statement that thin-layer, i.e. film-structures possess better superconductive characteristics. If we compare the results expressed by 25, 51 and 66, it is clear that:

$$\mathcal{W}_S > \mathcal{W}_A > \mathcal{W}_I \gg \mathcal{W}_B \equiv 0. \quad (70)$$

These expressions define the magnitude of the energy band narrowing in the films with respect to bulk band. We see that in the film-structures the allowed band of phonon energies is much smaller than the one in the corresponding massive sample. Taking into account the previous comment (the existence of the gap i.e. the rise of the ground state energy level) it is clear that the probability of the electron scattering on atomic vibrations is decreased (electric resistance decreases), but also that the effective – attractive – electron-phonon interaction "straightens" because virtual phonons possess more energy (phonons of the optical type). On the other hand, this can be used for the explanation of lower critical density of the electric current in the high-temperature superconductors (smaller number of phonons participates in the effective electron-phonon interaction), and less pronounced isotope effect (only higher energy phonons interact with electrons, so the role of the atoms is minority).

To support these statements, it is necessary to determine the density of states of the phonons at relevant energy levels, i.e. their distribution over the energies in film-structures. We have applied the well-known Debye's approach (Mahan, 1983; Jones & March, 1985), adapted for our model.

Following the standard definition (Maradudin, 1987; Cottam & Tilley, 1989; Callaway, 1974), the number of allowed values of the quasi-momentum $\vec{k} \equiv (k_x, k_y, k_z)$ per unit volume of $\vec{k}$ -space is: $\frac{N_x}{k_x^{max}} \cdot \frac{N_y}{k_y^{max}} \cdot \frac{N_z}{k_z^{max}}$, where, according to the model, $k_x^{max} = k_y^{max} = \frac{2\pi}{a}$, and $k_z^{max} <$

$\frac{2\pi}{a_z}$ (this value depends on the film kind). If we approximate the volume in the momentum space (in the long-wavelength approximation) by a cylinder of the basis πk^2 ($k^2 = k_x^2 + k_y^2$) and height k_z^{max} , in the frequency range $\omega, \omega + d\omega$ the total number of the phonon states can

¹⁷This is not an abstract theoretical conclusion, since the parameters of the system were chosen from and according to experimental data, and not for some general cases. We are sure that for some other set of the parameters, the theoretical result of the sputtering might even oppose to this effect, i.e. to decrease T_{ac} with respect to the undoped film. Our leading idea was to cast at least some light in the shadows surrounding the mechanism of high-temperature superconductivity, so that is the reason for our choice of data.

be expressed as:

$$\mathcal{N}_F = \frac{N_F}{4\pi} a^2 k^2; \quad N_F = N_x N_y N_z^F. \tag{71}$$

The density of phonon states is then:

$$\mathcal{D}_F(\omega)|_{\omega=\omega_F} \equiv \frac{d\mathcal{N}_F}{d\omega_F} = \left(\frac{d\omega_F}{dk}\right)^{-1} \frac{N_F}{2\pi} a^2 k/,,. \tag{72}$$

Long-wavelength approximation applied here allows us to choose and retain only the lowest possible value of the projection k_z : k_z^{min} . Taking this into account:

$$\omega_F \equiv \omega(k) \approx \Omega_F \left[\sqrt{a^2 k^2 + \Delta_F^2} + \Delta_F (1 - \delta_{FI}) \right]; \quad \Delta_F = \frac{\kappa_F}{N_z^F} \tag{73}$$

(magnitudes and values for κ_F and N_z^F are given in the Table 1) and expressions 23, 24, 49, 50, 64 and 65 we can determine:

$$\mathcal{D}_F(\omega_F) = \frac{N_F}{2\pi\Omega_F^2} [\omega_F - \Omega_F \Delta_F (1 - \delta_{FI})] \tag{74}$$

(the values for Ω_F are also given in Table 1).
Table 1 shown the values of the parameters used for the calculation and comparison of the densities of phonon states and Debye’s frequencies for the studied types of crystalline film-structures. The numerical values of the coefficients are calculated on the basis of the experimental data for high-temperature superconducting ceramics of the Y–Ba–Cu–O type from Refs. (Cava et al., 1987; Chu et al., 1987; Politis et al., 1987; Segre et al., 1987; Dietrich et al, 1987) and (Kuwahara, 1992; Notzel et al., 1992; Johnson, 1995); calculation procedure in details is given in our papers (Tošić et al., 1987; Šetrajčić et al., 1990; Djajić et al., 1987) and on conference talks (Ristovski et al., 1989; Djajić et al., 1991; Šetrajčić et al., 1994). One can clearly see from the expression (3.8) that the density of phonon states for a given value of the frequency $\omega = \omega_F(k)$ is lower than in the bulk structures, and the lowest in the (symmetrically) deformed films:

$$\mathcal{D}_S < \mathcal{D}_A < \mathcal{D}_I \ll \mathcal{D}_B \tag{75}$$

and that they are posses linear dependence on the frequency.
If one would “abandon” the long-wavelength approximation then the expression 74 would have slightly different form: instead of a linear function of ω , the density of states would turn into a δ -function, since $\Delta_F \rightarrow \mathcal{G}_F$ which has a finite discrete series of possible values¹⁸. In this way, one would confirm the results of the Einstein’s approach to the analyze of the density of phonon states (Jones & March, 1985).
At the end of this Section, let us determine the values of the Debye’s frequencies for all three kinds of films. According to the model described, if the sample contains N_F unit cells, than the total number of states is also equal to N_F , so from:

$$N_F \equiv \int_0^{\omega_D^F} \mathcal{D}_F(\omega) d\omega = \frac{N_F \omega_D^F}{4\pi\Omega_F^2} [\omega_D^F - 2\Omega_F \Delta_F (1 - \delta_{FI})] \tag{76}$$

¹⁸It can be seen from the expressions 15, 16, 44 and 61.

	$F = I$	$F = S$	$F = A$
κ_F	π	4,2	4,7
N_z^F	$N_z + 2$	$N_z + 3$	$N_z + 4$
Ω_F / Ω	1,00	1,12	1,21

Table 1. Debye’s parameters for different types ultrathin films

it follows:

$$\omega_D^F = 2\Omega_F \sqrt{\pi} \left[\sqrt{1 + \frac{\Delta_F^2}{4\pi} (1 - \delta_{FI})^2} + \frac{\Delta_F}{2\sqrt{\pi}} (1 - \delta_{FI}) \right]. \tag{77}$$

Simple analysis of this expression leads to another relation:

$$\omega_D^S < \omega_D^A < \omega_D^I \ll \omega_D^B. \tag{78}$$

For typical values of the parameters (already listed) one can estimate that Debye’s frequencies in the film-structures are 10 – 15 % lower than in the corresponding bulk-structures. This means that in thinlayered structures there exist “softer” phonons.

It is interesting to compare the values of the density of phonon states at Debye’s frequencies:

$$\frac{\mathcal{D}_F(\omega_D^F)}{\mathcal{D}_B(\omega_D^B)} = \frac{1}{\sqrt[3]{36\pi}} \frac{\Omega_B}{\Omega_F} \frac{N_z^F}{N_z^B}. \tag{79}$$

Since $N_z^F \sim 50$, and $N_z^B \sim 10^8$ it is clear that:

$$\mathcal{D}_F(\omega_D^F) \ll \mathcal{D}_B(\omega_D^B). \tag{80}$$

So, in the film-structures, i.e. the structures with broken translational symmetry, the population of phonons with Debye’s frequencies is extremely small – much smaller than in the corresponding unbounded and nondeformed crystalline structures.

The phonons with precisely Debye’s frequencies are responsible for the electrical and thermal transport properties of the materials, one can conclude that there will occur a large difference in these physical properties in bounded and deformed films with respect to the ideal and unbounded structures although there are no chemical or crystallographic differences. According to the results 78 and 80 – lower values of Debye’s frequencies and lower densities of phonon states in the films studied – one can expect that film-structures will be poorer electric (lower conductivity) and heat (lower capacity) conductors. This is well known and well tabulated fact, for examples for metals and metallic alloys (CRC HCP, 1989).

Since the idea to study such film-structures arose after the discovery of the high-temperature superconductors and their specific properties differing them from the classical superconducting materials, we can not avoid turning our attention at the end to the possible consequences that these results could bear to the superconducting properties.

Due to smaller phonon population and the appearance of softer phonons in small-grain perovskite structures (Bednorz & Müller, 1988) of Y–Ba–Cu–O type and the similar ones, one can conclude that the probability of Cooper’s pairs creation is smaller. This should result in the lower value of the (critical) density of (superconductive) current.

On the other hand, in the expression for matrix elements ($\mathcal{V}$) of the effective electron-electron interaction within the framework of the BCS theory there occur Debye’s frequencies: $\mathcal{V} \sim$

$\omega_D^{-1/2}$, which, taking into account the results obtained, undoubtedly indicates that the attractive interaction of the electrons is more intense for strongly bounded and deformed structures, so they can be "more strongly" coupled into Cooper's pairs. For the destruction of such pairs one needs more energy so the critical temperature of these structures is much higher.

If we remember the fact that the materials with poor conductive properties (in the normal phase) possess better superconductive characteristics, then following above presented analyzes and estimates, we can state that the boundness of the structure and the deformation of its crystal symmetry is one of the important elements which explain the peculiarities of the phenomenon, and even the very mechanism of high-temperature superconductivity, in part. At this stage we must notice that considerations presented here are only of qualitative nature and are the consequence of the incomplete¹⁹ analysis of the behavior of a single subsystem (phonons) – one of the participants in the effects of high-temperature superconductivity. We are trying to establish if it is possible that maybe for copper-oxide ceramics we also deal with the same (BCS, i.e. Cooper's) mechanism of superconductivity – the same one as for the classical superconducting materials, only under substantially different conditions. The continuation of the research which should include the behavior of the electron system in the studied film-structures (these results are now in the stage of numerical treatment), and especially the formation and the analysis of the effective electron-(virtual phonon)-electron interaction will either confirm or deny our above exposed statements.

4. Phonon thermodynamics of thin film-structures

Forasmuch as the properties of anisotropic structures are conditioned by the change of dispersion law, it is necessary to observe behavior of certain thermodynamic properties towards obtainment of better understanding about those properties. Phonon participation in thermodynamic properties (or heat capacitance temperature behavior, i.e. generally – in heat transferring) in thin film was found in our previous paper (Lazarev et al., 2000; Jaćimovski et al., 2004; Šetrajčić et al., 2007; Ilić et al., 2007; Šetrajčić et al., 2009).

Getting that, when $k \rightarrow 0$ (in long-wave approximation: $4 [\sin^2 (ak_x/2) + \sin^2 (ak_y/2)] \approx a^2 k^2$, $k^2 = k_x^2 + k_y^2$), energies of all three phonon branches have non-zero values, it can be utilized dispersion relations 22, 49 and 64, in somewhat simplified form:

$$E(\vec{k}) = \sqrt{a^2 k^2 E_0^2 + \Delta_f^2} . \tag{81}$$

where

$$\Delta_f = ak_z^{min} E_0 ; \quad E_0 \equiv \hbar \sqrt{\frac{C_\alpha}{M}} . \tag{82}$$

It should be specifically emphasized that verification of phonon dispersion law at very low values of k is virtually impossible, so that verification of existence of phonon gap detects itself in measurement of low temperature thermal capacitances in film and corresponding ideal structure.

¹⁹For completing of these analyzes it is necessary to determine the phonon contribution in the heat capacity of the system.

The thermal capacitance is analyzed, whereby at first internal energy is calculated in terms of standard form (Mahan, 1983; Jones & March, 1985; Maradudin, 1987; Callavay, 1974):

$$U_f = 3 \sum_{k_x, k_y, k_z} E(\vec{k}) \left[e^{E(\vec{k})/\theta} - 1 \right]^{-1}. \quad (83)$$

Going over from sum in last expression to integral in accordance with the formula²⁰:

$$\sum_{k_x, k_y, k_z} \rightarrow 3(N_z + 1) \sum_{k_x, k_y} \rightarrow \frac{3N_x N_y (N_z + 1) a^2}{4\pi^2} \int_0^{2\pi} d\varphi \int_0^{k_{max}} k dk,$$

and taking $k_{max} \approx k_D = \sqrt[3]{6\pi^2}$, after suitable notations:

$$\eta \equiv \sqrt{\frac{N_z^2}{3} + N_z + 1}; \quad \zeta \equiv \sqrt{1 + \left(\frac{N_z + 2}{\pi} \sqrt[3]{6\pi^2} \right)^2}$$

and adequate operations, expression for internal energy has been obtained in form:

$$U_f(x) = \frac{3N_f}{4\pi^2} \frac{\Delta_f^4}{E_0^3} x^2 \left\{ \left[Z_2\left(\frac{1}{x}\right) - \eta^2 Z_2\left(\frac{\eta}{x}\right) + \eta^2 \zeta^2 Z_2\left(\frac{\eta\zeta}{x}\right) - \zeta^2 Z_2\left(\frac{\zeta}{x}\right) \right] + \right. \\ \left. + 4x \left[Z_3\left(\frac{1}{x}\right) - \eta Z_3\left(\frac{\eta}{x}\right) + \eta \zeta Z_3\left(\frac{\eta\zeta}{x}\right) - \zeta Z_3\left(\frac{\zeta}{x}\right) \right] + \right. \\ \left. + 6x^2 \left[Z_4\left(\frac{1}{x}\right) - Z_4\left(\frac{\eta}{x}\right) + Z_4\left(\frac{\eta\zeta}{x}\right) - Z_4\left(\frac{\zeta}{x}\right) \right] \right\}, \quad (84)$$

where the symbol x is introduced for reduced temperature: $x = \frac{\theta}{\Delta_f}$, $N_f = N_x N_y (N_z + 1)$ and

$Z_r(X) = \sum_{j=1}^{\infty} j^{-r} e^{-jX}$ – the functions are called Dyson's functions.

For finding of expression for the thermal capacitance per a unit cell (here: per an atom), the standard definitional form (Mahan, 1983; Jones & March, 1985; Maradudin, 1987; Callavay, 1974) is used:

$$C_f = \frac{1}{N_f} \frac{\partial U_f}{\partial T} \equiv \frac{k_B}{N_f} \frac{\partial U_f}{\partial \theta} = \frac{1}{\Delta_f} \frac{k_B}{N_f} \frac{\partial U_f}{\partial x}. \quad (85)$$

In accordance with that it is obtained:

$$C_f(x) = \frac{3k_B}{4\pi^2} \left(\frac{\Delta_f}{E_0} \right)^3 \left\{ \left[Z_1\left(\frac{1}{x}\right) - \eta^3 Z_1\left(\frac{\eta}{x}\right) + \eta^3 \zeta^3 Z_1\left(\frac{\eta\zeta}{x}\right) - \zeta^3 Z_1\left(\frac{\zeta}{x}\right) \right] + \right. \\ \left. + 6x \left[Z_2\left(\frac{1}{x}\right) - \eta^2 Z_2\left(\frac{\eta}{x}\right) + \eta^2 \zeta^2 Z_2\left(\frac{\eta\zeta}{x}\right) - \zeta^2 Z_2\left(\frac{\zeta}{x}\right) \right] + \right. \\ \left. + 18x^2 \left[Z_3\left(\frac{1}{x}\right) - \eta Z_3\left(\frac{\eta}{x}\right) + \eta \zeta Z_3\left(\frac{\eta\zeta}{x}\right) - \zeta Z_3\left(\frac{\zeta}{x}\right) \right] + \right. \\ \left. + 24x^3 \left[Z_4\left(\frac{1}{x}\right) - Z_4\left(\frac{\eta}{x}\right) + Z_4\left(\frac{\eta\zeta}{x}\right) - Z_4\left(\frac{\zeta}{x}\right) \right] \right\}. \quad (86)$$

²⁰The transition $\sum_{\vec{k}} \rightarrow \int d\vec{k} = \int d^3k$ of Descartes coordinates for film must to be carried out to cylindrical coordinates due to finite thickness

It is known that the phonon part in thermal capacitance of the system is described with cubic temperature dependence. By introducing nondimensional reduced temperature, this dependence amounts to: $C_b(x) = \frac{12}{5} \pi^4 N_b k_B \left(\frac{\Delta_f}{E_D} \right)^3 x^3$. For comparison of these dependencies, these and expression 86 are divided by the constant: $C_0 = \frac{k_B}{2} \left(\frac{\Delta_f}{E_D} \right)^3$, whose dimension is equal to dimension of thermal capacitance, and nondimensional properties are compared: $C_{f/b} \equiv \frac{C_{f/b}}{C_0}$. On Fig.6 are shown relative (nondimensional) thermal capacitances of bulk (*b*) and film-structure (*f*) subject to the relative temperature *x* in low (a) and very low temperature region.

Fig. 6. Thermal capacitance vs. temperature at low and extremely low temperatures

On Fig.7 are shown relative (nondimensional) thermal capacitances of bulk (*b*) and film-structure (*f*) samples versus relative temperature *x*, for ultrathin – $N_z = 3$ (a), thin $N_z = 8$ (b) and thick $N_z = 48$ (c) film-structures, in comparison with bulk ones.

Fig. 7. Thermal capacitance in low temperature regime for ultrathin, thin, thick films

It can be seen that in low-temperature region (Fig.6) thermal capacitance of film is lower than that of massive specimens, whereas at the intermediate temperatures situation is reversed (Popov et al., 2003). Intersect point of two curves at low temperatures is moving – with increase of film-thickness – towards lower temperatures (Fig3 a $\rightarrow$ c). Besides, it is noticeable that thermal capacitance of film with decrease of temperature declines faster than that of corresponding ideal structure, or slowly rises with the increase of temperature – to a certain upper temperature. Hence, for film heating from certain lower to a certain upper temperature, it is necessary to use more thermal energy per mass unit than for heating the same quantity of corresponding (with the identical crystallographical parameters) unbounded structure to the same temperature. It is in accordance with the fact that phonons in film have non-zero excitation energy.

5. Conclusion

Studying and comparing the phonon spectra and states in the ideal unbounded and nondeformed (bulk) structures and the structures with broken translational symmetry (films) we have reached the following conclusions.

1. Mechanical vibrations in bulk structures are plane waves in all directions, while in the films they represent the superposition of the standing waves in z -directions (perpendicular to the boundary surfaces) and plane waves in XY -planes (parallel to boundary surfaces).
2. The amplitude of phonon displacements in the films depends on the film width and it is $\sim 10^4 \sqrt{2/N_z}$ times higher than in the ideal structures. This indicates their larger elastic "maneuvering space" without any negative effect to the mechanical properties of the given material (for example no breaking of interatomic bonds) which leads to higher resistance and higher melting point of the films with respect to bulk samples.
3. All three acoustic frequencies in bulk structures vanish for $\vec{k} \rightarrow 0$, while in the films they tend toward some minimal value depending on the film width. This means that phonons in the films possess the energy gap, that for their excitation (creation) one should spend certain energy, i.e. heat them up to certain – activation temperature, meaning that the system up to that temperature behaves as the "frozen" one, as if the phonons were not present.
4. Phonon gap, besides depending on the film width, depends also on the type of the atoms and their distribution along z -direction and also on the stoichiometric relation of the atoms injected in the films.
5. The densities of phonon states and Debye's frequencies have lower values in the films than in the corresponding bulk structures. This implies that in the films, phonon excitations are more "difficult" to appear, that they are less "present" and that created acoustic phonons of the optical type (above the activation temperature) are energetically "softer" than the classical ones which appear in the bulk structures.
6. Since phonons with Debye's frequencies define thermal and electrical properties of the materials, this means that films are worse thermal and electrical conductors.

These analyzes show that the films are better superconductors than the corresponding bulk samples, made from the same material with the same crystalline structure. This statement, which is an experimental fact is supported by the following of our results.

1. In the films there appear standing phonon waves along z-directions, the collective property specific for the macroscopic quantum-mechanical state which is the characteristics of the superconductors. In the ideal structures, where there exist only plane phonon waves, there is no such property.
2. Higher values of the amplitudes of phonon displacements in the films indicate to the possibility of the long-range phonon interaction with other excitations which can occur in the system (electrons or holes). This induces the higher possible coherence length, i.e. the larger radius of the Cooper's pairs which can be created here.
3. The appearance of the energy gap in the phonon spectrum of the films means that up to the activation temperature these systems behave as completely frozen, i.e. without any mechanical vibrations which would cause the real resistance to the electrical current conduction.
4. Lower values of Debye's frequencies in the films could result in the higher values of (BCS) matrix elements of the effective electron-electron interaction. The attraction between paired electrons is stronger, and one must spend more energy for their destruction, so the critical temperature of these systems is higher.

Comparing the results between the phonon behavior in the ideal and deformed films one can conclude that the strongest influence onto the change of phonon states and spectra has just the existence of finite boundaries of the system, while less important (although not negligible) influence has the disturbance of the atom distribution (due to doping) within the film – especially when we talk about symmetrical doping.

Since phonons with Debye's frequencies are responsible for electrically and thermally induced transport properties of material (Mahan, 1983; Jones & March, 1985), it follows that the nanofilm-structure will be inferior electrical and thermic conductor in contrast with the relative massive structures, providing there is no chemical and structural differences between them.

On the other hand, it is well known fact that the more inferior electrical conductor materials is (under normal conditions), the better superconductor it becomes (Maradudin, 1987; Callaway, 1974). Due to that, the experimental fact can be concluded and justified, that in spatially very confined structures more qualitative superconductive properties have been achieved.

In the region of low temperatures, the thermal capacitance of film is lower than in massive structures, while in medium temperatures it is reversed. Intersect point of two curves at low temperatures is moving – with increase of film-thickness – towards lower temperatures. Besides, it is noticeable that thermal capacitance of film with decrease of temperature declines faster than that of corresponding ideal structure, or slowly rises with the increase of temperature – to a certain upper temperature.

Hence, for film heating from certain lower to a certain upper temperature, it is necessary to use more thermal energy per mass unit than for heating the same quantity of corresponding (with the identical crystallographical parameters) unbounded structure to same temperature. It is well known that poorer electric conductors are better superconductors, so that in ultrathin films it is possible to achieve much better superconducting properties!

All these conclusions, derived on the basis of the results of the analyzes of this work, are of more or less qualitative nature and deal with the change of phonon states and spectra under the influence of the presence of boundaries and the breaking of crystalline symmetry of the structure, and the possible influence of these changes onto the macroscopic physical characteristics of these systems. Since we have taken only phonon contributions into account,

they could not be considered as definitive and final. The continuation of the research should study the influence of the boundaries onto spectra and states of other elementary charge carriers and their mutual interaction in the presence of the changed phonon field. On the basis of these results one might be able to say something more concrete about the order of magnitude of the superconductive characteristics of the films.

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