

APPLICATION OF SEVEN-PARAMETER VFF MODEL FOR INVESTIGATIONS OF LATTICE DYNAMICS IN QUASI-TWO-DIMENSIONAL Si AND Ge NANOSTRUCTURES

Dmitrii CRÎȘMARI

E.P. Pokatilov Laboratory of Physics and Engineering of Nanomaterials and Synergetics

Utilizând metoda celor mai mici pătrate, au fost obținuți parametrii interatomari ai interacțiunilor cu rază redusă de acțiune prin adaptarea frecvențelor fononice măsurate de-a lungul liniilor volumetrice principale de simetrie Δ , Σ și Λ . Astfel, a fost determinat câmpul forțelor de valență caracterizat de șapte parametri, în care energia potențială de deformare este compusă din șase tipuri de interacțiuni covalente. Parametrii obținuți pentru Si și Ge sunt prezentați în tabel. Au fost construite spectrele energetice fononice pentru nanopeliclele cu structura diamantului având o grosime de circa 3 nm; paralel sunt prezentate densitățile stărilor. De asemenea, utilizând legea dispersiei, au fost obținute vitezele fononice de grup, cu ajutorul cărora au fost determinate dependențele vitezelor medii de grup de energia fononică. În final, a fost efectuată o analiză comparativă a diferiților compuși cvasibidimensionali cu grosimea cuprinsă între 3 și aproape 7 nm. Pentru aceste nanostructuri a fost calculat parametrul important, care caracterizează proprietățile fononice și stabilește conductibilitatea lor termică, și anume: viteza medie de grup a fononilor acustici în aproximația undelor lungi. Rezultatele obținute permit a studia în continuare heterostructurile plane și a implementa în circuitele electronice nanoelementele cu factor de calitate înaltă.

Introduction

The importance of phonons and their interactions in bulk materials is well known to those working in the fields of solid-state physics, solid-state electronics, optoelectronics, heat transport, quantum electronics, and superconductivity. Nanodimensional structures (heterolayers, heterowires, multilayered quantum dots, quantum dot superlattices) at the present time are intensively studied in leading world scientific centers. In laboratories of physics of multilayered structures throughout tens years are conducted researches of vibrational, electronic and optical properties of nanostructures. Basically works are directed on the investigation of properties of atomic compounds. To investigate phonon properties of such compounds is necessary more exact calculation of the non-Coulomb interaction with a large number of force parameters (two-, three-, four-particle, etc., interatomic interactions). The question naturally arises as to the effect of dimensional confinement on the properties on the phonons in such nanostructures as well as the properties of the phonon interactions in nanostructures.

The theoretical model

According to this theory a covalent bond is formed between the two atoms by the overlap of half filled valence atomic orbitals of each atom containing one unpaired electron [1,2]. A valence bond structure is similar to a Lewis structure, but where a single Lewis structure cannot be written, several valence bond structures are used. Each of these valence bond structures represents a specific Lewis structure. This combination of valence bond structures is the main point of resonance theory. Valence bond theory considers that the overlapping atomic orbitals of the participating atoms form a chemical bond. Because of the overlapping, it is most probable that electrons should be in the bond region. Valence bond theory views bonds as weakly coupled orbitals (small overlap). Valence bond theory is typically easier to employ in ground state molecules.

Crystals with cubic structure are of major importance in the fields of electronics and optoelectronics. Indeed, zincblende crystals such as silicon (Si), germanium (Ge), and gallium arsenide (GaAs) may be regarded as two face-centered cubic (fcc) lattices displaced relative to each other by a vector $(a/4, a/4, a/4)$, where a is the size of the smallest unit of the fcc structure (Fig.1).

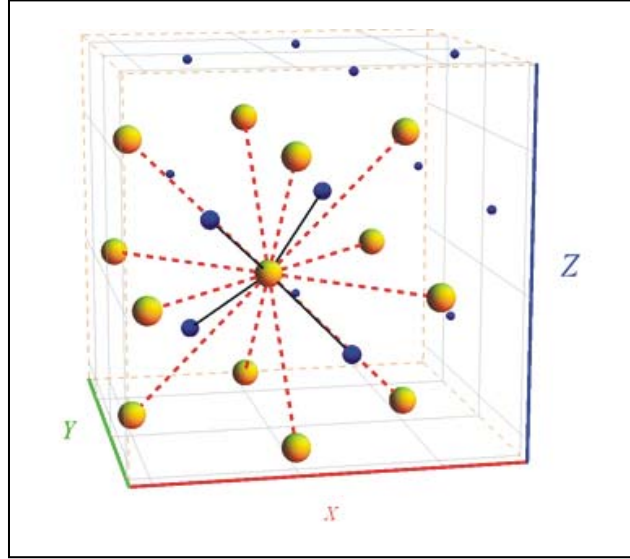


Fig.1. First two coordination groups of a lattice with the zincblende structure.

In the given figure the four big blue atoms compose the first sphere of interaction relatively to the central atom under consideration. The remaining nine little blue atoms, together with the four previous, form the second Bravais sublattice. The solid black lines show radiuses of short-range interactions. The twelve yellow atoms belong to the second coordination group; they with the central atom compose the first Bravais sublattice. The dashed red lines connect the atoms of long-range interactions. Thus, shown in the figure atoms represent fully the investigated diamond-like nanostructures and interactions in them.

The atom-atom force field $V(\vec{r}_i) = V_{SR}$ used here includes a short-range part V_{SR} , which describes the covalent bonding [3,4]. For atom i bonded tetrahedrally to atoms j , k and l , the short-range interaction is

$$V_{SR}(\vec{r}_i) = \frac{\kappa_{r1}}{2} \sum_j \delta r_{ij}^2 + \frac{\kappa_{r2}}{2} \sum_m \delta r_{im}^2 + \frac{\kappa_{\theta} r_0^2}{2} \sum_{j,k} \delta \theta_{ijk}^2 + \kappa_{r\theta} r_0 \sum_{j,k} \delta r_{ij} \delta \theta_{ijk} + \kappa_{rr} \sum_{j,k} \delta r_{ij} \delta r_{jk} + \frac{\kappa_{100} r_0^2}{2} \sum_{j,k,l} \delta \theta_{ijk} \delta \theta_{kjl} + \frac{\kappa_{200} r_0^2}{2} \sum_{j,k,l} \delta \theta_{ijk} \delta \theta_{jkl}, \quad (1)$$

where κ_{r1} , κ_{r2} , κ_{θ} , $\kappa_{r\theta}$, κ_{rr} , κ_{100} and κ_{200} are short-range force constants. r_0 is the equilibrium bond length. The first two terms in Eq. (1) are the Stretching-interactions between examined atoms and atoms of first and second coordination groups, respectively, and the third term is the Bending-interaction familiar from the commonly used Keating’s VFF models [5-7], the next term – the coupling Stretching-Bending-interaction, further – the Stretching-Stretching-interaction of two nearest bonds, while the remaining two terms describe the Bending-Bending-interactions with one and two centers, respectively. The summation over m corresponds to interactions of the central atom i with all atoms from second coordination group.

The atomic force constants $\Phi_{\rho,\sigma}(i, j)$ are obtained from the force field $V = V_{SR}$ as

$$\Phi_{\rho,\sigma}(i, j) = \frac{\partial^2 V}{\partial r_{i\rho} \partial r_{j\sigma}}, \quad (2)$$

where ρ and σ label the Cartesian coordinates. The phonon frequencies $\omega_{s\vec{q}} \equiv 2\pi\nu_{s\vec{q}}$ (of branch s and wave vector \vec{q}) and eigenmodes $\vec{Q}_{s\vec{q}}(\xi)$ of quasi-two-dimensional diamond-like nanostructures are then obtained by diagonalizing the dynamical matrix:

$$\sum_{\sigma, \xi'} [D_{\rho,\sigma}(\xi\xi' | \vec{q}) - \omega_{s\vec{q}}^2 \delta_{\rho\sigma} \delta_{\xi\xi'}] Q_{s\vec{q}}^\sigma(\xi') = 0. \quad (3)$$

Here ξ is the atomic index inside the primary cell, i.e., $\vec{r}_i = \vec{r}_\xi + \vec{R}_l$, where \vec{R}_l is a lattice vector. The matrix element $D_{\rho,\sigma}(\xi\xi'|\vec{q})$ is

$$D_{\rho,\sigma}(\xi\xi'|\vec{q}) = \frac{1}{\sqrt{M_\xi M_{\xi'}}} \sum_{l'} \Phi_{\rho,\sigma}(l\xi, l'\xi') e^{-i\vec{q} \cdot [\vec{R}(l) - \vec{R}(l')]}, \quad (4)$$

where M is the mass of atom. The displacement of atom i corresponding to the phonon eigenmode $\vec{Q}_{s\vec{q}}(\xi)$ is

$$\vec{u}_{s\vec{q}}(i) = \frac{1}{\sqrt{M_\xi}} \vec{Q}_{s\vec{q}}(i) e^{i\vec{q} \cdot \vec{R}_i}. \quad (5)$$

Thus, Valence Force Field model describes the interactions between uncharged atoms. Valence bond theory now complements molecular orbital theory, which does not adhere to the valence bond idea that electron pairs are localized between two specific atoms in a molecule but that they are distributed in sets of molecular orbitals which can extend over the entire molecule [8]. Molecular orbital theory can predict magnetic properties in a straightforward manner, while valence bond theory gives similar results but is more complicated. Valence bond theory views aromatic properties of molecules as due to resonance between Kekule, Dewar and possibly ionic structures, while molecular orbital theory views it as delocalization of the π -electrons. The underlying mathematics are also more complicated limiting valence bond treatment to relatively small molecules. On the other hand, valence bond theory provides a much more accurate picture of the reorganization of electronic charge that takes place when bonds are broken and formed during the course of a chemical reaction. In particular, valence bond theory correctly predicts the dissociation of homonuclear diatomic molecules into separate atoms, while simple molecular orbital theory predicts dissociation into a mixture of atoms and ions.

Results

As a result, it was established seven-parameter field, where the potential energy of deformation consists of six kinds of interatomic interactions (the Stretchings with first two coordination groups, the Bending, the double Stretching, the Stretching-Bending, the double Bendings with one and two centers). In the *table* below are presented the interaction parameters, obtained by solving the characteristic equation of sixth degree by minimizing the discrepancy of theoretical results and experimental data. Radial and angular parameters of the interatomic interactions are measured in different values; from the tabular numerical values it's possible to determine the contribution of an interaction in phonon dispersion dependences.

Table

Seven-parameter Valence Force Field for Si and Ge (*)

Silicon			Germanium		
№	Interaction constants	The numerical value	№	Interaction constants	The numerical value
1	$\kappa_{r1(Si)}$	1.303...	1	$\kappa_{r1(Ge)}$	1.246...
2	$\kappa_{r2(Si)}$	0.2460...	2	$\kappa_{r2(Ge)}$	0.2270...
3	$\kappa_{rr(Si)}$	-0.1099...	3	$\kappa_{rr(Ge)}$	-0.1162...
4	$\kappa_{\theta(Si)}$	0.1813...	4	$\kappa_{\theta(Ge)}$	0.1811...
5	$\kappa_{r\theta(Si)}$	0.2757...	5	$\kappa_{r\theta(Ge)}$	0.3035...
6	$\kappa_{1\theta\theta(Si)}$	$1.685... \cdot 10^{-3}$	6	$\kappa_{1\theta\theta(Ge)}$	$1.954... \cdot 10^{-3}$
7	$\kappa_{2\theta\theta(Si)}$	0.1071...	7	$\kappa_{2\theta\theta(Ge)}$	0.1079...

(*) Units: the Stretching and the Stretching-Stretching force constants are expressed in mdyne/Å, the Bendings and the Bending-Bending in mdyne·Å/rad², the Stretching-Bending in mdyne/rad. Ellipsis indicates that in the calculations were used and other significant numerals.

For estimation of conformity degree of the theory to experiment were calculated phonon dispersions along the main symmetry lines of investigated crystal diamond-like structure (directions $\Gamma \rightarrow X$, $\Gamma \rightarrow K$, and $\Gamma \rightarrow L$ in the Brillouin zone). Here we represent phonon energy spectra only along the main crystallographic direction 100 for bulk Si and Ge (Fig.2), because the results presented below (Fig.3,4) for planar nanostructures will correspond exactly to this direction. It's necessary to note that the inclusion of the four-particle Bending-Bending-interactions with one and two centers in addition to the two- and three-particle Stretching-, Bending-, Stretching-Bending- and Stretching-Stretching-interactions appears useful, since theoretically obtained phonon dispersion dependences began to describe more precisely experimental results. The account of many kinds of interatomic interactions with a large number of force parameters allows to describe more precisely phonon properties of planar nanostructures, wires, etc., that gives to this direction of researches necessary novelty.

We also explain that in Fig.2 the solid lines show double-degenerate dispersion dependences (they describe transverse vibrations), while the dashed lines mark once degenerate curves of longitudinal vibrations.



Fig.2. Experimental and calculated dispersion curves along the direction $\Gamma \rightarrow X$ for bulk Si (black) and Ge (red) crystals.

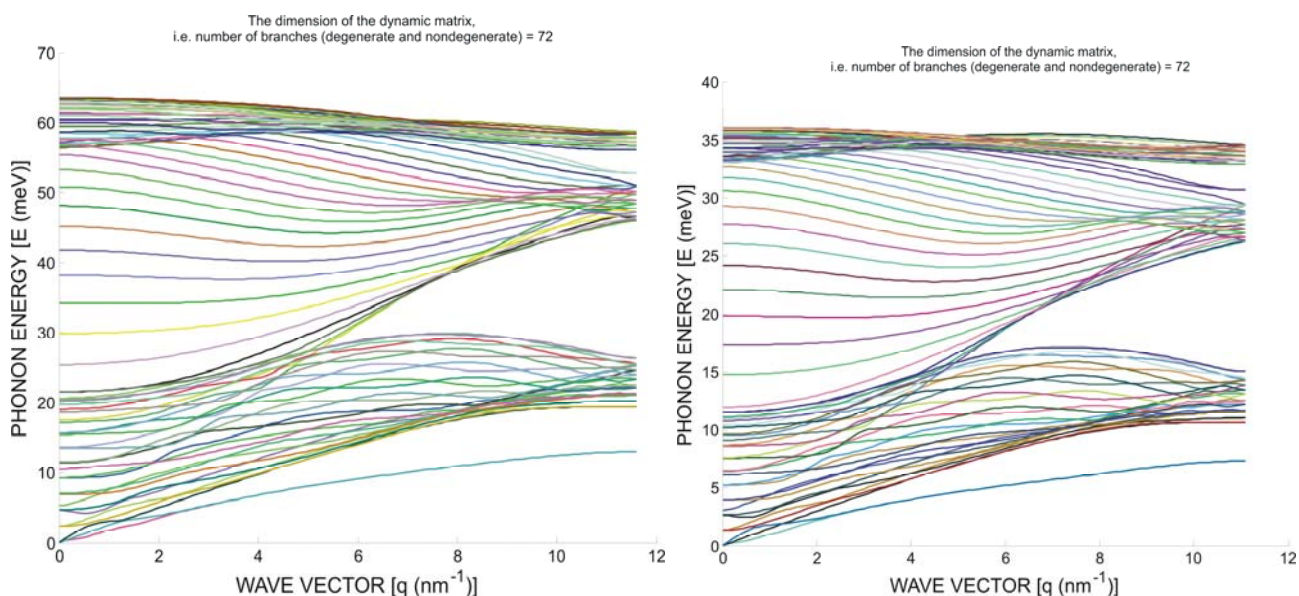
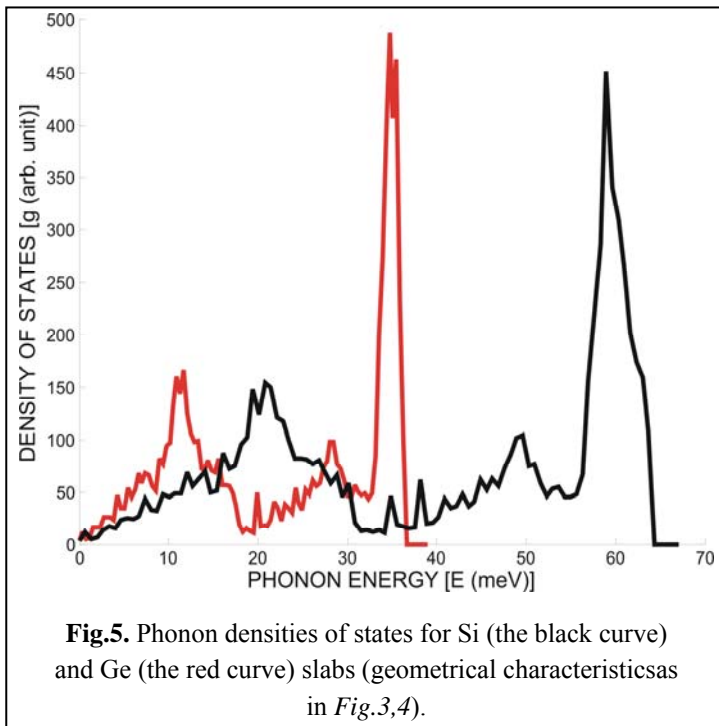


Fig.3,4. Phonon energy spectra for Si (the left figure) and Ge (the right figure) slabs with thickness of 24 monolayers along the main symmetry line (direction 100).

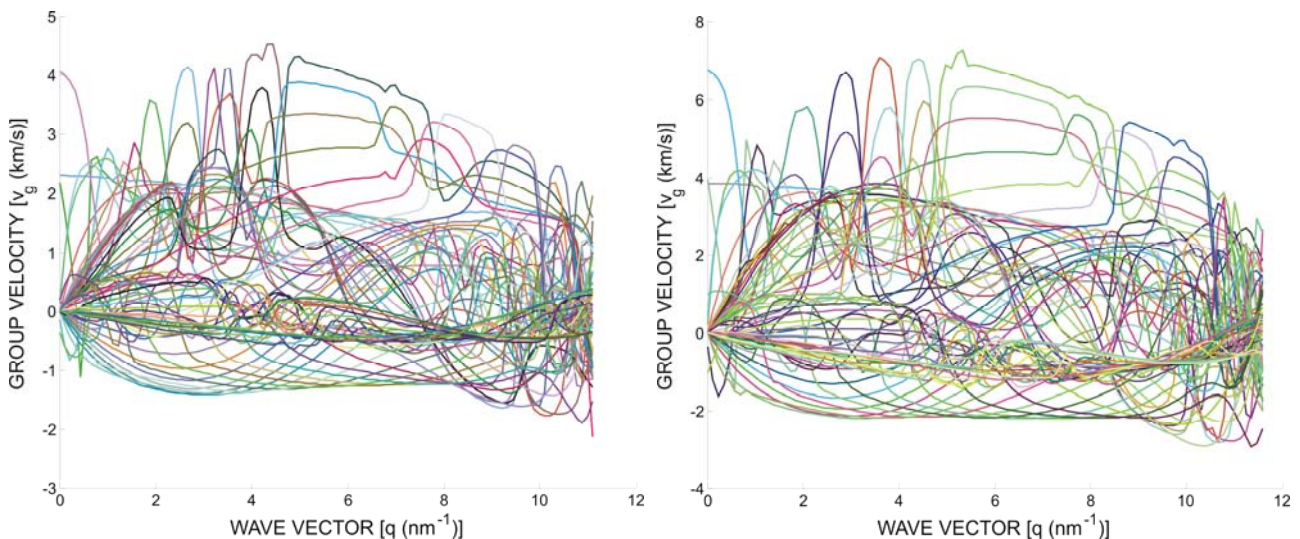
More visual representation of the phonon energy spectra (Fig.3,4) give the density of states shown in Fig.5. For example, for Si film we see three distinct peaks in the regions of 22, 50 and 60 meV. These peaks characterize the transverse acoustic, longitudinal acoustic and optical, and transverse optical vibrations, respectively.



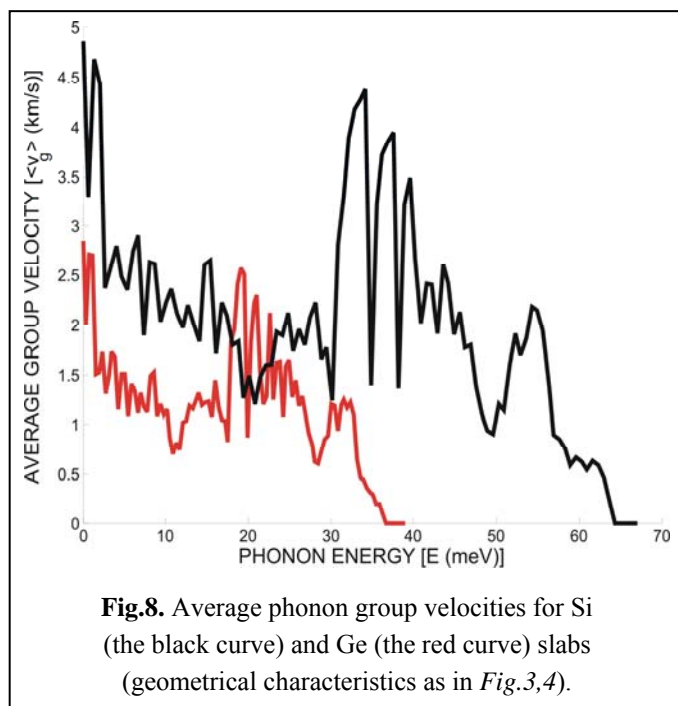
In Fig.6,7 are shown phonon group velocities obtained from the dispersion law. It's visible that in the Si film with thickness of 3.11 nm phonons possess velocities in the interval approximately from -3 to 7 km/s, but the Ge film with thickness of 3.25 nm phonon velocities vary from -2 to 4.5 km/s. Hence quanta of vibrational motion of atoms are characterized by higher velocities in Si slabs that should cause an increase of heat conductivity in these nanostructures in comparison with similar Ge compounds.

We also calculated average phonon group velocities for nanoslabs with thickness of 24 monolayers (ML). In Fig.8 are presented the dependences of these velocities on the phonon energy; the obtained curves give the resulting picture from all branches of group velocities from Fig.6,7. We see that for the phonons with zero energy their average phonon group velocities constitute 4.856 km/s for Si nanofilm with thickness of 3.11 nm

and 2.849 km/s in the case of 3.25 nm Ge quasi-two-dimensional nanostructure. At the same time, these velocities of phonons with energies approximately 37 meV for the corresponding Ge nanocompound (and with energies around 64 meV for Si) reduce to zero.



Finally, for the comparative analysis has been defined an important parameter characterizing phonon properties (the average group velocity of acoustic phonons in the long-wave approximation) in planar nanostructures with different thicknesses: 36 and 48 ML, in addition to 24 ML. So, in the case of Si, this value is equal to 4.941 km/s (thickness 4.74 nm) and 5.034 km/s (6.36 nm), and for Ge is 2.899 km/s (4.95 nm) and 2.965 km/s (6.64 nm). It's seen that at the increase in thickness of homogeneous nanodimensional films increases the average group velocity of acoustic phonons in the long-wave approximation, which is caused



by the increase in channel of heat extraction. These values reach 5.239 km/s in the case of bulk Si and 3.152 km/s for Ge. At the further studying of phonon properties in heterostructures, we can choose those or other combinations of materials for increase or decrease of heat conductivity in them that is the important factor at implementation of nanoelements, for example, in electronic circuits.

In summary we will note that application of Valence Force Field model has allowed to reproduce with high precision experimental dispersion dependences and to find a set of interatomic interaction parameters used in the given article for determination of the fundamental physical values, which characterize lattice dynamics (phonon energy spectra, group velocities, densities of states, etc.). These results will be necessary further for calculation of some kinetic coefficient (including heat conductivity) quasi-two-dimensional and other spatially limited nanostructures.

References:

1. Murrell J.N., Kettle S.F.A., and Tedder J.M. The chemical bond. - Chichester and New York: John Wiley & Sons, 1985.
2. Строшио М., Дутта М. Фононы в наноструктурах. - Москва: Физматлит, 2006.
3. Huaxiang Fu, Ozolins V., and Zunger A. Phonons in GaP quantum dots // Phys. Rev. B., 1999, vol.59, p.2881-2887.
4. Крышмарь Д., Покатилов Е. Вычисление кулоновского поля в дипольной решётке методом Эвальда в дополнение к модели VFF для расчёта колебаний ионного кристалла GaP // Stud. Univ., 2010, vol.37, p.65-69.
5. Tubino R., Piseri L., and Zerbi G. Lattice dynamics and spectroscopic properties by a valence force potential of diamondlike crystals: C, Si, Ge, and Sn // J. Chem. Phys., 1972, vol.56, p.1022-1039.
6. Wang H.X., and Messmer R.P. Valence-bond model for silicon force fields // Phys. Rev. B., 1990, vol.41, p.5306-5311.
7. Anderson A.B. Valence-force-field potentials for diamondlike crystals // Phys. Rev. B., 1973, vol.8, p.3824-3827.
8. Shaik S.S., and Hiberty P.C. A chemist's guide to valence bond theory. - New Jersey: Wiley-Interscience, 2008.

The work was supported in part by the Moldova State under Project No. 10.819.05.02F (17/ind) and 11.817.05.10F.

Prezentat la 30.09.2011