

Description of elastic properties of diamond- and sphalerite-structured diatomic crystals with the use of moment interaction

A.M. Krivtsov* and O.S. Loboda

St. Petersburg State Polytechnic University, St. Petersburg, 195251, Russia
Institute of Problems of Mechanical Engineering RAS, St. Petersburg, 199178, Russia

A mechanical model of diatomic lattice which takes into account force and moment interactions is proposed. Relations between macroscale elastic moduli and microscale longitudinal and transverse stiffnesses of interatomic bonds are derived. In the framework of the proposed model, crystals with diamond and sphalerite lattices are considered. It is shown that the model offers much universality allowing quite accurate description of elastic properties of a wide range of covalent crystals.

Keywords: elastic properties, diamond and sphalerite structures, moment interaction, mechanical model

DOI: 10.1134/S1029959912020129

1. Introduction

Carbon is an extremely significant chemical element. Carbon compounds constitute the basis for life and their properties govern to a great extent the range of conditions in which similar life forms can exist. There are numerous allotropic modifications of carbon much different in physical properties. The main and well-studied modifications of carbon are graphite and diamond. With advances in technologies, other forms of carbon such as fullerenes, carbon nanotubes and graphene were discovered; their unique mechanical properties open up new opportunities for practical application of the materials in various fields of science and technology. In this context, it becomes particularly urgent to develop models that allow adequate and unified description of mechanical properties of carbon, its modifications and compounds.

The variety of carbon modifications owes to the capability of carbon to form different chemical bonds. The electron orbitals of a carbon atom can vary in geometry depending on their hybridization. In all cases, the bond is directional (covalent); therefore, the simplest model in which atoms are represented by material points bound through pair force interaction is found inadequate. The approach considered in the paper consists in taking additional account of

pair moment interaction with the potentials dependent on the relative positions and rotations of two interacting particles. Thus, the interaction forces between atoms are no longer central: a transverse force, in addition to a longitudinal force, appears making it possible to account for directivity of bonds in covalent structures.

The use of moment interaction for description of crystalline structures is discussed in [1–8]. Noteworthy also are the works devoted to description of mechanical properties of carbon structures [9, 10].

In the paper, we follow and develop the approaches proposed in [3] where macroscale relations of elasticity for arbitrary polyatomic lattices were derived taking into account microscale moment relations. The developed approaches are applied to describe elastic properties of diamond-structured crystals (crystals of diamond, silicon, germanium and tin). The process under consideration is elastic deformation of the system. Each particle is taken to interact only with a limited number of neighbors, and this allows one to arrive at a local theory in going to the macroscale. The characteristics of elasticity are obtained with an energy approach in which strain energy expressions are compared giving a relation between micro- and macroscale parameters. The approach provides an easier way, compared to [3], to obtain required relations, particularly in the case of moment and many-body interactions. Relations between macroscale elastic moduli and parameters of longitudinal and transverse stiffnesses of interatomic bonds are derived.

* *Corresponding author*

Prof. Anton M. Krivtsov, e-mail: akrivtsov@bk.ru

It is shown that these relations can be successfully applied to description of compounds with sphalerite lattice, i.e., those whose lattice is similar to that of diamond but has atoms of two types in its nodes.

2. Derivation of equations

Let us derive expressions that define the stiffness tensor of a diatomic lattice with regard to force and moment interactions. Let there be a complex lattice whose elementary cell contains two atoms. By convention the atoms are termed atoms of the first and second type. Atoms of each type form a simple crystal lattice, with the lattices being congruent. Then, we choose one of the atoms of the first type and term it a reference atom. The atoms with which the reference atom interacts are numbered by indices α . The potential energy for the reference atom can be represented in the form:

$$W = \frac{1}{2V_0} \sum_{\alpha} \Pi(A_{\alpha}), \quad (1)$$

where Π_{α} is the interaction potential of the reference atom with an atom α . The factor $1/2$ in formula (1) appears because the potential Π_{α} describes the interaction of two atoms. The energy for the elementary lattice cell is determined by the formula

$$W \stackrel{\text{def}}{=} \frac{2}{V_0} \Pi = \frac{1}{V_0} \sum_{\alpha} \Pi_{\alpha}, \quad (2)$$

where V_0 is the elementary cell volume for an undeformed lattice; the factor 2 is required because the elementary cell contains two atoms (the energy per atom of the elementary cell is the same due to symmetry of the lattice).

The vectors directed from the reference atom to an atom α for an undeformed crystal are denoted as \mathbf{a}_{α} . The lattice atoms are modeled by solids whose displacement and rotation vectors with respect to their position in the undeformed crystal are denoted as \mathbf{u}_{α} and $\boldsymbol{\varphi}_{\alpha}$; the displacement and rotation vectors of the reference atom are designated as \mathbf{u} and $\boldsymbol{\varphi}$. Then, the interaction potential of atoms can be represented in the form [3]:

$$\Pi_{\alpha} = 1/2 \boldsymbol{\varepsilon}_{\alpha} \cdot \mathbf{A}_{\alpha} \cdot \boldsymbol{\varepsilon}_{\alpha} + \boldsymbol{\varepsilon}_{\alpha} \cdot \mathbf{B}_{\alpha} \cdot \boldsymbol{\kappa}_{\alpha} + 1/2 \boldsymbol{\kappa}_{\alpha} \cdot \mathbf{G}_{\alpha} \cdot \boldsymbol{\kappa}_{\alpha}, \quad (3)$$

where $\boldsymbol{\varepsilon}_{\alpha}$ and $\boldsymbol{\kappa}_{\alpha}$ are the strain vectors of interatomic bonds:

$$\boldsymbol{\varepsilon}_{\alpha} \stackrel{\text{def}}{=} \mathbf{u}_{\alpha} - \mathbf{u} + 1/2 \mathbf{a}_{\alpha} \times (\boldsymbol{\varphi}_{\alpha} + \boldsymbol{\varphi}), \quad \boldsymbol{\kappa}_{\alpha} \stackrel{\text{def}}{=} \boldsymbol{\varphi}_{\alpha} - \boldsymbol{\varphi}, \quad (4)$$

\mathbf{A}_{α} , \mathbf{B}_{α} and \mathbf{G}_{α} are the stiffness tensors of interatomic bonds (of the second order). Expression (3) has no term linear in strain and this means the absence of initial bonding forces (in the equilibrium state, the bonds in the crystal are free of stress). The use of the approximation is justified because in reality, the initial bonding forces are small due to fast weakening of the interaction. If we take these forces into account, the formulae will be too complicated and generally speaking we will have to resort to nonlinear theory.

On the macroscale, the specific (per unit volume) strain energy in a moment medium at small strains has the form [3]:

$$W = 1/2 \boldsymbol{\varepsilon} \cdot \mathbf{A} \cdot \boldsymbol{\varepsilon} + \boldsymbol{\varepsilon} \cdot \mathbf{B} \cdot \boldsymbol{\kappa} + 1/2 \boldsymbol{\kappa} \cdot \mathbf{G} \cdot \boldsymbol{\kappa}. \quad (5)$$

Here $\boldsymbol{\varepsilon}$ and $\boldsymbol{\kappa}$ are the macroscale strain tensors:

$$\boldsymbol{\varepsilon} \stackrel{\text{def}}{=} \nabla \mathbf{u} + \mathbf{E} \times \boldsymbol{\varphi}, \quad \boldsymbol{\kappa} \stackrel{\text{def}}{=} \nabla \boldsymbol{\varphi}, \quad (6)$$

where \mathbf{u} and $\boldsymbol{\varphi}$ are the displacement and rotation vectors of an element of the medium; ∇ is the vector differential operator; \mathbf{A} , \mathbf{B} and \mathbf{G} are the stiffness tensors of the medium (of the fourth order).

For homogeneous¹ deformation of the lattice, the following representations hold true:

$$\mathbf{u}_{\alpha} = \mathbf{u} + \mathbf{a}_{\alpha} \cdot \nabla \mathbf{u} + v_{\alpha} \boldsymbol{\zeta}, \quad \boldsymbol{\varphi}_{\alpha} = \boldsymbol{\varphi} + \mathbf{a}_{\alpha} \cdot \nabla \boldsymbol{\varphi} + v_{\alpha} \boldsymbol{\psi}, \quad (7)$$

where $\boldsymbol{\zeta}$ and $\boldsymbol{\psi}$ are the translational and angular residual vectors that describe respectively displacements and rotations of particles of one sublattice relative to particles of another sublattice; v_{α} is a coefficient that takes on the value 0 for atoms of the first type and the value 1 for atoms of the second type. Substitution of (7) in (4) gives the following relation between the strain vectors of bonds and the strain tensors of the medium:

$$\boldsymbol{\varepsilon}_{\alpha} = \mathbf{a}_{\alpha} \cdot \boldsymbol{\varepsilon} + v_{\alpha} \boldsymbol{\zeta} - 1/2 \mathbf{a}_{\alpha} \cdot \boldsymbol{\kappa} \times \mathbf{a}_{\alpha} + 1/2 v_{\alpha} \mathbf{a}_{\alpha} \times \boldsymbol{\psi}, \quad (8)$$

$$\boldsymbol{\kappa}_{\alpha} = \mathbf{a}_{\alpha} \cdot \boldsymbol{\kappa} + v_{\alpha} \boldsymbol{\psi}.$$

On the macroscale, it is as a rule sufficient to use momentless description of deformation of a medium, and therefore we turn to the transition to momentless theory. For this purpose, we restrict our consideration to deformation in which the first strain tensor remains symmetric. Then, using (6), we obtain

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}^S \Leftrightarrow (\nabla \mathbf{u})^A + \mathbf{E} \times \boldsymbol{\varphi} = 0 \Leftrightarrow \boldsymbol{\varphi} = 1/2 \nabla \times \mathbf{u}. \quad (9)$$

Geometrically the given relation means that all particles rotate together with the medium. For the second strain tensor, we obtain

$$\boldsymbol{\kappa} = \nabla \boldsymbol{\varphi} = 1/2 \nabla \nabla \times \mathbf{u}, \quad (10)$$

and hence for homogeneous deformation this tensor identically vanishes. We also assume that the angular residual $\boldsymbol{\psi}$ vanishes as well. Then, formulae (2), (3), (8) give

$$W = 1/(2V_0) \sum_{\alpha} \boldsymbol{\varepsilon}_{\alpha} \cdot \mathbf{A}_{\alpha} \cdot \boldsymbol{\varepsilon}_{\alpha}, \quad \boldsymbol{\varepsilon}_{\alpha} = \mathbf{a}_{\alpha} \cdot \boldsymbol{\varepsilon} + v_{\alpha} \boldsymbol{\zeta}, \quad (11)$$

from which it follows that

$$W = 1/2 \boldsymbol{\varepsilon} \cdot \mathbf{C}^* \cdot \boldsymbol{\varepsilon} + \boldsymbol{\varepsilon} \cdot \mathbf{C} \cdot \boldsymbol{\zeta} + 1/2 \boldsymbol{\zeta} \cdot \mathbf{C} \cdot \boldsymbol{\zeta}, \quad (12)$$

where

$$\mathbf{C}^* = 1/V_0 \sum_{\alpha} (\mathbf{a}_{\alpha} \cdot \mathbf{A}_{\alpha} \cdot \mathbf{a}_{\alpha})^S, \quad (13)$$

$$\mathbf{C} = 1/V_0 \sum_{\alpha} v_{\alpha} (\mathbf{A}_{\alpha} \cdot \mathbf{a}_{\alpha})^S,$$

$$\mathbf{C} = 1/V_0 \sum_{\alpha} v_{\alpha} \mathbf{A}_{\alpha}.$$

¹ Homogeneous deformation is understood as deformation in which the displacements and rotations are affine functions of coordinates.

Here symmetrization is over those vectors by which the symmetric tensor $\boldsymbol{\varepsilon}$ is multiplied in (12). The residual is found from the equilibrium conditions of material at specified $\boldsymbol{\varepsilon}$:

$$\begin{aligned} \partial W / \partial \boldsymbol{\zeta} = 0 \Rightarrow \\ \Rightarrow \boldsymbol{\zeta} = -\boldsymbol{\varepsilon} \cdot {}^3\mathbf{C} \cdot \mathbf{C}^{-1} = -{}^2(\mathbf{C}^{-1}) \cdot {}^3\mathbf{C}^T \cdot \boldsymbol{\varepsilon}, \end{aligned} \quad (14)$$

where

$${}^4\mathbf{C}^T \stackrel{\text{def}}{=} 1/V_0 \sum_{\alpha} v_{\alpha} (\mathbf{A}_{\alpha} \mathbf{a}_{\alpha})^S, \quad (15)$$

with symmetrization over the two right coefficients. Substitution of the resultant expression for $\boldsymbol{\zeta}$ in formula (12) gives

$$W = 1/2 \boldsymbol{\varepsilon} \cdot {}^4\mathbf{C} \cdot \boldsymbol{\varepsilon}, \quad {}^4\mathbf{C} \stackrel{\text{def}}{=} {}^4\mathbf{C}^* - {}^3\mathbf{C} \cdot {}^2\mathbf{C}^{-1} \cdot {}^3\mathbf{C}^T. \quad (16)$$

Thus, we have the stiffness tensor expression of macroscopic momentless theory of elasticity.

Let us consider that the stiffness tensors of force interaction between atoms are transversely isotropic; for simplicity, we restrict ourselves to the interaction with atoms of the first coordination sphere. Then, the stiffness tensors of bonds can be written in the form:

$$\begin{aligned} \mathbf{A}_{\alpha} = c_A \mathbf{n}_{\alpha} \mathbf{n}_{\alpha} + c_D (\mathbf{E} - \mathbf{n}_{\alpha} \mathbf{n}_{\alpha}), \\ \mathbf{n}_{\alpha} = 1/a \mathbf{a}_{\alpha}, \quad a = |\mathbf{a}_{\alpha}|, \end{aligned} \quad (17)$$

where c_A and c_D are the longitudinal and transverse stiffnesses of bonds. Substitution of this expression in (13) gives

$$\begin{aligned} {}^4\mathbf{C}^* &= \frac{a^2}{V_0} \sum_{\alpha} ((c_A - c_D) \mathbf{n}_{\alpha} \mathbf{n}_{\alpha} \mathbf{n}_{\alpha} \mathbf{n}_{\alpha} + c_D \mathbf{n}_{\alpha} \mathbf{E} \mathbf{n}_{\alpha})^S, \\ {}^3\mathbf{C} &= \frac{a}{V_0} (c_A - c_D) \sum_{\alpha} v_{\alpha} \mathbf{n}_{\alpha} \mathbf{n}_{\alpha} \mathbf{n}_{\alpha}, \\ {}^2\mathbf{C} &= \frac{1}{V_0} \sum_{\alpha} v_{\alpha} ((c_A - c_D) \mathbf{n}_{\alpha} \mathbf{n}_{\alpha} + c_D \mathbf{E}). \end{aligned} \quad (18)$$

Here we take $\sum_{\alpha} v_{\alpha} \mathbf{n}_{\alpha} = 0$.

Next, for simplicity, we restrict the consideration to crystal lattices for which $v_{\alpha} = 1$, i.e., the first coordination sphere holds only atoms of the second type. Besides the tensor $\sum_{\alpha} \mathbf{n}_{\alpha} \mathbf{n}_{\alpha}$ is assumed isotropic. Both these assumptions are valid for the diamond lattice which is considered below. The assumption made allow us to use the identities

$$\sum_{\alpha} \mathbf{n}_{\alpha} \mathbf{n}_{\alpha} = \frac{M}{d} \mathbf{E} \Rightarrow \sum_{\alpha} \mathbf{n}_{\alpha} \mathbf{E} \mathbf{n}_{\alpha} = \frac{M}{d} \mathbf{e}_k \mathbf{e}_n \mathbf{e}_k, \quad (19)$$

where M is a coordination number; d is the space dimension; \mathbf{e}_k is the orthonormal basis; hereinafter, summation is over repeated Latin indices from 1 to d . Then, formulae (18) take the form:

$${}^4\mathbf{C}^* = \frac{a^2}{V_0} \left((c_A - c_D) \sum_{\alpha} \mathbf{n}_{\alpha} \mathbf{n}_{\alpha} \mathbf{n}_{\alpha} \mathbf{n}_{\alpha} + \frac{M}{2d} c_D \mathbf{J}_{23} \right), \quad (20)$$

$${}^3\mathbf{C} = \frac{a}{V_0} (c_A - c_D) \sum_{\alpha} \mathbf{n}_{\alpha} \mathbf{n}_{\alpha} \mathbf{n}_{\alpha}, \quad (21)$$

$${}^2\mathbf{C} = \frac{M}{V_0 d} (c_A + d_1 c_D) \mathbf{E},$$

where

$$\mathbf{J}_{23} \stackrel{\text{def}}{=} \mathbf{e}_k \mathbf{e}_n \mathbf{e}_n \mathbf{e}_k + \mathbf{e}_k \mathbf{e}_n \mathbf{e}_k \mathbf{e}_n, \quad d_1 \stackrel{\text{def}}{=} d - 1. \quad (22)$$

Notice that the above assumptions fail to hold, e.g., for a hexagonal close-packed lattice (hcp), and complete formulae (18), rather than formulae (20), (21), should be used for it.

Let us write expression (16) for the resultant stiffness tensor ${}^4\mathbf{C}$ in the form:

$${}^4\mathbf{C} \stackrel{\text{def}}{=} {}^4\mathbf{C}^* - {}^4\mathbf{C}', \quad {}^4\mathbf{C}' \stackrel{\text{def}}{=} {}^3\mathbf{C} \cdot {}^2\mathbf{C}^{-1} \cdot {}^3\mathbf{C}^T, \quad (23)$$

where the tensor ${}^4\mathbf{C}^*$ is determined by formula (20), and for the correction stiffness tensor ${}^4\mathbf{C}'$, using (21), we obtain

$${}^4\mathbf{C}' = \frac{a^2 d}{V_0 M} \frac{(c_A - c_D)^2}{c_A + d_1 c_D} \sum_{\alpha} \mathbf{n}_{\alpha} \mathbf{n}_{\alpha} \mathbf{n}_{\alpha} \cdot \sum_{\beta} \mathbf{n}_{\beta} \mathbf{n}_{\beta} \mathbf{n}_{\beta}. \quad (24)$$

3. Diamond lattice

The crystal lattice of diamond is a complex diatomic lattice, i.e., it contains atoms of two types differing in geometric arrangement of atoms surrounding them. The packing density of the diamond lattice is very low, being a mere 46 % of the fcc lattice density, while the hardness of diamond crystals surpasses the hardness of all known minerals. Besides diamond, a similar lattice is characteristic of other group IV elements: silicon, germanium and α -tin. However, with an increase in atomic number, the covalent interaction is weakened with the result that tin can exist as well in metallic modification with characteristic close packing of atoms, and the next group IV element — lead — is found only in the form of close-packed metal.

Diamond is stable at high pressures and is metastable, though capable of existing for long, under normal conditions. When heated, diamond transforms into graphite (the transition temperature for synthetic micropowders is 450–500 °C; for crystals of size 0.6–1 mm, this temperature increases to 600–700 °C and depends on the structure perfection, amount and character of impurities).

An element of the diamond lattice is shown in Fig. 1. It is seen that the crystal has cubic symmetry. The atoms depicted in the figure are positioned at the cube corners, at the centre of its faces (atoms 1, 5, 7), and at the centers of four non-adjacent cube octants (atoms 2, 4, 6, 8). The lattice can be obtained from a body-centered cubic lattice (bcc) by removal of each second atom from the first coordination sphere such that the rest of atoms lie at tetrahedron vertices. Each atom is at the centre of the tetrahedron whose vertices are four nearest atoms; the angle between covalent bonds is 109°28'.

The diamond lattice is three-dimensional; the coordination number for it is determined as

$$M = d + 1, \quad d = 3, \quad (25)$$

and this allows writing formulae (20), (24) in the form:

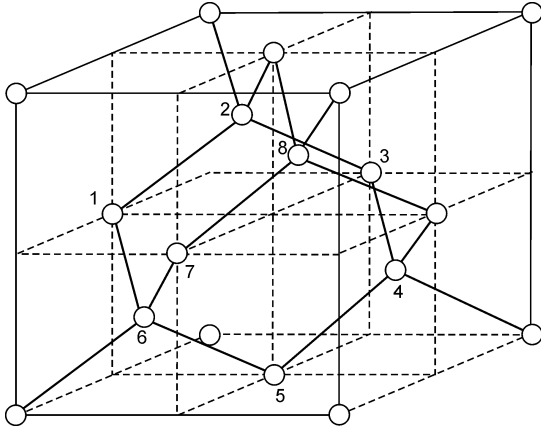


Fig. 1. Element of the diamond lattice

$${}^4\mathbf{C} \stackrel{\text{def}}{=} {}^4\mathbf{C}^* - {}^4\mathbf{C}', \quad (26)$$

$${}^4\mathbf{C}^* = \frac{a^2}{V_0} \left((c_A - c_D) \sum_{\alpha=1}^{d+1} \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha + \frac{d+1}{2d} c_D \mathbf{J}_{23} \right),$$

$${}^4\mathbf{C}' = \frac{d}{d+1} \frac{a^2}{V_0} \frac{(c_A - c_D)^2}{c_A + d_1 c_D} \sum_{\alpha=1}^{d+1} \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \sum_{\beta=1}^{d+1} \mathbf{n}_\beta \mathbf{n}_\beta \mathbf{n}_\beta.$$

Let us calculate the product

$$\begin{aligned} \sum_{\alpha=1}^{d+1} \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \sum_{\beta=1}^{d+1} \mathbf{n}_\beta \mathbf{n}_\beta \mathbf{n}_\beta &= \\ &= \sum_{\alpha, \beta=1}^{d+1} (\mathbf{n}_\alpha \cdot \mathbf{n}_\beta) \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\beta \mathbf{n}_\beta. \end{aligned} \quad (27)$$

Using the condition $\sum_{\alpha} \mathbf{n}_\alpha = 0$, it is easy to obtain that

$$\begin{aligned} \mathbf{n}_\alpha \cdot \mathbf{n}_\beta &= \begin{cases} 1, & \alpha = \beta, \\ -1/d, & \alpha \neq \beta, \end{cases} \Leftrightarrow \\ \Leftrightarrow \mathbf{n}_\alpha \cdot \mathbf{n}_\beta &= 1/d((d+1)\delta_{\alpha\beta} - 1), \end{aligned} \quad (28)$$

where $\delta_{\alpha\beta}$ is the Kronecker symbol. Substitution of formula (28) in (27) gives

$$\begin{aligned} \sum_{\alpha=1}^{d+1} \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \cdot \sum_{\beta=1}^{d+1} \mathbf{n}_\beta \mathbf{n}_\beta \mathbf{n}_\beta &= \\ &= \frac{d+1}{d^2} \sum_{\alpha=1}^{d+1} \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha - \frac{1}{d} \sum_{\alpha=1}^{d+1} \mathbf{n}_\alpha \mathbf{n}_\alpha \sum_{\beta=1}^{d+1} \mathbf{n}_\beta \mathbf{n}_\beta. \end{aligned} \quad (29)$$

This formula, in view of the relation

$$\sum_{\alpha=1}^{d+1} \mathbf{n}_\alpha \mathbf{n}_\alpha = \frac{d+1}{d} \mathbf{E}, \quad (30)$$

makes it possible to simplify the formula for the correction stiffness tensor:

$${}^4\mathbf{C}' = \frac{a^2}{V_0} \frac{(c_A - c_D)^2}{c_A + d_1 c_D} \left(\sum_{\alpha=1}^{d+1} \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha - \frac{d+1}{d^2} \mathbf{E} \mathbf{E} \right). \quad (31)$$

For lattices whose elastic properties are isotropic (e.g., graphene) or possess cubic symmetry (e.g., diamond), the formula from [4] is valid:

$$\sum_{\alpha} \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha = M_\kappa \mathbf{e}_\kappa \mathbf{e}_\kappa \mathbf{e}_\kappa \mathbf{e}_\kappa + M_\mu (\mathbf{J}_1 + \mathbf{J}_{23}),$$

$$\mathbf{J}_1 \stackrel{\text{def}}{=} \mathbf{E} \mathbf{E}, \quad (32)$$

where \mathbf{e}_κ are the unit vectors of the orthonormal basis which are directed either along the axes of cubic symmetry or arbitrary, as is the case for isotropy; M_κ and M_μ are the dimensionless coefficients determined by the formulae

$$M_\kappa = \frac{2M}{d} \frac{1 - \eta_c}{d\eta_c + 2}, \quad M_\mu = \frac{M}{d} \frac{\eta_c}{d\eta_c + 2}, \quad (33)$$

where η_c is the anisotropy parameter of the tensor $\sum \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha \mathbf{n}_\alpha$, and is coincident with the anisotropy parameter of the stiffness tensor of the material in pure force interaction.

Table 1 presents values of the dimensionless parameters for the diamond lattice.

The anisotropy parameter was calculated in the basis \mathbf{e}_κ (i.e., for direction 100). The volume of an elementary cell can be estimated using the following general formula (derived empirically):

$$V_0 = \sqrt{\frac{(d+1)^{d+1}}{d^d}} a^d, \quad d = 1, 2, 3. \quad (34)$$

The stiffness tensor moduli C_{11} , C_{12} and C_{44} , and also the bulk modulus K can be calculated by the formulae:

$$C_{11} = \frac{\sqrt{3}}{12a} (c_A + 2c_D), \quad C_{12} = \frac{\sqrt{3}}{12a} (c_A - c_D), \quad (35)$$

$$C_{44} = \frac{3\sqrt{3}}{8a} \frac{c_A c_D}{c_A + c_D}, \quad K = \frac{\sqrt{3}}{12a} c_A.$$

As one would expect, the bulk modulus depends only on the coefficients c_A (longitudinal stiffness of bond) and does not depend on the coefficients c_D (transverse stiffness).

4. Parameters of interatomic bonds

Crystals with cubic symmetry have three independent elastic moduli for which we can choose C_{11} , C_{12} and C_{44} . Let experimental values of these moduli be known. Then, given any two values and interatomic distance a , we can use formula (35) to determine the microscale characteristics of interatomic bonds — the coefficients c_A and c_D . Thus, the momentless macroscale characteristics of material allow us to find not only the pure force parameter of interatomic bond c_A , but also the coefficient c_D characterizing the transverse stiffness of interatomic bond and present only if moment interaction on the microscale is present. The value of the third elastic modulus can be used for estimation of the model error.

Table 2 presents experimental values of the elastic moduli of diamond, silicon, germanium and tin. As can be seen

Table 1
Dimensionless parameters for the diamond lattice

Parameters	d	M	η_c	M_κ	M_μ	$V_0 a^{-d}$
Values	3	4	∞	-8/9	4/9	$16\sqrt{3}/9$

Table 2
Experimental values of elastic moduli for crystals with diamond lattice (GPa)

Element	C_{11}	C_{12}	C_{44}	Source
C	1076	125	576	[11]
	1076	275	519	[12]
	1079	124	578	[13]
	1076	125	577	[14]
	1080	125	577	[15]
Si	168	65	80	[16]
	159	61	85	[17]
	160	57.8	80	[18]
	172	63	99	[19]
Ge	130	45	68	[17]
	126	44	67.7	[18]
	134	49	69	[20]
Sn	74.5	34.8	34	[18]

in the table, these values differ, at times greatly, from each other such that we can suggest only the most probable range of elastic constants.

Using the data of Table 2 for C_{11} , C_{12} and the interatomic distance α , formulae (35) give us the longitudinal and transverse stiffness coefficients of interatomic bonds in crystals given in Table 3. For example, the data from [11] and $\alpha = 0.154$ nm give the following values of stiffness of interatomic bonds in diamond crystals:

$$c_A = 472 \text{ N/m}, c_D = 338 \text{ N/m}. \quad (36)$$

According to the values in (36), the longitudinal to transverse stiffness ratio for bonds of carbon atoms in diamond crystals is equal to

$$c_D/c_A = 0.72. \quad (37)$$

The single value $c_D/c_A = 0.49$ obtained with the use of the experimental data from [12] is likely to be due to imperfection of the experiment in which the modulus C_{12} was found to be 275 GPa, which is suspiciously high. In silicon and germanium crystals, the interatomic distance is larger than that in diamond (0.235 and 0.245 nm, respectively) and the covalent bond is weaker. The ratio c_D/c_A for them lies between 0.34 and 0.39, which is much lower than that for diamond. Nevertheless, the transverse stiffness of bond is of significance and is to be taken into account. The difference in these values for silicon and germanium is within the experiment error. For tin with diamond lattice, the tendency is preserved: as the interatomic distance increases (0.281 nm), the effect of the transverse component of bond is weakened ($c_D/c_A = 0.28$).

Let us use the obtained longitudinal and transverse stiffness coefficients and formulae (35) to determine the value of the constant C_{44} (see Table 3). According to Table 3, experimental data that give no more than a 3% error in determination of C_{44} are available for each of the elements: diamond, silicon and germanium, and this fact counts in favor of the proposed model. However, the experimental data spread is fairly wide, resulting in a rather large deviation in the values of C_{44} . Possibly this owes to purely experimental errors.

Let us consider crystals with sphalerite structure. Sphalerite (zinc blende) possesses the geometric lattice of diamond; however, it consists of atoms of two different matters. The covalent bond is polar, which results from non-uniform electron density distribution due to differences in electronegativity of atoms. Let us demonstrate that the proposed procedure can be applied to advantage to this type of crystals, too. Table 4 presents experimental and calculation data for crystals with sphalerite structure. The experimental values of elastic moduli for boron nitride were taken

Table 3
Calculated values of elastic constants for crystals with diamond lattice

Element	c_A , N/m	c_D , N/m	c_D/c_A	$C_{44\text{exp}}$, GPa	$C_{44\text{cal}}$, GPa	Deviation, %
C, $a = 0.154$ nm	472	338	0.72	576	586	1.7
	578	285	0.49	519	605	17
	472	340	0.72	578	587	1.6
	472	340	0.72	577	586	1.6
	473	340	0.72	577	588	1.9
Si, $a = 0.235$ nm	162	55.9	0.35	80	91.4	14
	153	53.2	0.35	85	86.6	1.9
	150	55.5	0.37	80	88.0	10
	162	59.2	0.37	99	94.6	4.6
	159	54.3	0.34	80	89.0	11
Ge, $a = 0.245$ nm	125	48.1	0.39	68	71.9	5.8
	121	46.4	0.38	67	69.6	2.9
	131	48.1	0.37	69	73.6	6.6
Sb, $a = 0.281$ nm	93.4	25.7	0.28	34	38.4	13

Table 4

Experimental and calculated values of elastic constants for crystals with sphalerite lattice									
Element	a , nm	C_{11} , GPa	C_{12} , GPa	c_A , N/m	c_D , N/m	c_D/c_A	$C_{44\text{exp}}$, GPa	$C_{44\text{cal}}$, GPa	Deviation, %
BN	0.157	820.0	190.0	435	228	0.53	480	461	4.0
SiC	0.189	410.5	164.3	323	107	0.33	194	222	14
AlP	0.236	138.0	61.0	142	42.3	0.30	69.0	72.8	5.5
AlSb	0.266	89.4	44.3	109	27.7	0.25	41.6	44.9	8.1
GaP	0.236	141.1	63.5	146	42.3	0.29	70.3	73.7	4.8
GaAs	0.245	117.6	52.7	126	36.7	0.29	59.7	61.5	3.2
GaSb	0.264	88.4	40.3	104	29.4	0.28	43.2	46.0	6.5
InP	0.254	102.2	57.6	128	26.2	0.21	46.0	47.4	3.1
InAs	0.262	83.4	45.4	105	23.0	0.22	39.5	39.7	0.4
InSb	0.281	64.7	32.7	84.3	20.9	0.25	30.7	32.2	4.9
ZnS	0.235	97.6	59.0	117	20.9	0.18	45.1	42.6	5.5
ZnSe	0.245	80.3	45.1	96.7	20.0	0.21	39.9	37.4	6.2
ZnTe	0.264	71.1	40.7	92.9	18.5	0.2	31.3	32.6	4.2
CdS	0.253	73.3	50.9	102	13.0	0.13	30.2	26.8	11
CdTe	0.281	53.5	36.8	82.4	10.8	0.13	19.9	19.8	0.5

from [21]; those for the rest of the crystals, from [18]; and the data for interatomic distances, from [22]. The closest proximity to the elastic properties of diamond is found for boron nitride. It is seen from Table 4 that the interatomic distance in this element is somewhat larger (0.157 nm) and the transverse to longitudinal stiffness ratio of covalent bond is somewhat lower ($c_D/c_A = 0.53$) compared to those of diamond. The next element is silicon carbide ($a = 0.189$ nm, $c_D/c_A = 0.33$). However, in crystals with sphalerite structure, the interatomic bond is much more affected by ionization and metallization of covalent bond rather than by interatomic distance. As can be seen in Table 4, the ratio c_D/c_A varies from 0.13 to 0.3 while the interatomic distance varies slightly. For the majority of crystals (8 of 15), the deviation of the calculated values of C_{44} from the experimental values is no greater than 5 %. The maximum error for SiC is 14 %, which can be explained by a large experimental error for this crystal.

5. Conclusion

In the work, we proposed the mechanical model of a diatomic crystal lattice taking account of force and moment interactions. In the framework of the model, the expressions for the stiffness tensor and the relations between the macroscale elastic moduli and the microscale parameters of the longitudinal and transverse stiffnesses of interatomic bonds were derived. The proposed model was applied to describe the elastic properties of crystals with diamond and sphalerite lattices. For these crystals, the longitudinal and transverse stiffnesses of interatomic bonds were determined. The model error was estimated. The highest transverse to longitudinal stiffness ratio of interatomic bonds was found for diamond, $c_D/c_A = 0.72$, being indicative of strong co-

valent interaction and significance of the transverse stiffness. In the group of carbon (carbon, silicon, germanium and tin), the increase in interatomic distance causes weakening of the covalent interaction and a decrease in bond stiffness ratio: c_D/c_A for silicon, germanium and tin was about 1/3, which is lower than for carbon and yet it is not infinitesimal. Thus, the transverse stiffness of covalent bond is comparable with the longitudinal stiffness and is to be taken into account in description of covalent crystals.

In crystals with sphalerite structure, the covalent bond is affected, along with the interatomic distance, by nonuniform electron density distribution due to differences in electronegativity of atoms. Nevertheless the proposed model, in this case as well, does allow one to estimate the degree of covalence without introducing any correction terms into the formulae.

The foregoing suggests that the proposed moment model offers much universality, making possible a rather accurate unified description of elastic properties of a wide range of covalent crystals.

The work was supported by RFBR grant No. 11-01-00809-a and Program of the Presidium of RAS No. 11.

References

- [1] E.A. Ivanova, A.M. Krivtsov, N.F. Morozov, and A.D. Firsova, The description of particle crystalline packing in view of moment interactions, *Izv. RAN, MTT*, No. 4 (2003) 110 (*in Russian*).
- [2] E.A. Ivanova, A.M. Krivtsov, N.F. Morozov, and A.D. Firsova, *Theoretical Mechanics. The Description of Mechanical Properties of Crystalline Solids on Micro- and Macroscopic Level*, Izd-vo SPBSPU, St. Petersburg, 2004 (*in Russian*).
- [3] E.A. Ivanova, A.M. Krivtsov, and N.F. Morozov, Macroscopic elasticity relations of complicated crystal lattices in view of microscopic moment interactions, *Prikl. Mat. Mech.*, 71, No. 4 (2007) 595 (*in Russian*).

- [4] A.M. Krivtsov, *Elastic Properties of One- and Two-Atomic Crystals*, Izd-vo SPBSPU, St. Petersburg, 2009 (*in Russian*).
- [5] I.E. Berinskii, N.G. Dvas, A.M. Krivtsov, et al., *Theoretical Mechanics. Elastic Properties of One- and Two-Atomic Crystals*, Ed. by A.M. Krivtsov, Izd-vo SPBSPU, St. Petersburg, 2009 (*in Russian*).
- [6] I.E. Berinskii, Rod model of graphene crystal lattice, *Nauchn. Techn. Vedom. SPBSPU*, No. 3 (2010) 13 (*in Russian*).
- [7] V.A. Kuzkin and A.M. Krivtsov, Description of mechanical properties of graphene using particles with rotation degree of freedom, *DAN*, 440, No. 4 (2011) 476 (*in Russian*).
- [8] A.M. Krivtsov and E.A. Podolskaya, Modeling of elastic properties of HCP crystals, *Izv. RAN. MTT*, No. 3 (2010) 77 (*in Russian*).
- [9] R.V. Goldstein and A.V. Chentsov, Discrete-continual model of a nanotube, *Izv. RAN. MTT*, No. 4 (2005) 57 (*in Russian*).
- [10] I.E. Berinskii and A.M. Krivtsov, On the use of many-body interatomic potentials in calculations of elastic characteristics of graphene and diamond, *Izv. RAN. MTT*, No. 6 (2010) 60 (*in Russian*).
- [11] H.J. McSkimin and W.L. Bond, Elastic moduli of diamond, *Phys. Rev.*, 105 (1957) 116.
- [12] H.F. Markham, National Physical Laboratory measurements presented by M.J.P. Musgrave: *Diamond Conf.* (Reading, 1965) (unpublished).
- [13] H.J. McSkimin and P. Andreatch, Elastic moduli of diamond as a function of pressure and temperature, *J. Appl. Phys.*, 43 (1972) 2944.
- [14] M.H. Grimsditch and A.K. Ramdas, Brillouin scattering in diamond, *Phys. Rev. B*, 11, No. 10 (1975) 3139.
- [15] J.J. Gilman, Origins of the outstanding mechanical properties of diamond, *Mat. Res. Innovat.*, 6 (2002) 112.
- [16] G. Simmons and H. Wang, *Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook*, Cambridge, MA, MIT, 1971.
- [17] O.H. Nielsen and R. Martin, Stresses in semiconductors: Ab initio calculations on Si, Ge, and GaAs, *Phys. Rev. B*, 32 (1985) 3792.
- [18] S.P. Nikanorov and B.K. Kardashov, *Elasticity and Dislocation Inelasticity of Crystals*, Nauka, Moscow, 1985 (*in Russian*).
- [19] D.G. Clerc, Mechanical hardness: atomic-level calculations for diamond-like materials, *J. Mater. Sci. Lett.*, 17 (1990) 1461.
- [20] S. We, D.C. Allan, and J.W. Wilkins, Elastic constants of a Si/Ge superlattice and of bulk Si and Ge, *Phys. Rev. B*, 46 (1992) 12411.
- [21] M. Grimsditch, E.S. Zouboulis, and A. Polian, Elastic constants of boron nitride, *J. Appl. Phys.*, 76 (1994) 832.
- [22] D.M. Vasiliev, *Physical Crystallography*, Izd-vo SPBSPU, St. Petersburg, 1996 (*in Russian*).