
***Ab initio* Theory of Elastic Properties of Rare-Gas Crystals Under High Pressure**

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Abstract: The quantum mechanical model of deformable and polarizable atoms has been developed for the research of the elastic properties of rare-gas crystals Ne, Ar, Kr, and Xe over a wide range of pressure. It is shown that it is impossible to reproduce the observed deviation from the Cauchy relation $\delta(p)$ for Ne, Kr, Xe adequately taking into account the many-body interaction only. The individual dependence $\delta(p)$ for each of the crystals is the result of two competing interactions, namely, the many-body interaction and the electron-phonon interaction, which manifests itself in a quadrupole deformation of atoms electron shells due to displacements of the nuclei. The contributions of these interactions to Ne, Kr, and Xe compensated each other with high precision that provides δ with a positive value which is weakly dependent on pressure. In case of Ar the many-body interaction prevails. The compressed Ar has a negative deviation from the Cauchy relation the absolute value of which increases with the rise of pressure. The consideration of the quadrupole deformation is of great importance for heavy rare-gas crystals Kr and Xe. The represented *ab initio* calculated dependences of Birch elastic moduli $B_{ij}(p)$ and $\delta(p)$ are in good agreement with the experiment.

Keywords: Rare-Gas Crystals, High Pressure, Many-Body Interaction, Quadrupole Deformation of the Atomic Electron Shells

1. Introduction

Rare-gas crystals (RGS) are the simplest molecular crystals, that is why they are widely used as model objects when the theory is being tested. A large number of theoretical [1-9] and experimental [10-17] investigation of the elastic properties of RGS at high pressure are connected with their application as transmitting media in the diamond-anvil cells DAC [18]).

In 2009 the article by Sasaki et al. [10] was published. This article and other ones [11-13] has finished the series of the particularly accurate measurements elastic properties of RGS under pressure. Shimizu et al. [12] have determined a large deviation from the Cauchy relation (CR) δ for Ar in the range of pressures up to 70 GPa. These measurements have proved the fact that interatomic interaction in face-centered cubic rare-gas crystals cannot be described within

the framework of any models of the two-body potentials with the central interaction of atoms.

Usually, for crystals with any type of chemical bond (metals, dielectrics, semiconductors) the main reason for the deviation from the CR is considered to be non-pair interactions in crystals. Many attempts have been made to reach an agreement with experiment for theoretical values δ calculated in the framework of phenomenological, as well as microscopic descriptions of the non-pair forces (see, e.g., [1, 4, 7, and references therein]).

Within the framework of different models of the three-body interaction in RGS it is possible to successfully describe fcc-hcp transition [20, 21], equation of state [22, 1], elastic properties including the negative deviation from the Cauchy relation in RGS in the wide range of pressure [1-4, 7, and others]. In the work [10] Sasaki et al. sum up and discuss how well the nowadays theory describes the experiment concerning the deviation from Cauchy relation. In the

experiment the sequence $\delta_{Ne} > \delta_{Ar} > \delta_{Kr} > \delta_{Xe}$ for δ is observed at zero pressure only. With the rise of pressure, as experiment [10] showed, an individual dependence of δ on pressure can be observed, namely $\delta_{Ne} > \delta_{Kr} > \delta_{Xe} > \delta_{Ar}$ at $p \geq 10$ GPa. Sasaki *et al.* [10] mention that *ab initio* calculations in the density functional theory (DFT) [1] do not even qualitatively reproduce the deviation from the Cauchy relation $\delta(p)$. These calculations for δ show a negative pressure dependence for all RGS (Ne, Ar, Kr, Xe) with the coefficient directly proportional to the atomic weight of the elements.

This circumstance is associated with the fact that, apart from the many-body interactions, the violation of the Cauchy relation, as was shown for the first time by Herpin [23], is caused by the interactions related to the deformation of electron shells of the atoms. Herpin obtained the energy of atoms' interaction in the form of a series in powers of the distances between the pairs of the ions. The successive terms of this series are dipole, quadrupole, etc. bonds of the ions. Only the quadrupole terms lead to the violation of the CR for the crystals where each atom is the centre of the symmetry.

In this work, all the interactions which lead to the violation of the CR are researched *ab initio* within the framework of the theory of lattice dynamics with deformable atoms, which was developed by K. B. Tolpygo for ionic crystals [24, 25] and the rare-gas crystals [26].

In the quantum-mechanical model of polarizable and deformable ions by K. B. Tolpygo the crystal is considered as a set of N -point ions of Z valency (nucleus and internal electrons) and deformable shells, each of which consists of Z valent electrons interacting not only with ions but also among themselves. The similar shell model was brought forward by Dick and Overhauser [27] in 1958 and applied to homeopolar crystals by Cochran [28] in 1959. In this model, the atom was considered as consisting of a rigid core and rigid shell bound by quasi-elastic forces. The minimum quantity of parameters (for the elementary substances consisting of the same atoms) was four. They were defined from the comparison of the theory with the experimentally observed phonon spectrum.

In early works [26, 29, 30] (classical version of the model by K. B. Tolpygo) the parameters of the adiabatic potential were not calculated and could be found due to different experiments only. But these works have the common quantum-mechanical basis: the method implementing the adiabatic approximation and giving the general form of the adiabatic potential which parameters are expressed through the definite matrix elements of Hamiltonian of the electron subsystem on the atomic functions was offered. This research sets the problem to generalize the obtained results and to come to the wide range of questions which concern characteristics of the RGC lattice under pressure from the common point of view. Below, it will be shown that in this model, within a unified approach, allows one to obtain both the three-body short-range interaction and electron-phonon interaction related to the deformation of the atoms' electron shell due to displacement of the nuclei. To make establish the nature and ratio of the forces, which form the elastic

properties of the RGC under high pressures we use *ab initio* calculations dependencies of the functional dependencies and the values of the most important parameters which have been obtained by K. B. Tolpygo. As far as this system is many-electron, it is reasonable to choose the Hatree-Fock method as the basic analysis one. It is clearly formulated, precise enough and not very difficult for implementing on the modern computers [31].

The work is organized as follows. The method of the adiabatic potential of crystals with closed deformable shells and approximations which are in his basis is expounded in part 2. In part 3 the many-body interatomic potential was obtained and the simple form of the short-range three-body repulsive potential was offered. In part 4 expressions for Birch elastic moduli and the Cauchy relation with a glance at the three-body interaction and deformation of the electron shells are obtained. The calculation of the elastic properties, the comparison of our results for Ne, Ar, Kr, Xe with the experiment and other theories in the wide range of pressure are represented in part 5. In conclusions we summarize and discuss our results.

2. Deformation of Electron Shells in Lattice Vibrations and the Adiabatic Potential of the Crystal

Following the results obtained in [26, 32, 33], we derived the potential energy U of the lattice from the average Hamiltonian of the electron subsystem \bar{H} . For this purpose, we will minimize the Hamiltonian \bar{H} with respect to the parameters $c_i^l, c_{ij}^{ll'}$, describing the weak deformation of the electron wave function Ψ . Now, we define the weakly deformed (owing to the interatomic interaction and the displacement of the nuclei) "ground" state of the electrons

$$\Psi_0 = Ac \prod_l \psi^l, \quad \psi^l = c_0 \psi_0 + \sum_{i=1} c_i^l \psi_i^l; \quad (1)$$

where l is the number of the cell (atom), ψ_0^l is the ground state of the l -th individual atom, ψ_i^l is the i -th excited state of the l -th individual atom, and, $|c_i^l| \ll 1$. Then, we define the system of correlated doubly excited states

$$\Psi_{ij}^{ll'} = Ac \psi_i^l \psi_j^{l'} \prod_{l''} \psi^{l''}. \quad (2)$$

In state (2), the atoms l and l' are excited into the levels i and j , respectively, and the other atoms l'' are weakly deformed, as it is described by the function Ψ_0 (1). The state of the crystal will be sought in the form of a superposition of states (1) and (2)

$$\Psi = c_0 \Psi_0 + \frac{1}{2} \sum_{ll'ij} c_{ij}^{ll'} \Psi_{ij}^{ll'} \quad (3)$$

Now, we write the average Hamiltonian in the form

$$\bar{H} = \int \Psi^* \hat{H} \Psi d\tau \quad (4)$$

and substitute the function Ψ in the above formula from expression (3). Next, by minimizing the average Hamiltonian with respect to the coefficients c_i^l , $c_{ij}^{ll'}$ for arbitrary fixed displacements of the nuclei \mathbf{u}^l , arbitrary dipole moments of all atoms \mathbf{P}^l , and, in addition to [26], for arbitrary quadrupole $Q_{\alpha\beta}^l$ moments

$$\left. \begin{aligned} \mathbf{P}^l &= \sum_i e \int \mathbf{r}_i |\psi^l|^2 d\tau = const \\ Q_{\alpha\beta}^l &= \sum_i e \int (3x_\alpha x_\beta - \delta_{\alpha\beta} r^2) |\psi^l|^2 d\tau = const \end{aligned} \right\} \quad (5)$$

we express the relative minimum of the potential energy $U = \min \bar{H}$ in the function of all the quantities \mathbf{u}^l , \mathbf{P}^l , $Q_{\alpha\beta}^l$. Then, the equations of lattice vibrations can be written as

$$m \ddot{u}_\alpha^l = -\frac{\partial U}{\partial u_\alpha^l}, \quad \frac{\partial U}{\partial P_\alpha^l} = 0, \quad \frac{\partial U}{\partial Q_{\alpha\beta}^l} = 0. \quad (6)$$

Expression for U we will obtain in the form of (for more details see works [26, 32])

$$U = \min \bar{H} = const + \sum_l \left\{ \frac{(\mathbf{P}^l)^2}{2\alpha} + \frac{1}{2} \sum_{\alpha\beta} \frac{1}{2\beta_{44}} (Q_{\alpha\beta}^l)^2 + \right. \\ \left. \mathbf{P}^l \cdot \mathbf{P}^l + \frac{1}{2} \sum_{\alpha\beta} D_{\alpha\beta}^l Q_{\alpha\beta}^l - \frac{1}{2} \sum_r \left[\frac{C}{|\mathbf{r}^l - \mathbf{r}^r|^6} + \frac{C'}{|\mathbf{r}^l - \mathbf{r}^r|^8} + \frac{C''}{|\mathbf{r}^l - \mathbf{r}^r|^{10}} \right] + \right. \\ \left. \frac{1}{2} \sum_r K(\mathbf{P}^l, Q_{\alpha\beta}^l, \mathbf{P}^r, Q_{\alpha\beta}^r) + \frac{1}{2} \sum_r^{n.n.} U_{sr}(|\mathbf{r}^l - \mathbf{r}^r|) \right\} \quad (7)$$

Here, the first four terms describe the deformation of electron shells (α and β_{44} are the coefficients of the dipole and quadrupole polarizabilities). The next three terms describe the van der Waals forces, and K characterizes the Coulomb (in the classical sense) interaction of all the dipoles and quadrupoles with each other. Finally, the short-range forces are determined by the formula

$$\sum_r^{n.n.} U_{sr}(|\mathbf{r}^l - \mathbf{r}^r|) = \sum_r \left\langle \psi_0^l \psi_0^r \left| \hat{H}_{sr}^{ll'} \right| \psi_0^l \psi_0^r \right\rangle + \alpha (\mathbf{P}^l)^2 + \sum_{\alpha\beta}^9 \beta_{44} (D_{\alpha\beta}^l)^2 - 2 \left(\sum_i \frac{1}{E_i - E_0} \sum_r \left\langle \psi_0^l \psi_0^r \left| \hat{H}_{sr}^{ll'} \right| \psi_i^l \psi_0^r \right\rangle \right)^2 \quad (8)$$

Here, $\sum_{\alpha\beta}^9$ means that it is necessary to iterate over all nine combinations of the indices α, β (although among all the nine components $Q_{\alpha\beta}^l$, only five components are independent); $\sum_r^{n.n.}$ denotes the summation over the nearest neighbors; ψ_0^l, E_0^l and ψ_i^l, E_i^l are wave function and energies of the ground and i -th excited state of the l -atom.

$$\mathbf{P}^l = \frac{1}{\alpha} \sum_i \sum_r^{n.n.} \frac{\langle \psi_0^l | \mathbf{P}^l | \psi_i^l \rangle \langle \psi_i^l \psi_0^r | \hat{H}_{sr}^{ll'} | \psi_0^l \psi_0^r \rangle + c.c.}{E_i - E_0}, \\ D_{\alpha\beta}^l = \frac{1}{\beta_{44}} \sum_i \sum_r^{n.n.} \frac{\langle \psi_0^l | \hat{Q}_{\alpha\beta}^l | \psi_i^l \rangle \langle \psi_i^l \psi_0^r | \hat{H}_{sr}^{ll'} | \psi_0^l \psi_0^r \rangle + c.c.}{E_i - E_0}. \quad (9)$$

The matrix elements of the dipole and quadrupole moments are given by the expressions:

$$\langle \psi_0^l | \mathbf{P}^l | \psi_i^l \rangle = \int \psi_0^l \mathbf{P}^l \psi_i^l d\tau, \\ \langle \psi_0^l | \hat{Q}_{\alpha\beta}^l | \psi_i^l \rangle = \int \psi_0^l \hat{Q}_{\alpha\beta}^l \psi_i^l d\tau. \quad (10)$$

$$\langle \psi_i^l \psi_0^l | \hat{H}_{sr}^{ll'} | \psi_0^l \psi_0^r \rangle = \int \hat{H}_{sr}^{ll'}(\mathbf{r}, \mathbf{r}') \left(1 - \frac{1}{2} \hat{R}_{12} \right) \left[\begin{array}{l} \psi_i^l(\mathbf{r} \dots) \psi_0^l(\mathbf{r}' \dots) \\ \psi_0^l(\mathbf{r} \dots) \psi_i^l(\mathbf{r}' \dots) \end{array} \right] d\tau d\tau', \quad (11)$$

where \hat{R}_{12} is interchange operator of the electrons \mathbf{r}, \mathbf{r}' .

3. *Ab initio* Short-Range Many-Body Repulsive Potential

Adhering to [34, 35]. Let us consider the first term in expression (8). It should be noted that the wave functions of atoms $\psi_0^l(\mathbf{r}_1, \mathbf{r}_2 \dots)$ are the many-electron wave functions; however, in the one-electron approximation, these functions can be represented in the form of determinants constructed using the wave functions of electrons of an individual atom so that they satisfy the Hartree-Fock equation (Hartree-Fock approximation).

The expression written for the energy of short-range repulsion of atoms in the crystals in terms of the electron

orbitals of individual atoms $|\mathbf{l}\mathbf{s}\rangle$ and the orthogonalizing matrix \mathbf{P} has the form

$$E_{sr} = E^{(0)} + \Delta E(\mathbf{P}) + \Delta E(\mathbf{P}^2), \quad (12)$$

where $E^{(0)}$ is the interatomic interaction energy without regard for the orthogonalization of the orbitals of the nearest neighbor atoms, $\Delta E(\mathbf{P})$ is the orthogonalization correction linear in \mathbf{P} , and $\Delta E(\mathbf{P}^2)$ is the orthogonalization correction quadratic in \mathbf{P} . In expression (12) for the energy E_{sr} , the energy $E^{(0)}$ is given by

$$E^{(0)} = \sum_{\mathbf{l}} E_a^{\mathbf{l}} + \sum'_{\mathbf{l}, \mathbf{m}} \langle \mathbf{l}\mathbf{s} | V_{en}^{\mathbf{m}} + V_0^{\mathbf{m}} + V_{ex}^{\mathbf{m}} | \mathbf{l}\mathbf{s} \rangle, \quad (13)$$

Here, the prime of the sum sign denotes that $\mathbf{m} \neq \mathbf{l}$; further in the text, $\mathbf{l} \neq \mathbf{l}' \neq \mathbf{m}$ and $\mathbf{l} \neq \mathbf{l}' \neq \mathbf{m} \neq \mathbf{m}'$.

The first term in expression (13) is the sum of energies of individual atoms, which does not depend on the interatomic distances in the crystal. It can be included in the energy origin. The second term in expression (13) consists of two-center integrals, i.e., the matrix elements of the potential of the electron-ion interaction $V_{en}^{\mathbf{m}}$, the potential of the neutral individual atom $V_0^{\mathbf{m}}$, and the potential of the exchange interatomic interaction $V_{ex}^{\mathbf{m}}$ constructed using the atomic orbitals $|\mathbf{l}\mathbf{s}\rangle$.

The orthogonalization correction to the crystal energy, which is defined by expression (12) and is linear in \mathbf{P} , has the form

$$\begin{aligned} \Delta E(\mathbf{P}) = & -2 \sum_{\mathbf{l}\mathbf{l}'} \sum_{ss'} P_{ss'}^{\mathbf{l}\mathbf{l}'} (I - S)_{s's}^{\mathbf{l}\mathbf{l}'} \varepsilon_{\mathbf{l}\mathbf{s}} - \\ & 2 \sum_{\mathbf{l}\mathbf{l}'} \sum_{ss'} P_{ss'}^{\mathbf{l}\mathbf{l}'} \langle \mathbf{l}'\mathbf{s}' | V_0^{\mathbf{l}} + V_{ex}^{\mathbf{l}} | \mathbf{l}\mathbf{s} \rangle - \\ & 2 \sum_{\mathbf{l}\mathbf{s}\mathbf{s}'} P_{ss'}^{\mathbf{l}\mathbf{l}'} \langle \mathbf{l}\mathbf{s}' | \sum_{\mathbf{m} \neq \mathbf{l}} (\mathbf{v}_0^{\mathbf{m}} + \mathbf{v}_{ex}^{\mathbf{m}}) | \mathbf{l}\mathbf{s} \rangle - \\ & 2 \sum_{\mathbf{l}\mathbf{l}'} \sum_{ss'} P_{ss'}^{\mathbf{l}\mathbf{l}'} \langle \mathbf{l}'\mathbf{s}' | \sum_{\mathbf{m} \neq \mathbf{l}, \mathbf{m}' \neq \mathbf{l}'} V_0^{\mathbf{m}} + V_{ex}^{\mathbf{m}} | \mathbf{l}\mathbf{s} \rangle. \end{aligned} \quad (14)$$

where $\varepsilon_{\mathbf{l}\mathbf{s}}$ is the energy of the Hartree-Fock orbital $\varphi_s(\mathbf{r}-\mathbf{l})$.

The orthogonalization correction to the crystal energy, which is defined by expression (12) and is quadratic in \mathbf{P} , has the form

$$\Delta E(\mathbf{P}^2) = 2 \sum_{\mathbf{l}\mathbf{l}'\mathbf{m}\mathbf{m}'} \sum_{ss'tt'} P_{ss'}^{\mathbf{l}\mathbf{l}'} P_{tt'}^{\mathbf{m}\mathbf{m}'} \left\{ \begin{aligned} & 2 \langle \mathbf{l}'\mathbf{s}'\mathbf{m}'\mathbf{t}' | v_C | \mathbf{m}\mathbf{l}\mathbf{s} \rangle \\ & - \langle \mathbf{l}'\mathbf{s}'\mathbf{m}'\mathbf{t}' | v_C | \mathbf{l}\mathbf{s}\mathbf{m}\mathbf{t} \rangle \end{aligned} \right\} \quad (15)$$

We analyze the behavior of different terms in expressions (13)-(15) for the crystal under compression. Following [34-36], the modulus of the largest overlap integral S of the electron wave functions of the nearest neighbor atoms is chosen as the small parameter for evaluations. The calculation performed in [36] demonstrated that the expansion in S for the energy $E^{(0)}$ (13) begins with S^2 . The expansion of the elements of the matrix $\mathbf{P} = \mathbf{I} - (\mathbf{I} + \mathbf{S})^{-1}$ in powers of the matrix of overlap integrals S , has the form

$$P_{ss'}^{\mathbf{l}\mathbf{l}'} = S_{ss'}^{\mathbf{l}\mathbf{l}'} + O(S^2), \quad P_{ss'}^{\mathbf{l}\mathbf{l}'} = -(S^2)_{ss'}^{\mathbf{l}\mathbf{l}'} + O(S^3). \quad (16)$$

Then, expression (12) for the energy E_{sr} for electrons of the crystal can be written as the expansion in powers of the overlap integrals S

$$\begin{aligned} E_{sr} = & \frac{1}{2} \sum_{\mathbf{l}\mathbf{l}'}^{n,n} U_{sr}(\mathbf{r}^{\mathbf{l}} - \mathbf{r}^{\mathbf{l}'}) = E^{(0)}(S^2) + W_2(S^2) + \\ & W_3(S^3) + W_4(S^4) + W_5(S^5) + W_6(S^6) \end{aligned} \quad (17)$$

Here, W_2 is the orthogonalization correction quadratic in S

$$\begin{aligned} W_2 = & -2 \sum_{\mathbf{l}\mathbf{l}'} \sum_{ss'} P_{ss'}^{\mathbf{l}\mathbf{l}'} \langle \mathbf{l}'\mathbf{s}' | V_0^{\mathbf{l}} + V_{ex}^{\mathbf{l}} | \mathbf{l}\mathbf{s} \rangle - \\ & \sum_{\mathbf{l}\mathbf{m}} \sum_{ss'tt'} P_{ss'}^{\mathbf{l}\mathbf{l}'} P_{tt'}^{\mathbf{m}\mathbf{m}'} \langle \mathbf{l}\mathbf{s}'\mathbf{m}\mathbf{t}' | v_C | \mathbf{m}\mathbf{l}\mathbf{s}\mathbf{t} \rangle, \end{aligned} \quad (18)$$

where

$$\begin{aligned} \langle \mathbf{l}\mathbf{s}\mathbf{m}\mathbf{t} | v_C | \mathbf{m}\mathbf{l}\mathbf{s}\mathbf{t} \rangle = & \int \left(\begin{aligned} & \varphi_s^*(\mathbf{r}-\mathbf{l}) \varphi_t^*(\mathbf{r}'-\mathbf{m}) \\ & v_C(\mathbf{r}-\mathbf{r}') \varphi_s(\mathbf{r}'-\mathbf{m}) \\ & \varphi_t(\mathbf{r}-\mathbf{l}) d\mathbf{r} d\mathbf{r}' \end{aligned} \right), \\ v_C(\mathbf{r}-\mathbf{r}') = & \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}. \end{aligned}$$

The correction W_2 contains only the three-center integrals and corresponds to the two-body interactions in the crystal. The term W_3 is the third order correction in S , which contains the three-center integrals

$$\begin{aligned} W_3 = & -2 \sum_{\mathbf{l}\mathbf{l}'} \sum_{ss'} P_{ss'}^{\mathbf{l}\mathbf{l}'} (I - S)_{s's}^{\mathbf{l}\mathbf{l}'} \varepsilon_{\mathbf{l}\mathbf{s}} - \\ & 2 \sum_{\mathbf{l}\mathbf{l}'} \sum_{ss'} P_{ss'}^{\mathbf{l}\mathbf{l}'} \langle \mathbf{l}'\mathbf{s}' | \sum_{\mathbf{m} \neq \mathbf{l}, \mathbf{m}' \neq \mathbf{l}'} (V_0^{\mathbf{m}} + V_{ex}^{\mathbf{m}}) | \mathbf{l}\mathbf{s} \rangle - \\ & 2 \sum_{\mathbf{l}\mathbf{m}} \sum_{ss'tt'} P_{ss'}^{\mathbf{l}\mathbf{l}'} P_{tt'}^{\mathbf{m}\mathbf{m}'} \langle \mathbf{l}'\mathbf{s}'\mathbf{m}'\mathbf{t}' | v_C | \mathbf{l}\mathbf{s}\mathbf{l}'\mathbf{t} \rangle. \end{aligned} \quad (19)$$

The term W_4 is the fourth-order correction in S of the

mixed type

$$\begin{aligned}
 W_4 = & \sum_{\mathbf{l}} \sum_{ss'tt'} P_{ss'}^{\mathbf{ll}} P_{tt'}^{\mathbf{ll}} \left\{ \frac{2 \langle \mathbf{l}s' \mathbf{l}'t' | v_C | \mathbf{l}t \mathbf{l}s \rangle - \langle \mathbf{l}s' \mathbf{l}'t' | v_C | \mathbf{l}s \mathbf{l}t \rangle}{\langle \mathbf{l}s' \mathbf{l}'t' | v_C | \mathbf{l}t \mathbf{l}s \rangle} \right\} - \\
 & 2 \sum_{\mathbf{l}s's'} P_{ss'}^{\mathbf{ll}} \left\langle \mathbf{l}s' \left| \sum_{\mathbf{m} \neq \mathbf{l}} (V_0^{\mathbf{m}} + V_{ex}^{\mathbf{m}}) \right| \mathbf{l}s \right\rangle + \\
 & 2 \sum_{\mathbf{l}\mathbf{m}} \sum_{ss'tt'} \left\{ \frac{P_{ss'}^{\mathbf{ll}} P_{tt'}^{\mathbf{mm}} \langle \mathbf{l}s' \mathbf{m}t' | v_C | \mathbf{m}t \mathbf{l}s \rangle + P_{ss'}^{\mathbf{ml}} P_{tt'}^{\mathbf{lm}} \langle \mathbf{l}s' \mathbf{m}t' | v_C | \mathbf{l}t \mathbf{m}s \rangle}{\langle \mathbf{l}s' \mathbf{m}t' | v_C | \mathbf{m}t \mathbf{l}s \rangle} \right\} + \\
 & \sum_{\mathbf{l}\mathbf{m}} \sum_{ss'tt'} P_{ss'}^{\mathbf{ml}} P_{tt'}^{\mathbf{ml}} \left\{ \frac{2 \langle \mathbf{l}s' \mathbf{l}'t' | v_C | \mathbf{m}t \mathbf{m}s \rangle - \langle \mathbf{l}s' \mathbf{l}'t' | v_C | \mathbf{m}s \mathbf{m}t \rangle}{\langle \mathbf{l}s' \mathbf{l}'t' | v_C | \mathbf{m}t \mathbf{m}s \rangle} \right\} + \\
 & 4 \sum_{\mathbf{l}\mathbf{m}} \sum_{ss'tt'} P_{ss'}^{\mathbf{ml}} P_{tt'}^{\mathbf{ll}} \left\{ \frac{2 \langle \mathbf{l}s' \mathbf{l}'t' | v_C | \mathbf{l}t \mathbf{m}s \rangle - \langle \mathbf{l}s' \mathbf{l}'t' | v_C | \mathbf{m}s \mathbf{l}t \rangle}{\langle \mathbf{l}s' \mathbf{l}'t' | v_C | \mathbf{l}t \mathbf{m}s \rangle} \right\} + \\
 & 4 \sum_{\mathbf{l}\mathbf{l}'\mathbf{m}} \sum_{ss'tt'} \left\{ \frac{P_{ss'}^{\mathbf{ll}'} P_{tt'}^{\mathbf{mm}'} \langle \mathbf{l}'s' \mathbf{m}t' | v_C | \mathbf{m}t \mathbf{l}s \rangle + P_{ss'}^{\mathbf{ll}'} P_{tt'}^{\mathbf{m}'} \langle \mathbf{l}'s' \mathbf{m}t' | v_C | \mathbf{l}'t \mathbf{l}s \rangle}{\langle \mathbf{l}'s' \mathbf{m}t' | v_C | \mathbf{m}t \mathbf{l}s \rangle} \right\} + \\
 & 2 \sum_{\mathbf{l}\mathbf{l}'\mathbf{m}} \sum_{ss'tt'} P_{ss'}^{\mathbf{ll}'} P_{tt'}^{\mathbf{lm}'} \left\{ \frac{2 \langle \mathbf{l}'s' \mathbf{m}t' | v_C | \mathbf{l}t \mathbf{l}s \rangle - \langle \mathbf{l}'s' \mathbf{m}t' | v_C | \mathbf{l}s \mathbf{l}t \rangle}{\langle \mathbf{l}'s' \mathbf{m}t' | v_C | \mathbf{l}t \mathbf{l}s \rangle} \right\} + \\
 & \sum_{\mathbf{l}\mathbf{l}'\mathbf{m}\mathbf{m}'} \sum_{ss'tt'} P_{ss'}^{\mathbf{ll}'} P_{tt'}^{\mathbf{mm}'} \left\{ \frac{2 \langle \mathbf{l}'s' \mathbf{m}'t' | v_C | \mathbf{m}t \mathbf{l}s \rangle - \langle \mathbf{l}'s' \mathbf{m}'t' | v_C | \mathbf{l}s \mathbf{m}t \rangle}{\langle \mathbf{l}'s' \mathbf{m}'t' | v_C | \mathbf{m}t \mathbf{l}s \rangle} \right\}
 \end{aligned} \tag{20}$$

Similarly to W_5 , W_6 (for more details see [34, 35]).

The results of the calculations of the two-center integrals with the use of the tables presented in [37] are reported in our recent paper [38]. The regularities revealed in these calculations are conveniently used in approximating the three-center and four-center integrals whose dimensionality cannot be reduced according to the procedure proposed in [36]. In work [35] the approximate form of the three-body interaction in case when atoms l, l', l'' create the equilateral triangle is obtained:

$$\begin{aligned}
 W_3 = & - \sum_{ll'l''} \left(S(r^{ll''}) \right)^2 f \left(\left| \mathbf{r}^{l'} - \frac{1}{2} \mathbf{r}^{ll''} \right| \right), \\
 f \left(\left| \mathbf{r}^{l'} - \frac{1}{2} \mathbf{r}^{ll''} \right| \right) = & \frac{S \left(\left| \mathbf{r}^{l'} - \frac{1}{2} \mathbf{r}^{ll''} \right| \right)}{\left| \mathbf{r}^{l'} - \frac{1}{2} \mathbf{r}^{ll''} \right|}, \tag{21}
 \end{aligned}$$

where $S = S_{np_z np_z}^{ll'}$ is the largest overlap integral between the outer p-orbital of the electrons.

In Fig. 1 [22, 39-41] we present our short-range potentials, i.e., the two-body potential $V_{sr} = E^{(0)} + W_2(S^2)$ and the three-body potential W_3 , as well as the best empirical potentials as a function of the interatomic distance

$d = |\mathbf{r}^{ll'}| = a\sqrt{2}$, where a is one-half the cube edge (see. [22] and references therein).

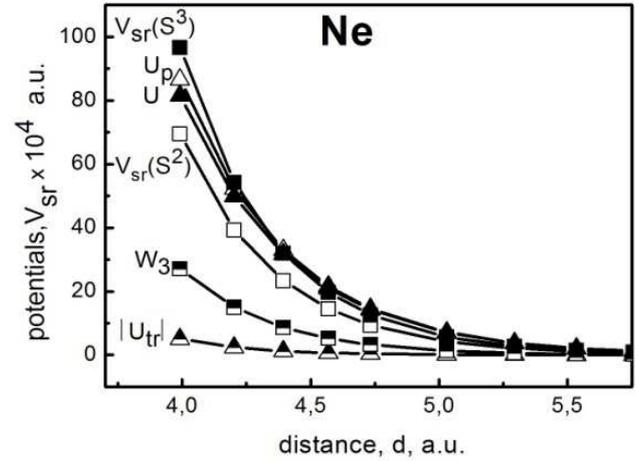


Fig. 1. Interatomic short-range potentials in Ne. $V_{sr}(S^3) = V_{sr}(S^2) + W_3$ is the present calculation; W_3 is the present calculation of the three-body potential (see (21)); $V_{sr}(S^2) = E^{(0)} + W_2(S^2)$ is the pair potential; U_p is the short-range part of the Aziz-Slaman pair potential [39, 40]; $|U_{tr}|$ is the short-range part of the Slater-Kirkwood three-body potential $|U_{tr}| = A \exp[-\alpha_{tr}(3a\sqrt{2})] \times (1 + 3 \cos^3 \pi/3)$ [22, 41]; U is the total potential $U = U_p - |U_{tr}|$.

As can be seen from Fig. 1, our pair potential $V_{sr} = E^{(0)} + W_2(S^2)$, calculated accurate to S^2 agrees fairly well with the best empirical Aziz-Slaman pair potential U_p [39, 40]. The three-body potential $W_3(S^3)$ (21) calculated by us and Slater-Kirkwood three-body potential $|U_{tr}| = A \exp[-\alpha_{tr}(3a\sqrt{2})] \times (1 + 3 \cos^3 \frac{\pi}{3})$ [41] and also corresponding sums are in good agreement with each other.

4. Birch Elastic Moduli and the Cauchy Relation in the Model of Deformable Atoms

Using the method of long waves [42] from equations of oscillations ([43] and references there), we can find expressions for the Birch elastic moduli B_{ij} , which are valid at any pressures [19, 44-46], taking into account the short-range three-body forces and the quadrupole deformation of the atoms electron shells. The long-range three-body forces [47] and the contribution of a quadrupole interaction to the van der Waals forces in compressed crystals at high pressures are less important; therefore, they are not presented in further expressions.

Then, the Birch elastic moduli B_{ij} can be written in a form

$$\begin{aligned}
B_{11} &= \frac{e^2}{2a^4} \left[G + H + 2F + 2E - \frac{2}{3}V_q - 0.980677B \right]; \\
B_{12} &= \frac{e^2}{2a^4} \left[\frac{1}{2}G - H - 2F + \frac{1}{3}V_q - \frac{1}{2}V_t - 0.864715B \right]; \quad (22) \\
B_{44} &= \frac{e^2}{2a^4} \left[\frac{1}{2}G + H + 2F - \frac{1}{2}T + \frac{1}{2}V_t - 0.26247B \right].
\end{aligned}$$

Here, we introduce the following dimensionless parameters of the short-range forces between the nearest neighbors.

$$\begin{aligned}
H &= H_0 + \delta H = \frac{4a^3}{e^2} \frac{1}{r_0} \frac{dV_{sr}}{dr} \Big|_{r_0} + \delta H; \\
G &= G_0 + \delta G = \frac{2a^3}{e^2} \left[\frac{d^2V_{sr}}{dr^2} \Big|_{r_0} - \frac{1}{r_0} \frac{dV_{sr}}{dr} \Big|_{r_0} \right] + \delta G, \quad (23)
\end{aligned}$$

the parameters of the short-range forces between the second neighbors F , E and the van der Waals parameter B are as follows:

$$F = H_0(2a); \quad E = G_0(2a); \quad B = \frac{6C}{a^5 e^2}. \quad (24)$$

Three-body corrections δH and δG , which lead to noncentricity of the pair interaction, are obtained on the basis of the expression for W_3 (21), have the form:

$$\delta H = -\frac{16a^3}{e^2} S(r_0) \left[\frac{2S_2(r_0)f(\eta) + 3S(r_0)f_2(\eta) - 2S_1(r_0)f_1(\eta)}{3S(r_0)f_2(\eta) - 2S_1(r_0)f_1(\eta)} \right] \quad (25)$$

$$\delta G = -\frac{16a^3}{e^2} \left[\frac{2S(r_0)S_3(r_0)f(\eta) + S_1^2(r_0)f(\eta) + 4S(r_0)S_1(r_0)f_1(\eta) + 9S^2(r_0)f_3(\eta)}{9S^2(r_0)f_3(\eta)} \right], \quad (26)$$

where $r_0 = a\sqrt{2}$ is a distance between the nearest neighbors, and $\eta = a\sqrt{6}/2$, e is the elementary charge, S_1, S_2, S_3 are expressed through the first and second derivatives of the overlap integral $S(r)$ with respect to argument modulus.

The expressions of these functions have the following form:

$$\begin{aligned}
S_1(r) &= \frac{a}{r} \frac{dS(r)}{dr}, \quad S_2(r) = \frac{1}{2r} \frac{dS(r)}{dr}, \\
S_3(r) &= \frac{1}{2r} \left(\frac{d^2S(r)}{dr^2} - \frac{1}{r} \left(\frac{dS(r)}{dr} \right) \right).
\end{aligned}$$

Similarly to f_1, f_2, f_3 .

The three-body interaction parameter can be represented in the form:

$$V_t = 64 \frac{a^3}{e^2} \left[S(r) \frac{a}{r_0} \frac{dS(r_0)}{dr_0} \right]_{r_0=a\sqrt{2}} \left[\frac{a}{R} \frac{df(\eta)}{dR} \right]_{R=a\sqrt{6}}. \quad (27)$$

The quadrupole interaction parameters V_q, T and dimensionless polarizability b have the form [43]:

$$V_q = \frac{b(2W - U)^2}{1 + 0.32673 \cdot b}; \quad T = \frac{8bW^2}{1 - 0.0661 \cdot b}; \quad b = \frac{2\beta_{44}}{a^5} \quad (28)$$

Here, W and U are expressed through the single different from zero tensor component $D_{\alpha\beta}^I$ (9)

$$\begin{aligned}
U &= \frac{1}{e} \left[\frac{a}{\sqrt{2}} \frac{dD_{xx}(r)}{dr} \Big|_{r_0} - D_{xx}(r_0) \right]; \\
W &= \frac{1}{e} \left[\frac{a}{\sqrt{2}} \frac{dD_{xx}(r)}{dr} \Big|_{r_0} + D_{xx}(r_0) \right]. \quad (29)
\end{aligned}$$

In this case, the deviation from the Cauchy relation, which is written through the Birch moduli, will not contain the pair interaction parameters (H_0, G_0, B):

$$\begin{aligned}
\delta &= B_{12} - B_{44} - 2p = \frac{e^2}{2a^4} \left[2\delta H - V_t + \frac{1}{2}T + \frac{1}{3}V_q - 4R_t \right]; \\
\delta_t &= \frac{e^2}{2a^4} [2\delta H - V_t - 4R_t], \quad R_t = -\frac{a^2}{6e^2} \frac{dW_3(a)}{da} > 0 \quad (30)
\end{aligned}$$

δ_t is the deviation from the CR only due to the three-body interaction. In terms of the expressions (25)-(27) and the fact that overlap integral of the outer p-orbitals is $S < 0$ we obtain $\delta G > 0$, $\delta H < 0$, $V_t < 0$ for all RGS under any pressure. The quadrupole interaction parameters, we have $V_q > 0$, $T > 0$ by definition (28). Thus, it is difficult to make an estimate of value and sign δ_t , and also it is difficult to make an estimate of the general meaning of deviation from the Cauchy relation δ . The explicit calculation for each crystal series Ne-Xe will give the individual dependence $\delta(p)$. It will allow defining the nature and correlation of forces forming the elastic properties under high pressures.

5. The Calculation of the Elastic Properties of RGC Under Pressure

It is seen from (28), (29), that compression dependence of V_q, T are determined by the matrix element $\langle \psi_i^l \psi_0^l | \hat{H}_{sr}^{ll'} | \psi_0^l \psi_0^l \rangle$, which can be expressed in terms of the matrix elements of the one-electron wave functions:

$$D_{\alpha\beta} \llcorner \langle \psi_i^l \psi_0^l | \hat{H}_{sr}^{ll'} | \psi_0^l \psi_0^l \rangle \llcorner \llcorner E^{(0)} + W_2 = V_{sr}.$$

Following, we accept [33, 43]

$$V_{sr} \approx A_i \frac{S^2(r^{ll'})}{|r^{ll'}|}, \quad (31)$$

where $|r^{ll'}|$ is a distance between atoms l and l' (for nearest neighbors, $|r^{ll'}| = a\sqrt{2}$), A_i is some coefficient which is weakly dependent on pressure [48].

Let us find parameters V_q and T by formulas (28), (29), using functional dependence (31)

$$V_q = L_1 \left(S \frac{dS}{dR} + \frac{5}{2} \frac{S^2}{R} \right)^2, \quad (32)$$

$$T = 8L_2 \left(S \frac{dS}{dR} + \frac{1}{2} \frac{S^2}{R} \right)^2 \quad (33)$$

where L_1 and L_2 are dimensionless coefficients containing dimensionless polarizability b which weakly depends on compression.

We set $T = 8V_q$. In this case, we neglect terms $O(S^4)$, as far as at consideration of the many-body interaction (17) we have used the term W_3 . Then the deviation from the CR due to the quadrupole deformation of the electron shell δ_q will take a form

$$\delta_q(p) = \frac{13}{3} \frac{e^2}{2a^4} V_q(p); \quad V_q(p) = A_i V_q^0 \frac{S^2 / |r^{ll'}|}{S_0^2 / (a_0 \sqrt{2})},$$

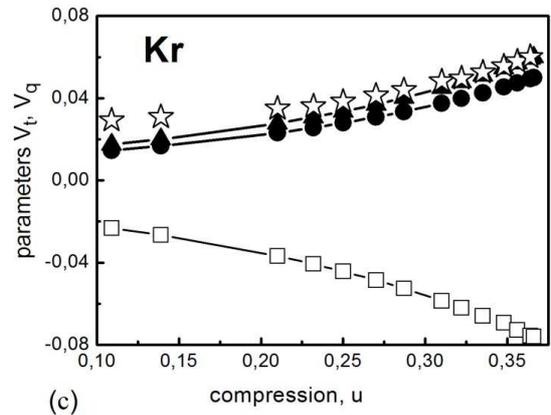
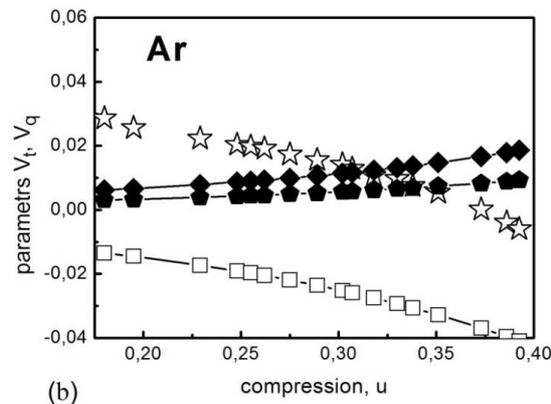
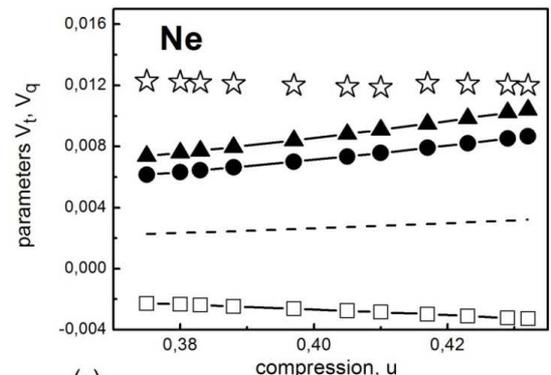
where V_q^0 and S_0 are the parameter of the quadrupole deformation of atomic electron shells and the overlap integral for $p=0$ accordingly.

Till now, the theory has not included fitting parameters since we could calculate all parameters of the two-body interaction (H_0, G_0, F, E) and the three-body interaction ($\delta H, \delta G, V_t, R_t$) with sufficient accuracy individually for each crystal of the series Ne-Xe. We found the functional dependence for the quadrupole parameter V_q but it seems to be impossible to determine its absolute value now (i.e., coefficients L, L_1 , and L_2) based on formulas (28), (29), (9). Therefore, we suggest to take the initial value of the parameter V_q^0 ($p \approx 0$) from experimental δ_{exp}^0 .

$$V_q^{\text{exp}} = \frac{3}{13} \frac{2a^4}{e^2} (\delta_{\text{exp}}^0 - \delta_t), \quad V_q^0 = V_q^{\text{exp}}. \quad (34)$$

In the case of lack of experimental values of δ_{exp}^0 , we can use exactly calculated parameter V_t and accept $V_q^0 = |V_t^0|$.

Figure 2 (a, b, c, d) shows the three-body interaction parameter V_t and the quadrupole parameter V_q for variation in A_i (31), depending on compression $u = \Delta V / V_0$ ($\Delta V = V_0 - V(p)$, where V_0 is volume as $p=0$), for Ne, Ar, Kr, Xe accordingly. The best possible fit with V_q^{exp} comes out when $A_i = 0.45$ for Xe and $A_i = 0.6$ for Kr. In case of light RGC such kind of the best agreement of the calculated $V_q(p)$ and $V_q^{\text{exp}}(p)$ cannot be observed. For the further calculations we choose $A_i = 0.5$ for Ne and $A_i = 0.1$ for Ar.



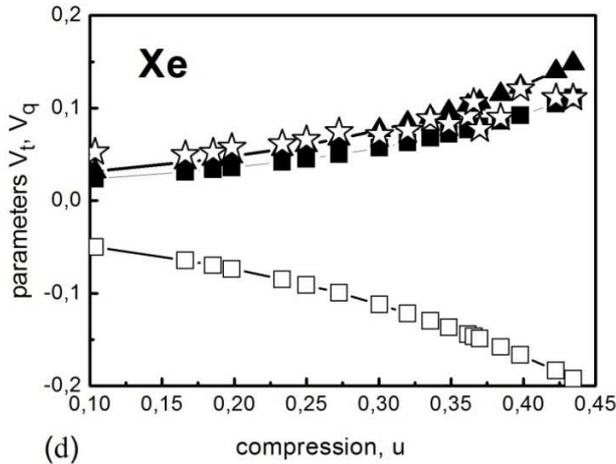


Fig. 2. Dependence of the three-body interaction parameter V_t and the quadrupole interaction parameter V_q on different coefficients A_i from compression for (a) Ne, (b) Ar, (c) Kr and (d) Xe. Filled triangle, circle, rhomb, pentagon and square are calculations the quadrupole parameters V_q with coefficients $A_i = 0.6, 0.5, 0.2, 0.1, \text{ and } 0.45$ (31), accordingly; the open square is the three-body interaction parameter V_t (27); dotted line is calculation from formula $V_q^0 = |V_t^0|$; stars is calculation of V_q^{exp} from formula (34) for $\delta = \delta_{\text{exp}}$ [10].

The parameters which are necessary for the calculation of the elastic moduli B_{ij} (22) and the deviation from Cauchy relation (30) are presented in the Table (see Appendix) for the series Ne-Xe. For comparison we give the pair interaction parameters in the Table which are defined with expressions (23)-(24) (see also [46]). As the Table shows the quadrupole parameters V_q and three-body parameters V_t have the same order, but both $|V_t| < V_q$ for Ne and $|V_t| > V_q$ for other crystals. The comparative role of the tree-body interaction is growing in the series Ne-Xe and is 0,5%, 2,6%, 4,7%, 7,4%, accordingly. In work [49] the contribution of the three-body interaction to the cohesive energy for Xe is 7% that is in good agreement with our calculations.

Birch elastic moduli B_{ij} (22) can be represented as

$$\begin{aligned}
 B_{ij} &= B_{ij}^0 + B_{ij}^t + B_{ij}^q, \quad K(p) = \frac{e^2}{2a^4}, \\
 B_{11}^t &= K(p)(\delta G + \delta H), \quad B_{11}^q = K(p)\left(-\frac{2}{3}V_q\right), \\
 B_{12}^t &= K(p)\left[\frac{\delta G}{2} - \frac{V_t}{2} - \delta H\right], \quad B_{12}^q = K(p)\left(\frac{1}{3}V_q\right), \\
 B_{44}^t &= K(p)\left[\frac{\delta G}{2} + \frac{V_t}{2} + \delta H\right], \quad B_{44}^q = -K(p)4V_q, \quad (35)
 \end{aligned}$$

where B_{ij}^0 are the Birch elastic moduli with pair interaction potentials previously calculated by us in the models M1, M3 and M5 [46] (see also Fig. 1). In the model M5 the short-

range part of the repulsive potential is calculated with respect to the accurate formula for W_2 (18) $V_{sr} = E^{(0)} + W_2(S^n)$, in other models M3 and M1 W_2 it is calculated in approximation S^2 . Moreover, in models M3 and M5 van der Waals constant $C \rightarrow C(1 - Ae^{-\beta r})$ is predetermined and “the second” neighbors are taken into account in the calculations of the short-range forces [46]. In the simplest model M1 $A = \beta = 0$ only the first neighbors are taken into account.

As it is seen from the Table and expression (35) the contributions of the elastic moduli B_{11}^t and B_{11}^q are compensated to a large extent, and we have the elastic modulus $B_{11} \approx B_{11}^0$. The main difference of B_{12} from B_{12}^0 is defined by the contribution of the three-body interaction of B_{12}^t which is positive. The contribution to shear modulus B_{44} due to the quadrupole deformation of the electron shells $B_{44}^q < 0$ and it has considerably bigger value than B_{44}^t ($|B_{44}^q| > |B_{44}^t|$). This analysis is true for all RGC at any

pressure. But the comparative value of contributions B_{ij}^t , B_{ij}^q is growing in the series Ne, Ar, Kr, Xe [34, 43, 48, 50]. The total contributions of the three-body and the quadrupole interactions in the elastic moduli B_{ij} are represented in the following figures the most visually.

In Figures 3 (a, b, c, d) – 6 (a, b, c, d) show the Birch elastic moduli and deviations from the Cauchy relation for Ne, Ar, Kr, Xe. The agreement of the theory and the experiment for elastic moduli depends on the model of calculation of B_{ij}^0 . M1 model fits best as a basic one for the calculation of B_{12}^0 in the crystals Ar, Kr, Xe. The inclusion of the contributions B_{12}^t and B_{12}^q in the calculation improves the agreement between theory and the experiment. The elastic moduli B_{ij}^0 calculated in the M3 model are in the best agreement with the experiment for Xe; this agreement becomes somewhat worse when the three-body interaction and the quadrupole deformation of the atomic electron shells are taken into account.

The elastic moduli B_{12} and B_{44} are presented in a wide range of pressure before the metallization region (see Figure 3 b, c – 6 b, c). Our results obtained for B_{12} and the results of other authors (ab initio calculations in DFT [1], and in calculations in the embedded atom model (EAM) with empirical potentials [2]) are in good agreement at moderate pressures.

As can be seen from Figs. 4 b – 6 b for the series Ar-Xe the calculation in EAM model is in the interval between our results obtained in the models M1 and M3. Our calculations

of B_{44} with consideration for the deformation of the electron shells B_{44}^q and the three-body interaction of B_{44}^t for Ne, Kr и Xe lie below than the calculations of B_{44} in DFT and the empirical model EAM with consideration for the three-body interaction only. But namely the consideration of B_{44}^q makes $B_{44} \leq 0$ at 75 GPa, that fits the transition of Xe from fcc into hcp phase [51].

The Figures 3 d – 6 d present the pressure dependence $\delta(p)$ for the series Ne-Xe. In case of Ne our calculations of

$\delta(p)$ in different approximations lay between the calculations of $\delta(p)$ in DFT and EAM. The consideration of the deformation of the electron shells for Ne gives the positive value $\delta(p)$ in agreement with the experiment. As can be seen from Figs 4 our calculations of $\delta = \delta_t + \delta_q$ are very close to the many-body calculations of $\delta(p)$, in particular, to the result which have been obtained in the work [3]. In case of Ar for the adequate description of the dependence of $\delta(p)$ the consideration of the many-body interaction only is enough.

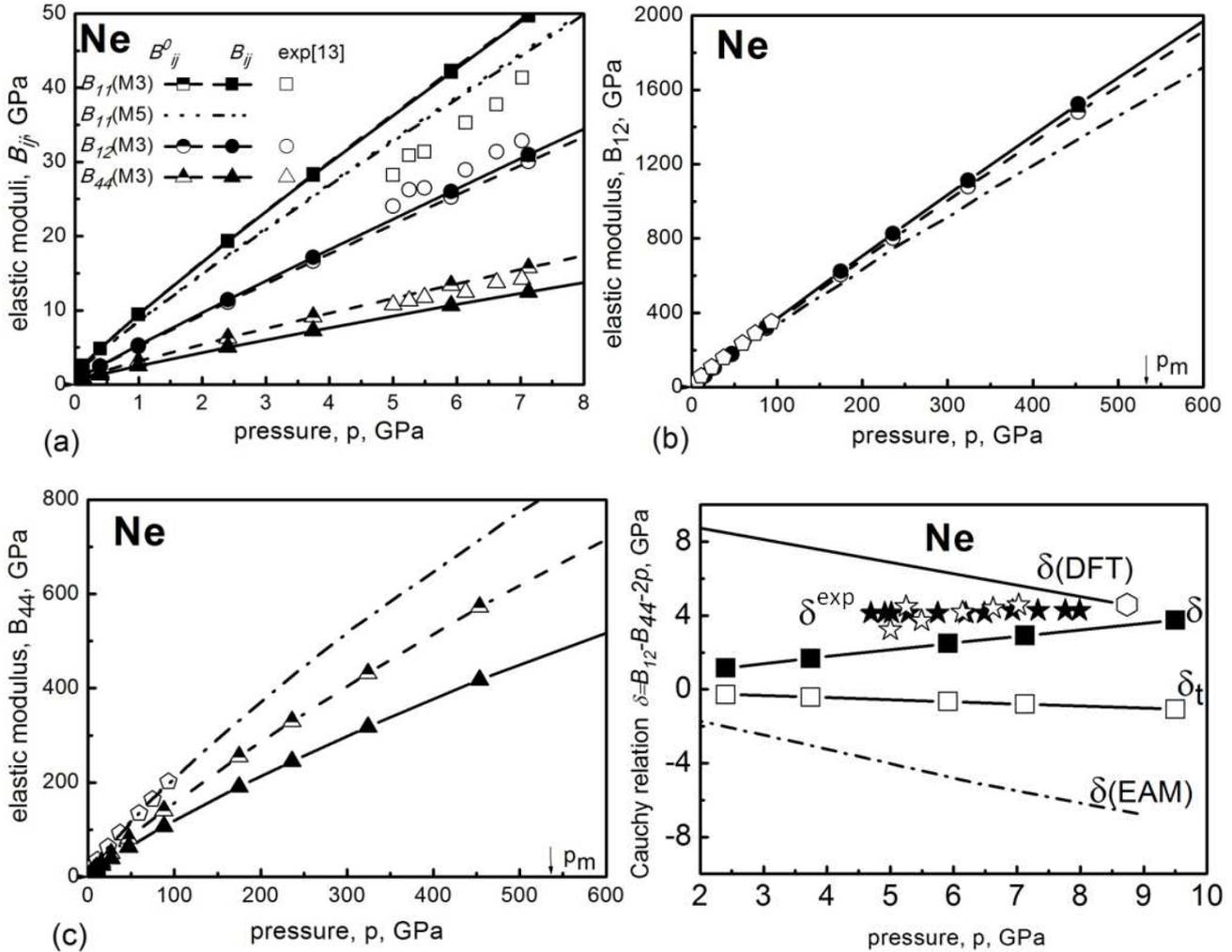


Fig. 3. Pressure dependencies of Birch elastic moduli [(a) B_{ij} , (b) B_{12} , (c) B_{44}] and deviations from the Cauchy relation $\delta = B_{12} - B_{44} - 2p$ (d) for Ne. (a–c) semi-filled symbols are calculations of $B_{ij}^0(M3)$ in the model M3 [46]; dotted line is calculation of $B_{11}^0(M5)$ in the model M5 [46]; filled symbols are calculations of B_{ij} in this work inclusion of the three-body and quadrupole interactions $B_{ij} = B_{ij}^0(M3) + B_{ij}^t + B_{ij}^q$; dashed-dot-dot line is calculation of $B_{11} = B_{11}^0(M5) + B_{11}^t + B_{11}^q$; open symbols are experiment [13]; dashed-dot line and open pentagon are calculations in EAM [2] and in DFT [1], accordingly. (d) Filled square are calculations with inclusion of the three-body and quadrupole interactions of $\delta = \delta_t + \delta_q$ at $V_q^0 = V_{exp}^0$, $A_i = 0,5$; open square is calculation taking into account only the three-body interaction $\delta_q = 0$; filled stars are average experimental data [10]; open stars are the experiments [13]. The arrows indicate the calculated metallization pressure $p_m = 540$ GPa [52, 53].

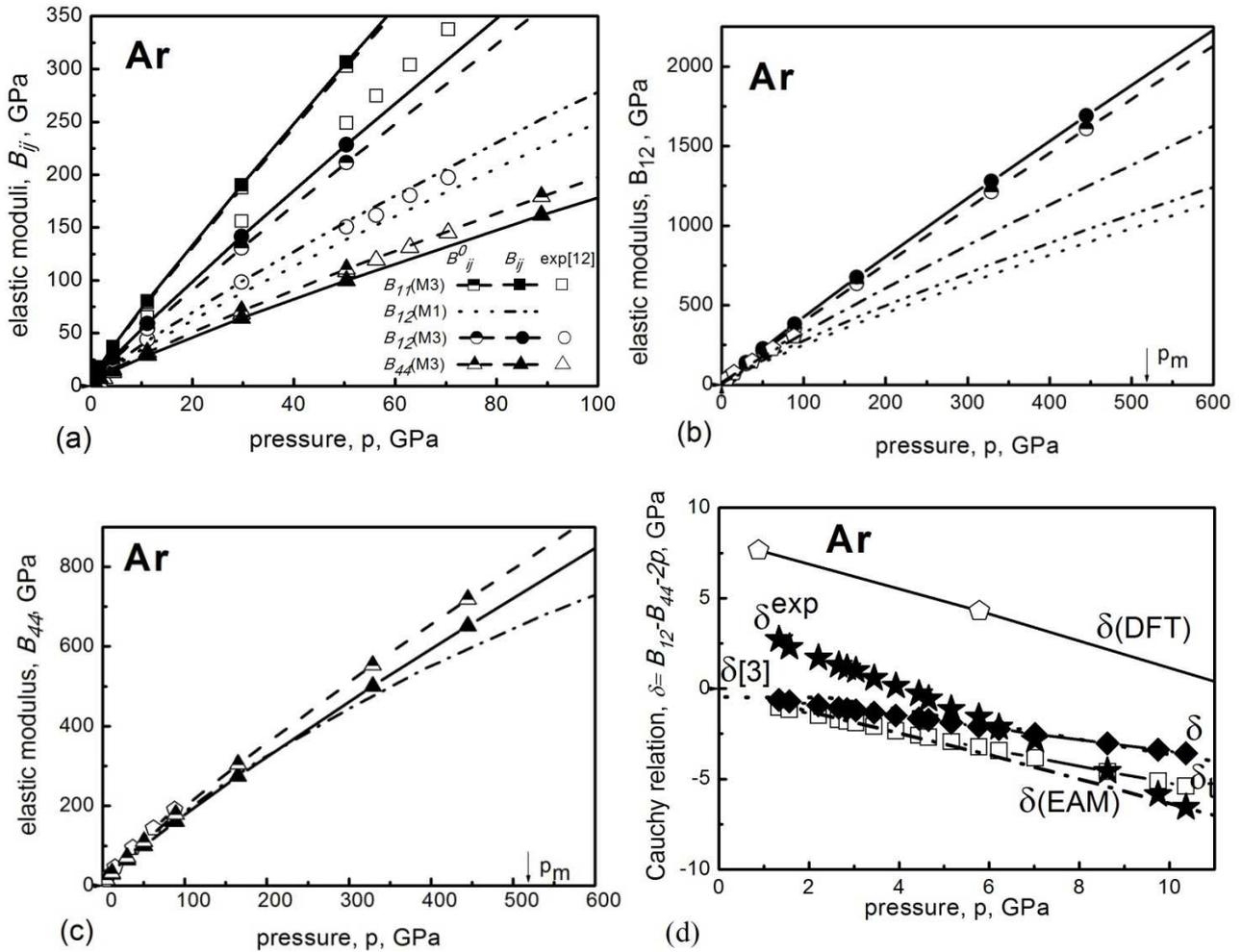
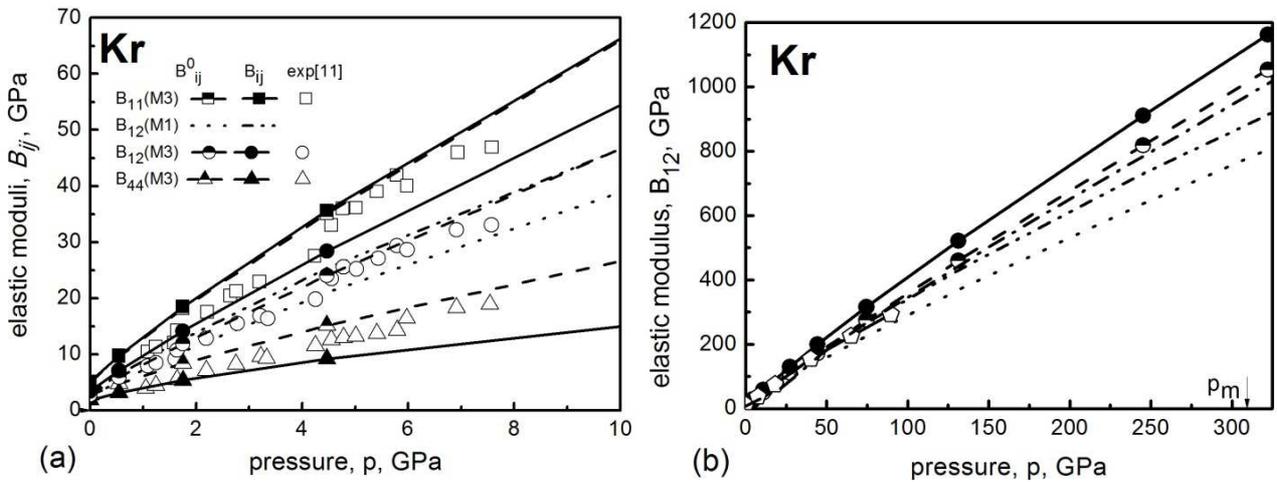


Fig. 4. Pressure dependencies of Birch elastic moduli [(a) B_{ij} , (b) B_{12} , (c) B_{44}] and deviations from the Cauchy relation (d) for Ar. (a–c) semi-filled symbols are calculations of $B_{ij}^0(M3)$ in the model M3 [46]; dotted line is calculation of $B_{12}^0(M1)$ in the model M1 [46]; filled symbols are calculations of B_{ij} in this work inclusion of the three-body and quadrupole interactions $B_{ij} = B_{ij}^0(M3) + B_{ij}^t + B_{ij}^q$; dashed-dot-dot line is calculation of $B_{12} = B_{12}^0(M1) + B_{12}^t + B_{12}^q$; open symbols are experiment [12]; dashed-dot line and open pentagon are calculations in EAM [2] and in DFT [1], accordingly. (d) Filled square are calculations with inclusion of the three-body and quadrupole interactions of $\delta = \delta_t + \delta_q$ at $V_q^0 = V_{exp}^0$, $A_i = 0, 1$; open square is calculation taking into account only the three-body interaction $\delta_q = 0$; filled stars are average experimental data [12]. The arrows indicate the calculated metallization pressure $p_m = 510$ [21].



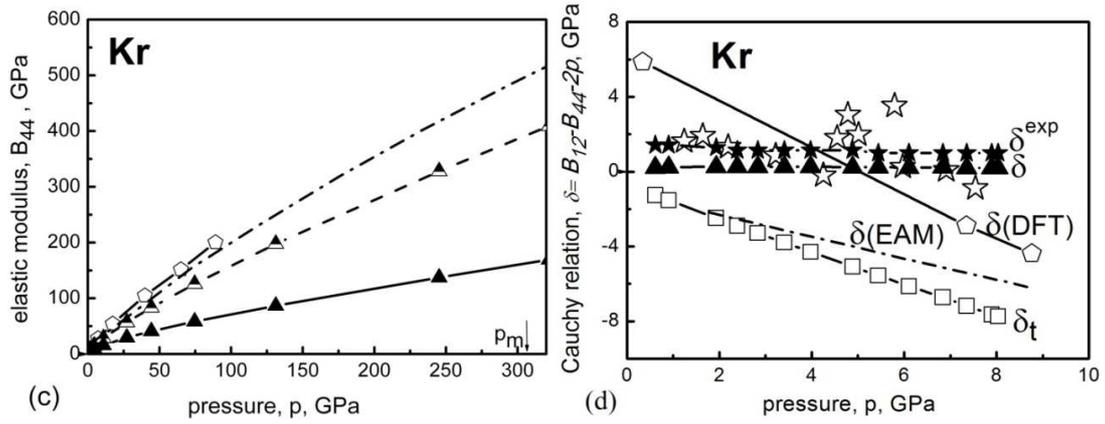


Fig. 5. Pressure dependencies of Birch elastic moduli [(a) B_{ij} , (b) B_{12} , (c) B_{44}] and deviations from the Cauchy relation (d) for Kr. (a–c) semi-filled symbols are calculations of $B_{ij}^0(M3)$ in the model M3 [46]; dotted line is calculation of $B_{12}^0(M1)$ in the model M1 [46]; filled symbols are calculations of B_{ij} in this work inclusion of the three-body and quadrupole interactions $B_{ij} = B_{ij}^0(M3) + B_{ij}^t + B_{ij}^q$; dashed-dot-dot line is calculation of $B_{12} = B_{12}^0(M1) + B_{12}^t + B_{12}^q$; open symbols are experiment [11]; dashed-dot line and open pentagon are calculations in EAM [2] and in DFT [1], accordingly. (d) Filled square are calculations with inclusion of the three-body and quadrupole interactions of $\delta = \delta_t + \delta_q$ at $V_q^0 = V_{exp}^0$, $A_i = 0,6$; open square is calculation taking into account only the three-body interaction $\delta_q = 0$; filled stars are average experimental data [10]; open stars are the experiments [11]. The arrows indicate the calculated metallization pressure $p_m = 310$ GPa [21].

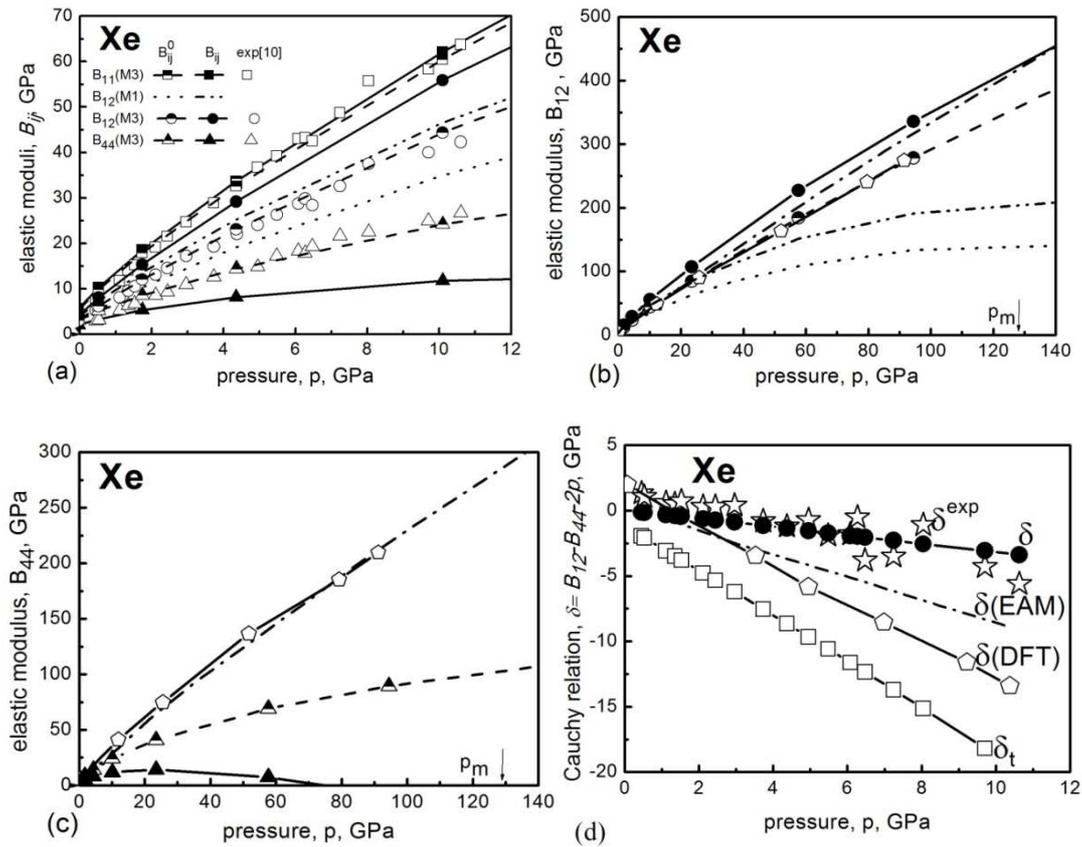


Fig. 6. Pressure dependencies of Birch elastic moduli [(a) B_{ij} , (b) B_{12} , (c) B_{44}] and deviations from the Cauchy relation (d) for Xe. (a–c) semi-filled symbols are calculations of $B_{ij}^0(M3)$ in the model M3 [46]; dotted line is calculation of $B_{12}^0(M1)$ in the model M1 [46]; filled symbols are calculations of B_{ij} in this work inclusion of the three-body and quadrupole interactions $B_{ij} = B_{ij}^0(M3) + B_{ij}^t + B_{ij}^q$; dashed-dot-dot line is calculation of $B_{12} = B_{12}^0(M1) + B_{12}^t + B_{12}^q$; open symbols are experiment [10]; dashed-dot line and open pentagon are calculations in EAM [2] and in DFT [1], accordingly. (d) Filled square are calculations with inclusion of the three-body and quadrupole interactions of $\delta = \delta_t + \delta_q$ at $V_q^0 = V_{exp}^0$, $A_i = 0,45$; open square is calculation taking into account only the three-body interaction $\delta_q = 0$; open stars are the experiments [10]. The arrows indicate the average metallization pressure p_m from 121 to 138 GPa [51, 54].

The Figures 5 d – 6 d present the pressure dependence of $\delta(p)$ on for heavy RGC. Our calculations are in good agreement with the experimental data. In Kr and Xe the obtained value δ has the weak dependence on pressure that makes our results substantially different from the results of other authors [1, 2]. The results of *ab initio* calculation in DFT [1] and EAM empirical model [2] are close to the experiment only when $p=0$, with the rise of pressure the distinction of kind can be observed. The proximity of the present calculations of $\delta(p)$ at different A_i and V_q^0 to δ^{exp} for the whole series RGC demonstrates the stability of the model and the controllability of made approximations

6. Conclusions

The presented results (see also [46]) of the calculations of the Birch moduli B_{ij} have demonstrated that, for their adequate description, it is sufficient to use a semiempirical effective pair interaction potential (B_{ij}^0 in model M3). The model M3 contains adjustable parameters A and β in the predefined van der Waals constant $C \rightarrow C(1 - Ae^{-\beta r})$ which make it possible to effectively take into account the many-body interaction, deformation of the atomic electron shells, and other effects. In this work, we have performed the *ab initio* investigation of a many-body interaction in the short-range repulsive potential within the framework of the dynamical theory of crystal lattices with deformable atoms (the *ab initio* version of the Tolpygo model). As follows from the calculation of the pressure dependences of the Birch modulus $B_{12}(p)$ for Ar, Kr and Xe within the M1 model (without adjustable parameters), we can successfully use the *ab initio* pair interaction potential $V_{sr} = E^{(0)} + W_2$ defined by expressions (13), (18) as well as the *ab initio* three-body interaction potential W_3 (21) proposed here instead of the semi empirical effective pair interaction potential [46]. This is understandable because the *ab initio* interaction potentials V_{sr} are in good agreement with the corresponding empirical potentials. In the Fig. 1 this agreement is shown for Ne. The simple form for the three-body potential obtained due to the calculation of the accurate expression W_3 (19) [37] allows to individually calculate the parameters of the three-body interaction through the overlap integrals of the external p-electrons the atomic orbitals.

It can be seen from Fig. 7 a for $\delta(p)$ the series Ne-Xe the consideration of the three-body interaction only leads to the relation $\delta_t^{\text{Ne}} > \delta_t^{\text{Ar}} > \delta_t^{\text{Kr}} > \delta_t^{\text{Xe}}$, similar to the calculations in DFT [1] and does not reproduce the observed dependence $\delta_{\text{Ne}} > \delta_{\text{Kr}} > \delta_{\text{Xe}} > \delta_{\text{Ar}}$. As it is presented in this work (see Fig. 7 b) for the adequate description of the observed dependence $\delta(p)$ in Ne, Kr and Xe it is also necessary to

take into account the deformation of the electron shells in the quadrupole approximation. The dependence of the deviation from the Cauchy relation on the pressure is the result of two competing interactions, namely the many-body and electron-phonon interactions, which manifests itself in the deformation of the atoms electron shells due to displacements of the nuclei. In case of Ne, Kr and Xe the contributions of these interactions in considerable measure are compensated that provides the weak dependence of $\delta(p)$ on pressure. The quantitative analysis of the contributions the three-body δ_t and the electron-phonon δ_q interactions to the deviation from the Cauchy relation showed the importance of the consideration of the information of the electron shells not only for the heavy RGC [48] but also for the light Ne. Furthermore, for Ne, we have $\delta_q > |\delta_t|$ which provides a positive value of δ in contrast to Xe, where we have $\delta_q < |\delta_t|$ which leads to the total negative value of δ in agreement with the experiment [10].

In our opinion to build the dynamic theory of crystal lattices in the model of the deformable atoms is of principal importance even when $p=0$ though in this case the electron-phonon interaction is small therefore the deformation of the electron shells is also small. The smallness of the interatomic interaction energy for the closed spherically symmetrical shells leads to that thing that atoms deform each other weakly. But it does not give grounds to ignore such a deformation since only this deformation is responsible for the coupling in the crystal that can be seen from the example of van der Waals. Such kind interaction, as it has been mentioned in the introduction, takes place in the shell model [27, 28, 55].

A somewhat different model is sometimes used, namely, the “breathing shell” model, in which the dynamic variables are the shell radii, which can elastically vary during the nuclear vibrations [56]. In our opinion, this model introduces nothing new in principle since the “breathing shell”, which retains the spherical symmetry, cannot originate long-range forces.

The previously suggested approximation of weakly (as a dipole) deformable atoms leads to the expressions for the adiabatic potential which are formally equivalent of the shell model. In this regard the shell model gets the quantum-mechanical justification (as Cochran notes in the work [28]). However, the sense of parameters turns out another, namely, the fundamental short-range action is performed between undeformable atoms (terms $\sim \mathbf{u}_1 \cdot \mathbf{u}_2$), the weaker forces are described by terms $\mathbf{u}_1 \cdot \mathbf{P}_2$ and $\mathbf{u}_2 \cdot \mathbf{P}_1$, and the weakest forces are described by terms $\mathbf{P}_1 \cdot \mathbf{P}_2$, where \mathbf{u}_i is the displacement of atom i , and \mathbf{P}_i it is dipole moment. This relation is actually a result of the comparison of the experiment with the phonon spectra. If to take into account the quadrupole function then it is a minor part in comparison with the dipole deformation and gives lesser corrections to the phonon energy. The quadrupole deformation cannot be described within the framework of cores and shells model.

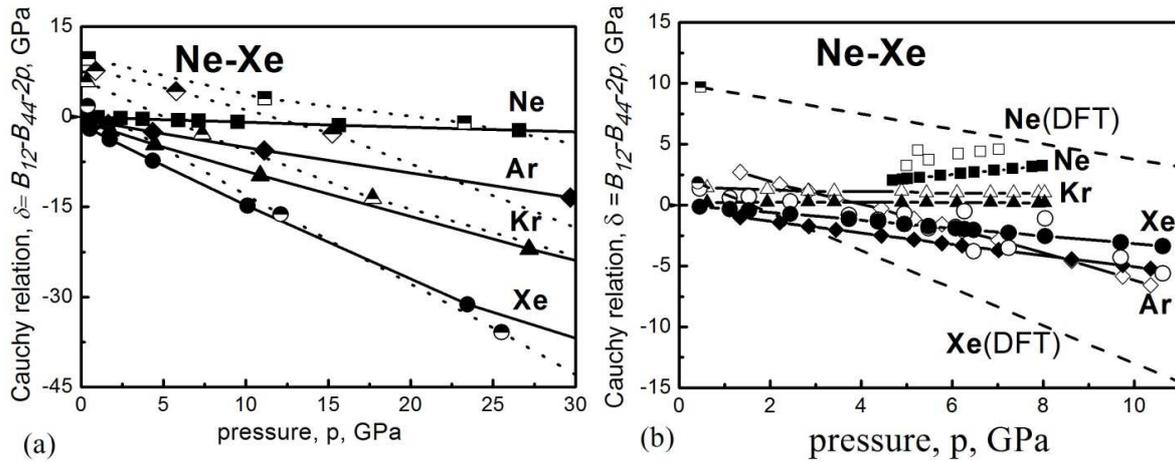


Fig. 7. Pressure dependence of the deviation from the Cauchy relation for Ne, Ar, Kr u Xe. (a) Filled symbols are calculations of $\delta(p) = \delta_i(p)$ without consideration of the quadrupole interaction $\delta_q = 0$; dashed lines with semi-filled symbols are *ab initio* DFT calculations [1]. (b) filled symbols are our calculations of δ with inclusion of the three-body and quadrupole interactions $\delta(p) = \delta_i(p) + \delta_q(p)$, open symbols are experiment for Ne [13], Ar [12], Kr [11] and Xe [10]. The other notations are as in the figure 7 a.

In the series of papers [57-59] we considered nonadiabatic effects, i.e., the electron-phonon interaction induced by the deformation of electron shells of the atoms in the dipole approximation. This corresponds to the inclusion of the lower order terms in the nonadiabaticity parameter. As is known [19] these terms do not contribute to the second-order elastic constants. The next order, i.e., the consideration of the electron-phonon interaction induced by the deformation of electron shells of the atoms in the quadrupole approximation leads to the appearance of the corresponding terms in expressions (35) for the elastic moduli. These terms make smaller contributions in comparison with those of the pair interaction potential, but they are comparable to the contribution of the three-body interaction (the parameters $|V_t|$ and V_q are of the same order of magnitude).

We have emphasized that the parameter δ does not depend on the parameters of the two-body potential. This makes it indispensable for the *ab initio* verification of the role of the

many-body interaction and the effects of the deformation of atomic electron shells.

The research of the CR violation gave us an opportunity to recognize the nature and the correlation of forces which form the elastic properties of crystals under high pressures.

Thus, it has been shown that the violation of the Cauchy relation for rare-gas crystals is caused by two factors: first, the three-body interaction forces associated with the overlap of electron shells of the atoms in the crystal, and second, the electron-phonon interaction related to the quadrupole deformation of electron shells of the atoms due to the displacement of the nuclei.

In conclusion we note that obtained in this work parameters can be confidently used in subsequent calculations of the dynamic matrix for the determination of the phonon energy, thermodynamic quantities, and other properties of rare-gas crystals at high pressures.

Appendix

Table. Dimensionless parameters of short-range pair interaction H_0 , G_0 , F , and E , three-body interaction δG , δH , R_t , and V_t , and electron-phonon interaction V_q as functions of the compression u .

u	p , GPa	$K(p)$, GPa	$H_0 \cdot 10^2$	$G_0 \cdot 10^2$	$F \cdot 10^2$	$E \cdot 10^2$	$\delta G \cdot 10^2$	$\delta H \cdot 10^2$	$R_t \cdot 10^2$	$V_t \cdot 10^2$	$V_q \cdot 10^2$
Ne: $V_q^0 = V_q^{\text{exp}} = 0.012$ ($p=4.6954$), $A_i=0.5$											
0	0.126	46.885	-1.280	9.190	-0.130	1.000	0.050	-0.024	0.010	-0.028	0.092
0.1	0.396	53.957	-1.860	13.330	-0.200	1.464	0.084	-0.041	0.018	-0.046	0.145
0.2	0.998	63.132	-2.830	20.100	-0.300	2.210	0.146	-0.072	0.032	-0.080	0.237
0.3	2.402	75.435	-4.530	31.730	-0.480	3.510	0.261	-0.132	0.060	-0.143	0.401
0.4	5.911	92.648	-7.720	52.930	-0.830	5.920	0.487	-0.252	0.119	-0.266	0.713
0.5	15.644	118.143	-14.22	94.470	-1.540	10.850	0.957	-0.510	0.250	-0.521	1.350
0.55	26.589	135.963	-20.00	130.189	-2.195	15.299	1.371	-0.745	0.372	-0.745	1.914
0.6	47.049	159.083	-28.98	183.950	-3.240	22.330	1.995	-1.107	0.567	-1.082	2.781
0.65	87.680	190.084	-43.47	267.700	-5.005	34.054	2.954	-1.682	0.884	-1.596	4.159
0.7	174.86	233.457	-68.03	403.930	-8.190	54.940	4.448	-2.613	1.417	-2.392	6.444
0.72	236.06	255.952	-82.533	482.004	-10.180	67.809	5.262	-3.137	1.725	-2.823	7.768

u	P , GPa	$K(p)$, GPa	$H_0 \cdot 10^2$	$G_0 \cdot 10^2$	$F \cdot 10^2$	$E \cdot 10^2$	$\delta G \cdot 10^2$	$\delta H \cdot 10^2$	$R_t \cdot 10^2$	$V_t \cdot 10^2$	$V_q \cdot 10^2$
0.74	324.01	282.534	-101.09	579.892	-12.830	84.842	6.237	-3.780	2.110	-3.339	9.437
0.76	453.33	314.355	-125.13	704.132	-16.432	107.79	7.402	-4.571	2.594	-3.953	11.563
Ar: $V_q^0 = V_q^{\text{exp}} = 0.0286$ ($p=1.338466$), $A_i = 0.1$											
0	0.016	23.197	-4.700	38.580	-0.030	0.420	1.012	-0.503	0.221	-0.564	0.141
0.1	0.507	26.696	-7.360	57.600	-0.070	0.820	1.633	-0.823	0.370	-0.907	0.216
0.2	1.650	31.236	-11.810	88.130	-0.150	1.650	2.692	-1.384	0.638	-1.491	0.343
0.3	4.358	37.323	-19.540	139.190	-0.320	3.390	4.528	-2.385	1.136	-2.498	0.563
0.4	11.127	45.839	-33.790	229.370	-0.750	7.380	7.763	-4.226	2.091	-4.270	0.968
0.5	29.705	58.454	-61.980	400.800	-1.880	17.290	13.490	-7.680	3.979	-7.402	1.751
0.55	50.404	67.270	-86.504	545.728	-3.108	27.480	17.798	-10.435	5.556	-9.758	2.410
0.6	88.875	78.709	-123.97	762.540	-5.300	45.130	23.397	-14.217	7.807	-12.819	3.376
0.65	165.051	94.047	-183.67	1100.93	-9.442	77.316	30.441	-19.352	11.012	-16.680	4.824
0.7	328.948	115.507	-284.19	1658.95	-17.790	140.00	38.778	-26.128	15.501	-21.254	7.048
0.72	444.701	126.637	-343.65	1984.54	-23.387	181.07	42.178	-29.306	17.720	-23.173	8.258
0.74	612.168	139.789	-419.99	2399.33	-31.176	237.44	45.489	-32.700	20.185	-25.031	9.718
Kr: $V_q^0 = V_q^{\text{exp}} = 0.029$ ($p=0.6163$), $A_i = 0.6$											
0	0.003	18.138	-6.700	55.500	-0.004	0.320	2.616	-1.297	0.579	-1.437	1.102
0.1	0.543	20.874	-10.500	80.840	-0.030	0.760	4.064	-2.063	0.946	-2.234	1.687
0.2	1.749	24.423	-16.640	119.350	-0.110	1.710	6.387	-3.336	1.579	-3.512	2.650
0.3	4.468	29.183	-26.830	179.630	-0.300	3.770	10.154	-5.484	2.693	-5.582	4.286
0.4	10.870	35.842	-44.420	277.880	-0.790	8.400	14.549	-9.136	4.680	-8.913	7.181
0.5	27.190	45.705	-76.560	447.440	-2.080	19.036	26.125	-15.562	8.368	-14.388	12.551
0.55	44.313	52.598	-102.69	579.961	-3.441	30.030	32.861	-20.279	11.225	-18.108	16.909
0.6	74.576	61.543	-140.40	766.380	-5.790	47.560	40.886	-26.341	15.068	-22.546	23.108
0.65	131.174	73.536	-196.82	1038.48	-10.026	77.446	49.822	-33.878	20.132	-27.491	32.088
0.7	245.234	90.315	-285.25	1455.30	-18.020	130.91	58.363	-42.708	26.543	-32.329	45.340
0.72	322.076	99.018	-334.89	1685.91	-23.106	163.73	60.996	-46.353	29.412	-33.883	52.331
Xe: $V_q^0 = V_q^{\text{exp}} = 0.05$ ($p=0.451$), $A_i = 0.45$											
0	-0.034	13.104	-9.690	82.620	-0.130	0.490	6.155	-3.051	1.401	-3.300	1.569
0.1	0.527	15.080	-15.300	118.300	-0.140	0.160	9.072	-4.767	2.246	-5.042	2.354
0.2	1.740	17.645	-24.100	169.400	-0.110	0.810	13.801	-7.433	3.619	-7.628	3.618
0.3	4.349	21.083	-38.100	243.110	-0.050	3.370	21.103	-11.744	5.938	-11.611	5.717
0.4	10.096	25.894	-60.490	349.730	-0.600	9.760	32.117	-18.717	9.889	-17.656	9.330
0.5	23.454	33.020	-97.140	505.280	-2.3400	26.010	47.859	-29.790	16.601	-26.377	15.813
0.55	36.372	38.000	-123.85	609.135	-4.2780	42.335	49.701	-34.064	19.896	-28.337	20.783
0.6	57.653	44.462	-158.80	737.480	-7.7600	69.540	67.202	-45.939	27.434	-37.010	27.981
0.65	94.445	53.126	-205.19	901.036	-14.180	116.29	75.048	-55.249	34.473	-41.554	37.874
0.7	162.717	65.249	-268.50	1124.15	-26.500	200.17	78.433	-63.609	41.848	-43.522	51.829

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