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TO THE THEORY OF FORCE CONSTANTS FOR MULTIATOMIC SYSTEMS IN THE TIGHT-BINDING MODEL (PART II)

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An approximate expression for the Coulomb interaction energy in solids has been obtained in the framework of the tight-binding model. The condition of adiabatic approximation and the procedure of quantum statistical averaging for the first (static) term in the expansion of the average potential energy in small nuclear shifts are analyzed, which allowed the electron contribution to the thermal expansion of solids to be calculated. An equation of state for a solid is obtained in the harmonic approximation by analyzing the internal energy and the thermal properties of the solid. A relationship between the specific heats C_v and C_p , which agrees with the Grüneisen law, is found.

Key words: theory of force constants, Coulomb interaction energy, energy of a multiatomic system, Grüneisen law.

1. Energy of a Multiatomic System and Coulomb Interaction in the Tight-Binding Model

In the spirit of the tight-binding approximation, we consider a multiatomic system consisting of atoms, the valence electrons of which are basically located near their “own” atoms and, due to the wave properties, interact with “other” surrounding atoms. For simplicity, all atoms are regarded to be identical. Below, atoms without their valence electrons will be referred to as nuclei.

The Hamiltonian of a system consisting of N atoms and Z electrons (Z is the atomic valency) looks like

$$\hat{H} = \sum_i \frac{p_i^2}{2m} - e^2 Z \sum_{i,k} \frac{1}{|\mathbf{R}_k - \mathbf{r}_i|} + \frac{e^2}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_j - \mathbf{r}_i|} + \frac{e^2 Z^2}{2} \sum_{k \neq l} \frac{1}{|\mathbf{R}_k - \mathbf{R}_l|} + \sum_k \frac{P_k^2}{2M}, \quad (1)$$

where the subscripts i and j enumerate the electrons, and the subscripts k and l the nuclei; m and M are the masses, and p_i and P_k the momenta of electrons and nuclei, respectively. Let us introduce the coordinates of electrons with respect to their “own” nuclei,

$$\mathbf{r}_i = \mathbf{R}_k + \mathbf{r}_{ik},$$

where \mathbf{r}_{ik} is the electron coordinate in the k -th atom, and the subscript i enumerates valence electrons. Then the Hamiltonian reads

$$\hat{H} = \sum_i \frac{p_i^2}{2m} - e^2 Z \sum_{i,k,l} \frac{1}{|\mathbf{R}_k - \mathbf{R}_l - \mathbf{r}_{il}|} + \frac{e^2}{2} \sum_{\substack{i,j,k,l \\ ik \neq jl}} \frac{1}{|\mathbf{R}_k + \mathbf{r}_{ik} - \mathbf{R}_l - \mathbf{r}_{jl}|} + \frac{e^2 Z^2}{2} \sum_{k \neq l} \frac{1}{|\mathbf{R}_k - \mathbf{R}_l|} + \sum_k \frac{P_k^2}{2M}. \quad (2)$$

Grouping the terms with $k = l$ in the sums over k and l , we obtain

$$\hat{H} = \sum_{i,k} \frac{p_{ik}^2}{2m} - e^2 Z \sum_{i,k} \frac{1}{|\mathbf{r}_{ik}|} + \frac{e^2}{2} \sum_{i \neq j,k} \frac{1}{|\mathbf{r}_{ik} - \mathbf{r}_{jk}|} + \sum_k \frac{P_k^2}{2M} - e^2 Z \sum_{i,k \neq l} \frac{1}{|\mathbf{R}_k - \mathbf{R}_l - \mathbf{r}_{il}|} + \frac{e^2}{2} \times \sum_{i,j,k \neq l} \frac{1}{|\mathbf{R}_k + \mathbf{r}_{ik} - \mathbf{R}_l - \mathbf{r}_{jl}|} + \frac{e^2 Z^2}{2} \sum_{k \neq l} \frac{1}{|\mathbf{R}_k - \mathbf{R}_l|}. \quad (3)$$

The first three sums give the internal energy of free atoms. The next sums are the kinetic energy of nuclei and the energy of interaction between electrons and nuclei (the energy of interatomic interaction), respectively. The latter will be denoted as $U(R, r)$, and,

together with the kinetic energy of nuclei, it equals the energy of nuclear motion. Hence, the Hamiltonian of the system is

$$\hat{H} = \hat{H}_0 + \hat{H}', \quad (4)$$

where $\hat{H}_0 = \sum_k \hat{H}_k$ is the sum of Hamiltonians of free atoms, and

$$\hat{H}' = \sum_k \frac{\hat{P}_k^2}{2M} + U(R, r), \quad (5)$$

where

$$U(R, r) = -e^2 Z \sum_{i,k \neq l} \frac{1}{|\mathbf{R}_k - \mathbf{R}_l - \mathbf{r}_{il}|} + \frac{e^2}{2} \times \\ \times \sum_{i,j,k \neq l} \frac{1}{|\mathbf{R}_k + \mathbf{r}_{ik} - \mathbf{R}_l - \mathbf{r}_{jl}|} + \frac{e^2 Z^2}{2} \sum_{k \neq l} \frac{1}{|\mathbf{R}_k - \mathbf{R}_l|} \quad (6)$$

is the energy of interatomic interaction. Some approximate simplifications in the expression for $U(R, r)$ can be made taking into account that the absolute value $|\mathbf{R}_k - \mathbf{R}_l| \neq 0$, and its minimum equals the distance between the neighbor atoms, so that $|\mathbf{R}_k - \mathbf{R}_l| > (|\mathbf{r}_i|, |\mathbf{r}_i - \mathbf{r}_j|)$. Then the dependences on i and j in the denominators can be neglected, and the summation over i and j can be carried out. As a result, we obtain

$$U(R, r) = -\frac{e^2 Z^2}{2} \sum_{k \neq l} \left(\frac{2}{|\mathbf{R}_k - \mathbf{R}_l - \mathbf{r}_l|} - \frac{1}{|\mathbf{R}_k - \mathbf{R}_l + \mathbf{r}_k - \mathbf{r}_l|} - \frac{1}{|\mathbf{R}_k - \mathbf{R}_l|} \right). \quad (7)$$

Let us analyze the expression for $U(R, r)$. It includes three Coulomb sums, each being a diverging series. However, at large enough distances, when $|\mathbf{R}_k - \mathbf{R}_l| \gg (|\mathbf{r}_i|, |\mathbf{r}_i - \mathbf{r}_j|)$, all three terms are mutually compensated, which testifies to the finiteness of $U(R, r)$. Moreover, we may talk about the relative smallness of this quantity if we take the virial theorem into account, according to which the average value of potential energy in a system of particles with the Coulomb interaction equals twice its kinetic energy. Then, since the kinetic energy of nuclei is low in comparison with that of electrons, the potential energy of nuclei $U(R, r)$ is also low in comparison with that of electrons, i.e. $U(R, r) \ll H_0$, which allows us to apply the standard perturbation theory.

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Bearing all that in mind, let us consider a change of the electron energy in the atom if the interaction is "switched on". The corresponding Schrödinger equation for the system is

$$(\hat{H}_0 + \hat{H}') \psi(R, r) = E\psi(R, r), \quad (8)$$

where

$$\hat{H}' = \sum_k \frac{\hat{P}_k^2}{2M} + U(R, r) \quad (9)$$

is considered now as a small perturbation. The Schrödinger equation for the eigenfunctions and the eigenvalues of the nonperturbed system looks like

$$\hat{H}_0 \psi_n^0(R, r) = E_n^0 \psi_n^0(R, r). \quad (10)$$

Since the Hamiltonian \hat{H}_0 is a sum of free-atom Hamiltonians, and the corresponding wave function is a product of atomic functions, E_n^0 is a sum of the energies of separate atoms in the n -th state, i.e. $E_n^0 = \sum_k \varepsilon_{nk}^0$. For identical atoms, $E_n^0 = N\varepsilon_n^0$, where N is the number of atoms, and ε_n^0 is the energy of one atom in the n -th state.

If the eigenfunction of free atoms $\psi_n^0(R, r)$ is taken for the wave function in the zeroth-order approximation, the first-order corrections to the energy equal

$$E_n^{(1)} = \int \psi_n^{0*}(R, r) U(R, r) \psi_n^0(R, r) d\mathbf{r} = U_{nn}(R). \quad (11)$$

Here, we took into consideration that $\psi_n^0(R, r)$ depends on R as a parameter that only enumerates the atoms. Therefore, the operator of the nuclear kinetic energy commutes with $\psi_n^0(R, r)$ and can be taken outside the integral. The following integration of the expression $|\psi_n^0(R, r)|^2$ over \mathbf{r} gives 1, and we obtain

$$\sum_k \frac{\hat{P}_k^2}{2M} \int |\psi_n^0(R, r)|^2 d\mathbf{r} = 0. \quad (12)$$

The corresponding energy E_n for the system of interacting atoms equals

$$E_n = E_n^0 + U_{nn}(R). \quad (13)$$

Note that $U_{nn}(R)$ is a double sum over the vectors and depends on their differences. Then, we may change to the sum over the vector differences with the corresponding multiplication of the sum by the

vector number, i.e. by the number of nuclei N (more exactly, by $N - 1$). At the same time, the potential $U(R, r)$, which includes the coordinates of electrons, does not possess this property. Hence, we may write $U_{nn}(R) = \frac{V}{v} U_{nn}^0$, where $V = Nv$ is the crystal volume, v is the volume of a unit cell, and the quantity $U_{nn}^0 = \frac{v}{V} U_{nn}(R)$ does not depend on the volume. Then $\frac{\partial U_{nn}(R)}{\partial \mathbf{R}_i} = \frac{V}{v} \frac{\partial U_{nn}^0}{\partial \mathbf{l}_i} \frac{\partial \mathbf{l}_i}{\partial \mathbf{R}_i}$, where \mathbf{l}_i is the lattice vector equal to the vector difference between the i -th lattice site and the lattice site at the coordinate origin.

The correction U_{nn} to the electron energy is a function of the coordinates of nuclei. It equals the energy of interaction between atoms, and its derivatives with respect to nuclear coordinates give expressions for the force constants of the corresponding order. By generalizing the Gell-Mann–Feynman theorem [2] about the differentiation of the energy with respect to atomic coordinates – namely, using the theorem proved by the author [3] about the arbitrary-order differentiation of the energy of a system with respect to atomic coordinates – we can write the following expression for the force constants of any order m :

$$\begin{aligned} \frac{\partial^m U_{nn}}{\partial \mathbf{R}_k^m} &= \int \psi_n^{0*}(R, r) \frac{\partial^m U(R, r)}{\partial \mathbf{R}_k^m} \psi_n^0(R, r) d\mathbf{r} = \\ &= \left(\frac{\partial^m U(R, r)}{\partial \mathbf{R}_k^m} \right)_{nn}, \end{aligned} \quad (14)$$

which, taking the statistical averaging into account, looks like

$$\frac{\partial^m \bar{U}_{nn}}{\partial \mathbf{R}_k^m} = \left(\frac{\partial^m \bar{U}(R, r)}{\partial \mathbf{R}_k^m} \right)_{nn}. \quad (15)$$

2. Energy of Nuclear Motion and Adiabatic Approximation

Let us consider the exact Schrödinger equation for a multiatomic system,

$$(\hat{H}_0 + \hat{H}') \psi(R, r) = E \psi(R, r). \quad (16)$$

The sought solution $\psi(R, r)$ is expanded in a series in eigenfunctions of the operator \hat{H}_0 , i.e.

$$\psi(R, r) = \sum_n a_n(R) \psi_n^0(R, r). \quad (17)$$

Since

$$\int |\psi_n^0(R, r)|^2 d\mathbf{r} d\mathbf{R} = 1,$$

we have

$$\int d\mathbf{R} \sum_n |a_n(R)|^2 = 1$$

and

$$a_n(R) = \int \psi_n^{0*} t(R, r) \psi(R, r) d\mathbf{r}.$$

Substituting expansion (17) into the Schrödinger equation,

$$\begin{aligned} \hat{H}_0 \sum_n a_n(R) \psi_n^0(R, r) + \hat{H}' \sum_n a_n(R) \psi_n^0(R, r) = \\ = E \sum_n a_n(R) \psi_n^0(R, r), \end{aligned} \quad (18)$$

multiplying the result by $\psi_n^{0*}(R, r)$, and integrating the product over \mathbf{r} , we obtain

$$\begin{aligned} \sum_n a_n E_n^0 \delta_{nn'} + \sum_n a_n \int \psi_n^{0*}(R, r) \hat{H}' \psi_n^0(R, r) d\mathbf{r} = \\ = E \sum_n a_n \delta_{nn'} \end{aligned} \quad (19)$$

or

$$\begin{aligned} \sum_n a_n \int \psi_n^{0*}(R, r) \sum_k \frac{\hat{P}_k^2}{2M} \psi_n^0(R, r) d\mathbf{r} + \sum_n a_n \times \\ \times \int \psi_n^{0*}(R, r) U(R, r) \psi_n^0(R, r) d\mathbf{r} = \\ = (E - E_n^0) a_n. \end{aligned} \quad (20)$$

In view of the commutativity of the operator of kinetic energy with $\psi_n^0(R, r)$, we obtain

$$\sum_k \frac{\hat{P}_k^2}{2M} a_n + \sum_{n'} a_{n'} U_{nn'}(R) = (E - E_n^0) a_n \quad (21)$$

or

$$\begin{aligned} \sum_k \frac{\hat{P}_k^2}{2M} a_n + U_{nn}(R) a_n + \sum_{n' \neq n} U_{nn'}(R) a_n = \\ = (E - E_n^0) a_n. \end{aligned} \quad (22)$$

Neglecting the non-diagonal terms $U_{nn'}(R)$ in this equation, we obtain the following equation for $a_n(R)$:

$$\left(\sum_k \frac{\hat{P}_k^2}{2M} + U_{nn}(R) \right) a_n = \varepsilon_n a_n, \quad (23)$$

where

$$\varepsilon_n = E - E_n^0. \quad (24)$$

The equation obtained for $a_n(R)$ is the Schrödinger equation for the wave function of the nuclear subsystem,

$$\hat{H}_R a_n = \varepsilon_n a_n. \quad (25)$$

Here,

$$\hat{H}_R = \sum_k \frac{\hat{P}_k^2}{2M} + U_{nn}(R). \quad (26)$$

Note that the functions describing the states of the electron and nuclear subsystems ($\hat{H}^0 \psi_n^0 = E_n^0 \psi_n^0$ and $\hat{H}_R a_n = \varepsilon_n a_n$) were separated provided that the non-diagonal matrix elements of the interaction energy calculated with the use of the wave functions of free atoms are small.

The non-diagonal structure of the matrix $U_{nn'}$ is related to the non-orthogonality of atomic wave functions for different atoms. If the adiabatic approximation is understood as a separate description of states belonging to either the electron or nuclear subsystem, it is satisfied in the tight-binding model under the condition $U_{nn'} \ll U_{nn}$. However, the independence of the description of the electron and nuclear subsystems turns out relative even if the adiabaticity condition is obeyed. Namely, the potential energy of nuclear motion is the potential energy of the system averaged over the electron states, and the wave function of the nuclear subsystem state depends on the quantum state of the electron subsystem. As a rule, if there are no considerable perturbations in the system, which are capable of inducing the electron transitions, it is the ground state of the electron subsystem.

Note that the theory of adiabatic approximation was first developed by M. Born [1]. However, while using the perturbation theory, a certain incorrectness was made, which consisted in that the kinetic energy of nuclei rather than the potential energy of their interaction was taken as a small perturbation, although the latter, in accordance with the virial theorem, has the same order of smallness as the former. As a result, the criterion of adiabaticity obtained in the form of harmonic approximation for the motion of the nuclear subsystem turned out too strict and little plausible, i.e. the adiabaticity of tracing the nuclear motion by electrons turned out dependent on the character of this motion, rather than on its quantum state.

Attempts to find a more acceptable criteria for the adiabatic approximation are discussed in the text-

books on quantum mechanics (e.g., by L.I. Glauber and O.S. Davydov). They are based on the non-commutativity condition for the operator of nuclear kinetic energy and the wave function of the electron subsystem depending on the coordinates of nuclei parametrically, rather than functionally. We consider this condition to be wrong. This is the more so, because it conflicts with the Gell-Mann–Feynman theorem of the differentiation of the energy of a multiatomic system with respect to the atomic coordinates [2].

The subsequent analysis of the Schrödinger equation for the nuclear subsystem is carried out in the standard way. The energy $U_{nn}(R)$ is expanded in a series in small shifts of the nuclei with respect to their equilibrium positions,

$$U_{nn}(R) = U_{nn}(R_0) + \sum_k \frac{\partial U_{nn}(R_0)}{\partial \mathbf{R}_k} \mathbf{u}_k + \frac{1}{2} \sum_{k,l} \frac{\partial^2 U_{nn}(R_0)}{\partial \mathbf{R}_k \partial \mathbf{R}_l} \mathbf{u}_k \mathbf{u}_l + \dots, \quad (27)$$

where R_0 means the equilibrium configuration of nuclei, for which all coefficients in the expansion are calculated. In the harmonic approximation, taking into account that the first derivatives of the potential energy with respect to the atomic coordinates in the equilibrium configuration equal zero, we obtain

$$U_{nn}(R) = U_{nn}(R_0) + \frac{1}{2} \sum_{k,l} \frac{\partial^2 U_{nn}(R_0)}{\partial \mathbf{R}_k \partial \mathbf{R}_l} \mathbf{u}_k \mathbf{u}_l, \quad (28)$$

which allows the equation for $a_n(R)$ in the harmonic approximation to be written in the form

$$\left(\sum_k \frac{\hat{P}_k^2}{2M} + \frac{1}{2} \sum_{k,l} \frac{\partial^2 U_{nn}(R_0)}{\partial \mathbf{R}_k \partial \mathbf{R}_l} \mathbf{u}_k \mathbf{u}_l \right) a_n^0(R) = \varepsilon_{n1} a_n^0(R), \quad (29)$$

where $a_n(R)$ was renamed as $a_n^0(R)$, and

$$\varepsilon_{n1} = \varepsilon_n - U_{nn}(R_0). \quad (30)$$

The obtained equation is the known one for the wave function of a multiatomic system in the vibration state. After changing to normal vibrations, the Hamiltonian transforms into a sum of the Hamiltonians for independent harmonic oscillators.

Let us designate the Hamiltonian in the harmonic approximation as \hat{H}_R^0 and write down the equation for a harmonic oscillator,

$$\hat{H}_R^0 a_{n\nu}^0 = \varepsilon_{n\nu} a_{n\nu}^0. \quad (31)$$

Here, ν is the quantum number of an oscillator. Then

$$\begin{aligned} \varepsilon_{n1} &= \sum_{\nu} \varepsilon_{n\nu} = \varepsilon_n - U_{nn}(R_0) = \\ &= E - E_n^0 - U_{nn}(R_0). \end{aligned} \quad (32)$$

Accordingly,

$$E = E_n^0 + U_{nn}(R_0) + \sum_{\nu} \varepsilon_{n\nu}. \quad (33)$$

The dynamics of a solid in the harmonic approximation has been studied in detail, which allowed the contribution of lattice vibrations to thermodynamic quantities and some thermal properties of crystals to be determined [4], in particular, the heat (thermal) capacity at a constant volume, C_v . However, the fact that the potential energy of nuclear motion is the value of the operator of potential energy of the system $U_{nn}(R_0)$ in the equilibrium configuration averaged over the electron states seems to be underestimated. Strictly speaking, it should be averaged, as any other observable physical quantity, not only quantum-mechanically, but also statistically. The term “equilibrium configuration” has to be related to the thermal equilibrium. Then it becomes evident that the equilibrium configuration itself depends on the temperature due to the thermal expansion. In the lattice dynamics, which is developed on the basis of the expansion of the potential energy (such expansion is unavoidable while distinguishing between the electron and vibrational states) in small atomic shifts, the static energy $U_{nn}(R_0)$ does not play a substantial role, and the statistical averaging is carried out only over the vibrational energy. In our opinion, the statistical averaging of the static component of the potential energy has to reveal its temperature dependence, which is responsible, in particular, for the thermal expansion of solids and, probably, for the electron contribution to the crystal heat capacity.

3. Thermal Properties of Solids

By the thermal properties, we understand, first of all, the heat capacity and the coefficient of thermal expansion. Thermodynamically, those properties have

been studied well enough. However, their quantitative calculation requires the application of quantum statistics.

The determination of those properties is associated with the calculation of the energy of the system and its derivatives with respect to nuclear coordinates. Such calculations become possible in principle as a result of both the generalization of the Gell-Mann–Feynman theorem of the differentiation of the energy of a multiatomic system with respect to the atomic coordinates, when the differentiation of wave functions is not needed, and the simplifications of the expression for the interaction energy $U(R, r)$.

In the harmonic approximation, the energy of nuclear motion equals

$$E_1 = U_{nn}(R_0) + \sum_{\nu} \varepsilon_{\nu}. \quad (34)$$

Hereafter, the subscript n at ε_{ν} , which enumerates the electron states, is omitted. The observable quantities in any system are its quantum-mechanically and statistically averaged operators. Therefore, the quantity E_1 has to be statistically averaged as well. The latter operation will be conditionally denoted by a bar over the corresponding symbol, so that

$$\bar{E}_1 = \bar{U}_{nn}(R_0(T)) + \sum_{\nu} \bar{\varepsilon}_{\nu}(T). \quad (35)$$

As a result of this averaging, the averaged values become dependent on the temperature T : $\bar{\varepsilon}_{\nu}(T)$ explicitly and $\bar{U}_{nn}(R_0(T))$ implicitly. Let us denote $\sum_{\nu} \bar{\varepsilon}_{\nu}(T)$ by E_k ; this is the well-known energy of vibrational nuclear motion, i.e. the thermal energy of the object, which governs—to a great extent, but not in full—its thermal properties. The proportionality between this energy and the crystal volume can be found when summing up over $\nu = (j, \mathbf{k})$, where j is the number of a normal vibration branch, and \mathbf{k} is its wave vector, with the corresponding density of states being proportional to the crystal volume. Therefore, we can write $E_k = V E_k^0$, where E_k^0 does not depend on the volume. Hence, the energy of the nuclear subsystem \bar{E}_1 turns out consisting of the thermal energy and the energy of interaction between the nuclei in a certain configuration. This static energy can be regarded as that having the mechanical origin, although this statement contradicts the viewpoint—to tell the truth, not substantiated [5]—that the internal energy

of a crystal cannot be divided into the thermal and mechanical ones. In our opinion, just this component of the energy governs all mechanical properties of a solid, and its temperature dependence determines the temperature dependence of mechanical characteristics of a solid, such as the elastic moduli and others. In what follows, in order to simplify notations, we put $\bar{E}_1 = E$.

One should pay attention to that the statistical averaging of the total crystal energy E_1 over the canonical Gibbs distribution is not possible because of its negative value, which is typical of the systems with coupled particles. At the same time, a partial averaging of its positive part (the vibrational energy) can be done [4]. Such opportunity follows from the structure of the canonical Gibbs distribution, which allows its factorization with respect to different types of energy. The negative values of energy \bar{E}_1 follows from the virial theorem, according to which $\bar{E}_1 = -K$, where K is the average kinetic energy of particles. On the other hand, $E_k = 2K$, so that $K = \frac{1}{2} \sum_{\nu} \bar{\varepsilon}_{\nu}$.

Nevertheless, the averaging of $U_{nn}(R)$ is still possible, at least formally, if we use the microcanonical Gibbs distribution and consider the solid as a closed system (in our opinion, this assumption is not too strict). In a closed system, the energy is constant, which results in the delta-like Gibbs distribution $\delta(U_{nn}(R) - U_{nn}(R, T))$ [6]. The normalizing multiplier is absent here owing to the deterministic character of both the coordinates of atoms in the lattice and the energy of interatomic interaction, from which the undetermined part in the form of the thermal energy is excluded. Therefore, we have

$$\bar{U}_{nn} = \int U_{nn}(R) \delta(U_{nn}(R) - U_{nn}(R, T)) dR = U_{nn}(T). \quad (36)$$

Now, let us make assumption – in our opinion, which is not deprived of plausibility – that, since U_{nn} depends only on the lattice vectors, R , the statistical averaging will result in the temperature dependence of the lattice vectors only. Moreover, since the crystal symmetry remains unchanged in rather a wide temperature interval, the temperature-induced variation of lattice vectors will result in the corresponding change of their lengths. Then

$$\bar{U}_{nn} = U_{nn}(R(T)) = \frac{V}{v} U_{nn}^0(R(T)) \quad (37)$$

and, respectively,

$$E = (U_{nn}^{01}(R(T)) + E_k^0)V, \quad (38)$$

where

$$U_{nn}^{01} = \frac{1}{v} U_{nn}^0. \quad (39)$$

In turn, according to the results of work [5],

$$\frac{\partial E}{\partial V} = -P. \quad (40)$$

Then

$$U_{nn}^{01}(R(T)) + E_k^0 = -P \quad (41)$$

and

$$E = -PV. \quad (42)$$

Accordingly, the relation

$$PV = \frac{1}{2} \sum_{\nu} \bar{\varepsilon}_{\nu} \quad (43)$$

can be considered as the equation of crystal state in the harmonic approximation. At high temperatures, $\hbar\omega_{\nu} \ll kT$, it transforms into the well-known classical expression

$$PV = \frac{3}{2} NkT. \quad (44)$$

Since

$$C_p = \left(\frac{\partial E}{\partial T} \right)_P, \quad (45)$$

we have

$$C_p = -P \frac{\partial V}{\partial T}. \quad (46)$$

On the other hand,

$$C_p = \frac{\partial}{\partial T} \left(\sum_{\nu} \bar{\varepsilon}_{\nu} \right) + \frac{d\bar{U}_{nn}}{dT}. \quad (47)$$

In turn,

$$\frac{d\bar{U}_{nn}}{dT} = \sum_k \frac{\partial \bar{U}_{nn}}{\partial \mathbf{R}_k} \frac{d\mathbf{R}_k}{dT}. \quad (48)$$

As a rule, in the course of the thermal expansion, the crystal keeps its symmetry in a wide temperature interval. Therefore, we assume that the vectors

$d\mathbf{R}_k$ and \mathbf{R}_k have the same direction. Multiplying each term on the right-hand side of Eq. (48) by $\mathbf{R}_k/\mathbf{R}_k = 1$, we obtain

$$\frac{d\bar{U}_{nn}}{dT} = \sum_k \frac{\partial \bar{U}_{nn}}{\partial \mathbf{R}_k} \frac{\mathbf{R}_k}{R_k} \frac{dR_k}{dT}. \quad (49)$$

We can demonstrate that the combination $\frac{1}{R_k} \frac{dR_k}{dT}$, which is a coefficient of the linear thermal expansion, does not depend on k for the cubic crystal. We will denote it by α_1 in contrast to the coefficient of bulk thermal expansion α . Note that the coefficient α_1 is related to the static (electron) part of the potential energy; therefore, it would be more proper to call it the electron contribution to the thermal expansion with regard for a probable phonon contribution, the calculation of which goes beyond the scope of the harmonic approximation.

So, we have

$$\frac{d\bar{U}_{nn}}{dT} = \alpha_1 \sum_k \frac{\partial \bar{U}_{nn}}{\partial \mathbf{R}_k} \mathbf{R}_k. \quad (50)$$

Let us introduce the notation

$$A_{nn} = \sum_k \frac{\partial \bar{U}_{nn}}{\partial \mathbf{R}_k} \mathbf{R}_k. \quad (51)$$

Then Eq. (50) reads

$$\frac{d\bar{U}_{nn}}{dT} = \alpha_1 A_{nn}. \quad (52)$$

Accordingly, for the heat capacities, we obtain

$$C_p = \frac{\partial}{\partial T} \left(\sum_\nu \bar{\varepsilon}_\nu \right) + \alpha_1 A_{nn} \quad (53)$$

and

$$\begin{aligned} C_v &= -V \frac{\partial P}{\partial T} = V \frac{\partial}{\partial T} (U_{nn}^{01} + E_k^0) = \\ &= \frac{\partial E_k}{\partial T} = \sum_\nu \frac{\partial \bar{\varepsilon}_\nu}{\partial T}. \end{aligned} \quad (54)$$

Here, we took into account that U_{nn}^{01} does not depend explicitly on the temperature. Formula (54) agrees with the result of work [4]. From Eqs. (53) and (54), it follows that

$$C_p = C_v + \alpha_1 A_{nn} \quad (55)$$

or

$$C_p - C_v = \alpha_1 A_{nn}. \quad (56)$$

Since A_{nn} does not depend explicitly on the temperature, the ratio $\frac{C_p - C_v}{\alpha_1} = A_{nn}$, being an expression of the Grüneisen law, allows one to determine the coefficient of linear thermal expansion,

$$\alpha_1 = \frac{C_p - C_v}{A_{nn}}. \quad (57)$$

By definition, $\alpha_1 = \frac{dR}{RdT}$ for a cubic crystal.

Let us determine the temperature dependence of the lattice vector

$$R(T) = R(0) e^{\alpha_1 T}, \quad (58)$$

where $R(0)$ is the corresponding value at the absolute zero temperature. Since $\alpha_1 T \ll 1$ within the whole interval of real temperatures, we may put

$$R(T) = R(0) (1 + \alpha_1 T). \quad (59)$$

4. Conclusions

As a rule [4], while analyzing the lattice dynamics, the abstract potential energy as a function of the nuclear coordinates, as well as its derivatives with respect to the nuclear coordinates, is used, without account for the possibility of their calculation. In this work, it is shown that, while describing the dynamics of nuclei, the corresponding dynamic equations include actually the averaged quantum-mechanical values of potential energy and its derivatives, which is a consequence of the division between the motions of the electron and nuclear subsystems. This division is carried out in the adiabatic approximation, the criterion of which is the smallness of the non-diagonal elements in the interaction energy matrix in comparison with the diagonal ones ($U_{nn'} \ll U_{nn}$). In addition, while expanding the potential energy in a series in small nuclear shifts from the equilibrium positions, it is necessary to take into account that the matter concerns the potential energy that is averaged statistically as well. As a result, there emerges the temperature dependence of not only the vibrational energy, but also the static one, U_{nn} , governing the thermal expansion, the temperature-induced shift of equilibrium positions, and the temperature dependence of force constants.

In this work, all preliminary conditions required for the calculation of both the average potential energy U_{nn} (with the use of $U(R, r)$) and its arbitrary-order derivatives with respect to the nuclear coordinates (force constants) are formulated. The main objective

of the work was to express all examined characteristics of a solid in terms of the quantum-statistically averaged interaction energy $\bar{U}_{nn}(R)$ and its derivatives.

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ДО ТЕОРІЇ СИЛОВИХ СТАЛИХ
БАГАТОАТОМНИХ СИСТЕМ У МОДЕЛІ
СИЛЬНОГО ЗВ'ЯЗКУ (ЧАСТИНА II)

Резюме

У роботі в моделі сильного зв'язку наведено наближений вираз для енергії кулонівської взаємодії в твердому тілі. Проаналізовано умову адіабатичного наближення та виконано аналіз квантово-статистичного усереднення першого (статичного) члена розкладу середньої потенціальної енергії по малих зміщеннях ядер. Такий аналіз дозволив визначити електронний внесок у теплове розширення твердого тіла. На основі аналізу внутрішньої енергії та теплових властивостей твердого тіла отримано рівняння стану твердого тіла в гармонічному наближенні. Відповідно знайдено зв'язок теплоємностей C_v та C_p , що узгоджується із законом Грюнайзена.