ISSN 1027-5495. Functional Materials, 26, No.4 (2019), p. 807-815.
doi:https://doi.org/10.15407/fm26.04.807 © 2019 — STC "Institute for Single Crystals"

Phase transitions in crystals: the electronic subsystem contribution

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Received March 13, 2019

The base energy of the electron subsystem of a condensed matter of a crystalline type was considered by quantum field theory methods. Here we considered monatomic condensates, because they are most simple from the point of view of the objects quantum description. In particular, evaluations were carried out for boron and the electronic subsystem was only taken into account. The exact value of the crystal internal energy as a function of temperature is obtained, and this dependence is completely determined by the Fermi-Dirac factor. Internal energy, as a function of this factor, has a sufficiently simple (parabolic) form. It is shown that the matrix elements included in the coefficients of this dependence are divided into two groups: centrally symmetric and anisotropic. Centrally symmetric matrix elements determine isotropic interactions. Such interactions are characteristic of liquids. Anisotropic matrix elements determine the interactions characteristic to crystals. It is shown that competition between them result in the phase transitions. The possibilities of analytical estimates for the contributions due to the electronic subsystem to the liquid-gas and crystal-liquid phase transition temperatures are analyzed.
Keywords: electronic subsystem, phase transitions, Fermi-Dirac factor.

Рассмотрена базовая энергия электронной подсистемы конденсированной среды кристаллического типа методами квантовой теории поля. Рассмотрение проводилось для одноатомных конденсатов, как наиболее простых с точки зрения квантового описания объектов. В частности, оценки проводились для бора, и учитывалась только электронная подсистема. Получено точное значение внутренней энергии кристалла как функции от температуры, причем эта зависимость целиком определяется фактором Ферми-Дирака. Внутренняя энергия, как функция от этого фактора, имеет достаточно простой (параболический) вид. Показано, что матричные элементы, входящие в коэффициенты этой зависимости, разделяются на две группы: центрально-симметричные и анизотропные. Центрально-симметричные матричные элементы определяют изотропные взаимодействия, характерные для жидкостей. Анизотропные матричные элементы определяют взаимодействия, характерные для кристаллов. Показано, что конкуренция между ними приводит к фазовым переходам. Анализируются возможности аналитических оценок вклада электронной подсистемы в температуры фазовых переходов жидкость-газ и кристалл-жидкость.

Фазові переходи у кристалах: внесок електронної підсистеми. *А.Д.Супрун, В.В.Дацюк, Л.В.Шмельова, С.М.Єжов*

Розглянуто базову енергію електронної підсистеми конденсованого середовища кристалічного типу методами квантової теорії поля. Розгляд проводився для одноатомних конденсатів, як найбільш простих з погляду квантового опису об'єктів. Зокрема, оцінки проводилися для бору, і враховувалася тільки електронна підсистема. Отримано точне значення внутрішньої енергії кристала як функції від температури, причому ця залежність цілком визначається фактором Фермі-Дірака. Внутрішня енергія, як функція від цього фактора, має досить простий (параболічний) вигляд. Показано, що

матричні елементи, що входять у коефіцієнти цієї залежності, розділяються на дві групи: центрально-симетричні й анізотропні. Центрально-симетричні матричні елементи визначають ізотропні взаємодії, характерні для рідин. Анізотропні матричні елементи визначають взаємодії, характерні для кристалів. Показано, що конкуренція між ними приводить до фазових переходів. Аналізуються можливості аналітичних оцінок внеску електронної підсистеми в температури фазових переходів рідина-газ і кристал-рідина.

1. Introduction

As is generally known, transformations of the aggregate state of substance behave to the first-order transitions. For these transitions the discontinuous changes of the first derivatives from thermodynamics potentials on the intensive parameters of the system (pressure and temperature) are characteristically. One of such derivatives is the specific volume of a unit mass of a substance, but the density of a condensed environment is used more often. Other such derivative is entropy, characterizing the change of degree of efficiency of the system. Methods of statistical physics [1 - 4] allow determine these parameters for the various aggregate states. Thus, thermodynamics potentials are first determined for every aggregate state, and then value of density and entropy. Further a density and entropy are analyzed for the purpose the estimation of points of phase transitions on a temperature and pressure.

Such statistical analysis does not give a complete answer for a question about physical nature of phase transformation. Except transformations of the aggregate state of substance, the first-order phase transitions are investigated and in other situations. It is possible to enumerate some examples: ferroelectrics [5], magnetic systems [6, 7], and thin-films for sunny elements [8], theory of superfluidity [9], proteinous and nucleic structures [10] and also many other physical systems [11 – 14]. Thus, model enough Hamiltonians are mostly used [15 – 17], actual for certain applications, and frequently not giving an answer for a question about physical reasons of the first-order transitions.

Understanding of primary causes of phase changes in the condensed environments is impossible without understanding of physical nature of changes of quality of the interatomic interactions due to electronic and phonon subsystems at such transitions.

Such consideration is conducted in the article by the methods of quantum theory of the field as it applies to the condensed environment. Exact expression is got for energy of condensate of crystalline type at a temperature $T = 0°K$. The feature of the got energy is that it contains dependence on a temperature as factors of Fermi-Dirac, and also on two types of interatomic interactions. One of them is characteristically for crystals and other for liquids. As shown in the article, a competition between these interactions at the change of temperature determines the contribution of electronic subsystem to the temperatures of phase transitions.

2. Materials and methods. Basic condensate energy and preliminary analysis

The operator of the electronic subsystem of the monoatomic condensate looks like in the particle number representation [18, 19]:

$$\widehat{H}=\sum_{f\mathbf{n}}\varepsilon_f b^+_{f\mathbf{n}}b_{f\mathbf{n}}-z\sum_{f\mathbf{n}}\sum_{\mathbf{l}}\sum_{g\mathbf{m}}{}''Q^{fg}_{\mathbf{nlm}}\,b^+_{f\mathbf{n}}b_{g\mathbf{m}}+\frac{1}{2}\sum_{f\mathbf{n}}\sum_{g\mathbf{m}}\sum_{f'\dot{\mathbf{n}}'}\sum_{g'\mathbf{m}'}V^{fgf'g'}_{\mathbf{nmn'm'}}b^+_{f\mathbf{n}}b^+_{g\mathbf{m}}b_{f'\dot{\mathbf{n}}'}b_{g'\mathbf{m}'}. \qquad (1)$$

This presentation can be used for not monoatomic condensates as a zero approximation. A double stroke near the signs of adding up means absence of element $n = l = m$.

The matrix elements of operator (1) have such determinations:

$$\varepsilon_f=\langle\varphi_f(\mathbf{r})|-\frac{\hbar^2}{2m}\Delta_r-zq(r)\,|\varphi_f(\mathbf{r})\rangle,\quad Q^{fg}_{\mathbf{nlm}}=\langle\varphi_{f\mathbf{n}}(\mathbf{r})|q(|\mathbf{r}-\mathbf{l}|)\,|\varphi_{g\,\mathbf{m}}(\mathbf{r})\rangle;$$

$$V^{fgf'g'}_{\mathbf{nmn'm'}} = \langle \varphi_{f\mathbf{n}}(\mathbf{r}_1)\,\varphi_{g\mathbf{m}}(\mathbf{r}_2)|q(|\mathbf{r}_1-\mathbf{r}_2|)\,|\varphi_{f'\mathbf{n'}}(\mathbf{r}_2)\,\varphi_{g'\mathbf{m'}}(\mathbf{r}_1)\rangle.$$

Here and further everywhere it denotes: $q(r) \equiv e^2/r$. The wave functions of single-electron ion of atom corresponding to the examined condensate were denoted $\varphi_{f\mathbf{n}}(\mathbf{r})$. The standard set of quantum numbers of hydrogen-like ion was denoted as f, and $\mathbf{n}$ is a spatial vector centering a wave function in accordance with property: $\varphi_{f\mathbf{n}}(\mathbf{r}) \equiv \varphi_f(\mathbf{r}-\mathbf{n})$. In crystals this vector coincides with the crystalline grate vector. In other cases it determines spatial position of atom. An operator (1) corresponds to the crystal that is at a zero temperature.

The creation (annihilation) operators $b^+_{f\mathbf{n}}$ ($b_{f\mathbf{n}}$) of the electronic states operate on a function $|\ldots,\ N_{f\mathbf{n}},\ \ldots\rangle$, the variables of that there are occupation numbers $N_{f\mathbf{n}}$. They take on only two values 0 and 1. Those operators operate on the electron state functions as:

$$b^+_{f\mathbf{n}}|\ldots,\ N_{f\mathbf{n}},\ \ldots\rangle = (-1)^{\sigma_{f\mathbf{n}}}(1-N_{f\mathbf{n}})\,|\ldots,\ 1-N_{f\mathbf{n}},\ \ldots\rangle;$$
$$b_{f\mathbf{n}}|\ldots,\ N_{f\mathbf{n}},\ \ldots\rangle = (-1)^{\sigma_{f\mathbf{n}}}N_{f\mathbf{n}}|\ldots,\ 1-N_{f\mathbf{n}},\ \ldots\rangle.$$

The parameter $\sigma_{f\mathbf{n}}$ is equal to the number of the states with energies below than energy of the state of $f\mathbf{n}$. Also next properties of the creation and annihilation operators are valid:

$$b^+_{f\mathbf{n}}b_{f\mathbf{n}}|\ldots,\ N_{f\mathbf{n}},\ \ldots\rangle = \mathrm{N}_{f\mathbf{n}}|\ldots,\ N_{f\mathbf{n}},\ \ldots\rangle, \tag{2}$$

and

$$b_{f\mathbf{n}}b^+_{g\mathbf{m}} + b^+_{g\mathbf{m}}b_{f\mathbf{n}} = \delta_{fg}\delta_{\mathbf{nm}}, \quad b_{f\mathbf{n}}b_{g\mathbf{m}} + b_{g\mathbf{m}}b_{f\mathbf{n}} = 0, \quad b^+_{f\mathbf{n}}b^+_{g\mathbf{m}} + b^+_{g\mathbf{m}}b^+_{f\mathbf{n}} = 0. \tag{3}$$

At a zero temperature electronic configuration of vacuum will be realized:

$$|0\rangle \equiv \left|\underbrace{1,...,1}_{N_e},0,...,0,...\right\rangle. \tag{4}$$

Here N_e is the total number of electrons in a condensate that occupy the lowermost energy states. Equation (2) for the vacuum state $|0\rangle$ can be written as:

$$b^+_{f\mathbf{n}}b_{f\mathbf{n}}|0\rangle = N^{(0)}_{f\mathbf{n}}\,|0\rangle. \tag{5}$$

Here $N^{(0)}_{f\mathbf{n}}$ marks set of the occupation numbers that describe the vacuum state. The equality takes place:

$$N^{(0)}_{f\mathbf{n}} = \begin{cases} 1, \text{if} f \le v; \\ 0, \text{if} f \ge c. \end{cases}$$

Here ν denotes the valence zone and c is the conductivity zone. It is obviously that the factor $N^{(0)}_{f\mathbf{n}}$ depends on the zone quantum states so, that reproduces Fermi-Dirac distribution at a zero temperature.

It is necessary to execute the averaging [20–22] of the operator (1) on the functions (4) for determination of internal energy of condensate $W = \langle 0|\widehat{H}|0\rangle$ and to add to the result the effective energy of the direct coulomb cooperation between nucleus. It is possible to get expression for the internal energy of crystal with help the commutation relations (3) and property (5):

$$W = z_n^2 {\sum_{\mathbf{nm}}}' q(|\mathbf{n}-\mathbf{m}|) - z_e {\sum_{\mathbf{nm}}}' {\sum_{f}} N^{(0)}_{f\mathbf{0}} Q^f_{\mathbf{n}-\mathbf{m}} + \frac{1}{2}{\sum_{\mathbf{nm}}}' {\sum_{fg}} N^{(0)}_{f\mathbf{0}} N^{(0)}_{g\mathbf{0}} K^{fg}_{\mathbf{n}-\mathbf{m}} - \frac{1}{2}{\sum_{\mathbf{nm}}}' {\sum_{fg}} N^{(0)}_{f\mathbf{0}} N^{(0)}_{g\mathbf{0}} R^{fg}_{\mathbf{n}-\mathbf{m}}$$

And also such denotations are used:

$$Q^{ff}_{\mathbf{nmn}} \equiv \int\limits_{(\infty)} \varphi^*_f(\mathbf{r}-\mathbf{n})\, q(|\mathbf{r}-\mathbf{m}|)\, \varphi_f(\mathbf{r}-\mathbf{n})\, d^3\mathbf{r};$$

$$V^{fggf}_{\mathbf{nmmn}} \equiv \int\limits_{(\infty)} d^3\mathbf{r}_2 \int\limits_{(\infty)} \varphi^*_f(\mathbf{r}_1-\mathbf{n})\, \varphi^*_g(\mathbf{r}_2-\mathbf{m})\, q(|\mathbf{r}_1-\mathbf{r}_2|)\, \varphi_g(\mathbf{r}_2-\mathbf{m})\, \varphi_f(\mathbf{r}_1-\mathbf{n})\, d^3\mathbf{r}_1;$$

$$V^{fgfg}_{\mathbf{nmnm}} \equiv \int\limits_{(\infty)} d^3\mathbf{r}_2 \int\limits_{(\infty)} \varphi^*_f(\mathbf{r}_1-\mathbf{n})\, \varphi^*_g(\mathbf{r}_2-\mathbf{m})\, q(|\mathbf{r}_1-\mathbf{r}_2|)\, \varphi_f(\mathbf{r}_2-\mathbf{n})\, \varphi_g(\mathbf{r}_1-\mathbf{m})\, d^3\mathbf{r}_1.$$

If a crystal is ideal (endless and defect-free), then energy over can be brought to the form:

$$W = z_n^2 {\sum_{\mathbf{nm}}}' q(|\mathbf{n}-\mathbf{m}|) - z_e {\sum_{\mathbf{nm}}}' {\sum_{f}} N^{(0)}_{f\mathbf{0}} Q^{\,f}_{\mathbf{n}-\mathbf{m}} + \frac{1}{2} {\sum_{\mathbf{nm}}}' {\sum_{fg}} N^{(0)}_{f\mathbf{0}} N^{(0)}_{g\mathbf{0}} K^{fg}_{\mathbf{n}-\mathbf{m}} - \frac{1}{2} {\sum_{\mathbf{nm}}}' {\sum_{fg}} N^{(0)}_{f\mathbf{0}} N^{(0)}_{g\mathbf{0}} R^{fg}_{\mathbf{n}-\mathbf{m}},$$

Here such denotations are used:

$$Q^{\,f}_{\mathbf{n}-\mathbf{m}} \equiv \int\limits_{(\infty)} \varphi^*_f(\mathbf{r})\, q(|\mathbf{r}+\mathbf{n}-\mathbf{m}|)\, \varphi_f(\mathbf{r})\, d^3\mathbf{r};$$

$$K^{fg}_{\mathbf{n}-\mathbf{m}} \equiv \int\limits_{(\infty)} d^3\mathbf{r}_2 \int\limits_{(\infty)} \phi^*_f(\mathbf{r}_1)\, \phi^*_g(\mathbf{r}_2)\, q(|\mathbf{r}_1-\mathbf{r}_2+\mathbf{n}-\mathbf{m}|)\, \phi_g(\mathbf{r}_2)\, \phi_f(\mathbf{r}_1)\, d^3\mathbf{r}_1 \equiv$$
$$\equiv \int\limits_{(\infty)} \phi^*_g(\mathbf{r})\, Q^{\,f}_{\mathbf{n}-\mathbf{m}-\mathbf{r}} \phi_g(\mathbf{r})\, d^3\mathbf{r}\ ;$$

$$R^{fg}_{\mathbf{n}-\mathbf{m}} \equiv \int\limits_{(\infty)} d^3\mathbf{r}_2 \int\limits_{(\infty)} \varphi^*_f(\mathbf{r}_1)\, \varphi^*_g(\mathbf{r}_2)\, q(|\mathbf{r}_1-\mathbf{r}_2+\mathbf{n}-\mathbf{m}|)\, \varphi_f(\mathbf{r}_2+\mathbf{m}-\mathbf{n})\, \varphi_g(\mathbf{r}_1+\mathbf{n}-\mathbf{m})\, d^3\mathbf{r}_1.$$

In an ideal crystal it is possible also to avoid one adding up in the double sums. We will define energy on one atom as: $w \equiv W/N_a$, where N_a the number of atoms in the basic area of crystal and will get:

$$w = z_n^2 \sum_{\mathbf{n}(\neq\mathbf{0})} q(|\mathbf{n}|) - z_e \sum_{f} N^{(0)}_{f\mathbf{0}} \sum_{\mathbf{n}(\neq\mathbf{0})} Q^{f}_{\mathbf{n}} + \frac{1}{2} \sum_{fg} N^{(0)}_{f\mathbf{0}} N^{(0)}_{g\mathbf{0}} \sum_{\mathbf{n}(\neq\mathbf{0})} K^{fg}_{\mathbf{n}} - \frac{1}{2} \sum_{fg} N^{(0)}_{f\mathbf{0}} N^{(0)}_{g\mathbf{0}} \sum_{\mathbf{n}(\neq\mathbf{0})} R^{fg}_{\mathbf{n}}. \qquad (6)$$

Here such denotations are used:

$$Q^{f}_{\mathbf{n}} \equiv \int\limits_{(\infty)} \varphi^*_f(\mathbf{r})\, q(|\mathbf{r}+\mathbf{n}|)\, \varphi_f(\mathbf{r})\, d^3\mathbf{r}; \qquad (7)$$

$$K^{fg}_{\mathbf{n}} \equiv \int\limits_{(\infty)} d^3\mathbf{r}_2 \int\limits_{(\infty)} \varphi^*_f(\mathbf{r}_1)\, \varphi^*_g(\mathbf{r}_2)\, q(|\mathbf{r}_1-\mathbf{r}_2+\mathbf{n}|)\, \varphi_g(\mathbf{r}_2)\, \varphi_f(\mathbf{r}_1)\, d^3\mathbf{r}_1 \equiv$$
$$\equiv \int\limits_{(\infty)} \varphi^*_g(\mathbf{r})\, Q^{\,f}_{\mathbf{n}-\mathbf{r}} \varphi_g(\mathbf{r})\, d^3\mathbf{r}\ ; \qquad (8)$$

$$R^{fg}_{\mathbf{n}} \equiv \int\limits_{(\infty)} d^3\mathbf{r}_2 \int\limits_{(\infty)} \varphi^*_f(\mathbf{r}_1)\, \varphi^*_g(\mathbf{r}_2)\, q(|\mathbf{r}_1-\mathbf{r}_2+\mathbf{n}|)\, \varphi_f(\mathbf{r}_2-\mathbf{n})\, \varphi_g(\mathbf{r}_1+\mathbf{n})\, d^3\mathbf{r}_1. \qquad (9)$$

The Coulomb energy $q(|\mathbf{n}|) \equiv e^2/|\mathbf{n}|$ depends on the modulus of the vector $\mathbf{n}$. One can show, using the definitions (7) and (8), that the matrix elements $Q^f_{\mathbf{n}}$ and $K^{fg}_{\mathbf{n}}$ also depend on $|\mathbf{n}|$. In this sense, they are centrally symmetric and provide only an isotropic bond between atoms, characteristic for liquids. In contrast, the matrix element $R^{fg}_{\mathbf{n}}$ depends on $\mathbf{n}$ as on a vector. That is, it depends on all its components, and makes an anisotropic contribution to the interaction, highlighting the crystallographic directions.

With account of separation of the matrix elements into centrally symmetric and anisotropic, we introduce the notation:

$$q_S \equiv \sum_{\mathbf{n}(\neq\mathbf{0})} q(|\mathbf{n}|); \quad Q_S^f \equiv \sum_{\mathbf{n}(\neq\mathbf{0})} Q_{\mathbf{n}}^f; \quad K_S^{fg} \equiv \sum_{\mathbf{n}(\neq\mathbf{0})} K_{\mathbf{n}}^{fg}; \quad R_A^{fg} \equiv \sum_{\mathbf{n}(\neq\mathbf{0})} R_{\mathbf{n}}^{fg}. \tag{10}$$

The subscript "S" indicates energies corresponding to centrally symmetric (liquid) contributions. The "A" index indicates energy corresponding to anisotropic (crystalline) contributions.

All the energy (6) then reduces to this form:

$$w = z_n^2 q_S - z_e \sum_f Q_S^f N_{f\mathbf{0}}^{(0)} + \frac{1}{2}\sum_{fg} K_S^{fg} N_{f\mathbf{0}}^{(0)} N_{g\mathbf{0}}^{(0)} - \frac{1}{2}\sum_{fg} R_A^{fg} N_{f\mathbf{0}}^{(0)} N_{g\mathbf{0}}^{(0)}.$$

Taking into account that the factor $N_{f\mathbf{0}}^{(0)}$ actually represents the Fermi-Dirac distribution at zero temperature, for a nonzero temperature this energy will have the form:

$$w\,(T) = z_n^2 q_S - z_e \sum_f Q_S^f N_{f\mathbf{0}}^{(T)} + \frac{1}{2}\sum_{fg} K_S^{fg} N_{f\mathbf{0}}^{(T)} N_{g\mathbf{0}}^{(T)} - \frac{1}{2}\sum_{fg} R_A^{fg} N_{f\mathbf{0}}^{(T)} N_{g\mathbf{0}}^{(T)}. \tag{11}$$

Since semiconductor type condensate is considered, only the highest valence band $f = \nu$ and the lowest conduction band $f = c$ are thermally active. Then it can be shown that:

$$N_{f0}^{(T)} = \begin{cases} 1, & \text{if } f < \nu, \\ N_{\nu 0}^{(T)}, & \text{if } f = \nu, \\ N_{c0}^{(T)}, & \text{if } f = c, \\ 0, & \text{if } f > c, \end{cases} \tag{12}$$

where

$$N_{v\mathbf{0}}^{(T)} = \frac{1}{1 + \exp\left(\frac{E_v - \mu}{kT}\right)}; \quad N_{c\mathbf{0}}^{(T)} = \frac{1}{1 + \exp\left(\frac{E_c - \mu}{kT}\right)}.$$

Here μ is the chemical potential restricted by condition: $E_v < \mu < E_c$. If a crystal is ideal (without admixtures), then with the good degree of precision the next value takes place: $\mu = \frac{E_v + E_c}{2}$. Expressions are just as a result:

$$N_{v\mathbf{0}}^{(T)} = \frac{1}{1 + \exp\left(-\frac{E_c - E_v}{2kT}\right)}; \quad N_{c\mathbf{0}}^{(T)} = \frac{1}{1 + \exp\left(\frac{E_c - E_v}{2kT}\right)}.$$

Obviously, that in this case is always executed condition: $N_{v\mathbf{0}}^{(T)} + N_{c\mathbf{0}}^{(T)} = 1$. As inequality $E_c > E_v$ is too executed always, then with the increase of temperature from 0 to infinity the factor $N_{c\mathbf{0}}^{(T)}$ increases too, but from 0 to 1/2. The factor $N_{v\mathbf{0}}^{(T)}$, vice versa, decreases from 1 to 1/2. Based on this, it is more suitable to choose a factor $N_{c\mathbf{0}}^{(T)}$ for analysis. Then expression (12) takes the form:

$$N_{f0}^{(T)} = \begin{cases} 1, & \text{if } f < \nu, \\ 1 - N_{c0}^{(T)}, & \text{if } f = \nu, \\ N_{c0}^{(T)}, & \text{if } f = c, \\ 0, & \text{if } f > c. \end{cases} \tag{13}$$

As a result the energy (11), with account the definition (13), takes the form:

$$w(T)=z_n^2 q_S - z_e\sum_{f\le v}Q_S^f+\tfrac{1}{2}\sum_{f\le v}\sum_{g\le v}K_S^{fg}-\tfrac{1}{2}\sum_{f\le v}\sum_{g\le v}R_A^{fg}+$$
$$+\left\{z_e\left(Q_S^v-Q_S^c\right)+\sum_{f\le v}\left(K_S^{fc}-K_S^{fv}\right)-\sum_{f\le v}\left(R_A^{fc}-R_A^{fv}\right)\right\}N_{c\mathbf{0}}^{(T)}+ \qquad (14)$$
$$+\left\{\tfrac{1}{2}\left(K_S^{vv}+K_S^{cc}-2K_S^{vc}\right)-\tfrac{1}{2}\left(R_A^{vv}+R_A^{cc}-2R_A^{vc}\right)\right\}\left(N_{c\mathbf{0}}^{(T)}\right)^2 .$$

Also next symmetries of matrix elements are here taken into account: $K_S^{fg}=K_S^{gf}$, $R_A^{fg}=R_A^{gf}$, that will be realized in the conditions of ideal crystal.

Further it is convenient to introduce the notations, which add to the expressions (10) and slightly reduce the analysis:

$$Q_S\equiv\sum_{f\le\nu}Q_S^f\equiv\sum_{f\le\nu}\sum_{\mathbf{n}(\neq\mathbf{0})}Q_{\mathbf{n}}^f\equiv\sum_{f\le\nu}\sum_{\mathbf{n}(\neq\mathbf{0})}\int\limits_{(\infty)}\varphi_f^*(\mathbf{r})\,q\left(|\mathbf{r}+\mathbf{n}|\right)\varphi_f(\mathbf{r})\,d^3\mathbf{r}; \qquad (15)$$

$$\mathrm{K}_S\equiv\sum_{f\le\nu}\sum_{g\le\nu}K_S^{fg}\equiv\sum_{f\le\nu}\sum_{g\le\nu}\sum_{\mathbf{n}(\neq\mathbf{0})}K_{\mathbf{n}}^{fg}\equiv\sum_{f\le\nu}\sum_{g\le\nu}\sum_{\mathbf{n}(\neq\mathbf{0})}\int\limits_{(\infty)}\varphi_g^*(\mathbf{r})\,Q_{\mathbf{n}-\mathbf{r}}^f\varphi_g(\mathbf{r})\,d^3\mathbf{r}; \qquad (16)$$

$$\mathrm{R}_A\equiv\sum_{f\le\nu}\sum_{g\le\nu}R_A^{fg}\equiv\sum_{f\le\nu}\sum_{g\le\nu}\sum_{\mathbf{n}(\neq\mathbf{0})}R_{\mathbf{n}}^{fg}\equiv$$
$$\equiv\sum_{f\le\nu}\sum_{g\le\nu}\sum_{\mathbf{n}(\neq\mathbf{0})}\int\limits_{(\infty)}d^3\mathbf{r}_2\int\limits_{(\infty)}\varphi_f^*(\mathbf{r}_1)\,\varphi_g^*(\mathbf{r}_2)\,q\left(|\mathbf{r}_1-\mathbf{r}_2+\mathbf{n}|\right)\varphi_f(\mathbf{r}_2-\mathbf{n})\,\varphi_g(\mathbf{r}_1+\mathbf{n})\,d^3\mathbf{r}_1\,; \qquad (17)$$

$$\kappa_S^{cv}\equiv\sum_{f\le v}\left(K_S^{fc}-K_S^{fv}\right)\equiv\frac{1}{2}\sum_{f\le\nu}\sum_{\mathbf{n}(\neq\mathbf{0})}\left(\int\limits_{(\infty)}\varphi_c^*(\mathbf{r})\,Q_{\mathbf{n}-\mathbf{r}}^f\varphi_c(\mathbf{r})\,d^3\mathbf{r}-\int\limits_{(\infty)}\varphi_v^*(\mathbf{r})\,Q_{\mathbf{n}-\mathbf{r}}^f\varphi_v(\mathbf{r})\,d^3\mathbf{r}\right); \qquad (18)$$

$$\rho_A^{cv}\equiv\sum_{f\le v}\left(R_A^{fc}-R_A^{fv}\right)\equiv$$
$$\equiv\sum_{f\le\nu}\left(\sum_{\mathbf{n}(\neq\mathbf{0})}\int\limits_{(\infty)}d^3\mathbf{r}_2\int\limits_{(\infty)}\varphi_f^*(\mathbf{r}_1)\,\varphi_c^*(\mathbf{r}_2)\,q\left(|\mathbf{r}_1-\mathbf{r}_2+\mathbf{n}|\right)\varphi_f(\mathbf{r}_2-\mathbf{n})\,\varphi_c(\mathbf{r}_1+\mathbf{n})\,d^3\mathbf{r}_1-\right. \qquad (19)$$
$$\left.-\sum_{\mathbf{n}(\neq\mathbf{0})}\int\limits_{(\infty)}d^3\mathbf{r}_2\int\limits_{(\infty)}\varphi_f^*(\mathbf{r}_1)\,\varphi_\nu^*(\mathbf{r}_2)\,q\left(|\mathbf{r}_1-\mathbf{r}_2+\mathbf{n}|\right)\varphi_f(\mathbf{r}_2-\mathbf{n})\,\varphi_\nu(\mathbf{r}_1+\mathbf{n})\,d^3\mathbf{r}_1\right)\,;$$

$$\eta(T)\equiv N_{c\mathbf{0}}^{(T)}\equiv\frac{1}{1+\exp\left(\frac{E_c-E_\nu}{2kT}\right)}. \qquad (20)$$

Then the energy (14), with account of these notations into account, takes the form:

$$w(T)=z_n^2 q_S - z_e Q_S+\tfrac{1}{2}\mathrm{K}_S-\tfrac{1}{2}\mathrm{R}_A+\left\{z_e\left(Q_S^v-Q_S^c\right)+\kappa_S^{cv}-\rho_A^{cv}\right\}\eta(T)+$$
$$+\left\{\tfrac{1}{2}\left(K_S^{vv}+K_S^{cc}-2K_S^{vc}\right)-\tfrac{1}{2}\left(R_A^{vv}+R_A^{cc}-2R_A^{vc}\right)\right\}\eta^2(T)\ . \qquad (21)$$

The matrix elements Q_S^ν, Q_S^c, $K_S^{\nu\nu}$, K_S^{cc}, K_S^{vc}, $R_A^{\nu\nu}$, R_A^{cc}, R_A^{vc} are defined by the general relations (10) using (7) ÷ (9).

3. Results and discussion. General analysis of the problem

Equation (21), taking into account (20), describes the influence of an external thermostat on the specific internal energy $w(T)$ of a monatomic condensate. Since the factor $\eta(T)$, defined in (20), also increases

with increasing temperature, it can be regarded as an overdetermined temperature. The dependence of the energy (21) on the factor η has a parabolic form:

$$w(\eta) = \left[U_S^{(0)} - (1/2)\,\mathrm{R}_A\right] + \left[U_S^{(1)} - \rho_A^{cv}\right]\eta + \left[U_S^{(2)} + U_A^{(2)}\right]\eta^2. \tag{22}$$

This form is convenient for qualitative analysis. Next denotations are here used:

$$U_S^{(0)} \equiv z_n^2 q_S + (1/2)\,\mathrm{K}_S - z_e Q_S; \quad U_S^{(1)} \equiv z_e Q_S^v + \kappa_S^{cv} - z_e Q_S^c; \tag{23}$$

$$U_S^{(2)} \equiv (1/2)\,K_S^{vv} + (1/2)\,K_S^{cc} - K_S^{vc}; \quad U_A^{(2)} \equiv R_A^{vc} - (1/2)\,R_A^{vv} - (1/2)\,R_A^{cc}. \tag{24}$$

The terms R_A and ρ_A^{cv} were given in (17), (19).

For the definiteness of the subsequent analysis were held qualitative estimates of all six quantities $U_S^{(0)}$, R_A, $U_S^{(1)}$, ρ_A^{cv}, $U_S^{(2)}$ and $U_A^{(2)}$ entering into the energy (22) and determined in (7) ÷ (9), (10), (15) ÷ (19), (23), (24). These estimates were based on the approximation of the far zone ($\{|\mathbf{r}|, |\mathbf{r}_1|, |\mathbf{r}_2|\} << |\mathbf{n}|$) in integrals of the type (7) ÷ (9). Such approaching is possible for quality estimations due to that in these integrals there are hydrogen-like wave functions that quickly (exponentially) decrease at $|\mathbf{n}| \to \infty$. Then in this approaching by all dependences on $|\mathbf{r}|, |\mathbf{r}_1|, |\mathbf{r}_2|$ it is possible to neglect if they appear together with $|\mathbf{n}|$.

All the centrally symmetric energies $U_S^{(0)}$, $U_S^{(1)}$ and $U_S^{(2)}$ are reduced to a combination of factors: $1/|\mathbf{n}|$, and all the anisotropic energies R_A, ρ_A^{cv} and $U_A^{(2)}$ are reduced to a combination of factors of the form: $\varphi_f(-\mathbf{n})\,\varphi_g(\mathbf{n})/|\mathbf{n}|$, where the indices of state f and g take the values v (valence band) or (conduction band).

In particular, for a semimetal such as boron, valence band in the simplest case is determined by $2p_x$, $2p_y$ states with wave functions:

$$\varphi_{v_x}(\mathbf{n}) = A\,|\mathbf{n}| \exp\left(-\frac{|\mathbf{n}|}{2}\right) \sin(\theta)\cos(\varphi); \quad \varphi_{v_y}(\mathbf{n}) = A\,|\mathbf{n}| \exp\left(-\frac{|\mathbf{n}|}{2}\right) \sin(\theta)\sin(\varphi), \tag{25}$$

and the conduction band is determined by the $2p_z$ state with the wave function:

$$\varphi_c(\mathbf{n}) = \left(A\Big/\sqrt{2}\right)\ \rho \exp\left(-\frac{|\mathbf{n}|}{2}\right) \cos\theta, \tag{26}$$

where $A \equiv (6/a_B)^{3/2}\Big/(8\sqrt{\pi})$ and a_B is the Bohr radius. In fact, all three states are defined by a superposition of the functions (25), (26) under the dominance of one of them. These functions have an odd symmetry in the sense of equality: $\varphi_f(-\mathbf{n}) = -\varphi_f(\mathbf{n})$. With account of this, we can estimate the coefficients at the powers of η on the right-hand side of (22) with respect to the functions (25), (26). In the far-field and nearest-neighbor approximation, and also under the assumption that $z_n = z_e \equiv z$, one can obtain the following estimates:

$$\left[U_S^{(0)} - (1/2)\,\mathrm{R}_A\right] = \frac{N_a e^2 \left(z^2 + z_{v_x}^* z_{v_y}^* \varphi_{v_x}(\mathbf{n})\,\varphi_{v_y}(\mathbf{n})\right)}{2|\mathbf{n}|}; \tag{27}$$

$$\left[U_S^{(1)} - \rho_A^{cv}\right] = \sum_{\substack{i,j=x \\ (i \neq j)}}^{y} \frac{N_a e^2 z_{v_i}^* \varphi_{v_i}(\mathbf{n}) \left(z_c^* \varphi_c(\mathbf{n}) - z_{v_j}^* \varphi_{v_j}(\mathbf{n})\right)}{2|\mathbf{n}|}; \tag{28}$$

$$\left[U_S^{(2)} + U_A^{(2)}\right] = \sum_{i=x}^{y} \frac{N_a e^2 \left(z_{v_i}^* \varphi_{\nu_i}(\mathbf{n}) - z_c^* \varphi_c(\mathbf{n})\right)^2}{4|\mathbf{n}|}. \tag{29}$$

Here, $z_{v_i}^*$ are the estimated parameters, which, like z_n and z_e, can have the meaning of effective charge numbers.

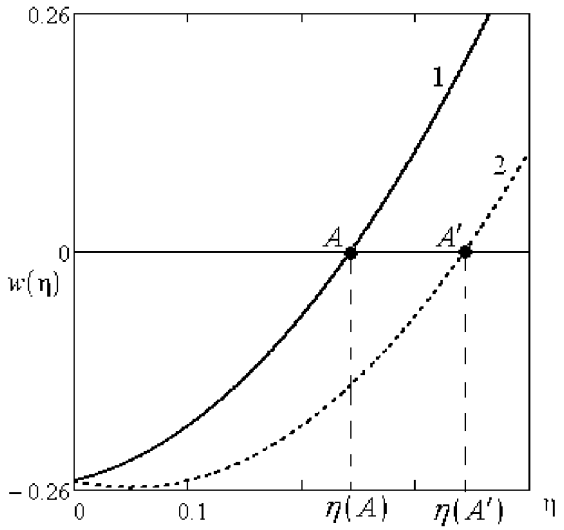

Fig. 1. The dimensionless representation of the energy $w(\eta)$ in units of N_aRy, where Ry is the Rydberg energy. For illustration, dimensionless parameter values were chosen: $w_0 = 0.25$ and $w_2 = 2.5$. For the parameter w_1 we took the values $w_1 = 0.25$ (curve *1*) and $w_1 = -2.5$ (curve *2*).

The second term in the numerator of the right-hand side of (27) can be negative in some directions. Indeed, if we take into account the definitions (25), then this term has the form: $z^*_{v_x} z^*_{v_y} A^2 \, |\mathbf{n}|^2 \exp(-|\mathbf{n}|) \sin^2(\theta) \sin(2\varphi) \big/ 2$. This function has a pair of opposite directions: $\varphi_1 = 3\pi/4$, $\varphi_2 = 7\pi/4$, where the second term in the numerator of the right-hand side of (27) is negative. Then in these directions the right-hand side in (27) has a minimum by the spatial variable $|\mathbf{n}|$, and the energy at the minimum point is negative: $\left[U_S^{(0)} - (1/2)\,\mathrm{R}_A\right] = -\left|\left[U_S^{(0)} - (1/2)\,\mathrm{R}_A\right]\right|$. That is, it corresponds to the bound state. In reality, when the superposition of states (25) and (26) is realized, there is more of such a pairs of directions and they determine the crystallographic directions. In the directions φ_1 and φ_2 the right-hand side in (28) is uniquely positive. That is, the condition is always fulfilled: $\left[U_S^{(1)} - \rho_A^{cv}\right] = \left|\left[U_S^{(1)} - \rho_A^{cv}\right]\right|$. This is fair for boron. But if we consider other substances, this component can take small negative values (in Fig. 1 - curve *2*). Finally, the right-hand side of (29) is always positive, because always $\left(z^*_{v_i}\varphi_{\nu_i}(\mathbf{n}) - z^*_c\varphi_c(\mathbf{n})\right)^2 > 0$. That is, the equality is always fulfilled: $\left[U_S^{(2)} + U_A^{(2)}\right] = \left|\left[U_S^{(2)} + U_A^{(2)}\right]\right|$.

Denoting further:

$$w_0 \equiv \left|\left[U_S^{(0)} - (1/2)\,\mathrm{R}_A\right]\right| > 0; \quad w_1 \equiv \left|\left[U_S^{(1)} - \rho_A^{cv}\right]\right| > 0; \quad w_2 \equiv \left|\left[U_S^{(2)} + U_A^{(2)}\right]\right| > 0,$$

the internal energy (22) can be represented in a compact form: $w(\eta) = -w_0 + w_1\eta + w_2\eta^2$.

Figure 1 (curve *1*) shows an illustrative graph of the energy dependence of $w(\eta)$.

The parameters were chosen so that the point $w(\eta) = 0$ (in the figure, point A) was sufficiently far from the value $\eta = 0.5$ (this value corresponds to an infinitely high temperature). The condition $w(\eta) = 0$ determines the value of the parameter η, which corresponds to the temperature of the liquid-gas phase transition. As this temperature is finite, then points A and A' on a Figure 1 represents approximate physical positions of such values on an axis η.

It is also quite obvious that the crystal-liquid phase transition must be determined by the condition of "switching off"the anisotropic contributions. It follows from the definition (22) that the "switching-off"of anisotropic contributions should be related to the condition: $U_A^{(2)}\eta^2 - \rho_A^{cv}\eta - (1/2)\,\mathrm{R}_A = 0$. This determines a certain value of the factor η (and the corresponding temperature) for the crystal-liquid phase transition.

Conclusions

In the article the exact expression for the internal energy of the condensate as a function of temperature was obtained. In particular, the exact value of the internal energy of condensate was obtained, as a function of temperature (only the electronic subsystem was taken into account). This dependence is completely determined by the Fermi-Dirac factor: $\eta = 1/(1 + \exp(E_g/2kT))$ (where E_g is the energy gap width). The internal energy, as a function of this factor, has a sufficiently simple form: $w(\eta) = -w_0 + w_1\eta + w_2\eta^2$. At zero temperature ($\eta = 0$) the condensate is an ideal crystal. This energy contains two types of interactions. These interactions contains in the coefficients w_0, w_1, w_2. Competition between them result in structural changes in the type of the phase transitions in the condensate when the temperature changes. On the one hand, these interactions are defining only an isotropic bond between atoms, what is characteristically of liquids. On the other hand, they contribute an anisotropic component into the interaction, define crystallographic directions and provide a crystal structure.

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