ЖУРНАЛ ФІЗИЧНИХ ДОСЛІДЖЕНЬ
т. 7, № 2 (2003) с. 161–166

JOURNAL OF PHYSICAL STUDIES
v. 7, No. 2 (2003) p. 161–166

A COMPUTATIONAL STUDY OF THE EFFECTIVE THREE-ION INTERACTION POTENTIALS IN LIQUID METALS WITH A HIGH DENSITY OF ELECTRON GAS

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(Received June, 25, 2002; received in final form December 25, 2002)

Based on the many-body theory of metals in the third order of the perturbation expansion in electron–ion interaction pseudopotential, the potentials of pair and three-ion interactions are calculated in liquid lead, aluminium and beryllium at their melting temperatures. The reducible and the irreducible three-ion interactions have an attractive nature on distances approximately equal to an average distance between ions in metals. It results in the shortening of average interatomic distance in an equilibrium state of metal. The potential landscapes created by a pair of fixed ions relative to the third ion are constructed. It is shown that with the increasing of an electronic density the contribution of reducible, as well as irreducible three-ion interaction is increased. It is also shown that the influence of reducible three-ion interaction on a potential landscape in a cluster of three ions is considerably larger than the influence of irreducible three-ion interaction.

Key words: liquid metals, pseudopotential perturbation theory, three-ion interaction, potential landscapes.

PACS number(s): 31.15.Md, 61.20.Gy, 61.20.Ne, 71.10.Ca

I. INTRODUCTION

The study of a nature of multi-ion interactions, their influence on different physical properties of metals is now an urgent problem of condensed matter physics. But it is very complicated and an insufficiently studied. The main task for the solution of this problem as a whole is the calculation of multi-ion interaction potentials. A few methods of calculation of effective multi-ion interactions in metals now exist. First, this is a microscopic many-body theory of metals [1], which is grounded on perturbation theory in electron-ion interaction pseudopotential. Second, the embedded atom method [2,3], and the 'glue potential' method [4–6], where the multi-parameter potential functions fitted to experimentally measured physical properties of metals are used. These two last methods are widely used, for example, in molecular dynamic simulations, but in fact are semiempirical methods. Gurskii and Krawczyk [7–9] proposed recently in a general fashion one new microscopic approach, which is grounded on density functional theory.

Nowadays the main microscopic method of multi-ion interaction study is the many-body theory of metals. Within the framework of this theory, some evaluations of equilibrium [1,10] and kinetic [11] properties of simple metals have been already carried out. These evaluations take into consideration the contributions of the higher orders of a perturbation theory in powers of pseudopotential, which are multi-ion interactions. However, the majority of these evaluations are carried out without considering multi-ion potentials. It means that calculations of energy are carried out in reciprocating space. This is a conventional method for a crystalline state of metals, where generally it is possible not to consider interaction potentials, and the usage of symmetry of a crystal allows for considerably simplified evaluations [1,10]. For a homogeneous liquid state, the evaluations also can be carried out in reciprocating space [11]. However, in this case there remains opened the question about relative quantity of the so-called reducible and irreducible contributions in multi-ion potentials and the question about their influence on the short-range order in a liquid. Therefore, in amorphous, liquid and inhomogeneous metals the calculations in configuration space are preferable.

Within the framework of the many-body theory of metals, it is possible to separate irreducible and reducible contributions into multi-ion potentials correctly. The latter arise out of the terms of a certain order of perturbation theory in pseudopotential, when coordinates of two or more ions coincide. Hasegawa for the first time obtained the corresponding formulas for the three-ion interaction [12]. However, the numerical computations were done only for equilateral configurations of three ions in liquid sodium and potassium. Moriarty carried out computations of three-ion potentials for isosceles ion configurations in some transition metals [13,14]. However, a systematic analysis of the three-ion potentials within the framework of the same approaches for a row of metals with differing valency and density of electron gas has not as yet carried out.

It is known that the contributions of the third order perturbation theory is most essentials for polyvalent simple metals with high density of electron gas [1,10]. Therefore, in the present paper for the analysis of three-ion interactions, we chose quadrivalent lead, trivalent aluminium and divalent beryllium. The latter has the largest density of electron gas from all simple metals. The objectives of this paper are as follows: a computation of reducible and irreducible three-ion interactions in these metals at their melting temperature; a determination of relative contribution of the three-ion interactions into full interaction potential of three ions; a clarification of the value dependence of these interactions on density of electronic subsystem of metal.

II. MANY-BODY THEORY OF METALS

In the context of many-body theory of non-transition metals, the energy of a metal is being calculated with using the adiabatic approximation for the electron–ion system. The energy of electronic subsystem E_e, if ion positions are fixed, is written as a series in terms of powers of electron–ion pseudopotential [1]:

$$E_e = E_e^{(0)} + E_e^{(1)} + \sum_{n\geq 2} E_e^{(n)}. \tag{1}$$

Here $E_e^{(0)}$ is the energy of homogeneous electron gas, $E_e^{(1)}$ is the contribution of the first order due to undotted ions, and the sum $\sum_{n\geq 2} E_e^{(n)}$ is the energy of band structure. In (1) one can separate the contributions independent of ion positions, dependent on the locations of separate ions, ion pairs, triplets, etc. Then [1]:

$$E_e = \varphi_0 + \sum_n \varphi_1(\mathbf{R}_n) + \frac{1}{2!}\sum_{m\neq n} \varphi_2(\mathbf{R}_n, \mathbf{R}_m)$$

$$+ \frac{1}{3!}\sum_{m\neq n\neq k} \varphi_3(\mathbf{R}_n, \mathbf{R}_m, \mathbf{R}_k) + \cdots. \tag{2}$$

Each term of series (2) describes indirect interactions of ion groups through the surrounding electron gas. Using (1) φ_2, φ_3, etc. can be represented as a series in terms of powers of pseudopotential:

$$\varphi_2(\mathbf{R}_1, \mathbf{R}_2) = \sum_{i=2}^{\infty} \Phi_2^{(i)}(\mathbf{R}_1, \mathbf{R}_2), \tag{3}$$

$$\varphi_3(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = \sum_{i=3}^{\infty} \Phi_3^{(i)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3), \tag{4}$$

where $\Phi_n^{(k)}(\mathbf{R}_1, ..., \mathbf{R}_n)$ represents the indirect interaction of the n ions through electron gas in the k-order perturbation theory in electron–ion interaction. So, pair interaction in the third order is the sum of a direct Coulomb repulsion of ions (we neglect by the overlapping of ion shells), indirect interaction in the second order $\Phi_2^{(2)}$ and indirect interaction in the third order $\Phi_2^{(3)}$ (the latter is called as reducible three-ion interaction):

$$\varphi_2^*(R) = \frac{(ze)^2}{R} + \Phi_2^{(2)}(R) + \Phi_2^{(3)}(R), \tag{5}$$

where z is the ion charge.

For simple metals good approximation is a local form of electron–ion pseudopotential. Then

$$\Phi_2^{(2)}(R) = \frac{1}{\pi^2}\int_0^\infty dq\, q^2 \Gamma^{(2)}(q)|W(q)|^2 \frac{\sin(qR)}{qR}, \tag{6}$$

$$\Phi_2^{(3)}(R) = \frac{3}{4\pi^4}\int_0^\infty dq_1\, q_1^2 \int_0^{q_1} dq_2\, q_2^2 \int_{-1}^{1} dx\, W(q_1)W(q_2)W(q_3)\Gamma^{(3)}(q_1, q_2, q_3) \times \left(\frac{\sin(q_1 R)}{q_1 R} + \frac{\sin(q_2 R)}{q_2 R}\right). \tag{7}$$

Here $\Gamma^{(2)}(q)$ and $\Gamma^{(3)}(q_1, q_2, q_3)$ are the sums of two- and three-pole diagrams, respectively; $W(q)$ is a form-factor of the local pseudopotential; $q_3 = (q_1^2 + q_2^2 + 2q_1q_2x)^{1/2}$.

The first term in series (4) is the irreducible three-ion interaction in the third order of perturbation theory. It is described by expression [12]:

$$\Phi_3^{(3)}(R_{12}, R_{23}, R_{13}) = \frac{3}{2\pi^4}\int_0^\infty dq_1\, q_1^2 \int_0^\infty dq_2\, q_2^2 \int_{-1}^{1} dx\, W(q_1)W(q_2)W(q_3)\Gamma^{(3)}(q_1, q_2, q_3)$$

$$\times \int_0^1 dy \cos\left(y\left(q_1 R_{12}\frac{R_{12}^2 + R_{23}^2 - R_{13}^2}{2R_{12}R_{23}} + q_2 R_{23} x\right)\right) \times J_0\left(q_1 R_{12}\left(1 - y^2\right)^{1/2}\left(1 - \frac{(R_{12}^2 + R_{23}^2 - R_{13}^2)^2}{4R_{12}^2 R_{23}^2}\right)^{1/2}\right)$$

$$\times J_0\left(q_2 R_{23}\left(1 - y^2\right)^{1/2}\left(1 - x^2\right)^{1/2}\right), \tag{8}$$

where $J_0(x)$ is the Bessel function of the zero-order; R_{12}, R_{23} and R_{13} are the distances between the vertices of a triangle formed by the ions.

III. COMPUTATION RESULTS

The pair and the three-ion interaction potentials were calculated at the melting points of lead, aluminium and beryllium. The corresponding values of Wigner–Seitz radii are $(r_s)_{\rm Pb} = 2.3560$, $(r_s)_{\rm Al} = 2.1677$ and $(r_s)_{\rm Be} = 1.9185$ (all the values in atomic units). For all the metals we use local two-parameter Animalu–Heine pseudopotential with the form-factor

$$W(q) = -\frac{4\pi e^2 z}{q^2\Omega_0}\left[(1+U)\cos(qR_0) - U\frac{\sin(qR_0)}{qR_0}\right] \times \exp\left(-0.03\left(\frac{q}{2k_{\rm F}}\right)^4\right). \qquad (9)$$

The permittivity function in the Vashishta–Singwi form was also used [15]. It provides a good description of exchange-correlation effects in an electron gas at small values of r_s. The parameters of the pseudopotential (9) for lead and aluminium are taken from [10], where they were fitted in the fourth order perturbation theory on requirements $p = 0$ and $C_{44} = C_{44(\rm exp)}$ (p is the pressure, C_{44} is the shear modulus). For beryllium the suitable data in the literature are absent, only the position of the first zero of pseudopotential form-factor it is known [16]. The aim of this paper was not an examination of the three-ion potential dependence from a choice of the pseudopotential form. Therefore, for beryllium we did not carry out the precise parameter adjustment procedure. The parameter R_0 was taken as equal to the ionic radius, and the second parameter U was fitted with use of condition $W(q_0) = 0$.

Fig. 1 shows computed potential $\varphi_2^*(R)$ (5) and its components. For all three metals reducible three-ion interaction $\Phi_2^{(3)}(R)$ has an attractive nature at short distances between two ions; therefore, the pair interatomic potential is strongly renormalized. In the first place, the first minimum position shifts towards shorter distances. This effect is almost identical for all three metals. Secondly, a minimum depth is largely increased. This effect is already unequal: it least for lead, slightly more for aluminium and most for beryllium. In beryllium at taking into account only the second order of the perturbation theory, the depth of the first minimum of pair potential is smaller than that the second minimum. Taking into account a reducible three-ion interaction $\Phi_2^{(3)}(R)$ leads to an increase of depth of the first minimum almost by five times. As a result, the potential $\varphi_2^*(R)$ in beryllium takes the form typical for simple metals (see Fig. 1(c)).

In the row of metals: lead, aluminium, beryllium, the values of r_s decrease while the contribution of $\Phi_2^{(3)}$ increases. Consequently, one can conclude that the importance of $\Phi_2^{(3)}$ consideration increases with a decrease of r_s. We note that this conclusion is in accordance with computations of pair interproton interaction in metallic hydrogen [17]. In this system at $r_s = 1.65$ pair potentials in the second order have not the minimum at all and only taking into account of $\Phi_2^{(3)}$ leads to its formation.

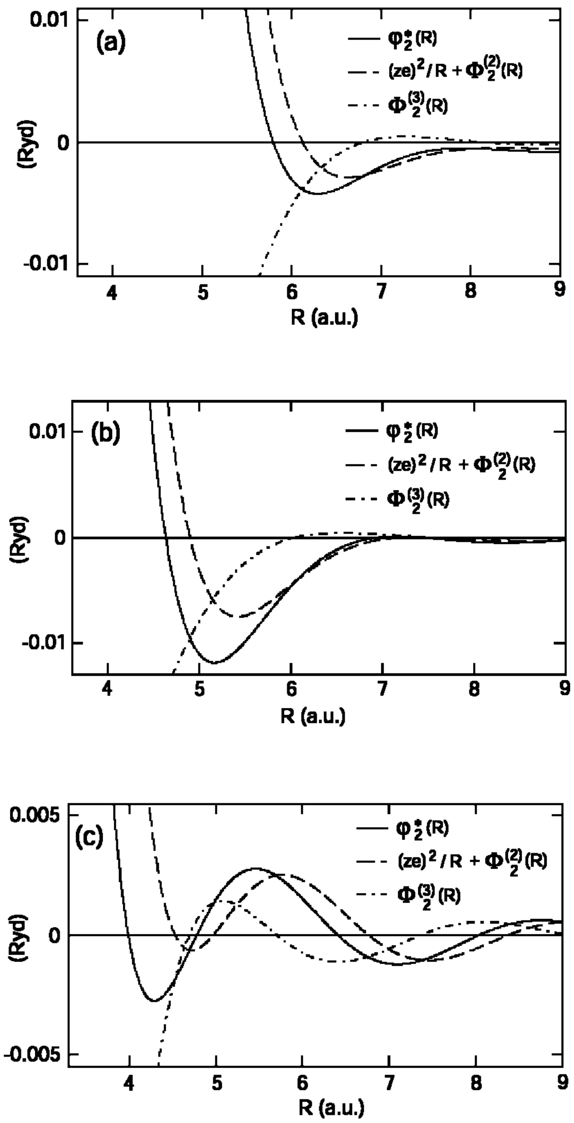

Fig. 1. Pair interaction potential and its components corresponding to (a) lead, (b) aluminium, and (c) beryllium.

The irreducible three-ion interaction potential $\Phi_3^{(3)}(R_{12}, R_{23}, R_{13})$ is the three-dimensional function and can be represented either as the table or graphically as the 'sections': surfaces or curves for certain configurations of ions. So, for example, Moriarty has presented the results of three-ion potential calculations in transition metals for isosceles ion configurations as a function of a vertex angle of an isosceles triangle [13,14]. For the application purposes the potential $\Phi_3^{(3)}$ should be tabulated or should be approximated by simple analytic function, however, for qualitative consideration preferably to present it as a potential landscape for a cluster of three ions (the table of $\Phi_3^{(3)}$ values for any ion configurations and its analytic approximation will be given elsewhere). We consider that such a form of result representation is visual and informative as it allows to clear up the behaviour of the potential and its influence on the potential landscape in a cluster.

Fig. 2 shows the irreducible three-ion interaction potential for a special case where three ions form a regular triangle. The dotted line in this figure corresponds to liquid sodium at melting point. It was computed for comparing (the data for computation was taken from [12]). As well as the reducible three-ion interaction potential $\Phi_2^{(3)}(R)$, the potential $\Phi_3^{(3)}(R,R,R)$ has an attractive nature on short distances between ions and oscillates on large ones.

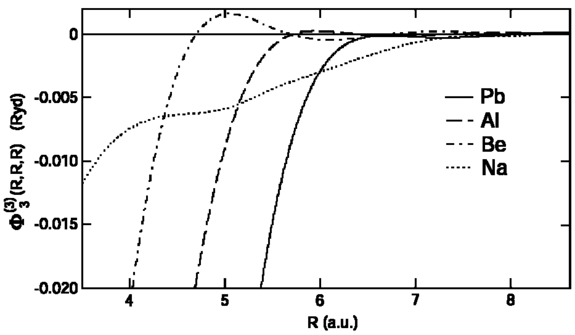

Fig. 2. The three-ion interaction potential for a regular triangle of ions.

In Figs. 3 and 4, two ions are located on an ordinate axis on fixed distance one from the other and a third ion is sited in the XY-plane. The potential landscapes in all these figures are shown only in one coordinate quarter, as they are symmetrical concerning the axes X and Y. The distance between two fixed ions for each metal is selected accordingly to the position of the first minimum of the pair potential $\varphi_2^*(R)$. This is 6.3 a.u. for lead, 5.16 a.u. for aluminium and 4.3 a. u. for beryllium (see Fig. 1). We note that these positions of the first minimum of $\varphi_2^*(R)$ are in good accordance with the corresponding experimental values of most probable distances between the neighbouring atoms.

The potential of irreducible three-ion interaction $\Phi_3^{(3)}$ is similar for all three metals (see Figs. 2–4). It has a sufficiently deep potential well (in beryllium it has even two potential wells which are separated by a saddle point). On large distances, the potential $\Phi_3^{(3)}$ has the damping oscillations. These oscillations are determined by Fridel's oscillations of electronic density. The distance from a bottom location of a potential well up to the fixed ions approximately equal an average interatomic distance for each of the metals.

Fig. 4 shows a potential landscape which is created by the ions pair and taking into account pair- and three-ion interactions. We do not show in this figure a potential landscape for lead, as here the potential $\Phi_3^{(3)}$ almost does not influence the landscape and the latter cannot be drawn in a reasonable scale. The drawing has been executed on radial directions from the origin of coordinates. A solid line corresponds to pair interaction in the third order taken into account that described by the function $\varphi_2^*(R_{23}) + \varphi_2^*(R_{13})$. A dotted line corresponds to pair and irreducible three-ion interaction taken into account that described by the function $\varphi_2^*(R_{23}) + \varphi_2^*(R_{13}) + \Phi_3^{(3)}(R_{\min}, R_{23}, R_{13})$. In these formulas indices 1 and 2 corresponds to the fixed ions and index 3 correspond to the free ion. The $R_{\min}$ are the positions of $\varphi_2^*(R)$ first minimum for each of the metals (see above).

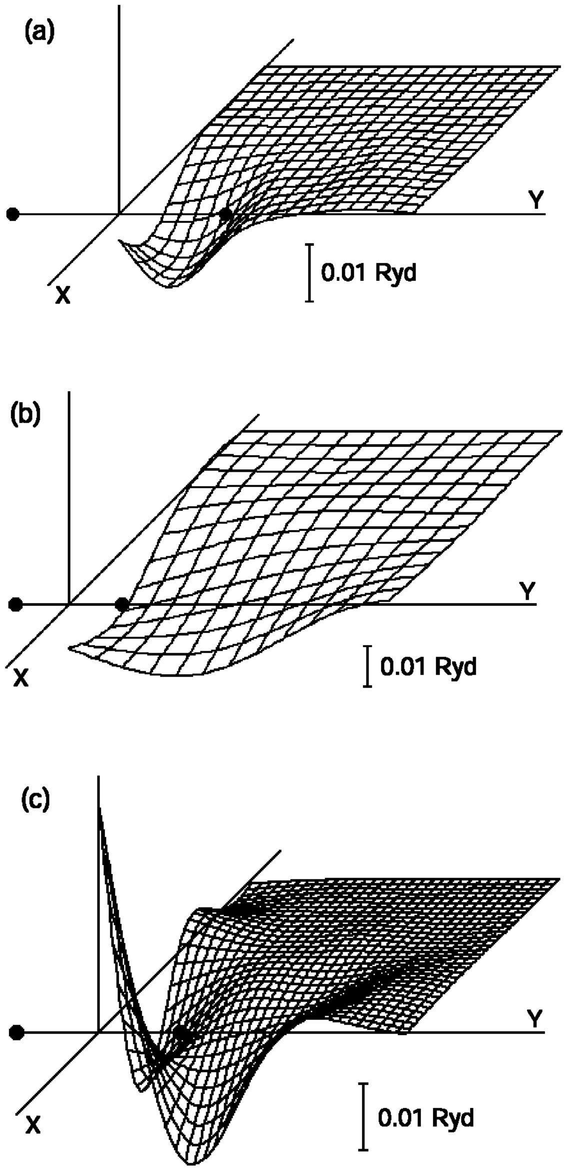

Fig. 3. Irreducible three-ion interaction potential corresponding to (a) lead, (b) aluminium, and (c) beryllium.

As noted above, the potential $\Phi_3^{(3)}$ almost does not influence a potential landscape in lead, it only increases insignificantly ($\sim$ 1%) a minimum depth in some directions. In aluminium (see Fig. 4(a)), an effect of irreducible three-ion interaction is something higher, but it shown is also small: $\sim$ 4% deepening the minimum on the X-axis (minimum A). In beryllium (see Fig. 4(b)) the contribution of $\Phi_3^{(3)}$ is rather significant that is especially noticeable in the direction of X-axis.

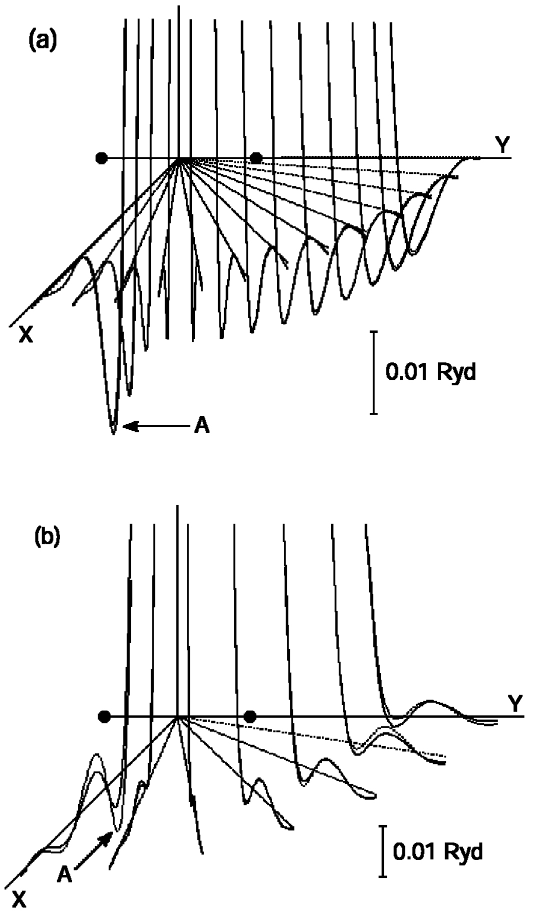

Fig. 4. A potential landscape created by two fixed ions for the third ion corresponding to (a) aluminium and (b) beryllium.

In this direction, the $\Phi_3^{(3)}$ potential taking into account results in the increase of the depth of the first minimum approximately twofold (minimum A) and in some increase of the depth of the second minimum. Thus in beryllium the effect of irreducible three-ion interaction is spread evenly to the second coordination shell.

IV. DISCUSSION OF THE RESULTS

There is an apparent tendency in a row of simple liquid metals with varied density of electron gas: with the increasing of density (decreasing of r_s) the contribution of both reducible and irreducible three-ion interactions increases.

Both reducible and irreducible three-ion interactions have an attractive nature on distances approximately equal to the equilibrium distance between ions. We note that the same nature has also indirect pair interatomic interaction in the second order $\Phi_2^{(2)}$. Thus, the attractive nature of all indirect interactions (in the second and in third order) leads to the shortening of an average interatomic distance in an equilibrium state of metal.

It is well known that the nature of pair interatomic interaction in the second order is identical for all of simple metals [18]. Our computations and the computations for liquid sodium and potassium [12] allow to draw the conclusion that the three-ion interactions are also similar in all simple metals.

For all metals the considered here the influence of reducible three-ion interaction $\Phi_2^{(3)}$ on a potential landscape in a cluster of three ions is considerably larger than the influence of irreducible interaction $\Phi_3^{(3)}$. This fact to some extent can be a ground for the approach when at calculations of the physical properties of metals the $\Phi_3^{(3)}$ is taken into account as perturbation at the accurate consideration of $\Phi_2^{(3)}$ [12] or the $\Phi_3^{(3)}$ contribution is neglected and only $\Phi_2^{(3)}$ is taken into account [19], especially for metals with low density of electron gas. However, the final answer to a question on importance of irreducible three-ion interaction in simple metals can be obtained only by calculating energy and different physical properties of metals with considering this interaction.

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ЧИСЕЛЬНЕ ДОСЛІДЖЕННЯ ПОТЕНЦІЯЛІВ ЕФЕКТИВНИХ ТРИЙОННИХ ВЗАЄМОДІЙ У РІДКИХ МЕТАЛАХ З ВИСОКОЮ ЩІЛЬНІСТЮ ЕЛЕКТРОННОГО ГАЗУ

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На основі багаточастинкової теорії металів у третьому порядку теорії збурень за псевдопотенціялом електрон–йонної взаємодії розраховано потенціяли парної та трийонної взаємодій у рідкому свинці, алюмінії і берилії при їхніх температурах плавлення. Редуковані та нередуковані трийонні взаємодії мають притягувальний характер на відстанях, які приблизно дорівнюють середній відстані між йонами в металах. Це скорочує середню міжатомну відстань у рівноважному стані металу. Побудовано потенціяльні рельєфи, які створюються парою фіксованих йонів щодо третього йона. Показано, що зі збільшенням електронної щільности внесок як редукованої, так і нередукованої трийонної взаємодії збільшується. Показано також, що вплив редукованої трийонної взаємодії на потенціяльний рельєф у кластері трьох йонів значно більший від впливу нередукованої трийонної взаємодії.