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Model pseudopotential of the electron – negative ion interaction*

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Generalization of the Anderson model to describe the states of electronegative impurities in liquid-metal alloys is the main aim of the present paper. The effects of the random inner field on the charge impurity states is accounted for selfconsistently. Qualitative and quantitative estimation of hamiltonian parameters has been carried out. The limits of the proposed model applicability to a description of real systems are considered. Especially, the case of the oxygen impurity in liquid sodium is studied. The modelling of the proper electron-ionic interaction potential is the main goal of the paper. The parameters of the proposed pseudopotential are analyzed in detail. The comparison with other model potentials have been carried out. Resistivity of liquid sodium containing the oxygen impurities is calculated with utilizing the form-factor of the proposed model potential. Dependence of the resistivity on impurity concentration and on the charge states is received.

Key words: *liquid metals, electronegative impurity, Anderson model*

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1. Introduction

The study of the properties of electronegative impurities in condensed matter has been provided for a long time and it is still actual. The basic results of this topic are gathered in monographs [1,2].

Let us consider the system of liquid-metal alloy containing electronegative impurities of such elements as H, O, Cl, N, C, F. It has practical application to the problems of corrosion resistance of materials. Liquid metals Li, K, Na, Pb and their mixtures Li_xPb_{1-x}, Li_xNa_{1-x}, Na_xK_{1-x} are used as the heat-carriers in nuclear reactors due to their large thermal capacity, thermal conduction and low melting temperatures [3–5].The utilization of these metal alloys in thermonuclear reactors is prospective as well [6].

*This paper is dedicated to Professor Myroslav Holovko on the occasion of his 60th birthday.

It still remains urgent to solve an important technological problem, caused by aggressive corrosive effect of liquid-metal phase on structural materials (steels). The dissolution of the constituent atoms of steel (Fe, Ni, Co, Mo, Cr and other) in a liquid phase takes place during the direct contact of the heat-carrier with structural material. It gives rise to violation of stoichiometric constitution of the surface layer of hard alloys. This predetermines the loss of valuable physical-chemical properties of this layer and its subsequent destruction. The dissolution of hard alloys in alkaline melts is a rather complicated physical and chemical process, which depends on numerous factors: chemical structure of a structural material and liquid-metal alloy, temperature, radioactivity, etc. Detailed discussion of experimental data for processes of structural materials interaction with alkaline metal alloys and their interpretation within the framework of simple kinetic and thermodynamic models can be found in [3,4].

Solubility kinetics of structural material in a metallic alloy essentially depends on the availability of electronegative impurities in the structure of the alloy. These impurities are always present in larger or smaller amounts in alkaline metal alloys. It was experimentally established that temperature dependence of the equilibrium solubility of gaseous impurities in liquid metals is approximately described by the expression $\ln C = A - BT^{-1}$, where C is concentration of impurities, A and B are certain constants, which have experimentally defined values for different alloys and for different impurities [3–5].

The mechanism of catalytic activity of gaseous impurities in alkaline alloys has not been fully investigated so far. Thermodynamic research methods in condensed metallic systems permit to define integrated (macroscopic) characteristics of alloys, to construct the diagrams of state. However, the microscopic reasons, which determine the impurity behaviour in alloys in such studies cannot be revealed. Therefore, the effect of different gaseous impurities on the properties of metals and their alloys cannot be predicted. Thus, from a technological point of view, undesirable effects cannot be deliberately excluded when liquid metals and structural materials are contacted.

Detailed research of the impurity behaviour at a microscopic level is important for a deeper understanding of interaction mechanisms of liquid-metal phase with structural alloys and for explaining the corrosive phenomena on a medium interface.

A computation of the following physical quantities is important in order to understand the microscopic processes:

- chemical potential or the coefficient of the activity of the impurities;
- maximum solubility of the impurities in liquid metals;
- charge impurity state;
- spin-polarized (magnetic) state;
- structure of the neighbouring environment of the impurity

and some others.

Let us consider a monocomponent metallic alloy of alkaline metal, in which gaseous impurities are included. The microscopic approach to the description of liquid alkaline metals Li, K or Na is identical. The only quantitative difference is due to microscopic parameters, which characterize these metals.

Let us give a qualitative estimate of impurity states in liquid alkaline metals. The experiments testify that the oxygen is the most dangerous in liquid sodium or in sodium based liquid alloys.

At least eight experiments provided by authors [7] show that oxygen exists in ionized form in liquid sodium due to its high electronegativity. The following chemical elements H, O, Cl, N, C, F belong to the class of electronegatives. Electronegativity is characterized by the capability of the atoms, which are included into the structure of a molecule and other compounds or a solvent, to join electrons. The electron affinity energy (E_0) is an important parameter of electronegativity.

An electronic structure of oxygen ($1s^2 2s^2 2p^4$) shows that a free atom can be in the state O^{2-} with two electrons additionally localized on the p-shell . However, the effective atomic charge state of oxygen in a condensed metallic medium can be changed from neutral to O^{2-}, taking any intermediate values, depending on the parameters of a system.

For the sake of simplicity we shall model atomic charge state of oxygen as localization process of electron from conductivity band to non-degenerate local s-level. The basic supposition in explaining the formation mechanism of a negative oxygen ion is the electron localization under the action of an effective one-particle potential. Twofold filling of a local level corresponds to the charge state O^{2-}. The formation of an effective charge of oxygen impurity in liquid metal can be presented as a process of hybridization of local level with the states from conductivity band. This qualitative interpretation of the formation of an effective impurity charge is explained within the framework of Anderson model [8].

The paper is organized as follows. In section 2 we generalize the Anderson model to describe the states of electronegative impurities in liquid-metal alloys. In section 3 we perform the analysis of the proposed effective pseudopotential of electron – negative ion interaction. The best method for testing the applicability of model pseudopotential in a real system is to calculate some material characteristics and compare them with the experimental data. Section 4 is devoted to the calculation of the change of impurity resistivity of liquid sodium containing the oxygen impurities.

2. Microscopic model of the system “metallic alloy – gaseous impurity”

Let us consider the separate gaseous impurity dissolved in liquid alkaline metal. The liquid-metal phase will be described within the framework of electron-ionic model, which for such metals gives satisfactory computational results of electronic and structural properties.

Let $\mathbf{R}_1, \ldots, \mathbf{R}_N$ be the coordinates of atoms of metallic alloy, which accept arbitrary values in volume V. The impurity has a coordinate $\mathbf{R}_0$. We selected the following full model Hamiltonian in coordinate representation:

$$\hat{H} = H_{\rm cl} + \hat{H}_{\rm el-i} + \hat{H}_{\rm el-el}\,. \tag{2.1}$$

Energy operator of electron-ion interaction is written as follows:

$$\hat{H}_{\rm el-i} = -\frac{\hbar^2}{2m}\sum_{1\leqslant i\leqslant N}\Delta_i + \sum_{1\leqslant i\leqslant N}\sum_{1\leqslant j\leqslant N} V(\mid \mathbf{r}_i - \mathbf{R}_j \mid) + \sum_{1\leqslant i\leqslant N_e} V_0(\mid \mathbf{r}_i - \mathbf{R}_0 \mid). \tag{2.2}$$

In this formula $\mathbf{r}_1,\ldots,\mathbf{r}_N$ are electron coordinates of a metallic subsystem, the amount of which coincides with the number of metal atoms due to one-valence of alkaline elements. It is assumed that the electrons of valence impurity shell remain localized on the impurity.

Pseudopotentials $V(|\mathbf{r}_i - \mathbf{R}_j|)$ and $V_0(|\mathbf{r}_i - \mathbf{R}_0|)$ describe electron scattering on the ions of metal and impurity, accordingly. The first term in formula (2.2) is the operator of a kinetic energy of a free electron subsystem.

The last term in (2.1) describes the energy of the pair electron-electron interaction

$$\hat{H}_{\rm el-el} = \frac{1}{2}\sum_{1\leqslant i\neq j\leqslant N}\Phi(\mid \mathbf{r}_i - \mathbf{r}_j \mid) = \frac{1}{2}\sum_{1\leqslant i\neq j\leqslant N}\frac{e^2}{\mid \mathbf{r}_i - \mathbf{r}_j \mid}. \tag{2.3}$$

Non-operator part $H_{\rm cl}$ describes the energy of classical ion-ionic interaction.

In order to represent the secondary quantization, as a base we shall use flat waves to decompose the field electronic operators

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}}\exp\left(\mathrm{i}\mathbf{k}\mathbf{r}\right) \tag{2.4}$$

and s-shell localized on the impurity

$$\psi_0(\mathbf{r}) = \frac{1}{\sqrt{\pi r_{\rm p}^3}}\exp\left(-\frac{|\mathbf{r}-\mathbf{R}_0|}{r_{\rm p}}\right). \tag{2.5}$$

Wave vector $\mathbf{k}$ in (2.4) goes through the specified values in impulse quasi-continuous space Λ:

$$\Lambda = \Big\{\mathbf{k}:\, \mathbf{k} = \sum_{1\leqslant\alpha\leqslant 3} 2\pi\, V^{1/3} n_\alpha \mathbf{e}_\alpha, \quad n_\alpha \in Z, \quad (\mathbf{e}_\alpha, \mathbf{e}_\beta) = \delta_{\alpha\beta}\Big\}.$$

Let us remark that $\psi_0(\mathbf{r})$ is not orthogonal to flat waves (2.4). Apart from this, its inclusion into the basis causes overfilling of the last. However, the errors introduced by such an approximate procedure will not affect the regularity of a qualitative picture. In the representation of the secondary quantization operator (2.1) with allowance for only a certain class of Coulomb electron-electron interactions we have the following:

$$\begin{aligned}\hat{H} \;=\;& H_{\rm cl} + \sum_{\mathbf{k}\in\Lambda}\sum_{\sigma=\pm1} E_k\, a^+_{\mathbf{k}\sigma}\, a_{\mathbf{k}\sigma} + \sum_{\sigma=\pm1} E_0\, d^+_{0\sigma}\, d_{0\sigma}\\ &+ \sum_{\mathbf{k}\in\Lambda}\sum_{\mathbf{q}\in\Lambda}\sum_{\sigma=\pm1}\left(V_q\, a^+_{\mathbf{k}\sigma}\, a_{\mathbf{k}-\mathbf{q},\,\sigma} + V_{0,q}\, a^+_{\mathbf{k}\sigma}\, a_{\mathbf{k}-\mathbf{q},\,\sigma}\right) + \sum_{\sigma=\pm1} U_0\, \hat{n}_{0\sigma}\hat{n}_{0,-\sigma}\\ &+ \sum_{\mathbf{k}\in\Lambda}\sum_{\sigma=\pm1}\left(W_k\, a^+_{\mathbf{k}\sigma}\, d_{0\sigma} + W^*_k\, d^+_{0\sigma}\, a_{\mathbf{k}\sigma}\right) + \sum_{\mathbf{k}\in\Lambda}\sum_{\mathbf{q}\in\Lambda}\sum_{\sigma,\sigma'=\pm1} P_q\, a^+_{\mathbf{k}\sigma}\, a_{\mathbf{k}-\mathbf{q},\,\sigma}\, \hat{n}_{\sigma'}\\ &+ \sum_{\mathbf{k}\in\Lambda}\sum_{\sigma\neq\sigma'}\left(U_k\, \hat{n}_{\sigma'}\, a^+_{\mathbf{k}\sigma}\, d_{0,\,\sigma} + U^*_k\, d^+_{0,\,\sigma}\, a_{\mathbf{k}\sigma}\, \hat{n}_{\sigma'}\right). \end{aligned} \tag{2.6}$$

Here, $a_{\mathbf{k}\sigma}(a^+_{\mathbf{k}\sigma})$ and $d_{0,\sigma}(d^+_{0,\sigma})$ are the annihilation (creation) Fermi-type operators for electrons in the states $\{\mathbf{k},\ \sigma\}$ and $\{\mathbf{R}_0,\ \sigma\}$, where $\sigma = \pm1$ is quantum spin number, which accepts two values according with two possible orientations of an electronic spin relatively to the quantization axis. $E_k = \hbar^2 k^2/2m$ is energy spectrum of the electrons in the states $\varphi_{\mathbf{k}}(\mathbf{r})$, and E_0 is the energy of the localized electronic state $\psi_0(\mathbf{r})$. $\hat{n}_\sigma = d^+_\sigma\, d_\sigma$ is the spin-dependent occupation number operator for the localized state.

The matrix elements V_q and $V_{0,q}$ characterize the processes of elastic scattering of electrons on the ions of metal and impurity. Their explicit analytical forms are as follows:

$$V_q = \frac{1}{N}\sum_{1\leqslant j\leqslant N} \mathrm{e}^{-\mathrm{i}\mathbf{q}\mathbf{R}_j}\, v(q), \qquad V_{0,\,q} = \mathrm{e}^{-\mathrm{i}\mathbf{q}\mathbf{R}_0}\, v_0(q). \tag{2.7}$$

Formfactors of scattering pseudopotentials

$$v(q) = \int\limits_V V(|\mathbf{r}|)\, \mathrm{e}^{-\mathrm{i}\mathbf{q}\mathbf{r}}\, \mathrm{d}\mathbf{r}, \qquad v_0(q) = \frac{1}{V}\int\limits_V V_0(|\mathbf{r}|)\, \mathrm{e}^{-\mathrm{i}\mathbf{q}\mathbf{r}}\, \mathrm{d}\mathbf{r} \tag{2.8}$$

depend only on the module of momentum transfer $\mathbf{q}$ due to the locality of pseudopotentials $V(|\mathbf{r}|)$ and $V_0(|\mathbf{r}|)$.

The processes of nonelastic scattering of electrons caused by their transition from the state localized on the impurity into conduction band and on the contrary, are characterized by a matrix element

$$W_k = \frac{1}{V}\int\limits_V \mathrm{e}^{-\mathrm{i}\mathbf{k}\mathbf{r}}\left(-\frac{\hbar^2\Delta_{\mathbf{r}}}{2m} + V_{\rm LF}(\mathbf{r})\right)\psi_0(\mathbf{r})\, \mathrm{d}\mathbf{r}. \tag{2.9}$$

Here,

$$V_{\rm LF}(\mathbf{r}) = \sum_{1\leqslant j\leqslant N} V(|\mathbf{r}-\mathbf{R}_j|) + V_0(|\mathbf{r}-\mathbf{R}_0|) \tag{2.10}$$

is the potential of a local field of metal ions and the impurity, which acts on the electron at a point $\mathbf{r}\in V$.

The term $\sum_\sigma U_0\, \hat{n}_\sigma \hat{n}_{-\sigma}$ in Hamiltonian (2.6) descends from the operator of Coulombic electron interaction and describes Hubbard repulsion of electrons localized on the impurity, with the intensity U_0.

$$U_0 = \int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2 |\psi_0(\mathbf{r}_1)|^2 \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} |\psi_0(\mathbf{r}_2)|^2 = \frac{5}{8}\frac{e^2}{r_\mathrm{p}}, \tag{2.11}$$

that for the atom of oxygen can be approximately about 1–5 eV.

The process of elastic scattering of electrons on the charged impurity is described by a matrix element

$$P_q = \int\limits_V \mathrm{e}^{-\mathrm{i}\mathbf{q}\mathbf{r}}\, \widetilde{\Phi}(\mathbf{r})\, \mathrm{d}\mathbf{r}. \tag{2.12}$$

Here, the value

$$\widetilde{\Phi}(\mathbf{r}) = \int\limits_V \Phi(|\mathbf{r} - \mathbf{r}'|)\, |\psi_0(\mathbf{r}')|^2\, \mathrm{d}\mathbf{r}', \tag{2.13}$$

has the sense of potential energy of the electron in a field, which is generated by the electron localized on the shell $\psi_0(\mathbf{r})$.

Matrix elements can be written down in the other form, structural multipliers being separated explicitly

$$W_k = \mathrm{e}^{-\mathrm{i}\mathbf{k}\mathbf{R}_0}\, w(k), \qquad U_k = \mathrm{e}^{-\mathrm{i}\mathbf{k}\mathbf{R}_0}\, u(k), \qquad P_k = \mathrm{e}^{-\mathrm{i}\mathbf{k}\mathbf{R}_0}\, p(k). \tag{2.14}$$

Coefficients

$$\begin{aligned} w(k) &= \frac{1}{\sqrt{V}} \int\limits_V \mathrm{e}^{-\mathrm{i}\mathbf{k}\mathbf{r}} \left(-\frac{\hbar^2 \Delta_\mathbf{r}}{2m} + V_\mathrm{LF}(\mathbf{r}) \right) \psi_0(\mathbf{r})\, \mathrm{d}\mathbf{r}, \\ u(k) &= \frac{1}{\sqrt{V}} \int\limits_V \mathrm{e}^{-\mathrm{i}\mathbf{k}\mathbf{r}}\, \widetilde{\Phi}(\mathbf{r})\, \psi_0(\mathbf{r})\, \mathrm{d}\mathbf{r}, \\ p(k) &= \frac{1}{V} \int\limits_V \mathrm{e}^{-\mathrm{i}\mathbf{k}\mathbf{r}}\, \widetilde{\Phi}(\mathbf{r})\, \mathrm{d}\mathbf{r} \end{aligned} \tag{2.15}$$

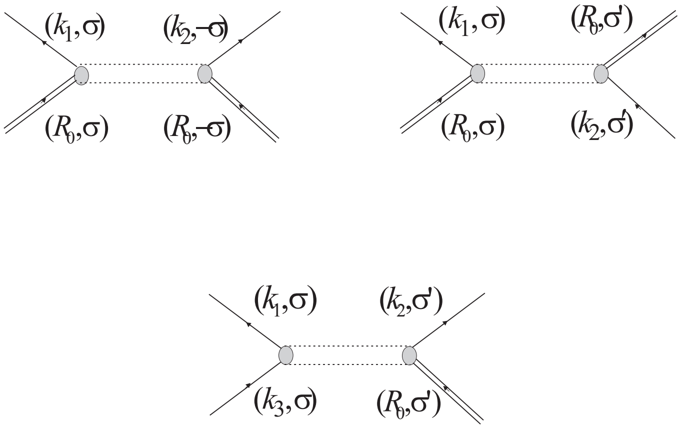

Figure 1. Feynman diagrams

do not depend here on the nodal index and are considered in the coordinate system related to the impurity.

Hamiltonian (2.6) does not take into account all processes with participation of two electrons. Specifically, processes represented by Feynman diagrams (figure 1) are neglected.

On the diagrams, as usually, the line, which exits from the top accords with the electron creation processes in the states indicated in the diagram, while the lines, which enter the top accord with annihilation processes, respectively. A double dashed line denotes the matrix element of Coulomb electron interaction operator. Actually, in Hamiltonian (2.6) only the electrostatic effects including two electrons are taken into account and the processes of exchange character are not considered.

3. The structure of the effective electron-ionic interaction potential

It is still an extremely difficult problem to calculate the total effective electron-ion interaction from the first principles with any degree of precision. Consequently, the potential is generally presented in a model form which includes in a simple parametric way all the features dictated by the physics of the situation. Ashcroft, Heine-Abarenkov, Cohen, Animalu model potentials are widely applicable in liquid metal physics. Parameters of these potentials have been investigated and approved completely enough ([11–13,20]). We have evaluated in chapter 5 the resistivity of the liquid sodium with Ashcroft's potential (including screening by the conduction electrons) [11].

$$v(r) = \left\{ \begin{array}{ll} 0, & r \leqslant r_{\mathrm{c}}, \\ -Ze^2/r, & r > r_{\mathrm{c}}. \end{array} \right. \tag{3.1}$$

where r_{c} is core radius.

The Fourier transform of the potential (3.1) is

$$v(q) = -\frac{4\pi Z e^2}{\Omega q^2}\cos(q r_{\mathrm{c}}). \tag{3.2}$$

Parameters for liquid sodium are $r_{\mathrm{c}}^{\mathrm{Na}} = 1.66$ a.u. $= 0.0878$ nm, $\Omega = 270$ a.u. – atomic volume of liquid Na at 100°C.

Screened function by the conduction electrons in Heldart-Vosko approximation is as follows [11]:

$$\begin{aligned} \varepsilon(q) &= 1 + \frac{4\pi Z}{\Omega q^2}(\frac{2}{3}E_{\mathrm{F}})^{-1}\lambda(\frac{q}{2k_{\mathrm{F}}})[1 - f(q)], \\ \lambda(y) &= \frac{1}{2} + \frac{1-y^2}{4y}\ln\left|\frac{1+y}{1-y}\right|, \\ f(q) &= \frac{1/2q^2}{q^2 + 2k_{\mathrm{F}}/(1 + 0.01574(\Omega/Z)^{1/3})}, \end{aligned} \tag{3.3}$$

where $k_{\mathrm{F}} = (3\pi^2 Z/\Omega)^{1/3} = 0.4786$ a.u.$^{-1}$.

Now let us consider the interaction between the electron and the negative ion. Besides Coulomb interaction $-(Z/r)$ there appears the term $-\alpha/r^4$ (α is ion polarizability). At large distances the pseudopotential has an asymptotic form at $r \to \infty$ [2]

$$U(r) \approx -\alpha/r^4. \tag{3.4}$$

Such an asymptotic behaviour of the potential is allowed to adsorb the effects of polarization since they affect the attraction electron and its localization at the impurity.

The potential of polarizative electron-ion interaction is selected in [14] as follows:

$$U(r) = -\alpha/2(r + r_{\rm p})^4, \tag{3.5}$$

where parameter $r_{\rm p}$ is the cutting radius, found for hydrogen $r_{\rm p} = 0.74a_{\rm B}$, polarizability $\alpha = 9/2a_{\rm B}^3$.

The effective potential chosen in [15] includes the observed polarizability in the following way:

$$U(r) = V(r) - \frac{\alpha e^2}{2(r^2 + r_{\rm p}^2)^2}, \tag{3.6}$$

where $V(r)$ is the central potential, parameter $r_{\rm p}$ is taken, somewhat arbitrary, to be the average distance from the nucleus of the outer electrons of the neutral atom. α serves as an eigenvalue once the binding energy E_0 is specified. The values of α reasonably agree with experimental values for ions O^-, C^-, F^-.

Similar form of the potential is adopted in [16]:

$$U(r) = U_{\rm HS}(r) + \frac{2(1 - e^{-r/r_0})}{r} - \frac{\alpha(1 - e^{-r/r_{\rm p}})}{(r^2 + r_{\rm p}^2)^2}, \tag{3.7}$$

where $V_{\rm HS}$ is the Hartree-Fock-Slater potential for the neutral atom. The parameter $r_{\rm p}$ was arbitrarily chosen to be $1.5a_{\rm B}, 2.5a_{\rm B}, 3.5a_{\rm B}, 4.5a_{\rm B}$, respectively, for all atoms in each of the successive rows of the periodic table. The atomic polarizability α is chosen as the best possible from the experimental and theoretical literature.

Theoretically, the value of ion polarizability can be found from the following formula

$$\alpha = 2e^2 \sum_{n \neq 0} \frac{|Z_{0n}|^2}{E_n - E_0},$$

Z is the operator of electron dipole moment, n characterizes the system state, E_n is the energy of this state. E_0 is electron energy of affinity. Short distance interaction permits to apply the zeroth radius potential method widely used in atomic physics. Wave function in the coupled s-state in δ-potential $\psi(r) = B\sqrt{\gamma/2\pi}\exp(-\gamma r)/r$. Then, polarizability $\alpha = B^2/2\gamma^4$. Parameters B, γ are in [10]. Assuming all the above mentioned, we will be modelling the potential of the interaction between the electrons and the negative ions. But following [15], we must note that the method of model potential has the following disadvantages. The semiempirical parameters α and $\mathbf{r}_{\rm p}$ do not arise naturally from the formalism. Thus, the only criterium we have for the accuracy of the method is its agreement with experimental results. So, we use the values of α [16] and $\mathbf{r}_\mathrm{p}$ [15], taken from the experiment.

We shall discuss herein the form of the electron wave function in the negative ion. Since the electron binding energy in the negative ion is considerably smaller than the electron binding energy in the atom, the size of negative ion is greater than the atomic size. The attraction of outer electrons takes place in the valence electron region. Thus, we can use one-electron approximation for a weakly bounding electron out of the atom. Radial electron wave function at large distances is as follows:

$$\psi_l(r) = \frac{C}{\sqrt{r}} K_{l+1/2}(\gamma r),$$

where l is the orbital electron moment, K is Macdonald's function. Wave function in such a form is used for these characteristics of a negative ion, which is determined by a weakly bounding electron. Other model wave functions one can find in a monograph [2].

We have to take the s-state wave function as:

$$\psi_0(r) = \frac{1}{\sqrt{\pi r_\mathrm{p}^3}} \mathrm{e}^{-r/r_\mathrm{p}}, \tag{3.8}$$

r_p is taken to be the average distance from the nucleus of the outer nl-electrons of the neutral atom.

3.1. Electron-neutral impurity interaction potential. The potential parameters

We shall select the effective potential of the interaction of electrons with neutral impurities as follows:

$$V_0(r) = \frac{A\mathrm{e}^{-r/r_\mathrm{p}}}{r^2} - \frac{\alpha}{(r^2 + r_\mathrm{p}^2)^2}, \tag{3.9}$$

$A > 0$, α, $r_\mathrm{p} > 0$ are potential parameters. The Fourier transform of the potential (3.9)

$$v_0(q) = \int\limits_V V_0(r)\, \mathrm{e}^{-\mathrm{i}\mathbf{q}\mathbf{r}}\, \mathrm{d}\mathbf{r}$$

can be written as follows:

$$v_0(q) = \frac{4\pi A e^2}{q} \mathrm{arctg}(q r_\mathrm{p}) - \frac{\alpha \pi^2 e^2}{r_\mathrm{p}} \mathrm{e}^{-q r_\mathrm{p}}. \tag{3.10}$$

The first term of expression (3.9) is some analytical approximation of repulsive interaction between electrons and neutral impurity.

The parameter A can be defined from physical reasons. It is a well known fact that the bound states spectrum of potential falling more rapidly than Coulomb potential, consists of finite number of energy levels or cannot contain them whatsoever. The energy of ground state level is supposed to coincide with the affinity energy. Then,

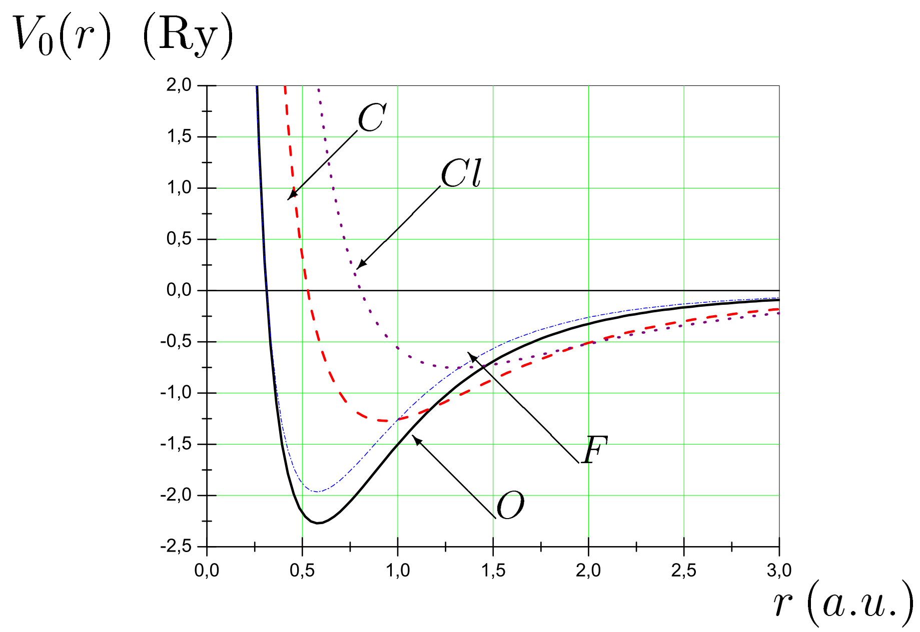

Figure 2. Pseudopotential of interaction between electrons and neutral impurities O, C, F, Cl.

the value of parameter A is chosen such that the resulting potential will support an s-state with the binding energy of the negative ion.

$$E_0 = 4\pi \int_0^\infty r^2 \left[\frac{\hbar^2}{2m} \left(\frac{\mathrm{d}\psi_0}{\mathrm{d}r} \right)^2 + V_0(r)\psi_0^2(r) \right] \mathrm{d}r$$

The equation for the parameter A is obtained as follows:

$$E_0 = \frac{\hbar^2}{2mr_\mathrm{p}^2} + \frac{4Ae^2}{3r_\mathrm{p}^2} - \frac{4\alpha I e^2}{r_\mathrm{p}^4},$$

where

$$I = \int_0^\infty \mathrm{d}x \frac{x^2}{(1+x^2)^2} \mathrm{e}^{-2x}, \qquad x = r/r_\mathrm{p}.$$

We have provided all calculations in the atomic system of units: 1 a.u. of energy $=$ 1 Ry $= e^2/2a_\mathrm{B} = 13.6$ eV, 1 a.u. of length $= 0.0529$ nm $= a_\mathrm{B}$, $\hbar = m = e = 1$.

Then, the potential (3.9) in the atomic system of units transforms into

$$V_0(r) = \frac{2A\mathrm{e}^{-r/r_\mathrm{p}}}{r^2} - \frac{2\alpha}{(r^2 + r_\mathrm{p}^2)^2},$$

where $A = 3/8r_\mathrm{p}^2 E_0 + 3\alpha I/r_\mathrm{p}^2 - 3/8$.

The pseudopotential of interaction between electrons and neutral impurities O, C, F, Cl is plotted in figure 2. All potential parameters are given in table 1.

Table 1. Parameters of model potential $V_0(r)$ of interaction between electrons and neutral impurities O, C, F, Cl. Experimental values are taken from [16] (*) and [17] (**).

Elements	r_{p} (a_{B}) [16]	$-E_0$ (Ry)	α (a_{B}^3)	A (a_{B})
O	1.2	0.1077	5.19*	0.278
C	1.71	0.09188	14.2*	0.527
F	1.16	0.2534	4.05*	0.249
Cl	2.046	0.2656	23.5**	0.968

3.2. Potential of interaction between electrons and charged impurity

We now turn to the matrix element (2.12). We calculate the effective pseudopotential of interaction between electrons and charged impurity in the Hartree-Fock approximation (see [18])

$$\widetilde{V}_0(r) = V_0(r) + \langle\hat{n}\rangle \int\limits_V \Phi(|\mathbf{r}-\mathbf{r}'|)\,|\psi_0(\mathbf{r}')|^2\,\mathrm{d}\mathbf{r}', \tag{3.11}$$

where $\langle\hat{n}\rangle$ is the spin-dependent occupation number operator for localized state. This value must be evaluated self-consistently. The system of equations for self-consistent calculation of charge impurity state is obtained in [18]. We can take here $0 \leqslant \langle\hat{n}\rangle \leqslant 2$ (according to the Pauli principle).

Now, the expression $\widetilde{\Phi}(\mathbf{r})$ can be written as follows:

$$\widetilde{\Phi}(\mathbf{r}) = \frac{4\pi e^2}{q^2 V}\sum_{\mathbf{q}}\frac{1}{q^2}\mathrm{e}^{\mathrm{i}\mathbf{q}\mathbf{r}}\rho_{1s}(\mathbf{q}),$$

here, we denote electron density Fourier coefficient

$$\rho_{1s}(\mathbf{q}) = \frac{1}{\pi r_{\mathrm{p}}^3}\int\limits_V \mathrm{d}\mathbf{r}'\mathrm{e}^{-2\mathbf{r}'/r_{\mathrm{p}}}\mathrm{e}^{-\mathrm{i}\mathbf{q}\mathbf{r}'} = \frac{q_0^4}{(q^2+q_0^2)^2}, \qquad q_0 = 2/r_{\mathrm{p}}.$$

Then,

$$\widetilde{\Phi}(\mathbf{r}) = \frac{q_0^4 e^2}{\pi r}\mathrm{Im}\int\limits_{-\infty}^{+\infty}\frac{\mathrm{e}^{\mathrm{i}qr}dq}{q(q^2+q_0^2)^2},$$

Finally, we obtain

$$\widetilde{\Phi}(\mathbf{r}) = \frac{e^2}{r}\left[1-\mathrm{e}^{-2r/r_{\mathrm{p}}} - \frac{r}{r_{\mathrm{p}}}\mathrm{e}^{-2r/r_{\mathrm{p}}}\right].$$

The effective pseudopotential of interaction between electrons and charged impurity (3.11) becomes as follows:

$$\widetilde{V}_0(r) = V_0(r) + \langle\hat{n}\rangle\frac{e^2}{r}\left[1-\mathrm{e}^{-2r/r_{\mathrm{p}}} - \frac{r}{r_{\mathrm{p}}}\mathrm{e}^{-2r/r_{\mathrm{p}}}\right]. \tag{3.12}$$

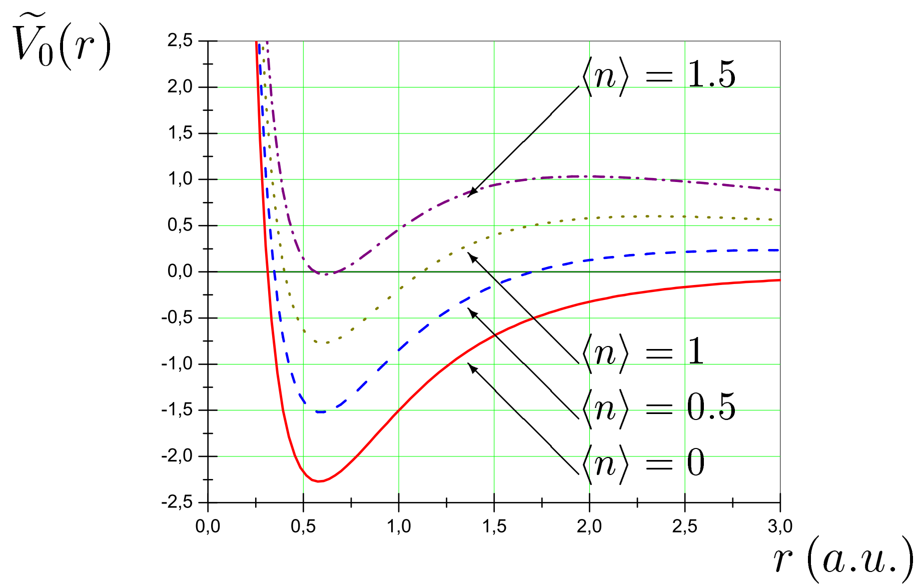

Figure 3. The pseudopotential of interaction between electrons and charged oxygen impurity at $0 \leqslant \langle\hat{n}\rangle \leqslant 2$.

The pseudopotential of interaction between electrons and oxygen impurity at $0 \leqslant \langle\hat{n}\rangle \leqslant 2$ is plotted in figure 3. The contribution from the Hartree-Fock potential increases when local level is occupied by one electron. It concerns the charge state O^-. When $\langle\hat{n}\rangle = 1.5$, the bound state of the electron with the ion is absent.

The form-factor of the effective impurity pseudopotential

$$\widetilde{v}_0(q) = v_0(q) + P_q\langle\hat{n}\rangle = \int \mathrm{d}\mathbf{r}\mathrm{e}^{-\mathrm{i}\mathbf{qr}}\Big[V_0(r) + \langle\hat{n}\rangle \int \mathrm{d}\mathbf{r}'|\psi_0(\mathbf{r}')|^2\Phi(|\mathbf{r}-\mathbf{r}'|)\Big]$$

contains the Hartree-Fock potential caused by the charge of impurities.

$$P_q = \frac{4\pi e^2}{q^2}\Big[1 - \frac{q^2 r_\mathrm{p}^2}{(4+q^2r_\mathrm{p}^2)}\Big(1 + \frac{4}{4+q^2r_\mathrm{p}^2}\Big)\Big]. \tag{3.13}$$

It can be rewritten in the atomic system of units as follows:

$$\begin{aligned}\widetilde{v}_0(q) &= \frac{8\pi A}{q}\arctan(qr_\mathrm{p}) - \frac{4\alpha\pi^2}{r_\mathrm{p}}\mathrm{e}^{-qr_\mathrm{p}} \\ &\quad + \langle\hat{n}\rangle\frac{8\pi}{q^2}\Big[1 - \frac{q^2r_\mathrm{p}^2}{(4+q^2r_\mathrm{p}^2)}\Big(1+\frac{4}{4+q^2r_\mathrm{p}^2}\Big)\Big].\end{aligned}$$

In the limit $q \to 0$, the form-factor $v_0(q)$ is as follows:

$$\begin{aligned} v_0(q) &= v_0(0) + \beta q + pq^2, \qquad q \to 0, \\ v_0(0) &= (8\pi A r_\mathrm{p} - 4\pi^2\alpha)/r_\mathrm{p}, \quad \beta = 4\alpha\pi^2, \quad p = -2\alpha\pi^2 r_\mathrm{p}/2. \end{aligned} \tag{3.14}$$

The form-factor $v_0^*(q) = v_0(q)/v_0(0)$, $q = qa_\mathrm{B}$ of the oxygen impurity is plotted in figure 4.

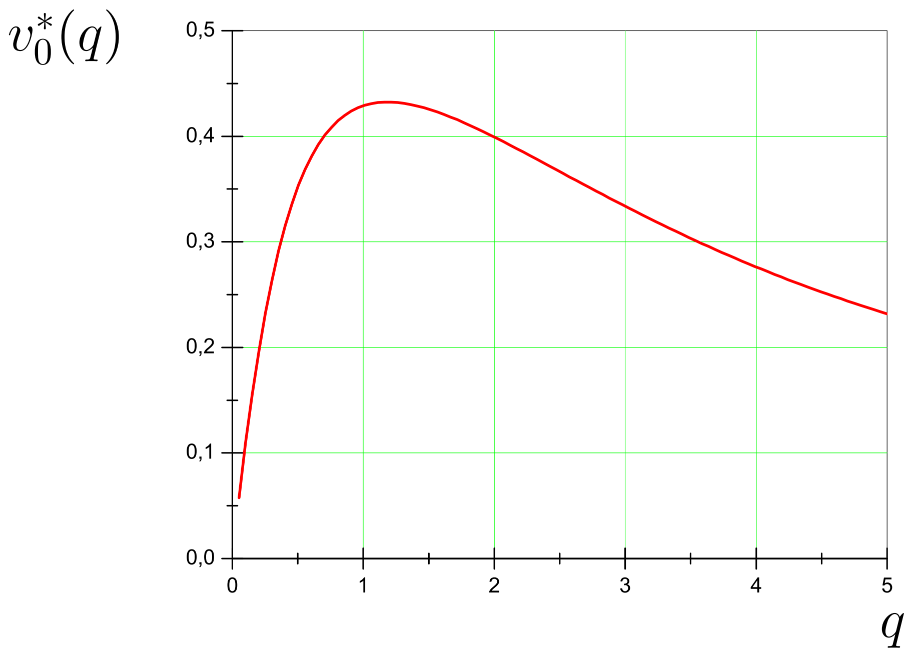

Figure 4. The form-factor $v_0^*(q)$ of the oxygen impurity.

The proposed pseudopotential will be helpful in calculating the charge and spin-polarized oxygen impurity states in liquid sodium. The system of equations for self-consistent calculation of charge impurity state is obtained in [18].

Calculating some material characteristics and comparing them with the experimental data is the best method for testing the applicability of model potential in a real system. We have to calculate the resistivity of liquid sodium with small concentration of the oxygen impurities in the next section.

4. Resistivity of liquid sodium containing the oxygen impurities

Liquid-metal resistivity is caused by the scattering of electron waves on the atomic thermal oscillations (i.e., phonon scattering). This is a thermal part of resistivity ρ_{T}. Besides this, an electron scattering on the impurities took place. This part is sometimes called the impurity or the residual resistivity $\Delta\rho_{\mathrm{C}}$.

$$\rho = \rho_{\mathrm{T}} + \Delta\rho_{\mathrm{C}},$$

where $\Delta\rho_{\mathrm{C}} \sim \Delta C$. The latter relation is used in the case of small concentration of impurities C [21].

Let us first discuss the pure liquid metal. In the liquid state all scattering is supposed to be confined to a spherical Fermi-energy shell. In the relaxation time approximation the solution of the Boltzmann equation for the relaxation time yields

$$1/\tau_{\mathrm{F}} = 2\pi n v_{\mathrm{F}} \int\limits_0^{\pi} \mathrm{d}\theta \;\; \sin\theta(1-\cos\theta)\sigma(q_{\mathrm{F}},\theta),$$

where $\sigma(q_{\mathrm{F}},\theta)$ is the differential scattering cross section per scattering center and v_{F} is the carrier velocity at the Fermi surface. Born approximation is used to determine σ. This, in turn, requires the square of the matrix element of the model potential that scatters the electrons $|v(q)|^2$:

$$\sigma(q_{\mathrm{F}},\theta) = \frac{1}{4\pi^2}(\frac{m}{\hbar^2})^2|v(q)|^2.$$

Since the scattering occurs on the spherical Fermi surface, we have $q = 2q_{\mathrm{F}}\sin\theta/2$, and hence

$$1/\tau_{\mathrm{F}} = \frac{1}{2\pi}\frac{m^2}{\hbar^4}\frac{\Omega}{2q_{\mathrm{F}}^4}\int_0^{2q_{\mathrm{F}}} |v(q)|^2 S(q) q^3 \mathrm{d}q.$$

$S(q)$ is liquid structure factor for the model of hard spheres. The theoretical structure factor is compared with the experimental data of Gingrich and Heaton [19] for the alkali metals by authors of [20]. It is apparent that up to and including the major diffraction peak, the structure factor is well reproduced by the model fluid.

$$S(q) = \{1 - nC(q)\}^{-1}, \tag{4.1}$$

where the direct correlation function in momentum space is given by

$$C(q) = -4\pi d^3 \int\limits_0^1 s^2 \frac{\sin qs}{qs}(\alpha + \beta s + \gamma s^2)\mathrm{d}s. \tag{4.2}$$

The parameters α, β, γ are functions of a packing-density parameter η:

$$\begin{aligned}
\eta &= (\pi/6)nd^3, \\
\alpha &= (1+2\eta)^2/(1-\eta)^4, \\
\beta &= -6\eta(1+\eta/2)^2/(1-\eta)^4, \\
\gamma &= (1/2)\eta(1+2\eta)^2/(1-\eta)^4.
\end{aligned}$$

For a long wavelength (i.e., small momentum transfer) the limit for the structure factor is known thermodynamically: $S(0) = nkT\chi_{\mathrm{T}}$, where χ_{T} is the isothermal compressibility. For sodium $nkT\chi_{\mathrm{T}} = 0.024$ at 100°C. The theoretical hard-sphere value is $S(0) = 1/\alpha = (1-\eta)^4/(1+2\eta)^2$. For $\eta = 0.45$, which is our fit to the sodium data, $S(0) = 0.025$.

The resistivity ρ_{T} may now be calculated from

$$\rho_{\mathrm{T}} = \frac{m v_{\mathrm{F}}\Omega}{Ze^2}\frac{1}{\tau_{\mathrm{F}}}. \tag{4.3}$$

Table 2. Comparison of liquid-metal resistivities for liquid Na, K at 100°C.

Metal	ρ_{exp}	$\rho_{\mathrm{H-A}}$ [20]	ρ_{A} [11]	ρ_{A}
Na	9.6	9.5	6.0	9.64
K	13	16.2	9.4	13.2

The resistivity for liquid metals is evaluated in [20] with Heine-Abarenkov potentials and the Animalu-Heine modification of this potential. The results are close to the experiment. We have calculated the sodium resistivity with Ashcroft's potential (3.1) (including screened function in Heldart-Vosko approximation (3.3)). In [11] the screened function has been used in Hartree approximation (without including electron exchange and correlation effects). The experimental value is $\rho_{\mathrm{exp}} = 9.6\ \mu\Omega\,\mathrm{cm}$ (see table 2).

So, we are convinced of the fact that the resulting value of resistivity is sensitive to the screened function and to small changes in the potential.

Now let us discuss the effect of the impurities on resistivity. When adding the impurity, the resistivity of liquid metal increases. The increment of resistivity is given as follows (the relation is obtained for crystals)

$$\frac{\Delta\rho}{\Delta C} = \frac{m v_{\mathrm{F}}}{e^2}\sigma, \tag{4.4}$$

where σ is total scattering cross section of conductivity electrons per impurity, ΔC is atomic part of the impurities.

$$\sigma = 2\pi \int_0^{\pi} (1-\cos(\theta))\sigma(q_{\mathrm{F}},\theta)\sin(\theta)\mathrm{d}\theta.$$

We have calculated the scattering cross section per pseudopotential $\tilde{v}_0(q)$ for a charged impurity.

$$\frac{\Delta\rho}{\Delta C} = \frac{m v_{\mathrm{F}}}{\pi e^2}\left(\frac{2m}{\hbar^2}\right)^2 \int_0^1 |\widetilde{v}(2q_{\mathrm{F}}z)|^2 z^3 \mathrm{d}z. \tag{4.5}$$

Concentration dependencies of the residual resistivity for several values $\langle n\rangle = 0, 1, 2$ are given in figure 5. The dash-dot line accords to experimental data [23]. Experimentally obvious relation is as follows:

$$\rho_{350^\circ\mathrm{C}} = \rho_{0\,350} + \Delta\rho = 18.9(1+\Delta C)\mu\Omega\,\mathrm{cm},$$

where $\rho_{350^\circ\mathrm{C}}$ is full resistivity of liquid Na at temperature 350°C, $\Delta\rho$ is the increment of resistivity caused by oxygen concentration rising, ΔC is the change of oxygen concentration (O_2 in at. %). The description of some experiments on controlling the oxygen impurity in Na is given in [22,23].

Dependence of the residual resistivity on the impurities charge states represented in figure 6 can be useful for impurity identification in liquid-metal heat-carriers.

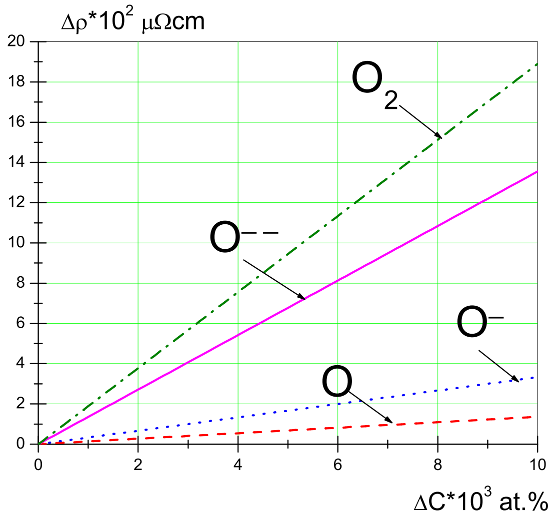

Figure 5. Concentration dependencies of the residual resistivity calculated for charged impurities $\langle n \rangle = 0, 1, 2$.

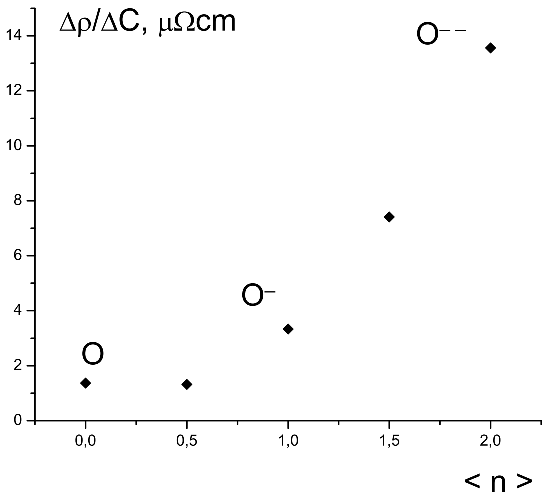

Figure 6. Dependence of the residual resistivity on the charge states of the impurities.

5. Conclusions

We have constructed the generalization of microscopic Anderson model to describe the states of electronegative impurities in liquid metal alloy. The case of oxygen impurity has been considered in detail. The proposed potential of interaction between conducting electrons and negative ions has been used in calculating the increment resistivity of liquid sodium containing oxygen impurities. The results are close to experimental data. The observed dependence of impurity resistivity on the concentration of the impurities and the charge states can serve as an effective method of controlling the impurities in liquid-metal heat-carriers. The form-factor of the potential will be used for self-consistent calculation of the charge and spin-polarized states of the oxygen impurity.

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Модельний потенціал взаємодії електронів з негативними іонами

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Узагальнюється мікроскопічна модель Андерсона з метою опису станів електронегативних домішок у розплавах рідких металів. Самоузгоджено враховується вплив випадкового внутрішнього поля на зарядові стани домішки. Проведена якісна і кількісна оцінка параметрів гамільтоніана, досліджуються межі застосовності мікроскопічної моделі до опису конкретних систем. Розглянуто конкретний випадок домішки кисню в рідкому натрії. У такій системі важливим є вибір потенціала взаємодії електронів з домішками. Детально проаналізовано параметри запропонованого псевдопотенціала, проведено порівняння з іншими модельними псевдопотенціалами. Використавши форм-фактор запропонованого потенціала, пораховано питомий опір рідкого натрію з домішками кисню. Отримано залежність домішкового питомого опору від зарядового стану домішок та їх концентрації.

Ключові слова: *негативні іони, рідкі метали, модель Андерсона*

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