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EFFECTIVE POTENTIALS OF INTER-ION INTERACTION OF TRANSITION METALS *

Abstract: The effective potential of inter-ion interaction in metals is a sum of direct inter-ion interaction and interaction by conducting electrons. Up to the present, satisfactory results of calculation of the effective potentials for transition metals have been determined with the use of perturbation calculation taking into account the second and third order corrections for 3d and 4d transition metals.

1. Introduction

One of the most important characteristics of metals that determine their equilibrium properties is an effective potential of inter-ion interaction. Usually the inter-ion interaction is represented in the form of a sum of pair-wise Coulomb potential and indirect interaction of ions through conducting electrons. Due to successful description of electron-ion interaction in simple metals by the method of model potential the nature of simple metals is well studied. An investigation of the inter-ion interaction for simple metals was performed in many works in which there were considered both the pair-wise interaction [1-4] (the second order of perturbation theory for the model potential) and the terms of perturbation theory of higher orders [5,6]. However, this problem is studied insufficiently in the case of transition and rare-earth metals, this fact being probably due to only a very slow progress in development of the pseudo-potential method for these metals.

Previously the calculation of effective potentials of the inter-ion interaction within the second-order perturbation theory for 3d transition metals was performed [7]. For determination of the shape-factors of the nonlocal model

potential (MP), the semilocal approximation of Fermi sphere was used. However, it is known that for quantitative calculations of the metals properties it is important to consider the electron-ion interaction nonlocality more precisely as well as the perturbation theory terms of higher orders for MP that correspond to many-particles correlations in the electronic subsystems.

2. Method

Let us introduce the effective potentials of inter-ion interactions of transition and rare-earth metals in the form of a sum of two terms: the potential of direct inter-ion interaction ($\frac{z^2}{r}$) and corrections of perturbation theory for MP [8]

$$V_{eff}(r) = \frac{z^2}{r} + \sum_{n>2} V^{(n)}(r) \tag{1}$$

It should be noted the corrections $V_2^{(n)}(r)$ describe indirect interaction between ions through conducting electrons. For the second order of perturbation theory for the MP is presented in the form [8]:

$$V^{(2)}(r) = \frac{\Omega_0}{2\pi^2}\int_0^\infty F^*(q)\frac{\sin kr}{kr}q^2 dq + \\ + \frac{\Omega_0}{2\pi^2}\int_0^{k_F}\sum_{m,R_j} A(R_j)\beta_{R_j}^m \frac{\sin kR_j}{kR_j}\left\{\left\langle \mathbf{k}\middle| w_{add}^{(0)}\middle|\mathbf{k}\right\rangle + \left\langle \mathbf{k}\middle| w_{hybr}^{(0)}\middle|\mathbf{k}\right\rangle\right\}k^2 dk \tag{2}$$

here β_R^m is the overlap integral of d- orbitals and m is quantum number. Summing over R_j is performed within first and second coordination spheres. The characteristic function of band structure of transition (rare-earth) metals $F^*(q)$ is as follows [9]:

$$F^*(q) = \frac{\Omega_0 q^2}{8\pi}\left\{\frac{1-\varepsilon_{d(f)}(q)}{\varepsilon^*_{d(f)}(q)}\left[\nu_q + \nu_{hybr}(q) + \delta\nu_{d(f)}(q)\right]^2 + \right. \\ + \frac{2\varepsilon_{d(f)}(q)}{\varepsilon^*_{d(f)}(q)} g_{d(f)}(q)\left[\nu_q + \nu_{hybr}(q) + \delta\nu_{d(f)}(q)\right] + \\ \left. + \left[1 - \frac{\varphi(q)}{\varepsilon^*_{d(f)}(q)}\right]\varepsilon_{d(f)}(q) g^2_{d(f)}(q) + h_{d(f)}(q)\right\} \tag{3}$$

here functions $g_{d(f)}(q)$ and $h_{d(f)}(q)$ are determined:

$$g_{d(f)}(q)=\frac{4}{\pi q^3\varepsilon_{d(f)}(q)}\left[\int_0^{k_F} f_{d(f)}(q)\ln\left|\frac{q-2k}{q+2k}\right|kdk+\right.$$
$$\left.+\int_{k_F}^{k_{D(F^*)}}\sin^2\frac{\beta(k)}{2}f_{d(f)}(q)\ln\left|\frac{q-2k}{q+2k}\right|kdk\right] \quad (4)$$

$$h_{d(f)}(q)=\frac{4}{\pi q^3}\left[\int_0^{k_F} f^2_{d(f)}(q)\ln\left|\frac{q-2k}{q+2k}\right|kdk+\right.$$
$$\left.+\int_{k_F}^{k_{D(F^*)}}\sin^2\frac{\beta(k)}{2}f^2_{d(f)}(q)\ln\left|\frac{q-2k}{q+2k}\right|kdk\right] \quad (5)$$

The indexes d and f are characteristics of transition and rare-earth metals, respectively. The potentials v_q, $v_{hybr}(q)$, $\delta v_{d(f)}(q)$ and the diagonal elements of additional potential ($\langle\mathbf{k}|w^{(0)}_{add}|\mathbf{k}\rangle$), hybridization potentials ($\langle\mathbf{k}|w^{(0)}_{hybr}|\mathbf{k}\rangle$) and dielectric constant ($\varepsilon^*_{d(f)}(q)$) are determined in [9].

Similarly we can write the correction of the third order to $V_{eff}(r)$:

$$V^{(3)}(r)=\frac{3\Omega_0}{4\pi^2}\int_0^{\infty}F^{(3)}(q)\frac{\sin kr}{kr}q^2dq \quad (6)$$

$$F^{(3)}(q)=\int_0^{\infty}q_1^2dq_1\int_{-1}^{1}\Phi(q,q_1)\Lambda^{(3)}(q,q_1,|\mathbf{q}+\mathbf{q}_1|)d\cos(\hat{\mathbf{q},\mathbf{q}_1}) \quad (7)$$

$$\Phi(q,q_1)=\frac{4}{\pi q^3}\int_0^{k_F}\langle\mathbf{k}|w|\mathbf{k}+\mathbf{q}'\rangle\langle\mathbf{k}+\mathbf{q}'|w|\mathbf{k}+\mathbf{q}\rangle\langle\mathbf{k}+\mathbf{q}|w|\mathbf{k}\rangle\ln\left|\frac{q-2k}{q+2k}\right|\ln\left|\frac{q_1-2k}{q_1+2k}\right|dk$$

Here $\Lambda^{(3)}(q,q_1,|\mathbf{q}+\mathbf{q}_1|)$ is electron threepole for which the expression obtained in [10] is used; form-factors of the screened MP $\langle\mathbf{k}+\mathbf{q}|w|\mathbf{k}\rangle$ are determined in [9].

Results and discussion

The effective potentials of inter-ion interaction obtained within the second-order correction of perturbation theory are presented in Figs 1-3.

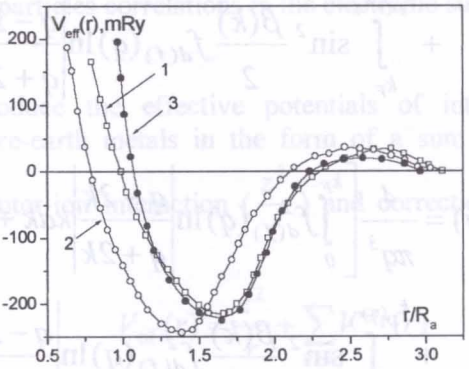

Fig. 1 Effective inter-ion interaction in 3d transition metals (1-Fe, 2-Co, 3-Ni)

In particular, Figure 1 shows the results of calculation of the pair-wise effective potentials of inter-ion interaction $V(r)$ for 3d transition metals (1-Fe, 2-Co, 3-Ni), Figure 2 – for 4d transition metals (1-Y, 2-Zr, 3-Mo) and Figure 3 shows potentials $V(r)$ for rare-earth metals (1-Ce, 2-Pr, 3-Eu)

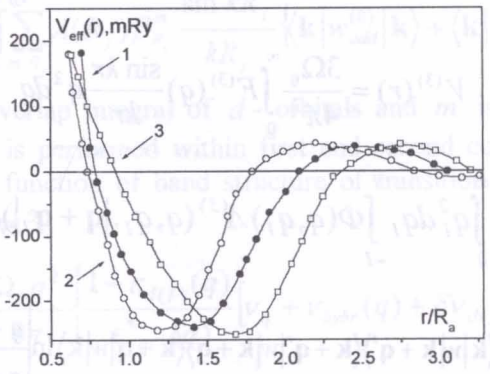

Fig. 2 Effective inter-ion interaction in 4d transition metals (1-Y, 2-Zr, 3-Mo)

In these figures one can see that obtained potentials are characterized by deep minimum which is defined by an exchange-correlation interaction between conducting electrons. At the long inter-ion distances we observe Friedel oscillations which are caused by logarithmic singularity of dielectric constant. An inclusion of the third-order correction of perturbation theory (according to

Eq.6) has an essential influence on a shape of effective potentials of inter-ion interaction. As an illustration of such influence we can show iron (Fe) potentials $V(r)$ in the Fig. 4, calculated with the consideration of the second (curve 1) and third (curve 2) order perturbation theory corrections for MP.

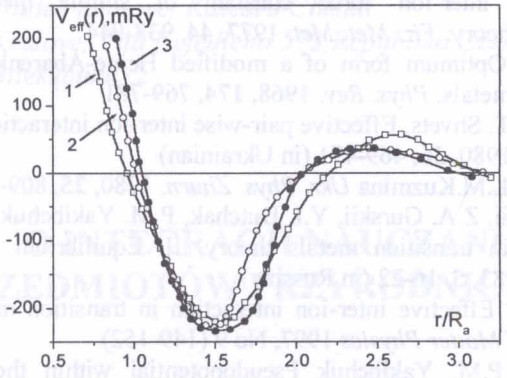

Fig. 3 Effective inter-ion interaction in rare-earth metals (1-Ce, 2-Pr, 3-Eu)

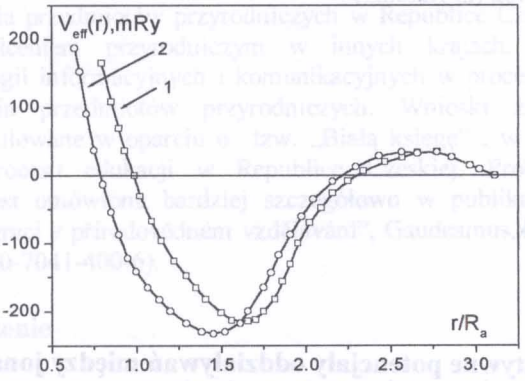

Fig. 4 Effective inter-ion interaction for Fe (1-the second-order correction, 2- the third-order correction)

As one can see (Figure 4), the third-order correction leads to increase of the first minimum and decrease of the equilibrium distance between ions. Within higher order corrections of perturbation theory the same tendency can be observed for other transition metals.

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Efektywne potencjały oddziaływań między jonami metali przejściowych

Streszczenie: Efektywny potencjał oddziaływania jonów w metalach jest sumą bezpośredniego oddziaływania jon-jon oraz sprzężenia za pośrednictwem elektronów swobodnych. Jak dotychczas, satysfakcjonujące wyniki obliczeń potencjału efektywnego uzyskano jedynie dla metali prostych. W pracy wyznaczono potencjały efektywne dla metali przejściowych stosując rachunek zaburzeń z uwzględnieniem poprawek drugiego i trzeciego rzędu dla metali 3d i 4d przejściowych.