Muffin-tin multiple-scattering theory for interatomic potentials in metals

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V E Egorushkin and K A Tarasenko

Institute for Physics of Hardness and Materials, Siberian Branch of the Russian Academy of Sciences, Pr. Academicheski 8, Tomsk 634055, Russia

Abstract. The muffin-tin multiple-scattering theory is employed to evaluate the interatomic forces in simple and transitional metals. In the framework of this theory the pair interatomic potentials have been calculated for K, Ni and Cu. The vacancy formation energy, the elastic constants and the phonon spectra have been obtained on the basis of the calculated potentials.

Many different methods can be used to calculate interatomic potentials in metals and alloys. The most consistent *ab initio* interatomic potentials are generated by pseudopotential theory for simple metals.

An *ab initio* method suitable in principle for the description of both simple and transitional metals was suggested in [1]. This was based on density-functional formalism and muffin-tin (MT) multiple-scattering theory. The pair potentials for Li, K and Rb have been calculated in [1]. The results of this analysis were satisfactorily close to the results obtained by pseudopotential theory. It would be interesting

(i) to investigate the interatomic potentials in transitional metals within the framework of the approach in [1],
(ii) to calculate some physical properties on the basis of these potentials and
(iii) to compare the results obtained with experimental data.

The purpose of our paper is to present the simplification of expressions for the interatomic potentials from [1] for systems which have an inversion centre, and to calculate the pair potentials, the vacancy formation energies, the elastic constants and the phonon spectra for K, Ni and Cu.

The following expression for the total energy of the system of MT scatterers in the approximation of rigid non-overlapping MT spheres has been obtained in [1]:

$$E(\{R_N\}) = \tfrac{1}{3} \sum_{i=1}^{N} \int_{\Omega_i} \mathrm{d}r \, n(R_i + r)[w^i(r) - w^i_{xc}(r)$$
$$+ \tfrac{1}{2} r \cdot \nabla w^i(r) - 2r \cdot \nabla w^i_{xc}(r)] \tag{1}$$

where $w^i(r)$ and $w_{xc}(r)$ are the total self-consistent one-electron and exchange–correlation potentials. $\{R_N\}$ is the total radius vector of N scatterers; $n(R_i + r)$

is the ground-state electron number density within the MT labelled i, which can be expressed as [2]

$$
n(R_i + r) = \begin{cases} \frac{2}{\pi} \operatorname{Im} \left(\sum_{L_1 L_2} \int_{E_{bb}}^{E_F} dE \, R_{l_1}(r, E) R_{l_2}(r, E) \right. \\ \qquad \left. \times Y_{L_1}(\hat{r}) Y_{L_2}(\hat{r}) \tau_{L_1 L_2}^{ii}(E) \right) & r \leqslant R_{MT}^i \\ n_{\text{const}} & r > R_{MT}^i \end{cases} \tag{2}
$$

where the electron energies are measured with respect to the MT zero, E_{bb} is the bottom of the conduction band, E_F is the Fermi energy, R_{MT}^i is the MT-sphere radius, $L \equiv (l, m)$ and $R_l(E, r)$ is the single MT radial wavefunction. $\tau_{L_1 L_2}^{ii}$ is Gyorffy's scattering path matrix given by [2]

$$
\tau_{L_1 L_2}^{ij}(E) = t_{l_1}^i \delta_{L_1 L_2} + \sum_{\substack{k \neq i, \\ L_3}} t_{l_1}^i G_{L_1 L_3}^0(E, R_{ik}) \tau_{L_3 L_2}^{k,j}(E) \tag{3}
$$

with

$$
t_l^i = -E^{1/2} \sin \delta_l^i(E) \exp[i \delta_l^i(E)]
$$

$$
G_{L_1 L_2}^0(E, R_{ij}) = -4\pi E^{1/2} \sum_{L_3} C_{L_1 L_2}^{L_3} i^{l_1 - l_2 + l_3 + 1} h_{l_3}^{(+)}(\sqrt{E} R_{ij}) \bar{Y}_{L_3}(\bar{R}_{ij}).
$$

Here t_l^i is the single-site scattering matrix, G^0 is the free-electron Green function, $h_l^{(+)}(x)$ are spherical Hankel functions, $Y_L(\hat{x})$ are real spherical harmonics and $C_{L_1 L_2}^L$ are the corresponding Gount numbers.

The separation of n-body contributions in the total energy is based on the addition of contributions which describe the scattering of electrons on n single MT potentials in the expansion for the scattering path matrix (3). Thus, we can obtain n-body decomposition for the total energy. For instance, the two-body (pair) interaction energy in the spherical frame of reference is given by [3]

$$
E^{(2)}(R_{ij}) = \frac{2}{3\pi} \sum_L \int_{E_{bb}}^{E_F} dE \operatorname{Im} \left({}^j \tau_{L_1 L_2}^{ii} - t_l^i \delta_{L_1 L_2} \right) Z_L^i(E) \delta_{L_1 L_2} \tag{4}
$$

where

$$
Z_L^i(E) = \frac{E}{\sin^2 \delta_l^i(E)} \int_0^{R_{MT}^i} dr \, [r R_l^i(r, E)]^2 p^i(r)
$$

$$
p^i(r) = w^i(r) - w_{xc}^i(r) + \tfrac{1}{2} r (d/dr)[w^i(r)] - 2r (d/dr)[w_{xc}(r)].
$$

This expression differs from the corresponding expression in [1]. The difference is that (4) takes into consideration the availability of the inversion centre in the system of scatterers (lattice, FCC, BCC, etc). Equation (4) can also be obtained using the spherically averaged electron number density in (1) instead of equation (2). The assumption about the spherically averaged electron density in (1) is probably not a

bad approach if the MT approximation gives satisfactory results for the electronic properties of metals (see, e.g., [4]).

The input data for the calculation of the interatomic pair potentials using equations (3) and (4) are $w(r)$, $w_{xc}(r)$, E_{bb}, E_F and R_{MT}. In this present paper we have taken the data [4] where workers have used the self-consistent Kohn–Sham method for all metals with an atomic number less than 50, i.e. $w(r)$, E_{bb}, E_F, R_{MT} and $\rho(r)$ in [4]. $\rho(r)$ is the total (core plus conduction) electron number density within the MT, from which $w_{xc}(r)$ was evaluated in the Hedin–Lundqvist approach (in accordance with [4]).

Information about the phase shifts $\delta_l(E)$ was input in the following way:

$$\cot \delta_l(E) = \{[n_l'(\mathcal{H}r) - n_l(\mathcal{H}r)L_l(E,r)]/[j_l'(\mathcal{H}r) - j_l(\mathcal{H}r)L_l(E,r)]\}\,|_{r=R_{MT}}.$$

Here $n_l(x)$ and $j_l(x)$ are spherical Neumann and Bessel functions, $L_l(E,r)$ are logarithmic derivations of $R_l(E,r)$ and $\mathcal{H} \equiv E^{1/2}$.

Table 1. The calculated and experimental values of the elastic constants C_{44} and C' and the vacancy formation energies.

		C_{44} (10^{10} dyn cm^{-2})	C' (10^{10} dyn cm^{-2})	E_v (eV)
K	Theory	2.9	0.30	0.41
	Experiment	2.7 [5]	0.35 [5]	0.39 [6]
Cu	Theory	80.9	48.5	1.39
	Experiment	75.6 [5]	23.6 [5]	1.05 [6]
Ni	Theory	120.0	64.7	1.63
	Experiment	118.0 [5]	45.0 [5]	1.4 [6]

The calculations have been performed for K, Ni and Cu. Angular momenta up to $l = 2$ (i.e. s, p and d electrons) have been included in the calculations. Core electrons have not been included explicitly. The results are shown in figure 1. The positions of the coordination spheres are indicated by arrows. The pair potential for K is very little different from that obtained in [1]. For an adequate examination of the interatomic potentials we have calculated the vacancy formation energies E_v (without lattice relaxation) and the elastic constants C_{44} and C'. The results are presented in table 1. One can see from the table that we have obtained, on the whole, satisfactory agreement with the experimental results [5, 6]. The calculated phonon spectra for K and Cu are shown in figure 2 and figure 3, respectively. The full curves correspond to our results, and the full circles to experimental data for K [7] and for Cu [8].

As seen from the results obtained, the above-cited method can be useful for the calculation or modelling of the properties of metal systems. The application of this method to more compound systems (e.g. Cu–Zn alloy) will be considered in subsequent papers.
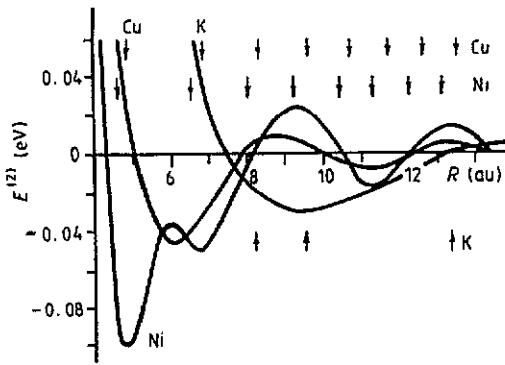
Figure 1. The calculated interatomic potentials for K, Ni and Cu. The positions of the coordination spheres are indicated by arrows.
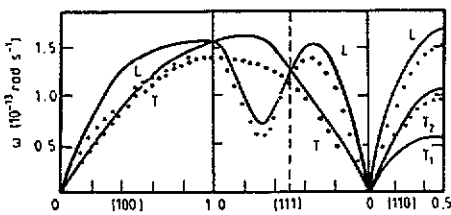

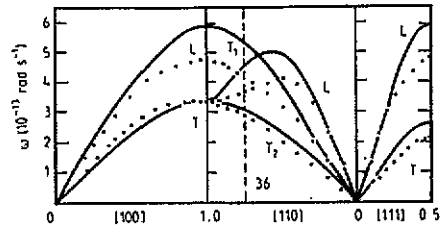**Figure 2.** The calculated (——) and experimental [7] (●) phonon spectra for K.

Figure 3. The calculated (——) and experimental [8] (●) phonon spectra for Cu.

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