

Electrical resistivity of liquid binary and ternary alloys

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Abstract New method of calculation of the electrical resistivity of liquid and amorphous alloys is presented. The method is based on the Morgan–Howson–Šaub (MHŠ) model but the pseudopotentials are replaced by the scattering matrix operators. The Fermi energy is properly determined by the accurate values of the phase shifts. The model depends on a very small number of universal parameters and gives stable results. The calculated values of the resistivity agree well with available experimental data for a substantial number of binary alloys. Moreover, the results for some ternary alloys were also obtained.

1 Introduction

Electron transport in liquid and amorphous materials has been extensively investigated by many authors. There are several theoretical models that describe electrical resistivity of disordered systems. The problem is very complex so that every approach requires some approximations which obviously cause the final results to be unreliable. On the other hand, theoretical models usually depend on a number of parameters that in many cases can be chosen in a way that allows us to reproduce experimental resistivities, even when there exist physical reasons for that such procedure should not succeed.

The commonly used Faber–Ziman (F-Z) model [1] represents a quasi-classical approach to this problem. Alloys are considered as the sets of ions, which relative positions are

described with use of the partial structure factors (which correspond to pair correlation functions), and the electron-ion interaction is represented by a pseudopotential. This method was used to reproduce resistivities of some simple alloys with rather good agreement with experiment [2, 3]. In our previous work we examined this model and came to the following important conclusions [4]:

1. The F-Z model gives very unstable results and the most important cause of this situation is the choice of the pseudopotentials. By suitable choice of the form of these pseudopotentials or by suitable choice of their parameters one can fit calculations to the experiment in almost every single case.
2. The F-Z model neglects multiple scattering effects. The comparison of the results obtained within the F-Z model and another one which involves the quantum effects of the multiple scattering shows that even for low resistive alloys the difference may be significant.

These two remarks suggest that the parameterization of the model may cause that some physical effects will not be seen. Since we cannot do anything better, we suggest that to obtain a useful model, which we may consider as physically correct, we should demand its universality, what would be the argument for a specific choice of the values of parameters.

Multiple scattering effects have been included in another model, formulated by Morgan et al. [5], usually called the ‘ $2k_F$ ’ scattering model (or MHŠ one), that is based on a different formalism than the F-Z model and similar ones. It is completely quantum model, based on the quantum kinetic equation. It gives a formula for the resistivity that may be interpreted as a rescaled F-Z one. In practice, obtaining the MHŠ results, when someone already has got the

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F-Z ones, requires just a few simple calculations and the results are much more physically sound, even if the parameterization allows for fitting resistivities in both models. Of course, since the MHS model gives the resistivity in a similar way as the F-Z one, the results are still unstable and the model has too many parameters to be useful in practice.

The Faber–Ziman model was extended by Evans et al. [6], who replaced the pseudopotentials by the scattering matrix operators that were calculated basing on the phase shifts of the wave functions. This approach was necessary particularly for the transition metals where the first Born approximation was not accurate enough [7–11]. What we have found examining this model is that the results here are much more stable than for the F-Z one, and that there is practically no free choice of parameters. The next step in our work was therefore a combination of the Evans model with the MHS one that included multiple scattering effects to obtain stable resistivities.

After elimination of the direct influence of the pseudopotentials on the transport lifetimes, we had to improve the precision of the Fermi energy determination, since the lifetimes were calculated as the integrals that depended on the Fermi radius. We have found that the Esposito method [12] is quite effective, and it does not require any additional parameters, so we have chosen this one for our model. Then, during the calculation process, we discovered that the phase shifts used for calculations required more precise approach. Many authors—in our opinion, which is based on the results they obtained—took phase shifts computed modulo π , or they assumed that the phase shift in zero-energy limit is equal to zero and continuous for the whole energy range. Although this approach does not cause any problems for obtaining the scattering matrix elements (since they are periodic functions that cut out all 2π phase shifts of the electron wave), it has a great importance when using the Lloyd formula for the electron number. The change we have made allowed us for elimination of one free parameter and for exact Fermi energy calculation even for heavier elements. We also generalized formulas to make calculations for multi-element systems.

In the whole process of constructing our model we focused on making it as general as possible. We could define parameters for each considered element that would allow us to predict the resistivity of any alloy of these elements. The results and the theory we present here work very well for most of simple metals. We did not introduce the temperature dependence of our model parameters, so the model cannot be used in a wide range of temperatures. It does not predict properly the resistivities of more complex elements, either. Nevertheless it gives very good results for many binary and ternary alloys, and these are presented in this paper.

2 Model

The resistivity in the ‘ $2k_F$ ’ scattering model is calculated as [5]

$$\rho = \frac{m_e^*}{ne^2\tau_{tr}}, \quad (1)$$

where:

$$\frac{1}{\tau_{tr}} = \frac{1}{\tau_{FZ}} \frac{1 + \frac{1}{2} \frac{\tau_{FZ}}{\tau} X^2 F_{MHS}^{1/2}(X)}{1 - \frac{3}{64} X^4 F_{MHS}(X)}. \quad (2)$$

Here τ_{FZ} stands for the transport lifetime and τ is one-electron lifetime (both taken from the F-Z model), $X = \hbar/(\tau E_F)$, and

$$F_{MHS}(X) = \left[2 \ln \frac{(1 + X^2)^{1/2} + 1 + 2^{1/2}[(1 + X^2)^{1/2} + 1]^{1/2}}{(1 + X^2)^{1/2} + 1 - 2^{1/2}[(1 + X^2)^{1/2} + 1]^{1/2}} \right]^2. \quad (3)$$

Instead of the original formula for F-Z lifetimes we follow Evans [6], taking

$$\frac{1}{\tau_{FZ}} = \frac{m_e^* \Omega_0}{4\pi \hbar^3 k_F^3} \int_0^{2k_F} dq \lambda(q) q^3, \quad (4)$$

$$\frac{1}{\tau} = \frac{m_e^* \Omega_0}{2\pi \hbar^3 k_F} \int_0^{2k_F} dq \lambda(q) q, \quad (5)$$

where Ω_0 is the average volume per one atom in the system, and for p -element alloy we generalized $\lambda(q)$ to be equal to

$$\lambda(q) = \sum_{\alpha=1}^p \sum_{\beta=1}^p \sqrt{c_\alpha c_\beta} S_{\alpha\beta}(q) t_\alpha(q) t_\beta^*(q). \quad (6)$$

In this equation c_i stands for the number concentration of the i th component, S_{ij} are the Ashcroft–Langreth partial structure factors [3] and $t_i(q)$ are scattering operator matrix elements (at the Fermi level):

$$t(q) = -\frac{2\pi \hbar^3}{\Omega_0 m_e^* k_F} \sum_l (2l+1) \sin \eta_l e^{i\eta_l} P_l(\cos \theta), \quad (7)$$

where P_l are the Legendre polynomials, $\cos \theta = 1 - q^2/(2k_F)^2$, and η_l phase shifts at the Fermi level for the l th band of the considered element.

2.1 Structure factors

We use the Ashcroft–Langreth partial structure factors [3] calculated by means of the method presented by Hoshino [13] that allows us to calculate these factors for multi-element systems. Following previous authors [8], in order

to reduce the number of parameters, we take the packing fraction according to Waseda's empirical rule [14]:

$$\eta = Ae^{-BT}, \quad (8)$$

where A and B are experimentally determined and given in [14]. Hard-sphere diameters are now given as

$$\sigma^3 = \frac{6\eta\Omega_0}{\pi} \quad (9)$$

and assumed constant with change of the composition.

For calculation of the Ω_0 we take densities linearly interpolated with temperature, using values given by Waseda [14].

For two-element alloys we assume that number density $n_0 = 1/\Omega_0$ changes linearly with composition.

2.2 Phase shifts

Phase shifts are calculated by solving the Schrodinger equation with the muffin-tin potential calculated by means of the Mattheiss prescription generalized for disordered systems by Mukhopadhyay [15, 16].

For the neutral atom the potential $v(r)$ is the sum of the Coulombic part $v_C(r)$ and the exchange correlation potential $v_{ex}(r)$. The first one is obtained from the Poisson equation and the second one reads:

$$v_{ex}(r) = -3\alpha e^2 \left[\frac{3}{8\pi} \rho(r) \right]^{1/3}. \quad (10)$$

The charge density $\rho(r)$ is calculated using wave functions given by the Herman–Skillman program [17] and α is the Slater exchange parameter.

For disordered systems with spherical symmetry the total Coulombic potential and the charge density are given, respectively, by

$$V_C(r) = v_C(r) + \frac{2\pi}{\Omega_0 r} \int_0^\infty dR R g(R) \int_{|R-r|}^{|R+r|} dt t v_C(t) \quad (11)$$

and

$$\rho_T(r) = \rho(r) + \frac{2\pi}{\Omega_0 r} \int_0^\infty dR R g(R) \int_{|R-r|}^{|R+r|} dt t \rho(t). \quad (12)$$

The exchange correlation potential for liquid alloy now is

$$V_{ex}(r) = -3\alpha e^2 \left[\frac{3}{8\pi} \rho_T(r) \right]^{1/3} \quad (13)$$

and the total potential is simply the sum:

$$V(r) = V_C(r) + V_{ex}(r). \quad (14)$$

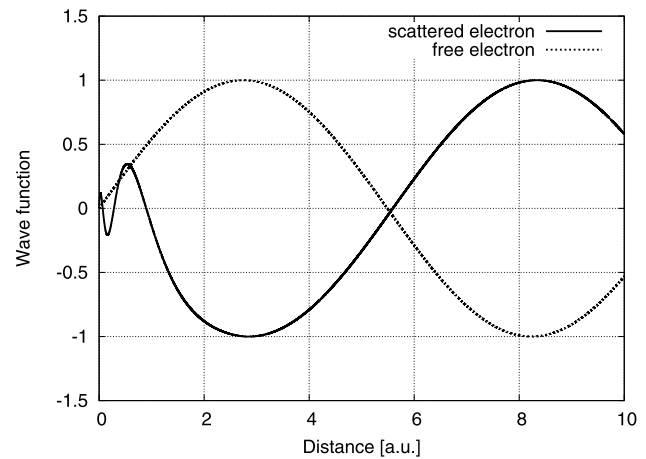


Fig. 1 Comparison of the scattered and free electron wave functions for Cu, $l = 0$

The muffin-tin zero is calculated as

$$V_0 = \frac{3}{(r_{WS})^3 - (r_{MT})^3} \int_{r_{WS}}^{r_{MT}} dr V(r), \quad (15)$$

where the Wigner–Seitz radius is

$$r_{WS} = \left(\frac{3\Omega_0}{4\pi} \right)^{1/3} \quad (16)$$

and the muffin-tin radius is taken as a half of the distance between the origin of the coordinate system and the first peak of the pair correlation function $g(r)$.

Comparison of the scattered electron wave function obtained as the solution of the Schrodinger equation with analytical free electron wave function allows us the phase shift determination; thus [18]

$$\tan \eta_l = - \frac{y(r_1)S(r_2) - y(r_2)S(r_1)}{y(r_2)C(r_1) - y(r_1)C(r_2)} \quad (17)$$

where $y(r)$ is the exact solution of the radial part of the Schrodinger equation, r_1 and r_2 are two distinct points in the asymptotic region, $S(r) = kr j_l(kr)$, $C(r) = kr n_l(kr)$, and j_l and n_l are the spherical Bessel and Neumann functions, respectively.

In such calculation every 2π component of the phase-shift is cut off, since the arc tan function is defined in $[-\pi, \pi]$ range. It is not a problem when we use phase shifts only in [7], where only periodic functions are considered, but for the Fermi energy calculation it is important to have full phase shift value. Figure 1 shows an example of the scattered and free electron wave function. It is apparent that the phase-shift here is about 3π , since the scattered electron wave function oscillates a couple of times before it reaches the asymptotic region.

In our method we count these oscillations to obtain proper values of the phase shifts. Figure 2 presents the phase shifts calculated in this way.

2.3 Fermi energy

Proper determination of the Fermi energy seems to be one of the most important steps of the calculations. Scattering operator matrix elements (7) depend on the phase shifts on the Fermi level, and since the phase shift usually changes rapidly with energy (especially for $l = 2$) it is crucial to determine the Fermi level as precisely as possible. Esposito et al. [12] suggested a consistent method to determine Fermi energy and effective valence Z^* . The method is based on Lloyd's formula for the integrated density of states [19]:

$$N(E) = N_0(E) + \frac{2}{\pi} \sum_l (2l+1) \eta_l + N_m(E), \quad (18)$$

where $N_0(E)$ is the free electron integrated density of states and $N_m(E)$ corresponds to multiple scattering effects. After neglecting of the last term the number of electrons may be written as:

$$Z = N(E_F) \approx N_0(E_F) + \frac{2}{\pi} \sum_l (2l+1) \eta_l. \quad (19)$$

Notice that the shift of the phase by 2π (or its multiplicity) cannot be neglected here. The η_l value is the biggest for small l (however it may be close to zero when counted modulo π), so the sum cannot be reduced to one term with η_2 . Also for heavier elements the sum must involve the term with $l = 3$ because it gives a significant contribution to the value of Z .

The Fermi vector dependence on the energy is:

$$k_F = \frac{(2m_e E_F)^{1/2}}{\hbar} \quad (20)$$

and the effective valence is:

$$Z^* = \frac{k_F^3 \Omega_0}{3\pi^2} = N_0(E_F). \quad (21)$$

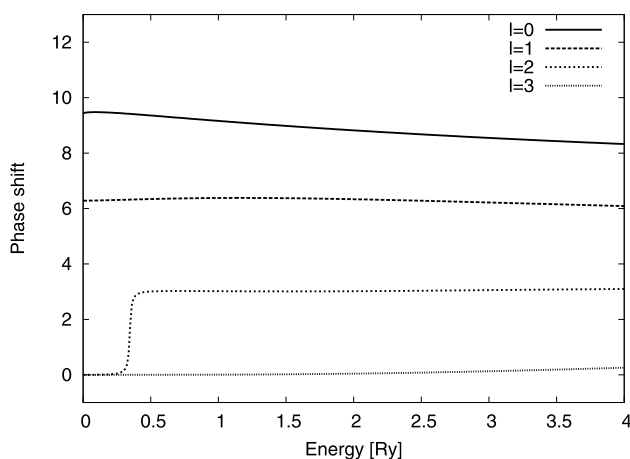


Fig. 2 Calculated phase shifts for Cu

The value of the Fermi energy E_F should satisfy (19) where Z is the atomic number.

Apart from the Esposito method there are also the Dreirach one [7] and several other propositions [8, 20], where the authors notice that the obtained resistivity may significantly differ from experiment and even the free electron model calculations may result in better agreement [21].

In this paper we decided to use the Esposito method, since it was free of any parameters and the shape of the resistivity curve as a function of concentration seemed to be in good agreement with experiment. We noticed that to achieve agreement in both of the shape and the absolute value of the resistivity one additional parameter for a given element should be used. We made the simplest choice which would be the effective mass as it appears in (1, 4, 5), and we assumed its linear dependence on the concentration.

3 Results

3.1 Binary alloys

We performed the calculations for the resistivity of more than 30 alloys, each time obtaining stable results. In order to make the model as universal as possible, we assumed that the parameters defined for the considered elements should not change for various alloys. We also neglected any temperature dependence of the model parameters (m_e^* , α). We assumed that α should be in the range from 0.6 to 1.0, since some authors reported that for metals it was approximately 0.7 or put full exchange with $\alpha = 1.0$. The reasonable values of the effective mass parameter m_e^*/m_e should be close to 1.0. The parameters used in calculations are gathered in the Table 1.

Figure 3 presents most successful calculations. It is well apparent that results agree with experimental data and the parameters given are universal. We performed calculations for all combinations of elements appearing in Fig. 3, which were available in literature thus we consider that the model

Table 1 Parameters used in calculations

Element	α	m_e^*/m_e
Al	0.7	0.85
Ca	0.98	0.78
Cd	0.75	1.11
Cs	0.6	0.82
K	0.6	1.2
Li	1.0	1.18
Mg	0.7	1.23
Na	0.7	1.0
Rb	0.6	1.3

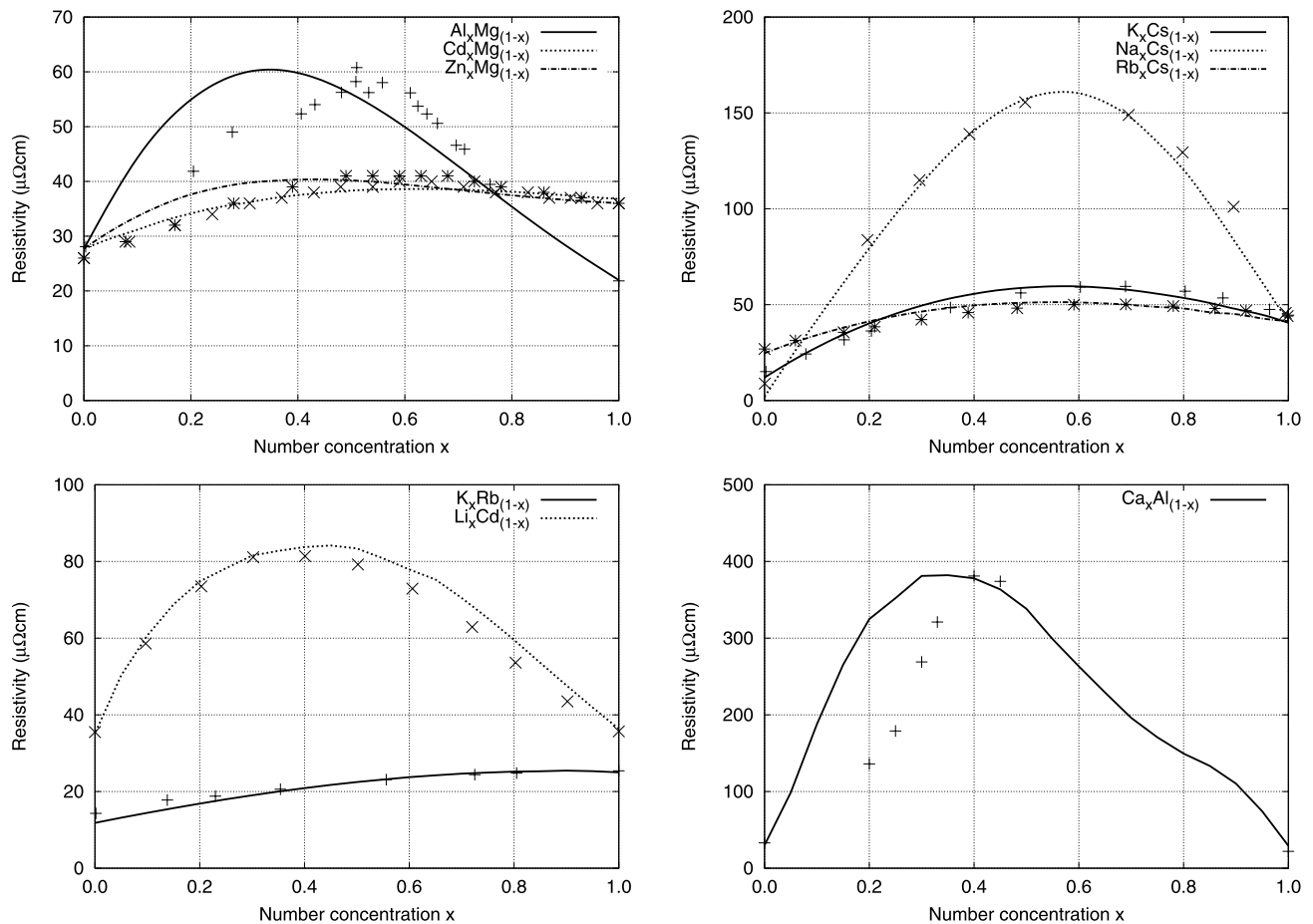


Fig. 3 Calculated values of the resistivity for alloys as a function of their composition. Crosses denote experimental values taken from literature: Al-Mg [22], Cd-Mg [23], Zn-Mg [24], K-Cs [25], Na-Cs [25],

Rb-Cs [26], K-Rb [27], Li-Cd [28], Ca-Al (amorphous) [29]. Details are given in the text

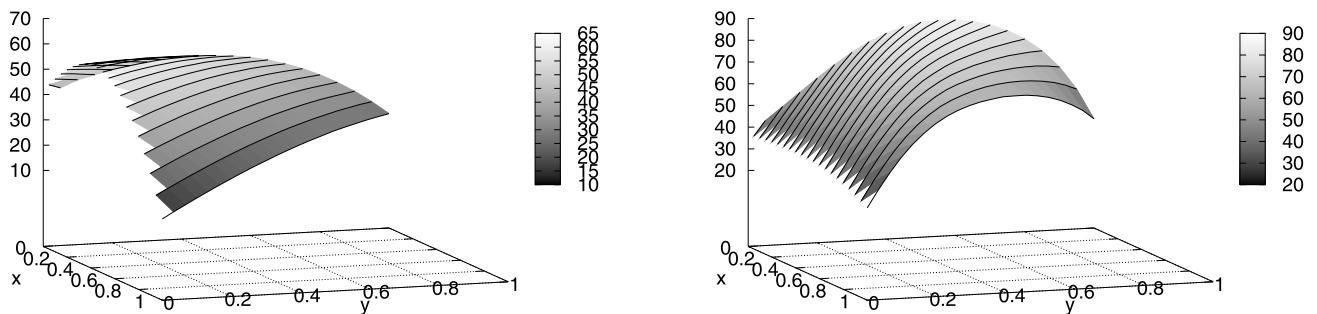


Fig. 4 Calculated values of the resistivity for two ternary alloys: K-Rb-Cs (on the left) and Mg-Li-Cd (on the right)

is universal for those elements and can be used for prediction of the resistivity.

3.2 Ternary alloys

While building the model we have generalized formulas to perform calculations for multi-element systems. Figure 4

presents exemplary calculations for two ternary alloys. Although we did not have experimental data for such systems, nevertheless for each pair of K-Rb-Cs elements we obtained good agreement with experiment, and same for Mg-Cd and Li-Cd (Fig. 3) while we did not have experimental data for Li-Mg.

The important fact that we notice here is that adding the third element does not increase the resistivity of the alloy over the highest value of any binary combination.

3.3 Discussion

There are several reasons that may cause differences between the results of the calculations and experimental data. Analytical models are created with some approximated assumptions like spherical symmetry, perfect isotropy and others. In our model we additionally have to interpolate values for alloys basing on the values for single elements assuming the linear dependence of the density, parameters α and m_{eff} on concentration or assuming constant hard-sphere diameters. The last ones are used to calculate the analytical structure factors and such methodology is the approximation too. Also the assumption that the atomic diameters for elements may be determined basing on the rule for the packing fraction η (8) may result in a worse match than a simple adjusting of the diameter values. Nevertheless we considered this approach as optimal, since the calculations were mostly made for composed systems for which the experimental data are difficult to obtain.

Moreover, there are many numerical effects that affect final results, like calculation of the pair density function $g(r)$ basing on the structure factors, by the Fourier transform. This process and also the calculation of the potentials require integration, and this should be performed to the infinity. In the numerical calculations it is obviously required to reduce the infinite integral to the finite sum (with parabolic interpolations).

We noticed two problems which we considered worth to mention separately. We can see some differences between experimental and theoretical values of the concentration where the resistivity reaches its maximum. We suppose that this may be caused by too simplified effective mass calculation. It probably does not change linearly as we assumed. To examine it we calculated the correlation factor between peak shift and the effective mass difference. The obtained value was equal to 0.66 that seems to confirm our supposition. We do not see any improvement which could eliminate this effect at the moment. The second effect is more serious. For several elements (Sn, Pb, Bi, Fe, Cu, Ge) we obtained results that did not match the experiment. We were able to easily fit the resistivity to experimental data for any single-element system, but for alloys the results were not satisfying. For some of considered alloys the calculated values of the resistivity were extremely high (over 1000 $\mu\Omega$ cm), and it is very likely that the model is reaching its limits. In other cases we had elements with complicated electron structure, for which the assumption of the spherical symmetry might not be adequate. The numerical errors in computation of the Fourier transform and other integrals may also be the reason of the

discrepancies between our calculations and the experiment. Nevertheless, our model presented here is much better than the previous one presented in [4] because of three reasons: (i) the calculations are more stable, i.e. the change in the resistivity due to a small change of parameters is also small; (ii) the number of free parameters is smaller than in the previous work [4]; (iii) the parameters are unambiguously assigned to each element used which results in the universality of the calculations.

4 Summary

We have developed the model for the resistivity of disordered alloys on the ground of our previous results. We improved the stability and precision by using the MHS model with the Evans correction. We have corrected the Esposito method for Fermi energy determination by improving the phase shifts calculations and finally we obtained two-parameter, fully quantum model, that can be used for multi-element alloys. The performed calculations have shown that the model can be considered as universal one for a quite large group of simpler elements.

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