TASK QUARTERLY 6 No 4 (2002), 669–680

COHERENT POTENTIAL APPROXIMATION TECHNIQUE IN A SIMPLE EXAMPLE OF RESISTIVITY CALCULATIONS FOR BINARY ALLOYS

MACIEJ WOŁOSZYN AND ANDRZEJ Z. MAKSYMOWICZ

Faculty of Physics and Nuclear Techniques,
University of Mining and Metallurgy,
Mickiewicza 30, 30-059 Cracow, Poland
woloszyn@novell.ftj.agh.edu.pl

(Received 15 May 2002)

Abstract: Technique of the Coherent Potential Approximation applied for calculations of the density of states in binary alloys A_xB_{1-x} is presented. Results of the calculations are also used to find the residual resistivity of the system versus concentration x.

Keywords: Coherent Potential Approximation, Green function technique, binary alloy, density of states, resistivity

1. Introduction

The Coherent Potential Approximation (CPA) method [1] is a powerful analytical technique for calculations of density of states $\rho(\omega)$ for binary alloys A_xB_{1-x}. Not only is density of states obtained but also so called coherent potential can be extracted from the calculations, and used in further studies. In this example we apply it to get the residual resistivity in alloys.

Before we proceed with the presentation of the CPA methods, some comments on the applicability or restrictions of this technique are necessary.

The two components of the alloy, elements A and B, must be expressed in terms of the same starting densities $\rho_0(\omega)$. This means, that we have to have the same bandwidth of A and B elements. Therefore compounds composed of two transition metals, such as Fe_xV_{1-x} alloy, are acceptable, while, for example, a transition metal and a rare earth compound would not be treatable correctly in the CPA, because the bandwidth of f-electrons of the rare earth elements is very narrow.

The CPA is a one electron approximation, and any corrections due to electron-electron correlations, or interaction of electrons with the lattice *etc.*, may only be incorporated by a suitable modification of the density of states of pure elements which is the input information for the CPA method. Also, within the CPA we do not get the dispersion relation or the wavefunctions. If, however, we are interested in a simplified description of the system, such as the density of states $\rho(\omega)$ only, the CPA is highly recommended.

The CPA technique is based on the concept of an effective medium, which replaces the actual environment seen by an electron. Due to the lack of translational invariance in alloys, the actual environment cannot be treated analytically. However, the effective medium restores the necessary symmetry for further mathematical treatment. This means, that we calculate the properties of the effective medium, described in terms of a coherent potential V (with a proper translational invariance), and we leave the problem of the optimal choice of V as a separate task. This is the essence of the CPA method – how to establish V.

In this paper we describe the CPA method answering the following questions:

- How is the density of states extracted from a given Green function of pure elements and any coherent potential V?
- Why is the potential V resulting from the CPA optimal?

Then we use the numerical findings specifically to translate the obtained V into a resistivity $1/\sigma$ of a binary alloy A_xB_{1-x} *versus* its concentration x.

In summary, CPA is a powerful technique; yet restricted to (a) alloys of the same electronic structure (density of states) of both components A and B of the alloy, (b) one electron calculations with all the consequences of this approximation.

In a sense, it may be considered as an alternative to the first principle (*ab initio*) tedious calculations, if a more detailed knowledge of the electronic structure – the dispersion relation or the wave functions – is not necessary.

2. Hamiltonian of an effective medium

The basic CPA method assumes the same shape of functions describing the density of states in components A, B of A_xB_{1-x} alloy. This condition assures identical kinetic energies of electrons $\varepsilon(k)$ for both A and B.

However, we allow different *atomic level* limits ε_i, $i=\mathrm{A}$, B. Thus, the Hamiltonian describing such system has the form:

$$H=\sum_k \varepsilon(k)a_k^\dagger a_k+\sum_i \varepsilon_i a_i^\dagger a_i, \tag{1}$$

where the dispersion relation $\varepsilon(k)$ is the same for both pure A or B elements, and index i stands not only for the *lattice site* i, yet also brings information which atom $i=\mathrm{A}$, B occupies this site (this is the ε_i value).

The first term, written in the Bloch representation, defines the kinetic energy of an electron. The scale and the origin of energy in this work is chosen so that $-1\le\varepsilon(k)\le 1$, and the width of the band is 2. In the CPA application we only need the density of states function $\rho_0(\omega)$ (normalized to unity) corresponding to $\varepsilon(k)$.

As we mentioned above, the second term $\sum_i \varepsilon_i a_i^\dagger a_i$ (the Wannier representation) describes the shift of atomic levels depending on the kind of atom occupying site i.

The above Hamiltonian cannot be solved, because the second term is not translationally invariant in general and, therefore, it cannot be converted into Bloch state and absorbed by the first term. The latter is true only for a special case of site independent atomic levels:

$$\varepsilon_i = \varepsilon = \text{const}, \tag{2}$$

when the obvious solution of a sheer rigid band $\rho(\omega) = \rho_0(\omega - \varepsilon)$ takes place.

Let us summarize the main points.

1. *The reference Hamiltonian*

$$H_0 = \sum_k \varepsilon(k) a_k^\dagger a_k, \qquad -1 \leq \varepsilon(k) \leq 1 \tag{3}$$

describes a virtual reference crystal with the dispersion relation $\varepsilon(k)$, or the corresponding density of states:

$$\rho_0(\omega), \qquad -1 \leq \omega \leq 1. \tag{4}$$

(This function $\rho_0(\omega)$ is the necessary information for the CPA.) The construction of the Green function $G(z)$ is equivalent to a more general Kramers-Kronig relation between $G(z)$ and the density of states:

$$\begin{aligned} G(z) &= \int_{-\infty}^{+\infty} \frac{\rho(\omega)}{z-\omega} \mathrm{d}\omega, \\ \rho(\omega) &= -\frac{1}{\pi} \operatorname{Im} G(\omega + \mathrm{i}0^+). \end{aligned} \tag{5}$$

Then, for the *reference crystal* we assume that

$$F_0(z) = \int_{-\infty}^{+\infty} \frac{\rho_0(\omega)}{z-\omega} \mathrm{d}\omega, \tag{6}$$

or

$$\rho_0(\omega) = -\frac{1}{\pi} \operatorname{Im} F_0(\omega + \mathrm{i}0^+), \tag{7}$$

are known, where F_0 stands for the reference Green function.

2. *Pure crystal* A *Hamiltonian* is given by

$$H_\mathrm{A} = \sum_k \varepsilon(k) a_k^\dagger a_k + \sum_i \varepsilon_\mathrm{A} a_i^\dagger a_i = \sum_k (\varepsilon(k) + \varepsilon_\mathrm{A}) a_k^\dagger a_k, \tag{8}$$

which of course is expressed by a stiff shift of the reference band only:

$$\rho_\mathrm{A}(\omega) = \rho_0(\omega - \varepsilon_\mathrm{A}), \tag{9}$$

$$G_\mathrm{A}(\omega) = F_0(\omega - \varepsilon_\mathrm{A}). \tag{10}$$

3. *Real binary alloy* $\mathrm{A}_x\mathrm{B}_{1-x}$ *Hamiltonian*

$$H = \sum_k \varepsilon(k) a_k^\dagger a_k + \sum_i \varepsilon_i a_i^\dagger a_i \tag{11}$$

is not directly convertible into the desired Bloch form, so we are forced to use the effective media ideology introduced below.

4. *Effective medium Hamiltonian*, for which we restore the symmetry is therefore

$$H_e = \sum_k \varepsilon(k) a_k^\dagger a_k + \sum_i V a_i^\dagger a_i = \sum_k (\varepsilon(k) + V) a_k^\dagger a_k \tag{12}$$

and is obtained by replacing ε_i by a site i-independent potential V. Now:

$$G_e(z) = F_0(z - V), \tag{13}$$

$$\rho_e(\omega) = -\frac{1}{\pi} \operatorname{Im} G_e(\omega + \mathrm{i}0^+), \tag{14}$$

yet $\rho_e(\omega)$ is no longer given by $\rho_e(\omega) = \rho_0(\omega - V)$ as this time we allow V to be complex and energy dependent:

$$V = V(\omega), \qquad \operatorname{Im} V \neq 0. \tag{15}$$

The effective medium will be discussed more in details within the CPA technique described in the next chapter. However, it is worth to note that at this stage we may propose for example:

$$\begin{aligned} &V = 0 && \text{for reference crystal,} \\ &V = \varepsilon_\mathrm{A},\ \varepsilon_\mathrm{B} && \text{for pure crystals A, B} \\ &V = x\varepsilon_\mathrm{A} + (1-x)\varepsilon_\mathrm{B} && \text{for alloy } \mathrm{A}_x\mathrm{B}_{1-x} \end{aligned} \tag{16}$$

within so called Virtual Crystal Approximation. All the above examples correspond to the *stiff band* picture when the energy independent and real V makes:

$$\rho_e(\omega) = \rho_0(\omega - V). \tag{17}$$

Within the CPA the simplest Virtual Crystal Approximation is replaced by:

$$V = V_\mathrm{CPA}(\omega), \qquad \operatorname{Im} V \neq 0 \tag{18}$$

and then $\rho_e(\omega) \neq \rho_0(\omega - V)$. The density of states of the effective medium must now be calculated from the basic formula (14). Below we discuss how to do it.

3. Coherent Potential Approximation for the effective medium

The main idea of the CPA is to replace the real system by an effective medium. Instead of using real potentials $\varepsilon_i = \varepsilon_\mathrm{A},\ \varepsilon_\mathrm{B}$ depending on atom remaining on site i, we use the average potential V, common for all sites. As it was shown in the previous section, the effective Hamiltonian is then:

$$H_e = \sum_k (\varepsilon(k) + V) a_k^\dagger a_k. \tag{19}$$

This yields the Green function (13) in terms of pre-calculated $F_0(z)$. The density of states of the effective medium, given by Equation (14), needs V in Equation (13) to be calculated. Here the CPA enters.

The idea is simple. First, we introduce a *single impurity* at the site $i=0$ defined by the potential

$$V_i=\begin{cases}\varepsilon_{\mathrm{A}} \text{ or } \varepsilon_{\mathrm{B}} & \text{for } i=0,\\ V & \text{for } i\neq 0,\end{cases} \tag{20}$$

which is a fully solvable case. The corresponding Green functions G_e^{A} or G_e^{B} at this impurity site are known in terms of the Green function of the medium:

$$G_e^{\mathrm{A}}(z)=\frac{G_e(z)}{1-(\varepsilon_{\mathrm{A}}-V)G_e(z)}, \tag{21}$$

and similarly

$$G_e^{\mathrm{B}}(z)=\frac{G_e(z)}{1-(\varepsilon_{\mathrm{B}}-V)G_e(z)}. \tag{22}$$

Now, with these partial Green functions we demand the net Green function G_e of the effective medium to be self consistent:

$$G_e=xG_e^{\mathrm{A}}+(1-x)G_e^{\mathrm{B}} \tag{23}$$

for $\mathrm{A}_x\mathrm{B}_{1-x}$ binary alloy, with the obvious density of states superposition rule

$$\rho_e(\omega)=x\rho_e^{\mathrm{A}}(\omega)+(1-x)\rho_e^{\mathrm{B}}(\omega) \tag{24}$$

as a consequence.

Applying Equations (21) and (22) to Equation (23) we get:

$$1=\frac{x}{1-(\varepsilon_{\mathrm{A}}-V)G_e^{\mathrm{A}}}+\frac{1-x}{1-(\varepsilon_{\mathrm{B}}-V)G_e^{\mathrm{B}}}, \tag{25}$$

which, after some simple algebra takes on a more often used form:

$$0=x\frac{(\varepsilon_{\mathrm{A}}-V)G_e^{\mathrm{A}}}{1-(\varepsilon_{\mathrm{A}}-V)G_e^{\mathrm{A}}}+(1-x)\frac{(\varepsilon_{\mathrm{B}}-V)G_e^{\mathrm{B}}}{1-(\varepsilon_{\mathrm{B}}-V)G_e^{\mathrm{B}}}. \tag{26}$$

In short, Equation (26) is the key CPA equation for suitable choice of V. Yet, since the Green functions G_e^{A} and G_e^{B} are energy ω-dependent, the $V_{\mathrm{CPA}}(\omega)$ also depends on energy. This means we have to apply Equation (26) for each energy ω. Not only is the density of states of the medium (14) now available, but we also get *partial* density of states for a single impurity ε_{A} in V_{CPA} medium:

$$\rho_e^{\mathrm{A}}(\omega)=-\frac{1}{\pi}\,\mathrm{Im}\,\frac{G_e}{1-(\varepsilon_{\mathrm{A}}-V_{\mathrm{CPA}})G_e}. \tag{27}$$

The concept of single impurity embedded in a medium may be illustrated as in Figure 1. Also, Equation (26) for Green function technique specialists is interpreted as a result of zero net scattering of an electron on the impurity.

Let us summarize the main points. For given $\rho_0(\omega)$, ε_{A}, ε_{B} and x the full algorithm may be constructed to calculate $\rho_e(\omega)$ and partial $\rho_e^{\mathrm{A}}(\omega)$, $\rho_e^{\mathrm{B}}(\omega)$ density of states for single impurities in the effective medium.

Still, we have not explored as yet the information concerning the imaginary part of V_{CPA}. This is discussed in the next section.

4. Resistivity and the Coherent Potential Approximation

The coherent potential V which is obtained as a result of the CPA calculations for the given energy ω is a complex number. Its imaginary part provides information

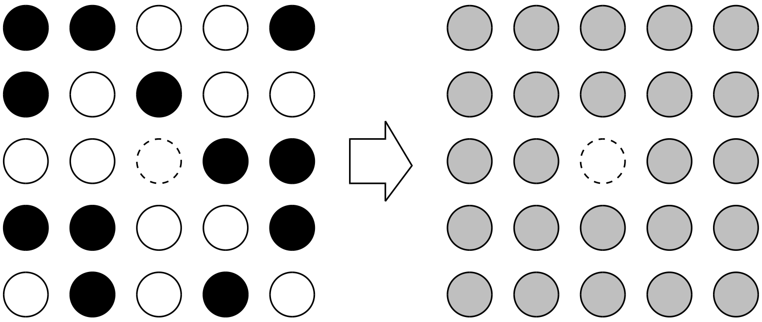

Figure 1. The idea of the CPA: components A and B (here shown as black and white circles) of a disordered system are replaced by an effective medium (grey ones). The reference site may be occupied by A with the probability x, or by B with the probability $1-x$

about relaxation time τ for an electron at the state of energy ω. As it is well known, the *stationary* solution of the Schrödinger equation has the time-dependent part of the wave function in the form:

$$\psi \propto e^{-i\omega t/\hbar}, \tag{28}$$

which makes the density of electrons $|\psi|^2$ at any position $\vec{r}$ in space a time-independent quantity.

However, the CPA idea of the formal replacement

$$\omega \to \omega + V \tag{29}$$

makes

$$|\psi|^2 \propto e^{-t/\tau} \tag{30}$$

with the relaxation time τ related to the CPA potential V

$$\frac{1}{\tau} \propto -\operatorname{Im} V. \tag{31}$$

On the other hand τ is related to the conductivity σ in simple Drude model (see *e.g.* [2]) as:

$$\sigma = \frac{ne^2}{m}\tau. \tag{32}$$

Thus, we obtain a relation between V and the residual resistivity (at $T=0$):

$$\frac{1}{\sigma_0} \propto -\operatorname{Im} V(\omega = E_F), \tag{33}$$

which is a part of the total resistivity $1/\sigma = 1/\sigma_0 + 1/\sigma(T)$ originating from the scattering on defects and impurities ($1/\sigma(T)$ is a temperature dependent result of scattering on phonons). The imaginary part of the potential V is taken at the Fermi level E_F.

In alloys, the concentration of elements is the parameter controlling the degree of disorder. Only for pure elements the lattice periodicity takes place and then the residual resistivity vanishes. For an alloy, a simple parabolic approximation often works. This is the Nordheim's rule [3] (see Figure 2):

$$\frac{1}{\sigma} \propto x(1-x). \tag{34}$$

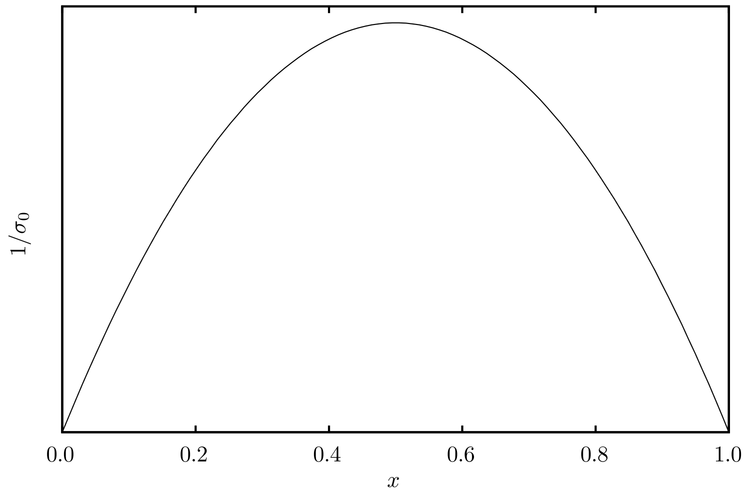

Figure 2. Illustration of the Nordheim's rule on parabolic resistivity dependence on concentration of alloy compound

The previously calculated density of states function $\rho(\omega)$ must be used for finding the Fermi level E_F from:

$$\int_{-\infty}^{E_F} \rho(\omega)\,\mathrm{d}\omega = n, \tag{35}$$

where the filling of the band in a binary alloy is $n = n_\mathrm{A}x + n_\mathrm{B}(1-x)$, if n_A and n_B denote the number of electrons for pure A and B elements.

5. Numerical procedure

Difficulties in finding analytical solutions of the CPA equation for more complicated (and thus closer to reality) functions ρ_0 lead to the necessity of using numerical procedures.

A convenient way to treat the problem is to consider an iterative formula equivalent to the CPA condition (26):

$$V^{(n+1)} = V^{(n)} + \frac{\langle T\rangle^{(n)}}{1+\langle T\rangle^{(n)} G_e(z)} \tag{36}$$

with

$$\langle T\rangle^{(n)} = \sum_{i=\mathrm{A,\,B}} p_i \frac{\varepsilon_i - V^{(n)}}{1-(\varepsilon_i - V^{(n)})G_e(z)} \tag{37}$$

and $p_\mathrm{A} = x$, $p_\mathrm{B} = 1-x$. In order to obtain the value of the coherent potential V, the iteration described by Equation (36) is repeated until $|V^{(n+1)} - V^{(n)}| < \epsilon$, where ϵ determines the requested precision of calculations.

Quite often a starting value of the potential V is the Virtual Crystal Approximation (VCA) potential:

$$V^{(0)} = V_\mathrm{VCA} = x\varepsilon_\mathrm{A} + (1-x)\varepsilon_\mathrm{B}. \tag{38}$$

6. Analytical results

For some specific $\rho_0(\omega)$ it is possible to solve the CPA Equation (26) analytically. One of these cases is that of the semi-elliptical bare density of states:

$$\rho_0(\omega)=\begin{cases}\frac{2}{\pi}\sqrt{1-\omega^2}, & |\omega|<1,\\ 0, & |\omega|\geq 1.\end{cases} \tag{39}$$

Using Equation (6) we obtain the expression:

$$F_0(z)=2(z-\sqrt{z^2-1}), \tag{40}$$

and from Equation (13) the form of the coherent potential may be written in terms of $G_e(z)=F_0(z-V)$:

$$V=z-\frac{1}{G_e(z)}-\frac{1}{4}G_e(z). \tag{41}$$

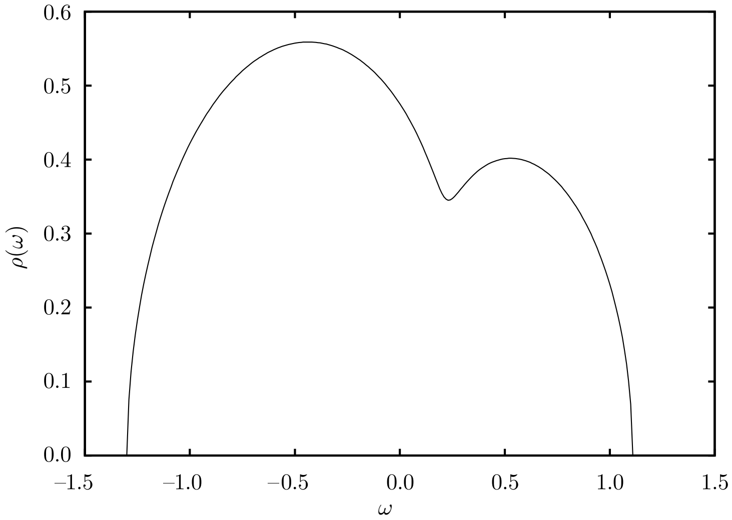

Figure 3. Density of states function $\rho(\omega)$ (normalized to unity) for binary alloy with $x=0.2$ and $\varepsilon_\mathrm{A}=-\varepsilon_\mathrm{B}=0.4$, found analitically for the semi-elliptical $\rho_0(\omega)$

Let us consider the example of a binary alloy ($\mathrm{A}_x\mathrm{B}_{1-x}$) with energies $\varepsilon_\mathrm{A}=\varepsilon$, $\varepsilon_\mathrm{B}=-\varepsilon$. The CPA Equation (26) in this case gives a cubic equation for G_e:

$$G_e^3-8zG_e^2+4\left[1-4\left(\varepsilon^2-z^2\right)\right]G_e-16\left[(2x-1)\varepsilon+z\right]=0. \tag{42}$$

The above equation has to be solved for all values of z to find the relation for the Green function $G_e(z)$ and consequently the density of states function $\rho(\omega)$ (see Figure 3), and then the residual resistivity presented in Figures 4 and 5.

7. Numerical results

To calculate the density of states for a given value of energy the following information on $\mathrm{A}_x\mathrm{B}_{1-x}$ alloy is needed:

- the density of states function $\rho_0(\omega)$ for both components of the alloy,
- atomic levels ε_i for $i=\mathrm{A}$, B,
- concentration x.

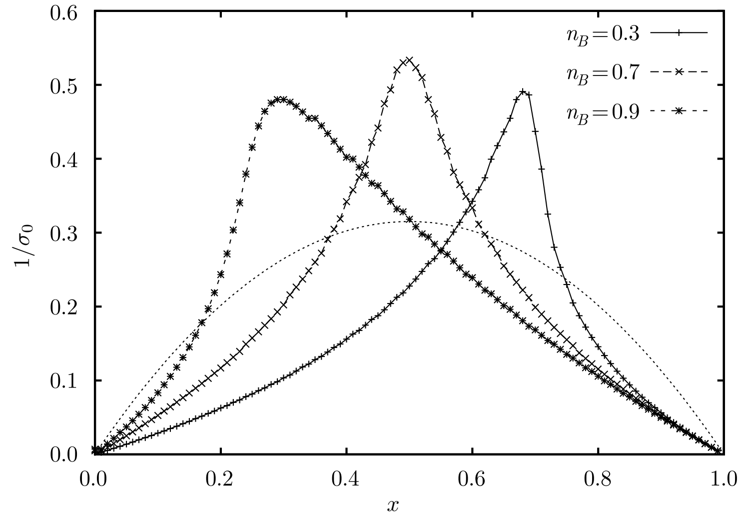

Figure 4. Residual resistivity $1/\sigma_0$ (in arbitrary units) as a function of concentration x for semi-elliptical $\rho_0(\omega)$ with $n_{\mathrm{A}} = 0.3$, $n_{\mathrm{B}} = 0.3$, 0.7, 0.9 and $\varepsilon_{\mathrm{A}} = -\varepsilon_{\mathrm{B}} = 0.4$. The solid line presents theoretical values from Nordheim's parabolic rule

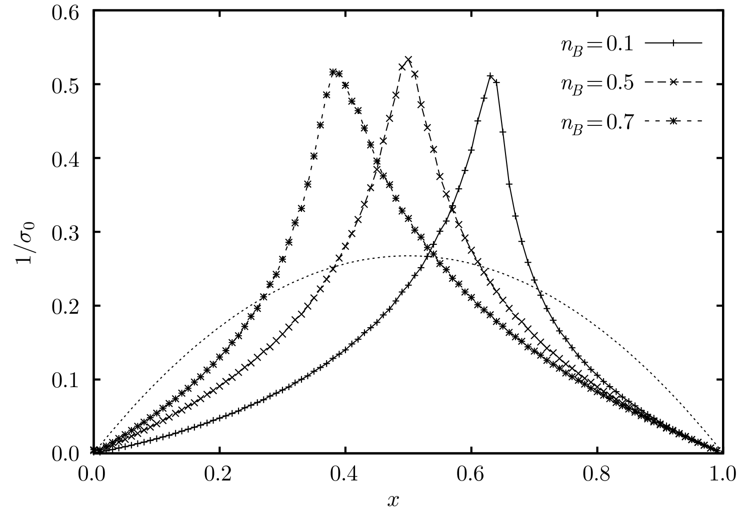

Figure 5. Residual resistivity $1/\sigma_0$ (in arbitrary units) as a function of concentration x for semi-elliptical $\rho_0(\omega)$ with $n_{\mathrm{A}} = 0.5$, $n_{\mathrm{B}} = 0.1$, 0.5, 0.7 and $\varepsilon_{\mathrm{A}} = -\varepsilon_{\mathrm{B}} = 0.4$. The solid line presents theoretical values from Nordheim's parabolic rule

For example, $\rho_0(\omega)$ can be approximated using any number of linear segments with the exception of vicinity of band edges, where we used the square root approximation to reproduce van Hove singularities:

$$\rho(\omega) \propto (\omega - \omega_0)^{1/2}. \tag{43}$$

$\rho_0(\omega)$ shown in Figure 6 is slightly modified (to account for the van Hove singularities) density of states proposed for transition metal alloys in some papers [4]. It was used to calculate all the results presented in this section. The values of atomic levels were $\varepsilon_{\mathrm{A}} = 0.5$ and $\varepsilon_{\mathrm{B}} = -0.5$.

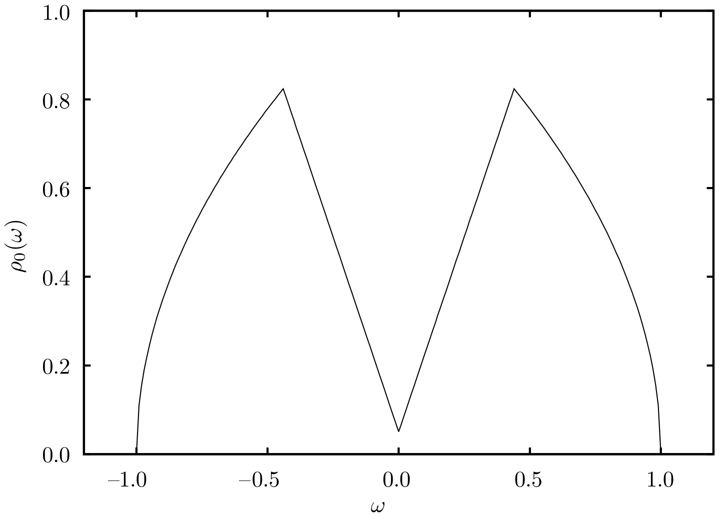

Figure 6. Function $\rho_0(\omega)$ proposed for transition metal alloys and used in numerical calculations

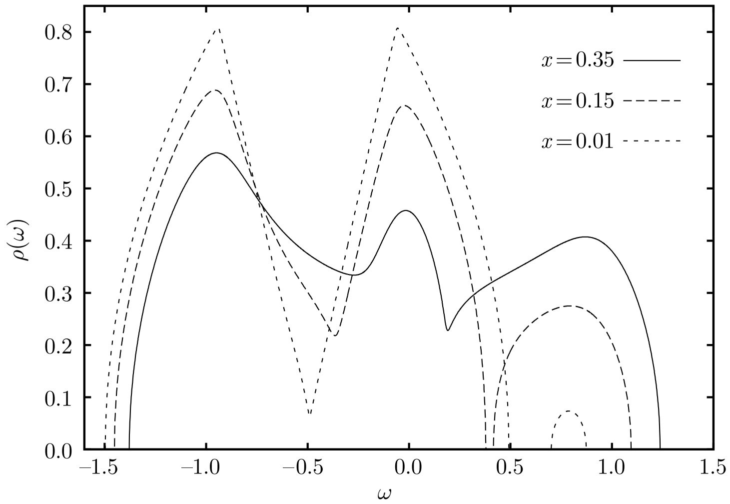

Figure 7. The results of the CPA calculations of density of states function $\rho(\omega)$ for a binary alloy A_xB_{1-x} ($\varepsilon_A = -\varepsilon_B = 0.5$)

The resulting density of states obtained for several values of the A component concentration x in binary alloy A_xB_{1-x} is shown in Figure 7.

Values of resistivity for different concentrations are presented in Figures 8 and 9. As expected, the maximum values of $1/\sigma_0$ were found for similar amounts of elements A and B. However, the obtained dependence is far from the parabola claimed by semi-empirical Nordheim's rule.

8. Conclusions

The Coherent Potential Approximation method was presented, then applied for calculations of the density of states in binary disordered alloys A_xB_{1-x}, and

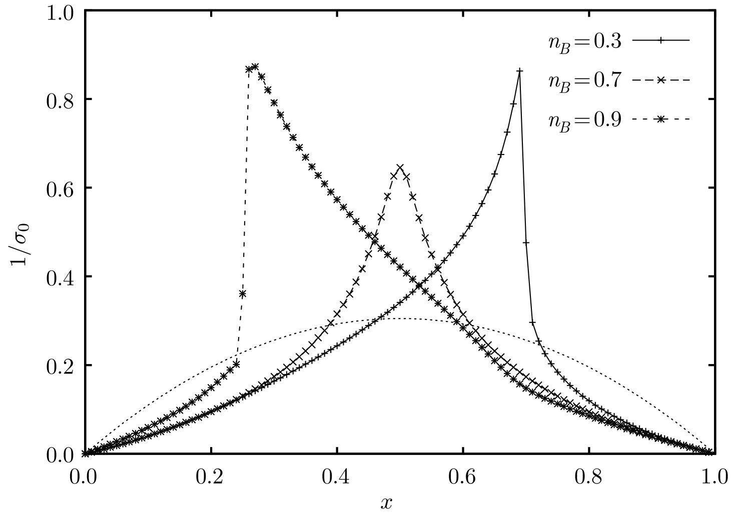

Figure 8. Residual resistivity $1/\sigma_0$ (in arbitrary units) versus concentration x for $n_B = 0.3$, 0.7, 0.9; in all cases $n_A = 0.3$ and $\varepsilon_A = -\varepsilon_B = 0.5$. The solid line presents theoretical values from Nordheim's parabolic rule

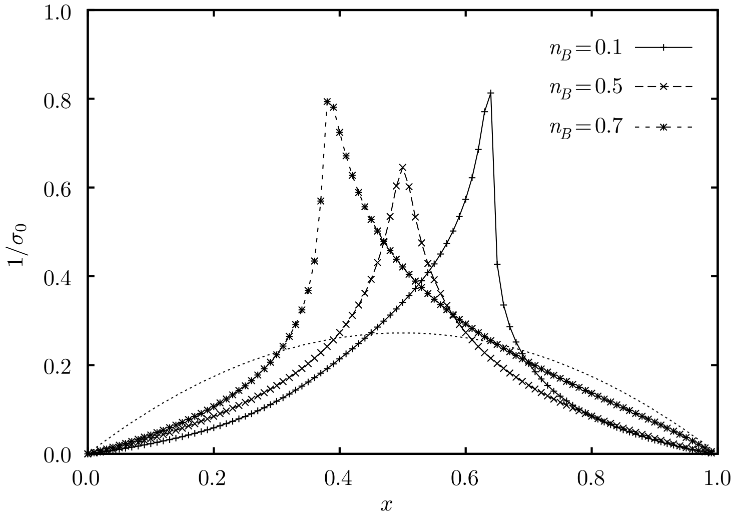

Figure 9. Residual resistivity $1/\sigma_0$ (in arbitrary units) versus concentration x for $n_B = 0.3$, 0.7, 0.9; in all cases $n_A = 0.5$ and $\varepsilon_A = -\varepsilon_B = 0.5$. The solid line presents theoretical values from Nordheim's parabolic rule

followed by a simplified approach to extract also the residual resistivity $1/\sigma_0$ from the complex form of the potential, which is specific to the Coherent Potential Approximation.

Comparison of the relation $1/\sigma_0$ versus concentration x of system components obtained for the semi-elliptical, analytically solvable $\rho_0(\omega)$, and that proposed for transition metal alloys (Figure 6) suggests a rather weak dependence of the resistivity $1/\sigma_0$ on the details of starting $\rho_0(\omega)$. Yet the shape of $1/\sigma_0 = f(x)$ is far from the parabola claimed by the Nordheim's rule.

References

[1] Velicky B, Kirkpatrick S and Ehrenreich H 1968 *Phys. Rev.* **175** 747

[2] Ziman J M 1972 *Principles of the Theory of Solids*, Cambridge

[3] Blatt F J 1968 *Physics of Electronic Conduction in Solids*, McGraw-Hill, Inc.

[4] Maksymowicz A Z 1982 *J. Phys.* **F 12** 537