Condensed Matter Physics 2007, Vol. 10, No 2(50), pp. 249–258

CONDENSED MATTER PHYSICS

Average replicated T-matrix approximation: valence band of non-crystalline metallic alloys

P.Yakibchuk, O.Volkov, S.Vakarchuk

The Ivan Franko National University of Lviv, 8 Kyrylo and Methodii Str., 79005 Lviv, Ukraine

Received April 23, 2007, in final form May 31, 2007

Here we present a new approximation for calculation of density of states of multi-component metallic alloys using Lloyd formula. We consider the average square of T-matrix as the pair replication of scattering system. The analytical expressions are probed on Ti_xMn_{1-x} and Al_xNi_{1-x} binary alloys. The results are in good agreement with the predicted behavior of density of states for such systems.

Key words: *density of states, T-matrix, Lloyd formula, atomic shell approximation, structure factor, binary alloy*

PACS: *71.22.+i, 71.20.Be, 71.15.La, 71.15.Mb, 71.15.Cr, 71.15.Hx, 71.10.-w*

1. Introduction

The Lloyd formula for the density of states (DoS) of a finite system on non-overlapping potentials in free space was derived in [1] by local integration of the Green function of the system in the r-space representation. Similarly, expressions which are valid within the muffin-tin single-site coherent potential approximation (CPA) were derived from the DoS per atom in a disordered binary substitutional alloy. It was stated in [2] and we also agree to the fact that the Lloyd formula is an elegant tool in multiple-scattering theory and it implicitly provides an analytical integration over energy and over all space and directly gives the number of states as a function of energy. However, the usual derivations of this formula are involved and the range of applicability of approximations used therein is somewhat physically obscure.

The significance of the Lloyd formula approach to the DoS calculation of metallic systems is proved by a series of works. So, in a general case it was studied in [3] and as the treatment of binary metallic alloys it was done in [4].

Furthermore, we should introduce our work by presenting some basic definitions and equations used in a multiple-scattering theory that were applied here. According to the Green function method, the definition of the DoS should be expressed as follows:

$$\mathrm{DoS}(E) = \frac{\mp}{\pi}\mathrm{Tr}\,\Im m\,\mathcal{G}^{\pm}(E). \tag{1}$$

Here $\mathcal{G}^{\pm}(E)$ is the Green function (advanced or retarded for "+" or "−", correspondingly) of the defined system and it satisfies the Dyson equation

$$\mathcal{G}^{\pm}(E) = \mathcal{G}_0^{\pm}(E) + \mathcal{G}_0^{\pm}(E)\widehat{V}\mathcal{G}^{\pm}(E), \tag{2}$$

where $\mathcal{G}_0^{\pm}(E)$ is the Green function of some known reference system (e.g. free electronic gas or medium of coherent potentials) and $\widehat{V}$ is the perturbation operator determined as the difference of the effective potential of electron-ion interaction in the defined system under consideration and the corresponding characteristic of the reference one.

Moreover, if only this is possible for the system of interest, the T-matrix operator is introduced by the following expression

$$\mathcal{G}^{\pm}(E) = \mathcal{G}_0^{\pm}(E) + \mathcal{G}_0^{\pm}(E)\widehat{\mathcal{T}}^{\pm}(E)\mathcal{G}_0^{\pm}(E). \tag{3}$$

Hence, comparing equations (2) and (3), the following Dyson equation for T-matrix of the system is also valid

$$\widehat{\mathcal{T}}^{\pm}(E) = \widehat{V} + \widehat{V}\mathcal{G}_0^{\pm}(E)\widehat{\mathcal{T}}^{\pm}(E). \tag{4}$$

It is worth noting that equation (4) leads to the optical theorem for T-matrices

$$\widehat{\mathcal{T}}^{\pm}(E) - \widehat{\mathcal{T}}^{\mp}(E) = \mp 2\pi\mathrm{i}\widehat{\mathcal{T}}^{\mp}(E)\widehat{\mathcal{T}}^{\pm}(E). \tag{5}$$

The applicability and usefulness of (5) for the case of transition metals were discussed in [5].

Using equations (1), (3) and presenting $\mathrm{DoS}_0(E) = \mp/\pi\, \Im m\, \mathrm{Tr}\, \mathcal{G}_0^{\pm}(E)$ – DoS of the reference system, the DoS of the system of interest can be decomposed

$$\mathrm{DoS}(E) = \mathrm{DoS}_0(E) + \delta\mathrm{DoS}(E), \tag{6}$$

where

$$\begin{aligned}
\delta\mathrm{DoS}(E) &= \frac{\mp}{\pi}\mathrm{Tr}\,\Im m\, \left[\mathcal{G}_0^{\pm}(E)\widehat{\mathcal{T}}^{\pm}(E)\mathcal{G}_0^{\pm}(E)\right] = \frac{\mp}{\pi}\Im m\ \mathrm{Tr}\, \left[\mathcal{G}_0^{\pm}(E)^2\widehat{\mathcal{T}}^{\pm}(E)\right] \\
&= \frac{\pm}{\pi}\Im m\ \mathrm{Tr}\, \left[\frac{d}{dE}\mathcal{G}_0^{\pm}(E)\widehat{\mathcal{T}}^{\pm}(E)\right] = \frac{\pm}{\pi}\Im m\ \mathrm{Tr}\, \left[\widehat{\mathcal{T}}^{\pm}(E)^{-1}\frac{d}{dE}\widehat{\mathcal{T}}^{\pm}(E)\right] \\
&= \frac{\pm}{\pi}\frac{d}{dE}\Im m\ \mathrm{Tr}\ \ln\, \widehat{\mathcal{T}}^{\pm}(E) = \frac{\pm}{\pi}\frac{d}{dE}\Im m\ \ln\ \det \widehat{\mathcal{T}}^{\pm}(E).
\end{aligned} \tag{7}$$

The latter expression (7) is the well-known Lloyd formula. Obviously, using the general properties of the matrix determinant and logarithm, one can state

$$\delta\mathrm{DoS}(E) = \frac{\pm}{p\pi}\frac{\mathrm{d}}{\mathrm{d}E}\Im m\ \ln\ \det\, \left[\widehat{\mathcal{T}}^{\pm}(E)^p\right]. \tag{8}$$

By defining the S-matrix operator $\widehat{\mathcal{S}}(E) = \widehat{\mathcal{T}}^{-}(E)^{-1}\widehat{\mathcal{T}}^{+}(E)$, the Lloyd formula (7) also validates the following expression

$$\delta\mathrm{DoS}(E) = \frac{\pm}{2\pi}\frac{\mathrm{d}}{\mathrm{d}E}\Im m\ \ln\ \det\, \left[\widehat{\mathcal{T}}^{\mp}(E)^{-1}\widehat{\mathcal{T}}^{\pm}(E)\right] = \frac{1}{2\pi}\frac{\mathrm{d}}{\mathrm{d}E}\Im m\ \ln\ \det \widehat{\mathcal{S}}(E) \tag{9}$$

and, furthermore, for diagonal presentation of S -matrix (matrix elements are $\mathcal{S}_{\alpha\beta}(E) = \delta_{\alpha,\beta}\mathrm{e}^{2\mathrm{i}\delta_\alpha(E)}$, where $\delta_\alpha(E)$ are generalized phase shifts of α^{th} state) equation (9) transforms to the generalized differential Friedel sum-rule

$$\delta\mathrm{DoS}(E) = \frac{1}{\pi}\sum_\alpha \frac{\mathrm{d}\delta_\alpha(E)}{\mathrm{d}E}. \tag{10}$$

In case of disordered systems, DoS in (1) depends on $\langle\mathcal{G}^{\pm}(E)\rangle$ – i.e., the average Green function taken in terms of the average over all possible spatial configurations of the system under consideration. If one applies the configuration averaging to the Dyson equation (2), then the corresponding equation for the average Green function of the system transforms to the following

$$\left\langle\mathcal{G}^{\pm}(E)\right\rangle = \mathcal{G}_0^{\pm}(E) + \mathcal{G}_0^{\pm}(E)\left\langle\widehat{V}\mathcal{G}^{\pm}(E)\right\rangle$$

and, introducing the so-called self-energy operator $\widehat{\Sigma}$ used to extract $\langle\mathcal{G}^{\pm}(E)\rangle$ in the second item of equation, this expression for the Green function average over configuration can be transformed to

$$\left\langle\mathcal{G}^{\pm}(E)\right\rangle = \mathcal{G}_0^{\pm}(E) + \mathcal{G}_0^{\pm}(E)\widehat{\Sigma}\left\langle\mathcal{G}^{\pm}(E)\right\rangle. \tag{11}$$

Taking the average of the equation (3), one can get

$$\left\langle\mathcal{G}^{\pm}(E)\right\rangle = \mathcal{G}_0^{\pm}(E) + \mathcal{G}_0^{\pm}(E)\left\langle\widehat{\mathcal{T}}^{\pm}(E)\right\rangle\mathcal{G}_0^{\pm}(E). \tag{12}$$

Hence one can see the fact that the average Green function is determined by the average T-matrix. Consequently, the Lloyd formula (7) for the case of a disordered system reformulates into

$$\delta\mathrm{DoS}(E) = \frac{\pm}{\pi}\frac{\mathrm{d}}{\mathrm{d}E}\Im m\ \left\langle\ln\ \det \widehat{\mathcal{T}}^{\pm}(E)\right\rangle = \frac{\pm}{\pi}\frac{\mathrm{d}}{\mathrm{d}E}\Im m\ \ln\ \det\, \left\langle\widehat{\mathcal{T}}^{\pm}(E)\right\rangle. \tag{13}$$

2. The replica-trick and Lloyd representation of DoS

There is a very useful mathematical technique to take the average over a configuration of systems with a high degree of topological disorder, such as metallic glasses and liquid alloys. It is called the replica-trick and is based on the application of the formula

$$\left\langle \ln \widehat{A} \right\rangle = \lim_{p\to 0} \left\langle \frac{\widehat{A}^p - 1}{p} \right\rangle = \lim_{p\to 0} \frac{\left\langle \widehat{A}^p \right\rangle - 1}{p} , \tag{14}$$

where the angle-brackets represent an average over all realizations of the disorder, and it also involves extending $\widehat{A}^p$, averaged for integer power p, to the case where p is no longer constrained to be an integer value, by positing that if $\widehat{A}^p$ can be calculated for all positive integers p then this may be sufficient to allow the limiting behavior as $p \to +0$ to be calculated.

Before applying (14) to the Lloyd formula (13) it might be necessary to show that the average T-matrix of the system under consideration with regard to optical theorem (5) can be represented by the following sequence

$$\left\langle \widehat{\mathcal{T}}^{\pm}(E) \right\rangle = \left\langle \widehat{\mathcal{T}}^{\mp}(E) \right\rangle \mp 2\pi\mathrm{i} \left\langle \widehat{\mathcal{T}}^{\mp}(E) \widehat{\mathcal{T}}^{\pm}(E) \right\rangle = \sum_{p=1}^{\infty} (\mp 2\pi\mathrm{i})^{p-1} \left\langle \widehat{\mathcal{T}}^{\mp}(E)^p \right\rangle. \tag{15}$$

So, the logical deduction regarding the power series in the last expression is the fact that the existence of an average T-matrix of the system of interest provides for the existence of an average $\widehat{\mathcal{T}}^p$ – operator for any positive integer power p and vice versa. Furthermore, this substantiates the implementation of (12) to be a sufficient condition of replica technique application.

Having regard to the validity of averaging procedure used in (12) it becomes possible to apply replica-trick to the first (upper) equality in (13)

$$\delta \mathrm{DoS}(E) \quad = \quad \frac{\pm}{\pi} \frac{\mathrm{d}}{\mathrm{d}E} \Im m \ \mathrm{Tr} \left\langle \ln \ \widehat{\mathcal{T}}^{\pm}(E) \right\rangle = \frac{\pm}{\pi} \frac{\mathrm{d}}{\mathrm{d}E} \mathrm{Tr} \lim_{p\to 0} \frac{1}{p} \Im m \left\langle \widehat{\mathcal{T}}^{\pm}(E)^p \right\rangle . \tag{16}$$

To satisfy the second (lower) equality in (13) we should apply the well-known approximation of the separation of mean values to the average $\widehat{\mathcal{T}}^p$ – operator in equation (16). Then it makes it possible to write $\langle \widehat{\mathcal{T}}^p \rangle = \langle \widehat{\mathcal{T}} \rangle^p$ and the Lloyd formula for the average T-matrix approximation can be got using the replica-trick backward.

Forestalling the current argumentation in this work, we state the fact that the average T-matrix of the system of interest depends on the density operator averaged over all the possible configuration and there is no way to express $\langle \mathcal{T} \rangle$ for the systems of high disorder in terms of analytical equations or it cannot even exist, but at the same time DoS for such systems exists (DoS exists for any system while one-electron approximation is valid). The self-average structure functions of such systems turn out to be the pair correlation functions (PCF) and the structure factors related to them [6]. To solve the problem we bring equation (15) into the following form

$$\left\langle \widehat{\mathcal{T}}^{\mp}(E) \widehat{\mathcal{T}}^{\pm}(E) \right\rangle = \sum_{p=2}^{\infty} (\pm 2\pi\mathrm{i})^{p-2} \left\langle \widehat{\mathcal{T}}^{\pm}(E)^p \right\rangle. \tag{17}$$

Item $\widehat{\mathcal{T}}^{\mp}\widehat{\mathcal{T}}^{\pm}$ keeps the self-average property while the Fermi golden rule is carried into effect. The existence of $\langle \widehat{\mathcal{T}}^{\mp}\widehat{\mathcal{T}}^{\pm} \rangle$ ensures the existence of $\langle \widehat{\mathcal{T}}^p \rangle$ for any integer $p > 1$. This condition is not sufficient for replica-trick application to $\langle \ln \widehat{\mathcal{T}} \rangle$, but at the same time it can be applied to $\langle \ln \widehat{\mathcal{T}}^2 \rangle$. Now the following suggestion becomes obvious which consists in applying another approximation $\langle \widehat{\mathcal{T}}^p \rangle = \langle \widehat{\mathcal{T}}^2 \rangle^{p'} |_{p'=p/2}$ to (16) (here p' is any positive integer power) instead of separation of mean values. Such an approximation enables us to get the following sequel for (16)

$$\delta \mathrm{DoS}(E) = \frac{\pm}{2\pi} \frac{\mathrm{d}}{\mathrm{d}E} \mathrm{Tr} \lim_{p\to 0} \frac{1}{p} \Im m \left\langle \widehat{\mathcal{T}}^{\pm}(E)^2 \right\rangle^p = \frac{\pm}{2\pi} \frac{\mathrm{d}}{\mathrm{d}E} \Im m \ \ln \ \det \left\langle \widehat{\mathcal{T}}^{\pm}(E)^2 \right\rangle . \tag{18}$$

We should note that the last expression could be got by taking the average of equation (8) if we set the power to square and then apply the replica-trick to a square T-matrix. This way of deriving (18) is direct but is not sufficiently substantiated in contrast to the one we used.

To accomplish the construction of calculation method we should define $\langle\widehat{\mathcal{T}}^2\rangle$. Formally, the structure of these matrix elements in k-space representation is the same as the formal structure of $\langle\widehat{\mathcal{T}}^{\mp}\widehat{\mathcal{T}}^{\pm}\rangle$. Hence, applying the derivation procedure which is similar to the Fermi golden rule, the following expression for $\langle\widehat{\mathcal{T}}^2\rangle$ matrix element, built on wave-vectors of initial and final states $\mathbf{k}_i$, $\mathbf{k}_f$, correspondingly, can be derived

$$\begin{gathered}\left\langle \mathbf{k}_i|\mathcal{T}^{\mp}\widehat{\mathcal{T}}^{\pm}|\mathbf{k}_f\right\rangle = \delta_{\mathbf{k}_i,\mathbf{k}_f}\sum_{\alpha,\beta}\sqrt{X_\alpha X_\beta}\sum_{\mathbf{k}} S_{\alpha\beta}(|\,\mathbf{k}_i-\mathbf{k}|)\left\langle \mathbf{k}_i|\underline{\widehat{t}^{\mp}_{\alpha}}|\mathbf{k}\right\rangle\left\langle \mathbf{k}|\underline{\widehat{t}^{\pm}_{\beta}}|\mathbf{k}_i\right\rangle \\ \Downarrow \\ \left\langle \mathbf{k}_i|\widehat{\mathcal{T}}^{\pm2}|\mathbf{k}_f\right\rangle = \delta_{\mathbf{k}_i,\mathbf{k}_f}\sum_{\alpha,\beta}\sqrt{X_\alpha X_\beta}\sum_{\mathbf{k}} S_{\alpha\beta}(|\,\mathbf{k}_i-\mathbf{k}|)\left\langle \mathbf{k}_i|\underline{\widehat{t}^{\pm}_{\alpha}}|\mathbf{k}\right\rangle\left\langle \mathbf{k}|\underline{\widehat{t}^{\pm}_{\beta}}|\mathbf{k}_i\right\rangle,\end{gathered} \tag{19}$$

where X_α is the fraction of α-component in the system of interest, $S_{\alpha\beta}(q)$ are the partial structure factors of scatterer subsystem in accordance with Ashcroft and Langreth [7] and $\left\langle \mathbf{k}'|\underline{\widehat{t}^{\pm}_{\alpha}}|\mathbf{k}\right\rangle$ are the matrix elements of single-site T-matrix defined for the site that is occupied by α-type scatterer interacting with the electron by means of self-consistent single-site potential $\widehat{v}_\alpha$. The following Dyson equation for such an average $\underline{\widehat{t}^{\pm}_{\alpha}}$ is implemented

$$\underline{\widehat{t}^{\pm}_{\alpha}}(E) = \widehat{v}_\alpha + \widehat{v}_\alpha\mathcal{G}^{\pm}_0(E)\underline{\widehat{t}^{\pm}_{\alpha}}(E). \tag{20}$$

The resolvent $\underline{\widehat{t}^{\pm}_{\alpha}}$ of the latter equation can be numerically found in case of the known potential $\widehat{v}_\alpha$ and the Green function of reference system $\mathcal{G}^{\pm}_0$.

We have called the technique suggested and developed in this work the *average replicated T-matrix approximation* (ARTA) for Lloyd formula of disordered metallic systems because the $\langle\mathcal{T}^p\rangle$-operators, or their particular case $\langle\mathcal{T}^2\rangle$, are the p-order multiple replications of T-matrix of the system considered within the replica technique. The square exponent corresponds to the pair correlation approximation and it is the most informative in case of highly disordered systems.

Finally, the conclusion of this section is that we have got a new method of calculating DoS of a disordered multi-component system founded on equations (18) and (19). The data required by this method are the partial structure factors and quantitative composition of the system under consideration, the single-site potentials in self-consistent field approximation of every component and finally the Green function of reference system. That is not an approximation of the method if we are positing the reference system to be a free electron gas, but at the same time it greatly simplifies the formalism for future development of computation method because the form of $\mathcal{G}^{\pm}_0$ is precisely known.

3. Approximations for numerical evaluation of DoS for binary metallic alloys

Now everything is ready on order to apply the computation technique that we used in evaluating the DoS of some binary metallic alloys within ARTA in this work.

The first objects to be define are the partial structure factors. This can be done using hard spheres solution of Ornstein-Zernike equation in Percus-Yevick approximation for multi-component system [8]. The matrix combined the partial structure factors $\boldsymbol{S}(q) = \{S_{\alpha\beta}(q)\}$

$$\boldsymbol{S}(q) = [\boldsymbol{I} - n\boldsymbol{X}^{1/2}\boldsymbol{c}(q)\boldsymbol{X}^{1/2}]^{-1}. \tag{21}$$

Here we present such values as: n is the atomic concentration of metallic alloy, $\boldsymbol{X} = \{\delta_{\alpha,\beta}X_\alpha\}$ is the fraction matrix of components and $\boldsymbol{c}(q) = \{c_{\alpha\beta}(q)\}$ is the matrix of Fourier transforms of direct correlation functions. The application of the Baxter "factorization technique" [9] leads to

$$\begin{aligned} c_{\alpha\beta}(q) = & - 4\pi\left[A_{\alpha\beta}\frac{S_\alpha S_\beta - C_\alpha C_\beta}{q^2} + B_{\alpha\beta}\frac{C_\alpha S_\beta + C_\beta S_\alpha}{q^3} + D_{\alpha\beta}\frac{S_\alpha S_\beta}{q^4}\right. \\ & + \left.\frac{4\pi\widetilde{\alpha}_0}{q^4}\left(\frac{C_\alpha C_\beta d_\alpha d_\beta}{4} + \frac{S_\alpha S_\beta}{q^2} - \frac{C_\alpha S_\beta d_\alpha + C_\beta S_\alpha d_\beta}{2q}\right)\right], \end{aligned} \tag{22}$$

where d_α is hard sphere diameter of α component, $S_\alpha = \sin(qd_\alpha/2)$, $C_\alpha = \cos(qd_\alpha/2)$ and abbreviating the p-order moments $\eta_p = \pi/6 \cdot n\sum_\alpha x_\alpha d_\alpha^p$, the other coefficients are defined as follows:

$$\begin{aligned} \widetilde{\alpha}_0 &= n\sum_\gamma X_\gamma\left[\frac{1-\eta_3+3d_\gamma\eta_2}{(1-\eta_3)^2}\right]^2, \\ \widetilde{\beta}_0 &= \frac{9\eta_2^2+3\eta_1(1-\eta_3)}{(1-\eta_3)^3}, \\ A_{\alpha\beta} &= \frac{(d_\alpha+d_\beta)(1-\eta_3)+3d_\alpha d_\beta\eta_2}{2(1-\eta_3)^2}, \\ B_{\alpha\beta} &= \frac{1}{1-\eta_3} - \widetilde{\beta}_0 d_\alpha d_\beta, \\ D_{\alpha\beta} &= 6\,\frac{\eta_2+(d_\alpha+d_\beta)(\eta_1+3\eta_2^2/(1-\eta_3))}{(1-\eta_3)^2}. \end{aligned} \tag{23}$$

The corresponding partial PCF is defined through the following Fourier-like transformation of the related structure factor

$$G_{\alpha\beta}(R) = 1-(X_\alpha X_\beta)^{-1/2}\frac{1}{2\pi n}\int_0^\infty [S_{\alpha\beta}(q)-\delta_{\alpha,\beta}]\,\frac{\sin qR}{qR}q^2\mathrm{d}q. \tag{24}$$

Solving equations (21-24) we can find all partial structure factors and PCFs for the system of interest and then start the next step of calculation, i. e., the construction of single-site self-consistent potential.

In this work, we treat the single-site potential of α-type scatterer as the atomic sphere approximation of the Kohn-Sham potential [10]

$$v_\alpha(r) = \begin{cases} -z_\alpha/r + v_H[\rho_\alpha(r)] + v_{xc}[\rho_\alpha(r)] & , \quad r \leqslant R_\alpha^\odot, \\ 0 & , \quad r > R_\alpha^\odot. \end{cases} \tag{25}$$

Here $R_\alpha^\odot$ is the radius of atomic sphere that is defined through electro-neutrality of the atomic cell, $-z_\alpha/r$ is the attractive Coloumb potential of α-type nucleus with atomic number z_α, $v_H[\rho_\alpha(r)]$ is Hartree potential of the repulsive electron-electron Coloumb interaction , $v_{xc}[\rho_\alpha(r)]$ is the local approximation of exchange-correlation potential. Both Hartree and exchange-correlation potentials are some functional of $\rho_\alpha(r)$ i. e., the single-site density of electron gas.

For the case of a disordered system, we find $\rho_\alpha(r)$ within Mattheis method [11] used in a series of works [13,12,14] applying the partial PCF and according to its definition

$$\rho_\alpha(r) = \rho_\alpha^{(at)}(r) - \frac{2\pi n}{r}\sum_\beta X_\beta\int_0^\infty \mathrm{d}R\, G_{\alpha\beta}(R)R\int_{|R-r|}^{R+r}\mathrm{d}r'\rho_\beta^{(at)}(r')r'. \tag{26}$$

Hence, the electron distribution around ion is spherically symmetric. Then Hartree potential can be presented as follows:

$$v_H[\rho_\alpha(r)] = \frac{4\pi}{r}\int_0^r \rho_\alpha(r')r'^2\mathrm{d}r' + 4\pi\int_r^{R_\alpha^\odot}\rho_\alpha(r')r'\mathrm{d}r' \tag{27}$$

and Slater approximation of $v_{xc}[\rho_\alpha(r)]$ [15,16] leads to

$$v_{xc}[\rho_\alpha(r)] = \overset{xc}{\alpha}\,\frac{3}{\pi}\left[3\pi^2\rho_\alpha(r)\right]^{1/3}, \quad \overset{xc}{\alpha} \in [2/3;1]. \tag{28}$$

Of course, we could use any of the more recent exchange-correlation corrections [17] but this causes some difficulties, so we simplify the calculation scheme.

In (26), we treat the atomic electron densities $\rho_\alpha^{(at)}(r)$ within the atomic shell approximation [18] via Gaussian-type decomposition

$$\rho_\alpha^{(at)}(r) = \sum_{i=0}^{N^{(\alpha)}} q_i^{(\alpha)} \mathrm{e}^{-\xi_i^{(\alpha)} r^2}. \tag{29}$$

Here, $\{q_i^{(\alpha)}\}$ and $\{\xi_i^{(\alpha)}\}$ are the parameter sets of predefined positive coefficients of $N^{(\alpha)}$-order electronic density decomposition for α-type atom. This presentation of electronic density reduces the (26) to

$$\begin{aligned} \rho_\alpha(r) &= \sum_{i=0}^{N^{(\alpha)}} q_i^{(\alpha)} \mathrm{e}^{-\xi_i^{(\alpha)} r^2} + \frac{\pi n}{r} \sum_\beta X_\beta \int_0^\infty \mathrm{d}R\, G_{\alpha\beta}(R) R \\ &\quad \times \sum_{i=0}^{N^{(\beta)}} \frac{q_i^{(\beta)}}{\xi_i^{(\beta)}} \left(\mathrm{e}^{-\xi_i^{(\beta)}(r-R)^2} - \mathrm{e}^{-\xi_i^{(\beta)}(r+R)^2} \right). \end{aligned} \tag{30}$$

The last equation takes the form that is optimized for a numerical solution and can be computed faster (e.g. we can apply Gauss-Hermite and Gauss-Laguerre quadrature rule to integration) and turns out to be more accurate than the equation (26).

The resolvent of (20) can be easily found for the case of central symmetric potential with the finite interaction range within partial wave decomposition. In this case the single-site t-matrix elements take the following form

$$\left\langle \mathbf{k}' | \underline{\hat{t}_\alpha^{\pm}} | \mathbf{k} \right\rangle = \frac{2\pi}{\Omega\sqrt{2E}} \sum_{l=0}^{\infty} (2l+1)(1 - \mathrm{e}^{2\mathrm{i}\delta_l^{(\alpha)}(E)}) P_l\left(\cos\angle(\mathbf{k}', \mathbf{k})\right), \tag{31}$$

where $\delta_l^{(\alpha)}(E)$ are the partial phase-shifts which satisfy the following boundary conditions

$$\delta_l^{(\alpha)}(E, 0) = 0, \qquad \delta_l^{(\alpha)}(E, R_\alpha^{\odot}) = \delta_l^{(\alpha)}(E) \tag{32}$$

of the well-known partial phase equation

$$\frac{\mathrm{d}}{\mathrm{d}r} \mathrm{tg}\delta_l^{(\alpha)}(E, r) = -\sqrt{2E} v_\alpha(r) r^2 \left[j_l(\sqrt{2E}r) - \mathrm{tg}\delta_l^{(\alpha)}(E, r) n_l(\sqrt{2E}r) \right]^2. \tag{33}$$

Turning back to ARTA equations(18,19) and reminding that we assume the reference system to be the free electron gas, the next equation for DoS can be got in a way similar to the one we used before in [19,20]

$$\begin{aligned} DoS(E) &= \frac{(2E)^{1/2}}{\pi^2 n} + \frac{1}{6\pi^3 n} \frac{d}{dE} \Bigg[(2E)^{3/2} \\ &\times \mathrm{arctg} \frac{\sum_{\alpha,\beta} \sqrt{X_\alpha X_\beta} \int_{-1}^{1} \mathrm{d}x S_{\alpha\beta}(q) \left[\Im m t_\alpha(x) \Re e t_\beta(x) + \Im m t_\beta(x) \Re e t_\alpha(x) \right]}{\sum_{\alpha,\beta} \sqrt{X_\alpha X_\beta} \int_{-1}^{1} \mathrm{d}x S_{\alpha\beta}(q) \left[\Im m t_\alpha(x) \Im m t_\beta(x) - \Re e t_\alpha(x) \Re e t_\beta(x) \right]} \Bigg], \end{aligned} \tag{34}$$

where $q = \sqrt{4E(1-x)}$, the imaginary and real parts of a single-site T-matrix according to (31)

$$\begin{aligned} \Im m t_\alpha(x) &= \frac{2\pi}{\Omega\sqrt{2E}} \sum_l (2l+1)[1 + \cos 2\delta_l^{(\alpha)}(E)] P_l(x), \\ \Re e t_\alpha(x) &= \frac{2\pi}{\Omega\sqrt{2E}} \sum_l (2l+1) \sin 2\delta_l^{(\alpha)}(E) P_l(x). \end{aligned} \tag{35}$$

Deriving these expressions we consider the trace to be the integral over the isoenergy surface that corresponds to free electron energy E.

So, the computation of DoS of a binary metallic alloy within the approximations suggested for ARTA, consists of the following steps:

1. Using the information about fractions of components, their hard sphere diameters and the packing parameter of alloy we should calculate the partial structure factors of the system according to Baxter's solution (21)–(23);

2. Using Fast Fourier Transformation we should get partial PCFs (24);

3. We should calculate the radial electronic density distribution (30) using the atomic shell approximation for all components of the alloy;

4. Constructing a singe-site potential (25,27,28) we should solve the corresponding phase equation (33) and find partial phase shifts for each component;

5. Using all these data in expressions (35) we calculate the ARTA DoS of binary metallic alloy within (34).

4. Ultimate calculation for Ti_xMn_{1-x} and Al_xNi_{1-x} liquid alloys

Probing the ARTA calculation scheme we choose two systems: Ti_xMn_{1-x} and Al_xNi_{1-x}. The first one is of interest because there are two close but distinguishable d-states that should perform hybridization effects in case of alloying. The second system consists of III-valent metal and magnetic transition metal. The main aspect of this system is the fact that systems of this type conserve its d-transition behavior for a small concentration of the transition metal.

We evaluate the hard sphere diameters of components using pure metal densities at the melting point (Al–2.37 g/cm^3, Ni–7.72 g/cm^3, Mn–5.97 g/cm^3, Ti–4.15 g/cm^3) and the fact that the packing parameter of the liquid metal fitted according to [21] is $\eta_3 = 0.48$. Conserving η_3 for the alloy we get the average concentration of the system n. From [22] we can get atomic shell approximation parameters in spatial convolution (30) $\{q_i^{(\alpha)}\}$ and $\{\xi_i^{(\alpha)}\}$. No other parameters are needed to perform the calculations.

In figure 1 we present our calculation results for the both systems studied. To perform the DoS dependencies on electron energy and fraction x of the first component (Al, Ti) we have reduced the DoS in (34) to $1/\pi^2 n$.

Evidently, the behavior of DoS for the both systems is in qualitative agreement with our hypothesis. DoS of Ti_xMn_{1-x} symmetrically transforms from pure Ti to pure Mn and and there is a distinguishable pseudo-gap caused by strong hybridization of two different d-bands in the intermediate concentration.

The other system Al_xNi_{1-x} is characterized by the d-resonance caused by a single d-band of Ni. It is conserved up to 10% fraction of Ni in the alloy and then it should vanish fast so that the DoS corresponds to a pure liquid Al. Such a behavior of the DoS provides the increase of the effect of the presence of the transition metal in the metallic alloy on its transport properties. Indeed, this is known to be associated with the broadening of the impurity d-states due to the interaction with the conduction band of the host metal [23,24]. The theoretical background to these works is based on Friedel concept of virtual bound d-states and Anderson theory of s-d mixing. According to their theory, the transition metal d-states are represented by simple Lorentzian bands of width 2Γ, located at an energy E_d, so that the partial DoS of spin-degenerated d-electrons is

$$\mathrm{DoS}_\mathrm{d}(E) \approx \frac{10}{\pi} \frac{\Gamma}{(E - E_\mathrm{d})^2 + \Gamma^2} \,. \tag{36}$$

The electronic transport properties of such alloys, where the host is aluminium and the add-on is a small fraction of any 3d-transition metal, are assumed to be due to resonance scattering from

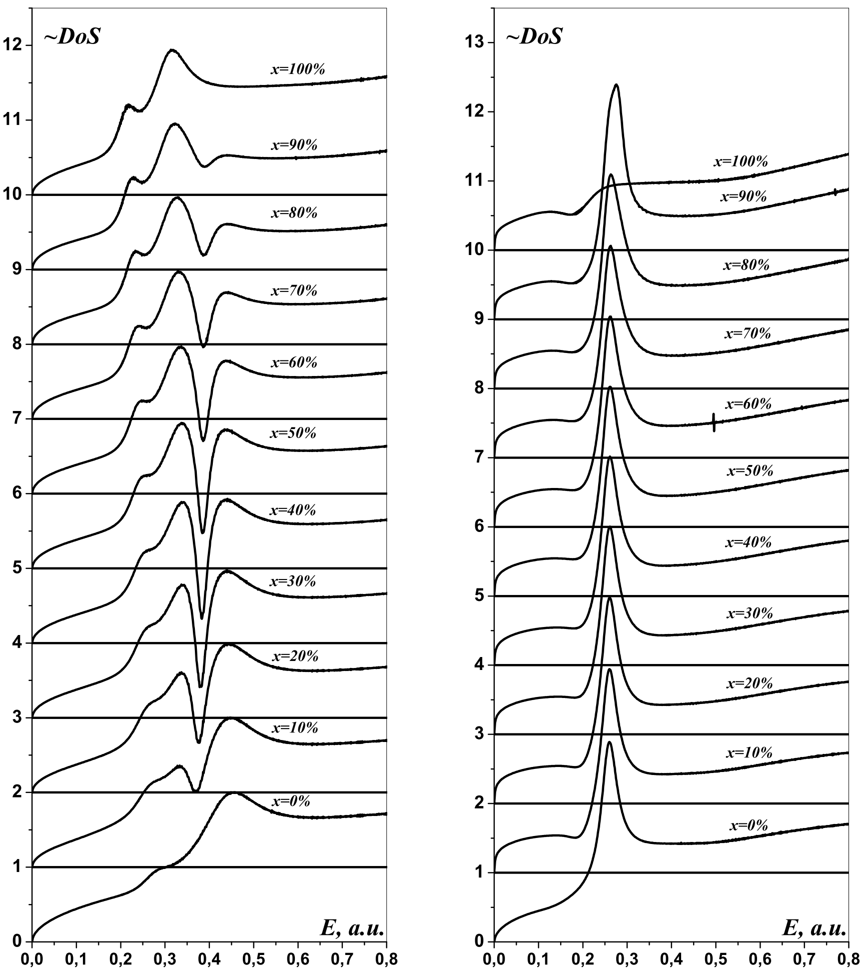

Figure 1. The dependence on energy of DoS of liquid alloys reduced by free electron density for the case of different fractions of components. The left figure presents Ti_xMn_{1-x} system and the right one corresponds to Al_xNi_{1-x}.

the virtual bound states dominated primarily by the d-wave phase shift $\delta_{\mathrm{d}}(E)$. So, in work [24], this hypothesis was proved experimentally for diluted Ni–Al alloys (the host metal was Al).

In regard to (36), the height of the resonance maximum is in direct proportion to reciprocal value of the half-width of the d-band $\sim 1/\Gamma$. Decreasing the fraction of Ni in an alloy we decrease the Ni–Ni correlation (i. e., enlarge the Ni–Ni interatomic distance) and then the d-shell overlapping becomes smaller. It is known that Γ is in direct proportion to these overlapping integrals. So, the resonance should increase the height of the maximum and at the same time should become narrower when the fraction of transition metal decreases. Comparing the 10% contribution of Ni to DoS of Al–Ni in figure 1 and 5–4% contribution of Ni to DoS – figure 2, we can see the proof of the correct behavior of a resonant d-band.

We should also mention that the DoS presented in this work keeps its sense so far as it is smaller than Fermi energy, the outer levels are not occupied by electrons. In case of Al–Ni where Fermi level located within the 0.2–0.25 a.u. range of energy (this is correct for small fraction of Ni) the effect of resonance should be definitely smaller than its maximum value because the corresponding Fermi energy is located near the beginning of d-band (left hill of the resonance). At the same time, the dependence of DoS on the fraction of transition metal in an alloy with non-transition metal for both large and small fraction of the transition metal cannot be in direct proportion to these fractions (experimentally shown in [24]).

The dependence of DoS on the fraction of Mn–Ti alloy is similar to the case of Al–Ni alloy though it is not obvious from figure 1. For intermediate concentration (20–80% of Ti) a significant density gap takes place and it is located between the d-band level of different components of the binary alloy. Anyway, it is obvious that this gap cannot be a superposition of those two different d-bands of Ti and Mn because it is even smaller than the free electron distribution.

5. Conclusion

The ARTA method based on the Lloyd formula developed in this work appears to be a useful technique for calculation of DoS of metallic alloys because it provides analytical expressions for direct evaluation of DoS through the series of simple mathematical equations. This method can be easily spread to the systems consisting of more than 2 components. It should be noted that it is also computationally fast and accurate. In comparison with the classical CPA and other applications of Lloyd, there is no need to use scattering perturbation and r-space average cluster representations. The results obtained in this study can be applied to the construction of reference system characteristics which can in turn be used in more precise techniques, e.g. the cluster approximation for CPA. And finally we claim that some mismatches of DoS behavior can be caused by approximations that we used in describing the atomic structure (e.g. density of alloy and hard sphere diameters). In our opinion the use of corresponding experimental data would improve the results of calculations.

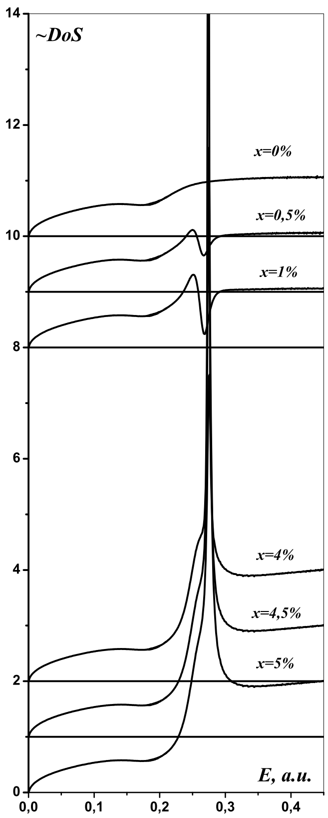

Figure 2. The dependence on energy of DoS of $Al_{1-x}Ni_x$ reduced by free electron density for the case of small Ni fractions.

References

1. Lodder A. The Lloyd formula and the muffin-tin CPA local density of states. J. Phys. F: Met. Phys., 1980, **10**, 1117.
2. Zeller R. An elementary derivation of Lloyd's formula valid for full-potential multiple-scattering theory. J. Phys.: Condens. Matter, 2004, **16**, 6453.
3. Lodder A., Braspenning P. J. Generalized Lloyd formula for the electron density of states. Phys. Rev. B, 1994, **49**, 10215.
4. Tatarchenko A. F., Kulikov N. I. Use of the Lloyd formula for binary alloys. Phys. Rev. B, 1994, **50**, 8266.
5. Schwartz L., Bansil A. Optical theorem and multiple-scattering theory. Electronic states in substitutional alloys. Phys. Rev. B, 1978, **18**, 1702.
6. Hansen J.-P., McDonald I.R. Theory of Simple Liquids. Academic Press, London, 1986
7. Ashcroft N. W., Langreth D. C. Structure of Binary Liquid Mixtures. I Phys. Rev., 1967, **156**, 685.
8. Lebowitz J. L., Rowlinson J. S. Thermodynamic Properties of Mixtures of Hard Spheres. J. Chem. Phys., 1964, **41**, 133.
9. Baxter R. J. Ornstein-Zernike Relation and Percus-Yevick Approximation for Fluid Mixtures. J. Chem. Phys., 1970, **52**, 4559.
10. Kohn W., Sham L. J. Self-Consistent Equations Including Exchange and Correlation Effects. Phys. Rev. A, 1965, **140**, 1133.

11. Mattheiss L.F. Fermi Surface in Tungsten. Phys.Rev A, 1965, No. 139, 1893
12. Mokhracheva L.P., Tskhai V.A., Geld P.V. One-centre exchange potentials in a crystal(TiC). Phys. St. Sol. B, 1976, **78**, 465.
13. Mokhracheva L. P., Tskhai V. A., Geld P. V. Chemical binding and energy band structure of vanadium monocarbide. Phys. St. Sol. B, 1977, **84**, 465.
14. Mokhracheva L. P., Tskhai V. A., Geld P. V. Charge Distribution and Ionicity of the Chemical Bonds in TiC, VC, and TiN. Phys. St. Sol. B, 1978, **87**, 49.
15. Slater J.C., Johnson K.H. Self-Consistent-Field X^{α} Cluster Method for Polyatomic Molecules and Solids. Phys. Rev. B, 1970, **5**, 844.
16. Geldart D.J.W., Rasolt M. Exchange and correlation energy of an inhomogeneous electron gas at metallic densities. Phys. Rev. B, 1976, **13**, 1477.
17. Perdew J.P., Chevary J.A., Vosko S.H., Jackson K.A., Pederson M.R., Singh D.J., Fiolhais C. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. Phys. Rev. B, 1992, **46**, 6671.
18. Constans P., Carbo R. Atomic Shell Approximation: Electron density fitting algorithm restricting coefficients to positive values. Jour. of Chem. Info. and Comp. Sc., 1995, **35**, 1046.
19. Yakibchuk P., Volkov O., Vakarchuk S. Density of states of disordered metals within scattering theory. Jour. of Phys. Studies, 2005, **9**, No. 1, 38 (in Ukrainian).
20. Yakibchuk P., Volkov O., Vakarchuk S. Electronic structure of disordered transition metals. Jour. of Phys. Studies, 2005, **9**, No. 2, 118 (in Ukrainian).
21. Ashcroft N. W., Lekner J. Structure and Resistivity of Liquid Metals. Phys. Rev., 1966, **145**, 83
22. Lluis Amat, Ramon Carbo-Dorca. Fitted electronic density functions from H to Rn for use in quantum similarity measures: cis-diamminedichloroplatinum(II) complex as an application example. Jour. of Chem. Info. and Comp. Sc., 1999, **20**, 911.
23. Auchet J., Terzieff P. The effect of Ti, V and Cr impurities on the transport properties of liquid aluminium. Journal of Alloys and Compounds, 1997, **261**, 295.
24. Terzieff P., Auchet J. Electronic structure of 3d-transition metal solutes in liquid aluminium. J.Phys.: Condens.Matter, 1998, **10**, 4139.

Наближення середньої реплікованої Т-матриці: валентна зона некристалічних металічних сплавів

П. Якібчук, О. Волков, С. Вакарчук

Львівський Національний університет імені Івана Франка

Received April 23, 2007, in final form May 31, 2007

В цій роботі ми пропонуємо нове наближення для розрахунку густини станів багато компонентних металічних систем за допомогою формули Ллойда. В цьому наближенні ми розглядаємо середнє значення квадрату Т-матриці, як парну репліку (відображення) системи розсіювачів. Аналітичний вираз, отриманий в рамках такої теорії, було апробовано на бінарних системах Ti_xMn_{1-x} та Al_xNi_{1-x}. Результати достатньо добре узгоджуються з прогнозованою поведінкою подібних систем.

Ключові слова: *густина станів, Т-матриця, формула Ллойда, наближення атомних оболонок, структурний фактор, подвійний сплав.*

PACS: *71.22.+i, 71.20.Be, 71.15.La, 71.15.Mb, 71.15.Cr, 71.15.Hx, 71.10.-w*