A theory for the electrical conductivity of an ordered alloy

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Abstract. A method for calculating the two-particle electron Green function (alloy conductivity) based on the cluster expansion for the scattering T-matrix is developed. Taking into account scattering processes on all pairs of atoms, an analytical expression for the conductivity of alloys with short-range and long-range order is obtained. The coherent potential approximation is selected as a zero approximation. It is shown that the change in the electronic spectrum due to ordering leads to an essential change in alloy conductivity.

1. Introduction

Essential progress in the theoretical investigation of various alloy properties has been achieved by the use of the best single-site approximation—the coherent potential approximation (CPA)—for the calculation of both the electronic density of states (one-particle Green function) and the kinetic coefficients (two-particle Green functions) [1]. However, the finer features of the density of states and transport phenomena cannot be described within the scope of the CPA. For example, describing Anderson localization requires account to be taken of interference due to electron scattering by different atoms [2,3], but vertex corrections to the electrical conductivity tensor vanish in the CPA [4]. Another type of statistical correlation of electron scattering by atoms caused by correlation in the atom distribution, i.e. by short-range order (SRO), is not taken into account in the CPA either.

There are a number of generalizations of the CPA that allow an account of the mentioned correlations.

Existing knowledge of the influence of SRO on alloy properties proceeds from considering electron scattering in the Born approximation, and therefore is unsuitable for noble and transition metals. Generalizations of the CPA are free from this limitation and applicable to alloys with an arbitrary value of the impurity potential. For example, a cluster extension of the CPA [1] was used in [5] to describe the influence of SRO on the electronic density of states, electron localization and metal–insulator transition in binary alloys using the idea of conditional averaging. But this theory faces the problem of the violation of translational symmetry (which is inherent in any cluster CPA [1]) and uses SRO parameters to describe the long-range order (LRO). In [6] an extension of the CPA based on the expansion of the small parameter R_0 [7] (R_0 is the decay length of the hopping integral for an electron in units of the lattice parameter) has been used to describe the effect of SRO on the electronic spectrum and conductivity of an alloy with an arbitrary relation between impurity potential and band width. It is shown that the influence of SRO on conductivity is caused not only by the change in electron relaxation time due to correlation in arrangement of atoms but also by the change in the electronic spectrum. The latter effect takes place only beyond the Born approximation for electron scattering and, as pointed out in [6], is essential in alloys with Fermi level situated near the spectrum edges.

On the other hand, in [8,9] the change in alloy electronic spectrum caused by SRO has been revealed also in the middle of a band. The density of electronic states exhibits a characteristic dip, which grows as SRO increases. It can be explained by a trend towards spectral change when LRO and a gap in the spectrum are being set up.

Thus it is of interest to study the influence of SRO and LRO on alloy conductivity, taking into account the mentioned change in the electronic spectrum in the middle of a band and the position of the Fermi level with respect to the arising dip or gap. In Smirnov's papers [10, 11] in the tight-binding approximation and for weak electron scattering, it is shown that LRO in alloys can lead to the formation of a forbidden band in the electronic spectrum. In particular, the supposition has been made about the possibility of a metal–insulator transition when the Fermi level is situated in the gap in the electronic spectrum. In [12] alloy conductivity for LRO was considered in the CPA, but the case when the Fermi level is in the gap in the electronic spectrum arising on ordering has not been studied.

To develop a consistent theory of conductivity in an ordered alloy, one should go beyond the scope of the CPA, taking account of statistical correlations in the arrangement of atoms, i.e. SRO and LRO, and the interference in the electron scattering by different atoms.

In [8,9] a new method has been developed that exceeds the scope of the CPA and takes statistical correlations into account. The conventional single-band model of diagonal disorder for a binary substitutional alloy has been employed. The CPA is used in this method as a zero approximation (the reference medium is described by the CPA). Then the corrections to the CPA corresponding to electron scattering on two atoms (all pairs of atoms), three atoms, etc., can be found. This has been achieved by summing the corresponding infinite series of the averaged scattering T-matrix. Statistical correlations are taken into account by considering the electron scattering by various clusters of atoms and with the aid of SRO and LRO parameters. A small parameter γ allowing one to account for the statistical correlations at scattering only by small clusters of atoms arises in their theory (see below). It is like the parameter introduced in [13] and is consistent with the Ioffe–Regel–Mott criterion [14]. In such a way in [8] the electronic density of states in an alloy with SRO and LRO was obtained by taking into account only scattering on all pairs of atoms. The above-mentioned dip and gap in the density of states have been revealed.

In this paper a theory of ordered alloy conductivity based on the described method is developed. The analytical expression for the conductivity tensor is obtained with account of pair statistical correlations. Contributions of scattering processes on clusters consisting of three or more atoms can be omitted when parameter γ is small. It is shown that such an approximation is valid in a rather wide range of alloy parameters. The theory developed allows the description of essential changes in alloy conductivity behaviour connected with the above-mentioned change in the electronic density of states arising on ordering. It should be noted that under the condition $\gamma \ll 1$ the corrections due to Anderson localization are small in the three-dimensional system considered [2] and are not taken into account.

In section 2 the alloy conductivity tensor is described in terms of the scattering T-matrix in the tight-binding approximation. The cluster expansions for the T-matrix and the conductivity tensor are considered. The procedure of configurational averaging is discussed with the aid of diagrams. Analytical expressions for the T-matrix, electronic density of states and conductivity taking into account the single-site scattering (CPA) and scattering by pairs of atoms are obtained. The small parameter of the theory, γ, is introduced.

In section 3 the influence of SRO on the electronic density of states and conductivity is described. Section 4 deals with the influence of LRO on the density of states and conductivity of an alloy. In section 5 the range of applicability of the theory developed (the behaviour of the parameter γ) and the experimental situation are discussed.

2. The conductivity tensor

For the calculation of the static alloy conductivity tensor in the case of elastic electron scattering, let us use the Kubo–Greenwood formula [4] (at $T = 0$)

$$\sigma_{\alpha\beta} = \frac{e^2\hbar}{2\pi N\Omega} \mathrm{Sp}\{\langle v_\alpha[G(E^+) - G(E^-)]v_\beta[G(E^+) - G(E^-)]\rangle\}_{E=\mu} \tag{1}$$

where

$$G(E^\pm) \equiv G(E \pm \mathrm{i}\delta) = (E^\pm - H)^{-1} \tag{2}$$

is the retarded or advanced Green function of the system (corresponding to sign '+' or '−'), H is the one-electron Hamiltonian of the alloy, E is the energy parameter, $\delta \to +0$, v_α is the α component of the operator of the electron velocity vector, $\Omega = \nu\Omega_0$ is the unit-cell volume, Ω_0 is the atomic volume, ν is the number of sublattices, N is the number of sublattice sites, e is the electron charge, μ is the Fermi level, and $\langle\ldots\rangle$ denotes averaging over the different atom distributions in an alloy (configurational averaging).

The Hamiltonian describing one-electron states of the binary alloy in a single-band model may be represented in the form

$$H = \sum_{(in),(jm)\neq(in)} |in\rangle h^{ij}_{nm} \langle jm| + \sum_{(in)} |in\rangle v_{in} \langle in|. \tag{3}$$

where h^{ij}_{nm} is the off-diagonal matrix element of the Hamiltonian (hopping integral) in the Wannier representation, v_{in} is the diagonal matrix element of the Hamiltonian, taking the value v_A or v_B depending on whether atom A or B is in the site (in), $|in\rangle$ is the electron eigenfunction (Wannier function), i is the sublattice number, and n is the sublattice site number. In the diagonal disorder approximation used here, the off-diagonal matrix elements of the Hamiltonian do not depend on the random distributions of atoms (they are not random quantities).

Let us express the Green function $G(E)$ in terms of the scattering T-matrix according to the relation

$$G(E) = \tilde{G}(E) + \tilde{G}(E)T(E)\tilde{G}(E). \tag{4}$$

Here

$$\tilde{G}(E) = (E - \tilde{H})^{-1} \tag{5}$$

is the Green function for the effective-medium Hamiltonian whose matrix elements are equal to

$$\tilde{H}^{ij}_{nm} = h^{ij}_{nm}(1 - \delta_{ij}\delta_{nm}) + \sigma_i\delta_{ij}\delta_{nm} \tag{6}$$

where σ_i is the diagonal matrix element of the reference ordered medium potential (coherent potential), which depends on sublattice number i. The operator T of scattering by the random potential V satisfies the equation

$$T = V + V\tilde{G}T \tag{7}$$

where

$$V = \sum_{(in)} \tilde{v}_{in} \qquad \tilde{v}_{in} = (v_{in} - \sigma_i)|in\rangle\langle in| \tag{8}$$

and the arguments E of the operators (the coherent potential also depends on E) are omitted for the sake of simplification.

It is easy to see that the relations

$$G(E^-) = G^+(E^+) \qquad \tilde{G}(E^-) = \tilde{G}^+(E^+) \qquad T(E^-) = T^+(E^+) \tag{9}$$

follow from the defintions of operators (2), (4) and (5). Substituting (4) into (1) and using the relations (9), one can express the alloy conductivity tensor in terms of the retarded Green function $\tilde{G}(E^+) \equiv \tilde{G}$ and corresponding T-matrix as follows:

$$
\begin{aligned}
\sigma_{\alpha\beta} = -\frac{e^2\hbar}{2\pi N\nu\Omega_0} \operatorname{Re} \sum_{(in)} \Bigg\{ & [v_\alpha(\tilde{G}-\tilde{G}^+)v_\beta(\tilde{G}-\tilde{G}^+)]_{nn}^{ii} \\
& + 2\sum_{(i_1 n_1)} [[\tilde{G}v_\alpha(\tilde{G}-\tilde{G}^+)v_\beta\tilde{G}]_{nn_1}^{ii_1} + [\tilde{G}v_\beta(\tilde{G}-\tilde{G}^+)v_\alpha\tilde{G}]_{nn_1}^{ii_1}]\langle T_{n_1 n}^{i_1 i}\rangle \\
& + \sum_{(i_1 n_1),(i_2 n_2),(i_3 n_3)} \{2[\tilde{G}v_\alpha\tilde{G}]_{nn_1}^{ii_1}[\tilde{G}v_\beta\tilde{G}]_{n_2 n_3}^{i_2 i_3}\langle T_{n_1 n_2}^{i_1 i_2} T_{n_3 n}^{i_3 i}\rangle \\
& - [[\tilde{G}^+ v_\alpha\tilde{G}]_{nn_1}^{ii_1}[\tilde{G}v_\beta\tilde{G}^+]_{n_2 n_3}^{i_2 i_3} + [\tilde{G}^+ v_\beta\tilde{G}]_{nn_1}^{ii_1}[\tilde{G}v_\alpha\tilde{G}^+]_{n_2 n_3}^{i_2 i_3}]\langle T_{n_1 n_2}^{i_1 i_2} T_{n_3 n}^{+i_3 i}\rangle\} \Bigg\}_{E=\mu}.
\end{aligned}
\tag{10}
$$

The matrix elements of the operator v_α in k-representation are equal to

$$v_{\alpha kk'}^{ij} = \frac{1}{\hbar}\frac{\partial h^{ij}(k)}{\partial k_\alpha}\delta_{kk'} \tag{11}$$

where $h^{ij}(k)$ is the Fourier representation of the hopping integral

$$h_{nm}^{ij} = N^{-1}\sum_k h^{ij}(k)\exp[ik(r_n + \rho_i - r_m - \rho_j)]. \tag{12}$$

Here r_n determines the origin of coordinates in the unit cell n of the ordered alloy and ρ_i is the site position of sublattice i in the unit cell. The wavevector k changes within the limits of the ordered alloy first Brillouin zone.

Without any limitation the Wannier functions can be selected to be real. It leads to the condition

$$h_{nm}^{ij} = h_{mm}^{ji}. \tag{13}$$

From (13) and (12) it follows that $h^{ij}(k) = h^{ji}(-k)$, and from the latter equation and (11) we have

$$v_{\alpha kk}^{ij} \equiv v_\alpha^{ij}(k) = -v_\alpha^{ji}(-k). \tag{14}$$

From (5), (6) and (13) it is possible to get

$$\tilde{G}^{ij}_{nm} = \tilde{G}^{ji}_{mn}. \tag{15}$$

The relation (15) in k-representation has the form

$$\tilde{G}^{ij}_{kk} \equiv \tilde{G}^{ij}(k) = \tilde{G}^{ji}(-k). \tag{16}$$

From (14) and (16) it follows that

$$[\tilde{G}v_\alpha\tilde{G}]^{ji}_{mn} = -[\tilde{G}v_\alpha\tilde{G}]^{ij}_{nm}. \tag{17}$$

According to formula (10), alloy conductivity is expressed in terms of the configurationally averaged matrix elements $\langle T^{ij}_{nm}\rangle$ of the scattering T-matrix and their products $\langle T^{i_1 i_2}_{n_1 n_2} T^{i_3 i_4}_{n_3 n_4}\rangle$.

To calculate the conductivity tensor, let us use the cluster expansion of the T-matrix [8,9]. As shown in [8] one can obtain the averaged T-matrix in closed analytical form taking into account only scattering by pairs of atoms (scattering by a single atom is taken into account in the Green function of the effective medium $\tilde{G}$ introduced with the help of the coherent potential and makes no contribution to the averaged T-matrix) and neglecting contributions from clusters that consist of three or more atoms. This is possible and the omitted terms are small if some parameter γ is small (see below). The expression obtained in [8] for the density of states appears to be applicable in a wide range of alloy parameters. The parameter of correlation in the arrangement of atoms is also considered to be small.

An analogous procedure may be developed to calculate the two-particle Green function (conductivity). It is necessary to substitute the T-matrix cluster expansion [8] into expression (10) and to carry out averaging over configurations. It will be shown below that scattering processes by pairs of atoms make the major contribution in the range of applicability of the given theory, as in the case of the one-particle Green-function calculation. The same quantity γ as well as the parameter of pair correlations in the arrangement of atoms on the lattice site serve as the small parameters. Then it is possible to pass from expression (10) to a simpler one

$$\sigma_{\alpha\alpha} = -\frac{e^2\hbar}{2\pi\nu\Omega_0}\,\mathrm{Re}\sum_i \left\{ [v_\alpha(\tilde{G}-\tilde{G}^+)v_\alpha(\tilde{G}-\tilde{G}^+)]^{ii}_{00} + 4\langle T^{ii}_{00}\rangle[\tilde{G}v_\alpha(\tilde{G}-\tilde{G}^+)v_\alpha\tilde{G}]^{ii}_{00} \right.$$

$$+ 2\sum_{(jm)\neq(i0)} [2\langle T^{ji}_{m0}\rangle[\tilde{G}v_\alpha(\tilde{G}-\tilde{G}^+)v_\alpha\tilde{G}]^{ij}_{0m} + (\langle T^{ji}_{m0}T^{ji}_{m0}\rangle - \langle T^{jj}_{mm}T^{ii}_{00}\rangle)[\tilde{G}v_\alpha\tilde{G}]^{ij}_{0m}$$

$$\left. \times [\tilde{G}v_\alpha\tilde{G}]^{ij}_{0m} - (\langle T^{ji}_{m0}(T^{ij}_{0m})^*\rangle - \langle T^{jj}_{mm}(T^{ii}_{00})^*\rangle)[\tilde{G}^+v_\alpha\tilde{G}]^{ij}_{0m}[\tilde{G}v_\alpha\tilde{G}^+]^{ij}_{0m}] \right\}_{E=\mu} \tag{10a}$$

in which relation (17) is used, and to substitute in it the expression for the scattering T-matrix taking into account only scattering by pairs of atoms [8].

For the system under consideration the T-matrix may be given as an expansion

$$T = \sum_{(in)} T_{in}. \tag{18}$$

Substituting (8) and (18) in equation (7) it is easy to show that

$$T_{in} = t_{in} + t_{in}\tilde{G} \sum_{(jm)\neq(in)} T_{jm} \tag{19}$$

where t_{in} is the operator of the single-site scattering matrix

$$t_{in} = (I - \tilde{v}_{in}\tilde{G})^{-1}\tilde{v}_{in}.$$

By making use of (18) and (19) one can obtain that

$$\begin{aligned}
T = \sum_{(i_1 n_1)} \tau_{i_1 n_1} |i_1 n_1\rangle\langle i_1 n_1| + \sum_{(i_1 n_1),(i_2 n_2)\neq(i_1 n_1)} \tau_{i_1 n_1} \tilde{G}_{n_1 n_2}^{i_1 i_2} \tau_{i_2 n_2} |i_1 n_1\rangle\langle i_2 n_2| \\
+ \sum_{(i_1 n_1),(i_2 n_2)\neq(i_1 n_1),(i_3 n_3)\neq(i_2 n_2)} \tau_{i_1 n_1} \tilde{G}_{n_1 n_2}^{i_1 i_2} \tau_{i_2 n_2} \tilde{G}_{n_2 n_3}^{i_2 i_3} \tau_{i_3 n_3} |i_1 n_1\rangle\langle i_3 n_3| + \dots \quad (20)
\end{aligned}$$

where τ_{in} is the diagonal matrix element of t_{in}, i.e.

$$\tau_{in} = [1 - (v_{in} - \sigma_i)\tilde{G}_{nn}^{ii}]^{-1}(v_{in} - \sigma_i).$$

Expressions (18)–(20) give the possibility of obtaining a cluster expansion of the T-matrix. Omitting, for example, the scattering processes by three or more atoms, one can obtain from (18) and (19) the following expression [8] (see also [9, 15, 16]) describing the contributions from scattering by individual atoms and pairs of atoms:

$$T = \sum_{(in)} \tau_{in}|in\rangle\langle in| + \sum_{(in),(jm)\neq(in)} \frac{\tau_{in}^2 \tau_{jm}\tilde{G}_{nm}^{ij}\tilde{G}_{mn}^{ji}|in\rangle\langle in| + \tau_{in}\tau_{jm}\tilde{G}_{nm}^{ij}|in\rangle\langle jm|}{1 - \tau_{in}\tau_{jm}\tilde{G}_{nm}^{ij}\tilde{G}_{mn}^{ji}}. \tag{21}$$

This expression is equivalent to series (20) in which only sums with one and two indices of sites are retained.

The average scattering T-matrix $\langle T_{n_1 n_2}^{i_1 i_2}\rangle$ and direct product $\langle T_{n_1 n_2}^{i_1 i_2} T_{n_3 n_4}^{i_3 i_4}\rangle$ that appear in expressions (10) and (10a) can be easily found with the aid of random occupation numbers C_{in}^λ having values 1 or 0 depending on the presence or absence of λ-type atom in the (in) site. Then any random quantity $X_{i_1 n_1 i_2 n_2 \dots i_l n_l}$ can be represented as

$$X_{i_1 n_1 i_2 n_2 \dots i_l n_l} = \sum_{\lambda_1 \lambda_2 \dots \lambda_l} C_{i_1 n_1}^{\lambda_1} C_{i_2 n_2}^{\lambda_2} \dots C_{i_l n_l}^{\lambda_l} X_{i_1 \lambda_1 i_2 \lambda_2 \dots i_l \lambda_l} \tag{22}$$

where $X_{i_1 \lambda_1 i_2 \lambda_2 \dots i_l \lambda_l}$ is the spectrum of a given random quantity. Using the property of random numbers

$$\sum_\lambda C_{in}^\lambda = 1$$

it can be shown that for the binary alloy

$$C_{in}^\lambda = C_i^\lambda + (C_i^B - C_i^B)(\delta_{\lambda B} - \delta_{\lambda A}) \qquad (\lambda = A, B)$$

$$\bar{P}_{i_1 n_1 i_2 n_2 \dots i_l n_l}^{\lambda_1 \lambda_2 \dots \lambda_l} = \bar{P}_{i_1 n_1 i_2 n_2 \dots i_l n_l}^{BB\dots B}(\delta_{\lambda_1 B} - \delta_{\lambda_1 A})(\delta_{\lambda_2 B} - \delta_{\lambda_2 A})\dots(\delta_{\lambda_l B} - \delta_{\lambda_l A}) \tag{23}$$

where

$$C_i^\lambda \equiv \langle C_{in}^\lambda \rangle$$

$$\bar{P}_{i_1 n_1 i_2 n_2 \ldots i_l n_l}^{\lambda_1 \lambda_2 \ldots \lambda_l} \equiv \langle (C_{i_1 n_1}^{\lambda_1} - C_{i_1}^{\lambda_1})(C_{i_2 n_2}^{\lambda_2} - C_{i_2}^{\lambda_2}) \ldots (C_{i_l n_l}^{\lambda_l} - C_{i_l}^{\lambda_l}) \rangle.$$

Here $C_i^A = x_i$, $C_i^B = y_i$ are the probabilities of occupation of the i sublattice by atoms A and B, which are equal to

$$x_i = x + (\nu_1/\nu)\eta \qquad y_i = 1 - x_i$$

for ν_1 sublattices of the first type and

$$x_i = x - (\nu_2/\nu)\eta$$

for ν_2 sublattices of the second type; here η is the LRO parameter, x, $y = 1 - x$ are the concentrations of the alloy components A and B, $\delta_{\lambda A}$, $\delta_{\lambda B}$ are the Kronecker symbols, and $\nu_1 + \nu_2 = \nu$.

In the considered approximation when processes of scattering by two or more atoms are not taken into account in average values of $\langle T \rangle$ and $\langle T \times T \rangle$, only two-atom (pair) correlations $\bar{P}_{injm}^{BB} \equiv \varepsilon_{nm}^{ij}$ appear. For homogeneous ordering they satisfy the relation

$$\varepsilon_{nm}^{ij} = \varepsilon_{0,m-n}^{ij} \equiv \varepsilon_{m-n}^{ij}.$$

As long as CPA is chosen as a zero approximation (see (4)–(6)) the contribution to $\langle T_{nm}^{ij} \rangle$ and $\langle T_{n_1 n_2}^{i_1 i_2} T_{n_3 n_4}^{i_3 i_4} \rangle$ from processes of scattering by individual atoms must be zero, i.e.

$$\langle \tau_{in} \rangle = 0 \qquad \langle \tau_{in} \rangle = x_i \tau_{iA} + y_i \tau_{iB}$$

$$\tau_{i\lambda}[1 - (\nu_\lambda - \sigma_i)\tilde{G}_{00}^{ii}]^{-1}(\nu_\lambda - \sigma_i) \qquad (\lambda = A, B). \tag{24}$$

This condition results in an equation for the coherent potential of the i sublattice

$$\sigma_i = \langle \nu_{in} \rangle - (\nu_A - \sigma_i)\tilde{G}_{00}^{ii}(\nu_B - \sigma_i) \tag{25}$$

with

$$\langle \nu_{in} \rangle = x_i \nu_A + y_i \nu_B.$$

Quantities $\tau_{i\lambda}$ entering $\langle T_{nm}^{ij} \rangle$ and $\langle T_{n_1 n_2}^{i_1 i_2} T_{n_3 n_4}^{i_3 i_4} \rangle$ satisfy the relations

$$\tau_{iA} = -y_i(\tau_{iB} - \tau_{iA}) \qquad \tau_{iB} = x_i(\tau_{iB} - \tau_{iA}) \tag{26}$$

which follow from (24).

Configurational averaging of the T-matrix and the product $T \times T$ can be put into a more instructive form with the aid of diagrammatic representations of $\langle T_{nm}^{ij} \rangle$ and $\langle T_{n_1 n_2}^{i_1 i_2} T_{n_3 n_4}^{i_3 i_4} \rangle$ (see figures 1 and 2), which follow from (20), (22) and (23). A point with a single outgoing line defines $\tau_{i\lambda}$, a point with two lines corresponds to $\tau_{i\lambda}^2$ and so on. Different points correspond to different lattice sites. A horizontal line represents $\tilde{G}_{nm}^{ij}$. The multiplier $\bar{P}_{i_1 n_1 i_2 n_2 \ldots i_l n_l}^{\lambda_1 \lambda_2 \ldots \lambda_l}$ is assigned to sites connected by a wavy line and $C_i^\lambda \equiv \langle C_{in}^\lambda \rangle$ is assigned to all the remaining sites. Summation over inside sites $(i_1 n_1)$, $(i_2 n_2)$ and over $\lambda_1, \lambda_2, \ldots$
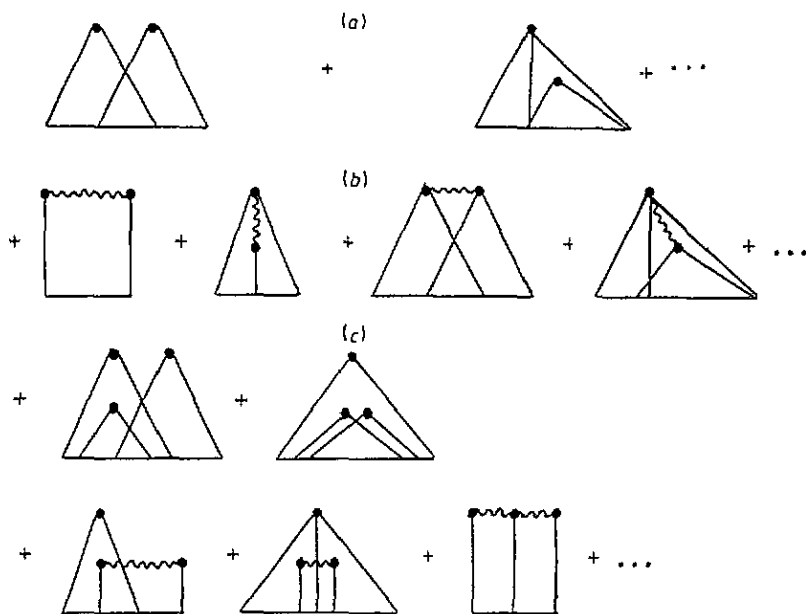
Figure 1. Diagram representation of the averaged T-matrix (T).

is performed. Diagrams (a) in figures 1 and 2 present the scattering processes without correlation in arrangement of atoms. Diagrams (b) represent the contributions connected with the pair interatomic correlations, which are described by parameters ε_{nm}^{ij}. Diagrams (c) representing scattering by clusters of three or more atoms are necessary for the evaluation of omitted terms. Diagrams containing seperate points with single outgoing line and diagrams corresponding to $\langle T_{n_1n_2}^{i_1i_2} T_{n_3n_1}^{i_3i_1}\rangle$ and $\langle T_{n_1n_2}^{i_1i_2} T_{n_2n_4}^{i_2i_4}\rangle$ are absent in figures 1 and 2. These diagrams do not make a contribution to conductivity owing to conditions (24) and $[\tilde{G}v_\alpha\tilde{G}]_{nn}^{ii} = 0$ (the latter condition follows from (17)).

Use of the described diagram representation and also the relations

$$\langle \tau_{in}^l \rangle = x_i y_i [x_i^{l-1} - (-y_i)^{l-1}](\tau_{iB} - \tau_{iA})^l$$

$$\tau_{iB}^l - \tau_{iA}^l = [x_i^l - (-y_i)^l](\tau_{iB} - \tau_{iA})^l$$

which follow from (26), make it possible to reduce the expressions for $\langle T_{nm}^{ij}\rangle$ and $\langle T_{n_1n_2}^{i_1i_2} T_{n_3n_4}^{i_3i_4}\rangle$ (without contributions from scattering by three or more atoms) to geometrical progression series. They may be summed exactly and the result for the conductivity is

$$\sigma_{\alpha\alpha} = -\frac{e^2\hbar}{2\pi v\Omega_0} \text{Re} \sum_i \left\{ [v_\alpha(\tilde{G} - \tilde{G}^+)v_\alpha(\tilde{G} - \tilde{G}^+)]_{00}^{ii} + 2 \sum_{(jm)\neq(i0)} (A_m^{ij})^{-1}(x_ix_jy_iy_ja_m^{ij}a_{-m}^{ji} + \varepsilon_m^{ij}) \right.$$

$$\times \{2[(x_i - y_i) + x_iy_i(x_j - y_j)a_m^{ij}a_m^{ji}]a_m^{ij}a_{-m}^{ji}(\tau_{iB} - \tau_{iA})[\tilde{G}v_\alpha(\tilde{G} - \tilde{G}^+)v_\alpha\tilde{G}]_{00}^{ii}$$

$$+ [1 - x_ix_jy_iy_j(a_m^{ij}a_{-m}^{ji})^2][2a_{-m}^{ji}(\tau_{iB} - \tau_{iA})[\tilde{G}v_\alpha(\tilde{G} - \tilde{G}^+)v_\alpha\tilde{G}]_{0m}^{ij}$$

$$- (\tau_{iB} - \tau_{iA})(\tau_{jB} - \tau_{jA})[\tilde{G}v_\alpha\tilde{G}]_{0m}^{ij}[\tilde{G}v_\alpha\tilde{G}]_{0m}^{ij}]\}$$

$$+ 4 \sum_{(jm)\neq(i0)} \text{Re}\left((A_m^{ij})^{-1}(x_ix_jy_iy_ja_m^{ij}a_{-m}^{ji} + \varepsilon_m^{ij})\right)$$
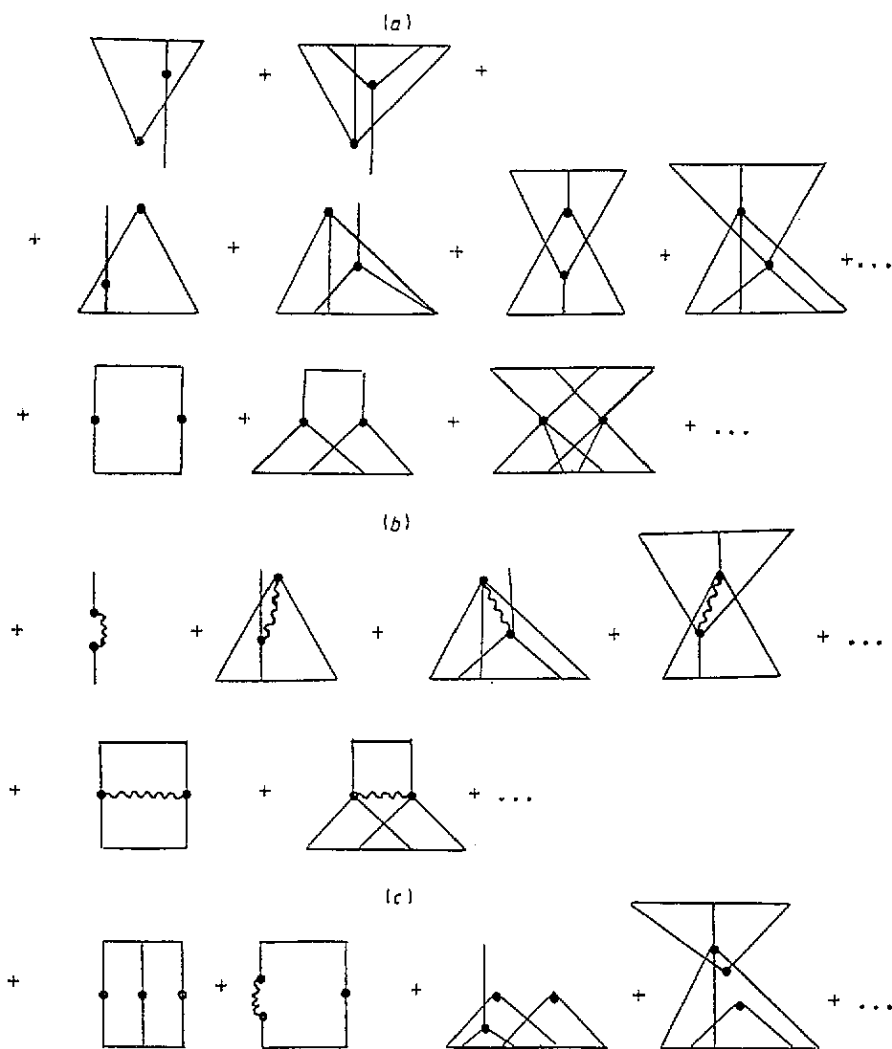
Figure 2. Diagram representation of the averaged direct product of T-matrices $\langle T_{n_1 n_2}^{i_1 i_2} T_{n_3 n_4}^{i_3 i_4} \rangle$.

$$\times [1 - x_i x_j y_i y_j (a_m^{ij} a_{-m}^{ji})^2] \frac{a_m^{ij}}{a_m^{ij} + a_m^{ij*}} \Bigg) (\tau_{iB} - \tau_{iA})^* (\tau_{jB} - \tau_{jA})$$

$$\times [\tilde{G} v_\alpha \tilde{G}^+]_{0m}^{ij} [\tilde{G}^+ v_\alpha \tilde{G}]_{0m}^{ij} \Bigg\}_{E=\mu} \tag{27}$$

where

$$A_m^{ij} = (1 - x_i x_j a_m^{ij} a_{-m}^{ji})(1 + x_i y_j a_m^{ij} a_{-m}^{ji})(1 + x_j y_i a_m^{ij} a_{-m}^{ji})(1 - y_i y_j a_m^{ij} a_{-m}^{ji})$$

$$a_m^{ij} \equiv a_{0m}^{ij} = (\tau_{iB} - \tau_{iA}) \tilde{G}_{0m}^{ij}.$$

The same result may be obtained by making use of analytical expression (21) in averaging the T-matrix and the direct product $T \times T$.

The alloy Fermi level μ in (27) is determined by the equation

$$Z = \frac{1}{2} \int_{-\infty}^{\mu} g(E)\, dE \tag{28}$$

where Z is the ratio of the number of occupied energy levels to the total number of levels in a band, and $g(E)$ is the electronic density of states per atom.

The electronic density of states $g(E)$ is connected with the one-particle Green function of an alloy by

$$g(E) = -\frac{2}{\pi \nu} \operatorname{Im} \sum_i \langle G \rangle_{00}^{ii}. \tag{29}$$

In accordance with (29) and (4) the density of states $g(E)$ is defined by the averaged T-matrix, which may be calculated as described above. The average T-matrix in k-representation has the form

$$\langle T \rangle_k^{ij} = \sum_{(j_1 m) \neq (i0)} (A_m^{ij_1})^{-1} (x_i x_{j_1} y_i y_j a_m^{ij_1} a_{-m}^{j_1 i} + \varepsilon_m^{ij_1})$$

$$\times \{ [x_i - y_i + x_i y_i (x_{j_1} - y_{j_1}) a_m^{ij_1} a_{-m}^{j_1 i}] a_m^{ij_1} a_{-m}^{j_1 i} (\tau_{iB} - \tau_{iA}) \delta_{ij}$$

$$+ [1 - x_i x_{j_1} y_i y_{j_1} (a_m^{ij_1} a_{-m}^{j_1 i})^2] a_m^{ij_1} (\tau_{j_1 B} - \tau_{j_1 A}) \exp(i\mathbf{k} \cdot \mathbf{r}_m) \delta_{j_1 j} \}. \tag{30}$$

Using (29), (4) and (30), one can obtain that

$$g(E) = -\frac{2}{\pi \nu} \operatorname{Im} \left(\sum_i \tilde{G}_{00}^{ii} + \sum_{i_1 (jm) \neq (i0)} (A_m^{ij})^{-1} (x_i y_j y_i y_j a_m^{ij} a_{-m}^{ji} + \varepsilon_m^{ij}) \right.$$

$$\times \{ [x_i - y_i + x_i y_i (x_j - y_j) a_m^{ij} a_{-m}^{ji}] a_m^{ij} a_{-m}^{ji} (\tau_{iB} - \tau_{iA}) (\tilde{G}^2)_{00}^{ii}$$

$$\left. + [1 - x_i x_j y_i y_j (a_m^{ij} a_{-m}^{ji})^2] a_m^{ij} (\tau_{jB} - \tau_{jA}) (\tilde{G}^2)_{m0}^{ij} \} \right). \tag{31}$$

The contributions of scattering by clusters of three or more atoms represented by diagrams (c) in figures 1 and 2 are neglected in expressions (27) and (31) for the conductivity and electronic density of states. The relative values of the neglected terms can be evaluated with the help of parameters

$$\gamma_{0m}^{ij} = \left| \sum_{(j_1 m_1) \neq (jm)} x_{j_1} y_{j_1} \left(\frac{\tilde{G}_{0m_1}^{ij_1}}{\tilde{G}_{0m}^{ij}} \right)^2 (a_{m_1 m}^{j_1 j})^2 \right| \tag{32}$$

which are calculated using the first main diagrams (c) in figures 1 and 2. The quantities γ_{0m}^{ij} as well as correlation parameters ε_m^{ij} are the small parameters of the theory. Evaluation of γ_{0m}^{ij} will be given below.

3. Influence of short-range order on alloy conductivity

In the absence of long-range order ($\eta = 0$), the dependence of the terms in (27) on the sublattice number i disappears. With the aim of analytical investigation of the basic features of the influence of short-range order on alloy conductivity, and also for carrying out numerical calculations, we shall use the following dispersion law for the Fourier representation $h(k)$ of hopping integral h_{nm} suggested in [6,7]

$$h(k) = W[1 + (kR_0)^2]^{-1} \qquad W < 0 \qquad (33)$$

where W is the position of the bottom of the pure metal energy band, and $v_A = 0$ is assumed as the energy origin. The dependence (33) corresponds to the exponential decrease of the hopping integral h_{nm} with distance between sites (R_0 is the characteristic decay length). The wavevector k changes within the first Brillouin zone.

Using equations (5), (6), (11) and (33) and also formula (12) for the transition from k-representation to the site one, we obtain the following explicit expressions for matrix elements of the Green function $\tilde{G}(E)$ and products of $\tilde{G}(E)$ and v_α that enter expression (27) for the alloy conductivity:

$$\tilde{G}_{00} = \frac{1}{E - \sigma} \left[1 + \frac{i}{4\pi} \frac{W}{(E - \sigma)} \left(\frac{\Omega_0}{R_0^3}\right) b \right]$$

$$\tilde{G}_{0m} = \frac{1}{4\pi} \frac{W}{(E - \sigma)^2} \left(\frac{\Omega_0}{R_0^3}\right) \frac{R_0}{r_m} \exp(ik_0 r_m)$$

$$[v_\alpha(\tilde{G} - \tilde{G}^+)v_\alpha(\tilde{G} - \tilde{G}^+)]_{00} = -\frac{2}{3} \frac{\Omega_0}{\pi \hbar^2} \frac{|E - \sigma|^2}{W\sigma''} \frac{(b_0')^3}{R_0}$$

$$[\tilde{G}v_\alpha(\tilde{G} - \tilde{G}^+)v_\alpha\tilde{G}]_{00} = -i\frac{\Omega_0}{6\pi\hbar^2} \frac{(E - \sigma^*)^2}{W(\sigma'')^2} \frac{(b_0')^3}{R_0} \left(1 - i\frac{3W\sigma''}{2|E - \sigma|^2} \frac{1}{b_0 b_0'}\right)$$

$$\sum_\alpha [\tilde{G}v_\alpha(\tilde{G} - \tilde{G}^+)v_\alpha\tilde{G}]_{0m} = -i\frac{\Omega_0}{2\pi\hbar^2} \frac{(E - \sigma^*)^2}{W(\sigma'')^2} \frac{b_0'(b_0^*)^2}{R_0} \left\{ \frac{\sin(k_0' r_m)}{k_0' r_m} - \frac{i}{4b_0'(b_0^*)^2} \frac{W\sigma''}{|E - \sigma|^2} \right.$$

$$\left. \times \exp(ik_0' r_m) \left[2b_0 + \frac{W\sigma''}{|E - \sigma|^2} \left(\frac{r_m}{R_0} - i\frac{3}{b_0}\right)\right] \right\} \exp(-k_0'' r_m) \qquad (34)$$

$$[\tilde{G}v_\alpha\tilde{G}]_{0m} = -i\frac{\Omega_0}{4\pi\hbar} \frac{W}{(E - \sigma)^2 R_0^2} \exp(ik_0 r_m)(l_\alpha \cdot l_m)$$

$$[\tilde{G}v_\alpha\tilde{G}^+]_{0m} = i\frac{\Omega_0}{2\pi\hbar} \frac{(b_0')^2}{R_0^2\sigma''} \left[\cos(k_0' r_m) - \frac{\sin(k_0' r_m)}{k_0' r_m} - \frac{W\sigma''}{2|E - \sigma|^2(b_0')^2} \sin(k_0' r_m)\right]$$

$$\times \frac{\exp(-k_0'' r_m)}{k_0' r_m}(l_\alpha \cdot l_m)$$

where

$$b = b_0 - i\frac{R_0}{\pi} \left[2k_m + k_0 \ln\left(\frac{k_m - k_0}{k_m + k_0}\right)\right] = b' + ib''$$

$$b_0 = \left(\frac{W}{E - \sigma} - 1\right)^{1/2} = b_0' + ib_0'' \qquad k_0 = \frac{b_0}{R_0} = k_0' + ik_0'' \qquad k_0'' > 0$$

$k_m = (6\pi^2/\Omega_0)^{1/3}$ is the Brillouin sphere radius, $l_m = r_m/r_m$, $\sigma = \sigma' + i\sigma''$ and $\sigma'' < 0$.

We shall carry out an analytical study of the main trends of the influence of SRO on alloy conductivity, neglecting in (27) at $\eta = 0$, in comparison with 1, quantities that are proportional to a_m, a_{-m}. This approximation corresponds to the calculation of conductivity in the CPA (the first term in (27)) including the main corrections caused by SRO (terms in (27) proportional to ε_m), i.e. this procedure takes into account in (1) the first terms of the diagram series for $\langle v_\alpha G(E_1) v_\beta G(E_2) \rangle$ (figures 1(b) and 2(b)). The contribution of the omitted terms is taken into account below in the numerical calculation of conductivity according to formula (27) (they account for about 20–30% of the total in the range of applicability of the used expansion on parameter γ).

Thus in the assumed approximation the alloy conductivity is equal to

$$\sigma_{\alpha\alpha} = \sigma_{\alpha\alpha}^{(0)} \left(1 - \sum_i C_i \alpha_i F(k_0' r_i) \exp(-2k_0'' r_i) \right)_{E=\mu} \tag{35}$$

where

$$
\begin{aligned}
F(z) = \frac{1}{z} &\left[\sin^2 z \left(\frac{1}{z} + \frac{W\sigma''}{2(E-\sigma')^2(b_0')^2} \right) - \frac{W\sigma'' \cos^2 z}{2(E-\sigma')^2(b_0')^2} \right] \\
&+ \frac{x - y}{xy} \frac{\sigma''}{\delta} \frac{1}{z^2} \left(\sin(2z) - \frac{3W\sigma'' \cos(2z)}{2(E-\sigma')^2(b_0^1)^2} \right) \\
&- \frac{1}{z^2} \left(\cos z - \frac{\sin z}{z} - \frac{W\sigma'' \sin z}{2(E-\sigma')^2(b_0')^2} \right)^2 + \frac{W^2(\sigma'')^2 \cos(2z)}{4(E-\sigma')^4(b_0')^4}
\end{aligned}
\tag{36}
$$

and

$$\sigma_{\alpha\alpha}^{(0)} = \frac{e^2}{3\pi^2\hbar} \frac{(E-\sigma')^2(b_0')^3}{W\sigma'' R_0} \bigg|_{E=\mu} .$$

Here $\delta = v_B - v_A$, $v_A = 0$, C_i, r_i are the coordination number and the radius-vector modulus for the i coordination sphere, and $\alpha_i = \varepsilon_i/(xy)$ is the Cowley SRO parameter.

The expression (36) for $F(z)$ consists of four terms. With the exception of the third term in (36) and the terms containing $\sigma''/(E-\sigma')$, the factor $F(k_0' r_i)$ in (35) is proportional to the imaginary parts of the matrix elements of the configurationally averaged scattering T-matrix $\langle T \rangle_k$ in k-representation (30). This part of $F(z)$ is caused by the change in damping of electronic states due to SRO. The contribution to the conductivity described by the third term in (36) and also by the terms containing $\sigma''/(E-\sigma')$ is proportional to the real part of $\langle T \rangle_k$ and caused by the change in the electronic spectrum due to SRO. It should be noted that the last contribution to the alloy conductivity is absent in the Born approximation of scattering theory [10, 11].

This change in the electronic spectrum may be revealed with the help of expression (31) at $\eta = 0$ (see also [8, 9]). Numerical calculations of electronic density of states of binary alloys with BCC structure are presented in figure 3. Concentration $y = 0.5$ and parameter $R_0 = 0.2a$ (a is the lattice parameter) are taken for the calculation. The energy is taken in units of the half-width of the pure metal energy band, $\frac{1}{2}|W - h(k_m)|$, and $\delta = -0.25$ is adopted. The SRO parameter for the first coordination sphere is $\alpha_1 = -0.1$. The energy dependences of the electronic density of states for a disordered alloy and for an alloy with
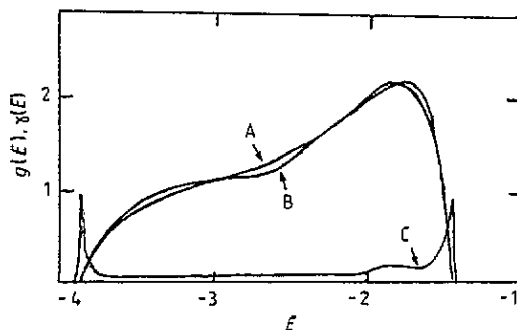
Figure 3. Energy dependences of the electronic density of states $g(E)$ of disordered alloy (curve A) and for the binary alloy with SRO (curve B) and parameter $\gamma(E)$ for the binary alloy with SRO (curve C).

SRO are depicted by curves A and B, respectively. Curve C in figure 3 presents the energy dependence of parameter γ.

These results show that for SRO a characteristic dip appears on the curve of the density of states $g(E)$ in the range of energies corresponding to the Brillouin zone boundary of the ordered alloy. The magnitude of this dip increases with increase of SRO. It shows a tendency to form a true gap in the energy band as a result of setting up of LRO (see figures 5 and 6).

The imaginary part of the coherent potential σ'' in formula (36) may be estimated with the help of the expression [8]

$$\sigma'' \simeq xy\delta^2 \operatorname{Im} \tilde{G}_{00} \simeq xy\delta^2 \frac{\Omega_0}{R_0^3} \frac{Wb'}{4\pi(E-\sigma')^2}. \tag{37}$$

At a low electron concentration Z when the Fermi level of an alloy μ (see (28)) is near the bottom of the conduction band and

$$k_0'r_1 \ll 1$$

the terms in $F(k_0'r_1)$ caused by the change in the energy spectrum may be neglected when $|\sigma''|$ is small enough in comparison with $|\mu - \sigma'|$. In this case the sign of the factor $F(k_0'r_1)$ in (35) becomes positive. It means that SRO in the first coordination sphere ($\alpha_1 < 0$) leads to an increase in the conductivity. This conclusion agrees with the results obtained in the Born approximation [10, 11].

At

$$(k_0'r_1) \sim \pi \qquad E = \mu \tag{38}$$

the terms in (36) caused by the change in damping of the electron states due to SRO may be neglected in comparison with the terms caused by the change in the electronic density of states. When the above-mentioned dip appears on the curve $g(E)$ for the energy range defined by condition (38) for SRO, the sign of the factor $F(k_0'r_1)$ in (35) becomes negative. It means that when the alloy Fermi level μ is in the region of the noted dip, the alloy conductivity decreases for SRO on the first coordination sphere ($\alpha_1 < 0$). The possibility of an essential contribution to alloy conductivity by a change in the energy spectrum due

to SRO was noted for the first time in [6]. However, the observed spectrum region was not investigated.

With further increase of the electron concentration, when the Fermi level μ goes out of the dip region, the factor $F(k_0' r_1)$ in (35) again becomes positive, and the conductivity behaves in the usual way, increasing for SRO.

These features of the conductivity behaviour for SRO are confirmed by the numerical calculation of the function $F(k_0' r_1)$ (it is verified that this factor reverses sign depending on the electron concentration value) and numerical calculations performed according to formula (27) at $\eta = 0$. The results of the calculation of the disordered alloy conductivity, $\sigma^{(0)}$, and that for the alloy with SRO, σ, for three values of the electron concentration characterized by the quantity z (see formula (28)) are given in table 1. The three different values of z correspond to three values of the Fermi level μ (28) positioned respectively at the bottom, in the dip and near the upper edge of a band (figure 3).

Table 1. Influence of SRO on alloy conductivity.

$Z =$	0.1	0.5	0.9
$\sigma^{(0)}$ (10^6 Ω^{-1} m^{-1})	1.04	1.06	2.63
σ (10^6 Ω^{-1} m^{-1})	1.31	0.97	2.68

4. Influence of long-range order on alloy conductivity

First we shall carry out an analytical investigation into the main trends of the influence of LRO on alloy conductivity in the single-site approximation. In this approximation the conductivity is described by the first term of equation (27).

Let us consider a binary ordered alloy with BCC lattice. In this case, the number of sublattices is two ($v_1 = v_2 = 1$). In the nearest-neighbour approximation the matrix elements of the effective-medium Green function $\tilde{G}(E)$ in k-representation have the form

$$\tilde{G}_k''(E) = (E - \sigma_2)/D_k \qquad \tilde{G}_k^{12}(E) = h^{21}(k)/D_k$$
$$\tilde{G}_k^{21}(E) = h^{12}(k)/D_k \qquad \tilde{G}_k^{22}(E) = (E - \sigma_1)/D_k \qquad (39)$$

where

$$D_k = (E - \sigma_1)(E - \sigma_2) - h^{12}(k)h^{21}(k) \qquad h^{12}(k) = h^{21}(k) = h(k)$$
$$h(k) = \sum_\rho h_{00}^{12} e^{ik\rho}$$

and ρ is the radius vector of a nearest neighbour in the alloy.

Let us use the semi-elliptical band model for the unperturbed density of states

$$g_A(\xi) = \begin{cases} (2/\pi w_A^2)(w_A^2 - \xi^2)^{1/2} & |\xi| \leqslant w_A \\ 0 & |\xi| > w_A \end{cases} \qquad (40)$$

where w_A is the half-width of the pure metal A energy band. Passing in (39) from k-representation to the site one according to formula (12) and substituting integration over
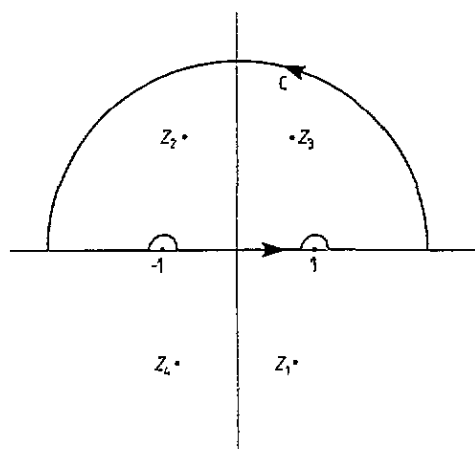
Figure 4. The contour C for integration in formula (42).

energy for summation over k with the use of (40), we obtain for the diagonal matrix elements of $\tilde{G}(E)$ in equation (25) for the coherent potential:

$$\tilde{G}_{00}^{11} = \frac{2}{w_A^2} \left[E - \sigma_2 - i \left(\frac{E - \sigma_2}{E - \sigma_1} \right)^{1/2} [w_A^2 - (E - \sigma_1)(E - \sigma_2)]^{1/2} \right] \tag{41}$$

$$\tilde{G}_{00}^{22} = [(E - \sigma_1)/(E - \sigma_2)]\tilde{G}_{00}^{11}.$$

Taking into consideration that according to (39) $\tilde{G}_k^{ij} = \bar{G}_{h(k)}^{ij}$, it is possible to obtain the relation

$$[v_\alpha(\tilde{G} - \tilde{G}^+)v_\alpha(\tilde{G} - \tilde{G}^+)]_{00}^{ii} = \int_{-\infty}^{\infty} d\xi\, \varphi(\xi) L(\xi, E) \tag{42}$$

where

$$\varphi(\xi) = \tfrac{1}{3} \sum_\alpha N^{-1} \sum_k v_\alpha^{12}(k) v_\alpha^{12}(k) \delta(\xi - h(k))$$

$$L(\xi, E) = [\tilde{G}_\xi^{21}(E) - \bar{G}_\xi^{12*}(E)]^2 + [\bar{G}_\xi^{11}(E) - \bar{G}_\xi^{11*}(E)][\bar{G}_\xi^{22}(E) - \bar{G}_\xi^{22*}(E)].$$

In crystals of cubic symmetry one may represent $\varphi(\xi)$ in the form [17]

$$\varphi(\xi) = \begin{cases} (2vv_m^2/3\pi)(w_A^2 - \xi^2)^{3/2} & |\xi| \leqslant w_A \\ 0 & |\xi| > w_A \end{cases} \tag{43}$$

where v_m is the maximum electron velocity in the energy band.

Taking into account (43), the integration in (42) is performed in the segment $[-1, 1]$ (assuming $w_A = 1$). In order to calculate the integral (42), analytical continuation of the integrand into the complex plane is carried out. The points $\xi = -1, 1$ are branch points of the integrand $\varphi(\xi)L(\xi, E)$. In the segment $[-1, 1]$ this function is real. At the other points of the real axis it is imaginary. Therefore,

$$\int_{-1}^{1} \varphi(\xi)L(\xi, E)\, d\xi = \operatorname{Re} \oint \varphi(\xi)L(\xi, E)\, d\xi.$$

The contour C is shown in figure 4.

The poles of the integrand are located at the points

$$z_1 = (A_1 A_2)^{1/2} \qquad z_2 = -z_1 \qquad z_3 = z_1^* \qquad z_4 = -z_1^*$$

$$A_1 = E - \sigma_1 \qquad A_2 = E - \sigma_2.$$

Performing the integration in (42) and substituting the result into (27), we shall obtain in the single-site approximation for alloy conductivity

$$\sigma_{\alpha\alpha} = \frac{4e^2 \hbar v_m^2}{3\pi \Omega_0} |I(E)|_{E=\mu} \tag{44}$$

where

$$I(E) = \frac{1}{|A_1 A_2|^2 \operatorname{Im}(A_1 A_2)} \operatorname{Re}\{[A_1 A_2 (1 - A_1 A_2)]^{1/2}$$

$$\times \{[|A_1 A_2|^2 [1 - (A_1 A_2)^* - \operatorname{Re}(A_1 A_2^*) + i \operatorname{Im}(A_1 A_2)] + (A_1 A_2)^* \operatorname{Re}(A_1 A_2^*)]\}\}$$

$$A_1 = E - \sigma_1 \qquad A_2 = E - \sigma_2.$$

Let us consider the expression (44) for the case of weak scattering when $\delta / w_A \ll 1$. In this case the solution of equation (25) for the coherent potential with the use of (41) may be presented as

$$\sigma_1 = \langle v \rangle - \tfrac{1}{2}\eta\delta + 2\delta^2 (x + \tfrac{1}{2}\eta)(y - \tfrac{1}{2}\eta)\left[E - \langle v \rangle - \tfrac{1}{2}\eta\delta - i \left(\frac{E - \langle v \rangle - \tfrac{1}{2}\eta\delta}{E - \langle v \rangle + \tfrac{1}{2}\eta\delta} \right)^{1/2} \right.$$

$$\left. \times [1 - (E - \langle v \rangle + \tfrac{1}{2}\eta\delta)(E - \langle v \rangle - \tfrac{1}{2}\eta\delta)]^{1/2} \right]$$

$$\sigma_2 = \langle v \rangle + \tfrac{1}{2}\eta\delta + 2\delta^2 (x - \tfrac{1}{2}\eta)(y + \tfrac{1}{2}\eta)\left[E - \langle v \rangle + \tfrac{1}{2}\eta\delta - i \left(\frac{E - \langle v \rangle + \tfrac{1}{2}\eta\delta}{E - \langle v \rangle - \tfrac{1}{2}\eta\delta} \right)^{1/2} \right.$$

$$\left. \times [1 - (E - \langle v \rangle + \tfrac{1}{2}\eta\delta)(E - \langle v \rangle - \tfrac{1}{2}\eta\delta)]^{1/2} \right]$$

$$\langle v \rangle = x v_A + y v_B = y\delta \qquad v_A = 0. \tag{45}$$

Analysis of expressions (41) and (45) shows that LRO leads to the formation of a true gap in the energy spectrum of the alloy with width $\eta|\delta|$ and with its centre at the point $\langle v \rangle = y\delta$.

When the Fermi level of the alloy is outside of the gap $\tfrac{1}{2}|\delta| \ll |\mu - \langle v \rangle| \leqslant 1$, it follows from (44) and (45) that

$$\sigma_{\alpha\alpha} = \frac{2e^2 \hbar v_m^2 [1 - (\mu - \langle v \rangle)^2]}{3\pi \Omega_0 \delta^2 (xy - \tfrac{1}{4}\eta^2)}. \tag{46}$$

Thus the dependence of the residual specific resistance $\rho = 1/\sigma_{\alpha\alpha}$ on the LRO parameter η obeys Smirnov's law [11]

$$\rho \sim (xy - \tfrac{1}{4}\eta^2).$$

When the Fermi level is near the gap $\frac{1}{2}\eta|\delta| < |\mu - \langle v \rangle| \sim \frac{1}{2}|\delta|$, the dependence of $\sigma_{\alpha\alpha}$ on the composition and degree of LRO is rather complicated. So, for alloys of stoichiometric composition ($x = y = 0.5$)

$$\sigma_{\alpha\alpha} = \frac{8e^2\hbar v_m^2[1 - \frac{1}{4}\delta^2(1 - \eta^2)]^{3/2}}{3\pi\Omega_0\delta^2(1 + \eta^2)}. \tag{47}$$

In the first case the resistance decreases with ordering, whereas in the second case the behaviour of $\sigma_{\alpha\alpha}$ (47) is quite the opposite: the resistance increases with ordering.

When $|\mu - \langle v \rangle| < \frac{1}{2}\eta|\delta|$ and the Fermi level μ is in the gap, it is possible to show that the alloy conductivity (44) is proportional to the small parameter $|\operatorname{Im}(A_1 A_2)/\operatorname{Re}(A_1 A_2)|_{E=\mu} = |\sigma_1''/(\mu - \sigma_1') + \sigma_2''/(\mu - \sigma_2')|$, and according to (45) it goes to zero together with the imaginary parts σ_1'' and σ_2'' of the coherent potentials of the sublattices.

Therefore, during ordering, when the Fermi level gets into the gap being formed, the alloy becomes similar to a dielectric in its electrical properties. This is, in fact, quantitative confirmation of the existence of a metal–insulator transition predicted by Smirnov [11].

The main features of the behaviour of the alloy conductivity $\sigma_{\alpha\alpha}$ at LRO remain valid in the general case when the ratio of the impurity scattering potential to the width of the band δ/w_A is arbitrary, though $\sigma_{\alpha\alpha}$ now depends on y, δ/w_A and η in a complicated way.

In figures 5 and 6 the results of numerical calculation of the electronic density of states (31) for alloys with various values of the LRO parameter η and correlation parameter for the first coordination sphere ε_0^{12} at $y = 0.5$ and $\delta/w_A = -0.5$ are presented. Figure 5 shows the density of states of the disordered alloy at various values of ε_0^{12}: (a) $\varepsilon_0^{12} = 0$, (b) $\varepsilon_0^{12} = -0.05$ and (c) $\varepsilon_0^{12} = -0.08$. Figure 6 shows the density of states for ordered alloy: (a) $\eta = 0.4$, $\varepsilon_0^{12} = -0.1$ and (b) $\eta = 0.98$, $\varepsilon_0^{12} = 0$. Broken curves depict the density of states calculated in CPA and corresponding to the first term in (31). Full curves depict the density of states in the two-site approximation. As can be seen from figure 5, the characteristic dip appears on the curve of the energy dependence of the density of states for formation of SRO, which is a precursor of the true gap arising on ordering (figure 6). In figures 7, 8 and 9 the results of numerical calculation of alloy conductivity are presented. The calculation has been performed according to formulae (44), (25) and (41) for the case $\delta/w_A = -0.5$, $y = 0.5$ and for three different values of electron concentration Z.

At $z = 0.8$ when the Fermi level μ (28) is outside of the gap near the upper edge of the band, the conductivity $\sigma_{\alpha\alpha}$ increases with the growth of the degree of LRO (figure 7).

At $z = 0.5$, when the Fermi level μ is in the middle of the gap, the behaviour of the conductivity is the opposite: on ordering it decreases by some orders of magnitude (figure 8).

At $z = 0.6$ the Fermi level μ for the disordered alloy is between the middle and the right edge of the gap formed on ordering. The position of the Fermi level μ depends on η and for complete LRO it goes outside of the gap area. (In figure 9 the points C and E correspond to the positions of the centre and the edge of the gap.) The non-monotonic change in the conductivity in the given case (figure 9) is explained by this circumstance.

It should be pointed out that the study of the conductivity behaviour for LRO in the CPA was carried out for the first time in [12]. However, the case of the Fermi level being in the gap was not considered in that work.

Let us consider the contribution of scattering by pairs of atoms (taking into account the interatomic correlations) to the ordered alloy conductivity. For this purpose the dispersion law $h(k)$ in (39) is taken in the form corresponding to an exponential decrease of the hopping integral h_{nm}^{ij} with distance between the sites

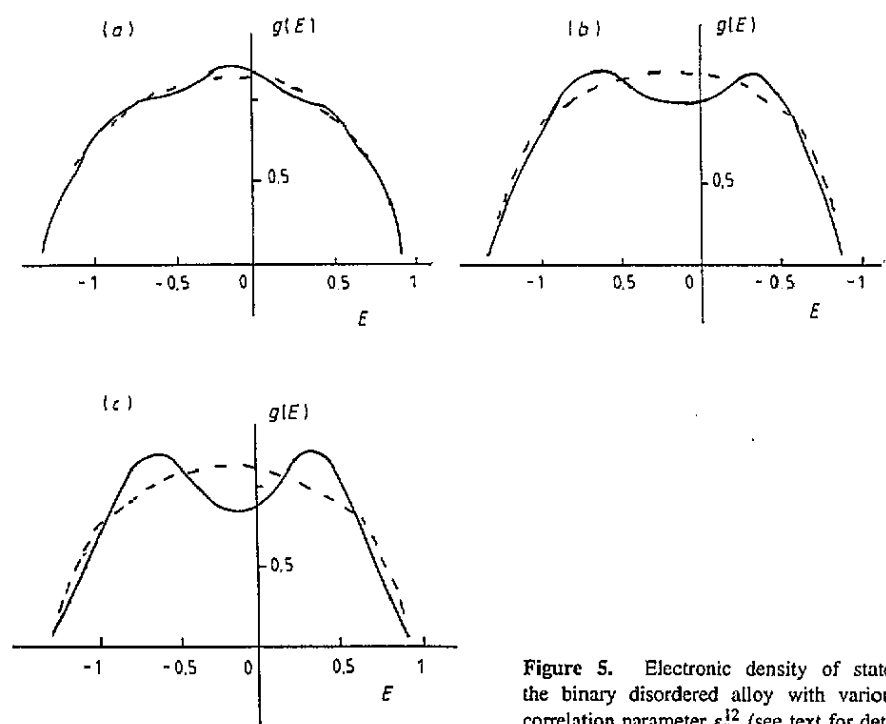$$h(k) = S(k) - S(k_m) \qquad S(k) = W[1 + (kR_0)^2]^{-1} \qquad W < 0. \tag{48}$$

Figure 5. Electronic density of states $g(E)$ for the binary disordered alloy with various values of correlation parameter ε_0^{12} (see text for details).
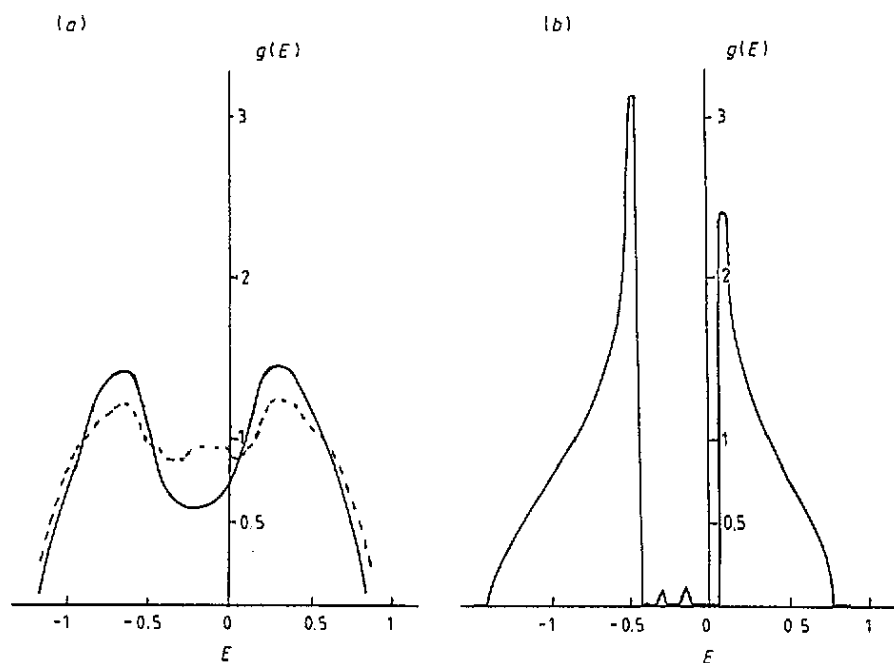

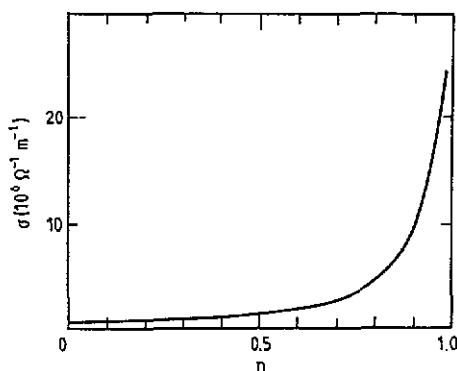**Figure 6.** Electronic density of states $g(E)$ for the ordered alloy (see text for details).

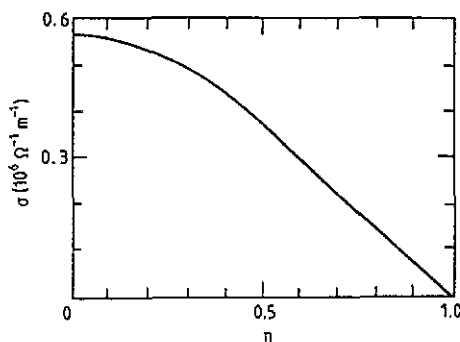**Figure 7.** Dependence of alloy conductivity σ on LRO parameter η ($z = 0.8$).

Figure 8. Dependence of alloy conductivity σ on LRO parameter η ($z = 0.5$).

The parameters W and R_0 are determined as in (33). The wavevector k changes in the range of the first Brillouin zone of the ordered alloy (k_m is the radius of the Brillouin sphere). The appearance of the constant term $S(k_m)$ in (48) is caused by the choice of the energy origin in the centre of the pure metal band.

The results of numerical calculation of the alloy conductivity (27) are presented in table 2. The alloy conductivity in the single-site approximation is denoted by $\sigma^{(1)}$ and σ is the conductivity obtained taking account of scattering by pairs of atoms. The calculation is carried out for different values of the LRO parameter η and of the pair correlation parameter for the first coordination sphere, ε_0^{12}. The scattering parameter $\delta = -0.5$ and $y = 0.5$. The results of the calculations for two values of the electron concentration, i.e. for $z = 0.9$ (the Fermi level is outside of the gap near the upper edge of the band) and $z = 0.5$ (the Fermi level is in the centre of the gap), are presented in table 2. As follows from the results obtained, it is possible to neglect the contribution of scattering by pairs of atoms to the conductivity of disordered ($\eta = 0$, $\varepsilon_0^{12} = 0$) and almost completely ordered ($\eta \simeq 1$) alloys. However, this contribution may be considerable for partially ordered alloys ($\eta \sim 0.5$).

5. Discussion

We have considered the corrections to the electronic density of states and the conductivity of alloys arising from electron scattering by pairs of atoms and the statistical correlations caused
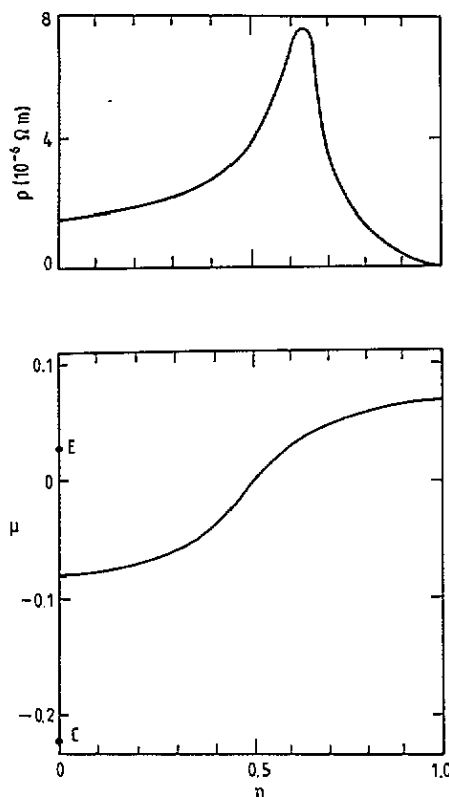
Figure 9. Dependence of alloy residual specific resistance ρ on LRO parameter η ($z = 0.6$).

Table 2. Contribution of pairs to the conductivity of ordered alloys.

	η	0	0	0	0.4	0.98
	ε_0^{12}	0	-0.05	-0.08	-0.1	0
$Z = 0.9$	$\sigma^{(1)}$ ($10^6\ \Omega^{-1}\ m^{-1}$)	0.337	0.337	0.337	0.389	1.63
	σ ($10^6\ \Omega^{-1}\ m^{-1}$)	0.340	0.359	0.377	0.471	1.63
$Z = 0.5$	$\sigma^{(1)}$ ($10^6\ \Omega^{-1}\ m^{-1}$)	0.543	0.543	0.543	0.433	0.347×10^{-2}
	σ ($10^6\ \Omega^{-1}\ m^{-1}$)	0.549	0.474	0.430	0.254	0.343×10^{-2}

by SRO and LRO. These corrections can lead to an essential change in the electronic spectrum and a corresponding change in behaviour of the conductivity owing to the formation of a dip or gap in the density of states.

It has been shown that SRO in the first coordination sphere ($\alpha_1 < 0$) can lead to an increase or decrease in the conductivity depending on the electron concentration, i.e., in fact, on the position of the Fermi level with respect to the dip formed in the electronic density of states and caused by SRO. This dip increases with increase of SRO, showing a tendency to form a gap in the density of states if LRO comes into being.

In the case of weak scattering ($|\delta|/w_A \ll 1$) the appearance of LRO leads to the formation of a true gap in the electronic density of states of width $\eta|\delta|$ (in the alloy model considered). Again the behaviour of the conductivity depends critically on the position of the Fermi level

with respect to the gap in the spectrum (see (46) and (47)). In particular, the Smirnov law [11] (decreasing resistivity during ordering) is obtained. When the Fermi level falls within a range of energy where the density of states is zero, the conductivity, of course, vanishes.

A more complicated situation arises when the electron scattering is not small. Then, at $\delta/w_A = -0.5$ and $y = 0.5$, numerical calculation shows the existence of a non-zero density of states in the range of energies corresponding to the Brillouin zone boundary of the partially ordered alloy (see figure 6(a)). A true gap appears in the considered model only at nearly complete order. The corresponding behaviour of conductivity is shown in figures 7–9.

The nature of the electronic states as well as the range of applicability of the theory developed may be established by means of a study of the behaviour of parameters γ (32) depending on alloy parameters. We consider the inequality $\gamma < \frac{1}{2}$ as the condition for the given theory to be valid and as the condition for the electronic states to be extended (not localized).

Let us first evaluate the parameter γ at $\eta = 0$. As shown in [8], the supposition of the existence of a single pole $k_0 = k_0' + i k_0''$ of the Green function $\tilde{G}_k$ in the upper half-plane of complex values of k leads to the expression

$$\tilde{G}_{0m} = \frac{e^{ik_0 r_m}}{k_0 r_m} \operatorname{Im} \tilde{G}_{00} \qquad (k_0' \gg k_0''). \tag{49}$$

It follows from (49) that the values of parameter γ (32) do not exceed the quantity

$$\gamma = xy \left| \sum_{m \neq 0} (a_m)^2 \right| = xy |(\tau_B - \tau_A)^2 [(\tilde{G}^2)_{00} - (\tilde{G}_{00})^2]|. \tag{50}$$

In accord with (49) the terms of the sum in (50) decrease with increase of the distance between the lattice sites as

$$\exp(-2k_0'' r_m)/|k_0 r_m|^2 \qquad k_0'' > 0.$$

Taking into consideration that $k_0'' \sim \operatorname{Im} \sigma$ and the relation following from condition (24) (see also [13])

$$[1 + xy|\tau_B - \tau_A|^2 |\tilde{G}_{00}|^2] \operatorname{Im} \sigma = xy|\tau_B - \tau_A|^2 \operatorname{Im} \tilde{G}_{00}$$

one may arrive at the conclusion that on the edges of the energy band (where $g(E) \sim \operatorname{Im} \tilde{G}_{00} \to 0$) the value of the parameter γ (50) is essentially larger than in the middle of the band.

For more precise evaluation of the parameter γ, let us transform (50) using the evident identity

$$-\left(1 - \frac{d\sigma}{dE}\right)^{-1} \frac{d\tilde{G}_{00}}{dE} = (\tilde{G}^2)_{00} \tag{51}$$

and also the relation

$$\frac{d\sigma}{dE} = \frac{\langle \tau_n^2 \rangle}{1 + \langle \tau_n^2 \rangle (\tilde{G}_{00})^2} \frac{d\tilde{G}_{00}}{dE} \tag{52}$$

obtained by differentiation of equation (24). Substituting (51) and (52) into (50) we obtain

$$\gamma = |P/(1 + P)|$$

$$P = -\frac{\langle \tau_n^2 \rangle}{1 + \langle \tau_n^2 \rangle (\tilde{G}_{00})^2} \left(\frac{1}{1 + \langle \tau_n^2 \rangle (\tilde{G}_{00})^2} \frac{d\tilde{G}_{00}}{dE} + (\tilde{G}_{00})^2 \right) \qquad (53)$$

The energy band edges correspond to the extremum points of the dispersion law $h(k)$, which may be represented in the vicinity of these points by a parabolic dependence for cubic crystals

$$h(k) = w + pk^2 \qquad w = \text{constant} \qquad p = \text{constant}.$$

Taking into account also the fact that, on the edge of the energy band (at $E \to E_l$), $\text{Im}\,\sigma \to 0$, equation (25) in the range of energy values near band edges may be solved analytically. As a result, it is possible to show that the derivative of the imaginary part of the Green function $\tilde{G}_{00}$ (and outside of the energy band, the derivative of the real part of $\tilde{G}_{00}$) with respect to energy tends to infinity at $E \to E_l$ as $(E - E_l)^{-1/2}$. Owing to this, parameter $\gamma(E)$ (53) on the edge of the energy band at $E \to E_l$ approaches its maximum value, which is equal to 1. In the energy range where $\frac{1}{2} \leqslant \gamma(E) \leqslant 1$, the cluster expansion of the scattering T-matrix converges badly. Thus the expressions for alloy conductivity obtained in the given work cannot be applied in the case when the value of the Fermi level μ falls within the mentioned range. However, the magnitude of this energy interval ΔE is insignificant with respect to the energy band width, and is determined for the energy band model (33) by the expressions:

$$\frac{|\Delta E|}{|W|} = \begin{cases} \dfrac{3}{(8\pi)^2} y^2 (1 - y)^2 \left(\dfrac{\delta}{W} \right)^4 \left(\dfrac{\Omega_0}{R_0^3} \right)^2 & \text{at } |\delta|/|W| \ll 1 \\[3mm] \dfrac{3}{(8\pi)^2} y^2 \left(\dfrac{\tilde{\delta}}{W} \right)^4 \left(\dfrac{\Omega_0}{R_0^3} \right)^2, \tilde{\delta} = \dfrac{\delta}{1 - \delta/W} & \text{at } y \ll 1, \dfrac{y}{1 - \delta/W} \ll 1. \end{cases}$$

For the alloy parameters that were used above, the value $|\Delta E|/|W| \sim 5 \times 10^{-4}$.

Numerical calculation of the parameter $\gamma(E)$ (32) shows that its values do not exceed 0.05 in the whole energy range, with the exception of the above-mentioned energy ranges on the edges of the band.

The arising of the gap in the electronic spectrum during ordering leads to the formation of new edges of the band where the parameter γ may not be small. The width of the corresponding energy intervals $\Delta E(\eta)$ may be evaluated at small value of LRO parameter η with the aid of (53). It has the form

$$\left| \frac{\Delta E(\eta)}{W} \right| = \left[y(1 - y) \left(\frac{\delta}{W} \right)^2 \right]^{2/3} \left(\eta \left| \frac{\delta}{W} \right| \right)^{1/3} \qquad y|\delta/W| \ll 1, \eta \ll 1. \qquad (54)$$

We should recall that in the model considered in section 4 the true gap at not very great η arises only in the case of weak scattering. Thus the results of section 4 for small η and small scattering are valied only outside of the interval $\Delta E(\eta)$ (54). In particular, at $\eta \leqslant 2\sqrt{2} y(1 - y)|\delta|/W$ the half-width of the gap is $\frac{1}{2}\eta|\delta| \leqslant \Delta E(\eta)$ and we cannot

say anything about the arising of a gap and the behaviour of the conductivity when μ falls within the region of the gap.

Experimental study of the influence of ordering on alloy conductivity has been performed in a number of works [11]. Most of them deal with the cases when the behaviour of the residual resistance obeys Smirnov's law, i.e. resistance decreases with ordering of an alloy.

However, the behaviour of the residual resistance in some cases exhibits more complicated character [18–20]. A non-monotonic dependence of the residual resistance on the annealing temperature was revealed in $CuAu_3$ alloys [18] near the point $T_c = 200\,°C$, which corresponds to the temperature of the order–disorder transition (figure 10). Taking into account that the Fermi level of this alloy is situated near a gap arising at ordering in the s band, it is natural to assume that such a behaviour of the alloy resistance is caused by a change in the electronic spectrum. Numerical calculation for the model alloy corresponding to this case is presented in figure 9. A similar behaviour of the resistance has been revaled in Co+72 at.% Fe alloy near $T_c = 300\,°C$ [19] and in Fe+25.5 at.%. Al alloy [20]. From the point of view considered it is interesting that the temperature dependence of the resistance of Cr–Al alloys shows semiconductor properties at concentration ~ 23.5 at.% Al and metallic ones at other concentrations of Al [21].
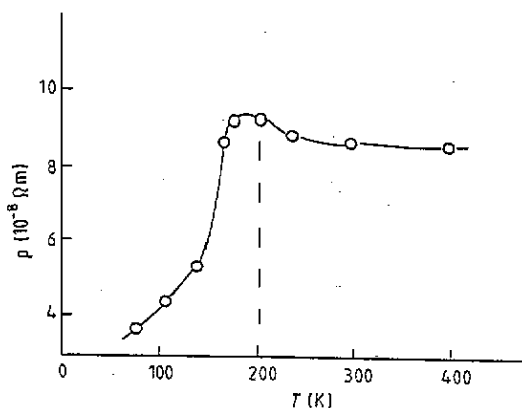

Figure 10. Dependence of residual specific resistance of $CuAu_3$ alloy on annealing temperature.

The experimental results presented cannot serve, of course, as authentic confirmation of the effects theoretically studied in the given work. In particular, it is necessary to determine experimentally SRO and LRO parameters as well as the conductivity of the alloy under consideration. On the other hand, to compare the theory developed in this paper with the experimental data, one will perhaps need to use the real electronic spectrum (in this work model spectra of the types (33), (40) and (48) have been used) and to extend the theory to the case of a two-band model. We hope to realize this in subsequent publications.

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