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The Theory of the Electrical Resistivity of Ordered Alloys

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The residual electrical resistivity of binary ordered alloys is examined in light of the many electron theory. It has been shown that the relation between the resistivity and the composition of the alloy and the degree of order is the same as in the one electron approximation. The correlation in alloys has also been calculated.

1. INTRODUCTION

THE quantum mechanical theory of the residual resistivity of disordered alloys was developed by Nordheim[1]. The theory of the residual resistivity of ordered solid solutions was constructed by Smirnov[2] for the general case of binary alloys of different structure, of arbitrary composition and degree of distant order. This article also explains the observations of the experimental dependence of the residual resistivity ρ_0 on the composition of the alloy and the degree of distant order. In the calculation of ρ_0 in references 1 and 2, two basic simplifying assumptions were made. In the first place, it was assumed that the absolute value of the difference $(V_A - V_B)$ of energies of interaction of valence electrons with the atoms of an alloy of the first and second type was sufficiently small. In the second place, it was assumed that the problem could be solved by the one electron approximation, i.e., the real system of interacting electrons could be replaced by a system of noninteracting electrons, moving in a potential field that is created by the ionic crystal lattices of the metal and by the remaining electrons.

The first of the indicated assumptions apparently is satisfied with sufficient exactness for many alloys. However, as has been noted repeatedly, the solution of the many electron problem with the help of the one electron approximation does not appear to have a theoretical basis in the case of metals. Among the results of theoretical examinations, some electronic properties of metals (for example, the possibility of passing electrons through an ideal crystal lattice without scattering, the appearance of the optical dispersion formula of metals) agree in the many electron and in the one electron theories[3,4]. In the present article, it is shown that the results in references 1 and 2, for the dependence of the residual resistivity upon the composition of the alloy and the degree of the order, are preserved also in the many electron theory, if only the assumption about the smallness of $(V_A - V_B)$ is used.

In articles 1 and 2, in calculating ρ_0, the coupling between the filling up of the various sites of a crystal lattice by atoms of the alloy was not taken into account, i.e., it was assumed that the atoms of the alloy are in a disordered distribution at the sites of a sublattice of the given type. In the particular cases of alloys with simple cubic lattices of stoichiometric systems, the coupling was studied with the help of the one electron approximation[5]. In the present article, formulas are developed for the residual resistivity, taking correlations into account; these are suitable for alloys of various structures and arbitrary composition.

2. DETERMINATION OF THE PROBABILITIES OF QUANTUM TRANSITIONS OF ELECTRONS FOR CONDUCTION UNDER THE ACTION OF DISORDER IN THE LOCATION OF THE ATOMS

We examine the binary ordered alloys A-B with the Brava-type crystal lattice having two types of sites in a well-ordered structure. Let us assume that this alloy was annealed at some temperature, as a result of which some equilibrium distribution of the atoms A and B at the junctions of the crystal lattice was established. Let us examine the electrical resistivity of this alloy, which has been quickly quenched to such a low temperature that the effect of the vibrations of the crystal lattice of the alloy on the movement of the electrons is negligibly small, so that one can assume that the ions are attached to the lattice sites.

For the identification of the stationary states of the system, strictly speaking, we should have

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solved the Schrödinger equation for all the electrons of the metal in the field of all the nuclei. Since, however, the inner electrons of the ions of the metal are bound considerably stronger than the valence electrons, and since they exist in discrete energy levels, it is possible to use the adiabatic assumption. According to this assumption, one can study the motion of the strongly bound electrons for given coordinates $\mathbf{r}_i$ of the conducting electrons. Afterwards, it is necessary to include this energy of the strongly bound electrons, which depends on $\mathbf{r}_i$, as a term in the potential energy of the conducting electrons. It is not possible to take the strongly bound electrons into account otherwise. In this case, we mean by strongly bound electrons, electrons lying in such deep electron shells of alloy atoms that the shells are practically unpolarized. All the remaining electrons refer to conduction electrons. This separation of valence electrons into a discrete subsystem is necessary so that it will be possible to formulate for just these electrons the smallness condition for the difference in interaction energy of the electrons with the ions in the lattice of different kinds:

$$|V_A - V_B| \sim \xi. \qquad (1)$$

Here the smallness of the parameter ξ implies that the solutions of the Schrödinger equation with the potential energies V_A and V_B differ by a small amount. The equation for a stationary system of N_e valence electrons in the field of the alloy ions has the form:

$$\left[-\frac{\hbar^2}{2m}\sum_i \Delta_i + \sum_i V(\mathbf{r}_i) + \sum_{i<k} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_k|}\right] \qquad (2)$$

$$\times\ \psi_n(\ldots \mathbf{r}_i \ldots) = E_n\psi_n(\ldots \mathbf{r}_i \ldots),$$

where $-\frac{\hbar^2}{2m}\Delta_i$ is the kinetic energy operator for the ith electron, $V(\mathbf{r}_i)$ is the potential energy of the ith electron in the field of the ions. As a zeroth approximation, as is customary[1,2], we shall take the state of the system of electrons, which are in the field of the completely ordered crystal lattice, consisting of effective ions. In this state, each effective ion creates a potential equal to average potential of the ions and alloy, occurring at the site of the given type. The perturbing function of the zeroth approximation is determined from the equation

$$\left[-\frac{\hbar^2}{2m}\sum_i \Delta_i + \sum_i \overline{V}(\mathbf{r}_i) + \sum_{i<k} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_k|}\right] \qquad (3)$$

$$\times\ \psi_n^0(\ldots \mathbf{r}_i \ldots) = E_n^0\psi_n^0(\ldots \mathbf{r}_i \ldots).$$

Equation (3) describes the motion of the system of electrons in the region of the periodic field $\overline{V}(\mathbf{r}_i)$, creating the effective ions. Using only the properties of the symmetric transformations, it is possible, as is known, to reduce the solution of Eq. (3) to the following form:

$$\psi_n^0(\ldots \mathbf{r}_i \ldots) \qquad (4)$$

$$= \sum_P (-1)^P P \exp\left[i \sum_{i=1}^{N_e} \mathbf{k}_i\mathbf{r}_i\right] u_n(\ldots \mathbf{r}_i \ldots),$$

where

$$P\exp\left[i \sum_{i=1}^{N_e} \mathbf{k}_i\mathbf{r}_i\right] u_n(\ldots \mathbf{r}_i \ldots)$$

results from the function

$\exp\left[i \sum_{i=1}^{N_e} \mathbf{k}_i\mathbf{r}_i\right] u_n(\ldots \mathbf{r}_i \ldots)$ by means of some permutations of position coordinates, $\sum_P$ denotes the summation over all permutations, and $(-1)^P$ equals $+1$ for an even number of transformations, corresponding to a given permutation, and equals -1 if the number of transformations is odd. The function $u_n(\ldots \mathbf{r}_i \ldots)$ remains unchanged for a displacement of all the electrons by the lattice constant a:

$$u_n(\ldots \mathbf{r}_i + \mathbf{a} \ldots) = u_n(\ldots \mathbf{r}_i \ldots). \qquad (5)$$

under the action of the perturbation energy

$$V'(\mathbf{r}_1 \ldots \mathbf{r}_{N_e}) = \sum_{i=1}^{N_e} [V(\mathbf{r}_i) - \overline{V}(\mathbf{r}_i)] \qquad (6)$$

the system can change from ψ_n^0 to another state, that is described by the wave function

$$\psi_m^0(\ldots \mathbf{r}_i \ldots) \qquad (7)$$

$$= \sum_P (-1)^P P \exp\left[i \sum_{i=1}^{N_e} \mathbf{k}_i'\mathbf{r}_i\right] u_m(\ldots \mathbf{r}_i \ldots).$$

The probability of this transition is proportional to the square of the modulus of the matrix element

$$V'_{nm} = \int \psi_n^{0*} V' \psi_m^0 d\tau_1 \ldots d\tau_{N_e} \qquad (8)$$

$$= \sum_{i=1}^{N_e} \int \Phi_{nm}(\mathbf{r}_i)\, \Delta V(\mathbf{r}_i)\, d\tau_i,$$

where

$$\Delta V(\mathbf{r}_i) = V(\mathbf{r}_i) - \overline{V}(\mathbf{r}_i), \tag{9}$$

$$\Phi_{nm}(\mathbf{r}_i) = \int \psi_n^{0*}(\mathbf{r}_1 \ldots \mathbf{r}_{N_e})\, \psi_m^0(\mathbf{r}_1 \ldots \mathbf{r}_{N_e}) \tag{10}$$

$$d\tau_1 \ldots d\tau_{i-1} d\tau_{i+1} \ldots d\tau_{N_e}.$$

Owing to the symmetry properties of the wave functions of the system relative to the periodic coordinates of the different electrons, the form of the function $\Phi_{nm}(\mathbf{r}_i)$ is not dependent upon the number i. Using Eq. (4) and the cyclic conditions, it is easy to see that

$$\Phi_{nm}(\mathbf{r} + \mathbf{a}) = e^{i\mathbf{q}\mathbf{a}}\Phi_{nm}(\mathbf{r}), \tag{11}$$

where

$$\mathbf{q} = \sum_i (\mathbf{k}_i' - \mathbf{k}_i).$$

Consequently, it is possible to introduce $\Phi_{nm}(\mathbf{r})$ in the form

$$\Phi_{nm}(\mathbf{r}) = e^{i\mathbf{q}\mathbf{r}} U_{nm}(\mathbf{r}), \tag{12}$$

where $U_{nm}(\mathbf{r})$ is a periodic function with period $\mathbf{a}$.

The potential energy of the ith electron $V(\mathbf{r}_i)$, as also in references 1 and 2, can be introduced in the form of a sum of potential energies which are formed by the separate ions of the alloy,

$$V(\mathbf{r}_i) = \sum_{s\chi} V^{\chi s}(\mathbf{r}_i - \mathbf{R}_s - \mathbf{h}_\chi), \tag{13}$$

where $\mathbf{R}_s$ denotes the vector drawn to the first site of the sth crystal cell, $\mathbf{h}_\chi$ is the vector, leading from the first site of the cell to the site of number χ of this cell, $V^{\chi s}$ is the potential energy of the electron in the field of the ion, occurring at the site of number χ of the sth cell, equaling V_A or V_B respectively, if atom A or B exists at this site. The summation in Eq. (13) is carried over all the sites of the crystal lattice of the alloy. The average of the potential energy $V(\mathbf{r}_i)$ equals

$$\overline{V}(\mathbf{r}_i) = \sum_{s\chi} \overline{V}^{\chi}(\mathbf{r}_i - \mathbf{R}_s - \mathbf{h}_\chi), \tag{14}$$

where $\overline{V}^{\chi}$ is the potential energy of the electron in the field of the effective ion, denoted by the site number χ. This energy is not related to the number of the cell s.

Substituting in Eq. (8) the Eqs. (12), (9), (13), and (14) and making in each term the change of variables

$$\mathbf{r}_i - \mathbf{R}_s - \mathbf{h}_\chi \to \mathbf{r}_i,$$

we obtain

$$V'_{nm} = N_e \sum_{s\chi} \exp\{i\mathbf{q}\mathbf{R}_{s\chi}\}\,(V^{\chi s}_{nm} - \overline{V}^{\chi}_{nm}). \tag{15}$$

Here

$$V^{\chi s}_{nm} = \int \exp\{i\mathbf{q}\mathbf{r}_i'\}\, V^{\chi s}(\mathbf{r}_i') \times U_{nm}(\mathbf{r}_i' + \mathbf{h}_\chi)\, d\tau_i', \tag{16}$$

$$\overline{V}^{\chi}_{nm} = \int \exp\{i\mathbf{q}\mathbf{r}_i'\}\, \overline{V}^{\chi}(\mathbf{r}_i') \times U_{nm}(\mathbf{r}_i' + \mathbf{h}_\chi)\, d\tau_i', \tag{17}$$

$\mathbf{R}_{s\chi} = \mathbf{R}_s + \mathbf{h}_\chi$ is the radius vector of the site of number χ of the sth cell, $V^{\chi s}_{nm}$ equals $V_{\mathrm{A}nm}$ or $V_{\mathrm{B}nm}$ depending on which atom occurs at the given site.

The square modulus of the matrix element $|V'_{nm}|^2$ on the basis of Eq. (15), equals

$$|V'_{nm}|^2 = N_e^2 \Big\{ \sum_{\chi s} (V^{\chi s}_{nm} - \overline{V}^{\chi}_{nm}) \times (V^{\chi s *}_{nm} - \overline{V}^{\chi *}_{nm}) + \sum_{\chi s \neq \chi' s'} \exp\{i\mathbf{q}(\mathbf{R}_{\chi s} - \mathbf{R}_{\chi' s'})\}\,(V^{\chi s}_{nm} - \overline{V}^{\chi}_{nm}) \times (V^{\chi' s' *}_{nm} - \overline{V}^{\chi' *}_{nm})\Big\}. \tag{18}$$

The first sum in Eq. (18) specifies the residual resistivity of the alloy in which there is the absence of coupling. This is the form of the sum calculated by Smirnov[2]. From this the following results have been obtained:

$$\sum_{\chi s} (V^{\chi s}_{mn} - \overline{V}^{\chi}_{nm})(V^{\chi s *}_{nm} - \overline{V}^{\chi *}_{nm}) = N' \Big[p_{\mathrm{A}}^{(1)} p_{\mathrm{B}}^{(1)} \sum_{\chi_1 = 1}^{\lambda_1} \Delta^{\chi_1}_{nm} + p_{\mathrm{A}}^{(2)} p_{\mathrm{B}}^{(2)} \sum_{\chi_2 = 1}^{\lambda_2} \Delta^{\chi_2}_{nm} \Big]. \tag{19}$$

Here

$$\Delta^{\chi j}_{nm} = |V^{\chi j}_{\mathrm{A}nm} - V^{\chi j}_{\mathrm{B}nm}|^2 \tag{20}$$

$$= \left| \int e^{i\mathbf{qr}} \left[V_{\mathrm{A}}(\mathbf{r}) - V_{\mathrm{B}}(\mathbf{r}) \right] U_{nm} (\mathbf{r} + \mathbf{h}_{\chi_j})\, d\tau \right|^2,$$

$p_{\alpha}^{(j)}$ is the substitution probability of a site of the jth kind by an atom α ($j = 1,2$; $\alpha = \mathrm{A,B}$), χ_j is the number of the site of the jth kind, and N' is the number of cells in the crystal lattice. The function $U_{nm}(\mathbf{r} + \mathbf{h}_{\chi_j})$ is different from $U_{nm}(\mathbf{r})$ by the order of magnitude of $|V_{\mathrm{A}} - V_{\mathrm{B}}|$. Therefore, as also in reference 2, the terms of all the $\Delta_{nm}^{\chi_j}$ are mutually equal

$$\Delta_{nm}^{\chi_1} \approx \Delta_{nm}^{\chi_2} \approx \Delta_{nm}. \tag{21}$$

correct to the cubic terms in $V_{\mathrm{A}} - V_{\mathrm{B}}$. Then Eq. (19) can be converted to the form:

$$\sum_{\chi s} (V_{nm}^{\chi s} - \overline{V}_{nm}^{\chi})(V_{nm}^{\chi s *} - \overline{V}_{nm}^{\chi *}) \tag{22}$$

$$= N\Delta_{nm} \left[c_1 c_2 - \frac{\nu}{1-\nu} \gamma^2 \eta^2 \right],$$

as was also done in reference 2. Here N is the number of sites of the crystal lattice of the alloy, c_1 and c_2 are the relative atomic concentrations of atom A and B in the alloy ($c_1 + c_2 = 1$), $\eta = (p_{\mathrm{A}}^{(1)} - c_1)/\gamma$ is the degree of distant order, ν is the ratio of the number of sites of the first kind to the total number of sites:

$$\gamma = \begin{cases} \dfrac{1-\nu}{\nu} c_1 & \text{where} \quad c_1 \leqslant \nu, \\ c_2 & \text{where} \quad c_1 \geqslant \nu. \end{cases} \tag{23}$$

The second sum in Eq. (18) equals zero, if coupling exists in the alloy [2]. If it is assumed that the coupling in the alloy is small, then it is possible, when computing this sum, to restrict the coupling parameter* to the linear terms. Therefore, we retain in the indicated sum only those terms that correspond to nearest neighbors. The remaining terms contain terms of a higher degree of smallness relative to the coupling parameter. Under these assumptions, the unknown sum can be put into the form:

$$\sum_{\chi s \neq \chi' s'} \exp \{ i\mathbf{q} (\mathbf{R}_{\chi s} - \mathbf{R}_{\chi' s'}) \} \tag{24}$$

$$\times \quad (V_{nm}^{\chi s} - \overline{V_{nm}^{\chi}})(V_{nm}^{\chi' s' *} - V_{nm}^{\chi' *})$$

$$\approx \sum_{k=1}^{z} \exp \{ i\mathbf{q}\delta\mathbf{R}_k \} \sum_{\chi s} (\overline{V_{nm}^{\chi s} V_{nm}^{\chi' s' *}} - \overline{V_{nm}^{\chi}}\, \overline{V_{nm}^{\chi' *}}).$$

Here the summation over χs, $\chi' s'$ is divided into a sum in which $\delta\mathbf{R}_k = \mathbf{R}_{\chi s} - \mathbf{R}_{\chi' s'}$ is constant. The summation over k is carried over all z nearest neighbors of a given site χs. At this site $\chi' s'$ is determined by the assignment of χs and k. The sum

$$\sum_{s} (\overline{V_{nm}^{\chi s} V_{nm}^{\chi' s' *}} - \overline{V_{nm}^{\chi}}\, \overline{V_{nm}^{\chi' *}})$$

depends only upon the kind of site χ and χ'. Introducing the probability $p_{\alpha\beta}^{(jl)}$ of the displacement of neighboring sites of type j and l ($j,l = 1,2$) to atoms α and β respectively, ($\alpha,\beta = \mathrm{A,B}$), the indicated sum can be transformed to the form:

$$\sum_{s} (\overline{V_{nm}^{\chi s} V_{nm}^{\chi' s' *}} - \overline{V_{nm}^{\chi}}\, \overline{V_{nm}^{\chi' *}}) \tag{25}$$

$$= N' \Big[p_{\mathrm{AA}}^{(jl)} V_{\mathrm{A}nm}^{\chi_j} V_{\mathrm{A}nm}^{\chi'_l *} + p_{\mathrm{AB}}^{(jl)} V_{\mathrm{A}nm}^{\chi_j} V_{\mathrm{B}nm}^{\chi'_l *}$$

$$+ p_{\mathrm{BA}}^{(jl)} V_{\mathrm{B}nm}^{\chi_j} V_{\mathrm{A}nm}^{\chi'_l *} + p_{\mathrm{BB}}^{(jl)} V_{\mathrm{B}nm}^{\chi_j} V_{\mathrm{B}nm}^{\chi'_l *}$$

$$- \left(p_{\mathrm{A}}^{(j)} V_{\mathrm{A}nm}^{\chi_j} + p_{\mathrm{B}}^{(j)} V_{\mathrm{B}nm}^{\chi_j} \right)$$

$$\left(p_{\mathrm{A}}^{(l)} V_{\mathrm{A}nm}^{\chi'_l *} + p_{\mathrm{B}}^{(l)} V_{\mathrm{B}nm}^{\chi'_l *} \right) \Big].$$

Here it is understood that the site numbers χ and χ' refer, respectively, to sites of the type j and l. By introducing the values ϵ^{jl}, which are determined by the relation

$$\varepsilon^{jl} = p_{\mathrm{AB}}^{(jl)} - p_{\mathrm{A}}^{(j)} p_{\mathrm{B}}^{(l)} = p_{\mathrm{BA}}^{(jl)} - p_{\mathrm{B}}^{(j)} p_{\mathrm{A}}^{(l)} \tag{26}$$

$$= -\left(p_{\mathrm{AA}}^{(jl)} - p_{\mathrm{A}}^{(j)} p_{\mathrm{A}}^{(l)}\right) = -\left(p_{\mathrm{BB}}^{(jl)} - p_{\mathrm{B}}^{(j)} p_{\mathrm{B}}^{(l)}\right),$$

Eq. (25) takes on the simpler form:

$$\sum_{s} (\overline{V_{nm}^{\chi s} V_{nm}^{\chi' s' *}} - \overline{V_{nm}^{\chi'}}\, \overline{V_{nm}^{\chi' *}}) \tag{27}$$

$$= -N' \varepsilon^{jl} \left(V_{\mathrm{A}nm}^{\chi_j} - V_{\mathrm{B}nm}^{\chi_j} \right)$$

$$\left(V_{\mathrm{A}nm}^{\chi' l *} - V_{\mathrm{B}nm}^{\chi'_l *} \right) \approx -N' \varepsilon^{jl} \Delta_{nm}.$$

In the last equation $(V_{\mathrm{A}nm}^{\chi_j} - V_{\mathrm{B}nm}^{\chi_j}) \left(V_{\mathrm{A}nm}^{\chi'_l *} - V_{\mathrm{B}nm}^{\chi'_l *} \right)$ is replaced by Δ_{nm}, which is correct only to the third order of the $|V_{\mathrm{A}} - V_{\mathrm{B}}|$ terms. Performing

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* The coupling parameter can be chosen, for example, in the same way as in reference 6.

the summations over χ and k in Eq. (24) and taking into account Eq. (27), we obtain the following expression for Eq. (24)

$$\sum_{\chi s \neq \chi' s'} \exp \{ i\mathbf{q} \, (\mathbf{R}_{\chi s} - \mathbf{R}_{\chi' s'})\} \, (V^{\chi s}_{nm} - \overline{V^{\chi}_{nm}}) \tag{28}$$

$$(V^{\chi' s' *}_{nm} - \overline{V^{\chi' *}_{nm}}) \approx - \Big[N_1 \varepsilon^{11} \sum_{k_1=1}^{z_1} \cos \mathbf{q}\delta\mathbf{R}_{k_1}$$

$$+ \; N_2 \varepsilon^{22} \sum_{k_2=1}^{z_2} \cos \mathbf{q}\delta\mathbf{R}_{k_2}$$

$$+ \, 2N_1 \varepsilon^{12} \sum_{k_3=1}^{z_3} \cos \mathbf{q}\delta\mathbf{R}_{k_3} \Big] \Delta_{nm}.$$

Here $N_1 = \nu N$ is the number of sites of the first type, $N_2 = (1-\nu) N$ is the number of sites of the second kind, z_1 is the number of sites of the first kind, adjacent to the sites of the first kind, z_2 is the number of sites of the second kind adjacent to the sites of the second kind, and z_3 is the number of sites of the second kind adjacent to the sites of the first kind.

If q is sufficiently small, such that for all k

$$\mathbf{q}\delta\mathbf{R}_k \ll 1, \tag{29}$$

then on the basis of Eqs. (18), (22), and (28), the quadratic modulus of the matrix element $|V'_m|^2$ equals

$$|V'_{nm}|^2 = a_{nm} f(c, \eta, \varepsilon), \tag{30}$$

where

$$a_{nm} = N_e^2 N \Delta_{nm}, \tag{31}$$

$$f(c, \eta, \varepsilon) = c_1 c_2 - \frac{\nu}{1-\nu} \gamma^2 \gamma_l^2 - \nu z_1 \varepsilon^{11}$$

$$- (1-\nu) z_2 \varepsilon^{22} - 2\nu z_3 \varepsilon^{12}$$

and ϵ denotes the set of values ϵ^{11}, ϵ^{22}, and ϵ^{12}. Here the coefficients, a_{nm}, correct to the terms of the highest (third) order of smallness relative to the $|V_A - V_B|$, do not depend upon c, η, and ϵ, i.e., they are single valued for all the quantum transitions. The latter case is essentially for what follows. In the case of the one electron approximation, inequalities similar to (29) are satisfied for all the quantum transitions in the case of "poor metals", i.e., of metals with a small number of valence electrons. If the number of valence electrons is large and the quantum transitions, for which the condition (29) is not fulfilled, play an essential role, then the coupling correction in Eq. (30) and (31) is too large in absolute magnitude. However, the basic contribution to the quadratic modulus of the matrix elements $|V'_{nm}|^2$ is the term (22), the calculation of which does not have a bearing on the condition (29) of small q. Therefore, without the coupling calculations in the alloy, Eq. (30) is correct for any q.

3. CALCULATION OF THE RESIDUAL RESISTIVITY

The average value of the electron current density can be determined by the equation:

$$I = \sum_{nm} w_{nm} I_{nm}, \tag{32}$$

where the series of values ω_{nm} introduces the matrix density, formulated by the wave functions ψ^0_n, which are determined by Eq. (4), and I_{nm} is the matrix element of the current density operator. In the absence of an electric field, the average electron current density equals zero, i.e.,

$$\sum_{nm} w^0_{nm} I_{nm} = 0, \tag{33}$$

where ω^0_{nm} designates the matrix density without the external field. If a large field F is applied to the metal, then the matrix element ω_{nm} can be written in the form:

$$w_{nm} = w^0_{nm} + \Delta w_{nm}, \tag{34}$$

while the average current density equals

$$I = \sum_{nm} \Delta w_{nm} I_{nm}. \tag{35}$$

The values of $\Delta\omega_{nm}$ are determined from the stationary condition, which requires

$$dw_{nm}/dt = 0. \tag{36}$$

in order that the matrix density does not change with time. Further, as in the derivation of the kinetic equation, we take into consideration the fact that the system of electrons exists in states of dynamic equilibrium, and the value of ω_{nm} change because of the presence of the field, also because of the diffusion of electrons on heterogeneities combined with an incompletely ordered distribution in an alloy of two types of atoms. The transformation of ω_{nm} per unit of time is some function of the field as a consequence of the first reason. The decomposition of this function into a power series in F does not include the zero order and can be written in the following form:

$$(\partial w_{nm}/\partial t)_{\text{field}} = \alpha_{nm}F + \ldots \qquad (37)$$

Since, according to Eqs. (30) and (31), the probabilities of any quantum transitions are proportional to the same function $f(c, \eta, \epsilon)$, then the change in ω_{nm} per unit time, connected with the heterogeneities of the alloy, is also proportional to this function:

$$(\partial w_{nm}/\partial t)_{\text{alloy}} = \lambda_{nm} f(c, \eta, \varepsilon), \qquad (38)$$

where λ_{nm} in the assumed approximation ($|V_A - V_B|$ small) does not depend upon c, η, or ϵ. The coefficients λ_{nm} appear as functions of the matrix elements of the density operator. The separation of these coefficients into a series in increments of $\Delta\omega_{pr}$ has the form:

$$\lambda_{nm} = \sum_{pr} \mu_{prnm} \Delta w_{pr} + \ldots \qquad (39)$$

Here the zeroth order term is zero, since in the absence of an electric field, Eq. (38) reduces to zero. From Eqs. (36), (37), (38), and (39), we obtain a system of equations for the determination of the values of $\Delta\omega_{pr}$:

$$f(c, \eta, \varepsilon) \sum_{p, r} \mu_{prnm} \Delta w_{pr} + \alpha_{nm}F = 0. \qquad (40)$$

Here the higher order terms of the decompositions (37) and (39) are rejected, which is justified for not too large fields, when Ohm's law is obeyed. The solution of the system of equations (40) has the form:

$$\Delta w_{pr} = c_{pr} \frac{F}{f(c, \eta, \varepsilon)}. \qquad (41)$$

Substituting the solution into Eq. (35), we obtain the final expression for the average density of electric current

$$I = \frac{F}{f(c, \eta, \varepsilon)} \sum_{nm} c_{nm} I_{nm}. \qquad (42)$$

Hence, the residual resistivity of the alloy equals

$$\rho_0 = A f(c, \eta, \varepsilon), \qquad (43)$$

where the constant A does not depend upon c, η, or ϵ.

It is evident,from Eq. (43), that the many electron theory, once the condition (29) is satisfied leads to a similar relation for the residual resistivity for a compound alloy, the degree of the distant order, and correlation in the alloy, as does the one electron approximation. According to this, the coefficient A, proportional to $|V_A - V_B|^2$ in the many electron theory, determines the same parameter as it does in the one electron theory.

Equation (31) for $f(c, \eta, \epsilon)$ takes a special form in the two cases:

1. For an inhomogeneous alloy, $\eta = 0$ and the function $f(c, \eta, \epsilon)$ equals

$$f(c, \varepsilon) = c_1 c_2 - z\varepsilon. \qquad (44)$$

Here the value of ϵ, determined by Eq. (26),is the same in an inhomogeneous alloy, for any neighboring sites, regardless of type, and z is the coordination number. The meaning of ϵ can be estimated with the aid of the statistical theory of conduction, taking into account the interaction only between nearest neighbors. According to Lifshitz[6] ϵ equals

$$\varepsilon = c_1^2 c_2^2 \frac{W}{kT}, \qquad (45)$$

correct to the quadratic terms relative to W/kT, where the energy of ordering $W = 2|v_{AB}| - |v_{AA}| - |v_{BB}|$ ($v_{\alpha\beta}$ is the energy of interaction of neighboring atoms α and β).

Equations (44) and (43), with $\epsilon = 0$, change to the corresponding equations in reference 1, not taking into account the coupling in the alloy. From the Eqs. (43), (44), and (45), it follows that the coupling (of nearest neighbors) diminishes the residual resistivity of ordered alloys ($W > 0$) and increases the residual resistivity of disordered alloys ($W < 0$). The effect of the nearest neighbor increases with a drop in the temperature T, at which the alloy was quenched. For given temperatures the coupling calculation gives a much larger correction to the electroresistivity, the nearer the composition of the alloys to the stoichiometric. We note that the correction of ρ_0, corresponding to the coupling calculation, is perhaps much too large. For example, at $c_1 = c_2 = ½$, $W/kT = 1/z$ (the temperature T is four times greater than the ordering temperature), the coupling diminishes in ordered alloys (in the case of "poor metals") by 25 per cent. (In the case of metals, in which the number of current carriers is not small, the coupling appears less influenced by the ordering). It would be interesting experiment-

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[6] I. M. Lifshitz, J. Exper. Theoret. Phys. USSR 9, 481 (1939)

ally to find the effect of nearest neighbors on the residual resistivity of alloys and to investigate this effect at different temperatures of annealing and different systems of alloys.

It should be noted that the reduced equations (44) and (45) cease to be correct at temperatures approximating the ordering temperatures, in which case the correction term $z\epsilon$ in Eq. (44) proves to be fairly large. In this case, it is not possible to restrict oneself to the linear terms relative to W/kT. The coupling not only between near neighbors must be considered.

2. In the case of the ordered alloy, in which each site is surrounded by neighboring sites only of a different type (for example, in alloys with a volume centered cubic lattice type, β-brass, alloys with a simple cubic lattice, etc.) $\epsilon^{11} = \epsilon^{22} = 0$, $\nu = \frac{1}{2}$, $z_3 = z$ and the function $f(c, \eta, \epsilon)$ can be written in the form:

$$f(c, \eta, \varepsilon) = c_1 c_2 - \gamma^2 \eta^2 - z\varepsilon^{12}. \tag{46}$$

In this case the value of ϵ^{12} in the approximation of nearest neighbors similar to Eq. (45), is equal to

$$\varepsilon^{12} = (c_1^2 - \gamma^2\eta^2)(c_2^2 - \gamma^2\eta^2)\frac{W}{kT}. \tag{47}$$

with exactness to the quadratic terms relative to to W/kT. Equation (46) is accurate only at temperatures considerably lower than the annealing temperature, for η close to unity, when the correction $z\epsilon^{12}$ is small. If it is assumed in this equation that $\epsilon^{12} = 0$, then Eq. (43) converts to the appropriate expression of reference 2. In the general case, the expression for ρ_0 in reference 2 results from Eqs. (43) and (31) when $\epsilon^{ij} = 0$.

In conclusion, we wish express our deep thanks to Prof. A. A. Smirnov for the repeated discussions of the article and his valuable advice.

Translated by D. F. Edwards