CALCULATION OF THE RESIDUAL TRANSPORT COEFFICIENTS BY MEANS OF THE 8-OPW MODEL WITH ITERATIVE SOLUTIONS TO THE RELAXATION TIME. APPLICATION TO ALUMINUM ALLOYS

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Abstract
In this work we calculate the electrical resistivity, Hall coefficient, and magnetoresistance associated with impurities of Zn, Ga, and Ge in an Al matrix. We have selected these impurities because experimental values of these parameters reported in the literature are very different from those calculated theoretically. The details of the electronic structure of aluminum are evaluated using the 8-OPW model. The full contributions of holes and electrons are obtained separately through the Fermi integrals, which are evaluated over the Fermi integrals of a particular form of the Boltzmann equation. The transposition coefficients are defined by the Fermi integrals, which are evaluated over the Fermi surface of the pure metal, or the "solvent" matrix in the case of dilute alloys. The dependence of the transport coefficients upon the Fermi surface obliges us to use an adequate band structure model which conforms to the true curvature of that surface [5], and not usual free electron model which has had some success for metals and alloys [6,7]. The literature on this subject; see, for instance, the works by Ascroft [8] and Kesternich, [9] who incorporate the models for characterization of two and three different regions of the Fermi surface in their studies about the Hall effect. Sorbello [10] and Fukai [11] incorporate the multiple plane wave model in the study of the residual electrical resistivity of dilute alloys, and finally Sorbello [12], Pfander et al. [13], Yonemitsu et al.[14] and Kaveh et al.[15] use a 4-OPW model to study the transport properties.

I. INTRODUCTION

The study of transport coefficients plays an important role in the characterization of metals and alloys, since such coefficients generate important information about the behavior of such materials under specific condition.

The starting point of this work is the Boltzmann equation [1,2,3,4]. Through the definition of a particular form of the equilibrium distribution function, the thermal, magnetic, and electrical effects capable of changing this distribution are incorporated and the different transport coefficients are associated with this change. The transport coefficients are defined by the Fermi integrals, which are evaluated over the Fermi surface of the pure metal, or the "solvent"
The intrinsic details of evaluation are the basic differences among those papers, and their results do not always agree with experiment.

The relaxation time, which appears in the transport integrals, also has been widely treated in the literature. It is a good approximation to consider it independent of applied fields. The two traditional ways to evaluate it are the so-called Ziman approximation [16], and the Taylor recurrent method [17], which lead to results which do not differ by more than 10% from experiment if the involved region of the Fermi surface is approximately spherical. The magnitude of the relaxation time is related inversely to the average scattering power of the impurity atoms, which obliges us to make an adequate choice of the potential. The empty core local model [18] with an adjustable parameter has been the most frequently used in this kind of calculation. Noticeable differences are found in these potentials owing basically to the deformation effect [11,12,13,14]. Undoubtedly those differences must influence the magnitude of the transport coefficients. The Heine-Abarenkov type pseudopotential [19] that we use in this work has had little success in the explanation of the electrical resistivity [20] and diffusional thermoelectric power [21] in dilute Al-Zn alloys; therefore we improve the pseudopotential by parametric adjustment in order to characterize the system under study.

In this paper we present explicitly all that concerns the evaluation of the transport coefficients in metals and alloys, emphasizing the details that have not yet received enough attention in the theory. The incorporation of the finite element method in the transport integral calculations enhances the interest in the work. The organization of this paper is as follows. Chapter II is dedicated to the transport theory. In chapter III we present the details related to the 8-OPW Fermi surface and its curvature. Chapter IV deals with the relaxation time approximation and the details of the calculation of the potential. In chapter V we present the calculation methods and, finally, in chapter VI we present the results and our conclusions upon applying the method to the Al-X system with X=Zn, Ge, and Ga.

II. TRANSPORT COEFFICIENTS

This subject has been widely studied by many authors, [1,3,17] who have used the Boltzmann equation to derive the transport coefficients. In this chapter we correlate the curvature of the Fermi surface with the transport coefficients, specifically the resistivity, Hall coefficient, and transverse magnetoresistance. These coefficients are derived from Boltzmann equation using the low field approximation, where conduction electrons are elastically scattered by impurities.

We know that the current density $J$ is regulated by the effects which external fields and collisions have upon conduction electrons. Thus the electronic flux in the $i$ direction is:

$$J_i = \frac{e}{4\pi^2 \hbar} \int \frac{\partial E}{\partial k_i} \Phi \left[ \frac{\partial f_0}{\partial E} \right] d^3k$$

(1)

where $e$ is the electron charge ($e$ positive for electrons), $f_0$ is the Fermi-Dirac distribution function, and the term $-\Phi \left( \frac{\partial f_0}{\partial E} \right) = f - f_0$ represents the deviation of the electronic distribution function $f_0$. The several coefficients will be defined through $\Phi$. Assuming a relaxation time $\tau(k)$, we obtain a differential equation for $\Phi$ from the Boltzmann equation [3] given by:

$$\Phi = -e\hbar^{-1} \left[ \tau(k) \varepsilon \nabla_k E + (c \hbar)^{-1} H G \Phi \right]$$

(2)

where $\varepsilon$ is the applied electric field, $H$ is the magnetic field, and $G$ is the differential operator, $G = \nabla_k E \times \nabla_k$.

For low fields, $\Phi$ can be iteratively determined by making the assumption that the second term in (2) does not participate in the first iterative step. For the $n$-th iterative step, $\Phi_n$ becomes:

$$\Phi_n = \left[ - (c \hbar)^{-2} \tau(k) H G \right]^n \left[ -e\hbar^{-2} \tau(k) \varepsilon \nabla_k E \right]$$

(3)

so that the function $\Phi$ in (1) is defined by:

$$\Phi = \sum_n \Phi_n$$

(4)

The current density $J$ can be expanded in increasing power of $H$, which allows us to
introduce the transport coefficients for crystals of arbitrary symmetry. For certain dilute Al alloys, particularly Al-Ge, the Hall coefficient has been reported [22] to be dependent upon \( H^2 \), thus we consider an expansion of \( \mathbf{H} \) to the third power. In our case, we identify the transport coefficients through the conductivity tensor \( \mathbf{\sigma} \), which is related, under isothermal conditions, to \( J \) and \( \mathbf{E} \) by:

\[
J_i = \sum_j \sigma_{ij} E_j
\]

(5)

If we orient the magnetic field \( \mathbf{H} \) parallel to \( \mathbf{z} \) axis and consider crystals of cubic symmetry, then \( J_i \) can be written as:

\[
J_i = -\frac{e^2}{4\pi^3 \hbar^2} \int \tau(k) \left( \frac{\partial E}{\partial k_x} \right) \left( \frac{\partial \mathbf{f}_0}{\partial E} \right) \times \sum_n \left[ \left( \frac{e\tau(k)H_z}{\hbar^2} \right)^n \left( \sum_l \frac{\partial E}{\partial k_l} E_l \right) \right] d^3k
\]

(6)

Here \( G_z \) is the \( z \) component of the \( \mathbf{G} \) operator, which allows us to make the transport coefficient depend upon a curvature tensor, specifically upon the Fermi surface curvature. In chapter III we show a new way to obtain the relation between the Tsuji curvature and the \( \mathbf{G} \) operator.

For isotropic solids, \( \sigma_{ij}(H) = \sigma_{ji}(-H) \), so that the principal diagonal elements of the conductivity tensor are even functions of \( H \) and the off-diagonal elements are odd functions of \( H \). Matching equations (5) and (6), we can write:

\[
\sigma_{xx}(H) = -\frac{e^2}{4\pi^3 \hbar^2} \int \tau(k) \left( \frac{\partial E}{\partial k_x} \right) \left( \frac{\partial f_0}{\partial E} \right) \times \left[ \frac{\partial E}{\partial k_x} + \left( \frac{e\tau(k)H_z}{\hbar^2} \right)^2 \right] G_z \left( \frac{\partial E}{\partial k_x} \right) d^3k
\]

(7)

where we have used \( \sigma_{xx} = \sigma_{yy} \) and \( \sigma_{xy} = -\sigma_{yx} \). Using eqs (7) we can define our transport coefficients as follows:

a) Electrical conductivity: \( \sigma_{xx}(0) \)

b) Hall coefficient:

\[
R = \left[ \frac{\sigma_{xy}(H)}{H} \left( \sigma_{xx}^2(H) + \sigma_{xy}^2(H) \right) \right]
\]

(8)

c) Transverse magnetoresistance:

\[
\frac{\Delta \rho}{\rho(0)} = \frac{\rho_{xx}(H) - \rho_{xx}(0)}{\rho_{xx}(0)}
\]

where,

\[
\rho_{xx}(H) = \frac{\sigma_{xx}(H)}{\sigma_{xx}^2(H) + \sigma_{xy}^2(H)}
\]

Note that the quadratic terms in these equations have implicit magnetic fields up to sixth power, but in the low field approximation, we consider field terms only power. Thus we can rewrite (7) as:

\[
\sigma_{xx}(H) = Y_0 + Y_1 H^2
\]

(9)

\[
\sigma_{xy}(H) = H \left( T_0 + T_1 H^2 \right)
\]
with

\[ Y_0 = -\frac{e^2}{4\pi^2\hbar^2} \int \tau(k) \left( \frac{\partial E}{\partial k_x} \right)^2 \left( \frac{\partial f_0}{\partial E} \right) d^3k \]

\[ Y_1 = -\frac{e^2}{4\pi^2\hbar^2} \int \tau(k) \left( \frac{\partial E}{\partial k_x} \right) \left( \frac{\partial f_0}{\partial E} \right) \left( \frac{e\tau(k)}{\hbar^2} \right)^2 \times \]

\[ G \left( \frac{\partial E}{\partial k_x} \right) d^3k \]

(10)

\[ \sigma_{xx}(0) = Y_0 \]

\[ R = \frac{T_0}{Y_0^2} + (HY_0)^2 \left( \frac{T_1}{T_0} - \frac{T_3}{T_0} - 2 \frac{T_0 Y_1}{Y_0^5} \right) \]

(11)

where the terms between brackets for \( R \) and \( \Delta \rho/\rho(0) \) correspond to the coefficient \( R_2 \) and \( P_1 \) in the paper by Boning et al. [22], and to the magnetoresistance in the Kestemich paper [9].

II.1. TRANSPORT COEFFICIENTS IN THE TWO-BAND MODEL

In this section we are going to combine individual transport coefficient of holes and electrons to obtain the measurable value of those coefficients. We group the contributions of the holes and electrons in two different bands that overlap. Let \( J^e \) and \( J^h \) be the current densities for electrons and holes in each band. The total current density is:

\[ J = J^e + J^h \]

(12)

II.1.1. ELECTRICAL CONDUCTIVITY

For an electric field in the \( x \) direction, we have:

\[ J = J^e + J^h = \left( \sigma^e_{xx} + \sigma^h_{xx} \right) \varepsilon \]

such that:

\[ \sigma_{xx} = \left( \sigma^e_{xx} + \sigma^h_{xx} \right) \]

(13)

This implies a parallel equivalent circuit between the bands. Note that in the case of a single band and two scattering processes, the equivalent circuit is in series, as is established by Mathiessen’s law.

II 1.2. HALL EFFECT

Let \( \varepsilon_x \) and \( \varepsilon_y \) be the components of the electric field perpendicular to the applied magnetic field. The respective current densities are defined by:

\[ j_i = \sum \sigma_{ii}^\alpha \varepsilon_t \]

(15)
with \( i.t = x, y \) and \( \alpha = e, h \).

From eqs. (12) and (15) we have:

\[
J_x = J_x^e + J_x^h = \left( \sigma_{xx}^e + \sigma_{xx}^h \right) \varepsilon_x + \left( \sigma_{xy}^e + \sigma_{xy}^h \right) \varepsilon_y
\]

\[
J_y = J_y^e + J_y^h = \left( \sigma_{xy}^e + \sigma_{xy}^h \right) \varepsilon_x + \left( \sigma_{yy}^e + \sigma_{yy}^h \right) \varepsilon_y
\]

(16)

Taking into account that \( J_y = 0 \) and, \( \sigma_{xy} = -\sigma_{yx} \), we obtained the Hall coefficient \( R_H \) :

\[
R_H = \frac{\varepsilon_y}{H J_x} = \frac{1}{H} \left[ \frac{\sigma_{xx}^e + \sigma_{xx}^h}{\left( \sigma_{xx}^e + \sigma_{xx}^h \right)^2 + \left( \sigma_{xy}^e + \sigma_{xy}^h \right)^2} \right]
\]

(17)

Let us write (17) in terms of \( R_H^e \) and \( R_H^h \):

\[
R_H^e \left[ \left( \sigma_{xx}^e \right)^2 + \left( \sigma_{xy}^e \right)^2 \right] + R_H^h \left[ \left( \sigma_{xx}^h \right)^2 + \left( \sigma_{xy}^h \right)^2 \right]
\]

\[
\left( \sigma_{xx}^e + \sigma_{xx}^h \right)^2 + \left( \sigma_{xy}^e + \sigma_{xy}^h \right)^2
\]

(18)

where:

\[
R_H^\alpha = \frac{1}{H} \left[ \frac{\sigma_{xy}^\alpha}{\left( \sigma_{xx}^\alpha \right)^2 + \left( \sigma_{xy}^\alpha \right)^2} \right]
\]

(19)

with \( \alpha = e, h \)

Applying the same considerations used to obtain (11), eqs. (18) can be written in terms of \( Y_o^\alpha, Y_1^\alpha, T_o^\alpha, \) and \( T_1^\alpha \), defined in (10); where \( \alpha = e, h \).

\[
R_H^e \left[ \frac{Y_o^e \left( Y_o^e \right)^2}{Y_o^e + Y_o^h} \right] + R_H^h \left[ \frac{Y_o^h \left( Y_o^h \right)^2}{Y_o^e + Y_o^h} \right] + 2H^2 \left( Y_o^e + Y_o^h \right)^2 \times \frac{R_H^e}{\left( Y_o^e + Y_o^h \right)^4} \left[ Y_o^e + T_o^e \right]^2 - \frac{Y_o^e}{\left( Y_o^e + Y_o^h \right)^2} \right]
\]

(20)
II.1.3. MAGNETORESISTANCE

In the same way as we obtained the previous coefficient, we have for the magnetoresistance:

$$\Delta \rho = \left( \frac{(\sigma^e_{xx} + \sigma^h_{xx})(\sigma^e_{xx}(0) + \sigma^h_{xx}(0))}{\rho(0)} \right) \left( \frac{(\sigma^e_{xy} + \sigma^h_{xy})^2}{(\sigma^e_{xy} + \sigma^h_{xy})^2 + (\sigma^e_{xy} + \sigma^h_{xy})^2} \right)$$

$$= H^2 (Y^e_o + Y^h_o)^2 \left[ \frac{Y^e_o + Y^h_o}{(Y^e_o + Y^h_o)^3} - \frac{2}{(Y^e_o + Y^h_o)^4} \right]$$

(21)

III. FERMI SURFACE

The introduction of impurities into a pure metal matrix necessarily introduces changes in the electronic density, which are reflected as a variation of the Fermi surface of the metal. For low concentrations of impurities, as in our case, we can nonetheless consider that the Fermi surface does not change significantly. Thus we use in our calculations the Fermi surface of pure aluminum. We have evaluated this Fermi surface using the method of eight orthogonalized plane waves (8-OPW). This method reproduces in detail such a surface, as well as the order parameters that involve derivatives over the Fermi surface, such as the electronic velocity and the Fermi surface curvature. The 8-OPW method is chosen because this is the minimum number of pseudoplane waves necessary to take into account the deformity effects [23]. The 8-OPW wave function \( \Psi \) is defined as a combination of eight orthogonalized plane waves, each one associated with a mode \( q_n \) of the reciprocal lattice, with normalization coefficients \( A_n \). Thus \( \Psi \) is written as:

$$|\Psi\rangle = \sum_{n=1}^{8} A_n |k - q_n\rangle$$

(22)

From the Schrödinger equation and (22) we get the secular equation

$$\det\left[ \frac{\hbar^2}{2m}(k-q_n)^2 - E_f \right] \delta_{nt} + |k - q_n| V |k - q_l| = 0$$

(23)

If we know the Fermi energy \( E_f \) and the matrix elements \( V(q_n) \), the Fermi surface can be evaluated completely. For computational purpose, (23) is written as:

$$D (k, E_f) = \det |F(k_x, k_y, k_z, E_f)|$$

(24)

where the function \( F \) means every term involved in (23). Relation (24) is evaluated by looking for the values of \( k \) which make \( D = 0 \); we require a coincidence to at least ten digits between two consecutive \( k \)'s that are solutions of (24).

III.1. FERMI CURVATURE AND FERMI VELOCITY

The Fermi surface geometry intervenes in the definition of the transport parameters through the differential operator \( C^m \) defined in (6), (7) and (10). This operator, through the electronic velocity component, \( v_i = h^{-1} \nabla_{k_i} E \), and its derivatives, allows us differential geometry to obtain the Fermi curvature [24, 25]. Let us define parametrically the wave vector \( k \) as a function of the parameters \( u \) and \( v \) as:

$$k(u,v) = \sum_{i=1}^{3} k_i (u,v) e_i$$

(25)

Also we define the average curvature \( \langle C \rangle \) of the Fermi surface in terms of the principal curvature \( C_1 \) and \( C_2 \) as:

$$\langle C \rangle = \frac{C_1 + C_2}{2} = \frac{(Ag - 2Ff + Ga)}{2P}$$

(26)
with

\[ A = k_u \cdot k_u; \quad F = k_v \cdot k_u; \quad G = k_v \cdot k_v \]
\[ a = P^{-1/2} [k_{uu} \cdot (k_u \otimes k_v)] \]
\[ f = P^{-1/2} [k_{uv} \cdot (k_u \otimes k_v)] \]
\[ g = P^{-1/2} [k_{vv} \cdot (k_u \otimes k_v)] \]
\[ P = A G - F^2 \]

We have used the following notation:

\[ k_u = \frac{\partial k}{\partial u} \quad \text{and} \quad k_{uv} = \frac{\partial^2 k}{\partial u \partial v} \]

For a surface family \( S \) \( (k_x, k_y, k_z, E) \), an adequate choice of parameter is:

\[ k_x (u,v) = k_x (u,0) = u \]
\[ k_y (u,v) = k_y (0,v) = v \]
\[ k_z (u,v) = k_z (u,v, S) \quad (27) \]

which allows to write the curvature of the surface \( S \) as a function of the first and second derivative of \( k_z \):

\[ \langle C \rangle = \frac{k_{z,yy} + \left(k_{z,x}\right)^2 + k_{z,xy} - 2k_z k_x k_z k_{x,xy}}{2 \left[ 1 + \left(k_{z,x}\right)^2 + \left(k_{z,y}\right)^2 \right]^{3/2}} \quad (28) \]

where the \( x \) and \( y \) subindexes after the comma are derivatives with respect to \( k_x \) and \( k_y \), respectively. We want to write (28) as a function of the Fermi energy; thus we use the first and second total differentials of the energy \( E(k_x, k_y, k_z) \) and of \( k_z \) \( (k_x, k_y, E) \), obtaining:

\[ k_{z,i} = - \frac{E_{z}^{-2}}{E_{z}^{-1}} [E_{z,ii} (E_{z})^2 + E_{z,zz} (E_{x})^2 - 2 E_{iz} E_{i} E_{z}] \quad (29) \]

If we substitute (29) into (28), and consider crystals of cubic symmetry, with \( E_{ij} = E_{ji} \), then:

\[ \langle C \rangle = \frac{3 [E_{xy} E_{x} E_{y} - E_{yy} (E_{x})^2]}{\left( (E_{x})^2 + (E_{y})^2 + (E_{z})^2 \right)^{3/2}} \quad (30) \]

Relation (30) represents the Tsuji formula for cubic crystals obtained in a different way \[4,26\].

The analytical dependence of the Fermi energy upon the wave vector is not known. This fact has caused the majority of investigators to use simple models where \( E(k) \) is supposed known; these models, however, as we know, do not reproduce well the complicated behavior of \( E(k) \) near the intersection of the Fermi surface with the Brillouin zone. In our case, relations (23) and (24) give all the information about the Fermi surface and can be evaluated numerically. Let us take the first and second total differential of \( D(k,E) \) and \( E(k) \); then the derivatives of the energy with respect to \( k \) are written as functions of \( D \):

\[ E_{,i} = - (D_{E})^{-1} D_{,i} \]
\[ E_{,ii} = - (D_{E})^{-2} [D_{E} D_{,ii} + D_{i} D_{,i} E_{,i} - D_{,i} D_{,i} E_{,i} + D_{,i} E D_{,i}] \]
\[ E_{,ij} = - (D_{E})^{-2} [D_{E} D_{,ij} + D_{,j} E_{,i} - D_{,j} D_{,j} E_{,i} + D_{,j} E_{,j}] \quad (31) \]

In this way the Fermi curvature is completely defined in terms of the secular equation that generates the surface, given by relation (24), their energy derivatives, given by (31), and the curvature expressions (28) and (30). In the same way the differential operator \( G \) that appear in the transport coefficients also can be written as functions of these energy derivatives:
\[ G^0_z = 1 \]
\[ G^1_z = E_y \nabla_x - E_x \nabla_y \]
\[ G^2_z = E_y (E_{yx} \nabla_x + E_{xy} \nabla_x - E_{xx} \nabla_y) - E_x \times \]
\[ (E_{yy} \nabla_x - E_{xy} \nabla_y, - E_{xy} \nabla_y) - 2 E_x E_y \nabla_{xy} \]
\[ G^3_z = (E_y \nabla_x - E_x \nabla_y) G^2_z \]

(32)

In these relations we have used:
\[ \nabla_x = \frac{\partial}{\partial k_x} \quad \text{and} \quad \nabla_{xy} = \frac{\partial^2}{\partial k_x \partial k_y} \]

**IV. ANISOTROPIC RELAXATION TIME**

**IV.1. FORMULATION**

Although the "exact" relaxation time, \( \tau (k) \), depends directly upon the applied fields [12] through the electronic distribution function, in the low field approximation \( \tau (k) \) does not depend upon the magnetic field but rather upon the direction of the electric field, which permits the electronic mean free path and the electronic velocity to be nonparallel. This relaxation field is called \( \tau^x (k) \) to emphasize its dependence upon the electric field, and can be obtained recursively [10] from the following relation:

\[ \tau^x (k) = \frac{1}{P(k,k') \, dk'} \left[ \int \tau^x (k') \, \frac{V_x (k')}{V_x (k)} \, P(k,k') \, dk' \right] \]

(33)

Here \( P(k,k') \) represents the transition probability between incident and scattered electrons with wave vectors \( k \) and \( k' \), respectively, and \( V_x \) is the component of the electronic velocity in the field direction.

In the evaluation of (33) we have taken as a first approximation the Ziman formula [16], which in an 8-OPW model is written as:

\[ \tau^{-1} (k) = \frac{C_0}{4\pi^2 \hbar} \left| \sum_{n} A_n (k) A_n' (k') S(q_{nn}) W(q_{nn}) \right|^2 \times \]

\[ \left[ \int \frac{3}{V(k)V(k')} \frac{\sum V_i (k)V_i (k')}{\nabla_k' E} \right] d\mathbf{s}' \]

(34)

where \( C_0 \) represents the initial impurity concentration, \( A_n \) are the wave function coefficients defined in (22), \( S(q_{nn}) \) is the impurity structure factor, which in our case is equal to \( 1/N \), \( W(q_{nn}) \) is the interaction potential between impurity atoms and matrix atoms, and \( q_{nn} \) is a wave vectors associated to \( k' - k + q_n - q_{n'} \), with \( q_n \) and \( q_{n'} \) equal to each of the eight wave vectors of the reciprocal lattice that participate in the 8-OPW model. The integral over all scattered \( k' \) is done over the Fermi surface.

**IV.2. PSEUDOPOTENTIAL SELECTION**

The success in obtaining goods results for the coefficients under study depends upon a proper selection of the scattering potential. For dilute alloys it has traditionally been evaluated by considering the weighted difference of the potentials of the involved elements, i.e., impurity atoms and pure matrix. Fukai [11] suggest this potential to have the form:

\[ W(q) = \frac{E_i (q) \omega_i}{E_s (q) \omega_s} w_i (q) - w_s (q) + \Delta S(q) w_s (q) \]

(35)

where the \( i \) and \( s \) subindexes refer to the impurity and matrix atoms, \( E(q) \) is the Hartree dielectric constant, \( w_j \) are the impurity and matrix pseudopotentials, and \( \Delta S(q) \) is the structural change caused by effect of the deformation produce when impurity atoms are introduced into the solvent matrix. The selection of \( w_j (q) \) is the
preferred procedure for local parametrical models, such as the Ashcroft one parameter potential, which has extensive use reported in the literature [10,11,12,27], and the point-ion model [20,21,28,29]. Recently we have applied the Cohen-Heine potential to the study of residual electrical resistivity during the clustering process [30]. One detail that has caught our attention is the difference between the pseudopotentials that are being used for the same element by different author. For this reason we propose a parametric potential determination form $w(q)$ in (35) from the potential $w_i(q)$ and $w_n(q)$ of elements considered pure, taken from the Heine-Animalu results reported by Harrison [19]. The use of these potentials in the relation (35) has been considered inadequate for the calculation of atomic properties of solids, particularly the electrical resistivity [20]; for this reason we correct the form factor of the elements under consideration, assuming a shifting of this factor by the alloying process. Our results become a modification of (35) [31], which can be rewritten as:

$$W(q) = F\left(\frac{a_1\Omega_r E_r}{\Omega_n E_n}\right) V_1(a_3q) - a_2 V_n(q) [1 - \Delta S(q)]$$

(36)

where the coefficients $a_i$ reflect adequately the normalization effect of the impurity atoms in the aluminum lattice, and their values are those which reproduce the electrical resistivity in the free electron model.

V. CALCULATION METHOD

In this chapter we describe the numerical analysis of the problem as well as the parameters used in the evaluation of the transport coefficients.

V.1. EVALUATION OF THE FERMI SURFACE OF THE ALUMINUM

In the evaluation of the Fermi surface we use relation (23); if the Fermi energy of aluminum and the matrix elements are known, we look for the value of $k$ that cause the secular determinant to vanish. This is accomplished by fixing two components of $k$ and varying the third one until the sign of the secular equation changes. Then by means of Aitken inverse interpolation [32] we adjust the value of $k$ until $|k - k_f|/k_f < 10^{-10}$. The parameters used in the evaluation of the Fermi surface are taken from Joss et al [23], and are shown in Table 1.

In Figure 1 we show the Al Fermi surface. Part 1-a corresponds to 1/16 of the second hole zone, and 1-b to an arm of the third electron zone, both in a reduced zone scheme, and constructed for planes of constant $k_z$. The maximum step was 0.05 a.u. in $k_z$ and 0.01 a.u. in $k_x$ and $k_y$. In critical points of degeneracy greater than 2, the steps were usually of 10^{-3} a.u. This guarantees a very precise Fermi surface with more than 5000 calculated points. Computing limitations for latter stages of this work obligated us to restrict the surface to slightly more than 1000 points.

![Fermi surface](image)

Fig. 1 (a) (001) cut through 1/16-th of the reduced second zone of the Fermi surface of aluminum (hole orbits). Over the diagonal, $k_x = k_y$, are shown the $k_z$ values in atomic units. A, B, C, D, E, and F correspond to $k_z$ equal to 0.745, 0.76, 0.78, 0.73, and 0.728 a.u., respectively. The arrow correspond to the maximal $k_z = 0.7273$ a.u. (b) (001) cut through an arm of the reduced third zone of the Fermi surface of aluminum (electronic orbits). The $k_z$ values are shown in atomic units. A, B, C, and D correspond to $k_z$.
equal to 0.05, 0.015, 0.25, and 0.33 a.u., respectively, the arrow corresponds to the maximal $k_z=0.3655$ a.u.

V.2 EVALUATION OF THE WAVE FUNCTION COEFFICIENTS OVER THE FERMI SURFACE

The Fermi surface for electrons and holes is covered by a mesh of 1032 points, at every one of which all the parameters associated with the Fermi surface are evaluated. In order to determine the eight coefficients $A_n$ associated with one of the 8-OPW waves, we rewrite the Schrödinger equation as:

$$\sum_{i=1}^{8} A_i (H-E_F) |k - q_i\rangle = 0$$

(22)

Multiplying on the left by $<k-q_i|$ and summing over the eight plane waves, we obtain a system of homogeneous equations with eight unknowns; when we introduce new variables $x_i = A_i / A_8$, it is rewritten as an overevaluated system. By means of the normalization condition, $\sum A_i^2 = 1$, we identify all coefficients $A_n$. In Figure 2 we show these coefficients for certain directions in the reciprocal space, for holes and for electrons. In Figures 2a and 2b the wave function coefficients are plotted as a function of the component $k_y$ of the wave vector, for a plane orbit corresponding to $k_z = 0$ a.u., while Figures 2c and 2d correspond to $k_z = 0.45$ a.u. Notice that for $k_z = 0$ there is a clear demarcation of the change of curvature observed in Figure 1a around the point (0.78,0.33). Note also the almost exclusive participation of the first four OPW waves in the definition of the transport coefficients. For the plane $k_z = 0.45$ a.u., Figure 1a does not show an accentuated change, $A_2$ and $A_5$ being the predominant coefficients for the calculation. In Figures 3a and 3b, we select the electronic orbit corresponding to $k_z = 0.3$ a.u., the closed character of this orbit (see Figure 1b) generates coefficients $A_i$ which are also closed, e.g., the coefficients $A_1$ and $A_3$ are degenerate while $A_2$ and $A_4$ are completely symmetric. There is total symmetric for the other coefficients, the waves corresponding to $A_1$, $A_2$, $A_3$, and $A_7$ being the ones with more weight in the definition of the transport coefficients. We wish to point out that an examination of the $A_i$ over the Fermi surface, for electrons or for holes, demonstrates the importance of having chosen the 8-OPW model, inasmuch as each of them becomes important at some point of the surface.

Fig. 2. (a) and (b). Wave function coefficients as a function of the $k_y$ component of the wave vectors, in the hole orbit given by $k_z = 0$ a.u. (a) $i = 1$, -o--; $i = 2$, -- -.; $i = 3$, -- o--; $i = 4$, -- -.-.. (b) $i = 5$, -o--; $i = 6$, --- -.; $i = 7$, -- -.; $i = 8$, -- -.-.
V.3. EVALUATION OF THE DERIVATIVES OVER THE FERMI SURFACE

The evaluation of all the derivatives, first, second and third, that appear in relations (10), (31), and (32) are made through the secular equation $D(E_i, k)$. As we know that the diagonal elements of $D$ depend on $E$ and $k$, their derivatives will be referred to the differentiation of the complementary minor of every element of the diagonal times, its respective lower order determinant. In Figures 4a and 4b we show the variation of the velocity $v_i = E_{i} / h$ as a function of the component of the wave vector $k$ over the Fermi surface for $k_z = 0$ and 0.45 a.u. The abrupt change of the curvature in the neighborhood of the point W of the first Brillouin zone is evident in every component of the velocity. In the Figures 4c, and 4d, we show the variation of $G_1^x(E, x)$, $G_2^y(E, y)$, and $G_3^z(E, y)$, as a function of $k_y$ for every hole orbit. Note that there is a multiplicative factor for each derivatives, and that for $k_z = 0$ there is a discontinuity around the point W. In the other hole orbit there is no observed discontinuity.

In Figure 5a we show the velocity of electrons in the third zone for the orbit $k_z = 0.3$ a.u. Notice that the velocity components in the directions $y$ and $z$ are overlapped, each one of these components being completely symmetric, and also that the absolute value of the velocity...
components is symmetric. The derivatives \( G_1^j \) for electrons are shown in Figure 5b, where a small asymmetry for \( G_2^2 \) and \( G_3^3 \) stands out. These results are doubtlessly very important since they show that in critical points of the Fermi surface the transport coefficients are magnified.

Our parameters for the Fermi surface have been matched with the 4-OPW calculation performed by Böning et al. [27], and at the level of Fermi velocity and Fermi curvature a good agreement is seen. The small differences found are due the extra parameters incorporated in our 8-OPW calculation. The numerical results of every calculated parameter (Fermi surface, Fermi velocity, derivatives over the Fermi surface and wave function coefficients) are available upon request from our research group.

![Graphs](image_url)

Fig. 4. (a) and (b). Velocity of electrons as a function of the \( k_y \) component of the wave vector over the Fermi surface. (a) In the hole orbit \( k_z = 0 \) a.u.: \( v_x, -v_y \); \( v_y, -v_x \); \( v_z, -v_{-z} \); \( v, -v_{-z} \). (b) In the hole orbit \( k_z = 0.45 \) a.u.: \( v_x, -v_y, -v_z \); \( v_x, -v_y, -v_z \). (c) and (b). Other energy derivatives \( G_1^j(E, j) \) vs. \( k_y \). (c) in the hole orbit \( k_z = 0 \) a.u.: \( i = 1, j = y \), multiplicative factor = 10^{63}, \( -v \); \( i = 2, j = x \), multiplicative factor = 10^{98}, \( -v \); \( i = 3, j = y \), multiplicative factor = 10^{134}, \( -v \). (d) In the hole orbit \( k_z = 0.45 \) a.u.: \( i = 1, j = y \), multiplicative factor = 10^{64}, \( -v \); \( i = 2, j = x \), multiplicative factor = 10^{102}, \( -v \); \( i = 3, j = y \), multiplicative factor = 10^{138}, \( -v \).
V. 4 EVALUATION OF THE FORM FACTOR

Relation (36) defines the form factor W(q) that intervenes in the evaluation of the relaxation time. Our pseudopotential for the different alloys studied is of the semiphenomenological Heine-Abarenkov type, and reproduces the electrical resistivity of impurities in the free electron model. The details of the computation are given by Luiggi [31], and the values of the parameters for the impurities studied are given in the Table 2.

V.5 INTEGRATION OVER THE FERMI SURFACE

All the integration that appear in this work are done over the Fermi surface using the finite elements method [33]. To do so we cover the second holes zone and the third electrons zone of the Fermi surface with a mesh of triangular elements which covers the 662 point of the second zone and the 370 points of the third zone. These surface are filled with 700 and 690 triangles, respectively. A preliminary calculation of these integrals in the reciprocal space was attempted, but the computation time was truly prohibitive. For this reason every triangle of the three-dimensional surface was projected onto a reference triangle, according to a linear nodal approximation, which has the advantage of defining a Jacobian which is independent of the transformation coordinates. Under this scheme the integration of (34) should be done as follows:

$$\tau^{-1}(k) = \text{const.} \sum_{M} \iint_{M} \langle \mathbf{P} \rangle [\mathbf{P}_{M}]^{-1} \{\mathbf{U}_{M}\} J_{S} \ d\alpha d\beta$$

where \(\alpha\) and \(\beta\) are the reference triangle coordinates and \(\langle \mathbf{P} \rangle\) is a three-component row vector which contains the polynomial basis of the approximation. \([\mathbf{P}_{M}]^{-1}\) is the inverse of the matrix \([\mathbf{P}_{M}]\) which is evaluated from \(\langle \mathbf{P} \rangle\) by means of the substitution of the coordinates of every point of the triangular element \(M\). In our case:

$$\langle \mathbf{P} \rangle [\mathbf{P}_{M}]^{-1} = (1 - \alpha - \beta, \alpha, \beta)$$

(39)

\(\{\mathbf{U}_{M}\}\) is a three-component column vector that stores the integrand value in each point of element \(M\). Note that this being a nodal approximation, the value of \(\{\mathbf{U}_{M}\}\) is the same in reciprocal space as in the reference space.

The Jacobian \(J_{S}\) becomes:
Once we know all the parameters defined in relation (33), we proceed by means of the methods already described to evaluate recursively the relaxation time associated with the Ga, Ge, and Zn impurities.

In Figure 6 we show the evaluation of the relaxation time for Al-Zn as a function of the component $k_y$ of the wave vector, for holes as well as for electrons. Figures 6a and 6b correspond to the orbits of electrons in the third zone for $k_z = 0$ and $k_z = 0.3$ a.u.. The evaluation sequence from the Ziman approximation up to three recursive steps is shown. Where only two curves appear there is total overlap of the second and third recursive steps. In these orbits we note an important fluctuation of the relaxation time associated with the change of the parameters over the Fermi surface. Figures 6c and 6d correspond to hole orbits for $k_z = 0$ and $k_z = 0.45$ a.u., we see an effect similar to that observed for electrons, but for $k_z = 0$ we note an important difference between the predicted behavior in the Ziman relation and the other recursive steps. In figure 7 we show the results for Al-Ga. The same differences are observed for holes and electrons.

Fig. 6. relaxation time vs. $k_y$ over the Fermi surface for a dilute Al-Zn alloy. In all cases the symbols have the following meaning: --Δ--, single step calculation (Ziman approximation); -o-, two recursive steps; ++-, three recursive steps. (a) Electron orbit for $k_z = 0$ a.u. (b) Electron orbit for $k_z = 0.3$ a.u. (c) Hole orbit for $k_z = 0$ a.u. (d) Hole orbit for $k_z 0.4$ a.u.
A difference from the previous potential is seen in Figure 7c, where for holes in the orbit $k_z = 0$, no convergence is obtained after three steps, which necessitates a fourth step. In Figure 8 we plot $\tau$ vs. $k_y$ for Al-Ge in the same orbits of holes and electrons. The same behavior seen earlier is observed here. A comparison of these results with those obtained by other authors is not possible since in general partial results are not show in other papers.

**Fig. 7.** Relaxation time $\tau$ vs. $k_y$ over the Fermi surface for a dilute Al-Ga alloy. The notation is the same as for a dilute Al-Ga alloy. The notation is the same as for Fig. 6.

**Fig. 8.** Relaxation time $\tau$ vs. $k_y$ over the Fermi surface for a dilute Al-Ge alloy. The notation is the same as for a dilute Al-Ge alloy. The notation is the same as for Fig. 6.
VI. RESULTS

Once we know the relaxation time associated with holes and electrons, we proceed to evaluate the coefficients in (11) for holes and electron, and then the total coefficients in (14), (20), and (21). The values between the braces in relation (20), and between brackets in relation (21), correspond to the same parameter designated by Pfander et al. [13] as $R_2$ and $R_3$, respectively. Note that this kind of calculation is quite different from that of Pfander et al. [13] as well as Yonemitsu et al., [14] who by 4-OPW considerations have merely introduced the effect of different zones of carriers, the final property weighting the contribution of each of these zones. In our case the calculation is complete for all the carriers in the second and third Brillouin zones in the scheme of reduced zones of Al. In Table 3 we show our results for Zn as the impurity. This Table gives individually the contribution of electrons and holes, as well as the total value in the two-band model. Rows 1, 2, and 3 refer to the Ziman approximation with two additional recursive steps. Row 4 is the experimental value given by Pfander et al., [13] while our final result, although an improvement of more than 30% over the result of Pfander et al., [13] is not better than that reported by Yonemitsu. [14]

3) The transverse magnetoresistances associated with holes and electrons have negative signs, although the total transverse magnetoresistance calculated in the two-band model has positive sign. In this case the second iterative step seems to be in agreement with the other results noted, while the third step departs somewhat. This is a consequence of the fact that our calculation does not adjust the property itself, but rather evaluates the relaxation time, and in this process small fluctuations are magnified because the parameter is raised to the fourth power.

4) The quadratic contribution of the Hall effect for holes and electrons is of variable sign, depending on the number of iterations, but our final result is quite close to the experimental value. The value of Pfander et al. for this contribution is quite exaggerated. [13]

In the Table 4 we present our results for the Ga impurity, where we notice the following:

1) The contribution of holes to the electrical resistivity is greater than that of electrons, as in the previous case. Our results within the Aiman approximation are quite close to those obtained by Pfander et al., [13] while our total result after three iterative steps differs by 14% from the experimental value; that is, our calculation improves this result by almost 60%.

2) The Hall coefficient is negative for electrons, and positive for holes is, but the total Hall effect obtained is negative, contrary to experiment. Without doubt this is a problem characteristic of the potential used.

3) Concerning the transverse magnetoresistance, the second and third iterative steps are quite close to the value reported by Pfander et al.[13]

4) The quadratic contribution of the Hall effect is positive in spite of the fact that the contributions of both holes and electrons are negative. Our value differs from that obtained by Pfander et al., [13] and we have no experimental result to compare with this value.
In Table 5 we present the results for the Ge impurity. We observe:

1) A greater value of the resistivity for electrons than for holes, contrary to the case for other impurities, with a recursive value in the third step closer to the experimental value than that reported by Pfander et al. [13] but lower than that reported by Yonemitsu et al. [14]

2) The Hall coefficient for electrons is negative and of magnitude greater than that for holes, which is positive. Our results in the third iterative step differ by 6% from experiment.

3) The value obtained for magnetoresistance is, in the third iterative step, 2.5 times greater than that obtained experimentally, although in the Ziman approximation is only 1.5 times greater.

4) The quadratic contribution to the Hall coefficient in the third iterative step is positive and differs by a factor of four from the experimental value, which is negative.

These results point out the important role that an adequate potential for every impurity plays in the evaluation of the transport coefficients, as well as the effect of the different parameters associated with the curvature of the Fermi surface, and also the other derivatives in critical points of such surface. We can follow the participation of holes and electrons in every property, but we are confident that the information given in Tables 3, 4, and 5 is the most complete that can be found in the literature for such calculations, and thus we feel that no additional discussion is necessary.

VII. CONCLUSIONS

We have achieved a complete calculation of the participation of holes and electrons in the electrical resistivity, Hall effect, transversal magnetoresistance, and quadratic component of Hall effect in the very dilute system Al-Zn, Al-Ge. The electronic details are considered with the 8-OPW method. The relaxation integrals are calculated by means of a finite element method, and the potentials are of the modified Heine-Animalu type. The dependence of all the electronic parameters upon the secular equation which defines the Fermi surface is developed and a different way to obtain the Tsuji relation for the curvature of such surface is shown. The application of all these details to the determination of the effect of Zn, Ga, and Ge impurities to an aluminum matrix allows us to conclude the following:

1) The details of the electronic structure as well as the characteristic of the scattering potentials are of paramount importance in obtaining good results for transport coefficients.

2) The recursive calculation of the relaxation time seems to converge for the electrical conductivity, but not necessarily for the other transport coefficients. Of course it has to be taken into account that our pseudopotential has been constructed with the intention of reproducing the magnitude of the electrical conductivity for spherical models of Fermi surface, which according to our results does not guarantee good convergence in other coefficients.

3) The contributions of holes and electrons are specified in the regions of the Fermi surface located in the second and third Brillouin zones of Al. We see that the electrical resistivity for holes is greater than for electrons for Zn and for Ga, but not for Ge; the different participation of other coefficients is also shown. Nonetheless, the electrical conductivity, because of its direct relationship with the relaxation time, is an important factor in other properties, as is shown in relations (20) and (21).

4) In general, the calculated coefficients show a better agreement with the experimental values than those obtained by Pfander et al. [13] We think our calculation can still be improved, at the level of a more adequate potential and a more exact calculation of the Fermi integral, considering, for instance, more triangles or different types of elements. Since the computational facilities in our group are very limited, a work of such magnitude can be hardly achieved in a short time.

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