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Theory of Electrical Conductivity in Disordered Binary Alloys. The Effect of *s-d* Hybridization*

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The coherent-potential approximation (CPA) of the conductivity theory of disordered alloys is generalized in order to calculate and to discuss the static conductivity of a two-*s*-*d*-band-alloy model relevant to noble- and transition-metal alloys. The vertex corrections are calculated and can be expressed in the CPA as a sum of single-site contributions. As in the one-band model and for the same physical reasons, these vertex corrections vanish if the potentials are short ranged. Three contributions are obtained for the electrical conductivity. They correspond to the propagation of a pair of *s* electrons, a pair of *d* electrons, and two hybridized *s*-*d* electrons. The scattering of *s* electrons is viewed as indirectly caused by the randomness of *d* levels acting through the hybridization interaction *s*-*d*. Two limiting cases are investigated and compared with previous treatments. In the weak-scattering limit, the present theory is shown to be equivalent to the Boltzmann approach. In the dilute-concentration limit, it is possible to reduce this formalism to previous calculations of the impurity-induced resistivity by defining in that limit an effective *s*-*d* scattering potential. A numerical application is presented. It is not directly related to any particular alloy but the physical parameters are reasonably chosen such that the computed resistivity reproduces qualitatively two types of deviations from the Nordheim behavior observed in some transition-metal-based alloys: (a) a change of slope of the resistivity-versus-concentration curve correlated with a minimum of the specific heat, and (b) an asymmetry of the resistivity curve with a peak in a range of concentration where the influence of *s*-*d* hybridization is dominant.

I. INTRODUCTION

The coherent-potential approximation (CPA) which has been applied by a number of authors[1-3] to provide a description of the equilibrium properties of elementary excitations in disordered crystals was recently extended in order to be applied to the transport properties. A theory of the linear response of electrons in substitutionally disordered binary alloys consistent with the single-particle CPA was presented in Ref. 4. In that paper the static electrical conductivity of a single-band model with short-ranged random scatterers was shown to be exactly soluble in the CPA. The solution gives the exact formulas in the limit of weak scattering and of dilute alloys and satisfies the energy and particle-number conservation conditions for all impurity concentration and any range of scattering strength. In two subsequent papers,[5,6] the frequency-dependent conductivity of the same model was calculated for all frequencies and the CPA was extended to more general transport coefficients where a diagrammatic way of calculating transport properties is needed.

The purpose of this paper is to extend the CPA theory to the calculation and the discussion of the static conductivity of a two-band model introduced by Levin and Ehrenreich.[7,8] This model, which contains some of the features of noble- and transition-metal alloys, emphasizes the effect of *s*-*d* hybridization and neglects the structure of the *d* band. The pure metals *A* and *B* are assumed to contain one *s* band of finite width and two resonant *d* energy levels ϵ_d^A or ϵ_d^B. These two *d* levels hybridize with the *s* band. In the alloy A_xB_{1-x} the *d*-level energy ϵ_d^N at a given site *n* may be ϵ_d^A or ϵ_d^B corresponding to whether the site *n* is occupied by an *A* or *B* atom. The unhybridized *s* bands and the hybridization constants are treated in the virtual-crystal approximation. By contrast, the *d* bands whose potentials are not expected to be weak are treated self-consistently in the CPA. In Ref. 8 the configuration-averaged density of states of this model was calculated for alloys of arbitrary concentration and reasonably strong scattering strengths and the limiting cases such as dilute alloy and split-band limit were investigated. In the theoretical discussion and the numerical calculation, Levin and Ehrenreich have neglected the width of the *d* levels due to *d*-*d* hopping. As a result of this approximation the alloy density of states exhibits hybridization gaps at the *d* levels. This feature of the theory had no importance as far as a discussion of the concentration dependence of the optical absorption edge was concerned. For our purpose, however, it was necessary to avoid these gaps and the model has been generalized to account for the width of the *d* level.

In contrast to previous theories[9,10] which were concerned with the effect of *s*-*d* scattering on the resistivity of transition-metal alloys, the theory of residual resistivity that we present in this paper is not restricted to dilute alloys and can be used for the complete range of concentrations. It provides, therefore, a useful tool for investigating possible deviations from Nordheim's[11] $x(1-x)$ law behavior of the resistivity of transition- and noble-metal alloys as well as the influence of s-d hybridization.

Mott[12] has emphasized that in transition metals and transition-metal alloys the resistance is mainly due to scattering processes in which an electron makes a transition from the s to the d band, the probability of such a transition being proportional to the density of states in the d band. With this picture, Mott has explained qualitatively the striking deviation from Nordheim's behavior of the residual resistivity in transition–noble-metal alloys which exhibit a Matterhorn-type behavior for rather large concentration (50–70%). Until now no detailed calculations had been performed to substantiate this explanation. On the other hand, deviations from Nordheim's rule have been observed in the small concentration region. Nellis *et al.*[13] recently measured an abrupt change in the slope of resistivity at about 7.5% of U in Pd, which is correlated with a minimum in the susceptibility and specific heat. It will be seen that with the formalism presented in this paper one can, at least qualitatively, account for these two types of behavior.

The paper contains three parts. The first part (Sec. II) generalizes Velický's formalism to the two-s-d-band model. The second part (Sec. III) discusses two interesting limiting cases, the weak-scattering limit and the dilute-concentration limit. The third part (Sec. IV) is an application of the theory to a model which shows deviations from Nordheim's rule observed in some alloys and is in agreement with Mott's prediction.

In Sec. II A, the two-s-d-band model is characterized. The most interesting feature of this two-band model is that the energy spectrum and the transport properties are determined by the scattering of s-d hybridized electrons by the random d levels. The self-energy corresponding to this scattering is then calculated self-consistently in the spirit of the CPA. This paper is restricted to nonmagnetic alloys, and therefore the model Hamiltonian is spin independent. The generalization to ferromagnetic alloys will be considered in a future paper. In Sec. II B, following Velický, we express the Kubo-Greenwood formula of conductivity in a form suitable for CPA calculations. In Secs. II C and II D we derive in the CPA expressions for $\langle G \rangle$ and $\langle GG \rangle$ the average one- and two-particle Green's functions. We establish a condition for the disappearance of the hybridization gap and then calculate the s and d density of states. The most important result of Sec. II C is the proof that, as in the one-band model and for the same physical reasons, the "random" vertex corrections in $\langle GG \rangle$ vanish. Physically this is equivalent to the vanishing of backscattering within a Boltzmann-equation context which results from the assumption that the scattering is short range and therefore isotropic. In a diagrammatic sense there are "hybridization" vertex corrections in the conductivity. They are included automatically in our formalism by defining "renormalized" ss and sd Green's functions which enter into the definition of the conductivity. In Sec. II E we use the results of Secs. II C and II D to derive the expressions for the three contributions to the conductivity, σ_{ss}, σ_{sd}, and σ_{dd}. The mixed term σ_{sd} comes essentially from the hybridized s-d character of the eigenstates of the model Hamiltonian. When the width of the d level is zero, the contributions σ_{sd} and σ_{dd} vanish.

Sections III A and III B deal with a discussion of two limiting cases. In Sec. III A, we discuss the weak-scattering limit and the formal equivalence of our formalism with the Boltzmann-equation approach is proved. The vanishing of the vertex corrections of the backscattering in the collision term of the transport equation are physically related. In Sec. III B, the dilute-concentration limit is investigated. Our point of view is essentially different from the localized-impurity approach. Host and impurity atoms are treated on the same footing and the s-d mixing of both atomic constituents is taken into account. However, it is possible in the dilute-concentration limit to reduce our formalism to previous calculations of the impurity-induced resistivity by defining in that limit an effective s-d scattering interaction.

The numerical application we present in Sec. IV is not related to a particular alloy but the physical parameters reasonably chosen are such that the computed resistivity can reproduce qualitatively two types of deviations from Nordheim's rule observed in some transition-metal alloys. The calculation and the comparison of the three contributions to the conductivity for different values of the Fermi energy illustrate the strong influence of s-d hybridization on the electrical conductivity of transition-metal-based alloys.

II. CALCULATION OF STATIC CONDUCTIVITY

A. Model

We want to calculate the configurationally averaged electrical conductivity of a completely disordered binary alloy A_xB_{1-x} whose Hamiltonian has the form

$$H^{\text{alloy}} = \sum_{k \in \mathrm{BZ}} E_s(k) | k_s \rangle \langle k_s | + \sum_{\substack{n,m \\ n \neq m}} t^d_{mn} | m_d \rangle \langle n_d | + \sum_n \epsilon^d_n | n_d \rangle \langle n_d | + \sum_{\substack{n \\ k \in \mathrm{BZ}}} \gamma(\epsilon^d_n)$$

$$\times(|k_s\rangle\langle n_d|e^{ikR_n}+\text{c.c.})\,, \quad (1)$$

where BZ means Brillouin zone and

$$t^d_{mn}=N^{-1}\textstyle\sum_k \epsilon_d(k)e^{ik(R_m-R_n)}\ . \quad (2)$$

The lattice is assumed to be monatomic with N sites in a large volume Ω. Each site n is occupied at random by an atom of type A or B, respectively, with probability x and $1-x$. There are c electrons per site. The crystal is supposed to have one s band and we assume the d band to be made of five independent and equal subbands. The two first terms represent the kinetic energy of the system. The function $E_s(k)$ is the dispersion relation of s electrons. Its interaction with the Brillouin-zone boundary determines the width $2w_s$ of the unhybridized s band. The matrix elements t^d_{mn} are the hopping integrals in the Wannier representation of d electrons. They give rise in the Bloch representation (2) to the dispersion relation of d electrons $\epsilon_d(k)$. The width of the unhybridized d band $2w_d$ will be calculated as in a nearest-neighbor tight-binding band and will have the general form

$$\epsilon_d(k)=w_d s(k) \quad (3)$$

with

$$-1\leq s(k)\leq 1\ .$$

Alloying is supposed to leave these two terms unchanged except for the bottom of the s band $\overline{\Gamma}_1$, which is supposed to be calculated in the virtual approximation

$$\overline{\Gamma}_1=x\Gamma_1^A+(1-x)\Gamma_1^B\ . \quad (4)$$

The third term is the only random term of the Hamiltonian which will be calculated self-consistently. The resonance energy of the d level ϵ^d_n can take one of two values depending on whether an A or a B atom is at site n. The last term describes the hybridization between s and d electrons. The coupling constant $\gamma(\epsilon^d_n)$ is assumed to be k independent. Moreover, we will suppose that it is evaluated at the average d resonance energy

$$\overline{\epsilon}^d_n=x\epsilon^A_n+(1-x)\epsilon^B_n\ .$$

The hybridization is thus reduced to the coupling of a d electron localized on site n with the s Wannier function of the same site n due to the average of sites $\neq n$ (see Appendix B).

The model represented by Hamiltonian (1) can be regarded as appropriate to the investigation of binary noble-metal alloys and paramagnetic transition-metal alloys.

B. CPA Kubo Formula

We start from the well-known Kubo-Greenwood formula[14]

$$\sigma^{\alpha\beta}=\frac{2\pi e^2}{m^2\Omega}\int d\eta\left(-\frac{df}{d\eta}\right)\times\mathrm{Tr}\ \langle p^\alpha\delta(\eta-H)p^\beta\delta(\eta-H)\rangle\ . \quad (5)$$

Here e and m are the electron charge and mass, respectively, and we use units in which $\hbar=1$. Greek letters refer to the Cartesian coordinates. The operators p^α and p^β are components of the linear momentum. The two spin orientations are taken into account by an extra factor of 2. The average over all configurations of the system is denoted by the brackets $\langle\cdots\rangle$. The function $f(E)$ is the Fermi-Dirac distribution function

$$f(E)=(1+e^{\beta(E-\mu)})^{-1}\,, \quad (6)$$

where the chemical potential μ and $\beta=(kT)^{-1}$ are related to the number of electrons per site c by the normalization condition

$$\mathrm{Tr}f(H)=cN\ . \quad (7)$$

In the model described by Hamiltonian (1) the momentum operator is configurational independent. Using the identity

$$\delta(\eta-H)=(2\pi i)^{-1}[G(\eta-i0)-G(\eta+i0)]\,, \quad (8)$$

we can, following Velický,[4] put Eq. (5) in a form more convenient for calculation in the CPA:

$$\sigma^{\alpha\beta}=\frac{2\pi e^2}{m^2\Omega}\int d\eta\left(-\frac{df}{d\eta}\right)I^{\alpha\beta}_{pp}(\eta,\eta)\,, \quad (9)$$

with

$$I^{\alpha\beta}_{pp}(\eta,\eta)=(4\pi^2)^{-1}\mathrm{Tr}p_\alpha[K(\eta^+,p_\beta,\eta^-)+K(\eta^-,p_\beta,\eta^+)-K(\eta^+,p_\beta,\eta^+)-K(\eta^-,p_\beta,\eta^-)] \quad (10)$$

and

$$\eta^\pm=\eta\pm i0\ .$$

The quantity to be averaged is a product of three operators (wherever possible, the argument z_1, z_2, and p will be omitted):

$$K(z_1,\ p,\ z_2)=\langle G(z_1)pG(z_2)\rangle\ . \quad (11)$$

To calculate K we will need the averaged Green's function

$$\overline{G}(z)=\langle(z-H)\rangle^{-1}\ . \quad (12)$$

C. CPA for G, s, and d Density of States

The averaged Green's function $\overline{G}(z)$ is supposed to be diagonal in the Bloch representation and can be determined in the CPA as usual by defining a k-independent self-energy operator. In the present case the self-energy has to be defined in the space of d states $\sum_k\Sigma_d(z)|k_d\rangle\langle k_d|$ and $\overline{G}_k$ can be written as a 2×2 matrix in the basis $\{|k_s\rangle,\ |k_d\rangle\}$:

$$\overline{G}_k = \begin{pmatrix} z - E_s(k) & -\overline{\gamma} \\ -\overline{\gamma} & z - \epsilon_d(k) - \Sigma_d \end{pmatrix}^{-1} . \tag{13}$$

The three Green's functions $\overline{G}_{ss}(k, z)$, $\overline{G}_{dd}(k, z)$, and $\overline{G}_{sd}(k, z) = \overline{G}_{ds}(k, z)$ are determined from (13):

$$\overline{G}_{ss}(k, z) = \{z - E_s(k) - \gamma^2[z - \Sigma_d - \epsilon_d(k)]^{-1}\}^{-1} , \tag{14a}$$

$$\overline{G}_{dd}(k, z) = \{z - \Sigma_d - \epsilon_d(k) - \gamma^2[z - E_s(k)]^{-1}\}^{-1} , \tag{14b}$$

$$\overline{G}_{sd}(k, z) = \gamma\{[z - E_s(k)][z - \Sigma_d - \epsilon_d(k)] - \gamma^2\}^{-1} . \tag{14c}$$

Following the standard procedure, the unaveraged propagator for the electrons in the alloy is expressed in term of $\overline{G}$ by defining a scattering operator $T(\Sigma)$:

$$G = \overline{G} + \overline{G}T\overline{G} . \tag{15}$$

The self-consistent condition

$$\langle T \rangle = 0 \tag{16}$$

is obtained by averaging (15). The multiple-scattering theory is used to express matrix T in the form of a sum of single-site contributions product of the atomic scattering matrix t_m and an effective wave factor. In the present case, the scattering matrix T is defined in the basis $\{ |n_s\rangle, |n_d\rangle\}$ by

$$\begin{pmatrix} 0 & 0 \\ 0 & \hat{T}^{dd} \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & \sum_{n_d} |n_d\rangle Q_n^{dd} \langle n_d| \end{pmatrix} , \tag{17}$$

with

$$Q_n^{dd} = t_n^d \left(1 + \overline{G} \sum_{m \neq n} |m_d\rangle Q_m^{dd} \langle m_d|\right) . \tag{18}$$

In the average of Q_n, the CPA neglects statistical correlation between t_n and the effective wave, and the self-consistent condition (16) is reduced to

$$\langle t_n^d \rangle = 0 , \tag{19}$$

with

$$t_n^d = (\epsilon_d^n - \Sigma_d)[1 - (\epsilon_d^n - \Sigma_d)F_{dd}(z, \Sigma_d)]^{-1} \tag{20}$$

and

$$F_{dd}(z, \Sigma_d) = N^{-1}\mathrm{Tr}_d\overline{G}(z) = N^{-1}\textstyle\sum_k \langle k_d|\overline{G}|k_d\rangle = \langle n_d = 0|\overline{G}|n_d = 0\rangle . \tag{21}$$

The CPA condition (19) yields the self-consistent relation for the self-energy

$$\Sigma_d(z) = \overline{\epsilon}_d - (\epsilon_d^A - \Sigma_d)F_{dd}(z, \Sigma_d)(\epsilon_d^B - \Sigma_d) , \tag{22}$$

where

$$\overline{\epsilon}_d = x\epsilon_d^A + (1 - x)\epsilon_d^B . \tag{23}$$

Equation (21) can be written explicitly as

$$F_{dd}(z, \Sigma_d) = \Omega_c(2\pi)^{-3} \int_{\mathrm{BZ}} d^3k \{z - \Sigma_d - \epsilon_d(k) - \gamma^2[z - E_s(k)]^{-1}\}^{-1} , \tag{24}$$

where Ω_c is the unit-cell volume.

To evaluate the function $F_{dd}(z, \Sigma_d)$ we will assume that in the pure metal both s and d unhybridized bands have the same shape and are related by a scaling factor α. We choose the energy origin such that $\epsilon_d^A = \frac{1}{2}\delta$ and $\epsilon_d^B = -\frac{1}{2}\delta$, where $\delta = \epsilon_d^A - \epsilon_d^B$ is the scattering strength parameter. In the pure metal ($\delta = 0$), the center of the unhybridized d band is located at the energy origin, while the center of the unhybridized s band is located at Δ_1. We therefore have

$$E_s(k) = \epsilon_s(k) + \Delta_1$$

and

$$\epsilon_d(k) = \alpha\epsilon_s(k) \tag{25}$$

with $\alpha < 1$. With these assumptions we can rewrite (24) in the form

$$F_{dd}(z, \Sigma_d) = \Omega_c(2\pi)^{-3} \int_{\mathrm{BZ}} d^3k \times \int_{-\infty}^{+\infty} \frac{\delta(E - \epsilon_s(k))}{z - \Sigma_d(z) - \alpha E - \gamma^2(z - E - \Delta_1)^{-1}} dE . \tag{26}$$

This expression can be simplified by defining the density of states (per site) in the unhybridized s band

$$\rho_{0s}(E) = \Omega_c(2\pi)^{-3} \int_{\mathrm{BZ}} d^3k \, \delta(E - \epsilon_s(k)) , \tag{27}$$

and its transform

$$F_{0s}(z) = \int_{-\infty}^{+\infty} \rho_{0s}(E)(z - E)^{-1} dE . \tag{28}$$

Equation (26) can be expressed in terms of $F_{0s}(z)$ as

$$F_{dd}(z) = [\alpha(E_+ - E_-)]^{-1}[(z - \Delta_1 - E_+)F_{0s}(E_+) - (z - \Delta_1 - E_-)F_{0s}(E_-)] , \tag{29}$$

with

$$E_\pm = \frac{1}{2}\left\{z - \Delta_1 + \frac{z - \Sigma}{\alpha} \pm \left[\left(z - \Delta_1 - \frac{z - \Sigma}{\alpha}\right)^2 + 4\frac{\gamma^2}{\alpha}\right]^{1/2}\right\} .$$

Quite similarly, the function

$$F_{ss}(z, \Sigma_d) = N^{-1} \sum_{k \in \mathrm{BZ}} \langle k_s|\vec{G}(z)|k_s\rangle \tag{30}$$

can be shown to be expressed in terms of $F_{0s}(z)$ as

$$F_{ss}(z) = (E_- - E_+)\{[(z - \Sigma)/\alpha - E_+]F_{0s}(E_+) - [(z - \Sigma)/\alpha - E_-]F_{0s}(E_-)\} . \tag{30'}$$

When $\alpha \rightarrow 0$, i.e., when the d levels are supposed not to overlap, Eq. (29) reduces to Eq. (2.24) of Ref. 8:

$$F_{dd}(z)(\alpha = 0) = (z - \Sigma)^{-1} + \overline{\gamma}^2(z - \Sigma)^{-2}$$

$$\times F_{0s}[z-\overline{\gamma}^2(z-\Sigma_d)^{-1}] \,. \tag{31}$$

It can be verified from (29) and (30′) that the two functions $F_{dd}(z, \Sigma_d)$ and $F_{ss}(z, \Sigma_d)$ are both analytic everywhere in the complex z plane except for branch cuts on the real axis, and because $F_{0s}(z) \to z^{-1}$ as $z \to \pm\infty$, the asymptotic behavior of $F_{ss}(z)$ and $F_{dd}(z)$ is z^{-1} for $z \to \pm\infty$.

The density of states of s and d electrons is derived from the discontinuity of $F_{ss}(z, \Sigma_d)$ and $F_{dd}(z, \Sigma_d)$ across the real axis. The average density of s and d states per atom are written, using Eq. (13),

$$\rho_s(E, \Sigma_d) = -2\pi^{-1}\,\mathrm{Im}F_{ss}(E+i0, \Sigma_d^{+}) \tag{32}$$

and

$$\rho_d(E, \Sigma_d) = -10\pi^{-1}\,\mathrm{Im}F_{dd}(E+i0, \Sigma_d^{+}) \,. \tag{33}$$

From the CPA definition of $\Sigma_d(z)$, Eq. (22), and the asymptotic behavior of $F_{dd}(z)$ one can verify that

$$\Sigma_d(z) - \overline{\epsilon}_d \to xy\delta^2 z^{-1} \quad \text{as } z \to \infty \,, \tag{34}$$

and because of the analyzity of Σ_d in both half-planes, the following dispersion relation for $\Sigma_d(z)$ can be derived:

$$\Sigma_d(z) = \overline{\epsilon} + \pi^{-1}\int_{-\infty}^{+\infty} dE(E-z)^{-1}\,\mathrm{Im}\Sigma_d(E+i0) \,, \tag{35}$$

from which one can obtain a family of sum rules, the two first of which are

$$\pi^{-1}\int_{-\infty}^{+\infty} \mathrm{Im}\Sigma_d(E+i0)\,dE = -xy\delta^2 \,, \tag{36}$$

$$\pi^{-1}\int_{-\infty}^{+\infty} E\,\mathrm{Im}\Sigma_d(E+i0)\,dE = xyE\delta^2 \,. \tag{37}$$

D. CPA for K

We will generalize the CPA determination of K discussed in Ref. 4 to the two-band model described by Hamiltonian (1). If we use expansion (15), the expression defining K can be written in the form

$$K = \overline{G}p\overline{G} + \overline{G}\Gamma\overline{G} \,, \tag{38}$$

where

$$\Gamma = \langle T\overline{G}p\overline{G}T \rangle \,. \tag{39}$$

In the first term of the right-hand side of (38), the two Green's functions are averaged independently. The second term is the so-called vertex correction due to the correlation in the motion of two particles appearing in K. In the $\{|n_s\rangle, \; |n_d\rangle\}$ basis, the operator $\hat{\Gamma}$ is written as

$$\hat{\Gamma} = \begin{pmatrix} 0 & 0 \\ 0 & \langle \hat{T}^{dd}\overline{G}p\overline{G}\hat{T}^{dd} \rangle \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & \hat{\Gamma}^{dd} \end{pmatrix} \quad . \tag{40}$$

The CPA expression for $\hat{\Gamma}^{dd}$ is obtained by replacing the scattering matrix $\hat{T}^{dd}$ in (40) by (19) and (18) and by neglecting in averaging the statistical correlations of the atomic t matrices and the effective wave factors for different sites. The operator $\hat{\Gamma}^{dd}$ is now a sum of single-site contributions:

$$\hat{\Gamma}^{dd} = \textstyle\sum_n \hat{\Gamma}_n^{dd} \,, \tag{41}$$

with

$$\hat{\Gamma}_n^{dd} = \langle \hat{T}_n^{dd}\hat{K}\hat{T}_n^{dd} \rangle - \langle \hat{T}_n^{dd}\overline{G}\,\hat{\Gamma}_n^{dd}\overline{G}\,\hat{T}_n^{dd} \rangle \,. \tag{42}$$

Equations (41) and (42) together with

$$\langle n_d|\hat{K}|n_d\rangle = \langle n_d|\overline{G}\hat{p}\overline{G}|n_d\rangle + \langle n_d|\overline{G}\textstyle\sum_m \hat{\Gamma}_m^{dd}\overline{G}|n_d\rangle \tag{43}$$

represent the CPA approximation for the quantity K.

The solution for $\langle n_d|\hat{K}|n_d\rangle$ can be found as in the one-band model by expressing the operator $\hat{T}_n^{dd}$ and $\hat{\Gamma}_n^{dd}$ in the Wannier basis of d electrons:

$$\hat{T}_n^{dd} = |n_d\rangle t_n^d \langle n_d| \,, \quad \hat{\Gamma}_n^{dd} = |n_d\rangle \Gamma_n^d \langle n_d| \,.$$

Equation (42) becomes

$$\Gamma_n^d = \mathfrak{L}^d \langle n_d|K|n_d\rangle \,, \tag{44}$$

with

$$\mathfrak{L}^d = \mathfrak{L}^d(z_1, z_2) = \langle t_n^d(z_1)t_n^d(z_2)\rangle$$
$$\times [1 + F_{dd}(z_1)\langle t_n^d(z_1)t_n^d(z_2)\rangle F_{dd}(z_2)]^{-1} \,. \tag{45}$$

Substituting (44) into (45) yields the relation

$$\langle n_d|\hat{K}|n_d\rangle = \langle n_d|\overline{G}\hat{p}\overline{G}|n_d\rangle$$
$$+ \mathfrak{L}^d \sum_{m_d} F_{n-m}^d(z_1)F_{m-n}^d(z_2)\langle m_d|\hat{K}|m_d\rangle \,. \tag{46}$$

This equation is solved by Fourier transformation and the solution analogous to Eq. (101) of Ref. 4 is given by

$$\langle n_d|\hat{K}|n_d\rangle = N^{-1}\sum_k e^{ikR_n}a_k(1-\mathfrak{L}^d\mathcal{A}_k)^{-1} \,, \tag{47}$$

with

$$a_k = \sum_{n_d} e^{-ikR_n}\langle n_d|\overline{G}p\overline{G}|n_d\rangle \tag{48}$$

and

$$\mathcal{A}_k = \sum_{n_d} e^{-ikR_n}F_n^dF_{-n}^d \,. \tag{49}$$

To determine the vertex correction the important quantity to calculate is

$$\langle n_d|\overline{G}p\overline{G}|n_d\rangle = N^{-1}\,\mathrm{Tr}_d(\overline{G}p\overline{G}) \,. \tag{50}$$

In the model described by Hamiltonian (1), where the hybridization coupling constant is k independent, it can be shown (see Appendix B) that the momentum operator is defined by

$$\langle k_i|\hat{p}^d|k_j'\rangle = \delta_{ij}\delta_{kk'}\,m\left(\frac{\partial}{\partial k_i^\alpha}\right)\epsilon_i(k) = mv_i^\alpha(k) \,, \tag{51}$$

with indices i and j taking the two values s and d. Since G is diagonal in the Bloch representation, we can rewrite (51) in the form

$$\langle n_d|\overline{G}p\overline{G}|n_d\rangle$$

$$=N^{-1}\sum_i\sum_k \langle k_d|\overline{G}|k_i\rangle\langle k_i|\hat{p}|k_i\rangle\langle k_i|\overline{G}|k_d\rangle\ . \qquad (52)$$

As in the one-band model, it can be shown that this quantity vanishes identically. By time-reversal symmetry one has

$$\epsilon_i(k)=\epsilon_i(-k)\ , \qquad (53)$$

and consequently [cf. Eqs. (14a)–(14c)]

$$\langle k_i|\overline{G}|k_j\rangle=\overline{G}_{ij}(k)=\overline{G}_{ij}(-k)\ , \qquad (54)$$

while the velocity operators are such that $v_i^\alpha(-k)=-v_i^\alpha(k)$. The integration of (52) over k gives zero, and looking back to Eqs. (42), and (47)–(49), we see that $\Gamma_n^d=0$.

In Sec. III A the vanishing of the vertex corrections will be shown to be directly related to the vanishing of the backscattering because the atomic scattering potentials are short ranged in the present model.

E. Expressions for *s-s*, *s-d*, and *d-d* Conductivity

With the vertex corrections identically equal to zero, expression (9) for the electrical conductivity in a cubic lattice ($\alpha=\beta$) reduces to

$$\sigma=\frac{2e^2}{\pi\Omega}\int d\eta\left(-\frac{df}{d\eta}\right)\operatorname{Tr}\langle v\operatorname{Im}G(\eta+i0)v\operatorname{Im}G(\eta+i0)\rangle\ . \qquad (55)$$

In the $\{|k_s\rangle,\ |k_d\rangle\}$ representation the operators v and G of (55) are 2×2 matrices. The trace is calculated and account is taken of relation (51). We obtain the following three contributions for the electrical conductivity:

$$\sigma=\sigma_{ss}+\sigma_{dd}+\sigma_{sd}+\sigma_{ds}\ , \qquad (56)$$

where

$$\sigma_{ss}=2\frac{2e^2}{\pi\Omega}\int d\eta\left(-\frac{df}{d\eta}\right)\sum_k v_s^2(k)\,[\operatorname{Im}G_{ss}(k,\eta+i0)]^2\ , \qquad (57a)$$

$$\sigma_{dd}=10\frac{2e^2}{\pi\Omega_c}\int d\eta\left(-\frac{df}{d\eta}\right)\sum_k v_d^2(k)\,[\operatorname{Im}G_{dd}(k,\eta+i0)]^2\ , \qquad (57b)$$

$$\sigma_{sd}=\sigma_{ds}=\sqrt{10}\,\sqrt{2}\,\frac{2e^2}{\pi\Omega_c}\int d\eta\left(-\frac{df}{d\eta}\right)\sum_k v_s(k)v_d(k)\times[\operatorname{Im}G_{sd}(k,\eta+i0)]^2\ . \qquad (57c)$$

Different coefficients appear in Eq. (57) because the total volume of s and d bands contain 2 and 10 electrons. These three terms represent the electrical conductivity corresponding, respectively, to the propagation of a pair of s electrons, a pair of d electrons, and two hybridized s-d electrons. The randomness of the d potentials acts upon the conductivity through the quantity Σ_d contained in the four Green's functions G_{ij}. It is appropriate to introduce the function defined between -1 and $+1$:

$$\phi(E)=N^{-1}\textstyle\sum_k v_s^2(k)\delta(E-\epsilon_s(k))\ . \qquad (58)$$

Using this function and the assumption (25),

$$\epsilon_d(k)=\alpha\epsilon_s(k)\ ,$$

the three expression (57) can be written more explicitly as

$$\sigma_{ss}=\frac{4e^2}{\pi\Omega_c}\int d\eta\left(-\frac{df}{d\eta}\right)\mathfrak{F}_{ss}(\eta)\ , \qquad (59a)$$

$$\sigma_{dd}=\frac{4\sqrt{5}\,e^2}{\pi\Omega_c}\int d\eta\left(-\frac{df}{d\eta}\right)\mathfrak{F}_{dd}(\eta)\ , \qquad (59b)$$

$$\sigma_{ds}=\sigma_{sd}=\frac{20e^2}{\pi\Omega_c}\int d\eta\left(-\frac{df}{d\eta}\right)\mathfrak{F}_{sd}(\eta)\ . \qquad (59c)$$

The three functions $\mathfrak{F}$ are given by

$$\mathfrak{F}_{ss}(\eta)=\gamma^4\Sigma_2^2(\eta)\int_{-1}^{+1}dE\,\frac{\phi(E)}{\{[(\eta-E-\Delta_1)(\eta-\Sigma_1-\alpha E)-\gamma^2]^2+[(\eta-E-\Delta_1)\Sigma_2]^2\}^2}\ , \qquad (60a)$$

$$\mathfrak{F}_{dd}(\eta)=\alpha^2\Sigma_2^2(\eta)\int_{-1}^{+1}dE\,\frac{(\eta-E-\Delta_1)^4\,\phi(E)}{\{[(\eta-E-\Delta_1)(\eta-\Sigma_1-\alpha E)-\gamma^2]^2+[(\eta-E-\Delta_1)\Sigma_2]^2\}^2}\ , \qquad (60b)$$

$$\mathfrak{F}_{sd}(\eta)=\alpha\gamma^2\Sigma_2^2(\eta)\int_{-1}^{+1}dE\,\frac{(\eta-E-\Delta_1)^2\,\phi(E)}{\{[(\eta-E-\Delta_1)(\eta-\Sigma_1-\alpha E)-\gamma^2]^2+[(\eta-E-\Delta_1)\Sigma_2]^2\}^2}\ . \qquad (60c)$$

We have made use of the explicit expression of $\overline{G}_{ss}$, $\overline{G}_{dd}$, and $\overline{G}_{ds}$ derived from definition (13), with $\Sigma_d(z)=\Sigma_1+i\Sigma_2$.

In the limit $\alpha=0$, the function $\mathfrak{F}_{dd}(\eta)$ and $\mathfrak{F}_{sd}(\eta)$ are identically zero and it is possible to simplify the form of $\mathfrak{F}_{ss}(\eta)$ by defining formally an s-electron self-energy $\Sigma_s=\gamma^2/(\eta-\Sigma_d)$, a quantity directly related to the relaxation time. For that reason we will use that limit for the discussion of two limiting cases in Secs. III A and III B. When $\alpha\neq0$, however, such a definition for Σ_s is not straightforward and we have to use the three integrals (60) to obtain the various contributions to the electrical conductivity.

III. DISCUSSION OF LIMITING CASES

It is interesting to investigate the usual limiting cases (weak-scattering and dilute-concentration limits) and to compare our results in these limits with previous treatments. The discussion is carried out for $\alpha = 0$ without lack of generality if we consider alloys whose Fermi energy E_F is far from the hybridization gap. In that case the function (60a) takes the simple form

$$\mathfrak{F}_{ss}(\eta) = \int_{-1}^{+1} dE\, \phi(E)$$
$$\times \{\mathrm{Im}[(\eta - E - \Delta_1) - \gamma^2(\eta - \Sigma_d)^{-1}]^{-1}\}^2 \;. \qquad (61)$$

A. Weak-Scattering Limit (Comparison with Boltzmann Equation)

In the weak-scattering limit it can be shown from Eq. (22) that Σ_2 is proportional to δ^2 and that $\Sigma_1 \simeq \bar{\epsilon}$. The quantity $\gamma^2/(\eta - \Sigma_d)$ in the denominator of (61) can be viewed as the self-energy Σ_s of s electrons. Since

$$\mathrm{Im}\Sigma_s = \gamma^2 \Sigma_2 [(\eta - \Sigma_1)^2 + \Sigma_2^2]^{-1} \;, \qquad (62)$$

we can use in the weak-scattering limit the formula (122) of Velický's paper[4] provided $\gamma/(\eta - \bar{\epsilon}) \gtrsim 1$. In that limit the s conductivity is thus

$$\sigma_{ss} = \frac{e^2}{\Omega_c} \int d\eta \left(-\frac{df}{d\eta}\right) \Delta^{-1} \mathrm{Im}\Phi(\eta - i0)\big|_{\Delta = \Delta(\eta)} \;, \qquad (63)$$

where

$$\Delta(E) = |\mathrm{Im}\Sigma_s(E)| \;, \qquad (64)$$

with

$$\Phi(z) = (\pi N)^{-1} \int_{-1}^{+1} dE (z - E)^{-1} \phi(E) \qquad (65)$$

being a function analytic in both half-planes and decaying as z^{-1} for $z \to \infty$. In (65), only the lowest-order term ($\sim \delta^2$) is kept and the exact criterion for this approximation is the inequality

$$\gamma^2(\eta - \bar{\epsilon})^{-1} \frac{\partial}{\partial \eta} \mathrm{Im}\Phi(\eta - i0) \ll \mathrm{Im}\Phi(\eta - i0) \;, \qquad (66)$$

which is equivalent to the London-Peieris criterion[15] for the applicability of the transport equation to Hamiltonian (1).

It is therefore of interest to compare this result to the solution of the Boltzmann equation in the hybridized model (1). We start from the velocity correlation function

$$\sigma_{ss}(\omega) = (e^2/i\omega\Omega)\mathfrak{D}(\omega + i0) \quad \text{as } \omega \to 0. \qquad (67)$$

$\mathfrak{D}(z)$ can be represented by a sum of diagrams in the ladder approximation which is valid in the weak-scattering limit (terms to order δ^2) (Fig. 1). We use for the Green's function of s and d electrons the expressions derived in Sec. II C, with $\alpha = 0$. In this approximation the Green's functions are equivalent to the corresponding expressions in Ref. 8.

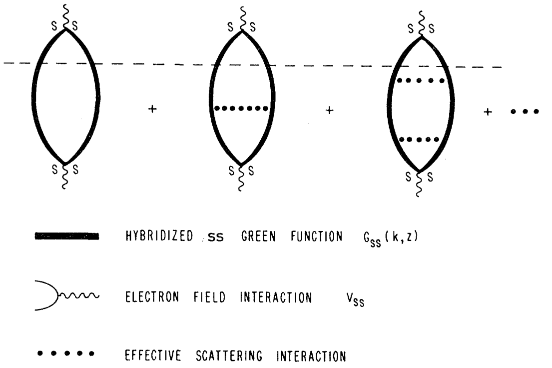

FIG. 1. Diagrammatic representation of the velocity correlation function $\mathfrak{D}(\omega)$ in the weak-scattering limit. The part of the diagrams under the dotted line defines the operator $\lambda_k^{ss}(z)$ which satisfies an integral equation represented by the diagrams of Fig. 2.

In the weak-scattering limit the self-energy Σ_d is equal to

$$\Sigma_d = \bar{\epsilon}_d + i\Sigma_2 \;, \qquad (68)$$

with

$$\Sigma_2 = \mathrm{Im}\Sigma_d(z) = \pi x y \delta^2 N^{-1} \sum_{k'} \delta\left(z - \bar{\epsilon}_d - \frac{\gamma^2}{z - E_s(k')}\right) \;. \qquad (69)$$

To calculate the electrical conductivity it is useful to introduce the function $\lambda_k^{ss}(z + i0,\ z - i0)$ which represents the sum of diagrams of Fig. 1 without the upper electron field interaction matrix element. This enables us to write for σ_{ss}

$$\sigma_{ss}(\omega) = -\,\omega^{-1} \textstyle\sum_k G_s(\eta + i0)\, G_s(\eta - i0 + \omega)$$
$$\times \lambda_k^{ss}(\eta + i0,\ \eta - i0) v_{ss}(k) \quad \text{as } \omega \to 0 \qquad (70)$$

which can be reduced for $\omega = 0$ to

$$\sigma_{ss}(0) = e^2 \Omega_c^{-1} \sum_k \int d\eta \left(-\frac{df}{d\eta}\right) \frac{v_{ss}(k) \lambda_k^{ss}(\eta + i0,\ \eta - i0)}{2|\mathrm{Im}\Sigma_s(\eta)|}$$
$$\times \delta\left(\eta - E(k) - \frac{\gamma^2}{z - \bar{\epsilon}_d}\right) \;. \qquad (71)$$

The function $\lambda_k^{ss}(\eta^+, \eta^-)$ has to satisfy the integral equation (cf. Fig. 2)

$$\lambda_k^{ss}(\eta^+, \eta^-) = v_{ss}(k) + \gamma^2 [G_{dd}^{\mathrm{NH}}(k, \eta^+)]^2 \sum_{k'} |\langle k| U - \bar{U} |k'\rangle|^2$$
$$\times [G_{dd}(k', \eta^-)]^2 \lambda_{k'}^{dd}(\eta^-) \;, \qquad (72)$$

where U is the scattering potential $\sum_n \epsilon_n^d |n_d\rangle\langle n_d|$ and G_d^{NH} is the nonhybridized interacting d Green's function. Equation (72) can be written more explicitly:

$$\lambda_k^{ss}(\eta^+, \eta^-) = v_{ss}(k) + 2\pi \frac{\gamma^2}{(\eta - \epsilon_d)^2}\, xy \frac{\delta^2}{N} \sum_{k'} \frac{\lambda_{k'}^{dd}(\eta^+, \eta^-)}{2|\mathrm{Im}\Sigma_d|}$$

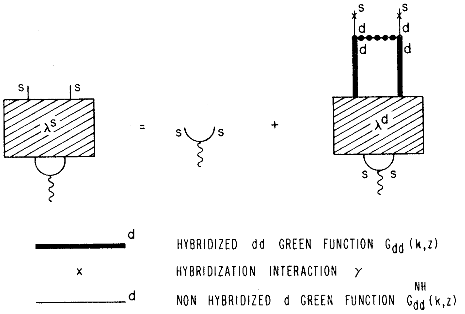

FIG. 2. Diagrammatic representation of the integral equation defining operator $\lambda_k^{ss}(z)$.

$$\times\delta\left(\eta-\bar{\epsilon}_d-\frac{\gamma^2}{\eta-E_s(k')}\right)\;. \tag{73}$$

If we introduce the notations

$$f_k^s=\frac{\lambda_k^{ss}}{2\,|\mathrm{Im}\Sigma_s|}\;,\qquad f_k^d=\frac{\lambda_k^{dd}}{2\,|\mathrm{Im}\Sigma_d|}\;, \tag{74}$$

we obtain the usual Boltzmann equation

$$v_{ss}(k)=\sum_{k'}W_{sd}(k,k')\,(f_k^s-f_{k'}^d)\;, \tag{75}$$

where the function $W_{sd}(k, k')$ is the probability of scattering of an s electron with wave vector k into a d state with wave vector k':

$$W_{sd}(k,k')\big|_{\epsilon_s(k)=\eta}=\frac{2\pi}{N}\,\frac{\gamma^2}{(\eta-\bar{\epsilon}_d)^2}$$

$$\times xy\delta^2\delta\left(\eta-\bar{\epsilon}_d-\frac{\gamma^2}{\eta-E_s(k')}\right)\;. \tag{76}$$

The k independence of $\langle k|U-\bar{U}|k'\rangle$ due to the short-range order of the scattering potential and the condition $v_{ss}(k)=-v_{ss}(-k)$ makes the backscattering vanish. A current-relaxation time can be introduced:

$$\tau^{-1}(k)\big|_{\epsilon_s(k)=\eta}=2\pi xy\delta^2\frac{\gamma^2}{(\eta-\bar{\epsilon}_d)^2}$$

$$\times\frac{1}{N}\sum_{k'}\delta\left(\eta-\bar{\epsilon}_d-\frac{\gamma^2}{\eta-E_s(k')}\right)\;. \tag{77}$$

The electrical conductivity becomes simply

$$\sigma=\frac{2e^2}{\Omega_c}\sum_k\int d\eta\left(-\frac{df}{d\eta}\right)\tau(k)\,v_{ss}^2(k)\delta(\eta-\epsilon_s(k)) \tag{78}$$

or

$$\sigma=\frac{2e^2}{\Omega_c}\int\left(-\frac{df}{d\eta}\right)\tau(\eta)\,\mathrm{Im}\Phi(\eta+i0)\;, \tag{79}$$

which coincides with Eq. (54) if, as is obvious from Eqs. (62), (69), and (77),

$$\tau^{-1}(k)=2\,|\mathrm{Im}\Sigma_s(\eta(k))|\;. \tag{80}$$

B. Dilute-Concentration Limit

It is also of interest to compare the dilute limit of the CPA hybridized s-d-band model with the expressions of the conductivity derived by Gomes[10] in dilute alloys of transition metals taking into account the s-s, d-d, and s-d scattering at the impurity.

In the dilute-concentration limit (A_xB_{1-x}, with $x\sim 0$), the expression for the s conductivity can be written in the same form as Eq. (63):

$$\sigma_{ss}=\frac{2e^2}{\Omega_c}\int d\eta\left(-\frac{df}{d\eta}\right)\tau^{-1}\,\mathrm{Im}\Phi(\eta-i0)\;, \tag{81}$$

where the transport relaxation time τ is defined by

$$\tau^{-1}(\eta)=2\,|\Delta|=2\gamma^2(\eta-\epsilon_d^B)^{-1}\Sigma_2(\eta)\;. \tag{82}$$

If we use definition (22) for Σ, in the dilute limit (82) τ^{-1} takes the explicit form

$$\tau^{-1}(\eta)=2\gamma^2\delta^2x(\eta-\epsilon_d^B)^{-1}\,\mathrm{Im}F_{dd}(\eta+i0,\epsilon_d^B)$$

$$\times[1-\delta F_{dd}(\eta+i0,\epsilon_d^B)]^{-1}\;. \tag{83}$$

In (83), the function F_{dd} depends only on the pure-host d resonance energy ϵ_d^B. When η is close to the energy resonance of the d level of the impurity ϵ_d^A, we can, using expression (31) for F_{dd}, write the relaxation times as

$$\tau^{-1}=\pi\delta^2x\frac{\gamma^4}{(\eta-\epsilon_B)^2}\,\frac{\rho_{0s}[\eta-\gamma^2/(\eta-\epsilon_d^B)]}{\{\eta-\epsilon_d^A-\gamma^2\,\mathrm{Re}F_{0s}[\eta-\gamma^2/(\eta-\epsilon_d^B)]\}^2+\{\tfrac{1}{2}\pi\gamma^2\rho_{0s}[\eta-\gamma^2/(\eta-\epsilon_d^B)]\}^2}\;. \tag{84}$$

If we now introduce the resonant density of d states of the impurity A near ϵ_d^A [see Eq. (2.45) of Ref. 8] we obtain

$$\rho_d^A(\eta)=\frac{5\gamma^2\rho_{0s}[\eta-\gamma^2/(\eta-\epsilon_d^B)]}{\{\eta-\epsilon_d^A-\gamma^2\,\mathrm{Re}F_{0s}[\eta-\gamma^2/(\eta-\epsilon_d^B)]\}^2+\{\tfrac{1}{2}\pi\gamma^2\rho_{0s}[\eta-\gamma^2/(\eta-\epsilon_d^B)]\}^2}\;. \tag{85}$$

The transport relaxation time of s electrons may be written in a form similar to Eqs. (12) and (13) of Gomes[10] (provided $V_{ss}=0$, since we do not consider direct interaction between s electrons):

$$\tau^{-1}=\frac{\pi}{5}\,\frac{\delta^2}{(\eta-\epsilon_d^B)^2}\,\gamma^2\rho_d^A(\eta) \tag{86}$$

if we introduce an effective matrix element for the s-d scattering potential,

$$V_{sd}^{\text{eff}} = \gamma\delta/(\eta - \epsilon_d^B) \ . \qquad (87)$$

In the formalism of the present paper the dependence of s-d scattering on the electron energy appears explicitly in the definition of $V_{s\text{-}d}^{\text{eff}}$.

The discussion was restricted to $\alpha = 0$, and therefore expression (87) for $V_{s\text{-}d}^{\text{eff}}$ is not valid for $\eta = \epsilon_d^B$. We will see, however, in the numerical example presented in Sec. IV that when $\alpha \neq 0$ the effective scattering potential is indeed maximum when the Fermi energy lies in the vicinity of the d resonance levels ϵ_d^B or ϵ_d^A.

IV. NUMERICAL EXAMPLES

The formalism presented in the preceding sections has been first applied to the calculation of the d-scattering-induced resistivity of the Levin-Ehrenreich model for Au-Ag discussed in Ref. 8. Here the d bands are filled and the s-d hybridization is not believed to affect significantly the behavior of the residual electrical resistivity of almost pure s electrons. As a matter of fact, the calculated curve of resistivity versus concentration shows only slight deviations from Nordheim's law. A quantitative comparison with experimental data, however, would require the calculation of the contribution to the resistivity produced by the direct s scattering mechanism due to the small difference in the position of the two s bands, which is not included in the present theory.

Instead, we will here focus on a more interesting, although purely theoretical, example which exhibits striking deviations from the linear dependence of resistivity versus concentration for small concentration and from Nordheim's $x(1-x)$ law for higher concentrations. As discussed in the Introduction, these two types of deviations have been observed in some transition-metal-based binary alloys. The maximum deviations to the $x(1-x)$ rule are expected to occur when the two d-band peaks in the alloy are split and when the d bands of the two constituents are unfilled. With increasing concentration the Fermi level moves from one d band to the other and crosses a region of minimum density of states. This minimum is expected to have some influence on the resistivity-versus-concentration curve, while the effect of s-d hybridization is expected to be important for concentrations such that the Fermi level lies in a region of large-d density of states. The artificial-alloy model presented hereafter exhibits these features. We shall now characterize this numerical example and first summarize the parameters describing the pure systems of the two constituents.

(i) For convenience the unhybridized s-band density of states is assumed to have the Hubbard semielliptic density of states

$$\rho_{0s}(E) = 2(\pi w_s^2)^{-1}(w_s^2 - E^2)^{1/2} \ , \quad -w_s \leq E < w_s \ . \qquad (88)$$

The half-bandwidth is $w_s = 7$ eV, which is a reasonable choice for noble and transition metals. Hereafter w_s will be taken as the unit of energy ($w_s = 1$). The unhybridized s band is flat and broad. It is not too different from a free-electron band for Fermi energies appropriate to most transition metals. We shall suppose that the s-band bottom is the same for the two constituents, and therefore we neglect the direct s scattering.

(ii) The unhybridized d band is assumed to have the same semielliptic shape as the s band with a scaling factor $\alpha = 0.05$. This is a value about two times larger than α_{min} calculated in Appendix A and not inconsistent with band calculations of transitions metals.

(iii) The scattering parameter is taken such that $\delta / w_s = 8\alpha$. This corresponds to a rather strong scattering (2.8 eV), although the conditions for the split-band limit defined in Ref. 8 are far from being fulfilled. In the units $w_s = 1$, and taking the energy origin such that $\epsilon_d^A = \frac{1}{2}\delta$ and $\epsilon_d^B = -\frac{1}{2}\delta$, the scattering parameter has the value $\delta = 0.4$. The difference between the bottom of the s band and ϵ_d^A is chosen to be 3 eV. This value lies between ϵ_d^{Ag} and ϵ_d^{Au} and is not far from the d resonance level generally attributed to Pd.

(iv) The hybridization constant is taken to be $\gamma = \gamma^{\text{Cu}}(\epsilon_d / \epsilon_d^{\text{Cu}}) = 0.314\epsilon_d$ when the values for Cu are obtained from Ref. 16. The scaling of γ based on the Cu value is here quite reasonable, since ϵ_d^{Cu} lies between ϵ_d^A and ϵ_d^B.

(v) The function $\phi(E)$ in Eqs. (60) is supposed, as in Velický's paper, to have the free-electron form

$$\phi(E) = \textstyle\sum_k v_s^2(k)\delta(E - \epsilon_s(k))\, \alpha(1 - E^2)^{3/2} \qquad (89)$$

and for simplicity we will put $T = 0$ in (59).

The numerical results of this model are summarized in Figs. 3–5. In Fig. 3, the impurity concentration x is fixed and has the value $x = 0.15$. The alloy d density of states corresponding to this concentration is the lower curve of Fig. 5(b). The three curves σ_{ss}, σ_{sd}, and σ_{dd} corresponding to the three contributions to the dc electrical conductivity [Eqs. 59(a)–59(c)] are plotted for a Fermi energy varying continuously from $-0.3w_s$ to $0.3w_s$. The total conductivity is represented by the dotted line. A logarithmic scale has been used for σ and the unit is chosen such that $\sigma_{sd} = 1$ for $E = 0$. Far from the peaks of the two d subbands centered on ϵ_d^A and ϵ_d^B there is one order of magnitude difference between the three conductivities. When the Fermi level lies in a region of large-d density of states in the vicinity of the two d resonance levels, σ_{ss}, σ_{sd}, and σ_{dd} conductivities are of the same order of magnitude, while the total conductivity is minimum. In the majority band, σ_{sd} and σ_{dd} can even

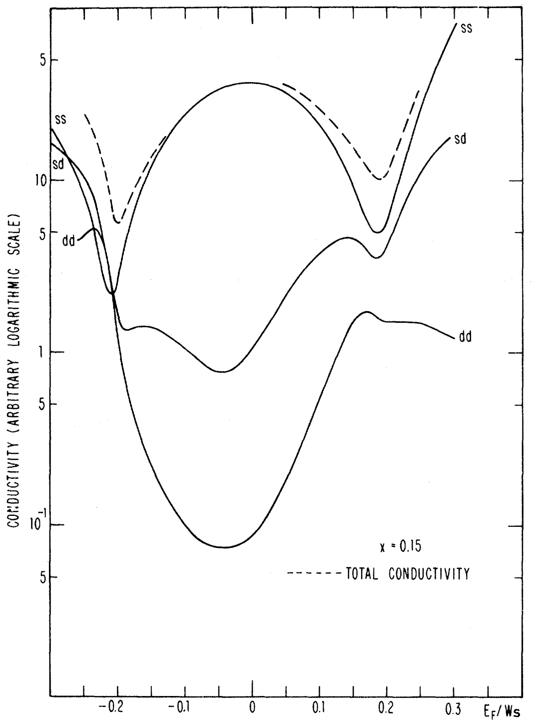

FIG. 3. Total dc electrical conductivity at $T=0$, σ_{ss}, σ_{sd} and σ_{dd} conductivities versus E_F (in units of half s bandwidth) for physical parameters corresponding to the lower curve of Fig. 5(b).

be larger than σ_{ss}. These features illustrate the strong influence of s-d hybridization on the conductivity. When $E \simeq \epsilon_d^A$ and $E \simeq \epsilon_d^B$, the cumulative effect of the large d density of states and of the indirect d scattering is maximum and the total conductivity is minimum.[17] The strong s-d hybridization interaction favors the scattering of s electrons to the d band and the three types of conductivities s, mixed sd, and d become of the same magnitude. As expected, the d conductivity is minimum when the self-energy Σ_d is maximum, i.e., between the two d-subband peaks, while in that region the s conductivity has a relative maximum. The behavior of s-d conductivity expresses its mixed character.

In Figs. 4 and 5, we examine the dependence of the residual resistivity versus concentration. The number of s and d electrons of the two constituents n_B and n_A is taken to be 10 and 6 such that in pure metals the d bands are unfilled. The number $n_B = 10$ corresponds to the number of valence electrons in Ni or Pd. We have chosen $n_A = 6$ for two reasons: (a) We are interested in describing, at least qualitatively, departures from the usual behavior of resistivity versus concentration like that exhibited by PdU.[18] (b) As the concentration of atoms B increases, the Fermi energy crosses the region of the density of states where non-self-consistent calculations give a poor description of the self-energy Σ_d (cf. Ref. 19) and where a CPA calculation is needed.

Figure 4 shows the residual resistivity versus concentration for this electronic population. The deviation of d conductivity from the $x(1-x)$ law has been calculated in the one-band model of Ref. 6. In the two-s-d-band model, because of the cumulative effect of the d scattering and of the hybridization coupling, the departure from the rigid-band behavior can be still more pronounced. The d conductivity, however, is small compared to the s conductivity in most of the s band, except in small regions, where they can be of the same order of magnitude (cf. Fig. 3). For that reason and because this is the total resistivity that is measured, we have only plotted the total resistivity curve. This curve is not symmetric about $x=0.5$ as Nordheim's rule suggests. The maximum occurs at $x=0.75$. For low concentration (this region is magnified in the upper left corner with the Fermi density of states versus concentration curve), the dependence is not linear and indicates a change of slope at about 6% correlated with a minimum in the density of states.[20]

With the results of Fig. 3 in mind, the detailed behavior of the resistivity can be understood by looking at the variation with concentration of the Fermi level E_F and of the impurity d density of states as shown in Figs. 5(a) and 5(b). For small

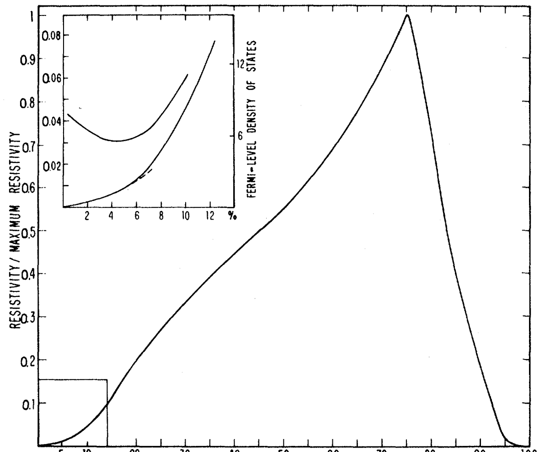

FIG. 4. Total residual resistivity versus concentration in units of its maximum value. The physical parameters are those of Figs. 5(a) and (b). The number of valence electrons is $6x + 10(1-x)$. The region of low concentration is magnified in the upper part of the picture and shows the change of slope of the resistivity curve correlated with a minimum in the density of states. The asymmetry of the total curve and the sharp maximum at 75% emphasizes the importance of s-d hybridization in that concentration range.

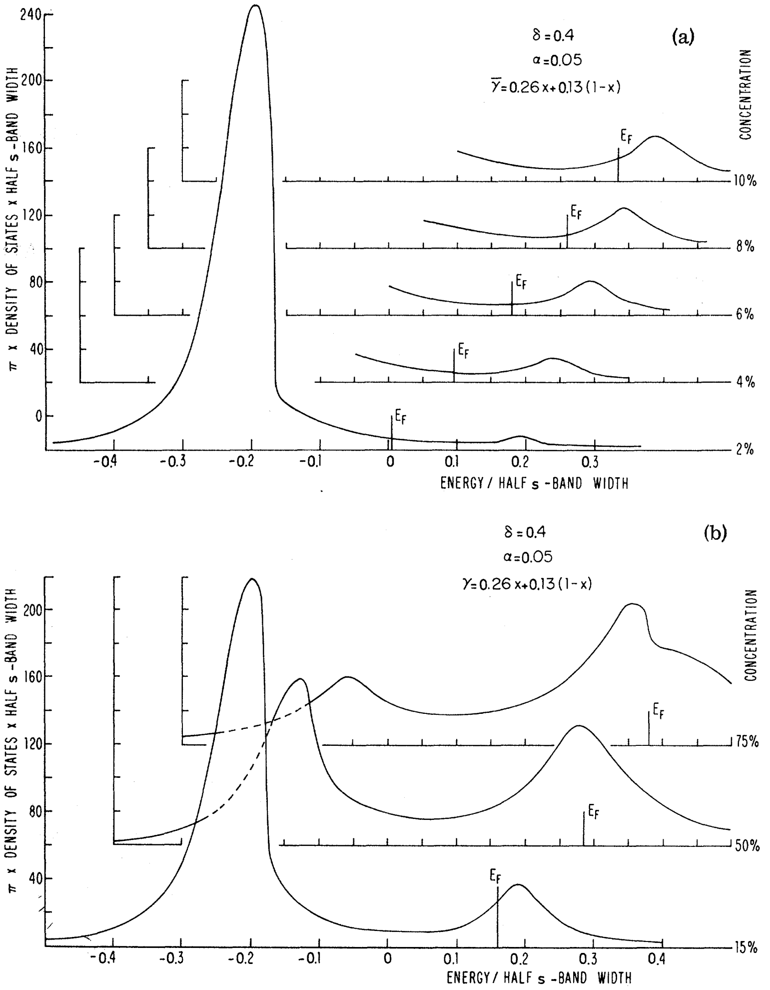

FIG. 5. The d density of states of the two s–d alloy model for various increasing concentrations. The parameters δ and $\bar{\gamma}$ are expressed in units $w_s = 1$. The half s bandwidth w_s is supposed to be equal to 7 eV. The Fermi level is calculated for a number of valence electrons equal to $6x + 10(1-x)$.

concentration, the d band of B metal is not filled, and with increasing concentration, E_F moves to the right in a region of decreasing density of states. At about 6%, the Fermi level moves into the impurity d resonance. The density of states at Fermi level now increases and this can be related to the change of the slope of the resistivity. This picture can give a possible explanation of the striking behavior of the specific heat and of the resistivity observed[13] in PdU if we suppose the existence of some f-d resonance level for U.[21]

In Fig. 5(b), we consider higher concentrations. The Fermi level changes more slowly. For 50%, it lies at the center of the d resonance peak of A. As shown in Fig. 3, the effect of s-d coupling on resistivity is now becoming important because the contributions of σ_{sd} and σ_{dd} are of the same order of magnitude as that of σ_{ss}. This explains the asymmetry of the resistivity curve, which in our example is maximum for 75%.

A similar type of deviation from Nordheim's rule has been observed in transition-metal–noble-metal alloys and interpreted by Mott as being caused by s-d scattering. The d bands of transition metals are unfilled and a strong s-d scattering occurs for concentrations such that the Fermi level lies in a region of high d density of states. Though the picture we used in this paper is somewhat different, our interpretation of this phenomenon is physically equivalent. We did not introduce a direct s-d scattering potential. The randomness of d levels acts on the conductivity of s electrons via the s-d hybridization coupling γ and gives rise to an indirect effective s-d scattering potential which is maximum in the middle of the d density of states peaks.

A quantitative calculation of the residual resistivity of disordered binary alloys requires much more information on the alloy density of states and Fermi surface. For instance, one cannot content oneself with simple model functions for $\rho_{0s}(E)$ and $\phi(E)$. We have shown, however, in Sec. III that a self-consistent CPA-model theory of the residual electrical conductivity can give a qualitative explanation of some features observed in transition-metal-based alloys and is a useful starting point for further investigation of the transport properties of this type of alloy.

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APPENDIX A: CONDITION FOR DISAPPEARANCE OF HYBRIDIZATION GAP

It is easy to derive the condition for the disappearance of the hybridization gap in the s-d model used in this paper if we choose for $\rho_{0s}(E)$ the Hubbard semielliptic density of states

$$\rho^H_{0s}(E) = 2(\pi w_s^2)^{-1}\,(w_s^2 - E^2)^{1/2} \quad \text{for } -w_s < E < w_s \ . \tag{A1}$$

The transform

$$F_{0s}(z) = \int_{-\infty}^{+\infty} \rho_{0s}(E)(z-E)^{-1}\,dE \tag{A2}$$

yields the explicit form

$$F^H_{0s}(z) = (2/w_s^2)\,[z - (z^2 - w_s^2)^{1/2}] \ . \tag{A3}$$

Using expressions (A1) and (A3), Eq. (20) for $F_{dd}(z)$ becomes

$$F_{dd}(z) = 2(\alpha^2 w_s^2)^{-1}\left(z - \Sigma + \alpha^2\,\frac{(z-\Delta_1-E_+)(E_+^2-w_s^2)^{1/2} - (z-\Delta_1-E_-)(E_-^2-w_s^2)^{1/2}}{\{[\alpha(z-\Delta_1)-(z-\Sigma)]^2+4\gamma^2\alpha\}^{1/2}}\right) \ . \tag{A4}$$

The condition for the disappearance of the gap in pure metal ($\Sigma = \epsilon_d = 0$) is simply

$$\operatorname{Im} F_{dd}(0) \geq 0 \ . \tag{A5}$$

This condition is equivalent to $|E_1| < w_s$ or

$$\gamma^2 < \alpha w_s(w_s + \Delta_1) \ . \tag{A6}$$

APPENDIX B: CALCULATION OF VELOCITY MATRIX ELEMENTS

In this appendix we show that the model Hamiltonian (1) implies the vanishing of velocity matrix elements $\langle k_s | v | k_d\rangle$ and $\langle k_d | v | k_s\rangle$ and that as a consequence we can write Eq. (51)

$$\langle k_i | \hat{p}^\alpha | k'_j\rangle = \delta_{ij}\delta_{kk'}\, m\left(\frac{\partial}{\partial k_i^\alpha}\right)\epsilon_i(k) = m v_i^\alpha(k) \ ,$$

where i and j can be either s or d.

To derive Hamiltonian (1) in the tight-binding approximation, one first solves the Schrödinger equation

$$H|\psi\rangle = (T + \textstyle\sum_i V_i)|\psi\rangle \ ,$$

where V_i is the atomic potential at site i, by expanding $|\psi\rangle$ in terms of atomic s and d orbitals,

$$|\psi\rangle = \textstyle\sum_n a_n^s |n_s\rangle + a_n^d |n_d\rangle \ .$$

The second step is to neglect matrix elements $\langle n_d | \sum_{l\neq m} V_l | m_d\rangle$ or $\langle n_d | \sum_{l\neq m} V_l | m_s\rangle$ with three different site indices and to keep only the off-diagonal hopping integrals $t_{mn} = \langle n_d | V_m | m_d\rangle$ and the diagonal hybridization constant $\gamma = \langle n_s | \sum_{l\neq n} V_l | n_d\rangle$. This interaction represents the hybridization of s and d electrons on site n due to the crystal field produced by all other atoms on sites $m \neq n$. Because off-diagonal matrix elements are neglected in the definition of γ, the hybridization constant is k independent in model Hamiltonian (1).

We can now define the velocity operator for the two-band model by generalizing a method used by Matsubara[22] to calculate the electrical conductivity of doped semiconductors. The spatial variables appearing in Hamiltonian (1) are site coordinates. The position operator in Wannier space is defined by[23]

$$\hat{R} = \textstyle\sum_n R_n |n_s\rangle\langle n_s| + R_n |n_d\rangle\langle n_d| \ , \tag{B1}$$

with

$$\hat{R}|n_s\rangle = R_n|n_s\rangle \ , \quad \hat{R}|n_d\rangle = R_n|n_d\rangle \ . \tag{B2}$$

The velocity operator is determined by using the equation of motion

$$\hat{v} = i[H, \hat{R}] = i(H\hat{R} - \hat{R}H) \ . \tag{B3}$$

After calculating the commutator, it is straightforward to show that because of (B2) and the k independence of γ, the matrix elements $\langle k_s | \hat{v} | k_d\rangle$ and $\langle k_d | \hat{v} | k_s\rangle$ vanish, while

$$\langle k_d | \hat{v} | k_d\rangle = i\sum_{m\neq n} t_{mn} R_{mn}\, e^{ikR_{mn}} = \frac{\partial}{\partial k}\sum_{m\neq n} t_{mn}\, e^{ikR_{mn}} \ , \tag{B4}$$

with $R_{mn} = R_m - R_n$.

If we restrict the summation over m and n to nearest neighbors, Eq. (B4) defines the group velocity of an electron of kinetic energy $(w_d/2)s(k)$,

$$v_d(k) = \frac{w_d}{2}\,\frac{\partial}{\partial k}\,s(k) \ , \tag{B5}$$

where w_d is the ordered d bandwidth and $s(k)$ is the dispersion relation discussed in Sec. II A. A similar expression holds for $\langle k_s | \hat{v} | k_s \rangle$ in the tight-binding approximation but quite generally can be expressed as

$$v_s(k) = \frac{\partial}{\partial k} E_s(k) , \tag{B6}$$

where $E_s(k)$ is the dispersion relation for s electrons.

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Retardation Effects in Azbel'-Kaner Cyclotron Resonance

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Corrections to the Azbel'-Kaner theory of the magnetic-field-dependent surface impedance of metals have been calculated. The results illustrate the effects of the finite transit time of the electrons in their passage through the skin layer. The cyclotron-resonance line shapes are modified from the Azbel'-Kanel results for both the high-$(\omega_c\tau)$ and low-$(\omega_c\tau)$ limits. The bearing of these results on experimental determinations of carrier effective masses and relaxation times are discussed. Finally, the background signals from the nonresonant electrons are calculated for an arbitrary cutoff angle for specular reflection of the electrons at the surface.

I. INTRODUCTION

Azbel'-Kaner cyclotron-resonance (AKCR) measurements have played an important role in the study of the Fermi surfaces of metals. The importance of the technique lies in the precise measurements provided of the effective masses and lifetimes of the carriers averaged over particular $\vec{K}$-space orbits. Recent advances in experimental techniques (the development of intense infrared sources of radiation[1,2]) and metals theory (the work on the electron-phonon interaction[3]) have focused interest on precise measurements of the frequency and temperature dependence of the electronic masses and relaxation rates. As the theoretically predicted mass shifts are small, careful consideration of line-shape effects are essential to proper interpretation of the experiments.[2]

The general problem of the magnetic-field-dependent surface resistance of a metal has not yet yielded an exact solution. The Azbel'-Kaner theory[4] is valid under the conditions of the extreme anomalous skin effect (ASE) provided also that the time of flight of the resonant electrons in their passage through the skin layer is small compared with the rf period. This last condition can break down