PHYSICAL REVIEW B VOLUME 35, NUMBER 11 15 APRIL 1987-I

Residual resistivity of defects in metals

Raju P. Gupta

Section de Recherches de Métallurgie Physique, Centre d'Etudes Nucléaires de Saclay, 91191 Gif-sur-Yvette Cédex, France

(Received 17 November 1986)

A simple expression for the residual resistivity of defects in metals is derived which includes the Bloch-wave character of the electronic structure of the host metal lattice at its Fermi surface. This expression involves, apart from Friedel phase shifts of the defect, only the average Fermi velocity and the average *s*, *p*, *d*, etc. partial-wave character of the electron states of the host metal atom at its Fermi energy, both of which are easily obtained in the course of a standard band-structure calculation. The explicit dependence on the partial-wave character makes the expression somewhat different from the well-known formula for the jellium matrix (which is, however, recovered in the free-electron limit), and the expression derived earlier by Gupta and Benedek. Calculations for impurities in copper show good agreement with experiment. We also show that the residual resistivities are extremely sensitive to the values of the Friedel phase shifts. Very minor changes in their values alter the residual resistivities dramatically. This indicates the major role played by these phase shifts in determining the residual resistivities, and the need for their accurate determination.

I. INTRODUCTION

The calculation of the residual resistivity of defects in metals is tedious since, even within the relaxation time solution of the Boltzmann equation, it requires the evaluation of rather laborious double integrations over the Fermi surface involving the matrix elements of scattering by the defect potential.[1] For simple-metal impurities in simple metals, these matrix elements have been evaluated using the pseudopotential theory and the linear-response approximation.[2] Such an approach is, however, unlikely to be valid for defects such as vacancies or interstitials, or interstitial impurities such as H, where the perturbation created is rather large and the linear-response theory no longer valid.[3,4] For the jellium matrix, an alternative approach based on the scattering theory can be used where the approximation of a weak perturbation is no longer necessary and the calculation is valid to all orders in the strength of the defect potential. The spherical nature of the Fermi surface allows the integrations to be performed analytically, and the resulting final formula for the defect resistivity is extremely simple and requires essentially the knowledge of the phase shifts of the potential of the defect at the Fermi energy.[5]

Indeed, similar problems are encountered elsewhere, especially in the evaluation of the electron-phonon coupling constant λ for the calculation of the superconducting transition temperature T_c in metals and compounds. There, also, one is required to evaluate tedious double-Fermi-surface integrals involving the matrix elements of the electron-phonon interaction.[6,7] In this case, however, a useful approximation has been introduced by Gaspari and Gyorffi[8,9] for transition metals, which results in a tremendous simplification. The integrations over the Fermi surface are performed analytically and the resulting final expression for λ is rather simple and involves essentially the phase shifts of the muffin-tin potential and the partial and the total densities of states at different atomic sites. This formula has been widely employed in the calculation of λ and the prediction of T_c for many metals and compounds, and the results obtained are, generally speaking, in rather good agreement with experiment.[10] This includes Nb and its compounds which have rather complicated Fermi surfaces. An attempt along similar lines was made by Gupta and Benedek[11] for the calculation of the residual resistivity. They obtained a formula very similar to that obtained by Friedel[12] for a jellium matrix. In their derivation, however, they also used the optical theorem,[1] which allowed the wave-function character at the Fermi surface to be expressed directly in terms of the total densities of states (DOS's) at the Fermi energy. This, unfortunately, puts serious limitations on the validity of their formula, not only in the case of transition metals of interest, such as Nb and Pd, with a strong *d* component at the Fermi energy, but also for noble metals such as Cu.[13,14]

In this paper we present an alternative derivation, without invoking the optical theorem, and obtain a formula for the residual resistivity which is similar, but not identical, to that obtained by Gupta and Benedek. The derivation of this formula is given in Sec. II, where we show that the residual resistivity of a solute or a defect is strongly dependent on the partial *s*, *p*, *d*, *f*, etc. -type DOS's of the host at its Fermi energy, and the Friedel phase shifts of the defect potential. Calculations of the defect resistivities for some substitutional impurities are presented in Sec. III and final remarks are given in Sec. IV.

II. DERIVATION OF THE FORMULA FOR RESIDUAL RESISTIVITY

As usual, we will use the Boltzmann equation to calculate the residual resistivity where it can be expressed in terms of an integral over the Fermi surface of the scalar product of the vector mean free path $\mathbf{\Lambda}(k)$ and the electron velocity $\mathbf{V}_k$ of an electron with wave vector $\mathbf{k}$ and band index n. In the relaxation-time approximation, $\mathbf{\Lambda}(k)$ is taken to be in the same direction as $\mathbf{V}_k$,

$$\mathbf{\Lambda}(k)=\tau(k)\mathbf{V}_k \ , \tag{1}$$

where $\tau(k)$ is the relaxation time due to the scattering by the defects. The residual resistivity ρ of the defect can then be written as

$$\frac{1}{\rho}=\frac{e^2}{12\pi^3}\int_{\mathrm{FS}}\frac{dS_k}{|\nabla_k E_k|}\tau(k)\mathbf{V}_k\cdot\mathbf{V}_k \ , \tag{2}$$

where FS denotes the integral over the Fermi surface. The relaxation time $\tau(k)$ is related to the probability $P(k,k')$ of scattering from an initial unperturbed state k to the final perturbed state k' through the relation

$$\frac{1}{\tau(k)}=n_i N\sum_{k'}P(k,k')(1-\cos\theta) \ , \tag{3}$$

where θ is the angle between $\mathbf{V}_k$ and $\mathbf{V}_{k'}$ ($\cos\theta=\mathbf{V}_k\cdot\mathbf{V}_{k'}/|\mathbf{V}_k\cdot\mathbf{V}_{k'}|$), n_i the number of defects, and N the number of units cells, each with volume Ω_0 ($N\Omega_0$ is the volume of the crystal). Further, $P(k,k')$ can be written as

$$P(k,k')=\frac{2\pi}{\hbar N^2}|T(k,k')|^2\delta(E_k-E_{k'}) \ , \tag{4}$$

where the transition matrix $T(k,k')$ is given by

$$T(k,k')=\langle\Psi_{k'}^s|\Delta V|\Psi_k\rangle \tag{5}$$

and describes the scattering of an electron from the initial state with wave function Ψ_k in the pure metal to the final state $\Psi_{k'}^s$ in the solid with the defect by the extra potential ΔV of the defect.

We now make the muffin-tin (MT) approximation in which the whole crystal is divided into touching spheres and the potential outside these spheres (the interstitial region) is assumed constant. Within the augmented-plane-wave (APW) formalism[15] the wave function inside a MT sphere of radius R in the unperturbed lattice can be written as

$$\Psi_k(\mathbf{r})=\frac{4\pi}{\sqrt{\Omega_0}}\sum_{l,m}i^l A_{lm}(k)R_l(k,r)Y_{lm}(\hat{\mathbf{r}}) \ , \tag{6}$$

where

$$A_{lm}(k)=\sum_{\mathbf{g}}a_{\mathbf{g}}(k)j_l(k_{\mathbf{g}}R)Y_{lm}^*(\hat{\mathbf{k}}_{\mathbf{g}}) \ , \tag{7}$$

and we have assumed the MT sphere to be situated at the origin. In Eq. (7), $a_{\mathbf{g}}(k)$ are the coefficients of expansion of the wave function ($\mathbf{g}$ is a reciprocal-lattice vector) which can be readily obtained in an APW calculation, j_l is the spherical Bessel function, Y_{lm} the spherical harmonics, $\hat{\mathbf{k}}_{\mathbf{g}}=(\mathbf{k}+\mathbf{g})/|\mathbf{k}+\mathbf{g}|$, and R_l is the radial wave function which, of course, depends on k only through the electron energy E_k and is normalized so that it is unity at the MT boundary, i.e., $R_l(k,R)=1$. Note that in the Korringa-Kohn-Rostoker (KKR) formalism[16] the coefficients A_{lm} can be obtained directly from the solution of the eigenvalue-eigenvector matrix. Taking the potential outside the MT sphere to be zero, the radial wave function in the interstitial region may be expanded in terms of the spherical Bessel (j_l) and Neumann (n_l) functions,

$$R_l(k,r)=\frac{1}{N_l(\kappa,R)}[j_l(\kappa r)\cos\delta_l(E)-n_l(\kappa r)\sin\delta_l(E)] \ , \tag{8}$$

where

$$N_l(\kappa,R)=j_l(\kappa R)\cos\delta_l(E)-n_l(\kappa R)\sin\delta_l(E) \ , \tag{9}$$

where $\kappa=\sqrt{E}$, and $\delta_l(E)$ is the phase shift of the muffin-tin potential $V(r)$ of the host metal evaluated at the energy E. Rydberg atomic units $\hbar=2m=e^2/2=1$ will be used throughout this paper.

In order to calculate the wave function Ψ_k^s in the presence of the defect, we assume that the potential of the defect is localized so that ΔV [$\Delta V(r)=V^s(r)-V(r)$, where $V^s(r)$ is the defect potential] vanishes outside the muffin-tin sphere. We also neglect here the size effect of the solute and, further, do not consider the case of magnetic impurities, although the generalization to these problems is quite straightforward. We restrict ourselves here to the case of substitutional impurities or defects with one atom per unit cell; the formalism can be extended rather simply to the case of interstitial impurities by filling the interstitial region with fictitious muffin-tin spheres of an appropriate radius and then treating the interstitial impurity as a substitutional defect. The wave function Ψ_k^s in the presence of the defect (assumed to be located at the origin) can be written as a sum of two terms, the wave function Ψ_k of the unperturbed lattice and an outgoing spherical wave Ψ^s,

$$\Psi_k^s=\Psi_k+\Psi^s \ . \tag{10}$$

The scattered wave Ψ^s can be expressed for $r>R$ in terms of Hankel functions $h_l=j_l+in_l$,

$$\Psi^s(\mathbf{r})=\sum_{l,m}i^l B_{lm}^s(k)h_l(\kappa r)Y_{lm}(\hat{\mathbf{r}}) \ , \tag{11}$$

where $B_{lm}^s(k)$ are constants to be determined. Inside the muffin-tin sphere of the defect, Ψ_k^s may, however, be written in terms of the solutions R_l^s of the radial Schrödinger equation [as in Eq. (6)] for the defect potential $V^s(r)$,

$$\Psi_k^s=\frac{4\pi}{\sqrt{\Omega_0}}\sum_{l,m}i^l A_{lm}^s(k)R_l^s(k,r)Y_{lm}(\hat{\mathbf{r}}) \ , \tag{12}$$

where again R_l^s is normalized to unity at $r=R$. Outside the MT sphere, R_l^s can be expressed in terms of the phase shifts δ_l^s of the defect potential,

$$R_l^s(r)=\frac{1}{N_l^s(\kappa,R)}[j_l(\kappa r)\cos\delta_l^s(E)-n_l(\kappa r)\sin\delta_l^s(E)] \ , \tag{13}$$

with

$$N_l^s(\kappa,R)=j_l(\kappa R)\cos\delta_l^s(E)-n_l(\kappa R)\sin\delta_l^s(E) \ . \tag{14}$$

The requirement that the wave function and its radial derivative determined from Eq. (10) be continuous to those determined from Eq. (12) determines both A^s_{lm} and B^s_{lm}. In particular,

$$A^s_{lm}(k)=e^{i(\delta^s_l-\delta_l)}\frac{N^s_l(\kappa,R)}{N_l(\kappa,R)}A_{lm}(k)\ , \tag{15}$$

which is the quantity of interest in the present work.

The transition matrix $T(k,k')$ can now be calculated using Eqs. (5), (6), and (12), and one obtains

$$T(k,k')=\frac{(4\pi)^2}{\Omega_0}\sum_{l,m}A^{*s}_{lm}(k')A_{lm}(k)\times\int_0^R R^s_l(k',r)\Delta V(r)R_l(k,r)r^2\,dr\ . \tag{16}$$

Note that Eqs. (2) and (4) impose the condition that k,k' in Eq. (16) be on the Fermi surface. Hence in what follows we drop the index k in $R_l(k,r)$, and the radial wave functions $R_l(r),R^s_l(r)$ and the phase shifts δ_l,δ^s_l will be assumed to be evaluated at the Fermi energy $E=E_F$. The radial integral in Eq. (16) can be easily evaluated (see Appendix for derivation) and expressed in terms of the phase shifts δ_l and δ^s_l of the host and the solute muffin-tin potentials at the Fermi energy,

$$\int_0^R r^2R^s_l(r)\Delta V(r)R_l(r)dr=-\frac{1}{\sqrt{E_F}}\frac{\sin\Delta_l}{N^s_lN_l}\ , \tag{17}$$

where $\Delta_l=\delta^s_l-\delta_l$, and N_l,N^s_l are the values determined from Eqs. (9) and (14) at $E=E_F$. With this and Eq. (15) we may rewrite Eq. (16) as

$$T(k,k')=-\frac{(4\pi)^2}{\Omega_0\sqrt{E_F}}\sum_{l,m}A^*_{lm}(k')A_{lm}(k)\frac{\sin\Delta_l e^{i\Delta_l}}{N^2_l}\ , \tag{18}$$

substituting Eq. (18) in Eq. (4), and then, in Eq. (3), we obtain, for the relaxation time $\tau(k)$ due to the scattering by the defect,

$$\frac{1}{\tau(k)}=\frac{n_i(8\pi)^2}{N\hbar\Omega_0E_F}\int_{\mathrm{FS}}\frac{dS_{k'}}{|\nabla_{k'}E_{k'}|}\left|\sum_{l,m}A^*_{lm}(k')A_{lm}(k)\frac{\sin\Delta_l e^{i\Delta_l}}{N^2_l}\right|^2(1-\cos\theta)\ . \tag{19}$$

Equation (2) in conjunction with Eq. (19) provides a vehicle for calculating the residual resistivity ρ of the defect. As can be seen from these equations, however, it remains a laborious task. In Sec. I we emphasized the great similarity between this problem and the calculation of the electron-phonon coupling parameter λ. As in the calculation of λ, we therefore invoke the spherical-band approximation proposed by Gaspari and Gyorffy[8,9] and write, at the Fermi energy,

$$A_{lm}(k)=a_l(E_F)Y_{lm}(\hat{\mathbf{k}})\ . \tag{20}$$

As noted by Gaspari and Gyorffy, although Eq. (20) is a serious approximation, it nonetheless retains most of the nonstructural features of a real band structure. With this approximation the integrals are easily performed analytically, and one obtains[17]

$$\rho=\frac{n_i}{N}\left[\frac{4\pi\hbar}{e^2}\right]\left[\frac{12\pi^2}{V^2_FE_F\Omega_0}\right]\sum_l(l+1)[A^2_l\sin^2\phi_l+A^2_{l+1}\sin^2\phi_{l+1}-2A_lA_{l+1}\sin\phi_l\sin\phi_{l+1}\cos(\phi_{l+1}-\phi_l)]\ , \tag{21}$$

which can be further rearranged and written as

$$\rho=C\sum_l[(2l+1)A^2_l\sin^2\phi_l-2(l+1)A_lA_{l+1}\sin\phi_l\sin\phi_{l+1}\cos(\phi_{l+1}-\phi_l)]\ , \tag{22}$$

where

$$A_l=\left|\frac{a_l(E_F)}{N_l}\right|^2\ , \tag{23}$$

$$\phi_l=\Delta_l+\theta_l\ , \tag{24}$$

$$C=\frac{n_i}{N}\left[\frac{4\pi\hbar}{e^2}\right]\left[\frac{12\pi^2}{V^2_FE_F\Omega_0}\right]\ , \tag{25}$$

and V_F is the electron Fermi velocity averaged over the Fermi surface. ϕ_l is the Friedel phase shift[1] which, in addition to Δ_l, may be allowed to include the contribution θ_l from the backscattering from the host lattice.[1]

The coefficients A_l depend on the partial-wave character, s, p, d, etc., at the Fermi surface of the host-metal atoms. Following Gaspari and Gyorffy,[8,9] the coefficients A_l can be expressed in terms of the partial DOS, $D_l(E_F)$, of one spin of angular momentum type l inside the muffin-tin sphere of the host-metal atom at the Fermi energy E_F through the relation

$$A_l=\frac{D_l(E_F)}{I_l(E_F)N(E_F)}\ , \tag{26}$$

where

$$N(E_F)=\sum_l D_l(E_F) \tag{27}$$

is the total DOS inside the muffin-tin sphere, and

$$I_l=\frac{\sqrt{E_F}}{\pi}(2l+1)\int_0^R dr\,r^2R^2_l(r)\ . \tag{28}$$

The integral I_l in Eq. (23) is directly related to the energy derivative of the logarithmic derivative, $L_l(E)$, evaluated at the Fermi energy E_F,

$$I_l = -R^2 \dot{L}_l(E_F) \ , \tag{29}$$

where $L_l = (1/R_l)(dR_l/dr)$ and $\dot{L}_l = dL_l(E)/dE$.

The coefficients A_l are easily obtained in the course of an electronic-structure calculation. A table of these coefficients has been given by Papaconstantopoulos *et al.*[10] for metallic elements with $Z \leq 49$. Equation (22) is the final result of this paper. It shows that in a metal where the DOS at the Fermi energy departs significantly from the free-electron behavior, the resistivity no longer depends only upon the differences $\phi_{l+1} - \phi_l$, but instead upon each individual component weighted appropriately by the corresponding partial-wave character at the Fermi surface. This equation rectifies the inherently inaccurate feature of the Gupta-Benedek model,[11] where the use of the optical theorem[1] constrained the coefficients A_l to be all equal and independent of their l value, thus ignoring the essential features of the Fermi surface.

It is easily seen that for a jellium matrix, one recovers from Eq. (22) the classic formula derived by Friedel,[12] since in this case the wave function inside the muffin-tin sphere can be written as

$$\Psi_k = \frac{4\pi}{\sqrt{\Omega_0}} \sum_{l,m} i^l j_l(kR) Y^*_{lm}(\hat{\mathbf{k}}) \left[\frac{j_l(kr)}{j_l(kR)} \right] Y_{lm}(\hat{\mathbf{r}}) \ . \tag{30}$$

From this, one obtains

$$A_l = j_l(kR) Y^*_{lm}(\hat{\mathbf{k}}) \ , \tag{31}$$

so that

$$a_l = j_l(kR) \ , \tag{32}$$

where k is the Fermi wave vector ($k = k_F$). Since the host-metal phase shifts $\delta_l = 0$ for a jellium matrix, one also has

$$N_l = j_l(kR) \ , \tag{33}$$

and hence, from Eq. (23), one obtains

$$A_l = 1 \ . \tag{34}$$

Substituting this in Eq. (22) and noting that $V_F = 2k_F$ and $E_F = k_F^2$ (in a.u.), and rearranging the terms, one obtains

$$\rho = \frac{n_i}{N} \left[\frac{4\pi\hbar}{e^2 Z k_F} \right] \sum_l (l+1)\sin^2(\phi_{l+1} - \phi_l) \ . \tag{35}$$

Equivalently, the resistivity ρ in $\mu\Omega\,\text{cm/at.}\,\%$ can be written as

$$\rho = 0.218 \left[\frac{4\pi}{Z k_F} \right] \sum_l (l+1)\sin^2(\phi_{l+1} - \phi_l) \ , \tag{36}$$

where Z is the valence of the matrix and k_F is in a.u. This is the formula which was first derived by Friedel[12] for the resistivity of a defect in a jellium matrix. Note that in Eqs. (35) and (36), $\phi_l = \delta_l^s$, the defect phase shift, in contrast to Eq. (22), where ϕ_l depends upon $\Delta_l = \delta_l^s - \delta_l$, the difference of the defect and the host-atom phase shifts, and ϕ_l, the backscattering contribution. From Eq. (34) we see that in the free-electron case $A_l = 1$, so that all partial waves are equally weighted. This is a result which is recovered in the electronic-structure calculations of Papaconstantopoulos *et al.*,[10] where one finds from their Table II that for Na, for example all A_l are nearly equal to unity, independent of the l value.

III. APPLICATION TO THE CASE OF COPPER

The expression of the residual resistivity, Eq. (22), has been derived here using the scattering theory without constraints on the strength of the defect potential and, in the spirit of the work of Gaspari and Gyorffy,[8,9] incorporates the effects of band structure in the spherical-band approximation. This is a general expression and is valid for both simple and transition metals. The residual resistivity of defects can be calculated simply, without performing laborious Fermi-surface integrals, from the Friedel phase shifts of the defect evaluated at the Fermi energy of the host matrix, and the average electron velocity and the average *s*, *p*, *d*, etc. partial-wave character of the electron states of the host metal at its Fermi surface. These quantities can be readily obtained from band-structure calculations.[10,18] The present formula for the residual resistivity is different from the previous work of Gupta and Benedek[11] in that it incorporates explicitly the *s*, *p*, *d*, etc. character of the electron states at the Fermi surface.

As an example of the application of this formula, here we calculate the residual resistivities of only a few impurities in copper, which is a well-studied metal and where experimental data are available. Most of the information needed here on copper (and for other metals) has been tabulated by Papaconstantopoulos *et al.*[10] With a lattice constant $a = 6.83$ a.u., these authors find the values of A_0, A_1, and A_2 to be 0.564, 0.862, and 0.928, respectively, and the densities of states of both spins, $N(E_F)$, equals 3.92 states/Ry atom at the Fermi energy $E_F = 0.598$ Ry of copper. The Fermi velocity V_F is unfortunately not available in these tables. This can be estimated from the Fermi surface and the DOS. From Ref. 1 we find the Fermi-surface area in Cu to be 0.98 times the corresponding area in the free-electron approximation. From this and the value of the DOS we deduce for V_F in copper a value of 1.044 a.u., which is to be compared to its value of 1.42 a.u. in the free-electron approximation. This allows us to obtain the presummation constant C in Eq. (22) and we find a value of 6.25 $\mu\Omega\,\text{cm/at.}\,\%$, which is substantially larger than its free-electron value of 3.80 $\mu\Omega\,\text{cm/at.}\,\%$. This difference indicates that it is not justified to replace the presummation constant in copper by its free-electron value.

Friedel phase shifts for several impurities in Cu have been given by Coleridge.[14] We have listed them in Table I for convenience. Coleridge distinguishes the d phase shifts of e_g and t_{2g} symmetry. In Table I we have given their mean value obtained by taking into account their orbital degeneracy. These phase shifts have been used to calculate the residual resistivities from Eq. (22). The resulting values have been listed in Table I, together with the experimental results from Ref. 14. Also listed in

TABLE I. Friedel phase shifts ϕ_0, ϕ_1, ϕ_2 (in rad from Ref. 14) and the impurity resistivity in $\mu\Omega$ cm/at. % in copper (from Ref. 14).

	Friedel phase shifts			Residual resistivity		
Alloy	ϕ_0	ϕ_1	ϕ_2	Coleridge	This work	Expt.
Cu(Zn)	0.197	0.193	0.132	0.36	0.32	0.33
Cu(Al)	0.201	0.398	0.227	1.30	1.35	1.13
Cu(Si)	0.634	0.829	0.232	4.02	4.28	3.95
Cu(P)	0.659	0.958	0.344	5.39	5.71	6.70
Cu(Au)	0.182	−0.087	−0.147	0.54	0.58	0.55
Cu(Ni)	−0.010	−0.060	−0.264	1.13	1.57	1.11
Cu(Pd)	−0.370	−0.190	−0.180	0.72	0.54	0.89
Cu(Pt)	0.500	−0.190	−0.230	2.13	1.92	2.10

Table I are the values calculated by Coleridge,[14] who used a set of 19 points in the irreducible $\frac{1}{48}$th portion of the Fermi surface (a total of approximately 900 points on the entire Fermi surface of copper) to perform the Fermi-surface integrals, and also did not put constraints on the nature of the vector mean free path (his calculation, however, shows that the relaxation-time approximation, which he refers to as the Ziman approximation, is an exceedingly good approximation for the calculation of the residual resistivities). A comparison in Table I shows that our calculated resistivities are, generally speaking, in fairly good agreement both with the experimental ones and those calculated by Coleridge, especially considering the fact that our Eq. (22) for the calculation of resistivities is an extremely simple formula which requires practically no calculations (on a computer). The worst agreement is obtained for three cases, Cu(Al), Cu(Ni), and Cu(Pd), where the calculated values differ from the experimental ones by 20—40%. One is tempted to interpret this discrepancy as the inadequacy of the approximations leading to Eq. (22), especially the spherical-band approximation. This interpretation is indeed not true since we notice from Table I that the resistivities calculated by Coleridge for Cu(Al) and Cu(P) by performing involved Fermi-surface integrations also differ from the experimental values by more than 20%. We note here that a direct comparison between our calculated values and those calculated by Coleridge is not meaningful since a total mesh of 900 points on the whole Fermi surface of copper is too coarse to call these calculations accurate, due to inherent numerical uncertainties.

The true cause of the discrepancy can be traced in the Friedel phase shifts which, in conjunction with the partial-wave-character coefficients A_0, A_1, and A_2, play the dominant role in determining the residual resistivities. As an example, if we choose the Friedel phase shifts for Cu(Al) calculated by Braspenning *et al.*,[18] $\phi_0=0.32$ rad, $\phi_1=0.39$ rad, and $\phi_2=0.19$ rad, we obtain for the residual resistivity ρ a value of $\rho=1.04$ $\mu\Omega$ cm/at. %, which is to be compared to the value of $\rho=1.35$ $\mu\Omega$ cm/at. % obtained from the phase shifts of $\phi_0=0.201$ rad, $\phi_1=0.398$ rad, and $\phi_2=0.227$ rad from Coleridge and the experimental value of $\rho=1.13$ $\mu\Omega$ cm/at. %. We notice that the two sets of Friedel phase shifts are not significantly different from each other, yet very minor differences change the resistivity by more than 30%. There are two terms in Eq. (22) which contribute to the residual resistivity. The contributions from the first term, which are always positive, can be identified as the *ss*, *pp*, and *dd* scattering terms, while those from the second, which are subtracted and can be either positive or negative depending on the phase shifts, can be identified as the *sp* and *pd* scattering terms. With the Friedel phase shifts of Coleridge, these five terms give contributions of 0.08, 2.09, 1.36, 0.46, and 1.72, respectively, to the residual resistivity, while those from Braspenning *et al.* give contributions of 0.20, 2.01, 0.96, 0.72, and 1.40, respectively. This comparison indicates the extreme sensitivity of each of these five terms to the Friedel phase shifts and demonstrates the controlling role of these phase shifts over the need of performing calculations involving rather elaborate Fermi-surface integrals, in determining the residual resistivity of a defect. In the particular case of Cu(Al), a comparison of calculated and experimental data seems to indicate that the Friedel phase shifts calculated by Braspenning *et al.* are preferable to those of Coleridge. If one chooses the Friedel phase shifts intermediate between those of Coleridge and Braspenning *et al.*, namely $\phi_0=0.26$ rad, $\phi_1=0.39$ rad, and $\phi_2=0.21$ rad, one obtains a value of $\rho=1.17$ $\mu\Omega$ cm/at. %, in excellent agreement with the experimental value of $\rho=1.13$ $\mu\Omega$ cm/at. %.

A similar picture emerges for Cu(Ni) and Cu(Pd). Braspenning *et al.* obtain Friedel phase shifts of $\phi_0=-0.06$ rad, $\phi_1=-0.04$ rad, and $\phi_2=-0.20$ rad for Cu(Ni), again not significantly different from those of Coleridge $\phi_0=-0.01$ rad, $\phi_1=-0.06$ rad, and $\phi_2=-0.264$ rad. The two sets of phase shifts yield values of residual resistivities $\rho=0.92$ and 1.57 $\mu\Omega$ cm/at. %, respectively, which differ from each other by more than 50%. Again, with phase shifts intermediate between these two sets, $\phi_0=-0.03$ rad, $\phi_1=-0.05$ rad, and $\phi_2=-0.23$ rad, we obtain a value of $\rho=1.20$ $\mu\Omega$ cm/at. % which is in good agreement with the experimental value of $\rho=1.11$ $\mu\Omega$ cm/at. % For Cu(Pd) it appears that the *d*-phase shift $\phi_2=-0.18$ rad is too small. Keeping ϕ_0 and ϕ_1 unchanged but with $\phi_2=-0.23$ rad instead, we obtain a value of $\rho=0.88$ $\mu\Omega$ cm/at. %, in excellent agreement with the experimental value of $\rho=0.89$ $\mu\Omega$ cm/at. %. This again shows the extreme sensitivity of the residual resistivity to the Friedel phase shifts. In view of this, given a set of Friedel phase shifts, only an order-of-magnitude agreement between calculated and experimentally determined residual resistivities can be reasonably expected.

IV. CONCLUSIONS

We have derived in this paper, a very simple expression, Eq. (22), for the calculation of the residual resistivities of defects in metals, which does not require the calculation of any laborious Fermi-surface integrals. The main ingredients which appear in the calculation are the Fermi velocity and the average partial-wave character of the host metal at its Fermi energy, and the Friedel phase shifts of the defect evaluated at the Fermi energy of the host matrix. The calculations have been presented for several impurities in copper where Friedel phase shifts are available, and the calculated values are, in general, in good agreement with available experimental data. We have also emphasized the extreme sensitivity of the calculated resistivities on the Friedel phase shifts. This is a point which has, to date, not been recognized in the literature and underlines the need for an extremely accurate determination of these phase shifts.

ACKNOWLEDGMENT

It is a pleasure to thank Dr. Y. Adda for discussions and his constant encouragement.

APPENDIX

Let us suppose

$$I=\int_0^R R_l(r)\Delta V(r)R_l^s(r)r^2\,dr$$
$$=\int_0^R U_l(r)\Delta V(r)U_l^s(r)\,dr\ , \tag{A1}$$

where $U_l=rR_l$ and $U_l^s=rR_l^s$, to be evaluated at $E=E_F$.

The radial Schrödinger equations for U_l and U_l^s at energy E are

$$-\ddot{U}_l+\left[V(r)-E+\frac{l(l+1)}{r^2}\right]U_l=0\ , \tag{A2}$$

$$-\ddot{U}_l^s+\left[V^s(r)-E+\frac{l(l+1)}{r^2}\right]U_l^s=0\ , \tag{A3}$$

where $\dot{U}_l=dU_l/dr$, $\ddot{U}_l=d^2U_l/dr^2$, etc. Multiplying (A2) by U_l^s and (A3) by U_l and subtracting, one obtains

$$\ddot{U}_l^sU_l-\ddot{U}_lU_l^s+[V(r)-V^s(r)]U_l(r)U_l^s(r)=0\ . \tag{A4}$$

Upon integration, one obtains

$$\int_0^R U_l^s(r)[V^s(r)-V(r)]U_l(r)\,dr$$
$$=(\dot{U}_l^sU_l-\dot{U}_lU_l^s)_0^R$$
$$=(\dot{U}_l^sU_l-\dot{U}_lU_l^s)_{r=R}\ . \tag{A5}$$

Noting that

$$U_l=rR_l,\quad \dot{U}_l=R_l+r\dot{R}_l\ ,$$

we obtain, from Eq. (1),

$$I=R^2(\dot{R}_l^sR_l-\dot{R}_lR_l^s)_{r=R}\ . \tag{A6}$$

We may now substitute the values of R_l and R_l^s from Eqs. (8) and (13), and making use of the Wronskian

$$j_l(X)\dot{n}_l(X)-n_l(X)\dot{j}_l(X)=1/X^2\ , \tag{A7}$$

we obtain

$$I=-\frac{1}{\sqrt{E_F}}\frac{\sin(\delta_l^s-\delta_l)}{N_l^sN_l}\ , \tag{A8}$$

where N_l and N_l^s are defined in Eqs. (9) and (14), respectively, and δ_l and δ_l^s are the phase shifts evaluated at $E=E_F$.

---

[1] P. T. Coleridge, N. A. W. Holwarth, and M. J. G. Lee, Phys. Rev. B **10**, 1213 (1974).

[2] Y. Fukai, Phys. Lett. **27A**, 416 (1968); R. Benedek and A. Baratoff, J. Phys. Chem. Solids **32**, 1015 (1971).

[3] R. Evans and M. W. Finnis, J. Phys. F **6**, 483 (1976); P. Jena, A. K. Gupta, and K. S. Singwi, Solid State Commun. **21**, 293 (1977).

[4] C. O. Almbladh, U. von Barth, Z. D. Popovic, and M. J. Stott, Phys. Rev. B **14**, 2250 (1976).

[5] C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963); M. Manninen, P. Hautojarvi, and R. Nieminen, Phys. Lett. **63A**, 60 (1977).

[6] W. L. McMillan, Phys. Rev. **167**, 331 (1968).

[7] B. N. Harmon and S. K. Sinha, Phys. Rev. B **16**, 3919 (1977).

[8] G. D. Gaspari and B. L. Gyorffy, Phys. Rev. Lett. **29**, 801 (1972).

[9] R. Evans, G. D. Gaspari, and B. L. Gyorffy, J. Phys. F **3**, 39 (1973).

[10] D. A. Papaconstantopoulos, L. L. Boyer, B. M. Klein, A. R. Williams, V. L. Morruzzi, and J. F. Janak, Phys. Rev. B **15**, 4221 (1977). Note that A_l in the present work is denoted by n_l/N_l by these authors.

[11] R. P. Gupta and R. Benedek, Phys. Rev. B **19**, 583 (1979).

[12] J. Friedel, Adv. Phys. **3**, 446 (1954).

[13] I. Mertig, E. Mrosan, and R. Schöpke, J. Phys. F **12**, 1689 (1982).

[14] P. T. Coleridge, J. Phys. F **15**, 1727 (1985).

[15] T. L. Loucks, *Augmented Plane Wave Method* (Benjamin, New York, 1967).

[16] J. M. Ziman, in *Solid State Physics,* edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1971), Vol. 16, p. 1.

[17] In the spherical-band approximation, the product $\hat{\mathbf{v}}_k\cdot\hat{\mathbf{v}}_{k'}$ is replaced by $\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}'$ and the integrands in Eqs. (2) and (19) by their values averaged over a spherical Fermi surface.

[18] R. Podloucky, R. Zeller, and P. H. Dederichs, Phys. Rev. B **22**, 5777 (1980); P. J. Braspenning, R. Zeller, P. H. Dederichs, and A. Lodder, J. Phys. F **12**, 105 (1982).