Impurity scattering and residual resistivity of transition metals

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We derive an expression for the residual resistivity of impurities in metals that incorporates both the Bloch-wave character of the electron states and backscattering by the host lattice. This expression, which involves the Friedel phase shifts, is closely analogous to a familiar relation for the jellium model, but its derivation is much more general. Calculations of impurities in noble-metal hosts based on our formula are in excellent agreement with the numerical calculations of Coleridge, Holzwarth, and Lee.

The calculation of the residual resistivity of impurities in metals requires both a knowledge of the scattering T matrix and a solution to the appropriate Boltzmann equation. The standard solutions to the Boltzmann equation lead to expressions for the resistivity that involve an integration of the square of the T matrix weighted by the momentum transfer. This Fermi-surface integral is tedious to evaluate in practice.

For simple-metal impurities in simple-metal hosts the T matrix is often calculated in the Born approximation under the assumption of weak pseudopotentials. If the electron states can be expressed as single orthogonalized plane waves (OPW), as in alkali metals, the Fermi-surface integrations are considerably simplified. If two or more OPW's are required, as in polyvalent simple metals,[1] a tedious Fermi-surface integration is necessary. For transition- and noble-metal hosts, the T matrix is more difficult to evaluate; however, a useful procedure based on a phase-shift formalism has recently been developed for this purpose.[2] Nevertheless, only a few calculations of the resistivity of impurities in noble-metal hosts[3] have been attempted so far because of the large amount of work involved in calculating the integrals over the Fermi surface. The purpose of this paper is to show that the residual resistivities of impurities may be estimated directly from the Friedel phase shifts, without elaborate Fermi-surface integrations. We demonstrate that a formula very similar to the familiar jellium result can be derived in a much more general framework. The formula is applied to impurities in noble-metal hosts and is found to agree well with the results of Coleridge, Holzwarth, and Lee[3] (CHL), who performed detailed numerical integrations over the Fermi surface.

The residual resistivity ρ can be expressed in terms of the vector mean free path $\vec{\Lambda}_{\vec{k}}$ and the Fermi velocity $\vec{v}_{\vec{k}}$ as an integral over the Fermi surface[3,4]:

$$\frac{1}{\rho} = \frac{e^2}{12\pi^3} \int_{FS} \frac{dS_{\vec{k}}}{\hbar v_{\vec{k}}} \vec{\Lambda}_{\vec{k}} \cdot \vec{v}_{\vec{k}} , \tag{1}$$

where $v_{\vec{k}} = |\vec{v}_{\vec{k}}|$ and e is the electronic charge. CHL have pointed out that a good approximation to the resistivity is obtained by assuming that the vector mean free path is parallel to the velocity. One then obtains

$$\frac{1}{\Lambda_{\vec{k}}} = \frac{\Omega c}{4\pi^2 \hbar v_{\vec{k}}} \int_{FS} \frac{dS_{\vec{k}'}}{\hbar v_{\vec{k}'}} |T_{\vec{k}\vec{k}'}|^2 (1 - \vec{v}_{\vec{k}} \cdot \vec{v}_{\vec{k}'}) . \tag{2}$$

Here c is the concentration of the impurity and Ω is the unit-cell volume. The transition matrix $T_{\vec{k}\vec{k}'}$ is given by

$$T_{\vec{k}\vec{k}'} = \langle \psi_{\vec{k}'}^i | \Delta V | \psi_{\vec{k}}^h \rangle , \tag{3}$$

which describes the scattering of an electron with wave function $\psi_{\vec{k}}^h$ in the pure host, by the extra potential of the impurity ΔV, to a final state $\psi_{\vec{k}'}^i$, in the solid with the impurity.

In order to evaluate $T_{\vec{k}\vec{k}'}$ we make use of the muffin-tin approximation familiar from the augmented-plane-wave (APW) and the Korringa-Kohn-Rostoker (KKR) methods of band-structure calculation.[5] For simplicity, we confine ourselves to cubic lattices with one atom per unit cell. The potential of the impurity atom is assumed to be localized so that $\Delta V(r)$ vanishes outside the muffin-tin well centered at the origin. We expand the Bloch function at the origin in terms of spherical harmonics:

$$\psi_{\vec{k}}^{i,h}(E, \vec{r}) = \sum_{lm} i^l a_{lm}^{i,h}(\vec{k}, E) R_l^{i,h}(E, r) Y_{lm}(\hat{r}) , \tag{4}$$

where $R_l(E, r)$ is the radial wave function and $\hat{r} = \vec{r}/r$. The superscript i (h) corresponds to the case of an impurity (host) atom at the origin. In principle, a cubic-harmonic representation would be more appropriate here; however, if the phase shifts for $l \geq 3$ are negligible, as is usually the

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case, the results are essentially unchanged.[6] Out-
side the muffin-tin radius, the radial wave func-
tion may be written as

$$R_l^{i,h}(E, r) = j_l(\kappa r) + i \sin\eta_l \, \exp(i\eta_l^{i,h}) h_l(\kappa r) \, . \quad (5)$$

Here j_l and h_l are the spherical Bessel and Han-
kel functions, respectively, η_l is the phase shift
of the scattering potential, and $E = \hbar^2\kappa^2/2m$ is the
energy measured from the muffin-tin zero, where
m is the electron mass. By a standard manipula-
tion $T_{\vec{k}\vec{k}'}$ can be converted into a surface integral.
Employing Eq. (5), one can then show that

$$T_{\vec{k}\vec{k}'} = -\frac{\hbar^2}{2m\kappa} \sum_{lm} a_{lm}^*(\vec{k}', E') a_{lm}(\vec{k}, E) A_l(\vec{k}, E)$$

$$\times \sin\Delta\eta_l \exp(i\Delta\eta_l) \, . \quad (6)$$

Here $a_{lm}^h \equiv a_{lm}$, and $a_{lm}^i = a_{lm}A_l$ where A_l
$\equiv |A_l| \exp(i\theta_l)$ is the renormalization factor that
describes the effect of backscattering by the host
lattice.[3] Since we are interested in scattering
between states on the Fermi surface, Eq. (6) is
evaluated at $E = E' = E_F$, the Fermi energy. $\Delta\eta_l$
$= \eta_l^i - \eta_l^h$ is the difference between the phase shifts
of the impurity and the host. Following Gaspari
Gyorffy,[7] we invoke a spherical band approxima-
tion to the coefficients a_{lm}:

$$a_{lm}(\vec{k}, E) = a_l(E) Y_{lm}(\hat{k}) \, . \quad (7)$$

Although this is clearly a severe approximation,
it nevertheless retains most of the nonstructural
features of a real band structure. Equation (7)
has been employed in the calculation of the elec-
tron-phonon coupling constant λ, which involves
similar integrations over the Fermi surface and
essentially similar matrix elements between scat-
tering states. These calculations have yielded ac-
curate values of λ for a large class of materials.[7]
Substituting Eqs. (7), (6), and (2) into (1) and per-
forming the integrations we find

$$\frac{\rho}{c} = \frac{3\pi\Omega}{16\pi^2 e^2 \hbar v_F^2} \left(\frac{\hbar^2}{2m\kappa}\right)^2$$

$$\times \sum_l (l+1)(|a_{l+1}|^2 S_{l+1} - |a_l|^2 S_l) \times \text{c.c.} \, , \quad (8)$$

where v_F is the average Fermi velocity and S_l
$= A_l \exp(i\Delta\eta_l) \sin\Delta\eta_l$. Using the optical theorem,
CHL have shown that the scattering factor S_l can
be expressed in the form

$$S_l = I_l^{-1} \sin\phi_l \exp(i\phi_l) \, , \quad (9)$$

where $\phi_l \equiv \Delta\eta_l + \theta_l$ is referred to as the Friedel
phase shift and

$$I_l = \frac{\Omega}{8\pi^2} \frac{\hbar^2}{2m\kappa} \int |a_{lm}(\vec{k}, E_F)|^2 \frac{dS_{\vec{k}}}{\hbar v_{\vec{k}}} \, . \quad (10)$$

Substituting Eq. (7) into Eq. (10), we obtain

$$|a_l|^2 = \frac{8\pi m\kappa}{\hbar^2} \frac{I_l}{N(E_F)} \, , \quad (11)$$

where $N(E_F)$ is the density of states of one spin at the
Fermi energy. With the help of Eqs. (9) and (11),
we can rewrite Eq. (8) in the form

$$\frac{\rho}{c} = \frac{3\pi\hbar\Omega}{[\pi e\hbar v_F N(E_F)]^2} \sum_l (l+1)\sin^2(\phi_{l+1} - \phi_l) \, . \quad (12)$$

One notes a remarkable similarity between Eq.
(12) and the corresponding relation in the free-
electron approximation. The presummation con-
stant on the right-hand side of Eq. (12) reduces
to $4\pi\hbar/e^2 k_F$ in the free-electron case. Equation
(12) does, however, incorporate several aspects
of band structure, viz., the average velocity of
the electron at the Fermi surface, v_F, the density
of states per spin at the Fermi energy of the host
$N(E_F)$, and the backscattering phase shifts θ_l.
Moreover, $\Delta\eta_l$ contains nonstructural informa-
tion about the host, in contrast to the free-elec-
tron formula, in which only the impurity phase
shift appears.

We have used Eq. (12) to calculate ρ for a var-
iety of impurities in noble-metal hosts.[8] The re-
sults are presented in Table I where they are
compared with the results of calculations by CHL,
who integrated Eqs. (1) and (2) numerically. Ex-
perimental values are also given. In the present
calculations, we employed the phase shifts given
by CHL, which were determined by fits to Dingle
temperatures[3] and/or Fermi-surface data[9] ob-
tained from de Haas–van Alphen experiments on
dilute alloys. The present results agree with
those of CHL and with experiment to within a few
percent in essentially all cases. Only in the case
of Au(Zn) does a substantial (>10%) discrepancy
exist; its origin is not presently understood. In
view of the simplicity of Eq. (12), the overall
agreement is remarkably good.

On the basis of Eq. (12), qualitative predictions
can be made about trends in the residual resistiv-
ity for a series of transition-metal impurities in
a given host material. Although the s and p phase
shifts of transition metals are not necessarily
small, d-wave scattering normally dominates the
resistivity, which reaches a maximum when ϕ_2
$\approx \frac{1}{2}\pi$. For transition-metal impurities in simple-
metal hosts, η_2^i constitutes the largest contribu-
tion to ϕ_2. The phase shift $\eta_2^i(E_F)$ decreases mon-
otonically as one crosses a transition-metal per-
iod. For impurities that belong to the first transi-
tion series in an Al host, the resistivity peaks at
Cr.[10] For this impurity a near-resonance occurs;
the phase shifts for elements on either side of Cr
depart increasingly from the resonance condition

TABLE I. Friedel phase shifts and residual resistivities for dilute noble-metal alloys.

Alloy	ϕ_0	ϕ_1	ϕ_2	Residual resistivity $(\mu\Omega\,cm/at.\,\%)$		
				expt.	Eq. (1) [a]	Eq. (12)
Cu(Ni) [b]	−0.069	−0.038	−0.258	1.11	1.11	1.10
Cu(Ge) [b]	0.15	0.748	0.18	3.79	3.79	3.76
Cu(Au) [b]	0.182	−0.087	−0.147	0.55	0.55	0.54
Cu(Fe) [b]	0.0	0.0	−0.93	11.5[c]	12.0	12.2
Ag(Au) [b]	0.176	0.087	−0.085	0.38	0.39	0.38
Ag(Sn) [b]	0.201	0.786	0.223	4.3	4.30	4.37
Au(Ag) [b]	−0.277	−0.072	0.051	0.36	0.36	0.34
Au(Cu) [b]	−0.210	0.077	0.103	0.45	0.46	0.48
Au(Zn) [b]	0.255	0.180	0.237	0.95	1.00	0.76
Cu(Al) [d]	0.21	0.48	0.28	1.1	1.6	1.44
Au(Ga) [e]	0.98	0.41	0.16	2.15	· · ·	2.09

[a] Resistivity values from Reference 3.
[b] Phase-shift values from Ref. 3.
[c] From Ref. 4.
[d] Phase-shift values from P. T. Coleridge, J. Phys. F **5**, 1317 (1975).
[e] Phase-shift values from Ref. 9.

and therefore lower resistivities are observed. For transition-metal impurities in transition-metal hosts, the trends are more difficult to predict because of cancellation between the phase shift of the impurity and that of the host. Furthermore, Eq. (12) is not strictly applicable to the case of an impurity with a localized spin.[10]

We were unable to test Eq. (12) on transition-metal hosts other than the noble metals, since accurate impurity phase shifts are not known. The spherical band approximation, Eq. (7), may seem inappropriate to materials with extremely anisotropic Fermi surfaces such as Mo, W, etc. It is possible, however, that this approximation still gives reasonable results in calculations of properties that involve *averages* over the Fermi surface. As mentioned earlier, surprisingly accurate values of the electron-phonon coupling constant λ were obtained for transition metals on the basis of the spherical band approximation.[7]

Two additional consequences of the present result, Eq. (12), deserve mention. The first concerns the sign of the Friedel phase shifts ϕ_l. Dingle-temperature data may be analyzed to determine $\sin^2\phi_l$, but not the sign of the individual phase shifts.[3] The resistivity is often used to help resolve this ambiguity and the present formula greatly simplifies this task. The second point concerns the *ab initio* calculation of the resistivity of vacancies. The calculations presently available

are based on pseudopotential treatments[11] or the jellium model,[12] which are applicable only to simple metals, at best. Recently an APW technique was developed to calculate the electronic charge density in a vacant lattice site in a metal.[13] This approach opens up the possibility of calculating the scattering potential of a vacancy in virtually any metal. The resistivity calculation would require the phase shifts of the host atom, the phase shifts associated with the vacancy potential (which can be calculated from the charge-density profiles), and the backscattering phase shifts θ_l. The latter can be determined by the method described by Lee, Holzwarth, and Coleridge.[9] Therefore, the calculation of the resistivity of vacancies in nonsimple metals should now be feasible.

Throughout our discussion we have assumed that the lattice relaxation around the impurity or point defect may be neglected, except insofar as it can be represented by a slightly modified Friedel sum,[3] according to the effective charge concept of Blatt.[14] For defects that produce a large distortion field, some reformulation of the theory becomes necessary.[15]

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[1] Y. Fukai, Phys. Rev. 186, 697 (1969); R. S. Sorbello,
J. Phys. F 4, 1665 (1974).

[2] G. J. Morgan, Proc. Phys. Soc. London 89, 365 (1966).
See also review papers by R. Harris, P. T. Coleridge,
and M. J. G. Lee, Phys. Condens. Matter 19, 185 (1975).

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

[4] P. T. Coleridge, J. Phys. F 2, 1016 (1972).

[5] J. M. Ziman, in Solid State Physics, Vol. 16 (Academic,
New York, 1971), p. 1.

[6] See, for example, the discussion in Phys. Condens.
Matter 19, 229 (1975).

[7] G. D. Gaspari and B. L. Gyorffy, Phys. Rev. Lett. 28,
801 (1972).

[8] $v_F N(E_F)$ is proportional to the area of the Fermi sur-
face which, in the case of noble metals, is close to the
free-electron value.

[9] M. J. G. Lee, N. A. W. Holzwarth, and P. T. Coleridge,
Phys. Rev. B 13, 3249 (1976).

[10] J. Friedel, Nuovo Cimento Suppl. 1, 287 (1958).

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

[12] M. Manninen, P. Hautojarvi, and R. Nieminen, Phys.
Lett. A 63, 60 (1977).

[13] R. P. Gupta and R. W. Siegel, Phys. Rev. Lett. 39, 1212
(1977).

[14] F. J. Blatt, Phys. Rev. 108, 285 (1957); 108, 1204
(1957).

[15] A. Lodder, J. Phys. F 6, 1885 (1976).