

Relation Between Local Order and Interference Effects in Electrical Resistivity for Metallic Alloys

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A relation is pointed out between the interaction of a pair of impurity atoms in a metal and the isotropic part of the interference term in their residual resistivity. The relation is established for weak, far apart, and magnetic or nonmagnetic scatterers in a free-electron gas. It should hold approximately down to the nearest-neighbor distance for alloys with normal or rare-earth components. In all cases, both effects are described by oscillating functions of the distance between the two scatterers, with the same phase. An increase of residual resistivity with local order results.

I. INTRODUCTION

THE nature of local order in metallic solid solutions has been much studied in recent years,¹ and its physical origin ascribed to the effect on its neighbors of the long-range oscillations of the perturbing potential due to a solute atom.² The setting up of such a local order is known to alter the electrical resistivity; and these changes have been explained fairly satisfactorily as due to changes in interference effects between scatterers.^{3,4}

The purpose of this note is to point out a direct relation between the interaction energy of two scatterers and the isotropic part of the interference in the resistivity. This relation will be proved for a gas of free electrons, and when the scatterers are spherically symmetrical, weak and not too near to each other. The scatterers can be magnetic or nonmagnetic. These conditions should apply approximately, even for impurities in nearest-neighbor positions, for normal or rare-earth metals; in semimetals it should only hold at very large distances; finally, the relation is not established for transitional matrices or scatterers.

When it holds, this relation is such that the establishment of local order under thermal equilibrium

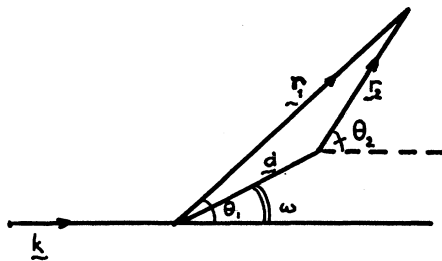


FIG. 1. Optical approximation.

¹ *Metallic Solid Solutions* (W. A. Benjamin and Company, Inc., New York, 1963).

² A. Blandin and J. L. Déplanté, *J. Phys. Radium* **23**, 609 (1962).

³ P. G. de Gennes and J. Friedel, *Phys. Chem. Solids* **4**, 71 (1958). M. T. Beal, *ibid.* **15**, 77 (1960).

⁴ M. T. Beal, thesis, Paris, June 1963 (unpublished); *Phys. Chem. Solids* (to be published); cf. also S. H. Liu, *Phys. Rev.* **132**, 589 (1963).

should always *increase* the isotropic part of the residual resistivity.

We first consider in detail the nonmagnetic case. The relation is then extended to magnetic scatterers.

II. NONMAGNETIC SCATTERERS

We consider two spherically symmetrical impurities, one at the origin, the second at point **d**. If they are weak scatterers, the optical approximation can be used to describe the wave function of an incoming electron **k** scattered by the pair

$$\psi \simeq e^{i\mathbf{k}\cdot\mathbf{r}_1} + \psi_{\text{scatt } 1}(\theta_1, \mathbf{k}, r_1) + e^{i\mathbf{k}\cdot\mathbf{d}} \psi_{\text{scatt } 2}(\theta_2, \mathbf{k}, r_2). \quad (1)$$

$r_1, r_2, \theta_1, \theta_2$ are explained in Fig. 1. $\psi_{\text{scatt } i}$ is the scattered part of the wave function of electron **k** when impurity *i* is isolated.

In writing (1), use has been made of the fact that the self-consistent potential *U* of the pair of scatterers only deviates from the sum of the potentials U_i of each scatterer, when isolated, by interference terms of the second order in U_i . Such terms are neglected in the optical approximation (1).

A. Interference Effect

At large distances from the scattering pair, formula (1) reduces to

$$\psi \simeq e^{i\mathbf{k}\cdot\mathbf{r}_1} + f_1(\theta_1) \frac{e^{i\mathbf{k}r_1}}{r_1} + e^{i\mathbf{k}\cdot\mathbf{d}} f_2(\theta_2) \frac{e^{i\mathbf{k}r_2}}{r_2}. \quad (2)$$

$|f_i(\theta_i)|^2$ is the differential cross section of the *i*th scatterer, when isolated.

The total resistivity cross section is thus, using well known relations,

$$\sigma(\omega, d) = \sigma_1 + \sigma_2 + \int f_1^*(\theta) f_2(\theta) e^{i\mathbf{K}\cdot\mathbf{d}} (1 - \cos\theta) \times \sin\theta d\theta + \text{c.c.} \quad (3)$$

$\mathbf{K} = (k_M \mathbf{r}) - \mathbf{k}_M$ is the scattering vector for an incoming electron at the Fermi level, with wave vector \mathbf{k}_M parallel to the electrical current; ω is the angle between **d** and \mathbf{k}_M (Fig. 1); σ_i the resistivity cross section for scatterer *i* when isolated.

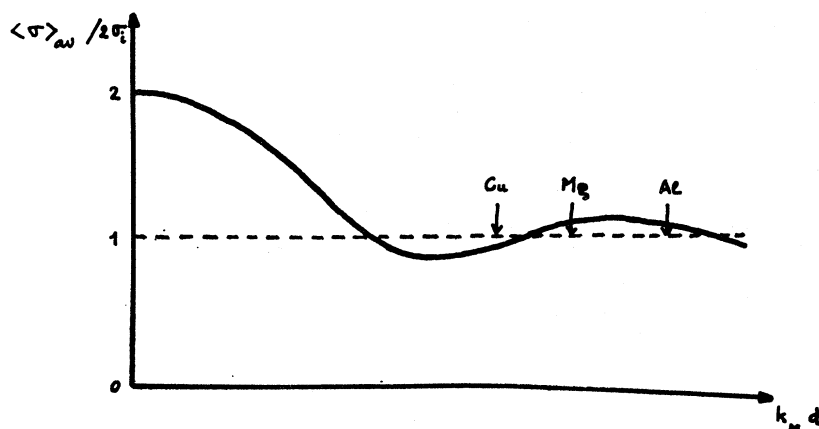


FIG. 2. Variation with distance d of the isotropic part of the electrical resistivity due to a pair of identical impurities.

Owing to the angular dependence with \mathbf{d} , the excess resistivity $\delta\sigma = \sigma - \sigma_1 - \sigma_2$ is anisotropic.⁵ It is however easy to check that the *average* cross section, for pairs oriented at random, is

$$\langle \sigma \rangle_{av} = \sigma_1 + \sigma_2 + \langle \delta\sigma \rangle_{av}, \quad (4)$$

with

$$\langle \delta\sigma \rangle_{av} \rightarrow 2(\sigma_1\sigma_2)^{1/2} \quad \text{for } d \rightarrow 0 \text{ (i.e., } k_M d \ll 1) \quad (5)$$

and

$$\langle \delta\sigma \rangle_{av} \rightarrow - \left[f_1^*(\pi) f_2(\pi) + \text{c.c.} \right] \frac{2 \cos 2k_M d}{k_M^2 d^2} \quad \text{for } d \rightarrow \infty \text{ (i.e., } k_M d \gg 1). \quad (6)$$

Let $U_i(\mathbf{r})$ be the potentials of the scatterers, with Fourier components

$$U_i(K) = \int U_i(\mathbf{r}) e^{-i\mathbf{K} \cdot \mathbf{r}} d\tau.$$

Using the relation $f(\pi) = -(1/2\pi)U_i(2k_M)$, Eq. (6) can also be written

$$\langle \delta\sigma \rangle_{av} \rightarrow - \frac{4}{\pi^2} U_1(2k_M) U_2(2k_M) \frac{\cos 2k_M d}{(2k_M d)^2} \quad \text{for } d \rightarrow \infty. \quad (7)$$

Figure 2 gives schematically the relative variation of the average residual resistivity $\langle \rho \rangle_{av} / (\rho_1 + \rho_2)$ of the pair, in the case of two identical scatterers.⁶

B. Energy of Interaction

The total scattering potentials U_i of the two impurities are made of a "bare" part V_i and of a "clothing" part W_i . The V_i 's are either the Coulomb field due to the excess nuclear charge describing a change of

⁵ B. Caroli, 3 Cycle, thesis, Orsay, 1961 (unpublished).

⁶ In drawing this curve, use has been made of the fact that, for likely scatterers, the expression between brackets in Eq. (6) is near to $(\sigma_1\sigma_2)^{1/2}$; it would be exactly equal to $(\sigma_1\sigma_2)^{1/2}$ only in the unphysical case of delta-function scatterers.

valency, or a change in "effective" potential, describing a change in period (cf. Ref. 2). The W_i 's are due to the reaction of the valence electrons, screening out the external perturbation V_i .

As long as the impurities are weak scatterers,

$$U_i(K) = V_i(K) / \epsilon_K, \quad (8)$$

where

$$\epsilon_K = 1 + \frac{2k_M}{\pi K^2} \left[1 + \frac{k_M}{k} \left(1 - \frac{K^2}{4k_M^2} \right) \ln \left| \frac{K+2k_M}{K-2k_M} \right| \right] \quad (9)$$

is the dielectric constant⁷ for wave number K of the valence electrons.⁸ Also the interaction energy between the impurities is, for weak scatterers, in atomic units ($e = \hbar = m = 1$),

$$w(d) = \frac{1}{(2\pi)^3} \int \frac{K^2}{4\pi} \epsilon_K U_1(K) U_2(K) e^{i\mathbf{K} \cdot \mathbf{d}} d^3\mathbf{K}. \quad (10)$$

The asymptotic form, valid for $k_M d \gg 1$, is

$$w(d) \rightarrow \frac{(2k_M)^4}{(2\pi)^3} U_1(2k_M) U_2(2k_M) \frac{\cos 2k_M d}{(2k_M d)^3} \quad \text{for } d \rightarrow \infty. \quad (11)$$

C. Discussion

For *normal metals*, the nearest-neighbor distance d_0 is such that $k_M d_0 \simeq 7$ to 10. The asymptotic formulas (6) or (7) and (11) thus hold for any distance d , giving an interference effect $\langle \delta\rho \rangle_{av} = \langle \rho \rangle_{av} - (\rho_1 + \rho_2)$ and an interaction energy w small, appreciable only at near-neighbor distances. In *semimetals*, with $k_M d_0 \ll 1$ for nearest neighbors, one expects on the contrary the asymptotic formulas for $d \rightarrow \infty$ to apply only at distances d very large compared with interatomic

⁷ As shown in the Appendix, no difficulty arises in the computation of $\langle \delta\sigma \rangle_{av}$ from the singularity of $U_i(K)$ for $K = 2k_M$.

⁸ J. Bardeen, Phys. Rev. **52**, 688 (1937). P. Nozières and D. Pines, Nuovo Cimento **9**, 470 (1958); A. Blandin, thesis, Paris, 1961 (unpublished); J. Friedel, *Low-Temperature Physics, Les Houches Summer School* (Presses Universitaires de France, Paris, 1961).

distances; for $d \ll k_M^{-1}$, formula (5) shows that the two impurities should scatter coherently: two identical impurities ($U_1=U_2$) should have a resistivity about twice as large as when they are separated; two impurities of opposite character ($U_1=-U_2$) should have very little total resistivity.

When relations (6) or (7) and (11) hold, it is seen that the change in average resistivity $\langle \delta\rho \rangle_{av}$ due to interference is directly *proportional* to the energy of interaction w , whatever the nature of the scatterers or their distance. The coefficient of proportionality is *negative*. Starting from a perfectly disordered solid solution and letting a local order appear under thermodynamical equilibrium, the pairs of solute atoms for which $w > 0$ (thus $\langle \delta\rho \rangle_{av} < 0$) should decrease in number, while those for which $w < 0$ (thus $\langle \delta\rho \rangle_{av} > 0$) should increase. Both types of movement lead, as stated above, to an *increase* in residual resistivity $\langle \delta\rho \rangle_T$. More precisely, it is easy to show¹ that, at temperature T , and for an atomic concentration c of scatterers,

$$\begin{aligned} \frac{\langle \delta\rho \rangle_T}{\rho_1 + \rho_2} &= \sum \frac{-w(d)}{k_B T} \frac{\langle \delta\sigma \rangle_{av}}{\sigma_1 + \sigma_2} c^2 + O\left(\frac{1}{T^2}\right) \\ &= \frac{16k_M^4}{\pi^3} \frac{1}{k_B T} \frac{U_1^2(2k_M)U_2^2(2k_M)}{U_1^2(2k_M) + U_2^2(2k_M)} c^2 \\ &\quad \times \sum \frac{\cos^2(2k_M d)}{(2k_M d)^5} + O\left(\frac{1}{T^2}\right), \quad (12) \end{aligned}$$

where the summation extends over all distances d between one lattice site and the others.

This conclusion strictly applies to weak nonmagnetic scatterers in normal metals. Normal substitutional or interstitial solid solutions fall roughly in this class. Experimental evidence, although scant, suggests that the relation established between $w(d)$ and $\langle \delta\rho(d) \rangle_{av}$ is observed as to the sign and order of magnitude.^{3,4} A number of restrictions must be stressed:

(a). $\langle \delta\rho \rangle_{av}$ is an isotropic average, for all possible directions of the electric current with respect to the pair. It is *not* exactly the average at fixed current direction, for all possible orientations of pairs of impurities in a crystal, because these are limited in number.

(b). The Born approximation used here is not very satisfactory: it is known^{8,9} to give not very good values for the resistivity of isolated impurities. The relation obtained is thus at best approximate in actual cases. This approximation might be poor for strong scatterers, such as vacancies or transitional impurities.^{4,8,10}

III. MAGNETIC SCATTERERS

A similar relation between $\langle \delta\sigma(d) \rangle_{av}$ and $w(d)$ holds for *magnetic* impurities, and is thus involved in both

⁹ J. Friedel, 1963 *Mol Summer School* (North-Holland Publishing Company, Amsterdam, 1964).

¹⁰ J. Friedel, *J. Phys. Radium* **23**, 692 (1962).

atomic and magnetic short-range order.^{3,4} It is again strictly valid within the Born approximation. It should thus apply very well to rare-earth impurities or pure rare-earth metals. It is *not* proved here for transitional impurities, although it might be that the resistance minimum observed at low temperature in alloys such as CuMn has the same physical origin.^{4,5,11}

A. Energy of Interaction

Let us take two magnetic impurities, one at the site \mathbf{R}_1 with spin \mathbf{S}_1 , the other at \mathbf{R}_2 with spin \mathbf{S}_2 . We suppose that the interaction between \mathbf{S}_1 and \mathbf{S}_2 is by indirect exchange, via the conduction electrons of the matrix considered as free electrons (spin \mathbf{s} , wave vector \mathbf{k}). The Hamiltonian for the two spins \mathbf{S}_1 and \mathbf{S}_2 is

$$H = -2J(\mathbf{r}-\mathbf{R}_1)\mathbf{s}\cdot\mathbf{S}_1 - 2J(\mathbf{r}-\mathbf{R}_2)\mathbf{s}\cdot\mathbf{S}_2. \quad (13)$$

$J(\mathbf{r}-\mathbf{R}_i)$ is the spin-dependent potential between \mathbf{s} and \mathbf{S}_i . A second-order perturbation calculation leads to the interaction between \mathbf{S}_1 and \mathbf{S}_2 ,

$$\begin{aligned} w(d) &= \text{Trace}[4(\mathbf{s}\cdot\mathbf{S}_1)(\mathbf{s}\cdot\mathbf{S}_2)] \int_{k < k_M} \frac{d^3\mathbf{k}}{(2\pi)^3} \\ &\quad \times \int_{k' > k_M} \frac{d^3\mathbf{k}' e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{d}} |J(\mathbf{k}-\mathbf{k}')|^2}{(2\pi)^3 [\frac{1}{2}k^2 - \frac{1}{2}k'^2]} + \text{c.c.}, \quad (14) \end{aligned}$$

where $\mathbf{d} = \mathbf{R}_1 - \mathbf{R}_2$.

This is the Yosida formulation,¹² with a general form for $J(K)$. We have only to suppose (cf. Appendix) that $J(K)$ is continuous and remains *finite* for all \mathbf{K} . It is well known¹² that (14) can be written:

$$w(d) = -\mathbf{S}_1 \cdot \mathbf{S}_2 \frac{k_M}{4\pi^4 d} \int_0^\infty K |J(K)|^2 F(K) \sin Kd dK \quad (15)$$

with

$$F(K) = 1 + \frac{4k_M^2 - K^2}{4k_M K} \ln \left| \frac{2k_M + K}{2k_M - K} \right|,$$

when k_M is the Fermi level. The asymptotic form analogous to (11) for $k_M d \gg 1$ is

$$w(d) \rightarrow \frac{(2k_M)^4}{(2\pi)^3} \mathbf{S}_1 \cdot \mathbf{S}_2 J^2(2k_M) \frac{\cos 2k_M d}{(2k_M d)^3}. \quad (16)$$

This is the Ruderman-Kittel-Yosida indirect interaction,¹² without particular restrictions about $J(2k_M)$ (cf. Appendix).

¹¹ A. J. Dekker, *Physica* **24**, 697 (1958); **25**, 1244 (1959). A. D. Brailsford and A. W. Overhauser, *Phys. Chem. Solids* **15**, 140 (1960), **21**, 127 (1961). T. Van Peski Tingergem and A. J. Dekker, *Physica* **29**, 917 (1963).

¹² M. A. Ruderman and C. Kittel, *Phys. Rev.* **96**, 99 (1954); K. Yosida, *ibid.* **106**, 893 (1957); T. Kasuya, *Progr. Theoret. Phys. (Kyoto)* **16**, 45 (1956).

B. Resistivity

The interference factor is the same as (3) for chemical interactions but

$$f_1^*(\theta)f_2(\theta) = \frac{1}{4\pi^2} |J(K)|^2 \langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle. \quad (17)$$

In terms of the density matrix, the correlations are evaluated as follows:

$$\langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle = \frac{\text{Trace}[\mathbf{S}_1 \cdot \mathbf{S}_2 \exp\{-w(d)/k_B T\}]}{\text{Trace}[\exp\{-w(d)/k_B T\}]} \quad (18)$$

For high temperatures, (18) can be expanded in powers of $1/T$. Then the total resistivity ρ due to the scattering of conduction electrons \mathbf{s} by \mathbf{S}_1 and \mathbf{S}_2 is

$$\frac{\rho}{\rho_1 + \rho_2} = 1 + \frac{\int_0^\pi \langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle e^{i\mathbf{K} \cdot \mathbf{d}} |J(K)|^2 (1 - \cos\theta) \sin\theta d\theta}{\sum_i \int_0^\pi \langle \mathbf{S}_i^2 \rangle |J(K)|^2 (1 - \cos\theta) \sin\theta d\theta}, \quad (19)$$

ρ_1 and ρ_2 being the individual incoherent resistivities of \mathbf{S}_1 and \mathbf{S}_2 . (18) and (19) lead at large distances d to

$$\frac{\rho}{\rho_1 + \rho_2} \rightarrow 1 + \frac{4J^2(2k_M) (2k_M)^4}{3k_B T (2\pi)^3} \times \frac{2S_1(S_1+1)S_2(S_2+1) \cos^2(2k_M d)}{S_1(S_1+1) + S_2(S_2+1) (2k_M d)^5} \quad \text{for } d \rightarrow \infty. \quad (20)$$

The excess resistivity $\rho - (\rho_1 + \rho_2)$ under thermal equilibrium, due to interference between the scatterers, is again *positive*, as for nonmagnetic impurities [formula (12)].

ACKNOWLEDGMENT

The authors thank Dr. A. Blandin for discussions, especially concerning the Appendix.

APPENDIX: ON THE VALIDITY OF THE ASYMPTOTIC FORM OF w AND $\delta\sigma$

The interaction energy as well as interference effects lead to similar integrations over K ; but the first is taken from $K=0$ to $K=\infty$, i.e.,

$$\frac{1}{d} \int_0^\infty f_1(K) \sin K d dK \quad (A1)$$

and the second stops at $K=2k_M$:

$$\frac{1}{d} \int_0^{2k_M} f_2(K) \sin K d dK, \quad (A2)$$

where $f_1(K)$ and $f_2(K)$ are functions of K given explicitly later.

The calculations of the corresponding asymptotic expressions for large distances d between the two scatterers involve integrations by parts, keeping only the smallest power of $1/d$. In this operation, attention must be paid to the structure of $f_1(K)$ and $f_2(K)$.

For magnetic scatterers,

$$f_1(K) = |J(K)|^2 F(K) K, \quad (A3)$$

where $F(K)$ is given by Eq. (15), and

$$f_2(K) = |J(K)|^2 K^2, \quad (A4)$$

where $J(K)$ is the Fourier transform of the exchange integral.

For nonmagnetic scatterers,

$$f_1(K) = |U(K)|^2 [K^2 \epsilon(K)] K \quad (A5)$$

and

$$f_2(K) = |U(K)|^2 K^2, \quad (A6)$$

where ϵ_K is given by Eq. (9) and the simplifying assumption is made that

$$U_1(K) = U_2(K) = U(K) = 4\pi Z / K^2 \epsilon(K), \quad (A7)$$

Z being the charge of each scatterer. $\epsilon(K)$ and $F(K)$ have no singularities but their derivatives are infinite for $K=2k_M$. $U(K)$ and $J(K)$ are assumed to be continuous and *finite* functions of K for all values of K .

Now, it is easy to verify that $f_1(0)$, $f_1(\infty)$ and $f_2(0)=0$. Then the leading term in the energy, in $1/d^2$, vanishes between the limits 0 and ∞ . The next term, in $1/d^3$, involves the derivative of $f_1(K)$, which has a singularity at $K=2k_M$. The main contribution to this term is in the immediate neighborhood of $2k_M$; it is in $\cos 2k_M d / d^3$, as computed in the text. But the leading term in the resistivity, in $1/d^2$, does not vanish for the limit $2k_M$. It is the term considered in the text. The next term involves the possible singularity at $2k_M$ in the derivative of $f_2(K)$; it is in $\cos 2k_M d / d^3$, thus negligible for $k_M d \gg 1$ compared with the first term in $1/d^2$.

More generally, for regular, finite potentials, with regular derivatives, there is no trouble. For a finite potential with infinite derivatives for some value $K=K_i$, the contribution to the energy comes from the neighborhood of K_i , but in the resistivity the singularity does not appear in the asymptotic form stopped at the leading term in $1/d$. The case of a step-function potential would be treated in the same way.