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Theory of the de Haas–van Alphen Effect in Dilute Alloys*

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Multiple-scattering theory is employed to determine the one-electron Green's function in the presence of a uniform external magnetic field and a dilute random arrangement of atomic potentials. The oscillatory part of the density of states is extracted and used to compute thermodynamic quantities. Explicit expressions for the frequency shifts and the amplitude diminution caused by inserting impurities into the free-electron gas are obtained.

I. INTRODUCTION

The de Haas–van Alphen (dHvA) effect has long been a useful tool for the investigation of extremely pure metals. In recent years it has been applied to the study of controlled dilute alloys in an attempt to elucidate the electronic properties of these relatively simple disordered materials.[1] One is primarily interested in the effect of alloying on the frequency of the dHvA oscillations, since this quantity depends directly upon the electronic states in the vicinity of the Fermi energy.

There have been several theoretical studies of the dHvA effect in dilute alloys. The earliest was the pioneering work of Dingle,[2] which was essentially a phenomenological treatment of the effect of impurity scattering on the amplitude of the oscillations. Dingle argued that the result of such scattering was to broaden the Landau levels (the quantized energy levels of an electron in a spatially uniform magnetic field). Since the dHvA effect arises from the passage of such levels through the chemical potential of the system, the broadening of the otherwise sharp levels manifests itself as a diminution in the amplitude of the oscillations. While correct in spirit, Dingle's treatment gave no prescription for calculating the lifetime causing the decrease in amplitude. Furthermore, it did not deal with the frequency shifts produced by alloying. Heine[3] did consider the question of what would happen to the frequency as impurities were added to the perfect crystal. His approach was a fundamental one, insofar as the effects of alloying in the absence of an external field were concerned, but did not attempt to deal with field-dependent effects in a basic way.

Bychkov[4] attempted to apply multiple-scattering theory to the problem. His work was limited to the case of a zero-range potential, and in any event was not concerned with the questions of frequency shifts. His expressions for the lifetime associated with the dHvA oscillations differ from those derived here and in Ref. (5) by the presence of apparently extraneous factors. Brailsford[5] discussed the question of frequency changes and amplitude reduction using what was essentially a ruse to avoid dealing with the multiple-scattering problem. He states that his formalism is not appropriate to situations where one has real or virtual bound impurity states. Since one can pass continuously from a weak-scattering limit to a strong-scattering virtual-state situation, it is difficult to delimit the domain of validity of Brailsford's theory.

In this paper we employ standard multiple-scattering theory to determine the one-electron Green's functions in the presence of a uniform external magnetic field and a dilute random arrangement of scatterers of arbitrary strength. The calculations, therefore, are in a strict sense only appropriate to a system which reduces to a free-electron gas as the concentration of the scatterers goes to zero. We express the frequency shifts and the lifetime in terms of the phase shifts produced by an individual scatterer. Because of our assumption of a spherical unperturbed Fermi surface the calculations are not immediately applicable to common experimental situations, which usually, for signal strength purposes, deal with small pieces of the actual distorted Fermi surface. An attempt is made to remedy this defect of our work in an intuitive manner.

II. FORMALISM

The Hamiltonian of the system is the sum of H_0, the nonrandom "unperturbed" part which in the present case describes the motion of an electron in a uniform external magnetic field, and V, the random potential describing the interaction of an electron with the impurities. The potential V can be decomposed into a sum of contributions from each impurity:

$$V(\vec{r}) = \sum_s v(\vec{r} - \vec{R}_s) \equiv \sum_s v_s \ , \tag{1}$$

where $\vec{R}_s$ denotes the position of the sth impurity.

The calculations will be performed using conventional multiple-scattering theory,[6,7] which will be briefly reviewed here. The unperturbed and perturbed Green's functions are defined by the expressions

$$G_0(z) = (z - H_0)^{-1} \ , \qquad \mathcal{G}(z) = (z - H_0 - V)^{-1} \ , \tag{2}$$

respectively, and the density of states at energy E is given by

$$\rho(E) = -\pi^{-1} \operatorname{Im} \operatorname{Tr} G(E + i\delta) \ , \tag{3}$$

where $G(z) = \langle \mathcal{G}(z) \rangle$, the angular brackets denoting an ensemble average over the position of the impurities, and δ is a positive infinitesimal. It is conventional to express the averaged Green's function G in terms of a self-energy operator Σ, defined implicitly by the equation

$$G(z) = (z - H_0 - \Sigma)^{-1} \ , \tag{4}$$

which in turn may be inverted to yield

$$G = G_0 + G_0 \Sigma G \ . \tag{5}$$

On the other hand, $\mathcal{G}$ may be expressed in terms of the total transition operator using the expression

$$\mathcal{G} = G_0 + G_0 \mathcal{T} G_0 \ . \tag{6}$$

Since $\langle \mathcal{G} \rangle = G$ and G_0 is not a statistical object, it follows that

$$G_0 + G_0 \Sigma G = G_0 + G_0 \langle \mathcal{T} \rangle G_0 \ , \tag{7}$$

which can be manipulated to yield

$$\langle \mathcal{T} \rangle = \Sigma (1 + G_0 \langle \mathcal{T} \rangle) \ , \tag{8}$$

The primary difficulty is the construction of a suitable approximate way of performing the average of $\mathcal{T}$. Lax[6] introduced the following procedure: $\mathcal{T}$ satisfies the equation

$$\mathcal{T} = V + V G_0 \mathcal{T} = \sum v_s (1 + G_0 \mathcal{T}) \ , \tag{9}$$

where the second form follows from the decomposition (1). Defining

$$\mathcal{T}_s = v_s (1 + G_0 \mathcal{T}) \ , \tag{10}$$

one finds that

$$\mathcal{T} = \sum_s \mathcal{T}_s \tag{11}$$

and

$$\mathcal{T}_s = t_s \Big(1 + G_0 \sum_{r \neq s} \mathcal{T}_r\Big), \tag{12}$$

where t_s is the single-atom t matrix satisfying the equation

$$t_s = v_s + v_s G_0 t_s \ . \tag{13}$$

In Refs. 6 and 7 it is shown in detail how Eq. (12) may be iterated to yield $\langle \mathcal{T}_s \rangle$ as the solution of an infinite coupled chain of equations. The result of these discussions is the following. Let $\langle \cdots \rangle_s$ and $\langle \cdots \rangle_{s,r}$ denote restricted ensemble averages, the first being one in which the position of the sth atom is held fixed, while in the second both the sth and the rth atoms are fixed. Then the first two of these coupled equations are

$$\langle \mathcal{T} \rangle = N \Omega^{-1} \int \langle \mathcal{T}_s \rangle_s d^3R_s \ , \tag{14a}$$

$$\langle \mathcal{T}_s \rangle_s = t_s (1 + \Omega^{-1} G_0 \sum \langle \mathcal{T}_r \rangle_{r,s} d^3R_r) \ , \tag{14b}$$

where N is the total number of impurities, Ω is the crystal volume, and we have assumed (as is appropriate to the small concentration limit) that all averages can be effected by integrating over the position of the impurities. The second of these equations is closed by making the approximate identification

$$\langle \mathcal{T}_r \rangle_{r,s} \simeq \langle \mathcal{T}_r \rangle_r \ , \tag{15}$$

in which case Eqs. (14a) and (14b) may be combined to yield

$$\langle\mathcal{T}\rangle = n\int t_s(1+G_0\langle\mathcal{T}\rangle)\,d^3R_s\ , \tag{16}$$

where $n = N\Omega^{-1}$ is the density of impurities. Combining (8) and (16) one finds that the self-energy operator is given by the expression

$$\Sigma = n\int t_s\,d^3R_s\ . \tag{17}$$

We now apply the multiple-scattering theory just outlined to the problem of an electron moving in an external magnetic field and the field of a (very dilute) random arrangement of impurities. Since we are interested here in the dHvA oscillations, which depend upon the field in a highly nonlinear way, it is necessary to treat the magnetic field exactly. We take the magnetic field to be in the z direction and work in the gauge in which the vector potential is given by $\vec{A} = (-By,\ 0,\ 0)$. The eigenfunctions and eigenvalues of

$$H_0 = (1/2m)[\vec{p} - (e/c)\vec{A}]^2 \tag{18}$$

are very well known.[8] In positional representation the eigenfunctions are

$$\langle\vec{r}\,|\,\nu, k_x, k_z\rangle = (2\pi)^{-1}e^{i(xk_x+zk_z)}\,u_\nu(y-y_0)\ , \tag{19}$$

where $u_\nu(y)$ is the harmonic-oscillator function

$$u_\nu(y) = (2\alpha/\pi)^{1/4}(2^\nu\nu!)^{-1/2}e^{-\alpha y^2}H_\nu[(2\alpha)^{1/2}y]\ , \tag{20}$$

in which $\alpha = eB/2\hbar c$ and $y_0 = k_x/2\alpha$. The eigenvalues are simply

$$E(\nu, k_x, k_z) = (\nu+\tfrac{1}{2})\,\hbar\omega + \hbar^2k_z{}^2/2m\ , \tag{21}$$

where $\omega = eB/mc$.

The Green's function $G_0(z)$ is given in terms of the kets $|\nu,\ k_x,\ k_z\rangle$ by the usual expression

$$\begin{aligned}\langle\vec{r}\,|\,G_0\,|\,\vec{r}\,'\rangle &= (2\pi)^{-2}\int dk_x dk_z \textstyle\sum_\nu \langle\vec{r}\,|\,\nu, k_x, k_z\rangle\langle\nu, k_x, k_z\,|\,\vec{r}\,'\rangle \\ &\quad\times[z - E(\nu, k_x, k_z)]^{-1}\ . \end{aligned} \tag{21}$$

Certain useful properties of G_0 may be established with the aid of gauge invariance arguments.[9] Let $\vec{a}$ be any constant vector. If $\phi(\vec{r})$ is an eigenfunction of H_0 with eigenvalue E, then $\phi(\vec{r}+\vec{a})$ is an eigenfunction of H_0' (with the same eigenvalue), where H_0' is H_0 with $\vec{r}$ replaced by $\vec{r}+\vec{a}$. But replacing $\vec{r}$ by $\vec{r}+\vec{a}$ is equivalent here to making the gauge transformation

$$\vec{A} \to \vec{A}\,' = \vec{A} - Ba_y\,\hat{i} = \vec{A} - \nabla(Ba_y x)\ .$$

This implies that

$$\phi(\vec{r}+\vec{a}) = e^{-2i\alpha a_y x}\phi'(\vec{r})\ ,$$

where ϕ' is some eigenfunction of H_0 corresponding to the same eigenvalue E. But since expression (21) involves a sum over all eigenfunctions, it follows that G_0 satisfies

$$\langle\vec{r}+\vec{a}\,|\,G_0\,|\,\vec{r}\,'+\vec{a}\rangle = e^{-2i\alpha a_y(x-x')}\langle\vec{r}\,|\,G_0\,|\,\vec{r}\,'\rangle\ . \tag{22}$$

Putting $\vec{a} = -\vec{r}\,'$ one finds

$$\langle\vec{r}\,|\,G_0\,|\,\vec{r}\,'\rangle = \exp[-2i\alpha y'(x-x')]\langle\vec{r}-\vec{r}\,'\,|\,G_0\,|\,0\rangle$$

or finally

$$\langle\vec{r}\,|\,G_0\,|\,\vec{r}\,'\rangle = e^{-i\alpha(y+y')(x-x')}F(\vec{r}-\vec{r}\,')\ , \tag{23}$$

where F is some unknown function.

The atomic t matrices have an analogous structure. In coordinate space they satisfy the equation

$$\begin{aligned} t_s(\vec{r}, \vec{r}\,') &= v(\vec{r}-\vec{R}_s)\delta(\vec{r}-\vec{r}\,') + v(\vec{r}-\vec{R}_s) \\ &\quad\times\int e^{-i\alpha(y+y'')(x-x'')}F(\vec{r}-\vec{r}\,'')t_s(\vec{r}\,'', \vec{r}\,')\,d^3r''\ , \end{aligned} \tag{24}$$

where we have used (23) for G_0. Direct substitution shows that t_s may be written in the form

$$\begin{aligned} t_s(\vec{r}, \vec{r}\,') &= \exp[i(\vec{r}-\vec{r}\,')\cdot(\vec{\alpha}\times\vec{R}_s) - i\alpha(xy - x'y')] \\ &\quad\times\tilde{t}(\vec{r}-\vec{R}_s, \vec{r}\,'-\vec{R}_s)\ , \end{aligned} \tag{25}$$

where $\vec{\alpha} = \alpha\hat{k}$ and $\tilde{t}$ satisfies

$$\begin{aligned} \tilde{t}(\vec{r}, \vec{r}\,') &= v(\vec{r})\delta(\vec{r}-\vec{r}\,') + v(\vec{r}) \\ &\quad\times\int e^{-i\vec{\alpha}\cdot(\vec{r}\times\vec{r}\,'')}F(\vec{r}-\vec{r}\,'')\tilde{t}(\vec{r}\,'', \vec{r}\,')\,d^3r''\ . \end{aligned} \tag{26}$$

The next step in the calculation is the determination of the matrix elements of the self-energy operator in the representation defined by the basis set (19). Using Eqs. (17), (19), and (25) one finds that the required matrix elements are given by the expression

$$\begin{aligned} \langle\nu, k_x, k_z\,|\,\Sigma\,|\,\mu, k_x', k_z'\rangle &= n(2\pi)^{-2}\int d^3r\,d^3r'\,d^3R \\ &\quad\times e^{i\phi}\,u_\nu(y+y_0)\,\tilde{t}(\vec{r}-\vec{R}, \vec{r}\,'-\vec{R})u_\mu(y'+y_0')\ , \end{aligned} \tag{27}$$

where the phase factor is

$$\begin{aligned} \phi &= (\vec{r}-\vec{r}\,')\cdot(\vec{\alpha}\times\vec{R}) - i\alpha(xy - x'y') \\ &\quad - (xk_x + zk_z) + (x'k_x' + z'k_z')\ . \end{aligned}$$

Replacing $\vec{r}-\vec{R}$ and $\vec{r}\,'-\vec{R}$ by $\vec{r}$ and $\vec{r}\,'$, respectively, the expression for the matrix elements (27) takes the form

$$\begin{aligned} &n(2\pi)^{-2}\int d^3r\,d^3r'\,d^3R \\ &\quad\times e^{i\phi}\,u_\nu(y+R_y+y_0)\,\tilde{t}(\vec{r}, \vec{r}\,')u_\mu(y+R_y+y_0') \end{aligned}$$

where ϕ is now defined by

$$\begin{aligned} \phi &= 2\alpha R_y(x'-x) + x'y' - xy + (x'k_x' + z'k_z') \\ &\quad - (xk_x + zk_z) + R_x(k_x' - k_x) + R_z(k_z' - k_z)\ . \end{aligned}$$

Performing the R_x and R_y integrations shows that the self-energy is diagonal in k_x and k_z:

$$\langle\nu, k_x, k_z\,|\,\Sigma\,|\,\mu, k_x', k_z'\rangle = \delta(k_x - k_x')\delta(k_z - k_z')\Sigma_{\nu\mu}(k_x, k_z)\ ,$$

where

$$\Sigma_{\nu\mu}(k_x, k_z) = n\int d^3r\,d^3r'\int_{-\infty}^{\infty}ds$$

$$\times \exp[ik_z(z'-z)+i\alpha(x'y'-xy)+2i\alpha s(x'-x)]$$
$$\times u_\nu(y+s)\,\tilde{t}(\vec{r},\vec{r}\,')u_\mu(y'+s) \qquad (28)$$

and we have introduced the integration coordinate $s=R_y+y_0$. The integration over s can be carried out exactly. One finds that

$$\int ds \exp[i\alpha(x'y'-xy)+2i\alpha s(x'-x)]\,u_\nu(y+s)u_\mu(y'+s)$$
$$=(\cdots)\exp[i\alpha(xy'-x'y)-\tfrac{1}{2}\alpha\rho^2]$$
$$\times L_\mu^{\nu-\mu}(\alpha\rho^2)[(x-x')+i(y-y')]^{\nu-\mu}, \qquad (29)$$

where $\rho^2=(x-x')^2+(y-y')^2$, L_μ^ν is the associated Laguerre polynominal, and $(\cdots)$ represents a factor which equals unity when $\nu=\mu$. Now because of the axial symmetry about the z axis, the operator $\tilde{t}$ that occurs in (28) is invariant under simultaneous rotation of $\vec{r}$ and $\vec{r}\,'$ about that axis. All of the factors in (29) are also invariant under such a rotation except for the last which behaves as $e^{i(\nu-\mu)\theta}$, where θ is the rotation angle. Consequently $\Sigma_{\nu\mu}$ vanishes unless $\mu=\nu$. Our final result for the self-energy matrix elements is, therefore,

$$\langle \nu, k_x, k_z|\Sigma|\mu, k_x', k_z'\rangle$$
$$=\delta_{\mu\nu}\delta(k_x-k_x')\delta(k_z-k_z')\Sigma(\mu,k_x,k_z), \qquad (30)$$

where

$$\Sigma(\mu,k_x,k_z)$$
$$=n\int d^3r\,d^3r'\exp[ik_z(z-z')+i\alpha(xy'-x'y)-\tfrac{1}{2}\alpha\rho^2]$$
$$\times \tilde{t}(\vec{r},\vec{r}\,')L_\mu^0(\alpha\rho^2). \qquad (31)$$

All of the preceding results, including the one concerning the diagonal nature of the self-energy, have been exact. Further progress is facilitated if it is recognized that the problem is replete with large and small parameters, and that we are interested at present in obtaining only those field-dependent quantities that are oscillatory in character. We first note that the range of integration in (31) is determined by the range of $\tilde{t}$. Since this is of the order of atomic dimensions, it follows that for the purpose at hand the term proportional to α in the exponential can be dropped. Furthermore, it is known that the dHvA oscillations arise from states of large Landau number. The Laguerre polynomial may then be approximated by

$$L_\mu^0(z)=e^{z/2}J_0([2(2\mu+1)z]^{1/2}),$$

where J_0 is the zeroth-order Bessel function. The self-energy matrix element (31) then takes the form

$$\Sigma(\mu,k_x,k_z)=n\int d^3r\,d^3r'\,e^{ik_z(z-z')}$$
$$\times J_0(2\rho\alpha^{1/2}(\mu+\tfrac{1}{2})^{1/2})\,\tilde{t}(\vec{r},\vec{r}\,'). \qquad (32)$$

But the addition formula for Bessel functions is

$$J_0(2\rho\alpha^{1/2}(\mu+\tfrac{1}{2})^{1/2})=\sum_{p=-\infty}^{\infty} J_p(k_\mu r_\perp)J_p(k_\mu r_\perp')\,e^{ip(\phi-\phi')}, \qquad (33)$$

where $r_\perp^2=x^2+y^2$ and ϕ is the azimuthal angle of $\vec{r}$, and we have defined a wave vector by $k_\mu^2=2\alpha(2\mu+1)$. Combining (32), (33), and the two-dimensional plane-wave expansion

$$e^{ik_\mu y}=\sum_{p=-\infty}^{\infty} J_p(k_\mu r_\perp)e^{ip\phi},$$

and making use of the cylindrical symmetry of $\tilde{t}$, we find for the matrix elements the expression

$$\Sigma(\mu,k_z)=n\int d^3r\,d^3r'\exp[ik_z(z-z')+ik_\mu(y-y')]$$
$$\times \tilde{t}(\vec{r},\vec{r}\,'). \qquad (34)$$

Using the notation $\tilde{t}(k_z,k_\mu)$ to denote the forward scattering matrix elements of $\tilde{t}$ for a wave vector with components k_z and k_μ, perpendicular and parallel, respectively, to the z axis, the self-energy matrix elements take the simple form

$$\Sigma(\mu,k_z)=n\tilde{t}(k_z,k_\mu). \qquad (35)$$

The operator $\tilde{t}$ satisfies Eq. (26) and in principle is itself a function of the external field because of the α in the exponential and the field dependence of F. However, as was discussed above, the exponential involving α is very close to unity for all reasonable fields and can therefore be ignored, at least insofar as we are only interested in oscillatory field-dependent quantities. It is shown in Ref. 10 that the quantity $F(\vec{r}-\vec{r}\,')$ is equal to the zero-field Green's function plus a correction term of order $(\hbar\omega/E)^{1/2}$, which can also be dropped, since we are interested in energies of the order of the Fermi energy. F, of course, also contains oscillatory terms, and therefore the t matrix itself has an oscillatory part. It can be shown that these terms can only lead to small corrections to the result derived below. The upshot is, therefore, that for the purpose at hand the operator $\tilde{t}$ can be replaced by the zero-field t matrix with no appreciable error. We shall henceforth drop the tilde and interpret the t matrix in this way.

We now calculate the zero field and the oscillatory part of the density of states. Since the self-energy is diagonal the Green's function $\langle\vec{r}|G|\vec{r}\,'\rangle$ is given by Eq. (21) with the substitution $z\rightarrow z-\Sigma$. Using the orthonormality of the Hermite polynomials, we find for the density of states (per unit volume)

$$\rho(E)=-(\alpha/2\pi^3)\,\mathrm{Im}\sum\nolimits_\mu\int dk_z$$
$$\times[E-(\mu+\tfrac{1}{2})\hbar\omega-\hbar^2k_z^{\,2}/2m-nt(k_z,k_\mu)]^{-1}. \qquad (36)$$

We introduce the following notation:

$$E=\hbar^2\epsilon/2m, \quad \hbar\omega=\hbar^2\epsilon_0/2m,$$

$$t(k_z, k_\mu) = (\hbar^2/2m)\tau((k_z^2 + k_\mu^2)^{1/2}) ,$$

where we have noted that for a spherical scatterer the forward part of the t matrix is a function only of the magnitude of the wave vector. Then we have

$$\rho(E) = -\tfrac{1}{4}\epsilon_0 C \operatorname{Im} \textstyle\sum_\mu \int dk_z \times [\epsilon - (\mu + \tfrac{1}{2})\epsilon_0 - k_z^2 - n\tau((k_z^2 + k_\mu^2)^{1/2})]^{-1} , \tag{37}$$

where $C = m\pi^{-3}\hbar^{-2}$. The sum over μ is evaluated using the Poisson sum formula, the result being

$$\rho(E) = -\tfrac{1}{4} C \operatorname{Im} \sum_{p=-\infty}^{\infty} (-1)^p \int_{-\infty}^{\infty} dk_z \int_0^\infty dx \times \exp\left(\frac{2\pi i p x}{\epsilon_0}\right) [\epsilon - x - k_z^2 - n\tau((k_z^2 + x)^{1/2})]^{-1} . \tag{38}$$

In this expression the variable x plays the role of the square of a wave vector whose direction is perpendicular to the z axis. It is convenient to change the integration variables to the pair (k, k_z), where $k^2 = k_z^2 + x$. One finds

$$\rho(E) = -\tfrac{1}{2} C \operatorname{Im} \sum_p (-1)^p \int_0^\infty k\,dk \int_0^k \exp\left(\frac{-2\pi i k_z^2}{\epsilon_0}\right) \times \exp\left(\frac{2\pi i k^2}{\epsilon_0}\right) [\epsilon - k^2 - n\tau(k)]^{-1} . \tag{39}$$

The inner integration is trivial for $p = 0$; for nonzero p it may be carried through once it is noted that insofar as the oscillatory terms are concerned the important values of k are of order the Fermi wave vector, which implies that the asymptotic limit $(k^2/\epsilon_0 \to \infty)$ may be taken. This approximation neglects field-dependent but nonoscillatory terms. The result is that for the purposes of the present paper one may write

$$\rho(E) = \rho_0(E) + \tilde{\rho}(E) , \tag{40}$$

where ρ_0, the zero-field density of states, is given by

$$\rho_0(E) = -C \operatorname{Im} \int_0^\infty k^2\,dk\,[\epsilon - k^2 - n\tau(k)]^{-1} \tag{41}$$

and

$$\tilde{\rho}(E) = -C\left(\frac{\epsilon_0}{2}\right)^{1/2} \sum_{p=1}^{\infty} (-1)^p p^{-1/2} \times \operatorname{Im} \int_0^\infty [\epsilon - k^2 - n\tau(k)]^{-1} \cos\left(\frac{2\pi p k^2}{\epsilon_0} - \frac{\pi}{4}\right) k\,dk . \tag{42}$$

While our primary purpose is a discussion of the dHvA oscillations, it is interesting to contrast the expressions for the zero field ρ_0 and for the oscillatory $\tilde{\rho}$. Equation (41) may be written in the form

$$\rho_0(E) = -C \frac{\partial}{\partial\epsilon} \int_0^\infty \operatorname{Im} \ln[k^2 + n\tau(k) - \epsilon]\, k^2\,dk , \tag{43}$$

where the partial derivative sign is meant to indicate that one does not differentiate with respect to the energy dependence of τ.

The limit of this expression as $n \to 0$ is of course the free-electron density of states. Of greater interest is the part of ρ_0 proportional to the concentration of impurities. We find that

$$\lim_{n\to 0} \frac{\partial\rho_0}{\partial n} = -C \frac{\partial}{\partial\epsilon} \operatorname{Im} \int_0^\infty \tau(k)\,[\epsilon + i\delta - k^2]^{-1} k^2\,dk . \tag{44}$$

It is easy to show that (44) is equivalent to

$$\pi^{-1} \frac{\partial}{\partial E} \operatorname{Im} \operatorname{Tr} G_0 t = -\pi^{-1} \operatorname{Im} \operatorname{Tr} G_0 t G_0 ,$$

where G_0 is here meant to denote the free-electron Green's function. Anderson and McMillian[11] have shown explicitly that the second form [which is equal to $\operatorname{Tr}(G - G_0)$, where G is the exact Green's function in the presence of a single impurity] yields the usual Friedel formula[12] for the change in the density of states per impurity

$$\Delta\rho(E) = \pi^{-1} \textstyle\sum (2l + 1) \dfrac{d\delta_l}{dE} , \tag{45}$$

where the δ_l are the phase shifts.

The point to be noted is that while the final result for the impurity contribution to the zero-field density of states involves only on-energy-shell quantities, obtaining this result by a momentum-space integration involves the forward part of t for all wave vectors. In particular, the off-energy-shell matrix elements of $\operatorname{Im} t$ enter in an important way. On the other hand, the rapid osicllations of the cosine factor in Eq. (42) ($k^2/\epsilon_0 \simeq 10^4$, if k is of the order of a Fermi wave vector) ensure that one gets significant contributions to the integral only in regions where the first factor is rapidly varying, i.e., only near the region where $\epsilon - k^2 - \operatorname{Re} n\tau = 0$. This means that $\tilde{\rho}$ will also depend only upon on-energy-shell quantities, but not necessarily those entering into ρ_0.

We evaluate the integral in (42) by expressing the cosine as a sum of exponentials and distorting the contour to the appropriate 45° line in the complex-k plane. Since the integral along the new contour yields field-dependent but nonoscillatory part of the density of states,

$$\tilde{\rho}(E) = C\left(\frac{\epsilon_0}{2}\right)^{1/2} \operatorname{Re} \sum_{p=1}^{\infty} (-1)^p p^{-1/2} \exp\left(\frac{2\pi i p(\epsilon - n\bar{\tau})}{\epsilon_0} - \frac{i\pi}{4}\right) , \tag{46}$$

where in this expression we have dropped prefactor terms proportional to the defect concentration n and $\bar{\tau} = \tau$ evaluated at $k = \epsilon^{1/2}$.

The final step in our calculations is the use of Eq. (46) to find the oscillatory part of the free energy, from which the dHvA oscillations in the susceptibility may be obtained. Denoting this part of the free energy by $\tilde{F}$, one has the usual formula

$$\tilde{F} = -(2/\beta)\int_0^\infty \ln[1 + e^{\beta(\mu - E)}]\,\tilde{\rho}(E)\,dE$$

or

$$\tilde{F} = 2\int_0^\infty [1 + e^{\beta(\mu - E)}]^{-1}\,\tilde{Z}(E)\,dE\,,$$

where $\beta = 1/kT$, μ is the chemical potential,[12] and

$$\tilde{Z}(E) = \int_0^E \tilde{\rho}(E)\,dE = \frac{1}{4}\,C\left(\frac{\epsilon_0^3}{2}\right)^{1/2}\,\mathrm{Im}\sum_{p=1}^{\infty}(-1)^p p^{-3/2} \times\exp\left(\frac{2\pi i p(\epsilon - n\bar{\tau})}{\epsilon_0} - \frac{i\pi}{4}\right). \qquad (47)$$

In this last equation we have again dropped prefactor terms proprotional to n. We have also ignored the fact that formal integration of Eq. (46) yields a spurious term arising from the lower limit of integration, or ultimately from the fact that we have only an asymptotic formula for $\tilde{\rho}$ and not one valid for all energies. In any event, no oscillatory terms would arise from the neglected term, even if it were carried along in the calculations.

The integral in (47) may be done by closing the integral in the upper half plane. One picks up poles at $E = \mu + (2r+1)\pi/\beta$, where r is an integer. To sufficient accuracy the value of $\bar{\tau}$ at the poles can be obtained by keeping only the first two terms of a Taylor expansion around μ. The result of summing over these poles is our desired formula

$$\tilde{F} = \left(\frac{C}{2\beta}\right)\left(\frac{\epsilon_0^3}{2}\right)^{1/2}\sum_{p=1}^{\infty}(-1)^p p^{-3/2}\,\frac{\cos[2\pi p(\mu - \Delta)/\hbar\omega - \frac{1}{4}\pi]}{\sinh[2\pi^2 p(1 - \Delta')/\hbar\omega\beta]} \times e^{-2\pi p\Gamma/\hbar\omega}\,, \qquad (48)$$

where we have written $n\bar{\tau} = 2m(\Delta - i\Gamma)/\hbar^2$ and dropped a small imaginary contribution to the argument of the hyperbolic sine. The quantity Δ' denotes $(d\Delta/dE)_\mu$, where one differentiates with respect to the full energy dependence of Δ.

The quantity $\Delta - i\Gamma$ is proportional to the forward part of the t matrix on the energy shell. An explicit expression is

$$\Delta - i\Gamma = -\frac{2\pi n\hbar^2}{mk_0}\sum_{l=0}(2l+1)\,e^{i\delta_l}\sin\delta_l\,, \qquad (49)$$

where k_0 is the Fermi wave vector. The lifetime τ_0 is defined by $\tau_0 = (nv\sigma)^{-1}$, where σ is the total scattering cross section per impurity and v is the Fermi velocity. Comparing (49) with the standard formula for the cross section shows that[13]

$$\Gamma = \tfrac{1}{2}(\hbar/\tau_0)\,.$$

The expression for Δ, which is the quantity that causes the frequency shift on forming the alloy, can be written in a variety of ways. An interesting one expresses it in terms of the frequency shift which would occur if the rigid-band model were applicable. If we imagine that the impurities have a valence difference of δz, and if $\delta\mu$ denotes the rigid-band shift in chemical potential that would occur with a density n of such impurities, then it is easy to show that

$$\Delta = -\delta\mu\left[\sum(2l+1)\cos\delta_l\sin\delta_l/\sum(2l+1)\delta_l\right], \qquad (50)$$

where the Friedel sum rule

$$\delta z = 2\pi^{-1}\sum(2l+1)\delta_l$$

has been used to express δz in terms of the phase shifts. While the actual values of the phase shifts depend upon the detailed nature of the scatterer, one can assume that in some situations only s and p scattering will be significant and plot the second factor in (50) against, say, δ_0 to see how close the result is to the rigid-band prediction. Such a plot is shown in Fig. 1 for the cases $\delta z = 1$ and 2, the valence difference entering in the determination of δ_1 as a function of δ_0. We note that Eq. (50) predicts that the shift is not the same as the rigid-band result, and in fact, for the current calculations is always smaller. The experimental observations on simple metal hosts and impurities are usually consistent with the rigid-band model. However, we note that (a) most of the data deal with the $\delta z = 1$ case, for which the departure of our result from the rigid-band predictions can be small, and (b) much of the published data would apparently also be consistent with a somewhat smaller slope of frequency vs impurity concentration than the rigid-band model would predict. We would encourage experimentation on systems for which the host-impurity valence difference is as large as possible.

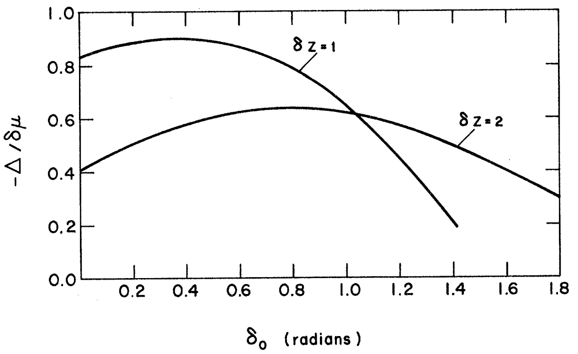

FIG. 1. Ratio of Δ to the rigid-band Fermi energy shift $\delta\mu$ for a situation in which only s- and p-wave phase shifts do not vanish. δz is the impurity-host valence difference and is used to express δ_1 in terms of δ_0 via the Friedel sum rule.

In those cases where one has a resonance for some l one would not expect that the "resonant electrons" would contribute to the oscillations. Equation (49) certainly show that a deep filled shell (e.g., the d electrons associated with a copper impurity) do not cause a shift in the oscillation frequency. The same conclusion holds in a situation where the resonance is exactly at the Fermi level. But according to Eq. (49) a partially filled shell (e.g., a transition-metal impurity not at the center or ends of a row in the Periodic Table) will contribute to the frequency shift.

Equation (48) shows that the presence of the impurity atoms will cause a shift in the temperature dependence of the oscillations, which is most easily described as being due to a change in the effective mass of the electrons involved in the oscillations. In view of the definition of the cyclotron frequency ω, the effective mass can be written in the form

$$\frac{m^*}{m} = 1 - \left(\frac{d\Delta}{dE}\right)_\mu .$$

It is perhaps important to note that the change from m to m^* in the temperature dependence has nothing whatsoever to do with the change in the zero-field density of states. That change is given by the Friedel result (45) and, in fact, Eq. (51) predicts that in a situation where a resonance is exactly at the Fermi level, and hence one has a large increase in the zero-field density of states, the effective cyclotron mass m^* will decrease.

At the present level of analysis it is impossible to relate, with any rigor, the results of this paper with observations involving the small pieces of highly distorted Fermi surfaces that often occur in real systems. Nonetheless, the following would appear to be a not implausible extension of the theory: According to Eqs. (50) and (51) the electrons (more accurately, the part of the spectral density) that is involved in the dHvA effect is characterized by the dispersion relation

$$\hbar^2 k^2 / 2m = E - \Delta .$$

The quantity $-\Delta$ thus plays the role of an energy shift (of the participating electrons) that is produced by making the alloy. Following Heine,[3] one would therefore argue that the change in area of a part of the Fermi surface which in the absence of impurities would be characterized by a cyclotron mass m_c would be

$$\delta S = -2\pi m_c \Delta / \hbar^2 .$$

To the extent that this is valid, we would expect that same relationship between our theory and the rigid-band model as was found above for the perfectly spherical Fermi surface.

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