from nonelectrostatic forces. From calculations of the elastic shear constants of beryllium[14] it is expected that the nonelectrostatic forces of interest are contributed by the kinetic energy of the conduction electrons and ion-core repulsive interactions. The relative importance assigned to these two contributions was found by Bernstein[14] to be sensitive to the energy-band model chosen for the calculations. Harrison[29] has attempted to calculate the physical properties of polyvalent metals from first principles and has obtained some information about the phonon spectrum in Zn, and for Al has obtained a dispersion relation. Further calculations of this type are needed to give an adequate description of the dispersion relations in polyvalent metals, and they are certainly desirable for giving a unified approach to various physical properties.

In calculating quantities such as frequency distributions, specific heat, and Debye-Waller factor for Be from the lattice dynamical models one would certainly expect to obtain the best results from the MAS model of DeWames *et al.*, in view of the better agreement between this model and the neutron-scattering data. Young and Koppel[10] have applied the extended Slutsky-Garland model to the calculation of coherent inelastic neutron scattering from polycrystalline Be, a case where there is justification for using a simpler model. This model fits the dispersion-relation data with maximum deviations of about 10%, although it does not satisfy the elasticity conditions in the long-wavelength limit. In view of the fact that an accuracy to within 10% is acceptable for the neutron-scattering kernel calculations, the simplified central-force model should suffice for this purpose and is expected to require less computation time than the more elaborate models.

## V. CONCLUSIONS

Comparison of the extended dispersion-relation data for Be with lattice dynamical models reveals continued discrepancies between the models and experimental data, although considerable improvement has been made in the modified axially symmetric model of DeWames *et al.* Application of Rosenstock's sum rule test to the dispersion-relation data demonstrates the presence of trace-variable or nonelectrostatic forces in the dynamics of the solid. From theoretical calculations of the elastic shear constants of beryllium it is expected that these nonelectrostatic forces are due to the kinetic energy of the conduction electrons and ion-core repulsive interactions.

## ACKNOWLEDGMENTS

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[29] W. A. Harrison, Phys. Rev. **129**, 2512 (1963); **136**, A1107 (1964).

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# Influence of Impurities on the de Haas–van Alphen Effect

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The influence of impurities, or solute atoms, upon the de Haas–van Alphen effect associated with a metal having a Fermi surface of arbitrary shape is investigated. It is shown that the well-known result of Dingle for the decrease in amplitude of the oscillations in the magnetic susceptibility may be derived without recourse to the additional phenomenological assignment of a specific line shape to each Landau level. The relaxation parameter used by Dingle is shown to be *twice* the lifetime of a state at the Fermi energy. This is compared with the relaxation time for electrical conduction for a class of impurity potentials of variable range in real space. The derivation of the Dingle result presented here depends only upon certain continuity arguments related to the effect of impurities on the electronic band structure. These are investigated in detail for the free-electron model. Simultaneously, the method yields the change in period of the oscillations upon alloying. The conditions under which the rigid-band model is applicable to this problem are derived and a possible generalization is suggested to account for the changes in period which are observed when the solute and solvent have the same valency. The information which can be obtained from experiment concerning the change in amplitude and period is correlated with previous theoretical studies.

## I. INTRODUCTION

THE qualitative aspects of the influence of impurities on the amplitude of the oscillatory component of the magnetic susceptibility of metals [de Haas–van Alphen (dHvA) effect] have been understood ever since the pioneering work of Dingle.[1] On the basis of an assumed Lorentzian line shape, characterized by a "relaxation time" $\tau$, for every Landau level, he showed that each harmonic in the oscillatory magnetization was modified in magnitude by the multiplicative factor $\exp[-2\pi l/\omega_c\tau]$, where $\omega_c=eB/mc$ is the cyclotron frequency and $l$ is the order of the harmonic. Moreover, Dingle's treatment, originally valid only for free electrons, has since been extended

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[1] R. B. Dingle, Proc. Roy. Soc. (London) **A211**, 517 (1952).

by Williamson *et al.*,[2] using the method of Lifshitz and Kosevich,[3] to describe the effect of impurities on the dHvA effect associated with a Fermi surface of arbitrary shape.

While one cannot dispute the fact that Dingle's treatment contains all the essential features for describing the amplitude reduction, it is, nevertheless, not entirely satisfactory from a fundamental point of view. For apart from the question of the precise significance of the parameter $\tau$, the artifice of ascribing a Lorentzian line shape to a state which is, despite the quantization of the energy of motion in the plane perpendicular to the field $\mathbf{B}$, part of a quasi-continuum, seems itself somewhat nebulous. Moreover, without further generalization, the treatment does not describe the accompanying change in the period of the oscillations. The approach, although undoubtedly partly successful, is essentially phenomenological in nature.

An attempt at a more rigorous treatment of the problem was made some years ago by Bychkov,[4] who used what are by now standard methods involving a temperature-independent Green's function.[5] Unfortunately, his treatment was restricted to free electrons, to the Fermi pseudo-potential approximation (i.e., Dirac $\delta$-function scattering potentials), and it is not readily generalized without *ad hoc* assumptions relating to the energy dependence of parameters which enter in this approach. Moreover, the interpretation of $\tau$, as derived by Bychkov, differs from that conjectured by Dingle, and in fact we will show it to be incorrect. In addition, changes in the period were not considered.

Nevertheless, the above approach is useful because it provides the clue to a simpler method of deriving the Dingle result. For under the circumstances inherent in Bychkov's work, namely no bound states either real or virtual, we have shown previously[6] that the results of the Green's-function method are simply equivalent to the statement that the number of band states is conserved upon addition of impurities. Thus by direct application of this principle one can circumvent a great amount of mathematical labor and obtain directly the physical properties of interest.

The purpose of the present paper is to show in detail how this leads to a simple, yet fundamental, derivation of the Dingle factor. Initially, in order to avoid the incidental mathematical approximations inherent in the Lifshitz and Kosevich approach, we shall consider the nearly free-electron model, where also one can examine the general conditions of validity in some detail. The generalization to a Fermi surface of arbitrary shape is found then to present no difficulty.

It is shown in general that the effect of impurities is precisely of the form derived by Dingle if his parameter $\tau$ is defined as *twice* the lifetime of a state at the Fermi energy, as determined by scattering off the impurities. This factor of two was mentioned by Dingle himself[1]; it is the difference between the line-shape parameter he derived using classical mechanics and that obtained from Weisskopf-Wigner perturbation theory.[7] Therefore, it is to be expected that this difference appear also in our final result, which is based upon quantum mechanics.

Simultaneously, the method presented here yields the accompanying change in the period of the oscillations. The conditions under which the previous rigid-band-model result of Heine[8] is valid are elucidated. By a slight generalization, suggested by the study of Williamson *et al.*,[2] a model is presented for describing those changes in period which arise when the impurity (solute) and host metal have zero relative valence.

In conclusion, the relation of the lifetime to the electrical resistivity relaxation time is discussed for a simple class of scattering potentials, and then compared with the experimental data presently available.

The paper is divided as follows. Section II contains a recapitulation of the derivation of the dHvA effect for free electrons and a treatment of the effect of impurities for this model. The assumptions involved are discussed in the Appendix. Section III is devoted to a generalization of the treatment to a Fermi surface of arbitrary shape. The significance of the relaxation time is discussed in Sec. IV, while Sec. V contains a brief summary of this work.

## II. NEARLY FREE ELECTRONS

In this section we shall consider the effect of impurities on an otherwise free-electron gas in a magnetic field. The treatment of the dHvA effect will follow Peierls' version of Landau's original method,[9] although slight modifications are included with an eye to later generalization.

It is necessary to recapitulate some of the standard results for the free-electron model. In the presence of a field $\mathbf{B}$, whose direction defines the $z$ axis, the energy levels, $\epsilon(n,k_z)$, are given by

$$\epsilon(n,k_z)=\hbar\omega_c(n+\tfrac{1}{2})+(\hbar^2k_z^2/2m), \tag{1}$$

where $n$ is a positive integer or zero, $\omega_c$ is the cyclotron frequency previously defined, and all other symbols have their usual significance. Each of the levels (1) is $d$-fold degenerate, $d$ being given by

$$d=(L^2eB/2\pi\hbar c), \tag{2}$$

if the normalization volume is taken as a cube of side

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[2] S. J. Williamson, S. Foner, and R. A. Smith, Phys. Rev. **136**, A1065 (1964).

[3] I. M. Lifshitz and A. M. Kosevich, Zh. Eksperim. i Teor. Fiz. **29**, 730 (1955) [English transl.: Soviet Phys.—JETP **2**, 636 (1956)].

[4] Yu. A. Bychkov, Zh. Eskperim. i Teor. Fiz. **39**, 1401 (1960) [English transl.: Soviet Phys.—JETP **12**, 977 (1961)].

[5] S. F. Edwards, Phil. Mag. **6**, 617 (1961).

[6] A. D. Brailsford, Proc. Roy. Soc. (London) **A292**, 433 (1966).

[7] For a full discussion see, for example, W. Heitler, *Quantum Theory of Radiation* (Clarendon Press, Oxford, England, 1957), p. 163 ff.

[8] V. Heine, Proc. Phys. Soc. (London) **A69**, 505 (1956).

[9] R. E. Peierls, *Quantum Theory of Solids* (Clarendon Press, Oxford, England, 1964), p. 147 ff.

length $L$. Thus, the number of states below an energy $\epsilon$, $Z(\epsilon)$ say, is (apart from spin, which we shall ignore in the detailed kinetics)

$$Z(\epsilon)=\frac{L}{\pi}\left(\frac{2m}{\hbar^2}\right)^{1/2} d \sum_{n=0} [\epsilon-\hbar\omega_c(n+\tfrac{1}{2})]^{1/2}, \tag{3}$$

where the summation in (3) extends over those values of $n$ for which the radicand is positive.

The Helmholtz free energy of the system $F$ is given by

$$F=N\eta-2\int_{-\infty}^{\infty} Z(\epsilon)f(\epsilon)d\epsilon, \tag{4}$$

where $f(\epsilon)$ is the Fermi function

$$f(\epsilon)=[1+\exp\{(\epsilon-\eta)/\kappa T\}]^{-1}, \tag{5}$$

$\eta$ is the Fermi energy, $N$ is the total number of electrons [including spin, which also accounts for the factor of 2 in (4)], $\kappa$ is Boltzmann's constant, and $T$ is the temperature.

It is well known that if the summation in (3) is approximated by an integration, the value of $Z(\epsilon)$ so obtained is identical with that for $\mathbf{B}=0$. Thus, in general, $Z(\epsilon)$ can be decomposed into two contributions

$$Z(\epsilon)=Z_0(\epsilon)+Z_1(\epsilon), \tag{6}$$

where $Z_0(\epsilon)$ is the number of states below the energy $\epsilon$ in the absence of a field and $Z_1(\epsilon)$ is an oscillatory function whose existence depends solely upon the quantization of the electronic motion in the plane perpendicular to $\mathbf{B}$. Thus $F$ may also be decomposed into two contributions,

$$F=F_0+F_1, \tag{7}$$

where

$$F_0=N\eta-2\int_0^{\infty} Z_0(\epsilon)f(\epsilon)d\epsilon, \tag{8}$$

is the free energy in zero field, by definition, and

$$F_1=-2\int_0^{\infty} Z_1(\epsilon)f(\epsilon)d\epsilon, \tag{9}$$

$$=2\int_0^{\infty} G(\epsilon)\frac{\partial f(\epsilon)}{\partial\epsilon}d\epsilon. \tag{10}$$

Here $G(\epsilon)$ is defined by

$$G(\epsilon)=\int_0^{\epsilon} Z_1(\epsilon')d\epsilon'. \tag{11}$$

The function $F_1$ contains the contribution from both the Landau diamagnetism and the dHvA effect. In order to separate these it is necessary to perform the decomposition (6) of $Z(\epsilon)$. This is achieved by the use of the Poisson summation formula,[9] which when applied to (3) yields

$$Z_1(\epsilon)=C\left\{\mathrm{Re}\sum_{l=1}^{\infty}\frac{(-1)^l}{2\pi i l}I_l(\epsilon)\exp(2\pi i l\epsilon/\hbar\omega_c)\right\}, \tag{12}$$

where $C=(2Ld/\pi)(2m\omega_c/\hbar)^{1/2}$, and

$$I_l(\epsilon)=\int_0^{(\epsilon/\hbar\omega_c)^{1/2}}\exp(-2\pi i l y^2)dy. \tag{13}$$

Hence, using the definition (11), after changing the order of the integration, we find

$$G(\epsilon)=C\left[\mathrm{Re}\sum_{l=1}^{\infty}(-1)^l\frac{\hbar\omega_c}{(2\pi l)^2}\times\left\{\left(\frac{\epsilon}{\hbar\omega_c}\right)^{1/2}-I_l(\epsilon)\exp(2\pi i l\epsilon/\hbar\omega_c)\right\}\right]. \tag{14}$$

The sum over $l$ in the first term in (14) yields the value $(-\pi^2/12)$. Since this part of $G$ is slowly varying, its contribution to $F_1$ may be approximated immediately from (10) by replacing $(\partial f/\partial\epsilon)$ by $-\delta(\epsilon-\eta)$ in the usual way.[10] One may verify that this leads to the Landau diamagnetism.[9] The remaining contribution to $F_1$ from (14) cannot be so evaluated because it varies rapidly over an energy interval $\sim\kappa T$, near $\epsilon=\eta$, if $\kappa T\sim\hbar\omega_c$. However, if one approximates $I_l(\epsilon)$ by $I_l(\infty)$ in (14), always a valid procedure except near the quantum limit, the resulting integration in (9) is evaluated easily by contour integration in the upper half of the complex energy plane. The only singularities of the integrand are the double poles of $(\partial f/\partial\epsilon)$ at the points $\epsilon=\eta+(2r+1)\pi i\kappa T$, where $r$ is an integer. One obtains then for this contribution to $F_1$, $F_{\mathrm{osc}}$ say, the result

$$F_{\mathrm{osc}}=2\kappa T\sum_{r=0}^{\infty}\mathrm{Re}[2\pi i Y\{\eta+(2r+1)\pi i\kappa T\}], \tag{15}$$

where

$$Z_1(\epsilon)=\mathrm{Re}Y(\epsilon), \tag{16}$$

with the above approximation for $I_l(\epsilon)$. Thus, with $I_l(\infty)=(1-i)/4\sqrt{l}$, from (12), (15), and (16), after summing over the residues we obtain the standard expression[9]

$$F_{\mathrm{osc}}=\frac{L^3\kappa T}{2\pi^2}\left(\frac{m\omega_c}{\hbar}\right)^{1/2}\times\sum_{l=1}^{\infty}\frac{(-1)^l}{l^{3/2}}\frac{\cos\{(2\pi l\eta/\hbar\omega_c)-\pi/4\}}{\sinh(2\pi^2 l\kappa T/\hbar\omega_c)}. \tag{17}$$

Although (17) will be of later interest for comparative purposes, the main reason for presenting the analysis is to bring out one important feature of this approach: If one is interested only in the dHvA effect terms (15), they can be obtained immediately from (9) with $I_l(\epsilon)$ replaced by $I_l(\infty)$ in the defining equation (12) for $Z_1(\epsilon)$. This approximation is invalid for small $\epsilon$, of course, and it is for this reason that $G(\epsilon)$ has to be introduced so that one may extract the Landau diamagnetism, which is associated with[9] the behavior of $Z(\epsilon)$ at small $\epsilon$. However, the point we

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[10] Reference 9, p. 92.

wish to emphasize here is that (15) and (16) are valid under general circumstances; they do not depend upon the free-electron model. This simplifying feature is extremely useful in the remaining analysis.

We are able now to determine the effect of impurities on $F_{\text{osc}}$. Let us suppose that as a result of virtual scattering off the impurities, a state at an energy $\epsilon$ in the absence of impurities is shifted upward in energy by an amount $\Delta(\epsilon)$, a function of energy alone. The quantity $\Delta(\epsilon)$ is to be calculated, say, by perturbation theory using the states pertaining to the levels (1) as a zero-order approximation. However, as we are interested in $\Delta(\epsilon)$ only for large quantum numbers, we shall anticipate that $\Delta(\epsilon)$ is for all practical purposes the value obtained for zero field. At present this is inessential. It may be regarded for the moment simply as a heuristic assumption; we shall return to the point later after obtaining the final result (23).

Under the preceding conditions, as long as $\Delta(\epsilon)$ varies slowly over an energy interval of the order of its own magnitude, the number of states below the energy $\epsilon$, $Z^i(\epsilon)$, in the impure "metal" is related to the corresponding quantity for the pure metal by

$$Z^i(\epsilon)=Z(\epsilon-\Delta(\epsilon)) \tag{18}$$

solely on the basis of continuity. This is all we need. For with the definition (16) and Eq. (12), after the decomposition (6) it follows that

$$Y^i(\epsilon)=C\sum_{l=1}^{\infty}\frac{(-1)^l}{4\sqrt{2}\pi i l^{3/2}} \times\exp[\{2\pi i l(\epsilon-\Delta(\epsilon))/\hbar\omega_c\}-\tfrac{1}{4}\pi], \tag{19}$$

for $\epsilon\gg\hbar\omega_c$. The essential point to notice at this juncture is that the contribution to $F_{\text{osc}}$ (15) from each residue contains a term involving the energy shift at an energy with a small positive imaginary component (it is presumed $\eta\gg\kappa T$, the terms for large $r$ are insignificant since the residue even with $\Delta=0$ is small). But from perturbation theory, ignoring the zero-order correction which is irrelevant, it is known that

$$\Delta(\epsilon)=\frac{P}{\pi}\int\frac{\Gamma(\epsilon,u)}{\epsilon-u}du, \tag{20}$$

where $P$ denotes the principal part and $\Gamma$ is defined by

$$\Gamma(\epsilon_k,u)=\pi\sum_{k'\neq k}|V_{kk'}|^2\delta(\epsilon_{k'}-u), \tag{21}$$

with $\epsilon_k=\epsilon$. (The notation is chosen to be analogous to that used in Green's-function methods.[6]) Hence[11]

$$\Delta(\eta_i+i\alpha)=\Delta(\eta_i)-i\Gamma(\eta_i) \tag{22}$$

as long as $\eta_i\gg\alpha$, where $\eta_i$ will denote the Fermi energy in the impure metal. Thus by virtue of (15), (19), and (22), after summing over the residues we find

$$F_{\text{osc}}{}^i=\frac{L^3\kappa T}{2\pi^2}\left(\frac{m\omega_c}{\hbar}\right)^{3/2}\sum_{l=1}\frac{(-1)^l}{l^{3/2}} \times\frac{\cos\{(2\pi^l\xi/\hbar\omega_c)-\pi/4\}\exp\{-(\pi l/\omega_c\tau)\}}{\sinh(2\pi^2 l\kappa T/\hbar\omega_c)}, \tag{23}$$

where

$$\xi=\eta_i-\Delta(\eta_i), \tag{24}$$

and

$$\tau^{-1}=(2\Gamma(\eta_i)/\hbar). \tag{25}$$

Since $\tau$, as defined, is the lifetime of a state at the Fermi energy, the additional amplitude factor in $F_{\text{osc}}{}^i$ [cf. Eq. (17)] is identical with Dingle's result if his relaxation time is equated to twice the lifetime, as we stated earlier. The additional numerical factors in the interpretation of Dingle's parameter suggested by Bychkov[4] do not arise. It will be noted also that, through the appearance of the parameter $\xi$, Eq. (24), we automatically include the change in period of the oscillations produced by the impurity. This will be discussed in more detail in the next section in connection with a Fermi surface of arbitrary shape.

Before proceeding to the generalizations, however, it is expedient to pause and assess the various approximations which have been made in deriving (23) in this, the one case where there seems any chance of carrying out a detailed investigation. The crux of the matter lies in our replacement of the shift by its value in zero field and in the use of (18). The first of these points is investigated in detail in the Appendix, where we consider the behavior of $\Gamma(\eta)$ using the wave functions appropriate to the levels (1), taking into account also the possibility of changes in the self-consistent potential which might arise if the impurity is charged. The end result is that our procedure should be valid as long as the quantum numbers are large, in accord with one's preliminary expectation. The second item, the use of Eq. (18), is adequate as long as $\Delta(\epsilon)$ is not rapidly varying with energy. Automatically, this excludes the possibility of discussing virtual bound states near the Fermi energy.[12]

## III. FERMI SURFACE OF ARBITRARY SHAPE

In this section the analysis is generalized to describe the effects associated with a Fermi surface of arbitrary shape, by adapting the methods of Lifshitz and Kosevich[3] to the formalism present in Sec. II.

Again, it is convenient to recapitulate the method for the pure metal. In this instance, the level spectrum is given by the implicit relation[13]

$$S(\epsilon,k_z)=(n+\gamma)(2\pi eB/\hbar c), \tag{26}$$

where $S(\epsilon,k_z)$ is the cross-sectional area of the surface $\epsilon_k=\epsilon$ in **k** space in the plane perpendicular to **B** (**B**

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[11] Since the denominator in the integrand of (20) never vanishes, the principal-part sign is irrelevant. It then reappears if one uses the operational identity $(x+i\alpha)^{-1}=(P/x)-i\pi\delta(x)$ for small $\alpha$. Also, $\Gamma(\eta)\equiv\Gamma(\eta,\eta)$.

[12] Yu. A. Izyumov, Advan. Phys. **14**, 569 (1965).

[13] L. Onsager, Phil. Mag. **43**, 1006 (1952).

taken along the $z$ direction), at a given value of $k_z$. In order to determine $Z(\epsilon)$, we shall neglect lattice broadening and assume the same $d$-fold degeneracy as in the free-electron model. The indications[14] are that this is a good approximation in those cases where the dHvA effect is expected to be observable in any event. Thus one obtains

$$Z(\epsilon)=(Ld/2\pi)\sum_{n=\epsilon}^{\infty}\int_0^{\epsilon}d\epsilon'\int_{S(\epsilon',k_z)>0}dk_z\,\delta\{S(\epsilon',k_z)-(n+\gamma)\alpha\}\frac{\partial S(\epsilon',k_z)}{\partial\epsilon'},\quad(27)$$

where $\alpha=(2\pi eB/\hbar c)$. We have assumed that the states are electron-like in order to be specific. Applying the Poisson summation formula to (27), and retaining only the oscillatory components, yields

$$Y(\epsilon)=(Ld/\pi)\sum_{l=1}^{\infty}e^{-2\pi il\gamma}\int_0^{\epsilon}d\epsilon'\int_{S(\epsilon',k_z)>0}dk_z\frac{\partial S(\epsilon',k_z)}{\partial\epsilon'}\times\exp[2\pi ilS(\epsilon',k_z)/\alpha].\quad(28)$$

Whence, upon evaluating the integral over $k_z$ by the method of steepest descent, we find

$$Y(\epsilon)=\frac{Ld}{\pi\sqrt{\alpha}}\sum_{l=1}^{\infty}\frac{\exp(-2\pi il\gamma-i\pi/4)}{\sqrt{l}}\times\int_0^{\epsilon}d\epsilon'\frac{(\partial S(\epsilon',k_0)/\partial\epsilon')\exp[2\pi ilS(\epsilon',k_0)/\alpha]}{\sqrt{|S''(\epsilon',k_0)|}},\quad(29)$$

where the primes on $S$ denote differentiation with respect to $k_z$, and $k_0$ is the value of $k_z$ for which $S(\epsilon',k_z)$ is a maximum. The denominator in the integrand of (29) is presumed to be a slowly varying function of $\epsilon'$ (it is a constant in the free-electron case). For large $\epsilon$, it may be assumed constant for the purposes of integration. Hence (29) becomes

$$Y(\epsilon)\simeq\frac{Ld\sqrt{\alpha}}{2\pi^2 i}\times\sum_{l=1}^{\infty}\frac{\exp[2\pi il[\{S(\epsilon,k_0)/\alpha\}-\gamma]-i\pi/4]}{l^{3/2}\sqrt{|S''(\epsilon,k_0)|}},\quad(30)$$

which, as evidenced by Eq. (31) below, leads to the result of Lifshitz and Kosevich for the pure metal.[3]

The effect of impurities may be analyzed as before. Since the entire approach here is semiclassical,[14] in the present context one is completely justified in using (18) with $\Delta(\epsilon)$ that value computed in zero field. Thus, by completely equivalent steps to those following Eq. (18), we obtain from (30) and (15) the result

$$F_{\text{osc}}{}^{i}=\frac{2L^3\kappa T(eB/2\pi\hbar c)^{3/2}}{\sqrt{|S''(\eta_i,k_0)|}}\times\sum_{l=1}^{\infty}\frac{\cos[(l\hbar c/eB)\xi-2\pi l\gamma-\pi/4]\exp(-\pi l/\omega_c\tau)}{l^{3/2}\sinh(2\pi^2 l\kappa T/\hbar\omega_c)},\quad(31)$$

where $\omega_c$ is now defined in terms of the cyclotron mass $m^*$,

$$m^*=(\hbar^2/2\pi)[\partial S(\epsilon,k_0/\partial\epsilon]_{\epsilon=\eta_i},\quad(32)$$

and

$$\xi=S(\eta_i,k_0)-(2\pi m^*\Delta(\eta_i)/\hbar^2)\quad(33)$$

to lowest order in $\Delta$. It will be observed that the decrease in amplitude associated with the presence of impurities has precisely the same form as in the free-electron model.[2] Specifically, the parameter $\tau$ is the lifetime of a state on the extremal cross section of the Fermi surface.

We will examine now the change in period of the oscillations produced by the impurity (solute). If $\eta_0$ is the Fermi energy in the pure metal, and each impurity has a relative valence $\nu$, then

$$Z^i(\eta_i)-Z(\eta_0)=N\nu\zeta,\quad(34)$$

where $N$ is the number of atoms in the crystal and $\zeta$ is the atomic fraction of impurities. Hence, by virtue of (18),

$$\eta_i-\eta_0-\Delta(\eta_0)\simeq\nu\zeta/n(\eta_0),\quad(35)$$

where $n(\epsilon)$ is the density of states per atom per unit energy range in the pure metal. In conjunction with (33), the relation (35) determines the fractional decrease in period, $R$ say. The parameter $k_0$, being the point of extremal area may be taken equal in the pure and impure metal to lowest order in $\Delta$. Thus, we find

$$R\simeq\frac{2\pi m^*\nu\zeta}{\hbar^2 n(\eta_0)S(\eta_0,k_0)},\quad(36)$$

a result first given by Heine[8] as a consequence of the rigid band model. However, it should be noted that the present derivation is somewhat more general, for we have shown that (36) is still valid even if the shift $\Delta$ is a variable function of energy. This is a further reflection of the fact that the dHvA effect is sensitive only to the properties of the system at the Fermi level. At the same time it must be recalled that (36) has been obtained under the assumption that the level shift depends upon energy alone. The experimental fact,[15] that the addition of Ag to Au [for which we presume $\nu=0$, and hence $R=0$ from (36)] produces, nevertheless, a change in period, indicates that the original premiss is too restrictive. And since we have not yet taken full cognizance of the peculiar characteristic of the dHvA effect, namely, its sensitivity only to the extremal area, it is not difficult to see how

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[14] A. D. Brailsford, Proc. Phys. Soc. (London) **A70**, 275 (1957).

[15] P. E. King-Smith, Phil. Mag. **12**, 1123 (1965).

one must extend the treatment to emphasize this feature. For, as the simplest generalization,[2] suppose $\Delta$ is a function of both $\epsilon$ and $k_z$. Equation (18) applies now only to each elementary slice of area $S(\epsilon,k_z)$ and thickness $\delta k_z$ separately. Thus (35) is replaced by the relation

$$\eta_i-\eta_0-\bar{\Delta}\simeq\nu\zeta/n(\eta_0)\,, \tag{37}$$

where $\bar{\Delta}$ is given by

$$\bar{\Delta}=\left\{\int\Delta(k_z)m^*(k_z)dk_z\right\}\bigg/\int m^*(k_z)dk_z\,, \tag{38}$$

the range of integration extending over the diameter of the Fermi surface parallel to the field direction. Consequently, the appropriate generalization of (36) is

$$R\simeq\left(\frac{m^*}{m_0}\right)\left(\frac{F_s}{F}\right)\frac{1}{\eta_s}\left\{\frac{\nu\zeta}{n(\eta_0)}+\bar{\Delta}-\Delta(\eta_0,k_0)\right\}. \tag{39}$$

The notation is that introduced by Shoenberg.[16] The quantity $F$ is the frequency of the oscillations in $B^{-1}$, $F_s$ is the value calculated for a free-electron gas of the same density [see (17)] with Fermi energy $\eta_s$, and $m_0$ is the free-electron mass. For the neck orbit[16] in Au, $(F_N/F_S)=0.0313$, and[15] $(m^*/m_0)=0.29$, with the field along $\langle 111\rangle$. The addition of 1% Ag is found[15] to decrease the neck size by $\sim$1%. Hence the result can be rationalized on the basis of (39) if $(\bar{\Delta}-\Delta_N)$ is negative and of magnitude $10^{-3}\eta_s(\sim 4\times 10^{-3}$ eV) at this concentration. Here $\Delta_N$ is the shift of a state at the neck. Since it seems reasonable to suppose $\bar{\Delta}\sim\Delta_B$, the belly shift [cf. (38)], we conclude from (39) that the effect of impurities on the belly frequencies should be comparatively small [specifically $(R_B/R_N)<(m_B^*F_N/m_N^*F_B)$]. In fact this is nothing new. It merely substantiates the experimental empirical rule[15] that the smaller the section of the Fermi surface under investigation, the greater is its sensitivity to perturbations of the pure metal.

We shall not carry the discussion of the change in period beyond this point. The "rigid-band" model result (36) has been discussed at length by Heine.[8] The reader is referred to his original work for further details.

## IV. THE RELAXATION TIME

It has become standard procedure[15] in the discussion of the effect of impurities upon the amplitude of the DHVA effect to express the result in terms of an apparent increment $x$ in temperature. The *concept* is valid only if $\kappa T>\hbar\omega_c$, but in any case it provides a useful means of parametrizing experimental results.

In our treatment $x$ is derived from (31). We find that

$$x=\hbar/\pi\kappa\tau_D=\hbar/2\pi\kappa\tau\,. \tag{40}$$

In order to avoid confusion we have explicitly introduced the Dingle parameter $\tau_D$; it is equal to twice the lifetime. Experimental results have been discussed in the past in terms of $\tau_D$, most extensively in the recent work of King-Smith.[15] He determined an "effective resistivity temperature," $x_\rho$ from the measured resistivity $\rho$ through the relation

$$x_\rho=\hbar/\pi\kappa\tau_\rho\,, \tag{41}$$

where

$$\tau_\rho=m_B^*/ne^2\rho\,, \tag{42}$$

($m_B^*$ being the belly cyclotron mass) and then examined the variation of $x_\rho$, $x_N$, and $x_B$ for a series of Au- and Ag-based alloys. The experimental results are conveniently discussed in terms of the ratios $(x_\rho/x_B)$, etc., where

$$(x_\rho/x_B)=(\tau_D/\tau_\rho)=(2\tau/\tau_\rho)\,, \tag{43}$$

and $\tau$ is here the value appropriate to the belly orbit.

The result to be anticipated for the ratio (43) depends of course upon the details of the states at the Fermi energy and upon the nature of the scattering potential. We shall not attempt any but the simplest anlysis; that for free electrons scattered by a potential of the type $V(r)\sim r^{-1}\exp(-q_0r)$, where $q_0^{-1}$ is a range parameter. Thus, since[17]

$$(\tau/\tau_\rho)=(I_1/I_0)\,, \tag{44}$$

where

$$I_r=\int_0^\pi P(\theta)(1-\cos\theta)^r\sin\theta d\theta\,,\quad (r=0,\,1)\,, \tag{45}$$

and $P(\theta)$ is the probability of scattering through an angle $\theta$, it is not difficult to derive the relation

$$(\tau/\tau_\rho)=\Phi(1+q_0^2/2k_F^2)\,, \tag{46}$$

where

$$\Phi(\lambda)=(\lambda-1)\left\{\tfrac{1}{2}(\lambda+1)\ln\left(\frac{\lambda+1}{\lambda-1}\right)-1\right\}, \tag{47}$$

and $k_F$ is the Fermi radius. The function $\Phi$ is illustrated in Fig. 1. As $(q_0/2k_F)\rightarrow\infty$, $\tau\rightarrow\tau_\rho$, the result for scattering by a delta-function potential. Schematically, Fig. 1 represents the effect of a variable range on the parameter $(\tau/\tau_\rho)$. Specifically, it relates to a scattering potential derived for a charged impurity in the Thomas-Fermi approximation,[18] when $q_0$ is found to be $\sqrt{3}$ times the ratio of the plasma frequency to the Fermi velocity. Thus, with the plasma frequency $\omega_p\sim 1.6(\eta_s/\hbar)$, we obtain $(\tau/\tau_\rho)\sim 0.7$.

After these preliminaries, it is possible to systematize the experimental results.[15] The major difference in any conclusions following our work, compared with the discussion of King-Smith, lies in the fact that we anticipate $(x_\rho/x_B)\leq 2$ for the isotropic model. This is twice the value obtained if $\tau_D$ itself is interpreted as the lifetime. In all of the 15 different samples listed in Ref. (15) our criterion is satisfied, whereas $(x_\rho/x_B)\geq 1$ in at least 5 instances. In fact $(x_\rho/x_B)$ exceeds the

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[16] D. Shoenberg, Phil. Trans. Roy. Soc. London **A255**, 85 (1962).

[17] N. F. Mott and H. Jones, *Theory of Metals and Alloys* (Clarendon Press, Oxford, England, 1936), p. 262.

[18] See Ref. 17, p. 87.

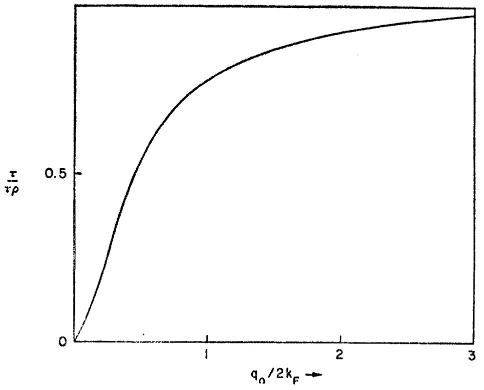

FIG. 1. The variation of the ratio of the lifetime of a state on the surface of the Fermi sphere to the electrical resistivity relaxation time as a function of the screening parameter $q_0$. The scattering potential is assumed to have the form $V(r)\propto r^{-1}\exp(-q_0 r)$.

Thomas-Fermi value of 1.4 (see above) in only one specimen, a Ag 0.57% Cu alloy. It may be necessary to invoke an effective potential giving greater weight to large angle scattering to explain this result,[15] but clearly further data are necessary in order to establish the necessity of this hypothesis. Apart from this one item of detail, no other significant difference arises between the present treatment and the original work of King-Smith, to which the reader is referred for further discussion.

## V. SUMMARY

The effect of the addition of impurities (solute atoms) upon the dHvA effect associated with a solvent with a Fermi surface of arbitrary shape has been investigated. The Dingle factor has been derived without recourse to phenomenology and the significance of his relaxation time has been elucidated. The change in period of the dHvA effect upon addition of small amounts of solute has been derived; the rigid-band-model result has been shown to have wider validity than its original derivation suggests. A tentative explanation has been presented of the change in period which occurs when the solute and solvent have the same valence. Finally, the relaxation of the lifetime to the electrical conductivity relaxation time has been discussed and correlated with a previous analysis of the dHvA effect in dilute alloys.

## APPENDIX

In this Appendix we discuss some of the mathematical aspects of the effects of impurities in the otherwise free-electron model. Specifically, we wish to discuss the validity of replacing the impurity-induced level shift by its value in zero magnetic field. Throughout it will be assumed that the impurities are distributed at random and that interference effects arising from scattering off different centers may be ignored. It is sufficient then to consider only one center at a time.

Our primary interest will be in the quantity $\Gamma_\lambda(u)$, defined by

$$\Gamma_\lambda(u)=\pi\sum_{\lambda'\neq\lambda}|V_{\lambda\lambda'}|^2\delta(\epsilon_{\lambda'}-u)\qquad\text{(A1)}$$

where $\lambda$ denotes the set of quantum numbers necessary to describe a state. The relation of $\Gamma$ to the level shift is given by Eq. (20). If the scattering potential is written as the series

$$V(\mathbf{r})=\sum_{\mathbf{q}}V(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{r}),\qquad\text{(A2)}$$

the form of $\Gamma$ is, with plane waves as basis states,

$$\Gamma_{\mathbf{k}}(u)=\pi\sum_{\mathbf{q}}|V(\mathbf{q})|^2\delta(\epsilon_{\mathbf{k}+\mathbf{q}}-u).\qquad\text{(A3)}$$

[The restriction on $\lambda'$ in (A1) makes a negligible difference to the sum; henceforth it is omitted.] We shall assume for simplicity that $V(\mathbf{r})$ is spherically symmetric so that $V(\mathbf{q})$ depends only upon $q$. For purposes of later comparison, (A3) will be expressed as an integral over variables appropriate to a cylindrical coordinate system. With the cylinder axis as the $z$ direction, one obtains

$$\Gamma_{\mathbf{k}}(u)=\frac{1}{4\pi^2}\int\int\frac{q_\perp dq_\perp dq_z|V(q)|^2}{\{4\epsilon_\perp\epsilon_q-(W-\epsilon_\perp-\epsilon_q)^2\}^{1/2}}\qquad\text{(A4)}$$

for unit normalization volume. Here $W=(u-\epsilon_{k_z+q_z})$, $\epsilon=(\hbar^2k_\perp^2/2m)$ and $\epsilon_q=(\hbar^2q_\perp^2/2m)$, where $k_\perp$ and $q_\perp$ are the magnitudes of components of the wave vectors in the basal plane of the coordinate system.

In the presence of a magnetic field, with the Landau gauge $\mathbf{A}=(0,Bx,0)$, the zero-order eigenfunctions are[9]

$$\psi_\lambda(\mathbf{r})\equiv\varphi_n(x-x_k)\exp i(k_y y+k_z z),\qquad\text{(A5)}$$

where $x_k=(\hbar ck_y/eB)$, and the $\varphi_n(x)$ are harmonic-oscillator wave functions (which, incidentally, are normalized to unity in infinite volume). The matrix element

$$M_{n'n}(\mathbf{q})=\int\varphi_n(x-x_k)\varphi_{n'}(x-x_{k'})\times\exp i[(k_y-k_y')y+(k_z-k_z')z+\mathbf{q}\cdot\mathbf{r}]d\mathbf{r}\qquad\text{(A6)}$$

vanishes unless $k_y'=k_y+q_y$, $k_z'=k_z+q_z$. The integration over $x$ may be performed by changing the origin and noting that

$$\varphi_{n'}(x-x_q)=\exp(-x_q d/dx)\varphi_{n'}(x).\qquad\text{(A7)}$$

The resulting operators in the exponentials in (A6) can be expressed in terms of annihilation and creation operators.[19] A Taylor-series expansion of the exponents then yields, after a little algebra, the result

$$|M_{n'n}(q)|=\mu^{1/2(n'-n)}e^{-1/2\mu}\left(\frac{n!}{n'!}\right)^{1/2}L_n^{n'-n}(\mu)\quad(n'>n),\qquad\text{(A8)}$$

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[19] P. A. M. Dirac, *Quantum Mechanics* (Clarendon Press, Oxford, England, 1947), p. 136.

where $\mu=(\epsilon_q/\hbar\omega_c)$ and the function $L_n{}^m$ is an associated Laguerre polynomial[20]

$$L_n{}^m(z)=\sum_{r=0}^{n}\binom{n+m}{n-r}\frac{(-z)^r}{r!}. \tag{A9}$$

For $n'<n$, $n$ and $n'$ are interchanged in (A8).

In the presence of a field, the $\Gamma_\lambda(u)$ is therefore

$$\Gamma_{n,k_z}(u)=\pi\sum_{\mathbf{q}}|V(q)|^2\sum_{n'=0}^{\infty}|M_{n'n}(q)|^2\delta \times\{W-\hbar\omega_c(n'+\tfrac{1}{2})\} \tag{A10}$$

with the previous definition of $W$. We shall not evaluate this expression for general values of the parameters. Instead, we consider two extreme cases in which the equivalence of (A10) and (A2) is reasonably easy to demonstrate. The first is embodied in the assumption that $V(\mathbf{r})$ is of short range, specifically a delta function.[4] With $V(q)=V_0$, a constant, the integration over $q_\perp$ becomes simply the normalization integral for the Laguerre functions. Then (A10) may be written

$$\Gamma_{n,k_z}(u)\simeq(mV_0/2\hbar^2)\int dq_z\int d\epsilon'(W-\epsilon') \tag{A11}$$

after approximating the summation over $n'$ by the corresponding integration. This is precisely equal to (A2) for the potential considered. The opposite extreme of a long-range potential is covered by the following analysis. For large $n$, we use the approximate relation[20]

$$z^{1/2m}e^{-1/2z}L_n{}^m(z)\simeq\frac{(n+m)!J_m[\sqrt{\nu z}]}{n!(\nu/4)^{m/2}}, \tag{A12}$$

where $\nu=(4n+2m+2)$, and $J_m(x)$ is the Bessel function of the first kind of order $m$. Combining (A12) and (A8), one finds that

$$|M_{n'n}(q)|^2\approx[J_m(\sqrt{\mu\nu})]^2, \tag{A13}$$

with $m=|n'-n|$, and $\nu=2(n+n'+1)$. Again, for large $n$, the order and the argument of the Bessel function may both be large. When the argument is the larger, there exists the following asymptotic expansion[21]:

$$[J_m(\sqrt{\mu\nu})]^2\simeq\pi^{-1}\{\mu\nu-m^2\}^{1/2}. \tag{A14}$$

{We have taken the mean value of the oscillations in $[J_m(z)]^2$ at large $z$.} Hence, upon replacing the summation over $n'$ by an integration and then using (A13) and (A14) we find[22]

$$\Gamma_{n,k_z}(u)\simeq\frac{1}{4\pi^2}\iint\frac{q_\perp dq_\perp dq_z|V(q)|^2}{\{4\epsilon_q(\epsilon_\perp+\epsilon_q)-(W-\epsilon_\perp-\epsilon_q)^2\}^{1/2}}, \tag{A15}$$

where here $\epsilon_\perp=\hbar\omega_c(n+\frac{1}{2})$. A comparison of (A15) with (A4) reveals that, for the same value of $\epsilon_\perp$ and $k_z$, the two expressions for $\Gamma$ are equivalent if $\epsilon_\perp\gg\epsilon_q$. Thus, for a potential of long range in real space for which $|V(q)|^2$ weights strongly the region of small $q$, the equivalence of (A2) and (A10) is again established. Unfortunately, the approximations inherent in the asymptotic expansions appear to preclude a demonstration of the detailed correspondence of (A2) and (A10) (at large quantum numbers) for an arbitrary $V(\mathbf{r})$, by this method. The alternative procedure, namely, direct evaluation of (A10), we are unable to carry out. However, we submit that the two examples we have discussed are strongly indicative of the general validity of neglecting the magnetic field in calculating the impurity-induced level shift. Of course, one might have invoked the correspondence principle at the outset and thereby avoided, seemingly, all the preceding analysis. But really this is simply a way of begging the question one is trying to answer.

A final comment is necessary if $V(\mathbf{r})$ is electrostatic in origin. Since an external potential is screened by the readjustment of the conduction electron density, if the (ionized) isolated impurity gives rise to a potential $V_e(\mathbf{r})$, the quantity $V(q)$ is given by $V(q)=\{V_e(q)/\epsilon(q)\}$, where $\epsilon(q)$ is the dielectric constant. Following Bardeen,[23] it is easy to show that with the eigenfunctions (A5), $\epsilon(\mathbf{q})$ is given by

$$\epsilon(\mathbf{q})=1-\left(\frac{2e^2m\omega_c}{\pi\hbar q^2}\right)\sum_{n,n'}\int dk_z|M_{n'n}(q)|^2 \times\left\{\frac{f(\epsilon_{n',k_z+q_z})-f(\epsilon_{n,k_z})}{\epsilon_{n',k_z+q_z}-\epsilon_{n,q_z}}\right\}, \tag{A16}$$

where $f(\epsilon)=1$ for $\epsilon<\eta$, and zero otherwise. In the Thomas-Fermi approximation, the last member of (A16) is approximated by its value in the limit $q\rightarrow 0$. Then, by virtue of (A8), only the term $n'=n$ contributes to the sum and (A16) becomes

$$\epsilon(\mathbf{q})\simeq1-\left(\frac{2e^2m\omega_c}{\pi\hbar q^2}\right)\sum_{n}\int dk_z\left[\frac{\partial f(\epsilon)}{\partial\epsilon}\right]_{\epsilon=\epsilon_{n,k_z}}. \tag{A17}$$

This yields the result $\epsilon(q)\simeq1+(q_0/q)^2$, where $q_0=\sqrt{3}\omega_p/v_F$, $\omega_p$ being the plasma frequency in zero field and $v_F$ is the Fermi velocity. This expression is the same as the zero-field value of $\epsilon(\mathbf{q})$. Thus, one is allowed to treat the potentials in (A3) and (A10) as the same in the manner we had assumed implicitly.

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[20] A. Erdelyi, *Higher Transcendental Functions* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. II, p. 153 ff.

[21] G. N. Watson, *Theory of Bessel Functions* (University Press, Cambridge, England, 1952), p. 244.

[22] The contribution from the regions where the order of the Bessel function is large compared with its argument is small (see Ref. 21, p. 243). It has been omitted for simplicity.

[23] J. Bardeen, Phys. Rev. **52**, 688 (1937).