dispersion relation discussed in Sec. II A. A similar expression holds for $\langle k_s | \hat{v} | k_s \rangle$ in the tight-binding approximation but quite generally can be expressed as

$$v_s(k) = \frac{\partial}{\partial k} E_s(k) , \tag{B6}$$

where $E_s(k)$ is the dispersion relation for s electrons.

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Retardation Effects in Azbel'-Kaner Cyclotron Resonance

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Corrections to the Azbel'-Kaner theory of the magnetic-field-dependent surface impedance of metals have been calculated. The results illustrate the effects of the finite transit time of the electrons in their passage through the skin layer. The cyclotron-resonance line shapes are modified from the Azbel'-Kanel results for both the high-$(\omega_c\tau)$ and low-$(\omega_c\tau)$ limits. The bearing of these results on experimental determinations of carrier effective masses and relaxation times are discussed. Finally, the background signals from the nonresonant electrons are calculated for an arbitrary cutoff angle for specular reflection of the electrons at the surface.

I. INTRODUCTION

Azbel'-Kaner cyclotron-resonance (AKCR) measurements have played an important role in the study of the Fermi surfaces of metals. The importance of the technique lies in the precise measurements provided of the effective masses and lifetimes of the carriers averaged over particular $\vec{K}$-space orbits. Recent advances in experimental techniques (the development of intense infrared sources of radiation[1,2]) and metals theory (the work on the electron-phonon interaction[3]) have focused interest on precise measurements of the frequency and temperature dependence of the electronic masses and relaxation rates. As the theoretically predicted mass shifts are small, careful consideration of line-shape effects are essential to proper interpretation of the experiments.[2]

The general problem of the magnetic-field-dependent surface resistance of a metal has not yet yielded an exact solution. The Azbel'-Kaner theory[4] is valid under the conditions of the extreme anomalous skin effect (ASE) provided also that the time of flight of the resonant electrons in their passage through the skin layer is small compared with the rf period. This last condition can break down

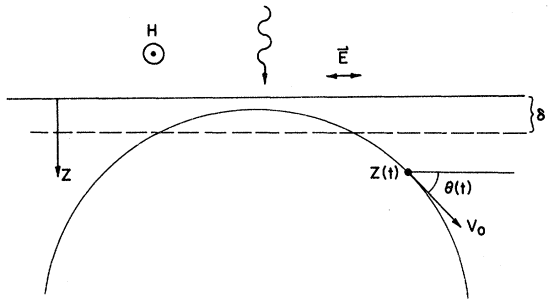

FIG. 1. The Azbel'-Kaner geometry in which the magnetic field is parallel to the sample surface and the rf E field is perpendicular to H.

at very high fields where the orbit is totally inside the skin layer and very low fields where the orbit curvature is very small. Fundamental contributions toward an understanding of the high-field case when the rf E field is along the applied H field has been made recently by Meierovich.[5] The importance of the low-field case was first pointed out by Koch and Kip[6] as a possible explanation of the low-field background signals often observed in AKCR experiments. They argued that a peak in the absorption might be expected when the time of flight of the electrons in their passage through the rf skin layer is one-half the rf period. From the geometry of the experiment (Fig. 1) the criterion for the maximum absorption they found was $\omega^2\delta/\omega_0 V_F = 1$. δ is the skin depth and ω_0 for circular orbits is $\omega_0 = eH/m^*c$, the cyclotron frequency. Smith[7] noted that the Koch-Kip mechanism can also be understood in terms of retardation effects in the current integrals. Thus, the stationary phase point is not at the top of the electron orbits as usually assumed but at a later time when $v_z \approx \omega\delta$, where v_z is the electron velocity z component. Although much of the low-field structure was subsequently identified as transitions between quantized surface levels,[8] a broad background absorption remains that can be related to retardation effects on the skimming electrons.

In this paper we discuss the effects of the finite time of flight of the electron through the skin layer on the surface impedance in the low-field limit, where the orbit dimensions are large compared with the rf skin depth δ. We obtain quantitative results for both the resonance signals and the nonresonant background signals. The bearing of these effects on the interpretation of measurements of m^* and τ will be discussed. In Sec. II the technique for calculating the surface impendance is outlined. In Sec. III the trajectory integrals are derived and evaluated. The results for cyclotron resonance and the background signals are then discussed in Secs. IV and V.

II. PRELIMINARIES

The surface impedance is calculated by a variational technique previously used by Prange and Nee.[8] We consider a high-frequency E field applied along one of the principal axis of the surface impedance tensor and write the following functional:

$$I = \left(-\frac{c^2}{i4\pi\omega}\int_0^\infty dz\ [E'(z)]^2 + \int_0^\infty dz\, E(z) J(z)\right) \Big/ [E(0)]^2 , \tag{1}$$

where z is measured into the metal and $J(z)$ is the rf current induced by the field $E(z)$ in the metal.

The integral is stationary with respect to $E(z)$ at the correct electric fields in the metal, where it takes the value $I = Z^{-1}$, where Z is the complex surface impedance.

In an applied magnetic field the surface resistance is often found to vary only slightly from the zero-field value. Under these circumstances a perturbation approach for calculating $Z(H)$ may be useful. Following Prange and Nee, the change in the surface admittance for small changes in the conductivity can be expressed as

$$Z^{-1}(H) - Z^{-1}(0) \simeq \int_0^\infty dz\, E(z)\, \Delta J(z) \tag{2}$$

or

$$\Delta Z \simeq - Z^2(0) \int_0^\infty dz\, E(z)\, \Delta J(z) . \tag{3}$$

In Eqs. (2) and (3) the $H = 0$ rf fields are to be used and ΔJ is the change in the current due to the change in the conductivity. It should be noted that this method correctly includes the effects of the first-order changes in $E(z)$ induced by the changes in the conductivity kernel.

$J(z)$ is calculated from the Chambers formula, which is equivalent to the Boltzman equation in the relaxation-time approximation

$$J(z, t_0) = \frac{e}{4\pi^3\hbar} \oint \left(\int_\infty^{t_0} dt\ \vec{v}(t) \cdot \vec{F}(z, t) e^{(t-t_0)/\tau} \right) \times \frac{\vec{v}(t_0)}{|v(t_0)|}\, dS , \tag{4}$$

where $F(z, t) = -eE(z, t)$ is the force on the electrons due to the rf fields and $\vec{v}(t)$ is the velocity of the electrons from the element dS of the Fermi surface. The electrons are assumed to have a relaxation time τ.

The analysis is greatly simplified by replacing the true (ASE) fields with exponential fields with an effective complex skin depth chosen to approximate the ASE fields

$$E(z) = E_0 e^{-z/\delta} , \tag{5}$$

where $\delta = \delta_1 - i\delta_2$ is found from the ASE surface impendance from

$$Z = -\frac{i4\pi\omega}{C^2}\frac{E(0)}{E'(0)} = \frac{i4\pi\omega}{C^2}\delta . \tag{6}$$

III. TRAJECTORY INTEGRALS

In the current integrals the electric fields must be evaluated as a function of position and time along the electron trajectories. For simplicity we consider a cylindrical section of Fermi surface of length K_y. The metal is taken to occupy the half-space $z>0$. The applied H field is along the y axis and the rf E field is along the x axis. The equation of motion of the electrons can be expanded about the effective point ($v_z=0$). For an electron at $z(t_0)$ with velocity $v_x=v_0\cos\theta$ at $t=t_0$, we have

$$z(t)\cong z(t_0)+v_0\sin\theta(t-t_0)+\tfrac{1}{2}\omega_0 v_0(t-t_0)^2 . \qquad (7)$$

$\omega_0=(eH/c\hbar)(v_0/K_0)$, where K_0 and v_0 are the radius of curvature of the Fermi surface and Fermi velocity at the effective point.

The terms higher order in $t-t_0$ in the equation of motion can be neglected for $|z(t)-z(t_0)|/R\ll 1$ where $R=v_0/\omega_0$ is the real-space radius of the trajectory at the top of the orbit, since the rf fields are small for $z>\delta$ and we have assumed that $\delta/R\ll 1$. Similarly, to the first order in δ/R the dot product $\vec{v}(t)\cdot\vec{F}(z,t)$ can be evaluated at $t=t_0$ as $ev_0E(z,t)\cos\theta$.

The following contributions to the current are considered: (i) J_{0b}: the bulk electrons $z(t_0)-v_0\sin^2\theta/2\omega_0\geq 0$ for $t_0-\pi/\omega_c<t<t_0$ (nonresonant contribution); (ii) J_{rb}: the bulk electrons for $t<t_0-\pi/\omega_c$ (resonant contribution); (iii) J_{0d}: the electrons which have collided with the surface $z(t_0)-v_0\sin^2\theta/2\omega_0<0$; (iv) J_{0s}: the specularly reflected electrons.

The skipping electrons ($v_x<0$) have not been considered. The quadratures become more complicated and moreover the work of Prange and Nee[8] on magnetic-field-induced surface-state resonances have shown that a quantum treatment is required for the contribution of these electrons. From Eqs. (2) and (3) it is seen that one must calculate the complex power integrals defined as

$$P=\int_0^\infty dz\,E(z)J(z) . \qquad (8)$$

Using the Chambers formula for the different current contributions, the corresponding power integrals become

$$P_{0b}=E_0J_0\int_0^\infty dz\exp\left(\frac{-2z}{\delta}\right)\int_{-1}^{x_m}dx\,(1-x^2)^{1/2}\exp\left(\frac{v_0x^2}{2\omega_0\delta}\right)\int_{-\infty}^{0}dt\exp\left[-\frac{v_0\omega_0}{2\omega_0\delta}\left(t+\frac{x}{\omega_0}\right)^2+i\bar{\omega}t\right] , \qquad (9)$$

$$P_{0d}=E_0J_0\int_0^\infty dz\exp\left(\frac{-2z}{\delta}\right)\int_{-1}^{x_m}dx\,(1-x^2)^{1/2}\exp\left(\frac{v_0x^2}{2\omega_0\delta}\right)\int_{-T}^{0}dt\exp\left[-\frac{v_0\omega_0}{2\delta}\left(t+\frac{x}{\omega_0}\right)^2+i\bar{\omega}t\right] , \qquad (10)$$

$$P_{0s}=E_0J_0\int_0^\infty dz\exp\left(\frac{-2z}{\delta}\right)\int_{x_m}^{1}dx\,P(\theta_s)(1-x^2)^{1/2}\exp\left(\frac{v_0x^2}{2\omega_0\delta}\right)\int_{-\infty}^{-T}dt\exp\left[-\frac{v_0\omega_0}{2\delta}\left(t-\frac{x}{\omega_0}+2T\right)^2+i\bar{\omega}t\right], \qquad (11)$$

$$P_{rb}=E_0J_0\left[\exp\left(\frac{i2\pi\bar{\omega}}{\omega_0}\right)-1\right]^{-1}\int_0^\infty dz\exp\left(\frac{-2z}{\delta}\right)\int_{-x_m}^{+x_m}dx\,(1-x^2)^{1/2}\exp\left(\frac{v_0x^2}{2\omega_0\delta}\right)\int_{-\infty}^{+\infty}dt\exp\left[-\frac{v_0\omega_0}{2\delta}\left(t+\frac{x}{\omega_0}\right)^2+i\bar{\omega}t\right], \qquad (12)$$

where

$$J_0=e^2K_yK_0v_0/4\pi^3\hbar , \qquad T=[x-(x^2-x_m^2)^{1/2}]/\omega_0 ,$$

$$x_m^2=2\omega_0z/v_0 ,$$

and

$$i\bar{\omega}=i\omega+1/\tau .$$

$P(\theta_s)$ is the probability of specular reflection of the surface electrons which strike the surface with angle θ_s:

$$\sin\theta_s=(\sin^2\theta-2z_0\omega_0/v_0)^{1/2} . \qquad (13)$$

For the resonant electrons P_{rb} is readily integrated using the properties of the complex error function to give

$$P_{rb}=E_0J_0\frac{\pi\delta^2}{v_0}e^{-\bar{\omega}2\delta/\omega_0v_0}\left[e^{i2\pi(\bar{\omega}/\omega_c)}-1\right]^{-1} . \qquad (14)$$

For the other integrals above it is convenient to evaluate the H-field derivatives, which is the quantity usually of most interest in the experiments. We define $P_0=P_{0b}+P_{0d}$, which is the appropriate power integral for the case of diffuse reflection of the electrons at the surface.

For $P(\theta_s)$ in Eq. (11) we consider the model in which the electrons are specularly scattered for θ_s less than a cutoff angle θ_0 and diffusely scattered for $\theta_s>\theta_0$.

After some tedious manipulation of these integrals and making use of the condition $\delta/R\ll 1$, one finds the following results:

$$\frac{dP_0}{dH}=\frac{J_0\delta^2}{2v_0H}[1-\sqrt{\pi}\,be^{b^2}\operatorname{erfc}(b)]^2 , \qquad (15)$$

$$\frac{dP_{0s}}{dH}=\frac{J_0\pi\delta^2}{2v_0H}\{-a(a+b)[e^{(a+b)^2}\operatorname{erfc}(a+b)]^2$$

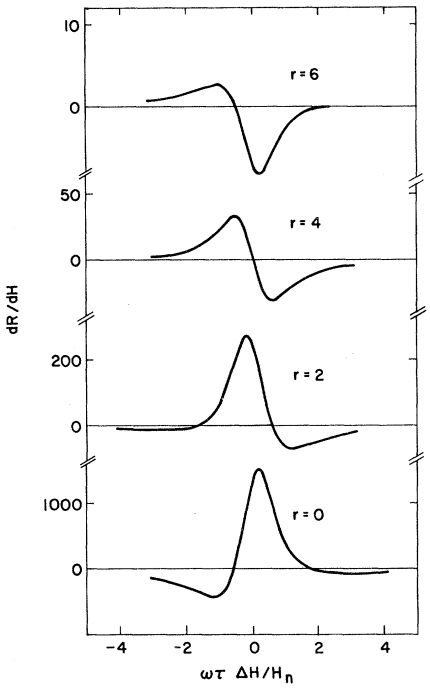

FIG. 2. The Chambers line shape in the presence of retardation effects. The retardation parameter is defined in the text. H_n is the resonance field for the nth subharmonic and $\Delta H = H - H_n$.

$$+ b\int_b^{a+b} [e^{t^2}\operatorname{erfc}(t)]^2\} \ , \quad (16)$$

where $b = i\bar{\omega}(\delta/2v_0\omega_0)^{1/2}$, $a = (v_0/2\delta\omega_0)^{1/2}\sin\theta_0$, and $\operatorname{erfc}(t)$ is the complex complimentary error function defined by $\operatorname{erfc}(b) = (2/\sqrt{\pi})\int_b^\infty e^{-t^2}dt$.

IV. CYCLOTRON RESONANCE

We first consider the contribution to the surface impedance of the electrons which return periodically to the skin layer. In the weak signal limit Eq. (14) gives

$$\Delta Z = -Z^2(0)P_{rb} = \left(\frac{4\pi\omega}{c^2}\right)^2 \frac{e^2K_y\delta^4}{4\pi^2\hbar^3} \times e^{-\bar{\omega}^2\delta/\omega_0 v_0}\,(e^{i2\pi(\bar{\omega}/\omega_c)} - 1)^{-1} \ . \quad (17)$$

Under Chambers line-shape conditions (i.e., weak signal and $\omega_c\tau \geq 50$), the resonance factor is usefully expressed as a sum of Lorentzian lines

$$[e^{i2\pi(\bar{\omega}/\omega)} - 1]^{-1} = \tfrac{1}{2}\{-1 + (\omega_c\tau/\pi)\sum_n [1 + i(\omega - n\omega_c)\tau]^{-1}\} \ . \quad (18)$$

Using Eq. (18) the Chambers result[9] is obtained with a complex prefactor due to the retardation effects. The retardation factor has the effect of reducing the amplitude of the resonance and mixing the real and imaginary parts of the Chambers result. Thus the resonance condition can differ from the Chambers result by an amount of order $\Delta H/H_0 \sim 1/\omega\tau$ and the relation for $\omega\tau$ in terms of the linewidth can also differ somewhat when retardation effects are considered. The cyclotron resonance line shape is shown in Fig. 2 for various values of

$$r = n\frac{m_c^* v_0}{\hbar K_0}\left|\frac{\omega\delta}{v_0}\right| \ .$$

Retardation effects on low-$(\omega_c\tau)$ data have a more insidious effect on the line shapes. The resonance factor in Eq. (17) can be expanded in powers of $e^{-i2\pi(\omega/\omega_c)}$, giving

$$[e^{2\pi i(\bar{\omega}/\omega_c)} - 1]^{-1} = \sum_{n=1}^{\infty} e^{-i2\pi n(\bar{\omega}/\omega_c)} \ . \quad (19)$$

For $\omega_c\tau \leq 10$ it is sufficient to keep the first term in the series so that ΔZ becomes

$$\Delta Z \cong \left(\frac{4\pi\omega}{c^2}\right)^2 \frac{e^2K_y\delta^4}{4\pi^2\hbar^3} e^{-\bar{\omega}^2\delta/v_0\omega_0} e^{-i2\pi\bar{\omega}/\omega_c} \ . \quad (20)$$

In this case the retardation factor inters the line shape in just such a way as to cause peak position shifts and amplitude reductions that could be misinterpreted to give erroneous effective masses and relaxation rates. We can determine the apparent mass m_a^* and relaxation rate τ_a^{-1} that would be obtained by analyzing these line shapes in the conventional way[10]:

$$m_a^* = m^* - \frac{\omega\hbar K}{2\pi v_0^2}\left[\delta_2\left(1 - \frac{1}{(\omega\tau)^2}\right) + \frac{2\delta_1}{\omega\tau}\right] \ , \quad (21)$$

$$\tau_a^{-1} = \tau^{-1}\left(1 - \frac{\omega\delta_2\hbar K}{\pi m^* v_0^2}\right) + \frac{\omega^2\delta_1\hbar K_0}{2\pi m^* v_0^2}\left(1 - \frac{1}{(\pi\tau)^2}\right) \ . \quad (22)$$

For circular orbits ($\hbar K_0 = m^* v_0$) the apparent masses and relaxation rates become

$$m_a^* = m^*\left\{1 - \frac{\omega}{2\pi v_0}\left[\delta_2\left(1 - \frac{1}{(\omega\tau)^2}\right) + \frac{2\delta_1}{\omega\tau}\right]\right\} , \quad (23)$$

$$\tau_a^{-1} = \tau^{-1}\left(1 - \frac{\omega\delta_2}{\pi v_0}\right) + \frac{\omega^2\delta_1}{2\pi v_0}\left(1 - \frac{1}{(\omega\tau)^2}\right) \ . \quad (24)$$

The result is an apparent frequency dependence of the mass and relaxation rate.

An analysis of AKCR data on bismuth at microwave frequencies appears to confirm these results.[2] τ_a^{-1} was determined from AKCR measurements at 8, 28, and 36 GHz on the same sample of bismuth with $\vec{H} \parallel$ binary axis. Since $\delta \propto \omega^{1/3}$ for the anomalous skin effect conditions, the retardation effect should produce a $\omega^{5/3}$ frequency dependence for τ_a^{-1}. The microwave results plotted

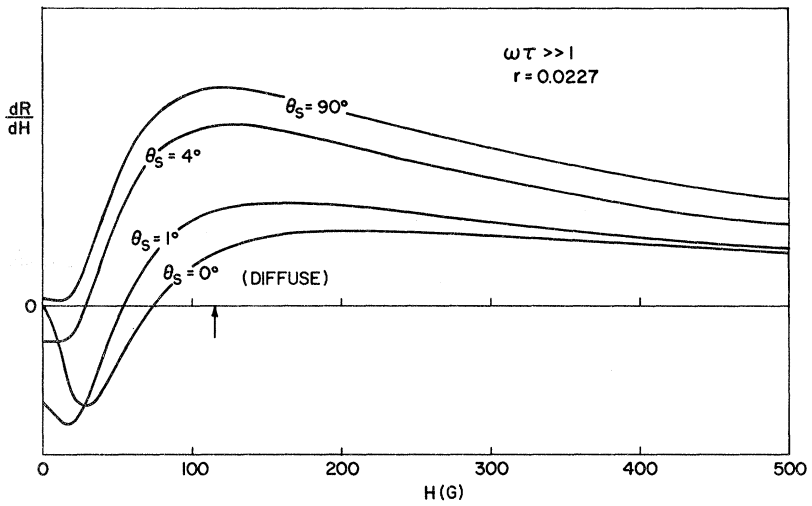

FIG. 3. The calculated low-field structure for copper in the $\omega\tau \gg 1$ limit. The parameters chosen were $f = 37.2$ GHz, $K_0 = 0.373 \times 10^8$ cm^{-1}, $v_0 = 1.11 \times 10^8$ cm/sec, and $\delta = 1.08 \times 10^5$ cm. θ_0 is the cutoff angle for specular reflection of the electrons at the surface. The arrow marks the field corresponding to the condition $\omega^2\delta/\omega_0 v_0 = 1$.

against $\omega^{5/3}$ gave a straight line with an increase in τ_a^{-1} of a factor of 8 between 8 and 36 GHz. At 36 GHz we estimate from the skin depth deduced from ASE surface impedance data $\omega\delta_2/\pi V_F \simeq 0.04$ and $\omega^2\delta_1/2\pi V_F \simeq 8\times 10^9$. The extrapolated τ_a^{-1} at zero frequency was $\sim 10^9$ sec^{-1}. Thus at 36 GHz the retardation effect dominates the amplitude decay of cyclotron-resonance subharmonics. No frequency dependence of m_a^* was observed in these data; however, the expected shift of $\sim 1\%$ was not significantly greater than the experimental accuracy.

These results have particular significance for the measurements of frequency- and temperature-dependent masses and relaxation rates recently reported in the literature. It is clear that careful attention must be taken of line-shape effects in evaluating such results.

V. BACKGROUND SIGNALS

Low-field background signals are often observed along with AKCR signals. Studies by Koch[11] and Khaiken[12] have shown that some of this structure is due to the skipping electrons, which can be described in terms of magnetic-field-induced surface quantum levels. However, an additional broad background signal still remains unaccounted for. That the retardation effects could account for low-field background signals was first suggested by Koch and Kip.[6] In the small-signal approximation we can calculate the nonresonant contribution of the skimming electrons. The result for diffuse scattering is

$$\frac{d\Delta Z_d}{dH} = -\left(\frac{4\pi\omega}{c^2}\right)^2 \frac{e^2 K_y \delta^4}{h^3 H}\,[1 - \sqrt{\pi}\, b e^{b^2}\,\mathrm{erfc}(b)]^2. \tag{25}$$

The specular scattering contribution has been determined for an arbitrary cutoff angle θ_0 for the specular reflection. For specular reflection the additional contribution is

$$\frac{d\Delta Z_s}{dH} = \left(\frac{4\pi\omega}{c^2}\right)^2 \frac{e^2 K_y \pi\delta^4}{h^3 H}\,\{-a(a+b) \times [e^{(a+b)^2}\,\mathrm{erfc}(a+b)]^2 + b\int_a^{a+b} dt\,[e^{t^2}\,\mathrm{erfc}(t)]^2\}. \tag{26}$$

It is of interest to note that the $H = 0$ limit of $d\Delta Z/dH$ predicted by Eqs. (25) and (26) is zero for diffuse reflection and nonzero for $\theta_0 \neq 0$. Since the total surface impedance is an even function of H, it follows that the contribution of the skipping electrons must be minus $d\Delta Z_s(0)/dH$ at $H = 0$.

These results are shown in Figs. 3 and 4, where dR/dH is plotted vs H for the high-frequency ($\omega\tau \gg 1$) case and the low-frequency ($\omega\tau \ll 1$) case for different choices of θ_s. For specular scattering a pronounced maximum is found in dR/dH whose field position is approximately given by $\omega^2\delta/\omega_0 v_0 = 1$ for $\omega\tau \gg 1$ and $\delta R/l^2 = 1$ for $\omega\tau \ll 1$.

Experimental data on the high-frequency background signals in carefully prepared samples of Cu have recently been measured by Doezema.[13] These same samples gave rise to strong magnetic-field-induced surface-state resonances, indicating a high degree of specularity. Parameters chosen to correspond to the known Fermi surface of Cu and the $H = 0$ surface resistance as measured by Pippard give good agreement for the over-all line shape and the peak position. The experimentally observed peak in dR/dH is 100 G, compared with our calculated peak at 118 G. Experimentally, dR/dH is found to go negative at high fields, in disagreement with the present theory. This effect is thought to be related to the nonresonant contribution to the surface resistance from the skipping electrons. Support for this view is given by the theoretical work of Kaner and Makarov[14] and recent experi-

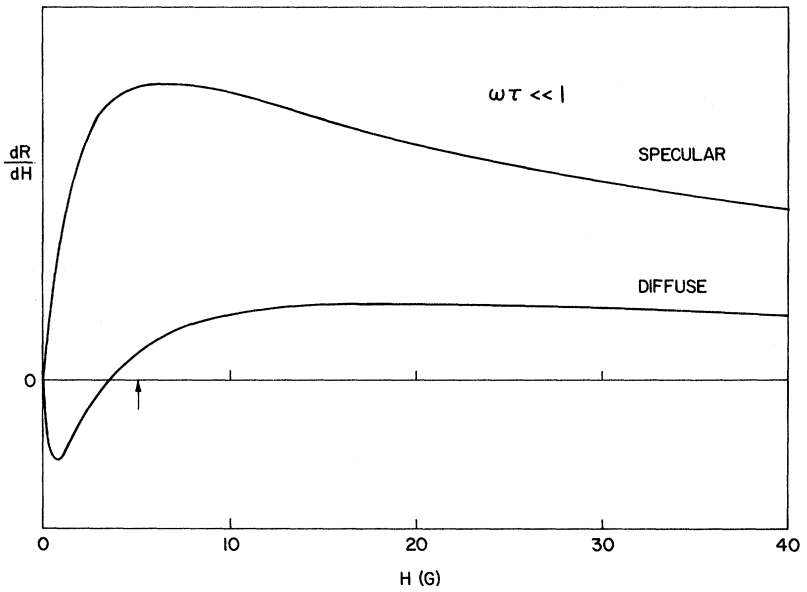

FIG. 4. The calculated surface resistance derivative for copper in the low-$\omega\tau$ limit. The parameters chosen were $f=5$ MHz, $K_0=0.373\times10^8\,\mathrm{cm}^{-1}$, $v_0=1.11\times10^8$ cm/sec, $l=v_0\tau=100\ \mu$, and $\delta=2\ \mu$. The arrow marks the field corresponding to the condition $R\delta/l^2=1$.

ments by Sibbald, Mears, and Koch.[15]

It is interesting to speculate that the retardation effect peak in dR/dH might provide a direct measure of δ. Doezema's results would indicate that δ in Cu at 100 G is 20% smaller than the zero-field value. From Eqs. (25) and (26) we estimate the total change in the surface impedance due to the skimming electrons to be the same order of magnitude. Also a decrease in δ is suggested from experiments[13] and theory[14] in the presence of the surface states of the skipping electrons. However, further experimental and theoretical work will be required to confirm this conjecture.

At low frequencies ($\omega\tau\ll1$), the experimental data[15] on highly polished Cu samples do not agree with the results presented here. In this case the skipping electrons can contribute much more significantly to the surface currents. Since $\omega\tau\ll1$, the rf fields can be regarded as time independent and each electron contributes to the current in proportion to the time it spends in the skin layer. The skimming electrons are curved out of the skin layer and for large enough fields spend less than their mean free time in the rf field. However, the skipping electrons always spend their entire mean free time in the skin layer.

VI. CONCLUSIONS

The above results are indicative of the retardation effects on the magnetic-field-dependent surface impedance of metals. Although some accuracy in the line shapes was undoubtably sacrificed by approximating the ASE fields as exponential, we believe that the main features are preserved. The major advantage of the present treatment is that it gives analytic results with Fermi-surface parameters, electronic lifetimes, and surface scattering parameters as adjustable parameters.

Our treatment of the background signals is incomplete in that we have not considered the skipping electrons. This is clearly a serious omission but one we have been unable to rectify. Our results should therefore be taken as indicative of one class of background signals that one might observe.

From the retardation parameter $r=|\omega^2\delta/\omega_0 v_0|$, one observes that retardation effects are important at high frequencies and low fields. With the present activity toward extending the cyclotron resonance studies into the infrared spectral region, it is clear that work on the line-shape theories will be essential. In addition to the retardation effects, one must also consider the consequences of the more nearly local conditions ($\delta/R_c<\!/<1$) and quantum aspects of the cyclotron resonance.[16]

Note added in proof. Retardation effects on AKCR line shapes have recently been observed in Ga by Kamgar, Henningsen, and Koch (unpublished). Both the subharmonics attenuation and the progressive modification of the Chambers line shape are clearly demonstrated.

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Fermi Level in Disordered Alloys*

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The Fermi level or electrochemical potential $\bar{\mu}$ is considered as a function of concentration in disordered alloys. In the case that the perturbation introduced by substituting one type of atom by another is localized around the site of substitution, $\bar{\mu}$ is a constant independent of concentration. Localization of the perturbation requires that there be no volume change in alloying and that the perturbation be shielded so that it decays in an exponential manner away from the site of substitution. When boundary conditions between the interior of the alloy and exterior to it are considered, nonlocalized perturbations are introduced which cause a variation of $\bar{\mu}$ with concentration. However, such nonlocalized perturbations do not change the microscopic properties of the interior of the alloy but cause simply a rigid shift in energy of the electronic structure.

I. INTRODUCTION

Because of the mathematical complication in treating disordered systems, it is always necessary to make some approximations in the calculations of their properties. In evaluating the validity of any approximation it is helpful to have as guidelines some exact results to which the calculation can be compared. Also, exact results themselves are helpful guides to suggest appropriate approximation or even to help directly in the calculation. Our fundamental understanding of disordered systems, even in a qualitative way, is still undeveloped, making it all the more important to have some exact results with which any approximate calculation can be compared.

In this paper it is proved that in a disordered metallic alloy, where the perturbation introduced by substituting one type of atom by another is localized about the site of substitution, the Fermi level or electrochemical potential $\bar{\mu}$ does not change with composition. The constancy of $\bar{\mu}$ was proved by Friedel for the case of very dilute alloys,[1] but he estimated that for any finite concentration, the Fermi level will vary in an exponential fashion.[2] The discrepancy between the result proved here and the previous result of Friedel will be shown to be due to the fact that Friedel inadvertently varied the potential origin as a function of concentration. In a real alloy the presence of a boundary will introduce long-range perturbations which will shift $\bar{\mu}$, but such an effect causes no change in the microscopic properties of the alloy in its interior, except for a rigid shift in energy.

Section II introduces some properties of the Green's functions which are used in Sec. III to prove that $\bar{\mu}$ is constant for localized perturbations. Sections IV discusses the effects introduced by considering boundary conditions. Section V consists of a discussion of the results, while Sec. VI gives a summary.

II. GREEN'S FUNCTIONS

To prove the desired result, we will calculate the change in the Fermi energy $\Delta\bar{\mu}$ caused by a small change in the concentration Δc and show that $\Delta\bar{\mu}/\Delta c \to 0$ as $\Delta c \to 0$. We prove that such a result is true for all values of the concentration, thus proving that $\bar{\mu}$ is independent of c.

In the course of proving this result we will find it convenient to introduce the Green's function of the alloy G_E defined as