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Electron Spin Resonance Absorption in Metals. II. Theory of Electron Diffusion and the Skin Effect*

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The theory of paramagnetic resonance absorption by the conduction electrons in a metal is worked out, taking into account the diffusion of the electrons in and out of the thin skin into which the radio-frequency field penetrates. Calculations are carried through in detail for the case of a flat metal plate. It is found that the diffusion has no marked effect on the width of the resonance absorption line, but has a radical effect on the shape of the line. In particular, for a piece of metal thick compared to the skin depth and with a relaxation time long compared to the diffusion time, the line is antisymmetrical about its center and has an unusual characteristic shape.

I. INTRODUCTION

The solid-state physics group at Berkeley has observed paramagnetic resonances arising from the conduction electrons in metals. Their experimental findings are reported in the preceding paper.[1] It was realized from the beginning of the conduction electron resonance work[2] that the diffusion of electrons in and out of the skin of the metal would have a decisive effect on the shape and intensity of the observed resonance lines. The present paper contains a quantitative theory of this effect, which the author worked out while attached to the Berkeley group during the summer of 1953. The comparison of theory with experimental results is not made here as it is included in the experimental paper.[1]

We build the theory upon a highly idealized model of the electrons in the metal. The electrons are assumed to diffuse like free particles, and the electron magnetic moments are treated like free-particle moments. This is necessary in order to make the theory of the diffusion effect reasonably simple. The comparison of the theory with experiment will then show to what extent the idealized picture is correct. The interest of the whole analysis will ultimately lie, not in the diffusion effect itself, but in the information which the experiments will give concerning the nature of the metallic state after the diffusion effect has been correctly taken into account.

The following is the plan of the present paper. In Sec. II the theoretical model is exactly described. Section III gives a sketch of the physical processes which we believe determine the line width; it is hoped that this rough discussion will make the subsequent mathematics easier to follow. Section IV begins the quantitative treatment. In Sec. V we give a simple theory which is mathematically exact for the limiting case of thick samples and long relaxation times, and which is valid whether the skin effect is in the classical or the anomalous range. This simple theory already contains the most important results of the whole investigation, and will be sufficient for many practical applications. Sections VI–VIII contain a more elaborate theory which is exact for a flat metal plate of any thickness and for any value of the relaxation time, but restricted to the domain of classical skin effect. The extension of this theory to anomalous skin-effect conditions would be possible in principle, but it is not done here. Section IX summarizes the results of the whole paper.

II. THE THEORETICAL MODEL

We suppose a piece of metal of volume V to be placed in a resonant cavity in which there is a radio-frequency magnetic field given by

$$\mathbf{H}_1(\mathbf{r})e^{-i\omega t}+\text{c.c.} \tag{1}$$

Here c.c. stands for "complex conjugate," ω is a fixed frequency, and $\mathbf{H}_1(\mathbf{r})$ is a complex vector function of the position $\mathbf{r}$. The whole cavity lies in a uniform magnetic field $\mathbf{H}$, which is varied slowly during the course of an experiment. The resonance frequency between the two spin states of an electron in the field $\mathbf{H}$ is

$$\nu=2\mu|\mathbf{H}|/\hbar, \tag{2}$$

where μ is the effective electron magnetic moment (not necessarily equal to the value for a free electron). We write

$$\alpha=\omega-\nu,\quad \gamma=\omega+\nu. \tag{3}$$

Under the influence of the field (1), a certain macroscopic magnetization,

$$\mathbf{M}(\mathbf{r})e^{-i\omega t}+\text{c.c.}, \tag{4}$$

will be created in the metal as a result of the turning of the magnetic moments of the conduction electrons. The field $\mathbf{H}_1(\mathbf{r})$ in turn depends on $\mathbf{M}$, because the penetration of radio-frequency field into the metal is changed by the magnetization. It is to be expected that $\mathbf{M}$ will show a resonant behavior and will become large

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[1] G. Feher, and A. F. Kip, preceding paper [Phys. Rev. 97, 337 (1955)]. The notations in the paper by Feher and Kip and in the present paper are somewhat different; their ω_0, χ_0, T_D, T_2 are respectively equal to our ν, χ, D, U; other symbols are the same in the two papers.

[2] Griswold, Kip, and Kittel, Phys. Rev. 88, 951 (1952); Kip, Griswold, and Portis, Phys. Rev. 92, 544 (1953).

when ν is nearly equal to ω; in the neighborhood of the resonance the distribution of $\mathbf{H}_1$ will also change. The experimentally observed quantity is the change in the Q-value of the cavity as ν or $\mathbf{H}$ varies. This quantity is a measure of the total energy absorbed in the metal both by eddy currents and by the resistive out-of-phase component of the magnetization. To interpret the experiment, we therefore need to calculate both $\mathbf{H}_1$ and $\mathbf{M}$ as functions of $\mathbf{H}$. The calculation naturally divides itself into two stages: first, to calculate the magnetization produced by a given $\mathbf{H}_1(\mathbf{r})$; second, to find self-consistent solutions of Maxwell's equations with this relation between $\mathbf{H}_1$ and $\mathbf{M}$. The problem is unusual because the magnetization is carried around by the electrons as they diffuse in the metal. Thus $\mathbf{M}$ at a given place and time depends on $\mathbf{H}_1$ at neighboring points and at earlier times.

The electrons which carry the magnetization are assumed all to lie at the top of the Fermi distribution of the conduction electrons and to move with constant velocity v. Let $P(\phi)$ be the probability per unit distance travelled and per unit solid angle that an electron changes its direction by an angle ϕ as a result of collision with lattice vibrations, other electrons, etc. Then each electron "loses its memory" of its direction of motion in a mean free path defined by

$$\Lambda = P^{-1}, \tag{5}$$

where P is the "transport collision probability,"

$$P = \int P(\phi)(1-\cos\phi)d\Omega. \tag{6}$$

A mean collision time τ is defined by

$$\tau = \Lambda/v. \tag{7}$$

We assume each electron to move as an independent classical particle, the changes of direction being random. If $F(\mathbf{r},t)$ is the probability distribution for the position $\mathbf{r}$ of an electron at time t, then over times large compared with τ the classical diffusion equation,

$$\partial F/\partial t = \tfrac{1}{3}v\Lambda\Delta F, \tag{8}$$

is satisfied. The boundary condition is

$$\mathbf{n}\cdot\mathrm{grad}F = 0, \tag{9}$$

where $\mathbf{n}$ is the normal vector at any point on the metal surface.

It is supposed that the spin of each electron is an independent quantum variable, which is only very weakly coupled to the electron's orbital motion. The spin is in general unaffected by collisions and reacts only to the local magnetic field at the place where the electron happens to be. However, the weak spin-orbit coupling exists and very occasionally, about once in every 10^5 collisions in the case of sodium, causes the spin state to change during a collision.[3] To take this effect into account, we do not introduce the spin-orbit coupling explicitly, but we assume a relaxation-time U with the following property. Given any time interval of length t, there is a probability $\exp(-t/U)$ that the spin state of an electron will be undisturbed by collisions during that interval, and a probability $[1-\exp(-t/U)]$ that the final spin state will be randomly distributed relative to the initial spin state.

The existence of such a relaxation time U produces a finite line width proportional to U^{-1} in the resonance signal from nondiffusing electrons. This we call the "natural width" of the line. Any other effects besides spin-orbit coupling which contribute to the natural width are supposed also included in U.

In Sec. VIII a more general model is introduced, in which the electrons have a finite probability of spin disorientation when they strike the metal surface, in addition to the steady relaxation effects included in U. For simplicity, the calculations are carried through in Secs. IV–VII for the model without surface relaxation. Exact results including surface relaxation are to be found at the end of Sec. VIII.

It is assumed that the electron magnetization is always far from saturation, so that $\mathbf{M}$ is small compared with $\mathbf{H}_1$. Terms of second and higher order in the static magnetic susceptibility χ of the metal are therefore neglected throughout the calculation. This makes it unnecessary to discuss the difficult question, whether the radio-frequency field which effectively acts on the electron spins is the field $\mathbf{H}_1$, or the magnetic induction $\mathbf{B}$, or something intermediate.[4] With an error at most of the order χ^2, we suppose $\mathbf{H}_1$ to be the effective field acting on the spins.

The penetration of the radio-frequency field into the metal will be limited by skin effect. The classical skin depth is given by

$$\delta = (c^2/2\pi\sigma\omega)^{\frac{1}{2}}, \tag{10}$$

where σ is the conductivity of the metal. If δ is large compared to Λ, we are in the domain of "classical skin effect" and the field penetration is controlled by δ. If δ is not large compared to Λ, we have "anomalous skin effect"[5] and the penetration is controlled by Λ.

III. QUALITATIVE ARGUMENT

It is convenient in what follows to use the symbol δ to mean the actual skin depth, given by (10) in the classical case and equal to Λ in the anomalous case. According to Eq. (8), an average electron will diffuse across the skin depth in a time of the order of

$$D = (3\delta^2/2v\Lambda). \tag{11}$$

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[3] This mechanism for the spin relaxation was proposed by R. J. Elliott, Phys. Rev. **96**, 266, 280 (1954). Reasons for believing that it is the controlling mechanism are given in the paper by G. Feher and A. F. Kip, reference 1, Sec. IV. C.2.

[4] For a discussion of this point see G. H. Wannier, Phys. Rev. **72**, 304 (1947).

[5] G. Reuter and E. Sondheimer, Proc. Roy. Soc. (London) **A195**, 336 (1948).

The amplitude and phase of the field $\mathbf{H}_1$ will change by factors of the order of e within the distance δ. Therefore the average electron will feel the radio-frequency field not with a fixed frequency ω but with frequencies spread over a band of width D^{-1}. At first glance this argument leads one to believe that diffusion should increase the width of the resonance line from U^{-1} to D^{-1} if $D<U$. The surprising fact is that the observed width remains equal to U^{-1}, although the intensity and shape of the line are changed by the diffusion. The aim of the following discussion is to explain this result in a qualitative way, and to draw an analogy to a more familiar physical example where a similar situation arises.

Suppose that the relaxation time U is long compared with D. The radio-frequency field seen by one electron will have the form

$$F(t)=f(t)e^{-i\omega t}+\text{c.c.}, \tag{12}$$

where $f(t)$ is a modulation factor with a frequency band of the order of D^{-1}. However, $f(t)$ is not a completely random function. It is composed of short pulses of duration D, extending over the time U and separated by irregular intervals. The pulses occur when the electron comes close to the surface and the amplitude of $f(t)$ is large; the intervals occur when the electron is far from the surface and $f(t)$ is almost zero. Two facts are here of decisive importance. (i) Each electron which leaves the surface has a high probability of returning, and so the $f(t)$ for an average electron contains more than one pulse. (ii) The phase of $f(t)$ returns to the same value each time the electron reaches the surface, and so the integral of $f(t)$ over a pulse has a finite average value which is not zero.

Now consider the form of the spectrum of $F(t)$. Each single pulse will give a smooth spectrum spread over a band of width D^{-1}. Two pulses separated by an interval I will give an interference pattern, with maxima and minima separated by a spacing of order I^{-1}, extending over the band width D^{-1}. There will always be constructive interference at the central frequency ω, because of point (ii). Three or more pulses will give a more complicated interference pattern over the band D^{-1}, still with the central maximum at ω. Now let this spectrum be squared to give the radio-frequency power spectrum seen by one electron, and let it then be averaged over many electrons. The interval-length I will vary at random over values from zero up to U. Therefore the interference patterns will average out to a smooth curve of width D^{-1}, except for the central maxima which will add constructively to give a single peak with width of the order of U^{-1}.

Thus we expect the observed absorption spectrum of radio-frequency energy, which is an average over many electrons of the power spectrum acting upon one electron, to have a structure of width U^{-1} superimposed upon a weaker background of width D^{-1}. This is in fact what is observed, although the conditions of the experiment are such as to make only the central structure clearly distinguishable.

The device invented by Ramsey[6] for observing molecular beam resonances with two separated oscillating fields is based on exactly the same principle. In Ramsey's apparatus the molecules pass through two short pulses of radio-frequency field. The phase relation of the two pulses is fixed, but the time interval between them depends on the velocity and so varies from molecule to molecule. The observed resonance line consists of a broad background with width determined by the duration of each pulse, and a narrow central structure with width determined by the interval between them. For obtaining sharp lines, it is essential that the molecular velocity is distributed at random over a wide range. This random element in Ramsey's apparatus plays precisely the same role as the random diffusion of the electrons in Feher's experiment.

The qualitative theory of this section would be exact if the only cause of radio-frequency energy absorption in a metal were the flipping of the electron spins. In fact, however, the eddy-current losses play an equally important part, and these have no analog in Ramsey's experiment. Therefore the qualitative theory explains only the fact that narrow lines are seen, and does not predict the shape of the lines correctly. The shape depends in a complicated way upon the phase relationships of electric and magnetic fields in the metal skin, and a simple physical picture of these effects is still lacking.

IV. CALCULATION OF THE MAGNETIZATION

We now begin the quantitative treatment of the model described in Sec. II. In this section we calculate the magnetization produced by a given magnetic field (1). Consider a single electron whose spin is described by the wave function

$$u(t)=a_1(t)\exp(-\tfrac{1}{2}i\nu t)u_1+a_2(t)\exp(\tfrac{1}{2}i\nu t)u_2. \tag{13}$$

Here u_1, u_2 are the states with spin parallel and antiparallel to the direction of $\mathbf{H}$. The amplitudes a_1, a_2 vary with time by virtue of the interaction energy,

$$\mu\boldsymbol{\sigma}\cdot\mathbf{H}_1(\mathbf{r}(t))e^{-i\omega t}+\text{c.c.}, \tag{14}$$

of the electron spin $\boldsymbol{\sigma}$ with the field (1). The Schrödinger equation for a_1 is

$$\begin{aligned} i\hbar\dot{a}_1=\mu(\mathbf{H}_1\cdot\mathbf{k}e^{-i\omega t}+\mathbf{H}_1{}^*\cdot\mathbf{k}e^{i\omega t})a_1 \\ +\mu(\mathbf{H}_1\cdot\mathbf{s}e^{-i\alpha t}+\mathbf{H}_1{}^*\cdot\mathbf{s}e^{i\gamma t})a_2. \end{aligned} \tag{15}$$

Here $\mathbf{H}_1$ stands for $\mathbf{H}_1(\mathbf{r}(t))$, $\mathbf{k}$ is a unit vector in the direction of $\mathbf{H}$, and $\mathbf{s}$ is the vector

$$\mathbf{s}=(u_1{}^*\boldsymbol{\sigma}u_2). \tag{16}$$

Since we are making the approximation of treating the magnetization as linear in $\mathbf{H}_1$, Eq. (15) may be solved by first-order perturbation theory. Consider an

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[6] N. F. Ramsey, Phys. Rev. 78, 695 (1950).

electron known to be in the state u_1 at any time t'. At a later time t its spin state will be determined by Eq. (15), and a simple calculation shows that the expectation value of its spin vector will be

$$\bar{\boldsymbol{\sigma}}(t,t')=\mathbf{k}+(i\mu/\hbar)\int_{t'}^{t} du[\mathbf{s}\cdot\mathbf{H}_1(\mathbf{r}(u))e^{-i\alpha u-i\nu t}\mathbf{s}^* \\ -\mathbf{s}^*\cdot\mathbf{H}_1(\mathbf{r}(u))e^{-i\gamma u+i\nu t}\mathbf{s}]+\text{c.c.} \quad (17)$$

For an electron in the state u_2 at time t', the expectation value of the spin at time t is given by the negative of (17). According to our model, there is a probability $U^{-1}\exp[-(t-t')/U]dt'$ that an electron observed at time t suffered its last random change of spin state during the time interval $(t', t'+dt')$. Further, each random change of spin state leads to the states u_1 and u_2 with unequal probabilities p_1 and p_2, because of the thermodynamical preference for the lower-energy state. Hence the weighted average of the spin-expectation value of an electron observed at time t is

$$\bar{\boldsymbol{\sigma}}(t)=(p_1-p_2)U^{-1}\int_{-\infty}^{t}\exp[-(t-t')/U]\bar{\boldsymbol{\sigma}}(t,t')dt' \\ =(p_1-p_2)\mathbf{k}+(i\mu/\hbar)(p_1-p_2) \\ \times\int_{-\infty}^{t}\exp[-(t-u)/U]du[\mathbf{s}\cdot\mathbf{H}_1(\mathbf{r}(u)) \\ \times e^{-i\alpha u-i\nu t}\mathbf{s}^*-\mathbf{s}^*\cdot\mathbf{H}_1(\mathbf{r}(u))e^{-i\gamma u+i\nu t}\mathbf{s}]+\text{c.c.} \quad (18)$$

We wish to calculate the macroscopic intensity of magnetization produced by the electrons observed in the neighborhood of a point $\mathbf{r}$ at time t. This is obtained if we average Eq. (18) over the possible previous histories of an electron which happens to be at $\mathbf{r}$ at time t. So let $G(\mathbf{r}',u,\mathbf{r},t)$ be the probability that an electron observed at $\mathbf{r}$ at time t was at $\mathbf{r}'$ at time u. Let N be the number of electrons per unit volume taking part in the magnetization. The product $N(p_1-p_2)$ is directly related to the static susceptibility χ of the metal by

$$\chi|\mathbf{H}|=\tfrac{1}{2}\chi\nu\hbar/\mu=-N\mu(p_1-p_2). \quad (19)$$

Averaging (18) over the electron histories and using (19), the magnetization density becomes

$$\mathbf{M}(\mathbf{r},t)=\chi|\mathbf{H}|\mathbf{k}+\tfrac{1}{2}i\chi\nu\int_{-\infty}^{t}\exp[-(t-u)/U]du \\ \times\int_V G(\mathbf{r}',u,\mathbf{r},t)d\mathbf{r}'[\mathbf{s}\cdot\mathbf{H}_1(\mathbf{r}')e^{-i\alpha u-i\nu t}\mathbf{s}^* \\ -\mathbf{s}^*\cdot\mathbf{H}_1(\mathbf{r}')e^{-i\gamma u+i\nu t}\mathbf{s}]+\text{c.c.} \quad (20)$$

This is the required nonlocal relation between $\mathbf{M}$ and $\mathbf{H}_1$.

It is required now to find solutions of the Maxwell equations consistent with (20). Assuming solutions varying with time like $\exp(-i\omega t)$ as in Eqs. (1) and (4), the Maxwell equations are

$$\text{curl}\mathbf{H}_1=(4\pi/c)\mathbf{j}, \quad (21)$$

$$\text{curl}\mathbf{E}=-(1/c)(d\mathbf{B}/dt)=(i\omega/c)\mathbf{B}, \quad (22)$$

$$\mathbf{B}=\mathbf{H}_1+4\pi\mathbf{M}. \quad (23)$$

Here $\mathbf{M}$ is given by Eq. (20) inside the metal and $\mathbf{M}=0$ outside. The current $\mathbf{j}$ is

$$\mathbf{j}=\sigma\mathbf{E}, \quad (24)$$

if the spin effect is in the classical range. When the spin effect is anomalous, $\mathbf{j}$ is a more complicated function[5] of $\mathbf{E}$ but is still independent of $\mathbf{M}$. The displacement current is in any case negligible inside the metal.

The experimentally observed quantity is the radiofrequency energy P absorbed into the metal per unit time and per unit area of surface. This is the real part of the normal component of the complex Poynting vector taken just outside the surface. It is convenient to define the complex surface impedance,

$$Z=(4\pi/c)[\mathbf{n}\cdot(\mathbf{E}_0\times\mathbf{H}_{10}^*)]/|\mathbf{H}_{10}|^2, \quad (25)$$

where $\mathbf{E}_0$ and $\mathbf{H}_{10}$ are the electric and magnetic fields immediately outside the surface, and $\mathbf{n}$ is the unit inward normal. This quantity Z is characteristic of the metal surface and depends on the direction of polarization but not on the magnitude of the field $\mathbf{H}_1$. The absorption rate P is then given by

$$P=(c/4\pi)^2|\mathbf{H}_{10}|^2(\text{Re}Z). \quad (26)$$

The imaginary part of Z gives the corresponding inductive load on the cavity, and would in principle be observable by a small shift in the resonant frequency of the cavity as the steady field $\mathbf{H}$ is varied.

V. SIMPLE THEORY FOR THICK SAMPLES AND LONG RELAXATION TIMES

In the case of a metal sample which has dimensions large compared to the skin depth (either classical or anomalous), we may idealize the problem by considering the surface to be the plane $z=0$, the metal occupying the half-space $z>0$, and the field $\mathbf{H}_1$ to be a function of z only. The integration over the x and y coordinates in Eq. (20) is then trivial. We may replace G by the Green's function for the diffusion equations (8) and (9) in one dimension, namely

$$G(z',u,z,t)=[(4/3)\pi v\Lambda|t-u|]^{-\frac{1}{2}} \\ \times\{\exp(-3(z-z'^2)/4v\Lambda|t-u|) \\ +\exp(-3(z+z')^2/4v\Lambda|t-u|)\}. \quad (27)$$

The integration over $\mathbf{r}'$ in Eq. (20) is replaced by an integration over z' from 0 to ∞.

In addition we make the approximation of a long relaxation time, that is to say we assume U to be long compared with the diffusion time D given by (11). This means that the time integration in Eq. (20) extends effectively over a time long compared with D, while the space integration extends only over values of z and z' of the order of δ. Comparing Eq. (27) with (11), the exponents in Eq. (27) will be small over the major part of the space and time integrations of Eq. (20). Therefore in the limit of long relaxation time we may replace both exponentials in Eq. (27) by 1 simply. The physical meaning of this approximation is clear; for long relaxation times the magnetization produced by the radio-frequency field at a depth z' in the skin will diffuse evenly over the skin in a way which becomes eventually independent of z'. Another consequence of the long relaxation time approximation is that the nonresonant term in γ in Eq. (20) becomes negligible compared with the resonant term in α. Substituting Eq. (27) into (20) with these approximations, the radio-frequency magnetization is equal to (4), with $\mathbf{M}(\mathbf{r})$ given by

$$\mathbf{M}(\mathbf{r})=\tfrac{1}{2}i\chi\nu\int_0^\infty dw[\tfrac{1}{3}\pi v\Lambda w]^{-\frac{1}{2}}\exp[-w(U^{-1}-i\alpha)] \times\int_0^\infty dz'\mathbf{s}\cdot\mathbf{H}_1(z')\mathbf{s}^*, \quad (28)$$

independent of the position $\mathbf{r}$. The time and space integrations are now separated and can be easily performed.

With error of order χ^2, we replace $\mathbf{H}_1$ by $\mathbf{B}$ in Eq. (28). The second Maxwell equation (22) becomes, for fields depending only on z,

$$(i\omega/c)\mathbf{B}=(d/dz)(\mathbf{n}\times\mathbf{E}), \quad (29)$$

and therefore

$$\int_0^\infty \mathbf{B}(z')dz'=(ic/\omega)(\mathbf{n}\times\mathbf{E}_0). \quad (30)$$

Thus Eq. (28) reduces to

$$\mathbf{M}(\mathbf{r})=-K(1-ix)^{-\frac{1}{2}}[\mathbf{s}\cdot(\mathbf{n}\times\mathbf{E}_0)]\mathbf{s}^*, \quad (31)$$

with

$$K=(\chi\nu c/2\omega)(3U/v\Lambda)^{\frac{1}{2}}, \quad (32)$$

$$x=\alpha U=(\omega-\nu)U, \quad (33)$$

and the complex square root in Eq. (31) to be taken with positive real part so that we have explicitly:

$$[1-ix]^{-\frac{1}{2}}=2^{-\frac{1}{2}}(1+x^2)^{-\frac{1}{2}}[\eta+i\xi], \quad (34)$$

$$\eta=[(1+x^2)^{\frac{1}{2}}+1]^{\frac{1}{2}},\quad \xi=(\mathrm{sgn}x)[(1+x^2)^{\frac{1}{2}}-1]^{\frac{1}{2}}. \quad (35)$$

By making use[7] of known results on skin effect, we can now complete the solution of the Maxwell equations with the constant magnetization $\mathbf{M}(\mathbf{r})$. The Eqs. (21) and (22), when written in terms of $\mathbf{B}$ and $\mathbf{E}$, are completely independent of the magnetization. This is true both with normal and with anomalous skin effect. Therefore the $\mathbf{B}$ and $\mathbf{E}$ fields inside the metal are given precisely by the usual theory of the skin effect without magnetization. The boundary condition at the surface is that the tangential components of $\mathbf{E}$ and $\mathbf{H}_1$ are continuous. Thus the fields immediately outside the surface are

$$\mathbf{E}_0=\mathbf{E}_0,\quad \mathbf{H}_{10}=\mathbf{B}_0-4\pi\mathbf{M}_\perp, \quad (36)$$

where $\mathbf{E}_0$ and $\mathbf{B}_0$ are the fields calculated without magnetization, and $\mathbf{M}_\perp$ is the tangential component of the magnetization given by Eq. (31).

We write Z_0 for the surface impedance of the metal without magnetization, given by

$$Z_0=(4\pi/c)[\mathbf{n}\cdot(\mathbf{E}_0\times\mathbf{B}_0^*)]/|\mathbf{B}_0|^2. \quad (37)$$

Let $\mathbf{b}$ be the complex polarization vector of $\mathbf{B}_0$,

$$\mathbf{b}=\mathbf{B}_0/|\mathbf{B}_0|,\quad (\mathbf{b}\cdot\mathbf{b}^*)=1. \quad (38)$$

By Eqs. (30) and (37), we have

$$(\mathbf{n}\times\mathbf{E}_0)=(c/4\pi)Z_0|\mathbf{B}_0|\mathbf{b}. \quad (39)$$

Substituting (31), (36), and (39) into Eq. (25), the surface impedance with magnetization becomes

$$\begin{aligned}Z&=Z_0[1+Kc(1-ix)^{-\frac{1}{2}}fZ_0]^{-1}\\&=Z_0-Kcf(1-ix)^{-\frac{1}{2}}Z_0^2, \quad (40)\end{aligned}$$

neglecting terms of order χ^2. We have written

$$\begin{aligned}f&=|(\mathbf{s}\cdot\mathbf{b})|^2=|(u_1{}^*\mathbf{b}\cdot\boldsymbol{\sigma}u_2)|^2\\&=(\mathbf{b}\times\mathbf{k})\cdot(\mathbf{b}^*\times\mathbf{k})+i(\mathbf{b}\times\mathbf{b}^*)\cdot\mathbf{k}, \quad (41)\end{aligned}$$

where $\mathbf{k}$ is the unit vector parallel to the steady field $\mathbf{H}$. In general, f is a real number lying between 0 and 2, measuring the proportion of the radio-frequency field which is circularly polarized in the positive sense about the direction of $\mathbf{H}$. The maximum value 2 is attained by f when $\mathbf{b}=2^{-\frac{1}{2}}(1,i,0)$, i.e., for pure circularly polarized radiation. In practice we shall usually be dealing with linearly polarized fields, in which case $\mathbf{b}$ is real and

$$f=\sin^2\phi, \quad (42)$$

where ϕ is the angle between the polarization directions of $\mathbf{H}_1$ and $\mathbf{H}$.

When the skin effect is anomalous, the Reuter-Sondheimer theory[5] will give the value of Z_0 to be used in Eq. (40). When the skin effect is classical, Eqs. (21), (22), and (24) give the classical result

$$Z_0=(1-i)(\sigma\delta)^{-1}. \quad (43)$$

Substituting this into (40), using Eqs. (26), (32), (10), and (11), we have the result

$$P=\tfrac{1}{4}\delta\omega|\mathbf{H}_{10}|^2[(1/2\pi)-\chi\nu f(DU)^{\frac{1}{2}}\xi(1+x^2)^{-\frac{1}{2}}], \quad (44)$$

with x and ξ given by Eq. (33) and (35). Thus the absorption line, in the case of a thick sample with long relaxation time and classical skin effect, has the unusual and characteristic shape given by the function $\xi(1+x^2)^{-\frac{1}{2}}$. Since ξ is an odd function of $(\omega-\nu)$, the line is in this approximation antisymmetrical about its center. The width is proportional to U^{-1} and independent of the diffusion time D. These are the most

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[7] The subsequent argument is due to Professor Kittel (private communication).

striking conclusions of the theory. The experiments[1] support them qualitatively; however for a quantitative comparison with experiment the discussion of a limiting case is insufficient, and the more detailed theory of the following sections is required.

VI. SOLUTION OF MAXWELL EQUATIONS FOR A FLAT PLATE

To give an exact theory for a metal sample which is not necessarily large or small compared with the skin depth, we must choose a definite shape for the metal. We shall confine ourselves to the case of a flat plate, which is a convenient shape both experimentally and theoretically. Other shapes could be handled by similar methods. We make no restriction on the relative magnitude of D and U, but we shall assume henceforth that we are in the domain of classical skin effect, i.e., that Eq. (24) is valid.

The metal will again be considered to be infinite in the x and y directions, thus it occupies the volume $0 \leq z \leq \theta$ where θ is the thickness. An important parameter in the problem will be the ratio of thickness to skin depth,

$$\lambda = \theta/\delta. \tag{45}$$

It is also convenient to introduce the dimensionless ratios:

$$R = (D/U)^{\frac{1}{2}}, \tag{46}$$

$$a = \lambda R = (3\theta^2/2v\Lambda U)^{\frac{1}{2}}. \tag{47}$$

As before, we assume the fields to depend on z only, so that the problem is essentially one-dimensional. We shall also make the arbitrary assumption that the magnetic field is equal on the two sides of the plate, i.e., an even function of $(z-\frac{1}{2}\theta)$. This assumption is made only to simplify the algebra; an unsymmetric field could be calculated in exactly the same way. In particular, for a thick plate $(\theta \gg \delta)$ the fields on the two sides are independent and the symmetric solutions apply unchanged to unsymmetric conditions; for example, the symmetric solutions may be used when the plate is thick and forms part of the wall of the cavity.

The idea of the following analysis is to reduce Eq. (20) to a tractable form by introducing the eigenfunctions $\psi_n(\mathbf{r})$, $n=0, 1, 2, \cdots$; these are defined as a complete orthogonal set of functions satisfying the eigenvalue equation

$$\Delta\psi_n = -\mu_n\psi_n, \tag{48}$$

with the boundary condition

$$\mathbf{n}\cdot\operatorname{grad}\psi_n = 0, \tag{49}$$

and the normalization

$$\int_V \psi_m{}^*\psi_n d\mathbf{r} = \delta_{mn}. \tag{50}$$

In particular, the first eigenfunction is a constant:

$$\psi_0(\mathbf{r}) = V^{-\frac{1}{2}}, \quad \mu_0 = 0. \tag{51}$$

The Green's function G which appears in Eq. (20) satisfies Eqs. (8) and (9) as a function of its arguments $(\mathbf{r},t)$ and reduces to a δ function, $\delta(\mathbf{r}-\mathbf{r}')$, for $t=u$. These conditions determine G as the series expansion:

$$G = \sum_n \psi_n{}^*(\mathbf{r}')\psi_n(\mathbf{r}) \exp[-\tfrac{1}{3}v\Lambda\mu_n(t-u)]. \tag{52}$$

Let the field $\mathbf{H}_1(\mathbf{r})$ inside the metal also be expanded in a series

$$\mathbf{H}_1(\mathbf{r}) = \sum_n \mathbf{h}_n\psi_n(\mathbf{r}), \quad \mathbf{h}_n = \int_V \psi_n{}^*\mathbf{H}_1 d\mathbf{r}, \tag{53}$$

where the coefficients $\mathbf{h}_n$ are vectors. Substituting from Eq. (52), (53) into Eq. (20), the space and time integrations can be performed immediately. The radio-frequency magnetization then appears in the form (4) with

$$\mathbf{M}(\mathbf{r}) = \tfrac{1}{2}v\chi i \sum_n \psi_n(\mathbf{r})[\eta_n(\mathbf{s}\cdot\mathbf{h}_n)\mathbf{s}^* - \zeta_n(\mathbf{s}^*\cdot\mathbf{h}_n)\mathbf{s}], \tag{54}$$

$$\eta_n = [U^{-1}+\tfrac{1}{3}v\Lambda\mu_n - i\alpha]^{-1}, \quad \zeta_n = [U^{-1}+\tfrac{1}{3}v\Lambda\mu_n - i\gamma]^{-1}. \tag{55}$$

The nonlocal relation between $\mathbf{M}$ and $\mathbf{H}_1$ given by Eq. (54), (55) is completely general, holding for a metal of any shape and for any kind of skin effect.

Now we specialize to the flat plate with classical skin effect and symmetrical fields which are functions of z only. The eigenfunctions which appear in Eq. (53) are then

$$\psi_n = [\epsilon_n/\theta]^{\frac{1}{2}} \cos[2\pi nz/\theta], \quad \mu_n = 4\pi^2 n^2/\theta^2, \tag{56}$$

where

$$\epsilon_0 = 1, \quad \epsilon_n = 2 \text{ for } n > 0, \tag{57}$$

and the normalization is per unit area of the plate. The Maxwell equations (21), (22), (23), (24) give, inside the metal,

$$\begin{aligned} 2i\delta^{-2}(\mathbf{H}_1+4\pi\mathbf{M}) &= (4\pi\sigma/c)(d/dz)(\mathbf{n}\times\mathbf{E}) \\ &= (d^2/dz^2)[\mathbf{n}\times(\mathbf{n}\times\mathbf{H}_1)] = -(d^2/dz^2)\mathbf{H}_\perp, \end{aligned} \tag{58}$$

where $\mathbf{H}_\perp$ is the component of $\mathbf{H}_1$ perpendicular to $\mathbf{n}$. Let $\mathbf{M}_\perp$, the component of $\mathbf{M}$ perpendicular to $\mathbf{n}$, be expressed as a series expansion

$$\mathbf{M}_\perp(z) = (1/4\pi)\sum_n \mathbf{m}_n\psi_n(z). \tag{59}$$

We multiply Eq. (58) by $\psi_n{}^*(z)$ and integrate over z between two limits lying just inside the surface at $z=0$, $z=\theta$. The right side is then integrated by parts twice, using Eqs. (49) and (48). The result is

$$\begin{aligned} &2i\delta^{-2}(\mathbf{h}_{n\perp}+\mathbf{m}_n) \\ &\quad = (4\pi\sigma/c)\psi_n{}^*(0)[(\mathbf{n}\times\mathbf{E}_\theta)-(\mathbf{n}\times\mathbf{E}_0)] \\ &\qquad\qquad - \int (d^2\psi_n{}^*/dz^2)\mathbf{H}_\perp dz \\ &\quad = -(8\pi\sigma/c)[\epsilon_n/\theta]^{\frac{1}{2}}(\mathbf{n}\times\mathbf{E}_0)+\mu_n\mathbf{h}_{n\perp}. \end{aligned} \tag{60}$$

Here $\mathbf{h}_{n\perp}$ is the component of $\mathbf{h}_n$ perpendicular to $\mathbf{n}$. The electric fields at the surfaces are $\mathbf{E}_0$ and $\mathbf{E}_\theta = -\mathbf{E}_0$ because of the assumed symmetry.

The information we need from the Maxwell equations is all contained in Eq. (60), while Eq. (54) gives the coefficients $\mathbf{m}_n$ in terms of the $\mathbf{h}_n$. One could solve Eq. (60) and (54) for the $\mathbf{h}_n$ and thus obtain the complete field-distribution inside the metal in terms of the electric field $\mathbf{E}_0$ at the surface.

The solution of the equations becomes simple because all the $\mathbf{m}_n$ are proportional to χ and may be treated as small. With an error of order χ, Eq. (60) implies that all the $\mathbf{h}_n$ are parallel to the vector $(\mathbf{n}\times\mathbf{E}_0)$, which is parallel to the polarization vector $\mathbf{b}$ defined by Eq. (38). Therefore we may write in Eq. (54), with an error of order χ^2,

$$(\mathbf{s}\cdot\mathbf{h}_n)=(\mathbf{s}\cdot\mathbf{b})(\mathbf{b}^*\cdot\mathbf{h}_n),\quad (\mathbf{s}^*\cdot\mathbf{h}_n)=(\mathbf{s}^*\cdot\mathbf{b})(\mathbf{b}^*\cdot\mathbf{h}_n). \tag{61}$$

A comparison of Eq. (54) with (59), using Eq. (61), gives the relation

$$(\mathbf{b}^*\cdot\mathbf{m}_n)=g_n(\mathbf{b}^*\cdot\mathbf{h}_n), \tag{62}$$

with g_n defined by

$$g_n=2\pi\nu\chi i[f\eta_n-f'\zeta_n]. \tag{63}$$

Here f is defined by Eq. (41) and f' by

$$f'=|(\mathbf{s}^*\cdot\mathbf{b})|^2=(\mathbf{b}\times\mathbf{k})\cdot(\mathbf{b}^*\times\mathbf{k})-i(\mathbf{b}\times\mathbf{b}^*)\cdot\mathbf{k}, \tag{64}$$

so that for linearly polarized fields

$$f'=f=\sin^2\phi, \tag{65}$$

with ϕ defined as in Eq. (42). Taking the scalar product of Eq. (60) with the vector $\mathbf{b}^*$ which is perpendicular to $\mathbf{n}$, and using Eq. (62), we obtain

$$\begin{aligned}(8\pi\sigma/c)[\epsilon_n/\theta]^{\frac{1}{2}}&[\mathbf{b}^*\cdot(\mathbf{n}\times\mathbf{E}_0)]\\&=[\mu_n-2i\delta^{-2}(1+g_n)](\mathbf{b}^*\cdot\mathbf{h}_n).\end{aligned} \tag{66}$$

The radio-frequency power absorbed per unit area of metal surface is given by Eq. (26) and (25). Since $\mathbf{H}_{10}^*$ is almost parallel to $\mathbf{b}^*$, with an error of order χ^2 the surface impedance Z may be written

$$Z=(4\pi/c)[\mathbf{b}^*\cdot(\mathbf{n}\times\mathbf{E}_0)]/(\mathbf{b}^*\cdot\mathbf{H}_{10}). \tag{67}$$

Since $\mathbf{H}_\perp$ is continuous across the surface, Eqs. (53) and (56) give

$$(\mathbf{b}^*\cdot\mathbf{H}_{10})=\sum\nolimits_n[\epsilon_n/\theta]^{\frac{1}{2}}(\mathbf{b}^*\cdot\mathbf{h}_n). \tag{68}$$

Substituting from Eqs. (68) and (66) into (67) gives the final explicit formula for Z:

$$Z^{-1}=(2\sigma/\theta)\sum\nolimits_n\epsilon_n[\mu_n-2i\delta^{-2}(1+g_n)]^{-1}, \tag{69}$$

or, neglecting terms in χ^2,

$$\begin{aligned}Z^{-1}=(2\sigma/\theta)\sum\nolimits_n\epsilon_n[&(\mu_n-2i\delta^{-2})^{-1}\\&+2i\delta^{-2}g_n(\mu_n-2i\delta^{-2})^{-2}].\end{aligned} \tag{70}$$

VII. EVALUATION OF THE LINE SHAPE FOR FOR A FLAT PLATE

In this section we first calculate in closed form the sum of the series (70). We then discuss in detail the shape of the observed resonance line for the various ranges of values of the parameters which can occur experimentally.

Using Eqs. (56) and (57), the summation in (70) may be replaced by a summation over integers n from minus to plus infinity. Taking the inverse of Eq. (70) and again neglecting terms of order χ^2,

$$Z=(2/\sigma\theta)\{F+\tfrac{1}{2}\pi\nu\chi a^2UF^2[fG(\alpha)-f'G(\gamma)]\}, \tag{71}$$

$$F=\Big[\sum_{-\infty}^{\infty}(\pi^2n^2-\tfrac{1}{2}i\lambda^2)^{-1}\Big]^{-1}, \tag{72}$$

$$G(\alpha)=\lambda^2\sum_{-\infty}^{\infty}(\pi^2n^2-\tfrac{1}{2}i\lambda^2)^{-2}[\pi^2n^2+\tfrac{1}{2}a^2(1-ix)]^{-1}, \tag{73}$$

where x, λ, a are given by Eqs. (33), (45), (47), respectively. Now introducing the notations

$$u=\tfrac{1}{2}\lambda(1+i),\qquad u^2=\tfrac{1}{2}i\lambda^2, \tag{74}$$

$$w=\tfrac{1}{2}a(\xi+i\eta),\quad w^2=\tfrac{1}{2}a^2(ix-1), \tag{75}$$

with ξ and η given by Eq. (36), the sums (72) and (73) become

$$F=-u\tan u, \tag{76}$$

$$\begin{aligned}G(\alpha)=\frac{i}{(w^2-u^2)^2}\bigg[&2u^2\frac{\cot w}{w}+(w^2-3u^2)\frac{\cot u}{u}\\&+(w^2-u^2)\operatorname{cosec}^2u\bigg].\end{aligned} \tag{77}$$

The real part of Z, determined by Eqs. (71), (76), and (77), gives the explicit form of the line shape for any values of the ratios λ and a. We now proceed to consider the simplifying approximations which can be made for values of λ and a lying in various ranges.

(a) Thin Case

$\lambda\leq 4$, or $\theta\leq 4\delta$.

For $\lambda\leq 1$, the term $n=0$ is much the greatest in the series (72) and (73), and we may neglect the other terms. Hence Eq. (71) becomes

$$Z=\frac{2\pi\theta\omega}{c^2}\bigg[-i+2\pi\nu\chi U\bigg(\frac{f}{1-iU\alpha}-\frac{f'}{1-iU\gamma}\bigg)\bigg]. \tag{78}$$

This result is entirely independent of electron diffusion. The energy absorption, which is proportional to the real part of Z, varies with $\mathbf{H}$ approximately as $[1+U^2\alpha^2]^{-1}$, and so gives an absorption line of the ordinary symmetrical Lorentz shape with the natural half-width U^{-1}.

The result (78) will still be reasonably accurate up to $\lambda=4$. The higher terms in (73), being small and spread out over a width greater than U^{-1}, will hardly be observable.

(b) Intermediate Case

$$\lambda \geq 4, \quad a \leq 4.$$

Experimentally the relaxation time U is of the order of 10^{-8} sec, while the diffusion time D is not shorter than 10^{-10} sec. So the ratio $R=(D/U)^{\frac{1}{2}}=(a/\lambda)$ is not less than about 1/10. Therefore, this intermediate case can occur only when $4 \leq \lambda \leq 40$, i.e., when the metal is thick but not very thick compared to the skin depth δ.

When $4 \leq \lambda \leq 10$ it will be convenient to calculate with the first few terms of the series (73), which still converges rapidly although the term $n=0$ is no longer predominant. When $10 < \lambda \leq 40$ and $a \leq 4$, it will be more convenient to use Eqs. (76) and (77) with the good approximations

$$\tan u = i, \quad \operatorname{cosec}^2 u = 0. \tag{79}$$

This gives for the central part of the absorption line, where $x = U\alpha \leq 1$, the shape

$$Z=(2/\sigma\theta)[-iu-i\pi\nu\chi a^2 U f(\cot w/w)]. \tag{80}$$

Naturally this intermediate case is more complicated to calculate than either the thin or the thick case. Fortunately, the intermediate case corresponds to metal thicknesses in the range 10^{-4}–10^{-3} cm, which is an awkward range for experimental preparation and will not often occur in practice.

(c) Thick Case

$$\lambda \geq 4, \quad a \geq 4.$$

These conditions are always fulfilled for sufficiently thick samples, say for $\theta > 40\delta$. And the results for this case will be independent of the shape of the metal, so long as the radius of curvature of the surface is everywhere large compared to δ.

The imaginary part of w given by Eqs. (75) and (35) is in this case always large compared to 1. Hence we may put $\cot w = \cot u = -i$ in Eq. (77). This gives for Z the formula

$$Z=(\sigma\delta)^{-1}[1-i-\pi\nu\chi D(fL-f'L')], \tag{81}$$

with

$$L=[R^2(x+i)-1]^{-2}\{4R^{-1}(\xi+i\eta)^{-1} + (1-i)[R^2(x+i)-3]\}, \tag{82}$$

and L' the same as L with α replaced by γ. In the absence of magnetization, Z reduces correctly to the classical formula (43) for a thick plate. Equations (81) and (82) are compact enough to be used for numerical calculation of the line-shape for any value of R. However, for a general discussion it is convenient to specialize further to the limiting cases $R \gg 1$ and $R \ll 1$.

(c1) *Thick Case, Broad Natural Line*

$$a \gg \lambda \gg 1, \quad R \gg 1.$$

Then, Eq. (75) reduces to

$$L=(1-i)R^{-2}(x+i)^{-1}, \tag{83}$$

and so

$$Z=(\sigma\delta)^{-1}\left[1-i+(1+i)\pi\nu\chi U\left(\frac{f}{1-iU\alpha}-\frac{f'}{1-iU\gamma}\right)\right]. \tag{84}$$

As with Eq. (78), this result is independent of diffusion. But the absorption line is now no longer symmetric, since the real part of Z varies approximately like

$$(1-U\alpha)/(1+U^2\alpha^2), \tag{85}$$

giving the algebraic sum of the real and imaginary parts of the electron susceptibility. That this result (85) holds in the absence of diffusion is well known.[8]

(c2) *Thick Case, Narrow Natural Line*

$$\lambda \gg a \gg 1, \quad R \ll 1.$$

This is the case which will usually occur in practice with bulk metal samples, and it shows the effects of diffusion in the most typical and interesting way. For these reasons we discuss this case in more detail than the others.

To simplify Eq. (82), knowing that $R \ll 1$, it is necessary to consider the center and wings of the absorption line separately. At the center, α is of the order U^{-1}, x is of order 1, and all terms in R^2 in Eq. (82) are negligible. Therefore,

$$L=2R^{-1}(\xi-i\eta)(1+x^2)^{-\frac{1}{2}}. \tag{86}$$

At the wings, α is of the order D^{-1}, and $R^2x=D\alpha$ is of order 1. In this case Eq. (82) gives

$$L=(D\alpha-1)^{-2}[2(\operatorname{sgn}\alpha-i)|D\alpha|^{-\frac{1}{2}}+(1-i)(D\alpha-3)]. \tag{87}$$

The approximations (86) and (87) overlap and are both valid in the range $U^{-1}<|\alpha|<D^{-1}$. The observed absorption of radio-frequency power per unit area is the quantity P defined by Eqs. (26) and (81). For the center of the line, Eq. (86) gives

$$P=\tfrac{1}{4}\delta\omega|\mathbf{H}_{10}|^2\left[\frac{1}{2\pi}-\nu\chi f(DU)^{\frac{1}{2}}(\operatorname{sgn}\alpha) \times\left(\frac{(1+U^2\alpha^2)^{\frac{1}{2}}-1}{1+U^2\alpha^2}\right)^{\frac{1}{2}}\right], \tag{88}$$

and for the wings Eq. (87) gives

$$\begin{aligned} P=\tfrac{1}{4}\delta\omega|\mathbf{H}_{10}|^2\{1/2\pi-\tfrac{1}{2}\nu\chi D[&f(D\alpha-1)^{-2} \\ &\times(2\operatorname{sgn}\alpha|D\alpha|^{-\frac{1}{2}}+D\alpha-3) \\ &-f'(D\gamma-1)^{-2}(2(D\gamma)^{-\frac{1}{2}}+D\gamma-3)]\}. \end{aligned} \tag{89}$$

The term in γ is small and slowly varying, and has been neglected in Eq. (88) compared with the rapidly varying α term.

Equation (88) is identical with the result (44) obtained from the simple theory of Sec. V. Equation (89)

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[8] C. Kittel, Phys. Rev. **73**, 155 (1948), Sec. IV.

shows that the simple theory is incorrect for frequencies far off resonance, even when the sample is thick and the relaxation time long so that the assumption $\lambda \gg a \gg 1$ is valid. However, the complicated and low-intensity wings of the absorption line will be difficult to measure with any accuracy. In the central part of the line, which is all that can be clearly seen in the experiments, the shape will be given by Eq. (88) provided the frequency ω is high enough so that $U \gg D$. As the frequency ω is lowered, D increases and the shape will gradually go over into Eq. (85).

VIII. THEORY INCLUDING SURFACE RELAXATION

The theory so far developed falls short of realism in one respect. The relaxation time U is supposed to take account of the disorientation of electron spins in collisions with lattice vibrations and other electrons. It is likely that such a relaxation time will exist and be roughly independent of position throughout the interior of the metal. However, an electron colliding with the metal surface may be subjected to stronger spin-dependent forces, arising from surface irregularities or paramagnetic surface impurities, than an electron in the interior. An electron colliding with the surface will therefore have a certain probability ϵ of spin disorientation during the collision, in addition to the steady probability U^{-1} per unit time which exists for all electrons. We assume this ϵ to be an average value taken over all collisions with the surface; it is not necessary that the probability be the same for electrons incident at different angles. In this section we shall recalculate the results of Secs. VI and VII, including the effects of surface relaxation as specified by the parameter ϵ.

The effect of the surface relaxation is to change the boundary condition Eq. (9) for the diffusion equation. The probability distribution $F(\mathbf{r},t)$ will now describe the probability of finding, at the point $\mathbf{r}$ at time t, an electron which has not suffered a spin disorientation by surface collision before the time t. Thus $F(\mathbf{r},t)$ describes a diffusion of particles which are lost with probability ϵ every time they hit the metal surface. To find the correct boundary condition, we observe that the mean velocity of the particles at any point is

$$\bar{v} = -\tfrac{1}{3}v\Lambda[\mathrm{grad}F/F], \tag{90}$$

at least when averaged over a time long compared with the collision time τ. Therefore, the number of particles lost per second per unit area of metal surface is

$$\tfrac{1}{3}v\Lambda(\mathbf{n}\cdot\mathrm{grad}F), \tag{91}$$

where $(\mathrm{grad}F)$ is taken at a point just inside the surface, and $\mathbf{n}$ is the inward normal vector. But the number of particles striking the surface per second per unit area is $\frac{1}{4}vF$, and the number lost is by hypothesis $\frac{1}{4}\epsilon vF$. Equating this number to Eq. (91), we find the desired boundary condition

$$\mathbf{n}\cdot\mathrm{grad}F = gF, \quad g = (3\epsilon/4\Lambda). \tag{92}$$

The Green's function G is now given by Eq. (52), where the ψ_n are still solutions of Eq. (48) but with the boundary condition,

$$\mathbf{n}\cdot\mathrm{grad}\psi_n = g\psi_n, \tag{93}$$

instead of Eq. (49). Specializing to the case of a flat plate and solutions even in $(z-\frac{1}{2}\theta)$, we find instead of Eqs. (56) and (57):

$$\psi_n = [\epsilon_n/\theta]^{\frac{1}{2}} \sec u_n \cos[2u_n(z-\tfrac{1}{2}\theta)/\theta], \tag{94}$$

$$\mu_n = 4u_n^2\theta^{-2}, \quad \epsilon_n = 2u_n^2(u_n^2+Q^2+Q)^{-1}, \tag{95}$$

where $u_0, u_1, u_2, \cdots$, are the positive roots of the equation

$$x\tan x = Q, \quad Q = \tfrac{1}{2}g\theta = (3\epsilon\theta/8\Lambda). \tag{96}$$

With these definitions, the results of Sec. VI up to Eq. (59) inclusive are still valid. However, the integration by parts which led to Eq. (60) now gives an additional term which by Eq. (93) reduces to

$$-2g[\epsilon_n/\theta]^{\frac{1}{2}}\mathbf{H}_{10}. \tag{97}$$

The additional term will be carried into the subsequent equations (66), (67) if $(\mathbf{n}\times\mathbf{E}_0)$ is replaced by

$$(\mathbf{n}\times\mathbf{E}_0) + (cg/4\pi\sigma)\mathbf{H}_{10}. \tag{98}$$

Therefore, Eqs. (69) to (71) will be correct with the new definitions of μ_n and ϵ_n, provided Z is replaced by

$$Z + (g/\sigma). \tag{99}$$

The formulas for the line shape are now, instead of Eqs. (71)–(73),

$$Z = (2/\sigma\theta)\{F-Q+\tfrac{1}{2}\pi\nu\chi a^2UF^2[fG(\alpha)-f'G(\gamma)]\}, \tag{100}$$

$$F = [2\sum_0^\infty u_n^2(u_n^2+Q^2+Q)^{-1}(u_n^2-u^2)^{-1}]^{-1}, \tag{101}$$

$$G(\alpha) = -4iu^2\sum_0^\infty u_n^2(u_n^2+Q^2+Q)^{-1} \times(u_n^2-u^2)^{-2}(u_n^2-w^2)^{-1}. \tag{102}$$

The sums can be evaluated in closed form by the following simple physical argument. The value of Z for $\chi=0$ is obviously independent of Q, since for zero magnetization it does not matter how rapidly the spins are disoriented. Therefore, $(F-Q)$ in Eq. (100) is equal to F given by Eq. (76), and the sum of the series (101) is

$$F = Q - u\tan u. \tag{103}$$

This result can be checked by direct evaluation of Eq. (101) using contour integration. Knowing Eq. (103), we deduce at once from Eq. (95):

$$G(\alpha) = iu(d/du)\{(w^2-u^2)^{-1}[F^{-1}(u)-F^{-1}(w)]\}$$
$$= \frac{i}{(w^2-u^2)^2}\left[\frac{2u^2}{w\tan w-Q}+\frac{w^2-3u^2}{u\tan u-Q} + (w^2-u^2)\frac{u^2\sec^2 u+Q}{(u\tan u-Q)^2}\right]. \tag{104}$$

We next briefly investigate the effects of surface relaxation on the line shapes of Sec. VII.

(a) Thin Case

$$\lambda \leq 4.$$

In this case, Q is small compared to 1, and the smallest root u_0 of Eq. (89) is approximately equal to $Q^{\frac{1}{2}}$. Keeping only the term $n=0$ in the series (101), (102), we find instead of Eq. (78):

$$Z=\frac{2\pi\theta\omega}{c^2}\left[-i+2\pi\nu\chi U\left(\frac{f}{1+\zeta-iU\alpha}-\frac{f'}{1+\zeta-iU\gamma}\right)\right], \tag{105}$$

$$\zeta=(U/T_S), \quad T_S=(2\theta/\epsilon v). \tag{106}$$

The surface relaxation leaves the Lorentz shape of the line unchanged, but increases the width from U^{-1} to $(U^{-1}+T_S^{-1})$. This was to be expected, since T_S is the average relaxation time for an electron travelling back and forth between the two surfaces of the plate and disorienting its spin with probability ϵ at each impact.

For a metal sample of arbitrary shape, and dimensions small compared with the skin depth, Eq. (105) will still hold with

$$T_S=4V/\epsilon vS, \tag{107}$$

where V is the volume and S the surface area of the metal. The physical interpretation of T_S as a relaxation time is the same as before. For example, for a small sphere of radius r,

$$T_S=4r/3\epsilon v. \tag{108}$$

(b) Thick Case

$$\lambda \geq 4, \quad a \geq 4.$$

Putting the approximations $\tan w=\tan u=i$ into Eq. (104), we find that Eq. (81) holds with

$$L=[R^2(x+i)-1]^{-2}\left[\frac{(2+(1+i)R\psi)^2}{R(\xi+i\eta+i\psi)}-2R\psi+(1-i)[R^2(x+i)-3]\right], \tag{109}$$

where we have written

$$\psi=(2Q/a)=\epsilon(3U/8\tau)^{\frac{1}{2}}. \tag{110}$$

The ratio (τ/U) is the probability of spin disorientation for an electron in a single scattering collision inside the metal, and in Li and Na may be of the order of 10^{-5}, while ϵ is the corresponding probability for a collision at the surface and may be larger by a considerable factor. We do not know *a priori* whether ψ will be large or small compared to 1.

(*b*1) *Thick case, broad natural line*

$$a \gg \lambda \gg 1, \quad R \gg 1.$$

In this case, the ψ-dependent terms in Eq. (109) are negligible and we still have the results (84) and (85).

(*b*2) *Thick case, narrow natural line*

$$\lambda \gg a \gg 1, \quad R \ll 1.$$

In this case, Eq. (109) gives for the central part of the line

$$L=4R^{-1}(\xi-i\eta-i\psi)[\xi^2+(\eta+\psi)^2]^{-1}. \tag{111}$$

Thus the central part of the observed absorption line has the shape given by

$$P=\tfrac{1}{4}\delta\omega|\mathbf{H}_{10}|^2\{(1/2\pi)-\nu\chi f(DU)^{\frac{1}{2}}(\operatorname{sgn}\alpha)\times[(1+U^2\alpha^2)^{\frac{1}{2}}-1]^{\frac{1}{2}}[(1+U^2\alpha^2)^{\frac{1}{2}}+\psi((1+U^2\alpha^2)^{\frac{1}{2}}+1)^{\frac{1}{2}}+\tfrac{1}{2}\psi^2]^{-1}\}. \tag{112}$$

If $\psi \ll 1$, this reduces to Eq. (88). For $\psi \gg 1$, the line has a different limiting shape:

$$P=\tfrac{1}{4}\delta\omega|\mathbf{H}_{10}|^2\{(1/2\pi)-2\nu\chi f\psi^{-2}(DU)^{\frac{1}{2}}(\operatorname{sgn}\alpha)\times[(1+U^2\alpha^2)^{\frac{1}{2}}-1]^{\frac{1}{2}}\}, \tag{113}$$

but is still approximately antisymmetrical about its center.

For making precise comparisons of theory with experiment in the thick case, the exact Eq. (109) must be used. However, it seems likely, from the rather sharp lines observed in experiments with small particles of metal,[9] that ψ is small compared to 1. If this is so, then the only effect of surface relaxation is a possible broadening of the lines in the thin case, and the results of Sec. VII will apply to the thick case without serious error.

IX. CONCLUSIONS

The results of this analysis may be summarized as follows:

(1) For thin samples ($\theta < 4\delta$), the absorption line has the usual symmetrical shape $[1+\alpha^2\bar{U}^2]^{-1}$, with a width $\bar{U}^{-1}=U^{-1}+T_S^{-1}$, where U and T_S are the volume and surface relaxation times.

(2) For thick samples the line has a central structure of width equal to the natural width U^{-1}, with wings extending over a band D^{-1} if $D<U$.

(3) The central structure is always markedly more intense than the wings, so that under normal experimental circumstances the apparent width of the line will be of the order of U^{-1}.

(4) The characteristic effect of electron diffusion is not to broaden the line but to make a radical change in its shape.

(5) For thick samples with a broad natural width

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[9] G. Feher and A. F. Kip, reference 1, Appendix A.

($\theta \gg \delta$, $D \gg U$), the line has the shape

$$[(1-\alpha U)/(1+\alpha^2 U^2)].$$

(6) For thick samples with a narrow natural width ($\theta \gg \delta$, $U \gg D$), and not too strong surface relaxation ($\psi \ll 1$), the central part of the line has the antisymmetrical shape

$$\operatorname{sgn}\alpha\left(\frac{(1+U^2\alpha^2)^{\frac{1}{2}}-1}{1+U^2\alpha^2}\right)^{\frac{1}{2}}. \tag{114}$$

(7) For thick samples, the intensity of the line at the center is reduced by the diffusion effect by a factor of the order of $(D/U)^{\frac{1}{2}}$. When $D \ll U$, the integrated intensity of the line comes mainly from the diffuse wings and not from the center.

(8) Results (1)–(7) are independent of the shape of the metal, although the detailed calculations of Secs. VI–VIII apply only to flat plates.

Experimentally, it is found convenient to measure not the actual energy absorption for a given **H** but the change in absorption resulting from a small modulation of **H**. Thus the measured quantity is the derivative of P with respect to ν. This has the effect of further accentuating the center of the line as compared with the wings. In particular, the shape (114) appears as a very strong symmetrical peak with shallow minima (depth about 6 percent of the central peak) on either side.

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Oscillatory Thermomagnetic Properties of a Bismuth Single Crystal at Liquid Helium Temperatures

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Measurements of the thermoelectric power, thermal conductivity, and electrical resistance have been made on a bismuth single crystal in magnetic fields up to 13 kilogauss at liquid helium temperatures. The results for two newly discovered effects, namely the oscillatory magnetic field dependence of both the thermoelectric power and the thermal conductivity, are presented in detail. The crystal was mounted transverse to the field with the trigonal axis parallel to the crystal length. The heat current was also parallel to the crystal length. Most of the data were taken with the magnetic field parallel to one of the crystalline binary axes where only one oscillating component was found. For this orientation the oscillations in the two thermomagnetic properties were periodic in H^{-1} with a period of 7.1×10^{-5} gauss^{-1}. This result is compared to the calculated period obtained from susceptibility oscillations (de Haas-van Alphen effect) of bismuth and found to agree very well. Temperature and field dependence of the amplitude of the oscillatory effects are discussed.

INTRODUCTION

THE thermal and electrical properties of bismuth have a long history of peculiar behavior especially when placed in a magnetic field. These peculiarities are emphasized when low temperatures are combined with strong magnetic fields. Thus, the pioneer work of de Haas and van Alphen[1] on the oscillatory susceptibility of Bi opened the door to susceptibility, magnetoresistance, and Hall effect experiments on many other metal single crystals. The latter two properties fall in the catagory of galvanomagnetic effects. Such measurements have been made on Bi and have revealed that both the magnetoresistance[2] and Hall coefficient[3] exhibit the same type of magneto-oscillatory behavior as the susceptibility. However, there has been only a little work done[4,5] on the thermomagnetic properties of Bi single crystals at low temperatures.

The present investigation was undertaken to determine if the thermoelectric power and thermal conductivity of Bi exhibit the same type of magneto-oscillatory behavior as do the susceptibility, magnetoresistance, and Hall coefficient. On the basis of thermodynamic arguments relating the galvanomagnetic and thermomagnetic coefficients,[6] it was believed that such properties as the thermoelectric power and thermal conductivity would show the oscillatory dependence on the magnetic field strength. Bismuth was chosen as the metal to study since its magnetic behavior is much more pronounced than most other metals at

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