251 (1964).
[5]S. Sugano and Y. Tanabe, J. Phys. Soc. Japan 20, 1155 (1965).
[6]J. Hubbard, D. E. Rimmer, and F. R. A. Hopgood, Proc. Phys. Soc. (London) 88, 13 (1966).
[7]P. O. Offenhartz, J. Chem. Phys. 47, 2951 (1967).
[8]P. O. Offenhartz, J. Am. Chem. Soc. 91, 5699 (1969).
[9]R. G. Shulman and S. Sugano, Phys. Rev. 130, 506 (1963).
[10]K. Knox, R. G. Shulman, and S. Sugano, Phys. Rev. 130, 512 (1963).
[11]D. Ellis, A. J. Freeman, and P. Ros, Phys. Rev. 176, 688 (1968); H. M. Gladney and A. Villard, *ibid.* 180, 385 (1963).
[12]C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).
[13]C. Froese, Proc. Cambridge Phil. Soc. 53, 206 (1957).
[14]R. E. Watson, MIT Solid-State and Molecular Theory Group, Technical Report No. 12, 1959 (unpublished).
[15]C. C. J. Roothaan, Rev. Mod. Phys. 32, 179 (1960).
[16]I. G. Csizmadia, H. C. Harrison, J. W. Moskowitz, S. Seung, B. T. Sutcliff, and M. Barnett, MIT Cooperative Computing Laboratory, Technical Note No. 36, 1963 (unpublished).
[17]B. Kleinman and C. W. Kern (unpublished).
[18]I. Shavitt and M. Karplus, J. Chem. Phys. 36, 550 (1962).
[19]R. S. Mulliken, J. Chem. Phys. 23, 1833 (1955).
[20]For a discussion of the corresponding question in organic radicals, see J. P. Colpa, E. deBoer, D. Lazdins, and M. Karplus, J. Chem. Phys. 47, 3098 (1967).

PHYSICAL REVIEW B VOLUME 3, NUMBER 1 1 JANUARY 1971

Surface Relaxation and Quasiparticle Interactions in Conduction-Electron Spin Resonance*

M. B. Walker
Department of Physics, University of Toronto, Toronto, Ontario, Canada
(Received 16 February 1970; revised manuscript received 16 September 1970)

A modified Bloch equation for the conduction-electron magnetization density is developed starting from the Landau-Silin kinetic equation, and a boundary condition describing surface relaxation is formulated. These basic results include the effects of the drift magnetization current density and predict relaxation of the magnetization density to the instantaneous local value of the applied microwave field. The conditions of validity of this and previous theories are critically discussed, and it is shown that in the collision-dominated regime, for example, the modified Bloch equation is valid only under classical-skin-effect conditions. A way of obtaining useful results for anomalous-skin-effect conditions is then outlined. Formulas for the surface impedance and for the amplitude of the microwave field transmitted through a thin metallic slab are derived.

I. INTRODUCTION

The observation of spin-wave excitations in sodium and potassium metals by Schultz and Dunifer[1] has stimulated considerable theoretical interest[2,3] in conduction-electron spin resonance (CESR). Many, but not all, of the interesting features of the data[1] are explained by Platzman and Wolff's adaptation of the Landau-Silin Fermi-liquid theory.[4] Also, a conventional theoretical interpretation of certain anomalous features of the CESR experiments of Walsh, Rupp, and Schmidt[5] on potassium is lacking, although Overhauser and de Graaf[5] have suggested that the anomalous behavior may be due to charge density waves. Thus, it appears that, while current theories of CESR have had their successes, they merit closer examination, particularly in the limit of low temperatures and very pure metals.

The origin of many of our present ideas concerning CESR is Dyson's famous paper.[6] In it, he points out that each electron spin diffuses into and out of the skin depth many times before it relaxes, and argues that this is the reason such narrow lines are observed in CESR. He also puts forward a quantitative theory of the surface impedance. In another important development, Azbel', Gerasimenko, and Lifshitz[7] showed that electron spins could be excited by a microwave field in the skin depth on one side of a thin metallic slab, and could then, after diffusing across the slab, emit radiation out the far side. A comprehensive review of both theoretical and experimental developments has been given by Walsh.[8]

In this paper, a theory of CESR is developed which has as its basis the Landau-Silin theory of a Fermi liquid. It is shown that, in a linear theory, long-wavelength oscillations of the magnetization density are governed by a modified Bloch equation similar to that suggested by Torrey.[9] Relaxation of the conduction-electron spins at a surface is described by an appropriate boundary condition on the magnetization density, and solutions of the modified Bloch equation consistent with the boundary condition are obtained for cases of practical

interest. This paper presents extensions of previous theories of CESR in several respects, as will now be discussed.

To describe situations where the diffusion of the spin-magnetic moments is important, Torrey has developed a modification of the Bloch equation. [9] He pointed out that the magnetization current density is a sum of two terms, a drift current proportional to the force on a magnetic moment in an inhomogeneous magnetic field (i.e., proportional to the magnetic field gradient) and a diffusion current proportional to the gradient of the magnetization density. In contrast to the problem considered by Torrey, the drift currents can be quite large in metals due to the fact that the skin effect gives rise to large magnetic field gradients, and a theory of CESR should therefore include them.

It was Kaplan[10] who recognized the relation of Torrey's equation to the CESR problem; unfortunately, however, Kaplan did not include the drift currents in his analysis. Since Dyson's initial equation for the magnetization density[6] and Kaplan's version of the modified Bloch equation can be shown to be equivalent, [11] it is clear that drift currents are neglected in Dyson's work, and in the work of subsequent authors[2,11,12] making use of Dyson's initial equation. The drift currents appear naturally in the formulation of the problem used in this paper.

Due to the work of Platzman and Wolff, [2] it is now known that the spin oscillations of a Fermi liquid are qualitatively different according as the parameter

$$p = \left|(B_0 - B_1)\omega_0\tau_0/(1+B_0)\right| \qquad (1.1)$$

(where τ_0 is the orbital collision time of the electrons, ω_0 is the resonance frequency, and the B_n's are the Landau Fermi-liquid parameters) is greater or less than unity. If τ_0 is sufficiently long that $p \gg 1$, we are said to be in a collisionless regime and propagating spin-wave modes exist. On the other hand, if $p \ll 1$, we are by definition in the collision-dominated regime, and the spin density has a diffusive behavior. This behavior is accounted for in the modified Bloch equation by allowing the diffusion constant to be a frequency-dependent complex number; in the collision-dominated regime the diffusion constant is purely real, whereas in the collisionless regime the diffusion constant is a pure imaginary number.

The assumption that the diffusion current is proportional to the gradient of the magnetization density is valid only if the magnetization density is slowly varying spatially. Otherwise higher-order spatial derivatives of the magnetization density will also play a part in determining the diffusion current. The question of when it is necessary to take into account higher-order contributions to the magnetization current density is discussed briefly in Sec. VI. It is found that, in the collision-dominated regime, the condition for higher-order corrections to be negligible is

$$\lambda \gg v\tau_0 \ , \qquad (1.2)$$

where λ is a wavelength characteristic of the spatial variation of the magnetization density and v is the Fermi velocity. Note that $v\tau_0$ is the electron mean free path. In the collisionless regime, the corresponding condition is

$$\lambda \gg \frac{v(1+B_0)}{\omega_0\left|(B_0-B_1)(B_0-B_2)\right|^{1/2}} \ . \qquad (1.3)$$

Since, in simple metals, the B_n's have magnitudes much smaller than unity, [1] condition (1.3) is more restrictive than the condtion that λ be greater than the cyclotron radius. Conditions (1.2) and (1.3) are also the conditions which must be satisfied for the modified Bloch equation to be valid.

In a paper concerning the interpretation of CESR experiments Lampe and Platzman[12] calculated quantities such as the surface impedance and the amplitude of the microwave field transmitted through a thin metallic slab. The amplitudes of the experimentally measurable quantities were expressed in terms of the surface impedance, which, if the skin effect is anomalous, should be taken to be the anomalous-skin-effect surface impedance. A major limitation of the Lampe-Platzman theory is the assumption that the diffusive motion of the magnetization density can be calculated assuming a diffusion current proportional to the gradient of the magnetization density. As has just been pointed out, this assumption limits the validity of the theory to the classical-skin-effect regime [see Eq. (1.2)].

This limitation can be overcome by noting that the oscillating magnetization density in a metal is a sum of two different modes of motion, the relatively long-wavelength spin-wave modes, and the short-wavelength skin-effect modes. The spatial variation of the long-wavelength spin-wave modes can be determined by the modified Bloch equation, and this allows the position and shape of the observed resonance lines to be calculated. However, because the short-wavelength skin-effect modes cannot, under anomalous-skin-effect conditions, be calculated using the modified Bloch equation [see conditions (1.2) and (1.3)], it turns out that the final formulas for the experimentally measurable quantities contain a factor of unknown magnitude. The relevant calculations are discussed in Sec. V.

At low temperatures in very pure metals, the bulk relaxation time becomes sufficiently long that collisions with the metallic surfaces can become the dominant relaxation mechanism for the conduction-electron spins. The experiments of Schultz

and Latham[13] are an excellent example of this phenomenon. A theory of surface relaxation is presented in Sec. IV. There, a boundary condition is formulated which states essentially that the effective flux of magnetization out of the surface of the metal due to surface relaxation is $2\beta\epsilon$ times the number of particles striking the surface per unit time (β is the Bohr magneton and ϵ is the probability that an electron's spin flips when it hits the surface).

Surface relaxation has been discussed previously by Dyson, but our analysis differs from Dyson's in some important points. First, our discussion is carried out within the framework of Fermi-liquid theory. Second, by noting that is the instantaneous local quasiparticle energy which is conserved in the collision of a quasiparticle with the surface, a boundary condition is found which has the property of giving zero flux of magnetization out of the surface when the magnetization density at the surface is in instantaneous local equilibrium. Third, it is shown that, in the limit as the probability of a spin flip ϵ tends to unity, the magnetization density at the surface is maintained in thermal equilibrium; this leads to an infinitely broad resonance line.

This third statement can be understood by computing the z component of the magnetization density M_z at the surface for the case where the applied magnetic field is zero. Note that $M_z=\beta[n_{\uparrow i}-n_{\downarrow i}+n_{\uparrow r}-n_{\downarrow r}]$, where $n_{\uparrow i}$ is the density of spin-up electrons incident on the surface, whereas $n_{\uparrow r}$ is the density of spin-up electrons having just been reflected from the surface; if $\epsilon=1$, $n_{\uparrow r}=n_{\downarrow i}$ and $n_{\downarrow r}=n_{\uparrow i}$, giving $M_z=0$ at the surface.

The results of this paper, which combines a discussion of so-called Fermi-liquid theory effects with a theory of surface relaxation, will allow the interpretation of experiments carried out under a wide range of experimental conditions. In particular, it is now possible to analyze experiments carried out at low temperatures, on simple metals of sufficiently high purity that spin waves exist and surface relaxation is important.[14]

II. TORREY'S MODIFIED BLOCH EQUATION

To analyze CESR experiments, Maxwell's equations must be solved, and Kaplan[10] suggested using the equation of motion

$$\frac{\partial\vec{M}}{\partial t}=\gamma\vec{M}\times\vec{H}-\frac{\vec{M}}{\tau_s}+D\vec{\nabla}^2\vec{M} \tag{2.1}$$

as the constitutive relation between $\vec{M}$ and $\vec{H}$. This approach, which is equivalent to that of Dyson,[6] of Lampe and Platzman,[12] and even of Platzman and Wolff[2] if the diffusion constant D is interpreted properly, has the advantage of allowing a relatively elementary mathematical analysis of the problem.[11] However, arguments given by Torrey[9] suggest that certain corrections should be made to Eq. (2.1). These arguments can easily be adapted to the case of a degenerate electron fluid, and will be presented here since they provide a very simple understanding of one of the basic equations of this paper [Eq. (2.8)].

Let n_σ be the number of electrons in the spin state σ ($\sigma=\pm1$ refers to the spin quantum number). The current densities of the two types of particles are each written as the sum of a drift current and a diffusion current, i.e.,

$$\vec{j}_\sigma=n_\sigma\vec{v}_\sigma-D\vec{\nabla}n_\sigma\ . \tag{2.2}$$

Here, $\vec{v}_\sigma$ is the drift velocity of particles in the state σ. It was Onsager who originally pointed out the desirability of including the drift currents in this expression.[9] The drift velocity is taken to be proportional to the force $\vec{f}_\sigma$ on particles of type σ in an inhomogeneous magnetic field; thus

$$\vec{v}_\sigma=\mu\vec{f}_\sigma=\mu\sigma\vec{\nabla}(\beta H_z)\ . \tag{2.3}$$

The coefficient of proportionability μ is called the mobility and H_z is the z component of the magnetic field.

In thermal equilibrium the total current density $\vec{j}_\sigma$ must vanish. Since, for noninteracting electrons in thermal equilibrium,

$$\vec{\nabla}n_\sigma=\rho(\epsilon)\vec{\nabla}(\sigma\beta H_z)\ , \tag{2.4}$$

where $\rho(\epsilon)$ is the number of electron states per unit volume per unit energy, the mobility must be related to the diffusion constant (to lowest order in the magnetic field) by the relation

$$\mu n_{\sigma 0}=D\rho(\epsilon)\ , \tag{2.5}$$

where $n_{\sigma 0}$ is n_σ in zero magnetic field. Equation (2.5), valid for a degenerate electron fluid, is the analog of the Einstein relation $\mu=D/kT$ which is valid in the nondegenerate case considered by Torrey.

The current density $\vec{\Lambda}_z$ of the z component of the magnetization density can now be calculated, with the result

$$\vec{\Lambda}_z=\beta\textstyle\sum_\sigma\sigma\vec{j}_\sigma=-D\vec{\nabla}(M_z-\chi H_z)\ , \tag{2.6}$$

where $\chi=2\beta^2\rho(\epsilon)$ is the Pauli susceptibility. The rate of change of the magnetization density due to this flux is, by the continuity equation,

$$\frac{\partial M_z}{\partial t}\Big|_{\text{flux}}=-\vec{\nabla}\cdot\vec{\Lambda}_z=D\vec{\nabla}^2(M_z-\chi H_z)\ . \tag{2.7}$$

Similar expressions hold for M_x and M_y. Thus the Bloch equation should be written

$$\frac{\partial\vec{M}}{\partial t}=\gamma\vec{M}\times\vec{H}-\frac{\vec{M}-\chi\vec{H}}{\tau_s}+D\vec{\nabla}^2(\vec{M}-\chi\vec{H})\ . \tag{2.8}$$

An important property of Eq. (2.8) not possessed by Eq. (2.1) is that for fields varying sufficiently

slowly the time derivative $\partial\vec{M}/\partial t$ can be neglected, $\vec{M}(\vec{r}, t) = \chi\vec{H}(\vec{r}, t)$ is a solution. Alternatively, one can say that the magnetization density relaxes towards the instantaneous local value of the magnetic field.

Equation (2.8) has also previously been obtained by Brinkman and Englesberg[15] starting from the Landau Fermi-liquid kinetic equation and assuming that no uniform external magnetic field is present. In Sec. III, the extension of Eq. (2.8) to the case where a uniform external field is present is derived starting from the Landau-Silin kinetic equation.

A question which arises now is whether the additional term in the modified Bloch equation (2.8) relative to Eq. (2.1) is sufficiently small that it can be dropped, so that previous theories of CESR are immediately applicable, or whether this additional term is sufficiently large that it must be retained. The total magnetic field in the metal is $\vec{H}(\vec{r}, t) = \vec{H}_0 + \vec{H}_1(\vec{r}, t)$, where $\vec{H}_0$ is a strong static uniform field and $\vec{H}_1(\vec{r}, t)$ is the microwave field; similarly, $\vec{M}(\vec{r}, t) = \vec{M}_0 + \vec{M}_1(\vec{r}, t)$. The microwave field exerts a torque on the magnetization density of magnitude $\vec{M}_0 \times \vec{H}_1$. It is evident from Eq. (2.8) that the term $-(D/\gamma)\vec{\nabla}^2(\chi\vec{H}_1)$ also acts as an effective torque; since it is due to drift currents, it will be called the drift torque. To compare the magnitudes of these two torques note that the microwave field in the metal varies significantly in a distance the order of the skin depth δ. Thus

$$\left| \frac{D\vec{\nabla}^2(\chi\vec{H}_1)}{\gamma\vec{M}_0 \times \vec{H}_1} \right| \approx \frac{2D}{\omega_0\delta^2} \ , \tag{2.9}$$

where $\omega_0 = -\gamma H_0$ and $M_0 = \chi H_0$ have been used. If $2D/\omega_0\delta^2 > 1$, the drift torque due to the skin-effect field is greater than the torque $\vec{M} \times \vec{H}_1$ and cannot be ignored.

Now consider CESR in lithium at room temperature, the relevant parameters for which are (see Lewis and Carver[16]) $D = \frac{1}{3}v^2\tau_0 = 50\ \mathrm{cm^2\ sec^{-1}}$, $\omega_0 = 5 \times 10^{10}\ \mathrm{sec^{-1}}$, and $\delta = 1.5 \times 10^{-4}$ cm, which gives

$$2D/\omega_0\delta^2 = 10^{-1} \quad \text{at } 273\ ^\circ\mathrm{K} \ . \tag{2.10}$$

Thus, for lithium at room temperature, the drift torque is small enough that it can be neglected.

At liquid-helium temperatures the situation is different. Since, at 4.2 °K, in relatively pure crystals the orbital relaxation time τ_0 will be several orders of magnitude longer than at 273 °K, it is easily seen by comparison with Eq. (2.10) that

$$2D/\omega_0\delta^2 \gg 1 \quad \text{at } 4.2\ ^\circ\mathrm{K} \ . \tag{2.11}$$

Thus, at 4.2 °K, it is necessary to revise current theories to include drift currents.

III. DERIVATION OF MODIFIED BLOCH EQUATION STARTING WITH LANDAU-SILIN KINETIC EQUATION

In a series of papers,[17] Landau developed a semiphenomenological theory of a degenerate Fermi liquid. The extension of the theory to the case of a charged Fermi liquid is due to Silin.[4,18] Of particular interest here is the fact that Silin showed how this theory could be used to discuss the spin-dependent oscillations of an electron fluid in a static uniform magnetic field. Platzman and Wolff[2] and Ying and Quinn[3] have further extended the analysis of the kinetic equation with particular reference to the interpretation of CESR experiments. It should also be remarked that the problem of spin oscillations in liquid He^3 is somewhat similar to the problem discussed here, and has been treated by Leggett,[19] who was particularly interested in developing a nonlinear macroscopic equation.

In his book,[20] Nozières gives micoscopic derivation of the kinetic equation in the case that there is no uniform static field present. A recent paper by Van Zandt[21] derives the kinetic equation in the case where a uniform magnetic field is present.

To follow the development of this section, a familiarity with the paper of Silin[4] (whose notation is followed here) is necessary. Our starting point is Eq. (5) of Silin's paper for the spin distribution function $\vec{\sigma}(\vec{p}, \vec{r}, t)$, namely,

$$\frac{\partial\vec{\sigma}}{\partial t} + \left[\vec{v} \circ \frac{\partial}{\partial\vec{r}} + \frac{e}{c}(\vec{v} \times \vec{H}_0) \cdot \frac{\partial}{\partial\vec{p}} + \frac{2\beta}{1 + B_0}\vec{H}_0 \times \right] \times \left[\delta\vec{\sigma} - \frac{\partial f_0}{\partial\epsilon}\delta\vec{\epsilon}_2 \right] = \vec{J} \ . \tag{3.1}$$

The magnetization density can be found from $\vec{\sigma}$ by

$$\vec{M}(\vec{r}, t) = (2\pi)^{-3}\beta \int d^3p\ \vec{\sigma}(\vec{p}, \vec{r}, t) \ , \tag{3.2}$$

while the energy $\delta\vec{\epsilon}_2$ is given by

$$\delta\vec{\epsilon}_2(\vec{p}, \vec{r}, t) = -\beta\vec{H}_1(\vec{r}, t) + (2\pi)^{-3} \int d^3p'\ \psi(\vec{p}, \vec{p}')\delta\vec{\sigma}(\vec{p}', \vec{r}, t) \ . \tag{3.3}$$

For $\vec{p}$ and $\vec{p}'$ on the Fermi surface, the interaction $\psi(\vec{p}, \vec{p}')$ is given by

$$\frac{2\psi(\vec{p}, \vec{p}')}{(2\pi)^3} = \sum_l \frac{(2l+1)B_l v}{4\pi p^2} P_l(\cos\hat{\theta}) \ , \tag{3.4}$$

where the P_l's are Legendre polynomials, $\hat{\theta}$ is the angle between $\vec{p}$ and $\vec{p}'$, and the B_n's are called the Landau Fermi-liquid parameters. In (3.4), a departure from Silin's notation has been made in favor of that of Platzman and Wolff. It should be noted that Eq. (3.1) is a linearized version of the original kinetic equation.[4]

Now define the z axis of a coordinate system to be along $\vec{H}_0$, and also define the unit vectors $\vec{\epsilon}_\alpha$ ($\alpha = 0, \pm 1$) by $\vec{\epsilon}_0 = \vec{\epsilon}_z$ and $\vec{\epsilon}_{\pm 1} = (\vec{\epsilon}_x \pm i\vec{\epsilon}_y)/\sqrt{2}$. Thus

$$\delta\vec{\sigma} = \textstyle\sum_\alpha \delta\sigma_{-\alpha}\vec{\epsilon}_\alpha \ , \tag{3.5}$$

where $\delta\sigma_{\pm1} = \delta\sigma_{\pm} = (\delta\sigma_x \pm i\delta\sigma_y)/\sqrt{2}$. The components of Eq. (3.1) can now be written

$$\frac{\partial \delta\sigma_\alpha}{\partial t} + \left[\vec{v}\cdot\frac{\partial}{\partial \vec{r}} + \omega_c \frac{\partial}{\partial \phi} - i\alpha\Omega_0\right]\delta\bar{\sigma}_\alpha = J_\alpha \quad , \tag{3.6}$$

where

$$\delta\bar{\sigma}_\alpha = \delta\sigma_\alpha - \frac{\partial f_0}{\partial \epsilon}\,\delta\epsilon_{2\alpha} \tag{3.7}$$

is the departure of the distribution function from its instantaneous local equilibrium value, $\Omega_0 = \omega_0/(1+B_0)$, $\omega_0 = 2\beta H_0$, $\omega_c = eH_0/m^*c$, $m^* = p/v$, and ϕ is the angle shown in Fig. 1. Now introduce the functions $g_\alpha(\vec{p}, \vec{r}, t)$ defined for $\vec{p}$ on the Fermi surface by

$$\delta\sigma_\alpha = -\frac{\partial f_0}{\partial \epsilon}\, g_\alpha \tag{3.8}$$

and assume that all quantities have the time dependence $e^{-i\omega t}$. Equation (3.6) finally reduces to

$$-i\omega g_\alpha + \left[\vec{v}\cdot\frac{\partial}{\partial \vec{r}} + \omega_c\frac{\partial}{\partial\phi} - i\alpha\Omega_0\right]\bar{g}_\alpha = -\frac{\bar{g}_\alpha - \langle\bar{g}_\alpha\rangle}{\tau_0'} - \frac{\langle\bar{g}_\alpha\rangle}{\tau_s'} \quad , \tag{3.9}$$

where

$$\bar{g}_\alpha = g_\alpha + \delta\epsilon_{2\alpha} \tag{3.10}$$

and

$$\langle\bar{g}_\alpha\rangle = (4\pi)^{-1}\int d\Omega_p\, \bar{g}_\alpha(\vec{p}, \vec{r}, t) \tag{3.11}$$

is an angular average of $\bar{g}_\alpha$ over all directions of momentum. The collision integral J_α has been replaced by the simple relaxation-time approximation on the right-hand side of Eq. (3.9). Evidently τ_0' is a characteristic momentum reorientation time of the conduction electrons, whereas τ_s' is a characteristic spin reorientation time.

Equation (3.9) will be assumed to have a solution of the form

$$g_\alpha = g_{0\alpha} + \vec{v}\cdot\vec{g}_{1\alpha} \quad , \tag{3.12}$$

where $g_{0\alpha}$ and $\vec{g}_{1\alpha}$ are independent of the momentum direction. From this assumption, it follows that

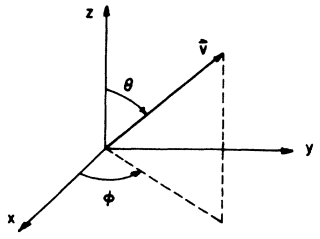

FIG. 1. Definition of the angles θ and ϕ.

$$\delta\epsilon_{2\alpha} = -\beta H_{1\alpha} + B_0 g_{0\alpha} + B_1\vec{g}_{1\alpha}\cdot\vec{v} \quad . \tag{3.13}$$

When Eqs. (3.10), (3.12), and (3.13) are substituted into (3.9), and (3.9) is multiplied by $\vec{v}$ and averaged over all directions of momentum, the result can be solved for $g_{1\alpha\gamma}$ (the components $\gamma = 0, \pm1$ of the vector $\vec{g}_{1\alpha}$); the result is

$$g_{1\alpha\gamma} = \frac{-i(1+B_0)}{\omega + \alpha\Omega_0(1+B_1) + \gamma\omega_c(1+B_1) + i/\tau_0} \times \vartheta_\gamma\left(g_{0\alpha} - \frac{\beta H_{1\alpha}}{1+B_0}\right) \quad , \tag{3.14}$$

where

$$\vartheta_{\pm1} = \frac{1}{\sqrt{2}}\left(\frac{\partial}{\partial x} \pm i\frac{\partial}{\partial y}\right), \quad \vartheta_0 = \frac{\partial}{\partial z} \tag{3.15}$$

and

$$\frac{1}{\tau_0} = \frac{1+B_1}{\tau_0'} \quad . \tag{3.16}$$

All that is needed now is an equation which determines $g_{0\alpha}$, since $g_{1\alpha\gamma}$ can then be found using (3.14). Note, however [see Eqs. (3.2), (3.8), and (3.12)], that a knowledge of $g_{0\alpha}(\vec{r}, t)$ is equivalent to a knowledge of $\delta M_\alpha(\vec{r}, t)$ and vice versa. We prefer to work with $\delta M_\alpha(\vec{r}, t)$ from here on, since the equation which determines it is a modified Bloch equation similar to Eq. (2.8) and can thus be readily interpreted.

The equation determining δM_α is found by multiplying Eq. (3.6) by β and integrating over all momenta. After some manipulation, one finds

$$-i\omega\delta M_\alpha = i\alpha\omega_0\delta\bar{M}_\alpha - \frac{1}{\tau_s}\,\delta\bar{M}_\alpha - \frac{\partial}{\partial\vec{r}}\cdot\vec{\Lambda}_\alpha \quad , \tag{3.17}$$

where $\tau_s = \tau_s'/(1+B_0)$, $\delta\bar{M}_\alpha = \delta M_\alpha - \chi H_{1\alpha}$ (χ is the static susceptibility of the interacting Fermi liquid) and

$$\vec{\Lambda}_\alpha = \beta\int\frac{d^3p}{(2\pi)^3}\,\vec{v}\delta\bar{\sigma}_\alpha \quad . \tag{3.18}$$

Furthermore, the components of $\vec{\Lambda}_\alpha$, namely, $\Lambda_{\alpha\gamma}$, are given by

$$\Lambda_{\alpha\gamma} = -D_{\alpha\gamma}\vartheta_\gamma\delta\bar{M}_\alpha \quad , \tag{3.19}$$

where

$$D_{\alpha\gamma}(\omega) = \frac{i(1+B_0)(1+B_1)\,\frac{1}{3}v^2}{\omega + \alpha\Omega_0(1+B_1) + \gamma\omega_c(1+B_1) + i/\tau_0} \quad . \tag{3.20}$$

Note that $\vec{n}\cdot\vec{\Lambda}_\alpha$ gives the flux of the αth component of $\vec{M}$ through a surface in the direction of the normal $\vec{n}$ to that surface. Combining (3.17) and (3.19) gives

$$\frac{\partial M_\alpha}{\partial t} = i\alpha\omega_0\delta\bar{M}_\alpha - \frac{\delta\bar{M}_\alpha}{\tau_s}$$

$$+\left[D_{\alpha\parallel}\frac{\partial^2}{\partial z^2}+D_{\alpha\perp}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\right]\delta\bar{M}_\alpha \ , \qquad (3.21)$$

where, since the time dependence $e^{-i\omega t}$ is assumed, $(\partial/\partial t)=-i\omega$. Also,

$$D_{\alpha\parallel}=D_{\alpha 0}=i(1+B_0)(1+B_1)\tfrac{1}{3}v^2\tilde{\omega}_\alpha^{-1} \qquad (3.22a)$$

and

$$D_{\alpha\perp}=\tfrac{1}{2}[D_{\alpha+}+D_{\alpha-}]$$

$$=i(1+B_0)(1+B_1)\tfrac{1}{3}v^2\,\tilde{\omega}_\alpha[\tilde{\omega}_\alpha^2-\bar{\omega}_c^2]^{-1} \ , \qquad (3.22a)$$

where $\tilde{\omega}_\alpha=\omega+\alpha\Omega_0(1+B_1)+i/\tau_0$ and $\bar{\omega}_c=(1+B_1)\omega_c$.

Equation (3.21) is the equation appropriate to the macroscopic description of the motion of small departures of the magnetization density from thermal equilibrium. Note that, apart from the anisotropy and frequency dependence of the diffusion constant, this equation has the same form as that proposed by Torrey [i.e., Eq. (2.8)]. As pointed out in the introduction, and as will be discussed in more detail in Sec. VI, Eq. (3.21) is valid only for relatively long-wavelength disturbances.

IV. BOUNDARY CONDITION

The modified Bloch equation (3.21) for the magnetization density in a metallic body does not have a unique solution unless some boundary condition on the magnetization density at the surface is specified. The derivation of the boundary condition presented here is based on the assumption that a quasiparticle has a probability ϵ of having its spin flipped on being reflected from the surface of a metal. This is similar to Dyson's fundamental assumption.[6] Our method of deriving the boundary condition is, however, somewhat different from that of Dyson, as is our final result.

The reflection of a quasiparticle from a smooth surface is interesting because it is not necessarily specular. Consider an electron with a momentum $\vec{p}'$ which, when reflected from the metallic surface $z=0$ (see Fig. 2), has a probability $1-\epsilon$ of emerging with some momentum $\vec{p}$ and its spin still up. Due to the translational invariance of the problem in the xy plane, the momenta p_x and p_y are equal to p'_x and p'_y, respectively. On the other hand, p_z is not necessarily equal to $-p'_z$, but is determined by the condition that the quasiparticle energy is conserved, i.e.,

$$\epsilon_{\vec{p}\uparrow}+\delta\epsilon_{\vec{p}\uparrow}=\epsilon_{\vec{p}'}+\delta\epsilon_{\vec{p}'\uparrow} \ . \qquad (4.1)$$

Here, $\delta\epsilon_{\vec{p}\uparrow}$ is the additional energy of a quasiparticle with spin up due to interaction with the magnetic field and other particles. Similarly, a quasiparticle with momentum $\vec{p}''$ and spin down has a probability ϵ of undergoing a spin flip when its momentum is changed to $\vec{p}$ by reflection. Thus the density of quasiparticles emerging with momentum $\vec{p}$ and spin up is just

$$n_\uparrow(\vec{p})=(1-\epsilon)n_\uparrow(\vec{p}')+\epsilon n_\downarrow(\vec{p}'') \ . \qquad (4.2)$$

This result is not quite as obvious as it appears at first, but can be deduced from a detailed consideration of the fluxes incident on and emerging from the surface. Because the quasiparticle energy is conserved in a collision with the wall [e.g., see Eq. (4.1)], the local instantaneous thermal-equilibrium values of all three quasiparticle distribution functions appearing in (4.2) are equal. Thus

$$\delta\bar{n}_\uparrow(\vec{p})-\delta\bar{n}_\uparrow(\vec{p}')=\epsilon[\delta\bar{n}_\downarrow(\vec{p}'')-\delta\bar{n}_\uparrow(\vec{p}')] \ , \qquad (4.3)$$

where $\delta\bar{n}_\uparrow(\vec{p})$ is the departure of the distribution function from its local thermal-equilibrium value (all formulas here refer to a given point at the surface of the metal). Note that the theory will still be correct to terms linear in the applied field if we now put $-p_z=p'_z=p''_z$.

Equations similar to (4.2) and (4.3) can be found involving $n_\downarrow(\vec{p})$. Thus, one can establish the result

$$\vec{n}\cdot\left[\beta\int\frac{d^3p}{(2\pi)^3}\,\vec{v}\,\delta\bar{\sigma}_z(\vec{p})\right]$$

$$=\vec{n}\cdot\left[2\epsilon\beta\int_{(-)}\frac{d^3p}{(2\pi)^3}\,\vec{v}\,\delta\bar{\sigma}_z(\vec{p})\right] \ , \qquad (4.4)$$

where $\delta\bar{\sigma}_z=\delta\bar{n}_\uparrow-\delta\bar{n}_\downarrow$, $\vec{n}$ is the unit outward normal and $\int_{(-)}d^3p$ means an integral over the region of space for which $p_z<0$. The term on the left-hand side is just the apparent flux of magnetization across the surface due to surface relaxation. Since $\delta\sigma_z=\delta n_\uparrow-\delta n_\downarrow$, the quantity on the right-hand side is $2\beta\epsilon$ times the number of spin-up particles hitting the surface minus a similar term for spin-down particles (or rather the departures of these quantities from their local equilibrium values).

There are important differences between the reasoning of previous paragraphs and the arguments of Dyson.[6] First, we have an additional factor of 2 on the right-hand side of Eq. (4.4). This is because we define ϵ to be the probability of a spin flip (the accompanying change in moment being 2β) whereas Dyson defines ϵ to be "the probability of spin disorientation" (the accompanying change in moment thus being only β). Second, the requirement of the conservation of the instantaneous local quasiparticle energy leads to an expression [Eq. (4.4)] involving the total (both drift and diffusion contributions) flux of magnetization across the surface, rather than an expression involving simply the diffusive contribution to the flux; the boundary condition is thus such that relaxation takes place towards instantaneous local equilibrium in the ap-

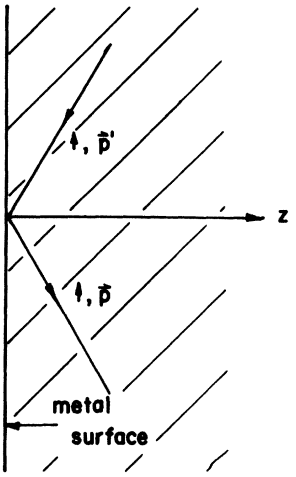

FIG. 2. Scattering of a quasiparticle by the metallic surface.

plied magnetic field. Finally, on the right-hand side of (4.4) we have a more sophisticated method of counting the number of particles hitting the surface per unit time, and this will be seen to lead to a profound difference between our result and that of Dyson for the limit $\epsilon \to 1$.

We shall assume that expressions similar to (4.4) hold for the fluxes of the x and y components of the magnetization also. Then, by computing the right-hand side of (4.4) using the results of Sec. III one finally arrives at the expression

$$\vec{n}\cdot\vec{\Lambda}_\alpha = \frac{\epsilon(1+B_0)v}{2(1-\epsilon)}\,\delta\bar{M}_\alpha \ . \tag{4.5}$$

Notice that in the limit as the probability of a spin flip at the boundary approaches unity, the magnetization density at the boundary is maintained in instantaneous thermal equilibrium, i.e., $\delta\bar{M}_\alpha = 0$, as one expects. This property is not possessed by Dyson's boundary condition, which lacks the factor $[1-\epsilon]^{-1}$ on the right-hand side of (4.5); our more sophisticated way of counting the number of quasiparticles hitting the surface gives rise to this difference in boundary conditions.

Some final comments on the effect of surface roughness are in order. While Eq. (4.3) is a very detailed statement which is valid only for the reflection of electrons from a smooth surface, Eq. (4.4), being an average over momentum directions of Eq. (4.3), contains much less detailed information. In fact, there is nothing in the physical interpretation of Eq. (4.4) (which balances the magnetization flux out of a surface against $2\beta\epsilon$ times the total number of particles striking the surface) which leads one to believe that this final form for the boundary condition is dependent on the surface properties, except insofar as the magnitude of ϵ is concerned. Thus, while the previous considerations concerning smooth surfaces were useful in establishing the correct form of the boundary condition, it is now possible to assert that the final results, Eqs. (4.4) and (4.5), can be used for both rough and smooth surfaces.

V. APPLICATION TO CESR

To obtain formulas relevant to the interpretation of experiments, consider an electromagnetic wave of time dependence $e^{-i\omega t}$ traveling in positive z' direction through a metallic slab bounded by planes $z' = \pm\frac{1}{2}L$. The static external field $\vec{H}_0$ is along the z axis. This geometry is sketched in Fig. 3.

Below, it will be shown that the magnetization density induced in the metal by a microwave field can be written as a sum of two terms, i.e., $\delta\vec{M} = \delta\vec{M}_{\rm skin} + \delta\vec{M}_{\rm sw}$. The skin-effect term $\delta\vec{M}_{\rm skin}$ is rapidly varying spatially, existing only in the skin depth, while the spin-wave contribution $\delta\vec{M}_{\rm sw}$ is relatively slowly varying. $\delta\vec{M}_{\rm skin}$ is a nonresonant function of the magnetic field[11] and can therefore be neglected if one is only interested in computing the resonant parts of the fields. The amplitude of $\delta\vec{M}_{\rm sw}$, on the other hand, exhibits resonant behavior. The problem is to find solutions of Maxwell's equations with $\vec{B}$ given by $\vec{B} = \vec{H} + 4\pi\delta\vec{M}_{\rm skin}$ and thus to obtain formulas for the surface impedance Z and for the amplitude of the transmitted field H_T. Such formulas have been previously obtained by Lampe and Platzman,[12] and later by Walker.[11] These formulas are

$$\frac{Z-Z_0}{Z_0} = 2\pi\,\frac{\vec{M}_{\rm sw}(-\frac{1}{2}L)\cdot\vec{H}_{1n}^{*}}{|\vec{H}_{1n}|^2} \tag{5.1}$$

and

$$\vec{H}_T = -cZ_0\vec{M}_{\rm sw\perp}(\tfrac{1}{2}L) \ , \tag{5.2}$$

where c is the velocity of light, Z_0 is the surface impedance for $\vec{M}=0$, and $\vec{M}_{\rm sw\perp}$ is the component of $\vec{M}_{\rm sw}$ in the plane of the surface. In conclusion, note

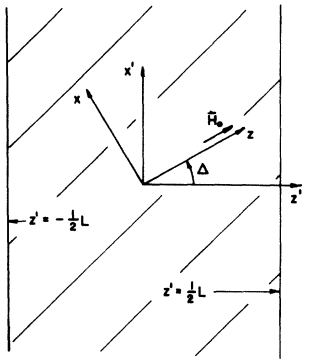

FIG. 3. Typical experimental geometry.

that it is necessary to calculate the amplitude of the magnetization density at the surfaces $z' = \pm \frac{1}{2}L$.

The magnetization density is determined by finding the solution of the modified Bloch equation (3.21) which is consistent with the boundary condition (4.5). Since it will be assumed that all fields depend only on the coordinate $z' = z\cos\Delta - x\sin\Delta$ (see Fig. 3), Eq. (3.21) becomes

$$\frac{\partial \delta M_-}{\partial t} = -i\omega_0 \delta \bar{M}_- - \frac{\delta \bar{M}_-}{\tau_s} + D_- \frac{\partial^2 \delta \bar{M}_-}{\partial z'^2} \tag{5.3}$$

where

$$D_- = D_{-\parallel}\cos^2\Delta + D_{-\perp}\sin^2\Delta \ , \tag{5.4}$$

whereas the boundary condition, Eq. (4.5), can be written

$$\left[\frac{d}{dz'} \pm C_-\right] \delta \bar{M}_-(z') \Big|_{z' = \pm 1/2\,L} = 0 \ , \tag{5.5}$$

with

$$C_- = [\epsilon(1 + B_0)v/2(1-\epsilon)D_-] \ . \tag{5.6}$$

Only the component M_- of $\vec{M}$ is considered in this section, since it is the only one which is resonant when $\omega = \omega_0$, and the notation $M_- = M$, $D_- = D$, and $H_{1-} = H$ is used.

Since the time dependence $e^{-i\omega t}$ is assumed, Eq. (5.2) can be written

$$\frac{d^2M}{dz'^2} + k_1^2 M = \kappa^2\left[1 + \frac{iD}{\omega_0}\frac{d^2}{dz'^2}\right] H \ , \tag{5.7}$$

where

$$k_1^2 = (D\tau_s)^{-1}[i(\omega - \omega_0)\tau_s - 1] \ , \quad \kappa^2 = i\chi_0\omega_0/D \ . \tag{5.8}$$

$H(z')$ is assumed to be a given function of z' which has been obtained by solving Maxwell's equations in the absence of M; i.e., $H(z')$ is the ordinary-skin-effect magnetic field. Equation (5.7) is thus an inhomogeneous differential equation, its most general solution being the sum of a particular solution and a linear combination of solutions of the corresponding homogeneous equation. A particular solution of Eq. (5.7) is

$$M_{\text{skin}}(z') = \frac{\kappa^2}{k_1}\int_0^{z'} dz'' \sin k_1(z' - z'') \times \left(1 + \frac{iD}{\omega_0}\frac{d^2}{dz''^2}\right) H(z'') \ , \tag{5.9}$$

as can be seen by substituting (5.9) into (5.7). Note that since $H(z'')$ is nonzero only within a skin depth of the surface $z'' = -\frac{1}{2}L$ (assuming that the exciting field is an incident only on this surface), the same is true for $M_{\text{skin}}(z')$. To Eq. (5.9) must be added solutions of the homogeneous equation proportional to $\cos k_1 z$ and $\sin k_1 z$ to obtain the complete solution which satisfies the boundary condition (5.5). The correct complete solution is finally found to be

$$M(z') = M_{\text{skin}}(z') + \tfrac{1}{2}\kappa^2\left[\int_{-1/2L}^{1/2L} H(z'')\,dz'' + \frac{C}{k_1}\int_{-1/2L}^{1/2L} \sin k_1\left(\tfrac{1}{2}L + z''\right) H(z'')\,dz''\right] \times \left[\frac{\cos k_1 z'}{k_1 \sin w - C\cos w} + \frac{\sin k_1 z'}{k_1\cos w + C\sin w}\right] \ , \tag{5.10}$$

where $w = \frac{1}{2}k_1 L$. The second of the two terms is obviously what we have called M_{sw} above; since solutions of the homogeneous equation exist in the absence of an exciting field, they are the so-called collective modes of the system. Notice that if the parameter p [see Eq. (1.1)] is much greater than unity, so that the collionless regime is obtained, the diffusion constant D [Eqs. (5.4) and (3.22)] will be a pure imaginary number. Now, if the sign of $\omega - \omega_0$ is the same as the sign of the imaginary part of D, k_1 [Eq. (5.8)] will be almost purely real for $|(\omega - \omega_0)\tau_s| \gg 1$ and the spin-wave modes are only weakly damped as they propagate into the metal.

The relation

$$\int_{-1/2L}^{1/2L} dz'\, H(z') = (ic^2/2\pi\omega) Z_0 \vec{\epsilon}_+^{\,*} \cdot \vec{H}_{1n} \ , \tag{5.11}$$

where H_{-1n} is the amplitude of the component H_- of the field incident on the surface $z' = -\frac{1}{2}L$, is useful in evaluating the amplitude of $M_{sw}(\pm\frac{1}{2}L)$ in terms of the surface impedance Z_0. Making use of (5.11) and (5.10), Eqs. (5.1) and (5.2) become

$$\frac{Z - Z_0}{Z_0} = \frac{c^2\chi Z_0(1 + C\delta')}{2D}\left|\frac{\vec{\epsilon}_+ \cdot \vec{H}_{1n}^{\,*}}{H_{1n}}\right|^2 \times \left[\frac{1}{k_1\tan w - C} - \frac{1}{k_1\cot w + C}\right] \tag{5.12}$$

and

$$\vec{H}_T = -\frac{c^3 Z_0^2 \chi(1 + C\delta')}{4\pi D}(\vec{\epsilon}_+^{\,*} \cdot \vec{H}_{1n})[\vec{\epsilon}_+ - (\vec{\epsilon}_{+'} \cdot \vec{\epsilon}_{z'})\vec{\epsilon}_z] \times \left[\frac{1}{k_1\tan w - C} + \frac{1}{k_1\cot w + C}\right] \ , \tag{5.13}$$

where δ' is an effective skin depth defined by

$$\delta' = \int_{-1/2L}^{1/2L} (\tfrac{1}{2}L + z')H(z')\,dz' \Big/ \int_{-1/2L}^{1/2L} H(z')\,dz' \quad . \tag{5.14}$$

It is of interest to consider the limit $|k_1 L| \ll 1$. In this case

$$\frac{1}{k_1 \tan w - C} = -\frac{2iD/L}{\omega - \omega_0 + i/T_{2\mathrm{eff}}} \quad , \tag{5.15}$$

where

$$\frac{1}{T_{2\mathrm{eff}}} = \frac{1}{\tau_s} + \frac{\epsilon(1+B_0)v}{(1-\epsilon)L} \tag{5.16}$$

is the effective resonance linewidth due to the combined effects of bulk relaxation and surface relaxation. This differs from the result of Dyson by predicting an infinitely broad line in the limit as the probability of a spin flip ϵ tends to unity and can be understood, as stated above, by noting that the magnetization at the surface cannot be excited from its thermal-equilibrium value when ϵ is unity.

Furthermore, it is of interest to note that, except for the factor $(1+B_0)/(1-\epsilon)$, Eq. (5.16) is just what would be predicted by a simple argument assuming that the electrons travel ballistically with velocity v back and forth between the two surfaces of the slab. For, in this case, the number of collisions a particle makes with the walls in time t is tv/L, and the effective relaxation time $T_{2\mathrm{eff}}$ is just that time such that $T_{2\mathrm{eff}}v/L = \epsilon^{-1}$. This argument is valid even if the electrons do not travel ballistically but are scattered from impurities, thus pursuing a random walk from one wall to the other. This can be seen by considering a kinetic-theory calculation of the pressure of a classical gas; the pressure is determined in terms of the number of particles colliding with the wall per unit time, and is the same whether we consider an ideal gas in which collisions between particles are ignored or a real dilute gas in which the particle motion is diffusive. For this argument to be valid, the electron must have time to diffuse back and forth across the slab at least once [i.e., $(D\tau_s)^{1/2} > L$]. In this case the number of collisions of the particular particle we are considering is the same as the number of collisions of a given particle averaged over all particles in the gas, which is the quantity entering the calculation of pressure.

In the case $(D\tau_s)^{1/2} < L$, there is no simple formula analogous to (5.16) for the linewidth, and analysis requires a detailed comparison of the experimental results with (5.12) and (5.13).

A comment on the effects of including drift-current contributions to the magnetization current density will be made here for the purpose of comparison with previous analyses[2,6,10-12] which have neglected these terms. For simplicity, consider the case $\epsilon = 0$, i.e., no surface relaxation. Previous work has concentrated on solving Eq. (2.1) with the boundary condition

$$\frac{dM_-(z')}{dz'}\bigg|_{z'=\pm 1/2L} = 0 \tag{5.17}$$

or some equivalent problem. In this paper, Eq. (5.3) is used, with the boundary condition (for $\epsilon = 0$)

$$\frac{d}{dz'}\left[M(z') - \chi H(z')\right]\Big|_{z'=\pm 1/2L} = 0 \quad . \tag{5.18}$$

It turns out that by neglecting both the term $-D\chi(d^2H/dz^2)$ in Eq. (5.3) [cf. Eq. (2.1)] and the term $d(H_-(z'))/dz']$ in Eq. (5.18) [cf. Eq. (5.17)] one makes two errors which exactly cancel each other, and the final formulas for Z and H_T obtained in this case agree with ours. If only one of these terms had been ignored, an error of the order of $|1 + 2D/\omega_0\delta^2|$ (which may be several orders of magnitude at liquid-helium temperatures) would have resulted in the magnitudes of Z and H_T.

In the above analysis leading to the formulas for the surface impedance and for the amplitude of the transmitted field, it is remarkable that nowhere was it necessary to make use of the explicit functional dependence of the skin-effect field $H_-(z)$ on z. Only Eq. (5.11), the relation between the integral of the skin-effect field and the surface impedance, was necessary. Thus, provided the behavior of magnetization density is accurately described by the macroscopic equation (5.3) and the boundary condition (5.5), the above formulas are valid for anomalous as well as classical-skin-effect conditions. A similar circumstance was noted previously by Lampe and Platzman[12] for the case where the motion of the magnetization density could be described by Eq. (2.1).

However, as mentioned in the Introduction, the basic macroscopic equations used above are valid, for collision-dominated conditions, only when $v\tau_0 \ll \lambda$, i.e., in the classical-skin-effect regime. Under collisionless conditions, the inequality (1.3) must be satisfied. While these inequalities are generally satisfied in practice if λ is taken to be a wavelength characterizing the spin-wave modes, they are not satisfied if the skin effect is anomalous, and λ is taken to be a wavelength characteristic of the skin-effect modes. Because the skin-effect modes play an important part in the determination of formulas for H_T and Z, particularly in so far as the magnitudes of these quantities are concerned, our above analysis is valid only under classical-skin-effect conditions.

To summarize: In spite of the fact that the derivation of the above formulas for H_T and Z did not involve any assumptions concerning the spatial dependence of $H_-(z)$, these formulas are still valid

only under classical-skin-effect conditions. The reason for this is that the basic equation of motion for the magnetization density is valid only under classical-skin-effect conditions.

To derive formulas valid under anomalous skin-effect conditions, assume that the spin-wave modes are of sufficiently long wavelength that they can still be described by the homogeneous equation corresponding to Eq. (5.7). The magnetization density in the metal will then still have the form

$$M(z') = M_{\text{skin}}(z') + M_{\text{sw}}(z') \quad , \tag{5.19}$$

$$M_{\text{sw}} = A\cos k_1 z' + B\sin k_1 z' \quad . \tag{5.20}$$

$M_{\text{skin}}(z')$ is that component of the magnetization density which falls off to zero within a skin depth of the surface. It cannot be determined by Eq. (5.7), since it varies much too rapidly spatially for Eq. (5.7) to be valid, and must be considered to be unknown. What allows us to obtain useful information in spite of the fact that M_{skin} is unknown is the assumption that it does not vary rapidly with frequency; i.e., it is nonresonant.

The boundary condition is still to be found by equating the flux of magnetization across a surface to $2\beta\epsilon$ times the number of particles striking the surface, or, more precisely, by Eq. (4.4). However, only that part of the distribution function $\delta\bar{\sigma}_\alpha$ corresponding to the long-wavelength spin-wave modes can be evaluated using the results of Sec. III. Thus, the boundary condition must be written in the form

$$\left(\frac{d}{dz'} + C_\alpha\right) M_{\alpha\text{sw}}(z')\Big|_{z'=l/2L} = 0 \quad , \tag{5.21}$$

$$\left(\frac{d}{dz'} - C_\alpha\right) M_{\alpha\text{sw}}(z')\Big|_{z'=-l/2L} = \frac{F_{\text{skin}}}{D_\alpha}(\vec{\epsilon}_+^{\,*}\cdot\vec{H}_{1n}) \quad . \tag{5.22}$$

In writing (5.21) and (5.22) it has been assumed, as above, that the slab is excited by a field incident on the surface $z' = -\frac{1}{2}L$. Thus, to a good approximation there is no skin-effect field near the surface $z' = +\frac{1}{2}L$, and (5.21) does not involve skin-effect fields. On the other hand, skin-effect fields are present near the surface $z' = -\frac{1}{2}L$ and, in writing (5.22), allowance has been made for this by including a factor F_{skin} on the right-hand side; F_{skin} could in principle be obtained explicitly by finding a solution of the kinetic equation valid at short wavelengths, but since this has not yet been done, F_{skin} must be treated as an unknown, which will depend on Δ, the angle which the external field makes with the normal to the slab.

The boundary conditions determine the constants A and B in Eq. (5.20), the final result for $M(z')$ being

$$M(z') = M_{\text{skin}}(z') + \frac{F_{\text{skin}}}{2D}\left(\frac{\cos k_1 z'}{k_1\sin w - C\cos w} + \frac{\sin k_1 z'}{k_1\cos w + C\sin w}\right)(\vec{\epsilon}_+^{\,*}\cdot\vec{H}_{1n}) \quad . \tag{5.23}$$

Also, the surface impedance and the amplitude of the transmitted field are given by

$$\frac{Z - Z_0}{Z_0} = \frac{\pi F_{\text{skin}}}{D}\frac{|\vec{\epsilon}_+^{\,*}\cdot\vec{H}_{1n}|^2}{|\vec{H}_{1n}|^2} \quad ,$$

$$\times\left[\frac{1}{k_1\tan w - C} - \frac{1}{k_1\cot w + C}\right] \tag{5.24}$$

and

$$\vec{H}_T = \frac{-cZ_0F_{\text{skin}}}{2D}\left[\frac{1}{k_1\tan w - C} + \frac{1}{k_1\cot w + C}\right]$$

$$\times[\vec{\epsilon}_+ - (\vec{\epsilon}_+\cdot\vec{\epsilon}_{z'})\vec{\epsilon}_{z'}](\vec{\epsilon}_+^{\,*}\cdot\vec{H}_{1n}) \quad . \tag{5.25}$$

An elementary application of the above results is the determination of the magnitude of ϵ from the experimental results of Schultz and Latham[13] on copper. Schultz and Latham have determined $(T_{2\text{eff}})^{-1} = 4\times10^8\ \text{sec}^{-1}$, in a slab thickness $L = 0.0038$ cm. The observation of increasing relaxation rates with decreasing L indicates that the relaxation is almost entirely due to surface relaxation. Thus

$$\epsilon = \frac{L}{v}\frac{1}{T_{2\text{eff}}} \approx 10^{-2} \quad ,$$

where $v = 1.6\times10^8$ cm/sec [22] has been used.

VI. VALIDITY OF MODIFIED BLOCH EQUATION

The assumption $g_\alpha = g_{0\alpha} + \vec{v}\cdot\vec{g}_{1\alpha}$ [see Eq. (3.12)] is only an approximation, and it turns out that it is valid only at relatively long wavelengths. Platzman and Wolff's work, [2] mentioned above, suggests that a criterion of validity for their analysis is $\lambda \gg R_c$, where λ is the characteristic wavelength of the disturbance, and $R_c = v/\omega_c$ is the cyclotron radius. Ying and Quinn[3] have explored the general problem of obtaining a spin-wave dispersion relation which is valid at all wavelengths. Here, a brief discussion is given of how to obtain higher-order corrections to the distribution function, and an assessment is made of the approximations used in Sec. III. [23]

Assuming that all quantities are proportional to $\exp[-i(\vec{q}\cdot\vec{r} - \omega t)]$, Eq. (3.9) determining g_α becomes

$$i\omega g_\alpha + \left[i\vec{q}\cdot\vec{v} + \omega_c\frac{\partial}{\partial\phi} - i\alpha\Omega_0\right]\bar{g}_\alpha = -\frac{\bar{g}_\alpha - \langle\bar{g}_\alpha\rangle}{\tau_0'} - \frac{\langle\bar{g}_\alpha\rangle}{\tau_s'} \quad . \tag{6.1}$$

Let (θ, ϕ) be the polar angles giving the direction of the momentum vector $\vec{p}$. Then $g_\alpha(\vec{p})$ can be expanded in terms of the spherical harmonics $Y_{lm}(\theta\phi)$, i.e.,

$$g_\alpha(\vec{p}) = \sum_{lm} g_{lm}Y_{lm}(\theta, \phi) \quad . \tag{6.2}$$

Note that since only one particular component, α,

is considered at a time, the subscript α need not be retained. Also, it follows that

$$\bar{g}_\alpha = \sum_{lm} \bar{g}_{lm} Y_{lm} - \beta H_\alpha \ , \tag{6.3}$$

where

$$\bar{g}_{lm} = (1+B_l) g_{lm} \ . \tag{6.4}$$

Now let $\vec{n}$ and $\vec{n}'$ be unit vectors in the directions of $\vec{v}$ and $\vec{q}$, respectively, so that

$$\vec{q} \cdot \vec{v} = qv(n_+ n'_- + n_- n'_+ + n_z n'_z) \ .$$

To understand the following developments, it is sufficient to note that the $n_{m's}$, i.e., $n_+ n_-$, and n_z, being the spherical harmonics Y_{1m}, have nonzero matrix elements only between spherical harmonics Y_{lm} and $Y_{l\pm1,m'}$.

Multiplying Eq. (6.1) by Y_{lm} and integrating over angles gives what will be called the (l,m)th equation. The (0, 0)th equation is

$$-i\omega \frac{g_{00}}{(4\pi)^{1/2}} - i\alpha\omega_0 \frac{g_{00}}{(4\pi)^{1/2}} - \frac{\beta H_\alpha}{1+B_0} + \frac{iqv}{(12\pi)^{1/2}} [n'_z \bar{g}_{10} - n'_+ \bar{g}_{11} + n'_- \bar{g}_{1-1}] = -\frac{1}{\tau_s} \frac{g_{00}}{(4\pi)^{1/2}} - \frac{\beta H_\alpha}{1+B_0} \ . \tag{6.5}$$

The $(1,m)$th equations are

$$-i\left[\omega + \alpha\omega_0 \frac{1+B_1}{1+B_0} - m\omega_c(1+B_1) + i\frac{1+B_1}{\tau'_0}\right] g_{1m} + ia_m \left(\tfrac{4}{3}\pi\right)^{1/2} (1+B_0)(qv) n'_m \frac{g_{00}}{(4\pi)^{1/2}} - \frac{\beta H_\alpha}{1+B_0} + iqv \sum_{m'} b_{mm'} g_{2m'} = 0 \ , \tag{6.6}$$

where $a_1 = -1$, $a_0 = 1$, and $a_{-1} = 1$ and the $b_{mm'}$ are coefficients depending on n'_m and having a magnitude the order of unity.

Note that if g_{2m} is arbitrarily assumed to be zero, Eq. (6.6) can be solved for g_{1m} in terms of g_{00}. When this result is substituted into (6.5), the results of Sec. III are obtained.

The first correction to the results of Sec. III is obtained by taking $g_{2m} \neq 0$, but assuming $g_{lm} = 0$, $l > 2$. To compute this correction, the $(2,m)$th equations are needed, which are

$$-i\left[\omega + \alpha\omega_0 \frac{1+B_2}{1+B_0} - m\omega_c(1+B_2) + i\frac{1+B_2}{\tau'_0}\right] g_{2m} + iqv \sum_{m'} d_{mm'} g_{1m'} = 0 \ . \tag{6.7}$$

Recall g_{3m} is assumed to be zero. The $d_{mm'}$'s are coefficients with magnitudes of order unity. Equation (6.7) is solved for g_{2m} and the result is substituted into (6.6). It now becomes evident that results similar to those of Sec. III will be obtained, except that the diffusion constant should be modified by a factor having a magnitude of the order of

$$1 + (qv)^2 b_{mm'} d_{m'm} \cdots \left[\left(\omega + \frac{\alpha\omega_0(1+B_2)}{1+B_0} - m\omega_c(1+B_2) + i\frac{1+B_2}{\tau'_0}\right)\left(\omega + \frac{\alpha\omega_0(1+B_1)}{1+B_0} - m'\omega_c(1+B_1) + \frac{i(1+B_1)}{\tau'_0}\right)\right]^{-1} . \tag{6.8}$$

If the results of Sec. III are to be valid, this factor should be close to unity.

The most restrictive conditions are obtained by putting $m = m' = 0$ in Eq. (6.8). Furthermore, take $\alpha = -1$ and $\omega = \omega_0$. Then it is seen that the results of Sec. III will be valid if

$$(qv)^2 \left[\left(\frac{(B_0 - B_1)\omega_0}{1+B_0} + \frac{i(1+B_1)}{\tau'_0}\right) \times \left(\frac{(B_0 - B_2)\omega_0}{1+B_0} + \frac{i(1+B_2)}{\tau'_0}\right)\right] \ll 1 \ . \tag{6.9}$$

In the collision-dominated regime this reduces to Eq. (1.2), i.e., $\lambda \gg v\tau_0$, whereas in the collisionless regime, the inequality (1.3) is obtained.

ACKNOWLEDGMENT

I would like to thank Dr. P. A. Wolff for stimulating discussions concerning the method used in Sec. VI.

*Supported by a grant from the National Research Council of Canada.

[1]S. Schultz and G. Dunifer, Phys. Rev. Letters 18, 283 (1967).

[2]P. M. Platzman and P. A. Wolff, Phys. Rev. Letters 18, 280 (1967).

[3]S. C. Ying and J. G. Quinn, Phys. Rev. 180, 218 (1969).

[4]V. P. Silin, Zh. Eksperim. i Teor. Fiz. 35, 1243 (1958) [Soviet Phys. JETP 8, 870 (1959)].

[5]W. M. Walsh, Jr., L. W. Rupp, Jr., and P. H. Schmidt, Phys. Rev. 142, 414 (1966).

[6]F. J. Dyson, Phys. Rev. 98, 349 (1955).

[7]M. Ia Azbel', V. I. Gerasimenko, and I. M. Lifshitz, Zh. Eksperim. i Teor. Fiz. 32, 1212 (1957); 35, 691 (1958) [Soviet Phys. JETP 5, 986 (1957); 8, 480 (1959)].

[8]W. M. Walsh, in *Solid State Physics*, edited by J. F.

Cochran and R. R. Haering (Gordon and Breach, New York, 1968), Vol. I, p. 127.

[9]H. C. Torrey, Phys. Rev. 104, 563 (1956).

[10]J. I. Kaplan, Phys. Rev. 105, 575 (1959).

[11]M. B. Walker, Can. J. Phys. 48, 111 (1970).

[12]M. Lampe and P. M. Platzman, Phys. Rev. 150, 340 (1966).

[13]S. Schultz and C. Latham, Phys. Rev. Letters 15, 148 (1965).

[14]A report of some of the results of this paper has already been published: See M. B. Walker, Phys. Letters 32A, 230 (1970); a misprint in Eq. (2) of that paper is corrected here.

[15]W. F. Brinkman and S. Englesberg, Phys. Rev. Letters 16, 1187 (1968).

[16]R. B. Lewis and T. R. Carver, Phys. Rev. 155, 309 (1967).

[17]L. D. Landau, Zh. Eksperim. i Teor. Fiz. 30, 1058 (1956); 32, 59 (1957) [Soviet Phys. JETP 3, 920 (1956); 5, 101 (1957)].

[18]V. P. Silin, Zh. Eksperim. i Teor. Fiz. 33, 495 (1957); 33, 1227 (1957) [Soviet Phys. JETP 6, 387 (1958); 6, 945 (1958)].

[19]A. J. Leggett, J. Phys. C 3, 448 (1970).

[20]P. Nozières, *Theory of Interacting Fermi Systems* (Benjamin, New York, 1964).

[21]L. L. Van Zandt, Phys. Rev. B 1, 3217 (1970); 1, 3223 (1970); 1, 3235 (1970).

[22]C. Kittel, *Introduction to Solid State Physics*, 2nd ed. (Wiley, New York, 1956).

[23]*Note added in proof.* Andrew Wilson and D. R. Fredkin [Phys. Rev. Abstracts 1, 10 (1970)] have recently obtained solutions of the kinetic equation valid for arbitrary wavelengths.

PHYSICAL REVIEW B VOLUME 3, NUMBER 1 1 JANUARY 1971

Sharp-Line Luminescence from Os^{4+} and Mo^{3+} in Cs_2HfCl_6 †

A. R. Reinberg

Texas Instruments Incorporated, Dallas, Texas 75222

(Received 30 July 1970)

Sharp-line luminescence spectra have been obtained for Os^{4+} ($5d^4$) and Mo^{3+} ($4d^3$) in single cubic crystals of Cs_2HfCl_6. For Os^{4+}, luminescence from both the $^1E(\Gamma_3)$ and $^1T(\Gamma_5)$ levels of the t^4 configuration to all the spin-orbit split levels of the $^3T_1$ ground state are observed. Luminescence spectra from the ^2E ("R" lines) of Mo^{3+} are reported for the first time. Sharp vibronic lines are observed in the vicinity of 1.1 μ due to coupling with odd-mode vibrations of the nearest-neighbor complex. Excitation spectra reveal pumping due to absorption into the $^4T_2$ and $^4T_1$ bands at 23.0×10^3 cm^{-1} and 19.5×10^3 cm^{-1}, respectively, and to the ^2T level at 14.0×10^3 cm^{-1}. The excitation bands do not correlate with the major absorption bands observed in these crystals, suggesting that other charge states of molybdenum are simultaneously present in the crystals.

I. INTRODUCTION

Compared to the large amount of information commonly available concerning the luminescent properties of the first transition-metal series, there is a general paucity of luminescence data for the second and third transition-metal series of ions as impurities in solids. Indeed, except for the notable work of Dorain and his co-workers,[1-3] there has been little detailed spectroscopy of any kind of the 4*d* and 5*d* ions as impurities in solids. Much of the prior work is concerned with the aqueous chemistry of complexes of these materials and hence consists primarily of absorption spectra. In a previous publication we described the sharp-line luminescence of $Re^{+4}(5d^4)$[4] in cubic single crystals of Cs_2ZrCl_6 and Cs_2HfCl_6 in the vicinity of 7000 Å. In this paper we report on the infrared luminescence of Os^{4+} ($5d^4$) and on the observation of "R" -line luminescence of Mo^{3+} ($4d^3$).[5] From the luminescence of Os^{4+} in Cs_2HfCl_6, we determine the energy of the lowest excited levels of the $^3T_1$ ground state. This level is split by a combination of the cubic field and the large spin-orbit coupling. The energies of these states have been calculated by Dorain, Patterson, and Jordan[2] but have not been verified by direct experimental observation.

To our knowledge, the spectrum of the R-line luminescence of Mo^{+3} has not been previously reported, although its excitation spectrum in glasses has been described elsewhere.[6]

II. EXPERIMENTAL

Although crystals of Cs_2HfCl_6 were grown by techniques described previously,[4] sufficient difficulty was encountered in producing good single crystals that a more detailed description of the process is warranted. In addition, there may be some question as to the charge state of the molybdenum impurity in similarly prepared material making the details worthwhile reporting. For reasons which we were unable to ascertain, considerably more success was had in preparing the hafnium salts over those containing zirconium. For that reason the data reported here were all taken with Cs_2HfCl_6. We believe that the results reported here are not peculiar to the hafnium compounds although they may not extend to such related compounds as K_2SnCl_6.