Paramagnetic Relaxation in Metals*

ALBERT W. OVERHAUSER†

Department of Physics, University of California, Berkeley, California

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The paramagnetic relaxation time of electron spins in a metal is calculated. Relaxation processes due to interaction with lattice vibrations, nuclear spins, other electrons, and impurity atoms are treated. It is found that the most important process of those considered is due to the interaction between electron magnetic moments and the fields caused by the translational motion of other electrons. A relaxation time of about one microsecond is calculated for this interaction at room temperature, and is approximately inversely proportional to the absolute temperature.

I. INTRODUCTION

If a metal is placed in a magnetic field, the spin magnetic moments of the conduction electrons tend to line up parallel to the field. Such an alignment of spins does not take place immediately, but is limited by the speed of the dynamical mechanisms that produce alignment. This relaxation process, which gives rise to a net magnetization of the metal, depends upon the interactions between the electron spins and other parts of the system. In order to calculate the effects of such interactions we shall treat the degenerate electron gas by means of the single particle model, so that all interactions are assumed to be small perturbations. The results will depend, of course, on the validity of this approach. A further approximation will be the use of plane waves, \( \exp(ik \cdot r) \), for the wave functions of the single particle states, and the expression, \( \hbar^2 k^2/2m \), for the kinetic energy of such a state.

In this paper we shall consider only the spin interaction terms which cause transitions that change the net magnetic moment of the spin system. In other words, we shall determine the various contributions to what is commonly called the “spin-lattice” relaxation time. Interactions which tend to broaden the magnetic energy states without producing magnetic relaxation should not be important in metals, as they are in crystals, in view of the high velocity of the conduction electrons and the weakness of the spin-spin interaction studied in Sec. V.

Let us assume that a metal with \( N \) conduction electrons per cc is placed in a constant magnetic field \( \mathcal{B} \) in the positive \( Z \) direction, which we shall call “up.”

The spin state of an electron can either be up or down, and, according to Fermi-Dirac statistics, the number of electrons \( n_+ \) or \( n_- \) per unit volume in \( k \) space with spin up or down is given by

\[
n_{\pm} = \frac{1}{8\pi^2} \left[ \exp \left( \frac{\hbar^2 k^2/2m \mp \mathcal{B} \mathcal{C} - \epsilon_{\pm}}{\kappa \Theta} \right) + 1 \right]^{-1}.
\]  

(1)

Throughout the calculations the volume of the metal is taken to be 1 cc, \( \mu \) is the Bohr magneton, and \( \Theta \), the absolute temperature. The parameters \( \epsilon_+ \) and \( \epsilon_- \) are the Fermi energies of the appropriate distributions. However, it follows from the fact that the total number of electrons is \( N \) that

\[
\epsilon_+ + \epsilon_- = 2\epsilon_0.
\]  

(2)

The constant \( \epsilon_0 \) is the Fermi energy of the electron gas before \( \mathcal{B} \) was applied. The one degree of freedom that remains permits the description of various amounts of bulk magnetization.

With approximations that are valid if \( \mathcal{B} \mathcal{C} \ll \epsilon_0 \) and \( \kappa \Theta \ll \epsilon_0 \), the total numbers of electrons \( N_+ \) and \( N_- \) with spin up and spin down are given by

\[
N_{\pm} = N/2 + m\kappa_0 (\epsilon_{\pm} - \epsilon_0 - \mathcal{B} \mathcal{C})/2\pi^2 \hbar^2.
\]  

(3)

The constant \( k_0 \) is the wave number (times \( 2\pi \)) at the top of the Fermi distribution, so that \( \epsilon_0 = \hbar^2 k_0^2/2m \). Equation (2) follows by setting \( N_+ + N_- = N \). Furthermore, the net magnetization at any instant is \( \mathcal{M} \), where

\[
\mathcal{M} = N_+ - N_-.  
\]  

(4)

The condition that the system of electrons with spin up, \( \{+\} \), and the system of electrons with spin down, \( \{-\} \), be in equilibrium is that \( \epsilon_+ = \epsilon_- \). From (3) and (4) the equilibrium value of \( \mathcal{M} \) is

\[
\mathcal{M}_0 = m\beta k_0 \mathcal{C} / \pi^2 \hbar^2.
\]  

(5)

The progress of the combined system, \( \{+\} + \{-\} \), towards equilibrium can then be described in terms of the process

\[
\mathcal{M} \longrightarrow \mathcal{M}_0.
\]

One expects that the variation of \( \mathcal{M} \) with time will be in accordance with the equation

\[
d\mathcal{M}/dt = (\mathcal{M}_0 - \mathcal{M})/T.
\]  

(6)

This equation serves as a definition of the relaxation time \( T \), and we shall prove that this equation has the correct form. If there are several independent mechanisms which produce orientation, then

\[
1/T = \sum 1/T_i
\]

where the \( T_i \) are the relaxation times to be associated.
with the individual processes. Short relaxation times are most important, whereas long ones can be neglected.

Six interactions which can induce transitions between the spin states in a metal so as to cause such a relaxation process are: (a) Interaction of the electron spin with magnetic fields arising from transverse lattice vibrations. (b) Interaction with electric fields arising from longitudinal lattice vibrations. (c) Interaction with nuclear spins. (d) Interactions with spins of other electrons. (e) Interaction with electric currents due to the translational motion of other electrons. (f) Interaction with impurities. These couplings with electron spins are small compared to the electron lattice interactions that are important, for example, in the theory of conductivity. This fact allows us to assume that in times which are short with respect to the action of the above processes and long compared to the collision time (10^{-13} \text{ sec}) of conductivity, \{+\} and \{-\} are independent but weakly interacting systems, each of which is in thermal equilibrium as regards its momentum distribution for the lattice temperature \theta. Therefore, the distribution (1) holds throughout the relaxation process with the Fermi energies \epsilon_+ and \epsilon_- as time varying parameters.

Each of the relaxation times will be determined by the following scheme. We shall compute the number of spins, \(W_{+,-}\), flipped per second from \{+\} to \{-\} and the number \(W_{-,+}\) flipped from \{-\} to \{+\}. The rate of change of \(D\) is then given by

\[
dD/dt = 2(W_{+,-} - W_{-,+}).
\]

In each case we shall find that this quantity is proportional to \(\epsilon_+ - \epsilon_-\), which, by (3), (4), and (5) is related to \(D_0 - D\):

\[
D_0 - D = mk_0(\epsilon_+ - \epsilon_-)/2\pi^2h^3.
\]

Therefore, (6) is proved to hold in each case and \(T\) can be identified from the coefficient of \(D_0 - D\). Also, since equilibrium obtains when \(dD/dt = 0\), one proves in a dynamical way that equilibrium is complete only if the Fermi energies are equal, which fact is, of course, a general result of statistical mechanics.

II. INTERACTION WITH TRANSVERSE PHONONS

In this section we shall compute the relaxation caused by the interaction between the electron magnetic moment, \(-\beta\sigma\), where \(\sigma\) is the Pauli spin vector, and the magnetic field \(3C'(t)\) produced by the lattice vibrations of the metal. We will assume for the present that there is no correlation between the translational motions of the free electrons and the vibrational motions of the lattice. The field \(3C'(t)\) arises from the current \(j(t)\) produced by the mass motion of the charged lattice points. If \(s(t)\) is the displacement vector describing the lattice vibrations, the current density is given by

\[
j = N\epsilon_s/dt.
\]

The assumption that there is one conduction electron per atom has been used here.

The magnetic field arising from such currents can be determined from the Maxwell curl equation.

\[
curl 3C' = (d\mathbf{D}/dt + 4\pi\sigma_0\mathbf{E} + 4\pi j)/c.
\]

(10)

However, the displacement current term is negligible and the conduction term is small for phonon frequencies greater than \(10^9\) per second. We may therefore use

\[
curl 3C' = 4\pi j/c.
\]

(11)

In writing Eq. (9) we have treated the positive ion lattice as a uniform distribution of positive charge. We shall also use the Debye model for the lattice vibrations and shall treat them by the method of field quantization. The displacement operator can then be written

\[
s = (\hbar/2\rho_0)eK_1(\sigma_{K1}e^{ik_1\cdot r} + \sigma_{K1}^*e^{-ik_1\cdot r}).
\]

(12)

The summation sign over \(K\) and \(\lambda\) has been omitted. \(eK_1\) and \(eK_1'\) are polarization vectors perpendicular to \(K\) and \(eK_1^*\) is parallel to \(K\). The velocity of sound in the metal is \(v\) and \(\omega = \omega K\). The density of the metal is \(\rho\), and \(\sigma_{K1}\) and \(\sigma_{K1}^*\) are destruction and creation operators, respectively, defined so that their nonzero commutators are 1. From (9), (11), and (12) the operator for the perturbing magnetic field is

\[
3C' = 4\pi Ne/(2\rho c^3K)|eK_1(\sigma_{K1}e^{ik_1\cdot r} + \sigma_{K1}^*e^{-ik_1\cdot r}).
\]

(13)

It can be shown that only transverse vibrations give rise to magnetic fields, so that \(\lambda\) is summed only over 1 and 2 in (13). Furthermore, \(eK_1 = -eK_1'\) and \(eK_2 = eK_1\).

We will quantize the free electron field with the following conventions. The creation and destruction operators for particles with spin up will be indicated by \(\psi\)'s, whereas the corresponding operators for electrons with spin down will be indicated by \(\psi\)'s. The field operator for the system \(\{+\}\) is then

\[
\psi = \psi e^{i\mathbf{k}_1\cdot r}.
\]

Similarly, the field operator for the system \(-\) can be taken:

\[
\psi = \psi e^{-i\mathbf{k}_1\cdot r}.
\]

The phonon electron interaction is \(\beta 3C'\cdot \sigma\), so that the perturbation operator of the electron phonon fields is

\[
H = \int \left( \frac{\varphi}{\psi} \right)^* 3C' \cdot \sigma \left( \frac{\varphi}{\psi} \right) d^3r.
\]

(14)

Evaluation of this expression gives

\[
H = 4\pi Ne\beta(h\nu/2\rho c^3K)^2\text{Tr}[(\hat{eK}_1)_{\nu}(\hat{eK}_1)_{\nu}]
\]

\[
\times \left[ (\delta_{\nu
-\nu'K} + b_{\nu'K}^*b_{\nu K}) + \delta_{\nu K'} + \delta_{\nu K} + \delta_{\nu'K} + \delta_{\nu K'} + \delta_{\nu K'} \right].
\]

plus four other terms which do not contribute to the relaxation process, and which we shall drop. The first term, for example, flips a spin up while absorbing a phonon. The conservation of wave number that obtains in emission or absorption of phonons is indicated by the symbols, $\delta k' - k - K = 0$. The above operator can be simplified by averaging the factors $(e_k e_k')^2 + (e_k e_k')^2$ which enter the squares of the matrix elements and by summing over both directions of polarization. A factor $4/3$ is obtained, so that we can set

$$H = 8\pi N e\beta(hu/6\rho e^2 K)(\delta k' - k - K)\delta k a_k + \delta k' - k - K b_k a_k + \delta k' - k - K\delta k' a_k + \delta k' - k - K b_k a_k' \tag{15}$$

We will now use first-order perturbation theory to calculate the number of electrons in $\{+\}$ which flip their spins down per second. Let us consider an electron in the state $k$ in $\{+\}$ and calculate the transition probability per second that it flips its spin due to phonon emissions of wave number in the interval $(K, K + dK)$. We will assume for the present that the states $k'$ in $\{-\}$ are unoccupied. The transition rate is given by

$$W_{k,k'} = (2\pi/\hbar)|H_{k,k'}|^2 \rho_f. \tag{16}$$

The matrix element is that due to the first term in (15) and the square of its magnitude is

$$(8\pi N e\beta)^2 hu(n_K + 1)/6\rho e^2 K.$$  

Here, $n_K$ is the average number of phonons in the state $K$. The density of final states, $\rho_f$, is

$$\rho_f = (m/4\pi\hbar^2)k_d K.$$  

Energy is conserved in the transitions so that we have

$$\hbar^2 k'^2/2m + \beta K = \hbar^2 k^2/2m + huK - \beta K. \tag{17}$$

There are similar transitions due to the absorption of phonons while the spins flip from up to down. The only difference is that $n_K + 1$ must be replaced by $n_K$, and the phonon term in (17) is of opposite sign. The transition probabilities for the analogous cases when spins are flipped up instead of down are the same.

We may now proceed to calculate the total number of spins flipped down per second. To do this we multiply the number of electrons in the wave-number interval $(k, k + dK)$ by the transition probability, $W_{k,k'} dK$ or $W_{k,k'} a_k dK$, and then also by the appropriate Fermi function to describe the probability that the final electron states $k'$ are unoccupied. We then integrate $dK$ from 0 to $\infty$ and $dK$ from $K_{min}$ to $K_{max}$. In order to account for the statistical factors we make the following definition:

$$g(k; x) = \left[\exp(\hbar^2 k^2/2m(x - x_0) + 1)^{-1}. \tag{18}$$

The number of electrons in $\{+\}$ with $k$ in the interval $(k, k + dK)$ is

$$(\hbar^2 dK/2\pi^2)g(k; \epsilon_k/k0 - \beta K/k0).$$

The probability that the final electron state is unoccupied in processes of phonon emission is

$$1 - g(k'; \epsilon_{-}/k0 + \beta K/k0).$$

On using (17) to eliminate $k'$, this expression becomes

$$1 - g(k; \epsilon_{-}/k0 - \beta K/k0 + huK/k0).$$

Using the above results and the analogous ones for the case of phonon absorption, the number of spin flips from $\{+\}$ to $\{-\}$ per second is

$$W_{+,-} = \frac{8m}{3\pi\rho}(\frac{Ne\beta}{\hbar})^2 \int \left[ g(k; \epsilon_k - \beta K/k0) \times \left[ 1 - g(k; \epsilon_k - \beta K/k0 + huK/k0) \right] \right] dK dkdK. \tag{19}$$

The corresponding expression for $W_{-,+}$ is obtained by interchanging $\epsilon_+$ and $\epsilon_-$ and by replacing $\beta K$ by $-\beta K$.

Before using (7) to obtain $dD/dt$, it is expedient to expand the functions $g(k; x)$ in a Taylor series about the point $x_0 = \epsilon_0/k0$. We will keep terms to the first order in the small quantities, $(\epsilon_+ - \epsilon_0)/k0$, $(\epsilon_- - \epsilon_0)/k0$, and $\beta K/k0$. In order to make the writing simpler, we will use the following notation:

$$g = g(k; x_0), \quad g' = \frac{dg(k; x)}{dx} \bigg|_{x = x_0}, \quad g_{\pm K} = g(k; x_0 \pm huK/k0), \quad g_{\pm K'} = \left[ \frac{dg(k; x)}{dx} \right]_{x = x_0 \pm huK/k0}.$$  

The last two notations are necessary because $huK/k0$ is not necessarily small. The integrand that occurs in the expression for $dD/dt$ after expansion and subtraction is

$$\left[ (\epsilon_+ - \epsilon_-)/k0 \right] \left[ g' \left[ 1 - g(k) + gg_{K'} \right] n_{K} + 1 \right] + \left[ g' \left[ 1 - g(k) - gg_{K'} \right] n_{K} + 1 \right] + \left[ g_{K'} + g(k) \left[ 1 - g(k) \right] n_{K} + 1 \right] + \left[ g_{K'} + g(k) \left[ 1 - g(k) \right] n_{K} + 1 \right] kdK. \tag{19}$$

It can be shown from the symmetry properties of $g(k; x)$ that

$$\int_{0}^{\infty} g_{\pm K'} kdK = \int_{0}^{\infty} g(1 - g_{\pm K})kdK. \tag{19}$$

The second term above therefore gives zero upon
integration, and we obtain

\[
dD = \frac{32\mu u}{3\pi p} \left( \frac{Ne\beta}{\hbar c^3} \right)^2 \frac{\varepsilon_+ - \varepsilon_-}{k_0} \int_{ggk}(n_k + 1)
\]

\[+gg-k'n_k]kd\kappa dK.
\]

The remaining integrations can be performed as indicated, but it is simpler and sufficient for our purposes to make use of the high temperature approximation, where we can neglect the difference between \(n_k+1\) and \(n_k\), and can set

\[n_k = k_0/\hbar uK_0.
\]

On integration and using (8) we obtain

\[
dD = \frac{16\pi N^2\varepsilon_0\theta(D_0 - D)}{3\hbar k_0 mc^4} \frac{K_{\text{max}}}{K_{\text{min}}} \log \frac{K_{\text{max}}}{K_{\text{min}}}.
\]

This equation is the desired result. We have only to discuss the determination of \(K_{\text{min}}\) and \(K_{\text{max}}\). At low phonon frequencies the induced electric fields resulting from the varying magnetic fields cause conduction currents which cancel out the magnetic fields. For such frequencies, there is a correlation between the electron motion and the lattice vibrations. It can be shown that this shielding effect decreases the magnitude of \(3\varepsilon_0\) by the factor \(K_0^2/(K_0^2 + K_{\text{min}}^2)\). The quantity \(K_{\text{min}}\) depends upon the electrical conductivity \(\sigma_0\) and is given by \(K_{\text{min}} = 4\pi \sigma_0 \theta / c^2\). Its value for metallic lithium is 600 cm\(^{-1}\).

If high frequency alternating fields are used to measure the relaxation time, the metal must be in the form of a fine powder of size small or comparable to the skin depth in order to prevent eddy current losses and excessive breadth of the absorption resonance due to the diffusion of the electrons in and out of the skin. The skin depth for Li is about 5\(\times\)10\(^{-3}\) cm for a frequency of 10\(^7\) cps, and 1/30 of this value for a frequency of 10\(^9\) cps. Particle sizes of about 10\(^{-3}\) cm and 10\(^{-4}\) cm, respectively, should be used. The minimum wavelength possible for phonons will be about twice the linear dimension of the particle. Assuming a spherical particle of diameter \(d\), and letting \(\lambda_{\text{max}} = \) the cube root of the particle volume, we obtain

\[(4\pi/3)^3K_{\text{min}} = 2\pi/d.
\]

\(K_{\text{min}}\) would be about 4.10\(^3\) and 4.10\(^4\), respectively. The restriction imposed by this last consideration would seem to be the more stringent in an ordinary practical case.

The expression for the maximum phonon wave number, as given by the Debye theory, is

\[(4\pi/3)^3K_{\text{max}} = 2\pi/a.
\]

Here, \(a\) is the cube root of the atomic volume. The ratio \(K_{\text{max}}/K_{\text{min}}\) is therefore \(d/a\).

The relaxation time due to the interaction with transverse phonons is therefore

\[T = \frac{3\mu h\kappa_0 c^4}{16\pi N^2\varepsilon_0\theta \log(d/a)}.
\]

(23)

For the case of Li at room temperature, this expression has the value 6\(\times\)10\(^{-2}\) sec.

III. INTERACTION WITH LONGITUDINAL PHONONS

In this section we shall compute the spin lattice relaxation caused by the interaction between electron spins and the electric fields of the lattice vibrations. The interaction energy of an electron spin with an electric field is given by\(^5\)

\[H = \beta(2\theta\mu)(\mathbf{E} \cdot \mathbf{p}).
\]

(24)

This term arises from the translational motion of the electron through the field, and is the origin of the spin orbit coupling in atoms, where \(E\) is taken to be the radial ion core field.

In metals and in the free electron approximation which we have been using, the fields that interest us are caused by the motion of the positive ions considered as a uniform distribution of positive charge. Electric fields will be associated with both longitudinal and transverse vibrations, but those due to the latter can be shown to be negligible. For longitudinal modes, however, the nonzero divergence of the lattice displacements will result in an accumulation of positive charge of amount

\[\delta\rho_+ = -Ne \text{ divs.}
\]

This charge density will in turn be the source of electric fields that will induce spin transitions by means of (24). The above accumulation of charge is cancelled out in part by a corresponding aggregation of conduction electrons. We shall calculate this effect by means of the Fermi-Thomas statistical approximation.

Let \(V(r)\) be the self-consistent potential arising from the accumulation of positive and negative charge. The maximum electron wave number, \(k_m\), at each point in the lattice is given by

\[\hbar^2 k_m^2/2m = \epsilon_0 + eV.
\]

The electron density as a function of position is then

\[n = [2m(\epsilon_0 + eV)]^{1/3}/(8\pi^3/\hbar^3).
\]

Since \(|eV| < \epsilon_0\), this expression can be expanded in a power series and we can write

\[n = (2m\epsilon_0)^{1/3}/(1 + 3\epsilon V/2\epsilon_0)^{1/3}/(8\pi^3/\hbar^3).
\]

Hence the accumulation of electric charge due to the electrons is

\[\delta\rho_+ = -me^2(2\theta\mu)/\pi^3/\hbar^3.
\]

Consider, now, a Fourier component of the lattice displacement vector

\[\mathbf{s}_k = \mathbf{s}_k^0 e^{i\mathbf{k} \cdot \mathbf{r}}.
\]

Reference 1, pp. 509 ff.
and of the resulting self-consistent potential

\[ V_K = V_K^0 e^{i K \cdot r} . \]

The Maxwell equation which obtains is

\[ \text{div} \mathbf{E} = 4\pi (\delta \rho_+ + \delta \rho_-) . \]

On inserting the expressions derived above, we obtain

\[ V_K = -\frac{4\pi NeKiK}{K^2 + 4\pi^2 \hbar^2 / \pi \hbar^2} . \tag{25} \]

The effect of electronic cancellation is given by the second term in the denominator. This interaction potential can be used, for example, to compute the electrical resistance of a metal and does in fact give results that agree with the more detailed theories. It seems reasonable to assume, therefore, that this simplified model will give a fair result for the relaxation problem at hand. It is easy to show that one does not make a significant error in neglecting spin orbit effects due to the ion core modulations of the crystalline field.

It is sufficient to compare \( (\Delta \varepsilon / a) \beta \) with (26) and to observe that they have the same magnitude. Here, \( \Delta \varepsilon \) can be taken to be the spin orbit splitting of the lowest \( p \) state in the atomic spectrum and \( a \) to be the lattice spacing.

If we expand (25) in a power series in \( K^2 \) and keep only the first term, we obtain for a Fourier component of the electric field,

\[ E_K = -K^2 \frac{\pi h^2 N}{2m^2 c e} \mathbf{s}_K / \hbar \mathbf{k}_0 . \]

The mean square matrix element for spin flip transitions due to (24) will then be

\[ |H|^2 = \frac{3}{2}(\beta K^2 \pi h^2 N / 2m^2 c e)^2 |\mathbf{s}_K|^2 . \tag{26} \]

By \( |\mathbf{s}_K| \) we mean:

- Phonon absorption: \( |\mathbf{s}_K| = (\hbar \omega / 2\rho_0) \delta_{K'-K} \).
- Phonon emission: \( |\mathbf{s}_K| = (\hbar \omega / 2\rho_0) \delta_{K'-K} \).

We have made use of the fact that \( E_K \) and \( \mathbf{p} \) are always about perpendicular due to conservation of energy and wave number. The factor \( \frac{3}{2} \) comes from the average over-all directions and is half the factor obtained in Sec. II where two polarization directions were included. To perform the rest of the calculation it is sufficient to compare (26) with the square of the coefficients in (15) since all other details are identical. The ratio of the two expressions is found to be

\[ \pi^2 h^2 K^4 / 128 m^2 \epsilon^2 \epsilon^2 \].

Furthermore, the final integration in \( K \) will be slightly different, so that the ratio of the relaxation times is

\[ \pi^2 h^2 K_{\text{max}}^4 / 512 m^2 \epsilon^2 \epsilon^2 \log(d/a) . \]

Therefore, on dividing (23) by this factor we obtain the spin lattice relaxation time due to interaction with electric fields.

\[ T = 96 \pi \hbar k_0 m^2 c^2 / \pi^2 N^2 h^2 K_{\text{max}} \hbar \theta . \tag{27} \]

The sound velocity \( u \) can be estimated from the relation

\[ u = \frac{\hbar K_{\text{max}}}{\pi D} . \]

For the case of Li at room temperature, assuming \( \theta_0 = 420^\circ \), we obtain a value of \( 3 \times 10^{-4} \) sec for the relaxation time.

### IV. Interaction with Nuclear Spins

In this section we will compute the paramagnetic relaxation due to the interaction of electron spins with the nuclear spins of the metal. We shall first consider the special case of a nucleus with spin \( \frac{1}{2} \) and magnetic moment \( \beta_n \) and shall generalize the calculation later for arbitrary nuclear spin. The most important interaction between the nuclear and electronic spins is that of the hyperfine coupling of an \( S \) state.\(^1\) Because this interaction occurs entirely at the point of the nucleus it will not be permissible to use the plane wave approximation for the electrons without making an error of \( 10^2 \) to \( 10^4 \). The perturbation can be written

\[ H = (8\pi/3) \beta \mathbf{\sigma} \cdot \mathbf{\sigma}(r) . \tag{28} \]

Here \( \mathbf{\sigma} \) is a Pauli spin operator for the nucleus and \( \delta(r) \) is a delta-function with \( r \) the relative coordinate of the electron and the nucleus under consideration. If we expand \( \mathbf{\sigma} \cdot \mathbf{\sigma} \) in terms of the raising and lowering operators, \( \sigma_\pm = \frac{1}{2}(\sigma_\pm - i \sigma_0) \), we obtain

\[ \mathbf{\sigma} \cdot \mathbf{\sigma} = 2 \sigma_+ \sigma_- + 2 \sigma_- \sigma_+ + \sigma_\pm \sigma_\pm \]

The first term flips an electron spin from \(+ \) to \(- \) and the nuclear spin from down to up. The transition probability per second for such a flip is

\[ W_{kk'} = (2\pi / h)(16\pi \beta \beta_n / 3)^2 |\psi(0)|^2 \rho_f . \]

Because of the point nature of the interaction there is no interference condition and \( |\psi(0)| \) is the magnitude of the wave function at the nucleus for an electron in the Fermi surface. The density of final states is

\[ \rho_f = m k^2 / 2\pi^2 h^2 . \]

The number of transitions of a given type will depend upon the distribution in spin states of the nuclei. Let \( M_+ \) and \( M_- \) be the number of nuclei with spin up and spin down, respectively. We have \( M_+ = M_- = N \), and we define

\[ \Delta = M_+ - M_- , \quad \Delta_0 = \beta \hbar N \beta / \pi \theta . \]

It follows that \( M_\pm = \frac{1}{2}(N \pm \Delta) \). The total number of electron flips per second from \(+ \) to \(- \) is accordingly

\[ W_{+-} = \int W_{kk'}(k^2 dh / 2\pi^2) M_- g(k, \epsilon_+ - \epsilon_0 / \beta \hbar + \beta \hbar / \pi \theta) \]

\[ \times \{ [1 - g(k'; \epsilon_- / \beta \hbar + \beta \hbar / \pi \theta)] - [1 - g(k'; \epsilon_+ / \beta \hbar + \beta \hbar / \pi \theta)] \} . \tag{29} \]

\(^1\) J. Korringa, Physica 16, 601 (1950).
The functions $g(k; x)$ are those defined in (18) and account for the Fermi statistics. The energy conservation equation for the above transitions is

$$\hbar^2 k^2/2m - \beta_3 c - \beta_2 c = \hbar^2 k^2/2m + \beta_3 c + \beta_2 c.$$  

Equation (29) can then be written

$$W_{+,-} = \frac{64 m^2 \beta_2}{9 \pi \hbar^8} |\psi(0)|^4 |\psi(N - \Delta)| \int g(k; \frac{e_- - \beta_3 c}{\kappa \theta})$$

$$\times \left[ 1 - g(k; \frac{e_- - \beta_3 c - 2\beta_2 c}{\kappa \theta}) \right] \hbar^4 dk.$$  

Transitions of the opposite type give a similar formula.

As in Sec. II, if we make a power series expansion of the functions in the integrands and compute $dD/dt$ by keeping only first-order terms in the small quantities that occur (including $\Delta/N$ and $\Delta_0/N$). After performing the various operations we have

$$\frac{dD/dt}{256 \pi m^2 k_0 N^2 \beta_3^2 \beta_2^2 \alpha^2 |\psi(0)|^4 (D_0 - D)/\hbar^4}$$

$$+ 256 m^2 k_0^2 \beta_2 \beta_3 \alpha \theta |\psi(0)|^4 (\Delta_0 - \Delta)/\hbar^4 \psi^2.$$  

(30)

We have thus derived in a dynamical way the conditions of complete statistical equilibrium for two interacting spin systems in a magnetic field; that is, $dD/dt = 0$ when $D = D_0$ and $\Delta = \Delta_0$. The calculation can be generalized to the case of arbitrary nuclear spin $I$ by making the substitutions:

$$N/2 \rightarrow N/(2I + 1), \quad \beta_n \rightarrow \beta_n/2I.$$  

We must also replace the square of the matrix element of $\sigma_{n+}$ and $\sigma_{n-}$, which is $I$ for $I = \frac{1}{2}$, by the quantity

$$G = \sum_{m=-I}^{I} (I + m + 1)(I - m) = \frac{2}{3} I(I + 1)(2I + 1).$$  

Furthermore, the quantities $\Delta$ and $\Delta_0$ must be redefined to mean the difference of the number of nuclei in adjacent magnetic states, so that we now have

$$\Delta_0 = \beta_n N 3c / I(2I + 1) \alpha \theta.$$  

Equation (30) becomes accordingly

$$\frac{dD/dt}{(D_0 - D)/T + G(\Delta_0 - \Delta)/T_0}.$$  

(31)

It should be noted that (6) does not hold in general for the interaction with nuclear spins because the electronic relaxation depends upon the nuclear spin distribution as is shown by the second term in (31). $T_n$ is the nuclear relaxation time and is

$$T_n = \frac{9 \pi \hbar^4}{64 m^2 k_0^2 \beta_2^2 \beta_3 \alpha^2 |\psi(0)|^4}. $$  

(32)

This is the same relaxation time as derived by Korringa and is equivalent to Eq. (9) of his paper, though in a different form. The constant $G$ appears in (31) because a given change in $\Delta$ requires $G$ times as many transitions as an equal change in $D$. $T$ is the electronic relaxation time and is

$$T = \frac{27 \hbar^4 I}{256 \pi m k_0 N \beta_3^2 \beta_2 (I + 1) |\psi(0)|^4}.$$  

(33)

It is interesting to note that this relaxation time is independent of temperature. It turns out that all other relaxation times increase with decreasing temperature, so that at very low temperatures this process will be the controlling one.

We will estimate this relaxation time for the isotope of lithium of mass seven, which has $I = \frac{3}{2}$. $|\psi(0)|^2$ can be determined as follows. We have defined it to be the square modulus of the metallic wave function, normalized in 1 cc, at the nucleus. Kohn and Bloembergen have computed the electron density at the nucleus for the conduction electrons in the metal and have compared it to the corresponding density of the valence electron for a lithium atom. They find the ratio to be 1.0. From the measured hyperfine structure splitting of Li and from the theoretical splitting of an S state, we find $|\psi(0)|^2 = 34$, which means that the density of conduction electrons at the nucleus is greater by 34 than if the charge cloud were perfectly uniform. The relaxation time obtained from (33) is then $2 \cdot 10^{-4}$ sec.

From (32) and (33) one can derive the ratio of the nuclear and electronic relaxation times due to their mutual interaction.

$$T_n/T = 8I(I + 1)\epsilon_0/9\kappa \theta.$$  

(34)

Since $T_n$ can be measured directly in a nuclear resonance experiment, $T$ could be determined from (34) without knowledge of the electronic wave functions.

V. INTERACTION WITH ELECTRON SPINS

In this section we shall begin a study of the paramagnetic relaxation resulting from electron-electron interactions. From the classical point of view there are two terms in the interaction Hamiltonian which exert forces on the spins. The first is the spin-spin interaction which has the form

$$H = (\beta^2/r_{12}^3)[(s_1 \cdot s_2)(r_{12}^2 - 3(s_1 \cdot r_{12})(s_2 \cdot r_{12})]. $$  

(35)

The second is the spin-current interaction which is the coupling between the magnetic moment of one electron and the magnetic field produced by the translational motion of another. This term has the form

$$H = (\beta/e/ncr_{12}^3)[(r_{12} \times p_2) \cdot s_1 + (r_{12} \times p_1) \cdot s_2].$$  

(36)

The exchange interaction does not have to be considered because it does not cause relaxation.

The spin-spin interaction can induce transitions in which there is a net flip of two spins up or down as well as those with a net flip of one spin up or down. On the other hand, the spin-current interaction can only cause single flip transitions. For the latter type processes both interactions must be treated simultaneously because interference effects are possible. The correct breakdown of the calculation is therefore into single flip relaxation and double flip relaxation. The relaxation time of the latter process is derived in this section, the former in the next.

We shall not use the above expressions for the electron-electron interaction because it is more convenient to use the relativistic wave equation of Dirac and to treat the interaction by the method of Møller. The calculations are thereby made more compact and the matrix elements are already provided. The Dirac equation for a free electron is

\[ E\psi = (\mathbf{p} \cdot \mathbf{p} + m^2)\psi. \]

Here, \( m = mc^2 \) and \( \mathbf{p} = c \) times the ordinary momentum vector. The plane wave solutions of positive energy are

\[ \psi = \psi_+ \exp \left(i\mathbf{p} \cdot \mathbf{r} / \hbar c\right), \quad \psi = \psi_- \exp \left(-i\mathbf{p} \cdot \mathbf{r} / \hbar c\right). \]

The coefficients of the exponential factors are spinors and are given to the first order in \( \hbar / \mu \) by

\[ \begin{align*}
\psi_+ &= (2\mu, 0, p_x, p_y, p_z)/2\mu, \\
\psi_- &= (0, 2\mu, p_x, -p_y, -p_z)/2\mu.
\end{align*} \]

(37)

We make use of the convention that for any vector \( \mathbf{F} \)

\[ F_\pm = F_x \pm iF_y. \]

(38)

The Hamiltonian operator representing the interaction between electron pairs will be of the form

\[ H = \frac{1}{2} \sum H_{\mathbf{p}' \mathbf{q}' \mathbf{p} \mathbf{q}} \psi_+^{\mathbf{p}'} \psi_+^{\mathbf{q}'} \psi_-^{\mathbf{p}} \psi_-^{\mathbf{q}}. \]

(39)

Here, the \( c_p, c_p^* \), etc. are either the \( b \)'s or \( d \)'s as defined in II, or the corresponding operators for negative energy states. Because we are concerned with first-order transitions of low energy, we will not have to take the negative energy states into account. The coefficients of the above terms are the matrix elements of the Møller interaction:

\[ H_{\mathbf{p}' \mathbf{q}' \mathbf{p} \mathbf{q}} = 4\pi \hbar^2 \mathbf{c} \mathbf{e} \left[ (u_{\mathbf{p}'}u_{\mathbf{p}})(u_{\mathbf{q}'}u_{\mathbf{q}}) \\
- (u_{\mathbf{p}'}^*u_{\mathbf{p}}^*)(u_{\mathbf{q}'}^*u_{\mathbf{q}}^*) \right] / (R^2 - \mathbf{e}^2). \]

(40)

Here \( \mathbf{R} = \mathbf{p} - \mathbf{p}' \) and \( \mathbf{e} \) is the energy of the state \( \mathbf{p} \) minus the energy of the state \( \mathbf{p}' \). In this calculation \( \mathbf{e}^2 \) can always be neglected in comparison to \( \mathbf{R}^2 \). The two term types in \( H \) which concern us here are: \( d_{\mathbf{p}'}^*d_{\mathbf{q}'}b_{\mathbf{p}'}b_{\mathbf{q}} \) which flip two spins down, and \( b_{\mathbf{p}'}^*b_{\mathbf{q}'}^*d_{\mathbf{q}'}d_{\mathbf{p}} \) which flip two spins up.

We will first treat the terms which flip two spins down. We must consider together all terms in (39) which connect the same initial and final states of the electron field, since they will interfere. Thus, for the transition \( d_{\mathbf{p}'}^*d_{\mathbf{q}'}b_{\mathbf{p}}b_{\mathbf{q}} \) we must take, instead of \( \frac{1}{2} H_{\mathbf{p}' \mathbf{q}' \mathbf{p} \mathbf{q}} \), the expression

\[ \frac{1}{2} (H_{\mathbf{p}' \mathbf{q}' \mathbf{p} \mathbf{q}} + H_{\mathbf{q}' \mathbf{p}' \mathbf{q} \mathbf{p}} - H_{\mathbf{q}' \mathbf{p}' \mathbf{q} \mathbf{p}} - H_{\mathbf{p}' \mathbf{q}' \mathbf{q} \mathbf{p}}). \]

However, \( H_{\mathbf{p}' \mathbf{q}' \mathbf{p} \mathbf{q}} = H_{\mathbf{q}' \mathbf{p}' \mathbf{q} \mathbf{p}} \), and \( H_{\mathbf{q}' \mathbf{p}' \mathbf{q} \mathbf{p}} = H_{\mathbf{p}' \mathbf{q}' \mathbf{q} \mathbf{p}} \). When we use the above expression with four terms, we must sum over only one-quarter of the terms in (39), so that if we sum over all of them anyway, we need only multiply the coefficients by an extra factor of \( \frac{1}{4} \). The matrix element can thus be taken:

\[ H' = \frac{1}{2} (H_{\mathbf{p}' \mathbf{q}' \mathbf{p} \mathbf{q}} - H_{\mathbf{q}' \mathbf{p}' \mathbf{q} \mathbf{p}}). \]

(41)

Using (37), (38), and (40) and letting \( \mathbf{S} = \mathbf{p} - \mathbf{q}' \), we obtain after some calculation the square modulus of (41):

\[ |H'|^2 = \left( \frac{\pi \hbar^2 \mathbf{c} \mathbf{e}}{2\mu^2} \right)^2 \left( \frac{R_+^2 R_-^2 S_+^2 S_-^2}{R^4} \right) \]

\[ - \frac{R_+^2 S_-^2 + R_-^2 S_+^2}{R^2 S^2}. \]

(42)

We will now consider in a group all possible transitions which can be specified by the magnitudes \( \rho, \eta \), and \( \mathbf{M} \), corresponding to the initial state, and the magnitude \( \rho' \). We treat all such cases together because they will all have the same Fermi factors. The total momentum \( \mathbf{M} = \mathbf{p} + \mathbf{q} \) is a constant during the collision. We can then average (42) over all possible orientations of the \( (\chi, \eta, \xi) \) axes with respect to the original \((X, Y, Z)\) axes; and then we must average this expression over the angle \( \phi \) between the planes of the initial and final states (see Fig. 1). A lengthy computation gives for the average value of (42),

\[ \langle |H'|^2 \rangle_{\mathbf{M}} = (2\pi \hbar^2 \mathbf{c} \mathbf{e})^2 / 10\mu^4. \]

(43)

The number of spin flips from \( + \) to \( - \) due to such double flip processes is given by

\[ W_{+, -} = 2 \int \left( 2\pi \mathbf{h} \right) \langle |H'|^2 \rangle_{\rho \eta} N_i \mathbf{G}_i \mathbf{G}_f. \]

(44)

Here, \( N_i \) is the number of initial states, \( \rho_f \) is the density

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of final states for each initial state, \( G_i \) and \( G_f \) are the appropriate Fermi factors for the initial and final states. The extra factor of 2 is due to the fact that each transition flips two spins, and the integration is over all differentials that are necessary to specify \( \rho_i \) and \( N_i \). Only electrons near the surface of the Fermi distribution, of momentum about \( p_0 \), will take part in such transitions. The phase space diagram will appear as in Fig. 2, which will serve as a definition of the quantities \( \theta_i, \rho_i, \lambda_i \) for the initial state and the corresponding ones, \( \rho_f', \lambda_f' \), for the final. The energies of the various states have the form

\[
E_p = e_p + (p_0/\mu)(p \sin \theta + \lambda \cos \theta) + \beta \mathbf{C}.
\]

The energy conservation equation, \( E_p + E_q = E_{p'} + E_{q'} \), gives

\[
\rho' = \rho + 2\mu \beta \mathbf{C}/p_0 \sin \theta. \tag{45}
\]

The number of initial states is

\[
N_i = (4\pi M^2 \hbar^2/4\pi \hbar^2) (2\pi p_0 \sin \theta \hbar \lambda dp/\hbar^2).
\]

The number of final states for a given initial state is

\[
Z_i = 2\pi p_0 \sin \theta \hbar \lambda dp'/\hbar^2.
\]

The spread in final energy is given by

\[
\Delta E_f = (2p_0/\mu) \sin \theta dp'.
\]

We therefore obtain the density of final states:

\[
\rho_f = (\pi \mu/\hbar^2) d\lambda'.
\]

In order to specify the appropriate Fermi factors, we make the following definitions:

\[
g(\rho, \lambda; x) = \{\exp[(p_0/\mu x)(\rho \sin \theta + \lambda \cos \theta) - x] + 1\}^{-1},
\]

\[
g(\rho, \lambda) = g(\rho, \lambda; 0), \tag{46}
\]

\[
g'(\rho, \lambda; x) = [\partial g(\rho, \lambda; x)/\partial x]_{x=0}.
\]

We have then

\[
G_i = g(\rho, \lambda; (\epsilon_+ - \epsilon_0)/\hbar \theta - \beta \mathbf{C}/\hbar \theta)
\]

\[
\times g'(\rho, -\lambda; (\epsilon_+ - \epsilon_0)/\hbar \theta - \beta \mathbf{C}/\hbar \theta).
\]

Using (45) we obtain similarly

\[
G_f = [1 - g(\rho, \lambda'; (\epsilon_+ - \epsilon_0)/\hbar \theta - \beta \mathbf{C}/\hbar \theta)]
\]

\[
\times [1 - g(\rho, -\lambda'; (\epsilon_+ - \epsilon_0)/\hbar \theta - \beta \mathbf{C}/\hbar \theta)].
\]

Each factor in (44) has now been evaluated. In order to determine the relaxation we must also consider the reverse processes which flip two spins from \( \{-\} \) to \( \{+\} \). We will obtain an equation like (44) with \( G_i \) and \( G_f \) replaced by \( G_i' \) and \( G_f' \), which differ from the former only in that \( \epsilon_+ \) and \( \epsilon_- \) are interchanged and \( \beta \mathbf{C} \) is replaced by \( -\beta \mathbf{C} \). Using (7) we obtain

\[
dD/dt = (8\pi \hbar/\hbar)(|H'|^2) \sum \rho N_i (G_i G_i' - G_i' G_i) \tag{47}
\]

We next expand \( G_i G_i' \) and \( G_i' G_i \) in terms of the small quantities \( (\epsilon_+ - \epsilon_0)/\hbar \theta, (\epsilon_- - \epsilon_0)/\hbar \theta \), and \( \beta \mathbf{C}/\hbar \theta \). For example,

\[
G_i = [g(\rho, \lambda) + g'(\rho, \lambda)(\epsilon_+ - \epsilon_0)/\hbar \theta]
\]

\[
\times [g(\rho, -\lambda) + g'(\rho, -\lambda)(\epsilon_- - \epsilon_0)/\hbar \theta].
\]

Only first-order terms are retained, and on using the relation

\[
1 - g(\rho, \lambda) = g(-\rho, -\lambda),
\]

we obtain

\[
G_i G_i' - G_i' G_i
\]

\[
= [(\epsilon_+ - \epsilon_-)/\hbar \theta] [g'(\rho, \lambda)g(\rho, -\lambda)g(-\rho, -\lambda')g(-\rho', -\lambda')
\]

\[
+ g(\rho, \lambda)g'(\rho, -\lambda)g(-\rho, -\lambda')g(-\rho', \lambda')
\]

\[
+ g(\rho, \lambda)g(\rho, \lambda')g(-\rho', \lambda')g(-\rho, -\lambda')
\]

\[
- (2\beta \mathbf{C}/\hbar \theta)[\epsilon_+ (\rho, \lambda)g(-\rho, -\lambda')g(-\rho', \lambda')
\]

\[
+ g(\rho, \lambda)g'(\rho, -\lambda)g(-\rho, -\lambda')g(-\rho', \lambda')
\]

\[
- g(\rho, \lambda)g(\rho, -\lambda')g'(\rho, -\lambda')g(-\rho', -\lambda')
\]

\[
- g(\rho, \lambda)g'(\rho, -\lambda)g(-\rho, -\lambda')g(-\rho', -\lambda').
\]

Now, each of the above terms in square brackets is integrated over \( dp, d\lambda, \) and \( d\lambda' \), and it can be seen that after integration the four terms in the coefficient of \( (\epsilon_+ - \epsilon_-)/\hbar \theta \) all give the same result. Thus the first term equals the second on the change of variable \( \lambda \rightarrow -\lambda \) in the second term; the third equals the fourth on the substitution \( \lambda' \rightarrow -\lambda' \) in the fourth; and, finally, the first term equals the third on the substitutions in the third, \( \rho \rightarrow -\rho, \lambda' \rightarrow -\lambda \) and \( \lambda \rightarrow -\lambda' \), while observing that \( g'(\rho, \lambda) = g(-\rho, -\lambda) \). The coefficient of \( 2\beta \mathbf{C}/\hbar \theta \) then integrates to zero and we can replace the coefficient of \( (\epsilon_+ - \epsilon_-)/\hbar \theta \) by \( 4g'(\rho, \lambda)g(-\rho, -\lambda)g(\rho, \lambda')g(-\rho', -\lambda') \). Combining the above results and remembering that \( M = 2p_0 \cos \theta \), (47) becomes

\[
\frac{dD}{dt} = \frac{128\mu \theta^2 p_0^3 (\epsilon_+ - \epsilon_-)}{5\pi^2 \hbar^2 \theta^3} \int g'(\rho, \lambda) g(-\rho, -\lambda) g(\rho, \lambda')
\]

\[
\times g(-\rho, -\lambda') \cos \theta \sin^2 \theta d\rho d\lambda d\lambda' \tag{48}
\]

The limits of integration are 0 to \( \pi/2 \) for \( \theta \) and \( -\infty \) to \( \infty \) for the remaining variables. The integrals can be evaluated, and on using (8) we obtain the relaxation equation

\[
dD/dt = 8\pi^2 e^2 \theta^2 (D_0 - D)/15\hbar^2 e^4. \tag{48}
\]
The relaxation time to be associated with the double flip action of spin-spin forces is therefore

$$T = 15m\hbar^2 c^2/\pi e^2 e^0. \quad (49)$$

It is interesting to note that (49) depends only upon the fundamental constants and the absolute temperature. The quadratic dependence of the relaxation rate with temperature results from the Fermi statistics. An electron in the Fermi surface can only collide with another electron in the Fermi surface, that is with a fraction of the electrons of about $\theta/\theta_0$. Similarly, of the possible final momentum states, only a fraction of about $\theta_0/\theta$ are permitted by the exclusion principle. Hence, two powers of $\theta/\theta_0$ would enter an order of magnitude calculation. For room temperature (49) has the value $6 \times 10^{-3}$ sec.

VI. INTERACTION WITH ELECTRON CURRENTS

In this section we shall calculate the relaxation rate due to electron-electron collisions in which there is a net flip of one spin up or down. Such transitions can be due to spin-spin forces or spin-current forces, but it will be seen that the latter interaction is several orders of magnitude larger than the former in so far as these processes are concerned.

There are four term types in (39) which produce a net flip of one spin from $\{+\}$ to $\{-\}$. These four types must be grouped in pairs since they can connect the same initial and final states. The first pair gives the following terms:

$$\frac{1}{2} \sum (H'_{a'\rightarrow a} b_{a'\rightarrow a} - H'_{a'\rightarrow a} b_{a\rightarrow a'})/\sqrt{2}. \quad (50)$$

It is necessary to make the distinction between $H'_{a'\rightarrow a}$ and $H'_{a\rightarrow a'}$ because the spin up spinor goes with the $p'$ in the first and with the $q'$ in the second. For a specific transition two terms of each type appear in (50), and, as before, one can show that the matrix element can be taken to be

$$H' = (H'_{a'\rightarrow a} - H'_{a\rightarrow a'})/\sqrt{2}.$$

Using (37), (38), and (40) one finds

$$H' = (\pi \hbar c/\sqrt{2} \mu) \left\{ [3i(\mathbf{R} \times \mathbf{M})] + [3i(\mathbf{R} \times \mathbf{S})] - R_+ R_+ / R^2 + [3i(\mathbf{S} \times \mathbf{M})]_+ + 3i(\mathbf{R} \times \mathbf{S})_+ + S_+ S_+ / S^2 \right\}.$$

We must average the square modulus of this expression over all orientations of the $(x, y, z)$ axes in Fig. 1. We obtain

$$\langle |H'|^2 \rangle_{\mathbf{a}'} = 8\pi^2 \beta^4 \left\{ [3(\mathbf{R} \times \mathbf{M})] + [3(\mathbf{R} \times \mathbf{S})] / 2 + 2R^2/15 + [3(\mathbf{R} \times \mathbf{S})] / 2 + 2(\mathbf{R} \times \mathbf{S})^2/6 + 2S^2/15 + \right\} / \langle |H'|^2 \rangle_{\mathbf{S}^2}.$$

Equation (51) must in turn be averaged over the angle $\varphi$. Near $\varphi = 0$, $R$ becomes very small; and near $\varphi = \pi$, $S$ becomes very small. The presence of these near singularities is due to the action of spin current forces which have an interaction energy that varies in distance as $1/r^2$, so that the total scattering cross section would be infinite. The presence of the magnetic field, however, removes the singularity because energy conservation for a collision in which one spin is flipped demands that $R$ and $S$ can never be smaller than

$$\delta = \mu_0 B / \rho_0 \sin \theta.$$

This quantity is small, however, so that integration over $\varphi$ makes several of the terms in (51) give a large contribution, of order of magnitude $\rho_0/\delta$, which is from $10^4$ to $10^6$ larger than the remaining terms, as can be seen only by a close examination. Equation (51) can therefore be replaced by

$$\langle |H'|^2 \rangle_{\mathbf{a}'} = 4\pi^2 \beta^4 \rho_0 F(\lambda, \lambda', \theta) / 3 \sin \theta \cos \theta. \quad (53)$$

Here

$$F(\lambda, \lambda', \theta) = (\cos \theta \sin \theta + 2 \cos \theta \sin \theta) \times [((\lambda - \lambda')^2 + \delta^2)^{-1} + ((\lambda + \lambda')^2 + \delta^2)^{-1}] + \delta^2 (\cos \theta \sin \theta - \cos \theta \sin \theta) \times [((\lambda - \lambda')^2 + \delta^2)^{-1} + ((\lambda + \lambda')^2 + \delta^2)^{-1}].$$

We can now compute the number of spin flips per second from $\{+\}$ to $\{-\}$ due to the spin-current interaction, and it is given by (54). The extra factor of 2 is now due to the extra two term types in the Hamiltonian operator, which in fact give the same transition rate as the two in (50). The factors $\rho_1, N_1$, and $G_1$ are the same as before, whereas $\langle |H'|^2 \rangle_{\mathbf{a}'}$ is given by (53) and $G_2$ is also new:

$$G_2 = \begin{cases} 1 - g(\rho, \lambda'; (\epsilon_1 - \epsilon_0 - \beta \mathbf{S}) / \mathbf{E}) \\ \times [1 - g(\rho, \lambda'; (\epsilon_1 - \epsilon_0 - \beta \mathbf{S}) / \mathbf{E})] \end{cases}.$$

The energy balance equation gives for this case

$$\rho' = \rho + \mu_0 B \rho_0 / \rho_0 \sin \theta,$$

so that, finally,

$$G' = \begin{cases} 1 - g(\rho, \lambda'; (\epsilon_1 - \epsilon_0 - 2 \beta \mathbf{S}) / \mathbf{E}) \\ \times [1 - g(\rho, \lambda'; (\epsilon_1 - \epsilon_0 - 2 \beta \mathbf{S}) / \mathbf{E})] \end{cases}.$$

Similar alterations must be made to $G_1$ for the inverse processes. The relaxation rate from (7) is

$$dD/dt = (8\pi^2/\hbar) \int \langle |H'|^2 \rangle_{\mathbf{a}'} \rho_2 N_2 G(\rho G_1 - \mathbf{G}_1 \mathbf{G}_2). \quad (54)$$
We have had to keep \(|H'\rangle\langle H'|_n\) inside the integral sign because it depends upon \(\lambda, \lambda', \theta\). However, \(|H'\rangle\langle H'|_n\) is invariant under the substitutions \(\lambda \rightarrow \lambda', \theta \rightarrow -\theta\), etc., so that we can use the same methods as in \(V\) to simplify \(G_G' - G_G\). Computation shows that this factor in the integrand can be replaced by

\[
2(e_\varepsilon - \varepsilon)g(r, \lambda)g(-r, \lambda)g(\rho, \lambda')g(\rho, -\lambda')/8\theta.
\]

From (8), (54), and the expressions for the various factors we find

\[
\frac{dD}{dt} = \frac{16\beta^2 \rho'^4 (D_0 - D)}{3c^4 \rho^2 \theta} \int F(\lambda, \lambda', \theta) g'(\rho, \lambda)
\times g(-\rho, \lambda)g(\rho, \lambda')g(\rho, -\lambda')d\theta d\rho d\lambda d\lambda'. \quad (55)
\]

The integrals can be evaluated and yield (see appendix)

\[
\frac{dD}{dt} = \frac{20e^4 \hbar^2 \theta (D_0 - D) \log(e \theta e^{1/\beta(3)}C)}{9m^2 c^4 \hbar}. \quad (56)
\]

Here \(\varepsilon = 2.718\). The relaxation time due to the spin-current interaction is therefore

\[
T = \frac{9m^2 c^4 \hbar}{20e^4 \hbar^2 \theta \log(e \theta e^{1/\beta(3)}C)}. \quad (57)
\]

It is interesting to note that this relaxation time is dependent to a large extent upon the field strength \(\theta\). For a magnetic field of 5 oersteds and a temperature of 293\(^\circ\)K, (57) gives \(8 \times 10^{-3}\) second.

**VII. INTERACTION WITH IMPURITIES**

In this section we shall estimate the relaxation caused by the presence of impurity atoms in the metal. If the impurity is paramagnetic, the electron spins in the conduction band can interact by means of a spin-spin interaction, as in (35), where the second electron is in a bound state of the impurity atom. The interaction energy will be of the order of magnitude of \(g^2 / a^2\) within the region of the atom, \(a\) is of the order of the atomic dimension. One can then show that, except for a numerical factor, the relaxation time due to such processes is given by

\[
T \sim \hbar^2 / mk_0 N \beta f. \quad (58)
\]

Here \(f\) is the fraction of paramagnetic impurity atoms in the metal. If \(f\) is \(10^{-3}\), (58) gives a value of \(10^{-3}\) sec.

Relaxation can also be caused by the atomic electric fields of all impurity atoms by means of a spin orbit interaction, (24). The magnitude of this interaction energy will be \(s \beta / a^2\), where \(s\) is the effective charge of the impurity atom as seen by a conduction electron. The relaxation time for such processes will therefore have the order of magnitude

\[
T \sim \hbar^2 / mk_0 N e^2 \beta^4 f. \quad (59)
\]

For an impurity content of \(10^{-4}\) and an effective charge \(z\) of say 3, an appropriate value which is sufficient to explain the contribution of impurities to the electrical resistance of metals, (60) gives a value of \(10^{-3}\) sec. One can conclude that such impurity processes do not play an important role in electron paramagnetic relaxation.

**VIII. CORRECTIONS TO THE RELAXATION TIMES**

The preceding calculations were based upon the free electron model and the effects of binding to the crystaline lattice and the Coulomb interaction between the electrons were neglected. We will now take account of these effects in so far as they influence the spin susceptibility of the conduction electrons and the density of single particle states at the top of the Fermi distribution. We continue to assume that the single particle model is a valid approximation.

Let \(\chi_0\) and \(\rho_0\) be the spin susceptibility and density of states for the free electron model without interactions, and let \(\chi\) and \(\rho\) be the corresponding quantities when lattice, and exchange and correlation interactions are accounted for. One can then show that the relaxation times must be multiplied by the factor

\[
(\chi / \chi_0) (\rho / \rho_0)^2 \text{ or } 4. \quad (60)
\]

The 4 in the exponent applies to the calculations in \(V\) and \(VI\), whereas the 2 applies to the others. The factor \(\chi / \chi_0\) occurs because a larger susceptibility, and hence larger equilibrium value of \(D_0\), means that the same number of electronic transitions will produce a fractional relaxation smaller by that same amount. A factor \(\rho_0 / \rho\) occurs for each integration over the surface of the Fermi distribution, including the one in the derivation of the formula for transition probability.

Since a complete treatment of exchange and correlation effects has not been made to date, even in the single particle model, the numerical values of the factors in (60) are unknown. However, experimental data on susceptibilities and electronic specific heats seem to indicate that these factors are not very different from unity.

**IX. CONCLUSION**

The most important relaxation process of those considered is that due to the spin-current interaction in \(VI\). The relaxation time of about 1 microsecond obtained for this process is at least two powers of ten shorter than the remaining ones, so that these latter processes may be neglected in comparison to the former. On the other hand, this figure is two or three powers of ten longer than the relaxation times characteristic of paramagnetic salts at room temperature.\(^{10}\) One would therefore expect that a paramagnetic resonance in metals could be easily observed, and that a very narrow

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line of about 100 kc or 0.1 oersted in width would be seen. However, a number of investigators have looked for such a resonance, by both microwave and radio-frequency techniques, and have failed to observe any resonance. It is at present difficult to explain these negative results. Yafet has shown that the energy of such a resonance would not be appreciably effected by interactions with the crystalline field.

A possible explanation is that an interaction resulting in a relaxation time of $10^{-10}$ sec or less has been overlooked. One might suspect that second-order processes play a more important role than the first-order processes considered, as is actually the case in paramagnetic salts. However, this possibility can be ruled out by a simple argument. If one considers the various second-order calculations (double phonon emission and absorption, phonon Compton effects, simultaneous collision of two electrons and emission of a phonon, etc.), one observes that the relation of the second-order calculation to the first is similar in structure and magnitude to the corresponding relation in the theory of electrical resistance. Since second-order processes do not play an important role in electrical resistance, otherwise the linear dependence of resistance on temperature would not result, therefore second order processes do not play an important role in paramagnetic relaxation. The second-order processes which involve only the electron-electron interaction are not included in this argument, but it is unlikely that they are important.

Note added in proof: The metallic spin resonance has been observed in Li, Na, and K at microwave frequencies. This recent success in finding the resonance resulted from the use of sufficiently small particle sizes, of the order of a micron or less, so that excessive width of such a resonance due to alternating current skin effects was reduced. Line widths of about 15, 80, and 120 oersteds were observed, respectively, in Li, Na, and K. These widths are probably caused by the modulation of the microwave field as seen by the electrons when they diffuse toward or away from the surface. More narrow lines would result, then, if even smaller particles or lower frequencies are used.

The author wishes to thank Professor Charles Kittel for proposing this problem and for helpful suggestions.

**APPENDIX**

We wish to compute the following integral occurring in (55):

$$
\int F(\lambda, \lambda', \theta)g'(\rho, \lambda)g(-\rho, \lambda)g(\rho, \lambda')g(-\lambda')d\theta d\rho d\lambda d\lambda'.
$$

Consider first the contribution of the first term of $F(\lambda, \lambda', \theta)$. We make the substitutions

$$
y = (p_0 \cos \theta / 2\mu_0 \theta)(\lambda + \lambda'), \quad x = p_0 \sin \theta / \mu_0 \theta,
y' = (p_0 \cos \theta / 2\mu_0 \theta)(\lambda - \lambda'), \quad \alpha = \beta \cot \theta / 2\theta.
$$

Hence,

$$
d\rho d\lambda d\lambda' = (2\mu_0 \theta / p_0 \sin \theta)(\mu_0 \theta / p_0 \cos \theta)^2 dxdydy'.
$$

The first term is, therefore,

$$
(9 \cos^2 \theta + 2 \cos \theta \sin^2 \theta) dxdydy'd\theta
$$

so that

$$
dx dy' = \frac{1}{2} dr ds.
$$

We obtain

$$
(\mu_0 \theta / p_0)^2 \int_{\lambda_0}^{\lambda_0} (2 \cos \theta \sin^2 \theta) dr ds dy dy'd\theta
$$

The integration in $s$ gives

$$
2y/(e^y - 1).
$$

The integral in $r$ gives

$$
\frac{\theta}{(e^\theta - 1 - 2y)/(e^\theta - 1)}.
$$

We obtain, therefore

$$
(\mu_0 \theta / p_0)^2 \int_{\lambda_0}^{\lambda_0} \int_{-\infty}^{\infty} \frac{(9 \cos^2 \theta + 2 \cos \theta \sin^2 \theta) xe^{x} (e^x - 1 - x) dx dyd\theta}{(x^2 + 4\alpha^2)^2 (e^\theta - 1)^2}.
$$

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11 Unpublished research.
13 Grisvold, Kip, and Kittel, Phys. Rev. 88, 951 (1952), and private communication.
The integration in \( x \) can be manipulated to give

\[
\int_0^\infty \frac{x^2 e^x dx}{(x^2 + 4\alpha^2)^{(c^2 - 1)^2}}
\]

If one takes advantage of the smallness of \( \alpha \), this integral can be shown to have the value \( \log(e/\alpha) \), where \( e = 2.718 \ldots \) We have then

\[
\left(\frac{\mu e}{\hbar}\right)^3 \int_0^\infty \frac{9}{(x^2 + 4\alpha^2)^{(c^2 - 1)^2}} (x^2 + 4\alpha^2) \log(2e/\alpha) \, dx \sin^2 \theta \, d\theta.
\]

This integration can be carried out and gives finally

\[
(20/3)\left(\frac{\mu e}{\hbar}\right)^3 \log(e/\alpha)^{0.45}/(\beta C).
\]

We will now compute the contribution of the second term in \( F(\lambda, \chi, \theta) \). We make the same substitution and analysis as before and obtain similarly

\[
\left(\frac{\mu e}{\hbar}\right)^3 \int_0^\infty \frac{9}{(x^2 + 4\alpha^2)^{(c^2 - 1)^2}} (x^2 + 4\alpha^2) \log(2e/\alpha) \, dx \cos \theta \, d\theta.
\]

If we integrate in \( x \), observing as before the smallness of \( \alpha \) for most all \( \theta \), this expression is

\[
(17/3)\left(\frac{\mu e}{\hbar}\right)^3 = (20/3)\left(\frac{\mu e}{\hbar}\right)^3 \log(e/\alpha)^{0.45}.
\]

We obtain on further integration in \( \theta \)

\[
(17/3)\left(\frac{\mu e}{\hbar}\right)^3 = (20/3)\left(\frac{\mu e}{\hbar}\right)^3 \log(e/\alpha)^{0.45}.
\]

On inserting the sum of the two terms we have evaluated into (55), we obtain (56).

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**Induced Conductivity in Luminescent Powders. II. AC Impedance Measurements**

**HARVEY KALMAN, BERNARD KRAMER, AND ARNOLD PERLMUTTER**

*Physics Department, New York University, Washington Square, New York, New York*

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Alternating current measurements of the impedance changes induced by ultraviolet, infrared, x-ray, and gamma-ray irradiation in (Zn:Cu)S luminescent powders are reported. These results are in agreement with previously reported dc measurements, and indicate that the observed impedance changes are primarily due to the change of the electron density in the conductivity band. Whereas the capacity changes show a monotonic increase, the \( Q \) values \( (X/R) \) show a pronounced minimum with increasing intensity. A model consisting of radiation sensitive and insensitive powder portions is proposed, and theoretical calculations based on such a model are shown to be in agreement with most of the experimental results. This ac measurement technique can be used to measure small exciting intensities (down to almost 1/1000 erg/sec cm\(^2\)).

1. INTRODUCTION

In a previous investigation\(^1\) of the conductivity induced in luminescent type materials (in powder form) by ultraviolet radiation it was found that a non-ohmic relationship between the induced current and the applied field existed at all voltages except when the highest field strengths were used. Similar non-ohmic relationships were found in later experiments in which x-rays were used as the exciting radiation. With light excitation the powders are not uniformly excited and this nonuniform excitation is certainly responsible for at least part of the non-ohmic relationship observed. The x-rays used for these experiments penetrated these thin layers layered uniformly; nevertheless, similar strong non-ohmic relationships were observed and this indicates that this non-ohmic characteristic is inherent to the powder structure. Since conductivity experiments with single crystals\(^2, 3\) irradiated with x-rays showed an ohmic relationship, this supports the idea that the non-ohmic characteristics are inherent to the grain structure.

With these results in mind it is assumed here, as a working hypothesis, that the powder has to be considered as an inhomogeneous system. Some parts of the powder sample (grain boundaries and air spaces) remain highly resistive even under strong excitation, while other parts, especially the interior of the grains, become highly conductive under excitation, much more than observed from dc measurements of the total resistance. To test this idea it was decided to duplicate many of the conductivity measurements with powders under ultraviolet, infrared, and high energy particle radiation using an alternating current field of low field strength instead of a dc field and measuring the effective resistive and reactive components of the impedance, hoping, in this way, to detect the true conductivity of the single grains.

Somewhat similar ac measurements have been reported by Garlick and Gibson,\(^4\) who have thoroughly

\(^{1}\) H. Kallmann and B. Kramer, Phys. Rev. 87, 91 (1952).

