Paramagnetic-Impurity Spin Resonance and Relaxation in Metals*

M. B. WALKER
Department of Physics, University of Toronto, Toronto, Ontario, Canada
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The response of a paramagnetic spin in a metal to applied time-dependent magnetic fields can be described in terms of frequency-dependent susceptibilities of the Kubo type. The diagrammatic technique used here to evaluate these susceptibilities has the advantage that approximations are made by expanding in powers of a small parameter, so that corrections to the results are known to be small if certain conditions are satisfied. For example, corrections to the formula given below for the transverse susceptibility are of order $\beta(\omega-\omega_R)$ and $\beta\Gamma_2$, where ω is the applied frequency, ω_R is the resonance frequency, and $\Gamma_2=T_2^{-1}$ is the transverse relaxation rate ($\hbar=1$); corrections to the formula for the longitudinal susceptibility are of order $\beta\omega$ and $\beta\Gamma_1$, where $\Gamma_1=T_1^{-1}$. An effective spin $S=\frac{1}{2}$ is assumed. The results of the diagrammatic analysis are interpreted in terms of the Bloch equations, modified to include relaxation to the instantaneous value of the magnetic field. The resonance frequency is calculated to second order in the interaction between spins and conduction electrons, while the relaxation times T_1 and T_2 are calculated to third order, and to this order all quantities are found to have a Kondo-like dependence on the logarithm of the temperature. The Korringa relation between the shift of the resonance frequency and T_1 is found to break down as the Kondo temperature is approached from above, but to third order in the interaction, the relation $T_1=T_2$ is found to be true for an isotropic interaction. Departures from thermal equilibrium of the conduction-electron system have been neglected in this work.

I. INTRODUCTION

IN 1946, Bloch[1] proposed a phenomenological equation describing the motion of a nuclear-spin system subjected to both a static and a time varying magnetic field. This equation successfully describes a wide variety of magnetic resonance experiments, although to obtain a valid description of low-frequency phenomena, it is necessary to modify the original equation so that relaxation takes place toward the instantaneous magnetic field.[2–4] Theoretical justification of the Bloch equation was provided by Wangsness and Bloch,[5] by Bloch,[6] and by Redfield.[7] The method of these papers was to develop an equation of motion for the reduced density matrix describing the spin system, and was found to be most useful when the perturbation responsible for the relaxation of the spin system had a very short correlation time. Sher and Primakoff[8] later examined the equation of motion for the density matrix in greater detail.

In the equation-of-motion approach,[2–7] the specification of the initial conditions involves the assumption of some explicit form for the density matrix describing the system (the system includes both the spin and its surroundings, which in the case studied below will be the conduction electrons in a metal). The choice made by Wangsness and Bloch[5] and others[3–7] corresponds to the hypothetical situation where the interaction between the spin and its surroundings is absent up until the time $t=0$, and that previous to the time $t=0$, the surroundings had achieved a state of thermal equilibrium at a given temperature. Furthermore, it was assumed that the surroundings remained in thermal equilibrium at all subsequent times. The artificiality of this method of specifying the initial conditions is certainly undesirable and not unavoidable in certain cases.[9] Also, it is important to be able to take into account the deviations from thermal equilibrium of the surroundings, since these are important in some instances, for example, in the theory of the phonon bottleneck, and in the description of the so-called bottleneck effect in paramagnetic resonance in metals.

An improvement in the general formulation of the theory was achieved by Kubo and Tomita[9] in their treatment of magnetic resonance absorption via a linear response theory. In this theory the important quantities are frequency-dependent susceptibilities, which are expressed in terms of spin correlation functions. The main purpose of this paper is to develop a field-theoretic method of evaluating these so-called Kubo formulas for the susceptibilities describing paramagnetic resonance and relaxation experiments. The result of our efforts is essentially a microscopic derivation of the Bloch equations.

To exploit field-theoretic techniques, and, in particular, Wick's theorem, a representation of spin operators in terms of fermion creation and annihilation operators is employed. This representation is due to Abrikosov,[10] and certain aspects of its application to

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[2] R. S. Codrington, J. D. Olds, and H. C. Torrey, Phys. Rev. **95**, 607 (1954).
[3] J. H. Van Vleck and V. F. Weisskopf, Rev. Mod. Phys. **17**, 227 (1945); M. A. Garstens, Phys. Rev. **93**, 1228 (1954); R. K. Wangsness, *ibid.* **98**, 927 (1955).
[4] A. Abragam, *Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961).
[5] R. K. Wangsness and F. Bloch, Phys. Rev. **89**, 728 (1953).
[6] F. Bloch, Phys. Rev. **102**, 104 (1956); **105**, 1206 (1956).
[7] A. G. Redfield. IBM J. **1**, 19 (1957).
[8] A. Sher and H. Primakoff, Phys. Rev. **119**, 178 (1960); **130**, 1267 (1963).
[9] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).
[10] A. A. Abrikosov, Physics **2**, 5 (1965).

the problem of paramagnetic impurity spin resonance in metals have been described in a previous paper.[11]

In its formal aspects, the calculation of the spin correlation functions describing paramagnetic resonance has many similarities to the evaluation of other transport coefficients, such as the electrical conductivity of a metal.[12,13] In particular, Holstein's paper[13] on the electrical conductivity of the electron-phonon gas has had a strong influence on our work. Thus, it will be shown that it is important to sum the so-called ladder diagrams occurring in the perturbation expansion of the two-particle Green's function, and to accomplish this, an equation for the external-field vertex function is obtained. Once the external-field vertex function is known, the spin correlation functions are easily found.

To interpret the work on spin-lattice relaxation in terms of more familiar concepts, the populations of the spin energy levels are introduced and related to the components of the external-field vertex function. The equation determining the external-field vertex function is then found to be very similar to the rate equation often used to determine the rate of decay of the populations from some initial nonequilibrium condition. However, inherent in the linear response theory, in terms of which the problem is formulated, is the fact that an external field has been applied to the spin system. This fact manifests itself in the rate equations in that the populations are found to tend toward values corresponding to thermal equilibrium in the instantaneous magnetic field. Similarly, the work on the paramagnetic resonance linewidth is interpreted in terms of a rate equation which is shown to be a transverse component of the Bloch equation, modified to include relaxation toward the instantaneous magnetic field.

A very important aspect of the method described below is that approximations are made by expanding various quantities in powers of a small parameter. In the theory of paramagnetic resonance line shapes, it is the value of the transverse susceptibility for frequencies ω close to the resonance frequency ω_R, which is of interest, and the expansion parameters are $\beta|\omega-\omega_R|$ and $\beta\Gamma_2$ where $\beta=(kT)^{-1}$ and Γ_2 is the transverse relaxation rate. In the theory of spin-lattice relaxation it is the value of the longitudinal susceptibility for frequencies close to zero which is of interest, and the expansion parameters are $\beta\omega$ and $\beta\Gamma_1$, where Γ_1 is the longitudinal relaxation rate. Thus, the susceptibilities are accurately determined at all frequencies closer than kT to the frequency at which they have a resonance.

[11] M. B. Walker, Phys. Rev. **176**, 432 (1968). Subsequently this paper will be referred to as I. Also, in referring to equations from I, Eq. (3.18) of I, for example, will be referred to as Eq. (3.18) of I.

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[13] T. Holstein, Ann. Phys. (N. Y.) **29**, 410 (1964).

The particular problem attacked below is that of an impurity spin in a metal interacting with the conduction electrons via an effective exchange interaction. The calculation of the resonance line shift is carried out to second order in the interaction strength, while the calculation of the transverse and longitudinal relaxation times is carried out to third order. Since the treatment is essentially perturbative in nature, the results are valid only at temperatures relatively high in comparison with the Kondo temperature. The calculations are of sufficiently high order, however, that the lowest order "Kondo-like" corrections to both the resonance frequency and the relaxation rates are obtained. Thus an idea is obtained of how these quantities change as the Kondo temperature is approached from above.

A fact which limits the domain of applicability of our theory is that deviations from thermal equilibrium of the conduction electrons have been ignored. It is hoped, in a future article, to extend the method used in this paper to the case where the deviations of the conduction electrons from thermal equilibrium are important.

The first detailed study of the paramagnetic resonance and relaxation of paramagnetic spins in a metal was that of Korringa,[14] who calculated both the resonance shift and the spin-lattice relaxation time and stated his now famous relation

$$T_1(\Delta\omega/\omega_0)^2=(\hbar/4\pi kT)(\omega_e/\omega_0)^2, \tag{1.1}$$

where $\Delta\omega$ is the shift of the impurity spin resonance frequency from ω_0 due to the conduction electrons, and ω_e is the conduction electron spin resonance frequency. The calculations below show that if ω_0 and ω_e are sufficiently different, Eq. (1.1), which is a valid result at high temperatures, becomes incorrect as the temperature approaches the Kondo temperature.

There is a good deal of recent work[15,16] on the problem of paramagnetic resonance in metals. This work will be referred to and compared with our own at appropriate places below. It is, however, perhaps not out of place to reiterate the distinctive features of the present paper. These are first, that approximations are made by expanding in powers of a small parameter so that the order of magnitude of the corrections to the various formulas is known, and is known to be small. Second, the calculation of the resonance linewidth has

[14] J. Korringa, Physica **16**, 601 (1950).

[15] H. Hasegawa, Progr. Theoret. Phys. (Kyoto) **21**, 483 (1959); B. Giovannini, M. Peter, and S. Koidé. Phys. Rev. **149**, 251 (1966); H. J. Spencer and R. Orbach, *ibid.* **179**, 683 (1969); R. Orbach and H. J. Spencer, *ibid.* **179**, 690 (1969); M. Peter, J. Dupraz, and H. Cottet, Helv. Phys. Acta **40**, 301 (1967); H. Cottet, P. Donze, J. Dupraz, B. Giovannini, and M. Peter, Z. Angew. Phys. **24**, 249 (1968); S. Schultz, S. R. Shanabarger, and P. M. Platzman, Phys. Rev. Letters **19**, 749 (1964); D. C. Langreth, D. L. Cowan, and J. W. Wilkins, Solid State Commun. **6**, 131, (1968).

[16] H. J. Spencer and S. Doniach, Phys. Rev. Letters **18**, 994 (1967); H. J. Spencer, Phys. Rev. **171**, 515 (1968); Y. L. Wang and D. J. Scalapino, *ibid.* **175**, 734 (1968); R. Orbach and H. J. Spencer, Phys. Letters **26A**, 457 (1968); B. M. Khabibullin, Fiz. Tverd. Tela **9**, 1874 (1967) [Soviet Phys. Solid State **9**, 1478 (1968)].

been carried out to third order in the interaction strength, at which point Kondo-like terms first show up. Thirdly, a discussion of the frequency-dependent longitudinal spin susceptibility is given.

II. PHENOMENOLOGICAL DISCUSSION OF PARAMAGNETIC RESONANCE LINE SHAPES

Suppose that a paramagnetic ion with an effective spin $S=\frac{1}{2}$ is subjected to a strong static magnetic field along the z axis and a small microwave field normal to the z axis. The interaction between spin and the static field is described by the Hamiltonian

$$H=\omega_0 S_z=-h_0 S_z. \tag{2.1}$$

Units $\hbar=1$ are used, and $h_0=\gamma H_0$, where γ is the gyromagnetic ratio and H_0 is the applied static magnetic field; henceforth, h_0 will also be referred as a magnetic field. Also, note that $\langle S_z\rangle=-\frac{1}{2}\tanh(\frac{1}{2}\beta\omega_0)$ and that the static susceptibility defined by $\chi_0=\partial\langle S_z\rangle/\partial h_0$, is given by $\chi_0=\frac{1}{4}\beta\,\mathrm{sech}^2(\frac{1}{2}\beta\omega_0)$. The interaction between the spin and the microwave field contributes, to the Hamiltonian of the system, a term

$$V(t)=-\tfrac{1}{2}(S_+h_{1-}+S_-h_{1+})e^{(-i\omega+\epsilon)t}, \tag{2.2}$$

where $S_\pm=S_x\pm iS_y$, $h_{1\pm}=h_{1x}\pm ih_{1y}$ and ϵ represents a positive infinitesimal, indicating that the microwave field is turned on adiabatically at an infinitely remote time in the past.

The response of the spin variable S_-, to first order in the driving microwave field, is given by[9]

$$\langle S_-\rangle_t=\chi_-(\omega)h_{1-}e^{-i\omega t}, \tag{2.3}$$

where

$$\chi_-(\omega)=\tfrac{1}{2}i\int_0^\infty dt\langle[S_-(t),S_+]\rangle e^{(i\omega-\epsilon)t}. \tag{2.4}$$

The subscript t in $\langle S_-\rangle_t$ indicates that the ensemble average is over an ensemble describing the nonequilibrium state of the system at the time t in the presence of the driving field. Note that Eq. (2.3) does not contain terms proportional to h_{1+}. This is because it has been assumed that $\langle[S_-(t),S_-]\rangle=0$.

The phenomenological equations of Bloch,[1] modified to include relaxation towards the instantaneous value of the magnetic field,[2–4] are known to provide an accurate description of a wide variety of paramagnetic resonance and relaxation experiments. It is thus reasonable to use the Bloch equations to obtain a phenomenological expression for $\chi_-(\omega)$. Pake[17] and Deutch and Oppenheim[18] have previously discussed certain aspects of the relation of the Bloch equations to the Kubo susceptibilities. It should be emphasized that it is essential to take into account the fact that relaxation is to the instantaneous value of the applied magnetic field if one is to obtain correct results at low frequencies, and in particular, for the longitudinal susceptibility. In our notation, the Bloch equations can be written

$$\frac{\partial\langle\mathbf{S}\rangle_t}{\partial t}=\langle\mathbf{S}\rangle_t\times\mathbf{h}(t)-\mathbf{i}\frac{\langle S_x\rangle_t-\langle S_z\rangle(h_{1x}/h_0')}{T_2}-\mathbf{j}\frac{\langle S_y\rangle_t-\langle S_z\rangle(h_{1y}/h_0')}{T_1}-\mathbf{k}\frac{\langle S_z\rangle_t-[\langle S_z\rangle+\chi_0h_{1z}(t)]}{T_1}, \tag{2.5}$$

where $\mathbf{h}(t)=\mathbf{h}_0'+\mathbf{h}_1(t)$ includes both the static and microwave applied magnetic fields. The static field $h_0'=h_0+h_{\mathrm{eff}}$, where h_0 is the externally applied field, and h_{eff} is the effective field at the impurity spin due to the conduction electrons. The circularly polarized component of Eq. (2.5) which is proportional to the vector $\mathbf{i}+i\mathbf{j}$ is

$$\frac{\partial\langle S_-\rangle_t}{\partial t}=-i\omega_R\langle S_-\rangle_t-\frac{\langle S_-\rangle_t-\langle S_z\rangle(h_{1-}/h_0')}{T_2}-i\langle S_z\rangle h_-(t). \tag{2.6}$$

In Eq. (2.6), the static field h_0' has been written $h_0'=-\omega_R$. Also, $h_-(t)$ is assumed to be a small quantity and only terms linear in $h_-(t)$ are retained. The assumption that $\langle S_-\rangle_t$ and $h_-(t)$ have the time dependence $\exp(-i\omega t)$ leads to the result

$$\chi_-(\omega)=\frac{-\omega_R+i\Gamma_2}{\omega-\omega_R+i\Gamma_2}\frac{\langle S_z\rangle}{h_0'}. \tag{2.7}$$

Two limiting cases of (2.7) are of interest. In the high-temperature limit, $\beta\omega_R\ll1$, $\langle S_z\rangle\simeq-\chi_0\omega_R$, giving

$$\chi_-(\omega)=\chi_0\frac{-\omega_R+i\Gamma_2}{\omega-\omega_R+i\Gamma_2},\quad \beta\omega_R\ll1 \tag{2.8}$$

whereas in the low-temperature limit $\beta\omega_R\gg1$, Eq. (2.7) gives

$$\chi_-(\omega)=-\frac{1}{2}\frac{1-i(\Gamma_2/\omega_R)}{\omega-\omega_R+i\Gamma_2},\quad \beta\omega_R\gg1. \tag{2.9}$$

The microscopic theory presented below demonstrates that the expressions (2.8) and (2.9) are correct so long as the conditions $\beta|\omega-\omega_R|\ll1$ and $\beta\Gamma_2\ll1$ are satisfied. Thus the validity of (2.8) is independent of whether the resonance frequency ω_R is large or small relative to the relaxation rate Γ_2; furthermore, note that the zero-frequency limit of $\chi_-(\omega)$ is $\chi_-(0)=\chi_0$, as it should be. With respect to the validity of (2.9), note that the

[17] G. E. Pake, *Paramagnetic Resonance* (Benjamin, New York, 1962).

[18] J. M. Deutch and I. Oppenheim, Advan. Mag. Res. 3, 43 (1968).

conditions $\beta\omega_R \gg 1$, $\beta\Gamma_2 \ll 1$ can only be satisfied when $\omega_R \gg \Gamma_2$; thus, to lowest order, $[1-i(\Gamma_2/\omega_R)]=1$, and in this order this microscopic theory obtained below agrees with (2.9).

The condition $\beta\Gamma_2 \ll 1$ for the validity of the theory can be understood in a simple way. Suppose, for example, that we estimate the contribution to the resonance linewidth which is due to the finite lifetime of the spin eigenstates by using ordinary time-dependent perturbation theory. The expression for the probability per unit time of a spin flip due to the scattering of a conduction electron contains a δ function expressing the law of energy conservation. The argument of the δ function will have an uncertainty equal to the uncertainty in the energy of the spin, which is the order of Γ_2. However, this uncertainty will not be important if the other energy-dependent factors in the expression for the transition probability vary little when their energy is varied by an amount of order Γ_2. Since the most rapidly varying factors are Fermi factors, which vary significantly when their energy is changed by kT, the usual expression for the transition probability will be a good approximation only when $\Gamma_2 \ll kT$. While exact expressions for the paramagnetic resonance line shape provide the starting point of the investigation below, it is found that, in the performance of certain integrals, it is convenient to neglect energy uncertainties in certain expressions and to approximate them by δ functions [e.g., see Eq. (4.32)]; the situation there is very similar to the one just described and leads to the conditions $\beta\Gamma_2 \ll 1$ and $\beta|\omega-\omega_R| \ll 1$ for the validity of our theory of line shape.

Spencer and Orbach[15] recently suggested that the transverse spin susceptibility should have the form (2.8) and showed how (2.8) could be derived in a phenomenological way by insisting that the impurity spins relax to the instantaneous microwave field. There is, however, some disagreement between various authors (see particularly Orbach and Spencer[15]) as to whether the exchange coupling between the spins and conduction electrons can cause relaxation to the instantaneous field or whether relaxation to the instantaneous field is due to other relaxation mechanisms. The microscopic derivation given below partially clarifies this point by showing that the exchange coupling between the spin and the conduction electrons does, in fact, cause relaxation to instantaneous value of the applied field, at least when the departures of the conduction electrons from thermal equilibrium can be neglected.

It is interesting to note that the assumption

$$\langle [S_-(t),S_+]\rangle = \langle [S_-(0),S_+]\rangle e^{-i\omega_R t-\Gamma_2|t|}$$

gives

$$\chi_-(\omega) = \langle S_z\rangle [\omega-\omega_R+i\Gamma]^{-1},$$

which is in marked disagreement with (2.7) if the resonance frequency is sufficiently low that it becomes comparable to the relaxation rate. On the other hand, the assumption

$$\langle \{S_-(t),S_+\}\rangle = \langle \{S_-(0),S_+\}\rangle e^{-i\omega_R t-\Gamma_2|t|}, \quad (2.10)$$

where $\{S_-(t),S_+\} = S_-(t)S_+ + S_+S_-(t)$, can be shown to lead to the correct results, (2.8) and (2.9), assuming $\beta\Gamma_2 \ll 1$ and $\beta|\omega-\omega_R| \ll 1$.

Besides demonstrating the correctness of the phenomenological equation (2.5) under certain conditions (these conditions have been outlined above), the microscopic theory described below gives quantitative estimates of ω_R and Γ_2, correct to second and third order in the interaction strength, respectively. Thus, ω_R is given by

$$\omega_R = \omega_0\{1+(J\rho)(\omega_e/\omega_0) - 2(J'\rho)^2 \times [\ln D/T + C - (\delta\omega/\omega_0)\ln 2]\}. \quad (2.11)$$

There is a misprint in Eq. (3.17) of I which, if corrected, gives (2.11).[19] The result obtained below for Γ_2 in the limit $kT \gg \omega_0, \omega_e$ is

$$\Gamma_2 = 4\pi(J'\rho)^2 kT \times \{\tfrac{1}{2}[1+(J/J')^2] - 4(J\rho)[\ln D/T + C]\}. \quad (2.12)$$

Here, D is the half-width of the conduction-electron energy band, ρ is the conduction-electron density of states, C is a constant approximately equal to unity, $\delta\omega = \omega_0 - \omega_e$, and J and J' are the longitudinal and transverse components of the exchange interaction defined by Eq. (4.3).

At temperatures well above the Kondo temperature, $kT_K = D\exp(-J\rho)^{-1}$, perturbation theory converges rapidly. It is then sufficient, for most purposes, to calculate corrections to the resonance frequency only to first order in J and J', and to calculate the linewidth to second order in J and J'. However, as is evident from (2.11) and (2.12), as the temperature is lowered toward the Kondo temperature, the next higher-order contributions to the resonance shift and relaxation rate become increasingly important. For temperatures lower than the Kondo temperature, (2.11) and (2.12) are completely inadequate, and a nonperturbative treatment is required.

The new result which is present in Eqs. (2.11) and (2.12) is the expression for the lowest-order (i.e., third-order) contribution to the relaxation rate Γ_2, which is logarithmic in the temperature. In I, it was shown that the individual level widths contained terms proportional to $\ln(D/T)$ in third order, but that these terms accounted for only a part of the full resonance linewidth Γ_2. Below, all contributions to Γ_2, to third order, have been calculated and the result is Eq. (2.12).

The other terms in (2.11) and (2.12) have been obtained previously. Townes, Herring, and Knight[20] estimated the magnitude of the first-order correction to

[19] I wish to thank R. Orbach for drawing this to my attention, and for a discussion of Eq. (2.5) in the limit $\beta\omega_R \gg 1$.

[20] C. H. Townes, C. Herring, and W. D. Knight, Phys. Rev. **77**, 852 (1950).

the resonance frequency and showed that this correction explained the shifts of the resonance frequencies of nuclei in metals observed by Knight.[21] (For nuclei, both ω_0 and J would be negative.) Shortly afterward, Korringa[14] gave a detailed calculation of the first-order resonance shift and the second-order contribution to spin-lattice relaxation and stated his now well-known relation [Eq. (1.1)] between them. The first direct calculation of the second-order contribution to the linewidth (T_2 had previously been inferred from the relation $T_1=T_2$, which is valid only when $J'=J$, and Korringa's result[14] for T_1) was given by Orbach and Spencer.[16] Interest in obtaining higher-order corrections was sparked by Spencer and Doniach's letter,[16] which showed that the second-order contribution to the g shift had a Kondo-like logarithmic dependence on temperature, and by Khabibullin's article,[16] which predicted a Kondo-like temperature dependence of the linewidth.

The interpretation of paramagnetic resonance experiments in metals is often carried out in terms of the surface impedance of the metal. The surface impedance can be determined in terms of the susceptibility $\chi_-(\omega)$. Suppose, for example, that the metal occupies the region of space $z>0$, that a static magnetic field is directed along the z axis and that a circularly polarized electromagnetic field proportional to $\mathbf{i}+i\mathbf{j}$ is normally incident on the metallic surface. The surface impedance can then be shown to be[22]

$$Z=-i\frac{k_0}{\sigma}[1+2\pi\tilde{\chi}_-(\omega)], \tag{2.13}$$

where $\tilde{\chi}_-(\omega)$ relates M_- to H_-, i.e., $M_-=\tilde{\chi}_-(\omega)H_-$. For $\beta\omega_R\ll 1$, $\tilde{\chi}_-(\omega)$ will be given by Eq. (2.8) with χ_0 replaced by $\tilde{\chi}_0$, where $\tilde{\chi}_0$ relates the equilibrium magnetization density M_z to the static field H_0, i.e., $M_z=\tilde{\chi}_0H_0$. The quantities $\tilde{\chi}_-(\omega)$ and $\chi_-(\omega)$ differ only because we have chosen to use reduced units throughout this paper. Also, in Eq. (2.13) σ is the electrical conductivity of the metal and $k_0=(1+i)\delta^{-1})$, where δ is the skin depth. Equation (2.13) could also have been obtained from the work of Dyson.[23]

III. PHENOMENOLOGICAL DESCRIPTION OF SPIN-LATTICE RELAXATION

In one type of paramagnetic relaxation experiment,[24] a radio-frequency magnetic field is applied along the z axis, which is taken to be the direction of the strong static external field. The effect of this radio-frequency field is accounted for by adding to the Hamiltonian of the system a term of the form

$$V(t)=-S_zh\exp[(-i\omega+\epsilon)t].$$

In analogy with (2.1) and (2.2), the response of the z component of the spin to this driving field can be written

$$\langle\delta S_z\rangle_t=\chi(\omega)he^{-i\omega t}, \tag{3.1}$$

where

$$\chi(\omega)=i\int_0^\infty dt\langle[S_z(t),S_z]\rangle e^{(i\omega-\epsilon)t} \tag{3.2}$$

and $\delta S_z=S_z-\langle S_z\rangle$, $\langle S_z\rangle$ being the value of S_z averaged over a thermal equilibrium ensemble.

The modified Bloch equation (2.5) may be used to obtain a phenomenological expression for the longitudinal susceptibility $\chi(\omega)$. By taking the z component of (2.5) and retaining only terms linear in h_{1z}, one finds the equation

$$\frac{\partial\langle S_z\rangle_t}{\partial t}=-\frac{\langle S_z\rangle_t-[\langle S_z\rangle+\chi_0h_{1z}(t)]}{T_1}. \tag{3.3}$$

The assumption that all quantities have the time dependence $e^{-i\omega t}$ and the use of (3.1) leads to the result

$$\chi(\omega)=\chi_0/(1-i\omega T_1). \tag{3.4}$$

Another way of arriving at an expression for the longitudinal susceptibility is to note that $\langle\delta S_z\rangle_t$ can be written

$$\langle\delta S_z\rangle_t=\tfrac{1}{2}[\delta n_\uparrow(t)-\delta n_\downarrow(t)], \tag{3.5}$$

where $\delta n_\sigma(t)=n_\sigma(t)-n_\sigma{}^0$ is the deviation of the population of the spin level σ, $n_\sigma(t)$, from its thermal equilibrium value $n_\sigma{}^0$. The populations obey the rate equations [cf. Eq. (30), Van Vleck and Weisskopf[3]]

$$\begin{aligned}\frac{d\delta n_\uparrow(t)}{dt}&=-w_{\uparrow\downarrow}\delta\bar{n}_\uparrow+w_{\downarrow\uparrow}\delta\bar{n}_\downarrow,\\ \frac{d\delta n_\downarrow(t)}{dt}&=w_{\uparrow\downarrow}\delta\bar{n}_\uparrow-w_{\downarrow\uparrow}\delta\bar{n}_\downarrow,\end{aligned} \tag{3.6}$$

where

$$\delta\bar{n}_\sigma=n_\sigma(t)-\bar{n}_\sigma \tag{3.7}$$

and

$$\begin{aligned}\bar{n}_\uparrow&=n_\uparrow{}^0+\chi(0)h_{1z}(t),\\ \bar{n}_\downarrow&=n_\downarrow{}^0-\chi(0)h_{1z}(t).\end{aligned} \tag{3.8}$$

The quantities $\bar{n}_\sigma$ defined by (3.8) are the values which the populations would have at time t if the system were to come instantaneously into thermal equilibrium in the total (static plus driving) magnetic field. Thus Eq. (3.6) assumes that the populations relax toward their instantaneous thermal equilibrium values. If all quantities in (3.6) are assumed to have the time dependence $e^{-i\omega t}$, these equations are easily solved, and the results, when combined with (3.5) and (3.1), give again the expression (3.4) for $\chi(\omega)$. One additional piece of information is obtained, however, and this is that the relaxation rate Γ_1 is given in terms of the

[21] W. D. Knight, Phys. Rev. **76**, 1259 (1949).
[22] This equation is the zero diffusion limit of Eq. (3.23) of M. B. Walker, Can. J. Phys. **48**, 111 (1970).
[23] F. J. Dyson, Phys. Rev. **98**, 349 (1955).
[24] C. J. Gorter, *Paramagnetic Relaxation* (Elsevier, New York, 1947).

transition probabilities $w_{\sigma\sigma'}$ by

$$\Gamma_1 = w_{\uparrow\downarrow} + w_{\downarrow\uparrow}. \tag{3.9}$$

The microscopic discussion given below shows that (3.6) is correct to third order in perturbation theory, in the sense that if the transition probabilities are calculated to third order using the results of ordinary time-dependent perturbation theory and are substituted into (3.6), correct results are obtained. To go to higher than third order it is necessary to use a renormalized interaction between the spin and the conduction electrons. The microscopic discussion also shows that (3.6) and (3.4) are valid only for $\beta|\Gamma|\ll 1$ and for frequencies sufficiently low that $\beta\omega \ll 1$.

Another point of interest is that the assumption

$$\langle\{\delta S_z(t), S_z\}\rangle = \langle\{\delta S_z(0), \delta S_z\}\rangle e^{-\Gamma_1|t|} \tag{3.10}$$

is equivalent to the assumption of the validity of (3.3) in that both lead to the same expression, Eq. (3.4), for the longitudinal susceptibility. To prove this, the identification $\chi_0 = \beta\langle(\delta S_z)^2\rangle$ should be made.

The above description applies to experiments which measure directly the susceptibility as a function of frequency.[24] A second type of experiment,[25] in which the transient recovery of the paramagnetic resonance absorption is observed following the application of a saturating pulse, is more difficult to describe theoretically, since the saturation of the spin system is a nonlinear process. It is possible, however, to think of a closely related experiment which can be described in terms of linear response theory. Suppose that one slowly switches on a small increment in the static field beginning at time $t=-\infty$ and then suddenly switches it off again at $t=0$. A measurement of the rate at which the magnetization decays to its thermal equilibrium value then gives the spin-lattice relaxation time. The perturbing part of the Hamiltonian associated with the prescribed process is

$$V(t) = -hS_z e^{\epsilon t}\theta(-t), \tag{3.11}$$

where $\theta(t)=0$, $t<0$ and $\theta(t)=1$, $t>0$. The increment in the magnetization is given by

$$\langle\delta S_z\rangle_t = -i\int_{-\infty}^{t} dt' \langle[S_z(t), V(t')]\rangle. \tag{3.12}$$

Again, the component of the linearized Bloch equation along the z axis can be used to obtain a phenomenological expression for the response. The solution of Eq. (3.3) with $h_{1z}(t) = h\theta(-t)e^{\epsilon t}$ is the required response, and is found to be

$$\begin{aligned} \langle\delta S_z\rangle_t &= \chi_0 h e^{\epsilon t}, \quad t<0 \\ \langle\delta S_z\rangle_t &= \chi_0 h e^{-\Gamma_1 t}, \quad t>0. \end{aligned} \tag{3.13}$$

Below, Γ_1 has been computed to third order in the interaction strength for a particular model [see Eq. (4.1)] of spins interacting with conduction electrons; the result obtained is valid when $\beta\omega_R \gg 1$ and when the temperature is higher than the Kondo temperature, and is given by

$$\Gamma_1 = 4\pi(J'\rho)^2 kT\{1-4J\rho[\ln(D/T)+C]\}. \tag{3.14}$$

As mentioned above, the second-order contribution to Γ_1 was obtained previously by Korringa. It is interesting that the Korringa relation (1.1) fails to be valid (unless $\omega_0=\omega_e$ and $J=J'$) as the temperature is lowered toward the Kondo temperature. By comparing (3.14) with (2.11) for the case of isotropic exchange, i.e., $J'=J$, it can be seen that a suitable extension of the Korringa relation to include the lowest-order Kondo-like correction is

$$T_1\left(\frac{\omega_R-\omega_0}{\omega_0}\right)^2 = \frac{\hbar}{4\pi kT}\left(\frac{\omega_e}{\omega_0}\right)^2\left(1-4J\rho\frac{\omega_0-\omega_e}{\omega_e}\ln\frac{D}{T}\right). \tag{3.15}$$

Another point of interest is that for an isotropic exchange interaction, the relation $T_1=T_2$ is correct to third order in J [cf. (3.14) and (2.12)].

IV. MICROSCOPIC DESCRIPTION OF PARAMAGNETIC RESONANCE LINE SHAPES

The evaluation of the transverse impurity spin susceptibility will be described in this section. The notation of I will be closely followed, and it will be assumed that the reader has an intimate knowledge of the first three sections of that paper. Before proceeding further, however, a few relevant points from I will be reviewed.

The paramagnetic impurity, which is characterized by an effective spin $S=\frac{1}{2}$, can occupy either of two eigenstates, $|\uparrow\rangle$ or $|\downarrow\rangle$. The first main point to note is that Abrikosov's[10] diagram technique for spins is used. Thus, for each spin eigenstate $|m\rangle$, a pair of pseudofermion creation and annihilation operators, $a_m^\dagger$ and a_m, which obey the usual fermion anticommutation relations, is introduced. In the pseudofermion representation, the spin operators are

$$S_- = a_\downarrow^\dagger a_\uparrow, \quad S_+ = a_\uparrow^\dagger a_\downarrow,$$

and

$$S_z = \tfrac{1}{2}(a_\uparrow^\dagger a_\uparrow - a_\downarrow^\dagger a_\downarrow) \tag{4.1}$$

and the explicit form of the Hamiltonian is

$$H_\lambda = \sum_m \lambda_m a_m^\dagger a_m + \sum_p \epsilon_p c_p^\dagger c_p + \sum_{mm'pp'} J_{mm'pp'} a_m^\dagger a_{m'} c_p^\dagger c_{p'}. \tag{4.2}$$

Here, $p\equiv(\mathbf{k},\sigma)$, and $\lambda_m = \lambda + \epsilon_m$, where

$$\epsilon_\uparrow = \tfrac{1}{2}\omega_0, \quad \epsilon_\downarrow = -\tfrac{1}{2}\omega_0,$$

and λ will eventually be allowed to tend to infinity so as to project out unphysical pseudofermion states. In

[25] P. L. Scott and C. D. Jeffries, Phys. Rev. 127, 32 (1962).

explicit calculations, $J_{mm'pp'}$ will be assumed to be independent of $\mathbf{k}$ and $\mathbf{k}'$ and denoted by $J_{mm'\sigma\sigma'}$; furthermore, its only nonvanishing values will be assumed to be

$$J_{\uparrow\uparrow\uparrow\uparrow}=J_{\downarrow\downarrow\downarrow\downarrow}=-J_{\uparrow\uparrow\downarrow\downarrow}=-J_{\downarrow\downarrow\uparrow\uparrow}=-(J/2\Omega)$$

and

$$J_{\uparrow\downarrow\downarrow\uparrow}=J_{\downarrow\uparrow\uparrow\downarrow}=-(J'/\Omega). \tag{4.3}$$

Note that Eq. (2.11) of I is incorrect and should be replaced by (4.3).

The single-particle pseudofermion propagator is defined to be

$$G_m(z_\nu)=-\int_0^\beta du\, e^{z_\nu u}\langle T\{a_m(u)a_m^\dagger\}\rangle \tag{4.4}$$

and can be written in the form

$$G_m(z_\nu)=[z_\nu-\lambda_m-M_m(z_\nu)]^{-1}. \tag{4.5}$$

The first- and second-order contributions to the self-energy are given by

$$M_m^{(1)}(z_\nu)=\sum_p J_{mmpp}f^+(\epsilon_p) \tag{4.6}$$

and

$$M_m^{(2)}(z_\nu)=\sum_{m'pp'}|J_{mm'pp'}|^2G_m(z_\nu+\epsilon_p-\epsilon_{p'})\times f^+(\epsilon_p)f^-(\epsilon_{p'}), \tag{4.7}$$

where $f^\pm(\epsilon_p)=[\exp(\pm\beta\epsilon_p)+1]^{-1}$. The rules for finding the higher-order contributions to $M_m(z_\nu)$ are given in I.

The quasiparticle approximation, which plays an important part in subsequent calculations, can be justified as follows: Consider the analytic continuation of the propagator $G_m(z_\nu)$ from the upper half-plane to the real axis, i.e., consider

$$G_m(\omega+i0^+)=[\omega-\lambda_m-\Delta_m(\omega)+i\Gamma_m(\omega)]^{-1}, \tag{4.8}$$

where $M_m(\omega+i0^+)=\Delta_m(\omega)-i\Gamma_m(\omega)$. $G_m(\omega+i0^+)$ is sharply peaked at the frequency $\omega=\lambda_m+\Delta_m(\omega)$ and in general, it is the value of $G_m(\omega+i0^+)$ for frequencies ω within Γ_m of the peak which is of interest. To proceed then, consider the function $f(\omega)$ defined by $f(\omega)=\omega-\lambda_m-\Delta_m(\omega)$. The renormalized energy $\tilde{\lambda}_m$ is defined to be the solution of $f(\tilde{\lambda}_m)=0$. The Taylor series expansion of $f(\omega)$ about the point $\omega=\tilde{\lambda}_m$ is

$$f(\omega)=(\omega-\tilde{\lambda}_m)Z_m^{-1}+(\omega-\tilde{\lambda}_m)^2Y_m^{-1}+\cdots, \tag{4.9}$$

where

$$Z_m^{-1}=1-\left.\frac{\partial\Delta_m(\omega)}{\partial\omega}\right|_{\omega=\tilde{\lambda}_m},\quad Y_m^{-1}=\left.\frac{\partial^2\Delta_m}{\partial\omega^2}\right|_{\omega=\tilde{\lambda}_m}. \tag{4.10}$$

A rough argument, to be sketched below, shows that the nth derivative of $\Delta_m(\omega)$ with respect to ω has a magnitude which is the order of $\beta^n\Gamma_m$. The expansion (4.9) is thus essentially an expansion in powers of the parameter $\beta(\omega-\tilde{\lambda}_m)$. Since the work of this paper will be restricted to situations where $\beta\Gamma_m\ll1$, the condition $\beta(\omega-\tilde{\lambda}_m)\ll1$ will be satisfied for all frequencies for which $G_m(\omega+i0^+)$ has an appreciable magnitude, and it will in general be a good approximation to keep only the first term in (4.9). Similarly, $\Gamma_m(\omega)$ can be replaced by $\Gamma_m(\tilde{\lambda}_m)$. Equation (4.8) can now be written as

$$G_m(\omega+i0^+)\approx Z_m/(\omega-\tilde{\lambda}_m+i\tilde{\Gamma}_m), \tag{4.11}$$

where $\tilde{\Gamma}_m=Z_m\Gamma_m$. Finally, it should be noted that if, in the rules for evaluating the diagrams, the propagators $G_m(\omega\pm i0^+)$ are replaced by the propagators

$$\tilde{G}_m(\omega\pm i0^+)=[\omega-\tilde{\lambda}_m\pm i\tilde{\Gamma}_m]^{-1}, \tag{4.12}$$

while, at the same time, the exchange interaction $J_{mm'pp'}$ is replaced by its renormalized value

$$\tilde{J}_{mm'pp'}=(Z_mZ_{m'})^{1/2}J_{mm'pp'}, \tag{4.13}$$

the final result for the contribution to any given diagram will remain unchanged.

It remains to show that $(\partial^n\Delta_m/\partial\omega^n)\sim\beta^n\Gamma_m$. On differentiating the expression (4.7) for the second-order contribution to the self-energy, it is found that

$$\frac{\partial M_m(\omega+i0^+)}{\partial\omega}=\sum_{m'pp'}|J_{mm'pp'}|^2\times\frac{\partial G_{m'}}{\partial\omega}(\omega+\epsilon_p-\epsilon_{p'}+i0^+)f^+(\epsilon_p)f^-(\epsilon_{p'}). \tag{4.14}$$

If the quasiparticle approximation is assumed on the right-hand side of (4.14), the differentiation of $\tilde{G}_{m'}(\omega+\epsilon_p-\epsilon_{p'}+i0)$ with respect to ω can be replaced by differentiation with respect to ϵ_p. An integration by parts then transfers the operation of differentiation to the Fermi factor $f^+(\epsilon_p)$ (the variation of $J_{mm'pp'}$ and the conduction-electron density of states with energy is relatively slow and can be neglected). Since $(\partial f^+(\epsilon)/\partial\epsilon)=-\beta f^+(\epsilon)f^-(\epsilon)$, one effect of the differentiation of $M_m(\omega)$ is to multiply it by the factor β. The extra factor of $f^-(\epsilon)$ in the integrand also reduces the domain of integration, since it goes to zero rapidly for $\epsilon<-kT$. Comparison of the expression for $\partial\Delta_m/\partial\omega$ with that for Γ_m now leads to the result $\partial\Delta_m/\partial\omega\sim\beta\Gamma_m$. Higher-order differentiations and higher-order diagrams can be discussed in the same way. This discussion has provided a self-consistent justification of the quasiparticle approximation, for the assumption of its validity on the right-hand side of (4.14) is shown to lead to the conditions which are necessary for its validity.

Since the quasiparticle approximation will be made throughout from this point on, it will be unnecessary to retain the tildes to denote renormalized quantities. Thus, Eq. (4.12) will be written

$$G_m(\omega\pm i0^+)=(\omega-\lambda_m\pm i\Gamma_m)^{-1} \tag{4.15}$$

from now on.

It is now possible to proceed to a study of the two-particle propagator $G_{-+}(x_\nu)$ defined by

$$G_{-+}(x_\nu)=-4\alpha\int_0^\beta du\, e^{x_\nu u}\langle T\{S_-(u)S_+\}\rangle\,, \quad (4.16)$$

where

$$\alpha=\tfrac{1}{4}e^{\beta\lambda_\downarrow}(1+e^{-\beta\omega_0})^{-1}\,, \quad (4.17)$$

and S_- and S_+ are given by Eq. (4.1). Once $G_{-+}(x_\nu)$ is known, $\chi_-(\omega)$ can be found from the relation

$$\chi_-(\omega)=-\tfrac{1}{2}G_{-+}(\omega+i0^+)\,. \quad (4.18)$$

$G_{-+}(x_\nu)$ is determined by the equation (see I)

$$(4\alpha)^{-1}G_{-+}(x_\nu)=\beta^{-1}\sum_{z_1}F_\nu(z_1) +\beta^{-2}\sum_{z_1,z_2}F_\nu(z_1)R_\nu(z_1,z_2)F_\nu(z_2)\,, \quad (4.19)$$

where the reducible particle-hole interaction R is given in terms of the irreducible interaction I by the Bethe-Salpeter equation

$$R_\nu(z_1,z_2)=I_\nu(z_1,z_2) +\beta^{-1}\sum_{z_3}I_\nu(z_1,z_3)F_\nu(z_3)R_\nu(z_3,z_2) \quad (4.20)$$

and

$$F_\nu(z_3)=G_\uparrow(z_3)G_\downarrow(z_3-x_\nu)\,. \quad (4.21)$$

If Eq. (4.20) is iterated, the result can be written symbolically in the form

$$R=I+IFI+IFIFI+\cdots\,. \quad (4.22)$$

Obviously the $(n+1)$th term differs from the nth by the presence of an additional factor FI. It will be seen explicitly below that the extra factor I contributes an extra factor of the order of magnitude of Γ_m to the $(n+1)$th term, whereas a partial fraction expansion of the term $F=G_\uparrow G_\downarrow$ [see (4.32)] shows that for frequencies close to the paramagnetic resonance frequency, it contributes an extra factor the order of Γ_m^{-1}. The product of these two additional factors is of the order of unity, indicating that all terms in the series on the right-hand side of (4.22) must be summed to obtain a good representation of R.

Now consider the external-field vertex function $\Lambda(z_1,\, z_1-x_\nu)$, defined in terms of the reducible particle-hole interaction by

$$\Lambda(z_1,\, z_1-x_\nu)=1+\beta^{-1}\sum_{z_2}R_\nu(z_1,z_2)F_\nu(z_2)\,. \quad (4.23)$$

Equation (4.20) can be combined with Eq. (4.23) to yield the basic equation

$$\Lambda(z_1,\, z_2-x_\nu)=1+\beta^{-1}\sum_{z_2}I_\nu(z_1,z_2) \times F_\nu(z_2)\Lambda(z_2,\, z_2-x_\nu)\,, \quad (4.24)$$

which will be used to determine Λ. Once Λ is known, the two-particle propagator can be determined using the relation

$$(4\alpha)^{-1}G_{-+}(x_\nu)=\beta^{-1}\sum_{z_1}F_\nu(z_1)\Lambda(z_1,\, z_1-x_\nu)\,. \quad (4.25)$$

To begin with, a treatment correct to second order in perturbation theory will be given. For this purpose, $I_\nu(z_1,z_2)$ can be written

$$I_\nu(z_1,z_2)=\int\frac{d\omega}{2\pi}\frac{I(\omega)}{z_1-z_2-\omega}\,, \quad (4.26)$$

as in Eqs. (4.9) and (4.10) of I.

The analysis of Eq. (4.24) begins with the conversion of the sum over z_2 to a contour integration. Thus,

$$\Lambda(z_1,\, z_1-x_\nu)=1-\frac{1}{2\pi i}\int_{C_1}dz_2\int\frac{d\omega}{2\pi}\frac{I(\omega)}{z_1-z_2-\omega}\left[\frac{1}{e^{\beta z_2}+1} +\frac{1}{e^{-\beta\omega}+1}\right]G_\uparrow(z_2)G_\downarrow(z_2-x_\nu)\Lambda(z_2,\, z_2-x_\nu)\,, \quad (4.27)$$

where the contour C_1 is shown in Fig. 1. The term $(e^{-\beta\omega}+1)^{-1}$ in the factor in square brackets is included to make the integrand nonsingular at the point $z_2=z_1-\omega$. It will now be assumed that the only singularities of the function $\Lambda(z_1,\, z_1-x_\nu)$, considered as a function of z_1, for fixed x_ν, are branch cuts at the lines $\mathrm{Im}z_1=0$, and $\mathrm{Im}(z_1-x_\nu)=0$. This assumption can be shown to be a self-consistent one. The integration over the contour C_1 can thus be replaced by an integration over the contour C_2 shown in Fig. 1. Finally, $\Lambda(z_1,\, z_1-x_\nu)$ is analytically continued in the z plane to the boundaries of its regions of analyticity, namely, $\mathrm{Im}z_1=0$ and $\mathrm{Im}(z_1-x_\nu)=0$, and x_ν is then put equal to $\omega_{\mathrm{ex}}+i0^+$, ω_{ex} being the externally applied frequency. The three different boundary value functions obtained by this procedure are

$$\Lambda_{++}(x,\omega_{\mathrm{ex}})=\Lambda(x+i0^+;\, x-\omega_{\mathrm{ex}}+i0^+)\,,$$
$$\Lambda_{--}(x,\omega_{\mathrm{ex}})=\Lambda(x-i0^+,\, x-\omega_{\mathrm{ex}}-i0^+)\,,$$

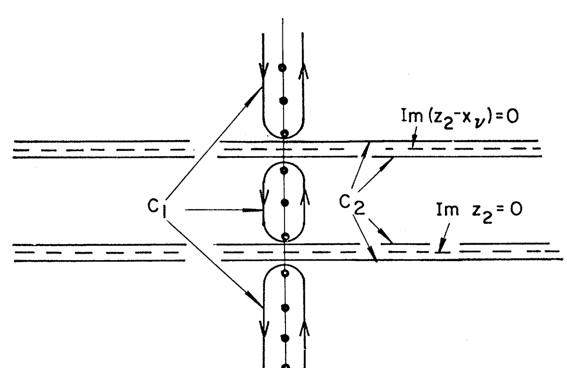

FIG. 1. Contours used in the evaluation of integrals (see text).

and

$$\Lambda_{+-}(x,\omega_{\text{ex}})=\Lambda(x+i0^+,\, x-\omega_{\text{ex}}-i0^+).$$

The three coupled integral equations obtained for these three functions can be summarized in the equation

$$\Lambda_{\eta_1\eta_2}(x,\omega_{\text{ex}})=1-\frac{1}{2\pi i}\int dx'\int\frac{d\omega}{2\pi}I(\omega)n(-\omega)\times\left\{\frac{G_\uparrow(x'+i0^+)G_\downarrow(x'-\omega_{\text{ex}}-i0^+)\Lambda_{+-}(x',\omega_{\text{ex}})}{x-x'-\omega+i\eta_1}-\frac{G_\uparrow(x'-i0^+)G_\downarrow(x'-\omega_{\text{ex}}-i0^+)\Lambda_{--}(x',\omega_{\text{ex}})}{x-x'-\omega+i\eta_1}+\frac{G_\uparrow(x'+i0^+)G_\downarrow(x'-\omega_{\text{ex}}+i0^+)\Lambda_{++}(x',\omega_{\text{ex}})}{x-x'-\omega+i\eta_2}-\frac{G_\uparrow(x'+i0^+)G_\downarrow(x'-\omega_{\text{ex}}-i0^+)\Lambda_{+-}(x',\omega_{\text{ex}})}{x-x'-\omega+i\eta_2}\right\},\quad(4.28)$$

where η stands for 0^+ or 0^-; also, the quantity $[\exp(\beta z_2)+1]^{-1}$ in (4.27) has been put equal to zero, since $z_2\to x'$ in (4.28), and only values of x' such that $x'\sim\lambda$ are important; $n(\omega)$ is defined by

$$n(\omega)=[e^{\beta\omega}-1]^{-1}.$$

The product $G_\uparrow(x+i0^+)G_\downarrow(x-\omega_{\text{ex}}-i0^+)$ can be expanded in the partial fraction expansion

$$G_\uparrow(x+i0^+)G_\downarrow(x-\omega_{\text{ex}}-i0^+)=-(\omega_{\text{ex}}-\omega_R+i\Gamma)^{-1}\times\left[\frac{1}{x-\lambda_\uparrow+i\Gamma_\uparrow}-\frac{1}{x-\omega_{\text{ex}}-\lambda_\downarrow-i\Gamma_\downarrow}\right],\quad(4.29)$$

where $\omega_R=\lambda_\uparrow-\lambda_\downarrow$ and $\Gamma=\Gamma_\uparrow+\Gamma_\downarrow$. Now, notice that the factor

$$\int d\omega n(-\omega)I(\omega)(x-x'-\omega+i\eta)^{-1}$$

in (4.28) is a slowly varying function of x' in the sense that it varies appreciably only when x' varies over an interval the order of kT. Furthermore, it will be assumed that $\Lambda_{\eta_1\eta_2}(x',\omega_{\text{ex}})$ is slowly varying in the same sense. [This assumption allows $\Lambda_{\eta_1\eta_2}(x,\omega_{\text{ex}})$ to be computed and the result, Eq. (4.35), is indeed a slowly varying function, a fact which provides a self-consistent justification of the original assumption.] On the other hand, the factor in square brackets in (4.29) is rapidly varying in the sense that it changes appreciably when x varies over an interval the order of Γ near $x\sim\lambda_\uparrow$ or $x\sim\lambda_\downarrow+\omega_{\text{ex}}$. (Recall that throughout this paper the assumption $\beta\Gamma_m\ll1$ is made, which allows us to make this distinction between slowly and rapidly varying functions.)

Now, consider the expansion

$$\frac{1}{x-\lambda_\uparrow+i\Gamma_\uparrow}=\frac{1}{x-\lambda_\uparrow+i0^+}+i\Gamma_\uparrow\frac{\partial}{\partial x}\left(\frac{1}{x-\lambda_\uparrow+i0^+}\right)+\cdots.\quad(4.30)$$

When integrating the product of (4.30) and some slowly varying (in the sense described above) function over x, an integration by parts transfers the operator $\partial/\partial x$ in the second term of (4.30) to the slowly varying function. Thus, for the purposes of a rough calculation, $\partial/\partial x$ can be replaced by β, and it can be seen that the expansion (4.30) is an expansion in the parameter $\beta\Gamma_\uparrow$. Since the quantity $\beta\Gamma_\uparrow$ will be considered a small quantity throughout this paper, it will be generally permissible to keep only the first term in expansions such as (4.30). In a similar way, it is possible to argue that the expansion

$$\frac{1}{x-\omega_{\text{ex}}-\lambda_\downarrow-i\Gamma_\downarrow}=\frac{1}{x-\lambda_\uparrow-i0^+}+(\omega_R-\omega_{\text{ex}}-i\Gamma_\downarrow)\times\frac{\partial}{\partial x}\frac{1}{x-\lambda_\uparrow-i0^+}+\cdots,\quad(4.31)$$

where $\omega_R=\lambda_\uparrow-\lambda_\downarrow$, is essentially an expansion in the parameter $\beta(\omega_R-\omega_{\text{ex}}-i\Gamma_\downarrow)$. Thus, (4.29) can be written as

$$G_\uparrow(x+i0^+)G_\downarrow(x-\omega_{\text{ex}}-i0^+)=\frac{2\pi i\delta(x-\lambda_\uparrow)}{\omega_{\text{ex}}-\omega_R+i\Gamma},\quad(4.32)$$

where $\Gamma=\Gamma_\uparrow+\Gamma_\downarrow$, provided $\beta\Gamma\ll1$ and the external frequency is sufficiently close to ω_R that $\beta|\omega-\omega_R|\ll1$. A similar expansion of the quantity

$$G_\uparrow(x-i0^+)G_\downarrow(x-\omega-i0^+)$$

shows that the first nonvanishing term is

$$G_\uparrow(x-i0^+)G_\downarrow(x-\omega-i0^+)=-\frac{\partial}{\partial x}\frac{1}{x-\lambda_\uparrow-i0^+}.\quad(4.33)$$

The corresponding expression for

$$G_\uparrow(x+i0^+)G_\downarrow(x-\omega-i0^+)$$

can be obtained by taking the complex conjugate of (4.33).

The expressions (4.32) and (4.33) are now substituted into (4.28). The second and third terms in the curly brackets on the right hand side of (4.28) can be neglected in comparison with the first and fourth terms, since they are smaller by the factor $\beta(\omega_{\text{ex}}-\omega_R+i\Gamma)$.

Thus, (4.28) becomes

$$\Lambda_{\eta_1\eta_2}(x,\omega_{\rm ex})=1-\frac{\Lambda_{+-}(\lambda_\uparrow,\omega_{\rm ex})}{\omega_{\rm ex}-\omega_R+i\Gamma}\int\frac{d\omega}{2\pi}n(-\omega)I(\omega)\times\left(\frac{1}{x-\lambda_\uparrow-\omega+i\eta_1}-\frac{1}{x-\lambda_\uparrow-\omega+i\eta_2}\right). \quad (4.34)$$

Equation (4.34) yields $\Lambda_{++}=\Lambda_{--}=1$, and

$$\Lambda_{+-}(x,\omega_{\rm ex})=1+\frac{in(-x+\lambda_\uparrow)I(x-\lambda_\uparrow)\Lambda_{+-}(\lambda_\uparrow,\omega_{\rm ex})}{\omega_{\rm ex}-\omega_R+i\Gamma}. \quad (4.35)$$

By putting $x=\lambda_\uparrow$ in (4.35), this equation becomes an equation for $\Lambda_{+-}(\lambda_\uparrow,\omega_{\rm ex})$, namely,

$$\Lambda_{+-}(\lambda_\uparrow,\omega_{\rm ex})=1-\frac{i\Gamma_v\Lambda_{+-}(\lambda_\uparrow,\omega_{\rm ex})}{\omega_{\rm ex}-\omega_R+i\Gamma}, \quad (4.36)$$

where

$$\Gamma_v=-\lim_{x\to\lambda_\uparrow}[n(-x+\lambda_\uparrow)I(x-\lambda_\uparrow)]. \quad (4.37)$$

The method of evaluating Eq. (4.25) for $G_{-+}(x_\nu)$ is much the same as the method just used for solving the equation for Λ. First the sum over z_1 is converted to a contour integral over the contour C_2 of Fig. 1 giving

$$(4\alpha)^{-1}G_{-+}(\omega+i0^+)=-\frac{1}{2\pi i}\int dx f(x)\times[(1-e^{\beta\omega})G_\uparrow(x+i0^+)G_\downarrow(x-\omega-i0^+)\Lambda_{+-}(x,\omega_{\rm ex})-G_\uparrow(x-i0^+)G_\downarrow(x-\omega-i0^+)+G_\uparrow(x+\omega+i0^+)G_\downarrow(x+i0^+)], \quad (4.38)$$

where the result $\Lambda_{++}=\Lambda_{--}=1$ has been used. It is important to note that at sufficiently low frequencies ω the factor $(1-e^{\beta\omega})\sim\beta\omega$ is a small quantity; thus, under certain conditions, all three terms in brackets in (4.38) can be of comparable magnitude, and it is not permissible to neglect terms proportional to

$$G_\uparrow(x+i0^+)G_\downarrow(x-\omega+i0^+)$$

and

$$G_\uparrow(x-i0^+)G_\downarrow(x-\omega-i0^+)$$

as was done in the derivation of the equation for Λ. When (4.32) and (4.33) are substituted into (4.38) and the integrals over x are performed, it is found to lowest order in $\beta\Gamma$ and $\beta|\omega-\omega_R|$ that

$$\chi_-(\omega)=-\tfrac{1}{2}G_{-+}(\omega+i0^+)=-\frac{\frac{1}{2}\tanh(\frac{1}{2}\beta\omega)\Lambda_{+-}(\lambda_\uparrow,\omega)}{\omega-\omega_R+i\Gamma}+\tfrac{1}{4}\beta. \quad (4.39)$$

It is now a simple matter to solve (4.36) for $\Lambda_{+-}(\lambda_\uparrow,\omega)$ and to substitute the result into (4.39), thus finally arriving at an expression for the transverse susceptibility comparable to that derived earlier by phenomenological arguments. Before doing this, however, the connection between Eq. (4.36) and the phenomenological equation of motion (2.6) for $\langle S_-\rangle_t$ will be demonstrated. This is easily done by first eliminating $\Lambda_{+-}(\lambda_\uparrow,\omega_{\rm ex})$ from (4.36) in favor of $\chi_-(\omega)$ using (4.39). Equation (4.36) then becomes an equation for $\chi_-(\omega)$, which can be written

$$-i\omega\chi_-(\omega)=(-i\omega_R-\Gamma_2)\chi_-(\omega)+\tfrac{1}{2}i\tanh\tfrac{1}{2}\beta\omega-\tfrac{1}{4}i\beta(\omega-\omega_R+i\Gamma_2), \quad (4.40)$$

where

$$\Gamma_2=\Gamma_\uparrow+\Gamma_\downarrow+\Gamma_v. \quad (4.41)$$

Since $\beta|\omega-\omega_R|\ll1$ is assumed, the function $\tanh\frac{1}{2}\beta\omega$ can be expanded in a Taylor series about the point $\omega=\omega_R$ giving, for the last two terms of (4.40), the expression

$$-i\langle S_z\rangle-i(\omega-\omega_R)(\tfrac{1}{4}\beta-\chi_0)+\tfrac{1}{4}\beta\Gamma_2. \quad (4.42)$$

The second of the three terms is negligible both when $\beta\omega_R\gg1$ and when $\beta\omega_R\ll1$. Furthermore, the third term is comparable to $\langle S_z\rangle$ only when $\beta\omega_R\ll1$ (since $\beta\Gamma_2\ll1$ is always assumed) and can therefore be replaced by $[\langle S_z\rangle/h_0']\Gamma_2$. Now, multiplying (4.40) by

$$h_-(t)=h_-\exp(-i\omega t)$$

and writing $\langle S_-\rangle_t=\chi_-(\omega)h_-\exp(-i\omega t)$ gives

$$\frac{d\langle S_-\rangle_t}{dt}=(-i\omega_R-\Gamma_2)\langle S_-\rangle_t+[\langle S_z\rangle/h_0']\Gamma_2h_-(t)-i\langle S_z\rangle h_-(t), \quad (4.43)$$

which is precisely Eq. (2.6).

It was shown in I that $\Gamma_\uparrow$ and $\Gamma_\downarrow$ correspond to the widths of the spin-up and spin-down energy levels as determined by the standard quantum-mechanical damping theory suitably generalized to take into account finite temperature effects. It was also stated in I that the paramagnetic resonance line width was not simply a sum of the two individual level widths, but that a complete theory should include vertex corrections as well. This complete theory has now been provided, the contribution Γ_v being the contribution of the vertex corrections to the transverse relaxation rate given by Eq. (4.41).

It is not difficult to generalize these results to third order in perturbation theory. To do this the expression for the third-order irreducible interaction is needed. This expression can be written

$$I_\nu(z_1,z_2)=\int\frac{d\omega}{2\pi}\frac{I(z_1,z_1-x_\nu;z_2,z_2-x_\nu;\omega)}{z_1-z_2-\omega}, \quad (4.44)$$

where

$$I(z_1,\, z_1-x_\nu;\, z_2,\, z_2-x_\nu;\, \omega)=2\pi \sum_{p_1p_2p_3m_1} J_{\uparrow m_1p_2p_1}J_{m_1\uparrow p_3p_2}J_{\downarrow\downarrow p_1p_3}f^+(\epsilon_{p_3})$$
$$\times[f^-(\epsilon_{p_1})G_{m_1}(z_1-\epsilon_{p_1}+\epsilon_{p_3})-f^-(\epsilon_{p_2})G_{m_1}(z_2-\epsilon_{p_2}+\epsilon_{p_3})]\delta(\omega-\epsilon_{p_1}+\epsilon_{p_2})$$
$$+2\pi \sum_{p_1p_2p_3m_1} J_{\downarrow m_1p_3p_2}J_{m_1\downarrow p_1p_3}J_{\uparrow\uparrow p_2p_1}f^+(\epsilon_3)[f^-(\epsilon_{p_1})G_{m_1}(z_1-\epsilon_{p_1}+\epsilon_{p_2}-x_\nu)$$
$$-f^-(\epsilon_{p_2})G_{m_1}(z_2-\epsilon_{p_2}+\epsilon_{p_3}-x_\nu)]+\text{two similar terms}. \quad (4.45)$$

The first two terms in (4.45) are the contributions of the two diagrams in Fig. 2, and the "two similar terms" referred to are the contributions of the two third-order diagrams identical to those of Fig. 2, but with the arrows on the conduction-electron lines reversed in direction.

The main point to note in (4.45) is that the third-order particle-hole interaction has the same analytic properties as the vertex function $\Lambda(z_1, z_1-x_\nu)$ examined above, that is to say, considered as a function of z_1 or z_2 for x_ν fixed, $I(z_1, z_1-x_\nu; z_2, z_2-x_\nu; \omega)$ has as its only singularities branch cuts when $\mathrm{Im}z_1=\mathrm{Im}(z_1-x_\nu)=\mathrm{Im}z_2=\mathrm{Im}(z_2-x_\nu)=0$. Thus, the contour integration and all the steps involved in the derivation of (4.36)–(4.43) from (4.23) and (4.25) can be carried out exactly as above. Instead of (4.37), however, the quantity Γ_v is defined by

$$\Gamma_v=-\lim_{x\to\lambda_\uparrow} n(-x+\lambda_\uparrow)I(x+i0^+,\, x-\omega_{\mathrm{ex}}-i0^+;\, \lambda_\uparrow+i0^+,\, \lambda_\uparrow-\omega_{\mathrm{ex}}-i0^+;\, x-\lambda_\uparrow) \quad (4.46)$$

where Γ_v is real. Formula (4.43) is again obtained.

The resonance line width and the shift of the resonance frequency can now be evaluated explicitly. This has been done for the simple *s-d* exchange interaction model described by (4.3). Furthermore, it was assumed that the temperature is sufficiently high that $kT\gg\omega_0,\omega_e$. To second order in perturbation theory, the resonance frequency is given by $\omega_R=\lambda_\uparrow-\lambda_\downarrow$. Since the λ_σ's are the renormalized spin energies, the resonance frequency can be written $\omega_R=\omega_0+\Delta_\uparrow-\Delta_\downarrow$ where ω_0 is the resonance frequency in the absence of the interaction. The level shifts $\Delta_\uparrow$ and $\Delta_\downarrow$ were calculated in I, and the result of this calculation was quoted earlier [see Eq. (2.11)].

Whereas terms depending logarithmically on temperature appear in the second-order result for the resonance shift, they do not appear in the linewidth calculation until third order. It thus seems to be consistent to calculate the linewidth to third order in perturbation theory, while calculating the resonance shift to second order. The individual level widths $\Gamma_\uparrow$ and $\Gamma_\downarrow$ were given in I to third order. Γ_σ can be evaluated to third order by substituting (4.45) into (4.46). Finally, $\Gamma_\uparrow$, $\Gamma_\downarrow$, and Γ_v can be combined as in (4.41) to give the transverse relaxation rate Γ_2; the explicit formula for the final result has already been given [Eq. (2.12)].

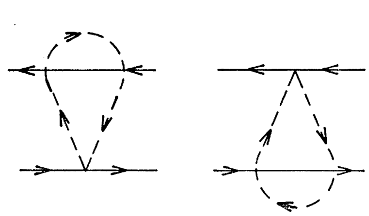

FIG. 2. Two of the four diagrams contributing to the third-order irreducible particle-hole interaction.

As pointed out at the beginning of this section, the exchange integral used in these calculations should be renormalized in accordance with the prescription (4.13). Note, however, that the first-order contribution to the self-energy (4.6) is frequency-independent, so that $(Z_mZ_{m'})^{1/2}=[1+O(J^2)]$. Thus it is permissible to use an unrenormalized exchange integral in (2.11) and (2.12) and still to have these expressions for the resonance frequency and the linewidth correct to second and third order, respectively.

V. MICROSCOPIC DESCRIPTION OF SPIN-LATTICE RELAXATION

The theory of spin-lattice relaxation presented here is based on the evaluation of the longitudinal susceptibility given by (3.2). The relevant Green's function is therefore

$$G'(u)=-\langle T\{S_z(u)S_z\}\rangle. \quad (5.1)$$

The prime indicates that the Abrikosov representation has not yet been introduced. In the Abrikosov representation, the Green's function (5.1) is written

$$G(u)=-\alpha\langle T\{n_\uparrow(u)-n_\downarrow(u),\, n_\uparrow-n_\downarrow\}\rangle, \quad (5.2)$$

where

$$\alpha=\tfrac{1}{4}e^{\beta\lambda_\downarrow}(1-e^{-\beta\omega_0})^{-1}. \quad (5.2')$$

The constant α has been determined in such a way that (5.1) and (5.2) are equal in the absence of the interaction between the spin and the conduction electrons. The presence of interactions modifies the value of the constant α, but the magnitude of this effect will not be estimated here. For further discussion of this point see I.

A few low-order contributions to the perturbation series for $G(u)$ are illustrated in Fig. 3. Notice that the irreducible particle-hole interaction, shown in Fig. 4, is conveniently represented by a matrix, its rows and columns being labeled by σ and σ', respectively. The rules for calculating the diagonal matrix elements $I_{\sigma\sigma;\nu}(z_1,z_2)$ are precisely the same as the rules for calcu-

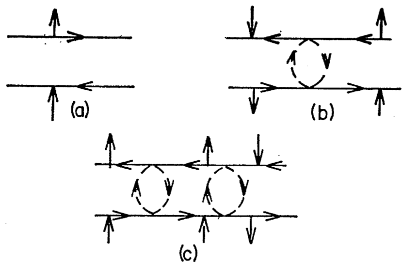

FIG. 3. Some low-order diagrams contributing to the Green's function describing the response to a longitudinal field (see Sec. V).

lating the irreducible particle-hole interaction used in the discussion of the linewidth (see I). However, an extra factor of (-1) must be included in the rules for the off-diagonal matrix elements $I_{\sigma\bar{\sigma};\nu}(z_1z_2)$. If there are an even number of off-diagonal $I_{\sigma\bar{\sigma}'s}$ in a given term, the product of these extra factors of (-1) is $(+1)$, as it should be, since such a term will contribute to $\langle T\{c_\uparrow^\dagger(u)c_\uparrow(u)c_\uparrow^\dagger c_\uparrow\}\rangle$ or $\langle T\{c_\downarrow^\dagger(u)c_\downarrow(u)c_\downarrow^\dagger c_\downarrow\}\rangle$. Alternatively, if there are an odd number of off-diagonal terms, the resulting factor of (-1) is necessary because such terms given contributions to $\langle T\{c_\uparrow^\dagger(u)c_\uparrow(u)c_\downarrow^\dagger c_\downarrow\}\rangle$ or $\langle T\{c_\downarrow^\dagger(u)c_\downarrow(u)c_\uparrow^\dagger c_\uparrow\}\rangle$.

The equation determining the Green's function is

$$\alpha^{-1}G(x_\nu)=\sum_1{}' F_1+\sum_{12}{}' F_1R_{12}F_2\,, \tag{5.3}$$

where the reducible particle-hole interaction R_{12} is determined by the Bethe-Salpeter equation

$$R_{12}=I_{12}+\sum_3{}' I_{13}F_3R_{32} \tag{5.4}$$

and

$$F_1=G_{\sigma_1}(z_1)G_{\sigma_1}(z_1-x_\nu)\,. \tag{5.5}$$

The index 1 in (5.3)–(5.5) stands for (σ_1,z_1) and $\sum_1{}'=\beta^{-1}\sum_1$.

The external-field vertex function is defined by the relation

$$\Lambda_1=1+\sum_2{}' R_{12}F_2\,, \tag{5.6}$$

and satisfies the equation

$$\Lambda_1=1+\sum_2{}' I_{12}F_2\Lambda_2\,. \tag{5.7}$$

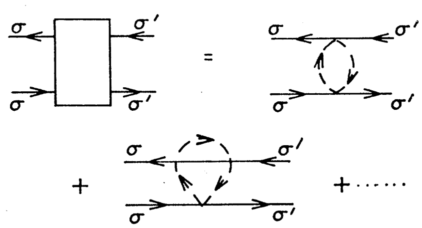

FIG. 4. Two of the diagrams contributing to the irreducible particle-hole interaction $I_{\sigma\sigma';\nu}(z_1,z_2)$.

When (5.7) is solved for Λ_1, the Green's function can be determined from

$$\alpha^{-1}G(x_\nu)=\sum_1{}' F_1\Lambda_1\,. \tag{5.8}$$

Except for the change of notation necessitated by the incorporation spin indices, σ, in the particle-hole interaction, these equations are very similar to Eq. (4.19)–(4.25) of the preceding section. A qualitative difference results, however, from the differences in the quantities called F and defined by (4.21) and (5.5). A partial fraction expansion of (5.5) similar to (4.29) and (4.32) yields

$$G_\sigma(x+i0^+)G_\sigma(x-\omega_{\rm ex}-i0^+) =2\pi i\delta(x-\lambda_\sigma)/(\omega_{\rm ex}+2i\Gamma_\sigma)\,. \tag{5.9}$$

The fact that this factor has a resonance when the external frequency is close to zero distinguishes it from (4.32), which has a resonance when the external frequency is close to the paramagnetic resonance frequency ω_R and can be shown to give rise ultimately to a resonance in the longitudinal susceptibility at zero frequency. The aim of subsequent work will be to develop an accurate expression for the longitudinal susceptibility where it is large, i.e., near zero frequency. This is shown to be possible for frequencies such that $\beta|\omega_{\rm ex}|\ll 1$, provided $\beta\Gamma_1\ll 1$.

The development of the theory of the longitudinal susceptibility parallels the development of the theory of the transverse susceptibility given in Sec. IV. To begin with, a calculation correct to second order in the interaction will be presented. First the sum over z_2 in (5.6) is converted to a contour integration over the contour C_2 specified in Fig. 1. Then approximations such as (5.9) which are correct to lowest order in $\beta|\omega_{\rm ex}|$ and $\beta\Gamma_1$ are introduced. This leads to an equation analogous to (4.36), namely,

$$\Lambda_{\sigma;+-}(x_1,\omega_{\rm ex})=1 +\sum_{\sigma_2}\frac{iI_{\sigma_1\sigma_2}(x_1-\lambda_{\sigma_2})n(-x_1+\lambda_{\sigma_2})\Lambda_{\sigma_2;+-}(\lambda_{\sigma_2};\omega_{\rm ex})}{\omega_{\rm ex}+2i\Gamma_{\sigma_2}}; \tag{5.10}$$

also, $\Lambda_{\sigma;++}=\Lambda_{\sigma;--}=1$. The factor $I_{\sigma_1\sigma_2}(\omega)$ appearing in (5.10) is defined in terms of the second-order irreducible particle-hole interaction $I_{\sigma_1\sigma_2}(z_1,z_2)$ by

$$I_{\sigma_1\sigma_2}(z_1,z_2)=\int\frac{d\omega}{2\pi}\frac{I_{\sigma_1\sigma_2}(\omega)}{z_1-z_2-\omega} \tag{5.11}$$

in analogy with Eq. (4.26).

The evaluation of the Green's function is begun by converting the sum over z_1 in Eq. (5.8) to a contour integration, which gives

$$\alpha^{-1}G(\omega_{\rm ex}+i0^+)=\frac{1}{2\pi i}\sum_\sigma\int_{-\infty}^{\infty}dxf(x)$$
$$\times[(1-e^{\beta\omega_{\rm ex}})G_\sigma(x+i0^+)G_\sigma(x-\omega_{\rm ex}-i0^+)$$
$$\times\Lambda_{\sigma;+-}(x,\omega_{\rm ex})-G_\sigma(x+\omega_{\rm ex}-i0^+)G_\sigma(x-i0^+)$$
$$+G_\sigma(x+\omega_{\rm ex}+i0^+)G_\sigma(x+i0^+)]. \quad (5.12)$$

Equation (5.12) should be compared with Eq. (4.38). Now, approximations similar to (4.32) and (4.33) are introduced, leading to the result

$$\alpha^{-1}G(\omega_{\rm ex}+i0^+)$$
$$=\beta\sum_\sigma e^{-\beta\lambda_\sigma}\left[\frac{\omega_{\rm ex}}{\omega_{\rm ex}+2i\Gamma_\sigma}\Lambda_{\sigma;+-}(\lambda_\sigma,\omega_{\rm ex})-1\right]. \quad (5.13)$$

Perhaps the simplest, and certainly the most straightforward, way of proceeding is to put $z_1=\lambda_{\sigma_1}$ in (5.10), to solve the resulting equation for $\Lambda_{\sigma;+-}(\lambda_\sigma;\omega_{\rm ex})$, and to substitute the solution into (5.13). It is, however, important to show that these results have an extremely simple interpretation in terms of a rate equation describing the time evolution of the populations of the spin energy levels. In the problem under consideration, the spin system is subjected to a driving field of frequency ω. Since only the linear response of the system is considered, the deviations of the populations from equilibrium have the same frequency, and can be written

$$\delta n_\sigma(t)=g_\sigma(\omega)he^{-i\omega t}, \quad (5.14)$$

where h is the magnitude of the applied magnetic field, as in Sec. III. Since the response of the system is given by $\delta\langle S_z\rangle_t=\frac{1}{2}[\delta n_\uparrow(t)-\delta n_\downarrow(t)]$ [see Eq. (3.5)], the susceptibility is given in terms of $g_\sigma(\omega)$ by

$$\chi(\omega)=\tfrac{1}{2}[g_\uparrow(\omega)-g_\downarrow(\omega)]. \quad (5.15)$$

Now note that (5.15) is in agreement with (5.13) [recall that $G(\omega+i0^+)=-\chi(\omega)$] if $g_\uparrow(\omega)$ and $g_\downarrow(\omega)$ are chosen to be

$$g_\uparrow(\omega)=-2\beta\alpha e^{-\beta\lambda_\uparrow}\left(\frac{\omega\Lambda_\uparrow}{\omega+2i\Gamma_\uparrow}-1\right),$$
$$g_\downarrow(\omega)=2\beta\alpha e^{-\beta\lambda_\downarrow}\left(\frac{\omega\Lambda_\downarrow}{\omega+2i\Gamma_\downarrow}-1\right), \quad (5.16)$$

where $\Lambda_\sigma\equiv\Lambda_{\sigma;+-}(\lambda_\sigma;\omega)$.

Now the equation determining Λ_σ must be transformed into an equation determining g_σ. The equation for Λ_σ is Eq. (5.10), with $z_1=\lambda_{\sigma_1}$, i.e.,

$$\Lambda_\sigma=1-\sum_{\sigma'}\frac{i\Gamma_{\sigma\sigma'}\Lambda_{\sigma'}}{\omega+2i\Gamma_{\sigma'}}, \quad (5.17)$$

where, by definition,

$$-\Gamma_{\sigma\sigma'}=\lim_{x\to\lambda_\sigma}n(-x+\lambda_{\sigma'})I_{\sigma\sigma'}(x-\lambda_{\sigma'}). \quad (5.18)$$

A comparison of $\Gamma_{\sigma\sigma'}$, just defined, with the transition probabilities $w_{\sigma\sigma'}$ computed in the first Born approximation shows that $\Gamma_{\uparrow\uparrow}=-w_{\uparrow\uparrow}$, $\Gamma_{\downarrow\downarrow}=-w_{\downarrow\downarrow}$, $\Gamma_{\downarrow\downarrow}=w_{\uparrow\downarrow}$, and $\Gamma_{\downarrow\uparrow}=w_{\downarrow\uparrow}$. Γ_σ can also be expressed in terms of the transition probabilities with the aid of the optical theorem (see I) which states $\Gamma_\sigma=\frac{1}{2}\sum_{\sigma'}w_{\sigma\sigma'}$. The elimination of Λ_σ from (5.19) in favor of g_σ, and the use of the relations between the quantities $\Gamma_{\sigma\sigma'}$, Γ_σ and the transition probabilities, gives the equations

$$-i\omega g_\uparrow=-w_{\uparrow\downarrow}g_\uparrow+w_{\downarrow\uparrow}g_\downarrow+4\beta\alpha w_{\uparrow\downarrow}e^{-\beta\lambda_\uparrow},$$
$$-i\omega g_\downarrow=w_{\uparrow\downarrow}g_\uparrow-w_{\downarrow\uparrow}g_\downarrow-4\beta\alpha w_{\downarrow\uparrow}e^{-\beta\lambda_\downarrow}. \quad (5.19)$$

These equations are now multiplied by $he^{-i\omega t}$, and $-i\omega$ on the left-hand side is replaced by the time derivative operator d/dt. Also, in dealing with the last term on the right-hand side, the static susceptibility

$$\chi(0)=\beta\langle(\delta S_z)^2\rangle=\beta[(1+e^{\beta\omega_R})(1+e^{-\beta\omega_R})]^{-1}$$

is introduced. In this way (5.19) can be written in the form

$$\frac{d\delta n_\uparrow(t)}{dt}=-w_{\uparrow\downarrow}\delta n_\uparrow+w_{\downarrow\uparrow}\delta n_\downarrow+\Gamma_1\chi(0)he^{-i\omega t},$$
$$\frac{d\delta n_\downarrow(t)}{dt}=w_{\uparrow\downarrow}\delta n_\uparrow-w_{\downarrow\uparrow}\delta n_\downarrow-\Gamma_1\chi(0)he^{-i\omega t}, \quad (5.20)$$

where $\Gamma_1=w_{\uparrow\downarrow}+w_{\downarrow\uparrow}$. These equations are simply the rate equations (3.6).

It is important to keep in mind that $\delta n_\sigma(t)$ has the time dependence $\exp(-i\omega t)$, and that (5.20) has a very limited range of validity, namely, it is valid for frequencies such that $\beta\omega\ll1$. Equation (5.20) is easily solved and the result (3.4) is obtained for the susceptibility.

The extension of the theory to third order in perturbation theory is accomplished by noting that, to third order, the irreducible particle-hole interaction can be written in the form

$$I_{\sigma_1\sigma_2}(z_1,z_2)=\int\frac{d\omega}{2\pi}\frac{I_{\sigma_1\sigma_2}(z_1,z_1-x_\nu;z_2,z_2-x_\nu;\omega)}{z_1-z_2-\omega}, \quad (5.21)$$

where $I_{\sigma_1\sigma_2}(z_1,z_1-x_\nu;z_2,z_2-x_\nu;\omega)$ is given by an expression similar to (4.28). Considered as a function of z_1 (or z_2) for fixed x_ν, $I_{\sigma_1\sigma_2}(z_1,z_1-x_\nu;z_2,z_2-x_\nu;\omega)$ has as its only singularities branch cuts along the lines $\text{Im}z_1=0$, $\text{Im}z_1=x_\nu$ (or $\text{Im}z_2=0$, $\text{Im}z_2=x_\nu$). It is easily seen that Eqs. (5.10)–(5.20) are unchanged by the substitution of (5.21) for (5.11), with the exception that Eq. (5.18) for $-\Gamma_{\sigma\sigma'}$ should be replaced by

$$-\Gamma_{\sigma\sigma'}=\lim_{x\to\lambda_\sigma}[n(-x+\lambda_{\sigma'})I_{\sigma\sigma'}(x+i0^+,x-\omega_{\rm ex}-i0^+;$$
$$\lambda_{\sigma'}+i0^+,\lambda_{\sigma'}-\omega_{\rm ex}-i0^+;x-\lambda_{\sigma'})], \quad (5.22)$$

where $\Gamma_{\sigma\sigma'}$ is real. The relations $\Gamma_{\sigma\sigma}=-w_{\sigma\sigma}$, and $\Gamma_{\sigma\bar{\sigma}}=-w_{\sigma\bar{\sigma}}$ can also be shown to hold to third order.

The calculation of the relaxation rate $\Gamma_1=w_{\uparrow\downarrow}+w_{\downarrow\uparrow}$ to third order in terms of the parameters J and J' of the model (4.3) is straightforward. The result has already been quoted [see Eq. (3.14)].

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Thermal Conductivity of Paramagnetic Salts at Low Temperatures*

V. Roundy and D. L. Mills†
Department of Physics, University of California, Irvine, Irvine, California 92664
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We present a simple theory of the effect of impurity-induced changes in atomic force constants and changes in atomic mass on the lifetime of coupled spin-phonon modes in paramagnetic crystals. The result is then employed to study the effect of impurity scattering, boundary scattering, and scattering of the coupled modes by longitudinal fluctuations in spin density on the temperature dependence of the thermal conductivity, and the frequency distribution of the heat flux. The theory can account for the experimental data on MgO doped with Cr^{2+} reported recently by Challis, McConachie, and Williams and offers support for the interpretation of the data presented by these authors.

I. INTRODUCTION

When paramagnetic ions are introduced into insulating crystals, phonons may induce transitions between the Zeeman levels. This spin-phonon interaction thus gives rise to spin-lattice relaxation,[1] shifts of the g factor,[2] and a number of other phenomena. When the wavelength of the resonant phonons (i.e., phonons with energy $\hbar\omega$ equal to the Zeeman energy) is large compared to the mean spacing between the ions, Jacobsen and Stevens[3] have pointed out that the normal modes of the system are coupled spin-phonon modes, in which the motion of different spins is correlated through the phonon field. The resulting modes have properties similar in many respects to the coupled magnon-phonon modes considered earlier by Kittel.[4]

In the theory of coupled spin-phonon modes in paramagnets, one linearizes the equations of motion by replacing the combination $S_z u$ by $\langle S_z\rangle u$, where u is the phonon amplitude, S_z the z component of spin, and the angular bracket denotes the thermal coverage. The normal modes are well defined only so long as this approximation is valid. The finite lifetime of the normal mode that results when the correction term $(S_z-\langle S_z\rangle)u$ is retained in the equations of motion was studied in an earlier work.[5] This term gives rise to a scattering of the coupled mode by spatial fluctuations in the z component of the spin of the ions. Since this work, other authors have also studied the lifetime of the coupled modes from other points of view.[6]

One finds that the scattering produced by the fluctuations in S_z has a resonant character, in the sense that the scattering rate is strongest for modes with frequency in the vicinity of the Zeeman frequency ω_0. The width of the resonance is roughly equal to the width of the frequency regime within which the coupled modes contain a large admixture of spin motion.

Detailed experimental studies of the thermal conductivity of crystals of MgO doped with Cr and other transition-metal impurities have recently been completed by Challis and co-workers.[7,8] The experiments were carried out in the liquid-He temperature range, and the Cr concentration ranged from 10^{-6} to 10^{-3}, depending on the sample. Also, the dependence of the thermal conductivity on the magnitude and direction of the magnetic field was measured.[8]

These authors analyzed their data in zero magnetic field[7] by employing a phenomenological model with a Debye spectrum of phonons combined with a frequency-dependent relaxation time. They included three terms in their expression for the inverse relaxation time $\tau^{-1}(\omega)$: a frequency-independent boundary scattering term, an impurity scattering contribution proportional to ω^4, and a resonant term proportional to $\omega^2(\omega^2-\omega_0^2)^{-2}$, where ω_0 and the coefficients of the various terms were determined by comparison with the data. It was suggested that the resonance term may possibly have its

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