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Electron paramagnetic resonance in exchange-coupled systems with unlike spins*

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Electron paramagnetic resonance in exchange-coupled systems with unlike spins (i.e, different g factors) is studied in the strong-isotropic-exchange limit. Arguments are advanced which show that in the long-wavelength low-frequency regime the dynamic magnetic susceptibility has a hydrodynamic component which can be identified with the dynamic susceptibility associated with the total spin. In an applied field the dynamic transverse susceptibility for the total spin develops an exchange-narrowed resonant peak. An expression for the effective g factor characterizing the resonance is obtained and evaluated. An equation for the linewidth is derived and estimates are given for the width in the infinite-temperature limit. Comparisons are made with previously published work on this problem, and possible experimental tests of the theory are suggested. The implications of this work for the analysis of the paramagnetic resonance of localized moments in nonmagnetic metals are discussed.

I. INTRODUCTION

The problem of characterizing the paramagnetic-resonance spectrum of an ensemble of exchange-coupled spins was recognized soon after the development of experimental techniques making possible detailed measurements on such systems. In a classic paper, Van Vleck[1] established the general features of the spectra in spin systems with both dipolar and exchange interactions. In Ref. 1 the distinction is made between systems with like spins (all magnetic atoms having the same g factor) and those with unlike spins. The development of the theory of magnetic resonance in systems of unlike spins (i.e., different g factors) has proceeded slowly. As will be discussed below, existing theories of paramagnetic resonance in systems with unlike spins where the Hamiltonian is dominated by the isotropic-exchange interaction are either incorrect or of limited applicability.

In this paper we will outline a theory of paramagnetic resonance in exchange-coupled systems with unlike spins which appears to overcome all the objections which can be raised against the previous theories. We derive a general expression for the effective g factor which we evaluate exactly in the high-temperature limit. We also investigate the resonance linewidth obtaining a formal expression for the width which involves time integrals of various spin-spin correlation functions. By approximating the integrals we obtain an estimate of the width in the infinite-temperature limit. Applications of the theory to disordered magnets have already been published.[2] Further applications will be reported elsewhere.

In Sec. II we introduce the Hamiltonian. Having done this we review existing theories for the effective g factor. In Sec. III we begin the development of the theory. This is done in two stages. First, the general problem of the low-frequency long-wavelength spin dynamics in systems with unlike spins is analyzed from a hydrodynamic point of view. Second, the important features of the dynamic magnetic susceptibility in the hydrodynamic regime are established. In Sec. IV we present a detailed analysis of the effective g factor and the linewidth. Section V is devoted to a general discussion of the theory and related experimental studies.

II. PRELIMINARY ANALYSIS

We begin this section by introducing the Hamiltonian for the system. With little loss in generality we specialize to a system having two types of spins, $\vec{S}_A$ and $\vec{S}_B$, with g factors g_A and g_B, where $g_A \neq g_B$. The Hamiltonian is written

$$\mathcal{H} = -\sum_{(Ai,Aj)} 2J_{AiAj}\vec{S}_{Ai}\cdot\vec{S}_{Aj} - \sum_{(Bi,Bj)} 2J_{BiBj}\vec{S}_{Bi}\cdot\vec{S}_{Bj} - \sum_{(Ai,Bj)} 2J_{AiBj}\vec{S}_{Ai}\cdot\vec{S}_{Bj} + g_A\mu_B H\sum_{Ai} S^z_{Ai} + g_B\mu_B H\sum_{Bi} S^z_{Bi} + \mathcal{H}_{\text{anis}}. \quad (1)$$

The first three terms make up the isotropic Heisenberg exchange interaction, where (,) denotes a sum over pairs; J_{AiAj} is the interaction between A spins, J_{BiBj} is the ineraction between B spins, and J_{AiBj} is the interaction between A and B spins. Also, μ_B is the Bohr magneton and H is the applied magnetic field. The symbol $\mathcal{H}_{\text{anis}}$ denotes the anisotropic terms, which can involve both dipolar and single-ion anisotropy.

We assume that there are non-negligible numbers of both A and B spins and that the two types are spatially intermingled. We do not make any additional assumptions about the relative positions of the spins. They can either be located at random or in a spatially ordered array. As noted, our analysis pertains to systems with strong isotropic exchange interactions. This will be the case if the exchange field seen by each one of the spins is large in comparison with the applied and the anisotropy fields. In addition, we assume that the A and B subsystems are strongly coupled to one another so that

$$-\sum_{(Ai,Bj)} 2J_{AiBj}\vec{s}_{Ai}\cdot\vec{s}_{Bj} \gg g_A\mu_B H\sum_{Ai} s^z_{Ai} + g_B\mu_B H\sum_{Bi} s^z_{Bi} + \mathcal{H}_{\text{anis}} . \quad (2)$$

This symbolic inequality will be reformulated and discussed in greater detail at the end of Sec. IV.

When the intersystem exchange integrals J_{AiBj} are equal to zero (and the anisotropic terms are small), the resonance spectrum is dominated by sharp peaks at $\hbar\omega = g_A\mu_B H$ and $\hbar\omega = g_B\mu_B H$. With increasing coupling between the A and B spins the lines broaden and begin to overlap. Finally, in the limit shown in Eq. (2) the spectrum is dominated by a single resonance at $\hbar\omega = g_{\text{eff}}\mu_B H$, where g_{eff} denotes the effective g factor. The shift from a two-peak to a one-peak spectrum is an example of exchange narrowing[1] which in this case is induced by the exchange coupling between the two subsystems.

The first calculation of g_{eff} in the exchange narrowed limit was reported by Pryce.[3] Treating the difference between the spins as a small perturbation he obtained the result

$$g_{\text{eff}} = \tfrac{1}{2}(g_A + g_B) . \quad (3)$$

Equation (3) shows no explicit dependence on temperature or on the relative concentrations and magnitudes of the A and B spins. It is rigorously correct only in so far as it applies to the case $N_A = N_B$, $s_A = s_B$, and $T = \infty$.

Subsequently, Bloembergen and Rowland[4] computed g_{eff} from the first moment of the Fourier transform of the magnetic moment correlation function. Their result took the form

$$g_{\text{eff}} = (g_A N_A + g_B N_B)/(N_A + N_B) , \quad (4)$$

where N_A (N_B) is the number of A (B) spins. However, as they point out Eq. (4) holds only for $s_A = s_B$ and $T = \infty$. In Sec. IV we will give a general expression for g_{eff} which reduces to the Bloembergen-Rowland result in the appropriate limit and is the proper generalization of their findings to finite temperatures and unequal angular momenta.

An alternative expression for the g factor can be obtained from the phenomenological equations for ferrimagnetic resonance[5]

$$\frac{d\vec{M}_A}{dt} = \frac{g_A\mu_B}{\hbar}\vec{M}_A \times (\vec{H} + \lambda\vec{M}_B), \quad (5)$$

$$\frac{d\vec{M}_B}{dt} = \frac{g_B\mu_B}{\hbar}\vec{M}_B \times (\vec{H} + \lambda\vec{M}_A) , \quad (6)$$

where λ is a molecular-field coupling constant, and $\vec{M}_A$ and $\vec{M}_B$ are the magnetic moments of the two subsystems:

$$\vec{M}_A = -g_A\mu_B\sum_{Ai}\vec{s}_{Ai} , \quad (7)$$

$$\vec{M}_B = -g_B\mu_B\sum_{Bi}\vec{s}_{Bi} . \quad (8)$$

The solution of the linearized version of Eqs. (5) and (6) is characterized by a low-frequency resonance with an effective g factor given by

$$g_{\text{eff}} = \frac{\langle M^z_A\rangle_T + \langle M^z_B\rangle_T}{\langle M^z_A\rangle_T/g_A + \langle M^z_B\rangle_T/g_B} , \quad (9)$$

where $\langle\cdots\rangle_T$ denotes an average carried out at temperature T. In the high-temperature limit, Eq. (9) becomes

$$g_{\text{eff}} = \frac{g_A^2 s_A(s_A+1)N_A + g_B^2 s_B(s_B+1)N_B}{g_A s_A(s_A+1)N_A + g_B s_B(s_B+1)N_B} . \quad (10)$$

It is apparent that Eq. (9) does not reduce to Eq. (4) when $s_A = s_B$. The failure to do so is attributed by Bloembergen and Rowland to the fact that the linearized form of Eqs. (5) and (6) are applicable only at low temperatures since they omit the effects of fluctuations in the exchange field.

Recently, Gulley and Jaccarino[6] have used equations similar to (linearized) (5) and (6), but augmented by damping terms, in order to characterize resonance in paramagnets with small concentrations of impurities. Although they obtain reasonable agreement with their measured values of g_{eff} in RbMnF_3: Ni (5at.%) their approach is incorrect whenever there is strong coupling between the two subsystems. When the coupling is strong the fluctuations in the AB exchange field in the paramagnetic phase are sufficiently large [cf. **Eq.** (2)] as to preclude characterization in terms of phenomenological impurity-host and host-impurity cross relaxation rates of the form employed. This is seen in the expression obtained for the high-temperature limit of g_{eff} in the presence of finite cross relaxation. Using the equations of Ref. 6 we find

$$g_{\text{eff}} = \frac{g_A^3 s_A(s_A+1)N_A + g_B^3 s_B(s_B+1)N_B}{g_A^2 s_A(s_A+1)N_A + g_B^2 s_B(s_B+1)N_B} . \quad (11)$$

Like (10), Eq. (11) is in disagreement with the Bloembergen-Rowland result when s_A is set equal to s_B. The origin of the disagreement can be traced to the cross-relaxation rates and detailed balance condition, which do not take proper account of the conservation of total spin. (This point is discussed in greater detail at the end of Sec. V.)

III. SPIN DYNAMICS

In this section we outline a hydrodynamic theory of the long-wavelength low-frequency spin dynamics in exchange coupled systems with unlike spins. In the interest of simplicity we will at first omit the anisotropic and Zeeman terms in the Hamiltonian leaving only the isotropic exchange interactions.

The Heisenberg Hamiltonian $\mathcal{H}_{\text{ex}}$ is characterized by the symmetry property that the total spin is a constant of the motion, i.e.,

$$[\vec{S}, \mathcal{H}_{\text{ex}}] = 0, \tag{12}$$

where

$$\vec{S} = \sum_{Ai} \vec{s}_{Ai} + \sum_{Bi} \vec{s}_{Bi}. \tag{13}$$

At finite temperatures the long-wavelength low-frequency response is governed by hydrodynamics.[7] In the paramagnetic phase the hydrodynamic modes characterize spin and energy diffusion. To illustrate this we denote the (spatial) Fourier transforms of the spin and energy densities by $\vec{s}(\vec{q}, t)$ and $\epsilon(\vec{q}, t)$, respectively [note $\vec{S} = \vec{s}(0, t)$, $\mathcal{H}_{\text{ex}} = \vec{\epsilon}(0, t)$]. The corresponding hydrodynamic equations take the form

$$\frac{\partial \vec{s}(\vec{q}, t)}{\partial t} = -D_S q^2 \vec{s}(\vec{q}, t), \tag{14}$$

$$\frac{\partial \epsilon(\vec{q}, t)}{\partial t} = -D_E q^2 \epsilon(\vec{q}, t), \tag{15}$$

where D_S and D_E are the spin and energy diffusion constants, respectively.

The operator of primary interest in magnetic studies is the magnetic moment density. We define its (spatial) Fourier transform $\vec{m}(\vec{q}, t)$ by

$$\vec{m}(\vec{q}, t) = -e^{i\mathcal{H}_{\text{ex}}t/\hbar}\Big[g_A\mu_B \sum_{Ai} \vec{s}_{Ai}\, e^{i\vec{q}\cdot\vec{r}_{Ai}} + g_B\mu_B \sum_{Bi} \vec{s}_{Bi}\, e^{i\vec{q}\cdot\vec{r}_{Bi}}\Big] e^{-i\mathcal{H}_{\text{ex}}t/\hbar}, \tag{16}$$

with the total moment $\vec{M}(t)$ equal to $\vec{m}(0, t)$. Since $\vec{M} = \vec{M}_A + \vec{M}_B$ does not commute with $\mathcal{H}_{\text{ex}}$, it would seem as though there was no hydrodynamic behavior associated with $\vec{m}(\vec{q}, t)$. However, this is not the case. The essential point here is that $\vec{M}$ has a finite projection onto $\vec{S}$.[8,9] This projection [or equivalently, the hydrodynamic component of $\vec{m}(\vec{q}, t)$] reflects the fact that the fluctuations in $\vec{M}$ are correlated with fluctuations in $\vec{S}$ as is evident in the nonzero value for the correlation function $\langle \vec{S} \cdot \vec{M} \rangle_T$.

In order to obtain expressions for the magnetic susceptibility which correctly incorporate the hydrodynamic behavior we make use of the projection operator formalism of Mori.[10] We designate the projection operator into the hydrodynamic variables by $\mathcal{P}$. In the absence of a magnetic field m^α couples only to s^α ($\alpha = x, y, z$). As a consequence it is sufficient to take $\mathcal{P}m^\alpha$, the hydrodynamic component of the magnetic moment, to be of the form

$$\mathcal{P}m^\alpha = (m^\alpha, s^{\alpha\dagger}) s^\alpha / (s^\alpha, s^{\alpha\dagger}), \tag{17}$$

with † denoting adjoint. In (17) and subsequent equations, (a, b) is defined for operators a and b by

$$(a, b) = \int_0^\beta d\lambda \langle e^{\lambda\mathcal{H}} a e^{-\lambda\mathcal{H}} b \rangle_T - \beta \langle a \rangle_T \langle b \rangle_T, \tag{18}$$

where $\mathcal{H}$ is the Hamiltonian and $\beta = 1/KT$, K being Boltzmann's constant. Using Eq. (17) we can separate m^α into its hydrodynamic and nonhydrodynamic components

$$m^\alpha = \mathcal{P}m^\alpha + (1 - \mathcal{P}) m^\alpha. \tag{19}$$

The separation displayed in (19) leads to a two-component expression for the dynamic magnetic susceptibility $\chi_{m^\alpha m^\alpha}(\vec{q}, \omega)$, a function of wave vector $\vec{q}$ and frequency ω.[8] Denoting the imaginary part by χ'', at small wave vectors we obtain the limiting form

$$\frac{\chi''_{m^\alpha m^\alpha}(\vec{q}, \omega)}{\omega \chi_{m^\alpha m^\alpha}(\vec{q})} = \frac{(M^\alpha, S^\alpha)^2}{(M^\alpha, M^\alpha)(S^\alpha, S^\alpha)} \frac{D_S q^2}{\omega^2 + (D_S q^2)^2} + \left(1 - \frac{(M^\alpha, S^\alpha)^2}{(M^\alpha, M^\alpha)(S^\alpha, S^\alpha)}\right) f(\omega), \tag{20}$$

where $\chi_{m^\alpha m^\alpha}(\vec{q})$ is the static magnetic susceptibility and $f(\omega)$ is a slowly varying function of $\vec{q}$ whose integral over the interval $-\infty \le \omega \le \infty$ is equal to π. The first term in (20) reflects the coupling to the total spin; the second is the remainder associated with the nonhydrodynamic part of $\vec{m}$. The functional form of $f(\omega)$ is not predicted by hydrodynamics. However its width in frequency $\Delta\omega$, can be estimated from the second moment of the autocorrelation function for the operator $(1 - \mathcal{P})M^\alpha$,

$$\Delta\omega \approx \left(\frac{\langle [(1-\mathcal{P})M^\alpha, \mathcal{H}_{\text{ex}}][\mathcal{H}_{\text{ex}}, (1-\mathcal{P})M^\alpha] \rangle_T}{\langle (1-\mathcal{P})M^\alpha (1-\mathcal{P})M^\alpha \rangle_T}\right)^{1/2}. \tag{21}$$

The diffusive form of the first term on the right-hand side of Eq. (20) is a consequence of the fact that $\vec{S}$ is a constant of the motion for the Heisenberg Hamiltonian. The presence of (weak) anisotropy in the spin Hamiltonian is accounted for by the replacement

$$D_S q^2 \to D_S q^2 + 1/T_2^A, \tag{22}$$

where T_2^A is identified with the spin-spin relaxation time. (Were spin-phonon interactions of importance, but not dominant, their contribution would appear as $D_S q^2 + 1/T_2^A + \omega_{\text{SL}}$, where ω_{SL} is the spin-lattice relaxation rate.)

The presence of an applied field modifies the above picture in two ways. First, there is a coupling between the energy and the longitudinal-spin diffusion modes which results in a spectrum for the longitudinal magnetic susceptibility which is characterized by two diffusive central peaks.[7,11,12] Second, for sufficiently large fields the hydrodynamic part of the transverse magnetic susceptibility develops a resonant peak at a frequency proportional to the field. The location and width of this peak will be discussed in Sec. IV.

IV. RESONANT FREQUENCY AND LINEWIDTH

The function of interest in paramagnetic resonance studies is the dynamic transverse magnetic susceptibility at $\vec{q}=0$. In Sec. III it was pointed out that in a magnetic field the transverse susceptibility develops resonant structure whose characteristic frequency is proportional to H. In order to see this we introduce the rotating wave, $\vec{q}=0$ susceptibility $\chi_{M^+M^-}(\omega)=\chi_{m^+m^-}(0,\omega)$ $(M^\pm = M^x \pm iM^y)$. Analogous to Eq. (20) we have

$$\frac{\chi''_{M^+M^-}(\omega)}{\omega\chi_{M^+M^-}} = \frac{(M^+, S^-)^2}{(M^+, M^-)(S^+, S^-)}\,\frac{\chi''_{S^+S^-}(\omega)}{\omega\chi_{S^+S^-}} + \left(1-\frac{(M^+, S^-)^2}{(M^+, M^-)(S^+, S^-)}\right) f(\omega)\,, \tag{23}$$

where $\chi_{S^+S^-}(\omega)$ is the dynamic susceptibility associated with the total spin $\vec{S}$. The first term in (23) arises from the projection of $\vec{M}$ onto $\vec{S}$ and is seen to be the generalization of the diffusive term in Eq. (20). In the second term, $f(\omega)$ has a width on the order of J_{AB} and does not contribute to a sharp resonance line in the usual cases [see Eq. (49) and the discussion following Eq. (50)].

In order to determine the location of the resonance we relate $\chi''_{S^+S^-}(\omega)$ to the relaxation function $(S^+(t), S^-)$ through the equation[13]

$$\chi''_{S^+S^-}(\omega) = \omega \,\mathrm{Re} \int_0^\infty dt\, e^{-i\omega t}(S^+(t), S^-)\,, \tag{24}$$

where Re denotes real part. Resonant structure in $\chi''_{S^+S^-}$ is equivalent to an asymptotic time dependence of $(S^+(t), S^-)$ of the form

$$(S^+(t), S^-) = (S^+, S^-)e^{i\omega_0 t-\gamma|t|} = \chi_{S^+S^-}\, e^{i\omega_0 t-\gamma|t|}\,, \tag{25}$$

having used the well-known expression for the static susceptibility $\chi_{ab}=(a, b)$.[14]

Equation (25) will be appropriate if the linewidth γ is small in comparison with the exchange frequency, a condition which will be discussed in more detail below. In the meantime, assuming (25) to be valid, we obtain an expression for the resonant frequency ω_0 from the equation[15]

$$\omega_0 = -i\left(\frac{dS^+}{dt}, S^-\right)\Big/(S^+, S^-) = -\frac{1}{\hbar}\langle[S^+, S^-]\rangle_T = \frac{-2\langle S^z\rangle_T}{\hbar(S^+, S^-)}\,, \tag{26}$$

having used the identity[14]

$$\left(\frac{da}{dt}, b\right) = \frac{-i}{\hbar}\langle[a, b]\rangle_T\,. \tag{27}$$

Equation (26) is one of the principal results of this study. It expresses the resonant frequency as the ratio of the expectation value of the total spin to the transverse spin susceptibility. By making use of the (approximate for noncubic systems) equality

$$(S^x, S^x)^0 = (S^y, S^y)^0 = (S^z, S^z)^0\,, \tag{28}$$

where $(\ ,\ )^0$ denotes evaluation in zero applied field, we can extract the effective g factor for the paramagnetic phase. In the small-field limit we find

$$g_{\text{eff}} = \frac{\hbar\omega_0}{\mu_B H} = -\frac{(S^z, M^z)^0}{\mu_B(S^z, S^z)^0}\,, \tag{29}$$

having identified $\langle S^z\rangle_T$ with $(S^z, M^z)^0 H$. Equation (29) is to be compared with the g_{eff} obtained from Eq. (9), which we can rewrite as

$$g_{\text{eff}} = -\langle M^z\rangle_T/\mu_B\langle S^z\rangle_T\,. \tag{9'}$$

In the paramagnetic phase, where $\langle M^z\rangle_T$ and $\langle S^z\rangle_T$ are proportional to H, Eq. (9′) becomes

$$g_{\text{eff}} = -(M^z, M^z)^0/\mu_B(S^z, M^z)^0\,, \tag{9''}$$

a result which is similar, but not identical, to Eq. (29).

Exact evaluation of Eq. (29) is possible only in the infinite temperature limit. As $T\to\infty$ we have

$$g_{\text{eff}} = \frac{g_A s_A(s_A+1)N_A + g_B s_B(s_B+1)N_B}{s_A(s_A+1)N_A + s_B(s_B+1)N_B}\,. \tag{30}$$

In the appropriate limits, Eq. (30) is seen to agree with Eqs. (3) and (4) but differs from Eqs. (10) and (11). We regard the agreement with the expressions of Pryce and Bloembergen and Rowland as strong evidence in support of the overall correctness of our approach.

Some indication of the temperature variation of g_{eff} is provided by an evaluation of Eq. (29) in the molecular-field approximation.[2] As an example we consider a spatially ordered AB array with nearest neighbor exchange integrals J_{AA}, J_{BB}, and J_{AB}. Defining functions C_1, C_2, C_3, and C_4 by

$$C_1 = [3KT - 2Z(B,B)\,J_{BB}\,s_B(s_B+1)]\,s_A(s_A+1), \tag{31}$$

$$C_2 = [3KT - 2Z(A,A)\,J_{AA}\,s_A(s_A+1)]\,s_B(s_B+1), \tag{32}$$

$$C_3 = 2Z(A,B)\,J_{AB}\,s_A(s_A+1)s_B(s_B+1)\,, \tag{33}$$

$$C_4 = 2Z(B,A)\,J_{AB}\,s_B(s_B+1)s_A(s_A+1), \tag{34}$$

where $Z(X,Y)$ denotes the number of nearest neighbors of an X spin which are of the type Y, we obtain the result

$$g_{\text{eff}} = \frac{(C_1 g_A + C_3 g_B)N_A + (C_2 g_B + C_4 g_A)N_B}{(C_1+C_3)N_A + (C_2+C_4)N_B}\,, \tag{35}$$

indicating a temperature dependence of the form $(x_1 + x_2T)/(x_3 + x_4T)$. Also, when $C_1 = C_2$, $C_3 = C_4$, and $N_A = N_B$, Eq. (35) reduces to the Pryce result, Eq. (3), independent of the temperature.

As noted, the appropriateness of Eq. (25) requires that the damping be small relative to the exchange frequency. To establish the conditions under which this is true we use a general expression for γ given by Mori[10]

$$\gamma = (S^+, S^-)^{-1} \int_0^\infty dt\, e^{-i\omega_0 t} \times \left(\exp[it(1-\mathcal{P})\mathcal{L}](1-\mathcal{P}) \frac{dS^+}{dt},\ (1-\mathcal{P}) \frac{dS^-}{dt} \right), \tag{36}$$

where $\mathcal{L}$ is the Liouville operator defined by

$$\mathcal{L}a = (1/\hbar)[\mathcal{H}, a]. \tag{37}$$

Since $[S^+, \mathcal{H}_{\mathrm{ex}}] = 0$, a nonzero value for γ reflects the presence of the Zeeman and anisotropy terms in the Hamiltonian. Although not contributing to dS^+/dt the isotropic exchange interaction does influence the dynamics through the time evolution operator $\exp[it(1-\mathcal{P})\mathcal{L}]$. As a consequence the resonance is strongly exchange narrowed. Because the Zeeman and anisotropy terms contribute independently to the damping (cross terms linear in the field give rise to a small frequency shift) the contribution of the former can be estimated from the zero-field relaxation rate

$$\gamma_{\mathrm{anis}} \approx \frac{1}{T_2^A} \approx [(S^+, S^-)^0]^{-1} \int_0^\infty \left(\frac{dS^+(t)}{dt}, \frac{dS^-}{dt} \right)^0 dt, \tag{38}$$

where the factor $(1-\mathcal{P})$ has been omitted from the time-evolution operator leaving

$$e^{it\mathcal{L}} \frac{dS^+}{dt} = \frac{dS^+(t)}{dt}, \tag{39}$$

which is usually satisfactory as a first approximation.

The calculation of the field-dependent part of the linewidth contains several novel features. From the commutator of S^+ with the Zeeman interaction we have

$$(1-\mathcal{P}) \frac{dS^+}{dt} = \frac{i\mu_B H}{\hbar} \left(\sum_{Aj} g_A s_{aj}^+ + \sum_{Bj} g_B s_{Bj}^+ \right) - \left(\frac{dS^+}{dt}, S^- \right) S^+ \Big/ (S^+, S^-). \tag{40}$$

Using Eqs. (26) and (29) we can rewrite (40) and obtain

$$(1-\mathcal{P}) \frac{dS^+}{dt} = \frac{i\mu_B H}{\hbar} \times \left(\sum_{Aj} (g_A - g_{\mathrm{eff}}) s_{Aj}^+ + \sum_{Bj} (g_B - g_{\mathrm{eff}}) s_{Bj}^+ \right). \tag{41}$$

Equation (41) leads to an approximate equation for the field-dependent part of the linewidth γ_H, which is of the form

$$\gamma_H \approx \frac{(\mu_B H/\hbar)^2}{(S^+, S^-)^0} \int_0^\infty dt (\{(g_A - g_{\mathrm{eff}}) \exp[it(1-\mathcal{P})\mathcal{L}] S_A^+ + (g_B - g_{\mathrm{eff}}) \exp[it(1-\mathcal{P})\mathcal{L}] S_B^+\}, [(g_A - g_{\mathrm{eff}}) S_A^- + (g_B - g_{\mathrm{eff}}) S_B^-])^0, \tag{42}$$

having omitted the factor $e^{-i\omega_0 t}$ since the integrand has a decay rate which is large in comparison with the Larmor frequency (in three dimensions).

From Eq. (42) it is apparent that γ_H is proportional to H^2 and involves the difference between g_{eff} and the g factors of the two subsystems. In addition, since $\vec{S}_A$ ($\vec{S}_B$) commutes with the AA (BB) exchange interactions, γ_H is large when the AB interactions are small. Furthermore, Eq. (42) is seen to be a generalization of the expression for the width in the two-frequency stochastic model where the resonance frequency flips from $g_A \mu_B H/\hbar$ to $g_B \mu_B H/\hbar$ at a rate which is rapid in comparison with $|g_A - g_B| \mu_B H/\hbar$.[16–18]

Quantitative estimates of the magnitude and temperature dependence of the linewidth can only come from detailed analyses of Eqs. (38) and (42). Such studies are beyond the scope of this paper. However qualitative estimates appropriate at infinite temperature are easier to come by. In the case of γ_{anis} we have

$$\hbar\gamma_{\mathrm{anis}} \approx g_{\mathrm{eff}} \mu_B \langle H_{\mathrm{anis}}^2 \rangle_\infty \langle H_{\mathrm{ex}}^2 \rangle_\infty^{-1/2}, \tag{43}$$

where $\langle H_{\mathrm{anis}}^2 \rangle_\infty$ is the mean-square anisotropy field and $\langle H_{\mathrm{ex}}^2 \rangle_\infty$ is the mean-square exchange field. The estimate of γ_H is not quite the analog of (43) because of the special role of the AB interactions. We find

$$\hbar\gamma_H \approx \mu_B^2 H^2 \hbar^{-1} [(g_{\mathrm{eff}} - g_A)^2 N_A s_A (s_A + 1) \bar{\tau}_A + (g_{\mathrm{eff}} - g_B)^2 N_B s_B (s_B + 1) \bar{\tau}_B] \times [N_A s_A (s_A + 1) + N_B s_B (s_B + 1)]^{-1}, \tag{44}$$

where $\bar{\tau}_A$ and $\bar{\tau}_B$ are given by the integrals

$$\bar{\tau}_A = \frac{3}{2N_A s_A (s_A + 1)} \int_0^\infty dt \langle \exp[it(1-\mathcal{P})\mathcal{L}] S_A^+ S_A^- \rangle_\infty^0, \tag{45}$$

$$\bar{\tau}_B = \frac{3}{2N_B s_B (s_B + 1)} \int_0^\infty dt \langle \exp[it(1-\mathcal{P})\mathcal{L}] S_B^+ S_B^- \rangle_\infty^0. \tag{46}$$

After making the Gaussian approximation to the integrand $(f(t) \approx f(0) \exp[\frac{1}{2} f''(0) t^2])$, we obtain the equations

$$\bar{\tau}_A = \left(\frac{\pi}{2} \right)^{1/2} \hbar \left(\frac{8}{3N_A} \sum_{Ai, Bj} J_{AiBj}^2 s_B (s_B + 1) \right)^{-1/2}, \tag{47}$$

$$\bar{\tau}_B = \left(\frac{\pi}{2} \right)^{1/2} \hbar \left(\frac{8}{3N_B} \sum_{Ai, Bj} J_{AiBj}^2 s_A (s_A + 1) \right)^{-1/2}. \tag{48}$$

which, when $N_A = N_B$ and $s_A = s_B$, lead to an expression for γ_H similar to that obtained by Yokota and Koide.[19]

In order to have slow exponential decay of $(S^+(t), S^-)$ it is necessary that γ_{anis} and γ_H be small in comparison with the decay rates of the integrands in Eqs. (38) and (42).[10] Generally speaking, this condition will be satisfied if the Hamiltonian has the properties postulated in Sec. II. In addition, if $\gamma_{\text{anis}} + \gamma_H \ll \omega_0$, the resonance in $\chi''_{S^+S^-}(\omega)$ will be sharp. Also, we note that if the Zeeman interaction is characterized by anisotropic g tensors, Eq. (26) is still applicable provided the z axis is identified with the direction of the thermal average of the total spin rather than the direction of the applied field.

Our final comment pertains to Eq. (2), the symbolic inequality relating to the strength of the AB exchange interactions. An equivalent statement of the inequality is that the breadth of the frequency distribution of the nonhydrodynamic part of $\chi_{M^+M^-}(\omega)$, $f(\omega)$, is large in comparison with the breadth of $\chi''_{S^+S^-}(\omega)$. From Eq. (21) we obtain the corresponding mathematical statement, appropriate when $\omega_0 \gg \gamma_{\text{anis}} + \gamma_H$,

$$(\Delta\omega)^2 = \frac{8[N_A s_A(s_A+1) + N_B s_B(s_B+1)]}{9N_A N_B} \times \sum_{Ai,Bj} J^2_{AiBj} \gg g^2_{\text{eff}}\,\mu_B^2\, H^2\,, \tag{49}$$

by evaluating the traces at infinite temperature.

V. DISCUSSION

The most significant aspect of the theory outlined in Secs. III and IV is the appearance of the dynamic spin susceptibility in the expression for the dynamic magnetic susceptibility. The presence of $\chi_{S^+S^-}(\omega)$ can be understood with the help of the fluctuation-dissipation theorem which relates $\chi''_{M^+M^-}(\omega)$ to the Fourier transform of the magnetic moment autocorrelation function.[14] Since fluctuations in the total moment are correlated with fluctuations in the total spin there is a contribution to the transform which can be identified with the spin-spin autocorrelation function. Such an identification is possible because the total spin is an approximate constant of the motion so that in zero field its Fourier transform is sharply peaked about $\omega = 0$. The relative weight of $\chi_{S^+S^-}(\omega)$, $(M^+, S^-)^2/(M^+, M^-)\,(S^+, S^-)$, which is less than or equal to one by the Schwarz inequality, is typically a slowly varying function of temperature with the limiting value

$$\frac{(M^+,S^-)^2}{(M^+,M^-)(S^+,S^-)} = \frac{[g_A s_A(s_A+1)N_A + g_B s_B(s_B+1)N_B]^2}{[g_A^2 s_A(s_A+1)N_A + g_B^2 s_B(s_B+1)N_B][s_A(s_A+1)N_A + s_B(s_B+1)N_B]}\,, \tag{50}$$

as $T \to \infty$. For realistic values of g_A, g_B, s_A, and s_B, Eq. (50) indicates that the hydrodynamic component has a large fraction of the total spectral weight. (In the case of like spins $\vec{M} = -g\mu_B\vec{S}$ so that the hydrodynamic component has all the spectral weight.)

An applied magnetic field induces resonant structure in the transverse magnetic susceptibility. This structure appears only in $\chi''_{S^+S^-}(\omega)$. Because $\vec{S}$ commutes with the isotropic exchange interaction the peak in $\chi''_{S^+S^-}(\omega)$ is exchange narrowed. In contrast, the nonhydrodynamic part of $\chi''_{M^+M^-}(\omega)$ [$f(\omega)$ in Eqs. (20) and (23)] is not expected to show any resonant structure. That part of $\vec{M}$, $(1-\mathcal{P})\vec{M}$, which is orthogonal to $\vec{S}$ is characterized by an autocorrelation function with a broad frequency distribution [cf. Eq. (49)]. Any resonant structure is washed out by the fluctuations in the exchange field since exchange narrowing does not come into play.

The expression obtained for the resonant frequency, Eq. (29), is of the standard hydrodynamic form; namely, it involves only equal time correlation functions. In contrast, the expression for the width, Eq. (36), is seen to involve time-dependent correlation functions. The distinction between time-dependent and time-independent functions is analogous to the situation occurring in the hydrodynamics of fluids, where the sound velocity is expressed in terms of thermodynamic functions and the damping is related to time integrals of various autocorrelation functions.[10]

The hydrodynamic model which has been postulated in the development of the theory is itself phenomenological. However, we believe its applicability to the paramagnetic resonance problem is justified when the AB exchange field is large. Also, the theory does make a number of detailed predictions. In particular, the high-temperature limit for g_{eff}, Eq. (30), is exact within the hydrodynamic approximation. Measurements of the paramagnetic resonance spectra of strongly exchange coupled systems with unlike spins seem so far to have been limited largely to the case of crystals with two inequivalent magnetic sites where there are equal numbers of identical magnetic ions on each of the sites.[20–24] In all of these cases the Pryce theory is applicable so that g_{eff} is given by Eq. (3) or its appropriate generalization in the case of anisotropic g tensors

$$\hbar\omega_0 = \tfrac{1}{2}\mu_B \left| \overleftrightarrow{g}_A \cdot \vec{H} + \overleftrightarrow{g}_B \cdot \vec{H} \right| . \qquad (51)$$

Measurements on systems with $s_A \neq s_B$ would be an important test of the theory outlined here as distinct from the analyses of Refs. 3 and 4. Furthermore such measurements, if sufficiently accurate, would establish the validity of our approach as opposed to alternative theories [e.g., Eqs. (10) and (11)].

Although the analysis up to now has been confined to the paramagnetic phase, Eq. (26) applies equally well to the ordered phase. This is verified in a calculation of (S^+, S^-) in the zero-temperature limit, where linearized magnon theory is appropriate. In the case of a two-sublattice ferrimagnet we have

$$(S^+, S^-) = \frac{-2\langle S^z\rangle_0(\langle S_A^z\rangle_0 + \langle S_B^z\rangle_0)}{\mu_B H(g_A\langle S_A^z\rangle_0 + g_B\langle S_B^z\rangle)} , \qquad (52)$$

which, when introduced into Eq. (26) yields a result identical to the zero temperature limit of Eq. (9).

We have established that Eq. (9) is valid in the low-temperature limit and invalid in the high-temperature limit. Thus the question arises as to the temperature where Eq. (9) breaks down and recourse has to be made to the more general result, Eq. (26). From the discussion in Sec. III we expect this to occur when the fluctuations in the AB exchange field become large. An equivalent criterion involves the exchange mode ($\vec{q} = 0$ optical magnon), which is the high-frequency resonance associated with Eqs. (5) and (6). The frequency of this mode, $(\mu_B \lambda/\hbar)(g_A\langle M_B^z\rangle_T + g_B\langle M_B^z\rangle_T)$, is proportional to the mean AB exchange field. When there are large fluctuations in the AB field the mode will be overdamped and the linearized form of Eqs. (5) and (6) [and hence Eq. (9)] will no longer be applicable. In most systems the high-frequency mode will become overdamped near the Curie temperature.

Also, we remark that the two components of the linewidth γ_{anis} and γ_H reflect fundamentally different aspects of spin dynamics. The former is related to the time integral of a four-spin correlation function, whereas the latter involves only integrals over two-spin functions. By making measurements at different frequencies it may be possible to isolate the two components thus inferring separate information about the two-spin and four-spin correlations.[25]

As a final comment it should be pointed out that the analysis in this paper appears to have important implications for the interpretation of the electron-paramagnetic-resonance spectra of magnetic impurities in metals. Previous analyses often have been based on linearized Bloch equations similar to (5) and (6), but augmented as in Ref. 6 by phenomenological damping terms.[26–29] The arguments in this paper suggest that such an approach is fundamentally incorrect for unlike spins when there is a strong isotropic exchange interaction between the conduction electrons and the local moments. Provided the system is paramagnetic the effective g factor in our theory is given by Eq. (29). In order to bring out the differences in the two approaches we introduce the *spin* susceptibilities of the ions and electrons, $\chi_i^S = (S_i, S_i + S_e)$ and $\chi_e^S = (S_e, S_i + S_e)$. Equation (29) then becomes

$$g_{\text{eff}} = (g_e\chi_e^S + g_i\chi_i^S)/(\chi_e^S + \chi_i^S) \quad . \qquad (53)$$

Equation (53) is not the same as the expression for g_{eff} obtained from the phenomenological equations of Refs. 26–29. In the absence of spin-lattice coupling this approach leads to the result

$$g_{\text{eff}} = (g_e\chi_e^M + g_i\chi_i^M)/(\chi_e^M + \chi_i^M) , \qquad (54)$$

where χ_i^M and χ_e^M are the *magnetic* susceptibilities of the ions and electrons, $\chi_i^M = (M_i, M_i + M_e)$ and $\chi_e^M = (M_e, M_i + M_e)$. Note that (54) reduces to Eq. (11), whereas (53) is equivalent to Eq. (30). The difference between Eqs. (53) and (54) is small for $g_i \approx g_e$, but may be important when the mismatch in gyromagnetic ratios is large.

When the electron-ion interactions are treated in the molecular-field approximation equation (53) *is* equivalent to the g_{eff} obtained from the Bloch equations derived by Barnes and Zitcova-Wilcox for an isotropic microscopic exchange Hamiltonian.[30] In the molecular-field approximation we have

$$\chi_i^S = \frac{\chi_i^{M_0}[1 + (g_i/g_e)\lambda\chi_e^{M_0}]}{g_i^2\mu_B^2(1 - \lambda^2\chi_e^{M_0}\chi_i^{M_0})} , \qquad (55)$$

$$\chi_e^S = \frac{\chi_e^{M_0}[1 + (g_e/g_i)\lambda\chi_i^{M_0}]}{g_e^2\mu_B^2(1 - \lambda^2\chi_e^{M_0}\chi_i^{M_0})} , \qquad (56)$$

where $\chi_e^{M_0}$ and $\chi_i^{M_0}$ are the electronic and ionic magnetic susceptibilities in the absence of electron-ion interactions and λ is a molecular-field constant. The agreement between the two theories comes about because, unlike Refs. 26–29, both approaches take proper account of the conservation of total spin.[31] In Ref. 30 this leads to a modification of the cross relaxation rates and the detailed balance condition relative to the expressions used in Ref. 28. It should be noted that this agreement does not imply that Eq. (1) is in any sense an appropriate Hamiltonian for the impurity problem. Rather, it is a consequence of the fact that Eq. (29), displaying no explicit dependence on the microscopic details of the Hamiltonian, is equally applicable to both metals and insulators provided the dominant interactions are isotropic and the system is in the hydrodynamic regime ($KT \gg g_{\text{eff}}\mu_B H$).

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[31] χ_i^S and χ_e^S, which are the weight factors in Eq. (53), are to be compared with the corresponding expressions for χ_i^M and χ_e^M, the weight factors in Eq. (54). According to Ref. 28 we have

$$\chi_i^M = \frac{\chi_i^{M0}(1+\lambda\chi_e^{M0})}{1-\lambda^2\chi_e^{M0}\chi_i^{M0}} ,$$

$$\chi_e^M = \frac{\chi_e^{M0}(1+\lambda\chi_i^{M0})}{1-\lambda^2\chi_e^{M0}\chi_i^{M0}} ,$$

in the molecular-field approximation.