Resonant and nonresonant effects of paramagentic spins on acoustic modes*

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The resonant and nonresonant effects of paramagnetic spins on acoustic velocity and attenuation are treated self-consistently and on the same footing. The acoustic waves are treated using elastic continuum theory and generalized Bloch equations are used for the spins although the same results can be obtained more formally using quantum-mechanical equations of motion and time-dependent correlation functions. Detailed formulas are derived for angular dependence and magnitudes of both resonant and nonresonant effects. Nonresonant velocity and attenuation changes are related to adiabatic and isothermal regimes and the transition between the two regimes. We suggest that nonresonant experiments can be used to measure spin decay rates and spin-phonon coupling constants in regimes or substances where resonant techniques cannot be used.

I. INTRODUCTION

Resonant spin-phonon coupling or acoustic magnetic resonance is used to study the internal structure of spin systems embedded in a lattice and has been adequately treated in the literature, usually in a way that emphasizes the quantum-mechanical nature of the spins.[1,2] On the other hand, the internal structure of molecules in fluids is studied acoustically using nonresonant techniques and is usually viewed in terms of rate equations and thermodynamic derivatives.[3] In this paper we treat both the resonant and nonresonant effects of paramagnetic spins on the acoustic velocity and attenuation on an equal footing. Our unified point of view is that both the resonant and nonresonant effects can be understood in terms of the coupling of acoustic modes to spin normal modes. We point out the way in which different and distinct spin correlation functions or spin normal modes couple differently to the acoustic modes and derive detailed formulas for a system with cubic symmetry. In particular, we emphasize that the "zero-frequency" resonant modes or longitudinal spin correlation functions can cause nonresonant velocity and attenuation changes. These changes can be used to study spin decay rates and spin-phonon coupling constants that may be difficult or impossible to study in resonant experiments.

In the rest of this section we will describe the spin-phonon Hamiltonian used and discuss the spin variables in terms of effective normal modes. Section II contains a calculation of the changes in velocity and attenuation on an arbitrary acoustic mode due to the spins. In Sec. III we apply the formalism to a specific lattice mode, connect up our formalism with other treatments, and suggest some possible experiments.

In this paper we shall consider only the interaction of spins in a cubic crystal environment with the lattice via the spin-phonon Hamiltonian[4]

$$\begin{aligned}\mathcal{H}_{S\text{-}P} = {} & \mu_B(g_{11}-g_{12})\sum_i H_i e_{ii} S_i + \mu_B g_{12}\vec{\mathrm{H}}\cdot\vec{\mathrm{S}}\sum_i e_{ii} \\ & + \mu_B g_{44}\sum_{i,j}{}' \tfrac{1}{2}(S_iH_j + S_jH_i)e_{ij} \\ & + \tfrac{3}{2}G_{11}\sum_i e_{ii}[S_i^2 - \tfrac{1}{3}S(S+1)] \\ & + G_{44}\sum_{i,j}{}' \tfrac{1}{2}(S_iS_j + S_jS_i)e_{ij}\ ,\end{aligned} \tag{1}$$

where $\vec{\mathrm{S}}$ is a spin operator, $\vec{\mathrm{H}}$ is an external magnetic field, and e_{ij} is the elastic strain

$$e_{ij} = \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)(1 - \tfrac{1}{2}\delta_{ij})\ , \tag{2}$$

where $\vec{\mathrm{u}}$ is the local lattice displacement. Latin indices denote Cartesian directions which coincide with the symmetry axes of the crystal and a prime on a summation over i and j means that the terms with $i=j$ are omitted. This is the most general form possible for a single spin in a cubic environment interacting with the lattice linearly in the e_{ij}. The first three terms correspond to a modulation of the spin's g factor by the lattice and the last two terms correspond to the acoustic modulation of a spin-orbit interaction or an interaction of the spins quadrupole moment with electric field gradients generated by the lattice. Equation (1) does not describe the most general form of spin-phonon coupling in that it does not include the lattice modulation of spin-spin interactions between spins at different sites. Finally, although we use the notation and vocabulary appropriate to electronic spins, the treatment is also valid for nuclear spins.

It will be our approximation to treat the lattice entirely by elastic continuum theory. In fact, this is entirely rigorous and the results obtained are identical to those obtained through quantizing the lattice in the harmonic approximation. This point will be considered again near the end of Sec. II. The treatment can also be easily generalized to substances in which cubic symmetry does not obtain.

Our treatment of the spin variables is somewhat more involved. We assume than an external magnetic field on the system $\vec{H}$ makes the polar angles (θ, ϕ) with the crystalline axes. In this case it is convenient to use the direction of $\vec{H}$ as the quantization axis for the spins but still use the crystalline axes for the lattice. In addition, we wish to express the spin operators in terms of the irreducible tensor spin operators[5,6] A_{lm}, where $|m| \leq l$ and $0 \leq l \leq 2S$. Terms in Eq. (1) linear in the vector spin operators S_i are proportional to dipole or $l=1$ operators and terms quadratic in the spin operators are proportional to quadrupole or $l=2$ operators. The irreducible spin tensor operators as applied to the type of problem being considered here are extensively discussed in Ref. 6. Under a wide variety of conditions these operators correspond to normal modes of the spin system and Bloch-like phenomenological equations can be written for them. Even in cases where the A_{lm} do not diagonalize the spin system, they are a convenient starting place and their use in no way restricts our treatment.

The appropriate transformation can always be carried out and will result in Eq. (1) being expressed as

$$\mathcal{H}_{S-P} = \sum_{l,m,i\leq j} f_{lm}(i,j) e_{ij} A_{lm} , \tag{3}$$

where $l=1, 2$ and m takes on integral values $|m| \leq l$. At least in simple spin systems the form of Eq. (3) emphasizes the coupling of the acoustic modes represented by e_{ij} to the spin modes represented by A_{lm}.

II. CALCULATION

In this section we shall obtain the changes in an arbitrary acoustic mode due to the presence of the spins. As discussed at the end of Sec. I, the spin-phonon Hamiltonian for a single spin can be transformed to Eq. (3). A straightforward transformation for the coefficients $f_{lm}(i,j)$ yields

$$f_{2,m}(i,j) = d(i,j;m)[\tfrac{3}{2}G_{11}\delta_{i,j} + 2G_{44}(1-\delta_{i,j})] , \tag{4a}$$

$$f_{1,m}(i,j) = \mu_B H\{d(i;m)d(j;0)[(g_{11}-g_{12})\delta_{i,j} + 2g_{44}(1-\delta_{ij})](3a_1)^{1/2} + g_{12}\delta_{ij}(3a_1)^{-1/2}\delta_{m,0}\} . \tag{4b}$$

In these equations the $d(i,m)$ transformation coefficients are

$$\begin{aligned} d(x;\pm 1) &= \mp(\cos\theta\cos\phi \pm i\sin\phi)/(6a_1)^{1/2} , \\ d(y;\pm 1) &= \mp(\cos\theta\sin\phi \mp i\cos\phi)/(6a_1)^{1/2} , \\ d(z;\pm 1) &= \pm\sin\theta/(6a_1)^{1/2} , \\ d(x;0) &= \sin\theta\cos\phi/(3a_1)^{1/2} , \\ d(y;0) &= \sin\theta\sin\phi/(3a_1)^{1/2} , \\ d(z;0) &= \cos\theta/(3a_1)^{1/2} , \end{aligned} \tag{5}$$

where $a_1 = [S(S+1)]^{-1/2}$. The transformation coefficients $d(i,j;m)$ are given in the Appendix of Ref. 5 and will not be reproduced here.

In the continuum limit the equations of motion for the lattice can be modified by turning the spin-phonon Hamiltonian into an additional energy density. Effectively this is accomplished by multiplying $\mathcal{H}_{S-P}$ by n_s, the density of spins, and replacing A_{lm} by $\langle A_{lm}\rangle$, the thermal average of A_{lm}. This is a valid procedure if the spins form a lattice or if the spins are randomly distributed and the average interspin distance is much less than an acoustic wavelength so that fluctuations in spin density can be ignored. Thus, there is an additional elastic energy density U_{S-P} associated with the spins which is given by the equation

$$U_{S-P} = \sum_{l,m,i\leq j} n_s f_{lm}(i,j) e_{ij} \langle A_{lm}\rangle . \tag{6}$$

The equation of motion for the lattice displacement $\vec{u}$,

$$\rho\left(\frac{\partial^2 u_i}{\partial t^2}\right) = f_i , \tag{7}$$

where ρ is the crystal mass density, is obtained in the usual way.[7] The additional energy density given by Eq. (6) yields an additional force Δf_i, where

$$\Delta f_i = \sum_{l,m,j} n_s f_{lm}(i,j)\left(\frac{\partial\langle A_{lm}\rangle}{\partial x_j}\right) . \tag{8}$$

We shall now derive semiphenomenological Bloch-like equations for the $\langle A_{lm}\rangle$. This will be generalized to a more rigorous formulation in terms of time-dependent spin correlation functions later in this section. However, the present treatment is probably easier to understand for most readers and makes the physics of the system easier to follow. For simplicity we assume that the spins feel an external magnetic field $H\hat{z}$, a driving torque due to $\mathcal{H}_{S-P}$, and some intrinsic decay mechanism. As in Ref. 6, this leads to effective Bloch equations

$$\left(\frac{d}{dt} + im\omega_0\right)\langle A_{lm}(t)\rangle = \frac{\langle[A_{lm}(t), \mathcal{H}_{S-P}]\rangle}{i\hbar} - \Gamma_{lm}[\langle A_{lm}(t)\rangle - \langle A_{lm}(t)\rangle_0] , \tag{9}$$

where $\omega_0 = \gamma H$, γ is the gyromagnetic ratio for a spin, and $\langle A_{lm}(t)\rangle_0$ is the instantaneous local equilibrium value of $\langle A_{lm}(t)\rangle$. All of the terms except the one proportional to Γ_{lm} arise rigorously from taking the expectation value of the Heisenberg equation of motion for A_{lm}. The last term includes spin relaxation phenomenologically and we assume that the $\langle A_{lm}\rangle$ are good normal modes of the spin system with decay rates Γ_{lm}.

In the rest of this paper we shall assume that the acoustic wave has the space-time dependence $\exp[i(\vec{q}\cdot\vec{r}-\omega t)]$. All of the quantities in Eq. (9) can be computed by methods identical to those used in Ref. 6. In the high-temperature limit ($kT \gg \hbar\omega_0$), some straightforward algebra yields

$$(-i\omega + im\omega_0 + \Gamma_{lm})\langle A_{lm}(t)\rangle = (im\omega_0 + \Gamma_{lm})\Big(-\beta\sum_{i\leq j} f^*_{lm}(i,j)e_{ij}\Big) , \quad (10)$$

where $\beta = 1/kT$ and $f_{l,-m} = f^*_{l,m}$. By combining Eqs. (2), (7), (8), and (10), we obtain the wave equation

$$(\omega^2 - v_0^2q^2)u_i = -\frac{\beta n_s}{\rho}\sum_{l,m,j,k\leq l} f_{lm}(i,j)f^*_{lm}(kl) \times q_j(q_k u_l + q_l u_k)(1-\tfrac{1}{2}\delta_{k,l})F_{lm}(\omega) , \quad (11)$$

where

$$F_{lm}(\omega) = (m\omega_0 - i\Gamma_{lm})/(m\omega_0 - \omega - i\Gamma_{lm}) \quad (12)$$

and v_0 is the acoustic velocity in the absence of the spins.

At this point we wish to point out that we have performed exactly the same calculation using harmonic quantized phonons and time-dependent spin-correlation functions. This calculation is similar to calculations already in the literature.[8,9] The results are exactly the same as Eq. (11) except that the phenomenological spin correlation functions $F_{lm}(\omega)$ are replaced by the exact spin correlation functions $\chi_{lm}(\vec{q},\omega)$ with the prescription

$$\beta F_{lm}(\omega) \to \chi_{lm}(\vec{q},\omega) , \quad (13)$$

where

$$\chi_{lm}(\vec{q},\omega) = \frac{i}{\hbar}\int_0^\infty dt\, e^{-i\omega t}\langle[A_{lm}(\vec{q},t), A^\dagger_{lm}(\vec{q},0)]\rangle . \quad (14)$$

In fact, it is somewhat obvious that such a replacement must be possible since the driving term in the Bloch equation given by Eq. (9) is exact because it was obtained from the Heisenberg equations of motion. Since only the deriving term determines which correlation functions enter an expression, the rest of our phenomenological treatment determines only the form of the correlation functions. Thus our equations can be generalized to spin systems with greater structure including non-Lorentzian decay and spin-spin interactions.

III. DISCUSSION

The results given in Eq. (11) are valid for any lattice mode and thus yield quite general angular dependences for resonant and nonresonant dispersion and absorption. In order to discuss the results in a less cumbersome manner, we will restrict the discussion in the rest of this paper to longitudinal phonons traveling in the $\hat{z}$ direction in the lattice coordinates. In this case the dispersion relation, Eq. (11), reads

$$\omega^2 - v_0^2q^2 = -\frac{\beta n_s}{\rho}q^2\sum_{l,m}|f_{lm}(z,z)|^2F_{lm}(\omega) . \quad (15)$$

Assuming that the right-hand side of Eq. (15) is much less than $v_0^2q^2$, the real and imaginary parts of this expression divided by $2v_0^2q^2$ are equal to $\Delta v/v$ and $-\Delta\alpha/q$, respectively, where Δv and $\Delta\alpha$ are the velocity shift and attenuation change due to the spins. Using Eqs. (4), (5), (15), and the Appendix of Ref. 5, we obtain

$$[(\Delta v/v) - i(\Delta\alpha/q)] = -(\beta n_s/2\rho v_0^2)(I_1+I_2) , \quad (16a)$$

$$I_1 = [\tfrac{1}{3}\mu^2H^2S(S+1)]\{\tfrac{1}{2}(g_{11}-g_{12})^2\sin^4\theta[F_{1,1}(\omega) + F_{1,-1}(\omega)] + [(g_{11}-g_{12})\cos^2\theta + g_{12}]^2F_{1,0}(\omega)\} , \quad (16b)$$

$$I_2 = a\{\sin^4\theta[F_{2,2}(\omega)+F_{2,-2}(\omega)] + \sin^2 2\theta[F_{2,1}(\omega)+F_{2,-1}(\omega)] + \tfrac{2}{3}(3\cos^2\theta - 1)^2F_{2,0}(\omega)\} , \quad (16c)$$

where

$$a = \tfrac{1}{120}(\tfrac{3}{2}G_{11})^2S(S+1)(2S-1)(2S+3) . \quad (17)$$

By decomposing the expression in this fashion it is easy to see the contributions from $l=1$ and $l=2$ separately. In addition, the real and imaginary parts of F_{lm} are F'_{lm} and F''_{lm}, respectively, where

$$F'_{lm}(\omega) - 1 = -\omega(\omega - m\omega_0)/[(\omega - m\omega_0)^2 \pm \Gamma^2_{lm}] , \quad (18a)$$

$$F''_{lm}(\omega) = \omega\Gamma_{lm}/[(\omega - m\omega_0)^2 + \Gamma^2_{lm}] . \quad (18b)$$

Equations (16) describe the usual $m=1$ and $m=2$ acoustic resonances from the ($l=2$) or quadrupolar terms. It also describes a distinct $m=1$ resonance from the ($l=1$) or dipole term. This resonance corresponds to a distinct normal mode which, in general, has a different line shape or decay rate than the ($l=1$, $m=1$) mode.

At large enough frequencies all of the $F_{lm}(\omega)$ are vanishingly small and $\Delta v/v$ is zero. In this limit the spins are decoupled from the lattice since they cannot respond to such a high frequency. This corresponds to the isothermal limit in that the spins remain in thermal equilibrium because they are unaffected by the lattice. In the opposite limit of $\omega \to 0$, all of the $F_{lm}(\omega)$ are one. This corresponds to the adiabatic limit since the driving frequency is so slow that the spins adiabatically follow the lattice and remain in local instantaneous equilibrium instead of thermal equilibrium. In other words, with respect to Eq. (9), $\langle A_{lm}\rangle = \langle A_{lm}\rangle_0$. Note that in this limit there is no attenuation and that $I_2 = \frac{8}{3}a$ and is independent of angle. This is necessary since $\vec{H}$ should have no effect in this limit. I_1 still depends on $\vec{H}$ since this quantity came from coupling terms which explicitly depend on $\vec{H}$.

Finally, let us consider the case where $\omega \ll \omega_0$ and so the terms with $m \neq 0$ are trivial. If we focus on just the $l=2$ contributions we obtain

$$I_2 = a\{\tfrac{8}{3} + \tfrac{2}{3}(3\cos^2\theta - 1)^2[F_{2,0}(\omega) - 1]\} . \quad (19)$$

In this case the attenuation is proportional to

$$\omega\Gamma/(\omega^2 + \Gamma^2) = \omega\tau/(1 + \omega^2\tau^2) , \quad (20)$$

where $\Gamma = 1/\tau$ refers to the $l=2$, $m=0$ mode. Similarly, the velocity change is proportional to

$$\omega^2/(\omega^2 + \Gamma^2) = (\omega\tau)^2/(1 + \omega^2\tau^2) . \quad (21)$$

In this case the adiabatic limit is $\omega\tau \ll 1$ and expressions similar to the situation in gasses obtain.[3]

We also wish to point out nonresonant experiments may be valuable in studying the spin relaxation rates either in systems where the resonant frequencies cannot be reached or in systems where inhomogeneous broadening entirely masks intrinsic linewidths. In the latter case the resonant frequencies of the $m \neq 0$ modes are severely and randomly altered but the $m=0$ mode remains essentially unaffected. In addition in many cases $\Gamma_{2,0}$ is magnetic field and temperature dependent in such a way that the region near $\omega\tau \sim 1$ can be passed through without varying the frequency.

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[3]See, for example, H. J. Bauer, in Ref. 2, Vol. 2A, Chap. 2.

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