

Broadening of Spin-Phonon Resonance Lines by Exchange and Magnetic Dipole Interactions*

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The second and fourth moments of the three principal ultrasonic free-spin absorption lines are calculated using a phenomenological form for the spin-phonon interaction. Both exchange and dipole interactions are taken into account, and it is found that exchange causes increased line width in all three cases. For the line at the Larmor frequency, the moments are compared with those for the corresponding photon absorption line, for which exchange narrowing occurs.

I. INTRODUCTION

IMPROVEMENTS in the technique of generating ultrasonic waves of microwave frequencies have led to increased interest in spin-phonon interactions in paramagnetic substances. Experimentally, Jacobsen, Shiren, and Tucker¹ have investigated the interaction between 9.2 kMc/sec ultrasonic waves and the spins of manganese impurities embedded in quartz crystals. They find the ultrasonic absorption line width to be somewhat smaller than the microwave line width for the same spin transition. The form of the spin-phonon interaction was first derived theoretically by Van Vleck² for the particular case of transitions between the lowest levels of the Cr⁺⁺⁺ ion in chrome alum. The interaction results from modulation of the spin-orbit coupling by the lattice vibrations and has the form of a sum of products of phonon creation and annihilation operators with quadratic functions of the spin components of a single paramagnetic ion. Using Van Vleck's spin-phonon interaction, Al'tshuler³ calculated absorption coefficients for ultrasonic waves in paramagnetic salts. He suggested that the exchange interaction might broaden the spin-phonon absorption lines but did not consider the shape of the lines in detail. Recently Mattuck and Strandberg^{4,5} have derived a formula for the spin-phonon interaction in a more general type of paramagnetic substance. They show that terms of the Van Vleck type dominate except when their matrix elements between the spin states involved vanish.

In this paper we use a phenomenological Hamiltonian for the spin-phonon interaction, which has the same form as Van Vleck's Hamiltonian, and is a generalization of a form of interaction used by Kittel.⁶ This Hamiltonian has been employed by Orbach⁷ to compute

the phonon lifetime, the spin-lattice relaxation time and the thermal resistance for a substance containing paramagnetic centers. The unknown coupling constant appearing in the phenomenological Hamiltonian could be determined in principle from an experimental value of the spin-lattice relaxation time due to single phonon processes, i.e., the low-temperature spin-lattice relaxation time, or perhaps from the effects of static strain on the resonance. It is our purpose here to present the results of calculations of the second and fourth moments of the spin-phonon resonance lines in the presence of exchange and magnetic dipole interactions.

II. MOMENT CALCULATION

We consider a system of N spins subjected to a magnetic field H along the z axis and interacting one with another via dipole-dipole and exchange forces. If β is the Bohr magneton and g is the Landé g factor, the Hamiltonian for the system is:

$$\mathcal{H} = g\beta H \sum_i S_i^z + \sum_{i < j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + g^2 \beta^2 \sum_{i < j} [r_{ij}^{-3} \mathbf{S}_i \cdot \mathbf{S}_j - 3r_{ij}^{-5} (\mathbf{r}_{ij} \cdot \mathbf{S}_i)(\mathbf{r}_{ij} \cdot \mathbf{S}_j)]. \quad (1)$$

The three terms here are the Zeeman, exchange and dipole-dipole energies. We assume all atoms to have the same spin angular momentum $\hbar S$. The subscripts i and j refer to the i th and j th atoms. It will be supposed throughout that the separation $g\beta H$ between the Zeeman levels is large compared with the breadth of these levels caused by the exchange and dipolar forces.

For the spin-phonon interaction we use the phenomenological form:

$$I = \sum_i [A(3S_i^z S_i^z - \mathbf{S}_i^2) + B(S_i^z S_i^+ + S_i^+ S_i^z) + B^*(S_i^z S_i^- + S_i^- S_i^z) + C S_i^+ S_i^+ + C^* S_i^- S_i^-], \quad (2)$$

where $S_i^\pm = S_i^x \pm iS_i^y$, and A , B , and C are linear functions of the phonon creation and annihilation operators. Note that I vanishes for $S = \frac{1}{2}$, so that it does not contain the terms in the spin-phonon interaction important for this particular spin value.^{4,5} To justify the form (2) we note that, except for $S = \frac{1}{2}$, the most important part of the interaction is required to be quadratic in the spin components, since it arises from a

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¹ E. H. Jacobsen, N. S. Shiren, and E. B. Tucker, Phys. Rev. Letters **3**, 81 (1959).

² J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

³ S. A. Al'tshuler, J. Exptl. Theoret. Phys. U.S.S.R. **28**, 38 (1955) [translation: Soviet Phys.—JETP **1**, 29, 37 (1955)].

⁴ R. D. Mattuck and M. W. P. Strandberg, Phys. Rev. Letters **3**, 369 (1959).

⁵ R. D. Mattuck, thesis, Massachusetts Institute of Technology, 1959 (unpublished).

⁶ C. Kittel, Phys. Rev. Letters **1**, 51 (1958).

⁷ R. Orbach, thesis, University of California, 1960 (unpublished).

perturbation theory procedure involving the spin-orbit coupling twice.² The expression (2) is the most general Hermitian form satisfying this requirement and in addition having the property $\text{Tr } I = 0$ evaluated for the eigenstates of the Zeeman term in (1), i.e., we require that I produce no over-all shift of the energy level spectrum.

The spin-phonon interaction I causes three types of transition between the levels of the spin system labelled by $S^z = \sum_i S_i^z$. The term containing A induces transitions in which S^z is conserved and gives rise to an aperiodic or zero-frequency line, which spreads to finite frequencies due to the broadening of the highly degenerate Zeeman levels by the dipole-dipole interaction. The terms involving B cause transitions between adjacent groups of Zeeman levels and give rise to an absorption line centered about the energy $g\beta H$, i.e., an absorption line in the same position as that observed in a microwave photon resonance experiment. Finally, the terms in C give rise to a line at twice the Larmor energy, that is, at energy $2g\beta H$.

The calculation of the moments of the photon absorption line for the system of interacting spins represented by (1) has been carried out by Van Vleck.⁸ The part of the Hamiltonian (1) which does not commute with the Zeeman term $g\beta HS^z$ gives rise with the interaction I to weak absorption lines at integral multiples of the Larmor frequency, whose intensities are reduced below those due to the part of (1) commuting with the Zeeman term by factors having the order of magnitude (average dipolar field at spin site/applied field H)². Following Van Vleck, we therefore truncate the Hamiltonian \mathcal{H} , retaining only the terms which commute with $g\beta HS^z$, leaving

$$\mathcal{H}' = g\beta H \sum_i S_i^z + \sum_{i < j} C_{ij} [S_i^+ S_j^- + S_i^- S_j^+] + \sum_{i < j} D_{ij} S_i^z S_j^z, \quad (3)$$

where

$$C_{ij} = -\frac{1}{4} g^2 \beta^2 r_{ij}^{-3} (1 - 3 \cos^2 \theta_{ij}) + \frac{1}{2} J_{ij}, \quad (4)$$

$$D_{ij} = g^2 \beta^2 r_{ij}^{-3} (1 - 3 \cos^2 \theta_{ij}) + J_{ij},$$

and θ_{ij} is the angle between r_{ij} and the z axis.

The mean second and fourth powers of the frequency for an absorption line are given by⁹:

$$\langle \nu^2 \rangle_{\text{av}} = -\text{Tr} [\mathcal{H}', I']^2 / h^2 \text{Tr } I'^2; \quad (5)$$

$$\langle \nu^4 \rangle_{\text{av}} = \text{Tr} [\mathcal{H}', [\mathcal{H}', I']^2] / h^4 \text{Tr } I'^2. \quad (6)$$

Here \mathcal{H}' is the truncated Hamiltonian given by (3) and I' is the part of the spin-photon or spin-phonon interaction responsible for the given absorption line. It is to be emphasized that these formulas for the second and fourth moments do not take into account the population differences between the initial and final states of the spin system. At temperatures sufficiently high for this

population difference to be approximately linear in the energy separation of the two states, the line shape deduced from the calculated values of (5) and (6) must be multiplied by an extra factor ν before being compared with the experimentally observed plot of phonon absorption versus frequency.

The actual calculation of the moments of the three absorption lines resulting from the interaction (2) is straightforward in principle, but involves a fair amount of tedious manipulation of the spin operators. We present here only the results. In all moments, factors of $[4S(S+1)-3]$ appearing in both the numerators and denominators of (5) and (6) have been cancelled, so the results do not apply for the case $S = \frac{1}{2}$.

1. Aperiodic Line

$$h^2 \langle \nu^2 \rangle_{\text{av}} = (16/N) S(S+1) \sum_{i < j} C_{ij}^2. \quad (7)$$

$$h^4 \langle \nu^4 \rangle_{\text{av}} = (64/N) S^2 (S+1)^2 \sum_{i \neq j \neq k} C_{ij}^2 C_{ik}^2 + (16/35N) S(S+1) \times \sum_{i < j} \{ 4C_{ij}^4 [188S(S+1) - 201] + C_{ij}^2 D_{ij}^2 [44S(S+1) - 53] \}. \quad (8)$$

2. Line at $g\beta H$

$$h^2 \langle \nu^2 \rangle_{\text{av}} = (2/3N) S(S+1) \sum_{i < j} [20C_{ij}^2 + D_{ij}^2]. \quad (9)$$

$$h^4 \langle \nu^4 \rangle_{\text{av}} = (1/9N) S^2 (S+1)^2 \times \sum_{i \neq j \neq k} \{ 624C_{ij}^2 C_{ik}^2 - 32C_{ij} C_{jk} C_{ki} D_{ij} + 112C_{ij}^2 D_{ik}^2 - 32C_{ij}^2 D_{ik} D_{jk} + 2D_{ij}^2 D_{ik}^2 \} + (2/105N) S(S+1) \times \sum_{i < j} \{ 8[1142S(S+1) - 569] C_{ij}^4 + 840[4S(S+1) - 3] C_{ij}^3 D_{ij} + 42[29S(S+1) - 13] C_{ij}^2 D_{ij}^2 - 14[4S(S+1) - 3] C_{ij} D_{ij}^3 + 7[3S(S+1) - 1] D_{ij}^4 \}. \quad (10)$$

Formulas (9) and (10) give the second and fourth moments about the center of the line, i.e., about the frequency $g\beta H/h$.

3. Line at $2g\beta H$

$$h^2 \langle \nu^2 \rangle_{\text{av}} = (8/3N) S(S+1) \sum_{i < j} [2C_{ij}^2 + D_{ij}^2]. \quad (11)$$

⁸ J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

⁹ I. Waller, Z. Physik **79**, 370 (1932).

$$\begin{aligned}
h^4\langle\nu^4\rangle_{av} = & (16/9N)S^2(S+1)^2 \\
& \times \sum_{i \neq j \neq k} \{18C_{ij}^2C_{jk}^2 - 8C_{ij}C_{jk}C_{ki}D_{ij} \\
& + 7C_{ij}^2D_{ik}^2 + C_{ij}^2D_{ik}D_{jk} + 2D_{ij}^2D_{ik}^2\} \\
& + (16/105N)S(S+1) \\
& \times \sum_{i < j} \{8[26S(S+1) - 17]C_{ij}^4 \\
& + [452S(S+1) - 309]C_{ij}^2D_{ij}^2 \\
& + 14[3S(S+1) - 1]D_{ij}^4\}. \quad (12)
\end{aligned}$$

The moments in this case are taken about the frequency $2g\beta H/h$.

III. DISCUSSION

The construction of an analytic approximation to the functional form of the shape of an absorption line from a knowledge of the moments of the line has been considered by Wright.¹⁰ We limit ourselves here to a consideration of the moments of the absorption line at the Larmor frequency. The other two absorption lines may be discussed in a similar manner. It is instructive to consider the second and fourth moments given by the formulas (9) and (10) in two limiting cases: (i) dipole-dipole interaction dominates the exchange interaction; (ii) exchange interaction dominates the dipole-dipole interaction.

(i) Putting $J_{ij}=0$, we have from (4):

$$D_{ij} = -4C_{ij} = g^2\beta^2 r_{ij}^{-3}(1 - 3\cos^2\theta_{ij}). \quad (13)$$

The second and fourth moments then reduce to:

$$h^2\langle\nu^2\rangle_{av} = (3/2N)S(S+1)\sum_{i < j} D_{ij}^2. \quad (14)$$

$$\begin{aligned}
h^4\langle\nu^4\rangle_{av} = & (1/48N)S^2(S+1)^2 \\
& \times \sum_{i \neq j \neq k} D_{ij}^2[61D_{ik}^2 - 8D_{jk}D_{ki}] \\
& + (1/1680N)S(S+1) \\
& \times [3018S(S+1) - 961]\sum_{i < j} D_{ij}^4. \quad (15)
\end{aligned}$$

The lattice sums appearing in Eqs. (14) and (15) are easily evaluated for a simple cubic lattice in the special case when the magnetic field H points along a (100) direction. The moments are then:

$$\langle\nu^2\rangle_{av} = 10.0S(S+1)g^4\beta^4\hbar^{-2}d^{-6}, \quad (16)$$

$$\langle\nu^4\rangle_{av} = 3[\langle\nu^2\rangle_{av}]^2\{1 - 0.348 - [0.034/S(S+1)]\}, \quad (17)$$

where d is the distance between neighboring magnetic

atoms. If the line shape were exactly Gaussian, the fourth moment would be $3[\langle\nu^2\rangle_{av}]^2$. It is seen from Eq. (17) that the line departs somewhat from Gaussian shape, being slightly less sharply peaked.

It is interesting to compare these moments with those obtained for the corresponding photon resonance absorption line.⁸ The second moment is exactly the same as that of the phonon resonance line, being given by Eq. (14). We write down the fourth moment only for the particular case of a simple cubic lattice with the magnetic field a (100) direction:

$$\langle\nu^4\rangle_{av} = 3[\langle\nu^2\rangle_{av}]^2\{1 - 0.160 - [0.021/S(S+1)]\}. \quad (18)$$

The line shape again departs from Gaussian, but to a lesser extent than the phonon absorption line. The second moments of the two lines being equal, the photon absorption line is the more sharply peaked, since it has the larger fourth moment, but the difference between the two line widths is small.

(ii) Neglecting the dipole-dipole interaction, we have from (4):

$$D_{ij} = 2C_{ij} = J_{ij}. \quad (19)$$

We adopt the approximation of assuming the exchange interaction to be negligible except between nearest-neighbor spins, but note that the longer-range contributions to the exchange energy may be of importance for small percentages of magnetic impurities. If the value of the exchange coefficient for nearest neighbors is J and the number of such neighbors is z , then:

$$h^2\langle\nu^2\rangle_{av} = 2S(S+1)zJ^2. \quad (20)$$

$$\begin{aligned}
h^4\langle\nu^4\rangle_{av} = & S^2(S+1)^2z^2J^4 \\
& \times \left[\frac{19(z-1)}{3} + \frac{859}{z} - \frac{1444}{210zS(S+1)} \right]. \quad (21)
\end{aligned}$$

For the simple cubic lattice, Eq. (21) can be written in the form,

$$\langle\nu^4\rangle_{av} = 3[\langle\nu^2\rangle_{av}]^2\{1 - 0.390 - [0.095/S(S+1)]\}, \quad (22)$$

so that the line shape is not very different from that in the zero exchange case given by Eq. (17).

In the photon case exchange does not contribute to the second moment but appears in the fourth moment, giving rise to the phenomenon of exchange narrowing of the absorption lines. It is seen that for the phonon resonance absorption lines, exchange contributes to both the second and fourth moments and thus acts to increase the width of the line.

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¹⁰ A. Wright, Phys. Rev. **76**, 1826 (1949).