PHYSICAL REVIEW B VOLUME 11, NUMBER 3 1 FEBRUARY 1975

Spin-resonance line-shape changes induced by intraspin cross relaxation*

Peter A. Fedders

Laboratory for Ultrasonics, Physics Department, Washington University, St. Louis, Missouri 63130

(Received 16 October 1974)

Intraspin cross relaxation induced by static quadrupole electric fields is investigated. Equations of motion pertaining to electromagnetic and acoustic spin-resonance experiments on a system of spins of arbitrary magnitude are derived. Explicit solutions are obtained and plotted for simple systems. In conjunction with other decay mechanisms, intraspin cross relaxation can lead to considerable structure in spin-resonance spectra including dips, additional broadening, and narrowing. Our analysis suggests that these effects may occasionally be observed and misinterpreted.

I. INTRODUCTION

As is well known, static-electric-field gradients in a crystal lead to shifts in the energy levels of nuclear and electronic spins via a quadrupolar interaction.[1] The simplest effect on the spin-resonance spectra induced by these shifts is merely a shift and/or splitting of the resonance line. In the presence of spin-spin interactions there are additional complications because the intrinsic spin decay rates themselves change. However, even if the intrinsic decay rates do not change, the line-shape spectra can be drastically altered by intraspin cross relaxation, which is the interference between different decay routes.[2]

The equations for intraspin cross relaxation have been worked out for the electromagnetic excitation of a spin-1 system and used to explain the EPR line shape of Ni^{++} impurities in MgO.[2] In this paper we investigate intraspin cross relaxation for spins of arbitrary magnitude excited by electromagnetic or acoustic probes. It turns out that the results depend very strongly on these two factors. We also extensively discuss the validity of the equations for systems with various intrinsic decay mechanisms. Our analysis shows that intraspin cross relaxation is often just as important as simple quadrupole splitting when a distribution of static strains or impurities is present. It may be responsible for observed anomalous dips, broadening, and narrowing in some experimental spectra.

In the remainder of this section we shall discuss decay rates and cross relaxation in terms of generalized Bloch equations and a multipole-sphere analogy. The basis equations describing the phenomena are derived and solved in Sec. II. In Sec. III the results are discussed and explicit plots are given. Some of the more tedious details of the derivation are included in the Appendix. In what follows we shall use notation appropriate to nuclear spins, although the equations are equally valid for electronic spins.

Most spin-resonance experiments can be interpreted in terms of the magnetization components M_+, M_-, and M_z corresponding to the spin operators I_+, I_-, and I_z. However, for a single spin of magnitude I, one needs a complete set of $(2I+1)^2$ operators in order to obtain a complete dynamical description.[3] In the high-temperature limit, where kT is much greater than any spin energy, the most convenient complete set is the set of irreducible tensor operators $A_{l,m}$.[3-5] These spin multiple operators are orthonormal in that

$$\mathrm{Tr}[A_\alpha(A_\beta)^\dagger]=\delta_{\alpha,\beta}(2I+1)\ , \tag{1}$$

where we use the shorthand notation $A_\alpha = A_{l,m}$ and $\alpha=(l,m)$. These operators can be expressed in terms of the usual vector spin operators, where m takes on all integral values $|m|\leq l$ and l takes on integral values from 0 to $2I$. The quantity $A_{0,0}=1$, while $A_{1,+1}$, $A_{1,-1}$, and $A_{1,0}$ are proportional to I_+, I_-, and I_z, respectively. Some relevant properties of these operators are listed in the Appendix.

One reason that the irreducible multiple operators are a convenient complete set in the high-temperature limit is that their expectation values satisfy a set of Bloch-like equations under a wide variety of circumstances. That is, in the presence of a magnetic field $H_0\hat{z}$, a set of spins which interact with the lattice or some other independently fluctuating field satisfies the equations[6]

$$\left(\frac{d}{dt}+im\omega_0\right)\langle A_{l,m}(t)\rangle = -\Gamma_{l,m}[\langle A_{l,m}(t)\rangle - \langle A_{l,m}(t)\rangle_0]\ . \tag{2}$$

In this equation $\omega_0=\gamma H_0$, where γ is the spin's gyromagnetic ratio, $\langle A(t)\rangle$ is the average value of $A(t)$ in the canonical ensemble, and $\langle A(t)\rangle_0$ is the instantaneous equilibrium value of $\langle A(t)\rangle$. The quantity $\Gamma_{l,m}$ is the decay rate or inverse lifetime of the mode (l,m). The reasons that the $\langle A_{l,m}\rangle$ satisfy Eq. (2) are that the commutator of A_α with I_z is proportional to A_α and that in the high-temperature limit the density matrix is essentially 1. Thus the trace of A_α and $A_\beta^\dagger$ weighted by the density matrix is proportional to $\delta_{\alpha,\beta}$. The physical meaning of Eq. (2) is that each $\langle A_{l,m}\rangle$ corresponds to an independent normal mode of the system. This is analogous to the normal modes on a sphere whose angular dependences go as $Y_{l,m}$, whose eigenfrequencies are $m\omega_0$, and where each normal mode decays independently with a decay rate $\Gamma_{l,m}$.

Actually Eq. (2) is much more general than stated above. If one has a lattice of spins interacting via spin-spin interactions and the Zeeman energy or isotropic exchange energy is much greater than the anisotropic exchange energy, then Eq. (2) can be generalized[5] to

$$(\omega - m\omega_0)\langle A_{l,m}(\vec{q},\omega)\rangle = [\pi_{l,m}(\vec{q},\omega) - i\Gamma_{l,m}(\vec{q},\omega)] \times[\langle A_{l,m}(\vec{q},\omega)\rangle - \langle A_{l,m}(\vec{q},\omega)\rangle_0] \; . \tag{2'}$$

In this equation π and Γ are the real and imaginary parts of a self-energy and

$$A(\vec{q},\omega) = \sum_{\vec{r}} \int dt A(\vec{r},t)\, e^{i(\omega t - \vec{q}\cdot\vec{r})} \; , \tag{3}$$

where the summation is over lattice sites $\vec{r}$. Even if the anisotropic exchange energy is not small, only $A_{l,m}$'s with the same l are mixed.

The effects of a driving term, an externally applied electromagnetic or acoustic field, can easily be incorporated into Eqs. (2) and (2′). However, with Eq. (2′), one is limited to linear response theory. Finally, consider the effect of an static quadrupolar ($l=2$) field on the spin system. In Sec. II we shall show that even if this term is small compared to the Zeeman term, the independent normal modes (l, m) described above are mixed and the decay scheme for $\langle A_{l,m}\rangle$ becomes quite complex. In the case where the spin decay rates $\Gamma_{l,m}$ are due to some independently fluctuating quadrupole field, the $\Gamma_{l,m}$ are not changed and the generalization of Eq. (2) is straightforward. In the case where spin-spin interactions are important, the $\Gamma_{l,m}$ themselves are modified and the modifications of Eq. (2′) are not so straightforward. However, if the static quadrupole energy shifts are much less than the spin-spin interaction, the modifications are again straightforward. An example is the case where the exchange energy is greater than the quadrupole splittings but the dipolar energy is less than the quadrupole splittings. This paper is limited to these straightforward cases although a procedure for handling the general case is suggested at the end of Sec. II.

II. SOLUTIONS

In this section we shall first consider only spins which decay via an independent fluctuating field. Spin-spin interactions are considered at the end of this section. In addition, we shall assume that the static quadrupole splittings are much less than the Zeeman splitting and so only the diagonal part of the static quadrupolar field need be used. For spins excited by an electromagnetic field, we use the Hamiltonian[2]

$$H = -\hbar\omega_0 I_z + \hbar\omega_q[I_z^2 - \tfrac{1}{3}I(I+1)] + \tfrac{1}{2}\hbar\omega_{1,1}(I_+ + I_-) \tag{4}$$

and the relaxation mechanism which yields Eq. (2). The strength of the static quadrupole field is expressed in terms of the frequency ω_q and $\omega_{1,1} = \gamma H_1$, where H_1 is the strength of an external probe field. All time-dependent quantities are assumed to vary as $e^{-i\omega t}$. By using only the diagonal part of the quadrupole Hamiltonian, we are neglecting terms of order ω_q^2/ω_0 compared to ω_0. The inclusion of higher-order terms is discussed later. The above approximation is valid if ω_q^2/ω_0 is much less than ω_0 and the $\Gamma_{l,m}$'s.

The generalization of Eq. (2) to include the driving and quadrupolar terms is

$$\omega\langle A_{l,m}\rangle = \langle [A_{l,m},\; H]\rangle/\hbar - i\Gamma_{l,m}(\langle A_{l,m}\rangle - \langle A_{l,m}\rangle_0) \; . \tag{5}$$

Since we are doing only linear response and the driving term is proportional to $A_{1,1}$ and $A_{1,-1}$, only the $\langle A_{l,m}\rangle$ with $m=\pm 1$ are affected and $\langle A_{l,m}\rangle$'s with different m's are not coupled. Thus Eq. (5) can be rewritten as

$$(\omega - \omega_0 + i\Gamma_{l,1})\langle A_{l,1}\rangle + \omega_q[D(l,1)\langle A_{l-1,1}\rangle + D(l+1,1)\langle A_{l+1,1}\rangle] = i\Gamma_{l,1}\langle A_{l,1}\rangle_0 - \tfrac{1}{2}\omega_{1,1}[l(l+1)]^{1/2}\langle A_{l,0}\rangle_0 \; , \tag{6}$$

where

$$D(l,1) = -C(l,1)/3a_2\sqrt{5} \; . \tag{7}$$

In obtaining these equations, Eqs. (A1) and (A9) from the Appendix have been used. The quantities a_2 and $C(l,1)$ are defined in Eqs. (A2) and (A8). The only nonzero $\langle A_{l,m}\rangle_0$'s are $\langle A_{1,0}\rangle_0$, $\langle A_{1,1}\rangle_0$, and $\langle A_{2,0}\rangle_0$, which can easily be evaluated to lowest order in $1/k/T$.

It is most convenient to normalize the solution to Eq. (6) as

$$\chi_{l,1}(\omega) = \sqrt{6}\, a_1\langle A_{l,1}\rangle/\beta\hbar\omega_{1,1} \; , \tag{8}$$

where $\beta = 1/kT$, a_1 is defined by Eq. (A2), and $\chi_{l,1}(\omega)$ is a generalized susceptibility. The spectral-shape function is the imaginary part of $\chi_{l,1}(\omega)/\omega$. Equation (6) is a set of $2I$ coupled equations which is conveniently written in matrix form as

$$[\chi] = [M]^{-1}\cdot[f] \; . \tag{9}$$

In this equation $[\chi]$ and $[f]$ are $2I\times 1$ column matrices whose elements are

$$[\chi]_{l,1} = \chi_{l,1}(\omega) \; , \tag{10a}$$

$$[f]_{l,1} = (-\omega_0 + i\Gamma_{1,1})\,\delta_{l,1} + \omega_q D(2,1)\delta_{l,2} \; . \tag{10b}$$

The quantity $[M]$ is a $2I\times 2I$ symmetric matrix whose only nonzero elements are

$$[M]_{l,l}=\omega-\omega_0+i\Gamma_{l,1}\,,\qquad [M]_{l,l+1}=[M]_{l+1,l}=\omega_q D(l+1,1)\,. \tag{10c}$$

In the Appendix a procedure is described for generating a recursion relation among the $D(l, m)$'s. The recursion relation for $D(l, 1)$ reads

$$D(l,1)=f(l,1)[g(l,1)]^{1/2}\,, \tag{11a}$$

$$f(l+1,1)=(2I-1)-g(l,1)f(l,1)\,,\quad 1\le l\le 2I-1 \tag{11b}$$

$$g(l,1)=\left[\frac{(2I+l+1)(2l-1)(l-1)}{(2I-l+1)(2l+1)(l+1)}\right]\,, \tag{11c}$$

where $f(1,1)=f(2I+1,1)=0$.

The equations for acoustically excited spin systems are quite similar to those for the electromagnetic case. For acoustic $\Delta m=1$ transitions

$$H=-\hbar\omega_0 I_z+\hbar\omega_q[I_z^2-\tfrac{1}{3}I(I+1)]+\tfrac{1}{2}\hbar\omega_{2,1}(\{I_+,I_z\}+\{I_-,I_z\}) \tag{12}$$

replaces Eq. (4). The solution is the same as the one described by Eqs. (8)–(11) except that

$$\chi_{l,1}(\omega)=\sqrt{30}\,a_2\langle A_{l,1}\rangle/\beta\hbar\omega_{2,1} \tag{8$'$}$$

replaces Eq. (8) and

$$[f]_{l,1}=\omega_q D(2,1)\delta_{l,1}+(-\omega_0+i\Gamma_{2,1})\delta_{l,2}+\omega_q D(3,1)\delta_{l,3} \tag{10b$'$}$$

replaces Eq. (10b).

For acoustic $\Delta m=2$ transitions

$$H=-\hbar\omega_0 I_z+\hbar\omega_q[I_z^2-\tfrac{1}{3}I(I+1)]+\tfrac{1}{2}\hbar\omega_{2,2}(I_+^2+I_-^2) \tag{13}$$

replaces Eq. (4). The solution is a set of $(2I-1)$ coupled equations which is written in matrix form

$$[\chi]=[M']^{-1}\cdot[f']\,. \tag{14}$$

In this equation $[\chi]$ and $[f]$ are $(2I-1)\times 1$ column matrices whose elements are

$$[\chi]_{l,1}=\chi_{l,2}(\omega)=-\sqrt{30}\,a_2\langle A_{l,2}\rangle/\beta\hbar\omega_{2,2}\,, \tag{15a}$$

$$[f']_{l,1}=(-2\omega_0+i\Gamma_{2,2})\delta_{l,1}+\omega_q D(3,2)\delta_{l,2}\,. \tag{15b}$$

The quantity $[M']$ is a $(2I-1)\times(2I-1)$ symmetric matrix with nonzero elements

$$[M']_{l,l}=(\omega-2\omega_0+i\Gamma_{2,l+1})\,,\qquad [M']_{l+1,l}=[M']_{l,l+1}=\omega_q D(l+2,2)\,. \tag{16}$$

The recursion relation for the $D(l, 2)$'s is

$$D(l,2)=f(l,2)[g(l,2)]^{1/2}\,, \tag{17a}$$

$$f(l+1,2)=4(I-1)-g(l,2)f(l,2)\,,\quad 2\le l\le(2I-1) \tag{17b}$$

$$g(l,2)=\left[\frac{(2I+l+1)(2l-1)(l-2)}{(2I-l+1)(2l+1)(l+2)}\right]\,, \tag{17c}$$

where $f(2,2)=f(2I+1,2)=0$.

The results derived in this section depend upon two critical assumptions. One assumption is that ω_q/ω_0 is small enough so that only the diagonal part of the static quadrupole Hamiltonian is needed. The other assumption is that the $\Gamma_{l,m}$ are not affected by the static quadrupole Hamiltonian. First consider the case where the decay of the spins is dominated by their interaction with some independent fluctuating field. In this case the $\Gamma_{l,m}$ can dedend only on the spin Hamiltonian via the spin energy levels.[6] Thus the $\Gamma_{l,m}$ are virtually unchanged by the static quadrupolar Hamiltonian as long as $\omega_0\gg\omega_q$. The effects of intraspin cross relaxation will be greater than the effects of second-order quadrupole splitting if $\Gamma_{l,m}\gg\omega_q^2/\omega_0$. If this is not true, then second-order terms must be included.

With spin-spin interactions the situation is more complex because the fluctuating field that each spin feels is due to the other spins and not due to an independent mechanism. Thus the problem must be solved self-consistently. In Ref. 5 a scheme is derived for generating integral equations for spin spectral functions. This scheme can be generalized to include any spin-spin interactions or static fields. In particular, it is easily seen that $\Gamma_{l,m}(\vec{q},\omega)$ is generated by an integral of Green's functions over all $\vec{q}$ and ω. Thus $\Gamma_{l,m}(\vec{q},\omega)$ is virtually unchanged as long as the quadrupolar frequency ω_q is much less than all the $\Gamma_{l',m'}(\vec{q}\,',m'\omega_0)$ over almost all of the Brillouin zone. Thus the equations of this section can be generalized to the case with spin-spin interactions by the substitution

$$\Gamma_{l,m}\to\Gamma_{l,m}(\vec{q},\omega)+i\pi_{l,m}(\vec{q},\omega)\,. \tag{18}$$

This substitution is valid if

$$\omega_q\ll\langle\Gamma_{l,m}(\vec{q},m\omega_0)\rangle\,, \tag{19}$$

where the $\langle\Gamma\rangle$ denotes an average over the Brillouin zone. The wave vector $\vec{q}$ in Eq. (18) denotes the wave vector of the exciting field, which is essentially zero in almost all electromagnetic experiments and acoustic experiments.

Equation (19) is not so stringent as to rule out all interesting cases. For example, consider an exchange-narrowed system where the exchange frequency ω_e is much greater than the dipolar frequency ω_d. In this case, $\Gamma_{1,1}\sim\omega_d^2/\omega_e$ and $\Gamma_{l,m}\sim\omega_e$ for $l>1$. Thus there is a range

$$\omega_d^2/\omega_e<\omega_q<\omega_e\,, \tag{20}$$

where cross-relaxation effects are important and where the equations are valid. If ω_q is much less than all the $\Gamma_{l,m}(q,m\omega_0)$, the effects are very small.

III. DISCUSSION

In this section we consider in detail the solutions for $I=1$ and $I=\frac{3}{2}$. From these two cases some generalizations can be made about higher-spin solutions. In order to avoid confusion we shall label the solutions $\chi_{l,m}(\omega, I)$, where I is the spin in the case under consideration, $(l=1,\ m=1)$ refers to the electromagnetic response due to an electromagnetic probe, and $(l=2,\ m=1 \text{ or } 2)$ refers to the acoustic response due to an acoustic probe.

The $I=1$ and $I=\frac{3}{2}$ solutions to the matrix equations in Sec. II read

$$\chi_{1,1}(\omega, 1) - 1 = -\omega\Omega_{2,1}/D_{1,1}\ , \qquad (21a)$$

$$\chi_{2,1}(\omega, 1) - 1 = -\omega\Omega_{1,1}/D_{1,1}\ , \qquad (21b)$$

$$\chi_{1,1}(\omega, \tfrac{3}{2}) - 1 = -\omega(\Omega_{2,1}\Omega_{3,1} - 1.6\omega_q^2)/D_{3/2,1}\ , \qquad (21c)$$

$$\chi_{2,1}(\omega, \tfrac{3}{2}) - 1 = -\omega\Omega_{1,1}\Omega_{3,1}/D_{3/2,1}\ , \qquad (21d)$$

$$\chi_{2,2}(\omega, \tfrac{3}{2}) - 1 = -\omega\Omega_{3,2}/D_{3/2,2}\ , \qquad (21e)$$

where

$$\begin{aligned} \Omega_{l,m} &= \omega - m\omega_0 + i\Gamma_{l,m}\ , \\ D_{1,1} &= \Omega_{1,1}\Omega_{2,1} - \omega_q^2\ , \\ D_{3/2,1} &= \Omega_{1,1}\Omega_{2,1}\Omega_{3,1} - 0.2\omega_q^2(8\Omega_{1,1} + 12\Omega_{3,1})\ , \\ D_{3/2,2} &= \Omega_{2,2}\Omega_{3,2} - 4\omega_q^2\ . \end{aligned} \qquad (22)$$

Often static quadrupole fields are due to a random distribution of defects. A small concentration of defects usually leads to a Lorentzian distribution of field gradients.[1,7] Thus the susceptibilities appropriate for most experiments are given by Eqs. (21) averaged over a Lorentzian distribution of ω_q. Equations (21) averaged over the function

$$\omega_1/\pi[(\omega_q - \omega_2)^2 + \omega_1^2] \qquad (23)$$

are

$$\chi_{1,1}(\omega, 1) - 1 = -(\omega\Omega_{2,1}/2b_1)[(b_1 + i\omega_1 - \omega_2)^{-1} + (b_1 + i\omega_1 + \omega_2)^{-1}]\ , \qquad (24a)$$

$$\chi_{2,1}(\omega, 1) - 1 = -(\omega\Omega_{1,1}/2b_1)[(b_1 + i\omega_1 - \omega_2)^{-1} + (b_1 + i\omega_1 + \omega_2)^{-1}]\ , \qquad (24b)$$

$$\chi_{1,1}(\omega, \tfrac{3}{2}) - 1 = -(\omega b_2/2\Omega_{1,1})[(b_2 + i\omega_1 - \omega_2)^{-1} + (b_2 + i\omega_1 + \omega_2)^{-1}] - (\omega/5\Omega_4)[2 - b_2(b_2 + i\omega_1 - \omega_2)^{-1} - b_2(b_2 + i\omega_1 + \omega_2)^{-1}]\ , \qquad (24c)$$

$$\chi_{2,1}(\omega, \tfrac{3}{2}) - 1 = -(\omega b_2/2\Omega_{2,1})[(b_2 + i\omega_1 - \omega_2)^{-1} + (b_2 + i\omega_1 + \omega_2)^{-1}]\ , \qquad (24d)$$

$$\chi_{2,2}(\omega, \tfrac{3}{2}) - 1 = -(\omega\Omega_{3,2}/2b_3)[(b_3 + i\omega_1 - \omega_2)^{-1} + (b_3 + i\omega_1 + \omega_2)^{-1}]\ . \qquad (24e)$$

In these equations

$$\begin{aligned} b_1 &= (\Omega_{1,1}\Omega_{2,1})^{1/2}\ , \\ b_2 &= (\Omega_{1,1}\Omega_{2,1}\Omega_{3,1}/4\Omega_4)^{1/2}\ , \\ b_3 &= (\Omega_{2,2}\Omega_{3,2})^{1/2}\ , \\ \Omega_4 &= 0.4\Omega_{1,1} + 0.6\Omega_{3,1}\ , \end{aligned} \qquad (25)$$

where the imaginary parts of all the b_i are positive. The distribution given by Eq. (23) describes a Lorentzian distribution of width ω_1 about a center at ω_2. Usually ω_2 is zero. Since for $I=1$ there is only one Γ with $m=2$, there is no $\Delta m=2$ intraspin cross relaxation.

Before looking at plots of these functions we shall first make some general remarks which hold for all I. First, if all of the $\Gamma_{l,m}$ are the same for a given m, the b's equal the Ω's and there is no intraspin cross relaxation. The only effect is then the usual splitting of the energy levels. Intraspin cross relaxation effects tend to become more pronounced as differences in the Γ's grow. Also intraspin cross-relaxation effects can be as important as the direct energy-level shifts due to the static quadrupolar field. Static-quadrupole shifts are of order ω_1 while effective-decay-rate shifts are of order $\Delta\Gamma \sim \Gamma_l - \Gamma_{l+1}$ if $\omega_q \gg \Delta\Gamma$ and of order $\omega_1^2/\Delta\Gamma$ if $\omega_1 \ll \Delta\Gamma$. If $\omega_1 \sim \Delta\Gamma$ the static shifts and effective-decay-rate shifts are comparable. Thus, unless the $\Gamma_{l,m}$'s are nearly equal for fixed m, both effects must be included.

There is a similarity between $\chi_{2,2}$ for an integral (half-integral) spin system and $\chi_{1,1}$ for a half-integral (integral) spin system. The reason is that for a half-integral spin system the electromagnetically allowed $(-\frac{1}{2} \to +\frac{1}{2})$ transition is not changed directly by the quadrupole field. The same is true for the $(-1 \to +1)$ acoustically allowed transition in an integral spin system. However, the $\chi_{1,1}(-\frac{1}{2} \to \frac{1}{2})$ transition [or the $\chi_{2,2}(-1 \to 1)$ transition] is affected greatly by intraspin cross relaxation. For example, if ω_1 is large and only direct quadrupole effects were included, one would obtain

$$\chi_{1,1}(\omega, \tfrac{3}{2}) - 1 \sim -0.4\omega/(\omega - \omega_0 + i\Gamma_{1,1})\ , \qquad (26)$$

since 0.4 of the spectral weight belongs to the unaffected $(-\frac{1}{2} \to \frac{1}{2})$ transition. However, the correct formula from Eq. (24c) is

$$\begin{aligned} \chi_{1,1}(\omega, \tfrac{3}{2}) - 1 &\sim 0.4\omega/(\omega - \omega_0 + i\Gamma_4)\ , \\ \Gamma_4 &= 0.4\Gamma_{1,1} + 0.6\Gamma_{3,1}\ , \end{aligned} \qquad (26')$$

that is, the decay rate is drastically altered. This is because the $l=1,\ m=1$ mode can relax through other $m=1$ channels. The quantity $\chi_{2,1}$ is different because the $(-\frac{1}{2} \to +\frac{1}{2})$ transition is not allowed acoustically.

From Eqs. (24) it can be seen that $\chi_{1,1}(\omega, 1)$, $\chi_{2,1}(\omega, 1)$, and $\chi_{2,2}(\omega, \frac{3}{2})$ have the same functional form. The other χ's become more complex but figures of $\chi_{1,1}(\omega, 1)$ for different Γ's and ω_1's show what can happen. In Fig. 1 the imaginary part of $\chi_{1,1}(\omega,1)/\omega$ is plotted versus $\omega-\omega_0$ for various values of Γ_1, Γ_2, and ω_1 with $\omega_2=0$. For comparison, the Lorentzian line with static quadrupole splittings but no cross relaxation is included. Since the results are symmetric about the origin of $\omega-\omega_0$, only the positive half is shown.

From these figures and from other cases we have plotted, several more generalizations can be made. For example, the center of the resonance is affected qualitatively much more by intraspin cross relaxation than the wings are. In addition, no matter how large ω_1 is with respect to $\Delta\Gamma$, the center of the resonance can be qualitatively altered. One can also see that a split line or a line with a dip in the center can be caused by intraspin cross relaxation. This unfortunately means that there are at least three distinct mechanisms that can cause such an effect. They are (a) a net strain on a crystal so that the average quadrupole splitting is not zero

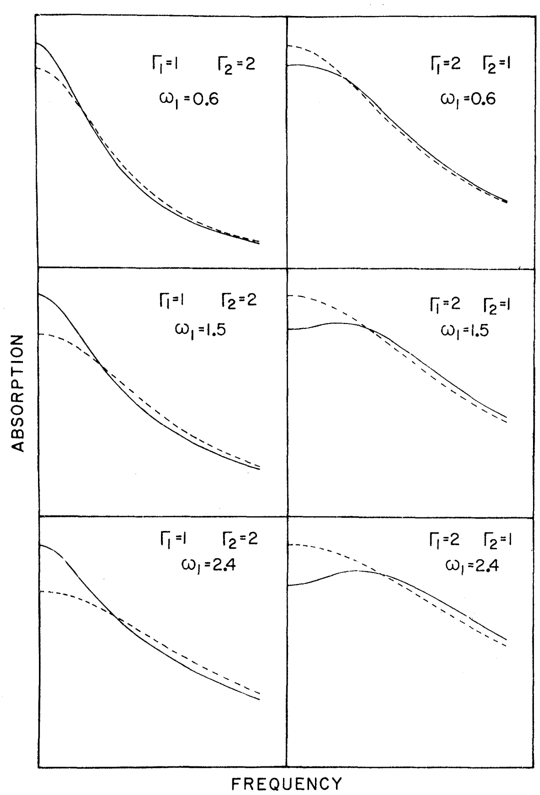

FIG. 1. Imaginary part of $\chi_{1,1}(\omega, 1)/\omega$ in arbitrary units vs $\omega-\omega_0$ for different values of Γ_1, Γ_2, and ω_1 with $\omega_2=0$. All frequencies are in the same arbitrary units and the length of the x axes is 4.5 of these units. The solid curve is computed using Eq. (24a). The dashed curve is computed by neglecting intraspin cross relaxation.

[that is, ω_2 in Eq. (23) is not zero]; (b) long-ranged sample-shape-dependent effects from imperfections described in Ref. 7; (c) intraspin cross relaxation.

Although it may not be easy to find the dominant mechanism or mechanisms in a given material, some essential differences in the mechanisms are (i) Mechanisms (a) and (b) are due to static quadrupole splittings and should affect the electromagnetic and the acoustic $\Delta m=1$ and $\Delta m=2$ spectra in similar way. Mechanism (c) can affect the three different spectra quite differently. One or two might have a huge hole in the center, while the other one or two may not. (ii) The angular dependences of the three mechanisms are different. Mechanism (c) has only the symmetry of the crystal. Mechanism (a) has the symmetry of the crystal folded into the symmetry of the static strain. That is, there must be some preferred axis, not just equivalent preferred directions. Similarly, mechanism (b) has the symmetry of the crystal folded into the symmetry of the crystal geometry. Thus, say, not all [100] directions are equivalent for mechanisms (a) and (b).

From Eqs. (24) and Fig. 1 one more important generalization can be made. The most dramatic effects (such as a dip in the center of the spectrum) will occur for $\chi_{l,m}$ when $\Gamma_{l,m}$ is greater than $\Gamma_{l\pm1,m}$. Except for the special case of $I=1$, one almost always has $\Gamma_{1,1}<\Gamma_{2,1}<\Gamma_{3,1}$ and $\Gamma_{2,2}<\Gamma_{3,2}$. This is certainly the case for dynamic quadrupole relaxation.[6] For spin-spin exchange interactions the second moment of $\chi_{l,m}(\omega)$ is proportional to $l(l+1)$ except for $l=1$, when the second moment is zero. Thus $\chi_{2,1}(\omega)$ (Δm is one acoustic transition) is more likely to yield dip than $\chi_{1,1}(\omega)$ (electromagnetic transitions) or $\chi_{2,2}(\omega)$ (Δm is two acoustic transitions). For this reason we believe that recent work on Ta,[8,9] showing a sharp dip in the center of the acoustic $\Delta m=1$ transition but no such structure in the acoustic $\Delta m=2$ transition, is due to intraspin cross relaxation. Calculations with $\Gamma_{l,m}$ proportional to $[l(l+1)]^{1/2}$ for $l\neq1$ and with $\Gamma_{1,1}$ much smaller show that a very sharp dip can be induced in the spectrum of $\chi_{2,1}(\omega)$ with very little change in $\chi_{2,2}(\omega)$. The peak in $\chi_{1,1}(\omega)$ is broadened with these parameters. We also suspect that some acoustic results in III-V compounds are likely candidates for this mechanism.[10]

Finally, let us consider the effects of intraspin cross relaxation on $m=0$- or T_1-type correlation functions. To first order in the static quadrupole field, $\chi_{l,0}$ is not affected. However, to second order $\chi_{l,0}$ is mixed with $\chi_{l',m}$ and $\Gamma_{l,0}$ can be effectively changed to order $\omega_q^2\Gamma_{l,m}/\omega_0^2$, where $m\neq0$. Even if $\omega_0\gg\omega_q$ this can be a sizable effect if spin-spin interactions are important. For example, $\Gamma_{l,0}$ is not affected by either dipolar or exchange interactions. However, $\Gamma_{1,\pm1}$ is affected by dipolar interactions and $\Gamma_{l,m}$ with $l \geq 2$ is affected by both. Thus $\Gamma_{l,m}$ $(m \neq 0)$ could be much greater than $\Gamma_{1,0}$.

APPENDIX

In this Appendix we evaluate some commutators of the irreducible spin-multipole operators. For reference here and in the text, the operators through $l = 2$ are listed below in terms of the usual vector spin operators:

$$\begin{aligned} &A_{0,0} = 1 \,, \\ &A_{1,0} = 3^{1/2} a_1 I_z \,, \quad A_{1,\pm1} = \mp \tfrac{3}{2}^{1/2} a_1 I_\pm \,, \\ &A_{2,0} = \mp 45^{1/2} a_2 [I_z^2 - \tfrac{1}{3} I(I+1)] \,, \\ &A_{2,\pm1} = \mp \tfrac{15}{2}^{1/2} a_2 \{I_\pm, I_z\} \,, \quad A_{2,\pm2} = \tfrac{15}{2}^{1/2} a_2 I_\pm^2 \,, \end{aligned} \tag{A1}$$

where

$$a_1 = [I(I+1)]^{-1/2}, \quad a_2 = [I(I+1)(2I-1)(2I+3)]^{-1/2}, \tag{A2}$$

$I = I_x \pm i I_y$, and the curly brackets $\{A, B\}$ denote the anticommutator of A and B. These and the other operators can be derived from the relations[3]

$$\begin{aligned} &\sum_{m=-l}^{m=+l} Y_{l,m} t^m = -t I_+ + 2 I_z + I_-/t \,, \\ &A_{l,m} = Y_{l,m}/(C_{l,m})^{1/2} \,, \\ &C_{l,m} = \frac{(2I+1+l)!\,(l!)^2 (2l)!}{(2l+1)!\,(2I-l)!\,(l-m)!\,(l+m)!\,(2I+1)} \,, \end{aligned} \tag{A3}$$

The commutator of operators A_α and A_β is written as

$$[A_\alpha, A_\beta] = \sum_\gamma C(\alpha; \beta; \gamma) A_\gamma \tag{A4}$$

and the following useful identities are easily proved:

$$\begin{aligned} C(\alpha; \beta; \gamma) &= -C(-\alpha; -\beta; -\gamma) = -C(\beta; \alpha; \gamma) \\ &= (-1)^{\beta_m} C(\gamma; -\beta; \alpha) \,, \end{aligned} \tag{A5}$$

where $-\alpha$ denotes $(l, -m)$ if α denotes (l, m). Because the A_α are in irreducible form, the commutators with A_α with the spin vector operators or irreducible operators of the first rank are trivial:

$$\begin{aligned} &[I_z, A_{l,m}] = m A_{l,m} \,, \\ &[I_\pm, A_{l,m}] = [l(l+1) - m(m\pm1)]^{1/2} A_{lm} \,. \end{aligned} \tag{A6}$$

Because $A_{2,0}$ is a second-rank tensor

$$\begin{aligned} [A_{l,m}, A_{2,0}] &= C(l, m; 2, 0; l-1, m) A_{l-1,m} \\ &+ C(l, m; 2, 0; l+1, m) A_{l+1,m} \,. \end{aligned} \tag{A7}$$

From Eq. (A5) one can show that

$$C(l, m; 2, 0; l+1, m) = C(l+1, m; 2, 0; l, m)$$

and, if we define

$$C(l, m) = C(l, m; 2, 0; l-1, m) \tag{A8}$$

we obtain

$$[A_{l,m}, A_{2,0}] = C(l, m) A_{l-1,m} + C(l+1, m) A_{l+1,m} \,. \tag{A9}$$

A recursion relation between the $C(l, m)$'s can be derived by taking matrix elements of Eq. (A9). In order to evaluate these matrix elements we write the Wigner-Eckart theorem[11] as

$$\langle I, I | A_{l,m} | I, I-m \rangle = \frac{\langle I \| A_l \| I \rangle \langle I, I-m; l, m | I, l, I; I \rangle}{(2I+1)^{1/2}} \,. \tag{A10}$$

Using Racah's[12] formula for the Clebsch-Gordan coefficient we obtain

$$\begin{aligned} \langle I, I | A_{l,m} | I, I-m \rangle &= \left(\frac{(2I)!\,(2I-m)!\,(l+m)!}{(2I+l+1)!\,(2I-l)!\,m!\,(l-m)!} \right)^{1/2} \\ &\times (-1)^m \langle I \| A_l \| I \rangle \,. \end{aligned} \tag{A11}$$

The matrix element is easily evaluated for $m = l$ by using Eq. (A3). This yields $\langle I \| A_l \| I \rangle = [(2I+1)(2l+1)]^{1/2}$ and thus

$$\begin{aligned} \langle I, I | A_{l,m} | I, I-m \rangle &= (-1)^m \\ &\times \left(\frac{(2l+1)(2I+1)!\,(2I-m)!\,(l+m)!}{(2I+l+1)!\,(2I-l)!\,m!\,(l-m)!} \right)^{1/2} \,. \end{aligned} \tag{A12}$$

By taking matrix elements of Eq. (A9) and using Eq. (A12) with $m = 1$ and $m = 2$, one obtains Eqs. (11) and (17) of the text.

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*Supported in part by the National Science Foundation.

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