

Cross Relaxation in Dilute Paramagnetic Systems*

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The theory of cross relaxation developed by Bloembergen, Shapiro, Pershan, and Artman is applied to the case of highly diluted paramagnetic salts. We find that the second moment for cross relaxation between two diluted paramagnetic species may be far greater than the sum of the second moments of individual lines which would be obtained from ordinary line width measurements. We can thus explain the dominance of cross relaxation in cases where the separation between the interacting resonances is up to twenty times the sum of the diluted linewidths.

I. INTRODUCTION

IN two recent papers,^{1,2} the theory of cross relaxation in paramagnetic salts was developed. These papers show that dipolar coupling between paramagnetic ions of the same or different types tend to equalize the spin temperature of pairs of energy levels. An impressive number of experiments³⁻⁵ have verified this theory, at least qualitatively, in the case of coupling between different resonance lines of the same paramagnetic ion. In addition Pershan² obtained good quantitative agreement of theory and experiment for the case of cross relaxation between the nuclear spins of Li and F in pure LiF crystals. This experiment was similar to those performed by Abragam and Proctor⁶ and explained most of the results obtained by the latter authors.

The theoretical papers above^{1,2} treated in detail only the case of concentrated crystals. The practical computations in reference 1 and 2 and in Shapiro and Bloembergen⁷ were based on replacement of the second moment for cross relaxation with the sum of the moments of the individual ordinary resonance lines. This approximation is useful for concentrated crystals as shown in Sec. III.⁸ However, we prove below (Sec. IV) that this approximation will not suffice for the case of diluted salts.

In this paper we shall investigate the cross relaxation between paramagnetic ions of different species. The theory follows closely that given by BSPA. We will concentrate however on the case of highly diluted systems although the formulation of the problem and

some of the results are quite general in this respect. For simplicity, we assume that there are no zero field splittings in either paramagnetic species and for detailed results, take $S=\frac{1}{2}$. We also consider a situation where the higher order terms in the spin-spin interaction (i.e., terms which do not conserve angular momentum even approximately) are of no consequence. These last two restrictions limit the applicability of the theory somewhat, but it will be shown that a number of important cases in paramagnetic resonance can be treated by these methods. In a later paper we hope to remove some of the restrictions discussed above.

Section II below contains a brief outline of Bloembergen's theory of cross relaxation. Section III is devoted to the computation of the second moment. In Sec. IV we prove that a Gaussian distribution is always a good approximation for the effective "line-shape" for cross relaxation and estimate the actual cross-relaxation time in a simple case.

II. CROSS-RELAXATION INTERACTIONS

Consider a crystal in which two paramagnetic species α and γ have been substituted for the diamagnetic host. We assume that the resonance frequencies of α and γ are nearly equal. For simplicity we assume that in paramagnetic resonance only allowed transitions ($\Delta S=\pm 1$) occur and that the energy levels of both species are equally spaced (no zero field splittings). The resonant frequencies in a magnetic field H_0 are given by $\omega_\alpha = g_\alpha \beta H_0$ and $\omega_\gamma = g_\gamma \beta H_0$ where the g are the spectroscopic splitting factors of the α and γ species and $\beta = e\hbar/2mc$. As stated above $|g_\alpha - g_\gamma|/g_\alpha \ll 1$. In addition we require the linewidth to be much less than the Zeeman frequency and $g_\alpha \beta H_0 \ll kT$.

The Hamiltonian for this system can be written as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{12}, \quad (1)$$

$$\begin{aligned} \mathcal{H}_0 = & g_\alpha \beta H_0 \sum_p S_{zp} + \sum_{p>q} A_{pq} \mathbf{S}_p \cdot \mathbf{S}_q + \sum_{p>q} B_{pq} S_{zp} S_{zq} \\ & + g_\gamma \beta H_0 \sum_\xi I_{z\xi} + \sum_{\xi>\eta} a_{\xi\eta} \mathbf{I}_\xi \cdot \mathbf{I}_\eta + \sum_{\xi>\eta} b_{\xi\eta} I_{z\xi} I_{z\eta} \\ & + \sum'_{p,\xi} C_{p,\xi} S_{zp} I_{z\xi}, \quad (2) \end{aligned}$$

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¹ N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. **114**, 445 (1959). This paper will be referred to as BSPA.

² P. S. Pershan, Phys. Rev. **117**, 109 (1960).

³ J. A. Giordmaine, L. E. Alsop, F. R. Nash, and C. H. Townes, Phys. Rev. **109**, 302 (1958).

⁴ K. D. Bowers and W. B. Mims, Phys. Rev. **115**, 285 (1959).

⁵ C. H. Townes, *Quantum Electronics* (Columbia University Press, New York, 1960), several papers from pp. 293-369.

⁶ A. Abragam and W. G. Proctor, Phys. Rev. **109**, 1441 (1958).

⁷ S. Shapiro and N. Bloembergen, Phys. Rev. **116**, 1453 (1959).

⁸ This result was proved independently by Pershan. However the details of our second moment result seems to differ somewhat. Our value for the second moment of the cross-relaxation process described below is about twice the sum of the second moments of the individual resonance lines in the absence of exchange.

$$\begin{aligned}
A_{pq} &= J_{pq}^\alpha - g_\alpha^2 \beta^2 r_{pq}^{-3} (1 - 3 \cos^2 \theta_{pq}), \\
a_{\xi\eta} &= J_{\xi\eta}^\gamma - g_\gamma^2 \beta^2 r_{\xi\eta}^{-3} (1 - 3 \cos^2 \theta_{\xi\eta}), \\
B_{pq} &= \frac{3}{2} g_\alpha^2 \beta^2 r_{pq}^{-3} (1 - 3 \cos^2 \theta_{pq}), \\
b_{\xi\eta} &= \frac{3}{2} g_\gamma^2 \beta^2 r_{\xi\eta}^{-3} (1 - 3 \cos^2 \theta_{\xi\eta}), \\
C_{p\xi} &= (j_{p\xi} + g_\alpha g_\gamma \beta^2 r_{p\xi}^{-3}) (1 - 3 \cos^2 \theta_{p\xi}).
\end{aligned} \tag{3}$$

It may be useful to note that Latin subscripts indicate summation over the α system of paramagnetic ions and Greek subscript for summation indices over the γ system. J^α and J^γ are the isotropic exchange terms between like ions; j is the anisotropic exchange α and γ ions. \mathbf{S} and \mathbf{I} are the nondimensional spin operators of the α and γ systems, respectively. The quantity $\cos \theta_{p\xi}$ is the direction cosine for the radius vector, $\mathbf{r}_{p\xi}$, between lattice points p and ξ and the magnetic field vector \mathbf{H}_0 . Since we are dealing with the case of paramagnetic resonance at microwave frequencies and have assumed the local fields to be much smaller than the Zeeman field H_0 , we have omitted the terms which do not conserve angular momentum in Eq. (2) and in Eq. (4) below. (That is, terms like $S_{zp}S_{+q}$, $I_{+z}I_{+\eta}$, $S_{+p}I_{+\xi}$, etc.) The terms given in Eqs. (2) and (4) are the ones which come closest to conserving energy and should dominate the higher order terms. The cross relaxation interaction \mathcal{H}_{12} is given by

$$\begin{aligned}
\mathcal{H}_{12} &= - \sum_{p,\xi} \frac{1}{4} C_{p\xi} (S_{+p}I_{-\xi} + S_{-p}I_{+\xi}) \\
&= - \sum_{p,\xi} \frac{1}{2} C_{p\xi} (S_{xp}I_{x\xi} + S_{yp}I_{y\xi}).
\end{aligned} \tag{4}$$

The summations are taken over all lattice points which are occupied by an α ion or a γ ion. Hence a product like $S_{+p}I_{-\xi}$ gives a nonzero contribution to the sum only if site p is occupied by an ion of type α with $M_s < +S$ and site ξ is occupied by an ion of type γ with $M_I > -I$. The similar requirements for the other products are obvious.

Following reference 1, a "hybrid" method may be used to compute the cross-relaxation rate. The cross-relaxation rate for the α system may be shown to be¹

$$\begin{aligned}
W_{12}^\alpha &= (2\pi/\hbar^2) (n_\gamma/N) \frac{1}{16} (S - M_s)(S + M_s + 1) \\
&\times (I + M_I)(I - M_I + 1) g_{12}(\omega_\alpha - \omega_\gamma) \sum_{\xi}' C_{p\xi}^2. \tag{5}
\end{aligned}$$

The summation now extends over *all* the magnetic sites which can be occupied by γ ions except the p th site when α and γ occupy equivalent sites. The use of the upper limit of summation will always indicate summation over all lattice points in what follows. n_γ is

the total number of ions of type γ . The treatment of lattice sums for dilute salts in this case follows from the work of Kittel and Abrahams.⁹

In Eq. (5), the higher order lattice rearrangements are included in the effective line shape factor $g_{12}(\omega)$. The shape function $g_{12}(\omega)$ may be easily shown to be identical for the two different relaxation processes considered above (i.e., relaxation of α or γ). Equation (5), as it stands, is of limited value unless some detailed information concerning the shape function is available. For high concentrations of α and γ , $g_{12}(\omega)$ will prove to be close to

$$g_{12} \simeq \int_{-\infty}^{\infty} g^\alpha(\omega) g^\gamma(\omega') \delta(\omega + \omega') d\omega d\omega', \tag{6}$$

as postulated in reference 1. The $g^\alpha(\omega)$ and $g^\gamma(\omega)$ are the line shapes of α and γ , respectively. However, at very low concentrations there will be large deviations from this form. We shall use the method of moments in deriving expressions for $g_{12}(\omega)$ (see Sec. III and IV).

III. COMPUTATION OF SECOND MOMENTS

The only practical method of computing line shape is the application of the method of moments. This method is discussed at great detail in the papers of Waller,¹⁰ Pryce and Stevens¹¹ and especially Van Vleck.^{12,13} The tractability of this method depends on the use of invariant sums. Since the trace of an operator is independent of the representation, one may choose a representation in which each ion is separately quantized (although these states are not proper states of \mathcal{H}_0).

Due to the complexity of the higher orders sums, we will evaluate only the second moment and use this in a Gaussian approximation to $g_{12}(\omega)$. In Sec. IV we will prove that a Gaussian is an excellent approximation to the shape of $g_{12}(\omega)$.

The second moment of $g_{12}(\omega)$ is given by^{12,1}

$$\langle \omega^2 \rangle_{av} = - \frac{\text{Trace} [\mathcal{H}_0, \mathcal{H}_{12}]^2}{\hbar^2 \text{Trace} \mathcal{H}_{12}^2}. \tag{7}$$

The computation of the commutators in Eq. (7) is tedious but straightforward. We obtained the following equations. (The summations below are understood to extend over all the subscripts which occur unless otherwise indicated.) Only occupied sites give a contribution

⁹ C. Kittel and E. Abrahams, Phys. Rev. **90**, 238 (1953).

¹⁰ I. Waller, Z. Physik **79**, 370 (1932).

¹¹ M. H. Pryce and K. W. Stevens, Proc. Phys. Soc. (London) **A63**, 36 (1950).

¹² J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

¹³ J. H. Van Vleck, Suppl. Nuovo cimento **6**, 993 (1952).

to the sum.

$$\begin{aligned}
& -\text{Trace} [\mathbf{H}_0, \mathbf{H}_{12}]^2 \\
& = \frac{1}{2} \text{Trace} (S_{yp}^2 S_{zq}^2 I_{x\xi}^2) \sum'' (B_{pq}^2 \\
& \quad + 2A_{pq}^2 + A_{pq} B_{pq}) C_{p\xi}^2 \\
& + \frac{1}{2} \text{Trace} (S_{yp}^2 I_{z\xi}^2 I_{x\eta}^2) \sum'' (b_{\xi\eta}^2 \\
& \quad + 2a_{\xi\eta}^2 + a_{\xi\eta} b_{\xi\eta}) C_{p\xi}^2 \\
& + \frac{1}{2} \text{Trace} (S_{zp}^2 S_{xq}^2 I_{y\xi}^2) \sum'' C_{p\xi}^2 C_{q\xi}^2 \\
& + \frac{1}{2} \text{Trace} (S_{yp}^2 I_{z\xi}^2 I_{x\eta}^2) \sum'' C_{p\xi}^2 C_{p\eta}^2 \\
& + \frac{1}{2} \text{Trace} (S_{xp}^2 S_{zp}^2 I_{y\xi}^2 \\
& \quad + S_{xp} S_{yp} S_{zp} I_{x\xi} I_{y\xi} I_{z\xi}) \sum' C_{p\xi}^4 \\
& + \frac{1}{2} \text{Trace} (S_{yp}^2 I_{z\xi}^2 I_{x\xi}^2 \\
& \quad + S_{xp} S_{zp} S_{yp} I_{x\xi} I_{y\xi} I_{z\xi}) \sum' C_{p\xi}^4. \quad (8)
\end{aligned}$$

In Eq. (8) above we have omitted terms which contain summations like $\sum'' B_{pq} C_{q\xi} C_{p\xi}^2$. Simplifying the lattice sums in a manner analogous to reference 9 and substituting the values for the traces which occur we obtain for the special case $S=I=\frac{1}{2}$.

$$\begin{aligned}
\hbar^2 \langle \Delta\omega^2 \rangle_{av} & = \left[-\frac{1}{4} \frac{n_\alpha}{N} \sum_p' B_{pq}^2 + \frac{1}{4} \frac{n_\gamma}{N} \sum_p' C_{p\xi}^2 \right] \\
& + \left\{ -\frac{1}{4} \frac{n_\alpha}{N} \sum_p' (2A_{pq}^2 + A_{pq} B_{pq}) \right\} \\
& + \left[-\frac{1}{4} \frac{n_\gamma}{N} \sum_\xi' b_{\xi\eta}^2 + \frac{1}{4} \frac{n_\alpha}{N} \sum_\xi' C_{p\xi}^2 \right] \\
& + \left\{ -\frac{1}{4} \frac{n_\gamma}{N} \sum_\xi' (2a_{\xi\eta}^2 + a_{\xi\eta} b_{\xi\eta}) \right\} \\
& - \frac{1}{4} \left[\frac{n_\alpha}{N} \sum_v' B_{pj}^2 C_{vj}^2 + \frac{n_\gamma}{N} \sum_\xi' b_{j\xi}^2 C_{j\xi}^2 \right. \\
& + \frac{n_\alpha + n_\gamma}{N} \sum_\xi' C_{j\xi}^4 \left. \right] / \sum_\xi' C_{j\xi}^2 \\
& + \sum_\xi' C_{j\xi}^4 / \sum_\xi' C_{j\xi}^2. \quad (9)
\end{aligned}$$

The first two terms in square brackets are the ordinary second moments of the α and γ ions, respectively. These brackets each consist of a "resonant" term and the nonresonant interactions of one type of ion on the other. These terms have been discussed by Van Vleck¹² and Kittel and Abrahams⁹ in the theory of linewidth in paramagnetic resonance.

The terms in curly brackets are new and arise from the fact that $\sum A_{pq} \mathbf{S}_p \cdot \mathbf{S}_q$ does not commute with \mathcal{H}_{12} contrary to the case considered by Van Vleck.¹² The curly brackets can lead to a substantial increase in the cross-relaxation second moment in concentrated salts

particularly when the exchange interaction is very large. The appearance of these terms are a manifestation of the fact that line shape of paramagnetic resonance lines deviates from a Gaussian and that even a slight deviation in the wings of the line can lead to important cross-relaxation effects.

The negative term is a correlation term which tends to reduce the second moment.¹⁴

The last term in Eq. (9) is due to the "quasi-resonant" interaction between two paramagnetic species. This term is independent of the concentration. At low concentrations we shall be especially interested in this since it will clearly be dominant. In fact, for concentrations of the two ions of less than 10%, only the concentration independent terms need be considered.

The concentration independent part may be evaluated fairly easily for special direction of a simple cubic lattice. If we neglect exchange terms (which are usually negligible at low concentrations) we find for the 100 directions of a simple cubic lattice

$$\langle \Delta\omega^2 \rangle_{av} = \frac{2.6g^4\beta^4}{\hbar^2 d^{-6}}. \quad (10)$$

In Eq. (10) d is the lattice distance between nearest magnetic sites. g is the appropriate average of g_α and g_β .

IV. MAGNITUDE OF CROSS-RELAXATION TERMS

It has been pointed out by Van Vleck and others, that the second moment is not sufficient to determine the line shape accurately. Since the fourth moment will have a different concentration dependence from the second the line shape may differ at different concentration. In our case, it can be seen that at low concentrations the dominant terms in the fourth moment contain only two indices, i.e.,

$$\begin{aligned}
\hbar^4 \langle \omega^4 \rangle & = -\text{Trace} [\mathcal{H}_0, [\mathcal{H}_0, \mathcal{H}_{12}]]^2 / \text{Trace} \mathcal{H}_{12}^2 \\
& [\mathcal{H}_0, [\mathcal{H}_0, \mathcal{H}_{12}]] \simeq \\
& -\sum_{p\xi}' C_{p\xi}^3 D_{p\xi} [S_{xp} S_{zp} I_{y\xi}, S_{zp} I_{z\xi}] + \dots \quad (11)
\end{aligned}$$

It may be shown that for spin $\frac{1}{2}$

$$\frac{\langle \Delta\omega^4 \rangle_{av}}{\langle \Delta\omega^2 \rangle_{av}} \simeq 3.0 + (\text{terms dependent on concentration}).$$

For a perfect Gaussian, the ratio of the fourth moment to the square of the second moment is exactly 3.^{12,9} Hence at low concentrations, the Gaussian distribution should be an excellent approximation. It is

¹⁴ If α and γ do not occupy equivalent sites [e.g., LiF, the two magnetic complexes of Cr^{3+} in $\text{K}_3\text{Cr}(\text{CN})_6$], the second and third terms in the correlation bracket do not occur.

interesting to note that this result holds even though the individual line shapes are far from Gaussian (which is usual at low concentrations).

It should be noted that for spin $\neq \frac{1}{2}$, the Gaussian approximation is not as good. However, since there are no terms which depend on the reciprocal concentration (in contradistinction of reference 9) it is still useful in diluted salts. I have not studied the case of high concentration but it seems likely that a Gaussian holds in this case as well.

In view of the above we can write the effective "shape function" for cross relaxation as

$$g_{12}(\omega_\alpha - \omega_\gamma) = \frac{\exp[-(\omega_\alpha - \omega_\gamma)^2/2\langle\Delta\omega^2\rangle_{av}]}{(2\pi\langle\Delta\omega^2\rangle_{av})}, \quad (12)$$

where $\langle\Delta\omega^2\rangle_{av}$ is given by Eqs. (9) and (10).

From Eqs. (5) and (12) we can write the cross-relaxation rate of the α system as

$$\begin{aligned} W_{12}^\alpha &= 5 \times 10^{-13} (n_\gamma/N) g_\alpha g_\gamma \lambda^{\frac{1}{2}} \sigma^{-1/2} d^{-3} \\ &\quad \times \exp[-(\omega_\alpha - \omega_\gamma)^2/1.3 \times 10^{-24} g_\alpha^2 g_\gamma^2 \lambda \sigma d^{-6}] \\ &= 5 \times 10^{-13} (n_\gamma/N) g_\alpha g_\gamma \lambda^{\frac{1}{2}} \sigma^{-1/2} d^{-3} \\ &\quad \times \exp[-(\omega_\alpha - \omega_\gamma)^2/1.33 \times 10^{-24} g_\alpha g_\gamma \lambda \sigma d^{-6}], \quad (13) \end{aligned}$$

where

$$\begin{aligned} \lambda &= \frac{1}{d^6} \sum_{\xi}^N r_{j\xi}^{-6} (1 - 3 \cos^2 \theta_{j\xi})^2, \\ \sigma &= \sum_{\xi}^N r_{j\xi}^{-12} (1 - 3 \cos^2 \theta_{j\xi})^4 / \left[\sum_{\xi}^N r_{j\xi}^{-6} (1 - 3 \cos^2 \theta_{j\xi})^2 \right]^2. \end{aligned}$$

Equation (13) holds even when the resonant frequencies of the different species are identical. For the 100 direction of simple cubic crystal

$$\begin{aligned} W_{12}^\alpha &= 4 \times 10^{-12} \frac{n_\gamma}{N} g_\alpha g_\gamma d^{-3} \\ &\quad \times \exp[-(\omega_\alpha - \omega_\gamma)^2/3.5 \times 10^{-24} g_\alpha^2 g_\gamma^2 d^{-6}]. \end{aligned}$$

For $d = 10^{-7}$ cm, $g_\alpha = g_\gamma \simeq 2$,

$$W_{12}^\alpha = 1.6 \times 10^{10} \frac{n_\gamma}{N} \exp[-(\omega_\alpha - \omega_\gamma)^2/5.7 \times 10^{19}].$$

If $n_\gamma/N = 0.005$,

$$W_{12}^\alpha \simeq 8 \times 10^7 \exp\{-[(\nu_\alpha - \nu_\gamma)/1.9 \times 10^8]^2\}.$$

Thus even for lines separated by 6×10^8 cps (200 gauss), the cross-relaxation time is of the order of 10^{-4} sec which may dominate the spin-lattice relaxation time at low temperatures. For some diluted crystals the above separation corresponds to at least 15–20 times the linewidth of a resonance line. Indications of such effects have been observed in $\text{K}_0\text{Cr}(\text{CN})_6$.^{15,7}

From Eqs. (12) and (10) we see that the effective linewidth for cross relaxation is proportional to d^{-3} . Since our estimate of 10^{-7} cm for d is rather larger than what is normally found, the cross-relaxation linewidth will usually be 2 to 10 times the above estimate of $\langle\Delta\omega^2\rangle_{av}$. In addition it is seen from Eq. (13) that the maximum cross-relaxation rate ($\omega_\alpha = \omega_\gamma$) also goes as d^{-3} and will thus be increased over the above estimate in most crystals.

It is seen from Eq. (13), that $g_{12}(0)$ and hence the cross-relaxation rate $W_{12}(0)$ depends on $(\langle\Delta\omega^2\rangle_{av})^{-\frac{1}{2}}$. Since the second moment in diluted salts is much larger than that used in Eq. (6) the maximum value of the cross-relaxation rate may be greatly reduced from that computed in Eq. (6). When $W_{12}(0)$ is much greater than the spin-lattice relaxation rate, the increase in the effective "linewidth" for cross relaxation will more than make up for decrease in $W_{12}(0)$ for separated resonances. This is due to the rapid decrease of the exponential for $(\omega_\alpha - \omega_\gamma)^2 > 2\langle\Delta\omega^2\rangle_{av}$.

One must be careful in attempting to apply the above theory to commonly used paramagnetic crystals. For usually $S > \frac{1}{2}$ and zero field splittings generally occur. For example, this theory should have order of magnitude validity for computing the cross relaxation between two nearly degenerate resonance frequencies of an $S = 1, \frac{3}{2}, \dots$ crystal if no other resonance line is approximately double or triple the average of the two resonance frequencies. It should also give cross coupling between ions of two magnetic complexes as well as coupling between nearly equal resonance lines of different paramagnetic species under the same conditions as above. of course, an effective g value will have to be used which depends on the eigenfunctions of the states under consideration.

In cases where one line has nearly double or triple the resonance frequency of another, higher order spin coupling terms are required for quantitative agreement.

In a later paper we shall treat some of these complicated cases in a more exact manner.

¹⁵ J. G. Castle, P. F. Chester, and P. E. Wagner, Phys. Rev. 119, 953 (1960).