REVIEWS OF MODERN PHYSICS VOLUME 25, NUMBER 1 JANUARY, 1953

Exchange Narrowing in Paramagnetic Resonance

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In this paper the problem of the line shape in paramagnetic resonance when large exchange interaction is present is discussed from the standpoint of a simplified mathematical model. The mathematical model can be called the model of "random frequency modulation": It is assumed that the atom absorbs a single frequency, which varies over a distribution determined by the dipolar local fields, but that this frequency varies randomly in time at a rate determined by the exchange interactions.

The predicted line shape in the case in which exchange is large is of resonance type in the observable center of the line, but falls off more rapidly in the wings. This line shape has been verified experimentally in a number of cases. This conclusion seems quite independent of any assumption about the type of random frequency modulation, etc. The quantitative conclusions are reached in the following way: It is suspected, since the exchange motion is the superposition of the effects of a number of neighbors which is not particularly small, that a good approximation to the modulation function is Gaussian noise with a Gaussian spectrum. This, of course, is what would result from the superposition of a large number of rather small effects. Under this assumption both the second moment (which is independent of exchange) and the fourth moment of the line shape can be calculated. This kind of modulation is the simplest one which does give a finite fourth moment; a Markoffian, or "jump," type of modulation, which might seem more reasonable at first, does not. These moments are then compared with the moments computed by Van Vleck [Phys. Rev. **74**, 1168 (1948)] to fix the two adjustable parameters, mean square frequency, and average rate of change of frequency, of the theory.

The result as to line breadth, which is essentially

$$\Delta \simeq \frac{\langle(\Delta\omega^2)\rangle_{\text{Av}}\ \text{dipole-dipole}}{J/\hbar},$$

if J is the exchange integral, can be compared with observed line breadths by estimating J from Curie-Weiss constants for a number of materials. The results are quite satisfactory if the theory is extended in two ways: (a) When the exchange frequency is larger than the resonance frequency, it can be shown that the off-diagonal elements of the dipolar interaction must be included, leading to a line-width larger by a factor of roughly 10/3; (b) in a number of cases hyperfine and Stark splitting is contributing importantly to the width.

The good agreement with experiment in the cases we have investigated leads us to believe that a quantitative approach to the paramagnetic resonance line breadth problem, using only the already known concepts of dipolar interaction, exchange narrowing, and fine structure splitting, will probably explain all the observed phenomena.

I. INTRODUCTION

THE phenomenon of exchange narrowing was first suggested as a possibility by Gorter and Van Vleck[1] and was demonstrated mathematically by Van Vleck.[2] These authors pointed out that in most pure salts the exchange interaction cannot broaden the paramagnetic resonance line because it commutes with the components of the total magnetic moment and, therefore, has no direct effect on either the Zeeman energy ($\sim S_z$) or the radiating dipole moment (S_x). On the other hand, exchange can cause rapid motion in the spin system, which can result in averaging out the effects of the broadening interactions such as magnetic dipolar interactions, thus narrowing the line.

At nearly the same time Bloembergen, Purcell, and Pound[3] observed that temperature motion of atoms in liquids and some solids had much the same kind of narrowing effect on nuclear magnetic resonance lines. These authors considered these narrowing phenomena in a way roughly similar to our present theory, but with a somewhat less schematized and therefore less quantitative model. With their considerations they deduced that narrowing occurred if the rate of motion (which we shall call ω_e) is rapid compared to the amplitude in frequency of the perturbations, which we call ω_p; and that then the line breadth is roughly

$$\Delta\omega \simeq \omega_p^2/\omega_e. \tag{1}$$

We have applied a similar model to the problem of narrowing by motion in the spin system because of exchange. In our model we assume the system to be absorbing a single frequency, which varies in a random way over a certain range determined only by the magnitude of the perturbations (primarily because of the magnetic interactions) but at a rate controlled by the motions. This is not an entirely new concept (see, for example, reference 1), but we have tried to carry the work through in a consistent, at least semiquantitative way, and to give the model as good a justification as possible.*

With this model it becomes possible to compute the actual line shape and line width, in contrast to the method of Van Vleck in which only the second and fourth moments of the line shape can be practically

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[1] C. J. Gorter and J. H. Van Vleck, Phys. Rev. **72**, 1128 (1947).

[2] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

[3] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

* This justification, as well as some of the other more mathematical parts of the theory, will not be given fully here; we hope to cover these points more completely in a later publication.

calculated. This is important because these moments fail to describe the line shape with any accuracy just when exchange narrowing becomes important. In all the possible forms of the model the line shape is of resonance type in the center when the narrowing is large, falling off more rapidly on the wings near the frequency ω_e. This agrees with the results of a number of experiments.[4,5]

We have also found it possible, picking the "Gaussian" form of the model which is most suited to the exchange problem, to compute second and fourth moments and, comparing these with those of Van Vleck, to fit the adjustable constants ω_p and ω_e of the theory. That the forms of these moments are such as to make this possible in the first place is confirmation of the essential physical correctness of the model. When certain corrections are made, also suggested by the model, we find quite excellent agreement with measured line widths, using exchange integrals computed from paramagnetic Curie-Weiss constants.

In this quantitative aspect we feel that our theory, in spite of its apparent arbitrariness, is valuable both as an aid to understanding, particularly in regard to the corrections which have to be made, and as an extrapolation method encouraging one to try to use the rough relation (1) quantitatively. We feel that the success we have had indicates that the concepts already available are completely adequate to explain most of the observed phenomena; there seem to be no important mysteries left.

II. THE MODEL OF RANDOM FREQUENCY MODULATION

It is true in general[6] that the spectrum of the radiation or absorption of any quantum-mechanical system is given by the Fourier integral of the Heisenberg operator for the dipole moment S_x:

$$I(\omega)=\text{Trace}\left|\int S_x(t)e^{i\omega t}dt\right|^2, \tag{2}$$

where

$$i\hbar\frac{dS_x}{dt}=HS_x-S_xH. \tag{3}$$

In our problem the Hamiltonian consists of three parts:

$$H=H_0+H_p+H_{ex}. \tag{4}$$

H_0 is the unperturbed Hamiltonian,

$$H_0=g\beta H\sum_j S_{zj}, \tag{5}$$

which causes the energy-splittings leading to the lines we are investigating. H_p is the "perturbing" Hamiltonian, for the time being assumed to be due to the dipolar interactions, which causes the broadening of these lines (Van Vleck, reference 2, has written it out in full); and H_{ex} is the exchange Hamiltonian,

$$H_{ex}=\sum_{j,k} J_{jk}\mathbf{S}_j\cdot\mathbf{S}_k. \tag{6}$$

We now calculate the spectral intensity (2) for a given absorption line (state $i\rightarrow$state j) under the following assumptions:

$$\text{(a)}\quad i\hbar\dot{H}_p=[H_0+H_{ex}, H_p]\simeq[H_{ex}, H_p]. \tag{7}$$

This is not really an assumption, but merely the expression of the fact that the perturbation of the dipolar interactions varies in time because of the exchange Hamiltonian, according to the standard commutator law. Since very many states are available to the system, and since thermal energy is large compared with all the Hamiltonians of (4), this time variation will be a random one, the order of magnitude of the rate being given by $H_{ex}/\hbar$. We write down (7) as an assumption to emphasize two facts: first, that H_{ex} does not commute with H_p, and thus it does cause a time variation of H_p; and second, that we leave out, at least for the time being, the time variation due to H_0; this is only justifiable on the basis of the later assumption (d), by which we throw away all the parts of H_p which are off-diagonal in H_0 as being, in the language of reference 3, nonsecular perturbations. In a later section we will consider the case in which $H_0\ll H_{ex}$; then, of course, no part of H_p is any more "secular" than any other part, and we retain assumption (a) but leave in all parts of H_p.

$$\begin{aligned}&\text{(b)}\quad [H_{ex}, H_0]=0.\\&\text{(c)}\quad [H_{ex}, S_x]=0.\end{aligned} \tag{8}$$

These two easily verified assumptions express the fact that H_{ex} causes narrowing rather than broadening, since it cannot directly change the unperturbed energies (by b) or interrupt the radiation in any way (by c).

(d) Finally, the assumption is made that H_p is so small as to have no important matrix elements connecting different unperturbed states of H_0. This is the assumption which is most vital to the model, since it expresses the assumption that H_p changes only the frequency of the radiation from the system, without causing transitions or changing the amplitude.

This assumption is obviously not a rigorous one, since H_0 has many states of the same energy (e.g., all states of given S_z, no matter what S^2 is, have the same energy). Thus obviously H_p will have important off-diagonal elements. However, the assumption is very far from being as bad as this reasoning would make it appear. In the first place, it always turns out that we need not leave out of our calculation the off-diagonal elements of H_p; we need only treat them as if they were

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[4] Unpublished work by R. T. Weidner on diphenyl picryl hydrazyl.

[5] Kumagai, Ono, Hayashi, Abe, Shimada, Shôno, and Ibamoto, Phys. Rev. **83**, 1077 (1951).

[6] P. W. Anderson, Phys. Rev. **76**, 647 (1949).

diagonal† For instance, in the present theory, we use Van Vleck's full mean square value of H_p, including both diagonal and off-diagonal effects.

A second way of thinking of assumption (d) is as an "isolated-atom" assumption; for the isolated atom H_p will not have important off-diagonal elements, so that we get qualitatively right answers; and then we renormalize by using the full perturbation as mentioned above.

It now becomes possible to compute the spectral intensity (2) for a given spectral line, which we pick out by using only the $i\rightarrow j$ matrix element of $S_x(t)$ in (2). This matrix element, from Eq. (3) and assumption (c), satisfies the equation

$$\begin{aligned} i\hbar(\dot{S}_x)_{ij} &= [H_0+H_p, S_x]_{ij} \\ &= [H_{0ii}+H_{pii}(t)]S_{xij}-[H_{0jj}+H_{pjj}(t)]S_{xij}. \end{aligned} \tag{9}$$

Here assumption (d) has eliminated all off-diagonal elements, and assumption (b) shows that

$$H_{0ii}-H_{0jj}=\hbar\omega_0, \tag{10}$$

the unperturbed resonant frequency, is not a function of time. The solution of (9) is obvious:

$$(S_x(t))_{ij}=(S_{xij})_0 \exp\left[-i\omega_0 t - i\int_0^t \Delta\omega_{ij}(t')dt'\right], \tag{11}$$

where

$$\Delta\omega_{ij}(t)=\frac{1}{\hbar}[H_{pii}(t)-H_{pjj}(t)] \tag{12}$$

is the randomly varying frequency introduced by the perturbation H_p, which in turn varies in time due to Eq. (7).

Equation (11) introduced into (2) gives

$$I_{ij}(\omega)\sim\left|\exp\left[-i(\omega-\omega_0)t-i\int_0^t \Delta\omega_{ij}(t')dt'\right]\right|^2. \tag{13}$$

Equation (13) is the basic equation of the random frequency-modulation model; it states that the spectrum is that which one would obtain from a frequency which varies about the mean frequency ω_0 in a random way, with amplitude controlled by the size of H_p but rate determined by H_{ex} through Eq. (7).

Before going on to the actual exchange narrowing problem let us introduce some transformations. First, we shall always think in terms of frequency differences from the line center, so that instead of $\omega-\omega_0$ we write simply ω; ω_0 enters nowhere else in the problem except in assumption (a). Second, we transform to the correlation-function form of the Fourier integral by the well-known process of Wiener and Khinchin:

$$I_{ij}(\omega)=\int_{-\infty}^{\infty} e^{i\omega\tau}\varphi(\tau)d\tau, \tag{14}$$

$$\begin{aligned} \varphi(\tau) &= \langle S_{xij}(t)S_{xij}^*(t+\tau)\rangle_{\text{Av}} \text{ over } t \\ &= \left\langle \exp\left[i\int_t^{t+\tau}\Delta\omega_{ij}(t')dt'\right]\right\rangle_{\text{Av}}. \end{aligned} \tag{15}$$

Equation (15) forms the basis for our mathematical manipulations. It should also be noted that Eq. (15) is a very simple way of understanding the phenomena of exchange and motional narrowing. Namely, since I and φ are Fourier transforms of each other, if φ has a "breadth" T in time, i.e., falls off appreciably in time T, then the breadth of I is $1/T$.

Now, first suppose $\Delta\omega_{ij}(t')$ varies quite slowly in time. Then the integral in (15) will become appreciable when $\Delta\omega_{ij}\tau\simeq 1$, so that if ω_p is some average of $\Delta\omega_{ij}$ we have $\omega_p T\simeq 1$, and thus the line breadth $\simeq\omega_p$, as in the case of no narrowing; the rate of change is unimportant.

But now suppose ω_e, the rate of change of $\Delta\omega_{ij}$, is much faster than its average ω_p. Then before $\int\Delta\omega_{ij}$ can have reached any large value the integrand $\Delta\omega_{ij}$ will have changed sign, and the whole integral will roughly average out. Thus $\varphi(\tau)$ becomes very much broader, and $I_{ij}(\omega)$ correspondingly narrower.

III. THE SPECTRUM FOR GAUSSIAN RANDOM MODULATION; EXCHANGE NARROWING

Before any progress can be made in finding the correlation function, we must make a decision as to what the amplitude and random properties of the function $\Delta\omega_{ij}(t)$ are. This decision must be made, in the present state of the theory of random functions,[7] more on the basis of mathematical convenience than anything else; fortunately, in the exchange narrowing case physical realism is probably also satisfied fairly well.

The most easily handled type of random function is the Gaussian type. This may be defined in a number of ways: The physical way is to appeal to the law of large numbers and say that the superposition of the small effects of a large number of random causes is always a Gaussian random function, e.g., Brownian motion or the voltage due to motion of electrons in a resistor. A way of producing a Gaussian random function is to put "white" Gaussian noise—that is, Gaussian noise with an equal amount of energy in every frequency range, such as is produced by electrons in a resistor—through an arbitrary electrical filter. All the probability distributions, for instance the probability of finding a given amplitude in a given frequency range, are Gaussian. On the other hand, it must be emphasized that the ac-

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† Thus we follow the procedure—remarkably successful quantitatively—of the "adiabatic approximation" in pressure broadening, replacing the transition effects of off-diagonal elements by equivalent energy perturbations.

[7] For a reference on random theory see M. C. Wang and C. E. Uhlenbeck, Revs. Modern Phys. **17**, 323 (1945). The authors are indebted to Dr. Shannon and Dr. McMillan of Bell Laboratories for helpful discussions of this subject.

tual spectrum, corresponding to the type of filter in the above example, is still completely arbitrary.

In exchange narrowing the frequency $\Delta\omega_{ij}(t)$ is due to the random perturbing effects on the frequency of a number of neighbors, 6–10 or more, which is not large in the usual sense but from experience with random theory seems to be fairly large in the sense we need. In addition, Van Vleck has shown that the mean fourth moment of the value of $\Delta\omega_{ij}$ is near to that expected from the Gaussian shape. Measured shapes, when narrowing is small, are indeed roughly Gaussian. This, of course, does not insure that all distributions are Gaussian, as is required for the true Gaussian random function, but it does verify our reasoning that the function should be Gaussian. One can be sure that this assumption is by far the least drastic of this theory.

Once one has picked the Gaussian type of random function one still has the freedom, as pointed out above, of choosing either the spectrum or the correlation function of the random modulation in a completely arbitrary way. This spectrum characterizes the properties of the motion due to exchange, in contrast to the amplitude of the random function $\Delta\omega_{ij}$, which is a consequence of the dipolar interactions alone. We should emphasize that now we speak of the spectrum of $\Delta\omega_{ij}(t)$, which we call $I_{\Delta\omega}(\nu)$; the corresponding correlation function, related by (14) to $I_{\Delta\omega}$, we call $\varphi_{\Delta\omega}(t)$. Fortunately, Van Vleck's computations again furnish us a very useful condition: The mean fourth moment even with exchange is finite, which one can show requires that the spectrum not have an anomalously long "tail"; it must fall off at large ν more rapidly than ν^{-3}. In particular, this excludes the Markoffian type of random modulation in which the motion proceeds in jumps, such as one might expect from the oversimplified picture of electrons jumping back and forth due to exchange. It is more realistic to think of exchange causing fields which cause the electrons to precess at rates not much greater than $J/\hbar$.

Again we appeal to the fact that the exchange effect is also the superposition of the effects of a number of neighbors which is not particularly small, to assume that $I_{\Delta\omega}(\nu)$ is Gaussian. Here our assumption is not really quite so sound, but we can be sure that with the condition that the fourth moment is finite, and assuming a reasonably smooth spectrum, the final results will be quite typical of those we would obtain with other spectra.

The assumptions then are:

$\Delta\omega_{ij}(t)$ is a Gaussian random function

$$\varphi_{\Delta\omega}(t)=\frac{\langle\Delta\omega_{ij}(t')\Delta\omega_{ij}(t'+t)\rangle_{\mathrm{Av}}}{\langle\Delta\omega_{ij}^2\rangle_{\mathrm{Av}}}=\exp\left[-\frac{\pi}{4}\omega_e^2t^2\right]. \quad (16)$$

[Equation (16) is equivalent to assuming $I_{\Delta\omega}$ Gaussian; ω_e is an average exchange frequency, of order $J/\hbar$.]

We now find that these assumptions make it possible to compute (15). First we use a well-known theorem relating to Gaussian random functions: The distribution of any linear combination of values of a Gaussian random function is itself Gaussian. Now the integral in the exponent of (15),

$$X=\int_t^{t+\tau}\Delta\omega_{ij}(t')dt', \quad (17)$$

is itself just such a linear combination, so that we know the distribution of X,

$$P(X)dX=\frac{1}{[2\pi\langle X^2\rangle_{\mathrm{Av}}]^{\frac{1}{2}}}\exp\left(-\frac{X^2}{2\langle X^2\rangle_{\mathrm{Av}}}\right)dX,$$

where $\langle X^2\rangle_{\mathrm{Av}}$ is the average value of X^2,

$$\langle X^2\rangle_{\mathrm{Av}}=\left\langle\int_0^\tau dt\int_0^\tau dt'\Delta\omega_{ij}(t)\Delta\omega_{ij}(t')\right\rangle_{\mathrm{Av}}.$$

This, after manipulation, can be shown to be

$$\langle X^2\rangle_{\mathrm{Av}}=2\omega_p^2\int_0^\tau dt(\tau-t)\varphi_{\Delta\omega}(t). \quad (18)$$

Here we have defined ω_p^2 as the mean square of $\Delta\omega_{ij}$:

$$\omega_p^2=\langle\Delta\omega_{ij}^2\rangle_{\mathrm{Av}}. \quad (19)$$

With the distribution of X, $P(X)$, known, we can immediately take the average of (15)

$$\varphi(\tau)=\int_{-\infty}^{\infty}dXP(X)e^{iX},$$

$$\varphi(\tau)=\exp\left[-\frac{\langle X^2\rangle_{\mathrm{Av}}}{2}\right]$$

$$=\exp\left[-\omega_p^2\int_0^\tau dt(\tau-t)\varphi_{\Delta\omega}(t)\right]. \quad (20)$$

Thus we see that with the Gaussian assumption, we can relate the correlation function for the spectral line to a rather easily performed integral (18) of the correlation function $\varphi_{\Delta\omega}$ of the random modulation, together with the second moment ω_p^2 (19) of the original distribution.

Before going on to discuss the Gaussian form for $\varphi_{\Delta\omega}$ (16) which is of most interest to us, we shall obtain a few rather general conclusions which are valid in the limiting cases.

Case I: $\omega_p\gg\omega_e$ so that $\varphi_{\Delta\omega}(t)$ is constant at its value for $t=0$, unity, throughout the region in which the exponent of (20) takes on appreciable values. Then we have

$$\varphi(\tau)_{\text{case I}}\simeq\exp\left[-\omega_p^2\int_0^\tau dt(\tau-t)\right.$$

$$\left.=\exp\left(-\frac{\omega_p^2\tau^2}{2}\right). \quad (21a)\right.$$

This can easily be shown, through Eq. (14), to give a Gaussian line of mean width ω_p^2. This is, of course, exactly what we started out with; other forms of modulation function have been tried, but the general conclusion can always be drawn that in case *I* the modulation has no effect whatever.

Case II: $\omega_e \gg \omega_p$. In this case $\varphi_{\Delta\omega}$ will have caused the integrand in (20) to vanish long before t can take on a value comparable to τ. Then

$$\varphi(\tau)_{\text{case II}} \cong \exp\left[(-\omega_p^2)\tau \int_0^\infty \varphi_{\Delta\omega}(t)dt\right] \tag{21b}$$

$$= \exp\left(-\frac{\omega_p^2\tau}{\omega_e}\right). \tag{21b}$$

Here ω_e can be defined by the equation (consistent with 16)

$$\frac{1}{\omega_e} = \int_0^\infty \varphi_{\Delta\omega}(t)dt,$$

and it is clearly a good measure of the inverse of the total width of $\varphi_{\Delta\omega}$, and thus of the true width of the spectrum $I_{\Delta\omega}(\nu)$. This Eq. (21b) is also remarkably general, holding as well for other types of random modulation. The line shape resulting from (21b) is the resonance shape:

$$I_{ij}(\omega) = \frac{2}{\pi} \frac{(\omega_p^2/\omega_e)}{\omega^2 + (\omega_p^2/\omega_e)^2}. \tag{22}$$

Clearly, if $I(\omega)$ is to have a finite second moment, as it must if $\Delta\omega_{ij}$ is Gaussian, (22) cannot hold throughout the frequency spectrum. It can be shown that the wings of the spectrum, which are determined primarily by $\varphi(\tau)$ at very small τ, where (21b) is no longer valid, fall off more rapidly than (22) indicates. In fact, (22) is a good approximation out to the frequency ω_e, beyond which the wings fall off quite rapidly.

As mentioned in the introduction, in a number of experimental cases of extreme narrowing[4,5] the resonance shape (22) has been found to be correct. We feel that the shape (22) is probably the most accurate conclusion of the theory.

Some of the moments of the distribution can also be found from Eq. (20) directly. The theorem which is most convenient to use is easily proved from Eq. (14), and is

$$\langle\omega^n\rangle_{\text{Av}} = i^n \frac{d^n\varphi}{d\tau^n}\bigg|_{\tau=0}. \tag{23}$$

For the second moment this gives

$$\langle\omega^2\rangle_{\text{Av}} = -\frac{d^2}{dt^2}\left\{\exp\left[-\omega_p^2 \int_0^\tau dt(\tau-t)\varphi_{\Delta\omega}(t)\right]\right\}\bigg|_{\tau=0}, \tag{24}$$

$$\langle\omega^2\rangle_{\text{Av}} = \omega_p^2.$$

We see that the second moment is completely independent of the effect of exchange, a fact which Van Vleck derived for the rigorously correct model.

The fourth moment is somewhat more complicated to derive from (23), but we shall write it down:

$$\langle\omega^4\rangle_{\text{Av}} = 3\omega_p^4 - \omega_p^2 \frac{d^2}{d\tau^2}\varphi_{\Delta\omega}(\tau)\bigg|_{\tau=0}. \tag{25}$$

Note that this will not be finite unless the spectrum of $\Delta\omega_{ij}(t)$ has a finite second moment, as stated previously.

With the specific Gaussian form (16) for the correlation function of $\Delta\omega_{ij}$, we can immediately write down the correlation function for this case. It is

$$\varphi(\tau) = \exp\left(-\frac{\omega_p^2\tau}{\omega_e}\int_0^{\omega_e\tau} e^{-(\pi/4)x^2}dx + \frac{2\omega_p^2}{\pi\omega_e^2}\left[1-\exp\left(-\frac{\pi}{4}\omega_e^2\tau^2\right)\right]\right). \tag{20a}$$

The actual spectral line shape is not of much interest except in the limiting cases, in which (22) and (21a) are quite satisfactory. It is of interest to go ahead and compute the fourth moment in this special case [(24) of course being quite satisfactory for the second moment]. One can do this quickly with (25) and obtain

$$\langle\omega^4\rangle_{\text{Av}} = 3\omega_p^4 + \frac{\pi}{2}\omega_p^2\omega_e^2. \tag{25a}$$

IV. COMPARISON WITH EXPERIMENT

These general formulas, containing ω_p and ω_e as adjustable parameters, represent the extent of this model's ability to give quantitative information. We know only that

$$\omega_p \sim H_p/\hbar \simeq (g^2\beta^2/\hbar a^3)$$

and $\omega_e \sim J/\hbar$ as to order of magnitude.

Fortunately, there is a way to make the method quantitative. We can use Van Vleck's values for the second and fourth moments and compare these with our values (24) and (25a). This gives two relations for our two parameters, ω_e and ω_p, so that then we can use (22) (at least in the extreme narrowing case) to predict the breadth. Thus we plan to use our model to "extrapolate" Van Vleck's numbers to get the entire line shape. Naturally no accurate limits of error may be set on such a procedure; nonetheless, one would be quite surprised if our assumptions combined to give an error of more than a factor of two, and less than this would be far more likely. For example, the two most extreme spectra $I_{\Delta\omega}(\nu)$ one could expect, the square spectrum and the simple exponential ($e^{-\nu/\omega_e}$), lead to errors of only about 1.5 in our extrapolation procedure, one in one direction and one in the other. The true deviation from the Gaussian is probably far less than these.

TABLE I. Exchange narrowing in Fe^{+++} and Mn^{++} salts.

Salt	θ	H_p	H_e	ΔHcalc$^{(1)}$	ΔHobs	$(10/3)\Delta H$calc$^{(1)}$
A. Extreme narrowing, $H_e \gg H_0$						
$FeNH_4(SO_4)_2$	13°K	840 oe	13 800 oe	51 oe	290 oe	170 oe
$Fe_2(SO_4)_3$	70	1200	74 100	19	90	64
$MnCl_2$	16	1750	17 000	175	625	585
$MnSO_4$	24	1600	25 400	100	330	330
B. $\theta \simeq 0$, weak narrowing						
$MnCl_2 \cdot 4H_2O$	3	750	<3000	>175	670	Upper limit ~1000
$MnSO_4 \cdot 4H_2O$	2	730	<2000	>250	570	
$MnSO_4 \cdot 5H_2O$	3	630	<3000	>125	625	
$MnSiF_6 \cdot 6H_2O$	~0	460	(0)		800	

The moments as given by Van Vleck are, for a simple cubic lattice structure,

$$\hbar^2\langle\omega^2\rangle_{\text{Av}} = 36.8\left(\frac{g^2\beta^2}{a^3}\right)^2 \frac{S(S+1)}{3} \times(\lambda_1^4+\lambda_2^4+\lambda_3^4-0.187), \quad (26a)$$

$$\hbar^4\langle\omega^4\rangle_{\text{Av}} = 3(\hbar^2\langle\omega^2\rangle_{\text{Av}})^2+490\left(\frac{g^2\beta^2}{a^3}\right)^2 J^2\left(\frac{S(S+1)}{3}\right)^2 \times(\lambda_1^4+\lambda_2^4+\lambda_3^4-0.187). \quad (26b)$$

The notation is: $g = g$-factor, $\beta =$ Bohr magneton, $a =$ lattice constant, $\lambda_{1,2,3}$ are direction cosines of the external field with respect to crystal axes, $S =$ spin quantum number per atom, and $J =$ exchange integral.

We should point out that the remarkable similarity between (26b) and (25a) in general form is not a necessary result of either theory; for instance, terms of form $(g^2\beta^2/a^3)^3$ can and do occur, but are extremely small, according to Van Vleck, and he drops them; while the coefficient of $\langle(\omega^2)\rangle_{\text{Av}}^2$ is not exactly, but approximately 3. The angular dependence is also an "accident." It seems to us that this agreement is good evidence for the physical sense of our model.

The uncertainties we already have seem bad enough that we need not worry about either crystal structure or directional properties very much, so we shall use the isotropic averages of (26). We then find for the two parameters

$$\omega_p^2 = \frac{15.2}{3}\left(\frac{g^2\beta^2}{\hbar}\right)^2 n^2 S(S+1), \quad (27)$$

$$\omega_e^2 = \frac{8.48}{3}\left(\frac{J}{\hbar}\right)^2 S(S+1). \quad (28)$$

n is the density of spins per cubic centimeter. The line breadth is then (half-width at half-power)

$$\Delta\omega = \omega_p^2/\omega_e. \quad (29)$$

In terms of magnetic field, as most measurements are made, this gives us the following fields corresponding to ω_e and ω_p:

$$H_p^2 = 5.1(g\beta n)^2 S(S+1), \quad (27a)$$

$$H_e = 2.83\frac{J}{g\beta}[S(S+1)]^{\frac{1}{2}}, \quad (28a)$$

and

$$\Delta H = H_p^2/H_e \quad (29a)$$

is the predicted half-width at half-power.

Kumugai and co-workers[8] have measured or compiled the line breadths for a number of salts of Mn^{++} and Fe^{+++}, where crystal anisotropy broadening is minor and thus powder data are reliable. For most of these salts an estimate of the exchange integral can be made from the Curie-Weiss law $\chi = C/(T+\theta)$, with θ obtained from the Weiss molecular field equations as

$$3k\theta = 2JZS(S+1). \quad (30)$$

Z is the number of nearest neighbors, which we always set equal to six for consistency with our previous assumption of simple cubic lattices. These salts are also advantageous in that crystal splittings do not contribute importantly to θ.

In Table I we make a comparison of our predicted line breadths from Eq. (29a) (column labeled $\Delta H_{\text{calc}}^{(1)}$) with the observed breadths (under ΔH_{obs}). The comparison is valid only for those salts with large θ which are collected in Table IA, both because the θ measurements are in most cases not valid to more than ±2°K, even if nothing but exchange is important, and because for the other salts the H_e values are not extreme enough to make our limiting formulas correct.

We see that in spite of the belief that our calculations should be good within a factor 2 at most, the comparison is bad, since errors as large as a factor 6 appear. This discrepancy is the same as that noticed by Kumugai *et al*,[8] using the simple order-of-magnitude formula (1). Fortunately, we can show that two very important sources of broadening have been so far neglected, and that their inclusion leads to good agreement with experiment.

The first source is the following. In Van Vleck's computation of the mean square broadening he leaves

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[8] Kumugai, Ono, and Hayashi, Phys. Rev. **85**, 925 (1952).

out terms in H_p which connect different Zeeman energy levels. (These are terms mixing $S_z\pm1$ and $S_z\pm2$ with S_z.) Van Vleck is perfectly correct in doing so, since when $H_p\ll H_0$, as in all resonance experiments, and when exchange is not too large, these terms contribute only in second order to the main line. On the other hand, because they mix up the S_z states they can lead to satellites at frequencies 0, $2\omega_0$, and $3\omega_0$, which are so far from the main line that in spite of their weakness their mean square breadth contribution is large.

In the present exchange narrowing cases, on the other hand, H_{ex} is not small compared to H_0, which introduces a new effect. One can show in a number of ways, by quantum-mechanical thinking or by the reasoning of reference 3, for instance, that these terms should no longer be omitted. Namely, the rapid variation of these terms due to exchange makes the fact that their "natural" unperturbed frequency is not zero immaterial.‡

One can demonstrate this on our model by assuming that these terms have a Gaussian spectrum centered not about zero but about ω_0. Van Vleck points out that the total mean square amplitude of these terms is 7/3 of that contributed by the zero-frequency terms, so that we may write

$$\langle\Delta\omega_{ij}^2\rangle_{\text{Av}}\varphi_{\Delta\omega}(t)=\exp\left(-\frac{\pi}{4}\omega_e^2t^2\right)\left[\omega_p^2+7/3\omega_p^2\cos\omega_0t\right]. \quad (31)$$

This equation embodies the assumption that the frequency ω_e of exchange motion is the same for the two types of terms, but otherwise is the only simple way to represent the situation. Using (31) one immediately sees that, if $\omega_e\gg\omega_0$, $\varphi_{\Delta\omega}$ will be zero long before $\cos\omega_0t$ can vary much from unity, so that we can for practical purposes use (16), just multiplying ω_p^2 by 10/3 in obtaining the breadth. On the other hand, if $\omega_e\ll\omega_0$ the cosine term will be rapidly varying and will eventually average to zero in its contribution to the main line. In the last column of Table IA we see that the factor 10/3 greatly improves the agreement with experiment, bringing the ratio of theory and experiment within the factor of two we have allowed ourselves.

We can still improve this agreement, however, as is suggested by a glance at Table I. Those cases in which H_p is least still seem to have too great an observed breadth. Can there be still another source of broadening? A number of authors[9–11] have measured very appreciable fine structures, of order 1000 to 2000 gauss in total width, in dilute salts of Mn^{++} and Fe^{+++}. These fine structures are due both to the nuclear hyperfine splitting and to crystal field splittings. Naturally, the latter, major, source of splitting varies from crystal to crystal, but the order of magnitude is roughly constant; and there is no reason whatever to believe that the forces causing these splittings are not operative in the more concentrated salts. It is known (see, e.g., reference 2) that such splittings will be narrowed out by exchange just like dipolar interactions; but nonetheless they represent an extra interaction which must be added in with the dipolar interactions to compute the full width.

This extra contribution is taken into account in the following rough manner: we assume the fine structure fields to be roughly constant, of mean square magnitude H_H^2, in all salts. H_H^2 will represent only in order of magnitude the true mean square width of the fine structure since we know only to order of magnitude how to compute the corresponding exchange narrowing; even given the mean fourth moment we certainly could not use the Gaussian assumptions. The introduction of H_H^2 has been done graphically in Fig. 1 as follows. We assume, for extreme narrowing,

$$\Delta H=[(10/3)H_p^2+H_H^2)]/H_e,$$

which may be written $H_e\Delta H=(10/3)H_p^2+H_H^2$. Thus if, as in Fig. 1, we plot $H_e\Delta H$ against $(10/3)H_p^2$ for various salts we should get points which cluster around a line of slope unity with a positive intercept on the $H_e\Delta H$ axis, of order of magnitude $H_H^2\simeq10^6$. The figure shows that this is the case; the slope of the line is 1 ± 20 percent or so, the intercept $1\pm1\times10^6$. The agreement is excellent considering the variations of crystal structure effects from salt to salt which are to be expected.

In the second half of Table I we list those salts with small θ. We can certainly make no definite predictions

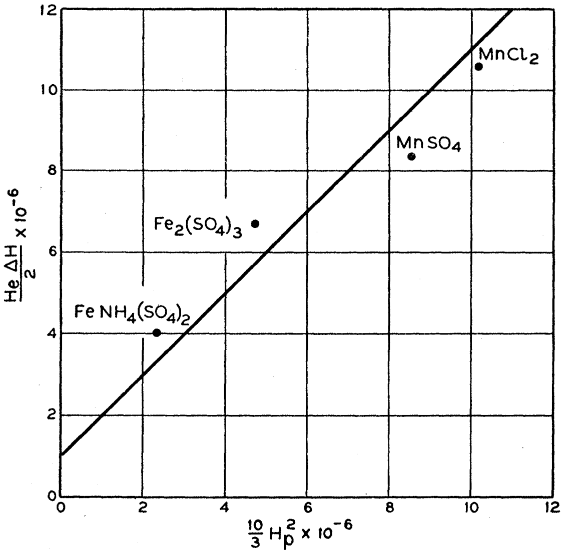

Fig. 1.

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‡ F. Keffer has arrived independently at the same conclusion (thesis, University of California, Berkeley, 1951).

[9] Bragguley, Bleaney, Griffiths, Penrose, and Plumpton, Proc. Phys. Soc. (London) **61**, 551 (1948).

[10] B. Bleaney, Physica **17**, 175 (1951).

[11] Ubbink, Poulis, and Gorter, Physica **17**, 213 (1951).

about these salts, in view of the experimental and theoretical uncertainties, but we have listed, first (H_p^2/H_e) taking H_e the maximum possible as a lower limit, and second $\sim(H_p^2+H_H^2)^{\frac{1}{2}}$ as an upper limit, to the predicted breadths. All cases lie within the limits.

The first three salts seem on the face of it to agree excellently with H_p, i.e., the Van Vleck theory, and to need no exchange narrowing correction. However, it is a little hard to believe that the authors who measured θ could be in such great error as to mistake $\theta=0$ for $\theta=2$ or 3, as would be required to explain this fact. The fourth salt, the fluosilicate,[12] is included to show that the agreement with Van Vleck can be illusory; we see that this salt has a breadth considerably larger than H_p, so that certainly there is a considerable H_H contribution. Thus we believe that the other three salts do indeed have exchange narrowing effects, with H_e of order 10^3 gauss, compensating the extra width owing to fine structure.

It is worth mentioning one other substance we have considered, $CuSO_4\cdot 5H_2O$. Bagguley and Griffiths[13] have measured single crystal lines at a number of frequencies and in a number of directions. Cu^{++}, under conditions of roughly axial symmetry as in this salt, shows a fairly large anisotropy both of g and of hyperfine structure, with the width of the hyperfine structure being usually fairly negligible perpendicular to the axis. In this direction the half-width is about 25 oersted at their highest frequency, which leads one to estimate an exchange field of ~1600 oe. The Curie point is about 0.7°K,[14] which corresponds to 2400 oe exchange field, in quite good agreement; while Bagguley and Griffiths were themselves able to estimate an exchange field, from the frequency at which they could resolve certain lines owing to the two molecules per unit cell, of around 2000 oe. In addition, at their lowest frequency (~3 cm) these authors found a slight increase in line widths, as would be predicted because here the "10/3 effect" should be beginning to appear.

It would be of interest to measure more directly the "10/3 effect" in a salt in which the exchange frequency can be bracketed by two measuring frequencies. It is extremely important, however, to avoid difficulties which are due to anisotropy broadening by using either single crystals or salts with $L=0$, and to be sure that spin lattice broadening is not present (i.e., that the spin-spin interactions make the lines reasonably broad).

Thus we find that in no cases we have considered are the data in appreciable disagreement with values predicted from our theory, if the corrections for off-diagonal elements of the dipolar interactions and for fine and hyperfine structure are taken into account. We feel that the theory and the concepts it uses are thus essentially correct. There seem in paramagnetic substances to be no unexplained sources of broadening such as are present in ferromagnetic materials and in antiferromagnetic materials near their Curie points.

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[12] The measurement here is an unpublished one by W. A. Yager.

[13] D. M. S. Bagguley and J. H. E. Griffiths, Proc. Roy. Soc. (London) **A201**, 366 (1950).

[14] This value comes from de Haas and C. J. Gorter, Leiden Comm. 210d. K. S. Krishnan and A. Mookerji, Phys. Rev. **54**, 841 (1938) find a considerable anisotropy of θ, with only the roughest agreement with the above value found for the powder. Both sets of measurements are at 14°K or higher. T. H. Gaballe and W. F. Giauque, J. Am. Chem. Soc. **74**, 3513 (1952), working along a single axis, agree somewhat better at liquid helium temperatures with the earlier 0.7°K value than with the 1.8°K value found for this axis by Krishnan and Mookerji. In view of the uncertainties in the susceptibility work it is best to regard our agreement above as somewhat fortuitous.