The Dipolar Broadening of Magnetic Resonance Lines in Crystals

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In regular crystals, the width of the absorption lines arising from the magnetic moment of the electron or nucleus is caused primarily by the interaction between the magnetic dipoles. It is prohibitively difficult to determine the precise shape of the absorption line theoretically, but the invariance of the diagonal sum in quantum mechanics permits the calculation of the second moment of the frequency deviation, and hence the r.m.s. line breadth. The latter agrees excellently with the observations of Pake and Purcell on the magnetic absorption of the F nucleus in CaF_2, both in absolute magnitude, and in the dependence on the direction between the magnetic field and the principal cubic axes. The fourth moment was also computed to examine how good an approximation is the conventional assumption of a Gaussian shape. As long as no exchange is present (the nuclear case) the Gaussian model is moderately good. For the 100 direction in a cubic crystal, the theoretical ratio of root mean fourth to root mean square breadth is 1.25. Pake and Purcell's measurements yield 1.24. A Gaussian model would require 1.32.

The theory is extended to include crystals with two kinds of spin moments (two types of nuclei, or simultaneous nuclear and electronic spin). Coupling between unlike moments is less effective (by a factor $\frac{2}{3}$ in the r.m.s. width) than that between like in broadening the lines.

In the paramagnetic absorption caused by electronic spin, it is imperative to include the effect of exchange coupling. This interaction does not contribute to the second moment, but greatly increases the fourth. As a result, the lines are peaked much more sharply than one would compute from the second moment with the Gaussian model for line shape. This "exchange narrowing" explains why microwave paramagnetic absorption lines are much narrower than one first conjectures from the amount of dipolar coupling.

The theoretical calculations are given in Sections II–IV. The final sections V–VI give the comparison with the experiments of Pake and Purcell, and with the model of Bloembergen, Purcell, and Pound, for r-f absorption in liquids.

I. INTRODUCTION

THE present paper[1] deals with the broadening of the absorption lines of crystals by dipolar interaction, with emphasis primarily on the r-f and microwave regions. The theory is much better tested by measurements in these domains than at ordinary optical wave-lengths since with the latter the line broadening is exceedingly small compared to the proper frequency and also it may not be safe to neglect, as we do, the influence of Doppler and radiation broadening.

We shall deal exclusively with media in which the atoms are regularly spaced, i.e., with crystals. The material may, however, be either a single crystal or a powder. The broadening which we consider is caused essentially by the magnetostatic interaction of the atomic dipoles, and is hence "adiabatic" in character. The mechanism is thus quite different from that in gases, where non-adiabatic collisions are the main factor, as shown in the theory of Bloembergen, Purcell, and Pound.[2]

[1] A preliminary account of the present paper was given at the 1947 Chicago meeting of the American Physical Society. For abstract see Phys. Rev. **73**, 1229 (1948).

[2] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

We shall assume throughout that the moments responsible for the absorption are magnetic, and arise from spin, be it nuclear or electronic. The influence of the crystalline electric field will be neglected, and the material will be supposed non-ferromagnetic. This procedure is well warranted in experiments on nuclear resonance absorption. The effect of the crystalline Stark effect on the absorption by electronic spin will be examined in a later paper. In another article the theory will be extended to the ferromagnetic case to provide a microscopic derivation of the Kittel formula for the resonance frequency.

The energy terms attributable to magnetic spin-spin interaction and to application of the external constant magnetic field will be called, respectively, the dipolar and Zeeman energies. We believe that these names are less ambiguous than the word magnetic, which can relate to either term according to the usage of the author. It will be supposed throughout that the applied field is sufficiently large that the dipolar interaction is small compared to the Zeeman member. This condition is fulfilled at the field strengths used in most experiments on resonance absorp-

tion at the Larmor frequency. The resonance wave-lengths are ordinarily in the r-f or microwave region according as the spin is nuclear or electronic. In a later article, Miss Wright will extend the theory to the case of non-resonant absorption at very low frequencies such as are used in the Dutch experiments on paramagnetic relaxation.

An important feature of the present paper is the inclusion of exchange interaction. Except for the exclusion of ferromagnetism, no restriction need be made on the size of the exchange coupling

in our calculations, as it commutes in matrix multiplication with the Zeeman term, so that both energies can be simultaneously diagonal.

The mathematical theory will be developed in Sections II, III, and IV. Comparison with experiment will be made in Section V, and readers not interested in theoretical calculations may wish to proceed directly to this section. In Section VI a qualitative comparison will be made with the theory of Bloembergen, Pound, and Purcell on relaxation phenomena in gases or liquids.

II. CALCULATION OF THE MEAN SQUARE ABSORPTION FREQUENCY

We shall suppose that the constant magnetic field H is applied in the z direction, and that the oscillating field whose absorption is being studied is along the x axis. Because of the dipolar interaction, the absorption is not strictly monochromatic at the frequency $Hg\beta/h$, and the present paper attempts to estimate the amount of the diffusion. Here and elsewhere, β denotes the Bohr magneton, nuclear or electronic as the case may be, and g is the corresponding Landé factor.

The Hamiltonian matrix is

$$\mathfrak{K} = Hg\beta\Sigma_j S_{zj} + \Sigma_{k>j}\tilde{A}_{jk}\mathbf{S}_j\cdot\mathbf{S}_k + g^2\beta^2\Sigma_{k>j}[r_{jk}^{-3}(\mathbf{S}_j\cdot\mathbf{S}_k) - 3r_{jk}^{-5}(\mathbf{r}_{jk}\cdot\mathbf{S}_j)(\mathbf{r}_{jk}\cdot\mathbf{S}_k)]. \tag{1}$$

Here the first, second, and third members are, respectively, the Zeeman, exchange, and dipolar energies. The symbol S_{zj} denotes the z matrix-component of the spin angular momentum (electronic or nuclear) of atom j, measured in multiples of the quantum unit $h/2\pi$. All atoms are assumed to have the same g-factor, and same spin quantum number S. This restriction will, however, be removed in Section IV. We make the usual assumption that the exchange coupling can be calculated on the basis that the atoms are effectively in S states, so that the exchange term has the isotropic form proportional to the scalar product of the two spins. If each atom has z electrons not in complete shells, and if these electrons are treated as equivalent, then the constant of proportionality in the second member of (1) is connected[3] with the usual exchange integral J_{jk} by the relation $\tilde{A}_{jk} = -2z^2 J_{jk}$. The exchange interaction is present only in the electronic, and not in the nuclear case since the orbital exchange energy is correlated by the exclusion principle with the alignment of electronic rather than nuclear spin.

For our purposes it is advantageous to use a system of quantization in which the z component of spin is diagonal. In order to exhibit more clearly the effects of this quantization, we write scalar products such as $\mathbf{r}_{jk}\cdot\mathbf{S}_j$ in the explicit form $r_{jk}(\alpha_{jk}S_{xj} + \beta_{jk}S_{yj} + \gamma_{jk}S_{zj})$, where α_{jk}, β_{jk}, γ_{jk} are the direction cosines of $\mathbf{r}_{jk}$ relative to the x,y,z axes. When this is done, Eq. (1) becomes

$$\mathfrak{K} = Hg\beta\Sigma_j S_{zj} + \Sigma_{k>j}\tilde{A}_{jk}\mathbf{S}_j\cdot\mathbf{S}_k + \Sigma_{k>j}g^2\beta^2 r_{jk}^{-3}\{\mathbf{S}_j\cdot\mathbf{S}_k - 3\gamma_{jk}^2 S_{zj}S_{zk} - \tfrac{3}{4}(\alpha_{jk}^2 + \beta_{jk}^2)(S_{j+}S_{k-} + S_{j-}S_{k+})\}$$
$$+ [\Sigma_{k>j}g^2\beta^2 r_{jk}^{-3}\{-\tfrac{3}{4}(\alpha_{jk}^2 - \beta_{jk}^2)(S_{j+}S_{k+} + S_{j-}S_{k-}) + \tfrac{3}{2}i\alpha_{jk}\beta_{jk}(S_{j+}S_{k+} - S_{j-}S_{k-})$$
$$- \tfrac{3}{2}\gamma_{jk}(\alpha_{jk} - i\beta_{jk})(S_{j+}S_{zk} + S_{zj}S_{k+}) - \tfrac{3}{2}\gamma_{jk}(\alpha_{jk} + i\beta_{jk})(S_{j-}S_{zk} + S_{zj}S_{k-})\}]. \tag{2}$$

Here we have used the abbreviations S_{j+}, S_{j-} for the combinations $S_{xj} + iS_{yj}$, $S_{xj} - iS_{yj}$ which are introduced in order to simplify the selection rules. Namely, the selection rules for S_{j+}, S_{j-} are, respectively, $\Delta M_j = +1$, $\Delta M_j = -1$ and hence are sharper than those $\Delta M_j = \pm 1$ for S_{xj} or S_{yj}. Here M_j is the magnetic quantum number for atom j, supposed individually space quantized relative to the z axis. We shall use the letter M for the total magnetic quantum number $\Sigma_j M_j$.

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[3] For a discussion of the dependence of exchange energy on spin alignment, see, for instance, J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, 1932), p. 316 ff.

Were it not for the portion of (2) inclosed in heavy brackets, the z component of total angular momentum, i.e., $\Sigma_j S_{zj}$, would be a constant of the motion, and would be specified by the usual total magnetic quantum number M. The x component of magnetic moment would then conform rigorously to the selection rule $\Delta M = \pm 1$, and the absorption would be entirely in the vicinity of the Larmor frequency $g\beta H/h$. The inclusion of the bracketed part of (2) introduces matrix elements in the Hamiltonian function of the type $\Delta M = \pm 1, \pm 2$. The addition of these elements makes the selection rule $\Delta M = \pm 1$ for the x component of moment cease to be rigorous. As a result, transitions of the form $\Delta M = 0, \pm 2,$ ± 3 are allowed, corresponding to changes in Zeeman energy amounting to 0, $2g\beta H$, $3g\beta H$. (Still larger changes in M are allowed if the perturbation calculation is carried further, but the intensity is so low as to be negligible.) The subsidiary lines whose frequencies are near 0, $2g\beta H/h$, $3g\beta H/h$ are not those of interest to us, and so we shall henceforth drop the bracketed part of (2). This omission is not to be regarded as merely a simplification. Retention of the omitted part of (2) would, in fact, be completely erroneous in the ensuing computation of various mean powers of the frequencies by the commutator method. If the commutator with the complete Hamiltonian were used, we would include the contribution of the lines centering about 0, $2g\beta H/h$, $3g\beta H/h$ as well. Then we could not use the departure of the mean square frequency from $g^2\beta^2H^2/h^2$ as a measure of the mean square line breadth of the main line. The subsidiary lines are, to be sure, much fainter than the primary Larmor component, but differ so much from the latter in frequency that their contribution to the mean square frequency deviation is of the same order as the mean square
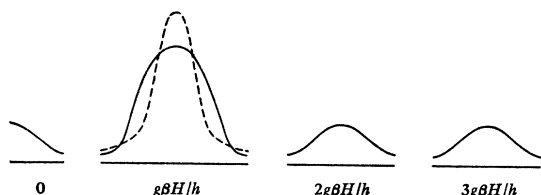

FIG. 1. Schematic illustration of main and subsidiary absorption lines. The dashed curve indicates how the shape of the main line is distorted by exchange coupling.

breadth of the dominant line. The situation is illustrated schematically in Fig. 1.[4]

Let the letter n denote the characteristic values of the expression (2), exclusive of the bracketed part, which is henceforth supposed omitted. Also let $(S_x)_{nn'}$ be the matrix element of $S_x = \Sigma_j S_{xj}$ which connects the states n and n'. The corresponding frequency is, of course, $\nu_{nn'} = (\mathfrak{3C}_n - \mathfrak{3C}_{n'})/h$. Then by definition the mean square absorption frequency, i.e., the frequency computed by weighting each fine-structure component with the associated squared amplitude, is

$$\langle \nu^2 \rangle_{Av} = \frac{\Sigma_{n, n'} \{ \nu_{nn'}{}^2 | (S_x)_{nn'} |^2 \}}{\Sigma_{n, n'} | (S_x)_{nn'} |^2}. \tag{3}$$

The trick is now to note that both the numerator and denominator of (3) can be expressed as diagonal sums. If the notation Tr be used for the trace or diagonal sum, then (3) can be written as

$$\langle \nu^2 \rangle_{Av} = - \text{Tr}[\mathfrak{3C}S_x - S_x\mathfrak{3C}]^2 / h^2 \text{Tr}(S_x)^2. \tag{4}$$

The great advantage of (4), which provides the standard method for computing mean square frequencies, is that the invariance of the diagonal sum makes it unnecessary to know the individual characteristic values $\mathfrak{3C}_n$. Instead the diagonal sum can be computed in an arbitrary system of quantization, most conveniently one in which each spin is individually space-quantized. It would, of course, be hopeless to try and compute the various characteristic values $\mathfrak{3C}_n$, since the number of them is comparable with the number of atoms composing the crystal. Rigorously, these characteristic values form a discrete rather than continuous manifold. When, however, there are 10^{20} or so fine-structure components to a line, it has effectively a continuous structure, as sketched in Fig. 1.

The retained part of (2) can be written as

$$\mathfrak{3C} = Hg\beta\Sigma_j S_{zj} + \Sigma_{k>j} A_{jk} \mathbf{S}_j \cdot \mathbf{S}_k + \Sigma_{k>j} B_{jk} S_{zj} \cdot S_{zk}, \tag{5}$$

[4] A sketch similar to Fig. 1, except for the exchange modification, is given by L. J. F. Broer in his thesis, Amsterdam, 1945, and also in Physica 10, 801 (1943). Broer discusses the orders of magnitude of the intensities and breadths of the main and subsidiary lines, but does not essay a quantitative calculation of the r.m.s. width.

with

$$A_{jk} = \tilde{A}_{jk} + g^2\beta^2 r_{jk}{}^{-3}[\tfrac{3}{2}\gamma_{jk}{}^2 - \tfrac{1}{2}], \quad B_{jk} = -3g^2\beta^2 r_{jk}{}^{-3}[\tfrac{3}{2}\gamma_{jk}{}^2 - \tfrac{1}{2}]. \tag{6}$$

The reader should be careful to distinguish between the symbols $\tilde{A}_{jk}$ and A_{jk}. Both appear as coefficients of the scalar product $\mathbf{S}_j \cdot \mathbf{S}_k$, but $\tilde{A}_{jk}$ embodies the effect of exchange alone, whereas A_{jk} also contains a dipolar contribution. The distinction can perhaps be remembered most easily by thinking of the wavy line as indicative of the transposition involved in exchange. Any coefficient without this line above it does not arise solely in virtue of exchange coupling. All B coefficients are purely dipolar in origin.

The scalar product $\mathbf{S}_j \cdot \mathbf{S}_k$ commutes with $S_x = \Sigma_j S_{xj}$. Hence the second member of (5) has no influence on $\langle \nu^2 \rangle_{\text{Av}}$. As a result we can conclude that exchange has no effect on the mean square absorption frequency.

We can evaluate traces in (4) with the aid of the familiar commutation and trace relations, $viz.$,

$$S_{xj}S_{yk} - S_{yk}S_{xj} = \delta_{jk}S_{zj}i, \quad \text{Tr}S_{zj}{}^2 = \tfrac{1}{3}S(S+1)(2S+1)^N, \quad \text{Tr}S_{zj} = 0, \tag{7}$$

where S is the spin quantum number of an individual atom. The traces over the different atoms can be computed independently. Thus

$$\text{Tr}S_{xj}S_{xk} = \text{Tr}S_{xj} = \text{Tr}S_{xk} = 0 (j \neq k), \quad \text{etc.}$$

Proceeding in this fashion, we find that

$$\text{Tr}(S_x)^2 = \tfrac{1}{3}NS(S+1)(2S+1)^N, \tag{8}$$

$$\mathcal{3C}S_x - S_x\mathcal{3C} = Hg\beta i\Sigma_j S_{yj} + i\Sigma_{k>j}B_{jk}(S_{yj}S_{zk} + S_{yk}S_{zj}),$$
$$-\text{Tr}(\mathcal{3C}S_x - S_x\mathcal{3C})^2/(2S+1)^N = \tfrac{1}{3}Ng^2\beta^2H^2S(S+1) + (2/9)S^2(S+1)^2\Sigma_{k>j}B_{jk}{}^2, \tag{9}$$

where N is the total number of atoms in the crystal.

One can easily convince oneself that the line structure (apart, of course, from the usual powers of ν) is symmetrical about a center located at the Larmor frequency $Hg\beta/h$. This statement can be proved from the fact that to every characteristic value of the expression (5), there is another one wherein the Zeeman energy is reversed in sign, but in which the dipolar and exchange energy is unaltered. Hence every fine-structure component on the high frequency side of $Hg\beta/h$ has a mirror image on the other side, with the same line strength, since the transition probability is unaffected by consistent reversal of the sign of the magnetic quantum number. Thus it follows from (4), (8), and (9) that the mean square deviation of the frequency from the Larmor value is

$$\langle \Delta\nu^2 \rangle_{\text{Av}} = \langle (\nu - g\beta H/h)^2 \rangle_{\text{Av}} = \langle \nu^2 \rangle_{\text{Av}} - g^2\beta^2H^2/h^2 = \tfrac{1}{3}S(S+1)h^{-2}\Sigma_k B_{jk}{}^2, \tag{10}$$

with B_{jk} defined as in (6). We suppose all atoms similarly situated, so that the sum at the end of (10) is independent of j.

If the crystal has cubic symmetry, it is found that when the definition (6) of the B_{jk} is used, the expression (10) becomes

$$\langle \Delta\nu^2 \rangle_{\text{Av}} = \tfrac{3}{8}g^4\beta^4h^{-2}[a + b(\lambda_1{}^4 + \lambda_2{}^4 + \lambda_3{}^4)]S(S+1), \tag{11}$$

where λ_1, λ_2, λ_3 are the direction cosines of the applied field H relative to the principal cubic axes X, Y, Z. The constants a, b are independent of λ_1, λ_2, λ_3, and have the values

$$a = \Sigma_k r_{jk}{}^{-6}[7 - 9(\mu_{jk}{}^4 + \nu_{jk}{}^4 + \xi_{jk}{}^4)], \quad b = \Sigma_k r_{jk}{}^{-6}[-9 + 15(\mu_{jk}{}^4 + \nu_{jk}{}^4 + \xi^4)]. \tag{12}$$

Here μ_{jk}, ν_{jk}, ξ_{jk} are the direction cosines of $\mathbf{r}_{jk}$ relative to the X, Y, Z axes. For a simple cubic lattice, the sums over k are readily computed, and (11) becomes

$$\langle \Delta\nu^2 \rangle_{\text{Av}} = 36.8g^4\beta^4h^{-2}d^{-6}[\tfrac{1}{3}S(S+1)][(\lambda_1{}^4 + \lambda_2{}^4 + \lambda_3{}^4) - 0.187]. \tag{13}$$

Here d is the spin-lattice constant, i.e., the distance between neighboring magnetic atoms located on a simple cubic grating. (Our constant d need not be the same as the conventional lattice constant, since there may be intervening atoms devoid of spin which are irrelevant for our problem.)

With a powder, rather than single crystal, we can replace the powers of the direction cosines by their averages over a sphere, and then (11) reduces to

$$\langle \Delta \nu^2 \rangle_{\text{Av}} = \tfrac{3}{5} g^4 \beta^4 h^{-2} S(S+1) \Sigma_k r_{jk}^{-6}. \tag{14}$$

It may be noted that the value $\langle \Delta \nu^2 \rangle_{\text{Av}}$ is larger by a factor $(\tfrac{3}{2})^2$ than it would have been had we computed this quantity in a naive fashion by erroneously assuming that because of the Larmor precession only the z component of moment of each atom is effective in the interatomic coupling. In other words, if we had assumed that the effective dipolar part of (2) was $\Sigma_{k>j} g^2 \beta^2 r_{jk}^{-3} (1 - 3\gamma_{jk}^2) S_{zj} S_{zk}$, the values of the constants a and b in (11) would be 4/9 as great as given by (12). This fact has already been demonstrated by Bloembergen, Pound, and Purcell.[2] When only the z components of moment are retained, the calculation becomes particularly simple, as it is then essentially magnetostatic rather than quantum-mechanical. Unfortunately the higher moments, say $\langle \Delta \nu^n \rangle_{\text{Av}}$, cannot, in general, be correctly obtained by multiplying the results obtained with the simplified model by a factor $(\tfrac{3}{2})^n$.

Our formula (14) for the mean square frequency deviation in an isotropic medium or powder is exactly 3/10 as large as the corresponding expression which Waller[5] derived for the mean square frequency in the absence of any external field. Waller used the same method as ours, except that in the numerator of (4) he took the commutator of S_x with the complete Hamiltonian function (1) or (2), inclusive of the bracketed terms. In his case, the inclusion of the bracketed terms was, of course, appropriate, since without the external field the separation into different frequency bands in accordance with the harmonic of the Larmor frequency is no longer relevant. By a very slight extension of Waller's calculation, it can be proved that in an applied field of arbitrary strength, the mean square frequency, inclusive of all lines, is equal to $g^2 \beta^2 H^2 h^{-2} + 10\langle \Delta \nu^2 \rangle_{\text{Av}}/3$, where $\langle \Delta \nu^2 \rangle_{\text{Av}}$ is given by (14). In strong fields, the subsidiary lines, of frequencies approximately 0, $2\beta H/h$, $3\beta H/h$, make a contribution $7\langle \Delta \nu^2 \rangle_{\text{Av}}/3$ to this mean square. This contribution is independent of H because in strong fields, as Broer[4] has noted, the amplitudes of the "forbidden" lines are inversely proportional to H, whereas the frequencies are approximately linear in H. In weak fields there is, of course, no essential distinction between the main lines and the subsidiaries or harmonics.

The usual assumption is that the frequencies have a Gaussian distribution

$$f(\nu) = [1/2\pi \langle \nu^2 \rangle_{\text{Av}}]^{\frac{1}{2}} \exp[-(\nu - g\beta H/h)^2/2\langle \Delta \nu^2 \rangle_{\text{Av}}]. \tag{15}$$

Then the full "half-width," i.e., twice the deviation in frequency from the central value at which the intensity has dropped to half its maximum, is

$$\Delta \nu_{\frac{1}{2}} = 2(\log\sqrt{2})^{\frac{1}{2}} \sqrt{2} [\langle \Delta \nu^2 \rangle_{\text{Av}}]^{\frac{1}{2}} = 2.35[\langle \Delta \nu^2 \rangle_{\text{Av}}]^{\frac{1}{2}}, \quad \Delta \nu_{\text{m.sl.}} = 2[\langle \Delta \nu^2 \rangle_{\text{Av}}]^{\frac{1}{2}}. \tag{16}$$

We also include in (16) the formula for the frequency separation $\Delta \nu_{\text{m.sl.}}$ of the two points of maximum slope $(df/d\nu)_{\text{max}}$ in the absorption curve.

One of the main points to be made in the present paper is that extreme caution must be exercised in using (15). A good idea as to the applicability of (15) may be formed by reckoning out the fourth moment, as we shall do in the next section, and examining whether it comes at all near to being equal to $3[\langle \Delta \nu^2 \rangle_{\text{Av}}]^2$, as (15) would require. We shall see that if exchange forces are important, (15) is necessarily far from the truth. On the other hand, in the case of nuclear resonance, where exchange does not enter, the error involved in (15) is not so serious.

[5] I. Waller, Zeits. f. Physik **79**, 380 (1932).

III. CALCULATION OF THE MEAN FOURTH POWER OF THE FREQUENCY

We now proceed to the more difficult calculation of the fourth moment. The standard formula,[6] analogous to (4), for the mean fourth power of the frequency is

$$h^4\langle\nu^4\rangle_{Av}=\text{Tr}[\mathfrak{IC}U-U\mathfrak{IC}]^2/\text{Tr}(S_x)^2, \tag{17}$$

where U equals $\mathfrak{IC}S_x - S_x\mathfrak{IC}$ and in our case is given by (9). Using the commutation rules (7) one finds

$$\mathfrak{IC}U - U\mathfrak{IC} = +H^2g^2\beta^2\Sigma_jS_{xj}+\Sigma_{k>j}\{[jk]+[kj]\}+\Sigma_{l>k>j}\{[jkl]+[klj]+[ljk]\}, \tag{18}$$

where

$$[jk]=2Hg\beta B_{jk}S_{xj}S_{zk}+B_{jk}^2S_{xj}S_{zk}^2+A_{jk}B_{jk}[-S_{zj}S_{xk}S_{zk}+S_{yk}S_{yj}S_{xj}-S_{yj}^2S_{xk}+S_{xj}S_{zk}^2],$$
$$[jkl]=2B_{jk}B_{kl}S_{zj}S_{xk}S_{zl}+[-B_{jl}A_{jk}+B_{kl}A_{jk}-B_{jl}A_{kl}+B_{jk}A_{kl}][S_{zj}S_{xk}S_{zl}-S_{yj}S_{xk}S_{yl}],$$

with $A_{jk}=A_{kj}$, $B_{jk}=B_{kj}$ defined as in (6).

Since the frequencies are symmetrically distributed about a centroid $g\beta H/h$, the relation $\langle\nu^4\rangle_{Av}=\langle(g\beta Hh^{-1}+\Delta\nu)^4\rangle_{Av}$ gives

$$\langle\Delta\nu^4\rangle_{Av}=\langle\nu^4\rangle_{Av}-6H^2g^2\beta^2h^{-2}\langle\Delta\nu^2\rangle_{Av}-H^4g^4\beta^4h^{-4}. \tag{19}$$

In order to work out the trace in (17), it is necessary to use, besides (7), relations such as

$$\text{Tr}S_{xj}^3=\text{Tr}S_{xj}^2S_{yj}=0,\quad \text{Tr}S_{xj}S_{yj}S_{zj}=\tfrac{1}{6}iS(S+1)(2S+1)^N,$$

$$\text{Tr}S_{zj}^4=\tfrac{1}{5}[S^2(S+1)^2-\tfrac{1}{3}S(S+1)](2S+1)^N,\quad \text{Tr}S_{xj}^2S_{yj}^2=\tfrac{1}{5}[\tfrac{1}{3}S^2(S+1)^2+\tfrac{1}{6}S(S+1)](2S+1)^N. \tag{20}$$

With the aid of the preceding formulas, it is finally found that

$$h^4\langle\Delta\nu^4\rangle_{Av}=N^{-1}\Sigma_{j,k,l\neq}[3B_{jk}^2B_{jl}^2+2A_{jk}^2(B_{jl}-B_{kl})^2+2A_{jk}A_{kl}(B_{jl}-B_{jk})(B_{jl}-B_{kl})$$
$$+2A_{jk}B_{jk}(B_{jl}-B_{kl})^2][\tfrac{1}{3}S(S+1)]^2+2N^{-1}\Sigma_{k>j}\{B_{jk}^4\cdot\tfrac{1}{5}[S^2(S+1)^2-\tfrac{1}{3}S(S+1)]$$
$$+2B_{jk}^3A_{jk}\cdot\tfrac{1}{5}[\tfrac{2}{3}S^2(S+1)^2-\tfrac{1}{3}S(S+1)]+\tfrac{1}{2}B_{jk}^2A_{jk}^2[\tfrac{4}{5}S^2(S+1)^2-\tfrac{3}{5}S(S+1)]\}. \tag{21}$$

Here the notation $j, k, l\neq$ means that none of the indices are to be equal. There are thus six times as many terms in the triple sum in (21) as in the type $l>k>j$ employed in (18). The $\neq$ convention makes it possible to write (21) more compactly than otherwise. In (18), however, it was desirable to use the $>$ rather than $\neq$ scheme in order to exhibit clearly the fact that terms differing by simple permutations must be added before rather than after squaring.

An interesting check on the arithmetical correctness of (21) is that all terms involving the A's cancel if $S=\tfrac{1}{2}$ and if, in addition, all the B_{jk}, etc., are formally given a value B independent of the subscripts. Under these restrictions, simple general considerations show that the exchange terms (i.e., those proportional to A_{jk}) should have no effect on the spectrum. Namely, the exchange energy $\Sigma_{k>j}\bar{A}_{jk}S_j\cdot S_k$ (or equally well the energy $\Sigma_{k>j}A_{jk}S_j\cdot S_k$ defined by (6), which contains in addition a dipolar contribution) commutes with Σ_jS_{zj} or Σ_jS_{xj}, and hence with the Zeeman energy, as well as with the dipole moment responsible for the absorption. This energy also commutes with the remaining dipolar Hamiltonian

$$B\Sigma_{k>j}S_{zj}S_{zk}=\tfrac{1}{2}B[(\Sigma_jS_{zj})^2-\Sigma_jS_{zj}^2],$$

if $S=\tfrac{1}{2}$, for then S_{zj}^2 has the unique value $\tfrac{1}{4}$, making the term $\Sigma_jS_{zj}^2$ merely an additive constant. Hence the exchange energy can be diagonalized without affecting in any way the matrix elements relevant to our absorption problem, and should hence not be involved in the moments of any order. As soon as B_{jk} depends on the subscripts, this statement is no longer true, for then the exchange energy does not commute with the dipolar part of the Hamiltonian.

The fact that (21) contains terms of the form A^2B^2 and AB^3, rather than just B^4, shows that the exchange (i.e., $\bar{A}$) terms influence the fourth moment, even though they do not enter in the second moment. This behavior is possible only if the absorption tapers off less sharply in the wings than the

[6] Compare, for instance, I. Waller, Zeits. f. Physik 79, 381 (1932).

Gaussian distribution would predict, but at the same time is peaked more sharply in the immediate vicinity of the center of the line, so that the original value of the mean square is unaltered. The half-width, and also the width between the points of maximum slope, is then smaller than given by (16). A rough, schematic illustration of the situation is given in Fig. 1; here the solid and dashed curves are, respectively, exclusive and inclusive of the effect of exchange coupling. It is thus not surprising that experimentally (see Section V) the absorption lines caused by electronic spin are often sharper than one would predict from dipolar interaction alone. Just how much the "exchange narrowing" amounts to cannot be inferred just from the second and fourth moments alone, since a detailed theory of the line shape which we do not have at present would be necessary. We shall allude to this question briefly in Section VI.

Explicit Computation of the Fourth Moment for a Simple Cubic Lattice. In order to evaluate (21) more explicitly, we shall assume a simple cubic grating, since this is the simplest to calculate, as well as one of the commonest to occur. We shall, for the present, neglect terms of the type $\bar{A}B^3$, and also the purely dipolar contribution to the fourth moment, as sums of the type $\bar{A}B^3$ or B^4 will be small compared with those of the $\bar{A}^2B^2$ variety if exchange is preponderant. When this order of approximation is made, we can replace A_{jk} by $\bar{A}_{jk}$ (cf. Eq. (6)), thus making the A terms arise entirely from exchange. We shall make the usual assumption that the exchange coefficients $\bar{A}_{jk}$ are negligible except between neighboring atoms, and have a constant value $\bar{A}$ when j is a neighbor of k. We shall furthermore disregard the dipolar terms connecting atoms separated by distances greater than $2d$, where d is the grating spacing. The resulting error amounts to only a very few percent, since the sums converge rapidly. The distance occurs to the inverse sixth power in expressions of the type $\bar{A}^2B^2$, inasmuch as $B\sim r^{-3}$. Furthermore in (21) the great bulk of the long-range terms in $\bar{A}^2B^2$, i.e., those in the triple sum, involve only the difference of the B's sharing the same terminal atom, and then the convergence is even better, since $(B_{jl}-B_{kl})^2\sim r_{jl}^{-4}$ as $r_{jl}\rightarrow\infty$, if k is a neighbor of j. In calculating grating sums, it is highly advantageous to have only such differences involved, and it is for this reason that we have grouped the terms in the way that we have in (21).

When the summations in (21) are explicitly performed with the simplifications mentioned in the preceding paragraph, it is found that

$$h^4\langle\Delta\nu^4\rangle_{Av}=4.9\times10^2g^4\beta^4d^{-6}\bar{A}^2[\tfrac{1}{3}S(S+1)]^2[\lambda_1{}^4+\lambda_2{}^4+\lambda_3{}^4-0.187]$$
$$+\tfrac{1}{4}g^4\beta^4d^{-6}\bar{A}^2[\tfrac{4}{5}S^2(S+1)^2-\tfrac{3}{5}S(S+1)]\cdot81[\lambda_1{}^4+\lambda_2{}^4+\lambda_3{}^4-\tfrac{1}{3}], \quad (22)$$

where d is the spin-lattice constant, i.e., the distance between neighboring magnetic atoms.

If the Gaussian assumption (15) were valid, the value of $\langle\Delta\nu^4\rangle_{Av}$ would be $3[\langle\Delta\nu^2\rangle_{Av}]^2$. The formula for $\langle\Delta\nu^2\rangle_{Av}$ is given in (13). Hence

$$\frac{\langle\Delta\nu^4\rangle_{Av}}{3[\langle\Delta\nu^2\rangle_{Av}]^2}=\frac{0.12\bar{A}^2}{g^4\beta^4d^{-6}}[\lambda_1{}^4+\lambda_2{}^4+\lambda_3{}^4-0.187]^{-1}. \quad (23)$$

In calculating this ratio, we have omitted the contribution of the second line of (22), which is smaller than the first and which vanishes entirely if $S=\tfrac{1}{2}$. The value of $\bar{A}$ at which the ratio (23) equals unity is a measure of amount of exchange coupling required to distort the shape of the line appreciably. (In this connection it should be remembered that the numerator of (23) omits the purely dipolar contributions which alone are sufficient to give a ratio about unity.) Simple dimensional examination of (21) shows that this critical value of $\bar{A}$ is given by a formula of the type $\bar{A}=cg^2\beta^2/d^3$, where c is a dimensionless constant. From (23) it is seen that the value of c will depend on direction. When the field H is along the 100 axis (X axis), c equals 2.6, while for the 111 direction c becomes 1.1. The phenomenon of "exchange narrowing" should hence be somewhat more pronounced for the 111 than the 100 application of the field, but the resulting anisotropy in the line shape is probably not large. (Incidentally, it appears to be purely an accident that the subtractive constant is 0.187 in both (13) and the first line of (22).)

We have tacitly supposed that dipolar interaction alone does not cause significant departures from the Gaussian distribution. This assumption may be tested by calculating the fourth moment by means of (21) with omission of all but dipolar terms. In this connection, it should be noted that in (21) the dipolar coupling not only enters through the B constants, but also through the A's, since by (6) the value of A_{jk} is $-\frac{1}{3}B_{jk}$ when there is no exchange. Thus it is no longer allowable to neglect all the A_{jk} except those joining neighboring atoms, although such terms have a distinctly dominant effect. When A_{jk} is replaced by $-\frac{1}{3}B_{jk}$, the expression (21) can be written

$$\langle \Delta \nu^4 \rangle_{Av} = \{3(\Sigma_k B_{jk}{}^2)^2 - \frac{1}{3}N^{-1}\Sigma_{jkl \neq}B_{jk}{}^2(B_{jl}-B_{kl})^2 - \frac{1}{5}\Sigma_k B_{jk}{}^4[8+\frac{3}{2}(S^2+S)^{-1}]\}\{\frac{1}{3}S(S+1)\}^2. \quad (24)$$

If only the first right-hand member were present, the fourth moment would have precisely the Gaussian value. Even for a simple cubic lattice, explicit evaluation of (24) would be laborious for an arbitrary angle between the applied field and the principal axes; also the angular dependence in the resulting analytical formula would be cumbersome, involving the direction cosines to the eighth rather than fourth power as in (22). We have therefore calculated (24) for a simple cubic lattice for the special case that H is directed along the 100 axis. Then we find that (24) becomes

$$\langle \Delta \nu^4 \rangle_{Av} = 3[\langle \Delta \nu^2 \rangle_{Av}]^2[1-0.160-0.021(S^2+S)^{-1}]. \quad (25)$$

If $S=\frac{1}{2}$, Eq. (25) yields a root mean fourth deviation $[\langle \Delta \nu^4 \rangle_{Av}]^{\frac{1}{4}}$, which is 1.25 times the root mean square $[\langle \Delta \nu^2 \rangle_{Av}]^{\frac{1}{2}}$. With a Gaussian distribution, the ratio would be 1.32 instead of 1.25. The departures from Gaussian form caused by pure dipolar interaction are thus not great. They tend to blunt the absorption curve, rather than peak it more sharply as the exchange corrections do. For a rectangular shaped curve, the ratio would be 1.16.

Rough numerical examination of (24) for the case that H is along the 111 direction indicates that for this orientation the departures from the Gaussian form are smaller than for the 100. The ratio of the root mean fourth to root mean square deviation is about 1.30.

If exchange effects are present, and if H is directed along the 100 axis, the fourth moment is the sum of the expressions (22) and (24), with $\lambda_1 = 1$, $\lambda_2 = \lambda_3 = 0$ in (22). The existence of terms of the form $\bar{A}B^3$ when (6) is substituted in (21) implies that this additivity is not rigorous. However, the contribution of the terms of structure $\bar{A}B^3$ turns out to be small, and may be considered zero within the accuracy to which we have evaluated the grating sums.

IV. CALCULATION FOR A CRYSTAL WITH TWO MAGNETIC INGREDIENTS

It is not difficult to extend the analysis to a grating which contains two different types of atoms, having, respectively, g-factors g and g', also spins S and S'. This situation arises when the crystal contains two species of atoms, both with nuclear (or both with electronic) spin. A further example of particular interest is encountered when a small percentage of atoms with electronic spin is added to a crystal whose nuclear resonance is being studied.

With two ingredients, it is necessary to distinguish which type of atom is active in the resonance. Without loss of generality we can assume that the atoms with unprimed spin are responsible for the absorption at the wave-length being utilized. It is supposed throughout the present section that the two g-factors are sufficiently different so that the resonances for the two varieties of atoms do not overlap. This condition is abundantly fulfilled when one of the spins is nuclear and the other electronic. In applying our formulas, the same definition of the magneton β must be used for both ingredients; hence g will be different by a factor of the order 10^3 for the nuclear and electronic constituents. If both spins are nuclear, their g-factors will in general differ, so that our calculations are applicable. It is not necessary that the spin quantum numbers S and S' be unlike. If both spins are electronic, both g and g' are presumably nearly 2, though there can be deviations from the ideal value 2 because of spin-orbit interaction. Then one must be careful to see whether g and g' differ sufficiently to separate the two resonances and make the present calculation relevant. The separation can, of course, be increased by augmenting the applied magnetic field. A limiting case which we do

not calculate, but which might ultimately prove of interest, and which could be treated by the general mathematical methods of the present paper, is that of atoms with identical g-factors but unlike spin quantum numbers. The general case in which the difference between the two Larmor frequencies is comparable with the dipolar broadening would present an intricate mathematical problem.

We shall throughout use primed and unprimed letters to distinguish the two varieties of atoms. Since the unprimed component is responsible for the resonance, the x component of moment S_x to be used in (4) or (17) involves only the summation $\Sigma_j S_{xj}$ over the unprimed atoms. A point particularly to be emphasized is that in constructing the Hamiltonian function $\mathfrak{IC}$, it is essential to exclude matrix elements of the type $\Delta M_j = +1$, $\Delta M_{k'} = -1$, or $\Delta M_j = -1$, $\Delta M_{k'} = +1$. Here M_j, $M_{k'}$ denote the magnetic quantum numbers appropriate to separate spatial quantization of atoms j and k', respectively. The effect of such elements would be to create a subsidiary absorption line at a Zeeman frequency $(2g-g')\beta H/h'$, and also to modify very slightly the irrelevant absorption at $g'\beta H/h$ due primarily to the primed system. These elements should thus be excluded, just as the heavily bracketed part of (2) was dropped in Section II to avoid inclusion of the subsidiary lines in Fig. 1. Generalized to the present problem, Fig. 1 would contain two main lines of frequency $g\beta H/h$, $g'\beta H/h$ respectively, and a variety of minor ones, of frequency $(2g-g')\beta H/h$, $2g\beta H/h$, $(g+g')\beta H/h$, etc. We are essaying the calculation of the width of the main line at $g\beta H/h$.

In virtue of the remarks made in the preceding paragraph, parts of the Hamiltonian function having factors of the form $(S_{xj}+iS_{yj})(S_{xk'}-iS_{yk'}) = S_{j+}S_{k-'}$ or $S_{j-}S_{k+'}$ should be omitted, although they must be retained when both letters are primed, or both unprimed. In a scalar product such as $\mathbf{S}_j \cdot \mathbf{S}_{k'} = S_{xj}S_{xk'}+S_{yj}S_{yk'}+S_{zj}S_{zk'}$ only the term $S_{zj}S_{zk'}$ is relevant. Hence, when one letter is primed and the other unprimed, even more of the dipolar terms should be discarded than those bracketed in (2). The effective exchange and dipolar potential coupling together two unlike atoms j,k' is thus $C_{jk'}S_{zj}S_{zk'}$ where

$$C_{jk'} = \tilde{A}_{jk'} + (1-3\gamma_{jk'}{}^2)gg'\beta^2 r_{jk'}{}^{-3}. \tag{26}$$

The total Hamiltonian to be employed in place of (5) is

$$\mathfrak{IC} = Hg\beta(\Sigma_j S_{zj}+\Sigma_{j'}S_{zj'})+\Sigma_{k>j}(A_{jk}\mathbf{S}_j\cdot\mathbf{S}_k+B_{jk}S_{zj}S_{zk})$$
$$+\Sigma_{k'>j'}(A_{j'k'}\mathbf{S}_{j'}\cdot\mathbf{S}_{k'}+B_{j'k'}S_{zj'}S_{zk'})+\Sigma_{j,k'}C_{jk'}S_{zj}S_{zk'}. \tag{27}$$

Here $A_{j'k'}$, $B_{j'k'}$ are to be understood defined as in (6) except for the addition of primes. The commutator $U = \mathfrak{IC}S_x - S_x\mathfrak{IC}$ is given by the expression

$$U = ig\beta H\Sigma_j S_{yj}+i\Sigma_{k>j}B_{jk}(S_{yj}S_{zk}+S_{yk}S_{zj})+i\Sigma_{j,k'}C_{jk'}S_{yj}S_{zk'},$$

which replaces (9). One finds that

$$\mathfrak{IC}U - U\mathfrak{IC} = (\mathfrak{IC}U - U\mathfrak{IC})_0+\Sigma_{l'}\Sigma_{k>j}\{2C_{jl'}B_{jk}S_{xj}S_{zk}S_{zl'}+2C_{kl'}B_{jk}S_{xk}S_{zj}S_{zl'}$$
$$+A_{jk}(C_{jl'}-C_{kl'})(-S_{zj}S_{xk}S_{zl'}+S_{xj}S_{zk}S_{zl'})\}$$
$$+\Sigma_j\Sigma_{l'>k'}\{A_{k'l'}(C_{jk'}-C_{jl'})(S_{yj}S_{yk'}S_{xl'}-S_{yj}S_{xk'}S_{yl'})+2C_{jk'}C_{jl'}S_{xj}S_{zk'}S_{zl'}\}+\Sigma_{j,k'}C_{jk'}{}^2S_{xj}S_{zk'}{}^2,$$

where $(\mathfrak{IC}U - U\mathfrak{IC})_0$ denotes the value which would result were there no primed atoms, and which is given by the right side of (18).

The same procedure that was used previously, based on Eqs. (4), (17), and (19), can now be employed to calculate the second and fourth moments. The following expressions are finally obtained for the mean square and mean fourth power frequency deviation:

$$\langle\Delta\nu^2\rangle_{\text{Av}} = \tfrac{1}{3}S(S+1)h^{-2}\Sigma_k B_{jk}{}^2+\tfrac{1}{3}S'(S'+1)h^{-2}\Sigma_{k'}C_{jk'}{}^2, \tag{28}$$

$$h^4\langle\Delta\nu^4\rangle_{\text{Av}} = h^4[\langle\Delta\nu^4\rangle_{\text{Av}}]_0+N^{-1}[\tfrac{1}{3}S(S+1)][\tfrac{1}{3}S'(S'+1)]\Sigma_{l'}\Sigma_{k>j}\{6B_{jk}{}^2(C_{jl'}{}^2+C_{kl'}{}^2)$$
$$+2A_{jk}{}^2(C_{jl'}-C_{kl'})^2+4B_{jk}A_{jk}(C_{jl'}-C_{kl'})^2\}+N^{-1}\Sigma_j\Sigma_{l'>k'}[2A_{k'l'}{}^2(C_{jk'}-C_{jl'})^2$$
$$+6C_{jk'}{}^2C_{jl'}{}^2][\tfrac{1}{3}S'(S'+1)]^2+N^{-1}\Sigma_{j,k'}C_{jk'}{}^4\cdot\tfrac{1}{5}[S'(S'+1)-\tfrac{1}{3}]S'(S'+1). \tag{29}$$

Here N is the number of unprimed atoms, and $h^4[\langle \nu^4 \rangle_{Av}]_0$ denotes the right side of (21), or in other words the mean fourth power deviation which would result were the coupling to the primed system completely absent. The expression (29) would have the value corresponding to the Gaussian hypothesis only if we could omit from (29) all terms except the two with factor 6, also from (21) all terms except that with factor 3, and if, in addition, we could disregard the exclusion of equal indices, replacing a sum of the type $\Sigma_a \Sigma_{c>b}$ by $\frac{1}{2}\Sigma_{a, b, c}$, etc. Actually, of course, these conditions are not fulfilled.

The results (28) and (29) doubtless appear rather formidable, but have several interesting implications, which we shall now summarize.

(a) All other things being equal, dipolar coupling between unlike atoms is less effective than that between like ones in broadening the lines. This prediction follows from the fact that the mean square broadening (28) involves coefficients B_{jk} and C_{jk} symmetrically, along with the fact that the definition (6) of B_{jk} involves a factor $\frac{3}{2}$ not contained in the dipolar part of the expression (26) defining C_{jk}. Hence the contributions of like atoms to the mean square are enhanced by a factor 9/4 as compared with those of unlike ones, apart from any allowances for diversity in magnitude of the g-factor or of the spin quantum number. This greater effectiveness of coupling between like atoms has its physical origin in resonance, and is expressed mathematically by the irrelevance of more terms of the Hamiltonian when the atoms are unlike.

(b) Exchange interaction between unlike atoms tends to broaden absorption lines. This prediction is a consequence of the fact that the definition (26) of C_{jk} includes a term involving the exchange coefficient $\tilde{A}_{jk}$, whereas that (6) of B_{jk} does not. Hence exchange coupling between dissimilar atoms, unlike that between similar ones, contributes to the mean square broadening (28). This diversity in behavior has arisen because $\tilde{A}_{jk}\mathbf{S}_j \cdot \mathbf{S}_k$ commutes in matrix multiplication with the x component of moment $S_x = \Sigma_k S_{xk}$, whereas $\tilde{A}_{jk} S_{zj} S_{zk'}$ does not.

(c) Both dipolar and exchange interactions between atoms of the primed system contribute to the fourth, but not to the second moment.

This one sees from the presence in (29), but absence in (28), of terms containing $A_{j'k'}$. The definition (6) of $A_{j'k'}$ includes both dipolar and exchange members. Hence there will be a narrowing effect and deviations from the Gaussian structure, in case either the exchange or dipolar interaction between the primed atoms is sufficiently large compared to the dipolar coupling between unprimed atoms, and also to both the exchange and dipolar interactions between unlike atoms.

(d) Exchange interaction between the unprimed atoms does not contribute to the second moment, but enhances the fourth moment, even if the dipolar broadening is caused primarily by interplay between unlike rather than exclusively unprimed atoms, i.e., by the addition of "foreign atoms." This statement expresses the presence in (29) of terms of the form $A_{jk}^2 C_{jl'}^2$, which will be more important than those of the form $A_{jk}^2 B_{jl}^2$ in (21), if $\Sigma_{k'} C_{jk'}^2 \gg \Sigma_k B_{jk}^2$.

A distinction should be noted between effects (a), (b) and (c), (d). Namely, (a), (b) are both operative on the mean square, and do not necessarily imply that the Gaussian assumption is a bad one. On the other hand, (c), (d) involve mechanisms influencing only the fourth and higher moments, and hence are consequential only if there are significant deviations from the Gaussian distribution.

Exchange integrals involving nuclear spins are presumably negligible. Hence only item (a) is of interest in experiments on nuclear resonance in materials devoid of any electronically paramagnetic atoms. A possible, but infrequently occurring exception is that the dipolar mechanism in (c) might make the broadening smaller than one would compute from (a) with the Gaussian hypothesis if the nuclei of the "foreign" atoms, i.e., those of the primed system not responsible for the resonance, are numerous and also have g-factors or spins materially greater than those of the primary (unprimed) atoms. Effect (b) of consequence only if both components have electronic spin.

Items (a) and (c) are of particular interest in case experiments are made on the broadening of nuclear resonance lines by the addition of a relatively small number of foreign atoms with electronic spin. Then g'/g is of the order 10^3,

TABLE I. Calculated and observed r.m.s. frequency deviations in CaF_2.[*]

Direction	$\Delta\nu_2$(calc.)	$\Delta\nu_2$(calc.)	$\Delta\nu_2$(obs.)
100	14.4 kc	3.60 gauss	3.68 ± 0.20 gauss
110	10.0	2.24	2.25 ± 0.20
111	6.1	1.53	1.77 ± 0.20

[*] The experimental measurements are by Pake and Purcell.

and Eq. (28) shows that, as one would guess, the foreign atoms will begin to influence the width of the absorption line when they are about 10^{-6} as abundant as the atoms responsible for the nuclear resonance. The broadening influence of the impurity will, however, be somewhat smaller than one would expect by simple extension of the formulas for a one-component system. In the first place, as already mentioned, the diversity in the definitions (6) and (26) of B_{jk} and C_{jk} diminishes the second or foreign part of (28) by a factor 4/9 compared to what one would expect by extrapolation of the first part. Far more important, however, is the fact that, as soon as the impurity becomes abundant enough to influence the line shape, the dipolar, not to mention the exchange, coupling between the foreign atoms enhances the fourth moment very materially, and hence makes the effective line-breadth considerably less than one would calculate from the mean square with the Gaussian hypothesis. One's first reaction is perhaps that any dipolar interaction between the foreign atoms is a higher order effect because of their unabundance. We have seen that only a small amount of paramagnetic impurity is needed to influence the mean square breadth of the nuclear resonance. Inspection of the structure of (29), however, shows that the dipolar coupling between the foreign or primed atoms yields contributions to the fourth moment of the order $(N'/N)^2 g^2 g'^6/d^{12}$, as compared with terms of the order $(N'/N)^2 g^4 g'^4/d^{12}$ from the square of the contribution of the foreign atoms to the mean square. (Mathematically, this statement is a consequence of appearance of terms of the form $A_{k'l'}{}^2 C_{jk'}{}^2$ coordinately with those of the form $C_{jk'}{}^2 C_{jl'}{}^2$ in the sum of type $\Sigma_j \Sigma_{l'>k'}$ in (29), and by definitions (6) and (28) one has $|A_{k'l'}| \sim (g'/g)|C_{jk'}|$ if $\bar{A}_{k'l'}=0$.) The dipolar interaction between the impurity atoms hence necessarily makes the line shape non-

Gaussian if they are abundant enough to be the main broadening agency.

V. COMPARISON WITH EXPERIMENT

As yet, the experimental data available to test our theory are rather meager. However, the rapid development of radiofrequency and microwave spectroscopy leads us to expect greatly enhanced evidence in the future.

Diamagnetic Crystals with One Type of Nuclear Spin. The simplest case theoretically is that of a crystal with a single variety of nuclear spin, and devoid of any electronic paramagnetism. Since we have assumed throughout that the influence of the crystalline field is negligible, it is essential that the nuclei be devoid of quadrupole moments unless the field is cubic. Otherwise a significant part of the broadening may be caused by the interaction of the quadrupole moment with the crystalline electric field. (A crystalline field which is of cubic symmetry will not, however, interact with a nuclear quadrupole moment.)

If there are no quadrupolar complications, the broadening of the resonance line should be due solely to the dipolar coupling between the nuclear spins, inasmuch as exchange forces involving nuclear spins are negligible. The mean square deviation of the frequency from its central value should then be computable from (13).

Calcium fluoride is a crystal *par excellence* for testing the theory of pure dipolar broadening mentioned in the preceding paragraph. The only spin is that of the fluorine nucleus, and the fluorine nuclei are arranged in a simple cubic lattice. Furthermore, the spin of the F nucleus is $\frac{1}{2}$, so that there can be no complications arising from quadrupole moments. The nuclear resonance absorption by a single crystal of CaF_2 has been measured by Purcell, Bloembergen, and Pound.[7]

The directional effects are most simply tested in a preliminary way by study of the variation of the peak absorption at the center of the line when the orientation of the magnetic field relative to the principal axes of the crystal is changed. The peak is easier to measure than the breadth,

[7] E. M. Purcell, N. Bloembergen, and R. V. Pound, Phys. Rev. 70, 988 (1946).

and exhibits the salient features of the directional trends. With the Gaussian assumption (15), the peak absorption should be inversely proportional to the r.m.s. line breadth, and so should have an angular factor which is the square root of the reciprocal of that given in (13). The angular dependence calculated on this basis when the magnetic field is rotated through various positions in the 110 plane is shown by the dashed line in Fig. 2, taken from the paper by Purcell, Bloembergen, and Pound. The measured peak absorption is shown by the solid line. The constant of proportionality is determined so as to give agreement in the 001 direction.

On the whole, the accord between theory and experiment in Fig. 2 is satisfying. Exact agreement cannot be expected, since the Gaussian assumption on which the theoretical curve is predicated is not rigorous. Since, experimentally, only the relative rather than absolute values of the peak absorption are known, measurements of the type shown in Fig. 2 do not provide a test of the calculated absolute magnitude of the line breadth.

In order to examine the absolute value of the width, and in order to study its directional dependence in a refined fashion not contingent on the Gaussian hypothesis, the r.m.s. width has recently been directly determined experimentally for three angles by Pake and Purcell.[8] The ingenious technique which they employed is described in the following paper; it involves a quite accurate determination of the line shape, so that the various points on the absorption curve can be weighted in accord with their r.m.s. frequency deviation and integrated. The comparison of theory and experiment is given in Table I. In making this comparison we follow the customary practice of expressing the frequency in terms of the magnetic field which will produce a Zeeman shift equal to the frequency interval in question. We also, however, include the values of the theoretical line widths in kilocycles. The abbreviated notation $\Delta\nu_n$, used in Table I and the ensuing discussion, has the significance $\Delta\nu_n = (\langle\Delta\nu^n\rangle_{Av})^{1/n}$.

Pake and Purcell have pushed the comparison of theory and experiment a step further by

[8] G. Pake and E. M. Purcell, Phys. Rev. **74**, 1184 (1948).

measuring the root mean fourth frequency deviation for the 100 direction. The observed value of the ratio $\Delta\nu_4/\Delta\nu_2$ is 1.24; our theory gives 1.25. The rectangular, triangular, and Gaussian approximations to the line shape would yield ratios 1.158, 1.245 and 1.316.

The agreement is certainly gratifying, especially when it is recalled that no undetermined constants are involved. Still, the good accord cannot be regarded as too much of a surprise, for, theoretically, in an ideal crystal one cannot envisage any important mechanism for broadening other than the dipolar one, whose moments we calculate rigorously. We believe that our example of CaF_2 is the first case of a substance, either solid or gaseous, where it has been possible to make an unambiguous comparison of a theoretical and observed line breadth with a high degree of accuracy.

It is to be emphasized that in Table I we compared the theoretical value of the r.m.s. frequency deviation with the same quantity observed experimentally, and not with half the frequency difference between the points of maximum slope in the absorption curve. For a Gaussian curve, $\frac{1}{2}\Delta\nu_{m.sl.}$ and $\Delta\nu_2$ would be identical. The observed values of $\frac{1}{2}\Delta\nu_{m.sl.}$, *viz.*, 4.4, 3.5, and 2.4 gauss for the 100, 110, and 111 directions are considerably higher than $\Delta\nu_2$. This fact shows that the Gaussian model is not an accurate one. In the 100 direction, the ratio $\frac{1}{2}\Delta\nu_{m.sl.}/\Delta\nu_2$ is 1.22. This value is reasonable; it
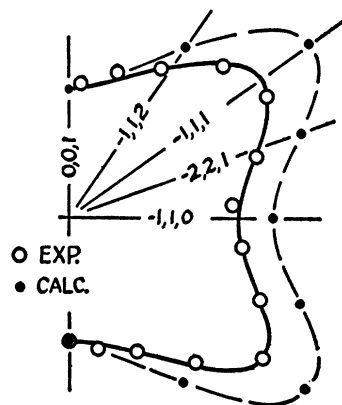

FIG. 2. Peak absorption intensity as a function of direction in a CaF_2 crystal. The solid curve gives the measurements of Purcell, Bloembergen, and Pound. The dashed curve is calculated from the theoretical r.m.s. breadth, under the assumption that the lines are Gaussian.

is a little nearer the ratio 1.0 for a Gaussian shape than that 1.73 for a rectangular one. The ratio $\Delta\nu_4/\Delta\nu_2$ of root mean fourth to root mean square frequency deviation was likewise intermediate between the Gaussian and rectangular models, but somewhat closer to the former.

We saw in Section III that the deviations of the fourth moment from the Gaussian value should be smaller for the 111 than the 100 direction. It is tempting to examine whether this fact will explain the somewhat different angular variation of the peak intensity in Fig. 2 than that provided by the Gaussian model. The corrections calculated on this basis, however, operate in the wrong direction. A rectangle has a value of peak intensity lower by a factor $(\pi/6)^{\frac{1}{2}}$ than that for a Gaussian curve of the same $\Delta\nu_2$. Thus the greater deviations from the Gaussian shape in the 100 direction would tend to increase, relatively, the prongs of the dotted curve in Fig. 2 in the 111 orientation. Dr. Pake tells us that probably the discrepancy in Fig. 2 is to be explained in terms of the fact that the crystal is not ideal. The mean square frequency deviation is considerably smaller for the 111 direction than for other nearly adjacent orientations, and the peak absorption higher. Hence, if the crystal is not perfectly cut, what one thinks is the 111 axis is not really this, but a sort of mixture of nearby directions. As a result, the measured value of $\Delta\nu_2$ for supposedly the 111 axis may be too high, and the peak absorption too low, in accord with the trend in Table I and Fig. 2. The estimates of experimental error in Table I relate to the uncertainty in the integration to obtain the root mean deviation; they do not include any error caused by crystal imperfections. The good agreement for the 111 and 110 directions suggests that the error attendant to the integration has been overestimated. The existence of crystalline imperfections does not immediately explain why the ratio $\frac{1}{2}\Delta\nu_{m.sl.}/\Delta\nu_2$ actually has a value (1.36) for 111 greater than that (1.22) for 100. The closer validity of the Gaussian model, which gives unit ratio, for the 111 direction would offhand suggest that even with crystal imperfections a trend should be expected which is the reverse of the observed. However, the value of $\Delta\nu_{m.sl.}$ is sensitive to small perturbations, and the maximum slope of the curve may well come from a spurious wing contributed by a microcrystal not perfectly aligned.

Diamagnetic Crystals with Two Types of Nuclear Spins. In paragraph (a) of Section IV it was pointed out that, because of less resonance, dipolar coupling between nuclei of unequal g-factors is less effective in broadening the lines than the corresponding dipolar interaction between like nuclei of comparable magnetic moment (more accurately, of magnetic moment equal to the geometric mean of that of the two dissimilar components). Unpublished work of G. Pake on the fluorine resonance in KHF_2 confirms this prediction. The second moment has not been measured with as high precision as in CaF_2. However, his data show clearly that without the theoretical reduction factor 4/9 caused by the dissimilarity of the moments in the H-F interactions, the calculated second moment would be much too high to agree with observation. (X-ray measurements do not fix the positions of the H atoms, but chemical and other evidence indicates that they are on lines connecting F nuclei; if H is midway on an $F-F$ line the calculated moment is too high without the reduction factor; it is increased further if the proton is not at the midpoint but instead resonates between two unsymmetrical locations.)

Nuclear Resonance in Crystals with Paramagnetic Impurities. If atoms with electron spin are added to an otherwise diamagnetic crystal, but not to so great an extent that electronic absorption masks the nuclear, then the nuclear resonance lines should be widened. However, the discussion at the end of Section IV shows that the action of both the exchange and dipolar forces connecting electronic spins make the effective half-width much smaller than that calculated from the second moment on the assumption of a Gaussian distribution. Unfortunately, no adequate data are yet available to test the theory on this subject. Bloembergen, Purcell, and Pound do indeed find that the widening of nuclear resonance lines in diamagnetic *liquids* by the addition of paramagnetic ions is smaller than the Gaussian model would lead one to expect. These authors, however, show that this behavior is explicable on the grounds that the paramagnetic ions migrate rapidly in the liquid, thus

diminishing the coherence and effectiveness of the dipolar forces coupling together nuclear and electronic spins. Thus there are two alternative mechanisms, both of which appear adequate to explain why paramagnetic impurities are not more potent in widening nuclear resonance lines in liquids. Probably the Bloembergen-Purcell-Pound migration effect is the dominant factor, for reasons to be discussed near the end of Section VI. The migration mechanism would not be relevant if the measurements were made on crystals rather than liquids, and so experiments are obviously desirable on nuclear resonance of crystals with paramagnetic atoms substituted for diamagnetic in a small percentage of the lattice points.

Absorption Arising from Electronic Spin in Paramagnetic Crystals. A number of experiments[9, 10] have been performed by now at various laboratories on resonance absorption by electron spin in paramagnetic crystals. In several instances, the line breadth is considerably smaller than one would calculate from dipolar broadening alone if one makes the Gaussian hypothesis and so uses Eqs. (14) and (16). Some examples are given in Table II. These discrepancies are, we believe, to be attributed to the phenomenon of "exchange narrowing," of which the theory was developed in Section III. We there showed that exchange interactions between atoms with electron spins makes the mean fourth power frequency deviation considerably larger than one would calculate with the Gaussian hypothesis from the mean square broadening caused by dipolar interaction, and that consequently the lines are more peaked and so effectively narrower than one would at first expect.

In connection with Table II it should be noted that part of the line broadening may originate in other causes than the dipolar mechanism. In particular, the crystalline Stark effect has a widening action in manganous salts, as does anisotropy in the g-factor in the cupric salts, whose effect we shall discuss elsewhere.[11] The broadening caused by this anisotropy is proportional to the magnitude of the applied

TABLE II. Approximate observed values of the width between the points of half the maximum absorption, contrasted with the values calculated from dipolar coupling under the assumption that the curve has a Gaussian shape.

	$\Delta\nu_{\frac{1}{2}}$ Observed*	$\Delta\nu_{\frac{1}{2}}$ Calculated
$CuCl_2 \cdot 2H_2O$	125 gauss	750 gauss
$CuSO_4 5H_2O$	175	475
$MnSO_4 4H_2O$	400	1500
$MnSO_4$	300	3500

* See references 9 and 10.

field, and hence can be reduced by using rather low resonant frequencies. Hence in an endeavor to eliminate as much as possible all but dipolar broadening, we give in Table II the half-breadths for copper furnished by the measurements of Zavoisky[9] at 200 cm, rather than the larger ones yielded by the data of Cummerow and Haliday,[10] also Arnold and Kip,[12] at about 3 cm.

When it is taken into account that other factors besides dipolar coupling may be responsible for some of the line width, the need of invoking the exchange effect to reduce the dipolar broadening becomes even more patent.

An additional piece of evidence may be mentioned in favor of the basic correctness of our model of "exchange narrowing." Exchange forces are relatively short-range, and so should be an effective factor only in materials with a fairly high concentration of magnetic ions. Actually, only in such compounds do the measured line widths prove conspicuously lower than those computed under the assumption of a Gaussian distribution. Glaring discrepancies such as those reported in Table II do not appear for the alums, with their many water molecules of hydration. Also, in Table II, the anhydrous salt $MnSO_4$ shows the greatest disparity between experiment and the Gaussian theory. Precisely this behavior is to be expected, since with no waters of coordination the paramagnetic ions will be closer together, and the "exchange narrowing" consequently greater.

Non-Resonant Paramagnetic Absorption at Low Frequencies. A number of experiments have been performed in Holland by Gorter and others[13] on

[9] E. Zavoisky, J. Phys. U.S.S.R. 10, 170, 197 (1945).
[10] R. L. Cummerow, D. Haliday, and G. E. Moore, Phys. Rev. 70, 433 (1946), 72, 1233 (1947).
[11] For preliminary abstract see Phys. Rev. 73, 1249 (1948).

[12] R. D. Arnold and A. F. Kip, Phys. Rev. to be published; abstract in 73, 1247 (1948).
[13] For a survey of this subject, and references, see Gorter's book, *Paramagnetic Relaxation* (Elsevier Publishing Company, Inc., Amsterdam and New York, 1947).

absorption at low frequencies, either in the absence of a magnetic field, or in a weak field comparable with the dipolar interaction. Here again there is evidence for "exchange narrowing" inasmuch as in magnetically concentrated materials the line breadth turns out less than that calculated by a Gaussian treatment of the dipolar effect. This subject has been briefly discussed in a letter to the editor by Gorter and the writer,[14] and we shall not pursue it here since the present paper aims to treat primarily resonant absorption wherein the Zeeman frequency is much greater than the line width. The adaptation of the mathematical methods used in the present paper to the non-resonant, low frequency case will be made in a future paper by Miss Wright.

VI. RELATION TO THE RELAXATION THEORY OF BLOEMBERGEN, POUND, AND PURCELL

A very interesting explanation of nuclear absorption and relaxation phenomena in gases, liquids, or in solids with molecular rotation has been presented by Bloembergen, Pound, and Purcell.[2] These authors point out that the migrations of atoms in fluids change the distances between spins and also the orientations of the axes connecting them. In molecular solids collisions alter the orientations of the molecular axes and hence of spin-spin axes if the molecule involves more than one spin. All these factors spoil the coherency of the action between the different electron spins, and so make the perturbing effect of the dipolar coupling in broadening the lines less than one would compute from the Gaussian model. As Gorter[14] has noted, the mechanism presented in the present paper has considerable analogy to that employed by Bloembergen, Pound and Purcell, provided that in our case we regard the coherency as spoiled by spin waves rather than collisions or migrations. It is well known that exchange, as well as dipole interaction, has the effect of making the spatial components of individual spins cease to be constants of the motion, and gives rise to a continual turning over of spins, which can be envisaged as waves of spin reversal being propagated through the crystal. Bloch showed that at low tem-

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

peratures this wave picture can be taken literally; at higher temperatures, the term "spin wave" is to be construed only in a generalized sense as meaning that the spins are in a constant state of upheaval because of the exchange forces. It is for this reason that exchange narrows the lines.

The calculation of the fourth moment can be given in rather general terms so as to apply to fluids. We shall show that the results of Bloembergen, Pound, and Purcell,[2] can be interpreted in terms of our moment criteria. Let q symbolize the coordinates other than spin variables which are involved in the dipolar potential. The q's then specify the orientation of the line joining two dipoles, and their distance of separation. The complete Hamiltonian function of the mechanical system will include a portion $\mathcal{3C}_2$ which commutes with the total spin moment responsible for the resonance, but which does not commute with the q's. For example, $\mathcal{3C}_2$ might be the intermolecular coupling which reorientates molecules at collisions, or even simply the translational kinetic energy associated with the migrations of ions. Then a sort of relaxation time for a variable q may be defined by

$$\frac{1}{\tau_c{}^2} = \frac{\mathrm{Tr}[\mathcal{3C}_2 q - q\mathcal{3C}_2]^2}{-\hbar^2 \mathrm{Tr} q^2}. \qquad (30)$$

This quantity τ_c is essentially the same as that which Bloembergen, Pound, and Purcell denote by the same letter. If $\mathcal{3C}_2$ is large compared with the dipolar part of the Hamiltonian, or, more precisely, if $1/\tau_c{}^2 \gg \langle \Delta \nu^2 \rangle_{Av}$, then the mean fourth power deviation as calculated from (17) and (19) will be of the order

$$\langle \Delta \nu^4 \rangle_{Av} = \langle \Delta \nu^2 \rangle_{Av} / \tau_c{}^2. \qquad (31)$$

According to the theory of Bloembergen, Pound, and Purcell, the half-width will be materially lower than $[\langle \Delta \nu^2 \rangle_{Av}]^{\frac{1}{2}}$ if $1/\tau_c{}^2 \gg \langle \Delta \nu^2 \rangle_{Av}$. Inspection of (31) shows that this is precisely the condition that the fourth moment appreciably exceed the Gaussian value $3[\langle \Delta \nu^2 \rangle_{Av}]^2$. Both approaches, i.e., the relaxation and moment methods, thus agree as to the conditions under which narrowing phenomena should appear.

Instead of thus applying moments to fluids, one can, vice versa, try to adapt qualitatively the relaxation theory to spin waves in crystals. In

this fashion one can obtain an estimate of the order of magnitude of the half-width when exchange narrowing is important—something we could not do by the method of moments. According to the theory of Bloembergen, Pound, and Purcell, the half-width is of the order $\tau_c \langle \Delta \nu^2 \rangle_{Av}$ if $1/\tau_c{}^2 \gg \langle \Delta \nu^2 \rangle_{Av}$. As applied to our problem of spin interaction, the variables q must be considered as including functions of the spin coordinates, and the Hamiltonian $\mathfrak{K}_2$ symbolizes the exchange energy. The relaxation time for the spin waves furnished by (30) is then of the order $h/\tilde{A}$, where $\tilde{A}$ is the exchange integral. Analogy to the relaxation theory thus suggests that the effective half-width is of the order $h \langle \Delta \nu^2 \rangle_{Av}/\tilde{A}$. Too much reliance, especially quantitatively, should not be placed on this estimate, as it is derived in a rather superficial way, and conveys little more information than one might conjecture from dimensional considerations.

The action of the spin waves associated with exchange forces only influences energy transfers internal to the spin system, and so does not help in securing thermal equilibrium between this system and the rest of the universe. In this respect there is a difference between the adaptation of the relaxation theory to the spin system, and its original use in connection with atomic migrations. With the latter, energy balance is secured by energy transfer between the spin system and the translations or rotations of atoms or molecules, which thus serve as a thermostat if the relaxation time τ_1 for this transfer is sufficiently short. If τ_c is small enough to permit applicability of (31), $1/\pi \tau_1$ should be comparable with the half-width $\Delta \nu_{\frac{1}{2}}$ of the absorption line and of the order $\langle \Delta \nu^2 \rangle_{Av} \tau_c$. In the experiments of Bloembergen, Pound, and Purcell on nuclear resonance in liquids with paramagnetic impurities, it is found that $\Delta \nu_{\frac{1}{2}}$ as measured by direct observation of the line width is very nearly equal to $1/\pi \tau_1$ when τ_1 is determined by measurements of incipient saturation or departures from thermal equilibrium caused by use of excessive power. This fact suggests that the narrowing of nuclear resonance lines in liquids is caused primarily by migration effects, for one would expect to have $1/\tau_1 \ll \Delta \nu_{\frac{1}{2}}$ if the narrowing were due mainly to dipolar or exchange coupling between paramagnetic ions as suggested in paragraph (c) of Section IV. In monatomic crystals, on the other hand, $1/\tau_1$ is millions of times smaller than $\Delta \nu_{\frac{1}{2}}$, and then our adiabatic calculation of the line breadth is well warranted.

In closing, it should be stressed once more that the theory of dipolar broadening of resonance lines in crystalline solids as developed in the present paper is entirely an adiabatic one, regardless of whether there are modulations by exchange forces. Our calculations thus throw no light on the mechanism which keeps the spin system in thermal equilibrium with the rest of the universe in crystals.