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# Theory of Line Narrowing by Double-Frequency Irradiation*

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Starting from the general equation for the distribution matrix, magnetic resonance absorption in crystals is treated by introducing the Fourier transform of the resonance line which is shown to have the convenient form of a simple trace. The method is first applied to rederive some earlier results of Van Vleck, concerning the moments of the line. It is then extended to include the case of the following experimental paper, where resonance absorption of one magnetic ingredient is observed while another magnetic ingredient is at the same time subjected to a strong resonant rf field. It is shown that the absorption line exhibits a center line and faint sidebands, and formulas for the intensity and shape of these lines are developed. In particular, it is shown that the total second moment of the absorption is unaltered by irradiation of the other ingredient. A quantitative measure for the observed narrowing of the center line is found through the reduction of its second moment, which is compensated by the contribution of the sidebands to the total second moment.

## 1. INTRODUCTION

THE rigorous analysis of the dipolar broadening of nuclear magnetic resonance lines in crystals represents a formidable mathematical problem. Even in external magnetic fields, strong enough to permit treatment of the dipolar energy as a small perturbation in comparison to the Zeeman energy, one deals with a secular problem where the matrices have a rank determined by the extremely high degeneracy of the unperturbed system. The greatly simplifying restriction to the lowest energy levels, which permits a treatment of the somewhat analogous problem of ferromagnetism near saturation,[1,2] is here not applicable under normal experimental conditions since they are so far from those of complete saturation that all the greatly numerous energy levels of the system are of practically equal importance. Van Vleck[3] has made a significant contribution to the problem by showing that one can nevertheless obtain quantitative information if one foregoes the attempt to calculate the detailed shape of resonance lines, but, instead, restricts oneself to compute their various moments. The very lowest moments are of the greatest practical importance since the complexity of the computation, as well as the difficulties of an experimental determination, increases very rapidly for the higher moments.

It is shown in the following paper, by Sarles and Cotts, that the dipolar broadening of a resonance line can be modified by choosing the applied alternating field to cause rapid changes in the orientation of the nuclear moments pertaining to another magnetic ingredient in the crystal. The following analysis of this effect will be carried out by a suitable adaptation of Van Vleck's method. In order to clarify the various simplifying assumptions of the method, the theory of relaxation, recently presented by the author,[4] will be used as a starting point. It will first be applied to the single resonances, considered by Van Vleck, before generalizing the treatment to include the discussion of experiments with double resonance, reported in the following paper.

## 2. GENERAL EQUATIONS AND NOTATIONS

It has been shown that the behavior of a general spin system can be derived from the distribution matrix $\sigma$, satisfying the equation[5]

$$d\sigma/dt+i[E,\sigma]=\Gamma(\sigma). \tag{1}$$

$E$ represents the total energy of the spin system, divided by $\hbar$, and can be written here as

$$E=B+C+D, \tag{2}$$

where the first part represents the Zeeman energy, determined by the external constant magnetic field $H_0$; the second, the dipolar energy; and the third, the contribution due to external alternating magnetic fields.[6] The term on the right side of Eq. (1) originates from the coupling of the spin system to the lattice, which acts as a heat reservoir at a given temperature. The presence of such a term is evidently required to account both for thermal relaxation and for a finite absorption of the spin system, but for the purposes of this paper it is sufficient to note that, besides being linear in $\sigma$, it should be regarded as being exceedingly small. Indeed, its order of magnitude is given by the inverse of the thermal relaxation time $T_1$, which may be assumed to be of the order of several seconds or even considerably

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[1] F. Bloch, Z. Physik **61**, 206 (1930); **74**, 295 (1932).

[2] F. J. Dyson, Phys. Rev. **102**, 1217 (1956).

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

[4] F. Bloch, Phys. Rev. **102**, 104 (1956); **105**, 1206 (1957). These two papers will be referred to as "II" and "III," respectively.

[5] Equation (2.56) in III; the small corrections Δ and Γ appearing in this equation are here omitted since they are negligible with respect to the principal part $E$, used in Eq. (2) of this paper.

[6] This notation is the same as of Eq. (4.1) in II; the coupling term $C$, however, does not have the form, given by Eq. (4.7) in II which is appropriate for liquids, but is to be replaced by that arising from the interaction of dipoles in fixed positions.

longer.[7] On the other hand, the width of the observed absorption lines is of the order of 10 kilocycles and is a measure for the magnitude of the dipolar term $C$ in Eq. (2). Compared to this term, that of the right side of Eq. (1) should thus be considered to have a relative order of magnitude of $10^{-4}$ or less.

Considering first a single magnetic ingredient of nuclei with spin $I$ and gyromagnetic ratio $\gamma$, the spin vector operator for a given nucleus $j$ will be denoted by $\mathbf{I}_j$. Choosing the $z$ component in the direction of the constant field, the components of $\mathbf{I}_j$ will be replaced by three operators $I_j^\lambda (\lambda=-1,0,1)$ which are related to the components of the vector $\mathbf{I}_j$ by the equations,

$$I_j^0=(I_j)_z; \quad I_j^{\pm 1}=(I_j)_x \pm i(I_j)_y, \tag{3}$$

and which satisfy the commutation rule[8]

$$[I_j^\lambda, I_k^\tau]=(-1)^{\lambda+\tau}(\lambda-\tau)I_j^{\lambda+\tau}\delta_{jk}\cdot(\lambda,\tau=-1,0,1). \tag{4}$$

Following the notation of Van Vleck[3] in the case of a second ingredient with nuclei of spin $I'$ and gyromagnetic ratio $\gamma'$, the spin vector operator of a given nucleus $j'$ of this ingredient will be denoted by $\mathbf{I}_{j'}$. The definition and commutation rules of the corresponding operators $I_{j'}^\lambda$ are obtained by replacing, in Eqs. (3) and (4), $j$ by $j'$ and $k$ by $k'$; any two operators, of which one has a primed, the other an unprimed lower index, commute of course with each other. It is finally useful, for further purposes, to introduce the total spin operators

$$I^\lambda=\textstyle\sum_j I_j^\lambda \quad (\lambda=-1,0,1), \tag{5}$$

for one ingredient and $I'^\lambda$ in case of a second ingredient, obtained by replacing $j$ by $j'$ in Eq. (5). With these notations, the Zeeman part $B$ of Eq. (2) can then be written in the form

$$B=-\omega_0 I^0, \tag{6a}$$

in the presence of one ingredient and

$$B=-\omega_0 I^0-\omega_0' I'^0, \tag{6b}$$

in the presence of two ingredients with

$$\omega_0=\gamma H_0, \quad \omega_0'=\gamma' H_0. \tag{7}$$

The dipolar part $C$ of Eq. (2) will, for a single ingredient, be written in the form,

$$C=\sum_{j<k} C_{jk}, \tag{7a}$$

where

$$\hbar C_{jk}=\hbar^2\gamma^2[r_{jk}^{-3}(\mathbf{I}_j\cdot\mathbf{I}_k)-3r_{jk}^{-5}(\mathbf{r}_{jk}\cdot\mathbf{I}_j)(\mathbf{r}_{jk}\cdot\mathbf{I}_k)] \tag{8}$$

represents the well-known interaction energy of two magnetic dipoles $j$ and $k$ with moments $\boldsymbol{\mu}_j=\hbar\gamma\mathbf{I}_j$ and $\boldsymbol{\mu}_k=\hbar\gamma\mathbf{I}_k$, respectively, separated from each other by the radius vector $\mathbf{r}_{jk}$ with magnitude $r_{jk}$. Using the operators defined in Eq. (3), one has

$$C_{jk}=\sum_{\lambda,\tau} c_{jk}^{\lambda\tau} I_j^\lambda I_k^\tau, \tag{9}$$

where the summation extends over the values $-1$, 0, 1 of $\lambda$ and $\tau$ and where the coefficients $c_{jk}^{\lambda\tau}$ are readily obtained by introducing in Eq. (8) the operators $I_j^\lambda$ for the nucleus $j$ defined by Eq. (3), and the corresponding operators $I_k^\tau$ for the nucleus $k$.[9] Since $C_{jk}$ is a Hermitian operator, the coefficient $c_{jk}^{-\lambda-\tau}$ is conjugate complex to $c_{jk}^{\lambda\tau}$.

In the presence of a second ingredient, one has, instead of (7a),

$$C=\sum_{j<k} C_{jk}+\sum_{j'<k'} C_{j'k'}+\sum_{jk'} C_{jk'}, \tag{7b}$$

with the same significance of Eqs. (8) and (9) for primed as for unprimed indices and with the replacement of $\gamma^2$ in Eq. (8) for the second term of Eq. (7b) by $\gamma'^{,2}$ for the third by $\gamma\gamma'$.

To obtain the part $D$ of Eq. (2) it will be assumed, in the case of a single ingredient, that the applied alternating field contains only a single frequency $\omega_1$ in the vicinity of the resonance frequency $\omega_0$. Its effect upon the nuclei can be described, in the customary manner, by that of a rotating field of magnitude $H_1$ with an $x$- and $y$-component, given by $H_1\cos\omega_1 t$ and $-H_1\sin\omega_1 t$, respectively. With the notations (3) and (5) one then has

$$D=-h_1(I^1 e^{i\omega_1 t}+I^{-1}e^{-i\omega_1 t}), \tag{10a}$$

with

$$h_1=\gamma H_1/2. \tag{11a}$$

In order to treat the case of double-resonance in the case of two ingredients, the alternating field will be assumed to contain, besides the frequency $\omega_1$, a second frequency $\omega_2$ in the vicinity of the resonance frequency $\omega_0'$ of the second ingredient. Because of the presence of an additional rotating field of magnitude $H_2$ and frequency $\omega_2$, one has therefore in this case

$$\begin{aligned} D=&-h_1(I^1 e^{i\omega_1 t}+I^{-1}e^{-i\omega_1 t}) \\ &-h_1'(I'^1 e^{i\omega_1 t}+I'^{-1}e^{-i\omega_1 t}) \\ &-h_2(I^1 e^{i\omega_2 t}+I^{-1}e^{-i\omega_2 t}) \\ &-h_2'(I'^1 e^{i\omega_2 t}+I'^{-1}e^{-i\omega_2 t}), \end{aligned} \tag{10b}$$

where the first and second terms on the right side con-

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[7] For the NaF crystal of the following paper [L. R. Sarles and R. M. Cotts, Phys. Rev. **111**, 853 (1958)], $T_1 \cong 1$ sec; since the thermal relaxation is here primarily due to the presence of paramagnetic impurities one can expect to find increasingly larger values of $T_1$ for higher purity of the crystal. In the case of relatively pure single crystals of LiF, one observes in fact thermal relaxation times which are of the order of several minutes and which would probably be even longer if the amount of paramagnetic impurities could be further reduced.

[8] Apart from expressing the fact that the spin operators of different nuclei $j$ and $k$ commute, this form of the commutation rule for $j=k$ can be readily verified, in virtue of Eq. (3), to be equivalent to the customary form $[I_x,I_y]=iI_z$ and its cyclical permutations.

[9] These coefficients appear explicitly in Van Vleck's Eq. (2), reference 3, where instead of the above notation $I^0$, $I^1$, $I^{-1}$, spin operators are denoted by $S_z$, $S^+$, $S^-$, respectively.

tain the action upon the primed and unprimed ingredient, respectively, of the field with frequency $\omega_1$, the third and fourth term that of the field with frequency $\omega_2$, and where

$$h_1=\gamma H_1/2, \quad h_1'=\gamma' H_1/2, \quad h_2=\gamma H_2/2, \quad h_2'=\gamma' H_2/2. \tag{11b}$$

Either in the case of a single ingredient or of two ingredients, it will be assumed that one observes signals of frequency $\omega_1$ so that the direct experimental information concerns the resonance characteristics of the contribution $M=M_x+iM_y$ to the complex polarization which is due to the unprimed ingredient.[10] Referring to a unit volume of the crystal, it is given by

$$M=\hbar\gamma\langle I^1\rangle, \tag{12}$$

where $\langle I^1\rangle$ stands for the expectation value of the operator $I^1$, defined by Eq. (5). In view of the general manner in which the distribution matrix determines the expectation value of a spin function,[11] one obtains from a solution $\sigma$ of Eq. (1)

$$\langle I^1\rangle=\mathrm{Tr}(I^1\sigma). \tag{13}$$

As a function of time, $M$ varies under stationary conditions with the frequency $\omega_1$; besides, it will be assumed that the magnitude $H_1$ of the corresponding rf field is sufficiently small, so that only linear terms in this quantity have to be retained. The resonance of the unprimed ingredient is then characterized by measuring the complex susceptibility

$$\chi=M/(H_1e^{-i\omega_1 t})=\chi'+i\chi'', \tag{14}$$

in its dependence upon $\omega_1$ and, particularly, by the imaginary part $\chi''$ of this expression, which corresponds to absorption.

### 3. SINGLE RESONANCE WITH A SINGLE MAGNETIC INGREDIENT

The formalism, outlined in the preceding section, will be applied in this section to the simplest case, where the crystal contains a single magnetic ingredient and where the alternating field is assumed to contain only one frequency $\omega_1$, so that the three parts $B$, $C$, and $D$, on the right side of Eq. (2) are given by the Eqs. (6a), (7a), and (10a), respectively. While it will yield no results beyond those already derived by Van Vleck,[12] the treatment of this case is presented in a manner which leads up to that of double resonance to be considered in the following section.

Starting with Eq. (1), a unitary transformation will first be applied to the distribution matrix $\sigma$ whereby the transformed matrix

$$\sigma_T=T\sigma T^{-1}, \tag{15}$$

is defined by means of the transformation operator

$$T=\exp(-i\omega_1 t I^0), \tag{16}$$

and its inverse $T^{-1}$.

It can be seen[13] that the result of this transformation upon the operator $I_j^\lambda$ is given by

$$TI_j^\lambda T^{-1}=e^{-i\lambda\omega_1 t}I_j^\lambda. \tag{17}$$

Indicating from now on the result of the transformation throughout by the subscript $T$, one obtains from Eqs. (5) and (17)

$$(I^\lambda)_T=e^{-i\lambda\omega_1 t}I^\lambda \tag{18}$$

and, with the trace invariant against the transformation, from Eq. (13)

$$\langle I^1\rangle=\mathrm{Tr}(I_T{}^1\sigma_T)=e^{-i\omega_1 t}\,\mathrm{Tr}(I^1\sigma_T). \tag{19}$$

The time dependence of this quantity, just as that of the complex polarization $M$ of Eq. (12), is contained in the exponential, multiplying the trace, so that the latter has to be independent of time. To meet this requirement, it is necessary to exclude transient effects and it is further sufficient to find the stationary part of the matrix $\sigma_T$ since the operator $I^1$ is independent of the time. This suggests finding a form of $\sigma_T$ which is altogether stationary. On the other hand, it follows from Eqs. (1), (2), and (15) that $\sigma_T$ has to satisfy the differential equation

$$d\sigma_T/dt+i[E_T,\sigma_T]=\Gamma_T(\sigma_T). \tag{20}$$

By dividing the operator $E_T$ into three parts in analogy to Eq. (2), so that

$$E_T=B_T+C_T+D_T, \tag{21}$$

one can verify from Eqs. (6a), (15), and (18) that

$$B_T=\omega_1 I^0+TBT^{-1}=\Delta_1 I^0, \tag{22}$$

with

$$\Delta_1=\omega_1-\omega_0. \tag{23}$$

It is further seen from Eqs. (7a), (9), and (17) that

$$C_T=TCT^{-1}=\sum_{\lambda\tau}\sum_{j<k}c_{jk}{}^{\lambda\tau}I_j{}^\lambda I_k{}^\tau e^{-i(\lambda+\tau)\omega_1 t}, \tag{24}$$

and from Eqs. (10a) and (18) that

$$D_T=TDT^{-1}=-h_1(I^1+I^{-1}). \tag{25}$$

A rigorously stationary solution of Eq. (20) is precluded by the time dependence of $C_T$, contained in the terms with $\lambda+\tau\neq 0$ of Eq. (24). On the other hand,

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[10] In applying the results, obtained below, to those of the following paper, the unprimed and primed ingredient will consist of the nuclei of $Na^{23}$, and $F^{19}$, respectively, contained in a crystal of NaF.

[11] See Eq. (2.6) of II.

[12] Sections II and III, reference 3.

[13] The simplest proof of Eq. (17) is obtained by noting that it holds at the time $t=0$ and by verifying that, in virtue of Eqs. (4) and (5) and, hence, of the commutation rule of $I^0$ with $I_j{}^\lambda$, the equality holds for the time-derivative.

the omission[14] of these terms involves a negligible error, provided that the conditions

$$(|\Delta_1|,\ |c_{jk}{}^{\lambda\tau}|,\ |h_1|)\ll\omega_1 \tag{26}$$

are satisfied. This is indeed the case under normal experimental conditions where the constant field $H_0$ is so strong that the Larmor frequency $\omega_0=\gamma H_0$ is very large compared to the frequencies on the left side of the relation (26) which represent a measure for the effective magnitude of the operator $E_T$ of Eq. (20). The same holds in the vicinity of resonance for the frequency $\omega_1$ so that the rapid alternation of the terms with $\lambda+\tau\neq 0$ justifies their omission.[15] It is therefore permissible to substitute for the expression (24) its time average

$$A=\sum_{j<k}\left[c_{jk}{}^{00}I_j{}^0I_k{}^0+c_{jk}{}^{1-1}I_j{}^1I_k{}^{-1}+c_{jk}{}^{-11}I_j{}^{-1}I_k{}^1\right]. \tag{27}$$

Another simplification arises from the fact that $h_1$ may be considered sufficiently small so that quadratic and higher terms in this quantity may be neglected. Let

$$\sigma_T=\sigma_0+\sigma_1, \tag{28}$$

where $\sigma_0$ is the stationary solution of Eq. (20) obtained for $h_1=0$ and where $\sigma_1$ is proportional to $h_1$. Since $D_T$, given by Eq. (25), is itself linear in $h_1$, it follows to this order from Eqs. (20) and (22) with the substitution (27) for $C_T$ that a stationary solution for $\sigma_1$ has to satisfy the equation

$$[\Delta_1 I^0+A,\ \sigma_1]+i\Gamma_T(\sigma_1)=h_1[I^1+I^{-1},\ \sigma_0]. \tag{29}$$

To obtain the quantity $\sigma_0$ which appears on the right side of this equation, it is to be noted that, for $H_1=0$, the spin system is in thermal equilibrium with the lattice, so that the stationary solution of Eq. (1) can be written in the form[16] $\zeta e^{-\beta E_0}$ where $\beta=\hbar/kT$ and where $E_0$ represents the principal part of the energy of the spin system, divided by $\hbar$. In the presence of a sufficiently strong constant field $H_0$, this part is given by the Zeeman energy $B$ of Eq. (6a) and one may therefore write

$$\sigma_0=\zeta\exp(\kappa I^0), \tag{30}$$

with

$$\kappa=\beta\omega_0=\hbar\omega_0/kT, \tag{31}$$

and

$$\zeta=[\mathrm{Tr}\exp(\kappa I^0)]^{-1}. \tag{32}$$

Although this result for $h_1=0$ refers to the stationary solution of Eq. (1), it applies also to that of Eq. (20) and hence to the quantity $\sigma_0$ of Eqs. (28) and (29). Indeed, this quantity is seen to remain unchanged under the transformation (15) since the operator $T$ of Eq. (16) commutes with $\exp(\kappa I^0)$.

In order to solve Eq. (29) for $\sigma_1$, it is most convenient to choose a representation in which the quantity $A$, given by Eq. (27), is diagonal with eigenvalues $\omega_n$. This quantity can be seen to commute with the operator $I^0$, in view of the definition (5) and the relations (4), so that it is possible to assign a definite eigenvalue $m$ of $I^0$ to each of the states $n$. It follows that the quantity $\Delta_1 I^0+A$ is, in this representation, likewise diagonal with eigenvalues

$$(n|\Delta_1 I^0+A|n)=m\Delta_1+\omega_n, \tag{33}$$

as well as the quantity $\sigma_0$ of Eq. (30) with eigenvalues

$$(n|\sigma_0|n)=\zeta e^{\kappa m}. \tag{34}$$

As a consequence of the commutation relations between $I^0$ and $I^{\pm1}$, one has the selection rule that $(n|I^{\pm1}|n')$ vanishes unless the eigenvalues $m$ and $m'$ of $I^0$ for the states $n$ and $n'$, respectively, satisfy the relation $m'=m\mp1$. Disregarding, for the time being, the imaginary relaxation term on the left side of Eq. (29), one obtains therefore from this equation, together with Eqs. (33) and (34),

$$(n|\sigma_1|n')=\zeta h_1(1-e^{-\kappa})(n|I^{-1}\exp(\kappa I^0)|n')/(\omega_n-\omega_{n'}-\Delta_1), \tag{35}$$

for $m'=m+1$ and an analogous expression for $m'=m-1$, while all other matrix elements of $\sigma_1$ vanish. Since the matrix, representing the contribution $\sigma_0$ to $\sigma_T$ in Eq. (28), is diagonal, it follows further from the selection rule for $I^1$, that one can write Eq. (19) in the form,

$$\langle I^1\rangle=e^{-i\omega_1 t}\sum_{nn'}(n|\sigma_1|n')(n'|I^1|n), \tag{36}$$

and that the expression (35) may be inserted on the right side of this equation.

The relaxation term, which was temporarily neglected, can be considered to be very small and thus to have an appreciable effect upon the result (35) only if $\omega_n-\omega_n{}'$ is in the immediate vicinity of the value $\Delta_1$, given by Eq. (23). This effect can be described by adding to the denominator on the right side of (35) a term $-i\Gamma_{nn'}$ with a real and positive coefficient $\Gamma_{nn'}$, which is of the order of magnitude of the inverse thermal relaxation $T_1$ and thus according to Sec. 2, very small compared to the width of the absorption line.[17] With this correction in Eq. (35) and with Eqs. (11a), (12), (13), and (36), one obtains from Eq. (14) the complex susceptibility

$$\chi(\Delta_1)=\tfrac{1}{2}\zeta\hbar\gamma^2(1-e^{-\kappa})\sum_{nn'}(n|I^{-1}\exp(\kappa I^0)|n')\times(n'|I^1|n)/(\omega_n-\omega_{n'}-\Delta_1-i\Gamma_{nn'}), \tag{37}$$

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[14] This omission is equivalent to that of the heavy-bracketed part of the Hamiltonian in Van Vleck's Eq. (2), reference 3.

[15] Treated as a perturbation, the omitted terms yield in first approximation contributions of small amplitude to $\sigma_T$ which vary with frequencies $\omega_1$ and $2\omega_1$ and correspond to the existence of faint subsidiary absorption lines, pointed out by Van Vleck.

[16] Equation (2.35) of II and (1.1) of III.

[17] The origin of this coefficient and the proof that it must be real and positive is analogous to that of the quantity $\Gamma_{ab}$ of Eq. (3.8) in II.

with the imaginary part

$$\chi''(\Delta_1)=\tfrac{1}{2}\zeta\hbar\gamma^2(1-e^{-\kappa})\sum_{nn'}(n|I^{-1}\exp(\kappa I^0)|n')\times(n'|I^1|n)f_{nn'}(\Delta_1). \quad (38)$$

The function

$$f_{nn'}(\Delta_1)=\Gamma_{nn'}/[(\omega_n-\omega_{n'}-\Delta_1)^2+(\Gamma_{nn'})^2] \quad (39)$$

attains appreciable values only if $\Delta_1$ differs from $\omega_n-\omega_n'$ by an amount comparable or small compared to $\Gamma_{nn'}$.

In view of the smallness of this coefficient, mentioned above, it is therefore permissible to replace the function $f_{nn'}(\Delta_1)$ in (38) by a $\delta$ function, multiplied by $\pi$ for reasons of normalization, and to write[18]

$$\chi''(\Delta_1)=(\pi/2)\zeta\hbar\gamma^2(1-e^{-\kappa})\sum_{nn'}(n|I^{-1}\exp(\kappa I^0)|n')\times(n'/I^1|n)\delta(\Delta_1-\omega_n+\omega_{n'}). \quad (40)$$

This quantity determines the absorption of weak rf fields in its dependence on the applied frequency $\omega_1=\omega_0+\Delta_1$ and contains thus the complete information, both with regard to magnitude and detailed shape of the resonance absorption line. It is, however, more convenient to write it as a Fourier integral in the form

$$\chi''(\Delta_1)=K\int_{-\infty}^{+\infty}\varphi(t)e^{i\Delta_1 t}dt, \quad (41)$$

where

$$K=\tfrac{1}{4}\zeta\hbar\gamma^2(1-e^{-\kappa}). \quad (42)$$

The moments of the absorption line, defined by

$$\langle\Delta_1{}^s\rangle_{\text{Av}}=\int\Delta_1{}^s\chi''(\Delta_1)d\Delta_1\Big/\left[\int\chi''(\Delta_1)d\Delta_1\right] \quad (43)$$

are then directly obtained from the Fourier transform

$$2\pi K\varphi(t)=\int_{-\infty}^{+\infty}e^{-i\Delta_1 t}\chi''(\Delta_1)d\Delta_1, \quad (44)$$

in the form

$$\langle\Delta_1{}^s\rangle_{\text{Av}}=i^s\varphi^{(s)}(0)/\varphi(0), \quad (45)$$

where $\varphi^{(s)}(t)$ represents the $s$th derivative of the generating function $\varphi(t)$. A simple expression for this function is obtained by inserting the result (40) for $\chi''(\Delta_1)$ in the right side of Eq. (44) and using the value (42) of $K$, so that one has

$$\begin{aligned}\varphi(t)&=\sum_{nn'}(n|I^{-1}\exp(\kappa I^0)|n')(n'|I^1|n)e^{i(\omega_{n'}-\omega_n)t}\\&=\sum_{nn'}(n|I^{-1}\exp(\kappa I^0)|n')(n'|e^{iAt}I^1e^{-iAt}|n).\end{aligned}$$

The last equality is based upon the fact that the matrix, representing the operator $A$ of Eq. (27), is diagonal and has the eigenvalues $\omega_n$ and $\omega_{n'}$ in the states $n$ and $n'$, respectively. Through the rules of matrix multiplication and the definition of the trace, one obtains thus[19]

$$\varphi(t)=\mathrm{Tr}(e^{iAt}I^1e^{-iAt}I^{-1}\exp(\kappa I^0)). \quad (46)$$

As a further simplification it is permissible, under normal experimental conditions, to assume $\kappa=\hbar\omega_0/(kT)\ll 1$ and, hence, to replace the operator $\exp(\kappa I^0)$ by unity[20] so that

$$\varphi(t)=\mathrm{Tr}(e^{iAt}I^1e^{-iAt}I^{-1}). \quad (47)$$

The principal problem of evaluating $\varphi(t)$ and, hence, through Eq. (41) the function $\chi''(\Delta_1)$, resides with the time development

$$I^1(t)=e^{iAt}I^1e^{-iAt} \quad (48)$$

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[18] This procedure was used from the start by Van Vleck and its significance is intuitively clear. Nevertheless, it may be well to add some remarks in regard to the calculation of moments. According to Eqs. (38) and (39), the observed absorption line is actually to be understood as the conglomerate of very many, very narrow lines of Lorentzian shape with a negligible contribution to the absorption as soon as $\Delta_1$ is outside of the range of the frequencies $\omega_n-\omega_{n'}$, i.e., outside of the width of the observed line. However, since for large values of $\Delta_1$ this contribution decreases merely as $1/(\Delta_1)^2$, it contributes an ever-increasing amount to the second and higher even moments, the larger the range of values of $\Delta_1$ is chosen. On the other hand, this range is, in practice, restricted to a few times the observed width $w$ of the line so that the Lorentzian wings of the actual line are immaterial, provided only that the width $\Gamma_{nn'}$ of the individual lines is small compared to $w$. In fact, choosing a range $\alpha w$ with $\alpha\gg 1$ on both sides of the observed line, it is readily shown that the contribution from this origin to the $s$th moment ($s$ even) is of the relative order of magnitude $\alpha^{s-1}|\Gamma|/w$ where $|\Gamma|$ represents a weighted average of the various values of $\Gamma_{nn'}$ and may be estimated from the observed values of $T_1$ to be in our case no more than $10^{-4}w$. Thus even the choice of quite large values of $\alpha$ is permissible without noticeably affecting the values of the lower moments.

[19] While the author introduced the Fourier transform merely as a formal device, he is grateful to Dr. K. Halbach for having pointed out to him that it has a simple physical significance which permits a more direct derivation of the expression for $\varphi(t)$, given in Eq. (46). Restricting oneself to effects, linear in the applied rf field, one may in fact consider the effect of a $\delta$ pulse of the rf field at the time $t=0$ as the result of the superposition of monochromatic fields with a uniform spectrum over the frequency $\omega_1$. The quantity, given by Eq. (44), can then be interpreted as representing the signal observed at a time $t>0$. Conversely, one can integrate Eq. (1), assuming that for $t<0$ one has $\sigma=\sigma_0$, keeping for $t>0$ only terms linear in the applied rf pulse and neglecting damping effects which arise from the term $\Gamma(\sigma)$. With the use of the Eqs. (12) and (13) one is thus led to an expression for $M$ which vanishes for $t<0$ and which is proportional to $\varphi(t)$. The expression (46) for this function is obtained by the same approximation as that which leads to the replacement of $C$ by its average value $A$ and the neglected part can likewise be seen to correspond to faint subsidiary absorption lines (see reference 15). The fact that the signal, following an rf pulse, can be expressed in terms of traces of operator products, was pointed out before by I. J. Lowe and R. E. Norberg, Phys. Rev. **107**, 46 (1957), who applied it to the calculation of free induction decays in crystals.

[20] The presence of this operator in Eq. (46) indicates a temperature dependence of the line shape which, however, is normally too slight to be observable. It might seem that it could be neglected only under the far-too-stringent condition $N\kappa\ll 1$ since the range of eigenvalues of the operation $I^0$ is of the order of magnitude $N$ of the number of nuclei present in the sample. Upon writing $\exp(\kappa I^0)$ as a product of operators, pertaining to the various nuclei, it can be seen, however, that the overwhelming majority of the factors cancel out in the expression (45) for the moments so that the condition $\kappa\ll 1$ is indeed sufficient to replace the remaining ones by unity. The effect of a finite temperature upon the line shape has also been pointed out by M. H. L. Pryce and K. W. H. Stevens, Proc. Roy. Soc. (London) **A63**, 36 (1950).

of the operator $I^1$ under the influence of the dipolar Hamiltonian $\hbar A$.

To find this development is equivalent to solving the differential equation

$$dI^1(t)/dt=i[A,I^1(t)], \tag{49}$$

with the initial condition

$$I^1(0)=I^1. \tag{50}$$

Although no simple solution can be expected for arbitrary values of the time $t$, it is easy to give a power series expansion, valid for a sufficiently short time $t$.[21] Indeed, the coefficients of this expansion are directly obtained from Eq. (49), and from successive differentiations of this equation which yield the derivatives of $I^1(t)$ at the time $t=0$ in terms of the corresponding successive commutators of $A$ with $I^1$.

From the expressions (46) and (47) it is seen, for the same reason, that the derivatives of $\varphi(t)$ at the time $t=0$ and, therefore, in view of Eq. (45), the moments of the absorption line, are simply obtained in the form of traces, involving these commutators. In particular, using $\varphi(t)$ in the form given by Eq. (47) and noting the fact that the trace of an operator product does not change by a cyclical permutation of the factors, one finds, for the second moment,

$$\langle\Delta_1^2\rangle_{\text{Av}}=\text{Tr}([I^1,A][A,I^{-1}])/\text{Tr}(I^1I^{-1}), \tag{51}$$

and, for the fourth moment,

$$\langle\Delta_1^4\rangle_{\text{Av}}=\text{Tr}\{[[I^1,A],A][A,[A,I^{-1}]]\}/\text{Tr}(I^1I^{-1}), \tag{52}$$

in agreement with the corresponding expressions derived by Van Vleck.[22] While the numerator of these expressions contains the trace of even products of spin operators $I_j^\lambda$, it can be seen, since the quantity $A$ of Eq. (27) is bilinear in these operators, that all odd moments are determined by odd products and, hence, vanish identically. The absorption line is therefore symmetrical around the value $\Delta_1=0$ or, according to Eq. (23), around the point at which the frequency $\omega_1$ of the applied rf field is equal to the Larmor frequency $\omega_0$ in the constant field.

## 4. DOUBLE RESONANCE WITH TWO MAGNETIC INGREDIENTS

While the results for the second and fourth moment, derived in the previous section, merely confirmed those of Van Vleck in the simplest case of a single ingredient, the method of their derivation permits a considerable generalization. In the first place, it can be readily extended to include the case of two ingredients in the presence of an alternating field with a single frequency, thus leading to the corresponding results of Van Vleck.[23] The further extension to the case of an rf field with two frequencies will be seen, under special conditions, to lead likewise to these results. More generally, however, there appear here new featured which will be particularly discussed in this section.

Before entering into a more rigorous discussion, it seems worth while to present some qualitative considerations, based upon purely classical arguments. Since only the dipole interaction between nuclei of different ingredients is relevant for these arguments, that between nuclei of the same ingredient will be neglected for purposes of simplicity. In the absence of any rf field the nuclei of one ingredient are thus considered to be acted upon by the external constant field and by a relatively weak internal field, arising from the dipoles of those neighboring nuclei which belong to the other ingredient. Because of the Larmor precession of these dipoles, the internal field alternates around an average value determined by their constant component parallel to the external field. The alternating part may be neglected because of its high frequency so that one deals with an effective constant field which deviates from the external strong field by an amount determined by the average value of the internal field. This amount is different at different sites in the crystal and leads thus to a broadening of the observed absorption line of the nuclei of one, the "unprimed," ingredient by the interaction with the dipoles of the other, the "primed," ingredient.

It will now be assumed that the latter are subjected to an additional external field of strength $H_2$, perpendicular to the constant field and rotating with a frequency $\omega_2$ in the vicinity of their Larmor frequency $\omega_0'$. Referring to a rotating coordinate system, it can readily be seen that, as an effect of magnetic resonance, the component of the dipoles, parallel to the constant field, is no longer constant, but alternates with a circular frequency

$$f=[(\gamma' H_2)^2+(\omega_2-\omega_0')^2]^{\frac{1}{2}}, \tag{53}$$

around a static value which is smaller than that in the absence of the rf field and obtained from the latter by multiplication with the factor

$$r=(\omega_2-\omega_0')/f. \tag{54}$$

This behavior of the dipoles is reflected upon the effective field to which the nuclei of the unprimed ingredient are exposed insofar as its previously-mentioned deviation from the external field is concerned. This deviation thus contains a static part, modified from its previous value by the factor $r$, and it provides in addition a

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[21] The required shortness of the time $t$ can be stated to demand that $1/t$ be large compared to the effective magnitude of $A$, measured by that of the coefficients $c_{jk}$ of Eq. (27) which pertain to the dipolar interaction of neighboring nuclei $j$ and $k$. Physically, this magnitude is of the order of the frequency width of the resonance absorption line.

[22] See reference 3, Eqs. (4) and (7). The fact that these equations contain the $x$-component $S_x$ of the total spin, rather than the complex combinations $I^1$ and $I^{-1}$ of the $x$- and $y$-component represents a merely formal difference between the results of Van Vleck and those given above.

[23] See reference 3, Sec. IV.

partial modulation of the effective field with the frequency $f$. In the reaction of the unprimed nuclei upon the applied rf field, this modulation of the effective field can be replaced by an equivalent modulation of the frequency $\omega_1$. As a consequence, there appear sidebands of the absorption of the unprimed ingredient, separated from the center line by integer multiples of the modulation frequency $f$. For sufficiently high values of the modulation frequency, the intensity of the other sidebands is small compared to that of the sidebands with the separation $f$ and $-f$ and the intensity of these two sidebands is, in turn, small compared to that of the center line. The width of the center line, which is then the only one of appreciable intensity, is determined by the static part of the deviation of the effective from the external field and will thus exhibit a reduction, measured by the factor $r$ of Eq. (54). Under conditions of exact resonance for the primed ingredient, i.e., for $\omega_2=\omega_0'$, the requirement of a high modulation frequency $f$ is, according to Eq. (53), equivalent to that of high values $H_2$ of the rf field. With this requirement fulfilled, the result $r=0$ for $\omega_2=\omega_0'$ indicates that the width of the resonance line of the unprimed ingredient is here totally unaffected by the presence of the primed ingredient, and this fact is indeed born out by the observations, reported in the following paper.

It is gratifying that the simple considerations, presented above, permit an intuitive understanding of the effects, which may be expected under conditions of double resonance and they formed indeed the basis for the original suggestion of an experimental investigation.[24] Nevertheless, they are only qualitatively correct and a quantitative derivation calls for a more rigorous treatment, analogous to that of the preceding section.

For this purpose, one has to introduce two essential changes. In the first place, the discussion of the Boltzmann equation (1) will be based upon the parts (6b), (7b), and (10b) of the spin energy, divided by $\hbar$. In the second place, the transformation operator $T$ of Eq. (16) is here to be replaced by

$$T=\exp(-i\omega_1 tI^0-i\omega_2 tI'^0). \tag{55}$$

While Eqs. (19), (20), and (21) remain still valid, one obtains instead of the expressions (22), (23), and (24)

$$B_T=\Delta_1 I^0+\Delta_2 I'^0, \tag{56}$$

$$\begin{aligned}C_T=\sum_{\lambda\tau}\Big[\sum_{j<k} c_{jk}{}^{\lambda\tau}I_j{}^{\lambda}I_k{}^{\tau}e^{-i(\lambda+\tau)\omega_1\tau}&\\+\sum_{j'<k'} c_{j'k'}{}^{\lambda\tau}I_{j'}{}^{\lambda}I_{k'}{}^{\tau}e^{-i(\lambda+\tau)\omega_2 t}&\\+\sum_{jk'} c_{jk'}{}^{\lambda\tau}I_j{}^{\lambda}I_{k'}{}^{\tau}e^{-i(\lambda\omega_1+\tau\omega_2)t}\Big],&\end{aligned} \tag{57}$$

$$\begin{aligned}D_T=-h_1(I^1+I^{-1})-h_1'[I'^1e^{i(\omega_1-\omega_2)t}+I'^{-1}e^{-i(\omega_1-\omega_2)t}]&\\-h_2[I^1e^{-i(\omega_1-\omega_2)t}+I^{-1}e^{i(\omega_1-\omega_2)t}]&\\-h_2'[I'^1+I'^{-1}],&\end{aligned} \tag{58}$$

respectively, where

$$\Delta_1=\omega_1-\omega_0;\quad \Delta_2=\omega_2-\omega_0'. \tag{59}$$

In contrast to the treatment of Sec. 3, there appear here time-dependent terms not only in $C_T$ but also in $D_T$. Through an analogous consideration these operators can, however, be replaced by their time averages if both frequences $\omega_1$, $\omega_2$ as well as their difference $\omega_1-\omega_2$ are large, compared to the frequencies $\Delta_1$, $\Delta_2$, $h_1$, $h_2'$, and those given by the various coefficients $c^{\lambda\tau}$ in Eq. (57). Barring the accident that the gyromagnetic ratio of the primed ingredient is either very close to zero or to that of the unprimed ingredient, these conditions are no more stringent than those, expressed by the relations (26) and are satisfied in external constant fields of comparable magnitude. As in Sec. 3, the term with $\lambda+\tau\neq 0$ in the first and second sum on the right side of Eq. (57) can thus be omitted. All terms in the third sum of Eq. (57) except those with both $\lambda=0$ and $\tau=0$ are likewise to be omitted as well as the second and third term on the right side of Eq. (58). Assuming again $h_1$ to be small and keeping only terms linear in this quantity, the further considerations are the same as those of the preceding sections. In particular, the basic equation (29) for $\sigma_1$ retains its validity and one may therefore still make use of the results (41), (45), and (47) for the imaginary part of the complex susceptibility, the moments of the absorption line due to the unprimed ingredient and the generating function $\varphi(t)$ for $\kappa\ll 1$, respectively.[25] The only essential difference between the treatment of the cases, considered in this and the preceding section, originates from the presence of additional terms in the time averages of the operators $C_T$ and $D_T$ so that the definition (27) of the time average $A$ has to be modified.

In order to distinguish the origin of the various parts which enter in this new definition, let

$$A=A_0+a. \tag{60}$$

The part

$$A_0=\Delta_2 I'^0-h_2'(I'^1+I'^{-1}) \tag{61}$$

arises from the operator $B_T$ and from the operator, obtained by the time average of $D_T$ according to the

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[24] The earlier observations by J. T. Arnold [Phys. Rev. **102**, 136 (1956)] of the influence of the resonance of one group of nuclei upon that of another group in the same molecule and the underlying theory of this effect by the author (reference 4, II) were likewise suggestive although they refer to a somewhat different situation.

[25] The explicit form (30) of the distribution matrix $\sigma_0$ for $h_1=0$ has to be replaced by an expression which depends also upon the spin operators of the primed ingredient in a manner determined by the magnitude of the rf field with frequency $\omega_2$. For large magnitudes, this dependency expresses, in particular, the saturation of the primed ingredient which may cause an "Overhauser effect" (see II, Sec. 3) upon the intensity of the absorption due to the unprimed ingredient. It would, in this case, result in a change of the constant $K$ in Eq. (41), leaving, nevertheless, Eqs. (45) and (47) unaltered. Since the relaxation of the two ingredients is primarily due to impurities, rather than to their mutual interaction, the presence of such an effect is, however, not to be expected and has actually not been observed.

Eqs. (56) and (58), respectively, and consists, in fact, only of the contributions to these operators which are due to the primed ingredient, since the corresponding contributions, due to the unprimed ingredient, are separately contained in Eq. (29). The other part represents the time average of the operator $C_T$ of Eq. (57) and may thus be written in the form

$$a=b+b'+c. \tag{62}$$

The first term,

$$b=\sum_{j<k}\left[c_{jk}{}^{00}I_j{}^0I_k{}^0+c_{jk}{}^{1-1}I_j{}^1I_k{}^{-1}+c_{jk}{}^{-11}I_j{}^{-1}I_k{}^1\right], \tag{63}$$

on the right side of this equation arises from the dipole coupling between nuclei of the unprimed ingredient and is identical with the form (27) of $A$, used in the preceding section. The second term $b'$ represents the corresponding contribution from the primed ingredient and is obtained by replacing the indices $j$ and $k$ in Eq. (63) by $j'$ and $k'$, respectively. The third term,

$$c=\sum_{jk'} c_{jk'}{}^{00}I_j{}^0I_{k'}{}^0, \tag{64}$$

arises from the dipole coupling between nuclei of the primed and unprimed ingredient; for the purposes of this paper, it is the most important one, since it transmits the effect of the rf field upon the former to the observed resonance of the latter.

The results of Van Vleck, derived in the absence of a second rf field $H_2$ with frequency $\omega_2$ refer to a special case of the more general situation, considered here. Indeed, one has in this case $h_2'=0$ and $A_0=\Delta_2 I'^0$ according to Eq. (61). The operator $I'^0$ can be readily seen to commute with the operator $a$ of Eq. (62), since the specific form of $b'$ and $c$ results from the process of taking the time average and thus from the very omission of those terms which do not commute with $I'^0$. Since $I'^0$ also commutes with $I^1$, it follows that the operator $I^1(t)$ of Eq. (48) and, hence, the generating function (47) are here totally unaffected by the additional term $A_0$ in Eq. (60) so that $A$ may be replaced by $a$. In particular, this substitution in the expression (51) for the second moment will be indicated by writing

$$\langle\Delta_1{}^2\rangle_{\text{Av}}=\langle\Delta_1{}^2\rangle(a), \tag{65}$$

and Van Vleck's result[26] can then be verified and restated in the form

$$\langle\Delta_1{}^2\rangle(a)=\langle\Delta_1{}^2\rangle(b)+\langle\Delta_1{}^2\rangle(c), \tag{66}$$

with the corresponding significance of the symbols $(b)$ and $(c)$, i.e., that the first and second term on the right side of this equation are obtained by substituting in Eq. (51) for $A$ the operators $b$ and $c$, given by Eqs. (63) and (64), respectively.

Contrary to the case, considered by Van Vleck, the presence of an rf field with frequency $\omega_2$ requires that one uses for the calculation of the moments the full operator $A$ of Eq. (60), including the part $A_0$. Applying the same symbolism as in Eq. (65) this leads to the expression

$$\langle\Delta_1{}^2\rangle_{\text{Av}}=\langle\Delta_1{}^2\rangle(A) \tag{67}$$

for the second moment. However, it is seen from Eq. (61) that $A_0$ contains only spin operators of the primed ingredient so that it commutes with the operators $I^1$ and $I^{-1}$ of the unprimed ingredient and does not, therefore, contribute to the expression (51) for the second moment. One obtains thus

$$\langle\Delta_1{}^2\rangle(A)=\langle\Delta_1{}^2\rangle(a),$$

i.e., the effect of the rf field with frequency $\omega_2$ upon the primed ingredient does not alter the second moment of the absorption line due to the unprimed ingredient.

This conclusion appears, at first sight, to be in contradiction with the observed narrowing reported in the following paper and qualitatively explained at the beginning of this section. It has to be remembered, however, that the expression (51) or (67) refers to the second moment of the total absorption line, including the sidebands which have to be expected. The observed narrowing, on the other hand, refers only to the center line and one is thus led to the conclusion that the amount by which the second moment of this line is reduced, must be exactly compensated by the contribution from the sidebands. This conclusion is not invalidated but, on the contrary, supported by the fact that the intensity of the sidebands becomes very small for very large values of the modulation frequency $f$ of Eq. (53). Indeed, since this frequency measures also the separation of the sidebands from the center line, it is necessary that their intensity is inversely proportional to $f^2$ in order to obtain a finite compensation even in the limit of very large values of $f$. Accepting the existence of sidebands, it is evidently possible, in this limit, to obtain their intensity, relative to the center line, from the decrease of the second moment of the latter or vice versa. Separate information about either of the two would then require the consideration of the fourth moment which is indeed affected by the presence of the rf field with frequency $\omega_2$.

It appears preferable, instead, to discuss the absorption in its complete dependence upon the frequency $\omega_1$ and thus not only to demonstrate more rigorously the existence of a center line and two sidebands for large values of $f$ but also to derive formulas for the shape and the relative intensities of these individual lines. The discussion will be based upon the expression (47) of the generating function $\varphi(t)$; for the present purposes, it is advantageous to rewrite it by means of the Eq. (48) in the form,

$$\varphi(t)=\text{Tr}(I^1(t)I^{-1}), \tag{68}$$

where $I^1(t)$ satisfies the differential equation (49) with the initial condition (50), and with $A$ now being defined by Eq. (60). In order to examine the modifications due

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[26] See reference 3, Eq. (28).

to the presence of the term $A_0$ in Eq. (60), a new quantity

$$I_S^1(t)=SI^1(t)S^{-1} \tag{69}$$

will be introduced through the transformation operator

$$S=S_0e^{-iA_0t}. \tag{70}$$

$S_0$ shall have the property, in common with $A_0$, to be independent of the time and to operate only upon the spin vectors of the primed ingredient, so that both commute with $I^1$. As a consequence, Eq. (68) is therefore equivalent to

$$\varphi(t)=\mathrm{Tr}(I_S^1(t)I^{-1}), \tag{71}$$

where, in view of the Eqs. (49), (50), and (60), the operator $I_S^1(t)$ has to satisfy the differential equation

$$dI_S^1(t)/dt=i[a_S, I_S^1(t)], \tag{72}$$

with the initial condition,

$$I_S^1(0)=I^1 \tag{73}$$

and with

$$a_S=SaS^{-1}. \tag{74}$$

While the transformation by means of the operator $S_0$ leaves the spin vectors of the unprimed ingredient unaltered, it shall be further demanded to represent a rotation of the spin vectors of the primed ingredient by a suitable angle $\theta$ around the $y$ axis. The transformed components of the spin vector $I_{k'}$ are then given by

$$\begin{aligned} S_0I_{k'z}S_0^{-1}&=I_{k'z}\cos\theta-I_{k'x}\sin\theta,\\ S_0I_{k'x}S_0^{-1}&=I_{k'z}\sin\theta+I_{k'x}\cos\theta,\\ S_0I_{k'y}S_0^{-1}&=I_{k'y},\end{aligned} \tag{75}$$

and the same relations hold for the components of the total spin vector of the primed ingredient.[27] The angle $\theta$ will be determined so as to satisfy the equations

$$\sin\theta=\gamma'H_2/f,\quad \cos\theta=-\Delta_2/f, \tag{76}$$

with

$$f=[(\gamma'H_2)^2+\Delta_2^2]^{\frac{1}{2}}. \tag{77}$$

In view of the significance of $\Delta_2$ from the second equality (59), the value of $\cos\theta$ is identical with that of the reduction factor $r$ of Eq. (54) and the Eq. (77) agrees with the Eq. (53) for the modulation frequency, introduced in the qualitative discussion at the beginning of this section.

With the particular choice of the angle $\theta$, expressed by the Eq. (76) and with the identity

$$h_2'(I'^1+I'^{-1})=\gamma'H_2I_x',$$

it follows from the application of the relations (75) to the total spin vector of the primed ingredient, that

$$S_0A_0S_0^{-1}=-fI'^0. \tag{78}$$

In order to evaluate the operator $a_S$ of Eq. (74), the relation (78) will first be used to rewrite Eq. (70) in the form

$$S=\exp(ifI'^0t)S_0. \tag{79}$$

As a next step, let

$$S_0aS_0^{-1}=\textstyle\sum_n a^n, \tag{80}$$

with the significance that $a^n$ contains all those linear and biquadratic terms $I_{k'}^\lambda$ and $I_{j'}^\lambda\ I_{k'}^\tau$ for which $\lambda=n$ and $\lambda+\tau=n$, respectively, and for $n=0$ also those terms which contain only spin vectors of the unprimed ingredient. Since the original time averaging, which led to the operator $a$ of Eq. (62), results in the very omission of all terms with $n\neq0$, it is seen that the appearance of such terms in the sum of Eq. (80) requires a finite value of $\sin\theta$ and thus, according to Eq. (76), the presence of the field $H_2$ of frequency $\omega_2$. Because of the relation

$$\exp(ifI'^0t)I_{k'}^\lambda\exp(-ifI'^0t)=e^{i\lambda ft}I_{k'}^\lambda,$$

derived in the same manner as the relation (17) for the unprimed ingredient, one has then

$$\exp(ifI'^0t)a^n\exp(-ifI'^0t)=e^{inft}a^n,$$

and hence, with the form (79) for $S$ from Eqs. (74) and (80),

$$a_S=\textstyle\sum_n e^{inft}a^n. \tag{81}$$

The explicit form of the operators $a^n$ is obtained by applying the transformation formulas (75) to the spin operators of the primed ingredient. They occur in the terms $b'$ and $c$ on the right side of Eq. (62) while the term $b$ is unaffected by this transformation. With the same significance of the upper index $n$ for these terms as that used in Eq. (80), one has thus

$$a^n=b^n+b'^n+c^n,$$

with

$$\begin{aligned} a^0&=b+b'^0+c^0,\\ a^{\pm1}&=b'^{\pm1}+c^{\pm1},\\ a^{\pm2}&=b'^{\pm2},\end{aligned} \tag{82}$$

and with all operators $a^n$ vanishing for which $|n|>2$. Going from the component notation of the transformation (75) back to that with upper indices, it is seen from Eq. (64) that

$$c^0=(\sum_{jk'} c_{jk'}{}^{00}I_j{}^0I_{k'}{}^0)\cos\theta=c\cos\theta, \tag{83}$$

and

$$c^{\pm1}=-(\sum_{jk'} c_{jk'}{}^{00}I_j{}^0I_{k'}{}^{\pm1})\sin\theta/2. \tag{84}$$

The evaluation of the contributions, due to $b'$, in the formulas (82) is likewise straightforward but their explicit form is not needed for the purposes of this paper.

When inserted into the differential equation (72), the alternating terms in the expression (81) for $a_S$ can be

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[27] Explicitly, the choice of the operators $S_0$ can be expressed in the form $S_0=\exp(i\theta I_y')$, with the notation chosen in accordance with the analogous operator, given by Eq. (2.30) of II.

expected to average out the more effectively, the higher the frequency $f$, so that the constant term $a^0$ will become of dominant importance. It is therefore advisable to perform a further transformation by writing

$$I_S{}^1(t)=\exp(ia^0t)U(t)\exp(-ia^0t). \tag{85}$$

The transformed operator $U(t)$ is then seen, from Eqs. (72), (73), and (81), to satisfy the equation

$$\frac{dU}{dt}=i\sum_{n\neq0}[a^n(t),U]e^{inft}, \tag{86}$$

with the initial condition

$$U(0)=I^1, \tag{87}$$

and with the notation

$$a^n(t)=\exp(-ia^0t)a^n\exp(ia^0t). \tag{88}$$

The insertion of the form (85) for the operator $I_S{}^1(t)$ leads further from the Eq. (71) for the generating function to

$$\varphi(t)=\mathrm{Tr}(\exp(ia^0t)U(t)\exp(-ia^0t)I^{-1}). \tag{89}$$

Just as $I^1(t)$ and $I_S{}^1(t)$, $U(t)$ is function of the spin operators, pertaining to the primed as well as to the unprimed ingredient. To characterize its dependence upon the former, one may write

$$U=\textstyle\sum_m U^m, \tag{90}$$

where the significance of the upper index $m$ is analogous to that of the index $n$, introduced in Eq. (80). Thus, expanding $U$ into a sum of terms which contain products of the spin operators $I_{k'}{}^{\lambda}$, the part $U^m$ contains all those products for which the sum of the upper indices $\lambda$ is equal to $m$ and $U^0$, in particular, contains also all the terms in the expansion which are independent of the spin operators of the primed ingredient. It can be verified that this property is maintained in the operator $\exp(ia^0t)U^m\exp(-ia^0t)$ which appears in the trace of Eq. (89) upon insertion of the expression (90) for $U$ and that only the term arising from $U^0$ gives a nonvanishing contribution to the trace[28] so that

$$\varphi(t)=\mathrm{Tr}(\exp(ia^0t)U^0(t)\exp(-ia^0t)I^{-1}). \tag{91}$$

While it is prohibitively difficult to find an explicit solution of the Eq. (86) the problem is very greatly simplified if the frequency $f$ is assumed to be large compared to the effective magnitude $|a|$ of the operators $a^n$. Physically, this assumption implies that the expected sidebands of the absorption are displaced from the center line by an amount which is large compared to the width of either, i.e., that they are well separated from each other.

The discussion of this case is facilitated by restating the Eqs. (86) and (87) as a set of coupled differential equations for the operators $U^m$ in the form

$$\frac{dU^m}{dt}=i\sum_{n\neq0}[a^n(t),U^{m-n}]e^{inft}, \tag{92}$$

with the initial condition[29]

$$U^m(0)=I^1\delta_{m0}. \tag{93}$$

Starting with the approximate solution $U^m=I^1\delta_{m0}$, one obtains further successive approximations in inverse powers of $f$ by substituting the result of the previous approximation on the right side of Eq. (92) and integrating. The operators $U^m$ appear in this manner as a series of the form

$$U^m=\textstyle\sum_n U_n{}^m e^{inft},$$

where the coefficients $U_n{}^m$ are slowly varying operators in the sense that their relative rate of variation is of the order of a magnitude $|a|$ and thus small compared to the frequency $f$. Retaining only the contribution of lowest order in $|a|/f$ to those coefficients, one finds from the first approximation for $m\neq0$

$$U^m(t)=\frac{1}{mf}\{[a^m(t),I^1]e^{imft}-[a^m,I^1]\}, \tag{94}$$

and from the second approximation for $m=0$,[30]

$$U^0(t)=I^1+\sum_{n\neq0}\frac{1}{(nf)^2}[a^n(t),[a^{-n},I^1]]e^{inft}. \tag{95}$$

Inserting the expression Eq. (95) for $U^0(t)$ in (91) one finds

$$\varphi(t)=\textstyle\sum_n \varphi_n(t)e^{inft}, \tag{96}$$

with

$$\varphi_0(t)=\mathrm{Tr}(\exp(ia^0t)I^1\exp(-ia^0t)I^{-1}), \tag{97}$$

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[28] The foregoing statements are most easily verified by considering the operator $U$ in a representation in which $I'^0$ is diagonal with eigenvalues $m'$. As an equivalent definition of $U^m$, it can then be stated that its matrix elements $(1|U^m|2)$ between two states 1 and 2 of the spin system are different from zero only if $m_2'-m_1'=m$; it suffices then to note that the matrix elements of $a^0$ satisfy in this representation the selection rule $m_2'-m_1'=0$ and that the trace of an operator contains only the diagonal elements which likewise satisfy this selection rule.

[29] The fact that the sum of the upper indices on the right side of Eq. (92) must be equal to the upper index on the left side is again most easily shown by means of the selection rules, mentioned in reference 28. The initial condition (93) follows from the fact that $I^1$ commutes with $I'^0$ and satisfies therefore the selection rule $m_2'-m_1'=0$.

[30] The operator $U^m(t)$ of Eq. (94) satisfies the initial condition (93) by vanishing for $t=0$ but the additional requirement $U^0(0)=I^1$ is not rigorously satisfied for the operator $U^0(t)$ of Eq. (95). This is due to the fact that the operator $I^1$ represents the coefficient $U_0{}^0$ only in zero-order with omission of second-order terms of relative order of magnitude $|a|^2/f^2$ which, if retained, would merely lead to minor corrections in the center line. Although the remaining coefficients $U_n{}^0$ in the sum on the right side of Eq. (95) are likewise of this order of magnitude, they have been retained, since their presence accounts for the very existence of the sidebands.

and, using further Eq. (88) together with the fact that the trace of a product of operators does not change by a cyclical permutation of their order

$$\varphi_n = \frac{1}{(nf)^2}\mathrm{Tr}(\exp(ia^0t)[I^1,a^{-n}]\exp(-ia^0t)[a^n,I^{-1}]) \quad (98)$$

for $n\neq 0$. Of the four values $\pm 1$, $\pm 2$ of $n\neq 0$ for which the operators $a^n$ are not identically zero, there remain nonvanishing values of the functions (98) only for $n=\pm 1$. Indeed, the operators $b'^{\pm 2}$ of Eq. (82) commute with $I^{\pm 1}$, since $b'$ contains only spin operators of the primed ingredient, and one has therefore $\varphi_{\pm 2}=0$. For the same reason, only the operators $c^{\pm 1}$ contribute to $\varphi_{\pm 1}$ and one may therefore rewrite Eq. (96) in the form

$$\varphi(t)=\varphi_0(t)+\varphi_1(t)e^{ift}+\varphi_{-1}(t)e^{-ift}, \quad (99)$$

with $\varphi_0(t)$ given by Eq. (97) and with

$$\varphi_{\pm 1}(t)=\frac{1}{f^2}\mathrm{Tr}(\exp(ia^0t)[I^1,c^{\mp 1}]\exp(-ia^0t)[c^{\pm 1},I^{-1}]). \quad (100)$$

The existence of a center line and two sidebands, displaced by the frequency $\pm f$, is a direct consequence of the expression (99) for $\varphi(t)$. Indeed, inserting it into the formula (41) for the susceptibility, one obtains

$$\chi''(\Delta_1)=\chi_0''(\Delta_1)+\chi_1''(\Delta_1+f)+\chi_{-1}''(\Delta_1-f), \quad (101)$$

where the three functions $\chi_n''(n=-1,0,1)$ are obtained from the Fourier transform of the corresponding functions $\varphi_n$ in the same manner in which $\chi''$ in Eq. (41) is obtained from $\varphi$. Each of the functions on the right side of Eq. (101) assumes therefore appreciable values only within an interval of its argument of the order of the dipolar energy, divided by $\hbar$. This means that $\chi_0''$, $\chi_1''$ and $\chi_{-1}''$ represent a line located in the vicinity of the value 0, $-f$, and $f$ of $\Delta_1$, respectively, and that one deals thus, indeed, with a center line and two sidebands.

In order to investigate the effect of the rf field $H_2$ upon the center line, it is best to examine the behavior of the part $\chi_0''$ of the susceptibility through that of its Fourier transform, determined by the function $\varphi_0(t)$ of Eq. (97). This function can also be characterized as the result of replacing $A$ in Eq. (47) by the operator $a^0$. The same replacement by the operator $a$ was pointed out before to lead to the case of the absorption line in the absence of the field $H_2$ so that the center line differs from this case merely by the fact that the role of the operator $a$ is taken over by $a^0$.

Conversely, one can verify that the equality $a^0=a$ results as a special case of the preceding treatment and represents the situation, considered by Van Vleck in the sense that the sidebands disappear and that the center line becomes identical with the absorption line for $H_2=0$. Indeed, this situation corresponds to the choice $\theta=0$ of the angle $\theta$ which appears in the transformation equations (75). The operators $b'^0$ and $c^0$ are then equal to $b'$ and $c$, respectively, and $c^{\pm 1}$ vanishes according to Eq. (84); therefore, the generating functions $\varphi_{\pm 1}(t)$, given by Eq. (100), vanish likewise so that the sidebands are absent. Although the condition $H_2=0$ is, rigorously, sufficient for the special case, considered here, it is formally necessary to impose an additional condition on $\Delta_2$ because of the approximations, made in the preceding treatment. Since this treatment is valid only if $f\gg|a|$, it requires for $H_2=0$, according to Eq. (77), that $|\Delta_2|\gg|a|$. In order that one indeed obtains the case $\theta=0$ for vanishing values of $H_2$, Eqs. (76) demand therefore as a formal condition that $-\Delta_2\gg|a|$. On the other hand, this case can also be obtained for finite values of $H_2$, provided that one has not only $|\Delta_2|\gg|a|$ but also $|\Delta_2|\gg|\gamma' H_2|$. Physically, this means that even a finite rf field $H_2$ becomes ineffective if its frequency $\omega_2$ is sufficiently removed from the resonance frequency $\omega_0'$ of the primed ingredient.[31]

Another special case of interest is that where the resonance condition $\omega_2=\omega_0'$ is exactly fulfilled so that $\Delta_2=0$. In order to ensure the validity of the preceding treatment it is necessary, in this case, that the field $H_2$ is sufficiently strong to satisfy the condition $\gamma' H_2\gg|a|$. According to the defining Eq. (76), the angle $\theta$ has here the value $\pi/2$; the operator $c^0$ of Eq. (83) vanishes therefore and one obtains from Eq. (82) $a^0=b+b'^0$. Since the operator $b'^0$, just as $b'$, acts only upon the spin vectors of the primed ingredients, it commutes both with $b$ and with $I^1$ and can therefore be omitted upon insertion of the above expression for $a^0$ in Eq. (97). The generating function $\varphi_0(t)$ is therefore obtained by replacing $A$ in Eq. (47) by the operator $b$ which originates from the unprimed ingredient alone. One thus confirms the conclusion, reached in the qualitative discussion at the beginning of this section, that under these conditions of optimal line narrowing the center line is totally unaffected by the presence of the primed ingredient and identical with the absorption line which would have to be expected if the nuclei of the primed ingredients had a vanishing magnetic moment. The circumstance that this is actually not so is in this case manifested by the existence of the sidebands. For $\sin\theta=1$, they reach, in fact, their maximum intensity and are displaced from the center line by the amount $f=\pm\gamma' H_2$.

With $\gamma H_2'\gg|a|$, the condition of validity of the preceding treatment is satisfied for all values of $\Delta_2$.

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[31] Strictly speaking, the conditions $|\Delta_2|\gg|\gamma' H_2|$ leads, according to Eq. (76) either to the choice $\theta=0$ or $\theta=\pi$, depending upon whether $\Delta_2$ is negative or positive. The difference between the two choices is, however, only of formal nature since the rotation of all the spin vectors of the primed ingredient by 180 degrees does not alter the physical situation. In fact, the preceding treatment could have been equally well carried out by taking the square root in Eq. (77) with the negative sign. Together with the sign of $f$, that of $\sin\theta$ and $\cos\theta$ in Eq. (76) would thus have been inverted with a resulting change in the definition of $\theta$ by 180 degrees. The only other consequence of the opposite sign of $f$ would have consisted in an interchange of the sidebands.

By letting this quantity vary from large negative to large positive values, one covers the whole range of the angle $\theta$ from 0 to $\pi$ and all the corresponding intermediate modifications of the center line by the rf field $H_2$. Except for the two special cases which were discussed above, the effect of these modifications upon the detailed line shape cannot be described in simple terms. On the other hand, it requires only a minor change in Eq. (66), restating the result of Van Vleck, to arrive at a simple expression for the second moment of the center line. Since $b'^0$ commutes with $I^1$ and $I^{-1}$, it is seen that the only change upon replacing in Eq. (51) $A$ by the operator $a^0$ of Eq. (82) consists in the fact that $c$ has to be replaced by the operator $c^0$ of Eq. (83), i.e., that $c$ has to be multiplied with $\cos\theta$. This factor appears quadratically in the replacement of the part $\langle\Delta_1^2\rangle(c)$ of Eq. (66) by $\langle\Delta_1^2\rangle(c^0)$ so that the second moment of the center line is given by

$$\langle\Delta_1^2\rangle(a^0)=\langle\Delta_1^2\rangle(b)+\langle\Delta_1^2\rangle(c)\cos^2\theta, \tag{102}$$

with

$$\cos^2\theta=\Delta_2^2/[(\gamma' H_2)^2+\Delta_2^2], \tag{103}$$

according to Eqs. (76) and (77). The expression (102) for the second moment represents the simplest quantitative measure for the narrowing of the center line by the rf field $H_2$ and has, indeed, been used in the following paper [Eq. (1)] to experimentally verify the conclusions of the theory, presented here.[32]

Turning now to the sidebands, it is possible by the arguments, presented above, to obtain the sum of their intensities, relative to the center line, from the expression (102) for the second moment of this line and from that of the total absorption, given in Eq. (66). In view of their definition

$$i_{\pm1}=\left(\int\chi_{\pm1}''(\Delta_1)d\Delta_1\right)\Big/\left(\int\chi_0''(\Delta_1)d\Delta_1\right),$$

and the significance of the generating functions (97) and (100), the relative intensities of the two sidebands can also be derived from the values of these functions for $t=0$ in the form

$$i_{\pm1}=\varphi_{\pm1}(0)/\varphi_0(0). \tag{104}$$

Since

$$\varphi_0(0)=\mathrm{Tr}(I^1I^{-1}),$$

and

$$\varphi_{\pm1}(0)=\frac{1}{f^2}\mathrm{Tr}([c^{\mp1},I^1][I^{-1},c^{\pm1}]),$$

they are seen to be closely related to the expression $\langle\Delta_1^2\rangle(c)$, obtained by replacing $A$ by $c$ in Eq. (51). In fact, comparing the Eqs. (64) and (84), it is seen that, besides the factor $-\sin\theta/2$, $c^{\pm1}$ differs from $c$ merely by the replacement of the spin operator $I_{k'}^0$ by $I_{k'}^{\pm1}$. Noting further that the definition of these spin operators leads to the equalities

$$\mathrm{Tr}(I_{k'}^1I_{k'}^{-1})=\mathrm{Tr}(I_{k'}^{-1}I_{k'}^1)=2\,\mathrm{Tr}(I_{k'}^0I_{k'}^0),$$

one obtains therefore

$$\varphi_1^{(0)}=\varphi_{-1}^{(0)}=\frac{1}{2f^2}\sin^2\theta\,\mathrm{Tr}([c,I^1][I^{-1},c]),$$

and from Eq. (104), in view of the significance of $\langle\Delta_1^2\rangle(c)$, for the relative intensities of the sidebands

$$i_1=i_{-1}=(1/2f^2)\langle\Delta_1^2\rangle(c)\sin^2\theta. \tag{105}$$

In calculating the contribution of the sidebands to the second moment of the total absorption by the unprimed ingredient, one has to consider that they extend only over a relatively small region in the vicinity of the value $\Delta_1=\pm f$. One commits, therefore, an error of higher order in $|a|/f$ by computing this contribution of each sideband as the product of $f^2$ with its relative intensity. Adding the expression $\langle\Delta_1^2\rangle(a^0)$ for the second moment of the center line, one thus obtains the second moment of the total absorption in the form

$$\langle\Delta_1^2\rangle_{\mathrm{Av}}=\langle\Delta_1^2\rangle(a^0)+f^2(i_1+i_{-1}), \tag{106}$$

and with the Eqs. (102), (105), and (66) one has therefore

$$\langle\Delta_1^2\rangle_{\mathrm{Av}}=\langle\Delta_1^2\rangle(b)+\langle\Delta_1^2\rangle(c)\cos^2\theta+\langle\Delta_1^2\rangle(c)\sin^2\theta=\langle\Delta_1^2\rangle(a), \tag{107}$$

as a check on the fact that the second moment of the total absorption is unaffected by the presence of the rf field with frequency $\omega_2$.

In analogy to the discussion in the preceding section, it is also possible to show that the sidebands are symmetrically distributed around the values $\pm f$ of $\Delta_1$ and to obtain their even moments around this frequency from the corresponding derivatives at the time $t=0$ of the generating functions (100). In particular, for the second moment of the sideband centered around $\Delta_1=f$ one obtains in analogy to Eq. (45) for $s=2$

$$\langle(\Delta_1-f)^2\rangle_{\mathrm{Av}}=-\varphi_{-1}^{(2)}(0)/\varphi_{-1}(0)$$

or, from Eq. (100),

$$\langle(\Delta_1-f)^2\rangle_{\mathrm{Av}}=\mathrm{Tr}([[I^1,c^1],a^0][a^0,[c^{-1},I^{-1}]])/\mathrm{Tr}([I^1,c^1][c^{-1},I^{-1}]), \tag{108}$$

and a similar expression, obtained by replacing $c^1$ by $c^{-1}$ and vice versa, for the sideband, centered around $\Delta_1=-f$. The computational effort, required for their evaluation, is comparable to that of the fourth moment,

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[32] Instead of the notation of Eq. (102), characterizing the various parts by the operators from which they are obtained, that of Eq. (1) of the following paper points to their physical origin. Thus, the second moment of the center line is written as $(\langle\Delta_1^2\rangle_{\mathrm{Av}})_0$, and instead of $\langle\Delta_1^2\rangle(b)$ and $\langle\Delta_1^2\rangle(c)$ the symbols $(\Delta_1^2)_{\mathrm{Na-Na}}$ and $(\Delta_1^2)_{\mathrm{Na-F}}$ are used. Further, since the primed ingredient consists here of the nuclei of fluorine, the deviation from resonance of these nuclei is denoted by $\Delta_{\mathrm{F}}$ instead of $\Delta_2$ and their gyromagnetic ration by $\gamma_{\mathrm{F}}$ instead of $\gamma'$.

given by Van Vleck[33]; in fact, there exists a similar, although not nearly so simple relationship between the two as that between the intensity of the sidebands and Van Vleck's form of the second moment.

It would be of interest to verify experimentally not only the narrowing of the center line but also the existence of the sidebands. The fact that this has not been possible so far is due to the relatively small intensity of the sidebands. In order to permit their individual observation, it is necessary that the sidebands are well separated from the center line and the condition of validity $|f| \gg |a|$ of the theory, presented here, expresses this very circumstance. With $\langle\Delta_1^2\rangle(c)$ of the order of magnitude $|a|^2$, it follows from Eq. (105) that the intensity of well separated sidebands is necessarily small, compared to that of the center line, even in the most favorable case where $\sin^2\theta = 1$. Nevertheless, the observation may become possible if larger signal-to-noise ratios can be achieved.

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[33] See reference 3, Eq. (29).

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# Double Nuclear Magnetic Resonance and the Dipole Interaction in Solids*

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The nuclear magnetic dipole interactions in a polycrystalline sample of sodium fluoride have been investigated using an extension of the magnetic resonance technique. The resonance absorption of $Na^{23}$ was observed with a variable-frequency spectrometer in a fixed external magnetic field, and the mean square width of the line shape computed.

This width has two main sources: (a) the interaction of $Na^{23}$ nuclei with other $Na^{23}$ nuclei through the dipole fields of the magnetic moments, and (b) the interaction of $Na^{23}$ nuclei with neighboring $F^{19}$ nuclei by the same mechanism. The application of a strong rf field satisfying the resonance condition for $F^{19}$ nuclei in the same external field caused rapid transitions between the fluorine Zeeman energy levels, and thus altered the average field produced at the position of sodium nuclei by the nuclear magnetic moments of fluorine. By varying the strength of this rf field and also by varying the deviation from precise resonance of the $F^{19}$ spins, one could selectively alter the contributions of this source of line broadening.

The available rf field was not sufficiently intense to eliminate entirely the broadening caused by source (b). However, the detailed behavior of this contribution to the width as a function of the deviation from resonance agrees well with a theory of Bloch for the case of the rf field strong compared to the line widths involved.

## I. INTRODUCTION

THE line widths characteristic of nuclear magnetic resonance absorption in solids are commonly of the order of kilocycles/second, owing to the magnetic dipole interaction between nuclei localized in the crystal lattice. In general, the rigorous calculation of the line shape itself is prohibitively difficult because of the extremely large number of spins to be considered in a crystal of practical size. Recently Lowe and Norberg have made some progress in developing such a theory.[1] Van Vleck, however, has given a procedure[2] for calculating the moments of the line shape, and the second moment, in particular, is a measure of the mean square line width. In a crystal containing two magnetic ingredients, $A$ and $B$, the second moment of the resonance line of $A$ will have contributions from both the $A$-$A$ and the $A$-$B$ magnetic dipole interactions.

The present work concerns itself with a method of altering this natural line shape by applying a perturbation which affects the $A$-$B$ dipolar coupling. The accompanying paper by Bloch[3] presents a theoretical treatment of the experiment.

The concept of "averaging out" local fields in nuclear resonance experiments is not new. An early example is the explanation by Bloembergen, Purcell, and Pound[4] of the narrow lines observed in liquid samples. By virtue of the rapid molecular tumbling motions, nuclei are caused to sample many different local fields in a time short compared to that in which they would otherwise have lost phase coherence. As a result their instantaneous precession frequencies differ less from the mean than would be the case with no motion, and narrowing of the resonance line is observed.

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