effects. It is very easily possible to make serious errors through their neglect. The following paper by A. M. Portis discusses the saturation effects in detail.

VII. CONCLUSION

From the experiments and calculations described above it appears that one may with some confidence attribute to hyperfine interactions the width of the electron spin resonance line arising from F centers in alkali halide crystals. It appears further than an F-center wave function which is a linear combination of polarized atomic orbitals will give a fair quantitative representation of the hyperfine interactions. It is also possible to make reasonable empirical estimates of the line widths on the basis of the results for $K^{39}Cl$ and $K^{41}Cl$, together with the free atom hyperfine coupling constants for the atoms under consideration. Our interpretation of the observed resonance line is also supported in detail by observations by Portis and Kip[12] on the rf saturation behavior of the resonance.

We are glad to acknowledge again our indebtedness to the U. S. Atomic Energy Commission for the provision of the $K^{41}Cl$. We thank the U. S. Naval Radiological Defense Laboratory, San Francisco, for the x-ray irradiations and the University of California Radiation Laboratory for the electron bombardments. The planning of the $K^{41}Cl$ experiment was assisted greatly by the generous advice and encouragement of Professor E. Segrè. We have profitted from discussions with L. W. Alvarez, I. Estermann, W. D. Knight, and F. Seitz. This research was supported in part by the U. S. Office of Naval Research.

[12] A. M. Portis and A. F. Kip, Bull. Am. Phys. Soc. **28**, No. 2, 9 (1953); A. M. Portis (following paper), Phys. Rev. **91**, 1071 (1953).

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Electronic Structure of F Centers: Saturation of the Electron Spin Resonance

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It is shown that the unusual observed saturation behavior of the microwave electron spin resonance associated with F centers in KCl, NaCl, and KBr crystals can be accounted for if the overall width is ascribed to interaction between the F-center electrons and the nuclear magnetic moments of the ions adjacent to the F centers. The measured saturation factor gives for F centers in KCl a spin-lattice relaxation time of 2.5×10^{-5} sec at room temperature. The observed saturation behavior in which only the absorption saturates is in marked disagreement with the Kramers-Kronig relations. However it is shown, that the Kramers-Kronig relations are not applicable to saturated systems. Expressions which avoid the use of these relations are presented for saturable systems.

I. INTRODUCTION

IT is shown in this paper that the unusual saturation behavior of the microwave spin resonance absorption and dispersion associated with F centers in alkali halide crystals can be accounted for if the over-all width is caused by hyperfine interaction.[1] The details of the saturation behavior of a system depend markedly on the nature of the broadening mechanism. If the broadening arises from dipolar interaction between like spins or from interaction with the radiation field, then the thermal equilibrium of the spin system will be preserved during resonance absorption. This will also be true if the line width comes from some mechanism which is external to the spin system but is fluctuating rapidly compared with the time associated with a spin transition. This first case we call the *homogeneous* case. The consequence of homogeneous broadening is that the energy absorbed from the microwave field is distributed to all the spins and thermal equilibrium of the spin system is maintained through resonance. In an effort to understand the observed saturation results, our measurements were first compared with the behavior expected for this kind of broadening. This comparison is shown in Fig. 1. The observed and the theoretical behavior for a simple line of the observed shape were fitted so as to have the same slope at low microwave fields. It can be seen that the simple theory completely fails to account for our saturation results.

In attempting to account for our results we realized that if the line width were to come from variations in the local magnetic fields the physical response of the system would be markedly different. For this second case, which we call the inhomogeneous case, energy will be transferred only to those spins whose local fields satisfy the resonance condition. Further, the processes for spin-spin interaction will be slow as compared with the direct interaction of the spins with the lattice, since in order for spins in different local fields to come to equilibrium, energy will have to be transferred to the lattice. It is useful for this case to think of spin packets

[1] A preliminary account of this work was given by A. M. Portis and A. F. Kip, Bull. Am. Phys. Soc. **28**, No. 2, 9 (1953).

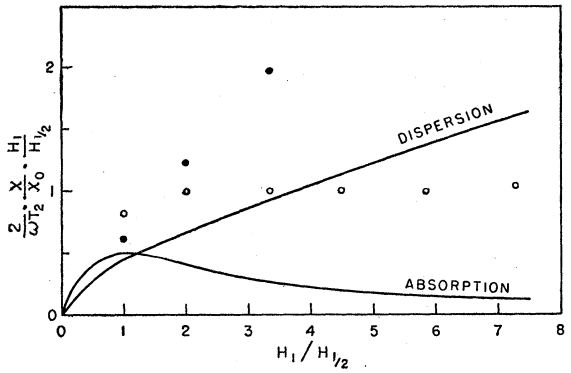

FIG. 1. Comparison between the observed saturation behavior of F centers in KCl and the simple theory of Sec. II.

having little or no interaction with each other and of width given by the simple dipole-dipole interaction. Then the over-all response of the spin system will be a superposition of the individual responses of the spin packets. It is clear that the broadening of the spin resonance in alkali halides where the width is from the distribution in hyperfine fields is of the inhomogeneous type. The excellent agreement between our results and the predicted saturation behavior for this case is shown in Sec. V.

By studying the way in which the system saturates at high-microwave fields it is possible to determine the spin-lattice relaxation time. Of course, for a steady-state experiment, one does not obtain directly the spin lattice relaxation time, T_1, but rather the product T_1T_2, where T_2 is the time associated with the width of the spin packets. This case is closely related to one considered by Bloembergen, Purcell, and Pound[2] where the over-all width comes from inhomogeneities in the applied magnetic field. At high-microwave fields the relation between absorption and dispersion deviated from the relationship developed by Kramers and Kronig.[3] This deviation has led here to a re-examination of the derivation of these relations. It has been found that certain assumptions made in the derivation regarding the behavior of the complex susceptibility are not valid for saturable systems. This problem is discussed in Sec. VI and Appendix I, where a scheme which introduces the Kramers-Kronig relations only in a restricted way is presented.

II. THE ELEMENTARY THEORY OF SATURATION

We consider here the saturation behavior of a system for which the broadening is of the *homogeneous* type. For simplicity we consider single electron spins so that only on the application of an external magnetic field is the spin degeneracy lifted. We then have two states per electron of frequency separation:

$$\omega_0 = g(e/2mc)H_0, \tag{1}$$

where g is the spectroscopic splitting factor and H_0 the applied magnetic field. These spin levels are not perfectly defined but are somewhat broadened. Sources of *homogeneous* broadening include:

(a) Dipolar interaction between like spins;
(b) Spin-lattice relaxation;
(c) Interaction with the radiation field;
(d) Motion of carriers in the microwave field;
(e) Diffusion of excitation through the sample;
(f) Motionally narrowed fluctuations in the local field.

We define N^+ to be the number of spins in the higher-energy spin state and N^- the number in the lower-energy state. For the entire spin system in thermal equilibrium we have

$$N^+/N^- = \exp(-\hbar\omega_0/kT_s), \tag{2}$$

where T_s is the effective spin temperature. If the spin system is in thermal equilibrium with the lattice at some temperature T_l,

$$N^+ = N_0^+, \quad N^- = N_0^-,$$

and

$$N_0^+/N_0^- = \exp(-\hbar\omega_0/kT_l). \tag{3}$$

We consider now the deviations of the spin system from equilibrium with the lattice under the interaction of the spin system with the radiation field and with the lattice. If we let $n = N^- - N^+$:

$$dn/dt = (dn/dt)_{\mathrm{rf}} + (dn/dt)_{\mathrm{sl}}, \tag{4}$$

where $(dn/dt)_{\mathrm{rf}}$ and $(dn/dt)_{\mathrm{sl}}$ give the rate of change of the difference in populations from interaction with the radiation field and spin-lattice interaction respectively.

The rate of change of the difference in populations from interaction with the radiation field at a frequency ω is given by

$$(dn/dt)_{\mathrm{rf}} = -\tfrac{1}{4}\pi\gamma^2 H_1^2 g(\omega-\omega_0)n, \tag{5}$$

where γ is the magnetomechanical ratio, H_1 the maximum amplitude of the microwave magnetic field, and $g(\omega-\omega_0)$ the normalized shape factor for the transition. Following Bloembergen,[2] we take for the interaction with the lattice:

$$(dn/dt)_{\mathrm{sl}} = (n_0 - n)/T_1, \tag{6}$$

where $n_0 = N_0^- - N_0^+ \simeq (\hbar\omega_0/2kT_l)N$ and T_1 is the spin-lattice relaxation time.

If the microwave power incident on the sample is varying slowly as compared with T_1, we obtain a quasi-steady state condition for which

$$dn/dt \cong 0,$$

and

$$n = n_0/[1+\tfrac{1}{4}\pi\gamma^2 H_1^2 T_1 g(\omega-\omega_0)]. \tag{7}$$

For the case where the microwave power is amplitude modulated at a frequency high compared with $1/T_1$,

[2] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).
[3] R. de L. Kronig, J. Opt. Soc. Am. **12**, 547 (1926); H. A. Kramers, Atti congr. intern. fis. Como **2**, 545 (1927).

n will not be able to follow the variations in microwave power over a modulation cycle but will respond to the average power. These two cases are examined in detail in Appendix II.

We are concerned here with the rate at which energy is absorbed from the radiation field:

$$P_a=-\tfrac{1}{2}\hbar\omega(dn/dt)_{\mathrm{rf}}. \tag{8}$$

Substituting from Eqs. (5) and (7), we find that

$$P_a=\tfrac{1}{2}\omega\left\{\tfrac{1}{2}\omega_0\left(\frac{\gamma^2\hbar n_0}{2\omega_0}\right)\cdot\frac{\pi g(\omega-\omega_0)}{1+\tfrac{1}{4}\pi\gamma^2H_1^2T_1g(\omega-\omega_0)}\right\}. \tag{9}$$

Noting that the complex part of the rf susceptibility is defined by

$$P_a=\tfrac{1}{2}\omega\chi''H_1^2, \tag{10}$$

and that the static spin susceptibility,

$$\chi_0=\gamma^2\hbar n_0/2\omega_0, \tag{11}$$

we have

$$\chi''(\omega)=\tfrac{1}{2}\chi_0\omega_0\frac{\pi g(\omega-\omega_0)}{1+\tfrac{1}{4}\pi\gamma^2H_1^2T_1g(\omega-\omega_0)}. \tag{12}$$

We define T_2 such that at the line center

$$g(0)=T_2/\pi. \tag{13}$$

Then

$$\chi''(\omega_0)=\tfrac{1}{2}\chi_0\omega_0T_2\frac{1}{1+\tfrac{1}{4}\gamma^2H_1^2T_1T_2}. \tag{14}$$

The expression derived in Appendix I for the real part of the rf susceptibility is

$$\chi'(\omega)=\tfrac{1}{2}\chi_0\omega_0\frac{1}{1+\tfrac{1}{4}\pi\gamma^2H_1^2T_1g(\omega-\omega_0)}\times\int_0^\infty\frac{2\omega'g(\omega'-\omega_0)}{\omega'^2-\omega^2}d\omega'. \tag{15}$$

III. THE GENERAL THEORY OF SATURATION

We considered in Sec. II the saturation behavior for *homogeneous* broadening of the spin levels. However, as in spin resonance from F centers in alkali halides, the over-all width may be caused by factors which do not maintain the spin system in equilibrium. Here one must take the results of Sec. II as applying to a spin packet of width approximately $1/T_2$. These lines must be then assembled under an envelope the shape of which is given by the details of the inhomogeneous broadening as illustrated in Fig. 2. The distinction between homogeneous and inhomogeneous broadening is that the inhomogeneous broadening must come from interactions outside the spin system and must be slowly varying over the time required for a spin transition. Examples of inhomogeneous broadening include:

(*a*) Hyperfine interaction,
(*b*) Anisotropy broadening,
(*c*) Dipolar interaction between spins with different Larmor frequencies,
(*d*) Inhomogeneities in the applied magnetic field.

The distribution in local fields is given by $h(\omega-\omega_0)$, which is normalized so that

$$\int_0^\infty h(\omega-\omega_0)d\omega=1.$$

We define T_2^* so that at the center of the distribution

$$h(0)=T_2^*/\pi. \tag{16}$$

Then we obtain in the general case for the absorption

$$\chi''(\omega)=\tfrac{1}{2}\chi_0\int_0^\infty\frac{\pi\omega'g(\omega-\omega')}{1+\tfrac{1}{4}\pi\gamma^2H_1^2T_1g(\omega-\omega')}h(\omega'-\omega_0)d\omega'. \tag{17}$$

The dispersion is given by

$$\chi'(\omega)=\tfrac{1}{2}\chi_0\int_0^\infty\frac{\omega'h(\omega'-\omega_0)d\omega'}{1+\tfrac{1}{4}\pi\gamma^2H_1^2T_1g(\omega-\omega')}\times\int_0^\infty\frac{2\omega''g(\omega''-\omega')d\omega''}{\omega''^2-\omega^2}. \tag{18}$$

As is shown in Appendix I, if the over-all broadening is large compared with the width of the spin packets, these expressions simplify to

$$\chi''(\omega)=\tfrac{1}{2}\chi_0\omega h(\omega-\omega_0)\int_0^\infty\frac{\pi g(\omega-\omega')}{1+\tfrac{1}{4}\pi\gamma^2H_1^2T_1g(\omega-\omega')}d\omega', \tag{19}$$

$$\chi'(\omega)=\tfrac{1}{2}\chi_0\int_0^\infty\frac{2\omega'^2h(\omega'-\omega_0)}{\omega'^2-\omega^2}d\omega'. \tag{20}$$

We note that the absorption line does not change shape on saturation since the integral in Eq. (19) will not be a function of ω. The details of the way in which

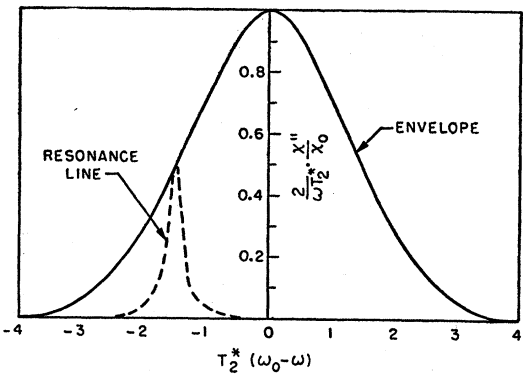

FIG. 2. Diagram illustrating the distinction between the resonance line for a spin packet and the envelope caused by inhomogeneous broadening.

$\chi''(\omega)$ changes in amplitude depend on the form of the shape function $g(\omega-\omega')$. As will be shown in Sec. V the observed behavior of the spin resonance is in good agreement with these results and allows further the determination of the shape of $g(\omega-\omega')$ even though it is masked by the over-all broadening.

IV. EXPERIMENTAL PROCEDURE

The experiments described in this and the preceding paper were performed at a frequency of approximately 8590 Mc/sec corresponding to a resonance field of about 3200 oersteds. A 2K39 reflex klystron nominally delivering 250 mw of microwave power was employed as the microwave source. The power was 100 percent modulated at 6 kc/sec by a microwave gyrator.[4] A simplified block diagram of the resonance equipment is shown in Fig. 3. The equipment for Pound stabilization, power monitoring, and power modulation of the microwave oscillator is not shown. The signal detected by a 1N23 crystal in the arm to the right of the magic-tee bridge is proportional to the difference in power reflected from the variable probe and the resonant cavity. In practice the bridge was first balanced by adjusting the position and depth of the variable probe until no microwave power reached the detecting crystal. The bridge was then unbalanced until about 1 μw of microwave power reached the detecting crystal.

One can unbalance the bridge in one of two ways, either by translating the probe along the guide or by decreasing the depth of its penetration into the guide. Translating the probe makes the bridge sensitive to variations in cavity frequency giving a signal at the crystal proportional to the dispersion. Raising the probe makes the bridge sensitive to variations in cavity Q giving a signal proportional to the absorption.

After unbalancing the bridge by raising the probe, the position of the probe along the guide was always readjusted for minimum power to the crystal in order to avoid a mixture of absorption and dispersion. In this way the amplitudes of the absorption and dispersion signals were compared over a range of 20 db in microwave power. After each power change the unbalance of the bridge was readjusted in order to maintain the same power on the detecting crystal. Using this procedure, it can easily be shown that the detected absorption and dispersion signals are proportional to $H_1\chi''$ and $H_1\chi'$ respectively.

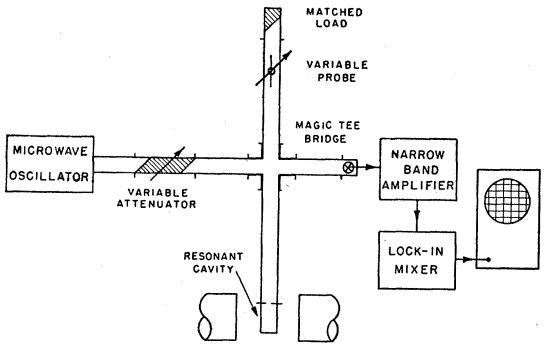

FIG. 3. Microwave apparatus.

[4] C. L. Hogan, Bell System Tech. J. **31**, 1 (1952).

The microwave field in the cavity was calculated from measurements of the loaded Q of the cavity, the voltage standing wave ratio in the cavity arm, and the power incident on the cavity. The power reflection coefficient of the cavity,

$$|\Gamma|^2=[(\beta-1)/(\beta+1)]^2, \tag{21}$$

where β is the voltage standing wave ratio and is equal to Q_e/Q_u, the ratio of the external Q to the unloaded Q of the cavity. It can be shown that the condition for optimum sensitivity is

$$\delta^2|\Gamma|^2/\delta Q_e\delta Q_u=0. \tag{22}$$

From differentiation of Eq. (21) it follows that for optimum sensitivity, assuming square law detection, the coupling iris should be chosen so that one-third of the incident power is reflected from the cavity. Since

$$1/Q_l=1/Q_u+1/Q_e, \tag{23}$$

where Q_l is the loaded Q, a measurement of Q_l and β will suffice to determine the unloaded Q of the cavity. If P is the power incident on the cavity it can be shown that

$$H_1^2=32\pi Q_u(1-|\Gamma|^2)P/\omega V, \tag{24}$$

where V is the volume of the resonant cavity.

V. ANALYSIS OF RESULTS IN KCl

The saturation results in crystals of KCl, KBr, and NaCl were qualitatively similar and further work is in progress. We will describe here only the results on KCl, for which a detailed study has been made at room temperature. Since at ordinary power levels the dispersion signal is nearly five times as strong as the absorption signal, the former was used for the analysis of line shape. Figure 4 presents a comparison of the results obtained for KCl with the theoretical Gaussian and Lorentz line shapes. As shown the line is essentially Gaussian in shape, in good agreement with the theory of hyperfine interaction as presented in the preceding paper. It was found further that the line width and line shape of both the absorption and dispersion were independent of the microwave power level.

Figure 5 presents the saturation results for KCl as a function of H_1. The parameters plotted are the peak absorption and dispersion signals, suitably normalized. $H_{\frac{1}{2}}$ is the value of the microwave field such that the saturation parameter at the line center,

$$S(\omega_0, H_1)=1/(1+\tfrac{1}{4}\gamma^2H_1^2T_1T_2)=\tfrac{1}{2}. \tag{25}$$

The results are compared with the theory of Sec. III with $g(\omega-\omega')$ taken to be Lorentz in shape.

It is clear from Fig. 1 that the results cannot be explained in any way on the basis of the simple theory of Sec. II. Equation (12) of that section gives for the absorption signal at the line center:

$$\frac{2}{\omega_0 T_2}\frac{\chi''(\omega_0)}{\chi_0}\frac{H_1}{H_{\frac{1}{2}}}=\frac{1}{1+(H_1/H_{\frac{1}{2}})^2}\frac{H_1}{H_{\frac{1}{2}}}. \tag{26}$$

For large H_1, on this basis, the absorption signal should go as $H_{\frac{1}{2}}/H_1$, as contrasted with the signal obtained, which is independent of H_1. Further, the theory of Sec. II predicts for a Gaussian line a flattening of the central portion of the line and a nearly twofold increase in line width over the range investigated. Neither of these effects was observed.

However, based on the theory of Sec. III, no change in line width or line shape should be expected. The saturation broadens and reduces the intensity of the absorption of the individual spin packets, but as long as the packets are narrow as compared with the inhomogeneous broadening of the resonance, this effect

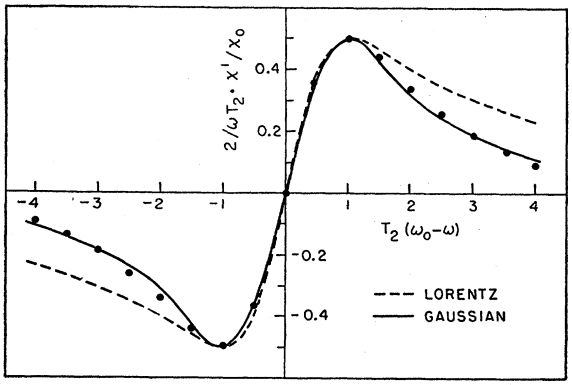

FIG. 4. Line shape (dispersion curve) of F centers in KCl.

will be reflected only in a reduction in the intensity of the absorption. As shown in Appendix I, the dispersion is not affected by the saturation of the spin packets, in agreement with the observations on KCl.

From Eq. (19), the peak absorption signal for the composite line is

$$\frac{2}{\omega T_2^*}\frac{\chi''(\omega_0)}{\chi_0}\frac{H_1}{H_{\frac{1}{2}}}=\int_0^\infty \frac{g(\omega-\omega')d\omega'}{1+(H_1/H_{\frac{1}{2}})^2\pi[g(\omega-\omega')/T_2]}\frac{H_1}{H_{\frac{1}{2}}}. \tag{27}$$

We wish to determine the form of $g(\omega-\omega')$ such that $\chi''(\omega_0)$ will behave in the observed way as a function of H_1. We require that for $H_1>H_{\frac{1}{2}}$

$$\int_0^\infty \frac{g(\omega-\omega')d\omega'}{1+(H_1H_{\frac{1}{2}})^2\pi[g(\omega-\omega')/T_2]}\frac{H_1}{H_{\frac{1}{2}}}\cong 1. \tag{28}$$

If $g(\omega-\omega')$ represents a Lorentz line, that is

$$g(\omega-\omega')=(T_2/\pi)[1/1+T_2^2(\omega-\omega')^2], \tag{29}$$

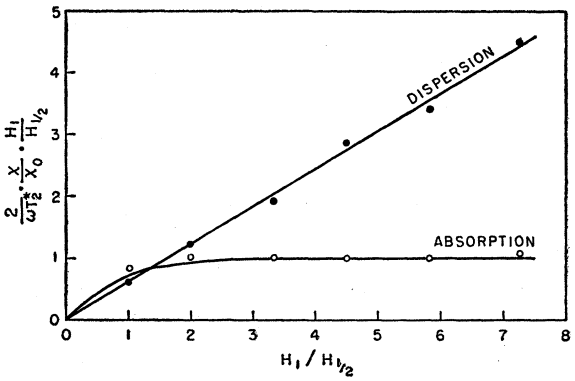

FIG. 5. Saturation behavior of F centers in KCl.

then the left side of Eq. (28) is equal to

$$\{1/[1+(H_1/H_{\frac{1}{2}})^2]^{\frac{1}{2}}\}(H_1/H_{\frac{1}{2}}), \tag{30}$$

which for large H_1 satisfies the required condition. If $g(\omega-\omega')$ were taken as cutting off more sharply in the wings than a Lorentz line, then the left side of Eq. (28) would be decreasing for $H_1>H_{\frac{1}{2}}$, in contrast with the observed behavior. On this basis we must conclude that the spin packets are very closely Lorentz in shape. This result is in good agreement with the arguments of Anderson[5] and the rigorous calculations of Kittel and Abrahams[5] of the frequency moments for dipolar broadening from paramagnetic ions randomly distributed on a simple cubic lattice. The result of Kittel and Abrahams is that, for a fractional magnetic population of less than 0.01, the resonance line is very nearly Lorentz with a half-width at half-maximum intensity,

$$\Delta H=5.3g\mu_B N, \tag{31}$$

where N is the concentration of paramagnetic ions. Substituting for N, the concentration of F centers in the sample studied as determined from the strength of the optical absorption in the F band, the value $2.9\times10^{17}/\text{cm}^3$, we obtain for the half-width of the spin packets:

$$\Delta H=0.028 \text{ oersted}.$$

Comparing this with the half-width at half-maximum intensity for the over-all line of 27 oersteds, it is clear that the assumption made that the packets be narrow as compared with the over-all line width is well justified.

From a study of the saturation behavior it is possible to estimate the spin-lattice relaxation time. The saturation parameter at the line center is defined as

$$S(\omega_0, H_1)=\chi''(\omega_0, H_1)/\chi''(\omega_0, 0). \tag{32}$$

For $H_1>H_{\frac{1}{2}}$ we find

$$S(\omega_0, H_1)\cong 0.012/H_1.$$

However, as shown in Appendix II, the form of the saturation factor will depend to some extent on whether $\omega_m T_1$ is less than or greater than unity, where ω_m is the

[5] P. W. Anderson, Phys. Rev. **82**, 342 (1952); C. Kittel and E. Abrahams, Phys. Rev. **90**, 238 (1953).

frequency of the modulation envelope of the microwaves. Since for F centers in KCl at room temperature,

$$\omega_m T_1 \sim 1,$$

one can at best make an estimate of T_1. Taking the saturation factor at the line center,

$$S(\omega_0, H_1) \simeq \frac{1.6}{\gamma (T_1 T_2)^{\frac{1}{2}}} \frac{1}{H_1},$$

we obtain

$$T_1 T_2 = 5.7 \times 10^{-11} \text{ sec}^2.$$

From the known concentration of F centers

$$T_2 = 1/\gamma \Delta H = 2.3 \times 10^{-6} \text{ sec}.$$

This gives for the spin-lattice relaxation time at room temperature

$$T_1 = 2.5 \times 10^{-5} \text{ sec}.^{6}$$

VI. ON THE KRAMERS-KRONIG RELATIONS

The Kramers-Kronig relations[3] give the form of the dispersion if the absorption is known for all frequencies and, conversely, the absorption if the dispersion is known,

$$\chi'(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\omega' \chi''(\omega')}{\omega'^2 - \omega^2} d\omega', \tag{33}$$

$$\chi''(\omega) = -\frac{2}{\pi} \omega \int_0^\infty \frac{\chi'(\omega')}{\omega'^2 - \omega^2} d\omega'. \tag{34}$$

Our experimental results are in strong contradiction with the above relations. We find that at high power levels χ' is independent of power level but χ'' decreases in amplitude with increasing microwave power. Neither the absorption nor the dispersion vary in shape or width. This strong discrepany led to a re-examination of the validity of these relations. Their derivation is presented clearly by Van Vleck,[7] and it is his presentation which will be examined here. The usual procedure is to define a complex susceptibility,

$$\chi(\omega') = \chi'(\omega') - i\chi''(\omega'), \tag{35}$$

where ω' is a complex frequency. One then integrates the function

$$\chi(\omega')/(\omega' - \omega),$$

where ω is real, along the real frequency axis closing the contour around the lower half of the complex frequency plane. Since for physically realizable systems the absorption is an even function of the frequency and the dispersion an odd function, and further stipulating that there be no singularities in the lower half of the complex plane, the relations Eqs. (33) and (34) are obtained.

It is in particular the stipulation that the complex susceptibility be analytic over the lower half of the complex frequency plane which we wish to examine here. Van Vleck establishes this condition on the basis of the linearity of the system. In considering the behavior of the complex dielectric constant, he expresses the electric polarization of the system in terms of a Fourier integral over the spectrum of the electrical disturbance by introducing a dielectric constant which is a function of frequency. It is concluded then that the dielectric constant can have no singularities in the lower half of the complex frequency plane, since if this were not the case one would have a response of the system preceding the arrival of the electrical disturbance. This situation is closely related to the impossibility of having exponentially increasing solutions for the response of a physical system in the absence of any excitation. We show here that if the system is nonlinear the treatment of Van Vleck does not apply, nor are his conclusions about the behavior of the system in the absence of any excitation valid. The susceptibility will in fact have singularities in the lower half of the complex frequency plane. The existence of these singularities is contingent on the presence of excitation, and it is in this important respect that linear and nonlinear systems differ. It does not follow then that for nonlinear systems the presence of singularities in the lower half of the complex frequency plane has as a consequence that there will be exponentially increasing solutions in the absence of excitation. Further, the response cannot precede the disturbance since it is the disturbance which creates the singularities.

Taking the results of Appendix I for the complex susceptibility in the simple case,

$$\chi(\omega) = \tfrac{1}{2}\chi_0\omega_0 \frac{\left\{\int_0^\infty [2\omega' g(\omega' - \omega_0)/(\omega'^2 - \omega^2)] d\omega'\right\} - i\pi g(\omega - \omega_0)}{1 + (H_1/H_2)^2 [\pi g(\omega - \omega_0)/T_2]}, \tag{36}$$

the complex susceptibility will have simple poles in the complex frequency plane for

$$[\pi g(\omega - \omega_0)/T_2]^{\frac{1}{2}} (H_1/H_{\frac{1}{2}}) = \pm i. \tag{37}$$

These poles must occur in conjugate complex pairs, from which it follows that if H_1 is nonvanishing there will be poles in the lower half of the complex frequency plane. The residues at these poles will be of order $(H_1/H_{\frac{1}{2}})^2$, so that for low power levels they can be disregarded. However, as has been seen at high power levels, the presence of these poles may profoundly alter the relation between χ' and χ'' so that their presence cannot be neglected. It does not seem possible in

[6] An estimate of the spin-lattice relaxation time from the hyperfine interaction, using the results of Waller for Raman processes [Z. Physik **79**, 370 (1932)], yields a value about ten times greater than this. However, because of the roughness of the estimate a more exact calculation might still be profitable.

[7] J. H. Van Vleck, Massachusetts Institute of Technology Radiation Laboratory Technical Report 735, 1945 (unpublished).

general to obtain an analytical expression, for example, for a saturated disperion line from a knowledge of the form of the saturated absorption line. It is possible on physical grounds to circumvent this problem as is done in Appendix I. It is required, however, that the form of the absorption in the absence of saturation be known.

As an example of the above considerations, we examine the solutions of the Bloch equations[8] for the behavior of a paramagnetic system in crossed constant and rotating magnetic fields. The importance of the Bloch equations here is that they yield expressions for the absorption and dispersion for any H_1 without the need for introducing the Kramers-Kronig relations. We obtain for a rotating microwave field of amplitude H_1

$$\chi'(\omega)=\tfrac{1}{2}\chi_0\omega_0T_2\{T_2(\omega_0-\omega)/[1+s+T_2^2(\omega_0-\omega)^2]\}, \quad (38)$$

$$\chi''(\omega)=\tfrac{1}{2}\chi_0\omega_0T_2\{1/[1+s+T_2^2(\omega_0-\omega)^2]\}, \quad (39)$$

where $s=\gamma^2H_1^2T_1T_2$.

$$\chi(\omega)=\chi'(\omega)-i\chi''(\omega)=-\tfrac{1}{2}\chi_0\omega_0\frac{\omega-[\omega_0-(i/T_2)]}{\{\omega-[\omega_0-(i/T_2)(1+s)^{\frac{1}{2}}]\}\{\omega-[\omega_0+(i/T_2)(1+s)^{\frac{1}{2}}]\}}. \quad (40)$$

The complex susceptibility will have poles at

$$\omega=\omega_0\pm(i/T_2)(1+s)^{\frac{1}{2}}.$$

The residue at the pole in the lower half of the complex plane is

$$-\tfrac{1}{4}\chi_0\omega_0[1-(1+s)^{-\frac{1}{2}}],$$

which is of order $(H_1/H_{\frac{1}{2}})^2$.

If one substitutes the expression of Eq. (39) for the absorption into Eq. (33), one does not obtain the expression of Eq. (38) for a nonvanishing microwave field. The solutions of the Bloch equation are then not in agreement with the Kramers-Kronig relations. They are, however, completely consistent with our Eqs. (12) and (15), which were derived using the Kramers-Kronig relations in only a very restricted way.

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APPENDIX I. DERIVATION OF THE SUSCEPTIBILITY EXPRESSIONS

In the absence of saturation we have, from Eq. (12),

$$\chi''(\omega)=\tfrac{1}{2}\pi\chi_0\omega_0g(\omega-\omega_0).$$

Since we are dealing here with an unsaturated system, we can obtain the unsaturated dispersion from Eq. (33), the first of the Kramers-Kronig relations. Then

$$\chi'(\omega)=\tfrac{1}{2}\chi_0\omega_0\int_0^\infty\frac{2\omega'g(\omega'-\omega_0)}{\omega'^2-\omega^2}d\omega'.$$

The saturation is introduced through Eq. (7), which gives the way in which the difference in populations of the spin levels decreases with increasing microwave power. Then, for arbitrary microwave field strength

$$\chi''(\omega)=\tfrac{1}{2}\chi_0\omega_0\frac{\pi g(\omega-\omega_0)}{1+\frac{1}{4}\pi\gamma^2H_1^2T_1g(\omega-\omega_0)}, \quad (12)$$

$$\chi'(\omega)=\tfrac{1}{2}\chi_0\omega_0\frac{\int_0^\infty[2\omega'g(\omega'-\omega_0)/(\omega'^2-\omega^2)]d\omega'}{1+\frac{1}{4}\pi\gamma^2H_1^2T_1g(\omega-\omega_0)}. \quad (15)$$

In the general case with both homogeneous and inhomogeneous broadening, we assemble the response of the spin packets under an envelope of shape $h(\omega-\omega_0)$. We obtain

$$\chi''(\omega)=\tfrac{1}{2}\chi_0\int_0^\infty\frac{\pi\omega'g(\omega-\omega')}{1+\frac{1}{4}\pi\gamma^2H_1^2T_1g(\omega-\omega')}h(\omega'-\omega_0)d\omega', \quad (17)$$

$$\chi'(\omega)=\tfrac{1}{2}\chi_0\int_0^\infty\frac{\omega'h(\omega'-\omega_0)d\omega'}{1+\frac{1}{4}\pi\gamma^2H_1^2T_1g(\omega-\omega')}\times\int_0^\infty\frac{2\omega''g(\omega''-\omega')}{\omega''^2-\omega^2}d\omega''. \quad (18)$$

For the case where the spin packets are narrow compared with the over-all line width, $g(\omega-\omega')$ will be appreciably different from zero only for $\omega'\sim\omega$. Since $h(\omega'-\omega_0)$ is slowly varying over this region, we obtain from Eq. (17)

$$\chi''(\omega)=\tfrac{1}{2}\chi_0\omega h(\omega-\omega_0)\int_0^\infty\frac{\pi g(\omega-\omega')d\omega'}{1+\frac{1}{4}\pi\gamma^2H_1^2T_1g(\omega-\omega')}. \quad (19)$$

To obtain Eq. (20), we first reverse the order of integration of Eq. (18)

$$\chi'(\omega)=\tfrac{1}{2}\chi_0\int_0^\infty\frac{2\omega''d\omega''}{\omega''^2-\omega^2}\times\int_0^\infty\frac{\omega'h(\omega'-\omega_0)g(\omega''-\omega')}{1+\frac{1}{4}\pi\gamma^2H_1^2T_1g(\omega-\omega')}d\omega'. \quad (41)$$

[8] F. Bloch, Phys. Rev. **70**, 460 (1946).

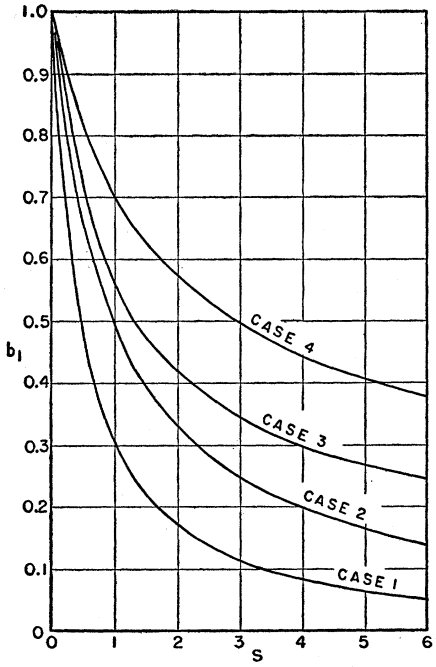

FIG. 6. Variation of the saturation parameter as a function of microwave power.

The contribution of the denominator in the integral over ω' will be of order T_2^*/T_2, so that we neglect it under the assumptions being made in this treatment. Then

$$\chi'(\omega)=\tfrac{1}{2}\chi_0\int_0^\infty \frac{2\omega''d\omega''}{\omega''^2-\omega^2}\int_0^\infty \omega' h(\omega'-\omega_0)g(\omega''-\omega')d\omega'.$$

Since $h(\omega'-\omega_0)$ is slowly varying in the vicinity of $\omega''\sim\omega'$, where $g(\omega''-\omega')$ is appreciable, and since

$$\int_0^\infty g(\omega''-\omega')d\omega'=1,$$

we obtain finally

$$\chi'(\omega)=\tfrac{1}{2}\chi_0\int_0^\infty \frac{2\omega''^2 h(\omega''-\omega_0)}{\omega''^2-\omega^2}d\omega''. \qquad (20)$$

It should be observed that this is just the dispersion that one obtains from the Kramers-Kronig relations for an absorption of shape $h(\omega-\omega_0)$.

APPENDIX II

Saturation Behavior for Power Modulated Microwaves

We have treated the microwave power level as varying slowly enough compared with T_1 so that we could consider the spin system as being in a quasi-steady state. However if ω_m, the frequency of power modulation of the microwaves, is of the order of or greater than $1/T_1$, the saturation behavior is somewhat altered. We consider here four cases:

Case 1. Homogeneous broadening and $\omega_m T_1<1$. The system will follow the variations in microwave power. Or if we take the saturation factor

$$S(\omega, H_1)=\chi''(\omega, H_1)/\chi''(\omega, 0),$$

the saturation factor will be periodic at the frequency ω_m.

Case 2. Homogeneous broadening and $\omega_m T_1>1$. For this case the system will not follow the variations in microwave power but will saturate at the average power level.

Case 3. Inhomogeneous broadening and $\omega_m T_1<1$. Here we will saturate spin packets individually rather than transferring power at once to the whole spin system. However, the spin packets will individually follow the periodic variations in power level.

Case 4. Inhomogeneous broadening and $\omega_m T_1>1$.

If the microwave field is power modulated, the power in the signal at the detecting crystal is given by

$$P_s=F\chi_0\omega_0 T_2 S(\omega_0, H_1)[1+\sin(\omega_m t)]P,$$

where P is the power incident on the microwave cavity and F is a factor which depends on the Q of the cavity, the filling factor for the sample, and the conversion loss of the detecting crystal. Since the detected signal is amplified by a narrow band amplifier and detected by a lock-in mixer, in the Fourier expansion of P_s:

$$P_s=F\chi_0\omega_0 T_2 P\sum_n a_n\cos(n\omega_m t)+b_n\sin(n\omega_m t),$$

the observed signal will be proportional to b_1. Our result is that for

Case 1: $b_1=(2/s^2)[(1+s)/(1+2s)^{\frac{1}{2}}]$;

Case 2: $b_1=1/(1+s)$;

Case 3: $b_1\simeq(1+0.60s)/(1+s)^{\frac{3}{2}}$;

Case 4: $b_1=1/(1+s)^{\frac{1}{2}}$,

where $s=\frac{1}{4}\gamma^2 H_1^2 T_1 T_2$.

These functions are plotted in Fig. 6 and behave in the expected way, with Case 1 saturating the most rapidly and Case 4 the most slowly.