Packet-Shifting Electron-Nuclear Double-Resonance Mechanisms

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Mechanisms of electron-nuclear double resonance (ENDOR) which involve the shift of spin packets are discussed in relation to experiments performed on phosphorus-doped silicon and irradiated frozen sulfuric acid. Both homogeneously saturated and inhomogeneously saturated electron-paramagnetic-resonance (EPR) transitions are considered. In the case of homogeneous packet-shifting ENDOR, the presence or absence of certain relaxation paths determines the sign and size of the ENDOR response. In the case of inhomogeneous packet-shifting ENDOR, the saturation and passage conditions also determine the nature of the ENDOR response.

I. INTRODUCTION

Electron-nuclear double resonance (ENDOR)[1] is the technique whereby transitions between nuclear-magnetic-energy levels are detected through their effect upon an electron-paramagnetic-resonance (EPR) signal. The nuclear transitions are stimulated, as in NMR, through the application of radio-frequency power, while a microwave EPR signal belonging to some convenient paramagnetic center in the material is monitored. In many cases, the EPR signal is affected by changes in the populations of the nuclear-magnetic levels. There are several possible methods of coupling between the electrons and nuclei which will give rise to these effects. The mechanism of interaction, the speed of response, and the sign of the effect (i.e., whether the EPR signal decreases or increases) depend on the material and the experimental conditions. The present work examines some relatively simple systems and exhibits the basic principles involved in their behavior.

A previous paper[2] dealt with a class of materials in which the ENDOR response depended on the existence of a nuclear polarization. The theory was an alternative to the original explanation[3] of Feher, for those cases in which Feher's theory obviously did not apply. The previous work also explained the "sign" of the ENDOR effect and the magnitude of its recovery time, both of which showed discrepancies between experiment and the predictions of a naive theory. The present work represents, at least in spirit, a continuation of that work.

This paper concentrates, however, on a description of ENDOR mechanisms involving the shift of spin packets, as proposed by Feher. Some mechanisms discussed are applicable to spin systems with homogeneously saturated resolved EPR transitions ("homogeneous" ENDOR). Others involve inhomogeneous saturation and packet-shifting within an inhomogeneous line ("inhomogeneous" ENDOR). Various types of ENDOR may be distinguished by these saturation conditions, the passage conditions, and the presence or absence of certain relaxation mechanisms. The size of the hyperfine interaction is another distinction, but in this paper only hyperfine interactions larger than a spin-packet width will be considered.

The principal system chosen for study was phosphorus-doped silicon. The reasons for this choice included the extensive work on relaxation phenomena in this material done by Feher and Gere.[4] This resonance center has both electron and nuclear spin equal to $\frac{1}{2}$ and hence is free from quadrupole effects. And yet because of the variety of relaxation paths available, some easily controlled, the system is of sufficient complexity to exhibit a variety of interesting ENDOR effects.

Additional experiments were performed on irradiated frozen sulfuric acid. When frozen at liquid nitrogen temperature and x-irradiated, this material exhibits a resonance due to trapped interstitial hydrogen atoms. Again both electron and nuclear spins are equal to $\frac{1}{2}$.

The experimental apparatus was described in I. The silicon was obtained from the Dow Corning Company, and had a resistivity 0.1–1.0 Ω. All experiments were performed at liquid-helium temperature, with the samples immersed. The frozen acid was irradiated at liquid-nitrogen temperature and transferred directly into the liquid-helium bath for measurement. Experiments on the silicon samples were performed in a darkened room unless the contrary is specified. Phase sensitive detection was used throughout this work, unlike the work reported in I. Depending on the observation, the magnetic field modulation frequency varied from 100 c/sec to 5 kc/sec.

Section II provides the theory behind the effects which are reported in the ensuing sections. In Sec. III, attention is restricted to resolved EPR transitions which are homogeneously saturated (modulation width exceeds linewidth), and dynamical passage effects are avoided. The effects then depend on the presence of various relaxation paths. Section IV is devoted to experiments performed with a modulation width narrow compared to the linewidth. Finally, Sec. V presents some general conclusions and a summary.

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[1] G. Feher, Phys. Rev. **103**, 500 (1956).
[2] J. Lambe, N. Laurance, E. C. McIrvine, and R. W. Terhune, Phys. Rev. **122**, 1161 (1961), hereafter referred to as I.
[3] G. Feher, Phys. Rev. **114**, 1219 (1959).
[4] G. Feher and E. A. Gere, Phys. Rev. **114**, 1245 (1959).

II. THEORY

A qualitative understanding of the sign and magnitude of the ENDOR responses is obtainable for many cases which have been studied experimentally.

Consider an electron paramagnetic center with an environment of nuclear spins. ENDOR responses from resolved lines are observed with all but one nuclear quantum number fixed. Ignoring possible zero-field splittings and nuclear quadrupole terms, one may write a Hamiltonian consisting of the electron and nuclear Zeeman terms and the hyperfine interaction,

$$H = g\beta \mathbf{H}\cdot\mathbf{S} - \gamma\beta_N \mathbf{H}\cdot\mathbf{I} + A\mathbf{S}\cdot\mathbf{I}. \tag{1}$$

In this expression, **H** is the applied magnetic field, **S** is the spin of the electron center, and **I** is the spin of the nucleus under consideration. The electron gyromagnetic ratio is g, the nuclear gyromagnetic ratio is γ, while β and β_N are the Bohr magneton and nuclear magneton, respectively. The hyperfine tensor is represented by the isotropic part only, A.

Ignoring inessential details from second-order perturbation theory, one may write the energy levels $E_{m_S m_I}$ of the electron (spin quantum number m_S) and the nucleus under consideration (spin quantum number m_I).

$$\begin{aligned}
E_{\frac{1}{2}\frac{1}{2}} &= \tfrac{1}{2}g\beta H - \tfrac{1}{2}\gamma\beta_N H + \tfrac{1}{4}A\,,\\
E_{\frac{1}{2}-\frac{1}{2}} &= \tfrac{1}{2}g\beta H + \tfrac{1}{2}\gamma\beta_N H - \tfrac{1}{4}A\,,\\
E_{-\frac{1}{2}\frac{1}{2}} &= -\tfrac{1}{2}g\beta H - \tfrac{1}{2}\gamma\beta_N H - \tfrac{1}{4}A\,,\\
E_{-\frac{1}{2}-\frac{1}{2}} &= -\tfrac{1}{2}g\beta H + \tfrac{1}{2}\gamma\beta_N H + \tfrac{1}{4}A\,.
\end{aligned} \tag{2}$$

It will be noticed that in general the allowed transitions $(-\frac{1}{2}\frac{1}{2} \to \frac{1}{2}\frac{1}{2})$ and $(-\frac{1}{2}-\frac{1}{2} \to \frac{1}{2}-\frac{1}{2})$ have different frequencies. When the inhomogeneous linewidth of the electron resonance does not exceed $\frac{1}{2}A$, the allowed transitions are resolved. The occupation of the state characterized by quantum numbers m_S, m_I, will be represented by $n(m_S,m_I)$ (Fig. 1).

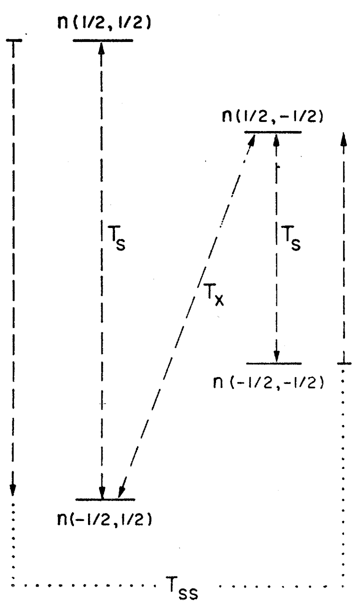

FIG. 1. Relaxation processes in simple systems with spin-$\frac{1}{2}$ nuclear species, spin-$\frac{1}{2}$ paramagnetic center. T_S is the electron spin-lattice relaxation time; T_x is the cross-relaxation time; and T_{ss} is the double-exchange scattering. The occupation probabilities of the spin states are indicated by $n(m_S,m_I)$.

It will be assumed that

$$\gamma\beta_N H \ll \tfrac{1}{2}A \ll kT \tag{3}$$

and the following auxiliary definition will be used:

$$\epsilon = g\beta H/kT. \tag{4}$$

Power absorption implies an eventual transfer of energy from the microwaves to the lattice. Consequently, the dynamical expressions for occupation and power depend upon the significant relaxation paths: electron spin-lattice relaxation with a relaxation time T_s; cross relaxation[5] with a relaxation time T_x; and double-exchange scattering[6] with a relaxation time T_{ss}. The effect of T_s and T_x processes is to establish a Boltzmann distribution between the energy levels involved. The process T_{ss} is different in that it attempts to equalize the temperature of two isolated systems. These relaxation processes are schematically indicated in Fig. 1, and are discussed by Feher and Gere.[4] They find T_s to be about 10 sec at 4.2°K, independent of light. In the dark, T_x and T_{ss} are found to be essentially infinite. When electrons are excited into the conduction band by absorbed light, T_{ss} becomes about 1 sec and dominates the relaxation scheme, while T_x may be as short as 8 min, leading to measurable effects. The nuclear spin-lattice relaxation time is assumed infinite.

The solutions of the relaxation equations involve the various relaxation times. The solutions of the rate equations in the presence of applied EPR power also involve these relaxation times, and, in addition, the transition rate W due to the applied microwaves. Without loss of generality, we consider the EPR monitor to be applied to the $(-\frac{1}{2}\frac{1}{2} \to \frac{1}{2}\frac{1}{2})$ transition. We shall present the rate equations' solutions only for two limiting cases, which approximate the experimental conditions to be reported.

T_x Infinite; T_{ss} Infinite

In the absence of T_x processes, no relaxation of nuclear spin polarization is possible (recalling that the nuclear spin-lattice relaxation has also been assumed infinite). The fractional nuclear polarization

$$P_N = [n(-\tfrac{1}{2},\tfrac{1}{2}) + n(\tfrac{1}{2},\tfrac{1}{2}) - n(\tfrac{1}{2},-\tfrac{1}{2}) - n(-\tfrac{1}{2},-\tfrac{1}{2})] \tag{5}$$

retains its initial value, providing a constant of motion which is found in the solution of the rate equation.

$$\begin{aligned}
n(\tfrac{1}{2},\tfrac{1}{2}) &= \tfrac{1}{4}(1+P_N)[1-\epsilon/(1+WT_s)],\\
n(-\tfrac{1}{2},\tfrac{1}{2}) &= \tfrac{1}{4}(1+P_N)[1+\epsilon/(1+WT_s)],\\
n(\tfrac{1}{2},-\tfrac{1}{2}) &= \tfrac{1}{4}(1-P_N)(1-\epsilon),\\
n(-\tfrac{1}{2},-\tfrac{1}{2}) &= \tfrac{1}{4}(1-P_N)(1+\epsilon).
\end{aligned} \tag{6}$$

[5] D. Pines, J. Bardeen, and C. P. Slichter, Phys. Rev. **106**, 489 (1957).

[6] P. W. Anderson, quoted in Feher and Gere (Ref. 4).

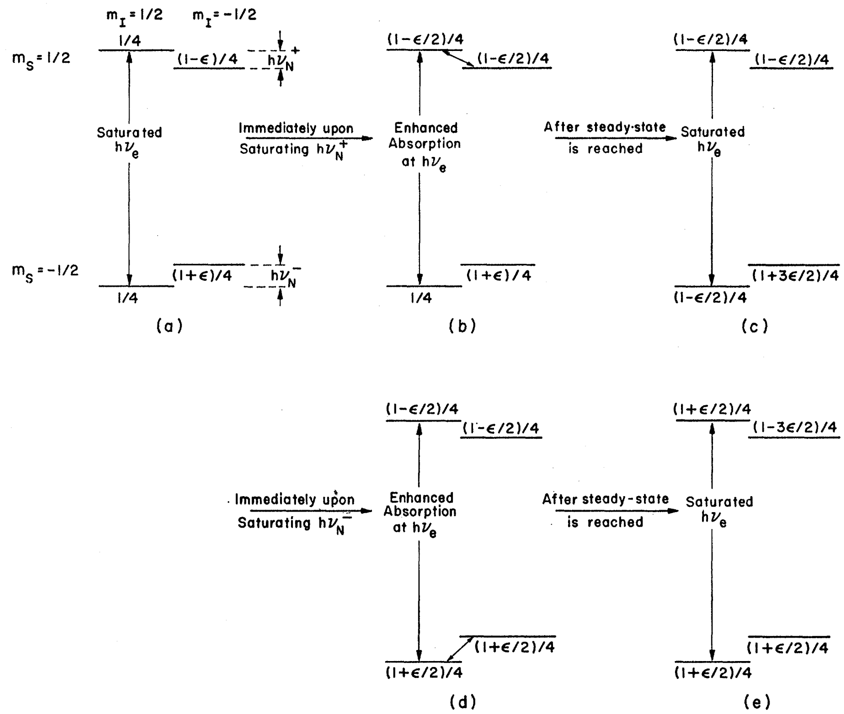

FIG. 2. ENDOR responses in the silicon system with electron spin-lattice relaxation as the only significant relaxation path. The relaxation times T_x, T_{ss}, and T_N are all so long that they may be neglected. The low-field EPR line is homogeneously saturated. (a) Steady-state EPR. Nuclear polarization $P_N=0$. (b) Transient ENDOR response at $h\nu_N^+$. (c) Steady-state EPR. Nuclear polarization $P_N=-\frac{1}{2}\epsilon$. No further ENDOR response at $h\nu_N^+$ until $h\nu_N^-$ is saturated. (d) Transient ENDOR response at $h\nu_N^-$. (e) Steady-state EPR. Nuclear polarization $P_N=\frac{1}{2}\epsilon$. No further ENDOR response at $h\nu_N^-$ until $h\nu_N^+$ is saturated.

T_x Finite; $T_{ss} \ll T_s$

For comparison with experiment when T_x is finite, we shall be concerned only with the conditions of dominant spin-exchange scattering. The solution is

$$\begin{aligned} n(\tfrac{1}{2},\tfrac{1}{2}) &= \tfrac{1}{4}[1-\epsilon], \\ n(-\tfrac{1}{2},\tfrac{1}{2}) &= \tfrac{1}{4}[1+\epsilon(2-WT_s)/(2+WT_s)], \\ n(\tfrac{1}{2},-\tfrac{1}{2}) &= \tfrac{1}{4}[1-\epsilon(2-WT_s)/(2+WT_s)], \\ n(-\tfrac{1}{2},-\tfrac{1}{2}) &= \tfrac{1}{4}[1+\epsilon]. \end{aligned} \quad (7)$$

The EPR signal in the absence of applied rf power may be deduced from these last equations (in which several small terms have been eliminated for purposes of clarity). Expressions for the EPR signal with applied rf (and consequently expressions for *steady-state* ENDOR responses) would be based on similar solutions calculated with NMR transitions saturated. The observed *transient* responses will be developed as required, along with qualitative discussion.

The simplified theory presented here is adequate to explain the reduction in magnitude or vanishing of ENDOR lines and the reversal in sign from the expected increase in absorption, in several cases studied experimentally. Therefore the simplified theory shall be used for clarity, although it has been verified that the proofs hold for a considerably more rigorous analysis.

III. HOMOGENEOUS ENDOR

Operationally, homogeneous ENDOR is achieved in an inhomogeneous line by using a slow-field modulation with a modulation field width exceeding the linewidth of the resonance. The entire resonance line responds uniformly to the ENDOR stimulus, approximating the behavior of a homogeneously broadened line. In the absence of passage effects, with homogeneous saturation, and for a spin-$\frac{1}{2}$ spin-$\frac{1}{2}$ system, one would expect the simplest ENDOR behavior. But even in this case, ENDOR lines may vanish or reverse in sign.

In the dark, a first approximation for the behavior of the n-type silicon spin system places $T_x = T_{ss} = \infty$, and the transient response of the EPR absorption signal to the saturation of the NMR transitions depends upon the previous state of nuclear polarization, by Eq. (6). A discussion of the transient responses in this case is given in the caption to Fig. 2. The important conclusions are (1) when the same NMR transition is saturated twice in a row, the second saturation does not lead to any change in the EPR signal; (2) when the saturation of one NMR transition is followed by the saturation of the other, the second signal causes the system to pass through a transient intermediate state to a new steady state. A large transient increase in EPR absorption occurs. Both of these conclusions are subject to the approximations of Eqs. (6) but relaxing these conditions only leads to the prediction of a small transient signal when the same NMR transition is saturated twice in a row.

The experimental results for phosphorus-doped silicon in the dark, shown in Fig. 3, amply demonstrate the validity of these conclusions. The nuclear transitions are located at 52 and 65 Mc/sec. To achieve the largest ENDOR responses, the oscillator had to be dialled back and forth between these frequencies. Both transitions

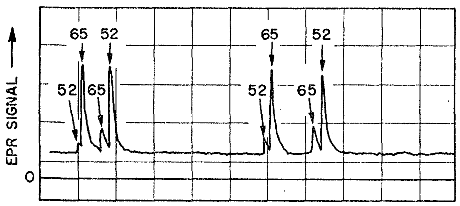

FIG. 3. Experimental observation of the response of an EPR signal in phosphorus-doped silicon to the excitation of NMR transitions. The sample was in the dark.

cause an increase in signal, the upper transition by depleting the population of the upper state being saturated, the lower transition by augmenting the population of the lower state being saturated. Had the high-field line $(-\frac{1}{2}-\frac{1}{2}\rightarrow\frac{1}{2}-\frac{1}{2})$ been saturated initially instead of the low-field line $(-\frac{1}{2}\frac{1}{2}\rightarrow\frac{1}{2}\frac{1}{2})$, identical results would have been obtained. The idealized case considered represents complete saturation. In practice sensitivity is greatest with only a partial saturation, since the resonance signal depends upon energy absorption.

Consider now the effect of shining light on the silicon sample. Free carriers are created, leading to a greatly reduced relaxation time for double exchange scattering T_{ss}. If this reduction were such that T_{ss} was still much longer than T_s, the ENDOR responses to the different NMR frequencies would still be of the same sign, but nonzero. But, in fact, the double-exchange scattering in illuminated phosphorus-doped silicon is more effective than the electron spin-lattice relaxation. This provides a strong tendency for the two occupation probability differences $[n(-\frac{1}{2},\frac{1}{2})-n(\frac{1}{2},\frac{1}{2})]$ and $[n(-\frac{1}{2},-\frac{1}{2})-n(\frac{1}{2},-\frac{1}{2})]$ to equalize.

The situation immediately after exposing the sample to light is illustrated in Fig. 4. Since $T_{ss}\ll T_s$, saturation of one line with a microwave field results in saturation of the entire system. The spin-exchange process communicates the infinite spin temperature of one population to the other and all four levels attain the same population. No ENDOR response can be obtained under this situation. Experimentally, this simple prediction is confirmed; within seconds after illuminating the sample, no ENDOR response is obtained.

However, the cross-relaxation time T_x must now be considered finite (although it is several minutes, and much longer than T_{ss}). After equilibration of the cross-relaxation process, the ENDOR effect is again observable, but a reversal in sign occurs for one of the ENDOR responses. The steady-state occupation probabilities are governed by Eqs. (7) and we assume complete saturation ($WT_s=\infty$). The situation 10 min or more after exposure to light is illustrated in Fig. 5. It is seen that upon saturation of the nuclear transition $h\nu_N^+$ the EPR absorption is increased, while upon saturation of the nuclear transition $h\nu_N^-$ the EPR absorption is turned into an emission. If the high-field EPR resonance line $(-\frac{1}{2}-\frac{1}{2}\rightarrow\frac{1}{2}-\frac{1}{2})$ were used the effect would be reversed: The upper nuclear transition would cause a decrease in signal and the lower nuclear transition would cause an increase.

The experimental observations for illuminated phosphorus doped silicon are shown in Fig. 6, while Fig. 7

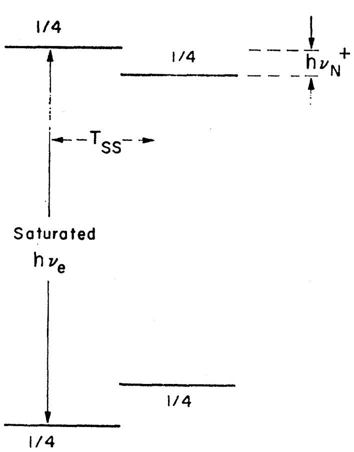

FIG. 4. Immediately upon illuminating a silicon sample: $T_{ss}\ll T_s$, and so all levels attain the same population ($n=\frac{1}{4}$). The nuclear transitions are already saturated, and there is no response to an applied ENDOR frequency.

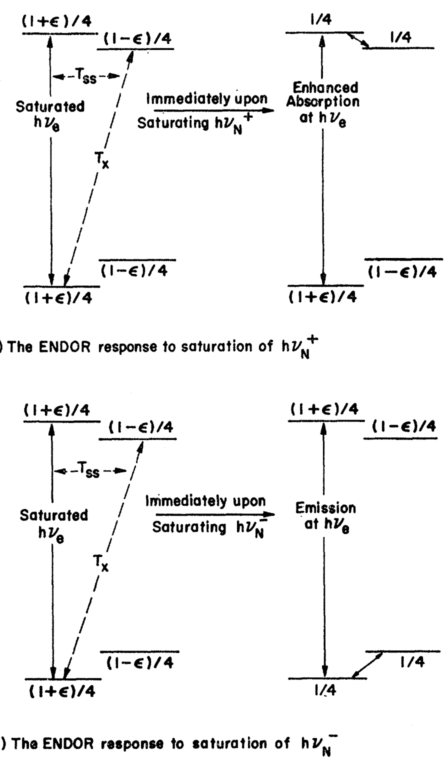

FIG. 5. ENDOR responses in a system with rapid spin-exchange scattering, finite cross-relaxation and electron spin-lattice relaxation times. The $(-\frac{1}{2},\frac{1}{2}\rightarrow\frac{1}{2},\frac{1}{2})$ EPR transition is the monitor, and is assumed to be heavily saturated. The combination of T_{ss} and T_x processes leads to a reversal of the usual ENDOR effect. Saturating $h\nu_N^-$ leads to an effect just opposite to that of saturating $h\nu_N^+$.

depicts experimental results on another system with rapid spin-exchange scattering: x-irradiated frozen sulfuric acid. In the first case, the high-field EPR line was used; in the second case, the low-field EPR line was the monitor. In both cases there was a difference between the signs of the two ENDOR responses, and all signs correspond to the predictions of our theory.

In Fig. 8 a system is depicted which has not been studied in these experiments: the system in which only spin-lattice relaxation T_s and cross-relaxation T_x occur. If the low-field EPR transition is used [Fig. 8(a)] only one ENDOR transition is possible, $h\nu_N^+$. If the high-field EPR transition is used as a monitor [Fig. 8(b)], then only the $h\nu_N^-$ ENDOR transition will be seen. This discrimination effect was used by Feher, Fuller, and Gere to determine the sign of the nuclear moment of phosphorus.[7] This case has been extensively treated in the past in the discussion of ENDOR, but is only one of the many possible cases.

In summary, these experiments demonstrate that even in the simple spin-$\frac{1}{2}$ spin-$\frac{1}{2}$ systems without

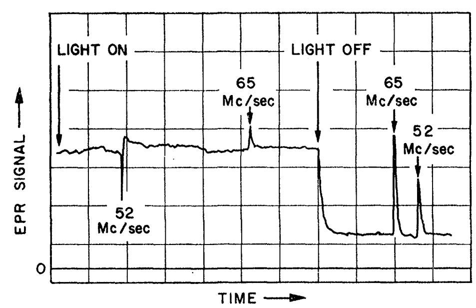

FIG. 6. Experimental observation of the response of an EPR signal in phosphorus-doped silicon to the excitation of nuclear transitions, with the sample illuminated.

dynamical complications, the response at expected ENDOR frequencies may be very small (or vanishing), may depend upon the previous state of nuclear polarization, or may change in sign from the expected absorption increase. Since such variety in behavior results from a variation in relaxation conditions, it is not surprising that even more variety may occur in experiments using rapid modulation or fast passage. Some of the passage effects are explored in the next section.

IV. INHOMOGENEOUS ENDOR

The previous section describes artificial experimental conditions normally not encountered in an EPR experiment. Usually the entire line is not swept, since resolution would be lost. Rather the modulation width is smaller than the linewidth. Attention will now be turned to more likely experimental conditions. In particular, one case of the diminution or reversal in sign of a phase-sensitive detector EPR response will be con-

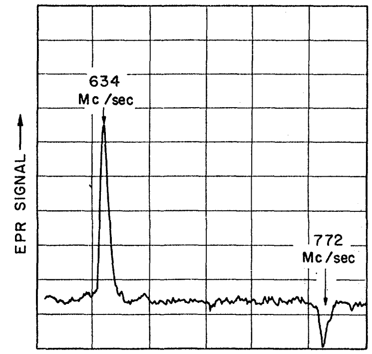

FIG. 7. Experimental observation of the response of an EPR signal in x-irradiated frozen sulfuric acid to the excitation of nuclear transitions.

sidered, under conditions of rapid field modulation of inhomogeneous lines.

The shape of the resonance signals observed in systems with inhomogeneously broadened lines is complex. A detailed analysis[8] of EPR signals has been made by Weger using as a prototype phosphorus-doped silicon. Weger confirmed the basic predictions[9] of Portis concerning the behavior of resonance signals from these systems, but carried the analysis further. He classified experimental cases according to the relative values of microwave field intensity, modulation width, modulation rate, spin-lattice relaxation time, and field scanning rate. The experimental method of Sec. III avoided these complications by employing a large modulation width and homogeneously saturating the lines.

ENDOR was observed also with a small modulation width, a modulation frequency of 5 kc/sec, and the magnetic field adjusted to the center of the resonance line. Weger terms this situation "fast" passage (modulation rate fast compared to spin-lattice relaxation rate).

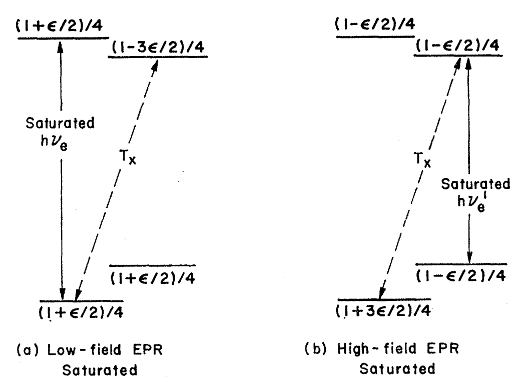

FIG. 8. ENDOR behavior of a system with no spin-exchange scattering. The combined effect of T_s and T_x determines the behavior. Only one of the expected ENDOR transitions causes any response. (a) When the low-field EPR line is saturated, only $h\nu_N^+$ ENDOR is observed. (b) When the high-field EPR line is saturated, only $h\nu_N^-$ ENDOR is observed.

[7] G. Feher, C. Fuller, and E. A. Gere, Phys. Rev. **107**, 1462L (1957).

[8] M. Weger, Bell System Tech. J. **39**, 1013 (1960).

[9] A. M. Portis, Phys. Rev. **104**, 584 (1956).

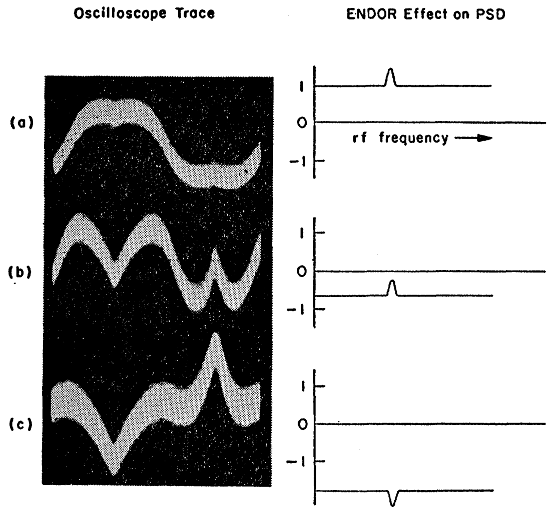

FIG. 9. Experimental observations of EPR line shapes and ENDOR responses under the field modulation conditions described in Sec. IV of the text. (a) Low-power case. ENDOR relieves saturation and increases PSD signal. (b) Intermediate-power case, with composite signal. ENDOR leads to a decrease in magnitude of the total PSD signal. (c) High-power case. ENDOR relieves the small degree of saturation present in the induction signal, and increases the magnitude of the PSD signal.

Except that our experimental situation involves fast passage rather than slow passage, it resembles Weger's case 3, an intermediate case between adiabatic and non-adiabatic conditions. Whether or not the magnetization vector can follow the instantaneous magnetic field is determined by the relative sizes of the microwave field intensity and the instantaneous rate of change of field. With sinusoidal modulation, a composite situation results. Conditions are adiabatic at the extrema and non-adiabatic in the center of the modulation cycle. The resulting signal is complex. Since the phase sensitive detector (PSD) selects one frequency, it is necessary to view the signals on an oscilloscope to observe their character.

The signal observed on the oscilloscope arises from two different physical situations. With the bridge tuned to the dispersion mode, one observes a signal from the dispersion of the spin packets being swept. One also observes an induction signal at the ends of the modulation cycle due to the adiabatic rapid passage of the spin packets. These two contributions appear with 180° phase difference. Their relative magnitudes depend on the microwave power level. In the case of low power, the dispersion component predominates, while for high power, the signal is due largely to the induction component (the dispersion signal saturates). For intermediate power, a composite signal appears. The PSD signal which results is large and of one sign at low power; large and of the opposite sign at high power. At some intermediate power level, the PSD signal vanishes. These simple predictions are observed experimentally, and Fig. 9 shows some actual oscilloscope traces and the PSD responses to ENDOR. The relief of saturation provided by the ENDOR transition leads to an increase in *magnitude* of the PSD response for low and high powers, but a decrease in *magnitude* of the PSD response at intermediate power.

In both this and the previous sections, the ENDOR effect has been assumed "thermal," i.e., dependent only on population differences and not phases. Two experiments verified this. The first duplicated the conditions of Fig. 2, where, after observing the ENDOR response to $h\nu_N^+$, it was necessary to saturate the other nuclear transition $h\nu_N^-$ before reobserving the ENDOR response $h\nu_N^+$. To confirm the thermal nature of the effect, the EPR field was taken off resonance while $h\nu_N^-$ was saturated. Upon returning to resonance and saturating $h\nu_N^+$, an ENDOR response was found identical to that which occurs when the field is left on resonance. This agrees with our explanation, but is inconsistent with a view that ENDOR is related to a dephasing of spin packets. A related experiment was performed under the experimental conditions of this section. The rf oscillator producing the driving signal for ENDOR observation was gated synchronously with the modulation cycle. This allowed the ENDOR effect to be stimulated at varying times during the modulation cycle. The ENDOR effect was independent of the phase, even in the high-power case where the signal arises only at the end of the cycle. This argues strongly in favor of the "thermal" interpretation of the ENDOR effect.

In addition to the foregoing ENDOR experiments, an additional effect was investigated. Studying a broad double resonance in silicon centered at 0.3 Mc/sec, Feher found it sensitive to the microwave power level,[3] and interpreted the effect as akin to Redfield's rotary-saturation phenomena.[10] Since the resonant spins are quantized in a frame rotating about the laboratory frame at the microwave frequency, it is possible to cause transitions with a field of frequency equal to the electron Larmor frequency in the rotating frame. For maximum rotary-saturation absorption, the additional field should be directed along the z axis. A signal similar to the one reported by Feher[3] was observed and the angle between the "ENDOR" driving coil and the static field direction was varied. The effect was a maximum when the coil's magnetic field was parallel to the z axis, as was to be expected. Moreover, the resulting signal was so large that the effect was easily observed with any orientation, unless special pains were taken to obtain a null condition. A small misalignment led to a rotary-saturation signal equal in size to the ENDOR signal.

Since the rotary-saturation effect is solely due to one spin species it should not show the "thermal" properties of ENDOR. To check this, the same gating experiments were performed as for the ENDOR measurements. The effect proved to be strongly phase-dependent. When

[10] A. G. Redfield, Phys. Rev. 98, 1787 (1955).

the rf was applied at the ends of the modulation cycle during the adiabatic fast passage signal, a clear rotary-saturation effect was observed. When the rf was applied during the center of the modulation cycle when adiabatic conditions are violated, no effect was observed. Thus, the effect is distinguishable from the true ENDOR effect.

V. SUMMARY AND CONCLUSIONS

A previous paper (I) included a discussion of the "depolarization" mechanism of ENDOR applicable to ruby and similar materials. The effect of the applied rf was to remove a dynamically established nuclear polarization in distant nuclei, and thus strongly affect the dispersion signal from an inhomogeneous EPR line. In the present work, the mechanisms discussed have all been of the "packet-shifting" type. The applied rf affects the population of the electron-spin system, shifting electrons between the resolved hyperfine levels.

Two main categories of "packet-shifting" ENDOR exist: homogeneous and inhomogeneous. In the first case the EPR line is saturated homogeneously by sweeping the entire line with a slow field modulation. In the second case, the field modulation is smaller in amplitude, and the EPR line is inhomogeneously saturated.

In homogeneous packet-shifting ENDOR, the detailed behavior depends on the presence or absence of certain relaxation paths. Phosphorus-doped silicon in the dark ($T_x = T_{ss} = \infty$) showed a dependence on the previous history of the sample. To obtain the largest ENDOR responses, one saturated the nuclear transitions alternately. Immediately upon exposing the sample to light ($T_{ss} \ll T_s$), no ENDOR responses were possible. However, after equilibrium was reached in light, the finite cross-relaxation time took effect (T_x finite, $T_{ss} \ll T_s$) and the two nuclear transitions again showed ENDOR responses, but of opposite sign. All these effects were explained in terms of the packet-shifting which occurs.

In inhomogeneous packet-shifting ENDOR, the small-amplitude field modulation usually employed in EPR measurements leads to an inhomogeneous saturation of the electron spin packets. The saturation and passage conditions of the modulation then affect the ENDOR response. During ENDOR experiments, the phase-sensitive detector signal sometimes increased, sometimes decreased, and sometimes reversed in sign. The complex signal was composed of two parts, resulting from different physical situations. One part was an induction signal due to the adiabatic rapid passage of the spin packets at the ends of the modulation cycle. The other part was a dispersion signal from the spin packets being swept. The relative sizes depended on the power level (saturation conditions), and the resulting composite PSD signal could be of either sign.

All packet-shifting ENDOR effects were shown to depend only upon population changes and not upon the dephasing of spin packets. In contrast to this "thermal" nature of the ENDOR responses, rotary-saturation effects were shown to be phase-dependent.

In summary, it was established that a great variety of ENDOR responses are possible, even in a system with nuclear spin $\frac{1}{2}$, electron spin $\frac{1}{2}$. These responses are consistent with the packet-shifting concept of ENDOR, and the details of the ENDOR response (sign and magnitude) depend on the presence or absence of various relaxation paths, on the saturation conditions, and on the passage conditions.

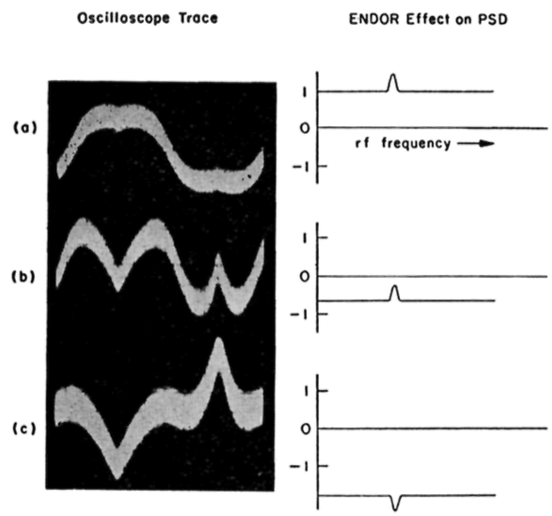

FIG. 9. Experimental observations of EPR line shapes and ENDOR responses under the field modulation conditions described in Sec. IV of the text. (a) Low-power case. ENDOR relieves saturation and increases PSD signal. (b) Intermediate-power case, with composite signal. ENDOR leads to a decrease in magnitude of the total PSD signal. (c) High-power case. ENDOR relieves the small degree of saturation present in the induction signal, and increases the magnitude of the PSD signal.