



RICE UNIVERSITY

Dynamic Polarization in Polymerized Alkynes

by

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ABSTRACT

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A measurement is reported of the proton polarization achieved in a polymer sample through the solid effect. The sample is a polymerized alkyne; the paramagnetism arises from free radicals trapped in the polymer structure. An enhancement factor of 12 was observed at 1.8°K. Growth and decay of the polarization was observed to consist of one component with time constant less than 1 second, another with time constant of 8 seconds.

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I. INTRODUCTION

Dynamic nuclear polarization by saturation of electronic transitions was first proposed by Overhauser¹⁾ in 1953, and subsequently verified by Carver and Slichter²⁾. Overhauser's proposal, which was concerned with the polarization effect in metals, was soon realized to be too restrictive and was generalized by Abragam³⁾ and Jeffries^{4,5)} to include paramagnetic substances. Since these proposals, dynamic polarization has been observed in a wide variety of substances, and several reviews of the subject are available⁶⁻¹³⁾.

This study is principally concerned with the "solid" effect, one of the techniques of dynamic polarization through saturation of "forbidden" transitions in the electronic resonance line. (The term "forbidden" will refer to a transition of the form $\Delta M = \pm 1, \Delta m = \pm 1$.) This technique has been applied to a number of materials. The largest nuclear polarization achieved has been in Nd doped crystals of $\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ ¹⁰⁾ (LMN) where 70 per cent polarization of the protons has been observed. The availability of such large polarizations has aroused considerable interest toward exploiting these effects to produce polarized targets for nuclear scattering experiments, and two such experiments have been carried out using polarized LMN¹²⁾. Polarizations of about 20 per cent were achieved in the LMN targets, a value adequate for the nuclear experiments.

The LMN crystals are not an ideal target material owing to the presence of a large number of nuclei other than protons in the target. These lead to considerable background scattering which obscures the events of interest, namely, the scattering from the protons.

The most obvious solution to this problem would be to work with solid hydrogen, but the properties of hydrogen in the solid state are such that no solid effect is observed. Dynamic polarization of solid deuterium has been achieved, but polarizations only on the order of one per cent have been observed. For reasons that are not well understood, attempts to polarize the protons in various hydrocarbons containing free radicals produced by irradiation at low temperatures have not yielded significant polarizations¹⁴⁻²⁰⁾. For a review of materials on which dynamic enhancement experiments have been performed, see references 10 and 11.

In this paper a measurement of the dynamic enhancement in polymerized acetylene is described. This polymer is paramagnetic owing to the trapping of free radicals into the polymer chain during its synthesis. It is hoped that an understanding of the dynamic polarization effect in this material might point the way for synthesizing an "ideal" nuclear target material, that is, one that contains only a small number of atomic species and that can be readily polarized. To the extent that no attempt has been made to synthesize an organic material with the properties of the ideal target, this represents a new approach to the polarized target problem.

In the following, the theory of dynamic polarization using the solid effect will be outlined, with emphasis on the points of principal interest in the present experiment. Then the experimental apparatus, techniques, and data are discussed. In the last section, the conclusions drawn from the experiment are summarized, and suggestions for proceeding with the study of the polymer samples are given.

II. THEORY

The polymer sample in this experiment is a hydrocarbon with a generally unknown structure, resulting from the polymerization of acetylene (C_2H_2) in the presence of a suitable catalyst. The physical properties and structure of this polymer will be discussed in detail in Section IV. For the moment, it will suffice to state that it is a non-crystalline solid exhibiting an electron paramagnetic resonance. The paramagnetism of the polymer is thought to arise from unpaired electron spins trapped in the polymer. Thus the polymer is essentially a free radical with long term stability. The density of paramagnetic centers is sufficiently small that the interaction between centers can be neglected.

Dynamic polarization experiments using the solid effect involve placing the sample in a resonant microwave cavity while simultaneously observing the nuclear resonance signal. It is observed that at magnetic fields displaced a few gauss to either side of the center of the electron resonance, the nuclear resonance signal increases in size when the microwave power is switched on. For fields lower than the electron resonance field, the nuclear signal is also inverted.

In the ideal case, as will be shown, the enhancement of the nuclear resonance signal should be on the order of the ratio of the electronic to the nuclear g-factor, or roughly 600. In practice, however, such is seldom the case, enhancement factors less than fifty being more common.

In the following development, first a simplified phenomenological theory will be developed, and this will be generalized to include the effects of spin diffusion and unresolved hyperfine spectra. Then an

alternate and more rigorous approach based upon a density matrix formulation will be outlined. The treatment given herein follows the treatment of Leifson and Jeffries²¹⁾ and Abragam¹³⁾. The density matrix approach follows Borghini's¹²⁾ extension of Redfield's²²⁾ treatment.

Simple Model

Consider a simple model containing N electron spins and n nuclear spins where $N \ll n$. Let $\hat{S}_k$ be the k^{th} electron spin and $\hat{I}_i$ the i^{th} nuclear spin. The spin Hamiltonian for the sample is

$$\mathcal{H} = g\beta \sum_k \hat{H} \cdot \hat{S}_k - g_n \beta \sum_i \hat{H} \cdot \hat{I}_i + \sum_{i,k} V_{ik} + \sum_{i>j} U_{ij} \quad 2.1$$

where β is the Bohr magneton, g_n the nuclear g-factor, and g the electron g-factor, assumed isotropic. The first and second terms represent the electron and nuclear Zeeman interactions, the third term represents the electron-nuclear interaction, and the fourth, the nuclear-nuclear interaction. The electron spins are presumed sufficiently dilute to preclude electron-electron interactions. For the case of principal interest here ($I, S = \frac{1}{2}$) quadrupole interactions need not be considered.

The electron-nuclear interaction term

$$V_{ik} = \hat{I}_i \cdot \vec{A}_{ik} \cdot \hat{S}_k - \frac{gg_n \beta^2}{r_{ik}^3} \left[\hat{I}_i \cdot \hat{S}_k - \frac{3(\hat{I}_i \cdot \hat{r}_{ik})(\hat{S}_k \cdot \hat{r}_{ik})}{r_{ik}^2} \right] \quad 2.2$$

consists of the sum of a contact type term and a dipole-dipole term.

In equation 2.2, $\vec{A}_{ik}$ is a tensor and $\hat{r}_{ik}$ represents the separation of $\hat{I}_i$ and $\hat{S}_k$. The fourth term in equation 2.1, which can be expanded

as

$$V_{ij} = \frac{g_i^2 \beta^2}{h_j^2} \left[\hat{I}_i \cdot \hat{I}_j - \frac{3(\hat{I}_i \cdot \hat{r}_{ij})(\hat{I}_j \cdot \hat{r}_{ij})}{r_{ij}^2} \right] \quad 2.3$$

represents the dipole-dipole interaction between $\hat{I}_i$ and $\hat{I}_j$.

For sufficiently large H_0 , the first two terms in equation 2.1 are much larger than the latter two. This implies that the electron and nuclear spins are effectively uncoupled, giving in zero order an energy level scheme composed of superimposed nuclear and electron Zeeman energy levels. The third term weakly couples the electron and nuclear spins systems together, and in doing so mixes the zero order states making possible so called "forbidden" transitions of the form $\Delta M = \pm 1$, $\Delta m = \mp 1$. Saturation of these transitions leads to the dynamic polarization effects of interest here.

The fourth term in equation 2.1 leads to a broadening of the NMR line, can add a structure to the line, and most significantly, leads to the possibility of spin diffusion. The electron-nuclear coupling leading to the possibility of exciting the forbidden transitions, and hence to the possibility of dynamic polarization, is a short range interaction. Therefore only the possibility of spin diffusion can lead to large enhancements over the whole of a sample rather than only in the vicinity of the electron spins.

For the moment, consider a simplified system where the nuclear resonance line has no structure, spin diffusion effects are negligible, and the electron resonance line is narrow enough that the forbidden transitions are well resolved from the allowed transitions. This model

demonstrates the essential features of the solid effect and can be generalized to incorporate the effects of spin diffusion and unresolved hyperfine structure subsequently.

Figure 2.1 represents the energy levels for the weakly coupled electron and nuclear spin systems. Take $g_n, g > 0$ corresponding to the case of interest; N_1 and $N_2 = N - N_1$, are the populations of the upper and lower electronic states respectively; and similarly $n_1, n_2 = n - n_1$ are the populations of the upper and lower nuclear states.

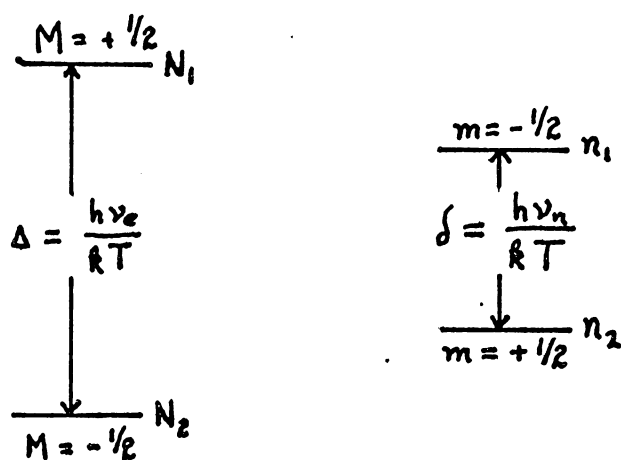


Figure 2.1. Energy level diagram and populations for a system of nuclear spins ($I=\frac{1}{2}$) loosely coupled to electronic spins ($S=\frac{1}{2}$).

Consider the case of two spins, nuclear and electronic, in weak dipolar coupling. The states of this two spin system are labeled by the zero order kets $|++\rangle, |+-\rangle, |-+\rangle, |--\rangle$ in figure 2.2.

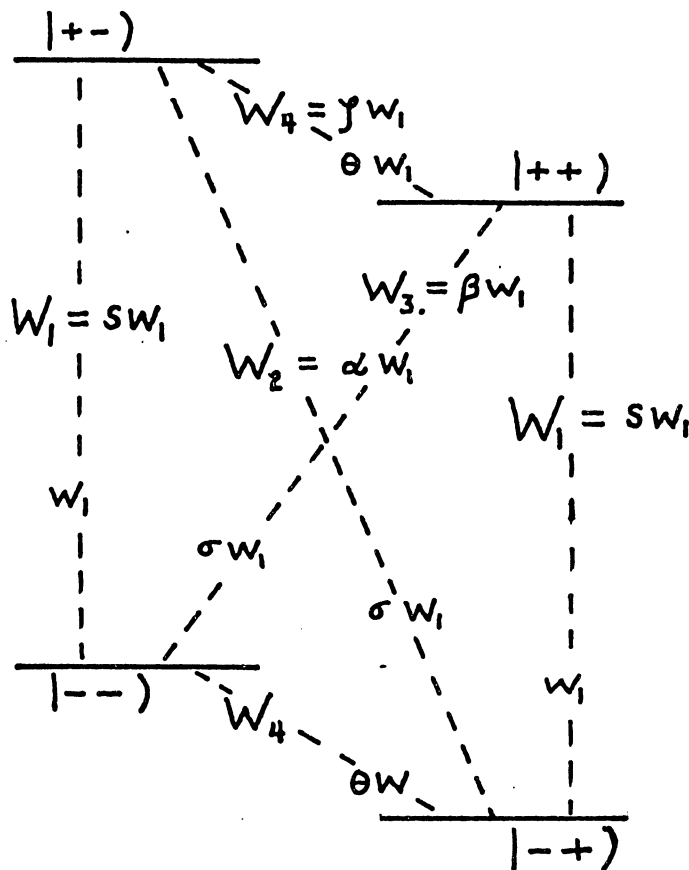


Figure 2.2. Energy level diagram and transitions of a nuclear spin $I=\frac{1}{2}$ in dipolar coupling with an electron spin $S=\frac{1}{2}$.

21)

Following Leifson and Jeffries, the thermal relaxation transition rates are labeled w_1 , σw_1 , θw_1 . The allowed transition $\Delta M = \pm 1, \Delta m = 0$ is the dominant electronic relaxation process and is labeled w_1 . In Appendix A, the weak dipolar coupling is shown to lead to a mixing of the zero order kets, making transitions of the form $\Delta M = \pm 1, \Delta m = \mp 1$ possible. These transitions occur at a rate σw_1 which is shown

to be

$$\sigma \approx \frac{3}{10} \left(\frac{g\beta}{Hr^3} \right)^2 \quad 2.4$$

In this experiment where $g \approx 2.0$, $H \approx 3300$ gauss, equation 2.4 gives $9.1r^{-6}$ where r is measured in angstroms. The relaxation process $\Delta M = 0$, $\Delta m = \pm 1$ may be present if the relaxation is not purely by way of the paramagnetic centers. The rate of this process is defined to be ϕw_1 . The transitions ϕw_1 arise because the dipolar admixtures are not ²¹⁾ constant in time. One expects $\phi < \sigma$ in general.

In addition to transitions due to thermal relaxation, transitions due to applied rf fields either at or near the electron resonance frequency or the nuclear resonance frequency can occur. Transition probabilities for various rf excited transitions are labeled W_1, W_2, W_3, W_4 . The first three of these occur in the range of 9 gc, the last near 14 mc. For convenience, these induced transition probabilities are related to w_1 by

$$\begin{aligned} W_1 &= S w_1 \\ W_2 &= \alpha w_1 \\ W_3 &= \beta w_1 \\ W_4 &= \gamma w_1 \end{aligned} \quad 2.5$$

Now consider a situation where $\phi, \sigma \ll 1$, i.e., the direct nuclear transitions and nuclear transitions via coupling with the electronic spins are much slower than the electronic relaxation transitions $\Delta M = \pm 1$, $\Delta m = 0$. And suppose, for example, that W_3 is now strongly excited by an applied rf field, equalizing the populations of $|++\rangle$ and $|--\rangle$. The electronic transitions w_1 between $|--\rangle \leftrightarrow |+-\rangle$ and $|+-\rangle \leftrightarrow |++\rangle$

will bring these states rapidly to a relative thermal equilibrium such that

$$\begin{aligned} N_{+-} &= N_{--} e^{-\Delta} \\ N_{-+} &= N_{++} e^{\Delta} \end{aligned} \quad 2.6$$

The nuclear polarization is given by

$$P = \frac{(N_{++} + N_{-+}) - (N_{--} + N_{+-})}{(N_{++} + N_{-+}) + (N_{--} + N_{+-})} \quad 2.7$$

Setting $N_{++} = N_{--}$ and using 2.6 one finds

$$P = \frac{(\sinh \Delta)}{(1 + \cosh \Delta)} \approx \frac{\Delta}{2} \quad 2.8$$

By a similar argument, saturation of W_2 leads to $p \approx -\Delta/2$. The thermal equilibrium polarization in the absence of dynamic polarization effects is $p_0 = \hbar \nu_n / kT \approx \delta/2$. Thus the effect of saturating the transition W_2 or W_3 is to increase the nuclear polarization by a factor $\pm \Delta/\delta = \pm g/g_n$. Thus the nuclei come to equilibrium as if their magnetic moment were the size of the electronic magnetic moment. Figure 2.3, again drawn from the excellent paper by Leifson and Jeffries, illustrates the effect.

An interesting statistical mechanical interpretation of the dynamic polarization effect has been given by Kittel²³⁾. He points out that in the derivation of the Boltzman distribution function, it is not the energy separation of two states that determines their equilibrium occupation numbers, rather it is the amount of energy the lattice receives or gives up in transitions between the states. In the usual case these energy transfers are identical with the energy separation of the states.

However, this is not the case when the electronic levels are disturbed by a saturating rf field. For example, consider the states $|++\rangle$ and $|+-\rangle$ in figure 2.2. When W_3 is saturated, the favored route for transitions from $|+-\rangle$ to $|++\rangle$ will be $|+-\rangle \rightarrow |--\rangle \rightarrow |++\rangle$. The transition $|+-\rangle \rightarrow |--\rangle$, a thermal relaxation process yields energy to the lattice, while the transition $|--\rangle \rightarrow |++\rangle$ takes no energy from the lattice, deriving this energy instead from the rf field. Thus in the process $|+-\rangle \rightarrow |++\rangle$, the lattice gains energy Δ ; in the inverse process, the lattice must give up energy Δ . On the other hand, in the absence of the

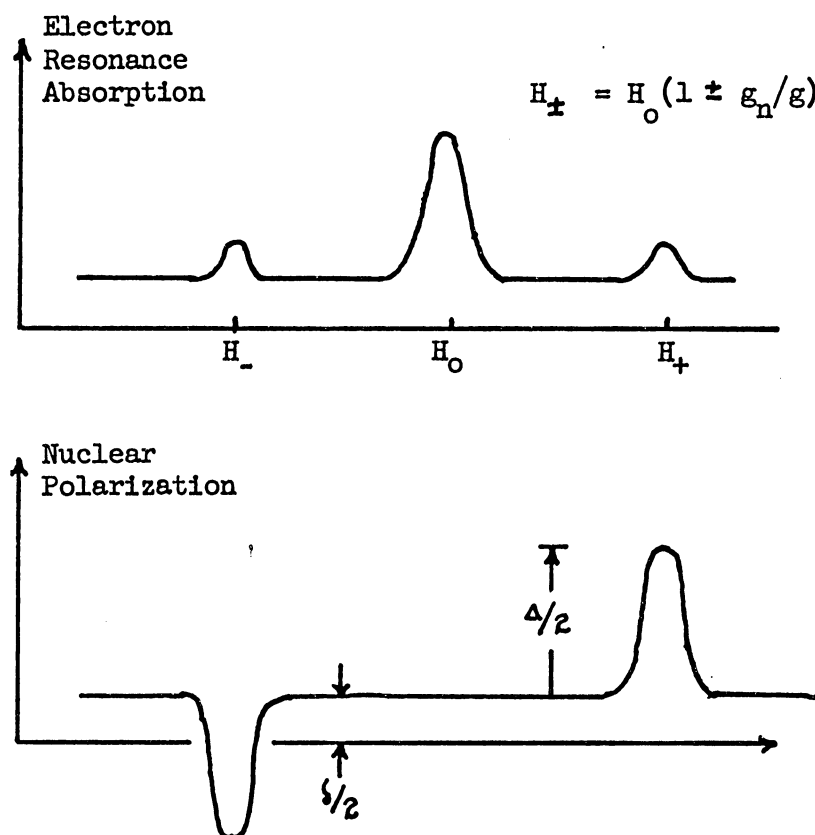


Figure 2.3. The effect of saturating various electronic transitions on the nuclear polarization.

applied fields the net gain in lattice energy for strictly thermal transitions $|+-\rangle \rightarrow |++\rangle$ is δ . Thus the population ratio of the states $|+-\rangle, |++\rangle$ is $e^{-\Delta}$ rather than $e^{-\delta}$.

This two spin model illustrates the effect, but cannot be a proper model for the total sample where the electron is surrounded by many nuclei at varying distances, all coupled with the electron to a greater or lesser degree. In equation 2.4 we see that the intensity of the forbidden transitions essential for the dynamic polarization falls off as r^{-6} . Only the nuclei near the electronic spin will be strongly polarized. Propagation of this polarization to distant spins must depend on spin diffusion.

As a first approach to accounting for the effect of the presence of the many nuclei about each electronic spin one can assume that the n nuclear spins share the N electron spins equally. Then the fraction $N/n \ll 1$ is the fraction of time a given nuclear spin may be interacting with an electron. With this assumption, one obtains equations for the time variation of the nuclear polarization p and the electronic polarization P ²¹⁾:

$$\begin{aligned} \frac{dp}{dt} = & -2w_1 \left[\psi + \left(\frac{N}{n} \right) (\theta + \sigma) \right] (p - p_0) - 2w_1 \beta p \\ & - w_1 (\alpha N/n) (p - P) - w_1 (\beta N/n) (p + P) \end{aligned} \quad 2.9$$

$$\begin{aligned} \frac{dP}{dt} = & -2w_1 (1 + \sigma) (P - P_0) - 2w_1 s P - w_1 \alpha (P - p) \\ & - w_1 \beta (P + p) \end{aligned} \quad 2.10$$

When $W_1 = W_2 = W_3 = 0$ and $f \approx 0$, corresponding to no microwave rf and an unsaturated NMR signal, equation 2.9 yields an exponential decay with time constant

$$T_{1n} = [2W_1 (\varphi + N/n(\theta + \sigma))]^{-1} \quad 2.11$$

This is defined as the nuclear relaxation time and represents the time constant of the decay of the polarization when the saturating microwave field is switched off. Similarly, one obtains from 2.10

$$T_{1e} \equiv [2W_1(1 + \sigma)]^{-1} \quad 2.12$$

for the electron relaxation time.

Equations 2.9 and 2.10 can also be solved for the transient approach to the final polarization after the microwave power is switched on. One finds, for instance, that on saturating W_3 , starting at $t = 0$, ²¹⁾ the polarization is given by

$$p(t) \approx p(\infty) [1 - \exp(-t/\tau_2)] \quad 2.13$$

The characteristic time τ_2 is approximately T_{1n} for low rf power (W_3 not saturated); for W_3 saturated, it becomes $\tau_2 \approx T_{1n} f(1 + f)^{-1}$, where f is defined below.

Taking the high temperature limit, $e^{-\Delta} \approx 1 - \Delta$, $e^{-\delta} \approx 1 - \delta$, the ^{state} steady/polarization to first order in δ/Δ is

$$p \approx \frac{\Delta(\alpha - \beta)(1 + \sigma)}{(\alpha - \beta)^2 - [2(1 + \sigma)f + \alpha + \beta + 2\gamma n/N][2(1 + \sigma) + 2s + \alpha + \beta]} \quad 2.14$$

where

$$f \equiv \left(\frac{n}{N}\right) \left(T_{ie}/T_{in}\right) \quad 2.15$$

The parameter f represents a "leakage" factor as we shall see. If, for example, W_3 is completely saturated, i.e., $\omega=0, S=0, P=0, \beta \neq 0$ then the steady state polarization becomes

$$P_{sat} = \frac{\Delta}{2} \frac{1}{1+f} \quad 2.16$$

Here it is assumed that $\sigma \ll 1$.

From equation 2.11, 2.12, and 2.15, the leakage factor is seen to be

$$f = \frac{n}{N} \frac{[\varphi + N/n(\theta + \sigma)]}{(1 + \sigma)} \approx \theta + \sigma + \frac{n}{N} \varphi \quad 2.17$$

The condition for obtaining the full polarization effect is that $f \ll 1$. For $\varphi \rightarrow 0, f \rightarrow \theta + \sigma \approx \sigma$ which is assumed to be small; the requirement of small f is seen to be equivalent to the requirement that nuclear relaxation processes be slow. For very dilute concentrations of electronic spins, the last term dominates, and $f \rightarrow \frac{n}{N} \varphi \ll 1$, yielding a low polarization. Or, from another view, equation 2.14 and the requirement $f \ll 1$, give the requirement

$$T_{ie} \ll \frac{N}{n} T_{in} \quad 2.18$$

That is, the electron spin must be able to "process" its share n/N of

the nuclear spins by mutual spin flips in a time less than T_{1n} -- otherwise the polarization is reduced.

If one defines E_{sat} as the observed enhancement factor ($E_{sat} = \rho_{sat}/\rho_0$) and E_i as the ideal enhancement factor equal to g/g_n , 2.15 gives

$$E_{sat} = E_i (1+f)^{-1}$$

Two factors can enter to make E_{sat} temperature dependent. First, f depends on the ratio T_{1e}/T_{1n} which is not necessarily temperature independent. Second, at higher temperatures, the electron resonance becomes progressively harder to saturate. The interplay of these two effects may lead to a maximum of E_{sat} at some temperature.

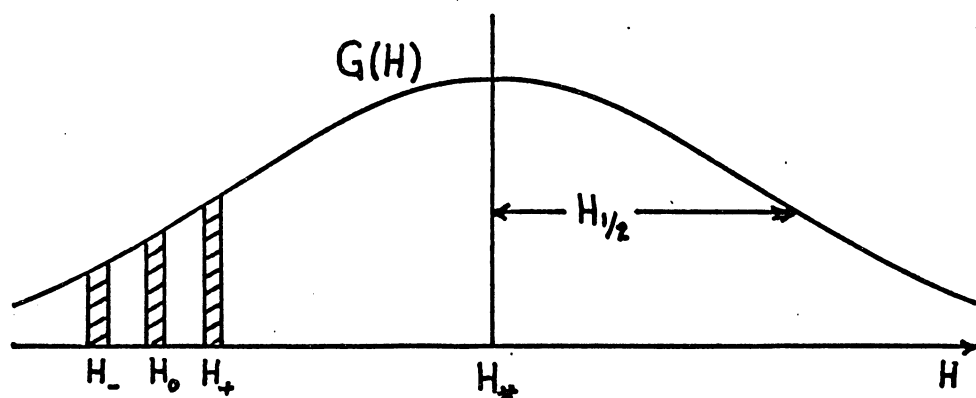
Unresolved Spectra

To this point it has been assumed that the separation $H_0 g_n/g$ of the forbidden transitions from the main electron resonance line is small compared to the width of the main resonance and hence that the transitions W_1, W_2, W_3 could be excited separately and independently. In the case of the polymerized acetylene samples, and indeed in most materials, this is not the case. The transitions W_2 and W_3 fall on the wings of the resonance line so that rf radiation saturating W_2 , for example, is certainly exciting W_1 and probably W_3 as well. The model developed so far must be generalized to account for this effect.

This generalization has been worked out, for the case of homo-
geneously and inhomogeneously broadened lines by Leifson and Jeffries 21)
and for inhomogeneously broadened lines with cross relaxation by
15,16)
Kessenikh and others . Both sets of authors used the rate equation
treatment for obtaining the population of the various electronic and

nuclear Zeeman levels following the treatment pioneered by Bloembergen,²⁴⁾ Purcell, and Pound. Though these treatments have lent insight into experimental results and were long thought to have general qualitative validity,²²⁾ Redfield has shown that the use of the rate equation approach can lead to wrong results for lines homogeneously broadened by the interaction of like spins. Redfield developed a density matrix approach to the treatment of the interaction of strong rf fields with solids.²⁵⁾ This treatment was extended by Provotorov to rf fields of arbitrary strength, and the application specifically to the solid effect¹²⁾ was developed by Borghini. We will first give the rate equation approach and then sketch the density matrix approach to the problem.

Inhomogeneously broadened line. The figure below schematically illustrates a completely inhomogeneously broadened line. The line is assumed to consist of a superposition of a large number of spin packets each of width $\delta \ll H_{1/2}$ and each packet thermally isolated from the others. The function $G(H)$ represents the observed shape of the electron resonance line. A large rf field at frequency $\nu_e = g\beta H_*/h$ is applied and the DC



magnetic field is taken to be H_0 . A fraction $G(H_0)$ of the spins will have the transition W_1 saturated, a fraction $G(H_-)$ will have W_3 saturated, and $G(H_+)$ will have W_2 saturated. The saturation of W_3 will give a partial polarization

$$E(H_0) = \frac{P_+ + P_-}{P_0} = \frac{\epsilon P_{ss}}{P_0} [G(H_-) - G(H_+)]$$

$$\approx \frac{\epsilon P_{ss}}{P_0} \left[-2H_0 \frac{\gamma_n}{g} \left(\frac{dG}{dH} \right)_{H_0} \right] \quad 2.20$$

Using $P_{ss} = \frac{A}{2} \left\{ \beta / [2f + \beta(1+f)] \right\}$ as the steady-state polarization arising from a partially saturated line (Equation 17b of reference 21), this gives

$$E(H_0) = - \frac{2 \epsilon H_0 \beta}{2f + \beta(1+f)} \left(\frac{dG}{dH} \right)_{H_0} \quad 2.21$$

for the curve of enhancement versus applied field. The feature of 2.21 of most significance for this work is that it predicts an enhancement curve proportional to the derivative of the EPR line.

Homogeneously broadened line. Let H_L be the intrinsic width of the spin packets of figure 2.4. For $H_L \approx \frac{\gamma_n}{g} H_0$, the assumptions underlying equation 2.21 become invalid. Suppose that $H_L \gg H_0 \frac{\gamma_n}{g}$, then at any value of H_0 within the resonance, all spins will have transitions W_1 , W_2 , W_3 simultaneously excited. If all transitions are strongly excited, the populations of all the states tend to become equal, and one questions whether any polarization could ever be observed. However, in the wings

of the line it is possible to saturate W_2 or W_3 preferentially yielding a saturation curve shaped roughly like the derivative of the resonance line. An expression for the polarization versus the magnetic field for this case is given in reference 21, equation 23. The shape of the enhancement curve is shown there to be heavily dependent on the value of the saturation parameter, $S_0 = (\gamma H_1)^2 T_{1e} T_{2e}$. Calculated enhancement curves for a reasonable case exhibit a maximum effect for $S_0 \approx 3$, the enhancement curve in this case peaking near H_+ and H_- . For larger S_0 , the maximum enhancement becomes progressively smaller, and the separation of the peaks of the enhancement curve becomes progressively larger ²¹⁾.

Spin Diffusion

In the simple model presented earlier, the many nuclear spins surrounding a paramagnetic center were simply assumed to share the center equally and any effects of the nuclear-nuclear coupling term in the Hamiltonian (equation 2.1) were ignored.

A variation of this problem was treated in 1949 by Bloembergen ²⁶⁾ in the course of developing a theory explaining the dominant role of very small numbers of paramagnetic centers in the nuclear relaxation process in diamagnetic crystals. Bloembergen realized that the nuclear-nuclear interaction leads to the possibility of diffusion of spin polarization and that the problem is therefore quite similar to the classical diffusion problem. Bloembergen's diffusion equation for spin polarization is

$$\frac{\partial p}{\partial t} = (\text{const}) \frac{(p - p_0)}{r_{ik}^6} - 2w_1 p p + D \nabla^2 p \quad 2.22$$

where D is the diffusion constant and r_{ik} is the electron-nuclear separation. The first term accounts for the nuclear relaxation induced by the electron, and the second accounts for the nuclear relaxation induced by the applied NMR rf field. The third term recognizes the tendency of the nuclear spin polarization to diffuse from regions of high, to regions of low, polarization. The mechanism for the spin diffusion is, of course, the mutual spin flips induced by the nuclear dipolar spin-spin coupling.

Equation 2.22 has been solved in various approximations²⁷⁾, yielding expressions for the nuclear relaxation time. The solutions predict that the growth or decay of polarization can be described by a single exponential in agreement with experiment.

The generalization of Bloembergen's approach to the treatment of the solid effect is straight forward and merely involves the addition to the diffusion equation of terms to account for generation of polarization by the paramagnetic centers in addition to their action as centers for relaxation^{10,17,21)}. Solution of the equation in general is difficult, but Jeffries¹⁰⁾ has treated two limiting cases.

Jeffries defines two distances: d , the "diffusion barrier" radius, and b , the "scattering length" of the nucleus. The diffusion barrier is that point where the dipole field of the electron begins to shift the nuclear Larmor frequency, decreasing the strength of the nuclear-nuclear coupling and hence the effectiveness of the spin diffusion process. The scattering length is the distance from the electron where the nucleus is equally likely to be flipped by the electron spin or by a neighboring nucleus.

For the case of $d < b$, with b assumed much less than the inter-electron spacing, and spin diffusion assumed to be effective in the bulk of the sample (the "free diffusion" case), the equilibrium polarization can be computed, and the theory predicts that polarization and depolarization will follow a single exponential in time.

The alternate case of $b < d$ (the "retarded diffusion" case), can also be treated, the result of principle interest here being that the theory again predicts that polarization and depolarization will follow a single exponential. Jeffries shows that investigation of the dependence of T_{1n} on T_{1e} and on the applied field H enables one to determine which of these cases holds for a particular material.

Density Matrix Theory

22) Redfield pointed out that the concept of spin temperature is invalid in the case of large applied rf fields. The applied field leads to coherent off-diagonal terms in the density matrix of the system, invalidating the use of a spin temperature. However, he further showed that one could regain the use of the temperature concept by transforming to a coordinate system rotating at the frequency of the applied field and then defining the temperature in the rotating frame. Redfield's 25) theory was valid only for rf fields far above saturation. Provotorov extended Redfield's theory to include arbitrary rf fields, and Borghini applied the Redfield-Provotorov approach specifically to the treatment of 12) the solid effect.

Borghini was able to treat the case of a homogeneously broadened electron spin system in detail, essentially by formulating and solving the diffusion equation in the rotating coordinate system. He showed

that polarization and depolarization should again follow an exponential law in this more general theory. Further, in contrast to the previous results of Leifson and Jeffries²¹⁾, he showed that one could, under the proper circumstances, observe an enhancement curve with the general shape of the derivative of ESR absorption in the homogeneous case as well as in the inhomogeneous case. Thus, a derivative-shaped enhancement curve is not sufficient evidence for homogeneous broadening as it was once believed to be. Borghini does not treat the inhomogeneously broadened case.

III. APPARATUS AND EXPERIMENTAL TECHNIQUES

NMR Spectrometer

The nuclear magnetic resonance spectrometer was of conventional design and is depicted schematically in figure 3.1. The rf bridge was a twin-T or Anderson bridge (figure C1). The microsource was simply a voltage divider to enable use of the low frequency function generator at a high output level to minimize zero drift. Use of the lock-in amplifier enabled the bandwidth of the system to be reduced to as little as 0.1 cps with a consequent increase in the signal-to-noise ratio.

The sample coil was enclosed in a double Dewar system such that measurements could be made from room temperature to 1.7°K. Use of the Dewars at room temperature was found to be advantageous for minimizing thermal drift of the bridge balance. The low temperature measurements were made by pumping on the He⁴ bath. Cooling from 4.2° to 1.7° required roughly one hour. Temperatures below 4.2° were determined by measuring the He⁴ vapor pressure with a mercury manometer.

As the DC magnetic field is varied linearly through the nuclear magnetic resonance, the lock-in amplifier detects that portion of the demodulated signal from the HRO-60 receiver that is in phase with the 100 cps reference signal. The output of the lock-in amplifier plotted on the xy-recorder represents either the derivative of the absorption or of the dispersion portions of the nuclear resonance signal, depending on the state of unbalance of the rf bridge. Discussion of the principles of phase-sensitive detection and lock-in amplification is available in
28) 13)
the books by Andrew and Abragam .

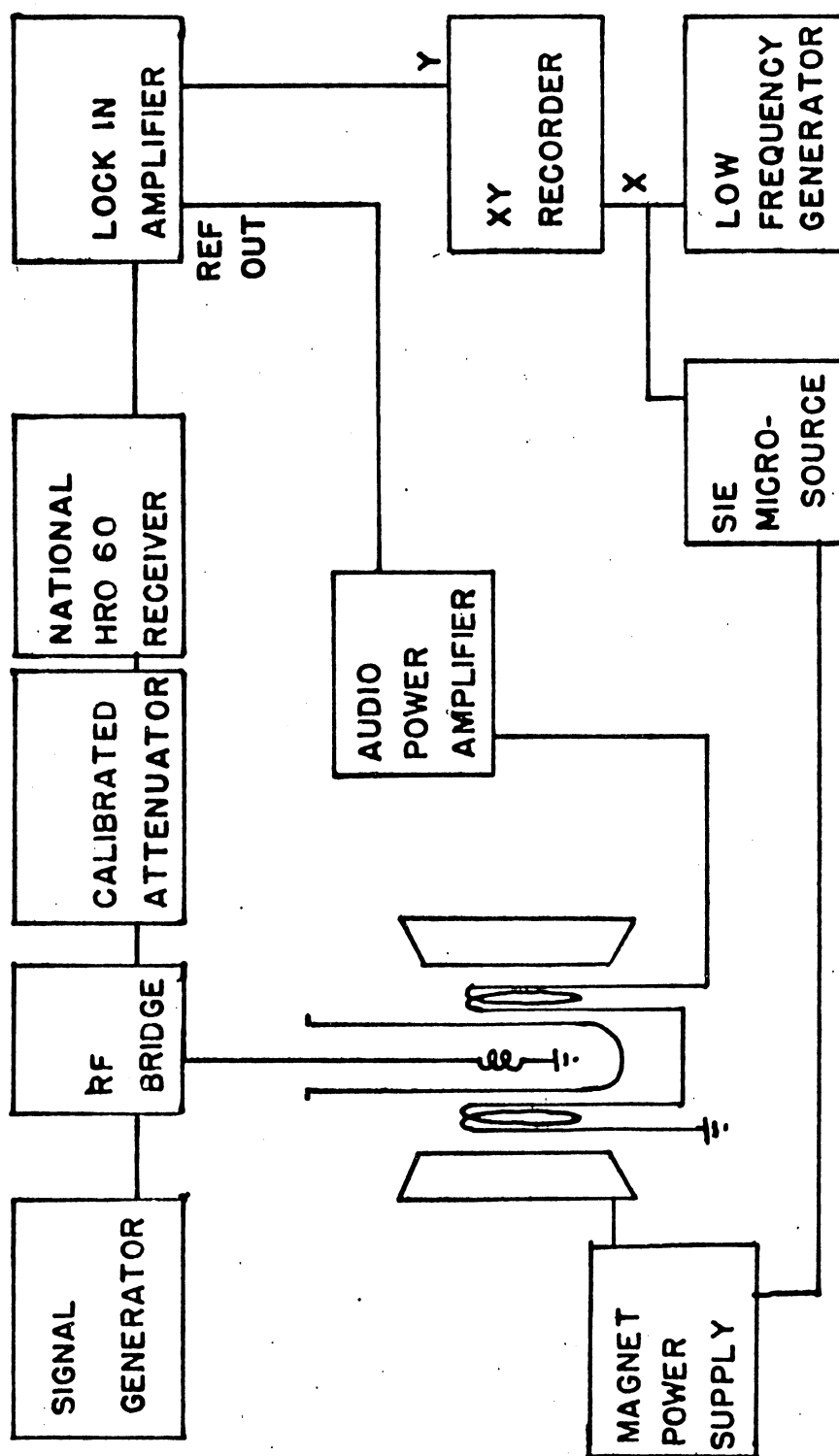


FIGURE 3.1 NMR SPECTROMETER

Calibration Procedures

Modulating field. A Harvey-Wells gaussmeter was used to calibrate the modulating field by observing the position of the proton resonance at two frequencies. Then $2\pi\Delta f/\gamma_p = \Delta H$ gives the separation of the two resonance positions in gauss, and the total width of the sweep is readily calculated. The calibration depends on the frequency of the modulation and, owing to varying degrees of core saturation, on the magnitude of the DC magnetic field.

Recorder base-line. The bridge was balanced at two slightly separated frequencies and the shift in position of the NMR signal gave a direct calibration of the recorder base-line in gauss. A frequency counter was used to measure the small changes in the frequency of the nominally 14 mc signal.

Experimental Techniques

Line-width measurements. Line-width measurements were made between points of maximum slope of the NMR line by observing the derivative of the absorption signal and measuring the separation of the two peaks of the trace.

Saturation measurements. The saturation level for the NMR line was found by measuring the signal height as the input signal was varied. The point at which a plot of signal height over input signal level, versus the input signal level, deviated from a horizontal line was taken as the level at which saturation became significant.

Electron Spin Resonance Spectrometer

The homodyne-balanced mixer spectrometer^{29,30)} depicted in figure 3.2 was found to be a happy compromise between sensitivity and simplicity for the purpose of this experiment. The spectrometer as shown is simplified somewhat from the spectrometer as used, in that elements such as isolators, wave meters, monitoring crystals, and the like which contribute in convenience, but not in principle, are not shown.

Interaction between the modulating field and the NMR coil leads led to a prohibitively high noise level when using the double resonance (DR) cavity for ESR measurements. For these measurements, therefore, a cavity designed specifically for ESR detection was used. The latter cavity differed from the DR cavity not only in the absence of the NMR coil, but also in its resonant mode. The resonant mode of the DR cavity was the TM_{110} mode and that of the ESR cavity was the TE_{011} mode. The resonant frequencies were approximately the same for the two cavities, around 9.3 gc at liquid helium temperatures.

The 3 db directional coupler in the sample cavity arm of the spectrometer was only necessary for stabilizing the klystron to the sample cavity at very low powers, in the range below 10 microwatts. The loss of signal entailed by the 3 db coupler was avoided by using a 10 or 20 db coupler at higher power levels or by stabilizing to a reference cavity at any power level. The power into the cavity was measured by tuning the slide-screw tuner for maximum reflected signal and closing the shorting switch. The power from the klystron arm of the circulator was then shunted to the thermistor mount.

Spin density measurements were made by comparing the ESR recorder traces from various samples with the traces of a standard. The standard

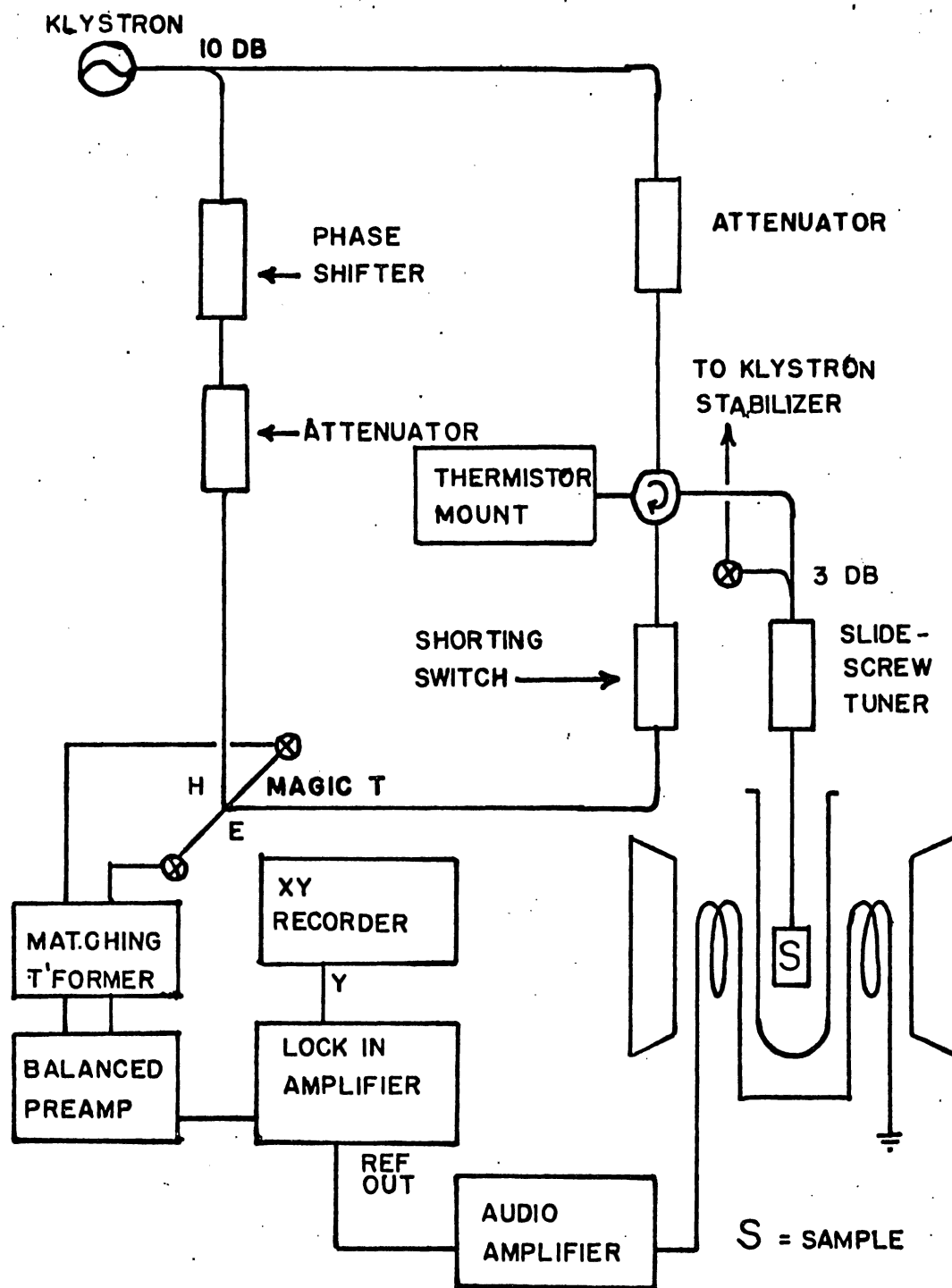


FIGURE 3.2 HOMODYNE BALANCED-MIXER SPECTROMETER

used was crystalline $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, assumed to have one electron spin per Cu atom. For a discussion of the method of correlating the ESR traces with the number of spins in the samples, see Appendix C.

The investigation of the ESR properties of various samples at liquid helium temperatures was facilitated by using an air lock as described by Estle and Walters³¹⁾ for changing samples with a minimum loss of helium.

Dynamic Polarization Technique

The apparatus for measure of the polarization enhancement consisted of the NMR spectroscope already described, plus the simple microwave arrangement depicted in figure 3.4.

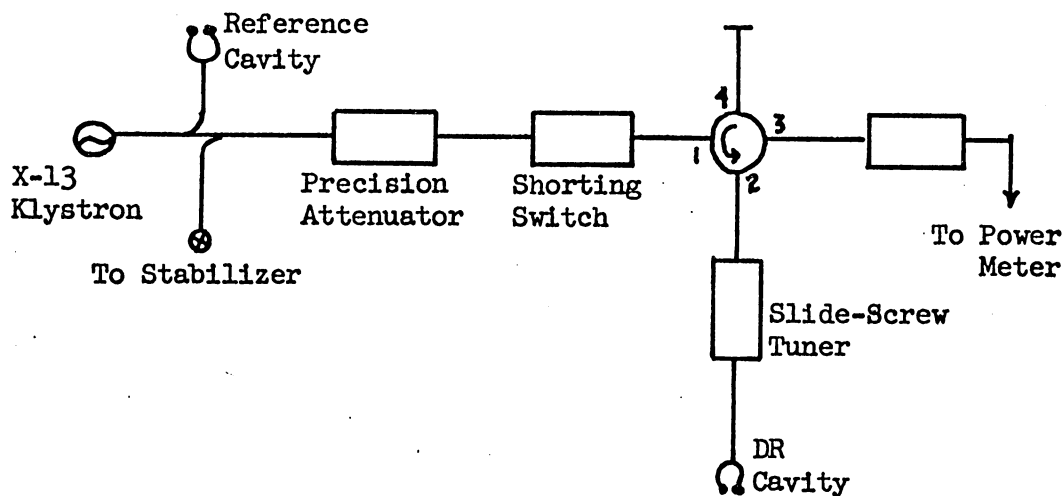


Figure 3.4. Microwave circuit for dynamic polarization.

The klystron frequency was stabilized to the reference cavity at the resonant frequency of the DR cavity. By opening and closing the shorting switch, the microwave power could be turned on and off in perhaps a fourth of a second. The power into the cavity was determined by adjusting the slide-screw tuner for maximum mis-match so that all power out of port 2 of the circulator was reflected back to the power meter. In previous measurements the power measurement obtained using this technique and that obtained by replacing the cavity with the thermistor mount was essentially the same. The maximum power available from the X-13 klystron was 64 mw, which proved to be ample.

The cavity for the dynamic polarization measurement was a right circular cylinder designed to be resonant in the TM_{110} mode at 9.3 gc. The sample was coaxial with the cavity, and a coil for NMR measurements encircled the sample holder inside the cavity. The leads for the NMR coil entered and left the cavity along the cylindrical axis, where, in the TM_{110} mode, the axial component of the E-field is zero.

It was assumed that the change in size of the derivative of the NMR signal was directly proportional to the change in polarization. Since the enhanced signal was observed to be larger in height, but unchanged in position or width, two methods were available for measuring the enhancement factor.

By observing the peak-to-peak height of the entire signal both in presence and in the absence of microwave power, the enhancement factor could be found. However, an alternate technique, with the added attraction of making the nuclear polarization time and the nuclear relaxation times accessible, was also possible. With the shorting

switch closed, the y-position of the xy-recorder pen was noted while the magnetic field was far off resonance. Then the DC magnetic field was manually tuned to the top of one peak of the derivative of the NMR absorption signal, this height being taken as p_0 . Using the time base mode of the xy-recorder with a sweep of, say, 10 sec per inch, the change in size of the NMR signal (i.e., the change in the polarization) as a function of time, both upon opening and closing the shorting switch, was obtained. The decay was not exponential, but was composed of a component with time constant less than one second and a component with a time constant of 8 or 9 seconds. In some cases there was evidence of an even longer time constant component, though this was obscured by the noise. The time constants were determined from a semilog plot of the data. The time constant of the short-lived component could not be evaluated as this was on the order of, or less than, the switching time for the microwave power.

IV. DESCRIPTION OF POLYMER SAMPLES

The samples investigated in this study were a series of polymers resulting from the catalytic polymerization of several alkynes, principally acetylene, as carried out by Watson³²⁾. In the polymerization process, acetylene is introduced into a container containing a solvent and a catalyst. As the polymerization proceeds, a solid precipitates from solution.

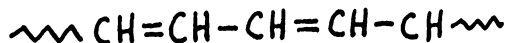
Depending on several parameters, such as concentration and composition of catalyst, sequence of addition of reagents, etc., the weight of solid polymer obtained represented varying percentages of the weight of alkyne added. One must assume that the polymers formed under varying conditions have somewhat different properties; different average molecular weights, different amounts of branching, and so forth. In this experiment, these quantities are unknowns.

The color of the polymers varied from rusty red to black. The texture varied from very fine to quite coarse, and the latter resembling a coarse black sand. The grain size and color seemed to be roughly correlated, darker samples being coarser. When the paramagnetic spin density was measured, it was found that the darker, coarser samples in general had higher spin densities.

The paramagnetism of the polymer is assumed to arise from free radical sites trapped in the polymer upon precipitation. If one postulates a mechanism of polymer growth such as:

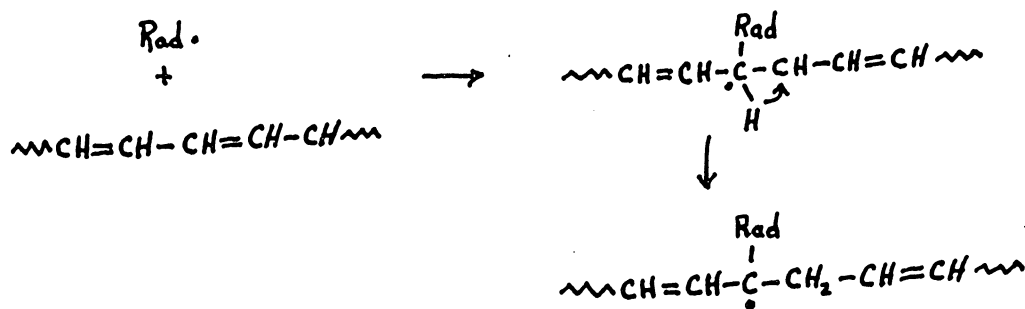
- 1) $\text{Rad}\cdot + \text{CH}\equiv\text{CH} \longrightarrow \text{Rad}-\text{CH}=\dot{\text{C}}\text{H}$
- 2) $\text{Rad}-\text{CH}=\dot{\text{C}}\text{H} + \text{CH}\equiv\text{CH} \longrightarrow \text{Rad}-\text{CH}=\text{CH}-\text{CH}=\dot{\text{C}}\text{H}$
- 3) etc.

then the structure of the polymer in the absence of branching or cross-linking would be



Trapping of the free radical ends of a growing chain is a well known process³³⁾. The end is surrounded by a "dead polymer cage" in the precipitate and is thus stabilized by the geometry of its surroundings.

Formation of radicals at branching sites in the polymer is conceivable, through a mechanism such as



Upon precipitation of the polymer, this type of radical site might also be trapped. The presence of both types of radical sites in the polymer would lead to two qualitatively different types of spin centers in the polymer. Possibly, this is the explanation for the two component relaxation and polarization times that were observed (Section V).

Previous studies of such trapped radicals, as well as of radicals formed by irradiation, are discussed by Ingram³³⁾. In general, exposure of polymers containing free radicals to atmospheric oxygen has a marked effect on their electron spin resonance signal. Examples are recorded (1) where an irradiated polymer displays no electron resonance signal prior to contact with oxygen, (2) where the polymer has a highly structured electron resonance line which disappears on contact with the

atmosphere, and (3) where a polymer has a broad, structured resonance which becomes a single, narrower line with long term stability upon exposure to oxygen. These effects are explained by assuming that molecular oxygen diffuses into the polymer and reacts with the unpaired electrons to localize the electrons near the oxygen molecules, forming a new radical ($R-O-O\cdot$).

Then either of two processes may occur: This radical may quickly decay to $R + HO_2\cdot$, the $HO_2\cdot$ then reacting to form some nonradical structure. Or the $R-O-O\cdot$ may be trapped, leading to a resonance line with long-term stability.

The interaction with oxygen has been shown to be reversible in several cases. Samples stored under vacuum at room temperature or higher often regain the structure lost upon exposure to oxygen³⁴⁾, or³⁵⁾ tend to recoup changes in T_{1e} that occurred upon exposure to oxygen.

The electron resonance signal for the polymerized acetylene samples was not observed prior to exposure of the polymer to the air. Electron spin density measurements made on some of the samples at times nearly five years apart showed that the spin density had decayed by a factor of ten to a hundred in this period (see table 5.2). These considerations, coupled with the lack of structure of the electron resonance line, indicate that the free radical sites in the polymer samples are of the form $R-O-O\cdot$. Again, there are possibly two types of these sites, resulting from oxygen reacting with trapped radicals either at chain ends or at branching sites.

V. EXPERIMENTAL RESULTS

NMR and ESR Line-Widths Versus Temperature

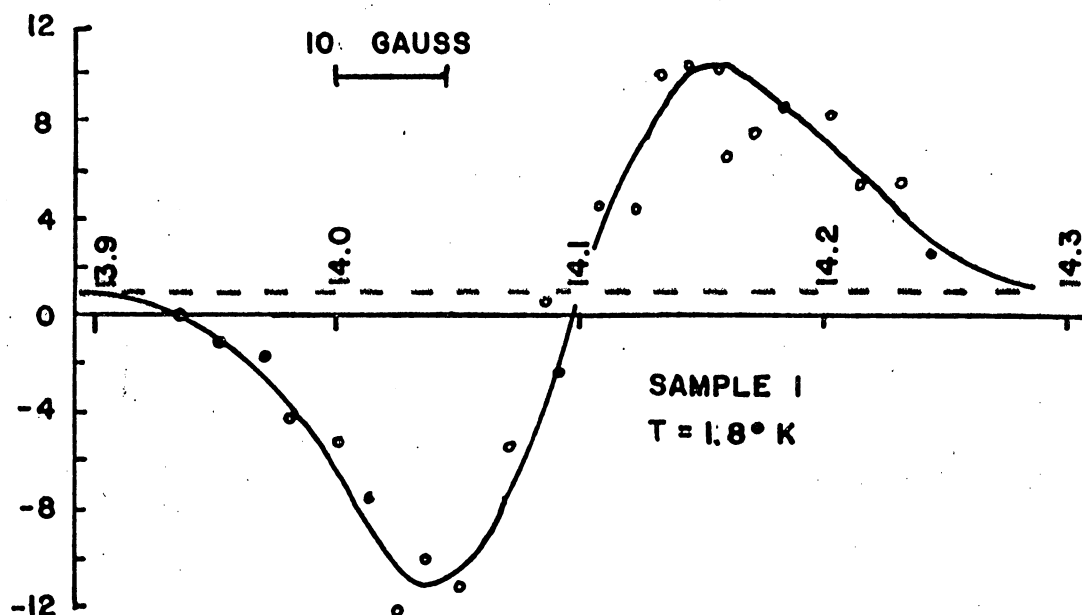
Table 5.1 summarizes the results of line-width measurements made at various temperatures.

Sample	Temperature (°K)	Line-width (gauss)	
		NMR	ESR
F2	300°	1.5 ± 0.3	13.0 ± 1.0
	77°	7.5 ± 0.3	14.3 ± 1.0
	4.2°	7.2 ± 0.3	14.3 ± 1.0
	1.8°	7.2 ± 0.3	14.0 ± 0.8
1	300°	--	7.8 ± 0.5
	77°	--	--
	4.2°	8.8 ± 1.0	12.7 ± 0.8
	1.8°	7.3 ± 1.0	11.9 ± 0.6

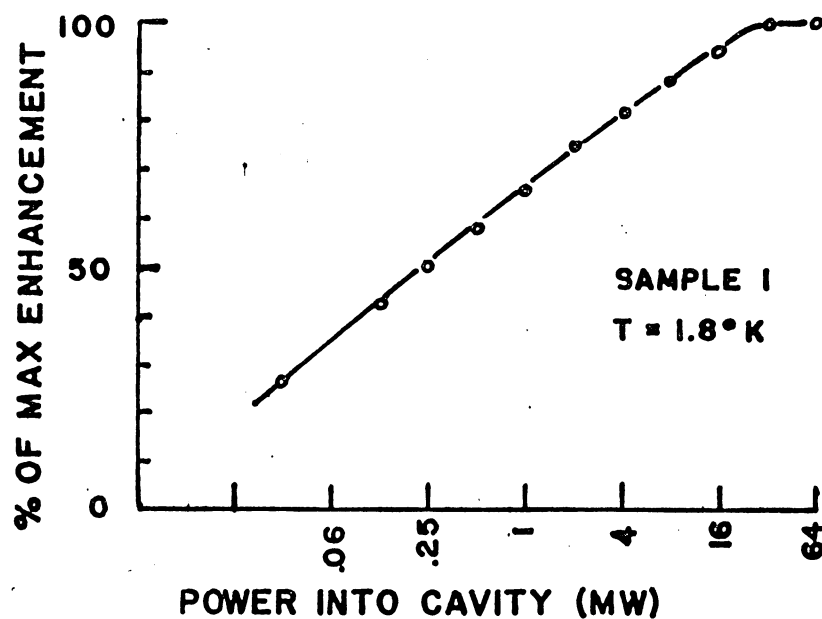
TABLE 5.1. Line-widths versus temperature.

Dynamic Enhancement

Sample 1 was chosen as a likely candidate for exhibiting a large dynamic enhancement effect, as it had the highest density of paramagnetic centers and the narrowest ESR line of any of the samples investigated. The observed enhancement as a function of NMR frequency is shown in figure 5.1. The scatter in the data points at 1.8°K arises to a large degree from uncertainty in the value of p_0 . This source of error could undoubtedly be reduced. A further contribution to the scatter results from the finite width of the NMR line relative to the width of the enhancement curve. If the magnetic field were not adjusted to exactly the same relative position on the NMR line for each frequency setting the measured enhancement might vary.



ENHANCEMENT VS NMR FREQUENCY



Similar measurements of enhancement versus NMR frequency were made at 4.2°K. The data there, while appearing to follow the 1.8°K data, contained considerable more scatter, which can perhaps be attributed to the modulation of the sample cavity by the boiling helium.

Note that the distance between enhancement peaks is about 26 gauss or roughly twice the distance between peaks of the derivative of the ESR signal.

The lower curve in figure 5.1 demonstrates that the power into the cavity was adequate to saturate the electron transitions and thus produce the maximum enhancement effect.

Electron Spin Density

Using the method described in Section III, the density of paramagnetic centers was measured in a number of polymer samples. These results along with ESR line-width data for the samples is summarized in table 5.2. In addition, results of similar spin density measurements performed nearly five years previously on some of the samples are given. Note that the spin density declined by one to two orders of magnitude during this interval. The spin densities are relative to $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, assumed to have one spin per copper atom. The accuracy of the spin density measurements is perhaps $\pm$ 30 per cent.

There is a rough correspondence between spin density and line-width, samples with higher spin densities tending to have narrower lines.

Sample 1, on which the polarization enhancement measurements were made, had the highest spin density and one of the narrower line-widths.

Sample	Average Spin Density (spins/gm)	Previous Spin Density Measurements	Line-width (gauss)
F2	6.9×10^{17}	--	13.0 ± 1.0
30B	5.0	146×10^{17}	9.7 ± 0.5
64B	1.5	138	8.7 ± 0.5
48	1.0	9.4	5.4 ± 0.5
1	140.0	--	7.8 ± 0.5
3	13.0	--	13.6 ± 0.8
E2	80.0	--	8.7 ± 0.5
A2	8.0	--	11.3 ± 0.5
E	10.0	--	10.1 ± 0.6
2	35.0	--	10.5 ± 0.5

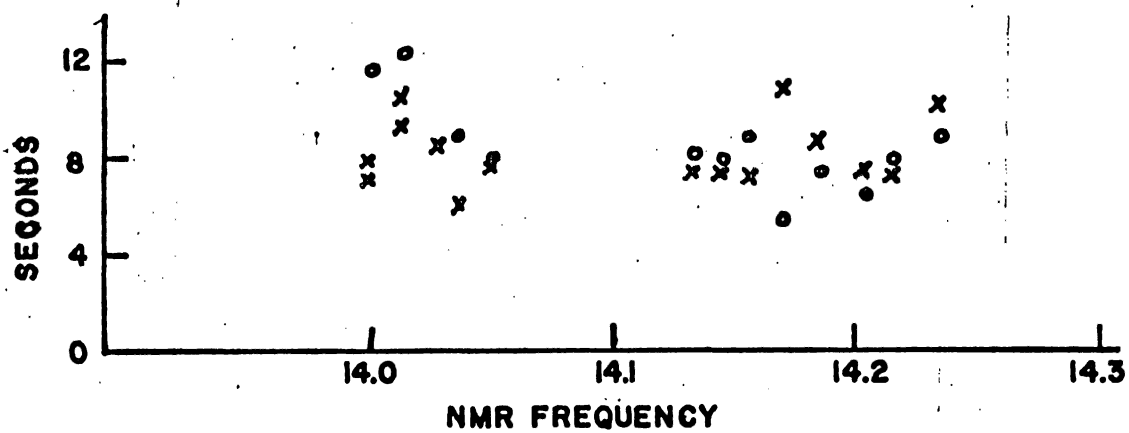
Table 5.2. Electron spin density data.

Polarization and Depolarization Time Constants

As described in Section III, the polarization and depolarization times were measured by monitoring the height of a peak of the derivative of the NMR line during its growth and decay after switching the microwave power on and off. The decay could not be described as exponential with a single time constant, rather, a semilog plot showed that the decay consisted of two components, one short- and the other long-lived.

The shorter time constant could not be measured with any accuracy as its decay occurred in a time comparable to, or shorter than, the switching time for the microwave power, say, something less than 1 second.

The time constants for the longer-lived component are given in figure 5.3. for a range of NMR frequencies. The polarization and depolarization times appear to be comparable, about 8 ± 1 seconds, within the accuracy of the experiment. Schacher³⁷⁾ performed similar measurements with several substances and observed that a plot of polarization time



**FIGURE 5.3 POLARIZATION AND DEPOLARIZATION
TIME VERSUS FREQUENCY**

versus magnetic field (or NMR frequency) exhibited a systematic variation over the width of the enhancement curve.

In general, Schacher observed that the polarization times were quite long near the center of the enhancement curve, lowest near the peaks of the curve, and higher again further out in the wings. Unfortunately, the signal to noise ratio in the present experiment preclude obtaining these time constants except in the regions of large enhancements, and even there the data exhibited considerable scatter. However, over the range in which the time constants could be measured, there is no evidence of the sort of variation Schacher observed.

Polarization Times Versus Microwave Power

The results obtained for the polarization time versus microwave power into the cavity are summarized below. Schacher observed an inverse linear relationship between the polarization time and the microwave power, higher powers giving lower polarization times. A similar effect has been observed by Swanenburg, et.al.,³⁸⁾ for the protons in LMN.

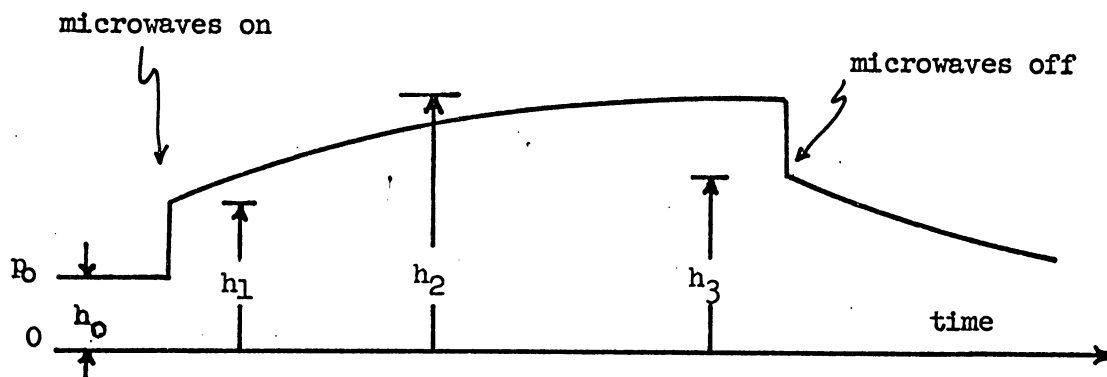
Power into Cavity (mw)	% Maximum Enhancement	Polarization Time Constant (sec)
64	100	5.0 ± 1.0
18	97	6.4 ± 1.0
8	89	6.8 ± 1.0
4	82	6.5 ± 1.0
.5	58	8.8 ± 1.0

There is slight evidence for this effect in the results of the present experiment, though the scatter in the data and the lack of ability to work with very small enhancements, prevent definite conclusions.

Further, all of these time constants are for the long-lived component; the variation of the time constant of the short-lived component with the magnetic field could not be investigated.

Analysis of Two Component Relaxation

In an attempt to determine the relative contribution to the enhanced NMR signal from the two components, the decay curve of the long-lived component, plotted on semi-log paper was extrapolated back to zero time to determine its initial height relative to the total enhanced signal. A typical polarization and depolarization curve is depicted below.



The signal heights h_i represent the following parameters of the curve:

- h_0 Unenhanced signal height
- h_1 h_0 + the additional signal from the enhancement of the short time constant component
- h_2 Enhanced signal height
- h_3 h_0 + additional signal from the enhancement of the long time constant component

The data from this analysis of the enhancement data (for sample 1 at 1.8°K) are plotted in figure 5.4. There the data are presented normalized to $h_0 = 1$, and uncertainties in h_0 are reflected in h_1 , h_2 , h_3 .

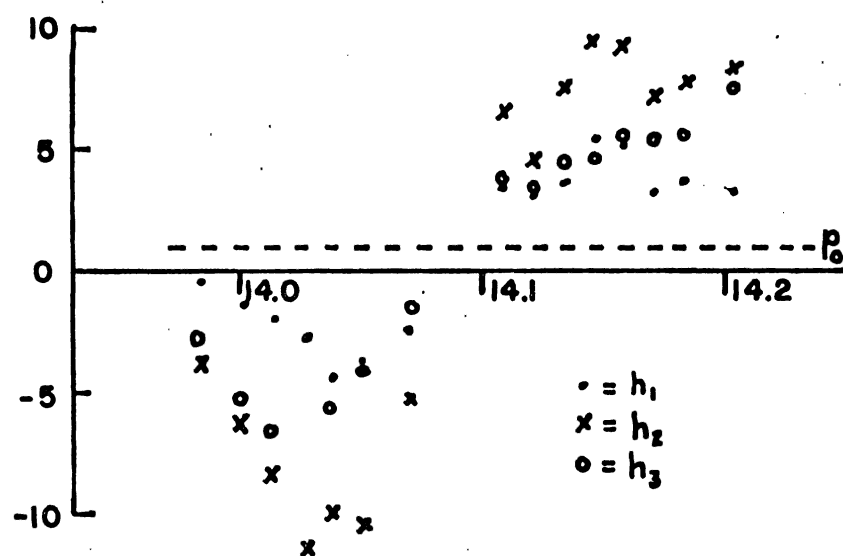


FIGURE 5.4

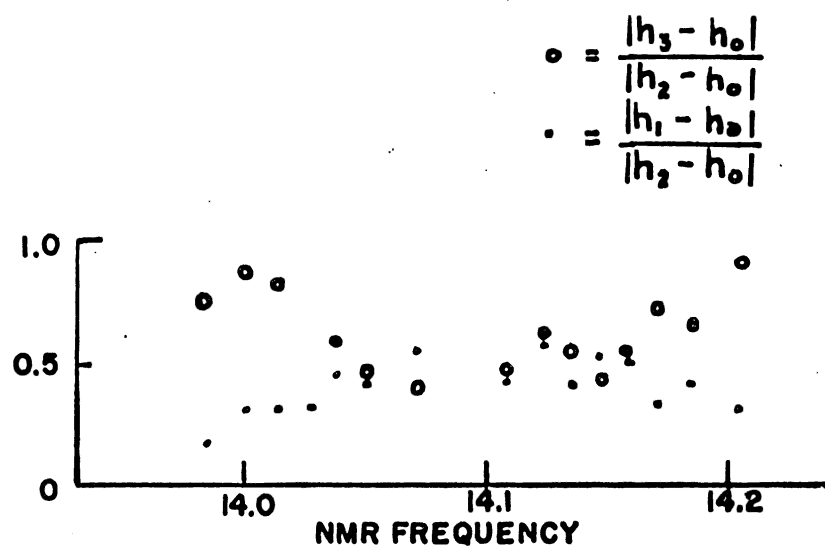


FIGURE 5.5

In figure 5.5, on the other hand, the quantities $|h_1 - h_0|/|h_2 - h_0|$ and $|h_3 - h_0|/|h_2 - h_0|$ are plotted. The quantity $|h_1 - h_0|/|h_2 - h_0|$ is the fractional enhancement attributable to the short time constant component when the microwave power is turned on, while $1 - |h_3 - h_0|/|h_2 - h_0|$ is the fractional change due to this component when the microwave power is turned off. One expects these quantities to be equal. From figure 5.5, it is apparent that this is approximately the case.

Note that the fractional change arising from the short time constant component decreases in the wings of the enhancement curve.

When the microwave power level was lowered, the short time constant component became progressively smaller and smaller until only the longer time constant component was present when the microwave power was attenuated 12 db (4 mw into the cavity). At this power level, the enhanced signal was roughly 50 per cent of its original level, although composed only of the long time constant component of the signal. The frequency of this measurement was 14.16 mc. Referring to figure 5.5, one sees that at this power the initial quick change of the NMR signal in both polarization and depolarization was about 50 per cent of the total signal height at that frequency. Evidently, much more power is required to bring the short time constant component factor to full enhancement than is required to enhance the longer time constant component.

Summary of Properties of Sample 1

The following summarizes the properties of sample 1 as they are known or can be estimated:

Composition - black, granular solid

32)

Density - estimated to be 0.9 to 1.0

Nuclear spin density - $n \approx 5 \times 10^{22}$ protons/gm

Electron spin density - $N \approx 1.5 \times 10^{19}$ spins/gm

Average separation of protons - $n^{-1/3} \approx 2.8$ angstroms

Average separation of electrons - $N^{-1/3} \approx 40$ angstroms

T_{1e} - estimated from saturation data: 10^{-2} to 10^{-4} sec

T_{1n} - two components; one about 8 seconds, the other less than 1 second

VI. INTERPRETATION OF DATA

Low Enhancement Factor

The prospects for use of sample 1 as a polarized target material are not particularly bright in view of the low observed enhancement factor. The unenhanced polarization at 1.8° in a field of 3300 gauss is 0.02 per cent; enhanced by a factor of ten, this gives 0.2 per cent for the enhanced polarization. An increase in the polarization by at least two orders of magnitude is necessary before a polarized target can be contemplated.

The reasons for the low enhancement factor are obscure, and only qualitative discussion can be given pending further experimental work. In particular, an investigation of the electronic relaxation time would be valuable. In general, a short nuclear relaxation time, implying a large "leakage factor" f (see equation 2.16), leads to a low enhancement factor. The quick decay of a portion of the nuclear spins upon removing the saturating microwave power indicates that at least some of the protons in the sample have a short relaxation time. The high microwave power required to bring these nuclei to full enhancement further supports this point.

If one takes one second as the maximum relaxation time of these short- T_1 nuclei, then equation 2.18 indicates that the T_{1e} of the associated electron spin would have to be 10^{-4} seconds or less for $f < 1$. This is on the lower edge of the electronic relaxation time estimated from saturation measurements.

Two Component Relaxation

The origin of the two components in the exponential growth and decay of the polarization must lie in the polymeric structure of the samples. Similar effects have not been reported for diamagnetic crystals. In particular, Jeffries¹⁰⁾ reports extensive experiments performed on LMN under a wide variety of electron spin densities and applied magnetic fields, all with relaxation describable by a single exponential. Further, as was emphasized in Section III, the various theoretical treatments of the solid effect, whether treating the case of retarded or free diffusion, homogeneously or inhomogeneously broadened ESR, all predict single time constants for polarization and depolarization.

On the other hand, a similar effect has been observed in a similar material, irradiated polyethylene¹⁴⁾. In measurements on polyethylene with 2.5×10^{18} electron spins per cc¹⁵⁾ at 1.6°K, the polarization was described by two exponentials with time constants of 25 and 80 seconds. Depolarization time constants were 50 and 180 seconds. Kessenikh,¹⁵⁾ et.al., concluded that the origin of the two component relaxation must lie in the existence of "crystalline" and "amorphous" phases in the polyethylene.

An alternate explanation may lie in the nature of the free radical in the polymer. To some extent, the unpaired electron may be delocalized over a number of carbons in the chain. With this assumption, the short time constant nuclei would be those most intimately associated with the electrons, the longer time constant nuclei would be those more remote from the electron that are polarized by spin diffusion along the polymer chain.

19)

Aleksandrov and Kessenikh have examined the nature of the thermal relaxation of the electron spins in polymer chains. They conclude that the assumption that the polymeric free radicals relax via the same mechanism as do paramagnetic centers in diamagnetic crystals is valid. The dominant relaxation mechanism in their theory is the coupling of the delocalized electrons with the longitudinal oscillations of the polymer chain. Assuming that Aleksandrov and Kessenikh are correct, the theory of the solid effect as developed for diamagnetic crystals may not be applicable in all particulars to polymers.

The similar effects observed in measurements on irradiated polyethylene and polymerized acetylene samples supports this view.

Future Measurements

The following suggestions are advanced for continuing the study of the polymerized alkyne samples:

1. Interpretation of the results of this experiment would be facilitated by measurement of the electronic relaxation time.
2. Future measurements of the polarization and depolarization times could be improved by utilizing electronic rather than manual switching in the microwave circuit. With faster switching time, the time constant of the shorter component of the nuclear relaxation could be measured.
3. A marginal oscillator NMR detector would have the advantage of making observations of the NMR line shape at constant H possible, though saturation of the sample might preclude use of this method.
4. The enhancement factor in samples other than 1 should be observed to see if similar effects are present.

APPENDIX A: NUCLEAR RELAXATION IN A DIAMAGNETIC
SUBSTANCE WITH PARAMAGNETIC IMPURITIES

3)
The following discussion follows a treatment by Abragam . We take the case of nuclear spins with $I=\frac{1}{2}$. The external magnetic field H is along the z -axis, and the z -component of the electronic and nuclear spins will be taken to be good or nearly good quantum numbers. The coupling of the nuclear spins with the lattice is assumed to be via their coupling with the electronic spins.

The most general interaction Hamiltonian for an electronic spin $\hat{S}$ and a nuclear spin $\hat{I}$ is

$$\mathcal{H}_i = \hat{I} \cdot \vec{\hat{A}} \cdot \hat{S} \quad A1$$

where $\vec{\hat{A}}$ is a symmetrical tensor. This can be written as

$$\mathcal{H}_i = -\hbar \gamma_n \hat{I} \cdot \hat{H}_e \quad A2$$

where $\hat{H}_e = -(I/\mu_n) \vec{\hat{A}} \cdot \hat{S}$ is the magnetic field produced by the electron at the nucleus.

For relaxation of the nuclear spins, two conditions must be met:

- (a) $\mathcal{H}_i$ must have matrix elements between states of the electron-nuclear system with different values of I_z , i.e., other elements of $\vec{\hat{A}}$ than A_{zz} must be non-zero. (b) The energy required for the nuclear transitions must be available.

The electronic field $\hat{H}_e$ fluctuates randomly in time and can be described as a random function of time. Condition (b) is equivalent to requiring that the spectrum of the random function $H_e(t)$ contain the frequency ω_0 . That is, the correlation function $\varphi(\tau) = \langle H_e(t) H_e(t-\tau) \rangle$ must have a non-vanishing value $J(\omega_0)$ for $\omega = \omega_0$.

The time variation of $\hat{H}_e$ can arise either from variation of $\vec{\hat{A}}$ or of $\hat{S}$. The first case, variation of $\vec{\hat{A}}$ arises, for example, from lattice vibrations in solids or Brownian motion of spins in liquids. The second case, time variation of $\hat{S}$, arises when the dominant relaxation mechanism for the electronic spins is some interaction other than that with the nuclear spins. Although both mechanisms could occur simultaneously, the second case, or relaxation arising from random flips of the electron spins, dominates in diamagnetic crystals with paramagnetic impurities²⁷⁾.

If one is interested only in the nuclear spins, it is permissible in some cases to treat the electron spins and the lattice together and neglect the distinction between the two origins of the fluctuating electronic field. In the Overhauser effect where the fact that the electronic spins are not in equilibrium is important, the electronic spins must be separated from the lattice and treated quantum mechanically.

The Hamiltonian for a nucleus interacting with an electron can be written as

$$\mathcal{H} = g\beta H_0 S_z - (\mu_N/I) H_0 I_z + \hat{I} \cdot \vec{\hat{A}}_0 \cdot \hat{S} + g\beta \hat{H}_T \cdot \hat{S} + \hat{I} \cdot \vec{\hat{A}}_1(t) \cdot \hat{S}$$

A3

Here, the first two terms represent Zeeman coupling with the external field, $\vec{\hat{A}}_0$ and $\vec{\hat{A}}_1(t)$ represent the static and the time-varying part of the tensor $\vec{\hat{A}}$, and $\hat{H}_T$ is a fluctuating magnetic field produced by the lattice.

For the case of nuclear spins in a solid, one assumes $\vec{\hat{A}}_1(t)$ can be neglected. The coupling between the electrons and nuclear spins is now

via $\hat{\mathbf{I}} \cdot \hat{\mathbf{A}}_0 \cdot \hat{\mathbf{S}}$ which we assume to be a dipolar coupling term. This can be written as

$$\hat{\mathbf{I}} \cdot \hat{\mathbf{A}}_0 \cdot \hat{\mathbf{S}} = \frac{gg_n\beta^2}{r^3} (A + B + C + D + E + F) \quad A4$$

The various terms in equation A4 yield the following changes in the electronic and nuclear spin states $I_z = m, S_z = M$:

$A = I_z S_z (1 - 3\cos^2\theta)$	$\Delta M = 0 \quad \Delta m = 0$	
$B = -1/4 (I_+ S_- + I_- S_+) (1 - 3\cos^2\theta)$	$\Delta M = \pm 1 \quad \Delta m = \mp 1$	
$C = -3/2 (I_+ S_z + I_z S_+) \sin\theta \cos\theta e^{-i\varphi}$	$\Delta M = 0 \quad \Delta m = 1$	A5
	$\Delta M = 1 \quad \Delta m = 0$	
$D = -3/2 (I_- S_z + I_z S_-) \sin\theta \cos\theta e^{+i\varphi}$	$\Delta M = 0 \quad \Delta m = -1$	
	$\Delta M = -1 \quad \Delta m = 0$	
$E = 3/4 I_+ S_+ \sin^2\theta e^{-2i\varphi}$	$\Delta M = 1 \quad \Delta m = 1$	
$F = 3/4 I_- S_- \sin^2\theta e^{+2i\varphi}$	$\Delta M = -1 \quad \Delta m = -1$	

In the absence of coupling the eigenstates of the electron-plus-nucleus system will be $|++\rangle, |+-\rangle, |-+\rangle, |--\rangle$. The effect of the dipolar coupling will be to mix into each term of these zero order wave functions a bit of each of the others. However, owing to the wide separation in energy of states with different M compared to states with only differing m , only the terms C and D leading to $\Delta M = 0, \pm 1, \Delta m = \pm 1, 0$ are significant. As can easily be found from perturbation theory this leads to the following first-order eigenstates

$ b'\rangle = +-\rangle + q ++\rangle$	$ b\rangle = --\rangle - q -+\rangle$	
$ a'\rangle = ++\rangle - \bar{q} +-\rangle$	$ a\rangle = -+\rangle + \bar{q} --\rangle$	A6

where $g = \frac{3}{4} \frac{\gamma\beta}{Hr^3} \sin\theta \cos\theta e^{-i\varphi}$ and a coefficient on the order of one in front of the zero order term is neglected. The energy states and levels of this system are depicted in figure A1.

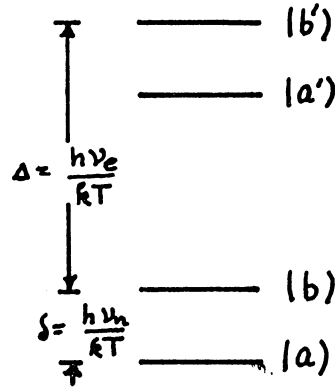


Figure A1. Energy levels for the system electron-plus-nucleus with weak dipolar coupling. ν_e = electron resonance frequency, ν_n = nuclear resonance frequency.

It is apparent that transitions from states $|b'\rangle \leftrightarrow |b\rangle$ or $|a'\rangle \leftrightarrow |a\rangle$ do not contribute to the nuclear relaxation. However, transitions such as $|b'\rangle \leftrightarrow |a\rangle$ or $|a'\rangle \leftrightarrow |b\rangle$, involving changes of the form $\Delta M = \pm 1, \Delta m = \mp 1$ do contribute to the nuclear relaxation. Since the fourth term in equation A3 is much smaller than the preceeding three terms, the first order eigenstates of these three terms can be considered as zero order eigenstates perturbed by the fourth term. Using this approach, the transition probabilities for these double spin flip transitions are found to be

$$W_{b' \leftrightarrow a} = g^2 \omega_1$$

A7

$$W_{a' \leftrightarrow b} = g^2 \omega_1$$

where w_1 is the transition probability of the allowed electronic transition $b' \leftrightarrow b$ or $a' \leftrightarrow a$ ^{3,10)}. This relates the nuclear relaxation time T_{1n} to the electronic relaxation time T_{1e} as

$$\frac{1}{T_{1n}} = \frac{3}{10} \left(\frac{g\beta}{r^3 H} \right)^2 \frac{1}{T_{1e}} \equiv \sigma \frac{1}{T_{1e}} \quad A8$$

The presence of small amounts of impurities other than the dominant impurity may lead to additional contributions to the nuclear relaxation. If these other impurities have much shorter T_{1e} than the T_{1e} of the major impurity then the nuclear relaxation time could be shortened out of proportion to the amount of the minor impurity present.

APPENDIX B: RF BRIDGE

The function of the rf bridge circuit in the NMR spectrometer is to balance out the major portion of the input voltage so that the signal voltage, which is a small modulation on a large ac carrier, can be amplified without saturating the receiver circuits. The balance conditions for the Anderson bridge (figure B1) are

$$RR_p\omega^2CC'(1 + C_2/C_1) = 1 \quad \text{B1}$$

$$\omega^2L[C + C_0 + C'(1 + C/C_1)] = 1 \quad \text{B2}$$

based on the assumption of a constant current source ³⁶⁾.

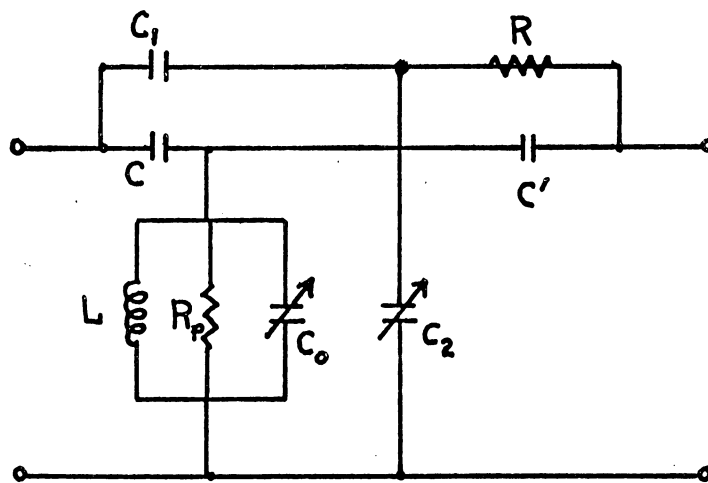


Figure B1. RF Bridge Circuit

In the course of balancing out the large ac portion of the signal, noise modulation of the signal source is also greatly reduced. Assuming that the noise modulation of the signal generator is totally eliminated, the noise at the output of the bridge is due only to the noise from the sample coil resistance plus noise from other dissipative elements in the bridge.

An alternate method of eliminating the carrier signal is the crossed coil or "induction" method of NMR detection. Here the receiver is attached to a coil oriented perpendicular to the dc magnetic field and to the rf coil driving the spin in the sample. At resonance, the precessing spins induce a voltage in the receiver coil which is amplified and displayed in a manner similar to the treatment of the output of the bridge circuit in the bridge method. However, in the induction method the only source of noise is the coil resistance. Thus the dissipative elements in the bridge represent a noise source over and beyond the minimum attainable in the induction method. The relationship between the signal-to-noise ratio for the two schemes is³⁶⁾

$$\left(\frac{S}{N}\right)_I = \eta^2 \left(\frac{S}{N}\right)_B \quad B3$$

where $\left(\frac{S}{N}\right)_I$ and $\left(\frac{S}{N}\right)_B$ represent, respectively, the signal-to-noise ratio in the crossed coils and in the bridge detection methods, and

$$\eta^2 = \left[1 + \frac{C}{C'} \left(1 + \frac{C_2}{C_1} \right) \right]^{-1} \quad B4$$

For maximum signal-to-noise ratio, the bridge circuit parameters should be chosen so that η^2 is as near one as possible.

APPENDIX C: ANALYSIS OF ESR SPECTROMETER

In this appendix, the electron spin resonance spectrometer circuit will be analyzed in some detail to enable the signal traces from the spectrometer to be related to the spin density in the samples. The circuit of the spectrometer is given in figure 3.2.

The sample in the sample cavity is subject to two orthogonal magnetic fields: (1) An rf field in the microwave range at the frequency ω_1 of the klystron, represented by $H_1 \cos \omega_1 t$; (2) a quasistatic field in the range of 3 kilogauss with a superimposed time variation. The time variation has two components, a linear sweep (S gauss/sec) and a low frequency (100 cps) sinusoidal modulating field. This is represented as

$$H_0 = H'_0 + St + H_2 \cos \omega_2 t.$$

Assuming the absence of saturation, slow sweep rate, and a small modulating field, i.e.,

$$S \ll \omega_1 H_1$$

$$H_2 \ll \Delta H$$

C1

where ΔH is the line-width, the time derivative of the magnetic susceptibility $\chi(\chi = \chi' - i\chi'')$ is given by

$$\frac{d\chi}{dt} = \frac{d\chi}{dH_0} \cdot \frac{dH_0}{dt} = - \frac{d\chi}{dH_0} \omega_2 H_2 \sin \omega_2 t$$

C2

where the derivative $d\chi/dH_0$ is evaluated at $H_0 = H'_0 + St$.

The cavity resonant frequency is represented by ω_0 . The small change in χ of the sample near resonance changes the voltage reflection coefficient R slightly. If we represent the wave incident on the cavity by

$$V_i = v_i e^{i\omega_1 t}$$

C3

the reflected wave is

$$V_r = R v_i e^{i\omega_1 t} \quad C4$$

The reflected voltage is the quantity monitored by the spectrometer, thus the sensitivity of the cavity is determined by the quantity $dR/d\chi$. The time derivative of R can be written as

$$\frac{dR}{d\chi} = \frac{d\chi}{dt} = - \frac{dR}{d\chi} \cdot \frac{d\chi}{dH_0} \omega_2 H_2 \sin \omega_2 t \quad C5$$

from equation C2. Thus at any H_0 ,

$$\begin{aligned} R &= \frac{dR}{d\chi} \frac{d\chi}{dH_0} H_2 \cos \omega_2 t \\ &= \frac{1}{2} \frac{dR}{d\chi} \frac{d\chi}{dH_0} H_2 \left(e^{i\omega_2 t} + e^{-i\omega_2 t} \right) \end{aligned} \quad C6$$

and equation C4 becomes

$$V_r = \frac{1}{2} \frac{dR}{d\chi} \cdot \frac{d\chi}{dH_0} H_2 v_i \left[e^{i(\omega_1 + \omega_2)t} + e^{i(\omega_1 - \omega_2)t} \right] \quad C7$$

Letting Q_0 be the unloaded cavity Q-value, Q represents the loaded Q-value, and η the filling factor, the reflected voltage can be shown to be ³⁰⁾ :

$$\begin{aligned} V_r &\approx \pi \eta Q_0 (1 - R'^2) v_i H_2 \times \\ &\left\{ \frac{d\chi'}{dH_0} [\cos(\omega_1 + \omega_2)t + \cos(\omega_1 - \omega_2)t] + \right. \\ &\quad \left. \frac{d\chi''}{dH_0} [\sin(\omega_1 + \omega_2)t + \sin(\omega_1 - \omega_2)t] \right\} \end{aligned} \quad C8$$

and that incident on b is

$$\begin{aligned} v_{ib} = & C_1 \frac{d\chi'}{dH_0} \left[\cos(\omega_1 + \omega_2)t + \cos(\omega_1 - \omega_2)t \right] \\ & + C_1 \frac{d\chi''}{dH_0} \left[\sin(\omega_1 + \omega_2)t + \sin(\omega_1 - \omega_2)t \right] \\ & + v_b \cos(\omega_1 t + \alpha) \end{aligned}$$

where $C_1 = \pi \eta Q_0 (1 - R'^2) v_1 H_2$. The crystal detector has the property of giving an output voltage V_0 such that the instantaneous magnitude of V_0 is a measure of the incident microwave power averaged over a number of cycles. The crystal detection law in this experiment was approximately

$$V_0 \propto (\bar{P}_i)^{1/2}$$

where P_i represents the incident power averaged over a time long compared to $1/\omega_1$, but short compared to $1/\omega_2$. (The actual detection law of the crystal, whether linear or square-law, affects the sensitivity, but not the principle of operation of the spectroscope.)

Squaring v_{1a} and v_{1b} , one finds that

$$\bar{P}_{ia} \propto v_b^2 \left\{ 1 + \frac{2C_1}{v_b} \left[\frac{d\chi''}{dH_0} \sin \alpha - \frac{d\chi'}{dH_0} \cos \alpha \right] \cos \omega_2 t \right\}$$

$$\bar{P}_{ib} \propto v_b^2 \left\{ 1 - \frac{2C_1}{v_b} \left[\frac{d\chi''}{dH_0} \sin \alpha - \frac{d\chi'}{dH_0} \cos \alpha \right] \cos \omega_2 t \right\}$$

C12

present on the klystron output leads to a convenient method for tuning the spectrometer. The noise at the output due to this fm klystron noise has the phase of the dispersion signal setting, that is, to the absorption signal ³⁰⁾. To tune to the dispersion signal, the phase is set midway between the two noise minima.

In the spin density measurements, the absorption derivative signal from various samples was compared with that of a standard. Choice of $\phi = \pi/2$ gives the absorption signal derivative, so the output signal to the recorder is

$$V_o = (\text{const}) \times \eta Q_o v_i H_i \frac{d\chi''}{dH_o} \quad \text{C16}$$

To estimate the functional dependence of $d\chi''/dH_o$, the Bloch equations are assumed to be valid, giving

$$\chi'' = \frac{\chi_o \omega_* T_2}{2} \frac{1}{1 + (\omega_o - \omega_*)^2 T_2^2} \quad \text{C17}$$

where ω_* is the frequency at the center of the resonance line. To convert equation C17 to field dependence, rather than frequency dependence, divide top and bottom by γ^2 , giving

$$\chi''(H_o) = \frac{\chi_o H_* T_2}{2 \gamma} \frac{1}{1 + (H_o - H_*)^2 T_2^2} \quad \text{C18}$$

From C18,

$$\frac{d\chi''}{dH_o} = \frac{\chi_o H_* T_2^3}{\gamma} \frac{(H_o - H_*)}{[1 + (H_o - H_*)^2 T_2^2]^2} \quad \text{C19}$$

Setting the differential of equation C19 equal to zero, one finds that the maxima of $d\chi''/dH_o$ occur at $(H_o - H_*) = \pm (\sqrt{3} T_2)^{-1}$. Thus the

separation of the maxima is

$$\Delta H = \frac{2}{\sqrt{3} T_2} \approx \frac{1}{T_2} \quad C20$$

The latter approximation is used throughout this paper to estimate T_2 .

Using C19 and C20, one finds that the values of $d\chi''/dH_0$ at the maxima are

$$\left. \frac{d\chi''}{dH_0} \right|_{\max} = \pm \frac{9}{16\sqrt{3}} \frac{\chi_0 H_* T_2^2}{\gamma} \quad C21$$

Using C16, C20, and C22, the maxima of the output voltage of the lock-in amplifier are

$$V_0|_{\max} = (\text{const}) \times \frac{\eta Q_0 \nu_1 H_z \chi_0 \omega_*}{(\Delta H)^2} \equiv S \quad C22$$

where S denotes the peak-to-peak signal height on the recorder trace.

Now, to relate S to the spin density in the samples, one can use the expression for the static susceptibility from the quantum generalization of the Langevin-Debye theory

$$\chi_0 = \frac{N \gamma^2 \hbar^2 I(I+1)}{3kT} \quad C23$$

where N is the number of spins per unit volume. This expression in C22 gives

$$S = (\text{const}) \times \frac{\eta Q_0 \nu_1 H_z N \gamma^2 \omega_*}{(\Delta H)^2} \quad C24$$

Solving for N,

$$N = (\text{const}) \times \frac{S (\Delta H)^2}{\eta Q_0 \nu_1 H_z \gamma^2 \omega_*} \quad C25$$

In practice, the various samples were compared with constant (determined by the cavity resonant frequency). Different γ 's were reflected in different positions of the center of the resonance. All comparisons were run at a constant temperature, and the filling factor and Q-factor can be assumed to be constant. Thus C25 simplifies to

$$N = (\text{const}) \times \frac{S (\Delta H)^2 H_x^2}{\nu_1 H_2} \quad \text{C26}$$

Determination of the spin density in an unknown, involves comparing the ESR signals from the unknown and a standard with the aid of C26.

VIII. BIBLIOGRAPHY

1. A. W. Overhauser, Phys. Rev. 89 (1953) 689.
2. T. R. Carver and C. P. Slichter, Phys. Rev. 102 (1956) 975.
3. A. Abragam, Phys. Rev. 98 (1955) 1729.
4. C. D. Jeffries, Phys. Rev. 117 (1960) 1056.
5. C. D. Jeffries, Phys. Rev. 106 (1957) 164.
6. W. A. Barker, Rev. Mod. Phys. 34 (1962) 173.
7. W. A. Barker, et. al., Rev. Mod. Phys. 36 (1964) 872.
8. Robert H. Webb, Am. J. Phys. 29 (1961) 428.
9. G. R. Khutsishvili, (Translation) Soviet Physics, Uspekhi 3 (1960) 285.
10. C. D. Jeffries, Dynamic Nuclear Orientation (Interscience, 1963).
11. C. D. Jeffries, Annual Review of Nuclear Science 14 (1964) 101.
12. A. Abragam and M. Borghini, Progress in Low Temperature Physics Vol. IV. (North Holland, 1964), Chapter VIII.
13. A. Abragam, The Principles of Nuclear Magnetism (Interscience, 1961).
14. V. I. Lushchikov, A. A. Manenkov, and Yu. V. Taran, (Translation) Sov. Phys. Solid State 3 (1962) 2541.
15. A. V. Kessenikh, V. I. Lushikov, and A. A. Manenkov, and Yu. V. Taran, (Translation) Soviet Physics Solid State 5 (1963) 321.
16. A. V. Kessenikh and A. A. Manenkov, (Translation) Soviet Physics Solid State 5 (1963) 835.
17. G. R. Khutsishvili, (Translation) Soviet Physics Solid State 5 (1964) 1983.
18. L. L. Buishvili and A. V. Kessenikh, (Translation) Soviet Physics Solid State 6 (1965) 2402.
19. I. V. Aleksandrov and A. V. Kessenikh, (Translation) Soviet Physics Solid State 6 (1964) 777.
20. R. H. Webb, Physics Letters 6 (1961) 611.

21. O. S. Leifson and C. D. Jeffries, Phys. Rev. 122 (1961) 1781.
22. A. G. Redfield, Phys. Rev. 98 (1955) 1787.
23. C. Kittel, Phys. Rev. 95 (1954) 589.
24. N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73 (1948) 679.
25. B. N. Provotorov, (Translation) Soviet Physics JETP 14 (1962) 1126.
26. N. Bloembergen, Physica 15 (1949) 386.
27. P. G. de Gennes, J. Phys. Chem. Solids 7 (1958) 345.
28. E. R. Andrew, Nuclear Magnetic Resonance (Cambridge University Press, 1955).
29. J. C. M. Henning, Rev. Sci. Inst. 32 (1961) 35.
30. F. A. Faulkner, Lab. Pract. (GB) 13 (1964) 1065.
31. T. L. Estle and G. K. Walters, Rev. Sci. Inst. 32 (1961) 1058.
32. W. H. Watson, Jr., W. C. McMordie, Jr., and L. G. Lands, Journ. of Polymer Science 55 (1961) 137.
33. D. J. E. Ingram, Free Radicals (Academic Press, 1958).
34. R. J. Abraham and D. A. Whiffen, Trans. Faraday Society 54 (1958) 1291.
35. J. G. Powles and B. I. Hunt, Physics Letters 14 (1965) 202.
36. D. Gheorghiu and A. Valeria, Nucl. Inst. and Methods 16 (1962) 313.
37. G. E. Schacher, Phys. Rev. 135A (1964) A185.
38. T. J. B. Swanenburg, N. J. Poulis, and L. J. Ancher, Physics Letters 15 (1965) 12.

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