Electron Paramagnetic Resonance Studies of a Radiation-Induced Defect Center in Anthracene Crystals

Emmitt O. Wright

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ELECTRON PARAMAGNETIC RESONANCE STUDIES OF A
RADIATION-INDUCED DEFECT CENTER IN ANTHRACENE
CRYSTALS

A Thesis
Presented to
The Faculty of the Department of Physics
The College of William and Mary in Virginia

In Partial Fulfillment
of the Requirements of the Degree of
Master of Arts

By
Emmitt O. Wright
August, 1967
APPROVAL SHEET

This thesis is submitted in partial fulfillment of the requirements for the degree of

Master of Arts

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LIST OF SYMBOLS

\( A \) = Hyperfine coupling constant

\( \beta_e \) = Bohr magneton

\( c' \) = Normal to a-b plane of anthracene crystal at intersection of a-b axes

\( e \) = Electronic charge

\( \Delta H \) = The line width at maximum slope of the absorption curve in terms of applied static magnetic field

\( \Delta \omega \) = The line width at maximum slope of the absorption curve in the r.f. microwave field

\( g \) = Electronic spectroscopic splitting factor

\( g(\omega - \omega_0) \) = The normalized line shape function

\( \gamma \) = The gyromagnetic ratio \( (\gamma = \frac{e}{mc} = 1.76 \times 10^1 \text{ Mc/gauss}) \)

\( H \) = Net applied external magnetic field

\( H_0 \) = The applied static magnetic field

\( H_1 \) = The circularly polarized component of the r.f. magnetic field

\( H_e \) = The effective applied magnetic field vector

\( h \) = Planck’s constant

\( \hbar \) = \( h/2\pi \)

\( \mathcal{H} \) = Spin Hamiltonian

\( I \) = Nuclear angular momentum vector

\( L \) = Orbital angular momentum vector
\( \lambda \quad = \quad \text{Spin-orbit coupling constant} \)

\( M \quad = \quad \text{The magnetization vector} \)

\( M_0 \quad = \quad \text{The static magnetization vector} \)

\( M' \quad = \quad \text{The magnetization vector as viewed in the rotating coordinate system} \)

\( P \quad = \quad \text{Average power } P \text{ absorbed per unit volume} \)

\( Q \quad = \quad \text{The cavity } Q \text{ [where } Q \text{ is defined as } \omega \text{ (energy stored/power lost) and } \omega = 2 \pi \times \text{frequency}] \)

\( S \quad = \quad \text{Spin angular momentum vector} \)

\( T_1 \quad = \quad \text{The spin-lattice relaxation time} \)

\( T_2 \quad = \quad \text{The so-called spin-spin relaxation time} \)

\( \omega \quad = \quad \text{The frequency of the applied r.f. microwave field} \)

\( \omega_0 \quad = \quad \text{The EPR resonance frequency} \)

\( \chi_0 \quad = \quad \text{Static susceptibility of the crystal } (M_0/H_0) \)

\( \chi \quad = \quad \text{The complex susceptibility of the sample relative to free space} \)

\( \chi' \quad = \quad \text{The real part of the complex susceptibility} \)

\( \chi'' \quad = \quad \text{The imaginary part of the complex susceptibility} \)
ABSTRACT

Electron paramagnetic resonance studies were conducted on an anthracene crystal which had been irradiated with 7 MeV electrons to a total integrated flux of $2 \times 10^{16}$ electrons cm$^{-2}$. Spectra obtained with a 9.5 and a 35 kMc spectrometer, operated at ambient temperatures and at very low power levels, were very similar. The dispersion mode spectra with the static magnetic field $H_0$ perpendicular to the b-crystallographic axis and parallel with the a-axis consisted of four lines equally spaced at 15 gauss apart and centered on a field value corresponding to a g-value of 2.0046 ± 0.0005. Rotation of the crystalline axis, such that the static field $H_0$ was parallel with the c-axis, caused the two central spectral lines to symmetrically approach one another and merge into one broad line of about 25 gauss in width centered at the same g-value as when $H_0$ was parallel with a-axis. The anthracene spectra were all highly susceptible to r.f. power saturation. Saturation was observable at r.f. power levels corresponding to an r.f. magnetic field vector as low as $4 \times 10^{-3}$ gauss. The observed absorption spectra are found, by curve fitting, to consist of four Gaussian lines with line widths of about 12 gauss and a hyperfine splitting of about 14 gauss. The intensity of the lines are found to be 1:3:3:1 implying that the hyperfine structure is arising from the interaction of the unpaired electron with three equivalent protons. Comparison with spectra from related aromatic hydrocarbons leads to the conclusion that the paramagnetic defect center is arising from a cross linking between two anthracene molecules within the crystalline structure.
ELECTRON PARAMAGNETIC RESONANCE STUDIES OF A RADIATION-INDUCED DEFECT CENTER IN ANTHRACENE CRYSTALS
INTRODUCTION

Studies and applications of spectroscopy are of critical importance to many aspects of manned and unmanned space travel and communications. Safe and reliable performance of both organic (including man) and inorganic materials, used in communication and other spacecraft component systems, are dependent upon an adequate knowledge of and thus the protection against, the potentially damaging effects of particulate and electromagnetic radiations encountered in space environments.

This study is concerned with defect centers produced in anthracene crystals (which are sometimes used as scintillation counters in the detection of particulate radiation). The study of radiation induced defects in organic crystals provide direct information about the production of free radicals in organic molecular structures such as may be produced under various radiation environmental conditions which will be encountered in space travel.

The present studies are concerned with a defect center produced in an anthracene crystal as a result of irradiation with 7 MeV electrons for a total flux of $2 \times 10^{16}$ electrons cm$^{-2}$. Three anthracene samples were exposed to the same electron beam but to different total fluxes ($10^{14}$, $10^{15}$, and $10^{16}$ electrons cm$^{-2}$). All three samples exhibited similar spectra under the same spectroscopic conditions except that the density of the defect centers as indicated by the signal amplitude of the spectra was a function of the total integrated
electron flux, as would be expected. However, because of the similarity in the spectra obtained, only one sample was used for detail analysis of the defect center characteristics (with respect to spatial dependence, etc.).

The technique used for investigating the nature of the defect center, produced in the anthracene crystal by radiation, was the method of electron paramagnetic resonance (EPR) spectroscopy. Spectrometers operating at two different microwave frequencies, 9.5 kMc and 35.0 kMc, were used for this investigation. The EPR method has been successfully used by many workers in recent years for the study of irradiated organic and inorganic solid state materials.
I. THEORY

In the construction of any electron paramagnetic resonance (EPR) model of an irradiation produced defect center in a crystalline material one is always faced with the problem of correlating the experimental information obtained from the various spectra with the atomic and nuclear structure of the system in question. The line shape of most EPR spectra is found to be either Lorentzian or Gaussian or some intermediate shape which can be determined by comparison with known line shapes. The processes that govern the line width are known as the relaxation phenomena. Two relaxation processes are generally used to describe a line width:

(1) the spin-lattice relaxation time $T_1$, a measure of the rate at which the spin system can lose its excess energy to the thermal reservoir or lattice structure, and

(2) the spin-spin relaxation $T_2$, a measure of the phase coherence of the precessing spin system. The coupling between spins and the crystalline lattice is strong, resulting in very short thermal relaxation times $T_1$, of the order of $10^{-4}$ to $10^{-10}$ sec. $T_1$ is strongly temperature dependent ($\sim T^{-4}$, where $T$ = temperature) since thermal agitations of neighboring ions results in variations of the crystalline electric field.

Another parameter which is determined from the EPR spectra is the so-called g-value (the spectroscopic splitting factor), a measure of the
anisotropic spin-orbit interaction. The g-value is modulated by the crystalline field effects since it arises from a mixing of the spin-orbit interactions which are affected by the crystalline field effects. The unknown g-value of a particular sample can be obtained by either measuring the magnetic field and microwave frequency with great precision or by the comparison technique using a dual sample cavity.

The general theory of magnetic resonance phenomena has been discussed by many authors in recent years [1 - 5]. The Hamiltonian \( \mathcal{H} \) for the magnetic interaction in a strong magnetic field is given by

\[
\mathcal{H} = g\beta_e H \cdot S + A_I \cdot S + \lambda L \cdot S
\]  

(1)

where the energy due to the interaction of the nuclear magnetic moment and external magnetic field and crystalline field effects have been neglected. The three terms of the expression are explained next.

There are two interactions involving the orbital angular momentum. One is the spin-orbit coupling which is given by the last term \( \lambda L \cdot S \) of equation (1) and the other is the interaction of the orbital momentum with the external field which has been neglected. The orbital angular momentum of an unpaired electron in a crystalline field is usually zero or in most cases it is quenched by the crystalline field. The constant \( \lambda \) is called the spin-orbit coupling constant.

The second term in equation (1) \( A_I \cdot S \) gives the hyperfine coupling between the magnetic moments of the nucleus and the electron. The constant \( A \) is called the hyperfine coupling constant. There are two fundamentally
distinct kinds of hyperfine interactions; one is concerned with the magnetic
field at the electron caused by the presence of a nuclear spin near the electron
but not right at the electron. This is the dipolar hyperfine interaction. The
other kind of hyperfine interaction is called the contact hyperfine interaction or
the Fermi contact interaction which is proportional to the electron density at
the nucleus.

\[ g \beta_e H \cdot S \]

The first term \( g \beta_e H \cdot S \) of equation (1) represents the interaction of
spin of the electron and the external magnetic field. The constant \( g \) is the
spectroscopic splitting factor. In a crystalline field these three constants
\((g, \lambda, \text{and } \lambda)\) are usually spatially dependent and in the present investigation
are found to be dependent upon the orientation of the crystallographic axes with
respect to the external magnetic field. The properties of the Hamiltonian are
discussed by many authors [1-5].

When a spin system comes under the influence of an externally applied
static magnetic field \( H_0 \), the applied field produces a torque on the randomly
orientated individual electron spin vectors which tends to align them with the
field \( H_0 \). On the other hand, random thermal motion tends to destroy the
alignment. Hence only a partially aligned system is obtained. This alignment
induced by an external magnetic field corresponds to the lowest energy state
of the spin system. While undergoing this alignment the spin system must
give up some of its energy to its surroundings, i.e., the crystalline lattice of
the solid. The characteristic time required for this energy exchange is called
the thermal or spin-lattice relaxation time \( T_1 \). Therefore in the absence of
interactions, other than crystalline field effects, the magnetization \( M_z \) of the
disturbed system along $H_0$ tends toward the equilibrium value $M_0$ given by

$$M_0 = \chi_0 H_0$$

(2)

where $\chi_0$ is the static susceptibility. The same interactions which cause changes in $M_Z$ tend to cause changes in the $M_X$ and $M_Y$ alignments also. This effect in addition to any irregularities in the magnetic field as seen by the individual electrons, produced by neighboring spins or other field inhomogeneities, will cause the individual electron spins which were originally precessing coherently to get out of phase with each other with a characteristic time constant $T_2$. The assumption that these processes may be described by an exponential decrease of the magnetization leads to the following simple decay equations

$$\frac{dM_x}{dt} = -\frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} = -\frac{M_y}{T_2}$$

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1}$$

(3)

where $T_1$ is the characteristic spin lattice relaxation time, and $T_2$ is the characteristic so called spin-spin relaxation time.

Newton's Law of motion for angular momentum may be expressed in terms of the net magnetization and applied external magnetic field vectors, $M$ and $H$ as

$$\frac{dM}{dt} = -\gamma (M \times H)$$

(4)
where $\gamma = \gamma e$, and $H$ is defined by equation (6). Then by combining equations (4) and (3) we get Bloch's phenomenological equations [2].

$$\frac{dM_x}{dt} = -\gamma (M_H y - M_y H) - \frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} = -\gamma (M_H z - M_y H) - \frac{M_y}{T_2}$$

$$\frac{dM_z}{dt} = -\gamma (M_H x - M_z H) + \frac{M_0 - M_z}{T_1}$$

where $H$ is given by

$$H = \hat{i}H_1 \cos\omega t + \hat{j}H_1 \sin\omega t + \hat{k}H_0,$$  \hspace{1cm} (6)

since all magnetic resonance experiments employ a small time varying external magnetic field $H_1$ perpendicular to the external static field $H_0$ which rotates with an angular velocity $\omega$ such that $H_1$ is a constant when viewed in a rotating coordinate system which rotates with the same angular velocity $\omega$.

In order to discuss the solution of equations (5), two concepts must be defined and investigated, i.e., rapid and slow passage conditions. By transforming equation (4) to a rotating coordinate system rotating with angular velocity $\omega$ and using equation (6) we get

$$\frac{\partial M'}{\partial t} = -\gamma [M' \times \{\hat{i}H_1 + \hat{k}(H_0 - \omega/\gamma)\}]$$

which states that physically in the rotating coordinate system the moment $M'$ acts as though it experienced effectively a static magnetic field $H_e$ given by

$$H_e = \hat{i}H_1 + \hat{k}(H_0 - \omega/\gamma).$$

Therefore, the magnetic moment $M'$ precesses in a cone of fixed angle about $H_e$ at an angular frequency of $\gamma H_e$. This situation is illustrated in Figure 1.
It is seen that the motion of the moment $M'$ is periodic and if it was initially oriented along the $z$-direction at time $t = 0$, then it periodically returns to that position. Notice from equation (7) and Figure 1 that if $H_0$ is above resonance ($H_0 > \frac{\omega}{\gamma}$), then the effective field has a positive $z$-component; but when $H_0$ lies below the resonance level ($H_0 < \frac{\omega}{\gamma}$), the effective field has a negative $z$-component; on the other hand if the resonance condition is fulfilled exactly, $\omega = \gamma H_0$, the effective field is simply $H_1$ and in the $x$-direction.

Therefore under resonance condition $M'$ in the rotating frame is seen to precess about $H_1$ with frequency $\gamma H_1$ and the axis of the precession cone is decreased from $\frac{\pi}{2}$ to zero.

Suppose that initially the magnetic field is far above resonance ($H_0 \gg \frac{\omega}{\gamma}$) and that the moment $M'$ is aligned in the $z$-direction. Now as the value $H_0 - \frac{\omega}{\gamma}$ is made to slowly decrease through zero to a large negative value, the angle $\theta$ of the effective field $H_e$ starts from essentially at $\frac{\pi}{2}$ and goes to $\pi$.

If the sweep through resonance is sufficiently fast so that the time taken to pass through resonance is short compared to the relaxation time $T_1$, then the magnetic moment vector $M'$ can follow the effective field and the spin system will be inverted. If, on the other hand, the sweep time is long compared to $T_1$, the relaxation processes $T_1$ and $T_2$ will cause $M'$ to relax back to $M_0$.

Physically this means that the time rate change of $\theta$ must be large, i.e., that

$$\frac{d\theta}{dt} \gg \frac{1}{T_1}$$

and from Figure 1 this can be written as

$$H_1^{-1} \left| \frac{d}{dt} \left[ H_0 - \frac{\omega}{\gamma} \right] \right| \ll \gamma H_1 .$$  

(8)
Also if \( \frac{1}{T_1} \) or \( \frac{1}{T_2} \) exceeds \( \gamma H_1 \), the relaxation processes will cause \( M' \) to decay before even one precession cycle of \( M' \) about \( H_e \) can occur, so in order that \( M' \) can follow the effective field \( H_e \) we have the restriction that

\[
\gamma H_1 \geq \frac{1}{T_2}.
\]

This condition is referred to as the rapid passage condition and points out the fact that the experiment must be performed in a time short compared to the relaxation time \( T_1 \). Further it can be shown that \( \frac{1}{T_2} \geq \frac{1}{T_1} \) [2].

In reality one takes \( T_1 \) and \( T_2 \) as nature gives them, but in most cases the requirements for rapid passage conditions cannot be fulfilled. Therefore, we are led to the discussion of the "slow passage" solutions. The solution for "slow passage" applies if the resonance is traversed in a time which is long compared to \( T_1 \) (the time required to maintain thermal equilibrium with the lattice or thermal reservoir).

The "slow passage" solution of Bloch's equations (5) is discussed by many authors [1-5]. In carrying out the solution, one defines the complex relative susceptibility of the sample as

\[
\chi = \chi' - i \chi'' \tag{10}
\]

where \( \chi \) is the susceptibility relative to free space. The real part of the susceptibility \( \chi' \) determines the in-phase magnetization while the imaginary part \( \chi'' \) determines the out-of-phase magnetization of the sample caused by the high frequency r.f. magnetic field. When an r.f. magnetic field \( H_1 \) is applied to the sample, an in-phase magnetization of \( \chi' H_1 \sin \omega t \) and an out-of-phase magnetization of the \( -\chi'' H_1 \cos \omega t \) is produced. The average power \( P \) absorbed
per unit volume of sample is given by

\[ P = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} H \frac{dM}{dt} \, dt = 2\omega \chi'' H_1^2. \]  \hspace{1cm} (11)

In evaluating this integral it is seen that the power absorbed by the sample from the \( H_1 \) field depends only on the out-of-phase component of the susceptibility.

Assuming slow passage and homogeneously broadened lines, the solution of the Bloch equation (5) for the imaginary part of the complex r.f. susceptibility can be shown to be [2]

\[ \chi'' = \frac{1}{2} \chi_0 \omega_0 \frac{\pi g(\omega - \omega_0)}{1 + \pi \gamma^2 H_1^2 g(\omega - \omega_0) T_1} . \]  \hspace{1cm} (12)

The normalized Lorentzian line shape function is defined by

\[ g(\omega - \omega_0) = \frac{T_2/\pi}{1 + T_2^2 (\omega - \omega_0)^2} \]  \hspace{1cm} (13)

and the normalized Gaussian line shape function is defined by

\[ g(\omega - \omega_0) = \frac{T_2}{\pi} e^{-\frac{(\omega - \omega_0)^2 T_2^2/\pi}{2}} . \]  \hspace{1cm} (14)

From equations (13) and (14) the line width at maximum slope of the shape functions can be shown for a Lorentzian line to be

\[ \Delta H = \frac{2}{\sqrt{3} \gamma T_2} \]  \hspace{1cm} (15)

and for a Gaussian line to be

\[ \Delta H = \frac{2\sqrt{\pi/2}}{\gamma T_2} \]  \hspace{1cm} (16)
where $\Delta \omega = \gamma \Delta H$ and $\Delta H$ is the separation of the absorption peaks in gauss.

Since $T_1$ is dependent upon lattice vibrations, the line broadening due to spin-lattice interactions can be reduced to zero by lowering the temperature of the sample. Clearly $T_2$ is not temperature dependent.

The crystal detectors used in most spectrometers operate in the linear range, i.e., with crystal detector biasing currents above 50$\mu$ amps. Therefore, what is detected and displayed is the change in the cavity reflection coefficient or the r.f. voltage from the detector which is proportional to $\chi''H_1$ rather than the power absorbed according to equation (11). Feher [4] develops this argument showing that a power absorption of $\frac{1}{2}\omega H_1^2\chi''$ gives rise to a change in the Q of the cavity which is proportional to $\chi''$ and independent of $H_1$.

Assuming that the field modulation amplitude is much less than the line width, the detected signal is

$$\frac{d(\chi''H_1)}{d(\omega - \omega_0)} = \frac{\chi_0 \omega_0 H_1 T_2^2 (\omega - \omega_0)}{[1 + T_2^2 (\omega - \omega_0) + \gamma^2 H_1^2 T_1 T_2]^2}.$$  \hspace{1cm} (17)

The maxima of this function occur at

$$(\omega - \omega_0) = \pm \sqrt{(1 + \gamma^2 H_1^2 T_1 T_2)/3T_2^2}.$$  \hspace{1cm} (18)

If equation (17) is evaluated at the peaks (equation 18) and then maximized with respect to $H_1$, we get

$$\frac{d}{dH_1} \left( \frac{d(\chi''H_1)}{d(\omega - \omega_0)} \right)_{\text{max}} = 0; \quad T_1 = \frac{1}{2T_2\gamma^2 H_1^2}$$

which shows that equation (17) will have its largest values when

$$H_1 = \frac{1}{\gamma\sqrt{2T_1 T_2}}.$$  \hspace{1cm} (19)
Therefore, the experimental technique is to determine whether the line shape is Lorentzian or Gaussian and then measure $T_2$ from the recorded spectra; then find that value of $H_1$ that gives the largest observed signal; finally, use equation (19) to find $T_1$ if the spectra are from a homogeneously broadened system, i.e., a Lorentzian line shape.

II. EXPERIMENTAL PROCEDURES AND RESULTS

The anthracene sample was cut from a single crystal which was supplied by the Isomet Corporation. It was cut and lapped to fit the 100 kc sample cavities of the X-band (9.5 kMc) EPR spectrometer. The final size of the sample was 2.5 mm × 0.5 mm × 90 mm long. The anthracene crystal (Fig. 12), which is monoclinic, was cleaved with the long flat surface containing the a-b crystallographic plane with the b-axis along the long direction of the sample [6-8]. Therefore, the sample orientation with respect to the crystallographic axes and the static magnetic field $H_0$ could be determined.

The sample, prior to the electron irradiation, was colorless and transparent and exhibited no EPR signals that could be detected. After the irradiation with electrons, the sample was still somewhat transparent but its color was now a yellowish-brown (indicative of some kind of radiation damage). Anthracene, $C_{14}H_{10}$, has a molecular weight of 178.2, and a melting point of 218°C. In the solid state form anthracene is a clear, colorless, transparent monoclinic crystalline structure. Each crystalline unit cell (Fig. 12) has a volume of 474.2 Å³ and contains two anthracene molecules. The anthracene molecule, Figure 13, is essentially planar. The long direction of the molecule
defines its L-axis; the short planar direction defines the M-axis: the axis normal to the plane of the molecule is the N-axis. The mean C-C bond length is about 1.4 Å and the mean C-H bond length is about 1.0 Å [8].

Figure 12 depicts the molecular disposition of the anthracene molecules within the unit cell. The unit cell dimensions are also shown in Figure 12. The molecules lie in the unit cell in two sets of parallel planes which are related by the mirror glide planes. The long axes (L-axis) of the molecules in the two planes are parallel to the c-axis of the crystal to within about 10 degrees. A molecule with its center located at (0, 0, 0) is surrounded by six other molecules in the a-b plane, those being located at: ± (0, 1, 0), ± (1/2, 1/2, 0) and ± (1/2, -1/2, 0). The upper end of the molecule located at (0, 0, 0) falls in the hollow between three molecules with centers at (0, 0, 1), (1/2, 1/2, 1) and (1/2, -1/2, 1) with its lower end being surrounded by molecules with centers at (0, 0, -1), (-1/2, -1/2, -1) and (-1/2, 1/2, -1). There are no C-C contacts within the unit cell. The H-H and the C-H distances are the shortest. Each molecule is involved in 26 contacts with 7 of these being crystallographically independent:

\[
\begin{align*}
H(C'; 0, 0, 0) -&- H(A'; 0, 0, 1) \quad 2.50 \text{ Å} \\
H(C'; 0, 0, 0) -&- H(A; \frac{1}{2}, -\frac{1}{2}, 1) \quad 2.91 \\
H(C'; 0, 0, 0) -&- H(B; \frac{1}{2}, -\frac{1}{2}, 1) \quad 2.96 \\
H(A; 0, 0, 0) -&- H(B; \frac{1}{2}, -\frac{1}{2}, 1) \quad 2.54 \\
H(B; 0, 0, 0) -&- H(F'; 0, 1, 0) \quad 2.79 \\
H(D; 0, 0, 0) -&- H(D'; 0, 1, 0) \quad 2.72 \\
C(D; 0, 0, 0) -&- H(F; \frac{1}{2}, -\frac{1}{2}, 0) \quad 2.67
\end{align*}
\]
It should be noted that the shortest C - H distance between adjacent molecules is 2.67 Å. This closeness is the cause of the C(D) and C(D') atoms b being deflected from the mean planes, and thus the slight but real deviation from the planarity of the molecule [8].

The sample was placed in a quartz sample tube having a 3 mm inner diameter. The sample tube was then inserted in the microwave EPR cavities and positioned with the static magnetic field \( H_0 \) normal to the b-axis so that \( H_0 \) could be rotated about the b-axis with the a-axis either parallel with or perpendicular to \( H_0 \).

With the above orientation of the sample the static magnetic field \( H_0 \) was always perpendicular to and could be rotated about the b-axis. The first derivative of the absorption mode spectra of the irradiated sample obtained at X-band, with the static field \( H_0 \) parallel with the a-axis, is shown in Figure 2. Figure 3 shows a spectrum obtained under the same spectrometer conditions, but with \( H_0 \) perpendicular to the a-axis. Figures 4 and 5 show spectra with \( H_0 \) at intermediate positions. Figures 6, 7, 8, 9, and 10 show the corresponding dispersion mode spectra under the same spectrometer settings as before. All of these spectra were obtained from the X-band spectrometer at ambient temperatures by using 100 kc field modulation and homodyne detection schemes at an r.f. microwave power level corresponding to an r.f. magnetic field vector, \( H_0 \) of about \( 4 \times 10^{-3} \) gauss.

Spectra were recorded as the static field \( H_0 \) was rotated about the sample from a position parallel with the a-axis through intermediate positions to a direction perpendicular to the a-axis. As the rotation proceeded, the two
lines forming the strong central doublet approached one another, and were simultaneously broadened until they finally formed a single broad central peak. The total width of this peak was then about 25 gauss as measured from the dispersion mode spectra. This strong central doublet could just be distinguished as being formed of two peaks, with a separation of about 7 gauss on each side of the center.

The spectrometer used for these studies was a standard Varian X-band (9.5 kMc) spectrometer with the 100 Kc field modulation unit. The two microwave cavities used were also supplied by the Varian Associates; those being the dual rectangular cavity assembly used for sample comparison purposes, and the cylindrical rotational cavity used for detailed spatial dependences. A block diagram of the essential components of the spectrometer is shown in Figure 11.

All spectra obtained at X-band from the anthracene sample were symmetrical and centered at 3394 gauss. Comparison (using the dual cavity) of the anthracene spectra with those of standard samples of diphenyl picryl hydrazyl (DPPH), and pitch in potassium chloride (KCl), showed the g-value to be 2.0046 ± 0.0005, with most of the uncertainty arising from the sample line width. The dispersion mode spectrum with $H_0$ along the a-axis consisted of four lines: a doublet spaced 7.5 ± 0.5 gauss on each side of the center and a second doublet of approximately one-third of the intensity of the first doublet spaced 22.5 ± 1.0 on each side of the center as measured. Thus, within experimental error, the dispersion mode spectrum (as can be seen from Fig. 6) consisted of four lines equally spaced at 15 gauss apart.
The observed absorption and dispersion spectra, Figures 2 and 6, appear to be made up of four unresolved lines. Their intensities (signal amplitude) suggest that the spectra consist of four equally spaced lines with relative intensities of 1:3:3:1 when the $H_0$ field is along the a-axis. The lines are seen to merge together as the sample is rotated about the b-axis.

By assuming that the spectra do consist of four unresolved lines with intensities of 1:3:3:1, the line width and splitting (that is the line separation) can be determined by curve fitting. The results of a computer program that was generated for this purpose indicates that the spectra do conform to a Gaussian shape (equation 16) consisting of four lines with a splitting of 14 gauss and a line width of 12 gauss. If a Lorentzian line shape, equation (15) is assumed, a splitting of (10) gauss and a line width of (14) gauss is found to be the best fit.

As the specimen was rotated from the position with $H_0$ along the a-axis to the position with $H_0$ along the c'-axis (Fig. 12), the two lines forming the strong central doublet are seen to approach one another and simultaneously broaden until finally they form a broad central peak (see Figs. 6 and 7). The total width of this peak was about 25 gauss in the dispersion mode, which could just be distinguished as being formed of two peaks. The outer two peaks have a separation of about 20 gauss on each side of the center, and are apparently somewhat reduced in relative intensity as compared with the intensity the outer doublet had in the first orientation of the specimen. Intensity measurements were, however, unreliable at this orientation because of the overlapping and irregular shape of the lines.
The spectra obtained at K-band (35.0 kMc) showed a close similarity to those at X-band (9.5 kMc). The center of the spectrum was still at approximately $g = 2$; the line structure, line width, and relative line intensities for various orientations were as described for the X-band. In particular, the K-band spectra exhibited the same general characteristics with respect to r.f. power saturation as did the X-band spectra.

R.f. saturation of the EPR spectra was found to occur at the rather low power levels characteristic of the short relaxation times of solid state materials. Some line broadening of the absorption mode signal was apparent at 19 $\mu W$ power in the cavity (40 db total attenuator setting on the Varian V 4502). Severe broadening was observed at 190 $\mu W$ r.f. power level, the absorption mode signal was so heavily saturated as compared with the dispersion signal that it could no longer be distinguished. Calculations for the cavities used, based on the klystron power measurements showed that a power saturation threshold of 19 $\mu W$ corresponded to a circularly polarized r.f. magnetic field vector of about $4 \times 10^{-3}$ gauss.

This rather low r.f. power level required to prevent saturation broadening set an effective lower limit of about one gauss on the modulation field amplitude which could be used. These conditions reduced signal-to-noise ratio thereby preventing any further resolution (at room temperature) of the hyperfine structure of the spectra.

III. DISCUSSION AND INTERPRETATION OF RESULTS

Analysis of the anthracene EPR data indicates that the spectra from the defect center consist of closely spaced clusters of lines centered on a magnetic
field value corresponding to a g-value of \( g = 2.0046 \pm 0.0005 \). The spectra was also found to be independent of the r.f. microwave frequency used (X-band or K-band), thus indicating that the defect center contained an unpaired electron of spin \( \frac{1}{2} \hbar \), whose orbital angular momentum (if nonzero) is essentially quenched by the crystalline field. Also the fact that the spectra are frequency independent indicates that the splittings are caused by hyperfine interactions rather than crystalline field effects. The observed hyperfine splitting must be due to either the carbon (C\(^{13}\)) or the hydrogen nuclei since these are the only two nuclei present whose nuclear magnetic moment is nonzero. Since the natural abundance of C\(^{13}\) is so low (only 1.108%), it must be concluded that the hyperfine splitting is due to the hydrogen nuclei whose nuclear spin is \( \frac{1}{2} \hbar \).

In order to discuss a possible model for the defect center produced by the irradiation, one must consider the chemical and crystallographic structure of the anthracene crystal. The anthracene molecular structure consists of a three benzene ring chain as shown in Figures 12, 13, and 14. Figure 15 depicts the delocalized "pi" electron distribution in the molecule. The anthracene molecule is almost planar with the mean C-C bond length being 1.4 Å and the C-H bond length being 1.0 Å \([8]\). The unit cell dimensions are defined in Figure 12. Anthracene is a monoclinic crystal with the cleavage plane containing the plane of the crystallographic a-b axes.

The anthracene molecules lie in two sets of parallel planes related by the mirror glide planes. The long molecular axis (L-axis, see Fig. 13) of the molecules of both sets of glide planes are parallel to the c-axis to within
about 10 degrees. The closest C-H distance between adjacent molecules is 2.67 Å: between the C(D) in the (0, 0, 0) molecule and the H(F) in the
\((\frac{1}{2}, -\frac{1}{2}, 0)\) molecule and, thus, between the C(D') in the (0, 0, 0) molecule and the H(F') in the \((-\frac{1}{2}, \frac{1}{2}, 0)\), and all other such crystallographically related pairs [8].

The EPR spectra of singly charged anthracene ions, both positive and negative, have been studied experimentally by Bolton, Carrington, and McLachlan [9] and theoretically by Sayetta and Momory [10]. The former authors, by using a very slow magnetic scan on samples in solution, were able to average out the large anisotropic hyperfine interactions caused by tumbling of the molecules; the resulting spectra contained many lines of 0.2 gauss line width. The splittings were interpreted as being due to isotropic Fermi contact hyperfine interactions. The magnitude of the splitting was about 6 gauss each for H(D) and H(D'); and about 3 gauss each for H(F), H(F'), H(B), and H(B'); and about 1 1/2 gauss each for H(A), H(A'), H(G), and H(G'); see Figures 12 and 13 for positional notation. The resulting spectra thus contained a triplet with approximately 6-gauss line separation, with each line split into a quintuplet with 3-gauss separation, and finally each of these smaller lines, in turn, formed a quintuplet of 1 1/2 gauss separation. Comparing these results for the anthracene ions in solution with the spectra of electron-irradiated anthracene crystals obtained in the present experiments, it is concluded that the defect center produced in this case is not that of the anthracene ions.
One is thus led to consider the possibility that the defect center is an anthracene radical, i.e., an anthracene molecule from which one (or more) hydrogen atoms have been removed. On the basis of chemical bond strengths, the most likely hydrogen atom to be removed is that at the D or D' position. Based on the work of Bolton, Carrington, and McLachlan [9], mentioned previously, it is estimated that the intramolecular isotropic hyperfine splitting which would be expected for a radical with an unpaired electron at the D position would consist roughly of a triplet with 3-gauss splitting, each line subdivided by the more distant hydrogen atoms. Anisotropic splittings would be of a similar order of magnitude [11]. Under limited resolution, the spectrum would consist of one line somewhat over 6 gauss in width. If one tentatively assumes that the defects are, in fact, largely such anthracene radicals, and that extramolecular hyperfine couplings cause the gross form of the EPR spectrum, then this intramolecular hyperfine structure, seen under limited resolution, would be of the right magnitude to explain the observed line widths. It should be noted, however, that the over-all splitting (approximately 14 gauss) of this intramolecular hyperfine structure for the anthracene ion, cannot be ruled out as inconsistent with the line widths actually observed.

From the above evidence it is concluded that the gross structure of the observed spectra is almost certainly due to extramolecular hyperfine interactions. By assuming the spectra to be made up of four lines spaced at 14 gauss apart with relative intensities of 1:3:3:1, the observed spectra can be reproduced by curve fitting. The most obvious source of extramolecular hyperfine interactions (for relative intensities 1:3:3:1 in the anthracene
crystal) would be three equivalent protons: the B-hydrogen and F-hydrogen of one molecule, and the F-hydrogen on a neighboring molecule. The F-hydrogen of the neighboring molecule would be located 2.67 Å above the D-carbon atom of the first molecule on a perpendicular from the plane of the first molecule [13]. The F-hydrogen atom of the neighboring molecule could have appreciable interaction with the π-electrons (Fig. 15) containing the unpaired electron of the radical or ion produced. The distance from the carbon atom to the hydrogen atom on an adjacent carbon atom within an anthracene molecule is 2.67 Å also (Fig. 13). Under these conditions the 1:3:3:1 spectra could be arising from the interaction of an unpaired electron at the D-carbon atom with three equivalent protons, the H(B), and H(F) proton of one molecule, and H(F) proton of another molecule. Thus the unpaired electron in this case is being shared by two different molecules within the crystalline lattice.

It has already been noted that r.f. saturation occurred at rather low power levels, corresponding to an r.f. magnetic field of about $4 \times 10^{-3}$ gauss. Using this value for $H_1$, then $\gamma H_1$ is of the order of $7.00 \times 10^{-2}$ Mc. The value of $1/T_2$ is of the order of $1 \times 10^2$ Mc for a Gaussian curve and $1.5 \times 10^2$ Mc for a Lorentzian curve. Hence the requirements for slow passage conditions (equations 8 and 9) have been attained. If a Lorentzian line is assumed, then $T_1$, the spin lattice relaxation time, is of the order of $3 \times 10^{-2}$ sec. Therefore, the thermal relaxation time is approaching the threshold for performing the experiment at ambient temperature since saturation effects begin to occur if $T_1$ exceeds about $10^{-5}$ seconds [2].
CONCLUSIONS

1. The results of the curve fitting computer program indicates that the observed spectrum does consist of four overlapping Gaussian lines of intensities 1:3:3:1 with line-width and line splittings of 12 and 14 gauss respectively. The observed hyperfine splitting probably results from extramolecular hyperfine interactions rather than intramolecular interactions. This conclusion is in agreement with the recent work of Dr. Blum and P. L. Mattern at the Brookhaven National Laboratory (reported at the APS Meeting in Chicago in April 1967). Blum and Mattern concluded that the line shape is Gaussian with extramolecular hyperfine structure having line intensities of 1:3:3:1.

2. The requirements for slow passage were experimentally achieved.

3. The spin-lattice relaxation time $T_1$ was found to be on the order of $10^{-2}$ seconds, at ambient temperature, indicating that the sample is still saturated even at this low r.f. power level.

4. Further attempts to perform the experiment at liquid nitrogen and liquid helium temperature should be made in an effort to study the behavior of the spin-lattice relaxation time as a function of temperature.

5. This is an excellent system for ENDOR experiments, and efforts should be made to conduct the ENDOR experiments.
6. Further work on the spatial dependence of the defect center should be performed, especially angular rotation of the specimen about the c' axis with respect to the static magnetic field.

7. Efforts should be made to obtain samples of selectively deuterated anthracene for irradiation. The difference between the hyperfine splittings due to the hydrogen nuclei (spin 1/2) and that of the deuterium nuclei (spin 1) should enable a more confident identification of the atoms which are causing the predominant splitting.

8. Electron irradiation at different energies and fluxes should be performed in order to study the defect production as a function of particle energy and flux.
REFERENCES


VITA

The author was born in Toxey, Alabama on October 22, 1932. He graduated from Southern Choctaw High School, Silas, Alabama in June 1951; the Newport News Shipbuilding and Dry Dock Apprentice School, Newport News, Virginia in September 1956; and received a Bachelor of Science in Physics from the Old Dominion College, Norfolk, Virginia (formerly The College of William and Mary, Norfolk Division) in June 1961. The author entered the graduate school of The College of William and Mary in February 1963. He is presently employed by the National Aeronautics and Space Administration, Marshall Space Flight Center, Huntsville, Alabama.
FIGURE 1. SUCCESSIVE MOTION OF THE MAGNETIC MOMENT VECTOR M' IN THE ROTATING COORDINATE SYSTEM. The position of the magnetic vector M' which is precessing about $H_\circ$ in the rotating coordinate system (a) is seen to follow $H_\circ$ as $\omega$ is swept through $\gamma H_0$; if the magnetization vector $M'$ is initially along $H_\circ$, then under rapid passage conditions it can be made to follow $H_\circ$ from (b) $\omega < \gamma H_0$ to (c) $\omega = \gamma H_0$ to (d) $\omega > \gamma H_0$. 
FIGURE 2. X-BAND ABSORPTION SPECTRA WITH $H_0$ ALONG THE $a$-AXIS

FIGURE 3. X-BAND ABSORPTION SPECTRA WITH $H_0$ ALONG THE $c'$-AXIS
FIGURE 4. X-BAND ABSORPTION SPECTRA WITH $H_0$ ROTATED WITH RESPECT TO THE $a$-AXIS OF THE CRYSTAL
FIGURE 5. X-BAND ABSORPTION SPECTRA WITH $H_0$ ROTATED WITH RESPECT TO THE a-AXIS OF THE CRYSTAL.
FIGURE 6. X-BAND DISPERSION SPECTRA WITH $H_0$ ALONG THE $a$-AXIS

FIGURE 7. X-BAND DISPERSION SPECTRA WITH $H_0$ ALONG THE $c'$-AXIS
FIGURE 8. X-BAND DISPERSION SPECTRA WITH H₀ ROTATED WITH RESPECT TO THE z-AXIS OF THE CRYSTAL.
Figure 9. X-Band Dispersion Spectra with $H_0$ Rotated with Respect to the a-Axis of the Crystal
FIGURE 10. X-BAND DISPERSION SPECTRA WITH $H_0$ ROTATED WITH RESPECT TO THE $a$-AXIS OF THE CRYSTAL
FIGURE 11. SCHEMATIC DIAGRAM OF EPR SPECTROMETER
FIGURE 12. ANTHRACENE MOLECULAR ARRANGEMENT IN THE UNIT CELL

- $a = 8.561 \text{ Å}$
- $b = 6.036 \text{ Å}$
- $c = 11.163 \text{ Å}$
- $\beta = 124^\circ 41'$
FIGURE 13. STRUCTURE OF THE ANTHRACENE MOLECULE
FIGURE 14. CRYSTAL STRUCTURE OF ANTHRACENE
FIGURE 15. DISTRIBUTION OF DELOCALIZED PI ELECTRONS OF THE ANTHRACENE MOLECULE