Final Report

SPIN RESONANCE PROPERTIES OF SAPPHIRES, CERTAIN $A_{11}B_{21}$ COMPOUNDS, AND CALCITE

Chihiro Kikuchi

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ABSTRACT

This report summarizes the electron-spin resonance properties of sapphires with various iron group impurities, of certain A_{II}B_{IV} compounds, and of calcite. A block diagram of a molecular electronic material, such as pink ruby, is given, to indicate possible directions for future investigations. Extensive references are given.
INTRODUCTION

Since the spring of 1956, when the first draft of the proposal for this contract was in preparation, dramatic developments have taken place in the field of electron spin resonance. At that time, this technique was considered to be merely a refined tool for basic research; accordingly, the essence of the proposed technical program was to use the electron as a microscopic and electric probe to ferret out microscopic details of solids that cannot be obtained by other methods. However, by the end of the same year, Bloembergen's suggestion of the solid-state maser became widely known, and its feasibility was demonstrated shortly afterwards by Scovil, Feher, and Seidel. By this time maser research and development programs were in progress in several physical laboratories; at the Lincoln Laboratory, McWhorter and Meyer discovered maser action in chrome cyanide about the middle of 1957, and this was followed by the demonstration of maser action in ruby on December 20, 1957, by the workers at The University of Michigan Willow Run Laboratories.

It is significant that the very class of materials proposed for basic studies under the present contract was found to have, and is being investigated for, technological applications. Before 1956, much of the efforts in electron spin resonance was concerned with the study of paramagnetic salts. About this time, a few investigators began the study of metal oxides and sulfides and other compounds. Of particular inspiration to the writer have been the papers by Hershberger and Leifer, by Van Wieringen, and by Hurd, Sachs, and Hershberger. These papers led to the study of Mn++ in zinc blende by Matarrese and Kikuchi; about the same time, the work on MgO was being carried out independently by Low and Wertz.

Consequently, when the problem arose of selecting an appropriate material for maser action, materials such as those mentioned above were considered. It was reasoned that a good maser material should have a large zero-field splitting, low nuclear magnetic moment density, high chemical stability, and a small number of nonequivalent sites. In the meantime, the measurements on ruby by Geusic came to the author's attention. A brief examination indicated that ruby has a number of desirable characteristics, and subsequently a program directed towards the determination of maser action in ruby was started early in 1957.

The chronological developments mentioned above serve to illustrate how basic research opens up new avenues of thinking and at the same time develops technical capabilities at an advanced level. For example, the paper by the workers at the Bell Telephone Laboratories, known for its tradition of research, was received in the Physical Review office on December 3, 1956, a little over a month after the publication of the paper by Bloembergen. At the Willow Run Laboratories, a few days after maser action in ruby had been
established, the writer prepared and submitted a proposal to Project MICHIGAN for the construction of a ruby maser for The University of Michigan 85-foot radiotelescope which had then not yet been completed. The above examples show that today the time scale from the conception of an idea to the demonstration of feasibility to the development of a device is very short, so that it is almost impossible, if not undesirable, to separate basic from applied research.

A list of publications resulting from this contract is given in Appendix A. A few general comments will be made about the results of our investigations and will be related to those reported from other physical laboratories.
I. RUBY (Al$_2$O$_3$:Cr$^{3+}$, $S = 3/2$)

At the time maser action in ruby was demonstrated by Makov, Kikuchi, Lambe, and Terhune, and confirmed three months later by the Russian workers, Zerev, Kornienko, Manenkov, and Prokhorov, ruby as a material had been studied to a very limited extent. The paramagnetism was apparently first noted by Rao and Liela from static susceptibility measurements. The electron spin resonance studies were made by Manenkov and Prokhorov, by Zaripov and Shamonin, and Geusic.

This paucity of information on ruby prior to 1957 is in sharp contrast to the wealth of information now available as the result of intensive investigations carried out in different physical laboratories. A partial list of references to ruby and other sapphires is given in Appendixes B and C.

The electron spin resonance (ESR) measurements of ruby show that the spin Hamiltonian of Cr$^{3+}$ in corundum ($\alpha$ - Al$_2$O$_3$) is given by

$$
\hat{H} = g_\parallel S_z B_z + g_\perp (H_x S_x + H_y S_y) - D(S_z^2 - 5/4)
$$

in which the axis of quantization $z$ is taken along the crystal $c$-axis. Because the spin is $3/2$, all Cr$^{3+}$ ions occupying the Al$^{3+}$ substitutional sites are magnetically equivalent and the crystalline electric field has axial (or strictly speaking, trigonal) symmetry. Schulz-DuBois indicates that the best values for the parameters in the Spin Hamiltonian at room temperature are

$$
2D = -0.3831 \pm 0.0002 \text{ cm}^{-1} = -11.493 \pm 0.006 \text{ kMc/sec}
$$

$$
g_\parallel = 1.9840 \pm 0.0006
$$

$$
g_\perp = 1.9867 \pm 0.0006
$$

The negative sign for $D$ was deduced first by Geusic from the relation

$$
2D = \lambda (g_\parallel - g_\perp)
$$

and from $g_\parallel < g_\perp$ and $\lambda > 0$ for Cr$^{3+}$, in which the d-shell is less than half full. The sign and magnitude of $D$ are in agreement with the low-temperature static susceptibility measurements by Daunt and Brugger. In addition, the sign of $D$ has been confirmed by Schulz-DuBois by making relative intensity measurements of the two fine structure satellites at 77$^\circ$K and 4.2$^\circ$K.
The zero-field splitting quoted above is in very good agreement with the measurements by Cross and Terhune\textsuperscript{17} made at zero magnetic field. The following values have been reported:

<table>
<thead>
<tr>
<th>Temp. (°K)</th>
<th>2D (kMc/sec)</th>
</tr>
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<tbody>
<tr>
<td>4</td>
<td>11.447</td>
</tr>
<tr>
<td>77</td>
<td>11.460</td>
</tr>
<tr>
<td>300</td>
<td>11.495</td>
</tr>
</tbody>
</table>

The indicated error is ±0.005 kMc/sec.

It is interesting to note that the nuclear quadrupole resonance splitting also decreases with decreasing temperature. According to Spence,\textsuperscript{18} the splittings are 180.1 and 178.5 kc/sec at room and liquid helium temperatures, in the ratio of 1.009. The corresponding ratio of the zero-field splittings is 1.004.

Spin-lattice relaxation times have been reported sporadically by a number of investigators such as Pashinin and Prokhorov,\textsuperscript{19} Kikuchi et al.,\textsuperscript{20} and others. The most notable, however, are the series of systematic measurements being made by Pace, Sampson, and Thorp.\textsuperscript{20} For example, the following values are reported for the 3/2 $\leftrightarrow$ 1/2 transition in pink ruby at 90° for 34.6 kMc/sec.

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>$T_1$(milliseconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>59</td>
</tr>
<tr>
<td>4.2</td>
<td>22.5</td>
</tr>
<tr>
<td>10.1</td>
<td>10.0</td>
</tr>
<tr>
<td>20.3</td>
<td>6.0</td>
</tr>
<tr>
<td>57</td>
<td>0.10</td>
</tr>
<tr>
<td>77</td>
<td>0.044</td>
</tr>
<tr>
<td>90</td>
<td>0.017</td>
</tr>
</tbody>
</table>

Unpublished measurements at Willow Run indicate that $T_1$ is strongly orientation dependent, being longest at 0°. Systematic measurements are needed for this angle, particularly in view of the fact that Mattuck and Strandberg\textsuperscript{21} have suggested spin phonon processes are of the quadrupole type.

Strandberg\textsuperscript{22} also points out that the line width in ruby cannot be accounted for by any simple phenomena such as the static field inhomogeneities, small changes in the orientation of the c-axis throughout the crystal, or the fluctuation in the crystalline electric field. Rather, it is suggested that the residual line width of approximately 42 Mc/sec is due to the clustering of chromium, possibly along lattice dislocations.

It should be noted that inhomogeneities arising from uneven distribution of chromium can be easily detected optically. These appear as light and dark striations spreading out in directions normal to the length of the ruby boule.
These inhomogeneities arise because the Al\textsubscript{2}O\textsubscript{3}-Cr\textsubscript{2}O\textsubscript{3} powder is tapped into the region where crystal growth is taking place. It seems that much research is needed for the development of a process to grow good single crystals of ruby and other sapphires.

The crystal structure of corundum can be visualized as rhombohedral arrangement of Al\textsubscript{2}O\textsubscript{3} molecules, each cell containing two molecules. When chromium is introduced into this lattice, it is reasonable to suppose that chromium ions occupy Al\textsuperscript{+++} lattice sites at random if the chromium concentration is sufficiently low. However, at higher concentrations pairs of chromiums can occur. The optical evidence was first pointed out by Schawlow, Wood, and Clogston,\textsuperscript{23} who suggested that the concentration-dependent lines lying on the long wavelength side of the fluorescence spectrum of ruby are due to Cr\textsuperscript{+++} pairs. The ESR evidence has been reported in a series of papers by the Raytheon workers at Waltham.\textsuperscript{24}

Recently, investigations have been carried out in different laboratories to determine the effect of the nuclear magnetic moment of Al\textsuperscript{27} upon the ESR spectrum, and the consequent effect upon maser action. The study of the effect of the saturating microwave power upon the nuclear resonance of Al\textsuperscript{27} was reported by Abraham, McCausland, and Robinson\textsuperscript{25} at Oxford, and by Cowen, Schafer, and Spence\textsuperscript{26} at Michigan State University. In the experiment of the latter group, one end of a ruby rod is thrust into a microwave cavity resonating at 9300 Mc/sec, and the other end is in the rf coil of a nuclear resonance spectrometer. With this arrangement, they examined the nuclear quadrupole resonance of Al\textsuperscript{27} as a function of microwave pumping. When the magnetic field was adjusted so that the chromium spin resonance occurred at the low field end of the magnetic field sweep, all components of the aluminum quadrupole resonance lines showed increased absorption, whereas emission resulted when adjusted to the high-field side.

The inverse of this effect, i.e., the effect of nuclear resonance transitions upon ESR has been reported by Terhune, Lambe, Makhov, and Cross.\textsuperscript{27} In this experiment, I.F. power is applied to a crystal of ruby located inside of a cavity by means of loops of wire wound around it. The wire is wound to permit frequency scanning from a few to over one hundred megacycles. A saturating microwave power is then applied to one edge of the chromium ESR line, say, -1/2 $\leftrightarrow$ 1/2, by holding the magnetic field and microwave frequency constant, and then the I.F. is varied. At the nuclear quadrupole resonance frequencies, sharp changes in the resonance at microwave frequency takes place.

The effect of this I.F. upon maser action has been reported by Makhov, Cross, Terhune, and Lambe.\textsuperscript{28} In one instance, the maser gain increased from 15 db to 35 db by merely turning on the I.F.

Natural chromium consists predominantly of even-even isotopes, but about 1.5\% of the odd neutron isotope Cr\textsuperscript{53} is present. This nuclide has spin I = 3/2, and so that hyperfine resonance is anticipated. The effect was first re-
ported by Terhune, Lambe, Makhov, and Cross. Later in a paper by Terhune, Kikuchi, Lambe, and Baker, it was indicated that the double resonance technique may be useful for the measurement of nuclear quadrupole moments. The hyperfine resonance of the group of states for \( S = 1/2 \) and \( 3/2 \) occur near 25 and 75 Mc/sec, respectively. An analysis of the spectrum gives \( A = 48.5 \) Mc/sec, in good agreement with Manenkov and Prokhorov's value 51 Mc/sec estimated from the hyperfine structure of ruby enriched with Cr\(^{53}\). Further study showed that the nuclear spin triplets associated with the different electron spin states cannot be accounted for completely by the proximity of the states \( M = 1/2 \) and \( 3/2 \). The inclusion of the nuclear quadrupole interaction leads to an estimate of \( 0.05 \times 10^{-24} \) cm\(^2\) for the quadrupole moment of Cr\(^{53}\).

The work on ruby has stimulated the study of a number of maser action schemes that can perhaps best be called four-level masers. The first was the push-pull scheme (see, for example, Kikuchi, Makhov, Lambe and Terhune) which makes use of the fact that the energy levels are symmetric at \( 54^\circ 44' \). Later this scheme was used by Ditchfield and Forrester and by Maiman to obtain maser action in ruby near liquid nitrogen temperatures. Furthermore, Minkovski has applied this scheme to chrome cyanide to obtain microwave emission at frequencies higher than the pump frequency. Other pumping schemes such as push-push, parallel pumping, harmonic pumping have been studied. For details the reader is referred to the unpublished notes by Makhov.

To date much of the maser research and development efforts have been made for angles such as \( 54^\circ 44' \), \( 90^\circ \) and others to meet the technical requirements of pump and signal frequencies. However, very little attention, if any, has been directed to the study of maser modes at \( 0^\circ \). For this reason a few comments will be made to point out some of the possibilities and also to point out how the \( 0^\circ \) maser can be used for polarization studies.

Let us examine the precession of a classical spinning magnetic top, to see how the effects of polarization come about.

In Figure 1, let the angular momentum \( \mathbf{\hat{A}} \) of the magnetic top be represented by the vector \( \mathbf{OP} \), and let the magnetic field \( \mathbf{H} \) be along the positive \( z \)-axis. Furthermore, assume that the magnetic moment \( \mathbf{M} \) is along \( Z \). We can then write

\[
\mathbf{\hat{M}} = \gamma \mathbf{\hat{A}} \tag{1}
\]

If \( \gamma \) is positive, \( \mathbf{\hat{M}} \) is parallel to \( \mathbf{\hat{A}} \), but if \( \gamma \) is negative, \( \mathbf{\hat{M}} \) is antiparallel to \( \mathbf{\hat{A}} \). The motion of the point \( P \) is given by

\[
\frac{d}{dt} \mathbf{\hat{A}} = \mathbf{\hat{T}} = \mathbf{\hat{M}} \times \mathbf{\hat{H}} = \gamma \mathbf{\hat{A}} \times \mathbf{\hat{H}}
\]
Consequently, for example, at the instant \( \dot{\mathbf{A}} \) as in the plane of the paper, \( d \mathbf{A} \) will be out from or into the plane of the paper, depending upon the sign of \( \gamma \). By tracing out the vector \( d \mathbf{A} \), it is easy to see that the Larmor precession.
will be either anti-clockwise or clockwise (when viewed from below the \( x \) \( y \) -plane),
for positive or negative magnetic moments, respectively. Therefore an anti-
clockwise rotating magnetic field will cause the flipping of bar magnet with
positive magnetic moment, and a clockwise rotating magnetic field will bring
about the same effect for a bar magnet with negative magnetic moment.

In quantum mechanics, the polarization relations can be derived from the
fundamental equation

\[
\text{in } \frac{\partial \psi}{\partial t} = H \psi = (H_0 + H') \psi \tag{3}
\]

Here we have separated the Hamiltonian \( H \) into the static part \( H_0 \) and the time-
dependent part \( H' \). The static part is given by

\[
H_0 = - \hat{\mathbf{M}} \cdot \hat{\mathbf{H}} \tag{4}
\]

\[
= - \gamma \hat{\mathbf{A}} \cdot \hat{\mathbf{H}} = - g\beta \mathbf{S} \cdot \mathbf{H}
\]

in which

\[
\gamma = g\beta / \hbar \tag{5}
\]

The eigenvalues then are

\[
E_M = - g\beta M \mathbf{H}
\]

The ordering of the levels will depend upon the sign of \( g \). The two cases are:

\[
g > 0 \quad \quad \quad \quad g < 0
\]

\[
\begin{array}{c}
M - 1 \\
M \\
M + 1
\end{array} \quad \quad \quad \quad \quad \quad \\
\begin{array}{c}
M + 1 \\
M \\
M - 1
\end{array}
\]

i.e., for positive magnetic moment, higher-energy states have smaller angular
momentum, etc. For the electron, the magnetic moment is known to be negative,
and so most frequently, the energy level diagram is as given as in the right
column. Consequently, instead of \( (4) \) we shall write
\[ \Psi_0 = g_0 S_2 H \] (4')

by taking the sign of \( g \) into account.

The time-dependent part is similar to (4'), i.e.,

\[ \mathcal{H}' = g_0 \vec{S} \cdot \vec{H}'(t) \]

It will be our purpose to show how the two counter-rotating fields will affect the transitions among the electron levels.

Consider first the case of anti-clockwise rotation. Such a field can be represented by

\[ H'_{ax}(t) = H'_a \cos \omega t \] (6)
\[ H'_{ay}(t) = -H'_a \sin \omega t \]

in which \( H'_a \) is the amplitude of the anti-clockwise magnetic field lying in the \( xy \) plane. Equation (6) then becomes

\[ \mathcal{H}'(t) = g_0 H'_a(S_x \cos \omega t - S_y \sin \omega t) \]
\[ = \frac{g_0 H'_a}{2}(S_+ e^{i\omega t} + S_- e^{-i\omega t}) \] (7)

Here

\[ S_\pm = S_x \pm i S_y \]

and are the well-known spin operators that increase or decrease the angular momentum by unity. Further, let \( \psi_M \) be the spin functions that satisfy

\[ \mathcal{H}_0 \psi_M = E_M \psi_M \] (8)
To find the solution of (3) we shall put

\[ \psi = \sum a_M(t) \psi_M e^{-iE_M t/\hbar} \]  \hspace{1cm} (9)

in which \( a_M(t) \) is the probability amplitude that the electron is in state \( M \) at time \( t \). The substitution of (9) into (3) gives

\[ a_M(t) = \frac{gM^4}{2\hbar} \sum_{M'} <M|S_+|M'> a_{M'}(t) \exp \left[ i(E_M - E_{M'}) + \omega_0 t/\hbar \right] \hspace{1cm} (10) \]

\[ + \frac{gM^4}{2\hbar} \sum_{M'} <M|S_-|M'> a_{M'}(t) \exp \left[ i(E_M - E_{M'}) - \omega_0 t/\hbar \right] \]

If at \( t = 0 \) the spin is in state \( M_0 \), then

\[ a_{M_0}(0) = 1 \hspace{1cm} (11) \]

with all other \( a \)'s equal to zero. Then the probability amplitudes will increase initially as

\[ a_M(t) = -\frac{gM^4}{2} <M|S_+|M_0> \exp \left[ i(E_M - E_{M_0}) + \omega_0 t/\hbar \right] \frac{1}{E_M - E_{M_0} + \omega_0} - \frac{1}{E_M - E_{M_0} - \omega_0} \hspace{1cm} (12) \]

Inspection of the above equation shows that the first part on the right-hand side will give rise to an increase in angular momentum upon emission of radiation, and the second part to absorption accompanied by decrease in angular momentum, i.e.,

\[ M_0 + M = M_0 + 1 \hspace{1cm} E_M = E_{M_0} - \omega_0 \hspace{1cm} (13) \]

\[ M_0 + M = M_0 - 1 \hspace{1cm} E_M = E_{M_0} + \omega_0 \]

On the other hand, for a clockwise rotating field

\[ H_{cx}'(t) = H' \cos \omega t \hspace{1cm} (14) \]

\[ H_{cy}'(t) = H' \sin \omega t \]
so that

\[ \hat{N}'(t) = \frac{g \beta H'}{2} \left[ S_{-} e^{i \omega t} + S_{+} e^{-i \omega t} \right] \]  

(15)

Note that the sign of the exponent for the above expression is the reverse of that of (7). The result corresponding to (12) is

\[ a_{M}(t) = -\frac{g \beta H'}{2} < M | S_{+} | M_{0} > \frac{\exp \left[ i \left( E_{M} - E_{M_{0}} \right) t/\hbar \right] - 1}{E_{M} - E_{M_{0}} - i \delta} \]

\[ -\frac{g \beta H'}{2} < M | S_{-} | M_{0} > \frac{\exp \left[ i \left( E_{M} - E_{M_{0}} + i \omega \right) t/\hbar \right] - 1}{E_{M} - E_{M_{0}} + i \omega} \]  

(16)

This result shows that the angular momentum and energy will increase or decrease together, i.e.,

\[ M_{0} \rightarrow M = M_{0} + 1 \quad E_{M} = E_{M_{0}} + \frac{\hbar \omega}{2} \]

\[ M_{0} \rightarrow M = M_{0} - 1 \quad E_{M} = E_{M_{0}} - \frac{\hbar \omega}{2} \]  

(17)

Let us now apply these results to ruby. At 0°, i.e., when the magnetic field is along the c-axis

\[ E_{\pm \frac{3}{2}} = \pm \frac{3}{2} g \beta H - D \]

\[ E_{\pm \frac{1}{2}} = \pm \frac{1}{2} g \beta H + D \]

The plot of these levels gives Fig. 2.

Inspection shows that the diagram can be divided into three regions with the ordering of energy levels as follows:

<table>
<thead>
<tr>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2</td>
<td>1/2</td>
<td>3/2</td>
</tr>
<tr>
<td>-1/2</td>
<td>3/2</td>
<td>1/2</td>
</tr>
<tr>
<td>3/2</td>
<td>-1/2</td>
<td>-1/2</td>
</tr>
<tr>
<td>-3/2</td>
<td>-3/2</td>
<td>-3/2</td>
</tr>
</tbody>
</table>

11
In region III, M increases with increasing energy, so that a clockwise field will induce an upward or downward transition between two adjacent levels. Consider next the top three levels in region II.

\[
\begin{align*}
3 & \quad \text{_________} \quad 1/2 \\
2 & \quad \text{_________} \quad 3/2 \\
1 & \quad \text{_________} \quad -1/2
\end{align*}
\]

These have been labeled 1, 2, and 3 in accordance with the usual maser notation. We note, however, that M increases by 1 in going from level 1 to 3, and decreases by 1 in going from 2 to 3. Therefore, from the conclusions reached above, \( H'_c \) will induce the 1-3 transition, and \( H'_a \) the 2-3 transition. These transitions can be used for the pump and signal of a 0° maser, provided thermal relaxation takes place between levels 1 and 2. Since Mattuck and Strandberg indicate that for \( S > 1/2 \), spin-phonon processes obey the quadrupole selection rule, a scheme such as suggested here should be studied for maser action.

Finally, the study of the interaction of electromagnetic radiation at microwave frequencies with those at optical frequencies being carried out by Wieder,\textsuperscript{34} by Geschwind, Collins, and Schawlow,\textsuperscript{35} and by Maiman\textsuperscript{36} should be mentioned. Much of these investigations were inspired by the thorough theoretical and experimental studies of the optical spectrum of ruby by Sugano\textsuperscript{37} and his associates.

It appears that the story of molecular electronic properties of ruby is just beginning to unfold.
II. VANADIUM SAPPHIRE \( (S = 1/2, 1, 3/2) \)

The study of this material was prompted by the need to have additional information about chromium in sapphire. The result has been the publication by Lambe and Kikuchi\(^{36}\) on the different oxidation states of vanadium in sapphire, and furthermore, ideas such as the use of the ESR technique in radiation solid-state chemistry and the application of high-energy radiation for the production of new solid-state electronic materials are being developed.

The theory of maser action in ruby is based on the assumption that chromium ions in sapphire are all isolated and are trivalent. However, at the time our investigations on vanadium sapphire were started, very little definitive information on the chemical condition of chromium was available. The effects of X-rays on ruby had been studied by Mathews and Lambe,\(^{39}\) but attempts to correlate these measurements with ESR were rather disappointing. A quick survey seemed to show that the presence of certain paramagnetic impurities reduces the intensity of the chromium lines in sapphire, but it did not seem possible to probe further.

The basic difficulty is that chromium does not have a well-recognizable signature. Natural chromium consists of over 90\% of the even-even isotopes Cr\(^{50}\), Cr\(^{52}\), and Cr\(^{54}\), but only 9.5\% of the odd-neutron isotope Cr\(^{53}\). The nuclear spin of the last nuclide is 3/2, but being an odd-neutron isotope, the h.f.s. splitting is small, so that the weak hyperfine structure components are almost obscured by the strong and relatively wide central component due to the even isotopes. It seemed then that it might be better to bracket the properties of chromium by first examining the ESR properties of other paramagnetic ions with readily recognizable signature. The obvious ones are vanadium \( (V - 51, I = 7/2, 99.75\%) \) and manganese \( (Mn - 55, I = 5/2, 100\%) \) flanking chromium to the left and right in the periodic table. Molybdenum, consisting of Mo-95 \( (I = 5/2, 15.7\%) \) and Mo-97\(^\d\) \( (I = 5/2, 9.5\%) \) offers another possibility; this element occurs directly beneath chromium in the periodic table and ESR studies in paramagnetic salts have shown that molybdenum behaves very much like chromium. However, our attempts to observe its resonance absorption spectrum have been so far unsuccessful.

The optical spectrum of vanadium spectrum appears to have been first investigated by Lov,\(^{40}\) and later in great detail by Pryce and Runciman,\(^{41}\) who have indicated 8 cm\(^{-1}\) as the value for the ground state splitting \( V^{+++} \). The ESR examination of this valence state of vanadium was observed first by Zverev and Prokhorov.\(^{42}\)

In addition, Kikuchi and Lambe have shown that the "raw" vanadium sapphire yields an ESR spectrum that can be ascribed to \( V^{4+} \). The spectrum can be seen only under very high gain, is isotropic, and consists of 8 components with
separation 140 gauss in contrast to the value of 110 gauss for $V^{3+}$. Moreover, the spectrum for $V^{4+}$ can be seen at room temperature, whereas the $V^{3+}$ can be observed only near 4.2°K. As indicated already, the spectrum due to $V^{4+}$ is very weak, and attempts to increase its intensity have been so far unsuccessful.

If the sample is subjected to ionizing radiation such as gamma or X-rays, a fraction of the $V^{3+}$ ions is converted to $V^{4+}$ ions, as evidenced by the room temperature ESR spectrum. The most readily interpretable results can be obtained with the K-band ESR spectrometer. At this frequency, $hv > 2D$, so the complications arising from cross-overs do not occur. At K-band frequency, the chromium lines, which occur as an impurity in the vanadium sapphire, moves along the group of 8 lines of vanadium. This fact shows that the spin of vanadium is $3/2$ and that the zero field splitting is comparable to that of $Cr^{3+}$. For $V^{4+}$, $D = 0.165 \ \text{cm}^{-1}$, in comparison to $D = 0.1917 \ \text{cm}^{-1}$ for $Cr^{3+}$. Furthermore, the h.f.s. coupling constant is isotropic with $A(V^{4+}) = 0.0085 \ \text{cm}^{-1}$. These values for $V^{4+}$ in sapphire are very close to the values of this ion in the Tutton salt. For the latter material, Baleezy, Ingram, and Scovil reported the values $A = B = 0.0088 \ \text{cm}^{-1}$ and $D = 0.158 \ \text{cm}^{-1}$.

The source of the electron for the process

$$V^{3+} + e \rightarrow V^{4+}$$

is not yet known. The process

$$2V^{3+} \rightarrow V^{4+} + V^{4+}$$

was considered, but no evidence for the increase of $V^{4+}$ spectrum with irradiation was found. Furthermore, the spectrum for $V^{4+}$ has been reported only for $0^\circ$. At other angles, for the samples investigated, the spectrum at K-band frequency was very complicated. It is possible that the axial symmetry of the crystalline electric is destroyed by the presence of the compensating electric charge in the vicinity of the $V^{4+}$ ion.

The investigation of these points will be resumed in the near future.

Although the comments in this section have been confined to the study of the oxidation states of vanadium in sapphire, it is clear that the techniques of ESR can be used to study changes in the oxidation states brought about radiations. These other aspects of radiation solid-state chemistry will be commented upon later in this report.
III. IRON AND MANGANESE SAPPHIRE \((S = 5/2)\)

The ESR properties of iron sapphire were first reported by Kornienko and Prokhorov,\(^4\)\(^+\) and later in greater detail by Bogle and Symmons.\(^4\)\(^5\) The latter investigators reported

\[
\begin{array}{cccc}
T(\degree K) & 4.2 & 77 & 299 \\
g & 2.003 \pm 0.001 & 2.003 \pm 0.001 & 2.003 \pm 0.001 \\
D & 1719 \pm 1 & 1716 \pm 1 & 1679 \pm 1 \\
|a| & 224 \pm 4 & 236 \pm 4 & 241 \pm 4 \\
a-F & +339 \pm 2 & +337 \pm 2 & +329 \pm 2 \\
\end{array}
\]

The values of \(D\), \(a\), and \(a-F\) are in units of \(10^{-4} \text{ cm}^{-1}\). These are to be compared with \(g = 2.003 \pm 0.001\), \(D = 1684 \pm 3\), \(|a| = 262 \pm 20\), \(a-F = 334 \pm 2\) reported by Kornienko and Prokhorov. The corresponding parameters for Mn\(^{++}\) in \(\alpha-\text{Al}_2\text{O}_3\) reported recently by Low and Suss\(^{46}\) are

\[
\begin{align*}
\varepsilon_{\parallel} & = 2.0017 \pm 0.001 \\
\varepsilon_{\perp} & = 2.0000 \pm 0.002 \\
D & = +208.3 \pm 1 \text{ gauss} \\
a-F & = 23.4 \pm 0.6 \text{ gauss} \\
A & = -85.0 \pm 0.5 \text{ gauss} \\
B & = -84.3 \pm 0.8 \text{ gauss} \\
\end{align*}
\]

It appears that the use of iron sapphire for zero-field maser occurred independently to three groups about the same time. Bogle and Symmons\(^4\)\(^7\) suggested the idea in their paper on iron sapphire. The experimental work was reported almost simultaneously by Kornienko and Prokhorov\(^4\)\(^9\) and by King and Terhune.\(^5\)\(^0\) The latter authors carried out the work upon the suggestion of the author, who had been considering the possibility of a zero-field maser since the fall of 1958. More extensive analysis of iron sapphire as a maser material and the measurements of the spin-lattice relaxation times have been given in a series of reports by the workers at the Royal Radar Establishment.

Significant result in the spectrum of Fe\(^{+++}\) and Mn\(^{++}\) spectra in sapphire is the splitting of the lines due to the paramagnetic ions occupying Al\(^{+++}\) sites in the two inequivalent Al\(_2\text{O}_3\) molecules in sapphire. This splitting comes about because \(S = 5/2\). In 1954, Hurd, Sachs, and Hershberger\(^7\) noted that the Mn\(^{++}\) lines in calcite are split into doublet and the correct explanation for the structure was provided independently by Kikuchi\(^5\)\(^1\) and McConnell.\(^5\)\(^2\) The details have been published by Kikuchi and Matarrese.\(^5\)\(^3\)
IV. OTHER SAPPHIRES

Limited studies have been made of sapphires containing other paramagnetic impurities. The ones that have come to the author's attention are:

1. Co^{++} (Ref. 54).

This spectrum was observed in the commercially available green sapphire at 1.6°K. The spin Hamiltonian parameters are:

\[ S' = \frac{1}{2} \]
\[ g_{\|}' = 2.316 \pm .005, \quad g_{\perp}' = 4.98 \pm .01 \]
\[ A/g_{\|}'B = 31.0 \pm 0.5 \text{ gauss}, \quad B/g_{\perp}'B = 42.0 \pm 0.5 \text{ gauss}. \]

2. Ni^{++} (Ref. 55).

The spin of Ni^{++} is 1, and Marshall reports the following values for the parameters:

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>300</th>
<th>77</th>
</tr>
</thead>
<tbody>
<tr>
<td>( g_{|} )</td>
<td>2.196</td>
<td>2.156</td>
</tr>
<tr>
<td>( g_{\perp} )</td>
<td>2.187</td>
<td>\n</td>
</tr>
</tbody>
</table>
V. AlPVI COMPOUNDS

As mentioned already, one source of inspiration to the author is the work by Van Wieringen on Mn$^{++}$ in ZnS, which is one of the AlPVI compounds. Subsequently, this material was studied in detail by Matarrese and Kikuchi, and the properties of Mn$^{++}$ ion in other cubic crystals have been reported by many investigators of which the most recent is the study of CdTe:Mn, by Lambe and Kikuchi. It should be noted that much of the theoretical interest in these materials was stimulated by Watanabe.56

From the standpoint of molecular electronics is the effect of optical radiation on the ESR spectrum of CdS, reported by Lambe, Baker, and Kikuchi.57

One of the surprising results58 in CdTe:Mn is the unexpectedly large value of the cubic field splitting $3a$. The following table gives a summary of the properties of Mn in CaF$_2$, MgO, ZnS, and CdTe, all of which are cubic.

<table>
<thead>
<tr>
<th>Material</th>
<th>g</th>
<th>$3a$ (cm$^{-1}$)</th>
<th>Coordination</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaF$_2$</td>
<td>1.998</td>
<td>.00019</td>
<td>8</td>
<td>Baker, Bleaney, and Hayes59</td>
</tr>
<tr>
<td>MgO</td>
<td>2.0014</td>
<td>.00558</td>
<td>6</td>
<td>Low60</td>
</tr>
<tr>
<td>ZnS</td>
<td>2.0025</td>
<td>.00233</td>
<td>4</td>
<td>Matarrese and Kikuchi61</td>
</tr>
<tr>
<td>CdTe</td>
<td>2.010</td>
<td>.0084</td>
<td>4</td>
<td>Lambe and Kikuchi</td>
</tr>
</tbody>
</table>

Baker, Bleaney, and Hayes have pointed out that the ionic assumption and the known anion-cation distances in CaF$_2$ and MgO lead to a ratio of cubic field splittings in reasonable agreement with the experimental values. However, they noted that there is a sharp disagreement between the calculated and the experimental values for CaF$_2$ and ZnS. The results by Lambe and Kikuchi on CdTe show that the discrepancy is even more pronounced. The calculated ratio of $a$(ZnS): $a$(CdTe) is 2.3; the measured ratio is 0.28. A systematic study of materials such as ZnTe is needed.

The study of ESR properties of paramagnetic ions in cubic crystals, combined with investigation of effects produced by ionizing radiation, has led to the idea of using polycrystalline cubic materials for the measurement of nuclear spins. That ESR technique is useful for nuclear spin measurements has been shown abundantly, particularly when appreciable quantities of the nuclear specie is available. For example, in the nuclear spin measurement of V-50 by Kikuchi, Sirvetz, and Cohen,62 samples enriched in V-50 were available in amounts sufficient to grow single crystals of the vanadium Tutton salt.
The situation is otherwise with radioactive isotopes such as V-49. To avoid the problem of growing single crystals, Weiss, Walter, and Gillian, and Cohen\textsuperscript{65} resorted to the study of a xylene solution of vanadium (IV) - cupferron chelate. The criticism of this procedure is that, besides taxing one's ability in organic chemistry, the ESR lines are in general quite broad and so the desired structure can be obscured by the presence of other impurities. In the case of the work just quoted, V-49 was prepared from a sheet of titanium metal by bombardment, but the small concentration of V-51 impurity present in the titanium metal was as much as 200 times that of V-49 after titanium had been removed.

To avoid some of the chemical procedures and also to reduce the line width, the author, in the summer of 1959 as a guest at the Brookhaven National Laboratory, undertook a search for a suitable solid diluent which would not require the growth of a single crystal. A little reflection showed that polycrystalline MgO, and CaO, and other cubic materials might be useful. Preliminary study indicates that the characteristics of vanadium in CaO are similar to those in MgO. In this report, comments will be confined to vanadium MgO. As is well known, V\textsuperscript{4+} in single crystals of MgO has been studied by Low and Wertz.

The following recipe was used to diffuse vanadium into MgO powder. Baker reagent grade MgO weighing about 4 grams was moistened with 2 cc of 0.02 molar solution of vanadyl chloride in HCl. Additional water was supplied to insure uniform wetting. The sample was then dried over a hot plate, and later fired in a muffle oven at 700°C for about 8 hours.

When the dried sample was studied, it exhibited a rather complex ESR spectrum which perhaps can be ascribed to the vanadyl ion V0\textsuperscript{4+}. The fired sample showed no paramagnetic resonance other than a weak but sharp line near g = 2, due possibly to chromium or iron impurities. However, after irradiation by X- or gamma rays, a spectrum characteristic of V-51 was produced. Measurements indicated that the component separations are identical to those of V\textsuperscript{4+} in a single crystal of MgO. Furthermore, the line is very narrow, about 2 gauss, and calculations indicate that quantities of V-49 of the order of a few micrograms give excellent signals. Also, because the spectrum is "clean" and the lines narrow, the lines of V-49 can be resolved from those of V-51 for a range of a magnetic moment ratio from 1.2 to 0.8. Work on certain chemical aspects of this problem is in progress, and the work will be reported in collaboration with Dr. Cohen of the Brookhaven National Laboratory.

An optical-microwave effect discovered by Lambe, Baker, and Kikuch\textsuperscript{57} in CdS, another AT\textsubscript{4}BV\textsubscript{4} compound, may ultimately become of considerable technological importance. The effect briefly is the appearance of ESR absorption of CdS at 4.2°K under irradiation of green light and its disappearance under infrared irradiation.

The structure and the angular dependence of the observed ESR signal indicate that the spin of the photosensitive center is 5/2. When the c-axis is
parallel to the magnetic field, a simple 5-line spectrum with the weak satel-
lites outside the strong ones is obtained. At 90°, the weak satellites lie
inside of the strong ones. The analysis of the spectra for these angles show
that $D/a_0 = -0.5$ with $|D| = 30 \times 10^{-4}$ cm$^{-1}$. For intermediate angles, the sat-
ellites split into doublets, as to be expected for paramagnetic ions of spin
$S = 5/2$ occupying inequivalent sites. In addition, the central component
$-1/2 \leftrightarrow 1/2$ line also shows angle-dependent splitting, due to second-order ef-
facts. Since spectroscopic analysis indicated the presence of iron, the photo-
sensitive center is assigned tentatively to Fe$^{+++}$.

The following tentative explanation of the effect has been given. When
free electrons and holes are produced by irradiation, Fe$^{++}$ traps a hole, there-
by becoming Fe$^{+++}$. The action of the 2-micron infrared radiation is to restore
the electron to the iron center, making it Fe$^{++}$.

Similar effects in SrS:Eu, Sm and ZnS:Gd have been reported by Title. In
the second materials the gadolinium resonance signal is observed to increase
under irradiation of 3850Å light. Title showed that this resonance is cor-
related with the onset of photo conductivity. The effect is observed at room
temperature.

These investigations and others on ruby indicate that an extensive program
on the study of the interaction of optical and microwave radiations will no
doubt be started in a number of physical laboratories.
VI. CALCITE (CaCO$_3$:Mn)

The potentialities of calcite as a maser material have been studied by Burkhardt.\textsuperscript{65} However, here we shall be concerned primarily with ESR properties of Mn$^{++}$ that have led to the clarification of the effects of the crystalline electric field upon paramagnetic ions.

As mentioned earlier, the first study of Mn$^{++}$ in CaCO$_3$ was carried out by Hurd, Sachs, and Hershberger. In particular, they noted that, for angles other than 0° and 90°, the fine structure satellites are split into doublets. Explanation of the experimental results were given independently by Kikuchi\textsuperscript{51} and McConnell.\textsuperscript{52} Additional results were presented by Kikuchi, Ager, and Matarrese\textsuperscript{66} and the details have been presented in a recent paper by Kikuchi and Matarrese.\textsuperscript{53}

For a crystal having an axis or 3-fold symmetry, the crystalline electric field effective for an iron-group ion is given by

\[
V_{\text{cryst}} = a_{20}Y_{20} + a_{40}Y_{40} + a_{43}Y_{43} + a_{4-3}Y_{4-3}
\]

By general arguments, it can be shown that if $S$ is less or equal to 3/2, only the term in the first line need be taken into account. However, for $S$ greater than 2, such as Mn$^{++}$ for which $S = 5/2$, the terms in the second line also have to be considered. An important point to note is that the nonaxial harmonics $Y_{4\pm3}$ must be included in additions to the axial harmonic $Y_{40}$. Furthermore, since the potential function must be real, it follows that

\[
a_{4-3} = -a_{43}^*
\]

Thus, the most general form for the crystalline field of 3-fold symmetry is given by

\[
V_{\text{cryst}} = a_{20}Y_{20} + a_{40} \left[ Y_{40} + b_3Y_{43} - b_3^*Y_{4-3} \right]
\]
Now, the crystalline electric field at the crystallographically nonequiva-
lent sites can be different. For example, in the case of CaCO₃ there are two
Ca⁺⁺ crystallographic sites, and an analysis of the crystalline electric field
shows that the two crystalline fields are related to each other by a reflection
in a plane containing the c-axis. If the two sites are represented by P and Q,
the electric field at the two sites are given by

$$V_{\text{cryst}}^{(P)} = a_{20}X_{20} + a_{40} \left[ Y_{40} + b_{3}^{(P)} Y_{43} - b_{3}^{(P)*} Y_{4-3} \right]$$

and

$$V_{\text{cryst}}^{(Q)} = a_{20}X_{20} + a_{40} \left[ Y_{40} + b_{3}^{(Q)} Y_{43} - b_{3}^{(Q)*} Y_{4-3} \right]$$

The two coefficients $a_{20}$ and $a_{40}$ are equal, for the two sites have a common
3-fold axis of symmetry. Because of the symmetry relation between the P and Q
site, it can be shown readily that

$$b_{3}^{(Q)} = b_{3}^{(P)*}$$

Further analysis shows that the ratio of the splittings of the strong and
weak doublets is 5:4; as observed by Hurd et al., the angular dependence of
the doublet splitting is given by

$$\sin^{3} \Theta \cos \Theta \cos 3\psi$$

and the magnitude of the maximum doublet splitting is calculated to be 24 gauss.
These points have been investigated and confirmed by Kikuchi and Matarrese.

Although the $\Theta$-dependence of the doublet splitting is valid only to the
first-order perturbation calculation the dependence on the azimuthal angle is
expected on very general symmetry arguments. This means that if the magnetic
field is varied on a cone-making angle constant $\Theta$ with the c-axis, the doublet
separation should exhibit the $\cos 3\psi$ dependence.

This point was demonstrated for both Mn⁺⁺ calcite and Fe⁺⁺⁺ in sapphire
by the following experiment. A crystal was placed in a TE₁₀₂ mode cavity in
such a way as to make the c-axis and the microwave field horizontal and par-
allel to each other. The magnet on a rotating mount was swung into an appro-
priate position, say 70°, with respect to the c-axis. The crystal itself was
attached to a graduated dial so that the azimuthal angle could be read ac-
curately. Figure 3 shows the azimuthal dependence of a doublet in iron sapphi-
re.
To the first order, the central components \(-1/2 \leftrightarrow 1/2\) do not split. However, these components can be split to the second order. For Mn\(^{++}\) in calcite, the spectrum is extremely complex due to the hyperfine structure, so that to date a structure due to the second-order splitting has not been found. However, for Fe\(^{+++}\) in CdS, the nuclear spin I is zero, the line is very narrow, so that evidence for the second-order splitting has been detected. Detailed measurements, however, have yet to be taken.
CONCLUSION

From the short survey presented above, it is clear that there are considerable gaps in our knowledge of such materials as sapphires and the \( \text{Al}_{2}\text{O}_{3} \) compounds. In particular, more information on the effect of electromagnetic radiation of one frequency upon another is very much needed.

The types of experiments discussed in this report can be summarized in Fig. 4. In the conventional ESR experiments, one is concerned with the flux of energy from the microwave pump field, to the electron-spin system, then to the lattice, and ultimately to the thermal bath. In the maser experiments, however, one is concerned with the return of energy to the electromagnetic field but at a different frequency. The experiments by the Oxford and Michigan State groups show how the microwave pump can affect the direction of flow of energy between the I.F. electromagnetic field, and the nuclear spin system. Furthermore, some of the experiments by Jacobson, Shiren, and Tucker show how microwave power flow can be gated by micro-acoustic radiation.

As indicated in the present report, very promising beginnings have been made in the study of the effects of optical radiations on the electron-spin system. It seems, however, that less attention has been paid to the lattice. By a combination of techniques, such as electron-spin resonance, Mossbauer effect, and neutron scattering, it would be possible to get a better understanding of the nature of the lattice and phonons.

Also, the above diagram is suggestive of molecular electronic systems; further basic investigations may very well lead to development which will be to the ruby maser as modern electronic systems are to the first triode by Lee deForest.
Figure 4.
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32. Minkowski, "Private Communication".

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APPENDIX A

REPORTS, PUBLICATIONS, AND PAPERS COMPLETED
UNDER CONTRACT NO. AF-47-(638)-68

TECHNICAL REPORTS


Kikuchi, C., and Sims, C., Resonance Absorption of Ruby at Low Magnetic Fields, Z-llO1, August, 1958.

PUBLICATIONS AND PAPERS


37


* This is essentially the same paper as Technical Report 2616-12-R, November, 1959.


APPENDIX B

W.R.L. MASER PUBLICATIONS AND PAPERS


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Ft. F. G. Nivril
Associate Technical Director
for Research
U. S. Naval Ordnance Lab.
White Oak, Silver Spring, Maryland
This report summarizes the electron-spin resonance properties of sapphires with various iron group impurities, of certain Al\textsubscript{2}Be\textsubscript{3} compounds, and of calcite. A block diagram of a molecular electronic material, such as pink ruby, is given, to indicate possible directions for future investigations. Extensive references are given.
The University of Michigan, The U. of Michigan Research Institute, Ann Arbor. SPIN RESONANCE PROPERTIES OF SAPPHIRES, CERTAIN \text{A}_{m}\text{B}_{n}\text{Y}_{m}\text{Z}_{n}\text{ compounds and calcite} by Chihiro Kikuchi. Final Report.
Oct. 60, 64 p. incl. illus., 67 refs.
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