

EPR SPECTROSCOPY – ANALYSIS OF 2, 2-DIPHENYL-1-PICRYLHYDRAZYL AND $MnCl_2$

Abhinav Gupta*¹

*¹Cambridge A Level Student, Kothari International School, Noida, Uttar Pradesh, India.

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ABSTRACT

Electron Paramagnetic Resonance (EPR) or Electron Spin Resonance (ESR) is a powerful tool for studying systems with unpaired electrons - paramagnetic ions. EPR is defined on the absorption of Electromagnetic Radiation, or microwave radiation. EPR of a paramagnetic sample when placed inside a magnetic field can help determine the identity, oxidation, and spin states of paramagnetic ion(s) and study the interactions of paramagnetic ion(s) with the lattice. DPPH (1,1 -diphenyl-2-picryl-hydrazyl) spectroscopy is done at room temperature, while $MnCl_2$ /Water solvent spectroscopy is done at temperatures as low as 100K. For this paper, samples were analyzed using a Varian E-3 X-Band EPR Spectrometer. The purpose of this paper is to analyze the spectra of DPPH and $MnCl_2$ samples using the following parameters: g-factor, line widths, and hyperfine constants. Post-analysis, measurements of experimental accuracy were made for each parameter, followed by the detection of random and systematic errors. Moreover, suggestions were made for improvements to the setup, and tactics to minimize errors were discussed to ensure the most accurate data.

Keywords: Spectroscopy, Electron Paramagnetic Resonance, Electron Spin Resonance, DPPH, $MnCl_2$ /Water.

I. INTRODUCTION

Electron Paramagnetic Resonance (EPR) relies on the Zeeman's effect: the interaction between magnetic field and the Spin Magnetic Moment of unpaired electrons in atoms. These substances - with at least one unpaired electron - are called paramagnetic ions. The 1,1 -diphenyl-2-picryl-hydrazyl (DPPH) sample is a widely used standard substance in quantitative EPR spectroscopy because of the high stability of its free radical, which comprises an unpaired electron and a negligible orbital magnetic moment owing to the molecule's existence in a highly delocalized orbit. Thus only the Electron Spin Magnetic Moment interacts with the microwave radiation to produce an EPR Spectra [1].

The $MnCl_2$ /Water Solvent sample, however, contains an Mn^{2+} ion with has a nuclei spin with a magnetic moment, this interacts with the magnetic moment of electrons, giving rise to hyperfine structures (discussed further in the paper). Many transition series ions, which have nuclei with spin, exhibit these hyperfine structures. [2]

The EPR Spectra will be analyzed by calculating the g-factor, a unit-less, directionless constant that can vary across species. The value for g is characteristic of both the orbital magnetic momentum and the electron spin - this is useful in analysis as it helps identify the type of sample inside the cavity. [3].

II. METHODOLOGY

Underlying Mechanism Behind EPR Spectroscopy

Electrons, an elementary particle, are characterized by a mechanical Angular Momentum known as Spin - represented by a vector \vec{S} .

Two spin orientations are possible relative to the z-axis (axis of quantization), which is created by the magnetic field, as shown in Figure 1. The figure also shows the spin angular momentum, with respect to the z-axis, the $S_z = m_s \hbar = S \cos \theta$, where m_s can be $+\frac{1}{2}$ or $-\frac{1}{2}$ and θ is the angle between the spin and the z-axis. The spin is an intrinsic property of an electron, which states that electron spin (s) = $\frac{1}{2}$. These states vary in orientation, although the magnitude of spin remains the same. [4]

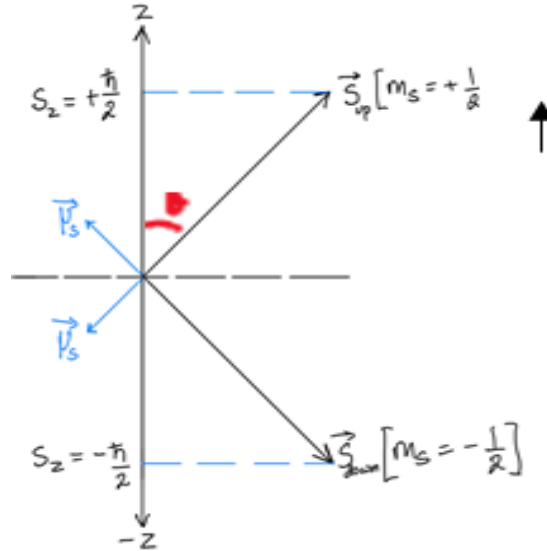


Figure 1. Representation of the Spin Angular momentum along z-axis

The magnitude of spin $|\vec{S}|$ is:

$$|\vec{S}| = \sqrt{s(s+1)}\hbar, \text{ where } s = 1/2, \hbar = \frac{h}{2\pi} \text{ and } h = \text{Planck's constant}$$

The magnitude of vector \vec{S} , for a single electron, when $s = 1/2$ is $\rightarrow |\vec{S}| = \sqrt{\frac{1}{2}(\frac{1}{2} + 1)}\hbar = \frac{\sqrt{3}}{2}\hbar$

Finally, the electron spin magnetic moment, $\vec{\mu}_s$, which is co-linear to the Spin Angular Momentum, is defined as:

$$\vec{\mu}_s = -g_e \frac{\mu_B}{\hbar} \vec{S} \text{ [}\mu_B = \text{Bohr Magnetron} = 9.27 \times 10^{-27} \text{ Am}^2 \text{] [5]}$$

EPR Spectroscopy - Theory

Electron Paramagnetic Resonance (EPR) relies on the interaction of electron spin in an external magnetic field \vec{B} - **Zeeman's Interaction** and splitting of electron spin energy in the presence of a magnetic field - **Zeeman's Effect**. Microwave radiation is used in EPR as its energy ($E = h\nu$) corresponds with a detectable splitting of electron spin states. In EPR, the source of microwave radiation is Klystron (vacuum tubes), and the frequency (ν) is kept constant due to the large bandwidth of EPR, while the magnetic field is swept from 0-1T. [2]

Energy of Interaction between $\vec{\mu}_s$ and $\vec{B} = \mathbf{E} = -\vec{\mu}_s \cdot \vec{B}$ [$\vec{\mu}_s = -g_e \frac{\mu_B}{\hbar} \vec{S}$]

$$\mathbf{E} = -g_e \frac{\mu_B}{\hbar} \vec{S} \cdot \vec{B} = m_s g_e \mu_B B$$

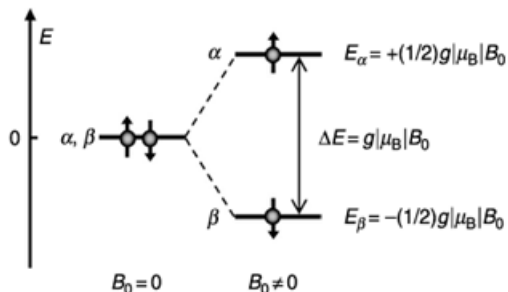


Figure 2a. The graphical representation of Zeeman's Effect [6]

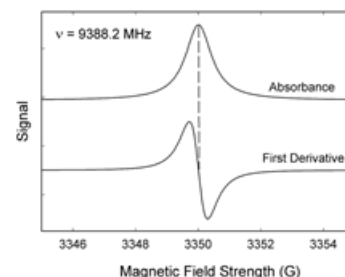


Figure 2b. EPR spectra with a single peak [7]

As shown in Figure 2a, when the magnetic field is zero, the electrons are in their degenerate states (zero energy). In the presence of a non-zero magnetic field, Zeeman splitting occurs as electrons absorb microwave radiation to jump to the excited state: the α spin state is shifted at high energy ($E_\alpha = +1/2 g_e \mu_B B$) and the β spin state at low energy ($E_\beta = -1/2 g_e \mu_B B$.) resulting in an EPR absorption line as shown in Figure 2b [6]. The transition from the degenerate state to the excited state is only possible when the energy of the photon ($h\nu$) absorbed is equal to the change in energy (ΔE):

$$\Delta E = E_{\alpha} - E_{\beta} = g_e \mu_B B = h \quad [8]$$

Rearrange the above equation to calculate the g-factor which is then further simplified by substituting the constants **h** and μ_B :

$$g_e = \frac{h\nu}{\mu_B B} \Rightarrow g_e = 0.71449 \frac{\nu(\text{GHz})}{B(\text{KG})} \quad [9]$$

Hyperfine Interaction

Hyperfine Interaction is observed when certain nuclei have a magnetic moment $\vec{\mu}_I$, which interacts with the magnetic moment of electrons to produce hyperfine splittings in the EPR spectra, this increases the number of signals (orientations) detected by the spectroscope. A paramagnetic ion has $(2I + 1)$ orientation/EPR signals, where I is the spin of the nuclei. [2]

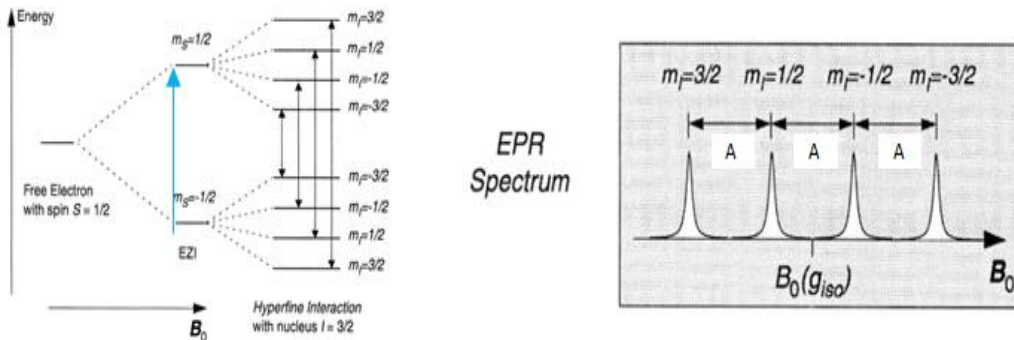


Figure 3a. Hyperfine Interaction for a spin system with an electron spin $s = \frac{1}{2}$ and nuclei spin $I =$

Figure 3b. Four equally spaced Absorption peaks with hyperfine constant (A) [10]

III. MODELING AND ANALYSIS

Experimental Design

Instrumentation: A Varian E-3 X-Band EPR Spectrometer was used to scan the EPR spectra of both samples: MnCl_2 and DPPH. DPPH spectroscopy was conducted at room temperature while MnCl_2 was done at 104K. **The following outline helps describe the process of EPR Spectroscopy referencing Figure 4:**

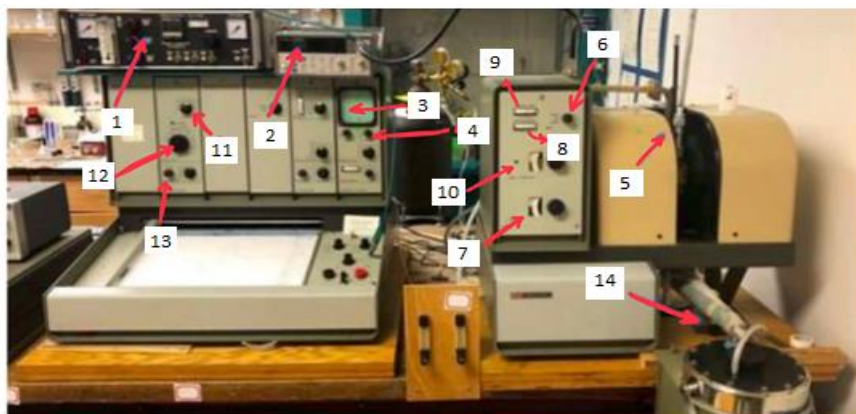


Figure 4. Varian E-3 X band EPR Spectroscopy [12]

For DPPH [12]:

1. Turn on the coolant water, located under the fume hood, to keep the electromagnet at around room temperature (298.15K). This implies the **Temperature Controller (1)** - monitors temperature and nitrogen flow - can remain off.
2. The frequency channel is set to three - this frequency is shown on the **Universal Controller (2)**, which displays frequency throughout the EPR run. Then, the intensity of the **Oscilloscope (3)** is attuned using the **Intensity Knob (4)** and set to the extreme right to start loading the EPR signal.

3. After the signal loads up, the sample is put inside the **Cavity (5)** and the **Mode knob (6)** is set to tune. A dip will be displayed on the oscilloscope. Adjust the horizontal dip, using the **Frequency Attenuator (7)** to superimpose on the black line of the oscilloscope. Furthermore, bottom the dip by turning the Teflon rod, which is situated behind the cavity.

4. After leveling out the dip, switch the mode knob to operate. Moreover, ensure proper positioning of the **Detector current (8)** and **Frequency error (9)** by adjusting Frequency and **Attenuation knobs (10)**

5. Finally, set the magnetic field mid-range, using **Thousandths Control (11)** and **Vernier Dial (12)**, and the **scan range (13)** to the appropriate value. Push the Scan Button to begin the EPR run.

For MnCl₂ [12]: Low-temperature Spectroscopy has some changes to the process described above. First, the Temperature Controller needs to be turned on after switching on the Coolant Water. During MnCl₂ spectroscopy, we freeze the sample at a temperature of around 100K using liquid nitrogen. Next, the nitrogen tank needs to be opened and nitrogen flow maintained at around 25 to 30 psi. **Dewar (14)** is then filled with liquid nitrogen. A tube, containing the sample, is inserted into another Dewar to cool the sample. The cooling needs to be slow otherwise the tube might shatter. Once the sample is cooled to the appropriate temperature, the sample is put into the cavity and the steps ahead are the same as for DPPH (described above).

IV. RESULTS AND DISCUSSION

DPPH:

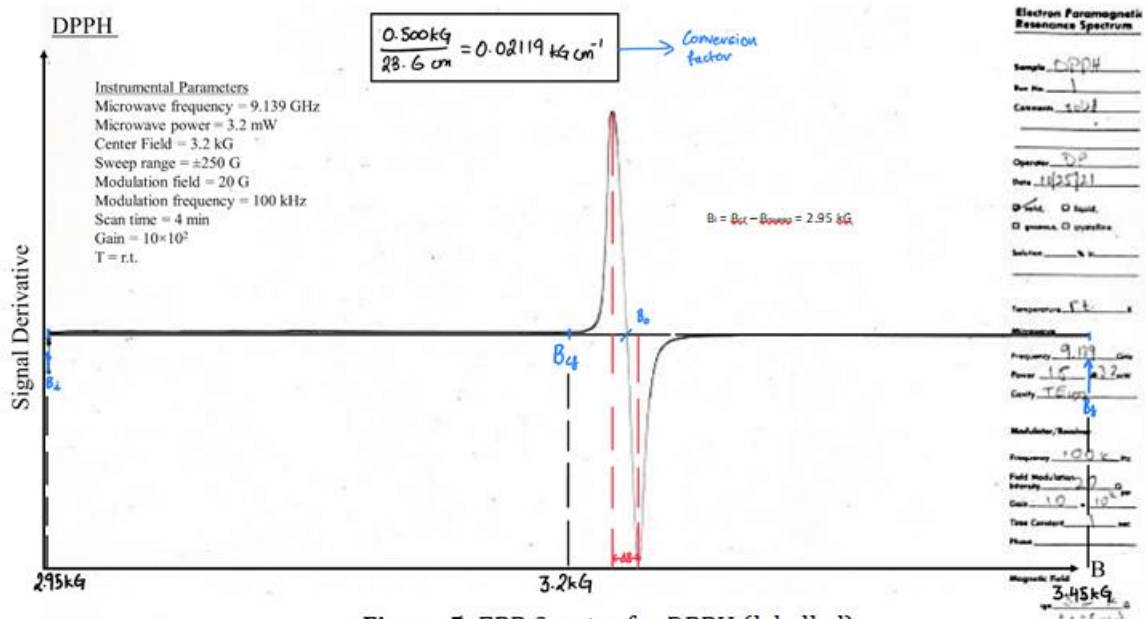


Figure 5. EPR Spectra for DPPH (labelled)

The length of the EPR spectra measures to be 23.6 cm, therefore the B_{cf} lies at the 11.8 cm mark with a value of 3.2 kG. From this, and the sweep range (B_{sweep}) = ±0.250 kG, we determine:

Table 1. Values for EPR Spectra Analysis of DPPH

Initial Magnetic Field (B _i)	Final Magnetic Field (B _f)	B ₀ (length)	Conversion Factor (refer to figure 5)	Resonance field = B ₀
2.95 kG	3.45 kG	13.1 cm	0.02119 kG cm ⁻¹	0.02119(13.1) + 2.95 = 3.2275 kG

Recalling the formula for the g-factor:

$$g = 0.71449 \frac{v}{B_0} [v = 9.139 \text{ GHz}] \Rightarrow g_e = 0.71449 \frac{9.139 \text{ GHz}}{3.2275} = 2.023$$

To calculate Line Width (ΔB):

Value of positive peak = 12.9(0.02119) + 2.95 = 3.223 kG

Value of negative peak = 13.4(0.02119) + 2.95 = 3.234 kG

$$\Delta B = 3.234 - 3.223 = 0.011 \text{ kG} = 11 \text{ G}$$

Value of negative peak = $13.4(0.02119) + 2.95 = 3.234$ kG

$$\Delta B = 3.234 - 3.223 = 0.011 \text{ kG} = 11 \text{ G}$$

Provided for DPPH - Literature g-factor = 2.0037 and Literature line width = 5.6 G [13]

$$\text{The percentage error in } g_e = \frac{2.023 - 2.0037}{2.0037} \times 100 = 0.96 \%$$

$$\text{The percentage error in } \Delta B = \frac{11 - 5.6}{5.6} \times 100 = 96.4 \%$$

The above analysis shows the experimental value of the g-factor is close to the literature value, within the limits of experimental accuracy. Thus, the g-factor of DPPH is 2.00, which is the g-factor of free electrons. This proves that the sample (DPPH) is a free radical. The Experimental line width (ΔB), however, has a significant 96.4 % deviation from the literature value. This could be because of a systematic error, magnetic dipole interactions, or local electric fields created by neighboring electrons/particles with a magnetic moment. [13] The error in line width could be due to several factors: instrumental errors being a major contributor. The error can be minimized by lowering the sweep field, so that the negative and positive peaks can be better measured, thus giving a more accurate value of ΔB . [14]

MnCl₂: For MnCl₂/Water sample, the length of the EPR Spectra is 23 cm, while the B_{cf} is placed at 11.5 cm with a value of 3.0 kG. The sweep field, B_{sweep}, is ± 2.5 kG. This can determine the initial (B_i = 0.5 kG) and final value (B_f = 5.5) of the magnetic field. The formula for Magnetic The field at any point in the spectra is **B_i + 0.21739d**, where d is the distance from B_i.

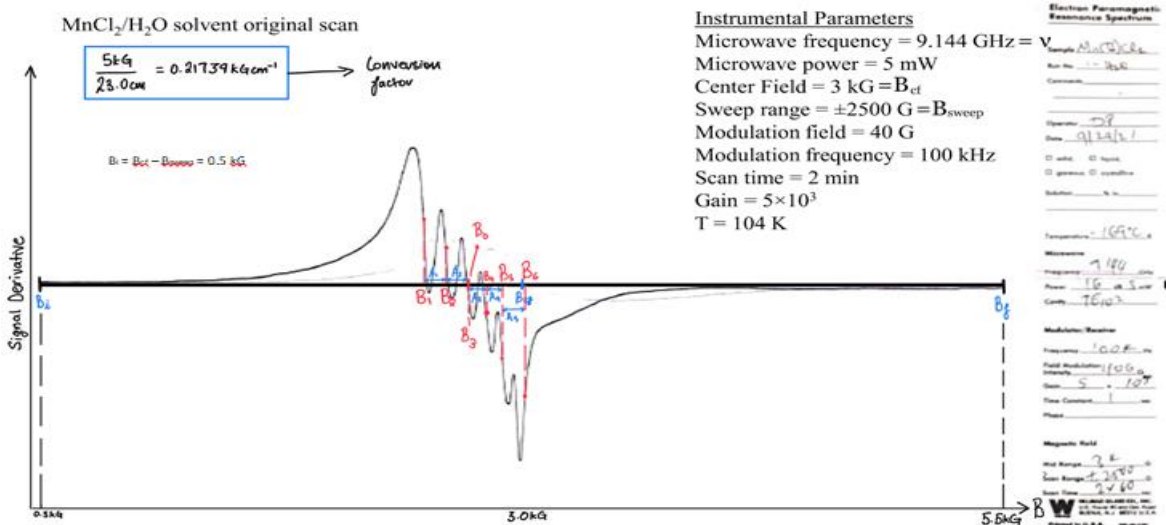


Figure 6. EPR Spectra for MnCl₂/Water Sample (labelled)

The g-factor is calculated by $g_e = 0.71449 \frac{\nu}{B_n}$ [B_n = resonant field and $\nu = 9.144$ GHz]

CONVERSION FACTOR = 0.21739 kG cm⁻¹

Table 2. Shows the g-factor and the hyperfine constants at each hyperfine line:

Hyperfine Line	Distance from B _i to B _n	B (in kG)	g-factor (g)	Hyperfine Constant (A)	
B ₁	9.2	2.5	2.61		
B ₂	9.7	2.61	2.50	A ₁ (B ₂ - B ₁)	0.11 kG
B ₃	10.3	2.74	2.38	A ₂ (B ₃ - B ₂)	0.13 kG
B ₄	10.7	2.83	2.31	A ₃ (B ₄ - B ₃)	0.09 kG
B ₅	11.2	2.93	2.23	A ₄ (B ₅ - B ₄)	0.10 kG
B ₆	11.6	3.02	2.16	A ₅ (B ₆ - B ₅)	0.09 kG

From Table 2, we know that the average g-factor value is $g_{\text{mean}} = \frac{\sum_0^6 g_n}{6} = \frac{14.19}{6} = 2.365$

The value of B_0 is where the signal derivative line crosses the baseline of the EPR spectra, which is the same as B_3 and has a value of 2.74 kG. Using the value of B_0 , the g factor:

$$g_o = .71449 \left(\frac{9.144}{2.74} \right) \Rightarrow g_o = 2.38$$

The percentage uncertainty between the g_o and g_{avg} with respect to g_{avg} (the smaller value) calculates to $\frac{2.38-2.365}{2.365} \times 100 = 0.63 \%$, which is acceptable within limits of experimental accuracy. However, in this paper, the value of g_o will be used as a comparison to the literature value.

The average value of the Hyperfine Constant = $A_{avg} = \frac{\sum A_n}{5} = \frac{0.52}{5} = 0.104 \text{ kG or } 104 \text{ G}$.

Literature values [15]:

- **g-factor = 2.00**
- **Hyperfine Constant = 90G**

The percentage uncertainty in the g-factor is $\frac{2.38-2.00}{2.00} \times 100 = 19\%$

The percentage uncertainty in Hyperfine Constant (A) = $\frac{104-90}{90} \times 100 = 15.6\%$

The percentage uncertainty in the g-factor and the Hyperfine constant is high. The reason behind the higher value of the g factor could lie in the solvent. The $MnCl_2$ sample used in EPR is an aqueous sample that has been frozen using liquid nitrogen. There may have been incomplete freezing, and water absorbs microwaves. Although not eliminated, this effect is lessened when the water is frozen, because as molecular motion decreases, microwave dielectric loss is also decreased. Incomplete freezing means more microwaves absorbed and a less accurate value for the g-factor. **The main method of improvement** (for DPPH and $MnCl_2$ analysis) will be to lower the sweep range, this will make it easier to locate the field position of the hyperfine line – the more accurate value of g-factor and Hyperfine Constant. [16]

Table 3: Summarizes the analysis of the two spectra:

Table 3. Summarizes all the information obtained in the analysis of the two spectra.

Results	Sample	
	DPPH	$MnCl_2$ /Water Solvent
Number of absorption peaks	1 (due to Zeeman’s splitting)	6 (due to hyperfine interaction)
B_0 (in kG)	3.2275	2.74
g-factor (g)	2.023	2.38
Line Width (ΔB)	11 G	-
Hyperfine Constant (A)	-	104 G
Percentage uncertainty in g	0.96 %	19 %
Percentage uncertainty in ΔB	94.6 %	-
Percentage uncertainty in A	-	15.6 %

V. CONCLUSION

The EPR analysis of a transition ions crystal like $MnCl_2$ and a hydrazyl, like DPPH vary in several ways. DPPH has a negligible orbital magnetic moment, and only the electron spin moment contributes to the absorption spectrum, thus it doesn’t show hyperfine interaction, with a g value of 2.02: The analysis is consistent with prior studies. $MnCl_2$, on the other hand, shows a deviation in the g value from existing research, this could be because of improper freezing (explained in the last section) or impurities in the sample creating an external magnetic field and interfering with the g factor calculations. However, the spectrum shows 6 hyperfine absorptions, implying a nuclear spin of $\frac{5}{2}$, which suggests the presence of Mn^{2+} ions.

In the past several decades, EPR has allowed us to study biological compounds, crystal samples, free radicals, etc. Future research for crystals should be conducted to account for as a solvent and alter the g-factor formula

to account for the water of crystallization. Furthermore, these systems should be researched to develop ways to detect impurities with the sample inside the cavity, thus minimizing the impact of any external magnetic field that might tamper with the analysis, thus giving more accurate results.

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