EPR Investigations of DPPH and Magnesium (II) Chloride

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Abstract

In the following paper, we discuss the basic theory of EPR in a simple manner, enough for even a beginner to understand. All theory is discussed, and nothing is assumed to be known. We then describe the experimental procedure, with the equipment and the samples. The systems in which the samples were run are also discussed, the low temperature of 104K was used, as well as room temperature of 293K. The results of the spectroscopy are then discussed, with all the other conditions which play a role being mentioned. In the end, we conclude by comparing the results we obtained with the theoretical results, and weigh the reasons for the differences.

Introduction

EPR, Electron Paramagnetic Resonance, is a spectroscopic technique, which gives us the ability to converse with electrons. The technique makes use of unpaired electrons as the medium to obtain information such as the g-factor of the electrons, the details of the atoms, interactions in the lattice, and more. The experiment focussed on carrying out EPR spectroscopy on two different samples, DPPH, and $MnCl_2$.

DPPH is an antioxidant, and a free radical. As it is a free radical, it has free electrons, and this property allows us to interact with the atoms. Similarly, $MnCl_2$ is paramagnetic, meaning it too has unpaired electrons.

The purpose of the experiment was for us to understand the basics of EPR spectroscopy, collecting, organizing and analysing the data, and comparing them with our expected results. It also helped us build respect for the experiment, and learn of its importance. I say this for it showed us how to identify free radicals, which are atoms which steal electrons from other molecules, giving rise to more free radicals, and more damage to cells. It causes many severe diseases, such as cancer, and cardiovascular diseases, and little is known about curing them. EPR is especially helpful, as we can identify the free radicals in the samples, and help save lives.

Background Theory

Electrons can only exist at certain energy levels, in specifically shaped orbitals. These rules are defined by quantum numbers, and the number m_s denotes the spin. The constant values of m_s are $\pm 1/2$, meaning that electrons have spin values of $+1/2$ or $-1/2$. Therefore, it seems obvious that pairs of electrons, which have to have opposite spins, will cancel out their spins, as $+1/2 + -1/2 = 0$. This is why we can only use unpaired electrons for the spectroscopy.

$$E = \frac{-13.6\ eV}{n^2}$$

-0.85eV

-1.5111eV

-3.4eV

-13.6eV

Figure 1. The different energy states for the electrons in the Hydrogen atom.

Electrons can only exist at certain discrete energy levels; however, they can jump between them. For an electron to jump between the energy states, it needs to absorb energy. However, the energy must be equal to the energy gap between the state it currently is at, and the state it is jumping to. This implies, that for an electron to jump from ground state to the 2nd state, it requires exactly 10.2eV of energy. The form in which this energy is provided is of electromagnetic radiation. The energy of the individual photons can also be found out.

$$\Delta E = E_{final\ state} - E_{initial\ state} = E_{photon}\ (\textbf{Equation 1})$$

$$E_{photon} = h\nu\ (\textbf{Equation 2})$$

Where h is plank's constant, and v is frequency.

In EPR, we run radiation through the sample, avoiding heating it. Our main goal is to push an electron to a higher energy state, and learn of values like the g-factor. We vary the magnetic field, and electrons spin states diverge, the ΔE is changing. When the value of
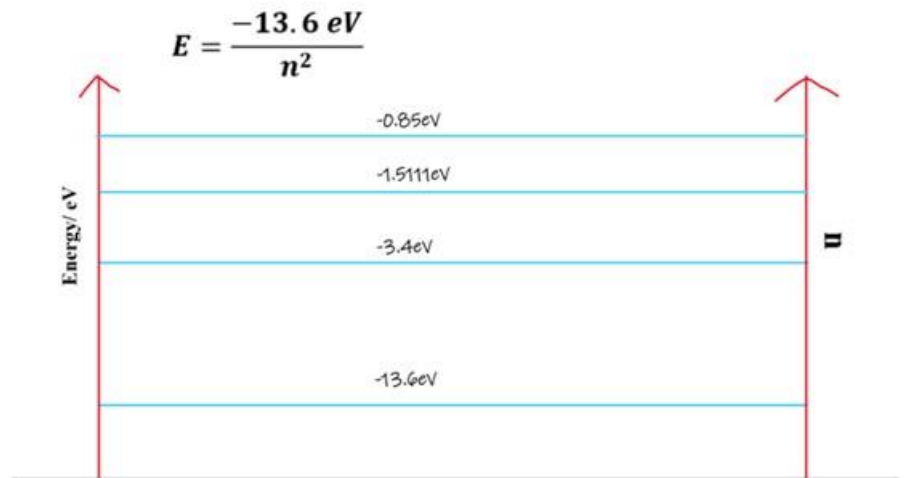
$+\frac{1}{2}g\mu_B B$

ΔE

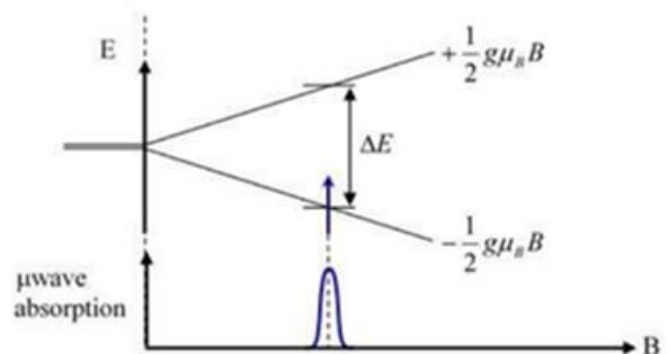μwave absorption

$-\frac{1}{2}g\mu_B B$

Figure 2. The diversion of the energy states the electron can be at, and the electron absorption signal – the Zeeman effect.

ΔE equals the energy of the photon, the electron will absorb the energy and jump to a higher state.

The energy difference, ΔE, is found out from the following equation:

$$E = g\mu_B B \text{ (\textbf{Equation 3})}$$

Where g is the g-factor, µB is the Bohr Magneton, and B is the magnetic field.

We can use this to satisfy equation 1, and obtain the resonance condition:

$$\Delta E = h\nu = g\mu_B B \text{ (\textbf{Equation 4})}$$

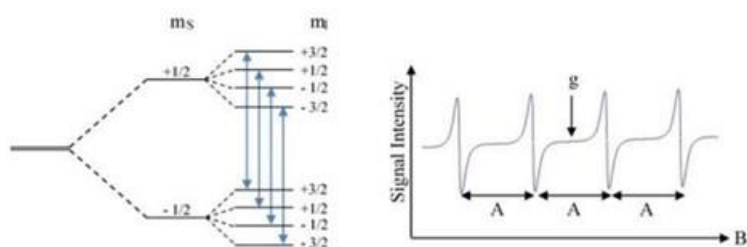$$g = 0.71449 \frac{\nu(GHz)}{B(kG)} \text{ (\textbf{Equation 5})}$$

Figure 3. m_S and m_I, and the different absorption signals detected – Hyperfine interactions are shown. The curve depicts the derivative lines.

In some instances, however, the nucleus itself has a spin, I. The spinning charged nucleus generates a magnetic moment. The magnetic moment will go on to add or subtract the external magnetic field's effects, $B \pm B_I$ and therefore, we will get multiple signals instead of 1.

Some things to note are that the m_S values will always have a difference of 1, while the m_I values will always have a difference of 0. There will always be 2I+1 number of values for m_I and it will go from -I to +I in intervals of 1.

We now know the resonance condition (equation 4). In the experiment, we obtain values for the magnetic field, and have fixed values for the Bohr Magneton and plank's constant. Lastly, the frequency of the wave is constant. Thus, we can find the g-value. The g-value of a free electron is constant; however, it varies for unpaired electrons due to their interactions with the magnetic field.

Placing a metal inside a molecule or crystal, there will be different interactions with the ligands,
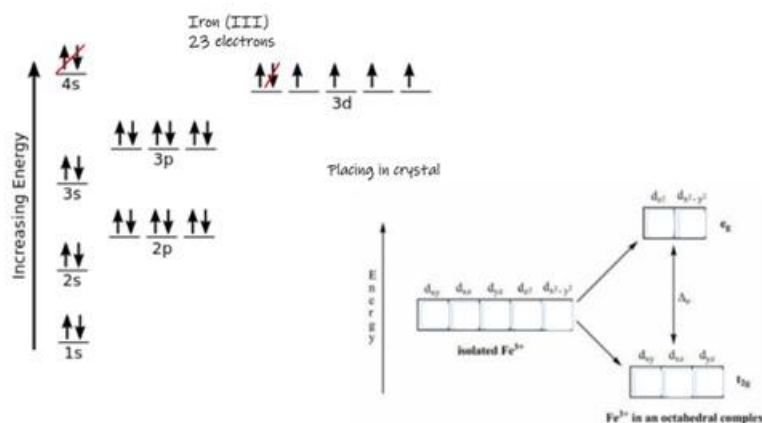
Figure 4. The arrangement of electrons in Fe (III), and the separation of the d-orbital electrons after placing the metal in a crystal, giving rise to a ΔE, which will decide whether the spin is high or low,

because of the orientations of the orbitals, and this will lead to a difference in energy of interactions. In octahedral symmetry, there will be two d-orbital with high energy, and three d-orbitals with low energy. In summary, the d-state orbitals will separate when the metal is placed inside a crystal, with ΔE being the energy separation. The same atoms can have different spin states, depending on the ΔE, which in turn depends on the interactions with the ligand molecules. If ΔE is small, some electrons can go up to the higher energy states, giving a higher spin, but if ΔE is large, the electrons will not have enough energy, and thus stay in lower energy states, giving a lower spin. They give a lower spin because they will have to form pairs, where the spins cancel out. The greater the spin, the greater the magnetism of the molecule.

Experimental Procedure:

Instruments used:

For the experiment, we used the Varian E-3 X-band EPR spectrometer, which allows liquid nitrogen to be added to reduce the temperature of the system. The frequency range of the spectrometer was 8.5GHz to 12GHz, with a temperature range of 80K to room temperature. The system was capable of going from 0G to 10000G (1T).

The sample was simply placed in the cavity, and the klystron is turned on, and our eyes were focused on the oscilloscope spectrum, waiting to see a dip on it. The dip signifies that the sample and cavity have absorbed the radiation. However, we have to first make sure that the guiding passage of the klystron's radiation is aiming directly through the iris of the cavity, and after noticing the dip on the power reading, we knew that the radiation passed through the iris to the cavity, and remained there, as there was no reflection. Simultaneously, liquid nitrogen flows through the cryostat, allowing us to run the test at 100K. The temperature is measured with a thermocouple thermometer which is built alongside the cavity. The thermometer has access to the cavity, and also the room temperature, and shows the temperature reading based on the difference between the two. We make sure that the temperature is maintained by simply by increasing the flow of liquid nitrogen when needed, and reducing it when needed.
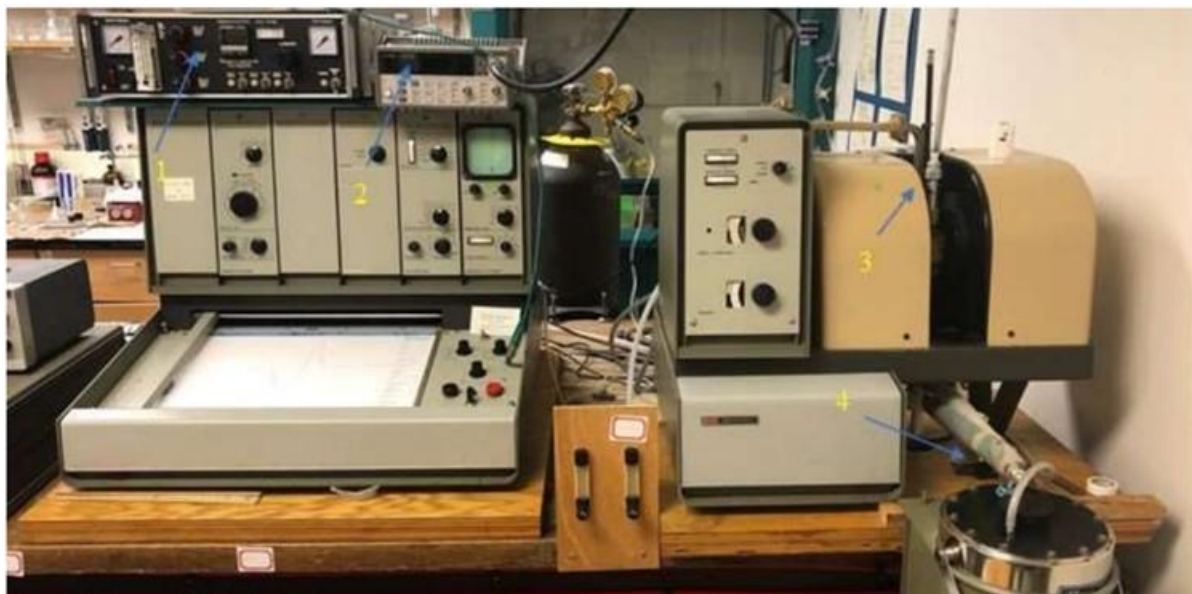
Figure 5. The Varian E-3 spectrometer. 1 is the temperature control, which not only monitors the temperature, but also controls the flow of Nitrogen. 2 is the universal counter which displays the frequency throughout the experiment. 3 is the cavity where the sample is contained. 4 is the dewar which stores liquid nitrogen.

Procedure:

The sample was placed in a special quartz glass without impurities, of a diameter of 3mm. A special material has to be used to hold the sample as EPR is an extremely sensitive. The DPPH sample was run through at room temperature, at 293K, and thus there was no need for liquid nitrogen to flow through. We had to first turn on the coolant, to make sure that the magnet doesn't overheat, but the temperature controller in this case was not turned on, as it was being run at room temperature.

For the DPPH, some grease was placed inside the EPR tube, and the DPPH sample was placed on the grease. The tube was now in the cavity, and the set up was initiated. The microwave radiation was now entering the cavity, through the wave-guides, and we waited for the dip in the radiation level to occur. The centre field and sweep range were set, at 3.2kG and 250G respectively. The microwave frequency was 9.139GHz and the microwave power was 3.2mW. The scan was run for 4 minutes, with a gain of 10×10^2.

For the $MnCl_2$ sample, we used a 9.144GHz frequency, at a power of 5mW. The centre field was set at 3kG and the sweep range was 2.5kG. The sample was dissolved in water, and the scan was run for 2 minutes, with a gain of 5×10^3, at a temperature of 104K, meaning it was a frozen solution. To reach this temperature, liquid nitrogen was flown

through the dewar flask, and the temperature controller was set up. The sample used water as the solvent, and was flash-frozen with liquid nitrogen before being placed in the cavity.

Results and Discussion:

The DPPH, 2,2-diphenylpicrylhydrazyl, which is a free radical, has a theoretical g value of 2.0036. The experiment was run at room temperature, at 293K. The B_i for the sample experiment was 2950G and B_f was 3450G, and B_0 was at 3227.425G. Using the formula (equation 5), where the microwave frequency was 9.139GHz, I obtained the value for g to be 2.023. The value was 0.0194 away from the theoretical value, a difference of 0.97%, meaning there were some issues that arose during the EPR scanning. The linewidth of the sample was 0.7cm, 7mm, 14.77G. The small linewidth shows us the energy that the electron absorbed, and emitted, meaning that the overall energy exchange.
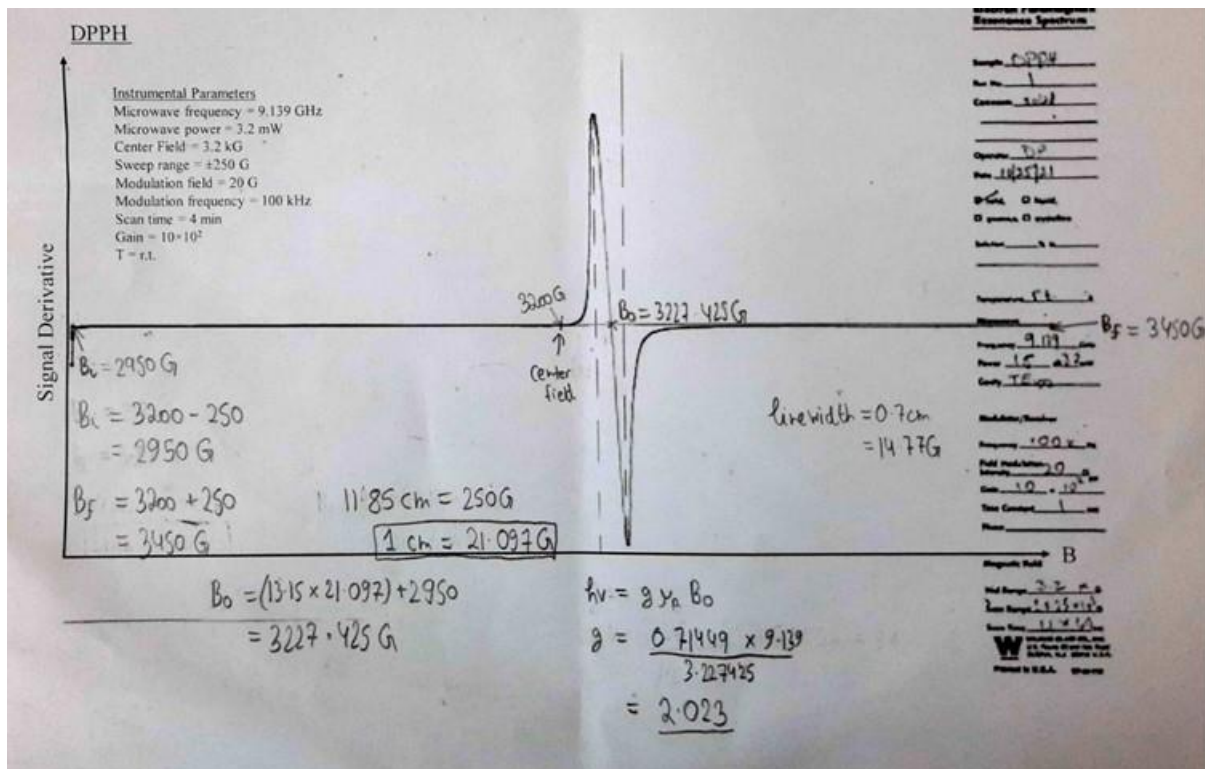

Figure 6. EPR absorption signals of DPPH at room temperature. The frequency was 9.139GHz, and the center field was 3.2kG and sweep range was 250G. B_0 had a value of 3227.425G, and the calculated g-value is 2.023. The scale was 1cm = 21.097G.

$MnCl_2$ has a nuclear spin of 5/2, meaning that there have to be ((5/2*2) +1) lines, 6 lines on the graph. Due to the nuclear spin, we will have a hyperfine interaction system, where we will have to average the values for the B in kilogauss to find the value to use in equation 5. I obtained a value of 2.354 which rounds up to 2.4. The theoretical value is around 2.0, meaning there were some errors.
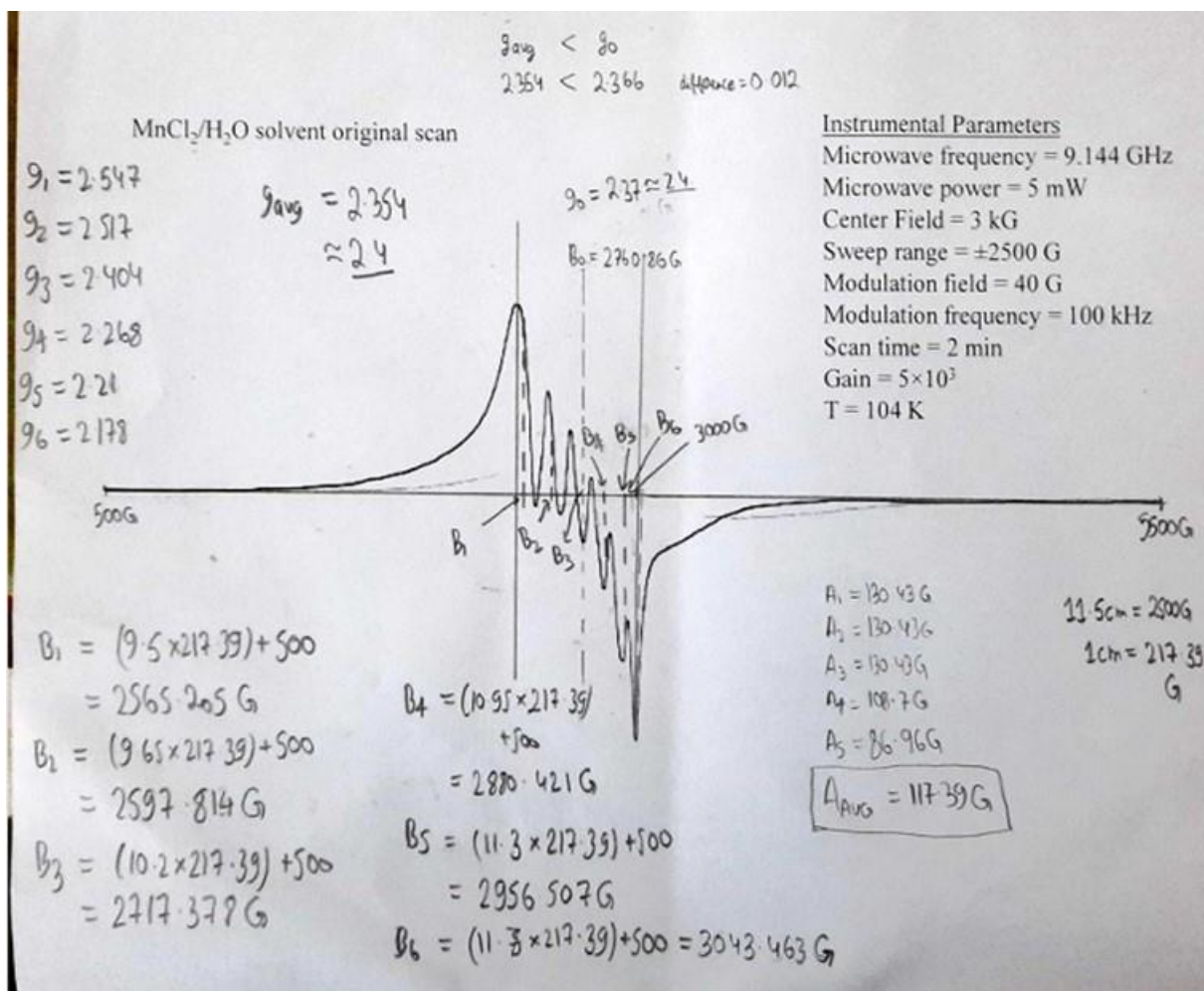
Figure 7. EPR absorption signals of MnCl$_2$ at 104K with water as the solvent. The frequency was 9.144GHz, and the center field was 3kG with a sweep range of 2500G. There were 6 magnetic field values, B$_1$ was 2565.205G, B$_2$ was 2697.814G, B$_3$ was 2717.378G, B$_4$ was 2880.421G, B$_5$ was 2956.507G, and B$_6$ was 2999.985G. I found out 6 g-values with these magnetic field values, and averaged the g-values to obtain 2.27 as the g-value. The scale of the spectrum was 1cm=217.39G

The B$_0$ value was 2760.86G, and the g-value from that was 2.37, which carries a difference of 0.012 from the g$_{avg}$ that I obtained.

The B$_0$ value is value named B$_3$ in the figure above, and it has a g-value of 2.404, which differs by only 0.04 from the g$_{avg}$ value.

The A, hyperfine constant had 5 different values, and upon further calculations, the average ended up being 117.39G.

Conclusion

To conclude, the samples of DPPH and $MnCl_2$ were run carefully, and their respective graphs were given to us. The DPPH was run at room temperature, while the $MnCl_2$ was run at 104K. The theoretical values and the final observed values for the samples are shown in table 1 below.

	Theoretical g-value	Final g-value	% Difference in the g-value
DPPH	2.0036	2.023	0.97
$MnCl_2$ with water solvent	2.0	2.4	20

Table 1. The g-values for DPPH and $MnCl_2$ respectively are shown, the theoretical, as well as the final. Alongside them are the difference in %.

As can be seen from table 1 above, the values for DPPH are quite accurate. This means that the sample run for the scan had no impurities in it, which kept is as accurate as possible. However, when it comes to the $MnCl_2$ sample, there was a difference of 20%. One possible reason for this difference is the presence of impurities. If any paramagnetic impurities were present in the samples, there would definitely be some errors, as they would affect the g-value. For the second sample of $MnCl_2$, the hyperfine constant has a value of 90G, and the value I obtained was 117.39G. The percentage difference is of 30%, and this again could have arisen from the presence of impurities in the sample. Another possible source of inaccuracy is the difference in the field range of the two samples, meaning that the accuracy for the $MnCl_2$ sample is a lot less.

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