Low Temperature Magnetic Susceptibility and the Partition Function

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Abstract

The magnetic susceptibility of paramagnetic compounds such as, gadolinium sulphate hydrate (GSH), chromium potassium sulphate hydrate (CPSH) and cupric acetate monohydrate (CAM) were investigated to see how they compared to each other at room temperature and how the susceptibility changed over a range of temperatures. The ratio of susceptibilities of GSH and CPSH at room temperature was 3.34 ± 0.2 which does not agree within uncertainty of the expected value of 4.2 however, it does still illustrate the effect or higher spin values on the susceptibility. The temperature dependence of GSH was illustrated and the Curie law was proved showing how the magnetic susceptibility of a paramagnetic compound is inversely proportional to temperature. The temperature dependence of CAM showed the effects of temperature on the susceptibility and gave a value for the exchange energy between the ground state and the triplet of excited states the Cu 2+ ions exist in to be $6.9 \times 10^{-20} j$.

Introduction

Magnetic properties such as the spin of electrons in ionic compounds have significant impacts on the reactions of that compound with diverse temperature stimulants. The partition function describes the statistical properties, such as electron spin, of a system in thermal equilibrium and the extent to which energy is partitioned among different possible states (J. Bevan Ott, 2000). The partition function (Z) can be described as follows, where ε_i are the possible states and k is the Boltzmann constant.

$$Z = \sum_i e^{\frac{-\varepsilon_i}{kT}} \quad (1)$$

The thermal average of any property X can be described by taking the sum of the probability of the property.

$$\langle X \rangle = \frac{1}{Z} \sum_i X_i e^{\frac{-\varepsilon_i}{kT}} \quad (2)$$

For a magnetic spin system, we can find its susceptibility using the partition function. The different energy states ε_i, when in a magnetic field, is the product of the magnetic moment which is the spectroscopic splitting factor (g), the Bohr magneton (μ_B) and the spin states (m_s) with the magnetic field (B).

$$\varepsilon_i = g m_s \mu_B B \quad (3)$$

Putting this into the partition function equation and summing over the different spin states (S) gives,

$$Z = \sum_{-S}^{S} e^{\frac{-g m_s \mu_B B}{kT}} \quad (4)$$

The temperature dependence of the susceptibility (χ) for low field measurements made at temperatures where the thermal energy kT is much greater than the energy level splitting can be shown as (Script, 2019),

$$\chi B = \mu_o M \quad (5)$$

Using this we can find the susceptibility for ionic compounds such as gadolinium sulphate hydrate (GSH), chromium potassium sulphate hydrate (CPSH) and cupric acetate monohydrate (CAM).

The susceptibility for GSH and CPSH is shown, where z is determined by the spin state of the magnetic compound (S = 7/2 and therefore z = 63/4 for GSH, and S = 3/2 and therefore z = 15/4 for CPSH)

$$\chi = \frac{\mu_o N}{V} \left(\frac{\mu_B^2 g^2}{3kT} \right) z \quad (6) \text{ (Script, 2019)}$$

The susceptibility of CAM is slightly different due to the difference in spin states between isolated Cu 2+ ions and Cu 2+ ions interacting in pairs. This results in one ground spin state and a triplet of excited spin states. J is the exchange energy between the ground state and the triplet of excited states.

$$\chi = \frac{\mu_o N}{V} \left(\frac{2\mu_B^2 g^2 e^{\frac{-J}{kT}}}{kT(1+3e^{\frac{-J}{kT}})} \right) \frac{63}{4} \quad (7) \text{ (Script, 2019)}$$

To measure the susceptibilities of paramagnetic compounds an apparatus as shown in **figure 1** is used, with two mutually inducting coils that produce voltages when the compound is put through each coil.
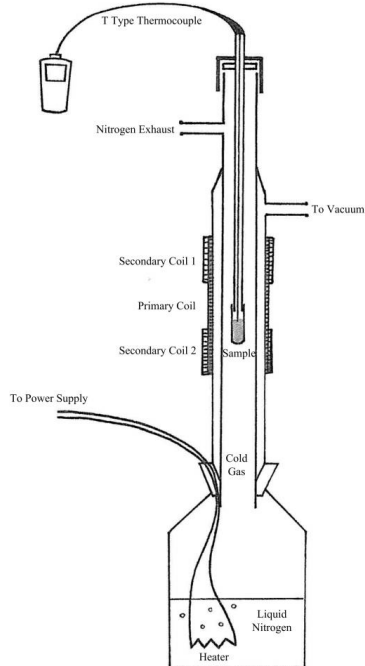

Figure 1: Diagram of mutually inducting coil set up (Script, 2019)

The voltage in each coil is shown as follows, where ω is the angular frequency from the waveform generator, i is the phase shift between voltage and current M is the mutual inductance.

$$V_1 = i\omega M_1 I_p \quad V_2 = i\omega M_2 I_p \text{ (8)}$$

The voltage difference combines the above equations,

$$\Delta V = V_1 - V_2 = i\omega I_p(M_1 - M_2) \quad \text{(9)}$$

When a compound is put through the first coil the mutual inductance changes based on the compound's magnetic susceptibility and its geometry (α).

$$\Delta V_{up} = i\omega I_p(M_1 - M_2) + i\omega\alpha\chi M_1 I_p \quad \text{(10)}$$

The same for the second coil is,

$$\Delta V_{down} = i\omega I_p(M_1 - M_2) - i\omega\alpha\chi M_2 I_p \quad \text{(11)}$$

The difference between these is as follows and considering that everything on the right side of the equation is constant it shows that the proportionality between Vup, Vdown and the susceptibility.

$$\Delta V_{up} - \Delta V_{down} = i\omega\alpha\chi I_p(M_1 + M_2) \quad \text{(12)}$$

Experimental Method

The magnetic susceptibility of GSH, CPSH and CAM was measured by investigating the response at room temperature and over a range of temperatures from room temperature down to approximately 80 Kelvin. Determining the exact magnetic susceptibility of a material is hard so the mutually inducting coil set up was used in order to find the voltage of the material in each coil and use this and its proportionality with susceptibility to determine how it changes from one material to another and how it changes in any material over a range of temperatures. The coil apparatus was connected to an offset control where the phase and amplitude of the signal can be aligned to produce readable results. This was then connected to a lock-in amplifier to isolate and amplify the very small signal and then it was connected to an oscilloscope so a good visual representation of what was happening could be seen. A diagram of the experimental set up is shown in **figure 2**.
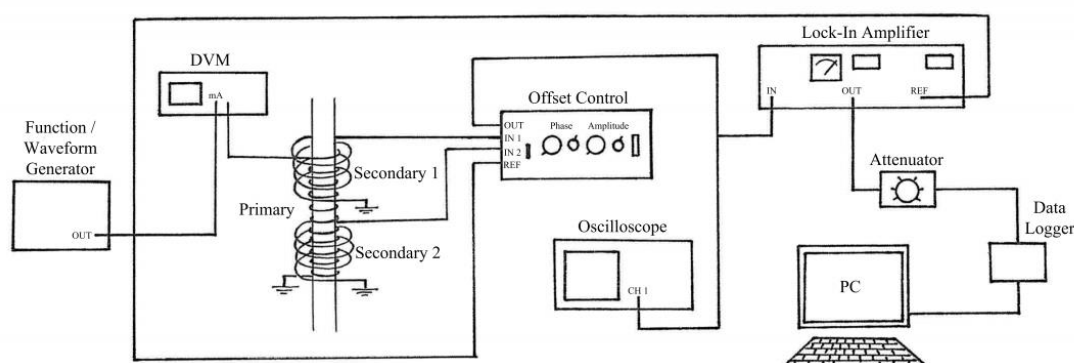
Figure 2: Experimental set up

To compare the susceptibility of GSH and CPSH each sample was individually placed in-between the coils and slowly moved up and down. Looking at the oscilloscope gave a good indication as to when the sample was in the middle of each coil and hence when to take voltage readings. If the signal from the coils was too large on the lock-in amplifier the sensitivity could be changed to see accurate results.

The temperature dependence of both GSH and CAM where investigated using the same experimental set up however instead of manually moving the sample up and down between the coils, each sample was attached to a stepper motor which moved the sample up and down between the middle of one coil to the middle of another. This was done for each sample at a range of temperatures starting at room temperature and then going down. The temperature was decreased by boiling off liquid nitrogen at a controlled rate. Once a full range of temperatures was found for each sample, the temperature dependence of the magnetic susceptibility could be plotted. From this plot the exchange energy could be found for the CAM sample. The output of one of the temperatures for the CAM sample is shown in **figure 3**.
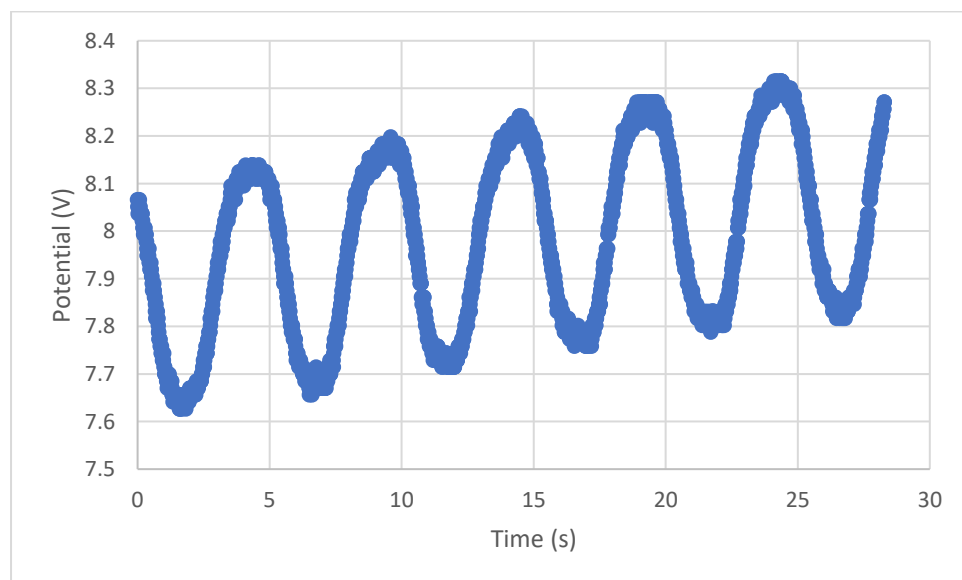

Figure 3: CAM sample at 196 K and 20 mV sensitivity

Results and Analysis

The room temperature susceptibility of the GSH sample is shown in **figure 4**. This shows how the voltage increases in amplitude as the sample enters each coil.
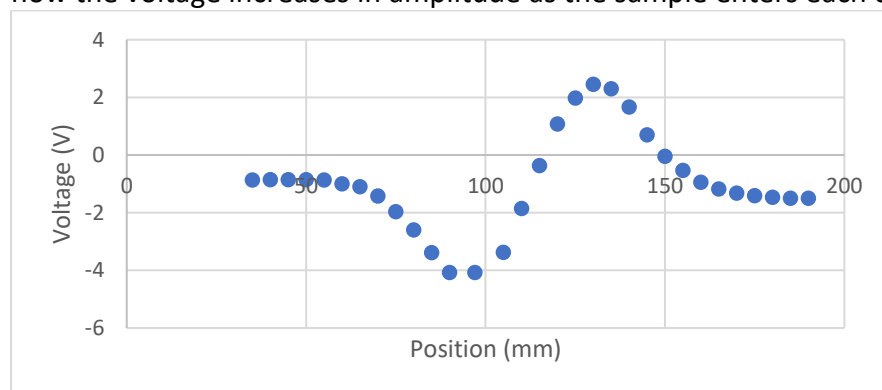

Figure 4: Output of GSH sample

From this, values for Vup and Vdown could be found.

$$V_{up} = 2.45 \pm 0.02 \; mV$$

$$V_{down} = -4.13 \pm 0.02 \; mV$$

Using equation (12) in conjunction with these values, the current of 5.36 mA, and incorporating the number of molecules (N) we can find a value proportional to the magnetic susceptibility.

$$\frac{V_{up} - V_{down}}{NI_p}$$

For the GSH sample, N is equal to 2n (number of moles) due to the two gadolinium ions in the compound.

$$N = 2 \times \frac{Mass \; (1.56g)}{Molar \; mass \; (747 \; gmol^{-1})}$$

$$N = \; 4.18 \times 10^{-3}$$

Therefore, the magnetic susceptibility is proportional to,

$$\chi = 293.9 \; \pm 7.3$$

For the CPSH sample the Vup and Vdown were found to be,

$$V_{up} = 0.05 \pm 0.02 \; mV$$

$$V_{down} = -1.7 \pm 0.02 \; mV$$

For CPSH, N is simply equal to n because there's only one chromium ion, therefore,

$$\chi = 87.9 \pm 2.2$$

The ratio of these two susceptibilities is 3.34 ± 0.2.

Investigating the effect of temperature on the magnetic susceptibility of GSH produced the following in **figure 5**. The figure proves the Curie law that the magnetic susceptibility of a paramagnetic substance is inversely proportional to temperature (byjus, 2019), this is proven by the straight line produced when comparing susceptibility and the inverse of temperature. The very small error bars were based on the uncertainties associated with the measurement devices.
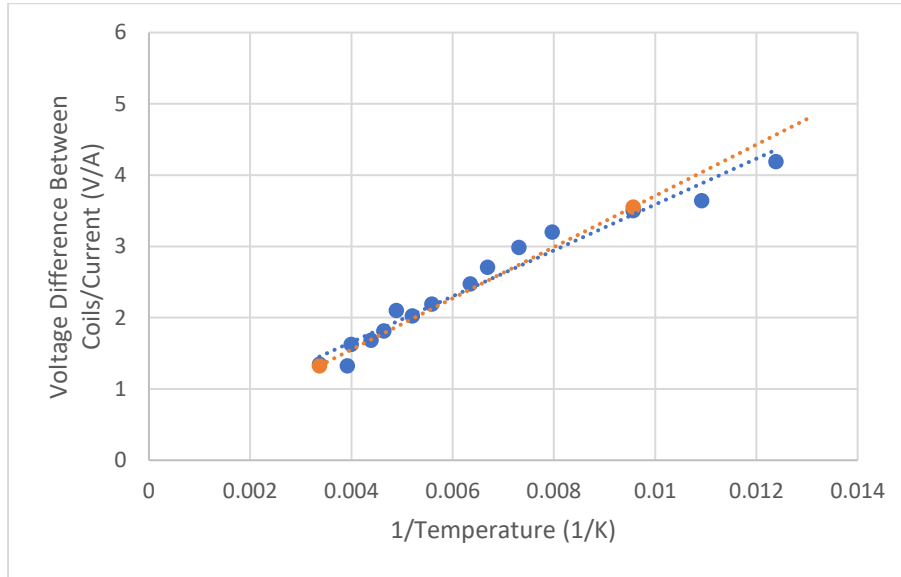

Figure 5: GSH temperature dependence

The temperature dependence of the magnetic susceptibility of CAM is shown in **figure 6**. The error bars increase in size as the inverse of temperature increases (temperature decreases) due to the increasing uncertainty when taking measurements at low temperatures.
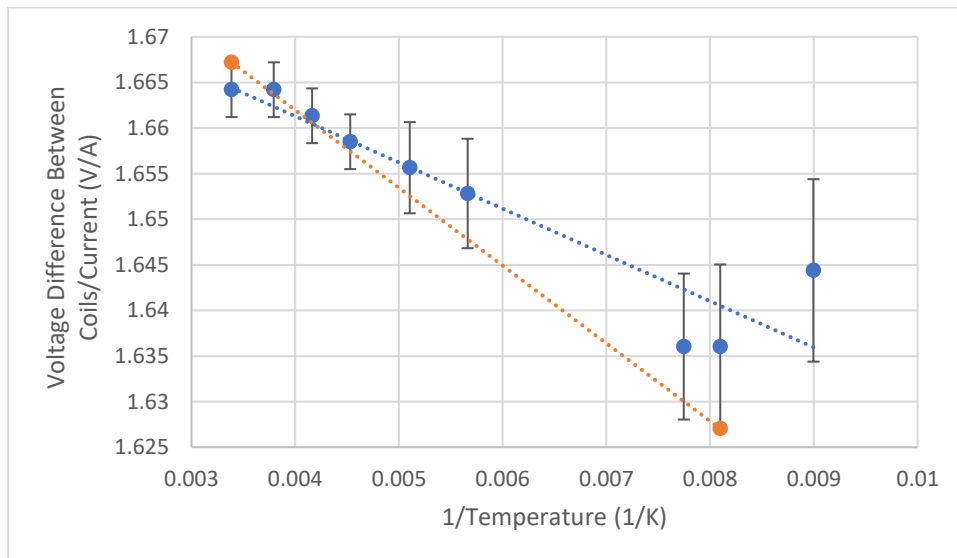

Figure 6: CAM temperature dependence, slope of -5.1 ± 1.8

From this graph we can determine the exchange energy (J) of the CAM sample as the slope of the function is equal to J/k. Therefore, the exchange energy is,

$$J = 6.9 \times 10^{-20} j$$

Discussion

The ratio of the magnetic susceptibility of GSH and CPSH was found to be 3.34 ± 0.2 which does not agree within uncertainty with the expected value of 4.2 or 63/15. However, this value does illustrate how the magnetic susceptibility changes between compounds with different magnetic properties. Both Gadolinium and Chromium ions have a 3+ charge however they have different sized valence orbitals. The Gd 3+ ion has 7 electrons in an f shaped valence shell which produces a spin value of 7/2. Comparing this to the Cr 3+ ion which has 3 electrons in a d shaped valence shell giving a spin value of 3/2. From this we can see why the magnetic susceptibility of GSH is larger than that of CPSH. The experimental value of the ratio of magnetic susceptibilities does not agree with theoretical values due to multiple factors. As shown in equation (10) the magnetic susceptibility is affected by the geometry of the sample. In the case of this experiment the samples of GSH and CPSH did not have the same geometry, GSH was in a longer thinner shape when compared to CPSH which was not accounted for in calculations. Another source of uncertainty came from finding the values of Vup and Vdown for both samples. In order to do this each sample had to be manually held in place so it was inside each coil. This was particularly difficult with this apparatus as you could not see where the coil was, so where the sample was held was purely based on looking at the oscilloscope. It was also hard to hold the sample in exactly the same place to take the same measurement for both samples. To reduce the error caused by these factors we could have ensured both samples were of the same geometry and could have used a clamp of sorts to secure each sample when it was in the middle of each coil so accurate measurements could be made.

From **figures 5** and **6** we can see how the magnetic susceptibility of both GSH and CAM were effected by temperature changes. For the GSH sample we can see how the Curie law was verified as we can see a linear relationship when comparing magnetic susceptibility to the inverse of temperature. While our results did imitate a linear relationship a lot of the points were around the line of best fit and not necessarily the most precise. This was due to the difficulty in holding a stable temperature for long enough to get an accurate result. Boiling off nitrogen was effective for reducing the temperature however it was quite hard to control the exact temperature in order to make a measurement. The time constant on the lock-in amplifier determined how long a stable temperature had to be held to make a measurement. In our case the time constant was 300 ms so in order to make a measurement the temperature had to be stable for 1.5 s. To try reduce this error two temperature values were taken, one at the start and one at the end of making the measurement and the average of these temperatures was used.

The error bars at low temperatures on **figure 6** are so large due to how sensitive the logging software could read the signal. At this temperature the signal received is very low and therefore the amplitude peaks of the signal are very undefined, so it is hard to see accurate values.

Conclusion

The room temperature comparison of GSH and CPSH showed the susceptibility of GSH to be greater than that of CPSH with the ratio being 3.34 ± 0.2. This does not agree with the expected value of 4.2. The temperature dependence of GSH and CAM showed the effects of temperature on magnetic susceptibility, with the GSH dependence proving the Curie law. From the CAM temperature dependence, a value of $6.9 \times 10^{-20} j$ was found for the exchange energy between the ground energy state and the triplet of excited energy states.

Bibliography

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