

Experiment 4: Measuring Metal Magnetism

The common ions of transition metals have 0-10 valence electrons in their *d*-orbitals. Magnetic measurements can be used to study these valence electrons, as the magnetic moment of a transition metal ion typically depends only on the number of unpaired electrons. The number of unpaired electrons is based on two factors – the charge of the ion, and its electron configuration. In this experiment, we will study ions of known charge in order to learn about their configurations, in particular, whether they exist in a high-spin state or a low-spin state.

Magnetic measurements provide a versatile tool for investigating the number of electrons present on a transition metal. Each unpaired electron can contribute to the total magnetic moment of a compound. While it is rare to find organic compounds with unpaired electrons, many transition metal complexes exist with unpaired electrons. Compounds with unpaired electrons are called *paramagnets*, and they will be attracted by magnetic fields. Due to the large variety of oxidation states available to transition metals, the number of unpaired electrons and the resulting paramagnetic moment will change greatly with a transition metal's chemical environment. Molecular compounds with no unpaired electrons are called *diamagnets*, and will be repelled by a magnetic field. Under certain conditions, superconductors can act as perfect diamagnets (expelling 100% of magnetic fields) and are therefore effective for levitation applications, such as the ones below. If all the magnetic spins in a paramagnet are aligned in parallel (as is the case for metallic iron at room temperature), the material is said to be a *ferromagnet* and will generate a magnetic force substantially stronger (~100X) than that of a paramagnet. In other materials known as *antiferromagnets*, the paramagnetic spins on neighboring metals align in an antiparallel configuration, giving a sample magnetization which is much less than that of the original paramagnetic state.

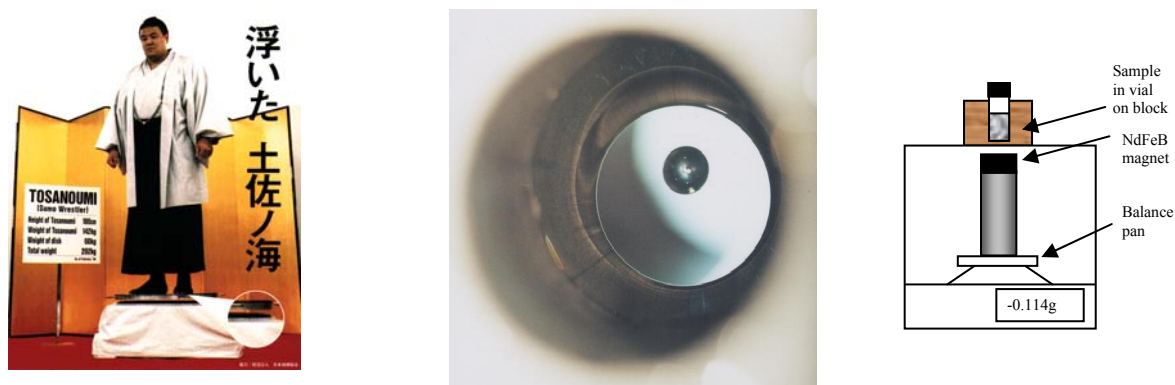


Figure 1. (left) Superconducting levitation of a 146kg sumo wrestler standing on a 60 kg magnet. (center) Diamagnetic levitation of a drop of H₂O in a 32T magnet producing a field 100 times stronger than the one we will use today. (right) Our experimental setup utilizing the Evan's Balance technique. The magnetic force (attractive or repulsive) that the sample exerts on a strong magnet is measured on a simple laboratory balance.

Instruments used for measuring magnetic moments are called magnetometers. A wide range of magnetometer designs are in use. The most sensitive magnetometers are inductive magnetometers such as SQUID magnetometers (superconducting quantum interference devices), which directly measure the number of magnetic flux quanta being produced by a sample as it moved through a set of detection coils. SQUID magnetometers typically operate at temperatures of 2-400K, and can give accurate magnetic data on samples with masses as small as 1 mg. However, the excellent sensitivity of a SQUID is generally offset by its large price tag. Simpler methods exist for measuring the magnetic moment of a sample, namely those which are sensitive to mass changes.

Paramagnetic and ferromagnetic materials move to align themselves with magnetic fields, and will move toward the region of highest magnetic field while diamagnetic materials are repulsed by magnetic fields and will move themselves toward the region of lowest magnetic field. The magnitude of the attractive or repulsive force can be determined if the mass change of the samples in the presence or absence of a magnetic field is measured – this is the principle of a Gouy balance. Thanks to Newton, we know that the force on the magnet is exactly the same magnitude as the force on the sample. An Evan's balance measures this force instead. Due to experimental considerations, it is generally simpler but less precise to measure magnetism using Evan's method. We will use a home-built Evan's balance to measure the magnetism of some inorganic compounds, as diagrammed in Figure 1.

For many common coordination compounds, the ligand field is sufficiently weak that electrons fill the *d*-orbitals to maximize the number of unpaired electrons. Magnetic properties can thus be used to identify the oxidation state (# of unpaired *d*-electrons) of a metal, or the ligand-field strength of a particular ligand. An example of using magnetism to assess ligand-field splitting (Δ_o) is shown below. Fe(II) with 6 O-donor ligands, as in $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, often experiences a weak ligand-field. In this compound, Fe(II) has a high-spin configuration with 4 unpaired electrons ($S = 2$). On the other hand Fe(II) with 6 CO ligands, as in $\text{Fe}(\text{CO})_6^{2+}$, experiences a strong ligand-field. Fe(II) in this complex has a low-spin configuration, with 0 unpaired electrons ($S = 0$). Only one of these configurations will have a paramagnetic moment – something we can easily measure in a magnetic balance.

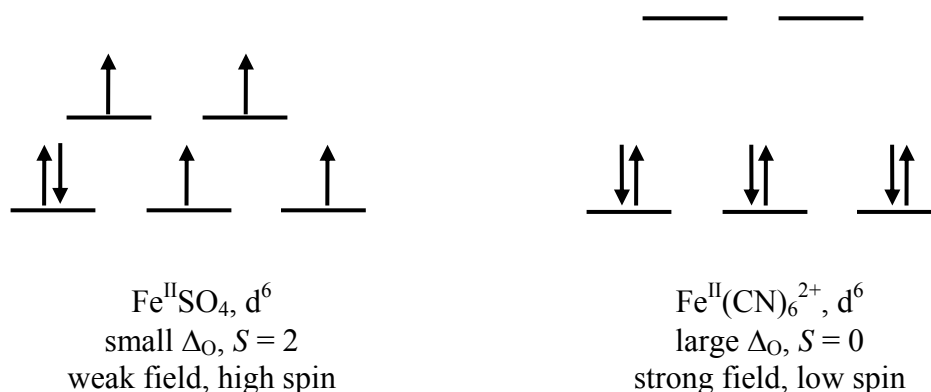


Figure 2. Changing the crystal-field splitting (Δ_o) can convert Fe(II) from a high-spin state to a low-spin state.

Magnetic metals are characterized by their effective magnetic moment, μ_{eff} , which depends on the number of unpaired electrons (n), or equivalently the total spin ($S = n/2$), and the Lande splitting factor, g . The effective magnetic moment, μ_{eff} , has units of Bohr magnetons (μ_B).

$$\mu_{eff} = g\sqrt{S(S+1)} \quad (1)$$

When there is no orbital momentum, $g \approx 2$ (the value seen for a free electron) and the effective magnetic moment will be the “spin-only” value: $\mu_{eff} = (\mu_{eff})_{s.o.}$. Another way to calculate the spin-only moment is eqn 2.

$$(\mu_{eff})_{s.o.} \cong \sqrt{n(n+2)} \quad (2)$$

Table 1. Magnetic Moments for Some Transition Metal Ions (3)

Ion	Theoretical ^a		Experimental ^a
	μ_S	μ_{S+L}	μ_{obsd}
V ⁴⁺	1.73	3.00	1.7–1.8
Cu ²⁺	1.73	3.00	1.7–2.2
V ³⁺	2.83	4.47	2.6–2.8
Ni ²⁺	2.83	4.47	2.8–4.0
Cr ³⁺	3.87	5.20	~3.8
Co ²⁺	3.87	5.20	4.1–5.2
Fe ²⁺	4.90	5.48	5.1–5.5
Co ³⁺	4.90	5.48	~5.4
Mn ²⁺	5.92	5.92	~5.9
Fe ³⁺	5.92	5.92	~5.9

^aData are in units of Bohr magnetons.

Experimental

WARNING: The magnets used in this lab generate extremely high magnetic fields (3000G). Do NOT move the magnets outside of the balances. Do NOT allow two magnets to approach each other, as they will violently slam into each other, potentially causing personal injury. Do NOT bring any credits cards near the magnets as they may be demagnetized. If you have a pacemaker, you are NOT allowed to perform this lab. Avoid bringing any strongly magnetic materials near these magnets. These magnets are brittle, and may be easily destroyed if mishandled.

The molar magnetic susceptibility (χ_M) is obtained by means of the Evan's method, which measures the attraction of a sample to a magnetic field. χ_M is calculated by use of the following equation, where C is a constant for the balance, m is the sample mass, MW is the sample molecular weight, L is the sample length, and $(R - R_o)$ is the balance reading (with minus without sample in holder). If you tare the balance before the measurement, R_o will be zero and your calculation will be simplified.

$$\chi_M = \frac{C \times L \times (R - R_o) \times (MW)}{m \times 10^9}$$

When the magnetic spins on the metal sites are weakly interacting (as they are for the salts we are measuring), it is possible to convert χ_{para} to μ_{eff} as shown below, where N_A is Avogadro's number, k is the Boltzmann constant, T is temperature in K, and β is a constant unit called the Bohr magneton (μ_B).

$$\mu_{\text{eff}} = \sqrt{\frac{3kT\chi_M}{N_A\beta^2}} = 2.828\sqrt{\chi_M T} \quad (\text{in units of } \mu_B)$$

Samples for this lab will be provided in sealed vials. Note that you need to know the mass and height of the sample within the vial before you can calculate its effective magnetic moment, μ_{eff} . Although the constant C used for calculating μ_{eff} can be analytically calculated if the magnetic field gradient is known, we will skip the math and instead use a sample of known magnetic moment to determine C and calibrate our magnetometer. In order to minimize errors from a non-linear field gradient, our vials have been prepared such that all the samples are of nearly constant height. You must be consistent in your sample placement between runs, as C will change if the height of the sample above the magnet varies. The sample must always be placed in the wood block and centered above the magnets.

Measure the mass change from an empty glass vial. Is there a measurable mass change on the balance? If so, you will need to either tare with an empty vial in the holder or subtract the vial signal from subsequent measurements (use the vial measurement as R_o).

The large magnetic moment on the high-spin compound $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ makes it a good material for standardizing our balance. You will get the biggest signal (and most accurate measurements) if the magnet is adjusted so that it is as close to the sample as possible. You should also make sure that the sample vial is centered over the magnet. Shift the position around until you find the region where the measured mass change of the magnet is maximized. What is the largest mass change on the balance you can get for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$? Calculate the constant C for your balance by assuming an effective magnetic moment of $4.87 \mu_B$ on each Fe atom.

Now measure the remaining samples. For each compound you measure, tabulate the values of the following: molecular weight (g/mol), mass (g), L (cm), R (filled), R_o (no sample), C, and χ_M . Turn in a table like the one below with your lab report. Remember that diamagnetic compounds do not have a moment (μ_{eff}) on their metal atoms.

Measure the vial containing a small amount of elemental Fe. How does this magnetism of this vial compare to the other vials. Why is there a large difference?

<i>Compound</i>	<i>Metal charge</i>	<i># valence electrons</i>	<i>HS μ_{eff} (predicted)</i>	<i>LS μ_{eff} (predicted)</i>	χ_M (calc)	μ_{eff} (calc.)	unpaired electrons (calc)
<i>MnSO₄•H₂O</i>							
<i>FeSO₄•7H₂O</i>							
<i>NH₄VO₃</i>							
<i>K₃[Fe(CN)₆]</i>							
<i>K₄[Fe(CN)₆]•3H₂O</i>							
<i>CoSO₄•7H₂O</i>							
<i>NiSO₄•6H₂O</i>							
<i>CuSO₄•5H₂O</i>							

The magnetism of paramagnetic compounds is highly dependent on temperature. Measure the molar susceptibility, χ_M , of one paramagnetic compound as a function of temperature. Do NOT set the cold sample directly on top of the glass on the balance – that could potentially crack the glass. Use the wooden holder to keep your sample separated from the glass lid of the balance. You will need to re-calibrate C when you use the wooden holder as the sample will be further from the magnet and will be experiencing a smaller field gradient. You can do this by comparing the room-temperature mass change of your sample with and without the wooden holder. Measure χ_M at three temperatures: 295K (room temperature), 195 K (dry ice / ethanol), and 77K (liquid N₂). Let your sample equilibrate in the cold temperature environment before quickly removing it and measuring its magnetism. Do some math while you are waiting.

WARNING: CRYOGENIC TEMPERATURES CAN BURN YOUR SKIN – AVOID DIRECT CONTACT WITH THESE VERY COLD SUBSTANCES, AND TRANSPORT YOUR COLD MAGNETIC SAMPLE WITH EXTREME CARE.

Plot your temperature-dependent data as $1/\chi_M$ vs. T and fit a line to the data. What is the x-intercept of this line? [This is a more general method that works even when the interactions between spins are NOT weak]. Use the slope of this line to calculate μ_{eff} for your sample based on the relation:

$$\frac{1}{\chi_m} = \frac{8.00}{\mu_{\text{eff}}^2} T \quad (3)$$

Also plot your data as χ_M vs T. Draw an appropriate curve through the data points.

Questions

1. Give examples of two classes of compounds made up of only 2nd period elements which have unpaired electrons and a paramagnetic moment.
2. Why is it important to know the height of the sample within the vial?
3. Calculate the spin-only magnetic moment for compounds with 0, 1, 2, 3, 4, and 5 unpaired electrons. Show your work.
4. Which compounds measured in this lab do you find to have no unpaired electrons? Draw the *d*-electron configurations of these compounds and explain why they are non-magnetic.
5. Which metal compounds investigated in this lab are present in the high-spin form? Where do their ligands fall in the spectrochemical series?
6. Which metal compounds investigated in this lab might have been in the high-spin form but are instead low-spin complexes? Where do their ligands fall in the spectrochemical series?
7. Which compound has a paramagnetic moment (μ_{eff}) that is well below that predicted by any spin model? What chemical cause might be responsible for this large deviation (20-40%) from the predicted spin-only moment? (hint: it is not orbital contributions, which would make the moment larger and not smaller)
8. Calculate the number of unpaired electrons for transition metals with 0-10 total electrons in the three most common situations: octahedral ligand geometry with a small Δ_{O} (high spin, HS), octahedral ligand geometry with a large Δ_{O} (low spin, LS), and tetrahedral ligand geometry (virtually always high spin due since $\Delta_{\text{T}} \sim 4/9 \Delta_{\text{O}}$). [None of our compounds are tetrahedral]

total # <i>d</i> electrons	# unpaired e ⁻ (tetrahedral, HS)	# unpaired e ⁻ (octahedral, HS)	# unpaired e ⁻ (octahedral, LS)
0		XXX	
1		XXX	
2		XXX	
3		XXX	
4			
5			
6			
7			
8		XXX	
9		XXX	
10		XXX	