

Pressure Induced Changes of the Magnetization of Mn₇ Molecules

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Abstract

The purpose of this project is to study the pressure dependence of the ground state spin of two different Mn₇ samples. Due to subtle differences in their structures, these Mn₇ samples have different ground spin states of $S = 11$ and $S = 16$. These types of molecular material are of wide interest for their applications in imaging and as a route to single-molecule magnets. The samples are placed inside a pressure cell at a temperature of approximately 4 K, and by increasing the pressure, we expect a change from the ground state to a higher state. The change of states is detected by using a resonant method based on a tunnel-diode oscillator. The reason for this project is to learn more about the physical properties of these two samples. Due to complications with the equipment, the Mn₇ samples were not studied, but the configuration and process to achieve this goal is described for continuing research.

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Introduction

Due to the fact that frequency can be measured with a great level of accuracy, resonant methods are precise and have high sensitivity for detecting physical properties of materials as function of temperature and magnetic field [1]. For this reason, the method was used for this project. Tunnel-diode oscillators have been used to study a variety of issues such as paramagnetic susceptibility in salts, penetration depth in superconductors, and phenomena in new materials like cuprate superconductors and borocarbide superconductors [1]. Therefore, this technique will be an excellent probe of phenomena related to the spin of different materials.

Another successful and increasingly important method for the study of solid-state phenomena is hydrostatic pressure. Historically, pressure measurements have been performed most commonly near room temperature or at very low temperatures, because of the limited standards for pressure calibration [2]. However, at low temperature it is possible to determine pressure using materials, such as lead and tin, for which its superconducting transition temperature is known.

Resistance thermometers are an important part of the project. The predictable change in electrical resistance of some material with respect to changing temperature allows the resistance thermometers to be useful as temperature sensors. Some resistance thermometers operating between 20 K and 300 K are made of platinum because of its linear relation between resistance and temperature and also because of its chemical inertness [3].

Using the aforementioned techniques, we want to put the samples under high pressure and low temperature conditions and see if we can detect any change in the physical properties of the material. The reason for this project is just a curiosity to know if the spin of these samples

can change under such conditions and maybe some other properties that we are not aware of may be detected as well.

Mn₇ Samples

The two samples that we want to study are Mn₇ samples that have a slight difference in their structure, so that one has a ground state spin of S = 11 and the second one S = 16 [4].

Figures 1 and 2 show the subtle differences in the structure of the samples.

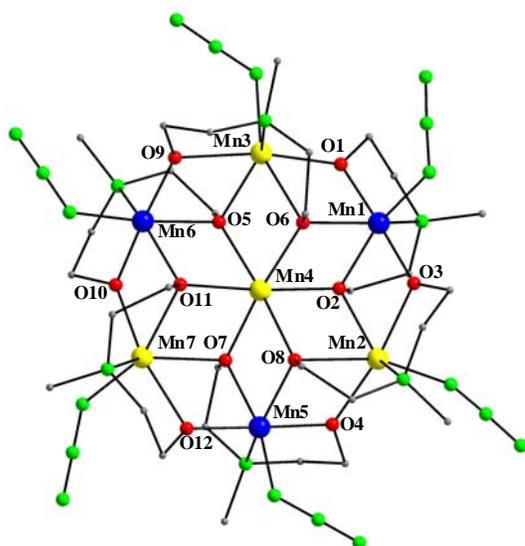


Figure 1. Mn₇ sample with S = 11

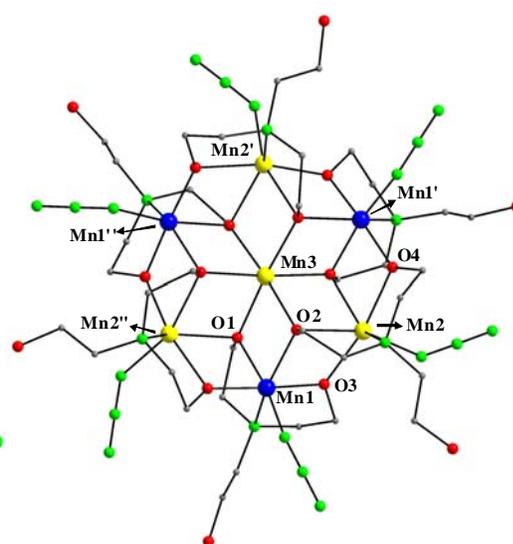


Figure 2. Mn₇ sample with S = 16

In Figure 1 we can see a near-planar Mn₇ unit comprising a central Mn atom held within a Mn₆ hexagon by six μ_3 -RO⁻ alkoxide arms of six mda²⁻ groups. The remaining mda²⁻RO⁻ arms bridge Mn₂ pairs of the hexagon, and the N atoms are terminally bound, as are the six N₃⁻ [4].

Figure 2 has the same symmetry as Figure 1 and is essentially the same structure with the difference of mda²⁻ vs teaH²⁻, the third alcohol arm being protonated and bound to Na⁺ ion instead of Mn [4].

Thermometry

The first part of this project deals with thermometry. Since the pressure cell will be at low temperatures, we need a thermometer that operates in the range of 4 K to 40 K. To achieve this goal, we built a resistance thermometer consisting of a Pt wire (length = 43.4 cm) wrapped around a cylindrical hollow piece of phenolic (length = 10.8 cm, radius = 0.46 cm). At each end of the platinum wire, two Cu leads were attached with silver epoxy, allowing a 4-wire resistance measurement to be made with a lock-in amplifier. The resistance of Pt as a function of temperature, $R(T)$, is expected to be linear from room temperature to approximately 50 K [5]. By measuring the resistance at room temperature $R(T_R = 298 \text{ K}) = 0.509 \Omega$, at liquid nitrogen temperature $R(T_{LN_2} = 77 \text{ K}) = 0.134 \Omega$, and in an ice and water mix $R(T_{ice} = 279 \text{ K}) = 0.471 \Omega$, we were able to verify the linear behavior of the Pt thermometer as shown in Figure 3.

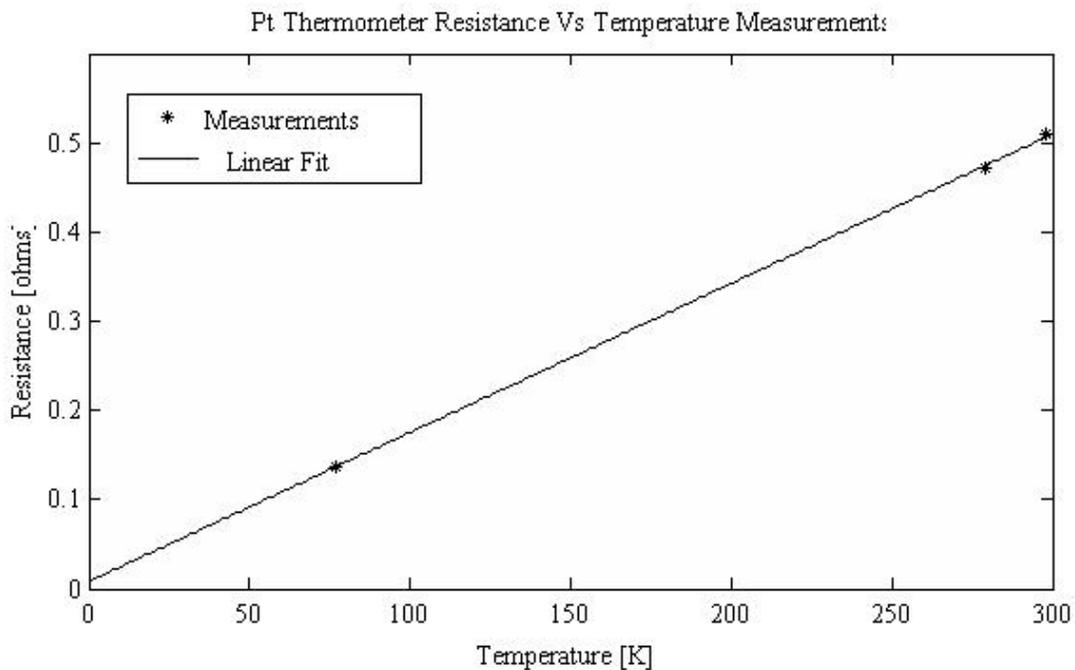


Figure 3. Linearity of platinum's resistance-temperature relation

Tunnel Diode Oscillator

The next part of the project involves the circuit for the tunnel diode oscillator (TDO). The circuit consists basically of a tunnel diode, a capacitor, and an inductor. A constant amplitude resonance is maintained by supplying the circuit with external power to compensate for dissipation. This power is provided by a tunnel diode that is forward biased with a voltage in the so-called negative resistance region [1]. This configuration makes a self-resonant circuit with a continuous oscillation and constant frequency. If any sample is inserted into the coil, there will be a change in frequency. Figure 4 shows the simplest circuit for a TDO. This circuit can be used as a base for more complex and precise circuits. In our case we built an RF choke to avoid undesired frequencies and noise, Figure 5.

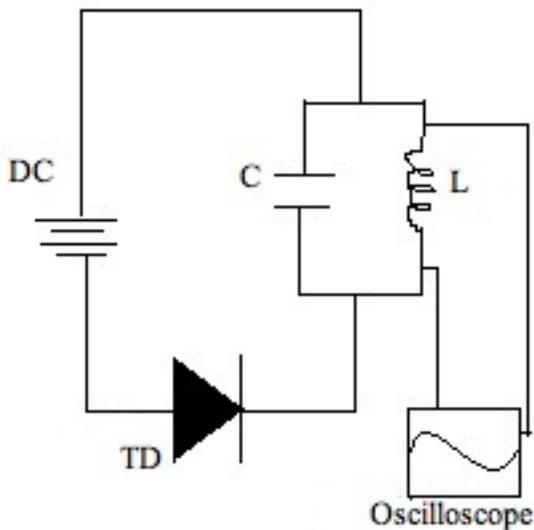


Figure 4. TDO Circuit

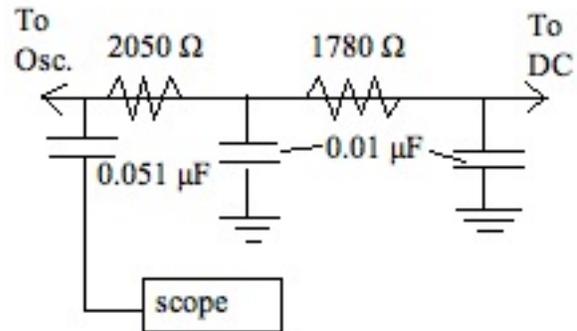


Figure 5. RF Choke

Pressure Cell

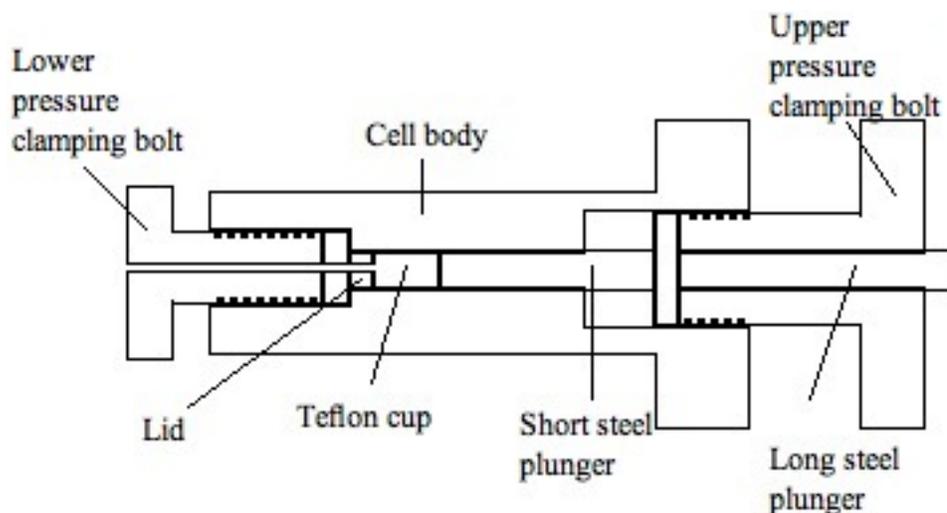


Figure 6. Pressure cell schematic

The pressure cell as shown in Figure 6 consists of a beryllium-copper main body with two clamping bolts, two boron-carbide steel plungers, two boron-carbide steel disks, and a Teflon cup. The Teflon cup goes inside the narrowest chamber of the pressure cell with the lid side towards the bottom of the cell because the lower clamping bolt and metal disk have a hole through which the wires of the coil inside the Teflon cup pass. On the other side of the Teflon cup there is a steel plunger, followed by a metal disk and then by the upper clamping bolt. This bolt is bigger and has a wider cavity in the center through which a second plunger can be introduced; this plunger extends about 1 cm from the top of the cell. By using a press we can apply pressure on the plunger, which at the same time is applying pressure to the metal disk, and the shorter plunger and also to the cup. To maintain this pressure we just turn the clamping bolt

and remove the pressure cell from the press and the longer plunger as well. With this cell we can achieve pressures up to 25 kbar.

The Teflon cup will contain a 1:1 n-pentane-isoamyl alcohol solution and a coil with the sample inside it. The leads of the coil come out the lid, which is sealed with “2850” black epoxy. The mixture of n-pentane-isoamyl alcohol is known to be a good hydrostatic pressure medium [2]. The coil is sealed in one end with filter paper and super glue and on the other end is partially sealed with filter paper and black epoxy, so that the solution can go inside the coil but the sample, a black powder-like material, cannot go outside it.

Probe Configuration and Experimental Procedure

With the pressure cell, the TDO circuit and thermometer ready, everything was mounted into a probe. This probe is going to be introduced into the cryostat and then the temperature will be lowered so that the measurements can be made using a LabVIEW program. First, the probe has 2 coaxial cables and 6 single wire connections. The pressure cell is held in a vertical position with screws that go from the base of the probe to the upper clamping bolt of the cell, Figure 7. The platinum thermometer is placed on top of the cell, wrapped with a piece of Cu foil to ensure good thermal contact with the cell and the four wires are connected each to one of the single wire connections of the probed. The phenolic had to be replaced by a smaller cylindrical piece of Teflon so that it could fit in the probe. The leads of the coil are soldered, one to the diode which has a 5 pF capacitor connected in parallel and the second one to the ground of the BNC cable. At the top of the probe the BNC connection goes to the RF choke, which is also connected to the DC and frequency counter. Since the BNC cables from the probe are long there is an attenuation of the signal and we used an RF amplifiers to improve the signal.

At first, we tried to use three small coils inside the Teflon cup, each coil with a different sample; one with lead and the other two with the different Mn_7 samples. The coils were so small and the leads so thin that we had problems making them oscillate and repairing them because wires broke. We tried coils made with a thicker wire with no success. Different size coils were made, and one of them seem to work fine it was small enough to fit in the cup but big enough to fit only one. It oscillated with the lead sample inside and it also oscillated inside the cup filled with solution, then when we put both at the same time we were not able to see any oscillations. Due to this type of problems with the coils, we were not able to make any pressure measurements for the samples or lead. The project will continue and hopefully these problems are solved soon so that results can be obtained.

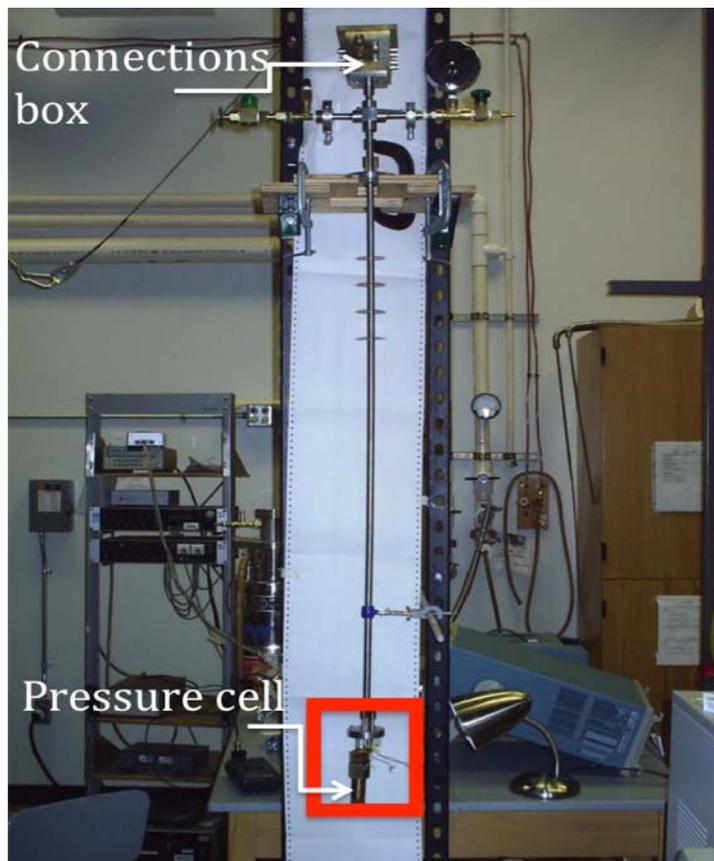


Figure 7. Probe configuration

Summary and Future Directions

In conclusion the projects objective is to discover if high pressure and low temperature can change the spin of Mn_7 samples. This objective can be achieved by using techniques such as resonant methods, resistance thermometry, and hydrostatic pressure methods. The next step that needs to be taken for the project is to pack Pb inside a coil and make sure that its superconducting transition can be detected by a change in frequency. If the transition for Pb is detected, then, the Mn_7 samples can be packed and loaded into the pressure cell and measurements can be made. With this last step we will be able to conclude if any changes occur.

Acknowledgements

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