Doping-Dependent Spin Reorientation Phenomenon in Holmium-based Orthoferrite
(Vibrating Sample Magnetometer Option)

http://education.qdusa.com/experiments.html
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In this Educational Module, students will synthesize and magnetically characterize samples of $HoFeO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$. $HoFeO_3$ undergoes a magnetic spin reorientation transition, and students will have the opportunity to investigate the effects of Cr doping on this phenomenon.

Introduction

There has been recent interest in rare-earth orthoferrites because of their magnetic properties and potential to create new spintronic devices. With a distorted perovskite structure, their chemical composition is $RFeO_3$, where R stands for rare earth ion. They contain two different magnetic ions, Fe^{3+} and R^{3+}. This suggests that there are three magnetic interactions R^{3+}- R^{3+}, R^{3+}-Fe^{3+}, and Fe^{3+}-Fe^{3+}, which lead to various magnetic phase transitions [1]. The most notable interaction is a spin reorientation (SR) transition during which the ordered spin systems rotate with respect to the crystal axes [1, 2]. The orientation of the strongly interacting spins of the R^{3+}-Fe^{3+} determines the temperature of the SR transition [3].

The origins of a material's magnetic behavior are complex and largely determined by the atomic configurations of its electrons following Hund's rules and the interactions between the electrons in the material environment (e.g. crystal field). In particular, key parameters that determine the magnetic behavior are the electron properties of spin (S), orbital angular momentum (L), and total angular momentum (J=S+L). The electrons can interact via direct exchange, superexchange, itinerant exchange, or indirect exchange. In direct exchange between valence electrons, the electrons can interact directly when

their charge distributions overlap. In superexchange, the electrons interact via the electrons from a mediating non-magnetic neighbor. Itinerant exchange occurs in metals when the conduction electrons interact with one another and mediate the interaction. For rare earth ions, the f-shell electrons can interact via both direct exchange and indirect exchange, whereby some f-shell electrons can be coupled due to interactions with electrons at the conduction level even though the valence charge distributions do not directly overlap [4].

The classic example of magnetic ordering is ferromagnetism, whereby the magnetic moments in a system spontaneously order along the same direction while below the Curie temperature. Antiferromagnetism, though it sounds to the contrary, is also a form of magnetic ordering whereby neighboring magnetic moments align antiparallel and sum to zero below the Néel temperature. Paramagnetic and diamagnetic systems do not possess a spontaneous net magnetic order and have magnetic moments that only align, or anti-align, with the application of magnetic field [5].

Orthoferrite compounds containing rare-earth and transition metal ions, such as $HoFe_{1-x}Cr_xO_3$ and $HoFeO_3$, possess magnetic ordering that depends on the competition between the spin configurations of the transition metals with those of the rare-earth ions [6]. At lower temperatures, the ordering of the rare-earth spins tends to dominate, which can lead to a spin reorientation (SR) transition [6]. Controlling the orientation of these spins can therefore lead to drastic changes in magnetic properties and offers unique functionality and potential as applications in future spintronic devices. Whereas conventional electronic devices utilize the electrical charge and current to perform computational operations, so-called spintronic devices would also use the associated magnetic spins to perform these tasks [7].

In this Educational Module, you will investigate the SR phenomenon in $HoFeO_3$ and then examine the effect of Cr doping on the SR. The investigation of new compounds created by careful doping has a rich history of tuning the physical properties of materials and even yielding surprising new behaviors.

Student Learning Outcomes

- Students will learn how to identify SR transitions from magnetic measurements.
- Students will develop proficiency in techniques for mounting samples for magnetic measurements.

- Students will operate the Vibrating Sample Magnetometer (VSM) Option of the VersaLab cryostat and gain experience in low temperature experiments.
- Students will apply foundational knowledge of relevant solid state physics to magnetic moment vs. temperature characterization.
- Students will learn how small chemical substitutions can affect a system's physical properties.

Materials List

Sample Preparation
Ho_2O_3, Fe_2O_3, and Cr_2O_3 Powder
Balance
Weighing Paper or Weighing Boats
Spatula or Scoopula
Mortar and Pestle
Alumina crucible
Muffle furnace
Hydraulic press
Pellet press die
Goggles, nitrile gloves, safety tongs, thermal gloves, and other PPE

Safety Information

Before attempting to perform any parts of this activity, please read the entire contents of: this Educational Module, the VersaLab User's Manual (1300-001), and the Vibrating Sample Magnetometer Manual (1096-100). Observe all instructions, warnings, and cautions. These are provided to help you understand how to safely and properly use the equipment, perform the experiments, and best achieve the student learning outcomes.

Quantum Design Inc. disclaims any liability for damage to the system or injury resulting from misuse, improper operation of the system, and the information contained in this Educational Module.

The safety warnings below apply to this Educational Module. Read them carefully and clarify any questions that you may have with your instructor before starting the work.

W A R N I N G !

Always use **P**ersonal **P**rotective **E**quipment (PPE) during every step of the sample preparation. Failure to do so might cause bodily harm.

W A R N I N G !

Acetone is hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Slightly hazardous in case of skin contact (permeator). For more information consult the Material Safety Data Sheet available on this website:

http://www.sciencelab.com/msds.php?msdsId=9927062.

C R U S H I N G   H A Z A R D !

Before using the die and hydraulic press, please read the entire contents of the manual specific to that equipment. Observe all instructions, warnings, and cautions. Failure to do so might cause bodily harm.

H O T   S U R F A C E !

Before using the furnace and combustion boats to sinter the samples, please read the entire contents of the manual specific to that equipment. Observe all instructions, warnings, and cautions. Failure to properly handle hot surfaces might cause bodily harm.

Sample Preparation

Be sure to use appropriate Personal Protective Equipment (PPE) before performing the synthesis.

The polycrystalline compounds of the $HoFeO_3$ and $HoFe_{1-x}Cr_xO_3$ (where x =0.5), are to be prepared by solid state reaction using purity > 99.9% powders of Ho_2O_3, Fe_2O_3, and Cr_2O_3 as starting materials [3,6].

1. Calculate the proper stochiometric ratios for:
    $Ho_2O_3 + Fe_2O_3 \rightarrow HoFeO_3$ (parent compound)
    $2Ho_2O_3 + Cr_2O_3 + Fe_2O_3 \rightarrow 4HoFe_{0.5}Cr_{0.5}O_3$ (Cr-doped compound)

2. Using a chemical spatula and weigh paper, weigh out appropriate amounts of Ho_2O_3, Cr_2O_3, and Fe_2O_3 in order to create both $HoFeO_3$ and $HoFe_{0.5}Cr_{0.5}O_3$.

3. For each sample, pour your powders into a mortar bowl and mix/grind with a pestle for at least 5 minutes or until well mixed. It is recommended to use a circular grinding motion on the pestle for best results (Figure 1).
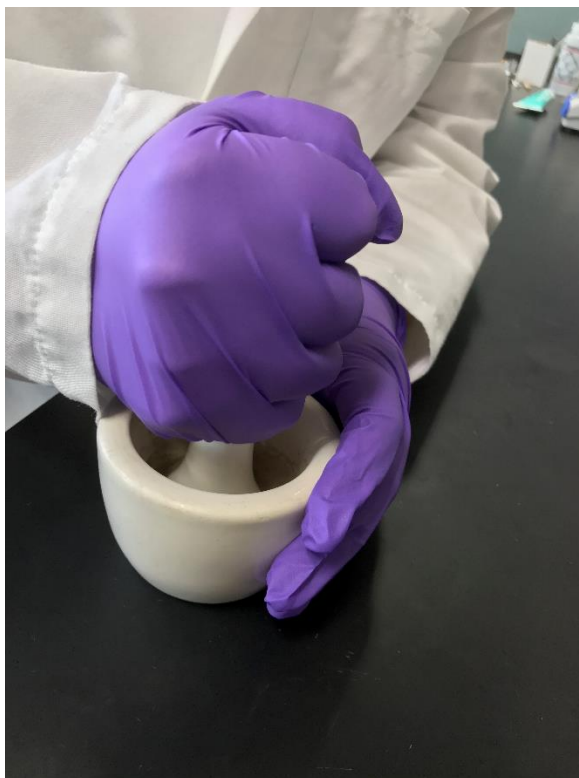
Figure 1. Grinding the powders with mortar and pestle.

4. Place the sample powders into their own alumina combustion boats. Sinter both compounds in a furnace in air at 1200 °C for 12 hours. A one hour ramp to 1200 °C followed by a one hour ramp down to room temperature after dwelling is suggested.

5. Once cooled, re-grind the powder. If a hydraulic press and die are available, form a pellet with the powder (Figure 2). Solid samples are highly recommended over powder samples.
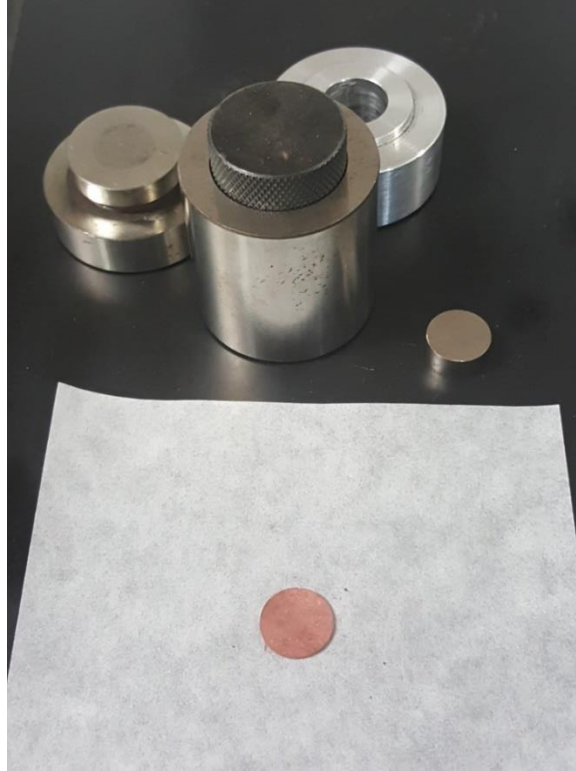
Figure 2. Pellet die and resulting pressed sample.

6. Perform a second sintering of the pellet (Figure 3) in air at 1400 °C for 24 hours [3].
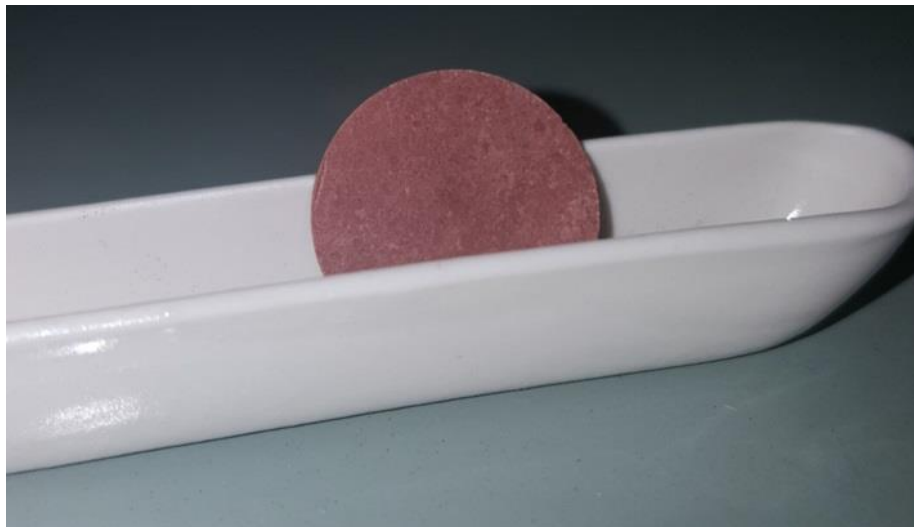

Figure 3. An alumina combustion boat is suitable for the sintering.

7. Only a few mg of sample is required for this experiment. This small sample can be obtained by chipping the large pellet by tapping it gently with a

sharp object. <u>Be sure to measure your mass!</u> Magnetization is typically reported in units of emu/g or emu/mole.

Sample Mounting with the VSM

Please refer to the VersaLab User's Manual (1300-001) and the Vibrating Sample Magnetometer Manual (1096-100) to properly load and measure samples. Samples may be mounted on either the brass holder or quartz paddle that comes standard with your VSM. GE 7031 varnish is a convenient medium to adhere samples to the holders, but time and care must be used to clean the varnish off with alcohol or toluene. Whatever you choose, be aware that mounting media may contribute to the measured signal, so it is best to establish what your experimental background is.

Please read Application Note 1096-306 [8] on VSM sample mounting on the QD website for more guidance on this topic. It is highly recommended to press the powders into a pellet and use a small solid piece for measurement. Great care should be taken to prevent any sample powder from contaminating the VersaLab sample chamber. If you are using another method that somehow encapsulates the powder, be sure that this method will not leave loose powder in the sample chamber. This may include the use of a gelatin cap, or in the very worst case, trapping the powder in a varnish, epoxy, or cement matrix. Be careful to measure the mass of the powder independent of the encapsulation medium.

For now, we will prepare to determine the measurement background from just your mounting medium (Kapton tape, GE varnish, etc.) <u>without your sample.</u> Place some of the mounting medium onto your sample holder 35 mm from its end. This is facilitated by the sample holder mounting station (Figure 4). For future reference, you should obtain the mass of the mounting medium.

Figure 4. Quartz paddle sample holder with sample in mounting station. The sample is held in place using 7301 varnish.

Sample Holder Measurement Using the VSM

Refer to your VersaLab manual to prepare the VSM for operation.

1) To load your sample into the VSM, first bring the temperature up to 300 K and allow it to stabilize. In MultiVu, click "Open Chamber" on the VSM Install/Remove Sample Wizard dialog box. You will notice the VSM motor head move to the top "load" position (Figure 5). Remove the black cap.

Figure 5. The VSM motor in "load" position.

2) Screw the sample holder onto the sample rod and gently insert that into the VSM. The end of the rod is held in place by a set of magnets, so you will feel a tug as the rod seats itself into place (Figure 6).
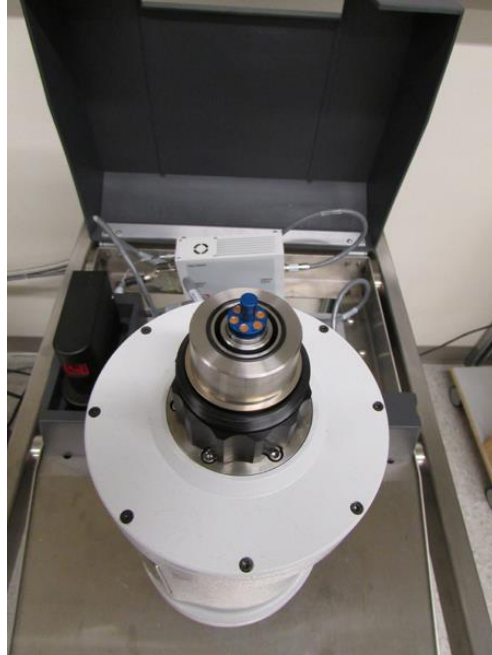

Figure 6. Inserted sample rod.

3) In MultiVu, click "Next" and then click on "Browse" to begin inputting your data file properties.

4) Clicking "Next" again will bring you to the sample centering dialog (Figure 7). Since this is only a measurement of your mounting media, we will choose a high field in order to determine what the maximum contribution might be. Feel free to set the field between 1 and 3 T (or 10,000 to 30,000 Oe).
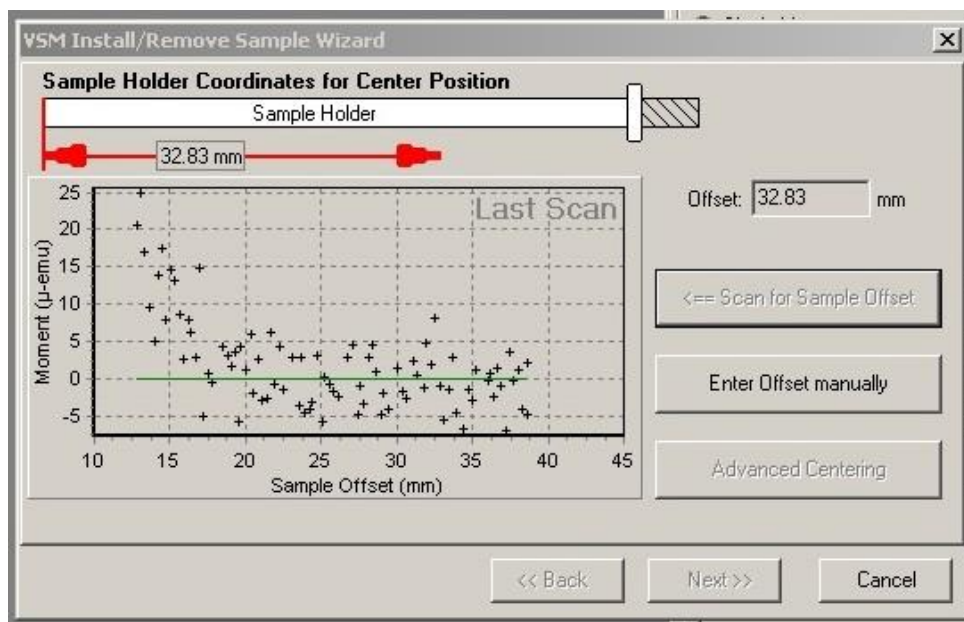
Figure 7. Sample centering scan dialog.

5) After the field settles, click "Scan for Sample Offset" and wait for the VSM. You will notice that the VSM motor drops down to the bottom "touchdown" position and then scans the holder. This will take a few seconds.

6) When the scan is complete, you may see something similar to that of Figure 8. The first dialog box will identify the center position. If you were attempting to measure something with a small magnetic moment that did not come up in the centering scan, you could enter the sample position manually. In this case, we see that the maximum background contribution of the holder at 3 T is 2×10^{-5} emu, which is sufficiently small for these particular samples.
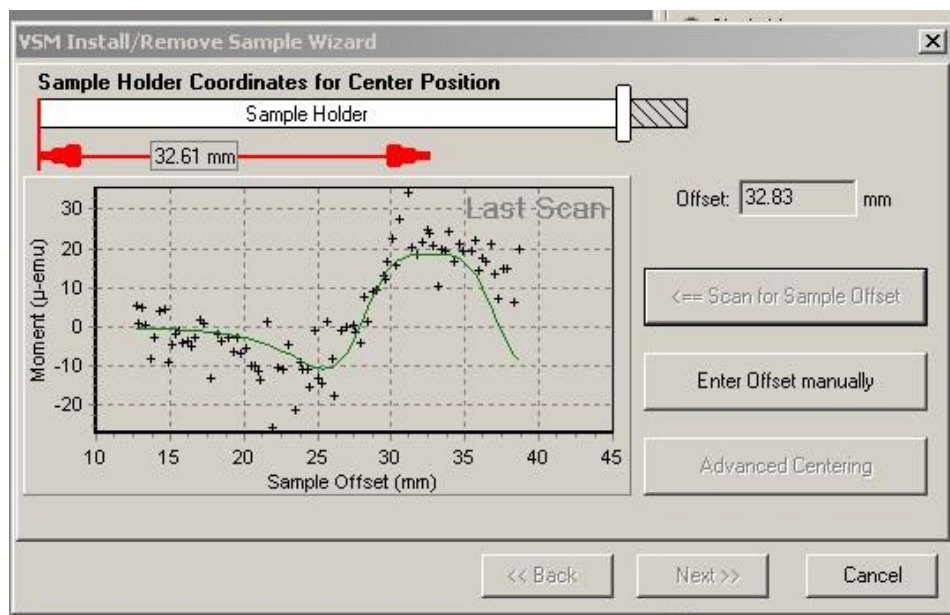
Figure 8. Sample centering result for the brass holder.

7) Ask your instructor if you should proceed to measure the Moment vs. Magnetic Field or Moment vs. Temperature properties of the sample holder. If your background contribution is large (10^{-3} or perhaps 10^{-4} emu), click "Back" on the dialog box until you get back to the first window that allows you to click on "Open Chamber." You need to either choose a new mounting medium or thoroughly clean your sample holder and mounting choice of any magnetic contamination.

If your instructor tells you to perform a scan, then click "Next" and "Close Chamber" on the next dialog. Wait for the chamber to pump down and for the "Finish" button to be active.

Write a short sequence using either the "Moment vs. Field" or "Moment vs. Temp" command, and hit "Run" when you are ready to go.

If, however, your instructor tells you to move on, then click "Back" repeatedly until you can return to the first dialog and click "Open Chamber" to remove the sample rod.

Sample Mounting

1) Weigh a sample of $HoFeO_3$. A small sample with a mass of a few mg should yield a good measurement. Again, a solid pellet piece is recommended, but if

you are using a powder encapsulation method, be sure to measure how much powder you have independent of the encapsulation medium.

2) Mount the sample 35 mm from the end of your sample holder using whatever medium you previously measured. Keep in mind that the sample will be oscillated by the motor, so be sure that it is secure!

3) In MultiVu, click "Open Chamber" in the VSM Install/Remove Sample Wizard dialog box and load your sample.

4) In MultiVu, click "Next" and then click on "Browse" to begin inputting your data file properties.

5) When an actual sample is mounted on the holder, a good initial scan field for centering is 1000 Oe. Set the field to this value.

6) When the field is stable, click "Next" to open the centering dialog window and perform a centering scan. There should be no problem in locating and centering the sample.

7) Click "Next" and check the "Extended Purge" box before you click on "Close Chamber." Extended Purge is a good idea since we will be cooling the sample and want to make sure that no water or water vapor is present, which can create an additional unwanted background at low temperatures (see application note 1014-210 from Quantum Design [9]). When the "Finish" button becomes available, click "Finish."

Characterizing Magnetization vs. Temperature -- M(T)

We will perform what is called a Zero Field Cooled (ZFC) measurement followed by a Field Cooled (FC) Cooling measurement. When doing a ZFC measurement, you cool the sample to the lowest temperature sought in the absence of any magnetic field. Before performing ZF cooling, ramp up the superconducting magnet to at least 1 T and then oscillate back down to 0 Oe to help remove remanence from the magnet (see application note 1070-207 from Quantum Design [10]). Once the magnetic remanence is removed, the sample is cooled to the desired temperature. The magnetic field is then applied, and the sample's magnetization is measured as it warms up. When doing a FC measurement, you measure the sample's magnetization as it cools in the presence of an applied magnetic field.

A sample sequence might look like this:

Set Temperature 300 K
Set Field 10,000 Oe
Wait for Field
Set Field 0 Oe, 200 Oe/s, Oscillate
Wait for Temperature, Field
Set Temperature 50 K
Wait for Temperature
Set Field 1000 Oe
Moment vs. Temperature, 50 K to 300 K, measure continuously, 1 K/min
     sweep
Moment vs. Temperature, 300 K to 50 K, measure continuously, 1 K/min
     sweep
Set Standby Mode
End Sequence

In the sequence above, we make sure to begin at room temperature with no applied magnetic field. Then we ZFC down to 50 K. The field is applied once the sample is cold, and the measurement occurs as the sample warms. Measuring continuously with a 1 K/min warming rate should yield good data that minimizes the temperature difference between the sample and coil thermometer. You may adjust the sweep and averaging parameters as you see fit. The second Moment vs. Temperature scan is the FC measurement. After that, Standby will return the system to 300 K and 0 magnetic field.

Although these measurements can take a long time to run, be sure to check on your data occasionally to look for errors and to make sure that the results make sense.

Do you see any spin reorientation transition or other interesting behavior?

Plot your data as the inverse molar susceptibility χ (in units of mole/emu) vs. Temperature (in units of Kelvin). This approach may allow you to better discover interesting features in your data.

Characterizing Magnetization vs. Magnetic Field -- M(H)

From your M(T) results, the SR transition temperature should be clear. You can also investigate whether your sample exhibits any transition between paramagnetic, antiferromagnetic, and ferromagnetic states using the Moment vs. Field measurement. Either create a new data file from the File tab of the VSM

command dialog window, or use the New Data File command in writing a sequence.

The idea is to obtain a Moment vs. Field scan at high and low temperatures in order to observe the effects of a transition.

A sample sequence might look like this:

New Data File
Set Temperature 300 K
Set Field 10,000 Oe
Wait for Field
Set Field 0 Oe, 200 Oe/s, Oscillate
Wait for Temperature, Field
Moment vs. Field, 0 Oe to 30,000 Oe, five quadrants, measure
       continuously, 10 Oe/s sweep
Set Field 0 Oe, 200 Oe/s, Oscillate
Wait for Field
Set Temperature 50 K
Wait for Temperature
New Data File
Moment vs. Field, 0 Oe to 30,000 Oe, five quadrants, measure
       continuously, 10 Oe/s sweep
Set Field 0 Oe, 200 Oe/s, Oscillate
Set Temperature 300 K

In the above, we open a new data file and then perform the Moment v. Field measurement at room temperature. Again, you may choose the measurement sweep parameters that fit your time constraints. Five quadrants can be selected in the Moment vs. Field dialog box by clicking and dragging so that a white field appears over the amplitude points (Figure 9). The measurement will start at 0 field, ramp up to the highest field at 3 T, then down to -3 T, and then back up to 3 T (five quadrants on the graph). This will yield a complete hysteresis loop, and yes, this will take a while depending on your sweep speed.
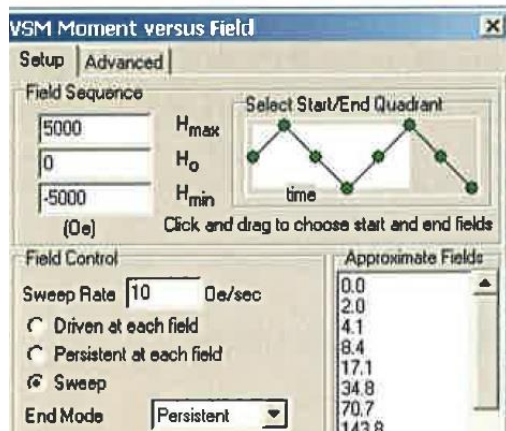
Figure 9. Moment vs. Field dialog showing the five-quadrant measurement sequence. Clicking and dragging on the white box removes or adds quadrants.

Afterwards, the field is set to 0 Oe in Oscillation mode to minimize the remnant field in the VersaLab magnet. The sequence then cools the sample in zero field and opens a new data file to obtain the Moment vs. Field measurement.
Do you observe any differences in the M(H) plots as you change temperature?

Repeat for HoFe$_{0.5}$Cr$_{0.5}$O$_3$

Now that you have your results for HoFeO$_3$, repeat the measurements with the Cr-doped sample and examine the differences in behavior.

As you perform your investigation, you may decide that you want to perform more measurements on both your samples to get a better understanding of what is occurring in the system.

Additional Moment Analysis

As mentioned before, you should convert your data to units of emu/mole. The reason to do this is that by plotting the inverse molar susceptibility χ^{-1} vs. temperature, with χ in units of emu/mole and temperature in Kelvin, the slope at high temperature yields the effective magnetic moment, i.e. the total magnetic moment in the paramagnetic phase. From [11] the magnetic susceptibility is,

$$\chi = \frac{M}{B} = \frac{Np^2\mu_B^2}{3k_BT} = \frac{C}{T}$$

where M is the magnetization, B is the magnetic field, N is the number of atoms, p is the effective moment, μ_B is the Bohr magneton constant, k_B is the Boltzmann constant, T is the temperature, and C is the Curie constant.

Plotting $(1/\chi)$ in units of Oe*mole/emu vs. T in the linear (paramagnetic) region, you can obtain

$$p \approx \sqrt{\frac{8}{slope}}$$

where p is the effective moment in units of μ_B and the slope is $\Delta(1/\chi)/\Delta T$ from the plot of your data. You can also determine the Curie-Weiss temperature from the T-intercept of your plot [12].

For $HoFeO_3$, the linear region of χ^{-1} vs T starts at 650 K and is out of the VersaLab's temperature range. However, you should be able to see a linear region in your $HoFe_{0.5}Cr_{0.5}O_3$ data approximately above 270 K [12].

Data and Discussion

1) Explain the fundamental physics principles of a VSM measurement. The VSM manual is a good place to start, and you should also explore other references, such as [5].
2) What is a spin reorientation transition?
3) What sort of technological application can you imagine that would use the SR transition?
4) What effect does Cr doping have on the SR transition of $HoFeO_3$? What is the physical reason for this?
5) Did you observe a difference between your ZFC and FC data? If so, can you explain the difference?
6) Based on your M(H) results, describe what sort of transitions, if any, your compounds undergo. Are your results due to the SR transition, or something else? Perform a literature search and even perform more measurements at other temperatures to help discover the answer.
7) How did the magnitude of magnetization compare between the two compounds. What reason might there be for this difference in behavior?

References

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