Fe_3O_4 Magnetic Characterization (Vibrating Sample Magnetometer Option)

http://education.qdusa.com/experiments.html

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In this Educational Module, students will characterize the magnetic properties of a sample of Fe_3O_4, more commonly known as magnetite. The primary emphasis will be to observe the Verwey transition, which is a structural phase transition accompanied by charge ordering. Although first reported in 1939, the underlying physics of the Verwey transition continues to be studied to this day.

Introduction

Imagine that you are hiking on a trail and stumble upon some dark rock, which perhaps may have some glittery specks in it. A paperclip falls out of your pocket and is magnetically attracted to this rock. You stop to investigate. How would you go about studying it? What might you discover?

Magnetite (Fe_3O_4) is a naturally occurring mineral that historically has been called “lodestone”. Lodestone was sought throughout antiquity due to its attractive ferromagnetic properties [1]. Today, magnetite is used in several industrial applications that include inks and cosmetics [2]. Furthermore, it has even been discovered to be produced and used by magnetotactic bacteria [3]. In 1939, E. J. W. Verwey investigated the resistivity vs. temperature behavior of Fe_3O_4 and identified a transition whereby the resistivity increased by two orders of magnitude (Fig. 1) [4, 5]. He attributed this behavior to a charge ordering transition, where the ordering of charge removed the necessary fluctuations required for metallic conduction, and his name has been associated with this phenomenon ever since.

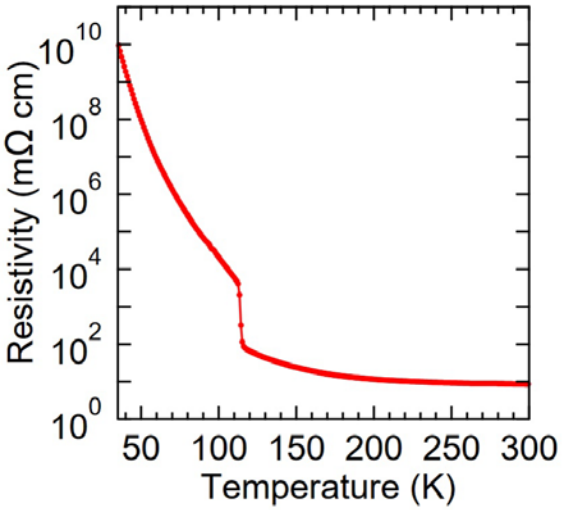

Figure 1. The Verwey transition as demonstrated by a plot of resistivity vs. temperature reproduced from [5].

Studies on the unique physical properties of Fe_3O_4 continued through the decades. A relatively more recent work probed the atomic structure of Fe_3O_4 via powder X-ray diffraction and Mössbauer spectroscopy [6]. From this work it was concluded that a structural phase transition results in a change from an inverse to normal spinel (Fig. 2) upon cooling through the Verwey transition temperature. However, this structural transition does not completely describe the presence of charge ordering, and recent studies suggest that the formation of a three site Fe trimeron sublattice is responsible for the electronic ordering [7]. As such, the subtle and interesting underlying physics of why the transition occurs continues to be studied to this day.

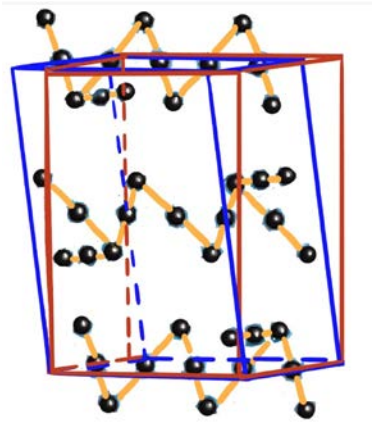

Figure 2. Sketch showing the Fe trimeron sublattice and the structural phase transition between the higher temperature cubic inverse spinel in red and the lower temperature monoclinic spinel in blue [6, 7].

Fe_3O_4 has been studied electrically via resistivity measurements and structurally via crystallographic techniques. It has also been reported that a change in the magnetic anisotropy – the directional dependence of a material's magnetic properties – due to the change in the crystalline symmetry can be observed at the Verwey temperature [8]. In this education module, you will have the opportunity to explore the Verwey transition via magnetic measurements.

Student Learning Outcomes

- Students will learn how to identify phase 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.

Safety Information:

Before attempting to perform any parts of this student experiment, please read the entire contents of: this Educational Module, the VersaLab User's Manual (1300-001), and the Vibrating Sample Magnetometer Manual (1096-100), and 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 reach the best 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 following Safety warnings apply to this Educational Module. We recommend that you study them carefully and discuss the details with your instructor before starting the work:

WARNING!

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

TOXIC HAZARD!

Acetone is toxic if swallowed. For more information consult the Material Safety Data Sheet available on this website:
http://www.guidechem.com/msds/110-20-3.html

Materials List

Sample Preparation
Magnetite Sample
Balance
Weighing Paper or Weighing Boats
Varnish

Fe_3O_4 Sample Preparation

Wearing proper personal protective equipment (PPE), break off a small piece of magnetite (Figure 3). One recommended procedure is to place the mineral in a bag and carefully strike it with a hammer. Be sure to measure the mass of your sample, as magnetization is often reported in units of emu/g.

Figure 3. Magnetite with pieces broken off. The small (~mm^3) fragments are sufficient for this VSM measurement.

Please refer to the VSM manual 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. You may also use Kapton tape or tightly wrapped Teflon tape to mount samples. Whatever medium you choose, be aware that it will contribute to the measured signal, so it is necessary to establish what your experimental background is first.

Please read Application Note 1096-306 [9] on VSM sample mounting on the QD website for more guidance on this topic.

Measuring the Background Signal

You will first measure the background of your mounting material to ensure that it does not significantly contribute to the measurement of your sample. Set aside the magnetite and, for now, choose your mounting medium (Kapton tape, GE varnish, etc.) and place that 35 mm from the end of your holder. This is facilitated by the sample holder mounting station (Figure 4). For future

reference, you should obtain the mass of the mounting medium so that you can measure your noise in emu/g.

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

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

1) In order to load your sample, first bring the temperature up to 300 K and allow it to stabilize for a few minutes. 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 it 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 the instrument (Figure 6).

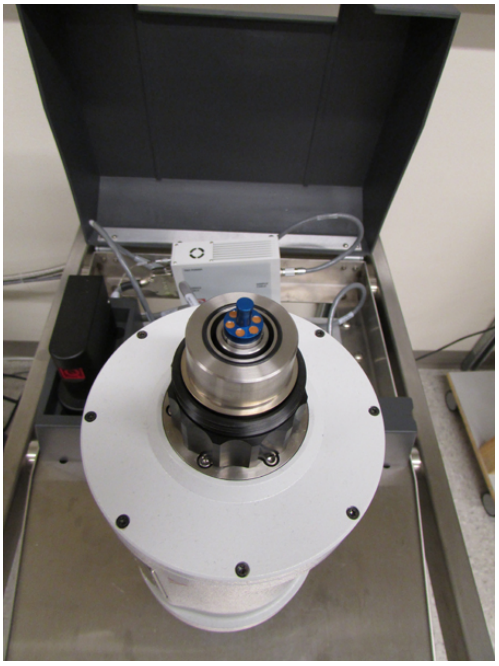

Figure 6. Inserted sample rod.

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 adhesive, we will choose a high field to determine what the maximum contribution might be. Feel free to set the field between 1-3 T (or 10,000-30,000 Oe).

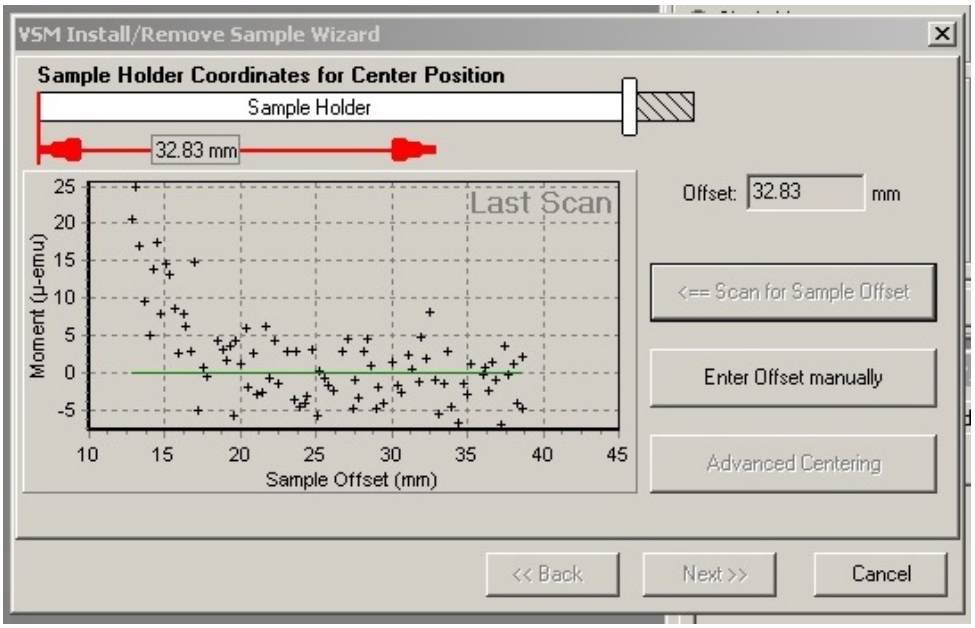

Figure 7. Sample centering scan dialog.

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. In this case, we see that the maximum background contribution of the holder at 3 T is 2×10^{-5} emu, which will be small compared to the signal we expect for our magnetite sample.

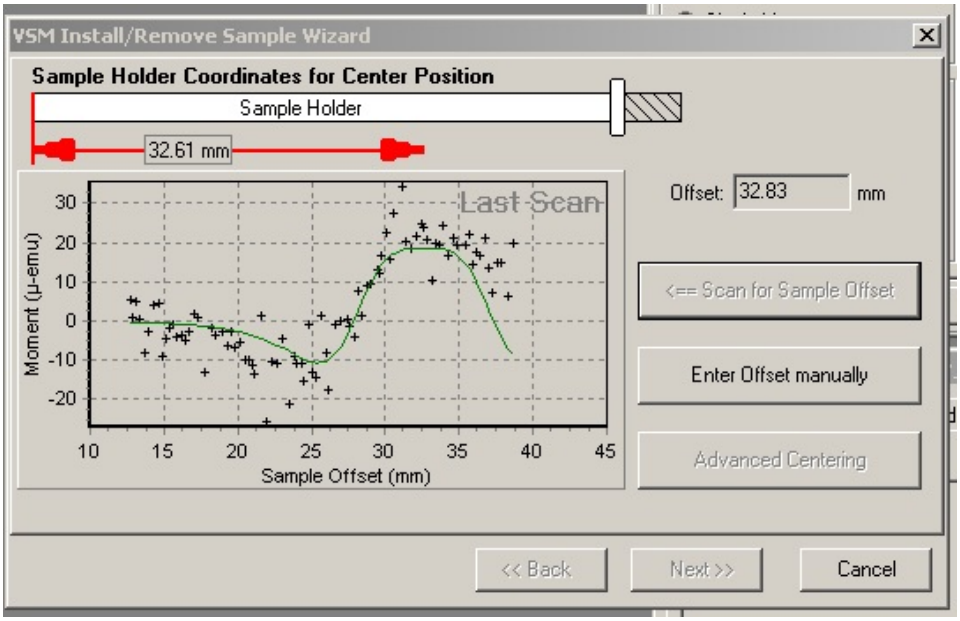

Figure 8. Sample centering result for the brass holder.

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}-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 complete background measurement 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.

At this point, it is a good idea to ramp up the magnet to at least 10,000 Oe and then set the field to *oscillate* back to 0 Oe. This procedure will help eliminate remnant field in the superconducting magnet that may have been left by a previous measurement.

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 to measure the magnetite sample, then click "Back" repeatedly until you can return to the first dialog and hit "Open Chamber" to remove the sample rod.

Sample Mounting

1) Weigh your Fe_3O_4 sample. A small piece with a mass of a few mg should yield enough magnetic material to ensure a good signal-to-noise ratio (SNR). You could also obtain a rough measurement of the volume of the sample.

2) Mount the sample 35 mm from the end of your sample holder using your mounting medium (Figure 4). 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 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 scan. There should be no problem in locating and centering the sample. The sample position found from scanning the sample using the installation wizard should be close to your own measurement of the sample offset, near 35 mm.

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 is present, which can create an additional unwanted background at low temperatures (see application note 1014-210 from Quantum Design [10]). When the "Finish" button becomes available, click "Finish."

Characterizing Magnetite: M(T)

We will perform what is called a Zero Field Cooled (ZFC) measurement followed by a Field Cooled (FC) 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 [11]). Once the lowest temperature has been reached, the field is turned on, 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 ZFC/FC measurement sequence might look like this:

Set Temperature 300 K
Wait for Temperature
Set Field 10000 Oe, 200 Oe/s, Linear
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
Wait for Field
Moment vs. Temperature, 50 K to 300 K, measure continuously, 2 K/s sweep
Moment vs. Temperature, 300 K to 50 K, measure continuously, 2 K/s 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 cool the sample down to 50 K in zero field. The field is applied once the sample is cold, and the ZFC measurement occurs as the sample warms. Measuring continuously with a 2 K/s 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.

As your measurement progresses, do you notice anything that indicates interesting behavior, such as the Verwey transition?

Characterizing Magnetite: M(H)

From your M(T) results, it should be clear what temperature the Verwey transition occurs. You can further characterize the sample's magnetic properties using the Moment vs. Field measurement routine. 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.

A sample sequence might look like this:

New Data File
Set Temperature 300 K
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, 50 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, 50 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 needs. 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. Note the estimated time in the VSM Moment vs. Field dialog box.

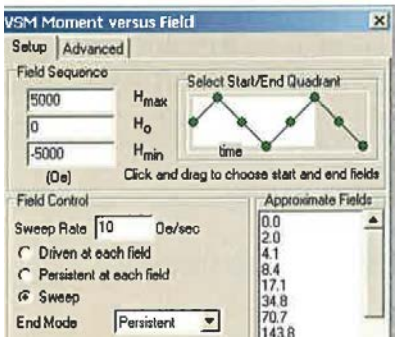

Figure 9. Moment vs. Field dialog showing the five quadrant measurement sequence. Clicking and dragging on the white box removes or adds quadrants.

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 at a lower temperature, to see if there is any difference.

Your obtained M(H) plot should be comparable to plots shown in text such as reference [12]. Fe_3O_4 is known to be ferrimagnetic, as a result of the competition between ferromagnetic and antiferromagnetic moments within the system [13].

If you have time, you may additionally perform a series of M(H) measurements at several temperatures spaced 1 K apart above and below the Verwey transition. You are encouraged to plot your sample's coercivity with respect to temperature.

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 [12].
2) Explain in more detail what the structural transition is for Fe_3O_4 at the Verwey temperature. How does it explain your results?

3) What is your Verwey transition temperature, and how do you know that you have identified the transition? Is this a first order phase transition?
4) Explain the difference between your ZFC and FC result of the Moment vs. Temperature. What is physically different between the two types of measurements, and what does it do to the sample? Reference [12] is a good starting point.
5) How do your M(H) plots compare between higher and lower temperature? What difference do you see, for instance, in the coercivity as you change the temperature?
6) What was the value of your saturation magnetization obtained from your M(H) plot? Would you consider this sample to be a "hard" or "soft" magnetic material? Why?

References

[1] A. Mills, "The lodestone: history, physics, and formation," *Annals of Science* 61, 273-319 (2003).
[2] Alfa Aesar chemical supply. https://www.alfa.com/en/catalog/012374/
[3] D.R. Lovley et al., "Anaerobic production of magnetite by a dissimilatory iron-reducing microorganism," *Nature* 330, 252-254 (1987).
[4] E.J. Verwey, "Electronic conduction of magnetite (Fe_3O_4) and its transition point at low temperatures," *Nature* 144, 327-328 (1939).
[5] S. Borroni et al., "On the Verwey transition in magnetite: the soft modes of the metal-insulator transition," https://arxiv.org/pdf/1507.07193.pdf.
[6] G. Kh. Rozenberg et al., "Structural characterization of temperature- and pressure-induced inverse normal↔spinel transformation in magnetite," *Physical Review B* 75, 020102 (2007).
[7] S. de Jong et al., "Speed limit of the insulator-metal transition in magnetite," *Nature Materials* 12, 882 (2013).
[8] M. Bohra et al., "Magnetic properties of magnetite thin films close to the Verwey transition," *Journal of Magnetism and Magnetic Materials* 321, 3738-3741 (2009).
[9] "VSM Sample Mounting Techniques," QD Application Note 1096-306, http://www.qdusa.com/sitedocs/appNotes/ppms/1096-306.pdf
[10] "Oxygen Contamination," QD Application Note 1014-210, http://www.qdusa.com/sitedocs/appNotes/mpms/1014-210.pdf
[11] "Using PPMS Superconducting Magnets at Low Fields," QD Application Note 1070-207, https://www.qdusa.com/sitedocs/appNotes/ppms/1070-207.pdf
[12] M. McElfresh, "Fundamentals of Magnetism and Magnetic Measurements" (1994). https://www.qdusa.com/sitedocs/appNotes/mpms/FundPrimer.pdf
[13] J. Stöhr, Chapter 7, *Magnetism: From Fundamentals to Nanoscale Dynamics*. Springer, 2006.