



Fe₃O₄ (Magnetite) Electronic Characterization (Electrical Transport Option)

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

**Prof. Stephen Tsui and Bailey Smith
California State University San Marcos**

In this Educational Module, students will characterize the resistive properties of a sample of Fe₃O₄, 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

Magnetite (Fe₃O₄) 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 Fe₃O₄ and identified a transition whereby the resistivity increased by two orders of magnitude (Figure 1) [4, 5] upon cooling. 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.

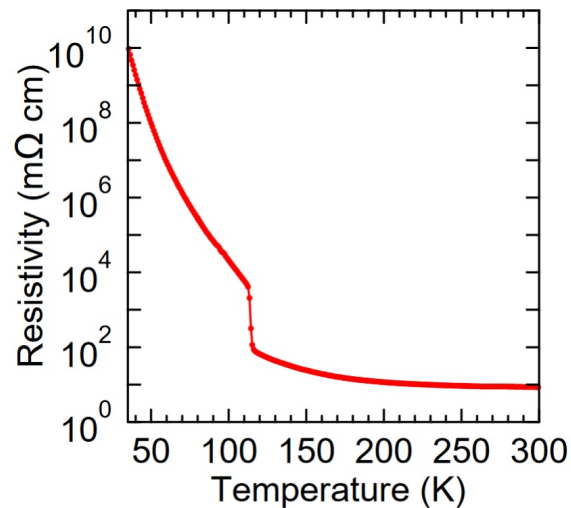


Figure 1. The Verwey transition as demonstrated by a plot of resistivity vs. temperature, reproduced from [5].

Studies on the unique physical properties of Fe_3O_4 continued through the decades. The atomic structure of Fe_3O_4 has been determined using 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 (Figure 2) structure 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.

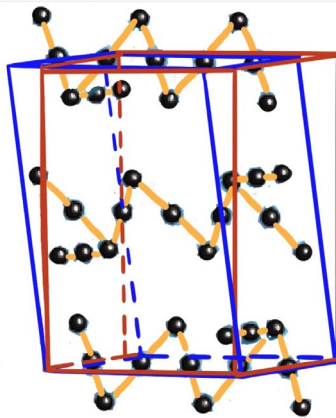


Figure 2. Sketch showing the Fe trimeron sublattice and the structural phase transition between the higher temperature cubic inverse spinel in red and the lower temperature monoclinic spinel in blue [6, 7].

In this education module, you will have the opportunity to observe the Verwey transition via an electrical resistance measurement, which is a powerful tool in examining various types of phase transitions.

Student Learning Outcomes

- Students will learn how to identify phase transitions from electric transport measurements.
- Students will develop proficiency in techniques for wiring and mounting samples for electric transport measurements.
- Students will operate the Electrical Transport Option (ETO) of the VersaLab™ cryostat and gain experience in low temperature experiments.
- Students will apply foundational knowledge of relevant solid-state physics to resistance 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 Electrical Transport Option (ETO) Manual (1084-700), 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 obtain 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:

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WARNING!

Always use **Personal Protective Equipment (PPE)** during every step of sample preparation. Failure to do so might cause bodily harm.



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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>



Measurement Background

Many fundamental materials characterization methods rely on the proper measurement of current and voltage. As such, experimental setups must be considered in terms of their equivalent electronic circuits in order to properly characterize a physical quantity. The heart of such a circuit is Ohm's law, $V = IR$, where V is the voltage drop across and I is the current through a resistance, R . From the extrinsic quantity *resistance*, one can obtain the material specific intrinsic quantity *resistivity*, ρ . In a typical sample measurement, the resistivity is calculated from the resistance as

$$\rho = \frac{RA}{L},$$

where R , A , and L are the resistance, cross-sectional area, and length (distance between voltage probes) of the sample, respectively.

The Resistivity Puck (Figure 3) clearly depicts three measurement channels, each with four gold-plated pads labeled $I+$, $V+$, $V-$, and $I-$ to be utilized for a conventional four-wire resistance measurement. It should be noted that the ETO does not support the use of Channel 3 (though other Quantum Design measurement options, e.g. the Resistivity Option, do). Note the ETO also allows for a two-wire measurement, which utilizes only the $I+$ and $V-$ pads. However, this is only appropriate for samples with a very large resistance, typically greater than 5 M Ω .

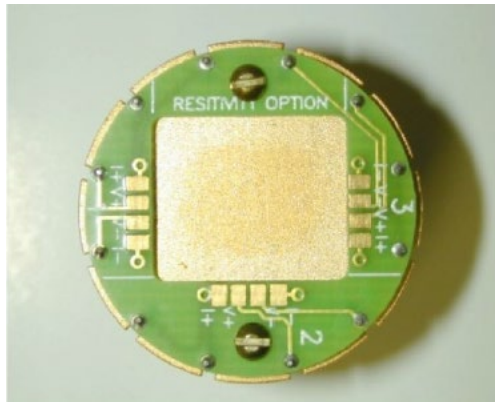


Figure 3. The Resistivity Puck. Notice the clearly labeled contact pads for the three measurement channels.

As a starting point, we consider a simple 2-lead measurement configuration, as illustrated below in Figure 4. For the 2-lead technique, current is supplied to the sample via two electrodes, and the voltage is read by a voltmeter in parallel, using the same two leads. Note that, in this configuration, the total voltage drop across the attached leads/contacts **and** the sample is measured. This type of 2-

lead measurement is commonly utilized when using a simple hand-held multimeter. The biggest drawback behind this technique is that the lead and contact resistances contribute to the total signal, and the resistance of the sample alone cannot be easily extracted. This is particularly true if the sample resistance is comparable to, or smaller than, the lead and contact resistances. However, in situations in which the sample resistance is known to be significantly larger than the contact/lead resistance, such a 2-lead measurement configuration is highly accurate.

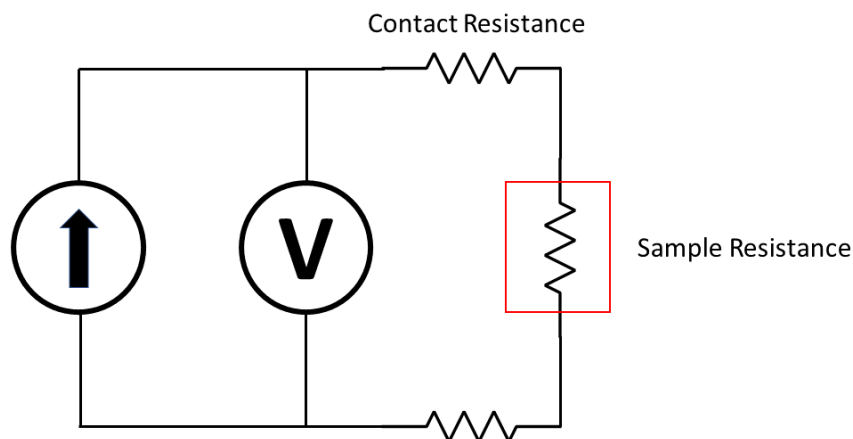


Figure 4. The circuit diagram for a typical 2-leads electronic configuration. Because the voltmeter is connected in parallel with the current source leads, the measured voltage drops occur over all leads and the sample, resulting in a total resistance measurement that encompasses the contact resistances and the sample resistance.

The 4-lead configuration illustrated in Figure 5 circumvents the lead/contact resistance issue faced by the 2-lead technique described above. It accomplishes this by using separate contacts/leads for the applied current and measured voltage. The current is applied via the two outermost contacts whereas the two innermost contacts are connected to a voltmeter. In principle, the voltmeter input is high impedance, thereby preventing the flow of measurement current in the innermost leads. As a result, the voltage drop that is measured occurs only between the two inner electrodes, eliminating any resistive contribution from the leads or contacts themselves. This is a very elegant and simple technique from an electronics standpoint.

The voltage reading, particularly for an AC measurement such as that utilized by the ETO, can be heavily dependent upon the contact geometry and quality. One should therefore always strive for good low-resistance *Ohmic contacts*. For example, a poor sample contact, e.g. an oxide barrier between the lead and sample, can result in a capacitive coupling and a large lag (or phase angle) between the source current and measured voltage in an ETO measurement.

The measured phase angle can therefore be used as a diagnostic tool to ascertain contact quality. Generally, a measured phase angle less than 1° is consistent with a good contact.

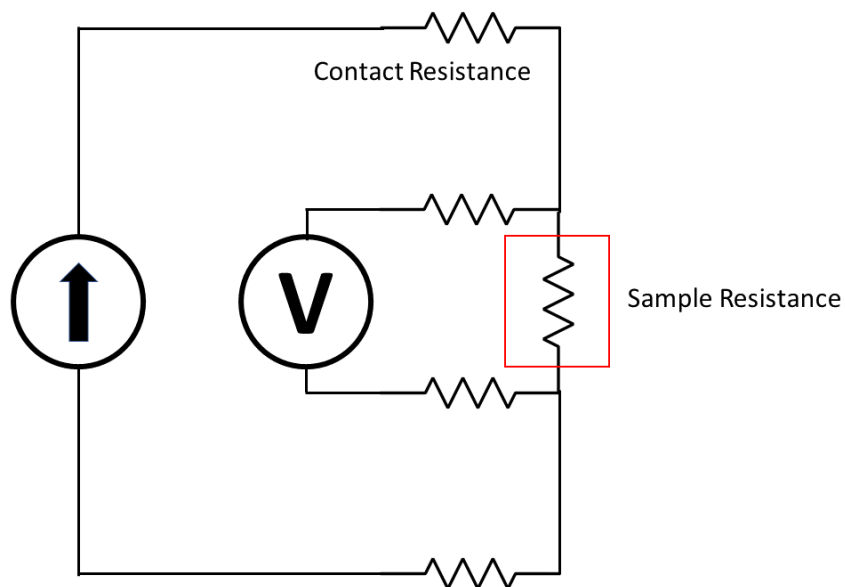


Figure 5. The circuit diagram for a typical 4-leads electronic configuration. Here, the voltmeter is attached to the sample via two leads separate from the current leads. Due to the negligible current in the voltmeter leads, the voltage drop, hence measured resistance, occurs only across the sample and ignores the contributions from the contact resistances.

Materials List

Sample Preparation
Magnetite Sample
Silver paint
Silver paint applicator
25 micron diameter Pt or Au wire
Apiezon N grease or GE7031 Varnish
Weighing or cigarette paper
Tweezers
Microscope
Scissors
Lighter
Soldering iron

Sample Preparation and Mounting

After making sure to wear proper personal protective equipment (PPE), such as gloves and safety glasses, break off a small piece of magnetite (Figure 6). One recommended procedure is to place the mineral in a bag and carefully strike it with a hammer. The piece must be small enough to fit onto the VersaLab™ Resistivity Puck but large enough for you to attach four wires. Flat surfaces are easier to work with, so you may consider sanding the sample or polishing it with a lapping device before attempting to mount it.



Figure 6. A typical magnetite specimen.

1) Cut a piece of weigh paper or cigarette paper (10 mm x 10 mm) in order to cover the central part of the Resistivity Puck and prevent the sample from shorting to the puck surface, which is grounded. Apply a thin layer of Apiezon N grease or GE7031 varnish to the gold area and lay the paper on top of it. It may be necessary to thin or dilute the GE7031 varnish with either toluene or methanol.

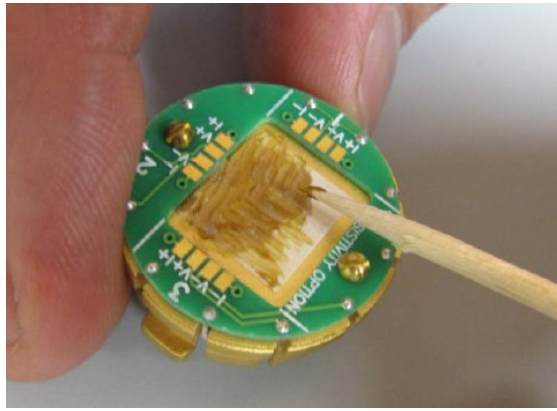


Figure 7. Apiezon N grease and paper application in order to: prevent a short from the sample to the puck surface, keep the sample in place, and provide good thermal contact.

- 2) Measure the thickness and width of the sample using calipers. These are required to determine the cross-sectional area, A , in order to calculate the intrinsic quantity resistivity, ρ .
- 3) Choose whether you wish to connect the sample to Channel 1 or Channel 2 (remember Channel 3 is not used with the ETO). Note, you may opt to measure two samples at the same time, and that may require you to reduce the sample sizes to fit both onto the puck. If not already done, this is a good time to coat (sometimes called tinning) the contact pads on the Resistivity Puck with a little bit of solder.

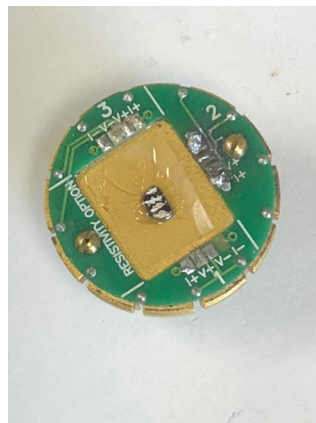


Figure 8. Sample mounted on the Resistivity Puck with contacts already in place.

- 4) Obtain a strand of Pt wire and run a lighter flame over it. This will soften/anneal the wire and make it easier to work with. If using Au wire, such a heat treatment is often not required. Cut the wire with some spare length to connect the samples to the puck channel pads.
- 5) Using tweezers and a microscope, attach four Pt (or Au) wires to your sample. As previously mentioned, it may be useful to sand the surface flat to facilitate

mounting the wires. The two inner wires will measure voltage while the two outer wires supply the current (Figure 9). It is recommended to use silver paint to attach the wires to the sample. Before getting started, it is suggested to first experiment with placing a drop of silver paint on weighing paper or a glass slide and get a feel for how its viscosity changes as it dries. Use a thin stick (e.g. toothpick) or needle to play with this and see if you can control placing a small droplet of paint on a surface.

When you are ready to work with the sample, one method to attach leads is to lay individual wires in the locations that you want and place a droplet of silver paint at the location with the small stick or needle. This is sufficient to measure the bulk properties of the sample, but painting stripes across the entire face of the sample can allow for greater bulk measurement coverage.

Any mistakes can be remedied with a cotton tip soaked in ethanol or the creative use of a needle, stick, or razor blade when the silver paint has dried. In an extreme case, the surface layer of the sample can be sanded clean.

This step is the most difficult portion of sample preparation and can take a lot of practice and patience!

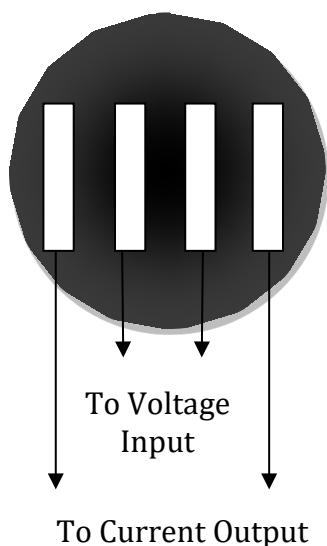


Figure 9. Four-lead measurement configuration.

6) Measure the distance between the inner voltage contacts, L , which, along with the cross-sectional area, is required to calculate the resistivity.

7) Place the sample onto the Resistivity Puck. Make sure it is adhered to the weigh or cigarette paper using a little extra Apiezon grease or GE7031 varnish, and solder the other ends of the wires to either Channel 1 or Channel 2 contact pads.

Note, it is recommended to simply heat the pre-coated solder on the contact pads, stick the Pt or Au wire in, and let the solder cool. Only use as much heat as required to melt the solder. Excessive heat could damage the Resistivity Puck.

8) There are several methods to check the quality of the contacts, but the most straightforward would be to insert the puck into the P150 diagnostic puck box accessory for the VersaLab™ and measure the resistances between any two leads using a hand-held multimeter.



Figure 10. Testing connections using the P150 wiring test station and a hand-held multimeter.

Sample Measurement Using the ETO

Refer to your VersaLab™ manual to prepare the cryostat for operation.

- 1) Place the puck in the insertion tool and lock it into place. Make sure that the puck is snug and does not rotate once locked.
- 2) Make sure that the VersaLab™ sample chamber is stable at 300 K with the magnet discharged. Use the VENT CONT command to vent the chamber, and then remove the KF25 blank flange/baffle set to open the sample chamber.
- 3) It is suggested to insert the puck with its keying notch aligned either to the right or left. When the tool has been inserted to the bottom of the sample chamber, rotate the tool such that the notch will turn towards you. You should feel the puck drop slightly once the notch is properly aligned with the key. Give the tool a gentle push downwards, release the lock, and lift the puck extraction tool out.

4) Replace the KF25 blank flange/baffle set and activate the PURGE AND SEAL command. Ensure that the sample chamber has been properly purged and there are no leaks to atmosphere.

5) Once the chamber has been purged, use the ETO resistivity console to perform a quick 4-wire measurement in immediate mode. The measured resistance should be comparable to that obtained using the P150 wiring test station and hand-held multimeter. The phase angle should also be less than 1° .

If the measured resistance value is significantly higher, or the phase angle large, inspect the integrity of the contacts.

6) Create a sequence to sweep temperature and measure the 4-wire resistance in zero magnetic field.

7) Run the sequence and display the measurement in real time. Hint, it may be useful to plot the data in log scale. Right click on the graph and click on Data Selection. Check the box to enable log scale (Figure 11). Once the data has been acquired, plot the resistivity vs. temperature using the dimensions of the sample and voltage lead placements that you previously measured.

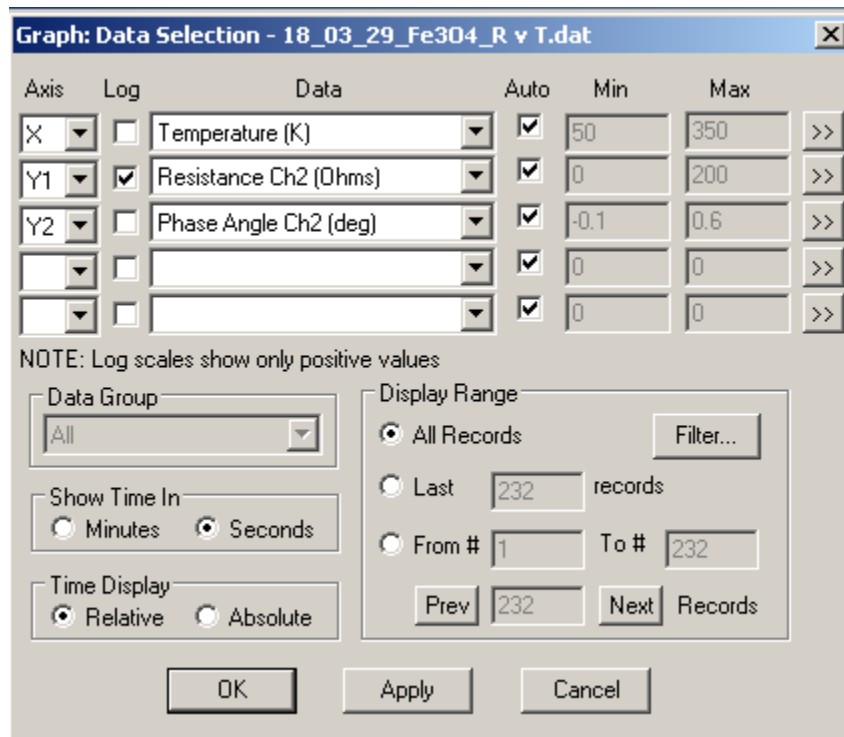


Figure 11. Data Selection popup window with log scale selected.

Data and Discussion

- 1) What is your Verwey transition temperature, and how do you know that you have identified the transition?
- 2) Does your sample behave like a metal or an insulator? Why do you say so?
- 3) Describe in more detail what the structural transition is for Fe_3O_4 at the Verwey temperature. How does it explain your results?
- 4) In your opinion, why is the Verwey transition significant? What could be some potential applications of this phenomenon?
- 5) The ETO essentially employs a digital lock-in amplifier to perform the 4-wire measurement. Perform some research and explain the measurement principle of a lock-in amplifier.

References

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- [2] Alfa Aesar chemical supply. <https://www.alfa.com/en/catalog/012374/>
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