Magnetic Analysis and Measurement (MAAM) Project

by Mikel Holcomb

Prefix: Things to Know About Research

One of the most challenging things to get used to for students starting research is understanding that research is almost never regularly scheduled, like a course would be. Sure, you might have regularly scheduled meetings, but the experiments will be different. You might plan them to happen at regular times, but things will inevitably change. In this project experience, we are going to do our best to schedule things for you and try to stick to a schedule, however, it is unrealistic to expect that your future research experiences will be like this. You are going to have take a little bit of agency for making sure you get things done and not expect anyone else to realize for you if you have not. In the end, you get out of this experience (and undergraduate research in general) what you put into it. A minimum effort will result in minimal output and a less than optimal experience for all - the undergraduate researcher, the faculty research mentor, and mentor's research group. No research can guarantee a paper, but you will learn many things along the way if you keep trying.

I collected some feedback from other faculty below.

"Be curious. It's unlikely you'll understand everything going on in the lab, especially at the beginning, and that's okay. If you **stay curious and ask lots of questions**, you'll understand things better. Curiosity is also a key skill in science and beyond, so it's great to use this opportunity to build the skill."

"You should **feel comfortable asking for help**. I was nervous about asking for help when I was beginning research as a student because I thought I was supposed to figure everything out on my own. I didn't know that that's not how science works, and it's through communication and asking questions and getting help from people that science (or anything) progresses."

Building independence:
While we don't expect you to figure out everything on your own, we do expect you to try. What and who are different resources you could try? Professor Holcomb may not be able to answer every one of your questions, so who are other resources you could try?

Chapter 1: A Brief Introduction to Magnetic Thin Films for Freshmen and Up

Disclaimer: This text is a work in progress. If you have ideas on how to make the material more clear to those just beginning, please provide that guidance to make this experience better for future students.

Condensed matter physics (CMP) is the largest subdiscipline of physics. It is also the easiest to translate to a wide variety of industry and government jobs. Why? Much of CMP has a component on material quality. What makes a material good and how to improve it is a question that comes up in many areas of our lives (and is highlighted in Chapter 2). For example, how do we make better computer chips, solar panels, sensors or even asphalt? Or even just how do we know if what we tried to make is what we made? While some industries just try many things (called an Edisonian approach), knowing some methods to test certain parameters can allow quicker optimization. Physics 471 (Introduction to Solid State Physics) is an elective class you could take your senior year to learn a lot more, but you can get a taste of this field without a ton of background knowledge.

> *Pro tip: Underlined words will be defined soon. For now, just accept that you'll understand this concept better soon. Not knowing jargon is unfortunately very common when starting. While it can get frustrating sometimes, there is some comfort in realizing that everyone goes through this phase. Don't let it deter you from asking questions.*

Due to Professor Holcomb's discovery of a new kind of magnetism (a novel kind of spontaneous magnetization reversal (SMR) in single-phase magnetic thin films), some of you are going to look for this effect for this project. However, even if your results do not show this behavior, you will be studying the main magnetic techniques to characterize magnetic materials, so your work has the potential to be publishable regardless of whether this new magnetism shows up in your measurements. (Other magnetic projects are also available, including several collaborations with other universities.)

What will you learn from this experience? Electricity and magnetism are some of the harder physics topics for students to visualize. Having hands-on experience with this research will help put the importance of this work into perspective and give you confidence that you can contribute to research, no matter your background level. In addition to learning about a new magnetic discovery, you will learn about materials growth and characterization, data analysis, and good research practices. While it would likely require work beyond this semester, your work is likely to be publishable.

This document is not designed to tell you everything about magnetism and characterizing materials, but is meant to give you a good start to understanding work in this and related condensed matter fields. Here are a few introductory references you might find helpful if you want a deeper discussion than what is explained in this brief workbook:

- Khan Academy: A brief history of magnetism and introduction of magnetic fields. https://blossoms.mit.edu/videos/lessons/mysteries_magnetism
- What is magnetism? https://www.explainthatstuff.com/magnetism.html
- Introductory experiments with magnets (includes additional resources): https://blossoms.mit.edu/videos/lessons/mysteries_magnetism
- Paper: Magnets in Biomedicine https://www.mdpi.com/2304-6740/8/1/6

What causes magnetism? All atoms contain electrons. The movement of these negatively charged electrons around the nucleus causes a magnetic field. While the movement of electrons is significantly more complex, you can picture this motion like the Earth going in its orbit around the Sun. In addition, the Earth spins about its axis, causing a 24 hour day. Likewise, the electron has a property called spin, that is often described as if it is spinning. It is not, but it creates a magnetic effect as if it were. Both the electron going around its orbit and the electron spin can cause magnetism. These two effects can sometimes cancel out; they can also sometimes result in a very strong magnetization.

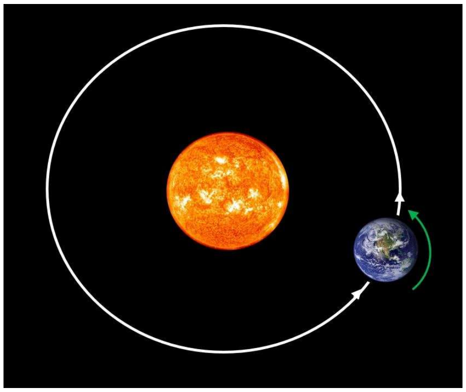


Figure 1: The Earth's motion from spinning around its axis of rotation and also from going around the Sun can be compared to the spin of an electron and the electrons motion around its atom.

One of the simplest and most familiar examples of a magnetic element is iron (Fe). You've probably seen that paperclips and nails made of iron can stick to magnets. That's because iron atoms have some unpaired electrons, and these electrons have spins that tend to line up in the same direction. When many of these aligned spins work together across a region of the material, they create what's called a magnetic domain. Even without an external magnetic field, these regions can give the material its own magnetic behavior. This is what makes iron a classic example of a ferromagnet—a material where the electron spins "like" to point the same way. For more details, see Appendix A.

In contrast, many other elements—like copper or gold—have all their electron spins paired up, with each spin-up canceled by a spin-down. These materials have no net magnetic moment, so they're not magnetic in the everyday sense. That's why a copper wire or a gold ring won't stick to a magnet, even though they also contain electrons. The key difference is whether there are unpaired spins and whether those spins prefer to align.

To explain our discovery of spontaneous magnetization reversal, it is helpful to briefly discuss a few well known types of magnetism. People are most familiar with **ferromagnets** (such as iron), which are frequently used to hold things on refrigerators or for other applications needing a permanent magnetization. Other applications include magnetic levitation, storing information on credit cards or computing chips, metallic sorting of materials, speakers, microphones, electric guitar pickups, generators, and medical use.

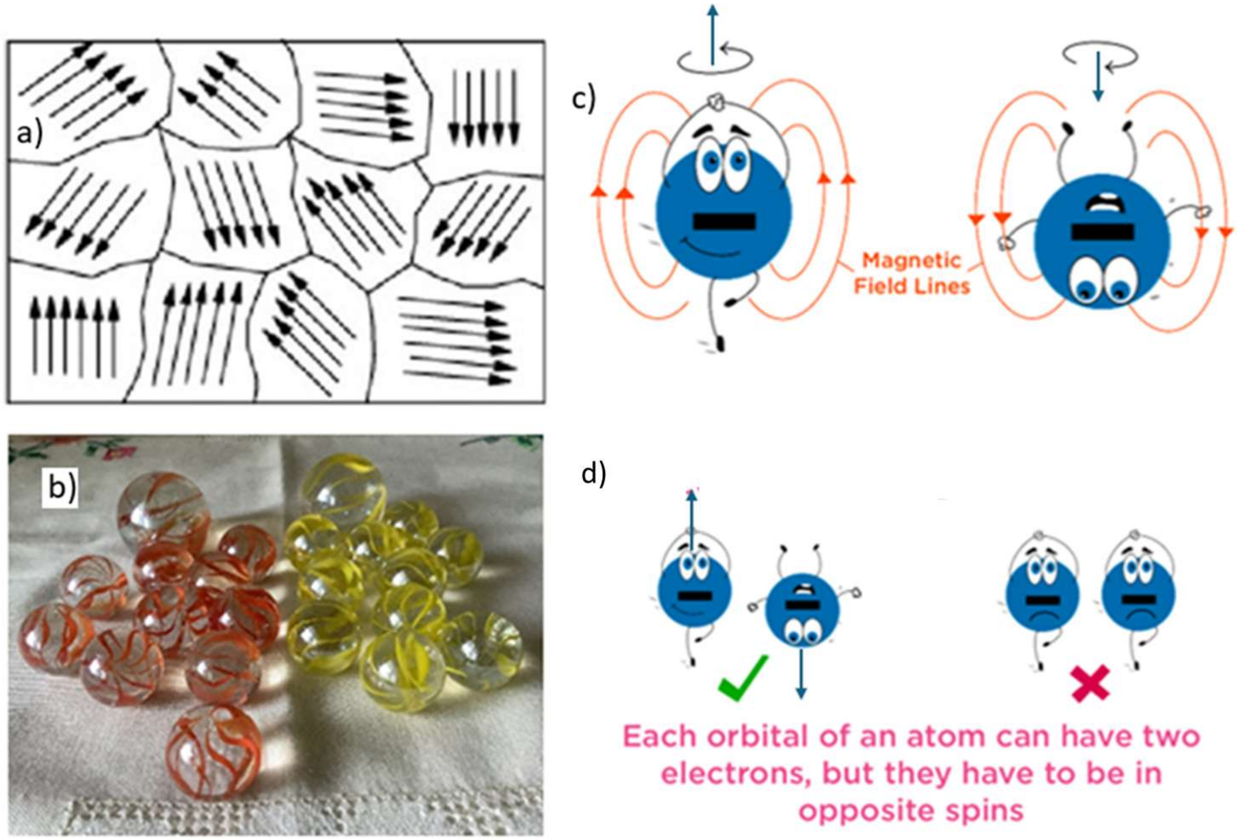


Figure 2: Marbles to help visualize electron spin.

Different types of magnets can be understood pictorially by how their electron spins like to align before and after an applied magnetic field (H) is applied. In a ferromagnet, even before a field is applied, nearby electron spins like to point in the same direction as shown in Figure 2a. While it is more complicated, let's think about why this might happen. Let's imagine the electron like a marble (for a visual, see Figure 2b) and its spin as if it were spinning. You can probably imagine that if one marble is spinning in a particular direction, say clockwise, that it would be easier for all the nearby electrons to marbles to spin in the same direction. We represent the direction of this "spin" with an arrow, as shown in Figure 2c. However, you might find another region of marbles spinning in a different direction, as happens in many materials. As you'll learn if you take modern physics, there are two opposite spins for each atomic energy level. The spins of the lower energy states will cancel, but not always in the higher energy states. For a little more detail on atomic levels (though not necessary to understand), see Appendix A.

Before a magnetic field is applied in a ferromagnet, the overall spin cancels out, as represented in Figure 2a. Once a magnetic field is applied, you can get these spins to align, and most of these spins will stay aligned, even after the field is removed, earning them the name **permanent magnet** (also known as ferromagnet). As shown in Figure 3, there are several types of magnetic properties. As we just learned, a ferromagnet will maintain its magnetism even after a field is removed (as long as its temperature is not raised above the magnetic ordering temperature, a useful trick for demagnetizing a material).

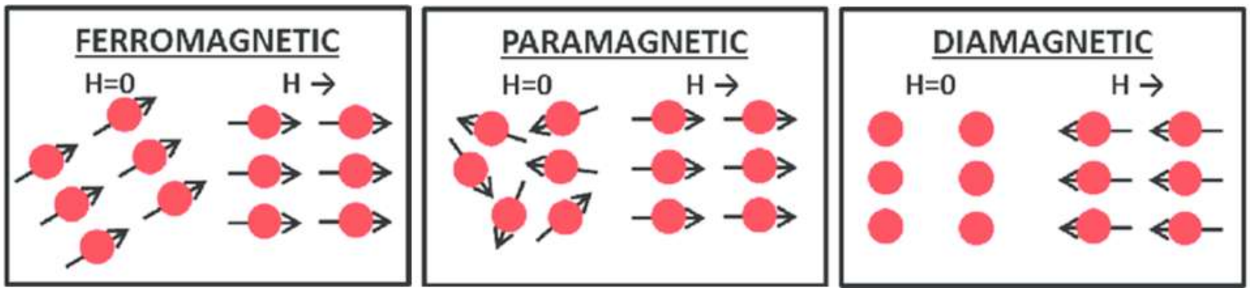


Figure 3: How the electron spins align before and after an applied magnetic field is applied in three common kinds of magnets.

The refrigerator that the refrigerator magnetic sticks to is coated with another kind of magnet called a **paramagnet**. The spins of a paramagnet are aligned randomly before a field is aligned, but will start to align more with the field, the stronger it gets. Paramagnets are useful when you would like to be able to magnetize something, but do not want it always sticking to things like something magnetic would. For example, if you drop a screw down an inconvenient place when doing a home project, a clever trick is to use a magnet to fish it out since the screw is paramagnetic.

While there are other types of magnetism, the final one that we need to discuss our SMR discovery is **diamagnetism**. A paramagnet will stick to a ferromagnet. A diamagnet will do the opposite and repel it. Thus, this effect can be used to levitate things from silly desk toys to trains! Except when coupled with superconductivity, this is normally a weak effect. The spins align opposite to the applied magnetic field, to try to cancel it out partway.

So, **what is SMR**? Spontaneous magnetization reversal is something that happens when both ferromagnetism and another type of magnetism occur at the same time. In our case, it was in the same material, but it has been observed between two different materials. Not only do they interact, but they interact in such a way that instead of aligning with the magnetic field when the applied field is small enough, the ferromagnetic phase aligns with the other phase, that acts a bit like a diamagnet, making the system point strongly in the opposite direction of the field, unlike typically weak diamagnets. In reality, it is probably a complicated coupling with antiferromagnetism, yet another kind of magnetism.

In brief, **antiferromagnetism** is a lot like ferromagnetism as shown in Figure 4. Within one plane, all spins line up just like a ferromagnet. However, in the next plane over, the spins point in the opposite direction, such that they can cancel out. (There is also something called a **ferrimagnet** where while they point in opposite directions, one direction is stronger than the other, so there remains a net effect.) The magnetization in antiferromagnets do not always perfectly cancel either, because sometimes these spin directions are not perfectly antiparallel. This effect called canted antiferromagnetism is shown by the tilted spins in Figure 5.

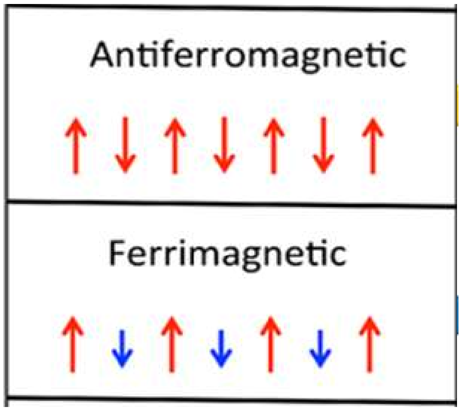


Figure 4: Spin alignment in antiferromagnets and ferrimagnets.

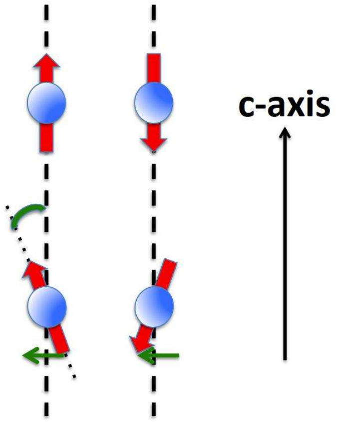


Figure 5: Bottom canted arrows shows how canted antiferromagnetism can result in a net magnetization (green arrow).
Source: https://www.eurekalert.org/multimedia/875339

Measuring Magnetization

To analyze your research, we will have to get slightly more mathematical. When an applied magnetic field **H** is applied to a material, the response is called its magnetic induction **B**. In some cases, the relationship between **H** and **B** can be linear, but that is often not the case. The equation relating **H** and **B** is

$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M} \text{ (cgs units)} \qquad \mathbf{B} = \mu_o(\mathbf{H} + \mathbf{M}) \text{ (SI units)}$$

where **M** is the magnetization of the material and μ_o is a constant called the permeability of free space. Note that two common systems of units are used, and it can be confusing to go between the two. Magnetization **M** is defined as the magnetic moment **m** per unit volume V,

$$\mathbf{M} = \mathbf{m}/V$$

A **magnetic moment m** is a measure of how strongly something acts like a tiny magnet. In atoms, it mainly comes from the spins and motion of electrons. If an atom has unpaired electrons (electrons without a spin partner), their tiny magnetic effects don't get canceled out. When those unpaired spins all point in the same direction, they add up, giving the atom a net magnetic moment. The more unpaired electrons, the stronger the moment. In simpler terms, a magnetic moment is like the magnetic strength of an atom or particle, caused mostly by the spins of unpaired electrons. In materials, if lots of atoms have magnetic moments that line up together, the whole material can behave like a magnet—this is what happens in a ferromagnet like iron.

Let's discuss the two most common ways to show the units of these variables. In cgs units (Centimeter-Gram-Second), the units for **M** are emu/cm^3 and **B** are gauss. In SI, **H** and **M** have the same units of A/m, and the units of **B** are tesla (T). [1 gauss = 10,000 tesla]

What kind of magnet a material is does not depend on the magnetization or induction, but instead how they vary when a magnetic field is applied. Thus, it is common to plot **M** versus **H**. The ratio of **M** to **H** is called the magnetic susceptibility

$$\chi = \mathbf{M} / \mathbf{H}$$

and it is commonly plotted versus temperature. **M** versus **H** and **M** (or susceptibility) versus temperature are the two most common ways to study magnetic materials. We will now point out the typical features of these common measurements, show in Figure 6. Both paramagnets and diamagnets have a linear dependence on the magnetization, but the magnetization of diamagnets is opposed to the applied field. As antiferromagnets have two countering sublattices, the magnetization will near by large and happens through canting of the sublattices, as shown in Figure 5. Ferromagnets and ferrimagnets both increase quickly with applied magnetic field and eventually saturate. You cannot tell the difference between these two types from this measurement, unless you have some way to know what your saturation magnetization should be. (Caution: it could also just be a film that is not grown as well as you would like that can reduce the magnetization. Good growth is an artform and not easy to master.)

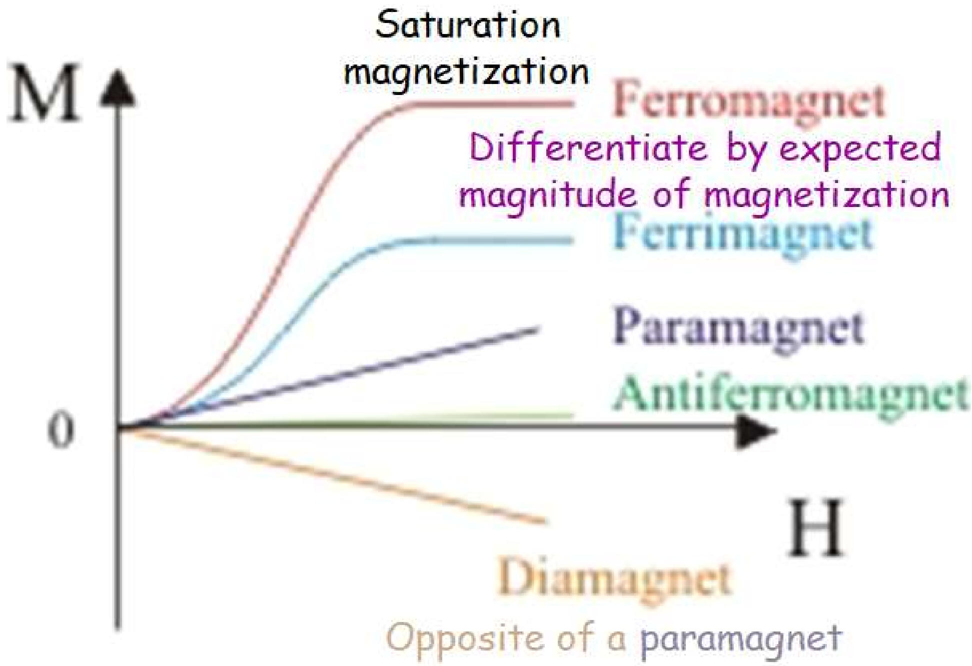


Figure 6: Comparison of magnetization **M** versus applied magnetic field **H** for a variety of types of magnetism.

If you turn down the applied magnetic field **H**, the curves for most of these magnet types would overlap with the curve created when increasing the field. As shown by the hysteresis loop in Figure 7, this is not the case for ferromagnets. Let us discuss why this happens. You can compare the ferromagnet curve in Figure 6 to the dotted line in Figure 7 when you are just turning on the field. It is not unusual to not even measure this line when reporting on ferromagnets. That is probably a mistake as we see some interesting differences for this curve in our new kind of magnetism. Perhaps some researchers saw these interesting features, but could not explain it and assumed they were doing the wrong thing. Assumptions can be problematic.

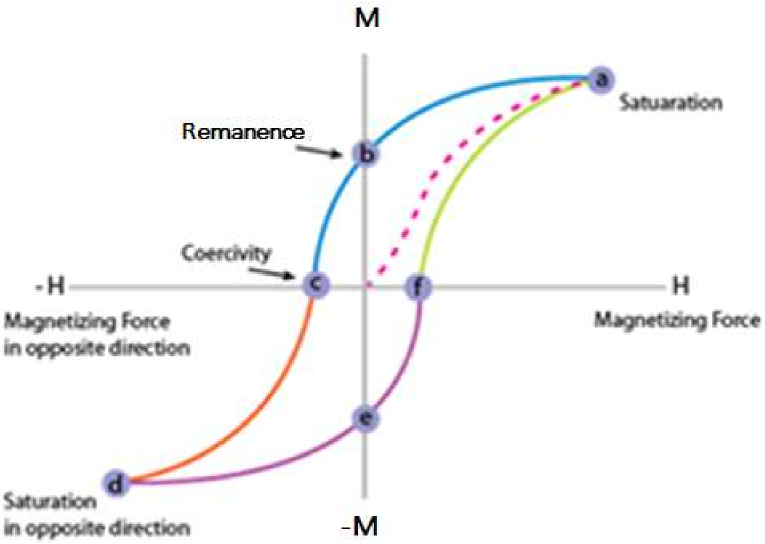


Figure 7: A diagram of the typical hysteresis loop for a ferromagnet along with some scientific terms often used to characterize these materials.

After increasing the field in Figure 7 to point **a**, when you turn down the field, it will follow the blue curve. You can see at point **b** the applied field is zero, but there is still a remaining magnetization (called the remanent magnetization). Now that you got all of the spins aligned, many of them are energetically happy with this alignment. It actually takes a magnetic field in the opposite direction (see path to **c**) to counter this energetic preference. If you turn up that negative field larger you will go to point d, which is the same situation at point a, but in the opposite direction. Turning off the field takes you to point **e**, which is exactly like point **b**, except in the opposite direction. Is this loop always symmetric around zero? Nope, but that happens when you have two different magnetic phases interacting. When it's not symmetric, it is called having **exchange bias**. You are unlikely to have this asymmetry (where point **c** is not equal to the negative of point **f**), but it does not hurt to check, as it is possible and is a feature that has application value. It is used in magnetic hard drives. By the way, ferrimagnets can have loops that look similar to Figure 7, but sometimes they look more complicated, as shown in Figure 8.

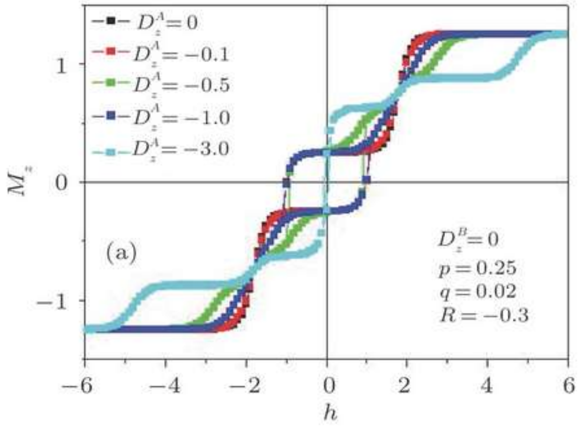


Figure 8: Calculation of a ferrimagnetic hysteresis loop with arbitrary units.
Source: https://cpb.iphy.ac.cn/article/2017/1916/cpb_26_12_127501.html

There are two common ways to plot the dependence on temperature. You can have either the magnetization or the magnetic susceptibility (**M**/**H**) on the y axis. As the magnetization is a little easier to understand, we will start there. However, it is the susceptibility versus temperature that is best able to distinguish between different types of magnetism. For simplicity, let's just discuss a ferromagnet's magnetization with temperature first, as shown in Figure 9.

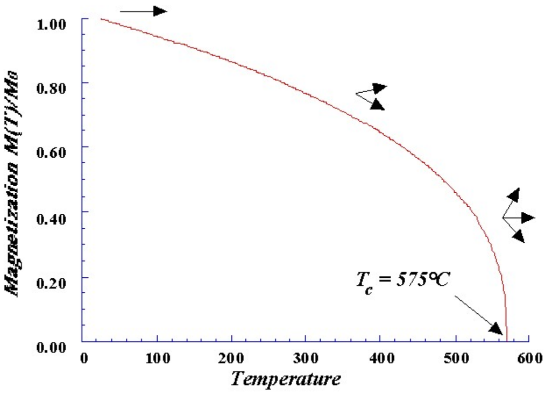


Figure 9: Normalized magnetization versus temperature for a ferromagnet

This ferromagnet has a critical temperature at 575 °C where it is no longer ferromagnetic beyond that point. Above their critical temperatures, almost all magnetic materials (except diamagnets) transition to paramagnetic materials. (There are some rare exceptions where a material might transition from ferromagnetic to antiferromagnetic or vice versa and then to paramagnetic at a higher temperature). For a ferromagnet, the critical temperature is called the Curie temperature. For a ferrimagnet or antiferromagnet, the critical temperature is called the Néel temperature. Note that at lower temperatures, the magnetization is larger, as the spins align more. At higher temperatures, thermal fluctuations contribute to the spins not aligning as well. It is not uncommon to normalize this curve (as done in Figure 8) to have the magnetization of the lowest temperature set to one. However, note that I would like you to find the actual value of the magnetization. We will practice. In Figure 10, we see the susceptibility versus temperature for several kinds of magnetism. Also shown are the typical basic formulas used to determine the critical temperatures.

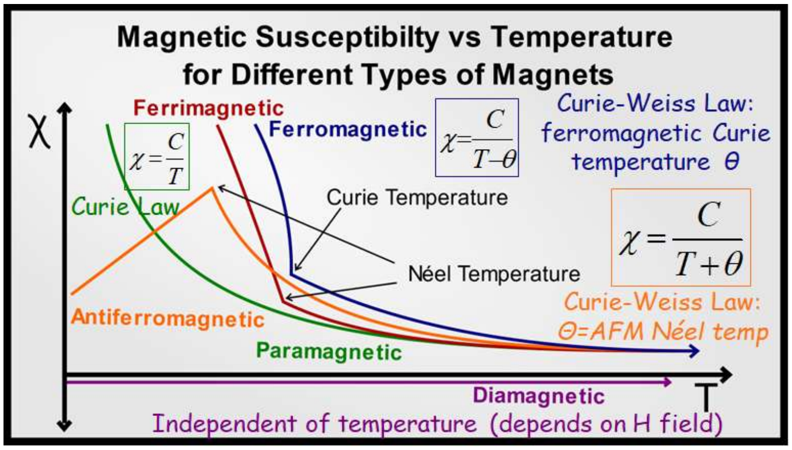


Figure 10: Susceptibility versus temperature along with basic formulas typically used to describe their temperature dependence and find their critical temperatures θ.

For finding the ordering temperature, another common graphing method is to plot one over the susceptibility versus temperature, as shown in Figure 11. Ferromagnets have positive order temperatures and antiferromagnets have negative temperatures.

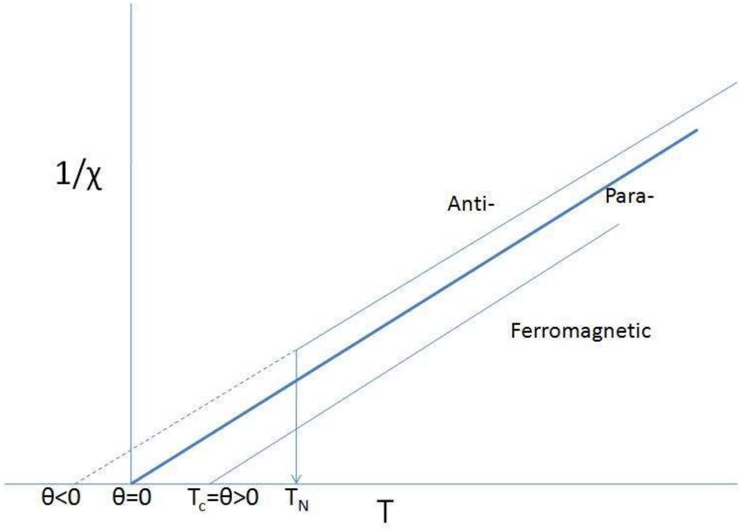
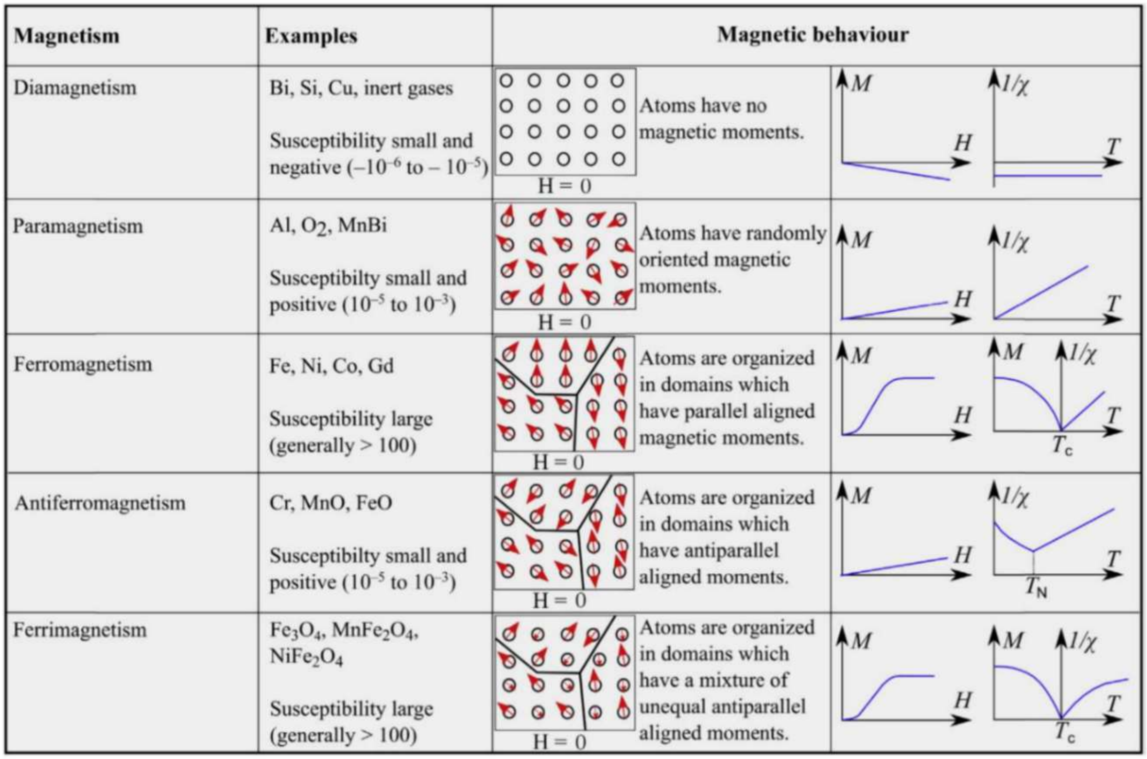


Figure 11: The inverse susceptibility versus temperature is often used to find the ordering temperature.

A nice summary of these magnetic behaviors can be found in Figure 12.



Magnetism	Examples	Magnetic behaviour
Diamagnetism	Bi, Si, Cu, inert gases Susceptibility small and negative (-10^{-6} to -10^{-5})	H = 0 Atoms have no magnetic moments.
Paramagnetism	Al, O_2, MnBi Susceptibilty small and positive (10^{-5} to 10^{-3})	H = 0 Atoms have randomly oriented magnetic moments.
Ferromagnetism	Fe, Ni, Co, Gd Susceptibility large (generally > 100)	H = 0 Atoms are organized in domains which have parallel aligned magnetic moments.
Antiferromagnetism	Cr, MnO, FeO Susceptibilty small and positive (10^{-5} to 10^{-3})	H = 0 Atoms are organized in domains which have antiparallel aligned moments.
Ferrimagnetism	Fe_3O_4, $MnFe_2O_4$, $NiFe_2O_4$ Susceptibility large (generally > 100)	H = 0 Atoms are organized in domains which have a mixture of unequal antiparallel aligned moments.

Figure 12: Summary of common forms of magnetism and their features. Note that the ferromagnetic and ferrimagnetic cases show both what magnetization and one over the magnetic susceptibility look like with temperature.

Source: https://www.sciencedirect.com/science/article/pii/B9780081001486000081?via%3Dihub

So, let's see how our samples look different. If you measure magnetization versus temperature in a large magnetic field, it will look exactly like Figure 9. Most scientists measure in a large magnetic field, as that makes the magnetization larger and more impressive. However, in a device, you'd rather not have to use a large magnetic field. If you measure in a smaller magnetic field the result you get depends on whether you cooled the sample in a field (red, field cooled) or not (blue, zero field cooled). When we did not apply a field during cooling, the magnetization switched directions! In Figure 13, you see the effect of changing the applied field during measurement and cooling. I have debated if this is too much for now, but I have included a brief further discussion of how you might imagine this negative region happening in Appendix B.

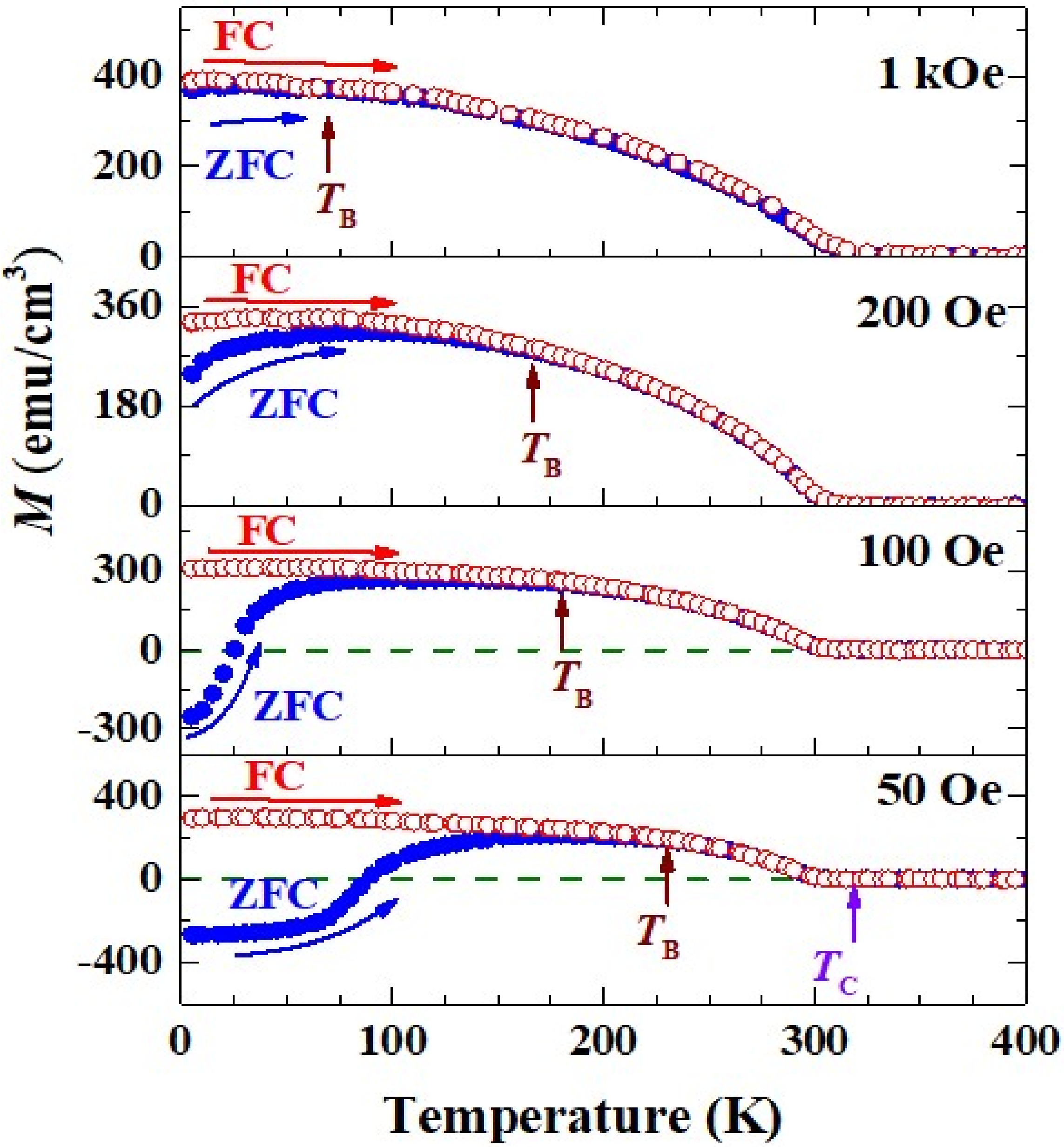


Figure 13: Magnetization versus temperature for our samples exhibiting spontaneous magnetization reversal.

But this was not the only weird behavior. The hysteresis loops for our samples in Figure 14 were odd too. The black parts of the curves are fairly typical. It is common for the width of these loops to change with temperature as shown. What is odd is the red part of the curve. If you look back at the dotted line in Figure 7, this part of the curve is supposed to start at zero. Instead, our films were immediately going against the field, if we zero field cooled our samples. (It is useful to note here, as you may see this discussion in some of the literature, that many people thought here that we had some artifact field in our magnet as we cooled it down. This is indeed possible and we have to carefully zero out the system to minimize it. However, we have done several checks, including in system were this artifact not possible and we still get the same results. This is the likely reason that anyone that saw this effect in the past, assumed they had messed up. What did we say about assumptions?) It is also important that the first time (recently) we apply the field, we need a larger field that what is needed in the later loop.

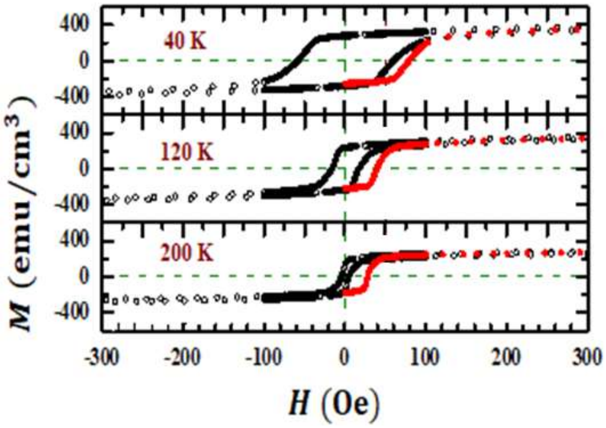


Figure 14: Hysteresis loops at 40, 120 and 200 K. Note that these loops are after background subtraction, as discussed in Appendix C. Ref: Our paper

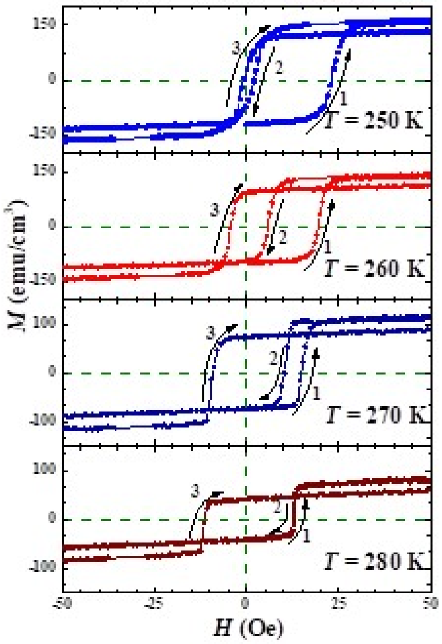


Figure 15: Hysteresis loops near the critical temperature.

Finally, the hysteresis loops are even more strange as we approach the critical temperature, which is a little above room temperature in our case. I will point out that unlike a lot of materials, this means our materials are likely useful for room temperature applications. There are not a huge number of room temperature magnets. The higher temperature hysteresis loops are shown in Figure 15. They are called inverted. After you turn the field up, when you lower the applied field, the magnetization actually reverses BEFORE you turn the field all the way down. A similar behavior is exhibited in nanoparticles called superparamagnetic. It is typically discussed being due to interactions between nanoparticles of different sizes with different critical temperatures. However, our films are of excellent quality. How do we know that? Well, we will have to discuss how you study the quality of materials. But, before we do, let me point out that there are still a lot of open questions about what is going on with these systems. Maybe you can help us figure it out!

A few papers showing interesting negative magnetization are listed below. You also might want to check out Appendix C, which shows some **excellent undergraduate questions** on this topic, shortly after being introduced to this topic.

(You do not have to read these, but in case you want to read further. Note that it takes time to get good at understanding papers. Even experts struggle)

The phenomenon of negative magnetization and its implications - ScienceDirect

https://www.sciencedirect.com/science/article/pii/S0304885303000763?via=ihub

Our first SMR paper: https://iopscience.iop.org/article/10.1088/1361-648X/aade14

PNAS paper: https://www.pnas.org/doi/10.1073/pnas.1819570116

Zigzag magnetic structure: https://journals.aps.org/prb/pdf/10.1103/PhysRevB.101.054442

So, **what's the story behind this discovery**? Were we looking for it? No. We were trying to solve a problem called magnetic dead layers. I came across this problem when trying to look at coupling between ferromagnetic and ferroelectric materials.

> *Ferroelectrics are the electrical equivalent of ferromagnets. A ferromagnet has a spontaneous magnetization, whose direction can be changed with an applied magnetic field. A ferroelectric has a spontaneous polarization—or separation of positive and negative charges—whose direction can be changed with an applied electric field.*

Anyway, the coupling effect went away whenever the magnetic layer got too thin. A diagram of a thin film is shown in Figure 16. While the thickness range varies depending on the topic, in what I do thin films can be anywhere from 1 atomic layer to about 100 nanometers thick, so that's still pretty darn thin!

You see, when magnetic layer gets smaller the magnetization drops, and faster than you would think based on the change in volume. This drop can be seen in Figure 17 for $LaSrMnO_3$ if you normalize the magnetization by volume.

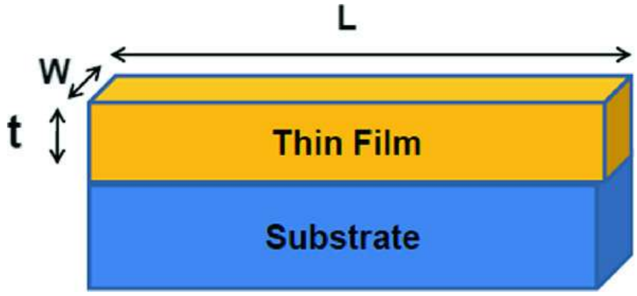


Figure 16: A thin film is grown on a substrate. What makes a good substrate choice for your thin film is addressed soon. Source: https://link.springer.com/chapter/10.1007/978-981-15-6116-0_1

As can be seen in Figure 17, above 26 unit cells (u.c.), the normalized magnetization does not change much. However, for thinner films, the magnetization drops. It was originally hypothesized that there was a portion of the film that was magnetically dead (thus the name magnetic dead layers) and as you made the film thinner, a greater fraction of the film was not magnetic. But theory did not agree that this should happen; theory suggested that even single atomic layers could be magnetic. This apparent dead layer occurs for a lot of materials. I wanted to understand why, partly because it was getting in the way of the layered coupling I was studying, and also because I realized that this problem would affect a lot of future technologies utilizing thin films.

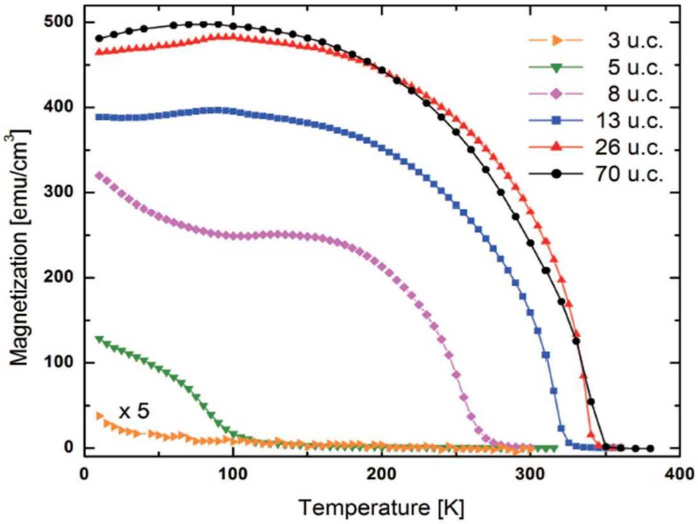


Figure 17: Magnetization versus temperature for LSMO of varying numbers of atomic layers or unit cells (u.c). Source: Huijben *et. al.* PRB 2008

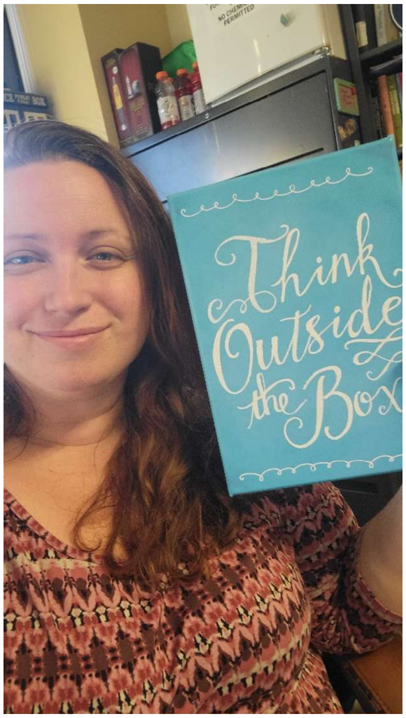


Figure 18: So I can always be thinking outside of the box

But this problem had been around for decades and no one had solved it yet. It gets increasingly hard to get funding for something the longer it has been studied. You have to convince the reviewers why *you* are the one that can solve it, despite a lot of people trying. That is not an easy thing to do, particularly since scientists tend to be pretty skeptical by training. So, I knew I needed to come up with something unique, some out of the box idea. I bought the box in Figure 18 to assist me. I like buying dumb things that amuse me (shrug).

So, the box was not really the catalyst, though that would almost be as good of a story. What I really did was gathered a bunch of the key papers about magnetic dead layers and tried to brainstorm what I could do differently. The first thing that I noticed was that most of these papers were by men, which historically been common in physics but should change! I laughed and thought, well maybe I have an advantage there. I wondered if there was a way to specifically think not like a guy. I figured, well I’m brainstorming, so why not mull over it for a few minutes. And to my surprise, I found my idea.

Absolutely no offense to men (we need your mindset too), but men have a tendency when discussing their research topic to focus on how big their material constants/properties are. For example, many assume a magnet with a larger magnetization would be better, and size indeed has a role to play. It’s also easier to compare numbers; these temperature or field dependence curves require a lot more brainpower to think about. But that magnetization number depends on how you measure it, as we have seen. If we measure in a larger magnetic field, the magnetization will be bigger. For this and other reasons, a lot of magnetic work is done in large applied magnetic fields. But, it’s not how big it is in a magnetic field that matters, but how you are going to use it. In a device, you don’t want to have to apply a large magnetic field because that requires a lot of energy. You’d ideally like your device to work with very small energy needs. So, if your magnet works in small fields, that is much better. Our spontaneous magnetization reversal is easily switched in small fields, so there is a lot of potential here.

Project Ideas

While we discuss a general analogy for what is going on in these novel magnetism systems, there are still many open-ended questions that need to be understood with which you could help. Here are some examples related to this effect, and later some other topics that might interest you as well. You are also welcome to come up with your own ideas. (I also have a number of collaborators with other magnetic projects; see following list.)

1. What about materials beyond manganites? Similar odd behavior has recently been seen in very different systems (Kumar *et. al.* 2021, Liang *et. al*. 2022, Bera *et. al*. 2023). Perhaps we can compare and contrast some things such as lattice parameter and strain. Taiwanese professor Eddie Chu is willing to grow us some other perovskite complex oxides.
2. Ferrites would be a natural material choice due to their reasonably high-temperature magnetism. Some of these systems (such as Holcomb's significant background in $BiFeO_3$) are also multiferroic, meaning you can control the magnetism with electricity. Multiferroics has a lot of interesting future potential applications. (Martin *et. al*. 2008, Yang *et. al*. 2009, Holcomb *et. al*. 2010)
3. Maybe the effect has more to do with HOW we are measuring it? What about elemental magnets? If we measured them heating up in between, could they also show inverted loops?
4. Perhaps we should repeat some old samples, such as to narrow in on particularly interesting temperature regimes or see if changes have occurred to the samples.
5. We could also look at LSMO samples from another group to compare. Collaborators from Carnegie Mellon University and Rice have both volunteered to provide LSMO samples.

Not all students need to be interested in this new magnetic effect. The researchers below (some from other institutions) have also agreed to help you if you are interested in their projects.

1. Rosalynn Quinones-Fernandez at Marshall University has a hypothesis that the magnetic properties of the dusting powder used to identify finger prints affects the quality of the fingerprinting. She has 8 powders to test. Your group could measure 1 or several of these. I promised to measure these samples for her soon, so this project would likely start the earliest. If there were interest, 8 different people in the class could measure each one of these.
2. Nearby female magnetism expert Sara Majetich from Carnegie Mellon University is studying thin films are predicted to be **altermagnetic**, a new class of magnetism that combines features of ferromagnetism and AFM. Interestingly, the altermagnetism effects have been seen in rutile thin films but not bulk. Is there something at the surface that's different?
3. Sara Majetich from Carnegie Mellon University is also looking at (Ba,Mn)O3 thin films --- "If it can be made with 70% Mn, it's predicted to be ferromagnetic. Paul's former student looked at this and got up to 60%, and our joint student has picked up the effort. It should be AF if it's not FM. AF measurements (M of T with a low H) are much trickier, as you know. The science of interest would be in looking at the ordering T as a function of composition, and hopefully getting something FM. Near the threshold, remanent loops could be useful to see if there's an ordered component --- and also to check on paramagnetic contributions."
4. Understanding how capping effects magnetic thin films grown by Lane Martin at Rice. (Valencia *et. al*. 2011)
5. Understanding the unusually large moment of $MnBe_2Te_4$ grown by Matt Brahlek at Oak Ridge and the resulting complicated defect chemistry. (Mazza *et. al*. 2022)
6. Understanding how nanoparticle shape (rods, spheres and shells) grown by Hari Srikanth at USF affect iron oxide nanoparticles and the resulting strain effects. (Attanayake *et. al*. 2023)

7. Understanding how superconductivity affects magnetism. (Snegirev e*t. al*. 2023) This project could be a collaboration with retired WVU professor Mohindar Seehra, who also has several old powder samples that could be explored.

You are also welcome to explore trying to get collaborators that I don't already know. However, please recognize that you'll need to contact them, and not all professors are quick about returning emails on usual requests. If you are going to do this, I suggest an email something to the effect of the following: (Copying my email address on the message is likely to dramatically improve your chances of getting a response.)

Dear Dr. XXXXXXXXXXXXX,

I am taking a magnetism research class that gives us hands-on measurement experience. While my professor (Dr. Holcomb, copied on this email) has given us several projects, she also has given us the option of seeking out a new collaborator. I was interested in your work on YYYYYYYYYYYYYYYY, or other projects you think might be interesting.

We plan to do measurements of M vs H and M vs T on a vibrating sample magnetometer. If you have any films that would be appropriate to explore, please let me know. Also please let me know if you are not interested, such that I can find another project quickly. Thank you.

Your Name

(The colored sentences are something good to include if you can identify what about their work interested you, but are not required. Also, you don't have to open it to other projects if you are really only interested in the topic you identified. It depends how important it is to you to focus on a specific topic, or if you are open to whatever the contact might be interested in currently or might benefit them. Nothing wrong with helping out a colleague; sometimes that could be the start of a valuable connection.)

A message like this **really needs to be sent right away** if you want to try this because it takes most scientists a little while to get back to you and/or send you a sample. Since it's the beginning of the semester, you might even send a short follow-up message if you don't get a response in 3-5 days:

I know it is the beginning of the semester, which is busy for many people, so I just wanted to send a friendly reminder about my email to make sure it didn't get lost or forgotten about. Thank you so much for your consideration!

You don't want to get delayed too much on your project. If you don't get a positive response within a week, I recommend you transition to one of the projects from our group, as those will likely have the quickest turnaround.

-Samples can be sent to: Mikel Holcomb, 135 Willey Street, Morgantown, WV 26506

Chapter 2: Understanding Your Sample Better (Anisotropy, Sample Quality, and More)

Out-of-Plane versus In Plane Measurements

Thus far, we have basically ignored spin direction with respect to the sample. But in real materials, the direction that magnetic moments (spins) prefer to point can actually matter a lot—this is known as **magnetic anisotropy**.

In simple terms, magnetic anisotropy describes how some directions inside a material are more “magnetically comfortable” than others. Just like it’s easier to roll a ball downhill than uphill, it’s easier for spins to align along certain directions in a crystal. This directional preference can affect how materials respond to magnetic fields and how stable their magnetic states are—something that's especially important in magnetic memory, sensors, and spintronics.

Magnetic anisotropy tends to play a major role in ferromagnets, ferrimagnets, and antiferromagnets, where spins interact strongly with each other and with the crystal structure. It's also relevant in more exotic systems like helimagnets, spin glasses, and skyrmion-hosting materials, though we will focus on the material systems we have discussed so far.

If you select a thin film to measure, you may want to measure in plane, out-of-plane or both, which will depend on your material. Part of your research into the material you select will be to decide whether in plane or out-of-plane measurements are likely to be more interesting. While not required, you will be allowed to also measure the opposite choice AFTER you’ve analyzed your first directional choice, if there is time and you are still interested. (If we run out of time during the class, there may still be the option to do this measurement after the course is over at a time of your choosing. Speak to Professor Holcomb if interested.)

When you're first trying to figure out whether **in-plane** or **out-of-plane** magnetic measurements will be more useful for your sample, think about the **shape and structure of the material**. For example, if your sample is a **thin film**—like a flat, pancake-shaped layer—it’s often the case that magnetic moments prefer to lie **in the plane**, because there’s more space and fewer energy penalties for aligning that way. On the other hand, some materials or growth conditions can encourage spins to point **out of the plane**, especially if certain atoms or layers stack in a way that favors vertical alignment. While not necessary, to understand what affects this energy, you can explore:

1. Shape Anisotropy (a.k.a. Demagnetizing Effects): This is one of the biggest factors in thin films. A thin film has a large area but very little thickness—like a sheet of paper. When spins align **out of the plane**, they create magnetic fields that extend outside the material more than if they stay in the plane. This costs **magnetostatic energy**, because the system "doesn't like" having magnetic field lines that go far into space. In contrast, if the spins lie **in-plane**, the magnetic field they create is more confined within the material, and that costs less energy. So, from an energy perspective, **in-plane alignment is often favored** in thin films.

2. Crystal Structure and Spin-Orbit Coupling: In some materials, the atomic arrangement and how electrons orbit the nucleus create a built-in preference for spins to align in certain directions. This is called **magnetocrystalline anisotropy**. Sometimes, depending on the stacking of atoms or the symmetry of the crystal, the lowest-energy direction (the “easy axis”) might be **out-of-plane**, even in a thin film. This is more rare, but it does happen—especially in engineered materials like multilayer films or those grown under strain.

3. Strain and Interface Effects: If the film is grown on a different material (a substrate), it might be **strained**—stretched or compressed slightly. That can shift the energy landscape and make **out-of-plane** alignment more favorable in some cases. Similarly, the chemical environment at the interfaces can tweak the spin orientation preferences.

So, in summary, **in-plane spins** usually generate less stray field energy (shape anisotropy), but **out-of-plane spins** can be favored if the crystal structure, strain, or interfaces create the right conditions. So how do you guess which orientation will be better for your material? Start by asking:

- Is the material shaped more like a flat sheet or a 3D chunk? (Thin films are flat.)
- Do you know anything about the **crystal symmetry**? (For more about how crystal symmetry can affect see section after diffraction, which introduces basic concepts of symmetry.)
- Has anything in the literature suggested a preferred magnetic direction?

In this class, part of your job as a researcher will be to make these kinds of guesses, test them experimentally, and adjust based on what you see. It’s totally fine if your first guess is wrong—that’s real science.

To guide you in this decision (and other understanding of materials characterization), we will now give some basics into how to understand what material you have. At the end of this chapter, after explaining a bit about crystal structure, we will come back to this idea of anistropy (differences) in magnetic directions.

A common question that comes up in materials research (whether its magnetic research or something totally different), is how do you even know if your material is good?

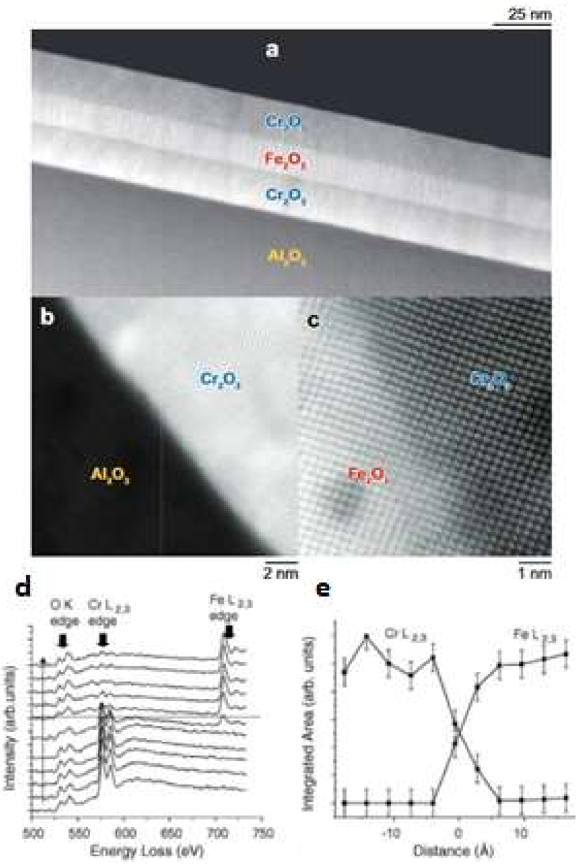


Figure 19: (a) Low-resolution scanning transmission electron microscopy images $Cr_2O_3/Fe_2O_3/Cr_2O_3$ grown on Al_2O_3. (b,c) Higher- resolution scanning transmission electron microscopy images revealing the cation rows at each interface. (d,e) It is not uncommon to do electron energy loss spectroscopy (EELS) to integrate the area under element edges, here Cr and Fe as a function of distance from the interface. Source: https://www.ctcms.nist.gov/hydrogen_storage/Material/PDFs/Transmission%20Electron%20Microscopy%20of%20Multilayer%20Thin%20Films%E2%88%97.pdf This paper reviews the use of a range of transmission electron microscopy techniques to discuss the structure, chemistry, and properties of multilayer thin films.

So, how do you know if you got a "good" sample? What even **makes a sample good**? The answer to this depends on who you ask and what the purpose of the sample is for. To address this, let us consider the example shown in Figure 19. The top panel shows a large scale view of a multiple layer film of $Cr_2O_3/Fe_2O_3/Cr_2O_3$ grown on top of an Al_2O_3 substrate. While the authors argue this is a high-quality film, the zoomed in images in Figures 19b-c show that there is still a lot of defects and variation. Instead of only using the images, sometimes this variation is also studied by element specific measurements that look at the atomic absorption edges (Appendix D) shown in Figure 19d. If you integrate these atomic edges, you can quantify the amount of each element across the thin film, as done in Figure 19e. In Figure 19e, you can see that the Cr concentration is high and the Fe at zero until you get close to the interface. Then it takes a few atomic layers before it is all Fe and no Cr. A perfect interface would be a step function, but interfaces are never perfect. I would say the interface in Figure 19 is a good interface, but there are sharper ones. The sharpness of the interface can also depend on the materials. No matter how much you finesse your growth, you may not be able to make a better interface with some materials. **Why does**

my field focus so much on uniformity? Well, the materials that people are still studying are very complex (if they are not, we typically finished studying them already). A general physicist's approach is to take something very complicated and try to simplify it. How do you do this in materials? Well, you make it as perfect as you possibly can. Once you understand the "perfect" film, then you can add imperfections and see how that changes the material. Sometimes it's not much, sometimes it's a lot.

A challenge is that nothing is perfectly perfect, even in materials that are not thin films (such as powders). There will always be some defects. But the line between how many defects is ok depends on who you are talking to and what they are using it for. There can be situations where defects are even beneficial, but this is not typically the case when we are first trying to understand a material. For example, samples with rough surfaces are beneficial for solar cells, as the roughness helps with light absorption. For an example of an even more uniform film, see Figure 20.

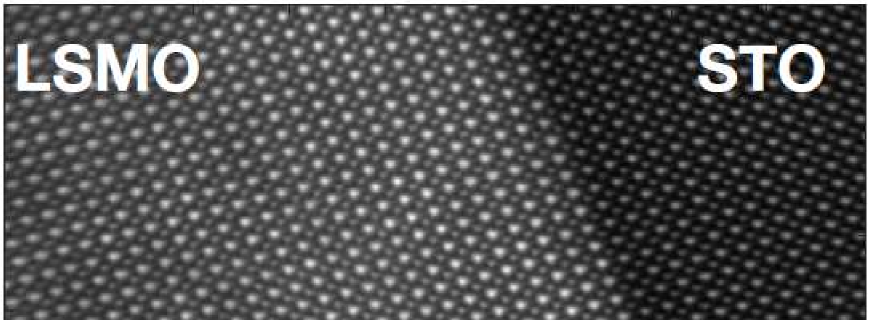


Figure 20: Cross-sectional transmission electron microscope image of our LSMO/STO thin films. While I do not claim it to be perfect, it is more uniform than the films in Figure 19.

The circles you are seeing are atoms (technically a column of atoms that stack up behind it). Crystal structures have a few different types of ways the atoms organize themselves. Figure 21 shows what is known as a body centered cubic lattice. There is also simple cubic that does have the atom in the center and face centered cubic that has atoms on the face centers of the cubes. There are other types of lattices. They can be more complicated.

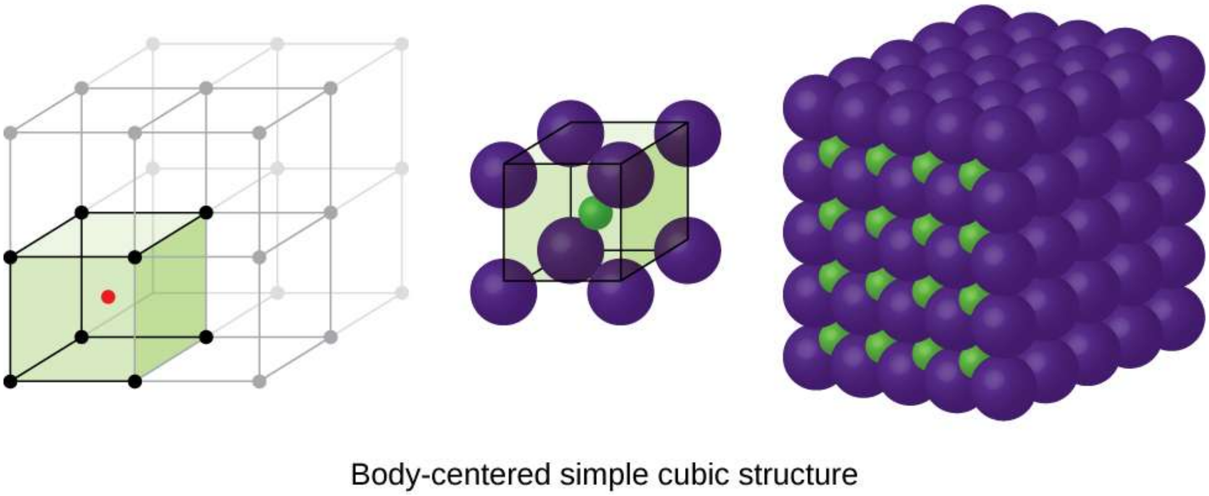


Figure 21: The body-centered cubic lattice. Source: https://iu.pressbooks.pub/openstaxchemistry/chapter/10-6-lattice-structures-in-crystalline-solids/

Based on the representation you see in Figure 21, you can see it is common to show the lattices as cubes. We will use a side view of these cubes (thus squares) to help demonstrate one meaning of high-quality thin films. The highest quality thin films are called epitaxial. Epitaxial means that the distances between atoms in your thin film is the same as the substrate you grow it on. The difference between eptaxial growth and relaxed is illustrated in the left side of Figure 22 in the matched region. As we stated, it is wise to pick a substrate where the distance between the atoms is similar to what you are trying to grow. If they match well, you have the potential for it to grow epitaxially; it is still hard to do. Even when those distances are close, it may not match well, as there is an energy cost associated with spacing the atoms closer or further from what they naturally like to be. The thicker you grow the film, the larger that energy to match becomes, and eventually there will be defects, such as the defect planes/lines shown on the right side of Figure 22.

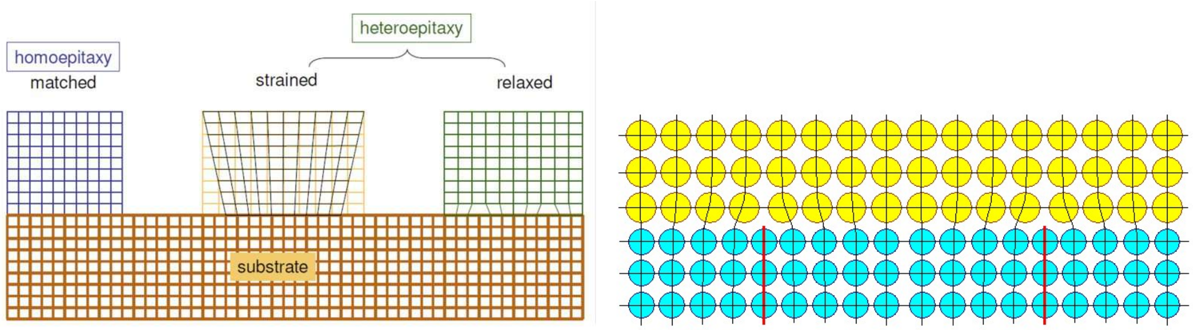


Figure 22: A thin film is grown on a substrate, that ideally has a similar distance between atoms as the film you are growing. If the amount is off by more than a couple percent, the film is not likely to match up and grow very smoothly. Source: https://www.mks.com/n/silicon-epitaxial-thin-films

You do not necessarily have to take transmission electron microscopy images of your films to get some judgement of their quality. In fact, I would not normally recommend TEM, as the process to do it destroys your sample. (There are cases where it is worth it, but I would say that is unlikely for our task here. I decided to introduce it to you anyway, however, as it is very visual and is a commonly shown characterization method that you will see in many papers.) There are nondestructive methods to characterize samples.

X-ray Diffraction

The most common method to learn about samples is x-ray diffraction (XRD). XRD is so common for many reasons. It is nondestructive, so it will not mess up your sample by doing measurements, unlike electron microscopy. It is relatively cheap, which is a big bonus. It also tells you a lot about your sample, not just information about its quality.

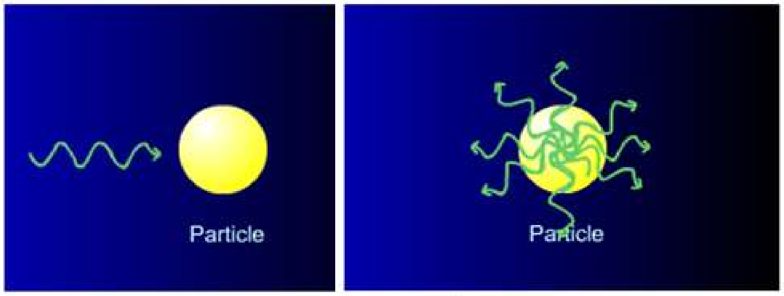


Figure 23: When x-rays are illuminated onto an atom, the atom can absorb that energy and reemit it in all directions but with lower intensity.

Before we go into what we can learn from XRD, let us discuss a little bit about diffraction in general. As illustrated in Figure 23, when x-rays interact with atoms you get scattering. Scattering is the emission of x-rays of the same energy and frequency as the incident x-rays in all directions (but with much lower intensity). When a bunch of atoms are together is some periodic fashion (as you find in a crystal), this outgoing light will have regions of constructive or destructive interference. In other words, the outgoing scattering of all atoms will sometimes cancel out, and sometimes add together. It is more common for it to cancel out, so you will get a limited number of peaks. Note that diffraction is not limited to x-rays or even electromagnetic (light) waves (Appendix F). For example, Figure 24 shows two very different examples of water waves.


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Figure 24: (Left) The superposition of waves created by two tennis balls wiggled in a lake. Note that destructive interference occurs when the two waves cancel out. (Right) You can see wave bending when the distance between the wave crests (the wavelength) is similar in size to obstructions (rocks).

You can imagine the atoms like the tennis balls, except there are a lot more atoms. Having more sources of the oscillations means you get more regions where the oscillations cancel out, but you will get some spots where they add up. Where the add up is where you get diffraction peaks.

The condition for constructive interference (when they add together) is often explained by Bragg's law. As we will see there are some additional considerations we will need, however, Bragg's law is a great introduction. When the path difference of waves from scattering off of different planes of atoms is off by an integer number (n) of wavelengths (as shown in Figure 23), you have the potential for constructive interference. Whether this happens, depends on the wavelength (λ) of the light, the distance between the planes (d) and the angle (θ) of the incident light. The formula for this condition is

$$n\,\lambda = 2d \sin(\theta)$$

Careful study of Figure 25 (not necessary though) will help you understand why this formula is the case. The path length of the green and red oscillations in Figure 25 are the same before and after they reach the triangles. For them to add up means that the extra path length has to be equal to another wavelength or multiple wavelengths. Some trigonometry will help you realize that if the distance between the horizontal planes is d then, the extra path length traveled for the green wave along each of the two triangles is $d\sin\theta$, and thus $2d\sin\theta$ has to be equal to some multiple of the wavelength in order for them to add up.

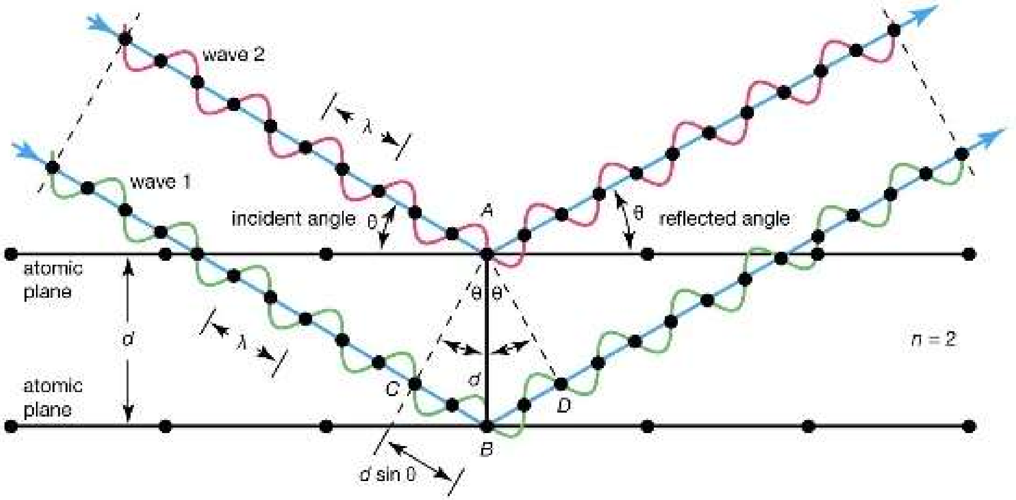

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Figure 25: Illustration of Bragg's law showing constructive interference. Source: https://www.britannica.com/science/X-ray-diffraction

All sets of atoms planes (see Figure 26 for some examples of different sets of lattice planes) MAY cause this destructive interference, but there are some notable exceptions and those exceptions are actually a great way to understand how the atoms organize in your material!

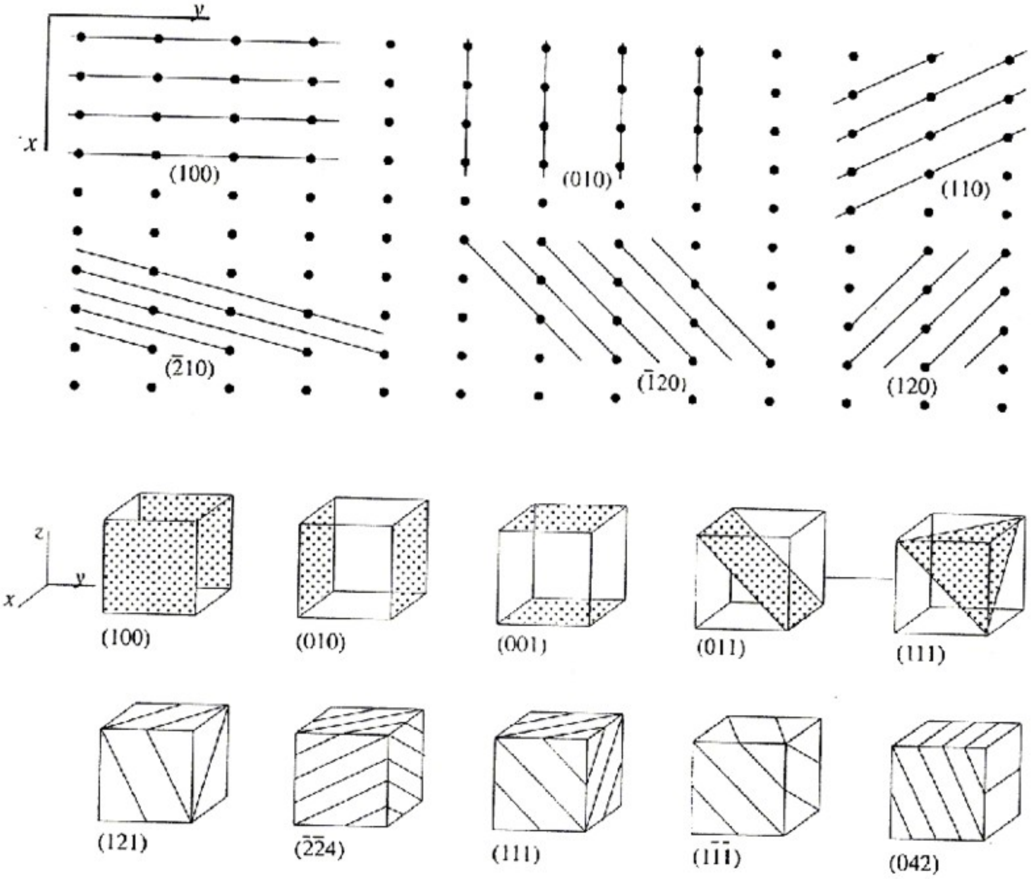


Figure 26: Representations of different lattice planes. We refer to these three numbers as **(h k l)**, known as Millier indices.

To understand why SOME sets of lattice planes do NOT give a peak like you might expect from Bragg's law, let us consider a very small deviation to Figure 25. Let's add one more set of lattice planes (in red) between the two we considered before (as shown in Figure 27), except let's make the atoms between the planes shifted in between the horizontal positions of the other two planes. Now, let's think about how this affects the scattered waves. Previously, in Figure 25, the x-rays scattered from the two original planes added together constructively when the Bragg condition was met. But now, with our extra set of lattice planes positioned in between, something interesting happens. The contributions cancel out. The vertical offset of the atoms is important for this extinction. Because the new atoms are not directly in line with the original planes, the x-rays they scatter will have a different phase compared to those from the original planes. Specifically, if these atoms are positioned halfway between the original planes, the x-rays they scatter will be shifted in phase by half a wavelength (λ/2) relative to the waves from the original planes. A phase shift of λ/2 means that the waves scattered from these intermediate atoms will be **out of phase** with the waves scattered from the original planes. This causes destructive interference, meaning the waves cancel each other out rather than adding up to form a peak.

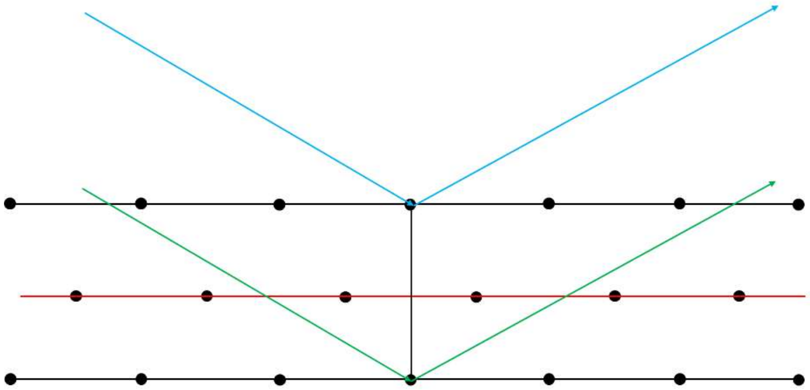


Figure 27: Adding in an offset plane of atoms will need to extinction, or the lack of a diffraction point where you might otherwise expect one.

Why Does This Matter?

This situation models what happens in certain crystal structures, like body-centered cubic (BCC) and face-centered cubic (FCC), where extra atoms inside the unit cell lead to systematic absences in the diffraction pattern. Because of their positions, the scattered waves from different atoms in the unit cell cancel each other out for certain reflections, even though Bragg's law might suggest a peak should appear. Thus, while Bragg's law tells us when diffraction *could* occur, the actual diffraction pattern depends on both atomic positions and interference effects. By analyzing which peaks are missing, we can learn important details about how atoms are arranged in a material.

So far, we have discussed why diffraction peaks occur, but there are multiple ways to collect the diffraction data. Which way you use depends on what kind of sample you have and what you are looking for. For example, if your sample were not perfectly ordered like the epitaxial films we discussed before, but were instead made of lots of grains like shown in Figure 28, you would do powder diffraction. When your film is oriented in many directions, there is no reason to rotate the sample, you can just sweep the detector around in a circle to collect all possible peaks. This is a common way to study powders and is an excellent method for determining the lattice type (simple cubic, body centered cubic, face centered, etc.), since all of the peaks that don't experience the extinction discussed above will show up.

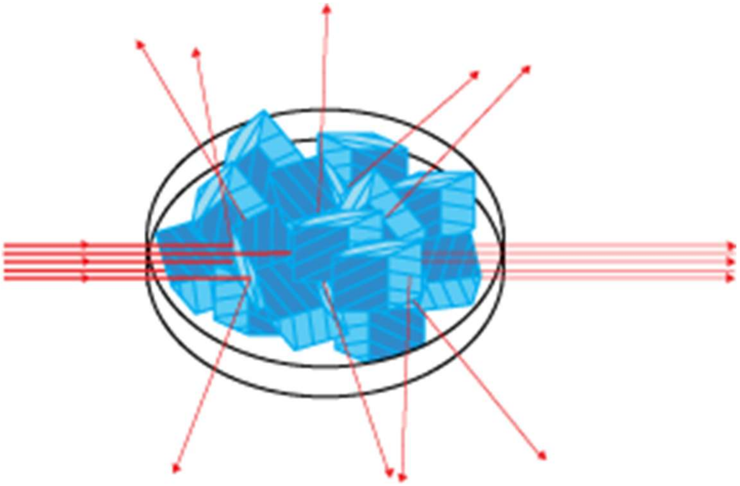


Figure 28: You still get diffraction peaks even if your material isn't all ordered in the same direction.

A typical powder diffraction experiment might give a result similar to that shown in Figure 29. The intensity of the peak is on the y axis and the angle of diffraction is on the x axis. It is common for the x axis to say 2θ instead of just θ, because that is actually how much the x-ray is deviated from if the beam went straight through the sample.

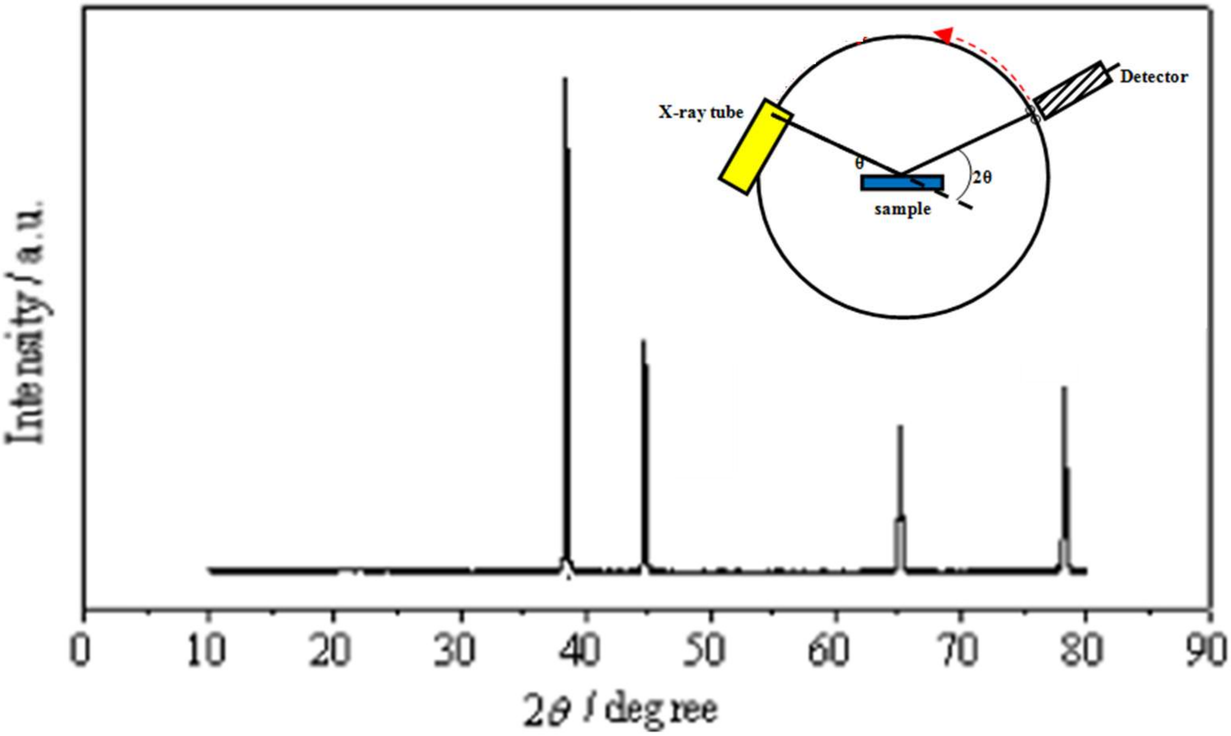


Figure 29: Example XRD powder diffraction data of some form of cubic lattice to help us figure out how to analyze this data. Inset shows a possible orientation, emphasizing that the beam reflection is 2θ away from the incoming beam direction.

So if I told you what angles these peaks occur at, how do we figure out what crystal lattice we have? We'll partly use Bragg's law [n λ = 2d sin (θ)], but we are going to need to know more about d, the distance between the planes, which depends on which planes we have (which we don't know). So, what do we do? Well, one option is to insert your data into a computer and sometimes it's good at telling you what you have. You could also painstakingly try to match it with stuff on you find on google images. But, both of those options might not work, so let's go through what the computer does. First of all, we need to relate the distance between the planes d to the lattice parameters of the material. The lattice parameter is the distance in a particular direction that you need to travel to repeat the unit cell. We could consider a cubic system or an orthorhombic system. In a cube system, the lattice parameter is just the side. An orthorhombic system still has 90 degree angles but the lengths of the sides are different; sides in the x direction are different than the y direction which are different than the z direction. Note: plenty of material systems do not have 90 degree angles, but those formulas get more complicated, so let's stick to some of the simpler ones for this discussion.

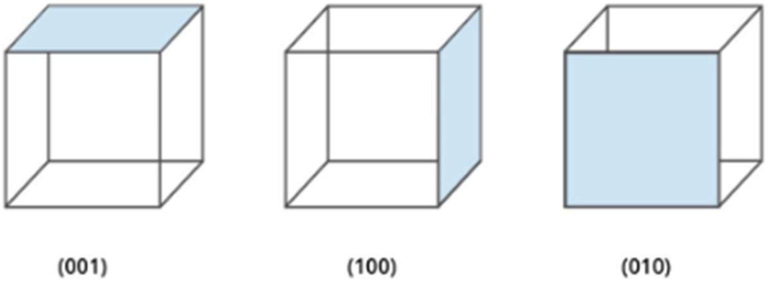


Figure 30: Half of the examples from the {100} family of planes. We don't use the negatives such as (-1 0 0) for peak labeling, as they are redundant with their positive counterparts.

In a cubic lattice, the distance between the 100, 010 or 001 planes are all equal to the lattice parameter a. Whereas in the orthorhombic system shown in Figure 31, the distances would be a, b, or c depending on if you wanted d_{100}, d_{010} or d_{001} respectively.

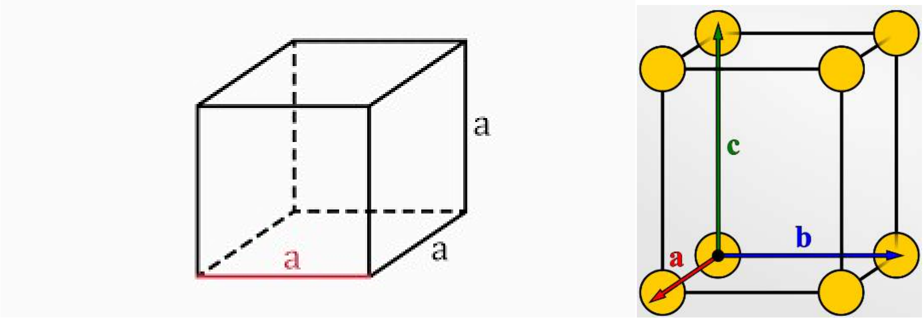


Figure 31: Lattice parameter of (left) a cube versus of (right) an orthorhombic system.

These distances get a little more complicated as the Miller indices (h k l) become larger. But the formula for the distance between planes for a cubic (a=b=c), tetragonal (a=b≠c) or orthorhombic (a≠b≠c) system can be generalized to:

Cubic
(a=b=c)

$$\frac{1}{d_{hkl}^2} = \frac{\left(h^2 + k^2 + l^2\right)}{a^2}$$

Tetragonal
(a=b≠c)

$$\frac{1}{d_{hkl}^2} = \frac{\left(h^2 + k^2\right)}{a^2} + \frac{l^2}{c^2}$$

Orthorhombic
(a≠b≠c)

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Note that the formula for an orthorhombic system when a is set equal to b and c simplifies to the cubic system, and similarly for the tetragonal formula. Formulas exist for more complicated systems where the angles between the lattice directions are not 90 degrees, but you really only need those if you suspect your system is not orthogonal (90 degree angles). If you have one of these more complicated lattice types, it's more common to use the computer program to fit things, but we want to get the idea here.

If we limit ourselves to the first order diffraction peaks (n=1) which will be at the lower angles, combining Bragg's law and the distance equation for a cubic system gives:

$$n\,\lambda = 2d \sin(\theta) \quad \text{but let's set } n=1$$

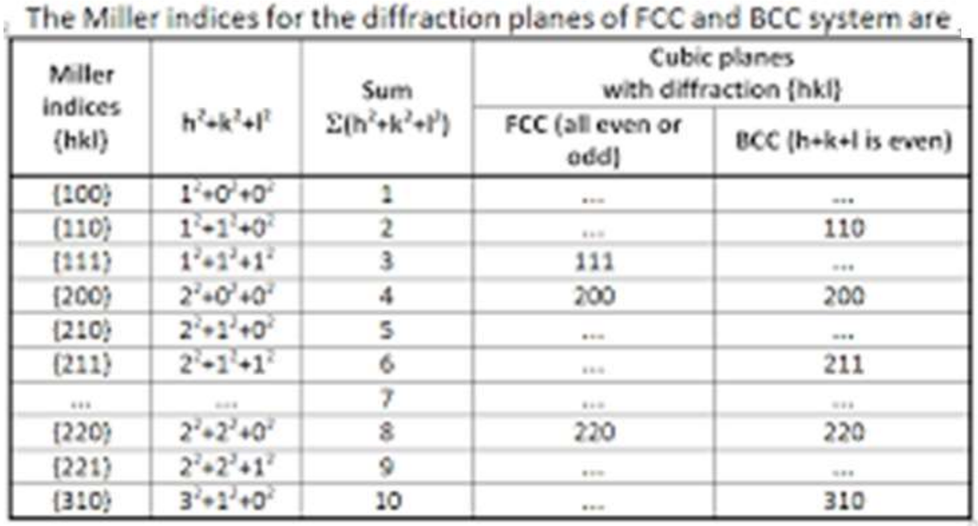
and square everything

$$\lambda^2 / 4d^2 = \sin^2(\theta)$$

Plug in for d

$$\sin^2(\theta) = \lambda^2 (h^2+k^2+l^2)/\,4a$$

For convenience the sum of $h^2+k^2+l^2$ is given for all simple cubic, body centered cubic (bcc) and face centered cubic (fcc) in Figure 30. All combinations of h, k and l are allowed for simple cubic, but bcc and fcc have only certain peaks, due to the extinctions we discussed. If you look at the bcc and fcc lattices in Figure 32, you will probably be able to see how you sometimes get those planes that are offset from the rest that cause extinctions. Note that even if a system has an orthorhombic structure (a≠b≠c), it can still have a bcc or fcc alignment of the atoms within that structure. We also still label the Miller indices (h k l) for the places the same whether the system is cubic, orthorhombic or even some more complicated structure.



The Miller indices for the diffraction planes of FCC and BCC system are

Miller indices {hkl}	$h^2+k^2+l^2$	Sum $\Sigma(h^2+k^2+l^2)$	Cubic planes with diffraction {hkl}	
			FCC (all even or odd)	BCC (h+k+l is even)
{100}	$1^2+0^2+0^2$	1	...	...
{110}	$1^2+1^2+0^2$	2	...	110
{111}	$1^2+1^2+1^2$	3	111	...
{200}	$2^2+0^2+0^2$	4	200	200
{210}	$2^2+1^2+0^2$	5	...	...
{211}	$2^2+1^2+1^2$	6	...	211
...	...	7	...	...
{220}	$2^2+2^2+0^2$	8	220	220
{221}	$2^2+2^2+1^2$	9	...	...
{310}	$3^2+1^2+0^2$	10	...	310

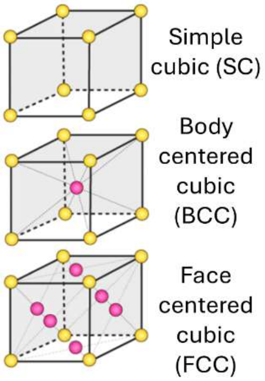


Figure 32: Expected diffraction peaks for face centered and body centered cubic. Simple cubic has peaks for every combination of h, k and l.

You still might be wondering how we are going to learn anything useful from the equation $\sin^2 (\theta) = \lambda^2 (h^2+k^2+l^2)/ 4a$ since we have several unknowns. There's a trick. We are going to divide $\sin^2 \theta_2$ by $\sin^2 \theta_{1.}$ θ_1 is the smallest angle at which a diffraction peak occurs and θ_2 is the second smallest angle. When I divide $\sin^2 \theta_2 / \sin^2 \theta_1$, the constants $\lambda^2/ 4a$ cancel out, leaving me with only the sum of the squares of the Miller indices for the first and second diffraction peaks.

Crystal lattice	1st	2nd	3rd	$\sin^2 \theta_2 / \sin^2 \theta_1$	$\sin^2 \theta_3 / \sin^2 \theta_1$
BCC	110	200	211	$2^2 / 1^2 + 1^2 = 2$	$2^2+1^2 +1^2 / 1^2+1^2 = 3$
FCC	111	200	220	$2^2 / 1^2 +1^2 +1^2 = 4/3$	$2^2 +2^2 / 1^2+1^2 +1^2 = 8/3$

Thus, the relative position of even the first two peaks can give you a lot of information about the crystal structure. (I should probably note that the ratios for SC and BCC are the same for the first several peaks, and thus they are difficult to distinguish from this trick alone, however you can normally guess which you should have depending on the ratio of the radii of the atoms in the structure. There is only one single element lattice that forms in the simple cubic structure, but many structures with more than one element are simple cubic. If you would like me to add here how to do this radial comparison, please let me know.)

Is there anything else we can learn from the diffraction pattern? Once you've figured out which lattice you have, you can also determine the lattice parameter (a, b and c), which tell you the distance between atoms. Why would we care about the distances between atoms? These distances can have a huge effect on how the atoms interact, affecting magnetism and bonding. The width of these peaks tells you about how consistent the lattice parameters are. If they vary, the peaks will spread out. As atoms bounce around due to thermal energy, diffraction peak widths can get bigger at higher temperatures, though not enough to worry about. Material structure can also sometimes change with temperature. Most XRD systems are fixed at room temperature, but there are special facilities in national labs if that were an important measurement for a new material you were studying.

Many of the samples we will study will not be powders but single or polycrystals. Both can still be studied by the same manner as powders, but you may see a lot less peaks. Polycrystals may still exhibit several peaks like powders, but you may not see all of the possible reflections because certain orientations may be preferred in your film. Thus, our trick of looking at the relative position of the first two peaks, might not work; though, it's still worth a check if you have the data.

Another complication of measuring films rather than powders is that you typically grow your film on a starting material called the substrate, as shown in Figure 16. The substrate is going to have its own set of diffraction peaks. An example is shown in Figure 31 of a thin film on top of a substrate. One material is $SrTiO_3$ and the other is (LaAlO3)0.3-(SrAl0.5Ta0.5O3)—nicknamed LSAT. Both materials are simple cubic. How do you figure out which is which? Notice that the width of the peak are different—one is very sharp and the other is less sharp. Substrates are typically purchased from a vendor that specializes in growing very high quality crystals, so that people can grow on top of them or use them for some other purpose, thus the spacing between the atoms is very consistent—producing a sharp peak.

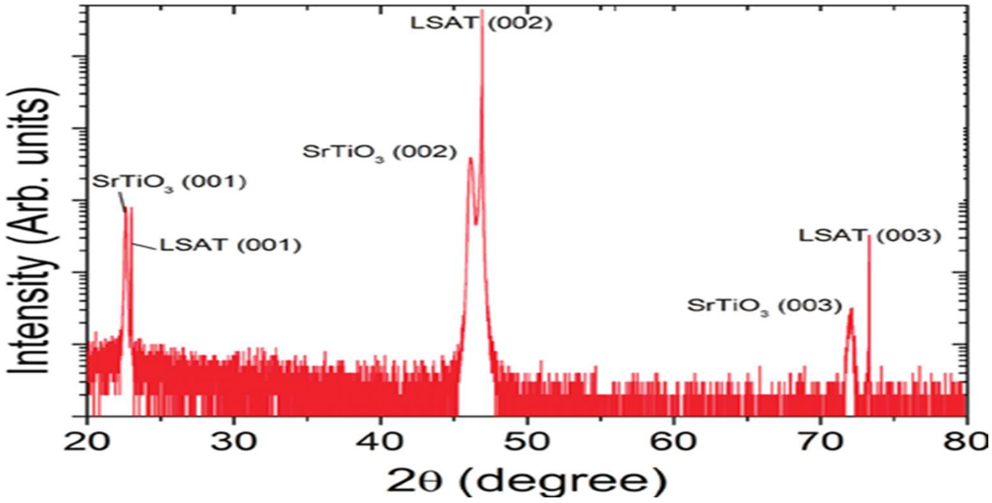


Figure 33: XRD of thin film on a substrate

A sharp eye might notice that all of the peaks in Figure 33 have similar indices: 001, 002 and 003. The second two are the higher order (n=2 and 3) of the (001) planes. Why don't the others show up? They might not show up anyway, but this particular measurement was done in a different way. Previously, we only rotated the detector. Now we are going to rotate the sample and the detector such that the reflection angle is the same, as shown in Figure 34. This is known as the Bragg-Brentano geometry and will only show the sets of planes that are perpendicular to the sample surface, so most sets of planes will not show up. This is helpful if you want to know what that perpendicular orientation is or if you are only interested in the lattice parameters of the film—perhaps you already know the lattice type from similar prior samples.

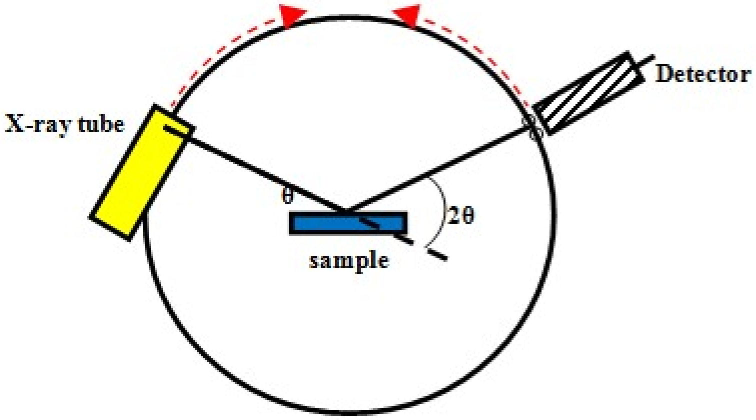


Figure 34: Bragg-Brentano geometry of XRD, common for single crystalline films

The sample in Figure 33 does not have any but there are other things that can complicate the diffraction pattern. Materials do not always grow how you expect them to. Even if you are trying to grow all one material, sometimes other materials form as well, known **as secondary phases**. To provide an example, I will show some samples grown by NASA. These are not magnetic samples, but rather superconducting samples.

Superconductors are materials that can carry electricity with zero resistance—meaning no energy is lost as heat. Once current starts flowing, it can keep going forever without needing more power. That's a big deal. Superconductors also be useful for lower energy power grids, MRI machines, magnetically floating trains, quantum computer and much more! NASA is using superconductors to make more sensitive detectors that can detect signal photons—similar to some work in quantum computing devices.

The problem (that we are helping them with) is that their superconducting films are not perfect, and it is influencing the performance of their devices. In this example, they are growing Nb superconductors, and the Nb is oxidizing. Several (Nb_2O_5, NbO_2, and NbO) different possible oxide states are possible, and some of these oxide states may be worse for their devices than others. Surface phases (due to interacting with the environment) are not the only possible kind of secondary phase that can form when growing a material, but it is what we will focus on for this example. (Another example of possible secondary phases might be if I were trying to grow a material made of elements A, B and oxygen O with the formula ABO_3, it might not be uncommon to get secondary phases A_2O_3 or B_3O_4. These other phases would give very different diffraction peaks, that would likely have much smaller peaks since their would probably be a lot less of this material.)

There are other methods of XRD, such as rocking curves (Appendix G) and reciprocal space maps (Appendix H), but they are more advanced than we need to consider now. There is also a related x-ray method that uses the same machine but is not a diffraction effect; this other method is called x-ray reflectivity (Appendix I) which is also somewhat common in the literature for verifying sample thickness, density and roughness. Reflectivity occurs when the angle from the sample surface is too small for diffraction. While not x-ray related, another tool in the same room as the XRD system is ellipsometry. While measurements beyond the magentic measurements are not required for this class, if you would like to learn more about ellipsometry, please see Appendix J.

Crystal Symmetry Effects on Magnetism

As we have discussed, x-ray diffraction can tell you what is your material's crystal symmetry. We previously discussed that crystal symmetry can affect your material's preferred magnetic directions. The **crystal symmetry** of a material influences how **magnetocrystalline anisotropy** behaves, which can give you clues about whether the spins prefer to point **in-plane** or **out-of-plane**. Here's how that works:

1. Symmetry Defines "Easy" and "Hard" Directions

Every crystal has certain directions that are more "special" than others—these are often called **high-symmetry axes**. Magnetization tends to prefer directions where the crystal looks the same in all directions around the spin—because that leads to a more stable (lower-energy) configuration. These are called **easy axes** of magnetization. In some crystals, one of those high-symmetry axes might point **out of the plane**—for example, in a material with a **hexagonal** or **tetragonal** crystal structure, the **c-axis** (the vertical axis) can be quite different from the in-plane directions (a and b axes). If the spin prefers to point along the c-axis, that's **out-of-plane anisotropy**.

2. Examples of Out-of-Plane Favoring Symmetries

- **Hexagonal close-packed (HCP)** materials: Often favor magnetization along the **c-axis** (out of plane), because it's the unique symmetry direction.
- **Tetragonal** structures: The **[001] direction** (perpendicular to the square base) may be favored, especially if there's strain or elongation.
- **Layered materials** (like some transition metal oxides): The bonding is different along the vertical direction, which can make spins want to align **perpendicular** to the layers.

3. How to Guess from Symmetry

Ask yourself:

- Does the crystal have a **unique axis** (like a c-axis in hexagonal or tetragonal crystals)?
- Are the in-plane directions **all equivalent**, but the out-of-plane one is different?
- Is the material made of **stacked layers**? If so, are the interactions between layers weaker or different?

If the answer to these is yes, then there's a good chance the **out-of-plane direction could be energetically favored** for magnetization. In summary, **differences between in-plane and out-of-plane directions**—especially in crystal structure—is a key clue that magnetization might prefer to be out-of-plane. This is something you can look up in the material's crystallographic data, find out via x-ray diffraction or test experimentally with magnetic measurements in both directions.

Appendix A: A Brief Introduction to Atomic Energy Levels and Electron Spin

Since iron is a well-known magnet, let's use it for our example. Figure A1 shows the electron configuration or energy levels of individual iron atoms. Note: only the lower levels are filled, as electrons like to fill the lowest levels unless given enough energy to excite from these levels, as can happen through heat or light absorption, for example.

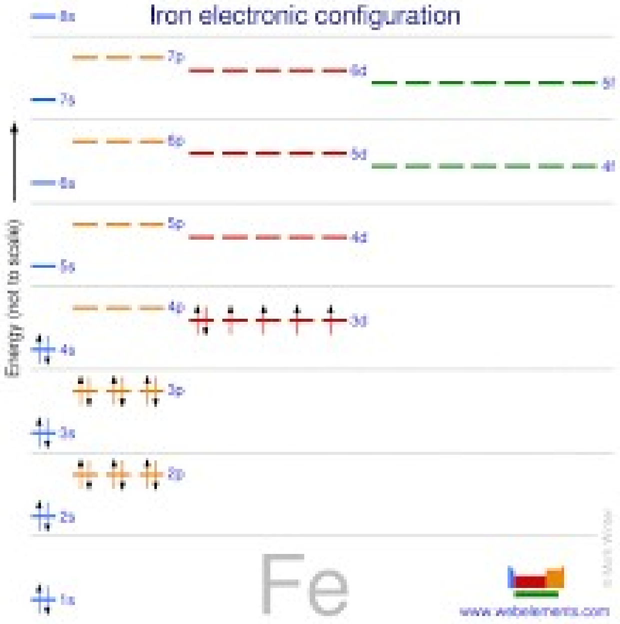


Figure A1: Energy levels of individual iron atoms. Source: https://www.webelements.com/iron/atoms.html

You will notice orbital labels of numbers (1-8) and letters (s, p, d and f). These are quantum numbers and you will learn more about them in modern and quantum physics. Note that all of the lower filled orbitals have arrows pointing up and down, thereby canceling out. It is only the 3d orbitals that have arrows that do not cancel out. The fact that they do not cancel out means that the magnetization of this material when introduced to a magnetic field will want to align with that magnetic field. What happens after the field is removed depends on what type of magnetism this material experiences (discussed further in the main text).

When electrons fill up the energy levels in an atom, there are some basic rules that help predict how the spins will arrange themselves. These are called **Hund's Rules**, and they help explain why some atoms—and therefore some materials—end up being magnetic.

Here's a simple version of what Hund's Rules say:

1. **Electrons prefer to stay unpaired** in different orbitals of the same energy (if space allows). Think of it like kids sitting on a school bus: they'd rather each take their own empty seat than sit next to someone right away.

2. **When electrons do stay unpaired, they tend to spin in the same direction.** This aligned spin gives the atom a **net magnetic moment**—it starts to “act magnetic.”
3. **If electrons must pair up (because all orbitals are full), they’ll do so with opposite spins**, canceling out their magnetic effects.

So, Hund’s Rules explain why atoms like iron (with several unpaired electrons spinning the same way) can be magnetic, while others like neon (with all electrons paired) are not.

Appendix B: A Rough Understanding of What Could Be Occurring in SMR

The following argument has been applied to non-single-phase systems exhibiting SMR. This may or may not be the case here. Let me remind you of the magnetization versus temperature for a ferr**o**magnet that we showed in Figure B1.

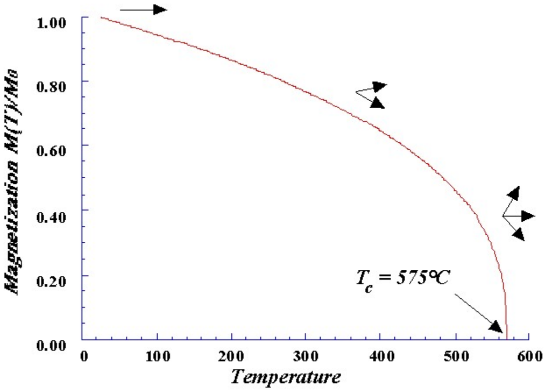


Figure B1: Normalized magnetization versus temperature for a ferromagnet

In a ferr**i**magnet, the magnetization of the two sublattices A and B work partly cancel each other out, but not completely. One example of how this my look for the magnetization versus temperature is shown in Figure B2.

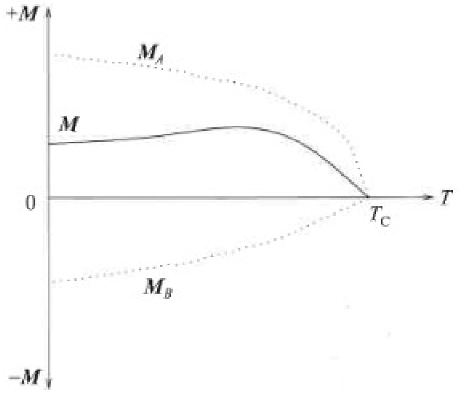


Figure B2: One possibility for how the magnetization versus temperature can look for a ferrimagnet.

However, it could be more complicated. For example, it is possible that the critical temperature of the two sublattices are different. If so, you have the potential to generate something more like Figure B2, which looks a lot more like what we found in Figure B3. The blue and red curves are the sublattice magnetizations, while the rest are the overall magnetizations we measure as we change the applied magnetic field in which we do the measurement. This is a mean field theory approach. You will note that the fit is very good. It is tempting to say this must be right. However, multiple magnetic sublattices can be observed via polarized neutron reflectivity. While we have measured many samples showing SMR, we have only observed one sample (which was purposefully made with a lot of missing oxygen) that showed any evidence consistent with more than one magnetic sublattice like that shown in Figure B2. Even if this interpretation is correct, it is unclear why the negative magnetization would be larger.

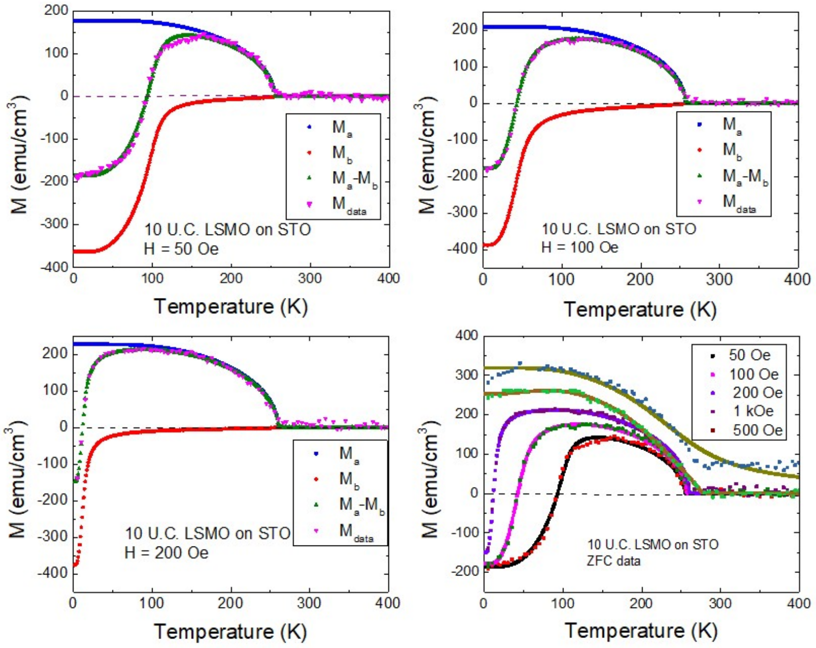


Figure B3: Magnetization versus temperature measured in different magnetic fields for two sublattices of different ordering temperatures, where the negative lattice has a lower ordering temperature and a stronger magnetization.

Appendix C: Interesting Student Questions

This appendix shows two questions I had gotten from Seth Richardson (a WVU undergraduate), a day after I told him about our magnetic finding in a way very similar to what is presented in this tutorial. The day after that discussion he read one of our papers (Observation and interpretation of negative remanent magnetization and inverted hysteresis loops in a thin film of La0.7Sr0.3MnO3). His questions are good and the answers to these questions get to the heart of some future directions I want to take. I also think that it is good for students to see that people new to the field can ask really probing questions for which I do not yet have complete answers. That means you have the ability to come up with ideas and experiments to test these questions and contribute significantly to this field. With your permission, maybe some of your questions will be featured in a future version of this document.

Question 1: Are negative remnant magnetization (NRM) and inverted hysteresis loop (IHL) activity only observed when using zero field cooling and a thin material?

My response: NRM and IHL are only observed with zero field cooling. It's possible that VERY tiny fields might also do it, but they'd probably have to be less than 10 Oersteds. I'm not sure about whether this is only observed in thin films (it takes a long time for us to grown films beyond 40 nm, which is still pretty thin). That's something I'd still like to test. I suppose we could grow a really thick sample. Alternatively, we could find another sample source. I have a colleague that grows LSMO. I suspect he is also mainly doing thin films, but he might be able to do longer depositions easier than us.

Question 2: What does it mean to state that the LSMO/STO material "is a mixture" of superparamagnetic (SPM) and ferromagnetic (FM) states? Does that simply mean there are clusters of LSMO material spread out on top of the film of the same material-film?

My response: First, let me make clear that these films are very high quality, and an visions of “clustering” should not be anything similar to the visions you might think about when considering nanoparticles or even films with a lot of grains. Whatever is going on, the film looks very consistent throughout. As we have discussed, there is not such thing as a perfect material without defects, but those defects are quite limited.

Navid (my former graduate student and the first author of that paper) and I actually discussed in depth whether it made since to call these phases superparamagnetic. While I agreed with him that they were behaving that way, I preferred to call them superparamagnetic-like, much in the same way that I called that other phase in my discussion diamagnetic-like. In the end, I allowed Navid to call it superparamagnetic in the paper; I'm still not sure if that was the right choice, but that's what we went with. To have a mixture means that for some reason, both ferromagnetic magnetism and some other kind of magnetism is occurring at the same time in slightly different locations. While I'm still not completely convinced on the topic, I'd say that the evidence is leaning more toward those locations being more or less equally spread out through the film. This spread could happen a few ways. For example, perhaps around defects (such as missing oxygen), the other kind of magnetism wins the competition, whereas ferromagnetism wins without those defects. We can discuss this more, but another thing that happens a lot in thin films (will be in the tutorial) is that the distance between the atoms change; that change can also affect whether FM or the other magnetic phase wins locally (in this case, I would think that the other phase would be more separated from the FM phase, which I'd say our data doesn't seem to agree with, but I'm still open to exploring the idea more. Yet another possibility is more abstract. So, we know there is competition between two phases. I suggested that defects or distances between atoms could be enough to change the winner of this competition. What if this competition isn't locally fixed? What if it's more quantum mechanical in nature? What if it's in a superposition of both? Intriguing question. Really tough to figure out how you would verify that, but perhaps we should find some people (like Ned) who specialize in quantum mechanical measurements with whom to brainstorm.

Appendix D: What is an absorption edge?

In Appendix A, we talked about the energy levels of atoms. When we shine light—or more precisely, X-rays—onto a material, the atoms in that material can absorb the energy if it’s just right. Each atom has electrons in different energy levels, like rungs on a ladder. The inner electrons (close to the nucleus) sit on the lower rungs, and it takes a lot of energy to knock them loose.

An **absorption edge** happens when the incoming X-ray has **just enough energy to eject an electron** from one of these tightly bound inner levels (like the 1s or 2p levels, depending on the element). If the X-ray doesn’t have quite enough energy, nothing happens. But once it hits that threshold, the atom suddenly starts absorbing a lot of X-rays—that’s the “edge.”

This sharp jump in absorption is called an **absorption edge**, and it's different for each element, kind of like a fingerprint. Scientists use these edges to study which elements are present in a material, and even learn about the way atoms are bonded or how their electrons behave.

So in short, an **absorption edge** marks the point where X-ray energy is high enough to knock a specific electron out of an atom’s inner shell. It’s like a doorway that opens only when you have the exact right key (energy).

Absorption edges are frequently studied to know what element are in a material, or even the position dependent location of elements, such as to judge whether an interface has a sharp transition between different materials. The Holcomb group using x-ray absorption spectrscopy for a wide range of scientific experiments, including helping NASA optimize their next-generation single photon detectors.

Appendix E: Magnetic Background Substraction

When we start taking magnetic data, you will notice that it looks different from what you might suspect. We have to do some background subtraction to get it to look like a normal hysteresis loop.

https://arxiv.org/ftp/arxiv/papers/1807/1807.01348.pdf Here is a link to a paper that explains that the substrate itself contributes to the total signal we observe. Remember that the system measures total magnetization, and the properties of the substrate (which is much larger than the thin film) will affect our results.

Here is a figure from that paper showing the raw data on the left and the subtracted data on the right.

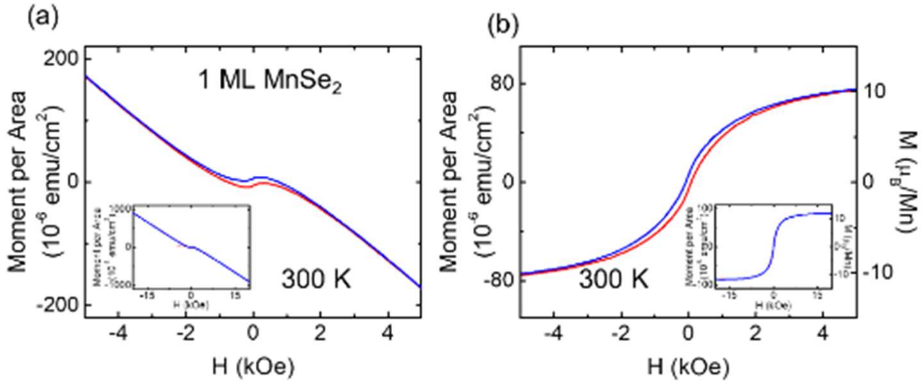
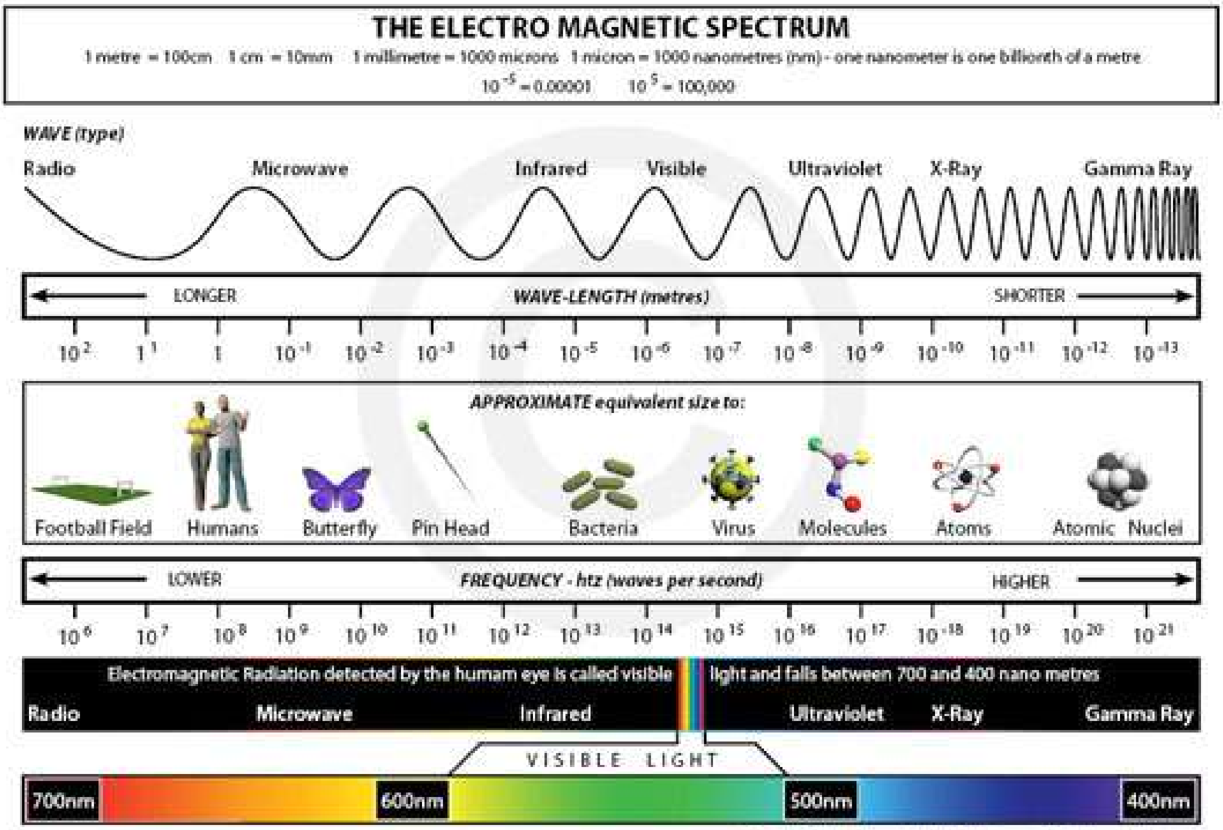


Figure 2. Room temperature, out-of-plane magnetic hysteresis loop of 1 ML MnSe$_2$. (a) Raw bulk magnetization loop showing diamagnetic background from substrate. Inset: Full range M(H) scan up to higher magnetic fields. (b) Bulk magnetization loop after linear diamagnetic background subtraction of raw data. Inset: Full range M(H) scan up to higher magnetic fields.

Appendix F: Electromagnetic (Light) Waves



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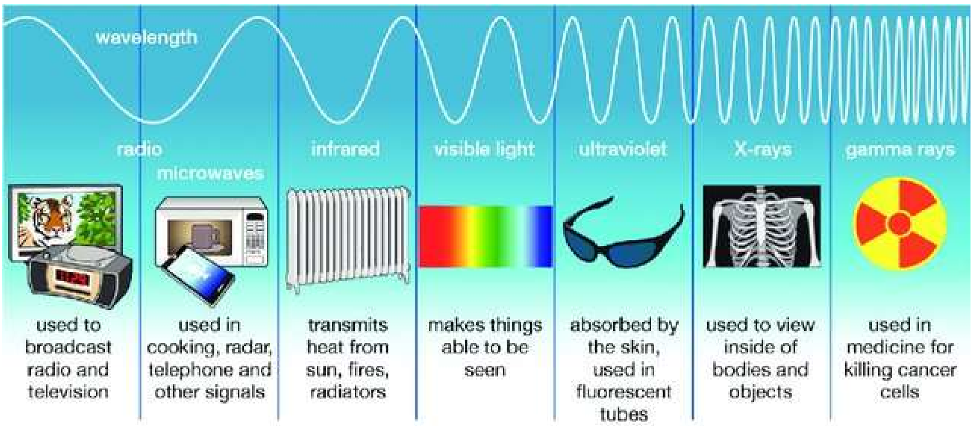
Electromagnetic energy travels in waves and spans a broad spectrum from very long radio waves to very short gamma rays. The human eye is only sensitive to a small portion of this spectrum called visible light. A radio detects a different portion of the spectrum, and an x-ray machine uses yet another portion. (Source: https://science.nasa.gov/ems/01_intro) The chart above gives the size and frequency of the electromagnetic spectrum. The figure below discusses some applications of different kinds of waves. (Source: https://www.researchgate.net/publication/328648666_Advanced_Ceramic_Materials_Sintered_by_Microwave_Technology)



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Appendix G: Rocking Curves

(Our current XRD system does not have this feature, but maybe a future one will.)

As we have discussed, X-ray diffraction (XRD) is a tool scientists use to study how the atoms are arranged in a crystal. A **rocking curve** is a special type of XRD measurement that tells us how perfectly aligned the crystal layers are.

Here’s the basic idea:

- In a normal XRD experiment, you shine X-rays at a crystal and measure how they bounce off (or “diffract”) from the crystal planes.
- In a **rocking curve**, you focus on one particular crystal plane and **slightly tilt (or “rock”) the sample** while keeping the X-ray angle nearly fixed.
- As you rock the crystal, the intensity of the reflected X-rays forms a peak.

The **width and shape of that peak** tell you how perfect the crystal is:

- A **narrow peak** means the crystal planes are very well aligned—like a smooth stack of paper.
- A **broader peak** means there’s some misalignment or defects—like a stack that’s a bit wrinkled or bent.

In short, a **rocking curve** is an XRD technique used to check how well-aligned the atomic layers are in a crystal. A sharper peak means a better crystal.

Appendix H: Reciprocal Space Maps

(Our current XRD system does not have this feature, but maybe a future one will.)

When we use X-ray diffraction (XRD) to study crystals, we often think about the pattern of atoms in **real space**—the actual arrangement of atoms. But sometimes it's more helpful to look at things in **reciprocal space**, which is a mathematical way to describe how X-rays interact with repeating structures in a crystal.

Here is an analogy to help make sense of reciprocal space:

When we have an oscillating wave, physicists often take the **Fourier transform** of it to understand what **frequencies** make up the wave. Instead of focusing on how the wave moves in time (real space), the Fourier transform shifts our perspective to the frequency domain (reciprocal space), where patterns and structures can be easier to interpret.

In the same way, reciprocal space gives us a clearer view of a crystal's internal structure by translating repeating patterns of atoms into a space where **angles, spacing, and strain** show up as simple shifts or shapes. While it's a more abstract concept, reciprocal space often **simplifies complex structures**. Even if a crystal is slightly **rotated, stretched, or distorted**, these changes are easier to see and measure in reciprocal space than by trying to trace every atom directly.

(Reciprocal space also becomes especially useful when exploring more advanced topics, like how **electronic energy bands** form in solids.)

A **reciprocal space map (RSM)** is like a 2D image that shows how X-rays diffract in two directions at once. It gives much more detail than a single diffraction peak. You can think of it like going from a **single point elevation reading** to a **full topographic map** that shows the shape and slope of the terrain—in this case, the alignment and strain within the crystal.

Why use it?

An RSM helps us answer questions like:

- **Is the film strained or relaxed?** (Strain shows up as shifts in peak positions.)
- **How well is the film aligned with the substrate?**
- **Are there imperfections or distortions in the crystal?**

In the map:

- Each bright spot is a **diffraction peak** that tells us about the spacing and orientation of atomic planes.
- The **shape and position** of the peaks tell us about **strain, tilts, and crystal quality**.

In short, a **reciprocal space map** is an advanced type of X-ray diffraction measurement that shows how a crystal’s structure behaves in two directions. It’s used to study strain, alignment, and overall crystal quality—especially in thin films.

Appendix I: X-ray Reflectivity

X-ray reflectivity (XRR) is done using the same instrument as XRD, but it focuses on something different. Instead of looking at diffraction (how X-rays bounce off atomic planes inside the crystal), XRR measures how X-rays are reflected from the surface of a material.

To do this, we use very shallow, or grazing angles, so the X-rays just skim the surface rather than going deep into the crystal. At these angles, the X-rays reflect like light bouncing off a pond. The way the intensity of the reflected X-rays changes with angle tells us important information about the surface and thin film layers.

What can XRR tell us?

- Thickness of thin films
- Density of each layer
- Surface and interface roughness

That's why XRR is especially useful for studying thin films—like the kind often grown on substrates in material science or nanotechnology.

How does it work?

When X-rays reflect off different layers in a film (like air/film and film/substrate), the reflections can interfere with each other—sometimes adding up, sometimes canceling out—just like waves on water. This creates a pattern of oscillations in the reflected signal (called Kiessig fringes), which scientists can analyze to learn how thick or smooth the layers are.

In short, XRR measures how X-rays reflect off a surface at shallow angles. It's like using a ruler made of X-rays to measure how thick a film is, how dense it is, and how smooth the surfaces and interfaces are.

Appendix J: Ellipsometry

Ellipsometry is a technique used to measure very thin films—often just a few nanometers thick—without ever touching the sample. It works by shining **polarized light** (light with a specific orientation) onto the surface and then measuring how that light **changes** after it reflects.

Unlike techniques like XRD or XRR that use X-rays, ellipsometry uses visible or ultraviolet light. The tool you might use—like the J.A. Woollam M-2000U White Light Ellipsometer —uses a range of wavelengths (white light) and analyzes how the polarization of light is altered by thin layers.

What does ellipsometry tell us?

- **Thickness** of thin films
- **Refractive index** (how the film bends light)
- Sometimes even **material composition** or **optical properties**

It’s especially useful for transparent or semi-transparent films, such as oxides, polymers, or coatings on semiconductors.

How does it work?

When polarized light hits a surface, it reflects in a slightly different way depending on the film’s thickness and optical properties. Ellipsometry measures two angles—called Psi (Ψ) and Delta (Δ)—that describe how the light's polarization has changed. From these values, software can calculate what the film is made of and how thick it is. In short, ellipsometry is a powerful, non-contact way to measure thin film thickness and optical properties using polarized light. It’s especially useful for transparent layers and gives very precise results—often down to a fraction of a nanometer.