Magnetism in Materials

TP3

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1 Introduction

1.1 Magnetic moment

The fundamental object in magnetism is magnetic moment. In classical electromagnetism this can be equated to a current loop. Consider a current \( I \) around an elementary loop of area \( dS \). The magnetic moment \( d\mu \) is then given by, \( d\mu = I \, dS \). This current loop is equivalent to magnetic dipole, consisting of two magnetic monopoles of opposite magnetic charge separated by infinitesimal distance, in the same direction as \( dS \).

A current loop occurs due to the motion of electrical charges. All the charges considered here are associated with particles that have mass. Therefore in all current loops there is orbital motion of both mass and charge. Hence the magnetic moment will always be coupled with angular momentum given by, \( \mu = \gamma L \), where \( \gamma \) is the gyromagnetic ratio. The relation between magnetic moment and angular momentum is demonstrated by Einstein-de Haas effect or Barnett effect.

The energy of a magnetic moment in a magnetic field is given by, \( E = -\mu \cdot B \). And the torque on the magnetic moment due to magnetic field is given by \( \mathbf{G} = \mu \times \mathbf{B} \). Since the magnetic moment is associated with angular momentum, the torque can be rewritten as \( \frac{d\mu}{dt} = \gamma \mu \times B \).

1.2 Magnetization

Magnetization \( M \) is defined as magnetic moment per unit volume. It is a vector field that expresses the density of permanent or induced magnetic dipole moments in a magnetic material.

In free space there is no magnetization. The magnetic field vectors \( \mathbf{B} \) and \( \mathbf{H} \) are linearly related by \( \mathbf{B} = \mu_0 \mathbf{H} \), where \( \mu_0 \) is the permeability of free space. \( \mathbf{B} \) and \( \mathbf{H} \) are scaled versions of each other with former measured in tesla (T) and latter in \( \text{Am}^{-1} \). When a magnetic solid (of magnetization \( M \)) is inserted into that free space the general relationship between the vector fields will be \( \mathbf{B} = \mu_0 (\mathbf{H} + M) \).

In a special case where \( M \) is linearly related to \( \mathbf{H} \) the solid is called a linear material, \( M = \chi \mathbf{H} \) where \( \chi \) is a dimensionless quantity called as magnetic susceptibility. Then the relationship between the vector fields can be re-written as \( \mathbf{B} = \mu_0 (1 + \chi) (\mathbf{H}) = \mu_0 \, \mu_r \, \mathbf{H} \). \( \mu_r = 1 + \chi \) is the relative permeability of the magnetic solid.

The root cause of magnetic behavior in magnetic solids is the presence of one or more unpaired electrons. The angular momentum associated with an electron orbiting around the nucleus of an atom is known as orbital angular momentum. The electron also possesses an intrinsic magnetic moment known as spin.

1.3 Localized moments

Consider an atom with a hamiltonian given by \( \hat{H}_0 = \sum_i (\frac{p_i^2}{2m_i}) + V_i \) which is a sum of the electronic kinetic and potential energy. Now in the presence of an external magnetic field the new hamiltonian can be written as

\[
\hat{H} = \hat{H}_0 + \mu_B (L + gS) \cdot B + \frac{e^2}{8\pi\epsilon_0} \sum_i (B \times r_i)
\]

The dominant perturbation to the original hamiltonian \( \hat{H} \) is \( \mu_B (L + gS) \cdot B \). This is the effect of atom’s own magnetic moment known as paramagnetic term. The third term \( \frac{e^2}{8\pi\epsilon_0} \sum_i (B \times r_i) \) is due to the diamagnetic moment.

All materials show some degree of diamagnetism, a weak, negative magnetic susceptibility. From a classical viewpoint the action of a magnetic field on the orbital motion of an electron causes a back e.m.f., which by Lenz’s law opposes the magnetic field which causes it. Diamagnetic susceptibilities are largely temperature independent.
Paramagnetism corresponds to a positive susceptibility so that an applied magnetic field induces a magnetization which aligns parallel with the applied magnetic field which caused it. The magnetization of a classical paramagnet is described by the Langevin function $L(y)$ such that $M \propto \frac{B}{T}$. And using $\chi = M/H$ susceptibility can be calculated as $\chi \propto \frac{1}{T}$. This demonstrates that the magnetic susceptibility is inversely proportional to the temperature, which is known as Curie’s Law.

1.4 Exchange interaction

Magnetic moments in a solid communicate with each other and potentially produce long range order. When two magnetic dipoles are separated by a distance their interaction energy depends on their separation and degree of mutual alignment. However this interaction is too weak to account for ordering in most materials.

Now let us discuss how the exchange interactions develop between magnetic moments. Since electrons are fermions they obey Pauli’s exclusion principle, where no two fermions can occupy the same quantum state. This means when two electrons are exchanged with respect to their spatial and spin coordinates, the overall wave function of the system will be antisymmetric. The overall wave function is the product of spacial and spin coordinates

$\Phi_a(r_1)\Phi_b(r_2) \pm \Phi_a(r_2)\Phi_b(r_1)$

**spatial:** $\Phi_a(r_1)\Phi_b(r_2)$

**spin:** $\alpha(1)\beta(2) \pm \alpha(2)\beta(1)$

**Direct exchange** Electrons on neighboring magnetic atoms interact via an exchange interaction. in this case the exchange interaction proceeds directly without the need for an intermediary.

Very often direct exchange cannot be an important mechanism in controlling the magnetic properties because there is insufficient direct overlap between neighbouring magnetic orbitals. Thus in many magnetic materials it is necessary to consider some kind of indirect exchange interaction.

**Superexchange** Exchange interaction between non-neighboring magnetic ions mediated by a non-magnetic ion(s) placed between the magnetic ions

**Anisotropic exchange** Exchange interaction between the excited state of one ion and the ground state of other ion

1.5 Magnetic structures

1.5.1 Ferromagnetism

A ferromagnet has spontaneous magnetization even in the absence of an applied field. All the magnetic moments lie along a single unique direction. For a ferromagnet in an applied field $B$ the appropriate Hamiltonian to solve is $\mathcal{H} = -\sum_{ij} J S_i S_j + g\mu_B \sum_j S_j B$, the exchange constants for nearest neighbors will be positive ($J > 0$), to ensure ferromagnetic alignment. In the above mentioned equation, the first term is Heisenberg exchange energy and the second term is Zeeman energy.

Let us make an approximation by defining an effective molecular field $B_{mf} = -\frac{2}{\mu_B} \sum_j J_{ij} S_j$. The exchange interaction term in the original Hamiltonian can be replaced by the effective molecular field to yield the effective Hamiltonian as $\mathcal{H} = g\mu_B \sum_i S_i (B + B_{mf})$.

This assumption is based on an approach that all magnetic ions experience the same molecular field. Since the molecular field measures the effect of ordering of the system one can assume that $B_{mf} = \lambda M$, where $\lambda$ is a constant that parametrizes the strength of the molecular field.

\[ L(y) = \coth(y) - \frac{1}{y} \]
Now we are able to treat this problem as if the system were a simple paramagnet placed in a magnetic field \((\mathbf{B} + \mathbf{B}_{\text{mf}})\). At low temperature the magnetic order is self sustaining. As the temperature is raised, thermal fluctuations begin to progressively destroy the magnetization and at critical temperature the order will be destroyed.

In every ferromagnetic system, below a certain temperature (Curie temperature \(T_c\)), non zero magnetization occurs and this grows as the material is cooled. The substance thus becomes magnetized even in the absence of an external field. This spontaneous magnetization is the characteristic of ferromagnetism. Applying a small field \(B\) at \(T \geq T_c\) will lead to a small magnetization \(M \propto \frac{B + \lambda M}{T}\), and the magnetic susceptibility can be written as \(\chi \propto \frac{1}{T - T_c}\).

The mean-field magnetization as a function of temperature calculated for different values of applied field \(B\) is shown in figure 1. The phase transition is only present when \(B = 0\).

![Figure 1: mean-field magnetization as a function of temperature calculated for different applied field \(B\)](image_url)

1.5.2 **Antiferromagnetism**

If the exchange interaction is negative \((J < 0)\) the molecular field is oriented such that it is favorable for nearest neighbor magnetic moments to lie antiparallel to one another. This is observed in systems that can be considered as two interpenetrating sublattices, with magnetic moment point up and down, as shown in figure 2.

![Figure 2: antiferromagnet decomposed into two interpenetrating sublattices](image_url)

1.6 **Hysteresis**

A ferromagnet contains a number of small regions called domains. In sufficiently large ferromagnets, magnetization of a single domain costs a large amount of magnetostatic energy, \(\int \mathbf{B} \cdot d\mathbf{M}\). To minimize this the material
breaks into multiple domains, where each domain is magnetized to saturation in the direction of one of the easy axes, but the sum of the domain magnetization is zero.

Domain walls are the boundaries between domains in which all spins are aligned in the direction of the easy axis. At the domain wall magnetic dipoles or spins have to reorient themselves, as shown in figure 3.

When a demagnetized ferromagnet is magnetized, it results in domain wall motion where the domains that are aligned favorably along the applied field grow at the expense of unfavorably aligned. This process will give rise to hysteresis in magnetization curves.

The energy dissipated by a ferromagnet is proportional to the area of the hysteresis loop. If the area is small then the material is said to be magnetically soft, and if the area is large then the material is said to be magnetically hard.
2 Measurement techniques

Various experimental techniques can be used to probe the magnetic order in real materials. The most conventional way to measure magnetic moment of a sample is by using a magnetometer.

2.1 Magnetometry

A magnetometer is an instrument that measures the dc magnetic response of bulk and nanoscale materials as a function of external control parameters like magnetic field, temperature etc.

Magnetometers operate on Faraday’s Law of Induction, where a changing magnetic field will produce an electric field. This electric field can be measured and tell us information about the sample moment.

When magnetic flux enclosed by a resistive coil changes, a voltage is induced across the terminals of the coil. This induced voltage is given by the rate of change of magnetic flux. This basic law of electromagnetism is known as Faraday’s law of induction.

\[ \nabla \times E = -\frac{\partial B}{\partial t} \], Maxwell-Faraday equation

Applying Stokes theorem, curl E can be rewritten as, \[ \oint E \cdot dl = -\frac{d}{dt} \int B \cdot ds = -\frac{d\Phi}{dt} \]

\[ V_{\text{induced}} = -N \frac{d\Phi}{dt}, \text{ for a coil of } N \text{ turns} \]

There are several different magnetometers available which can be classified based on their situation or intended use. During this practicals you will be using a vibrating sample magnetometer (VSM).

In a vibrating sample magnetometer (figure 4) the sample is inserted into the region of uniform magnetic field in the center. Then it is sinusoidally vibrated using a motor. When the sample is vibrated the flux on the sample changes, thereby inducing a voltage, according to Faraday’s law.

Pickup coils, which are opposite in polarity with each other, are placed in the sample space to detect the induced voltage. This is to ensure that voltages due to changes in the applied field are canceled out and only the signal from the sample remains.

Hence the induced voltage in the pickup coil \( V_{\text{induced}} \) is proportional to the sample moment but does not depend upon the magnitude of the applied magnetic field.

\[ V_{\text{induced}} \propto \text{moment} \]

The signal detected by the pick-up coil is then transmitted into a lock-in amplifier, which eliminates interfering signals and amplifies the signal-to-noise ratio (when the noise is removed, the signal is better).

There exist several magnetometers with different theory of operation, which can also be used to measure the magnetization of a sample. For example, in an extraction magnetometer the sample is placed at the center of the coil and then removed to a large distance, inducing a voltage in the coil. The magnetic flux \( \Phi \) produced by the sample is equal to \( \int V \ dt \).

SQUID (superconducting quantum interference device) is one of the most sensitive techniques that can be used to measure magnetic moment in a material. This consists of a superconducting ring with a ‘weak-link’, so that there is a Josephson junction in it, and the ring is therefore able to act like a very sensitive quantum
interferometer. If a sample is passed through the ring, the persistent current induced is proportional to the magnetization of the sample.

In the alternating gradient magnetometer, the sample is mounted on a piezoelectric strip and an alternating field is provided by counterwound coils, so that at the sample there is an alternating field gradient. This results in a force on the sample equal to \( (\mu \nabla) B \). The piezoelectric strip therefore deflects in time with the driving frequency and by an amount that can be measured by the piezoelectric signal, allowing \( \mu \) to be deduced.

In a torque magnetometer, the sample is suspended on a torsion fibre. The application of a magnetic field \( B \) on the sample produces a torque equal to \( \mu \times B \).

Vector magnetometers which can measure the magnitude as well as direction of the magnetic moment can be utilized in industries for various purposes. For example, they are used in hall-effect sensors which can be used for proximity sensing, positioning, speed detection, and current sensing applications.

Magnetometers have a very diverse range of applications, including geographic surveys like searching for natural resources, submarine detection, heart beat monitors, weapon systems positioning, sensors in anti-locking brakes etc. They can give an indication of auroral activity before the light from aurora (figure 5) becomes visible. A grid of magnetometers around the world constantly measures the effect of the solar wind on the Earth's magnetic field, which is then published on the K-index.

\[ \text{Figure 5: aurora} \]

2.2 Other techniques

An ac susceptometer can be used to study the dynamic response of sample properties. During ac susceptibility measurements, an ac field is applied to a sample and the resulting ac moment is measured. Because the induced sample moment is time-dependent, ac measurements yield information about magnetization dynamics which are not obtained in dc measurements, where the sample moment is constant during the measurement time.

Magnetic resonance techniques like NMR, \( \mu \)SR etc can be used to measure the temperature dependence of the magnetization of ferromagnets. They do not measure the average magnetization (like in dc magnetization measurements) but rather the magnetization at a particular crystallographic site, or individual sublattices. They can also give information about the spontaneous magnetization from within a magnetic domain, even if the sample as a whole is unmagnetized.

The most direct information on the arrangement of magnetic moments in a sample can be obtained from neutron scattering experiments. Nuclear scattering of neutrons results from interaction with the nucleus, rather than with the electron cloud. So the scattering power of an atom is not strongly related to its atomic number, unlike X-ray and electron scattering. Hence it is easier to sense light atoms, such as hydrogen, in the presence of heavier ones, and neighboring elements in the periodic table generally have substantially different scattering cross sections and can be distinguished. Neutrons are a highly penetrating probe, allowing the investigation non-destructively, of the interior of materials, rather than just the surface layers. This makes them extremely useful in studying magnetism in condensed matter.
3 Objectives

During the four days, you will learn to:

1. Understand the basics of vibrating sample magnetometer
2. Prepare and load samples for measurement
3. Perform various types of magnetization measurements
4. Analyze and interpret the magnetization profile

4 Experimental details

Our experiments will be carried out using EZ7 VSM as shown in figure 6. In the VSM, the sample is connected through a sample holder to a vibration shaft. The sample is then placed in the middle of a set of pickup coils in which a voltage is induced. An electromagnet surrounds the sample and pickup coils, and is used for varying the field to which the sample is exposed so that the magnetization can be measured as a function of applied field. EZ7 supports maximum field up to $\pm 1.8 \, \text{T}$.

By placing the sample in a cryostat or oven, temperature dependence of magnetic moment can be measured. This can be done using optional hardware in the form of a single temperature chamber which supports a temperature range from upto $\approx 900 \, \text{K}$.

Once can pre-define a sequence using one or more recipe file such that the measurements can be set up to extract many different magnetic parameters.

Figure 6: EZ7 VSM
4.1 Sample preparation

Various types of samples can be measured in the VSM. If you are measuring powders then you can use small acrylic cups which are provided with the system. If you are measuring thin films or single crystals then these can be directly mounted on the sample holder, explained subsequently.

4.1.1 Sample holder

Sample holders are quartz rods where the test sample is mounted on one end and where the other end is held in place inside the shaft of the vibrator. Sample holders are available in different sizes and shapes to accommodate different sample types and types of measurements.

As shown in figure 7, sample holders are either perpendicular or transverse. In addition acrylic cups are available to measure powder samples.

Depending on the signal level of your sample, contamination of your sample or sample holder can cause considerable background signals that may be of the same order or larger than the signal of the sample. Hence, it is very important to clean the sample holder before and after doing the measurements. In most cases, the sample holder can be cleaned sufficiently well enough using alcohol or acetone.

4.1.2 Mounting the sample

Sample is mounted on the holder using several different ways, using a double-sided tape, or teflon tape. When doing measurements at extreme temperatures, some extra measures have to be taken to mount the sample to the sample holder. Double-sided tape or vacuum grease will not be able to hold the sample reliably at either low or high temperatures.

Using the Optional Temperature Control System

Temperature dependence of magnetization can be performed by placing the sample in a cryostat or oven. This chamber fits easily and is used in conjunction with nitrogen gas.

For measurements at low temperature (up to $\sim 600$ K) teflon tape can be used to wrap the sample with sample holder, as shown in figure 8 and figure 9.

For measurements at high temperature ceramic adhesive can be used, which does not melt at high temperatures.

4.2 Inserting the sample holder

Important: This step has to be done by the student under the supervision of the instrument responsible. The student must call the instrument responsible every time when removing/loading a sample holder to avoid any damage to the instrument and accessories.

The sample holder is very fragile and has to be inserted carefully.

- Gently move the Vibrator assembly so that it rests on its rubber stops

\[\text{instrument responsible: nagabhushan.ganesh@epfl.ch}\]
• Carefully loosen the collet at the end of the vibrator shaft and insert the sample holder rod (sample is on other end)
• Gently push the rod inside the shaft as far as it can go and then tighten the collet. Do not over-tighten.
• When done, gently lower the Vibrator back into place.

4.3 Software

The software uses a Recipe File to perform a measurement. One or more Recipe Files are loaded into the Sequence Menu’s Sequence Table. When the Start Measurement button is pressed, the software reads the list of recipe files (and performs the desired measurements) sequentially until they are all completed.

Several types of pre-defined measurements are supported in the VSM

• Virgin curve: measures the magnetic behavior of a demagnetized sample as a function of the applied field.
• Hysteresis curve: measures the magnetic moment or the magnetization as a function of the applied field. Starting at the (positive or negative) maximum field, the field is decreased in steps and at each field the magnetization is measured and plotted.
• Temperature scan: this measurement is useful in obtaining the Curie temperature
• Time dependence: this measurement offers the possibility to investigate the stability of the magnetization at different applied fields.

5 Measurement data

5.1 Data manipulation

Although the voltage measured by VSM coils is an accurate measure of change in flux, not all the measured signal is caused by the magnetic material under investigation. A variety of other things can contribute to the signal that is measured. The purpose of the data manipulation software is to remove these distortions and the unwanted additions to the measured signal to allow us to recover/isolate the signal of the sample that we are

the summation of magnetization vectors of all the particles leads to zero
trying to measure.

Data manipulation is applied during or after the measurement to correct for background subtraction, demagnetizing field correction, smoothing data using cubic spline interpolation etc.

Important: These functions can significantly change the shape of the loops and curves plotted and the parameters calculated from the data. You should always use these functions with caution and always verify yourself that the resulting graphs look plausible and the calculated parameters are correct. If the graphs look odd, there is a good chance that insufficient or wrong data manipulation was applied.

5.2 Data analysis

The data analysis module will help you to analyze previously-measured data. The data analysis program allows you to show one or two previously-measured files at the same time, print their graphs, calculate parameters from them etc.

Alternatively, you can also export the data files and analyze using matlab/python or other softwares.
6 References


7. [Magnetometers](http://wikipedia)